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Optimal Low Density Materials with Architected Porosity from
the Nano to the Macro Scale

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Final Report

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14. ABSTRACT The research objective of this proposal is to unravel the deformation and failure mechanisms of ultra-low density hierarchical nano-architected metallic and hybrid materials, in order to develop optimized macroscale lattices with controlled topological features from the nanometer to the centimeter scale. The proposed materials will consist of a nanoarchitected thin film deposited on a carefully optimized polymeric lattice-type architecture, which is subsequently removed. This will result in a material with unique combinations of high strength and toughness and low density. Through a synergistic combination of novel synthesis approaches, state-of-the-art multi-scale characterization techniques and topology optimization algorithms, this program will combine, for the first time, the main advantages of cellular and nanoporous materials toward the development of highly engineered ultra-low density hierarchical nano-architected lattices. Although recently metallic hollow microlattices with exceptionally strong nanocrystalline Nickel walls have been demonstrated, the brittleness of the nc-walls and local buckling mechanisms at the lattice nodes limit the achievable lattice strength.					
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AFOSR Final Report

Contract/Grant Title: Optimal low-density cellular materials with architected structure from the nano to the macro scale

Contract/Grant #: FA9550-14-1-0352

Reporting Period: 9/15/14 to 9/14/19

Author:

Prof. Andrea M. Hodge, University of Southern California

Prof. Lorenzo Valdevit, University of California, Irvine

Abstract

The research objective of this proposal is to unravel the deformation and failure mechanisms of ultra-low density hierarchical nano-architected metallic and hybrid materials, in order to develop optimized macroscale lattices with controlled topological features from the nanometer to the centimeter scale. The proposed materials will consist of a nanoarchitected thin film deposited on a carefully optimized polymeric lattice-type architecture, which is subsequently removed. This will result in a material with unique combinations of high strength and toughness and low density.

Through a synergistic combination of novel synthesis approaches, state-of-the-art multi-scale characterization techniques and topology optimization algorithms, this program will combine, for the first time, the main advantages of cellular and nanoporous materials toward the development of highly engineered ultra-low density hierarchical nano-architected lattices. Although recently metallic hollow microlattices with exceptionally strong nanocrystalline Nickel walls have been demonstrated, the brittleness of the nc-walls and local buckling mechanisms at the lattice nodes limit the achievable lattice strength. Here we propose to address both limitations, by developing novel nanoarchitected walls and unveil novel optimized cellular architectures. The proposed nanoarchitected thin film will be a nanoporous metallic foam, with the pores infiltrated with a polymer, sandwiched between thin monolithic nanocrystalline face sheets. This topology will impart the film superior strength (by virtue of nanoscale phenomena at the foam ligament level and the small grain size of the face sheets), ductility in both tension and compression (thanks to the hybridization) and bending stiffness (coming from the sandwich configuration). Combined, these features will help overcome fracture and local buckling of the ligaments, which will result in greatly improved lattice strength.

The extensive use of topology optimization will lead to architectures that optimally exploit the features of the new films and improve properties, with the prospect of colonizing significant white space in the strength/density map. These lattices will provide controllable features, which can be tuned for applications requiring lightweight strong materials, such as aircraft, satellites and other deployable structures.

Main Accomplishments/Successes

- A. Developed a method for synthesizing hollow struts with architected walls as proof-of concept for a scaled up process on complex structures
- B. Leveraged modeling to identify optimal wall topologies to explore experimentally
- C. Demonstrated scalable fabrication approaches for macro-scale materials with optimized nano-scale porosity

Research Contributions:

The research contributions include

- A.R. Garcia Taormina, T. Juarez, J. S. Oakdale, J. Biener, and A. M. Hodge “Scaling-up of Nano-architected Micro-Structures: A Mechanical Assessment” *Advanced Engineering Materials*, DOI: 10.1002/adem.201900687, (2019).
- M-T Hsieh, B. Endo, Y. Zhang, S.W. Godfrey, J. Bauer, L. Valdevit, ‘The mechanical response of architected materials with spinodal topologies’, *Journal of Mechanics and Physics of Solids*, 125 (2019): 401-419.
- Bauer, Jens, et al. "Programmable Mechanical Properties of Two-Photon Polymerized Materials: From Nanowires to Bulk." *Advanced Materials Technologies* (2019): 1900146.
- T. Juarez, A Schroer, R. Schwaiger, A. M. Hodge “Evaluating sputter deposited metal coatings on 3D printed polymer micro-truss structures” *Materials and Design*, volume 140, 15 February 2018, Pages 442-450.
- T. Juarez, J. Biener, J. Weissmüller, A. M. Hodge “Nanoporous Metals with Structural Hierarchy: A Review” *Advanced Engineering Materials*, Volume 19, Issue 12, December (2017).
- Bauer, J., Meza, L. R., Schaedler, T. A., Schwaiger, R., Zheng, X., & Valdevit, L. ‘Nanolattices: An Emerging Class of Mechanical Metamaterials’, *Advanced Materials*, 15, 1701850–26. (2017).
- T. Juarez, A.M. Hodge, “Synthesis of nanoporous gold tubes”, *Advanced Engineering Materials* Volume: 18 Issue: 1 Pages: 65-69 (2016).

** Note: just attach journal paper at end versus recopying the information in the text

Transitions: (required for final report)

- 1. Methods to industry:
- 2. Students to employment (trained under grant) - **Ph.D. students** trained and graduated
 - Dr. Kamia Smith now researcher at Edwards Air force Research Laboratory
 - Dr. Theresa Juarez now researcher at JPL

- Alina Garcia, 4th year Ph.D. student

Post-Docs

- Dr. Angelica Saenz now Staff Scientist at
- Dr. Jens Bauer now Research Associate at UC Irvine

3. Techniques to AFRL (correspondence with AFRL researchers)

Collaborations:

1. AFRL - Edwards Air force Research Laboratory
2. DOD – Sandia National Lab
3. Others: e.g., NSF – Lawrence Livermore National Lab, Karlsruhe Institute of Technology, Germany
4. Industry: None
5. Student Internships - Northrop Grumman Corporation

Awards:

1. Best paper: Two invited review papers
 - T. Juarez, J. Biener, J. Weissmüller, A. M. Hodge “Nanoporous Metals with Structural Hierarchy: A Review” *Advanced Engineering Materials*, Volume 19, Issue 12, December (2017).
 - Bauer, J., Meza, L. R., Schaedler, T. A., Schwaiger, R., Zheng, X., & Valdevit, L. ‘Nanolattices: An Emerging Class of Mechanical Metamaterials’, *Advanced Materials*, 15, 1701850–26. (2017).
2. Recognition at school:
 - Professor Hodge received Hanna Reisler Mentoring Award (2018)
3. External recognition:
 - Professor Hodge received the “Early Career Achievement Award” at Northwestern University, 2017
 - Professor Hodge received the TMS Julia and Johannes Weertman Educator Award, 2020
 - Best Poster Award Nominee, T. Juarez and A.M. Hodge "*Synthesis of Architected Structures with Metal-Foam Walls*" 2015 MRS Fall Meeting & Exhibit, Boston, Massachusetts. November 30, 2015

Publications:

1. Patents: 0

2. Journal : 8

3. Conferences: 30

4. Posters: 5

Software:

Toolboxes available

Invited Talks:

- A.M. Hodge, Hamburg Collaborative Research Center SFB 986 Workshop “Tailored Metal Microlattices: Challenges and Outlook” Hamburg, Germany, June 2019
- A.M. Hodge, Controversies Colloquium 2018: Stability of Nanostructures “Exploring the thermal evolution of nanomaterials: From nanometallic multilayers to nanostructures UC Irvine, Irvine, CA February 2018. Invited.
- L. Valdevit, ‘Additive manufacturing approaches for micro/nano-architected materials’, NSF/AFOSR Integrated Future of Additive Manufacturing, Design, Production and Qualification Workshop, Washington, DC, July 23-24, 2018. Invited.
- L. Valdevit, ‘Stiffness, strength and fracture toughness of architected materials with spinodal topologies’, European Solid Mechanics Conference, Bologna, Italy, July 1-6, 2018
- L. Valdevit, ‘Fabrication of Multi-Material and Multi-Scale Metastructures - Challenges and Opportunities’, ARO Workshop on Metamaterials, Atlanta, GA, May 16, 2018. Invited.
- L. Valdevit, ‘Mechanical Metamaterials - Fabrication, Characterization, Modeling and Optimal Design’, University of Minnesota, Minneapolis, MN, April 24, 2018
- L. Valdevit, ‘Additive manufacturing and optimal design of micro/nano-architected materials’, Materials Research Society Spring Meeting, Phoenix, AZ, Apr 3-6, 2018. Invited.
- L. Valdevit, ‘Additive manufacturing and optimal design of micro/nano-architected materials’, Rutgers University, New Brunswick, NJ, Mar 26, 2018
- L. Valdevit, ‘Mechanical metamaterials: Fabrication, characterization, modeling and optimal design’, 1st International Conference on Aeronautics, Colon, Queretaro, Mexico, Oct 17-18, 2017. Invited.

Student Talks:

- A. Garcia Taormina, T. Juarez, R. Schwaiger, A.M. Hodge “*Development of Metal-Polymer Hierarchical Structures*” ASM International Student Poster Contest: Los Angeles Chapter, Garden Grove, CA. May 15, 2018.
- A. Garcia Taormina, T. Juarez, R. Schwaiger, A.M. Hodge “*Development of Metal-Polymer Hierarchical Structures*” USC Aerospace and Mechanical Engineering Industry Day, Los Angeles, CA. April 20, 2018.
- A. Garcia Taormina, T. Juarez, R. Schwaiger, A.M. Hodge “*Development of Metal-Polymer Hierarchical Structures*” 2018 SCSMM Spring Symposium, Los Angeles, CA. April 13, 2018.
- A. Garcia Taormina, A.M. Hodge, “*Coating of 3D printed microlattices via magnetron sputtering*” 2018 TMS Annual Meeting & Exhibition, Phoenix, AZ. March 12, 2018.
- A. Garcia Taormina

- , T. Juarez, R. Schwaiger, A.M. Hodge “*Development of Metal-Polymer Composite Microlattices*” USC Aerospace and Mechanical Engineering Board of Advisors Meeting, Los Angeles, CA. November 9, 2017.
- T. Juarez and A.M. Hodge “*Synthesis and characterization of metallic tubular nanoporous structures*” 2015 TMS Annual Meeting & Exhibition, Orlando, FL. March 17, 2015.
- T. Juarez and A.M. Hodge “*Synthesis and characterization of nanoporous gold tubes.*” First International Symposium on Nanoporous Materials by Alloy Corrosion. Lake Bostal, Germany. September 29-30, 2014.

Community Efforts:

1. Data Collects
2. Student events

References:

Changes in Research Objectives: None

Change in AFOSR Program Manager: There were 4 program managers during this project: Dr. Joycelyn Harris, Dr. Kenneth Goretti and Dr. Jay Tiley

Extensions Granted or Milestones Slipped: One year NCE extension given to Prof. Hodge due to death of spouse.

New discoveries, inventions, or patent disclosures: None

Append 1 – 3 Published Papers to the PDF file before submitting

Scaling-Up of Nano-Architected Microstructures: A Mechanical Assessment

Alina R. Garcia-Taormina, Theresa Juarez, James S. Oakdale, Juergen Biener, and Andrea M. Hodge*

Nano- and micro-architected materials generated by ultra-high-resolution 3D printing techniques, such as two-photon polymerization direct laser writing (TPP-DLW) or projection micro-stereolithography (PμSL), have garnered great interest due to their ability to achieve exceptional combinations of material properties. The scalability of these materials, however, remains a crucial challenge as larger high-resolution samples require stitching smaller blocks of the structure of interest together. Herein, scaling techniques and testing methodologies to investigate the effect of stitching on the integrity and mechanical behavior of TPP-DLW parts under tensile load are explored. Specifically, stitched log-pile I-beam specimens with relative densities of 21.5% and 54.7% are tested herein. The micro-tensile tests reveal that the higher-density log-pile samples exhibit brittle behavior with fracture loads at least four times higher than those of lower-density samples. The location of sample failure depends on the type of stitch introduced in the sample, as well as on the relative sample density. Overall, this study highlights the importance of stitching techniques and relative density for the design of nano- and micro-architected materials.

There has been a considerable amount of interest in two-photon polymerization (TPP) processes, such as direct laser writing (DLW), as they enable the fabrication of nearly any topology or complex structure with sub-micron resolution.^[1–3] For example, TPP can be used for generating nano- and micro-architected lattice materials with notable mechanical properties^[4,5] and unparalleled optical behavior.^[6] Accordingly, such DLW-architected materials offer advances in a wide range of applications, such as photonics,^[7–9] cell culture and tissue engineering,^[10–12] energy absorption,^[13] and lightweight structural components.^[14] A number of previous studies have further functionalized DLW printed materials through modification of the printing resin^[15,16] or by

deposition of ceramic and metallic coatings onto the scaffolds.^[17–21] These materials can achieve new combinations of strength, density, toughness, and stiffness when compared with conventional monolithic materials.^[22–24] However, in all these TPP studies, the absence of scalability has remained a prominent challenge.

Indeed, several authors have highlighted the inability to scale-up print volume as a critical issue in TPP fabrication.^[25–29] Consequently, recent studies have explored stitching techniques to produce millimeter-sized porous materials comprising micro-scale building blocks with nanoscale features.^[30–33] While these works demonstrated that stitching provides a viable approach to expand the overall print volume, they also revealed structural defects and other non-uniformities at the stitch boundaries, which may impact the macroscopic behavior of the material. To date, limitations

in print volume have also restricted the evaluation of DLW-architected structures to predominantly compression tests.^[4,22,32,34–36] Therefore, both scaling techniques and testing methodologies need to be developed to assess stitching, and its effect on structural integrity, which to the best of the authors' knowledge, is yet to be explored.

In this study, DLW I-beam micro-tensile specimens with log-pile architectures were printed with two different relative densities (21.5% and 54.7%) using three different stitch protocols: no stitch (C), a stitch line (S), and a stitch line with a 2 μm overlap (SO). The effect of the presence and nature of the stitch interface on the mechanical integrity of the DLW log-pile samples were then tested in tension using a custom micro-tensile machine.

This study focuses on several factors that may impact the scaling feasibility, such as sample relative density and stitching protocol. **Figure 1** shows the gage sections of both low- and high-density samples, as well as the as-printed feature dimensions. Cross-sectional scanning electron microscopy (SEM) micrographs, outlined in purple, show the characteristic log-pile architectures of the low- (78.5% porosity) and high-density (45.3% porosity) samples. The 1) width and 2) length of the elliptical voxels for both sets of samples were determined to be 250 and 850 nm, respectively (Figure 1c,d). The low-density samples were printed with an 3) XY spacing of 1.75 μm and a 4) Z spacing of 650 nm, whereas the high-density samples were printed with an XY spacing of 850 nm and Z spacing of 450 nm. A comparison of

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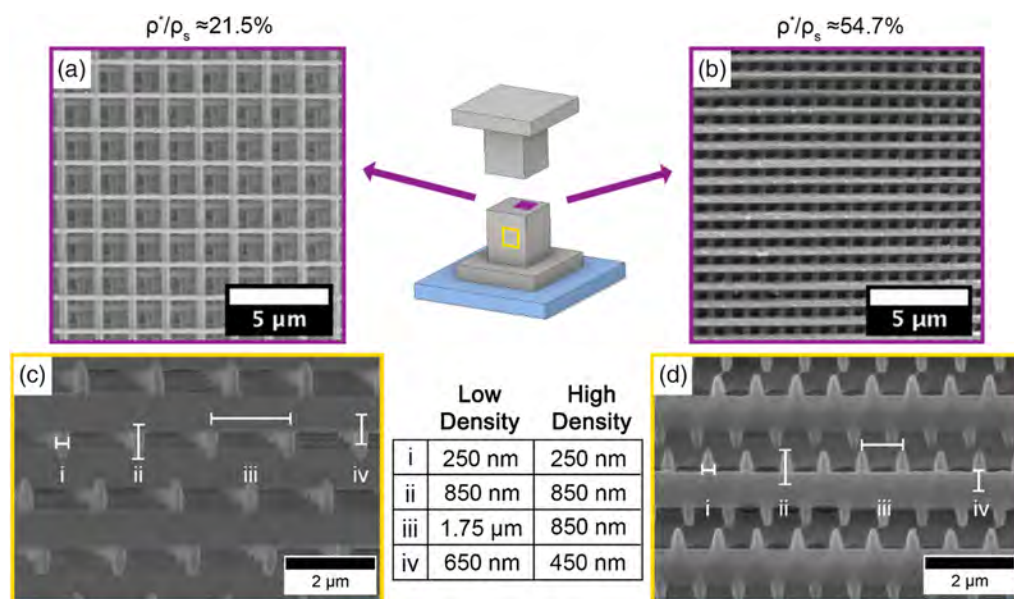


Figure 1. a,b) Representative cross-sectional SEM micrographs highlighting the relative density of the low- and high-density samples, respectively. c,d) Representative micrographs of the log-pile features with an accompanying table of the measured feature dimensions for the low- and high-density samples, respectively.

the as-designed to the as-printed feature dimensions indicates ≈ 12 –16% material shrinkage, consistent with the previously reported values for Nanoscribe's photoresist, IP-Dip.^[30,31,33] The effects of this shrinkage on the materials' functionality, however, can be widespread, and its impact on the mechanical integrity of the architected materials is still unknown. Representative SEM micrographs of the as-printed stitch protocols C, S, and SO

of the low-density samples (**Figure 2**) show several types of defects, such as warping and disruptions in continuity at the stitch interface that are similar to previously reported findings.^[30–33]

In general, the root cause of these defects is the non-uniform material shrinkage, which is typically concentrated at interfaces, such as at the substrate–sample interface and at the grip/gage

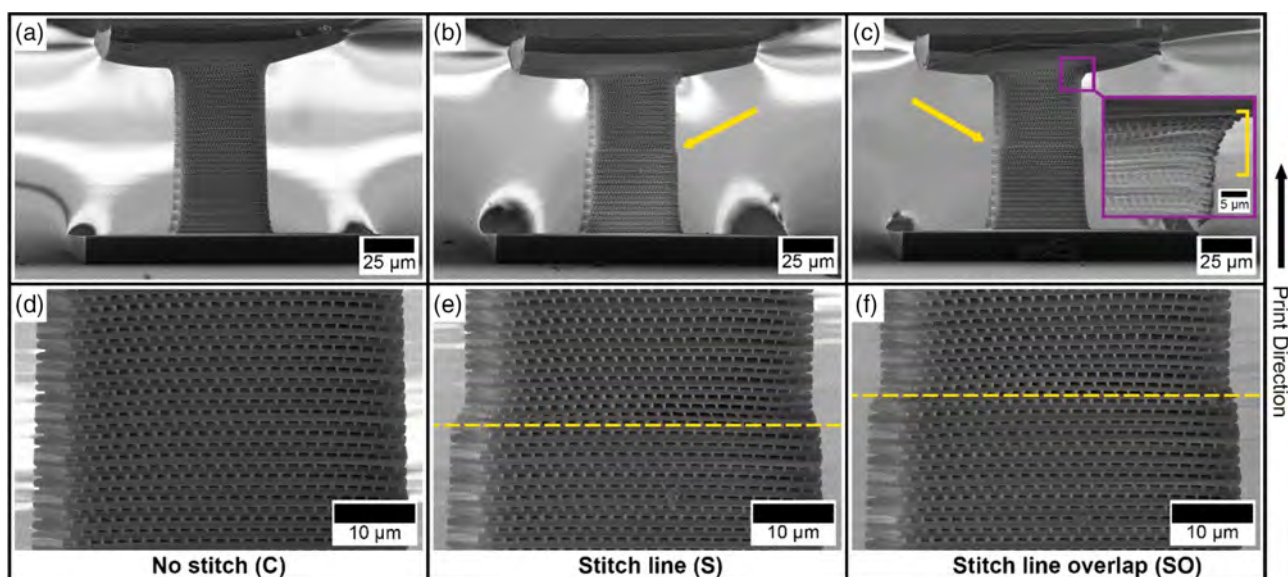


Figure 2. Representative SEM micrographs of low-density tensile specimens: a) no stitch samples, b) samples printed with a stitch line, and c) those with a stitch line and a 2 μm overlap. The yellow arrows indicate regions of stitch-induced defects. Micrographs d–f) show the corresponding gage sections, where the yellow dashed line highlights the location of the stitch line. Inset c) highlights a representative region of axial shear stress denoted by the yellow bracket.

transition, where the material properties, like density or modulus, change abruptly. Figure 2a–c shows the overall sample morphology of the low-density tensile specimens for the C, S, and SO protocols, whereas the higher magnification SEM micrographs in Figure 2d–f highlight the differences at the stitch interface region. Please note that Figure 2a,d does not contain a stitch interface and thus serve as a reference. Additionally, there is no observable difference at the stitch boundary between samples with the stitch line (Figure 2e) and those with the overlap (Figure 2f) as the only difference between the two protocols is the overlap, where the writing path starts at 2 μm into the already printed lower half of the specimen. All samples, irrespective of relative density or stitch type, show the expected regions of axial shear stress at the interfaces between the grip and gage sections due to non-uniform material shrinkage. An example of this type of shrinkage is highlighted in Figure 2c (additionally, see Figure S1, Supporting Information). Other researchers, such as Liu et al.,^[30] observed similar axial shear stress in analogous regions along the interface of a printed log-pile structure and in a fully dense “top cap,” which is comparable to the grip pieces printed in the present work. In addition, we also observe non-uniform shrinkage at the stitch line (marked by yellow arrows) as evidenced by the sudden noticeable change in gage width (Figure 2e,f). This is a surprising observation as the structures (and thus the density) above and below the stitch line are nominally the same. We hypothesize that non-uniform shrinkage at the stitch line is due to proximity effects,^[32,37,38] which leads to reduced oxygen inhibitor concentration within the photoresist at the writing front, which, in turn, increases the degree of conversion^[39] and ultimately reduces the extent of shrinkage observed for a given laser power.^[40] The abrupt pause and subsequent 5 min rest period of the stitched specimens allow the oxygen inhibitor concentration to return to its (higher) equilibrium value. Upon continuing the writing process, this results in a lower degree of

conversion and consequently greater degree of shrinkage. Nonetheless, it is clear that the regions of shrinkage-induced defects are exacerbated by the stitching process, which, in turn, could impact the viability of stitching for the scaling-up of DLW-architected structures.^[30,31,33,41]

Micro-tensile tests were performed to assess the impact of these defects on the mechanical performance. To our knowledge, no previous tensile tests have been reported on such types of samples. **Figure 3** shows the corresponding stress–strain curves normalized by the effective density (Table S1, Supporting Information) for low- (21.5%) and high-density (54.7%) samples, as well as representative images of the samples at failure. A minimum of two samples at each density and stitch type have been measured. The corresponding average maximum tensile load achieved for each type of specimen is shown in **Table 1**. The data show that the high-density samples failed at loads at least four times higher than the low-density samples, and of these, those with a stitch line overlap reached the highest average load of 48.0 mN before failure. In contrast, the low-density samples fractured at much lower loads, where the highest load of 10.8 mN was achieved in samples printed with no stitch. The observed trend with a varying relative density is similar to that of open-cell polymeric foams, where it has been observed that higher-relative density foams achieve higher maximum tensile stresses.^[42,43] However, as highlighted in Figure 3a, some ductility was observed in low-density samples, whereas the high-density samples exhibited brittle-like behavior. Polymeric foams are often brittle in tension^[43–46] but have also been shown to undergo ductile failure^[42] depending on the cell geometry and properties of the base material. To date, these materials have been mainly tested under compression and have been shown to follow the expected strength and stiffness scaling laws depending on their respective architectures.^[36,47,48] The only study to date exploring

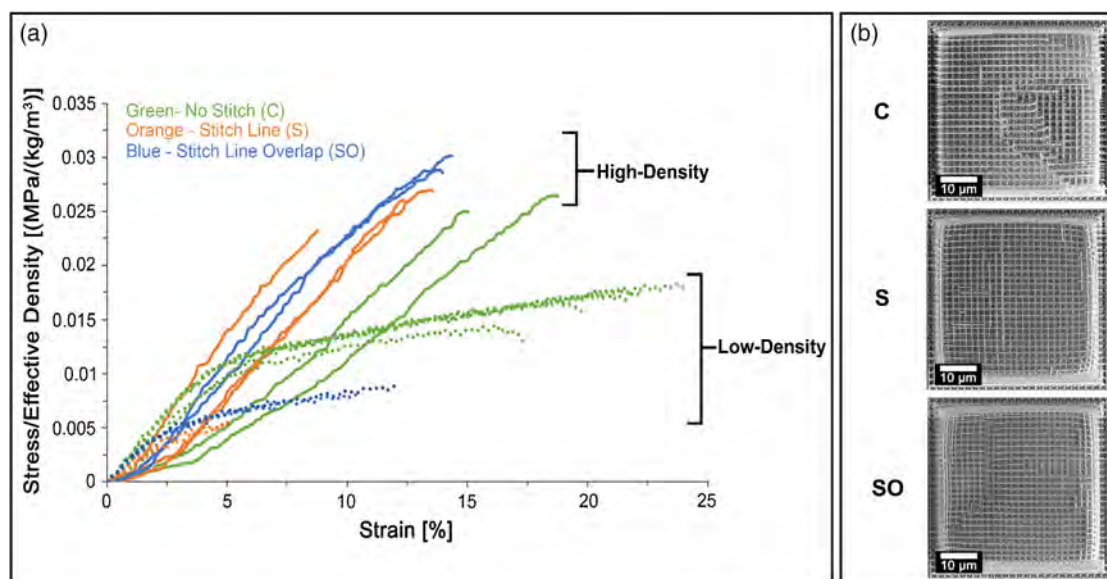


Figure 3. a) Representative stress–strain curves of uniaxial tension tests for low- and high-density log-pile I-beam samples, where the stress values are normalized by the effective density of the architected gage. Green curves show continuously (C) printed pillars, orange curves show samples printed with a stitch (S), and blue curves show samples printed with a stitch line overlap (SO). b) Representative SEM micrographs of fracture surfaces of the low-density samples for each type of stitch protocol.

Table 1. Summary of average maximum achieved load before failure.

	Stitch type	Max load achieved [mN]
Low density	C	10.8 ± 0.9
	S	3.6 ± 0.0
	SO	5.4 ± 0.2
High density	C	41.9 ± 1.1
	S	41.4 ± 2.6
	SO	48.0 ± 1.0

tensile characterization of DLW micro-architected structures reported that the strength of the structure was $\approx 50\%$ lower in tension than in compression,^[49] which is consistent with the results found in this study (see Table S2, Supporting Information).

To further understand the implications of stitching on the feasibility of scaling-up, the samples were characterized postmortem. As determined from camera images (not shown), all C printed samples failed in the grip region, whereas all S printed samples failed at the stitch interface in the midsection of the gage, irrespective of relative density. To further understand the effect of stitching on sample failure, Figure 3b highlights the representative SEM micrographs of the low-density fracture surfaces because these samples have been affected most by the stitching protocols. In contrast to the fracture morphology of C samples, where the fracture cuts through multiple layers, a clean fracture along the stitch plane was observed in S printed samples. The failure along the stitch line in S samples could be attributed to the stitching process and the rest period (see Experimental Section), which is expected to locally reduce the degree of polymerization at the stitch boundary due to increased oxygen inhibition.^[50,51] Similarly, it can be expected that the stitch line overlap (SO) protocol prevents failure at the stitch interface and enhances the strength of the structures due to the additional laser raster in the stitch region, which should locally increase the degree of crosslinking in the polymer.^[14,47] This was indeed observed for the high-density SO samples, which achieved the highest failure load among all samples. However, low-density SO samples show evidence of interplanar fracture, indicating that the stitch plane is no longer the weakest point of the sample.

The fracture near the stitch line in these samples can be attributed to the stress concentration within the stitch plane caused by non-uniform shrinkage and pre-existing axial stress in this region (see Figure 2). The discrepancy in failure location and mechanical performance among low- and high-density samples reinforces that relative density plays a significant role in the tensile behavior of stitched architected materials and needs further study.

The effect of stitching, a critical component of the scalability of TPP techniques, on the mechanical behavior of printed log-pile structures with two different densities and three different stitching protocols was investigated by performing micro-tensile tests. These tests revealed that the high-relative-density structures exhibited brittle behavior, whereas the low-relative-density samples demonstrated a more ductile mechanical response. Additionally, the relative density affected the location of failure and the maximum strength achieved by the samples, where the high-density samples failed at higher loads than the low-density samples. Overall, this study provides valuable insights into overcoming the scaling limitations of DLW-architected materials and lays the foundation for future studies on the role of stitching protocol and relative density.

Experimental Section

A Nanoscribe GmbH Photonic Professional GT in the dip-in configuration^[17] was used to fabricate $50 \times 50 \mu\text{m}^2$, $100 \mu\text{m}$ tall log-pile I-beam specimens. The piezo scan mode limits the maximum achievable print range of any structure to a $300 \mu\text{m} \times 300 \mu\text{m} \times 300 \mu\text{m}$ cube. The writing laser, a FemtoFiber pro near-infrared (NIR) laser supplied by TOPTICA operating at 780 nm with a 100 fs pulse duration and 80 MHz repetition rate, was focused through a Zeiss plan-apochromat $63 \times 1.4 \text{ NA}$ Oil DIC M27 objective, resulting in elliptical voxels with $\approx 3.5:1$ aspect ratio. Two sets of log-pile tensile test specimens with integrated grips were printed: “low-density” samples with a log-pile gage section programmed with a pitch size of $2 \mu\text{m}$ and a Z spacing of 750 nm and “high-density” samples with a pitch size of $1 \mu\text{m}$ and a Z spacing of 500 nm . Note that the gage section is defined as the entire architected area between the grips. SEM was used to assess the dimensions of the representative “as-printed” specimens. Prior to imaging, samples were coated with a thin layer of Pt using a Cressington 108 Manual Sputter Coater. All SEM imaging was performed on an FEI Nova NanoSEM 450 at 5 kV .

The specimens were fabricated by applying a drop of IP-Dip, Nanoscribe’s commercial acrylate-based photoresist, to a $25 \times 25 \times 0.7 \text{ mm}^3$ glass slide

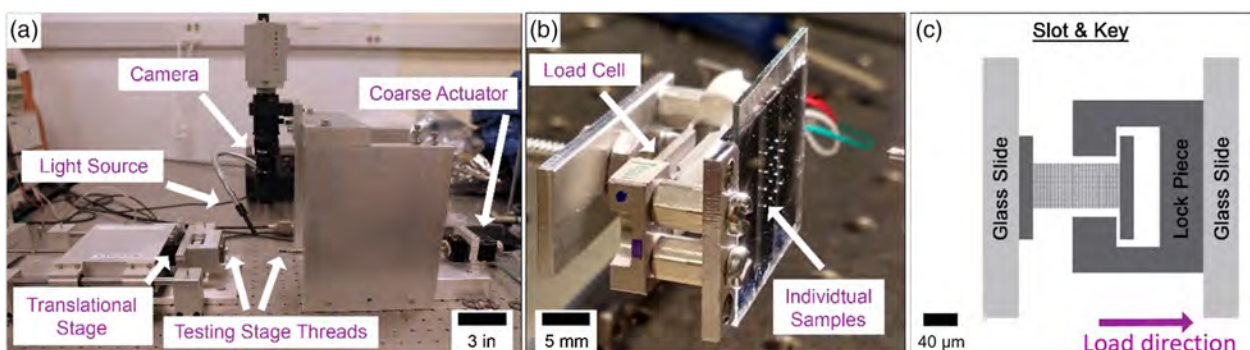


Figure 4. Photographs of a) a custom micromechanical testing apparatus and b) 1 N load cell with representative DLW I-beam tensile samples printed on the glass side. c) A top-view schematic showing the slot and key method for gripping tensile specimens: a mechanical grip in which samples are slotted into a lock piece and pulled in tension until fracture.

(obtained from Nanoscribe). Prior to printing, the glass slides were functionalized with alkoxy silane compounds to promote better adhesion to the polymer samples. Detailed functionalization steps can be referenced in the Supporting Information. The I-beam tensile specimens were printed under three varying stitching conditions: a group of samples were printed continuously with no stitch (C), a second set was printed with a 5 min rest period in the middle of the gage section with no overlap (S), and the last set was printed with a 5 min rest period and a 2 μm overlap in the middle of the gage section (SO). For stitched samples, the lower half of the structure was printed directly onto the glass slide, the print process was then paused for 5 min, and then the upper half was printed. No overlap is defined as restarting the printing process after the rest period directly on the structure surface, whereas the overlap (SO) protocol involves restarting the printing process following the rest period 2 μm within the already polymerized lower half.

Uniaxial tensile tests were carried out on a custom-built micromechanical testing apparatus (Figure 4), comparable with the mechanical testing apparatuses used by Slaby et al.^[52] and Balk et al.^[53] The machine, shown in Figure 4a, consists of a coarse actuator (ThorLabs DRV001), piezo actuator (ThorLabs PAZ015), 2D alignment stage, 1N load cell (Phidgets CZL639HD), camera (Pixelink PL-B782F), and light source. The glass slide with printed tensile specimens was directly attached to the load cell (Figure 4b). Control of the testing stages and data acquisition were carried out through a custom MATLAB script. Tensile tests were carried out using a slot and key method, as shown in Figure 4c. An optical camera above the sample stage was used for aligning and slotting the tensile specimens into a corresponding fully dense fabricated lock piece, as well for imaging the samples during testing. Once the I-beam specimen was slotted, the tensile tests were performed by moving the lock piece at a speed of 0.1 $\mu\text{m s}^{-1}$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Nanolattices: An Emerging Class of Mechanical Metamaterials

Jens Bauer,* Lucas R. Meza, Tobias A. Schaedler, Ruth Schwaiger, Xiaoyu Zheng, and Lorenzo Valdevit

In 1903, Alexander Graham Bell developed a design principle to generate lightweight, mechanically robust lattice structures based on triangular cells; this has since found broad application in lightweight design. Over one hundred years later, the same principle is being used in the fabrication of nanolattice materials, namely lattice structures composed of nanoscale constituents. Taking advantage of the size-dependent properties typical of nanoparticles, nanowires, and thin films, nanolattices redefine the limits of the accessible material-property space throughout different disciplines. Herein, the exceptional mechanical performance of nanolattices, including their ultrahigh strength, damage tolerance, and stiffness, are reviewed, and their potential for multifunctional applications beyond mechanics is examined. The efficient integration of architecture and size-affected properties is key to further develop nanolattices. The introduction of a hierarchical architecture is an effective tool in enhancing mechanical properties, and the eventual goal of nanolattice design may be to replicate the intricate hierarchies and functionalities observed in biological materials. Additive manufacturing and self-assembly techniques enable lattice design at the nanoscale; the scaling-up of nanolattice fabrication is currently the major challenge to their widespread use in technological applications.

1. Introduction

No solid material considerably lighter than water has been reported to date. To decrease the density beyond this point, materials must have a porosity, which generally comes at the

cost of a disproportional degradation of properties. For example, a foam with a relative density ($\bar{\rho}$), i.e., the volume fraction, of 10% will have a stiffness and strength that are 0.3% and 0.9% of the constitutive bulk material, respectively. In this sense, lighter than water and as strong as steel is intuitively a utopian property combination, yet it has recently been achieved with nanolattice materials.^[1–3]

Advances in material processing and availability have defined human progress since the Stone Age; the modern frontier for material design is that of nanomaterials. One- and two-dimensional nanomaterials, such as nanowires and thin films, are known to have exceptional properties. Although these nanoproperties are very desirable for many applications, they are intrinsically coupled to dimensional constraints such as surface-to-volume effects. When nanowires and thin films are scaled up, their size-affected properties are lost. Similarly, when they are clustered in a

composite, interfaces weaken their overall performance. To overcome this dilemma one can envision highly ordered three-dimensional architectures constructed from nanowires or thin films: This is what long-remained technologically infeasible—this is what nanolattice materials are.

Nanolattices have been rapidly developed over the past few years, redefining the limits of the accessible material property space. The key driving force for this advance was the evolution of high-precision additive manufacturing techniques, such as self-propagating photopolymer waveguides (SPPW),^[4] projection micro-stereolithography (PμSL),^[5] and direct laser writing (DLW),^[6,7] which have led to the production of progressively smaller lattice structures (**Figure 1**) reaching unit cell sizes below 1 μm.^[8] Self-assembly techniques have been used to synthesize nanolattices with unit cell sizes down to the order of 50 nm.^[2,3,9] Genetic engineering may be another potential method for nanolattice fabrication.^[10–12] Micro- and nanolattices possess unparalleled mechanical properties at extremely low densities, including effective strengths of up to 1 GPa,^[1–3,9,13,14] high deformability and recoverability with brittle constituent materials,^[13,15–18] and ultrahigh stiffness,^[19] all despite being composed of 50–99.9% air. Also, auxetic structures with negative Poisson's ratio,^[20] pentamode lattices with near zero shear modulus and a resulting fluid-like behavior,^[21] and lattices with exceptional non-mechanical properties, such as optical

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cloaking^[22,23] and broadband electromagnetic polarization,^[24] have been demonstrated.

While the concept of resilient lattice architecture is more than a century old and goes back to Alexander Graham Bell^[25] and Buckminster Fuller,^[26] today lattices can for the first time be made small enough to actually exploit nanoscale properties. It is this unique feature, which facilitates extraordinary strength, sometimes higher than that of the corresponding fully dense bulk material, as well as optical or electromagnetic properties. Other mechanical characteristics of nanolattices, including ductile-like behavior and high stiffness, arise from scale-independent structural effects.

At the nanoscale, size effects can tremendously alter the mechanical,^[27–31] magnetic,^[27] thermal,^[32,33] and electrical^[34,35] properties of a material compared to its corresponding bulk behavior. This is related to microstructural constraints, such as the size and distribution of dislocations, grain boundaries, cracks and voids, which in small scales can be affected by dimensional constraints. The presence of defects can have various effects in different materials systems. For example, plastic flow in metals occurs via dislocation motion, and defects such as grain boundaries hinder this process; thus, the yield strength of polycrystalline metals generally increases as the grain size is reduced.^[36] The chemical bonds in ceramics do not allow plastic deformation at room temperature, and stress concentrations at crack tips cannot be relieved by localized plastic flow; the size of cracks is therefore the limiting factor for their strength. The size of any defect is limited by the overall dimensions of an object, meaning the smaller the object, the higher its strength will be. Mechanisms governing strength can be more complex,^[27,30,31] but there is a clear overall trend that “smaller is stronger”. Metallic and ceramic ultrastrong nanoscale materials have been reported, such as 40-nm-thin and 5.6-GPa-strong gold wires,^[37] 20-nm-thin and 18-GPa-strong silicon wires,^[38] and carbon nanotubes (CNTs) and graphene reaching stresses as high as 100–130 GPa.^[37] Additionally, properties like ductility in silicon nanowires^[38–40] and metallic glass nanopillars,^[41,42] increased Young's modulus in carbon^[43–46] and nanoporous gold,^[47] as well as notch insensitivity in gold nanowires^[48] have also been observed. Future nanolattices may be able to further capitalize on these enhanced nanomaterial properties.

Using classical material fabrication methods, there appears to be little room for further expansion of the accessible material property space. To develop new materials, three fundamental approaches have been identified:^[49] i) by manipulation of the chemistry, metal alloys, polymer formulations, and ceramic or glass compositions may be developed; ii) manipulating the microstructure by thermomechanical processing controls the distribution of defects and phases, thereby modifying a material's properties without changing the chemistry. Searching for lighter, stronger, stiffer, and more durable materials, both approaches have systematically been exploited over centuries with great success; iii) controlling the architecture of multiple materials (composites) or a single material and space (cellular materials) creates hybrid materials. Introducing architecture into materials design allows for the tailoring of a vast range of material property combinations depending on the topology, i.e., the spatial layout of constituent materials.



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The mechanical properties of cellular materials are defined by their constituent material properties, relative density and architecture, and they are traditionally classified as bending- or stretching-dominated, depending on their topology.^[50] Stochastic structures such as foams commonly deform by bending of their ligaments, resulting in an inhomogeneous stress distribution and therefore poor material utilization. The effective strength and stiffness of bending-dominated structures scales

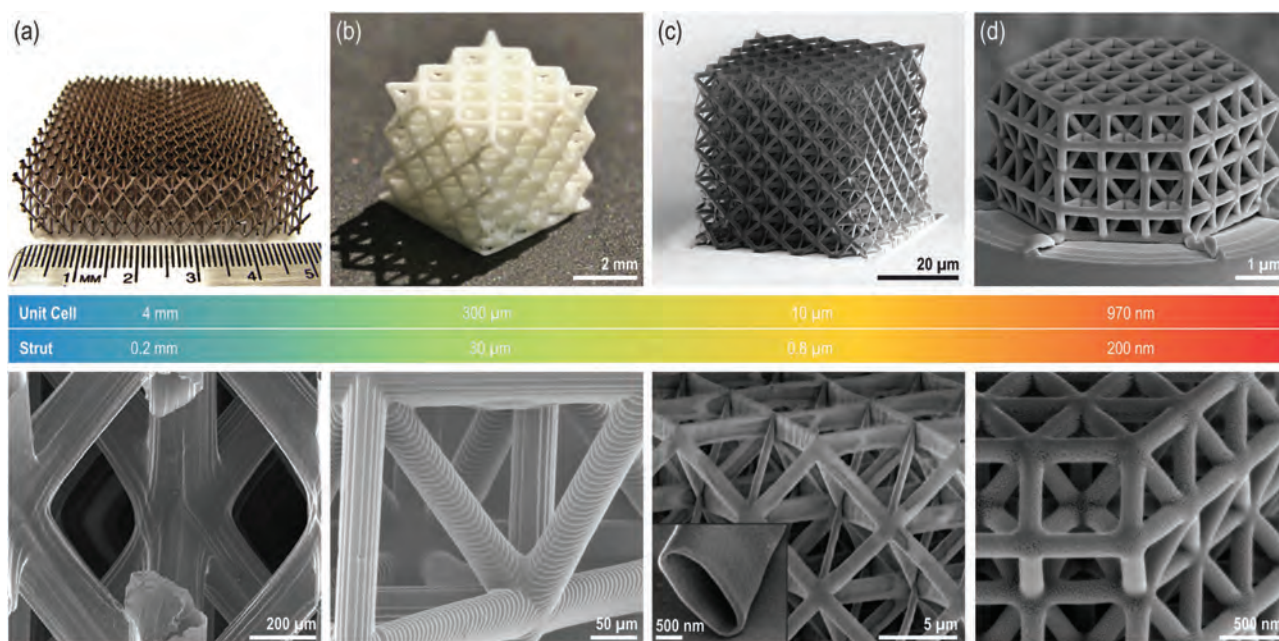


Figure 1. Lattice miniaturization—from the millimeter- to the nanoscale. Characteristic unit-cell dimensions and diameters of individual struts are indicated. a) Hollow-beam nickel lattice, manufactured using SPPW polymer templates, electroless nickel plating, and base etching to remove the polymer. b) Solid-beam alumina lattice fabricated by PμSL with a nanoparticle loaded resist and subsequent sintering. c) Hollow-beam alumina lattice fabricated by DLW, atomic layer deposition and oxygen plasma etching. d) Solid-beam glassy carbon lattice made by DLW and subsequent pyrolysis. a) Reproduced with permission.^[15] Copyright 2011, The American Association for the Advancement of Science (AAAS). b) Reproduced with permission.^[19] Copyright 2014, AAAS. c) Reproduced with permission.^[13] Copyright 2014, AAAS. d) Reproduced with permission.^[1] Copyright 2016, The Authors.

with their relative density as $\sigma_{\text{eff}} \propto \bar{\rho}^{1.5}$ and $E_{\text{eff}} \propto \bar{\rho}^2$ respectively.^[51] An ideal stretching-dominated material deforms via uniaxial compression and tension of its members, and has a linear scaling with the relative density of both strength ($\sigma_{\text{eff}} \propto \bar{\rho}$) and stiffness ($E_{\text{eff}} \propto \bar{\rho}$).

Bending- or stretching-dominated behavior of an open-cell topology generally depends on the rigidity of its pin-jointed counterpart (Figure 2).^[52] In 2D, the triangle is the only rigid polygon, and in 3D, polyhedral cells with fully triangulated surfaces are rigid. The connectivity (Z) of a structure, namely the average number of elements connected at a node, is a good indicator of rigidity. A topology constructed from rigid unit cells is necessarily fully rigid and stretching-dominated, with $Z = 6$ and $Z = 12$ for the 2D and 3D cases, respectively (Figure 2a). Topologies with lower connectivities can be periodically-rigid and theoretically still stretching-dominated (Figure 2b,c), but they are more sensitive to imperfections, which may easily activate deformation mechanisms that can cause bending. Nonrigid topologies are fully bending-dominated (Figure 2d). Although valid in many cases, the classification of cellular materials as bending- or stretching-dominated based on their topology does not account for influencing factors such as the loading conditions (Figure 2e) or the shape and rigidity of the nodes, which is of particular relevance for hollow-beam lattices. Therefore, the topology of a structure may not sufficiently indicate its bending- or stretching-dominated behavior.

Introducing lattice architecture into cellular materials can markedly expand the boundaries of accessible material property space, in particular, in the low density regime.^[49] A lattice material

is defined as a periodic network of structural elements such as slender beams or rods.^[49] Apart from the obvious case of lattice trusses, this definition includes shell-based designs such as honeycombs. For a lattice to be formally considered a material instead of a structure, the length scale on which a load is applied should be large compared to that of the lattice elements.^[49] The most common mechanically investigated lattices are rigid assemblies of octahedron and tetrahedron unit cells, named octet-trusses (see right three structures in Figure 1).^[52] Beyond high strength and stiffness at low weight,^[53,54] lattice architecture offers a range of other exceptional mechanical properties. Some of those properties, such as tunable energy absorption,^[55] can be incorporated into stretching-dominated designs. Others, including tailorable thermal expansion,^[56] origami-based adaptivity,^[57] and auxetic^[58] or fluid-like behavior,^[59] mostly involve hinge-like deformation and folding of bending-dominated topologies. These mechanisms are typical of mechanical metamaterials.^[60–62]

The behavior of metamaterials is determined by their topology rather than by their composition. Classically, photonic^[62–64] and phononic^[62,65,66] crystals derive their properties from wave phenomena, and therefore strongly depend on the length scale of their patterns. Photonic crystals for optical cloaking^[22] are nanolattices designed to direct light of a certain wavelength around an object, rather than scattering it; this would not be possible with lattices of the same topology at larger scales. By contrast, mechanical metamaterials rely on scale-independent deformation of their unit cells. Self-similar auxetic^[67] and pentamode^[21,59] metamaterials have been demonstrated both at the macro- and nanoscale.^[61]

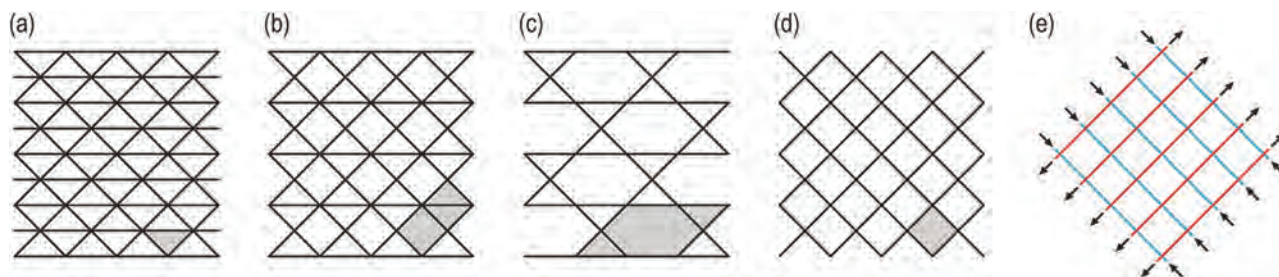


Figure 2. Bending- versus stretching-dominated behavior. a) Stretching-dominated, rigid topology ($Z = 6$) constructed from rigid triangular unit cells. b,c) Periodically-rigid, theoretically stretching-dominated topologies consisting of non-rigid unit cells, $Z = 5$ (b) and $Z = 4$ (c). d) Non-rigid, generally bending-dominated topology ($Z = 4$) constructed from non-rigid unit cells. e) Non-rigid topology which for the indicated load case behaves fully stretching-dominated representing the least weight optimum. Unit cells are shaded in gray.

Certain biological lattice architectures consist of nanoscale building blocks, allowing their mechanical properties to benefit from both optimized topology and material size effects (Figure 3).^[68,69] The architecture of diatoms,^[10,70] a common type of phytoplankton, is nanometer- or even molecular-scale, and has been shown to be remarkably strong.^[71] Other natural materials such as cancellous bone^[72] or Euplectella glass sponges^[73] have lattice elements on the scale of millimeters and are composed of a hierarchically structured constituent material. Cancellous bone grows adaptively according to the loading situation, with the thickness and the orientation of each ligament depending on the magnitude and orientation of loading.^[74,75] The resulting structure is an anisotropic network oriented in the direction of the principal tensile and compressive stresses.^[75] This architecture is a classic example of a least-weight design.^[76,77] Interestingly, these structures behave stretching-dominated, despite not being fully triangulated, because struts aligned with the principal stress direction experience no bending moment (Figure 2d).^[75] Hierarchical design of a solid material from nanoscale building blocks allows for the exploitation of extraordinary nanoscale strengths and enables high toughness at the macroscale.^[68] On the lowest level of hierarchy, solid bone,^[72] enamel,^[78] and nacre^[79] consist of ceramic-like elements on the order of 1–100 nm, held together by a small volume fraction of a soft organic matrix.

Nanolattice materials, or simply nanolattices, are a novel class of mechanical metamaterials; their effective properties are determined by both their topology and their nanoscale features, through which they are capable of exploiting unique size-affected material properties. The full potential of nanolattices is actively being discovered, and the remarkable properties that have been

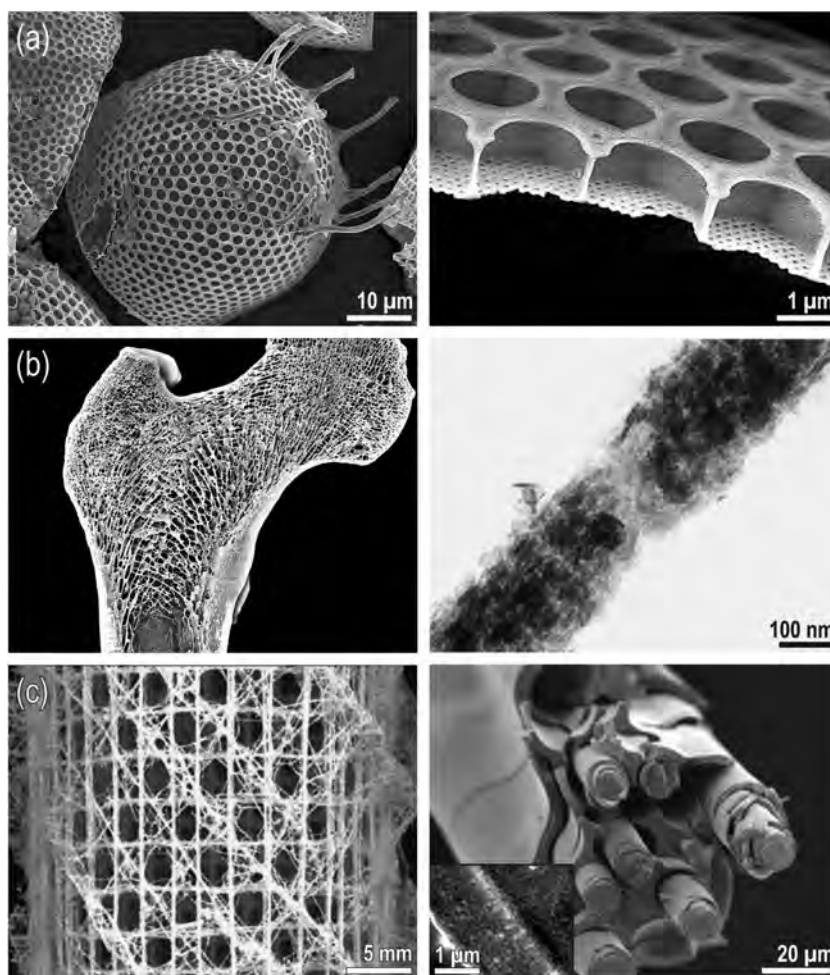


Figure 3. Biological hierarchical lattice materials gain high mechanical robustness from optimized topologies and mechanical size effects in their nanoscale basic building blocks. a) Hierarchical diatom lattice composed of nanoscale lattice elements. b) Cancellous bone network whose hierarchical solid material consists of arrays of mineralized collagen fibrils (left); mineralized collagen fibril of a turkey tendon which is assembled from 2–4 nm thick plate-like crystals (right). c) Euplectella glass sponge lattice (left) and its hierarchically structured base material with 25-nm-size nanoparticles on the lowest hierarchical level. a) Reproduced with permission.^[80] Copyright 2014, The Royal Society of Chemistry. b) (left) Reproduced with permission.^[81] Copyright 2017, Karlsruhe Institute of Technology. b) (right) Reproduced with permission.^[72] Copyright 1998, Annual Reviews. c) Adapted with permission.^[73] Copyright 2005, AAAS.

found to date may just be the tip of the proverbial iceberg. We still cannot mimic the complex hierarchical architecture of biological materials, and scaling-up nanolattices for use in technological applications without sacrificing their beneficial properties will be one of the future's challenges. Prototypes of bioinspired multiscale lattices, up to several centimeters in size, have recently demonstrated exceptional properties^[82,83] compared to their first-order counterparts.^[13,19] While they are still at the outset of their development, nanolattices may eventually lead us to a new era of lighter, stronger, and more durable multifunctional materials.

Here, we examine the unique mechanical properties of nanolattices. Key mechanisms governing the behavior are discussed in the context of lattice architecture and size effects, and shortcomings along with potential avenues for overcoming them are identified. We examine nanolattice performance in relation to large-scale lattice materials, disordered nanoporous materials, and bulk materials to provide a comprehensive review of their materials property space. We further investigate the evolution of nanolattice materials throughout other disciplines, and discuss multifunctionality, relevant fabrication methods, up-scaling approaches, and future directions.

2. Exploiting Nanolattice Architecture

Here we discuss the benefits of combining nanomaterials and lattice architectures with a particular focus on mechanical properties. Properties unique to nanolattices are identified, and their dependence on small-scale materials effects, architecture, or a combination of the two is examined. In this context, not all lattices presented here are fully nanoscale; for properties that rely on scale-independent effects, we discuss where nanoscale structuring may be advantageous for multifunctional reasons, and point out where the incorporation of material size effects has the potential to improve properties. We examine which of the presented characteristics may be successfully combined, and which ones are incompatible.

2.1. Strength

The strength of a nanolattice is defined by three factors: i) the architecture, ii) the length scale, which controls the effect of size-dependent strengthening, and iii) the solid material composition and microstructure, which are strongly affected by the fabrication methodology.

In the context of lightweight materials design, one of the most important figures of merit to evaluate a material's performance is its specific strength, i.e. the ratio between its strength and density. When considering specific strength, there are ultimately two necessary conditions to justify the enormous effort to process nanolattice materials. First, the architecture must provide a combination of strength and density, which may not be attained by any fully dense material. In relation to the material property space accessible by commercial bulk materials, this is often referred to as reaching the "white space". Second, nanolattice materials must capitalize on strength gains from

material size effects, otherwise the same performance could be realized by self-similar macroscale lattice materials, which are much easier and cheaper to fabricate.

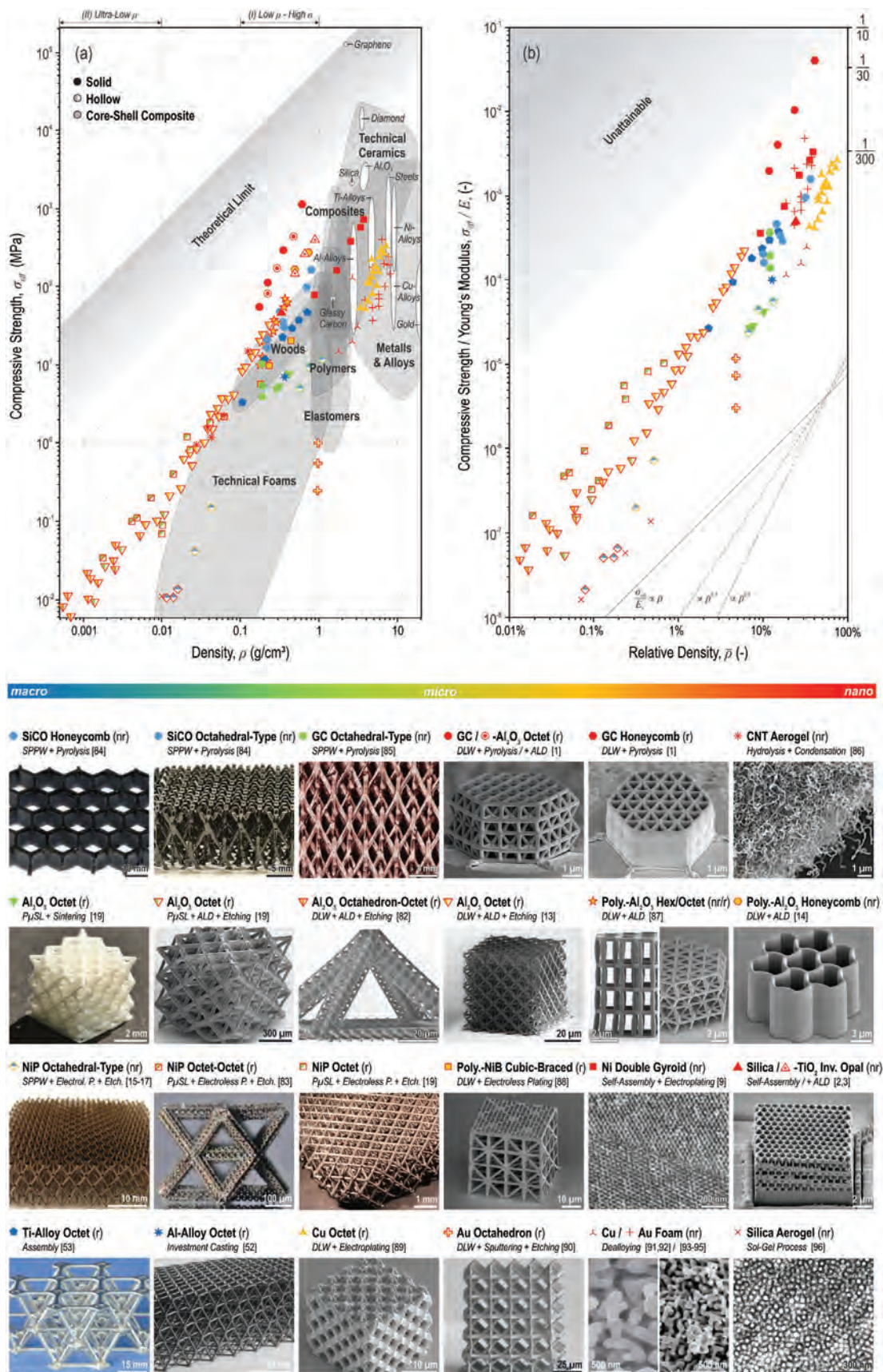
2.1.1. The Strength of Existing Nano-, Micro-, and Macrolattice Materials

The material-property chart in **Figure 4a** shows compressive strength versus density of a wide range of nano-, micro-, and macrolattices, as well as stochastic nanoporous foams and commercially available bulk materials. Lattices with rigid and non-rigid topologies and with different material compositions are included across all length scales. The dashed diagonal lines are design guidelines with a slope of one, two materials on the same line have the same specific strength. Correspondingly, the theoretical limit is defined using diamond, which has the highest specific strength of all bulk materials, and graphene,^[44] which exhibits the highest strength measured to date.

Overall, the specific strength of the lattice materials presented here roughly increases with decreasing structural length scale. This is demonstrated using a color scale, where materials with larger features are blue and those with smaller features are red. Depending on their material composition, some of the nanolattices reach far into the chart's "white spaces". The impact of architecture is evident when comparing the different carbon-based or hollow-beam nickel data, where the strength of stochastic nanoporous materials and lattices with nonrigid topologies falls short of the strength of rigidly architected lattices of similar size.

Two distinct density regimes best illustrate the exceptional performance of nanolattices. i) In the range of 0.1–1 g cm⁻³, glassy carbon nanolattices,^[1] self-assembled core-shell silicitanium inverse opals,^[2,3] and core-shell polymer-alumina honeycombs^[14] reach strengths of up to 400 MPa. Their strength-to-density ratios clearly outperform those of all bulk metals and alloys, polymers, technical and biological cellular materials as well as micro- and macrolattices and nanoporous foams. Glassy carbon honeycombs^[1] even reach strengths above 1000 MPa, leaving diamond as the only bulk material with a notably higher ratio of strength-to-density. ii) In the ultralow density regime, below 0.01 g cm⁻³, hollow-beam octet lattices composed of alumina shells on the order of 5–50 nm thickness are up to ten times lighter than the lightest technical foams, yet they still achieve strength-to-density ratios comparable to wood and certain aluminum alloys.^[13,82] These nanolattices are often built using multiscale architecture^[82,83] (Section 4), and they outperform other ultralow density materials such as nanoporous silica aerogels^[96] and hollow-beam nickel lattices fabricated by SPPW,^[15] by a factor of more than 10.

Reaching into the material property "white spaces" is not limited to nanolattices, as demonstrated by hollow-beam nickel and alumina lattices,^[19,83] which have notably larger dimensions than nanolattices but maintain similar or greater strengths. Any architected material made of a strong enough constituent material is capable of reaching into new material property spaces, as the diagonal guidelines in **Figure 4a** indicate. Nanolattices such as self-assembled nickel gyroids,^[9] core-shell polymer-nickel composite lattices^[88] or hollow-beam gold



lattices^[90] have comparable or lower strengths than bulk materials of equal density, despite their small dimensions.

To visualize the strength gain of nanolattice materials compared to larger-scale cellular materials and bulk solids, we normalize the data of Figure 4a with the constituent solid materials Young's moduli^[3,19,51,53,84,99–101] (E_s) in Figure 4b. Core-shell composite lattices are excluded from this analysis as samples have varying ratios of multiple constituent materials and therefore cannot be correlated to single equivalent bulk material. The guidelines ($\sigma_{\text{eff}}/E_s \propto \bar{\rho}$, ($\sigma_{\text{eff}}/E_s \propto \bar{\rho}^{1.5}$ and ($\sigma_{\text{eff}}/E_s \propto \bar{\rho}^2$, indicate different scaling laws classically associated with stretching-, bending- and buckling-governed behavior, respectively. As a point of reference, the strength of ductile bulk metals is typically on the order of $\sigma_s \approx E_s/300$,^[51] and brittle materials such as ceramics typically have a yield strain well below 1%,^[102] for which Hooke's law gives strengths on the order of $\sigma_s \approx E_s/100$.

In the range of $\bar{\rho} > 10\%$, nanolattices substantially outperform both macroscale cellular materials and the corresponding fully dense bulk solids from which they derive their properties. Glassy carbon nanolattices achieve up to 400% of the compressive strength of bulk glassy carbon^[99] even though their relative density is only 10–25%. Glassy carbon honeycombs resist compressive stresses 16 times as high as the corresponding bulk material at a relative density of 44%. Self-assembled nickel gyroids reach strengths in the range of $E_s/300$ at about 40% relative density. At these high relative densities, the relative contribution of nanoscale size effects to the strength is much greater than that from the architecture. This is best illustrated with stochastic nanoporous gold, which as well reaches strengths on the order of $E_s/300$ at relative densities of 20–40%.^[93–95] Despite their rigid topology, the strength of glassy carbon and hollow-beam alumina nanolattices as well as copper microlattices scale with relative density by the power of >1.5 , underperforming the prediction for stretching-dominated material strength.^[1,13,89]

For lower relative densities of $\bar{\rho} \leq 1\%$ the architecture has a more significant impact on the strength, and the effect of the length scale is less apparent. The strengths of both micro- and nanolattices with rigid topologies in this density regime scale linearly with the relative density, clearly outperforming lattices and nanoporous materials with nonrigid topologies. The guidelines in Figure 4b can be used to estimate that the

constituent materials' strengths are approximately equal to the corresponding bulk material strength. It is noted that essentially all lattices with $\bar{\rho} \leq 1\%$ are made from hollow shells with nanoscale thickness; no macroscale lattice has been reported that is capable of achieving this scaling at ultralight weights.

2.1.2. Architecture and Strength

The impact of architecture on the strength of a lightweight material is independent of any length-scale effects. Figure 5a shows the ratio between ideal stretching- and bending-dominated strength, which increases exponentially with decreasing relative density. For lattices with $\bar{\rho} > 10\%$, which corresponds to the strongest nanolattices, the strength gain of stretching- compared to bending-dominated behavior is less than three; this rises to above a factor of 30 in the ultralow density regime below $\bar{\rho} = 0.1\%$. The effective strength of cellular materials (σ_{eff}) can be approximated by the first-order scaling law:

$$\sigma_{\text{eff}} = C\bar{\rho}^a\sigma_s \quad (1)$$

where σ_s is the constituent solid material strength, C is a geometric parameter, and the exponent a is 1 for stretching- and 1.5 for bending-dominated behavior.^[50] For many open-cell topologies with near-isotropic effective strength, such as the octet lattice and stochastic foams, $C \approx 0.3$ has been found analytically and empirically.^[51,52] The normalized strength of glassy carbon nanolattices, whose architecture is designed to be stretching-dominated, with $\bar{\rho} \approx 25\%$ is about six times higher than that of nickel gyroids of comparable relative density with a nonrigid topology (Figure 4b). Based on Figure 5a, the architecture contributes to approximately a factor of two to this strength difference, meaning a factor of three can be attributed to the difference in constituent materials. In real structures, the difference between strengths likely has a greater dependence on material compositions, meaning architecture has a less significant impact on the effective strength for high relative density materials. In contrast, rigidly designed nickel lattices with $\bar{\rho} \approx 0.3\%$ ^[19] are 20 times stronger than those with non-rigid topologies;^[16] from Equation (1), this difference is almost entirely due to the architecture.

Figure 4. Compressive strength–density materials property chart of different nano-, micro-, and macrolattices as well as stochastic nanoporous and commercial bulk materials.^[1–3,9,13–17,19,52,53,82–96] Symbol shapes relate to the constituent material, symbol colors indicate the length scale of structuring (fillings = feature diameter, lines = shell thickness, if any). a) Absolute strength vs density plot showing that many nanolattices reach far into the low- ρ -high- σ , or the ultralow- ρ “white space”. For graphene^[44] the tensile strength is shown. b) Strength normalized by Young's modulus of the constituent solid material (E_s) vs relative density plot, showing that nanolattice materials are capable of exploiting material strengths up to the theoretical limit ($E_s/10$), whereas the bulk material strengths are often on the order of $E_s/300$. For each structure the material composition (GC = glassy carbon, Poly. = polymer), the unit cell topology including its rigidity (r = rigid, nr = non-rigid) and a brief description of the applied fabrication process is given. The following numbering corresponds to the “row-column” of the data legend images: 1-1, 1-2) Reproduced with permission.^[84] Copyright 2016, AAAS. 1-3) Reproduced with permission.^[85] Copyright 2011, Elsevier. 1-4, 1-5) Reproduced with permission.^[1] Copyright 2016, The Authors. 1-6) Reproduced with permission.^[97] Copyright 2007, American Chemical Society (ACS). 2-1, 2-2) Reproduced with permission.^[19] Copyright 2014, AAAS. 2-3) Reproduced with permission.^[82] Copyright 2015, The Authors. 2-4) Reproduced with permission.^[13] Copyright 2014, AAAS. 2-5) Reproduced with permission.^[87] Copyright 2016, Wiley-VCH. 2-6) Reproduced with permission.^[14] Copyright 2014, The Authors. 3-1) Reproduced with permission.^[15] Copyright 2011, AAAS. 3-2) Reproduced with permission.^[83] Copyright 2016, The Authors. 3-5) Reproduced with permission.^[9] Copyright 2017, Elsevier. 3-6) Reproduced with permission.^[3] Copyright 2016, Elsevier. 4-1) Reproduced with permission.^[53] Copyright 2015, Elsevier. 4-2) Reproduced with permission.^[52] Copyright 2001, Elsevier. 4-3) Reproduced with permission.^[89] Copyright 2015, Elsevier. 4-4) Reproduced with permission.^[90] Copyright 2015, American Society of Mechanical Engineering. 4-5-left) Reproduced with permission.^[92] Copyright 2006, Cambridge University Press. 4-5-right) Reproduced with permission.^[94] Copyright 2007, Elsevier. 4-6) Reproduced with permission.^[98] Copyright 1998, ACS.

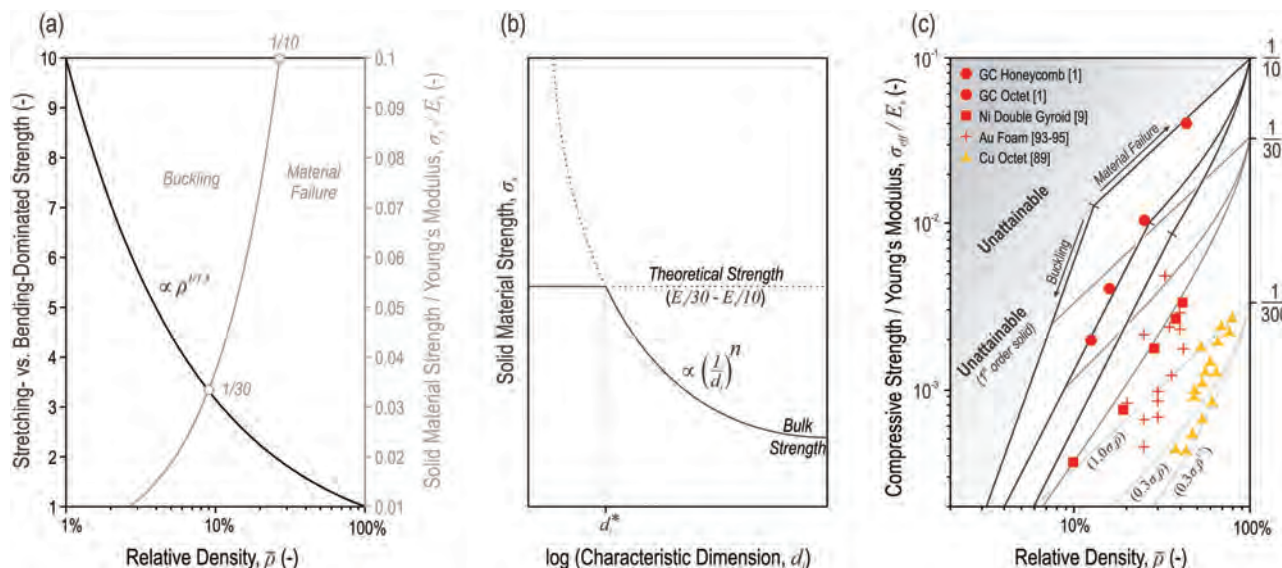


Figure 5. The impact of architecture and size effects on the strength of nanolattice materials. a) The strength gain of stretching- over bending-dominated behavior increases exponentially with decreasing relative density (black curve). Buckling before material failure becomes increasingly critical with a growing ratio of strength-to-Young's modulus (σ_s/E_s) of a lattice's constituent material; the gray curve shows the transition between Euler beam buckling and material failure of an ideal solid beam octet lattice with rigid joints. b) Schematic representation of size-dependent material strengthening. c) Normalized effective strength (σ_{eff}/E_s) vs relative density material property chart showing the interaction of size-dependent material strengthening and architectural instability. The cellular material bounds for σ_s of $E_s/300$, $E_s/30$, and $E_s/10$ are shown. Compare Figure 4 for data point legend.

Increasing the anisotropy of a topology can lead to a strength increase of a factor of up to three. Geometric parameters of up to $C = 1$ can be reached when lattice elements are added, removed, or varied in diameter, or when unit cells are stretched corresponding to a preferred loading direction.^[14,90,103] Due to the effects of anisotropy, lattices with non-rigid designs can have strengths comparable to rigid architectures and may outperform them in some cases. For example, lattices with stretched hexagonal-prismatic unit cells were shown to have a 20% increased strength compared to regular octet lattices.^[87] Values of $C = 1$ and $a = 1$ correspond to the Voigt bound (Equation (1)), which represents the maximum theoretical effective strength for any cellular material. It can be achieved when the entire solid material of a structure is aligned with the direction of an applied load and therefore is stressed uniformly, such as for ideal honeycombs under out-of-plane loading or a square lattice under biaxial loading (Figure 2e). Values of $C < 1$ arise due to the misalignment of lattice elements with respect to an applied load. In practice, bending of lattice elements, imperfections, Poisson expansion, instability effects, and experimental misalignment result in additional knockdown of this geometric prefactor.

At sufficiently low relative densities, lattice elements may be slender enough to collapse by elastic buckling before reaching the material strength. The effective strength can then be obtained by replacing σ_s in Equation (1) with the elastic buckling strength of a lattice element (σ_{eb}). The Euler buckling criterion of a slender beam is $\sigma_{eb} = k^2\pi^2IE_s/(Al^2)$, where E_s is the Young's modulus of the constituent material, I is the area moment of inertia, A is the cross sectional area, and l is the length.^[51,53,104] The constant k depends on the boundary conditions and is equal to 2 for rigidly jointed beams and 1 for pin-jointed beams. For a slender honeycomb wall under

out-of-plane loading, the buckling-strength relationship $\sigma_{eb} = KE_s/(1-\nu_s^2)(t/L)^2$ is valid, where ν_s is the Poisson's ratio of the constituent material, t is the thickness and L width of the cell wall, and K is the constraint factor, which is 2 for the pin-jointed and 6.2 for the clamped case.^[51,105] Correspondingly, the effective elastic buckling strength (σ_{eff}^{el}) is given by:

$$\sigma_{eff}^{el} = D\bar{\rho}^b E_s \quad (2)$$

where D is a geometric parameter and the exponent b is 2 for any open-cell material^[51] and 3 for honeycombs under out-of-plane loading.^[105] For stochastic foams $D \approx 0.05$, and for honeycombs $D \approx 6$ has been found.^[51,105] For an octet lattice with circular, rigidly connected, solid struts, a geometric parameter of $D \approx 0.123$ can be approximated.^[52,53] By relating Equation (1) and (2) it is possible to find the relative density at which the failure mode switches from yielding or fracture to elastic buckling as a function of the ratio between σ_s and E_s (Figure 5a).

Instability events like buckling are increasingly relevant for the design of nanolattices. Instability plays a role in the effective strength of a lattice when the constituent material strength is sufficient to prevent failure before the onset of the instability. If we take $\sigma_s \approx E_s/300$, as is the case for many macro-scale cellular metals and ceramics, material failure will generally occur well before the onset of any structural instabilities, meaning buckling will not play a role in the lattice strength (Figure 5a). This changes dramatically when the ratio between σ_s and E_s increases. From Equation (2), the failure of a solid-beam octet nanolattice will be governed by elastic buckling below $\bar{\rho} \approx 9\%$ when $\sigma_s = E_s/30$ and below $\bar{\rho} \approx 27\%$ when $\sigma_s = E_s/10$ (Figure 5a). Similar relationships can be found for other types of architecture. The high constituent material strength of carbon nanolattices can therefore explain the scaling behavior

of their effective strength; the failure of samples with a relative density between 13% and 16% is governed by elastic buckling. Hollow-beam lattices and hierarchical architectures can have significantly improved buckling resistance, facilitating linear scaling of the strength with relative density down to 0.01% (Figure 4b). Shell buckling may still limit the strength of very thin-walled structures, as low density hollow-beam nickel octet microlattices show.^[19]

As the relative density of a lattice increases beyond $\approx 10\%$, its elements start to become short and squat, and the first-order scaling laws in Equation (1), which are derived assuming lattices consist of slender beams, begin to break down.^[51] The theoretical maximum effective strength of an isotropic cellular material can be estimated across all relative densities using the nonlinear Hashin–Shtrikman (H–S) bounds^[9,106] of:

$$\sigma_{\text{eff}} = \frac{2\bar{\rho}}{\sqrt{4 + \frac{11}{3}(1 - \bar{\rho})}} \sigma_s \quad (3)$$

Below $\bar{\rho} \approx 10\%$, Equation (3) can be approximated by the first-order scaling relationship in Equation (1) with values of $a = 1$ and $C \approx 0.72$. This maximum strength bound is over two times higher than the ideal bound for near isotropic open-cell lattices, but may be attainable with closed-cell designs.^[107] Gibson and Ashby have defined the transition between true cellular solids and solids containing isolated pores to be at $\bar{\rho} \approx 30\%$.^[51] Above this relative density the nonlinear H–S-bounds can be used to explain the scaling behavior, such as of the copper octet lattices and nickel gyroids (Figure 5c).

The mechanical behavior of hollow-beam and core–shell composite lattices is not always well captured by classical lattice theory. The mechanistic underpinnings for their strength are complex and are a subject of current research. Hollow lattices are often observed to have a weaker strength than that predicted by Equation (1), and this is primarily attributed to localized bending of the hollow nodes. Strength is limited by the “weakest link”, so bending of hollow nodes may not have much effect on lattices with a bending-dominated topology, as is the case for hollow-beam nickel lattices made by SPPW,^[15] whose effective strength scaling is well described by Equation (1). However, hollow node bending can have a drastic effect on the strength of stretching-dominated topologies. Also, high sensitivity to processing-related imperfections such as waviness and nonideal beam cross-sections has been discussed.^[13,16,19,82] The linear strength scaling observed in rigid micro- and nanolattices at low $\bar{\rho}$ is up to 10 times lower than the strength predicted by theory (Figure 4b); using Equation (1) to estimate the constituent solid material strength (σ_s) of hollow-beam alumina lattices results in values of $\sigma_s \approx E_s/300$ (Figure 4b), despite values of $\sigma_s \approx E_s/30$ having been found for single lattice elements.^[108]

Shape optimization of lattice nodes may have the potential to improve the strength in particular of hollow-beam and core–shell nanolattices. In core–shell lattice materials, stress concentrations were shown to increase dramatically with an increasing stiffness gradient between the core and shell, with the extreme case being a hollow shell.^[3,87] For polymer–alumina core–shell lattices, stress concentrations were also shown

to cause substantial knockdown of the tensile strength with respect to the compressive strength.^[87] Hollow “shellular” lattices,^[109] namely lattices without struts that consist only of smooth interconnected nodes, were developed with the aim to reduce stress concentrations. Although despite their optimized node shape, they have a fairly low geometric parameter, C , and a high sensitivity to shell buckling instabilities, and show little improvement in strength with respect to non-shape-optimized hollow-beam octet lattices.^[109,110]

2.1.3. Size Effects and Strength

When the length scale of architecture of a cellular material is small enough to fully exploit size-dependent strengthening, its effective strength may be on the order of 30 times higher than that of self-similar macroscale materials. A brittle perfect crystal reaches the theoretical strength (σ_{th}) when the atomic bonds of two adjacent atomic layers break simultaneously. Based on an equilibrium analysis of the work required to cleave the crystal and the energy released in the formation of the new surfaces, σ_{th} has been estimated to be on the order of $E_s/10$.^[102] For ideal ductile materials, a theoretical strength of $E_s/30$ has been derived based on a shear failure criterion.^[102] In practice, the synthesis of monolithic bulk materials involves the introduction of imperfections such as dislocations, grain boundaries, voids and cracks, all of which give rise to typical bulk strengths of metals and ceramics on the order of $E_s/300$. The relative strength–density property chart in Figure 5c illustrates the cellular material bounds for different ratios of σ_s to E_s .

The strength of a material depends on the characteristic intrinsic size, i.e., the length scale of its microstructure meaning the size and distribution of its flaws. Corresponding to Griffith’s law,^[28] the fracture strength (σ_f) of brittle materials increases as:

$$\sigma_f = Y \frac{K_{Ic}}{\sqrt{\pi a_c}} \quad (4)$$

when the critical size of a crack (a_c) is reduced.^[102] The fracture toughness (K_{Ic}) quantifies a material’s resistance to crack growth, and Y is a nondimensional geometric parameter. In bulk technical ceramics, the size of cracks is typically on the microscale or larger, resulting in characteristically low fracture strengths.^[51] The yield strength (σ_y) of ductile metals is generally governed by the presence of obstacles to dislocation motion and may be described by:

$$\sigma_y = \sigma_0 + \frac{k}{l^n} \quad (5)$$

where σ_0 usually is the bulk strength and k and n are constants.^[30] The characteristic length (l) traditionally represents the size of grains or particles or the spacing between dislocations. When l is taken to be the grain size, Equation (5) is known as the Hall–Petch relation,^[111,112] which describes strengthening in polycrystals with decreasing grain size. In this equation, $n = 1/2$ and σ_0 is an estimate of the strength of a single crystal (for $l \rightarrow \infty$). Strengthening mechanisms like

the Hall–Petch relation are well established, although the grain sizes of bulk metals are typically above the nanoscale.

Ultimately the intrinsic size of a material is limited by its extrinsic size, i.e., its characteristic dimensions (d_i). As the size of a material approaches the nanoscale, this finiteness becomes “feelable” and it can be assumed that intrinsic features are on the same length scale as extrinsic ones, i.e., $a_c, l \sim d_i$. This leads to the well-known “smaller is stronger” phenomenon,^[27,29–31] where strength have been found that far exceed bulk values. There is no universal scaling law for size-affected material strengthening as it arises due to the complex interaction of a number of different intrinsic and extrinsic mechanisms, yet based on relations like those in Equation (4) and (5), the strength of both brittle and ductile solids (σ_s) is often estimated to increase as:

$$\sigma_s \propto \left(\frac{1}{d_i}\right)^n \quad (6)$$

at small scales (Figure 5b), where n generally is in the range of 0.5–1.^[29,30]

Below a certain critical dimension (d_i^*), which is typically on the order of 1–100 nm, σ_s can reach values as high as the theoretical strength. Theoretical strength has repeatedly been demonstrated with single crystalline ceramic and metallic specimens,^[37] where the confined extrinsic sizes result in a near ideal material. Flaw insensitivity has also been discussed for length scales below d_i^* .^[29] According to Equation (4), the stress needed to fracture a brittle material with a critical crack length smaller than $a_c^* \propto d_i^*$ would exceed the theoretical strength. Notch insensitivity in ductile single crystalline gold nanowires has been shown to result from strain hardening.^[48] No polycrystalline metals that reach σ_{th} have been found, and the critical dimension relates instead to the peak strength of the grain boundaries.^[27,31,113] When dislocation loops no longer fit inside grains, grain boundary strengthening breaks down.^[27] In size ranges below d_i^* , mechanisms such as sliding of grains at the free surfaces can induce a weakening effect.^[27,31,114]

In a lattice, the characteristic dimension (d_i) may be the beam diameter or the wall thickness of an individual lattice element, which in a nanolattice may be designed as small as the critical dimension (d_i^*). This mechanism allows nanolattice materials to substantially exceed the limits of macroscale cellular materials, as Figure 4b and Figure 5c show. By contrast, self-similar macrolattices with $d_i \gg d_i^*$ cannot benefit from the size-affected strengthening in Equation (6).

Pyrolytically derived ceramic nanolattices exploit material strengths on the order of the theoretical strength. Figure 5c shows that the effective strength of the glassy carbon honeycombs^[1] and the nanolattices with $\bar{\rho} \approx 25\%$ ^[1] reach the cellular-materials’ bounds for stretching-dominated behavior corresponding to $\sigma_s = E_s/10$ with $E_s = 28$ GPa.^[99] High purity of the starting resin results in a low population of flaws after the material is transformed into a ceramic.^[84] Polymer-resin-derived SiOC lattices and honeycombs with macroscale dimensions already achieve remarkable strength, and when the dimensions are reduced, the flaw sizes decrease correspondingly. For a solid-beam lattice, a surface crack along the diameter of a strut may be a critical strength-limiting

flaw. If a fracture strength of $\sigma_f = E_s/10$ is used, Equation (4) gives a critical flaw size of $a_c \approx 30$ nm for glassy carbon with $E_s = 28$ GPa,^[99] $K_{Ic} = 0.91$ MPam^{0.5},^[115] and $Y = 1$.^[116] The strut diameters of the glassy carbon nanolattices are in the range of 200 nm, flaws are likely to be much smaller than 30 nm, and based on Equation (4) it is reasonable to expect corresponding material strengths of $E_s/10$.

Atomic-layer-deposited hollow-beam ceramic and core–shell composite nanolattices notably benefit from material strengthening size effects, but they may not make full use of them in their effective properties. In agreement with Equation (6) with $n = 0.5$, tensile experiments on polymer–alumina composite lattice elements^[108] and bulge tests on suspended alumina membranes^[100] showed that the strength of atomic-layer-deposited alumina shells increases up to 5.5 GPa when their thickness is reduced below 50 nm. The theoretical strength of these materials has not been reached, a fact that may be attributed to the porosity of atomic layer deposited ceramics, which is as also reflected in their reduced density^[117] and Young’s modulus^[100] compared to the corresponding bulk material. Although strengths of 5.5 GPa are below the theoretical limit, they are as much as 20 times higher than the corresponding bulk strength.^[51,118] As described in Section 2.1.2, strength gains in hollow-beam and core–shell composite lattices are often not fully reflected in their effective strength due to their shell-based designs and their sensitivity to structural imperfections. The constituent material strength of sintered particle-based lattices^[19] is limited by their high flaw population, which may be rather independent of the length scale.

Single crystalline metallic nanolattices achieve material strengths in the range of the theoretical shear strength. Interpolating the measured effective strength of the nickel gyroids^[9] to that of the fully dense material gives $\sigma_s = E_s/30$ with $E_s = 214$ GPa^[51] (Figure 5c). Nickel gyroid films have a columnar polycrystalline structure with in-plane grain sizes of about 1.5 μ m. However, their constituent unit cell sizes of 45 nm enable strengths on the order of single crystalline nickel. Nanoscale single crystal metal specimens approach theoretical strengths via mechanisms such as dislocation starvation, wherein dislocations exit at free surfaces and leave behind a dislocation-free material.^[31] The critical dimension for face-centered cubic nickel can be approximated to be 13 nm using Equation (5), with k estimated from the Burger’s vector and the shear modulus and $n = 0.66$,^[119] this matches the strut diameter of the nickel gyroids.^[9] Similar relations can be found for nanoporous gold foams, whose effective strength has been described over a feature length scale range of 10–900 nm by replacing σ_s in Equation (1) with Equation (5);^[94] comparable systematic studies have not yet been performed for nanolattices.

The benefit of small-scale structuring may be limited in lattices made from polycrystalline metals. The strength of electrodeposited nanocrystalline nickel-based thin films, similar to those used in some hollow-beam microlattices,^[15,19,83] has been estimated to be ≈ 2 GPa.^[19,101] While this strength is higher than that of many bulk nickel alloys, strengths of 4.3 GPa have been found in amorphous nickel-based films of core–shell composite lattices.^[88] Compression tests of 7-nm-grained hollow lattice beams showed a drastic decrease in strength when wall thicknesses were reduced from 500 nm to 150 nm, the magnitude of

which could not be explained by geometry alone and was also attributed to the “smaller is weaker” effect that is induced by the sliding of grains at the free surfaces.^[101] A similar behavior may explain the drop in strength of hollow-beam nickel octet microlattices^[19] shown in Figure 4. As dimensions are reduced, the fraction of grains at the free surfaces increases, intensifying surface sliding weakening effects. This is distinctly reflected in low-strength hollow-beam gold lattices synthesized via sputtering,^[90] which have grain sizes of 25–50 nm and feature dimensions down to 200 nm. Copper microlattices with strut diameters in the range of 1–3 μm mostly consist of grains spanning entire lattice members.^[89] They are therefore neither fully single- nor polycrystalline, and corresponding strengthening and weakening effects may be present at the same time. The constituent material strengths of copper microlattices can be estimated to be on the order of $E_s/300$. However, their effective strength has been shown to be three times higher than the strength of 10- μm -thick polycrystalline copper films synthesized under identical conditions.^[89]

2.2. Stiffness

In quantifying the performance of lightweight materials, the specific stiffness, or the ratio between Young’s modulus and density, is as important as the specific strength. Lattice stiffness depends on architecture, and topologies that are optimized for high strength generally achieve high stiffness. In contrast to strength, reducing the length scale of lattice architectures has not been shown to lead to any size-affected increase in the stiffness of the constituent materials. Size effects in the stiffness are still a subject of current research and may be limited to a small number of materials, such as carbon.^[43–47] Taking advantage of stiffness size effects in nanolattices may require a further decrease in feature sizes beyond what is achievable today.

Despite a lack of size-affected benefit to their constituent stiffness, micro- and nanolattices have pioneered new regions in the stiffness versus density material property space. **Figure 6** compares different nano-, micro- and macrolattices, stochastic nanoporous foams and commercially available bulk materials. Rigid architectures of hollow-beam alumina^[13,19,82] and nickel-based^[19] nano- and microlattices populate the ultralight density “white space” below 0.01 g cm^{-3} . These materials have specific stiffnesses that do not considerably degrade over several orders of magnitude decrease in density. As a result, they substantially outperform nonrigid lattices of the same density and are demonstrably less dense than stochastic cellular materials of comparable stiffness. Ultralight micro- and nanolattices achieve new material property spaces for both stiffness and strength, but in higher density regimes of 0.1–1 g cm^{-3} , the stiffness of nanolattices does not reach the same “white space” that is reached for strength.^[1–3,14] This illustrates the beneficial impact of size effects on nanolattice strength and its corresponding absence in stiffness.

Analogously to strength, the effective stiffness of cellular materials (E_{eff}) versus relative density is classically modeled by the relationship:

$$E_{\text{eff}} = F\bar{\rho}^g E_s \quad (7)$$

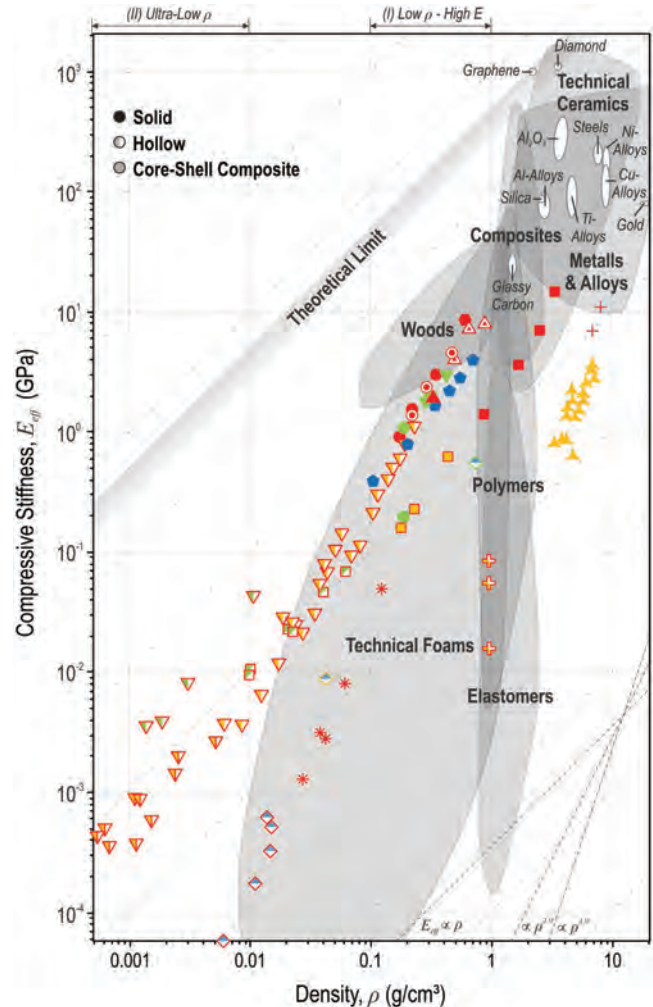


Figure 6. Compressive stiffness vs density materials property chart comparing different nano-, micro-, and macrolattices as well as stochastic nanoporous and commercial bulk materials. Certain hollow-beam micro- and nanolattices reach far into the chart’s ultralow- ρ “white space”. For graphene,^[44] the tensile stiffness is shown. See Figure 4 for data point legend.

where E_s is the Young’s modulus of the constituent solid material, F is a geometric parameter, and $g = 1$ and 2 are the exponents for ideal stretching- and bending-dominated behavior, respectively. The impact of bending on the stiffness is more pronounced than it is for the strength, which has a scaling exponent of $a = 1.5$ for bending-dominated behavior. In the ultralight regime, stochastic materials can have scaling exponents of $g = 3$.^[120] Geometric parameters for open-cell foams of $F \approx 1$ have been found,^[51] and for the octet lattice, $F = 1/9 - 1/5$ has been predicted mathematically^[52] depending on the loading direction. As is the case for the strength, anisotropy can lead to increased stiffness in a preferred loading direction but at the cost of decreased stiffness in other directions. The effective stiffness of certain closed-cell designs has been predicted to reach the H–S upper bound without sacrificing isotropy.^[107]

It can be seen in Figure 6 that the stiffness of many lattice materials does not scale perfectly linearly or quadratically with the density, but instead falls somewhere in between. This

occurs because the relationship defined in Equation (7) is only valid for lattices with slender beams. Equation (7) provides a useful guideline for quantifying the performance of a given topology, but it often obscures some of the more complex mechanical phenomena observed in actual lattices, particularly in those made from hollow beams or shells. The stiffness of lattices can also be affected by structural defects like missing strut members, stress concentrations at nodes, local shearing and bending in strut members, and waviness or misalignment of the struts;^[13,19] investigations into these effects are a topic of ongoing research.

2.3. Recoverability, Energy Absorption, and Damage Tolerance

The deformability of materials can be greatly enhanced through the addition of architecture. Micro- and nanolattices are able to take intrinsically brittle and low-elastic-limit materials—like ceramics and certain classes of metals—and use them to create metamaterials that are able to undergo large deformations of up to 80% compressive strain without catastrophic failure.^[13,15,18,82,83] This is primarily enabled by scale-independent architectures that deform in ways that accommodate large displacements and in part because of nanoscale constituent materials that can withstand larger elastic strains due to increased yield strengths. Enhancing the deformability gives rise to three important architected material properties: recoverability, energy absorption, and damage tolerance.

Hollow-beam micro-^[15,18] and nanolattices^[13,82] made from both ductile and brittle constituent materials have demonstrated near 100% recoverability after compression to 50% strain (Figure 7). A transition from brittle failure to recoverable deformation was observed below a certain critical wall-thickness-to-strut-diameter ratio (t/D). This phenomenon was attributed to shell buckling of thin-walled struts, which can form low stress hinges that prevent catastrophic failure and accommodate large macroscopic reversible strain.^[13,17,18] Recoverability has been shown with both rigid and nonrigid topologies, but

relative densities are generally required to be very low to enable shell buckling.

Controlling the activation of different failure mechanisms is key to enabling the enhanced deformability observed in nano- and microlattice materials. In a lattice the primary failure mechanisms are constituent material failure, beam buckling, and shell buckling in lattices with hollow members. The strength of the solid material (σ_s) is an intrinsic material property, but it can be greatly affected by feature size, as is discussed in Section 2.1.3. The beam buckling strength was defined in Section 2.1.2 for slender beams using the Euler buckling criterion of $\sigma_{eb} = k^2 \pi^2 E_s / (Al^2)$. The shell buckling strength for hollow circular beams is $\sigma_{sb} = E_s (t/R) / \sqrt{3(1-\nu^2)}$, where t is the wall thickness, R is the beam radius, and ν is the constituent material Poisson's ratio.^[121]

The failure mechanism that governs the initiation of failure can be determined by setting these three equations equal. The critical transitions ratios between material failure and beam buckling, material failure and shell buckling, and beam and shell buckling for a thin-walled hollow circular beam respectively are:

$$\left(\frac{R}{l}\right)_{s \rightarrow eb} = \frac{1}{\pi} \sqrt{\frac{\sigma_s}{2E_s}}$$

$$\left(\frac{t}{R}\right)_{s \rightarrow sb} = \frac{\sigma_s}{E_s} \sqrt{3(1-\nu^2)}$$

$$\left(\frac{tl^2}{R^3}\right)_{sb \rightarrow eb} = 2\pi^2 \sqrt{3(1-\nu^2)}$$

Using these relationships as guidelines, architected materials can be designed to undergo failure via one of these mechanisms using any constituent material.

Buckling is the cornerstone of much of the deformability, recoverability and energy absorption observed in micro- and

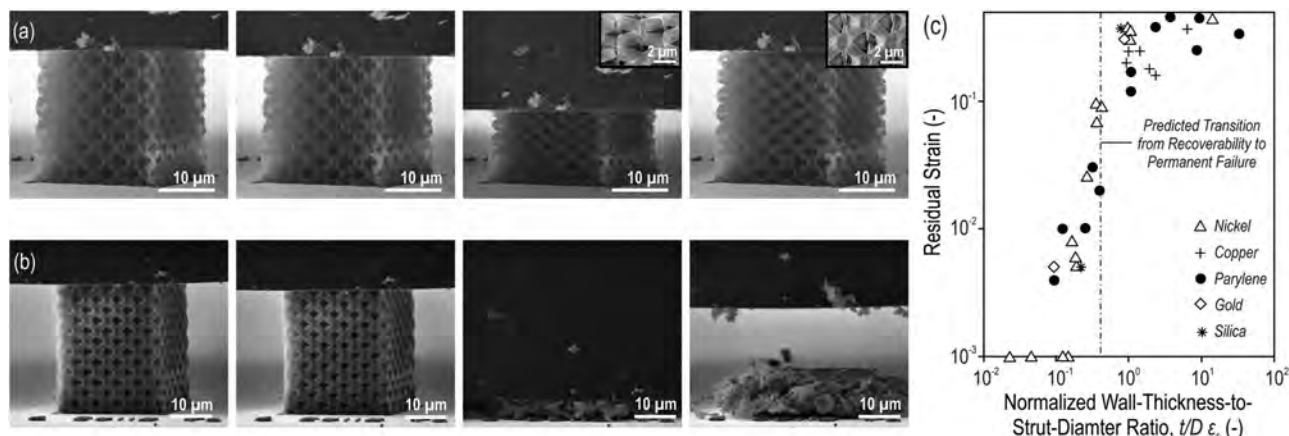


Figure 7. Recoverability of micro- and nanolattices. a) Compression of thin-walled and b) thick-walled hollow-beam alumina nanolattices, demonstrating the effect of shell buckling on increasing the deformability and recoverability of intrinsically brittle materials. c) Residual strain of hollow-beam microlattices fabricated via SPPW, after 50% compression vs wall-thickness-to-strut-diameter ratio (t/D) normalized by the yield strain of the constituent material. The critical ratio t/D that guarantees full recoverability from any imposed macroscopic strain can be estimated analytically. a,b) Reproduced with permission.^[13] Copyright 2014, AAAS. c) Adapted with permission.^[18] Copyright 2013, The Authors.

nanolattices. It is an intrinsically elastic phenomenon, meaning that if the stress in a post-buckled beam does not reach the yield or fracture strength of the material, a structure will be able to recover to its original shape. This recovery can occur independently of architecture, and lattices can simultaneously be designed to be recoverable and to have high strength and stiffness.

In lattices with beam buckling dominated failure, beams must be highly slender and nodes must either be reinforced or able to rotate in order to ensure post-failure recoverability. Node reinforcement, such as selectively increasing the material thickness at the node, can be done in any architecture, but node rotation is best enabled in architectures with nonrigid topologies like octahedral-type unit cells,^[122] which have intrinsic mechanisms that allow for a greater degree of deformation. In lattices with shell buckling dominated failure, shell walls must be thin and have large radii of curvature to improve structure recovery. In locally buckled sections of beams, a compliant hinge is formed that enables greater deformation.^[13,55] Permanent failure can and does often occur in these locally buckled regions, but structures can still globally recover if the failure is unable to propagate to the rest of the beam. This behavior has been observed experimentally, but there is not a well-developed theory on how to design geometries that form buckled hinges that can impede brittle failure propagation.

The ability of a recovered structure to retain its initial strength and stiffness is crucial to its utility as an engineering material. Due to the activation of certain failure modes and the buildup of local damage, the post-yield stiffness and strength of a recovered structure is generally lower than that of the undeformed material.^[15,55,82] Reducing the applied strain on a structure can help it to retain its strength, but it is difficult to completely preserve the initial mechanical properties. When repeatedly compressed to the same strain, structures often exhibit a stable cyclic behavior.^[15,55,82] This occurs because failure modes that were activated in the initial cycle can be reactivated, minimizing the accumulation of additional damage.

Fracture, plastic work, and intrinsic material damping dissipate energy in continuum materials; in recoverable lattices, buckling and other hysteretic instabilities are the dominant mechanisms that cause energy dissipation. Beams that buckle often exhibit a bi-stable behavior, during deformation they undergo a snap-through between a buckled and unbuckled state. This snap-through event induces high-frequency vibrations, which are eventually damped, resulting in energy dissipation. The character of the snap-through events can also be controlled by changing the type of buckling; for example, Euler buckled beams in uniaxial compression will maintain an approximately constant load, while shell-buckled beams will have a drop in load carrying capacity in their post-buckled configuration.^[123] In lattice architectures buckling and snap-through events can be coordinated to dissipate energy in a controlled manner, and structures can be designed to enable layer-by-layer deformation, uniform crushing, or localized failure.^[13,82,83,124–127] One important characteristic damping parameter is the mechanical loss coefficient, defined as $\eta = \Delta U / 2\pi U$, where U is the stored elastic strain energy and ΔU is the dissipated strain energy.^[128] It has been shown that lattices can be designed to have exceptionally high damping figures of merit $E_{\text{eff}}^{1/3} \eta / \rho$.^[55] Structures

with optimized damping will generally have low relative densities ($\bar{\rho} < 0.1\%$) and hence low strength and stiffness. High-density architected materials that dissipate energy via snap-through buckling of hinges while maintaining recoverability have been proposed.^[124–127]

When maximizing energy dissipation per unit mass, e.g., for the development of protection systems, plastic flow is the mechanism of choice. Polymer and ceramic–polymer composite nanolattices fabricated by interference lithography^[62] were shown to dissipate exceptional amounts of energy per unit mass.^[129–132] This was attributed to the ability of the structure to spread plastic deformation over a large volume; in a bulk material, failure is generally localized to a single shear band or necking region, whereas failure in lattices can occur homogeneously throughout a sample. Although plastically deformable nanolattices possess exceptionally high specific energy dissipation, their deformation is not recoverable and therefore not repeatable.

The design of damage tolerant and lightweight materials is still a major engineering challenge. The fracture toughness of a periodic lattice scales with the square root of the unit cell size, meaning that it decreases when the unit cell size is reduced.^[49,133–135] For octet or hexagonal lattices, a single “missing” beam introduces a stress concentration.^[133,135] In contrast, Kagome lattices are insensitive to flaws smaller than a certain transition length.^[133,136] This transition length scales with $1/\bar{\rho}$ and can be several times the unit cell size.^[133] In nanolattices, material strengthening size effects should counteract the size-dependent weakening of the architecture.^[135] Therefore, there may be a slight benefit to the toughness of nanolattices, but the substantial design challenge remains. A possible solution might be in the use of hierarchical designs, where larger unit cells could impart toughness, while smaller nested unit cells would be used to exploit size-dependent strengthening effects. Hierarchical micro- and nanolattices have also been observed to have increased recovery beyond that of simple periodic lattices because failure is localized to sections of hierarchical beams, allowing structures to undergo permanent damage while still recovering globally.^[82,83]

There are many other size-affected material properties like enhanced ductility,^[38,42] fatigue resistance,^[137] and fracture toughness^[29] that have been observed in nanomaterials but have not been used in practical implementations. Future developments in nanoarchitected material design may rely on these and other size affected material properties to push the limits of mechanical performance.

2.4. Auxetic Behavior

The concept of auxetics,^[138] namely materials with negative Poisson's ratio, holds great promise for adding new functionality to nanolattices. At the macroscale, auxetic structural designs are progressively employed in the development of novel products, especially in the fields of intelligent expandable actuators, shape morphing structures, and minimally invasive implantable devices.^[139] There is a wealth of possible auxetic designs, many of which rely on folding and unfolding mechanisms of nonrigid topologies, and there are many possibilities

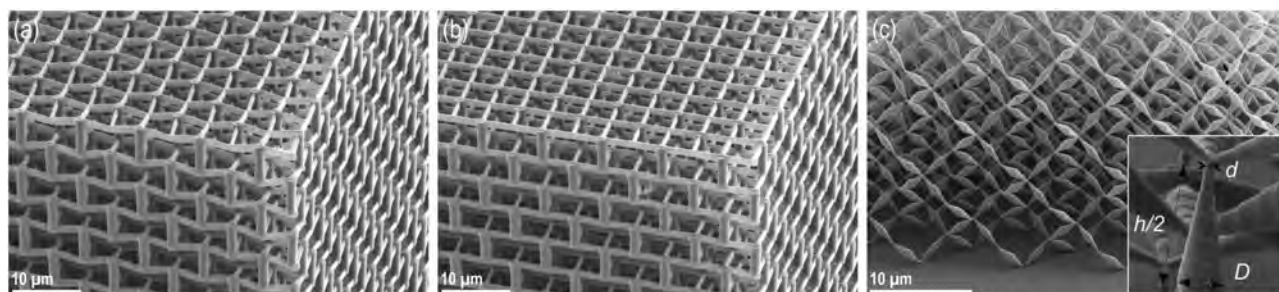


Figure 8. Nanolattices achieving extreme tunable mechanical properties. a,b) Auxetic lattices based on the bow-tie design with four-fold symmetry, subtle structural variation changes Poisson's ratio from -0.14 (a) to 0.01 (b). c) Pentamode lattices have a very large bulk modulus compared to the shear modulus. Ideally, the connecting points of the double-cones would be infinitely small and control the modulus ratio. Minimum cone diameters d of 550 nm were achieved. By increasing the cone diameter D , the mass density of the lattice can be adjusted. a,b) Reproduced with permission.^[20] Copyright 2012, Wiley-VCH. c) Reproduced with permission.^[21] Copyright 2012, AIP Publishing LLC.

for the creation of three-dimensional architectures that achieve Poisson's ratios down to -1 or lower.^[140] Poisson's ratio of zero describes a material that retains its lateral dimensions upon compression, while Poisson's ratio of -1 describes a material that will shrink laterally an equal amount to what it is compressed vertically, thereby keeping its shape but not its volume. Poisson's ratios of -0.8 have been demonstrated for macroscopic lattices, and a design for an ideal dilational metamaterial with Poisson's ratio of -1 has been proposed.^[67] Materials with Poisson's ratios of -1 require infinitesimal joints to achieve their performance. The small dimensions and enhanced material properties of nanolattices may be able to replicate such ideal joints.^[67] Auxetic lattices based on the bow-tie design were created (Figure 8a,b) exhibiting different Poisson's ratios depending on the precise shape of their bow-tie elements.^[20] In these materials, subtle design changes were used to shift Poisson's ratio from negative to zero or even positive values. Applying thin alumina coatings using atomic layer deposition to the polymer structures increased the stiffness while leaving Poisson's ratio unaffected. With the ever increasing precision in manufacturing capabilities, progressive size reduction of auxetic geometries may allow the exploitation of mechanical size effects in nanolattice materials with tailorable adaptivity.^[141]

2.5. Metafluidic Behavior

Pentamode metamaterials, also referred to as metafluids, have a very large bulk modulus compared to their shear modulus, which ideally is zero. A material with a very large bulk modulus will have little volume change during deformation, meaning its Poisson's ratio is close to 0.5 .^[21] A material with a very small shear modulus will "flow away" under shear in a manner similar to a fluid.^[21] Pentamode metamaterials combine these two principles to generate an elasticity tensor with only one non-zero eigenvalue and five eigenvalues that are negligibly small.^[60] Based on a concept by Milton and Cherkaev,^[142] these materials can be created using rigid, double-cone elements connected to each other at their point-like tips and arranged in a diamond-type lattice (Figure 8c).^[21] Actual structures are approximations of the ideal pentamode material having zero diameter of the cone ends, but minimum cone tip diameters of 550 nm have been achieved, resulting in bulk-to-shear modulus

ratios of approximately 1000 .^[21] The bulk modulus of such a double-cone lattice is mainly determined by the diameter of the cone tip; increasing the cone diameter will primarily affect the mass density of the lattice and has less significance for the modulus.^[143] If minimum cone diameters smaller than 550 nm were achieved, a further enhancement of the bulk-to-shear modulus ratio should be possible, which would facilitate the fabrication of three-dimensional transformation-elastodynamic architectures^[21,144] like free-space cloaks that render objects invisible to incident radiation. For elastomechanical cloaking, macroscale pentamode lattices with different modulus ratios were combined to render a physical object "unfeelable".^[145] The concept of reducing the dimensions of the connection points in a lattice was applied to design nanolattices with maximized anisotropy of the elastic modulus.^[146] These face-centered cubic nanolattices were created using interference lithography and achieved an elastic-to-shear-modulus ratio of four.

2.6. Non-Mechanical Properties & Multifunctionality

Photonic metamaterials^[62–64] are micro- or nanoarchitected to enable interaction with electromagnetic waves such as visible light (wavelength 400 – 700 nm). Notable examples include silicon woodpile lattices with engineered defects exhibiting near-infrared complete photonic bandgaps, chiral and bichiral polymeric photonic crystals featuring polarization stopbands, photonic quasicrystals, and polymeric woodpile lattices with spatially tailored density, providing invisibility cloaking at optical wavelengths.^[22,23] The development of tailored photoresists for multiphoton lithography and multilaser polymerization approaches based on stimulated emission depletion (STED) achieve significantly increased resolution,^[147–149] further enhancing the opportunity to design nanolattices with unique optical properties.

Phononic metamaterials^[62,65,66] are designed to interact with mechanical waves. Mechanical waves travel within a homogeneous and isotropic medium with the dispersion relation $\omega = ck$, where ω is the frequency, k is the wave vector, and c is the velocity of propagation in the longitudinal or shear direction. If the medium has an intrinsic periodicity though, a much more complex dispersion relation results, with several acoustic and optical branches. When properly designed, the periodic medium might

exhibit “bandgaps”, i.e., ranges of frequency where wave propagation is prohibited along any direction. Acoustic metamaterials with unit cells in the centimeter range have been developed extensively.^[150] Recently, DLW has been employed to fabricate phononic crystal at the microscale, which can tailor ultrasonic wave propagation.^[151] Phonons (thermal vibration within the atomic lattice) are largely responsible for heat conduction in non-metallic solids. In principle, nanoarchitected materials could be designed to interact destructively with phonons, possibly resulting in exceptionally low thermal conductivity; the key challenge is that phonons responsible for heat conduction have extremely low wave length, and hence can only interact with architected materials with periodicity on the order of ~ 1 nm.^[66]

Cellular materials have been exploited for thermal management for decades.^[51,152] When fabricated in ceramic constituent at very low density, they provide exceptionally low thermal conductivity and diffusivity; conversely, when fabricated in metal with open porosity, they enable active cooling and efficient heat transfer from the hot to the cold side.^[153] Optimized lattice architectures such as multiscale heat pipe structures^[154] substantially improve thermal properties compared to stochastic foams.^[155] In all these applications, length scale reduction promises performance improvements, thanks to size effects in the thermal conductivity.^[32,33,156]

Lattice materials with tunable thermal expansion can be designed by properly combining different constituent materials, or folding mechanisms similar to those of auxetic structures. A number of possible designs have been proposed and demonstrated at the macroscale.^[56,157–159] If fabricated at smaller scale, these multi-constituent architected materials would be useful for applications where dimensional accuracy is essential under continuous temperature excursions, e.g., positioning of micromirrors^[160] in space applications. Recently, multimaterial PμSL has been used to develop a bimaterial negative coefficient of thermal expansion polymeric lattice with unit cell size of ≈ 5 mm.^[161] In the context of thermal size effects, the ability to generate similar multi-material topologies with dimension reduced by several orders of magnitude may hold opportunities for novel applications.

Electrochemical phenomena such as upon lithiation/delithiation of electrodes for advanced lithium-ion batteries require very large surface area, interconnected porosity, and the ability to accommodate strains, up to several hundred percent, without mechanical failure. The ability to optimize the topology of a nanolattice can dramatically improve the combination of transport, electrochemical and mechanical properties over that of state-of-the-art stochastic porous materials. Self-assembly has been applied to develop energy storage and conversion devices such as solar cells, batteries, and fuel cells.^[162] Glassy carbon^[163] and copper–silicon^[164] nanolattices fabricated by interference lithography and DLW, respectively, were proposed as electrode materials. Although not quite a nanolattice, pillared graphene nanostructures have been shown to possess excellent specific capacitance and Coulombic efficiency, which are ideal properties for supercapacitors.^[165]

In biotechnology, micro- and nanolattices with controlled three-dimensional architecture have been successfully used for tissue engineering,^[166] as scaffolds for controlled cell cultures,^[167] and in minimally invasive medicine.^[168] Chemical

functionalization, as demonstrated with polymeric lattices generated using DLW, with pre-functionalized photomonomers^[169] potentially qualifies nanolattices for a variety of biomedical and biochemical applications.

3. Fabrication

Lattice structures with millimeter to centimeter scale periodicity can be efficiently fabricated via the assembly of folded and/or slotted thin sheets (similar to a cardboard box), or by modular assembly methods such as wire layup.^[170] Additive manufacturing (AM) technologies^[171] like selective laser sintering, selective laser melting, stereolithography and electron beam melting offer sub-millimeter resolution and increased design freedom, but at the cost of a lower production rate. The production rate of a manufacturing process generally scales inversely with its accuracy and resolution capacity. Fabrication techniques with micrometer and nanometer resolution, such as those required for fabricating nanolattices, are currently limited to a number of polymer-based, low-throughput, AM and self-assembly techniques. Those that have been most successfully applied to micro- and nanolattice fabrication are described in the following sections. We discuss the achievable resolution, productivity and design freedom, and give an overview on the most commonly used methods to convert polymeric structures into ceramic, metallic and composite lattices.

3.1. Self-Propagating Photopolymer Waveguides (SPPW)

SPPW is an angled exposure technique to fabricate polymer structures from self-propagating photopolymer waveguides.^[4,122] This technique exposes a photomonomer by ultraviolet (UV) light passed through a two-dimensional mask with a pattern of apertures as shown in **Figure 9a**. In the photomonomer, self-propagating photopolymer waveguides develop at each aperture in the direction of the UV collimated beam and cross at points of intersection, forming a three-dimensional interconnected array of polymer struts. After removing the uncured monomer, an open-cell polymer material is left behind. SPPW controls the architectural features of the bulk cellular material by controlling the strut angle, diameter, and three-dimensional spatial location during fabrication. The unit cell architecture is governed by the pattern of circular apertures on the mask and the orientation and angle on the collimated incident UV light beams. With standard UV exposure capabilities, lattices have been fabricated with strut diameters ranging from ≈ 10 μm to >1 mm and relative densities between $\approx 5\%$ and 30% . The overall material thicknesses can range from 100 μm to over 25 mm per exposure. The maximum achievable material thickness, which is dependent on the distance the waveguide can propagate, is roughly 100 times the lattice member diameter. To achieve higher thicknesses, multiple layers have to be exposed similar to other layer-by-layer AM techniques. The lattice strut angle relative to the exposure plane can be between $\approx 50^\circ$ to 65° for directly intersecting waveguides. Vertical or near vertical struts are also producible. Changing the aperture spacing and diameter on the mask enables variations

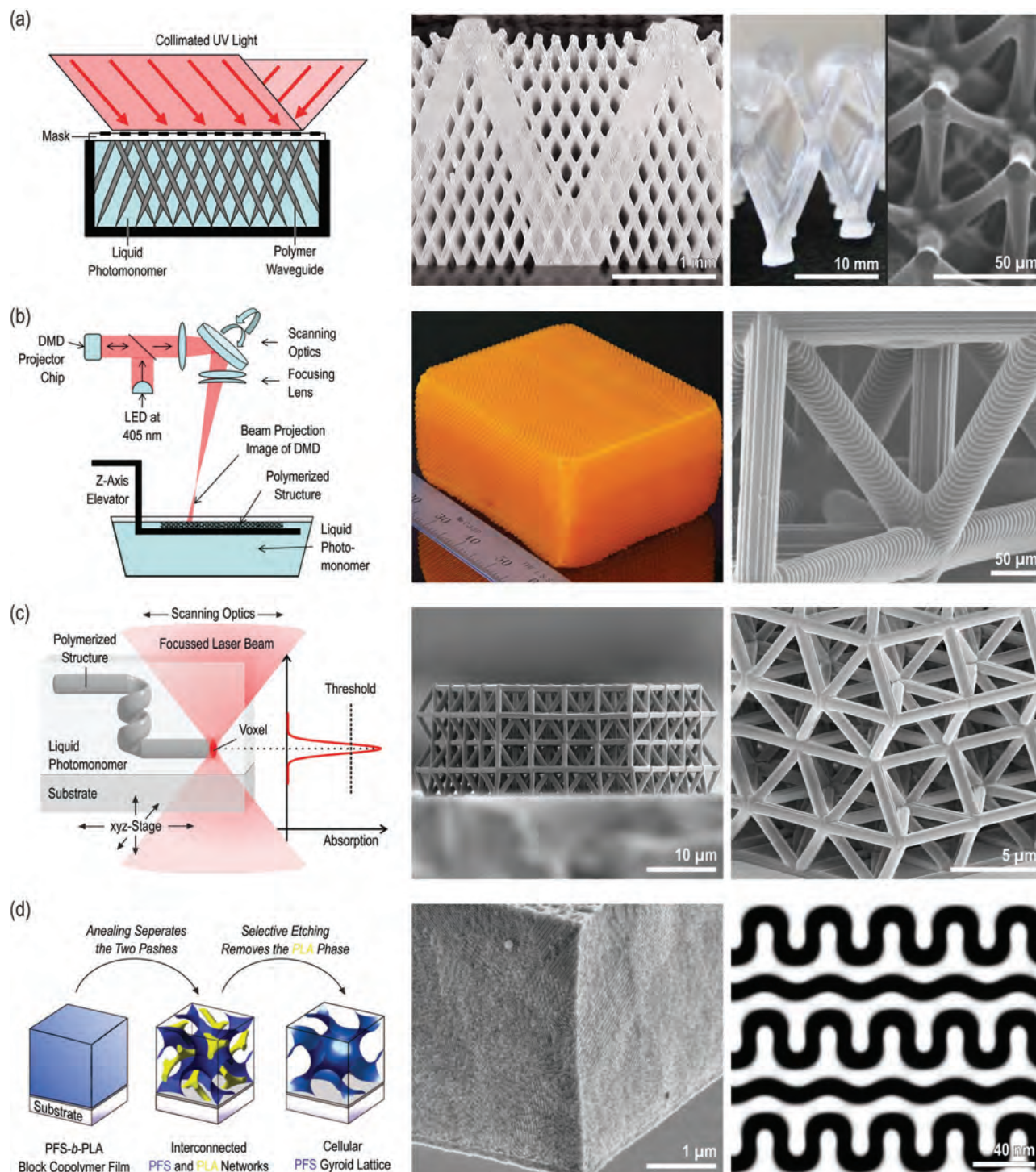


Figure 9. Selected processes for fabricating micro- and nanolattices. a) By UV-light exposure of a photomonomer through a two-dimensional mask, SPPW creates polymeric microlattices, tens of centimeters in size, within minutes; while topologies are limited to linear extensions of the mask, feature dimensions may be varied in a broad range, from >25-mm-thick single unit-cell structures to lattices with members $\approx 10\ \mu\text{m}$ in diameter, to hierarchical structures. b) Large area P μ SL creates centimeter-size arbitrary polymeric microstructures with minimal feature dimensions of 5–300 μm , in a layer-by-layer fashion by polymerizing the surface layer of a photomonomer bath through a digital mask. c) DLW processes focus a laser beam into a photomonomer, creating an ellipsoid-shaped polymer feature (voxel) down to 100 nm in size, via multiphoton polymerization. Scanning the laser beam and moving the sample stage forms arbitrary micro- and nanostructures of typically <1 mm overall size. d) Self-assembly, i.e., of block copolymers like poly(4-fluorostyrene-block-D,L-lactide) (PFS-b-PLA), can create a number of topologies such as gyroid lattices, with feature sizes down to 10 nm and overall dimensions of up to centimeters. a) Adapted with permission.^[173] Copyright 2010, The Authors. b–left & middle) Adapted with permission.^[83] Copyright 2016, The Authors. b–right) Adapted with permission.^[19] Copyright 2014, AAAS. c–left) Adapted with permission.^[174] Copyright 2017, Nanoscribe GmbH. c–middle) Adapted with permission.^[108] Copyright 2015, Elsevier. d) Adapted with permission.^[175] Copyright 2009, American Chemical Society.

in the lattice feature dimensions and unit cell sizes (Figure 9a). SPPW can only be used to fabricate architectures that are linear extensions of the mask; this allows a range of nonrigid lattice truss topologies and honeycombs, but prohibits rigid lattice topologies with struts parallel to the mask plane. Masks with larger apertures can be used to make negative templates for shellular topologies that are rigid and do not contain in-plane elements.^[109] The main advantage of SPPW compared to other high resolution AM approaches is the substantially higher speed and scalability. 30 cm × 30 cm × 20 mm polymer lattices have been fabricated in 1 minute, and rates of more than 1 m² per min are achievable with a continuous SPPW process. Interference lithography^[62] and other angled exposure techniques such as X-ray lithography can be used to create similar topologies to those made using SPPW and with feature diameters below 100 nm, albeit at the cost of considerably lower scalability.^[131] Multibeam interference lithography markedly extends the variety of topologies that can be created.^[62] A range of resin systems are available for SPPW that enable lattices from stiff,^[122] viscoelastic,^[172] or pre-ceramic^[84] polymers.

3.2. Projection Micro-Stereolithography (PμSL)

Projection micro-stereolithography is a layer-by-layer process for the fabrication of three-dimensional polymer microstructures (Figure 9b).^[5] For each layer, a reconfigurable digital mask and a UV light-emitting diode (LED) array project an image onto the surface of a liquid photomonomer bath, inducing polymerization in the shape of the projected image. The thickness of the resulting layer is in the range of 10–100 μm, depending on the penetration depth of the light, which is controlled by process parameters including light intensity,^[5,176,177] exposure time,^[176,178] and the concentration of photoabsorber^[179,180] and photoinitiator^[181] in the photomonomer. Lowering the polymerized layer into the resin bath forms a new liquid layer on top of the polymerized layer and the process is repeated until the desired object is completed. The spatial light modulator (SLM), which is usually a deformable mirror array (DMD), combined with projection optics defines the resolution and scalability. For example, a typical SLM with 1920 × 1080 pixels projected over an area of 15.36 mm × 8.64 mm combined with UV reduction optics with a reduction factor of 6:1 gives a final resolution of 1.3 μm per pixel at the projection focal plane. Three-dimensional lattices with feature sizes of 5 μm and 300 μm can be fabricated in areas of 1 mm and 5 cm in 1 to 2 hours, respectively. Further extending the scalability, Large Area PμSL^[83] combines an addressable SLM with a galvanometric mirror scanning system to produce microscale architectures over a large area. As the light is scanned, the image projected from the SLM changes corresponding to the respective location of the pattern. Hierarchical lattice materials with over 60 000 octet unit cells and with feature sizes <5 μm (see Section 4) can be fabricated with a speed of 1200 mm³ per hour. The main advantage of PμSL compared to high resolution AM techniques such as DLW is the increased fabrication speed, which, due to the projection technique, is not compromised as feature complexity increases. PμSL can work with a range of resins with inorganic nanoparticles,^[182,183] pre-ceramic polymers,^[184–186] as well as

resins with different colors,^[187] stiffness,^[188] and viscosities.^[189] Multimaterial PμSL with feature sizes in the millimeter range has also been shown.^[161]

3.3. Direct Laser Writing (DLW)

Direct laser writing (DLW) is a multiphoton lithography process that facilitates the fabrication of fully three-dimensional polymeric micro- and nanostructures (Figure 9c).^[6,7] In DLW, an optical microscope focuses a laser beam with a wavelength (λ) of typically 780 nm into a volume of liquid photoresist. The photoresist contains a photoinitiator that absorbs the laser light and causes polymerization of its monomers. The photoinitiator is transparent to light with a wavelength λ but absorbs light at $\lambda/2$, which has double the energy than light at λ . If two or more photons of wavelength λ are absorbed simultaneously, the sum of their energy is high enough to induce polymerization. This is known as multiphoton absorption, which is a second-order process that is several orders of magnitude weaker than the single-photon absorption used in SPPW or PμSL. In the DLW process, multiphoton polymerization is achieved by focusing of the laser light. As the absorption reaction depends on the square of the light intensity there is no polymerization along the path of the light but only in a small focus volume. The result is an ellipsoidal polymerized voxel, or volume pixel, that is typically ≥200 nm wide and ≥600 nm high.^[149,174] DLW with resolutions down to 100 nm have been achieved using more complex optical configurations.^[149,190] By moving the laser focus sample one can “write” three-dimensional structures into the photoresist. Piezoelectric xyz-stages with nanometer accuracy can move the sample in all directions at speeds of tens of micrometers per second. Galvo mirrors enable rapid in-plane scanning of the laser focus with a scan speed of up to m s^{−1}. In practice, both writing methods are combined to achieve typical writing speeds on the order of mm s^{−1}. The working area of both writing methods is generally limited to a few hundred micrometers, the fabrication of larger structures requires stitching of multiple writing fields. A range of positive^[24] and negative^[64,167,169,191,192] tone photoresists can be used in fabricating nanolattices.^[193] After samples are written, the remaining photomonomer is dissolved in a developing bath, leaving the finished structure behind. Super critical drying^[194] can be applied during the development stage to avoid distortion of the structure due to capillary effects. DLW has the highest achievable resolution of any fully three-dimensional AM technique, and it is therefore the method of choice for the fabrication of nanolattices. The main challenge DLW faces is its scalability; the size of fabricated samples typically ranges from hundreds of micrometers to centimeters depending on the complexity of the structures being written.

3.4. Self-Assembly

Self-assembly based approaches have shown great promise for the fabrication of complex micro- and nanostructures, and are therefore often seen as an alternative to additive manufacturing. As defined by Whitesides and Grzybowski, “Self-assembly is

the autonomous organization of components into patterns or structures without human intervention^[195]; this process is applicable at all length scales, although the first studies focused on the self-assembly of molecules.^[195]

Block copolymer self-assembly (Figure 9d) has been successfully used in the fabrication of a variety of periodic functional nanostructures with dimensions on the order of tens of nanometers.^[196,197] Block copolymers are macromolecules that form separate distinct domains based on microphase separation of their constituent polymer blocks. Depending on the molecular weights and the relative compositions of the copolymer, different nanodomain structures develop. A variety of three-dimensional morphologies can be assembled.^[198] Electroplating can be used in combination with self-assembled polymer templates to fabricate nanolattices from several inorganic materials. For example, three dimensionally periodic double-gyroids were fabricated with block copolymers and coated with nickel using electroplating; after removing the block copolymer, the resulting structure was a periodic double-gyroid nickel replica with strut sizes of 13 nm and a relative density of 38%.^[9] Vanadium pentoxide gyroid structures were fabricated using a similar process and with strut sizes of only 10 nm.^[199] Room-temperature oxidation of silicon containing triblock copolymers was shown to create silicon oxycarbide inverse double gyroids with strut sizes of ≈ 20 nm.^[200]

The self-assembly of colloidal crystals using nanoscale particles is another approach for the production of templates for ordered nanoporous structures. Inverse opals made using materials such as silica, nickel, and alumina have been reported.^[2,201] Typical pore sizes are in the range of a few hundreds of nanometers^[2,201,202] and strut thicknesses are on the order of 100 nm.^[2,201] The technological potential of colloidal self-assembly for large area fabrication has been demonstrated using nickel inverse opals that were fabricated covering 2 cm² areas.^[201] Inverse opals are open-cell structures, when close-packed colloidal spheres are used as a template. Closed-cell structures can be produced using a colloidal crystal template composed of close packed core-shell spheres that have been infiltrated with a precursor fluid.^[203] In a process similar to nanocasting,^[204] the precursor is converted into the target material and replicates the templated nanomorphology after the chemical removal of the hard template. Colloidal crystals made from carbon and silica and from silica spheres have been identified as the most promising template materials.^[204] While colloidal crystals from monodisperse spheres have a limited range of crystal structures, binary mixtures of differently sized colloidal particles were demonstrated to form more complex topologies.^[205,206]

Three-dimensional assembly of graphene and carbon nanotubes have been predicted by molecular dynamic simulations to possess a number of outstanding physical properties including mechanical, electrical, and chemical.^[207–210] Synthesis of nanostructures such as pillared graphene has been shown,^[211] but their structural order is limited and they generally do not possess a truly periodic architecture.

The application of self-assembly processes to the controlled fabrication of nanolattices is still in its infancy, but their implementation has great potential benefits for upscaling and mass fabrication. The two main advantages of self-assembly methods are their low-cost of synthesis and their rapid processing times.

The disadvantages are the limited topological diversity and the emergence of larger-scale defects that typically propagate through the entire material; these both need to be explored in more detail for self-assembly methods to be a truly effective nanolattice fabrication tool.

3.5. Synthesis of Composite, Ceramic and Metal Structures

To date, there are no metal- or ceramic-based AM processes with sufficiently high resolution for the synthesis of nanolattices. The majority of fabrication techniques are polymer-based, and a number of post-processing techniques exist that are used to overcome this limitation.

Atomic layer deposition (ALD) is a highly conformal deposition process that allows for the coating of complex 3D geometries with angstrom-level thickness control.^[212] ALD in its simplest form is a thermal process that works by depositing a monolayer of a precursor onto a surface then flowing a reactant over it, resulting in a single atomic layer of a given material. This cycle can be repeated until a specific material thickness is obtained. More complex forms of ALD can use multiple precursors and plasma ignition to facilitate less thermodynamically favorable chemical reactions. ALD is highly advantageous due to its lack of directional dependence and its ability to diffuse into small spaces, making it ideal for coating polymeric nanolattices to form core-shell composite structures.^[2,14] (Figure 10a). Composite structures can be cut open, e.g., by focused ion beam milling, allowing for the removal of the polymer core by etching or thermal treatment.^[13,202] The major limitation of ALD is its slow rate, which is normally on the order of nanometers per hour. ALD can be used to create a wide range of materials, including metals, ceramics, and semiconductors.^[213]

Electroless plating of metals is a well-established method for coating a broad range of shapes and materials.^[214] Preferred are metals with a reduction potential greater than that of water, so that they can be deposited in aqueous solutions. Ionic liquid based processes have been developed for important metals with a low reduction potential such as aluminum. Electroless deposition is a favorable method for the coating of lattice materials with metals due to the conformal, non-line-of-sight deposition characteristics.^[15] Electroless plating processes rely on an autocatalytic reaction to reduce the metal ions in solution; it therefore enables the uniform deposition into pores as long as mass transport is not limited. Hollow-beam metal lattices can be fabricated in a process analogous to that illustrated in Figure 10a.

Electroplating into negative templates enables the fabrication of solid-beam metallic lattices (Figure 10b).^[9,89] This process involves first spinning a positive tone photoresist, i.e., a photoresist that is designed to be removed after exposure to UV light, onto a conductive substrate. Transparent conductive substrates can be made using thin films of indium tin oxide (ITO) or gold, which remain sufficiently transparent when sputtered at thicknesses of <50 nm. Using AM techniques, a structure can then be written into the photoresist, with the requirement that it must span from the top of the spun photoresist to the conductive substrate in order to ensure a conductive path. After the exposed resist has been developed, the pores can be infiltrated with an electroplatable material. Electroplating is a

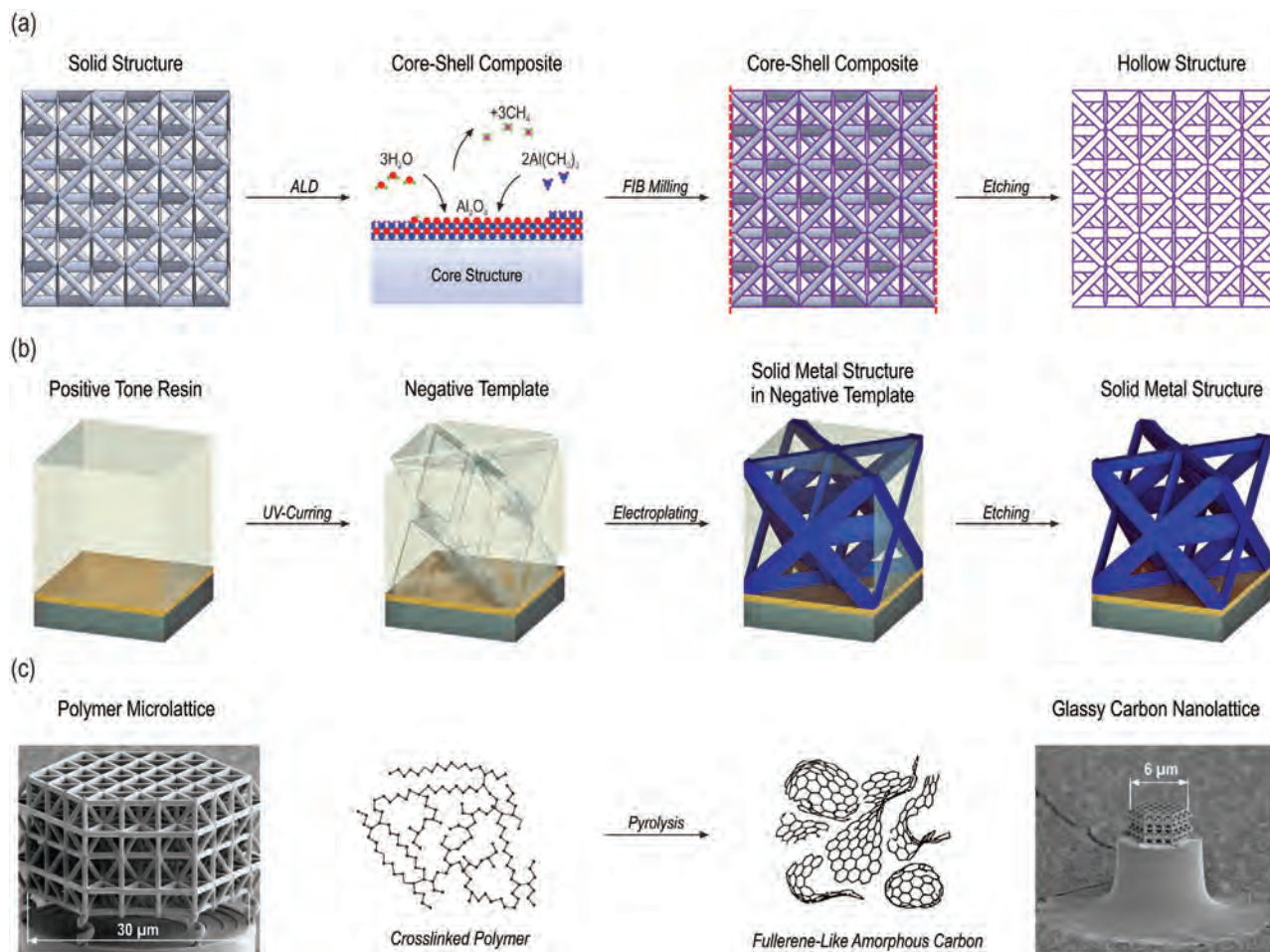


Figure 10. Post-processing routes for synthesizing ceramic, metallic, and composite nanolattices based on polymer templates. a) Hollow-beam ceramic lattices are fabricated by ALD, focused ion beam (FIB) milling, and etching; analogously, metal lattices can be made via electroless plating. b) Electroplating into a negative template creates solid-beam metal lattices. c) Accompanied by conformal shrinkage of up to 90%, pyrolysis of polymer lattices yields carbon-based ceramic lattices. a) Adapted with permission.^[13] Copyright 2014, AAAS. b) Adapted with permission.^[89] Copyright 2015, Elsevier. c) Adapted with permission.^[1] Copyright 2016, The Authors.

commonly utilized industrial process, and has been shown to offer a high degree of nanostructural material control.^[215] In contrast to electroless plating, electroplating uses an applied voltage from an external source to deposit a material from solution. Deposition rates are proportional to the current density in the part, which also depends on the electric field applied by the anodes. The application of a constant voltage can result in a moderate directional dependence and deposition that is limited by line of sight. With advanced electroplating techniques such as voltage pulsing and conformal anodes, metal can readily be deposited into complex, three-dimensional nanoscale pores. Multiple metals can be electroplated in parallel, but complexity increases exponentially with every additional metal; electroplating is therefore not well suited for the creation of multicomponent alloys. Care must be taken to ensure that the electroplating solution does not react with and erode the photoresist. After electroplating, the undeveloped photoresist can be removed using a developer, leaving behind a solid lattice.

Using pyrolysis, glassy-carbon-based structures (Figure 10c) can be made from thermosetting polymers, such as UV-cured

resins, that are thermally decomposed in vacuum or inert atmosphere at temperatures in the range of 1000–3000 °C.^[216] This process is accompanied by shrinkages of up to 90%.^[217] Glassy carbon is an amorphous carbon allotrope that primarily consists of nongraphitic sp²-bonded carbon.^[99,217] The fabrication of nanolattices using pyrolysis offers two unique benefits: i) Polymer templates are directly transformed to robust ceramic structures, avoiding procedures like coating, milling, and etching. Glassy carbon exhibits excellent chemical and thermal stability as well as biocompatibility and can achieve semiconductor-type electrical properties.^[217] Its Young's modulus is about 10 times higher than that of cross-linked epoxy resins,^[218] and strengths in nanolattices on the order of 3 GPa have been observed. Its low density^[99,216] of 1.3–1.5 g cm^{−3} is attributed to a fullerene-related closed-cell porosity.^[219] Silicon-based pre-ceramic resins can be used to fabricate pre-ceramic polymer lattices via UV-curing, which then can be converted to ceramics such as silicon-oxycarbide;^[84] ii) With appropriate designs, highly uniform shrinkage can be exploited to fabricate considerably smaller structures than what is achievable with

the applied fabrication method alone. A five-fold reduction in size was demonstrated with direct-laser written octet lattices (Figure 10c).^[1]

AM with particle-loaded polymers allows for the fabrication of macro- and microlattices from a variety of materials. The most common of these processes use inorganic particles like oxides embedded in a thermoset polymer that become sintered after the polymer is burned off.^[19] Metal particles can also be used, and good results have been achieved with copper and silver.^[220] Carbon fiber reinforced polymer composites^[221] as well as foam based ceramic lattices^[222] have also been processed. The major drawbacks of this method are that the final material is likely to possess a high flaw population, and the reduced resolution and feature quality. Both of these makes particle-loaded AM techniques difficult to use for the fabrication of nanolattices. Lithographically defined microstructures of graphene oxide flakes with feature sizes on the order of 1 μm ^[223] as well as high-quality, transparent fused silica microstructures^[224] have been shown, though.

sizes that are relevant for technological applications. Scaling-up the dimensions of a structure while keeping its smallest feature sizes at the nanoscale is inherently difficult, and current fabrication methods dictate a tradeoff between build volume, production rate and minimum feature size. The most straightforward workaround to overcome this problem is to combine large-scale, high-throughput processes with thin film deposition techniques to produce hollow structures, but any length scale gaps in the architecture will inevitably lead to shell buckling instabilities due to high ratios of diameter-to-wall-thickness.^[15]

Hierarchical architecture provides a means of expanding build volumes without sacrificing accuracy, resolution or structural integrity. The production rates of many AM processes scale proportionally to the relative density of the structure being manufactured. The effective relative density ($\bar{\rho}_{\text{eff}}$) of a hierarchical structure compounds with increasing hierarchical order, and for an architecture of order N is given approximately by:

$$\bar{\rho}_{\text{eff}} = \prod_{i=1}^N \bar{\rho}_i \quad (8)$$

where $\bar{\rho}_i$ is the relative density of the i^{th} level of hierarchy. When the order of hierarchy is increased, the compounding relative densities decrease the effective relative density without

4. Hierarchical Architecture and Scale-Up

The exceptional properties of nanolattices can only truly have an impact as engineering materials if they are scaled-up to

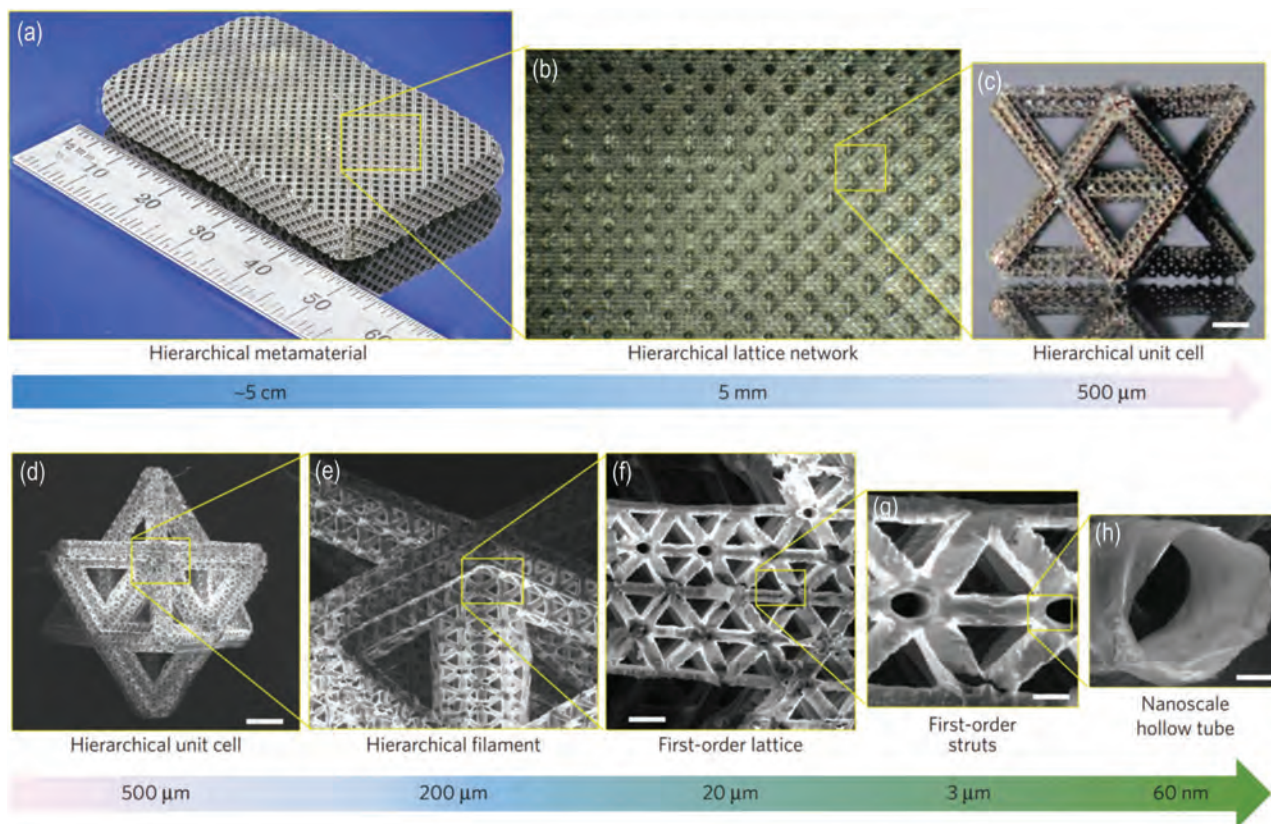


Figure 11. Centimeter-size hierarchical hollow-beam nickel microlattice material fabricated using large area projection micro-stereolithography. a–c) Optical microscope images of bulk hierarchical lattice material with a network of hierarchical octet unit cells. d–h) Scanning electron microscopy images showing the breakdown of structural hierarchy down to hollow-beam walls tens of nanometers in thickness. The scale bars in (c), (d), (f), (g), and (h) are 80 μm , 80 μm , 10 μm , 3 μm , and 2 μm , respectively. Adapted with permission.^[83] Copyright 2016, The Authors.

increasing the slenderness of individual structural elements, thereby maintaining structural stability.

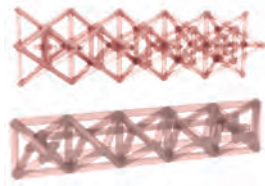
A scaled-up manufacturing of microlattices with nanoscale features from hundreds of micrometers to several centimeters has been demonstrated using large area PμSL.^[83] **Figure 11** shows a breakdown of the feature sizes in these materials, the length scale of each order of structural hierarchy decreases by a factor of ≈ 10 from one level to the next. The microlattice consists of a network of octet unit cells (**Figure 11c**) composed of strut members that are $\approx 200\ \mu\text{m}$ in diameter, each of which consist of a network of self-similar smaller-scale unit cells (**Figure 11h**). The first-order unit cells are made from hollow tube nickel-based struts (**Figure 11i**) with diameters on the order of $10\ \mu\text{m}$ and wall thicknesses ranging from $50\ \text{nm}$ to $700\ \text{nm}$ (**Figure 11j**). Similar orders of structural hierarchy have been shown in nanolattices made from both core-shell polymer-alumina and hollow alumina with first-order strut diameters below $1\ \mu\text{m}$ and shell thicknesses of $20\ \text{nm}$, and an overall structure size on the order of hundreds of micrometers.^[82]

Hierarchical architectures offer a range of unique mechanical properties that are widely taken advantage of in the natural world (**Figure 3**).^[68,69] Diatom frustules, Euplectella glass sponges, and bone have exceptional resilience to mechanical loading. Soft tissues such as skin and structures like bird's nests are highly compliant and able to undergo large deformations without failure. A number of man-made structures have been created that have hierarchical architectures, the most common of which are construction cranes and building scaffolding, and the most notable example being the Eiffel tower.^[225] One key advantage of both natural and engineered hierarchical structures is their increased resistance to buckling. Recalling the Euler buckling criterion from Section 2.1.2, the buckling strength of a beam scales with its length as $1/l^2$, and the resulting strength of a buckling-dominated lattice scales with relative density as $\sigma \propto \bar{\rho}^2$. In a hierarchical structure, the relative densities at each order of hierarchy are multiplied according to Equation (8), meaning beam length and relative density are decoupled. The length of the beams can therefore be much shorter for a given $\bar{\rho}$ compared to a single-order structure, resulting in an increase in the buckling resistance.

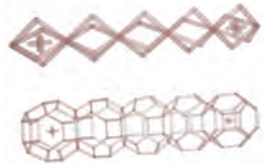
There are four different types of hierarchical lattice architectures that can be created using stretching- and bending-dominated constituent lattices (**Figure 12**).^[49] Combinations of self-similar architectures at adjacent hierarchical levels result in fractal-like lattices that are either stretching-stretching or bending-bending. Combining dissimilar architectures at neighboring hierarchies results in hybrid lattices that are either stretching-bending or bending-stretching. In all four cases, the effective strength (σ_{eff}) of a hierarchical structure of order N can be approximated by the first-order scaling law:

First Order Architecture

Stretching-Dominated

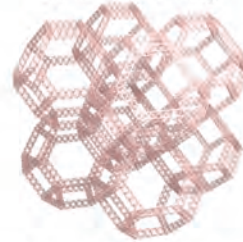


Bending-Dominated

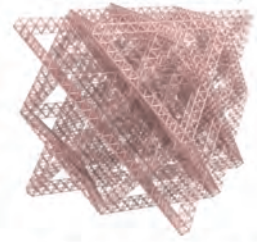


Second Order Architecture

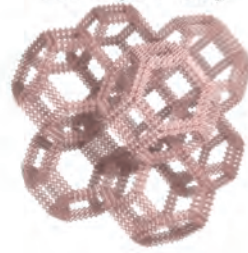
Bending-Stretching



Stretching-Stretching



Bending-Bending



Stretching-Bending

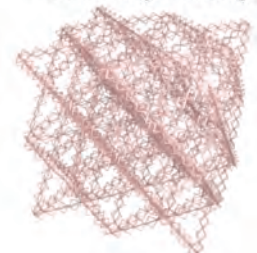


Figure 12. Different types of hierarchical lattice architectures. Mechanical behavior can be tailored for high strength and stiffness (stretching–stretching), high compliance (bending–bending) or the intermediate cases of both (bending–stretching, stretching–bending). Adapted with permission.^[83] Copyright 2016, The Authors.

$$\sigma_{\text{eff}} = C_{\text{eff}} \prod_1^N \bar{\rho}_i^{a_i} \sigma_s \quad (9)$$

where σ_s is the strength of the constituent solid material, C_{eff} is an effective geometric parameter, and a_i is the scaling exponent of each order. Similarly, the effective stiffness (E_{eff}) can be estimated by:

$$E_{\text{eff}} = F_{\text{eff}} \prod_1^N \bar{\rho}_i^{g_i} E_s \quad (10)$$

where E_s is the Young's modulus of the constituent solid material and F_{eff} is an effective geometric parameter.

Fractal-like stretching-dominated hierarchy can lead to superior strength at low density due to an increased buckling stability, potentially enabling access to ultralow density material property spaces that are inaccessible to first-order lattices. Tunable failure behavior and increased energy absorption has been demonstrated with lattices,^[82,83] honeycombs and sandwich panels,^[226–228] and corrugated truss^[229] and space frame structures.^[230] Fractal-like stretching-dominated micro-^[83] and nanolattices^[82] have exhibited near-linear scaling of strength and stiffness down to $\bar{\rho} \approx 0.01\%$ (**Figure 4** and **Figure 6**), while corresponding first-order lattices^[13,19] have scaling exponents as high as 2.7 below $\bar{\rho} \approx 0.1\%$. The geometric parameters of the hierarchical orders have a multiplying effect due to the underutilization of nonaxially oriented lattice elements; this can lead to a reduction in the effective properties. For example, the effective geometric parameter of an octet lattice decreases from $1/3$ to $1/9$ as a structure goes from first- to second-order, which results in a decrease of σ_{eff} by a factor of three. This same mechanism

has the effect of increasing the damage tolerance. After axially oriented lattice elements undergo failure, non-axially oriented elements are able to remain intact and distribute strain through bending or local elastic buckling, thereby accommodating large global deformation without failure.^[82] Recoverabilities of up to 98% of the original structure height after compression to $\geq 50\%$ have been reported.^[82] Corresponding to Section 2.3, the introduction of hierarchy increases the tailorability of failure modes and post-failure behavior. Based on classical lattice theory, stiffness cannot be increased by the addition of hierarchy to the architecture, but it has been postulated that the introduction of hierarchy can reduce local bending effects in certain structures, leading to an increase in the effective stiffness.^[82]

Fractal-like bending-dominated hierarchies can be used to create highly compliant structures. A second-order lattice with $g_1 = g_2 = 2$ has an effective scaling exponent between stiffness and relative density of four. This can potentially allow for large, super-elastic deformations even with brittle base materials. Combining bending-dominated architectures may not always result in an increased compliance. In contrast to stretching-dominated hierarchies, the geometric parameters of each bending-dominated hierarchical order add up, leading to an increased effective stiffness.^[227,231] This can be understood as a gain in flexural rigidity for a given relative density that occurs when replacing slender lattice elements with a bending-dominated network of smaller-scale, short and squat elements. A similar behavior applies for the effective strength.^[227]

Combining stretching- and bending-dominated architectures yields mixed behavior. A cuboid-octet microlattice optimized for tensile loading has been constructed by tessellating a first-order stretching-dominated topology with a second-order bending-dominated one.^[83] The microlattice was composed of brittle 60 nm nickel-based thin films but still demonstrated reversible elastic stretching up to 20% strain; this was achieved while simultaneously attaining specific tensile strengths substantially higher than commercial foams and comparable to those of first-order core-shell polymer-ceramic lattices^[87] synthesized using DLW.^[83] While the stiffness of these materials was governed by compliant hinges in the bending-dominated second-order of hierarchy, their high strength has been attributed to mechanical size effects in the hollow-beam walls of the first-order architecture. Ceramic honeycomb structures fabricated using direct foam writing with a bending-dominated first-order topology and a stretching-dominated second-order architecture were shown to possess highly tailorable stiffness.^[222] The effective geometric parameter of second-order bending-stretching architectures increases with respect to the first-order counterparts in a similar manner to fractal-like bending architectures. The reverse is true for stretching-bending type architectures; as the elements of the stretching-dominated lattice are replaced by bending-dominated ones, they deform by bending instead of stretching, resulting in reduced stiffness compared to the first-order stretching-dominated architecture.

5. Conclusion and Outlook

The introduction of lattice architecture at the micro- and nanoscale has set new boundaries on the accessible regions of

many material property spaces. Photonic and phononic metamaterials with periodicity comparable to the wavelength of optical or acoustic waves were the first drivers towards miniaturization. The high strengths of nanolattices have for the first time demonstrated the ability to exploit size effects in mechanical metamaterials. Nanolattice architecture can be simultaneously designed to enable unique scale-independent properties such as tailorable stiffness, deformability, thermal expansion, as well as auxetic behavior and pentamode meta-fluidity. It is the confluence of nanomaterials and architecture that engenders the huge diversity of properties of nanolattices, although not all properties explicitly benefit from miniaturization.

The extensive work on nanolattices in the recent years has laid the foundation for this emerging field. Data are still very limited, and key physical principles, including some of those described here, are the subject of some uncertainty. More in-depth characterization and modeling are still required to draw a comprehensive picture. Due to experimental limitations, investigations into the mechanical behavior of nanolattices has mostly been limited to compression tests, and proper assessment of their tensile, shear, and fracture properties needs to be done. Besides strength, many more mechanical, thermal and electrical properties exhibit size-dependent behavior. Incorporation of these effects in nanolattices would inevitably lead to major advances in the colonization of new material property space, and this bears the potential for creating new materials with superior multifunctionality. Approaches for creating metamaterials may vary widely across disciplines, but it is remarkable how similar optimal architectures and scales often are. Moving forward, nanolattices should not be thought of as photonic, phononic, auxetic, or light-weight metamaterials, but instead as a single class of multifunctional materials. As nature shows, the introduction of hierarchy is crucial to achieve both multifunctionality and optimized individual properties like mechanical robustness. Initial efforts for the introduction of structural hierarchy into nanolattices have been promising, and eventual designs may be able to fully mimic the material hierarchy of biological materials, leading to a new generation of multifunctional nanolattice materials.

Size effects in materials have been investigated for decades, and nanolattices provide a promising avenue for the preservation of superior size-affected properties in large-scale materials applications. A major future challenge will be to substantially push the current limits of scalability to create nanolattices with sizes that are relevant for technical applications. Some potential methods to increase production while maintaining nanoscale features are parallelization by diffractive beam splitting of laser techniques such as DLW, multistep self-assembly, and hybrid fabrication methods that combine AM with extrusion or injection molding. These fabrication methods have a number of technological challenges associated with their implementation, the most critical of which being that they avoid introducing macroscopic flaws that counteract the beneficial properties gained from using nanomaterials. Another challenge is extending the still narrow bandwidth of materials available for manufacturing of nanolattices.

The first market for nanolattices may be small-scale, small-lot components for biomedical, electrochemical, microfluidic and aerospace applications, which require highly customizable and

extreme combinations of properties. Should scalability become a reality, nanolattices will find application in a variety of light-weight structural components. Over the past few years, nanolattices have certainly caught the attention of scientists and engineers alike. The scientific and technological development over the next few decades will be critical for moving this exciting new class of materials from the lab bench to our everyday life.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

metamaterials, nanoarchitectures, nanolattices, size effects

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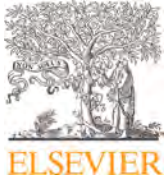
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The mechanical response of cellular materials with spinodal topologies

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ABSTRACT

The mechanical response of cellular materials with spinodal topologies is numerically and experimentally investigated. Spinodal microstructures are generated by the numerical solution of the Cahn-Hilliard equation. Two different topologies are investigated: ‘solid models,’ where one of the two phases is modeled as a solid material and the remaining volume is void space; and ‘shell models,’ where the interface between the two phases is assumed to be a solid shell, with the rest of the volume modeled as void space. In both cases, a wide range of relative densities and spinodal characteristic feature sizes are investigated. The topology and morphology of all the numerically generated models are carefully characterized to extract key geometrical features and ensure that the distribution of curvatures and the aging law are consistent with the physics of spinodal decomposition. Finite element meshes are generated for each model, and the uniaxial compressive stiffness and strength are extracted. We show that while solid spinodal models in the density range of 30–70% are relatively inefficient (i.e., their strength and stiffness exhibit a high-power scaling with relative density), shell spinodal models in the density range of 0.01–1% are exceptionally stiff and strong. Spinodal shell materials are also shown to be remarkably imperfection insensitive. These findings are verified experimentally by in-situ uniaxial compression of polymeric samples printed at the microscale by Direct Laser Writing (DLW). At low relative densities, the strength and stiffness of shell spinodal models outperform those of most lattice materials and approach theoretical bounds for isotropic cellular materials. Most importantly, these materials can be produced by self-assembly techniques over a range of length scales, providing unique scalability.

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1. Introduction

Cellular materials are porous materials consisting of one or more solid phases and void space. For all cellular materials, Young’s modulus, E and yield (or buckling) strength, σ_y , are a strong function of the relative density, $\bar{\rho}$ (i.e., the volume fraction of the solid phase), generally following a power-law behavior: $E \sim E_s \bar{\rho}^n$ and $\sigma_y \sim \sigma_{ys} \bar{\rho}^m$, with E_s and σ_{ys} the Young’s modulus and yield (or buckling) strength of the base material, respectively. The values of the exponents n and m have

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a dramatic effect on the mechanical efficiency of the material and are strongly affected by the topology of the unit cell architecture (Fleck et al., 2010).

The mechanical properties of open-cell, strut-based cellular materials like foams and lattices have been studied extensively (Ashby et al., 2000; Deshpande et al., 2001b; Gibson and Ashby, 1997). Depending on the coordination number (number of bars meeting at each node) and the balance between the number of states of self-stress and internal mechanisms, beam-based topologies can be either bending-dominated or stretching-dominated: in the former, local deformation upon global loading (e.g., compression) occurs primarily by bending of the struts (a weak deformation mode); by contrast, in the latter the vast majority of the strain energy is stored by axial deformation of the struts (Deshpande et al., 2001a). The implication is that stretching-dominated lattices are much more mechanically efficient than bending dominated lattices, with effective stiffness and yield strength scaling as $E, \sigma_y \sim (\bar{\rho})^1$ (versus $E \sim (\bar{\rho})^2$ and $\sigma_y \sim (\bar{\rho})^{1.5}$ for bending-dominated 3D lattices and stochastic foams) (Fleck, 2004). In all cases, at low relative density, strut buckling limits the strength of both stretching- and bending-dominated lattices. For nearly any strut-based lattice architecture, the effective elastic buckling strength scales with $\bar{\rho}$ as $\sigma_{el} \sim (\bar{\rho})^2$ (Ashby, 2006, 1983; Deshpande et al., 2001b), dramatically reducing mechanical performance at low relative densities. For most solid-strut topologies, the yielding-to-buckling transition occurs at a relative density of the order of $\sim 1\%$ (Gibson and Ashby, 1988).

Hollow-strut lattices can potentially delay the onset of buckling, shifting the yielding-to-buckling transition to $\bar{\rho} < 0.1\%$ (Bauer et al., 2017; Meza et al., 2014; Pingle et al., 2011; Schaedler et al., 2011; Torrents et al., 2012; Valdevit et al., 2013, 2011). However, their mechanical properties are often much worse than analytical predictions suggest: for example $E \sim (\bar{\rho})^{1.61}$ and $\sigma_y \sim (\bar{\rho})^{1.76}$ has been experimentally extracted for hollow-strut ceramic octet lattices (Meza et al., 2014). The hollow nodes of these lattices were shown to deform through bending (regardless of the coordination number); this phenomenon, coupled with stress concentration at the nodes, causes a knock-down from classical scaling laws, which do not account for nodal topology (Bauer et al., 2016a; Bauer et al., 2017; Meza et al., 2014; Portela et al., 2018; Torrents et al., 2012; Valdevit et al., 2013). Local node buckling (at low relative densities) and high sensitivity to imperfection (waviness of the strut and non-ideal strut cross section) during fabrication of these structures also contribute to the reduction of strength (Salari-Sharif et al., 2018; Valdevit et al., 2013). Adding fillets to the nodes efficiently reduces these stress concentrations, enhancing the strength of hollow-strut lattices. Increasing node-smoothing gradually converts hollow-strut lattices to shell-based cellular materials (Han et al., 2015).

Shell-based cellular materials can be classified in closed-cell and open-cell materials, based on the connectivity of their porosity. The former include closed-cell stochastic foams (Gibson and Ashby, 1988) and 3D periodic arrangements of polygonal cells, such as closed-cell octet and cubic-octet regular foams (Berger et al., 2017) and quasi closed-cell inverse opals (do Rosário et al., 2017). While some of these materials are remarkably efficient (e.g., the nearly-isotropic cubic-octet regular foam approaches the theoretical Hashin–Shtrikman stiffness bounds (Berger et al., 2017)), their topology still results in stress localization near face edges and vertices, and hence sub-optimal material utilization.

By contrast, open-cell shell-based materials can be constructed as a thin, smooth, interconnected membrane that occupies a 3D volume, with interconnected porosity. These topologies usually take the form of a locally area-minimized geometry (Meeks and Perez, 2011), and are characterized by a mean curvature approximately equal to zero everywhere on the surface. The most famous examples are triply periodic minimal surfaces (TPMS), such as the Schwarz P surface (Hyde et al., 1996; Schwarz, 1890), the Schwarz D surface (Hyde et al., 1996; Schwarz, 1890) and the gyroid surface (Schoen, 1970). The uniform curvature of these surfaces has been numerically shown to dramatically reduce local stress intensification upon macroscopic loading (Rajagopalan and Robb, 2006). Furthermore, Schwarz P shell and Schwarz D shell materials were shown to be stretching-dominated, with E and σ_y on par with or better than most of the existing lattice architectures (Han et al., 2017, 2015; Nguyen et al., 2017). A similar class of open-cell thin shell materials was derived from simple-cubic (SC), face-centered cubic (FCC), and body-centered cubic (BCC) tube-lattices. These topologies have tailorable anisotropy and can achieve elastic moduli higher than the hollow truss lattices they are derived from (Bonatti and Mohr, 2018).

Unfortunately, all these thin shell materials have two shortcomings: (i) they are significantly imperfection sensitive, as any surface roughness or waviness due to manufacturing imperfections would cause them to buckle prematurely under compression (Han et al., 2017; Hutchinson and Thompson, 2018); and (ii) they are generally difficult to fabricate with scalable manufacturing processes (inverse opal and gyroid materials can be fabricated at the nanoscale, but upscaling is challenging). The development of architected materials that can be fabricated at macroscale dimensions while still retaining dimensional control of their nano/micro-scale features is a very active research endeavor. The driving force has been the quest for scale-up of the well-known beneficial size effects on strength that metallic and ceramic materials exhibit when one or more component dimensions are reduced to the nanoscale. Excellent performance has been demonstrated in solid ceramic nanolattices (Bauer et al., 2016b), hollow metallic (Schaedler et al., 2011; Zheng et al., 2016) and ceramic (Meza et al., 2014) micro and nano-lattices and nano-shell-based cellular materials (Khaderi et al., 2014, 2017). The practical applicability of all these nano-architected materials, though, is dramatically hindered by scalability challenges that derive from their manufacturing process (Bauer et al., 2017; Bishop-Moser et al., 2018). Approaches based on self-assembly, possibly combined with additive manufacturing at a larger scale, have the potential to dramatically increase scalability.

Spinodal decomposition is a near-instantaneous diffusion-driven phase transformation that converts a single-phase material into a two-phase material (one possibly being void space), with the two phases arranged in a bi-continuous topology and separated by a surface with nearly uniform negative Gaussian curvature and nearly zero mean curvature (Cahn, 1961; Jinnai et al., 1997). Spinodal decomposition may occur by a variety of physical processes, e.g., the dealloying of an Au/Ag

solid solution (Hodge et al., 2007) or the heating/cooling of an emulsion gel through a critical point (Lee and Mohraz, 2010). The former results in a gold solid spinodal structure with ~50% porosity and nanoscale feature size (Fig. 1a), whereas the latter gives rise to a ~50%/50% mixture of two liquids with microscale feature size, called a bicontinuous interfacially jammed emulsion gel (bijel) (Fig. 1b). While thermodynamics favors the growth of the feature size over time, this process can be arrested (thereby controlling the length scale), by lowering the temperature (in the case of nano-porous metal) or by jamming the interface with solid nano-particles (in the case of bijels). Bijels can be used as templates for the development of structural and functional micro-architected materials, via a suite of materials conversion processes (Lee et al., 2013; Lee and Mohraz, 2011). For example, one of the liquid phases can be replaced by a photosensitive monomer, which is subsequently photopolymerized, and the other liquid phase removed, resulting in a ~50% dense polymeric cellular spinodal architecture. The surface of this cellular solid can be subsequently coated with metal or ceramic, and the polymer ultimately dissolved, with the end result being a stochastic shell-based architected material with spinodal topology (Lee and Mohraz, 2010) (Fig. 1c). This process is extremely scalable, and can result in rapid fabrication of macro-scale shell-based cellular materials with microscale feature size. The stochastic nature of this shell-based architecture, though, raises questions about its mechanical efficiency.

In this work, we thoroughly investigate the mechanical response of both solid and shell-based architected materials with spinodal topologies. We numerically generate 3D spinodal cellular materials with different relative densities and characteristic feature sizes and extract shell-based spinodal cellular materials from the interface between the solid and the void space. We compute stiffness and strength under uniaxial compression by finite element simulations, which are verified by mechanical experiments conducted on polymeric samples produced by 2-photon polymerization Direct Laser Writing. We show that while solid spinodal cellular materials scale poorly with relative densities, shell spinodal architected materials are remarkably efficient, with effective Young's modulus and yield strength scaling with the relative density as $\bar{\rho}^{1.2-1.4}$. Importantly, spinodal shell topologies are shown to be largely imperfection insensitive, and hence robust against elastic buckling failure modes at ultra-low densities. These findings reveal that shell spinodal architected materials perform better than many available periodic topologies (both strut and shell-based), particularly at ultra-low density. These mechanical characteristics, combined with the ability to self-assemble at multiple length scales, make shell-based spinodal architected materials a remarkable class of cellular solids.

2. Numerical construction of spinodal topologies

2.1. Generation of solid spinodal topologies

Spinodal structures are formed through spinodal decomposition, a diffusion-type phase transformation process that separates a compound into a mechanical mixture of phase A and phase B solid solutions by reducing the total free energy of the system (Porter et al., 1981). The phase separation processes during spinodal decomposition can numerically be described with phase field approaches (Biener et al., 2009; Crowson et al., 2009, 2007). One of the most commonly used formulations is the Cahn-Hilliard equation (Cahn and Hilliard, 1958; Sun et al., 2013), which can be written as:

$$\frac{\partial u}{\partial t} = \Delta \left[\frac{df(u)}{du} - \theta^2 \Delta u \right] \quad (1)$$

where $u(x, y, z, t)$, is the concentration difference between the two phases (phase A and phase B) at a coordinate (x, y, z) at the evolution time, t ($u(x, y, z, t)$ is bounded between -1 and 1 , with $u = -1$ denoting full phase A and $u = 1$ denoting full phase B), and Δ is the Laplacian operator. At time $t = 0$, the system is nearly homogeneous, with $u \sim 0$ everywhere. As the simulation starts, phase separation is driven by a free-energy function with a double well, which can be chosen as $f(u) = \frac{1}{4}(u^2 - 1)^2$. Regions of phase A and phase B quickly develop, with θ denoting the width of the interface between the two phases (here set to 1.1, as suggested by (Sun et al., 2013)). As time progresses the size of the single-region domains increases and the curvature of the interface decreases. For a cellular material, one of the two phases represents void space. This equation is discretized by the Finite Difference method, and solved on a cubic domain of $100 \times 100 \times 100$ nodes, subject to periodic boundary conditions. The solution procedure is nearly identical to that reported in (Sun et al., 2013); a synopsis is reported in Appendix 1 for completeness. Solid spinodal volumes at 5 different evolution times, $t_1 - t_5$ (and hence different domain sizes and surface curvatures) and 4 different relative densities, $\bar{\rho}_1 = 20\%$, $\bar{\rho}_2 = 30\%$, $\bar{\rho}_3 = 50\%$ and $\bar{\rho}_4 = 70\%$, are extracted for post-processing (Fig. 2). Spinodal volumes were subsequently sliced in 2D images and the stack of images was imported in the commercial software Simpleware ScanIP to generate a 3D tetrahedral finite element mesh for subsequent mechanical characterization.

2.2. Calculation of the characteristic feature size

Whereas periodic architected materials have a very well-defined unit cell size, for stochastic spinodal solid this definition is fuzzier. Nonetheless, a measure of the *characteristic feature size*, λ , is necessary to enable comparison with periodic cellular materials. This dimension can be defined as the inverse of the dominant frequency in a Fast Fourier Transform (FFT) of the spinodal model (Jinnai et al., 2004; Kwon et al., 2010). In order to graphically illustrate the relationships between real domain and frequency domain, FFTs are initially extracted on two-dimensional slices of the solid spinodal topologies (Fig. 3).

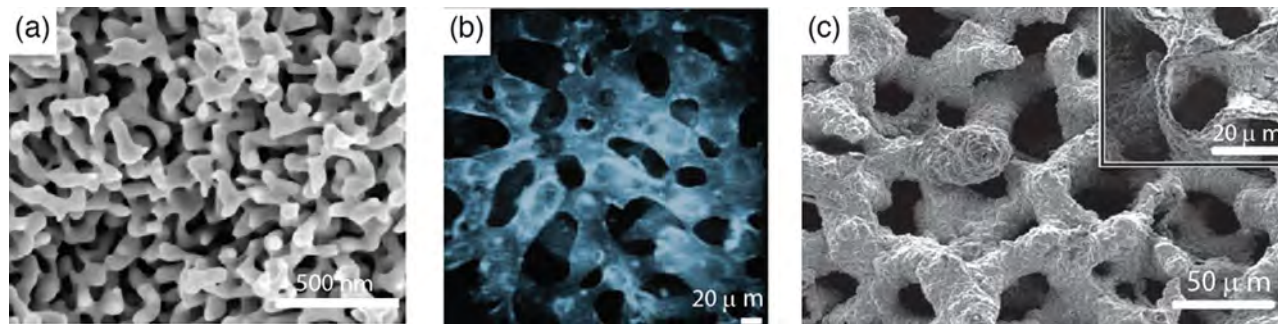


Fig. 1. Examples of self-assembled spinodal topologies at different length scales: (a) nano-porous Au, obtained by selective etching of Au/Ag solid solutions (reproduced from (Hodge et al., 2007)); (b) spinodally decomposed bijel (reproduced from (Lee and Mohraz, 2010)); (c) micro-porous metallic shell spinodal architected material, obtained by material conversion of spinodally decomposed bijels (reproduced from (Lee and Mohraz, 2010)).

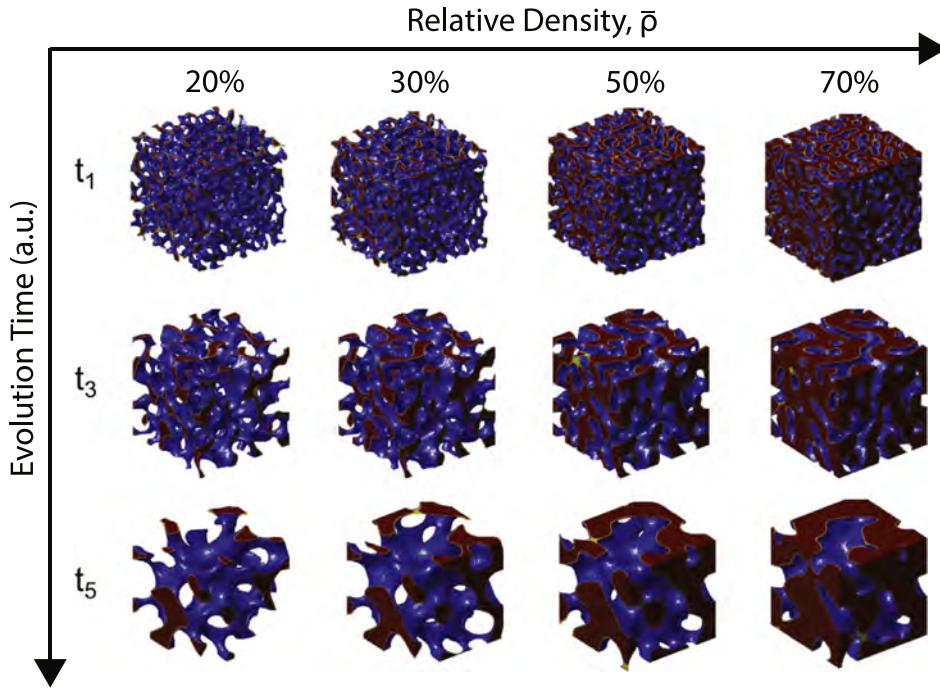


Fig. 2. 3D spinodal solid models with different relative densities, $\bar{\rho} = 0.2, 0.3, 0.5$, and 0.7 , extracted at different evolution times, t_1, t_3 , and t_5 .

The results show three important features: (i) the intensity profiles in the FFT images are all nearly axisymmetric, indicating that all our spinodal models are isotropic; (ii) the dominant frequencies shrink as the evolution time increases, indicating that the characteristic feature size increases with evolution time; (iii) the dominant feature size is unaffected by the relative density of the solid spinodal models and only depends on evolution time, suggesting that this unique characteristic length scale can be used to uniquely describe the morphology evolution of the system (*in lieu* of time), a description that we adopt henceforth for both solid and shell spinodal topologies.

To properly measure the characteristic feature size for each topology, FFTs are extracted for full three-dimensional spinodal models. Plots of amplitude VS frequency along the x-direction are extracted and depicted in Fig. 4a (the specific direction is immaterial, as the models were shown to be isotropic). Notice that if the frequency is multiplied by the domain size L in Fig. 4a, then the x-position of the dominant frequency peak represents the number of unit cells in the domain, $N = L/\lambda$, with λ the characteristic feature size.

Fig. 4a clearly shows that the characteristic feature size increases with evolution time, as qualitatively observed in the 2D FFTs. This time evolution is explicitly plotted in Fig. 4b, where the characteristic feature size is shown to scale with the cubic root of the evolution time, as expected by the LSW (Lifshitz-Slyozov-Wagner) theory of spinodal decomposition (Baldan, 2002; Kwon et al., 2010), for all but the first simulation. The slight disagreement on the first simulation point is attributed to an incomplete phase separation in the Cahn-Hilliard evolution model (i.e., evolution is not yet fully completed at that short time, and feature growth had not fully started). This finding confirms that the numerical topologies obtained with the technique described in Section 2.1 possess the characteristic features of naturally occurring spinodal structures.

2.3. Generation of shell spinodal topologies

Spinodal shell geometries are generated by extracting the interface between solid and void phases of spinodal solid models with a three-step process: (i) the stack of 2D images for each model is imported in Matlab and a 3D matrix containing the phase information of any point in the cubic domain at a particular instant in time is generated; (ii) the Matlab 'isosurface' function is used to extract the interface between solid and void phases; (iii) the Matlab 'surface smoothening' algorithm is applied the isosurface patches, in order to remove sharp geometric transitions. The resulting three-dimensional surface is then meshed with triangular shell elements within Matlab and subsequently imported in the commercial finite element software Abaqus for further mechanical analysis. The relative density of spinodal shell topologies is tuned by controlling the shell thickness in Abaqus. With this procedure, we generate spinodal shell topologies from each of the 5 solid spinodal topologies with 50% relative density discussed above (each with a different evolution time, and hence domain size and surface curvature); three such topologies are depicted in Fig. 5a. Once the surface area per volume ratio, S/V , of each model is extracted, the relative density of the shell spinodal model is calculated as $\bar{\rho} = bS/V$, with b the shell thickness. This relationship is plotted in Fig. 5b; notice that the shell thickness has been normalized by the characteristic domain size, λ , defined

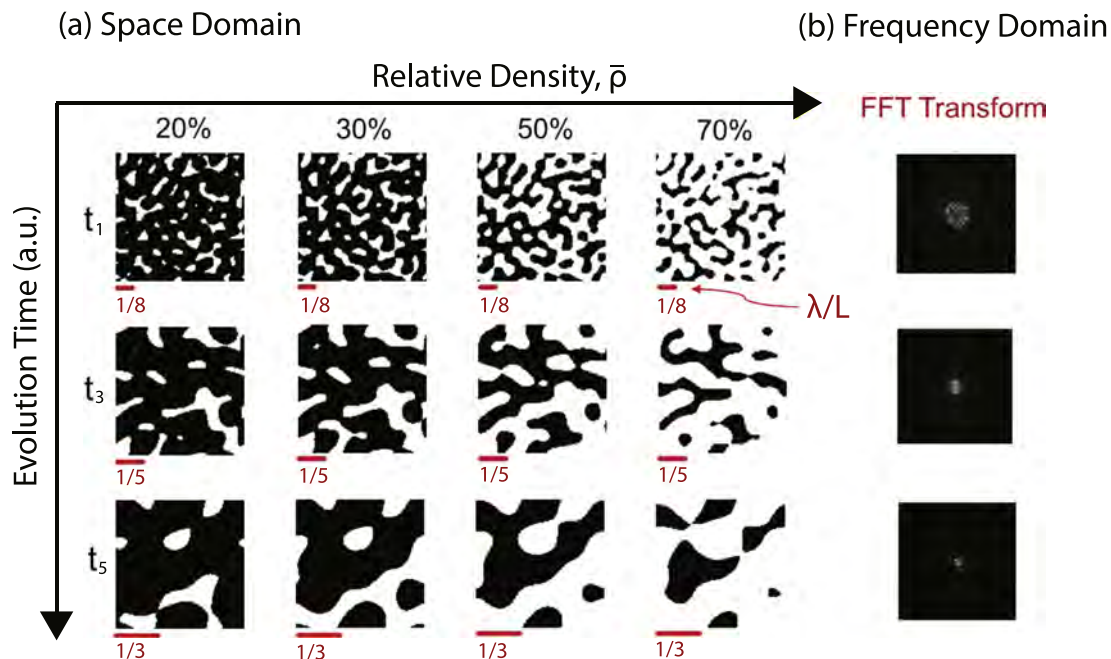


Fig. 3. 2D slices of spinodal solid models in (a) space domain and (b) frequency domain, at different relative densities ($\bar{\rho} = 0.2, 0.3, 0.5$, and 0.7) and different evolution times (t_1, t_3 , and t_5). The characteristic feature size is extracted from the FFT transforms of the models, and depends on the evolution time, but not on the relative density.

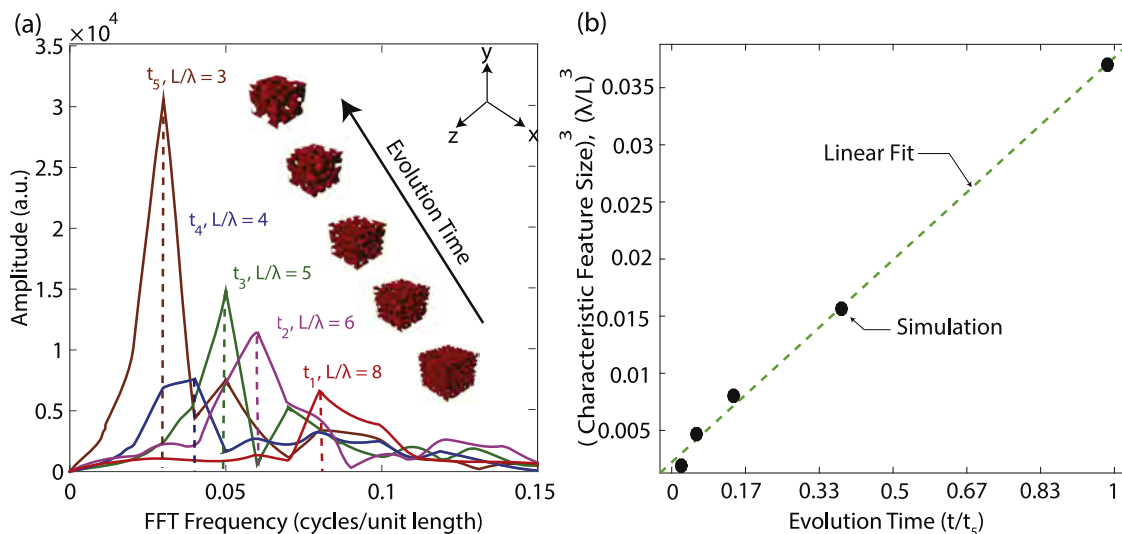


Fig. 4. Time evolution of the inverse of the characteristic feature size, as extracted from 3D FFT analyses of solid spinodal models. (a) FFT amplitude along the x direction at five evolution times; the frequency with highest amplitude is the inverse of the characteristic feature size. (b) The characteristic feature size scales with the cubic root of the evolution time (normalized by t_5), as predicted by the LSW theory of spinodal decomposition.

in Section 2.2 above. Using this approach, we generate shell spinodal structures with relative densities, $\bar{\rho} = 0.01\%, 0.1\%, 1\%, 5\%, 7\%$, and 10% for further analysis.

2.4. Calculation of the surface curvature

While clearly stochastic in nature, spinodal structures possess a remarkable uniform distribution of surface curvatures, with every surface patch characterized by a near-zero mean curvature and negative Gaussian curvature. Mean and Gaussian curvatures can be expressed in terms of the principal curvatures as $H = \frac{1}{2}(\kappa_1 + \kappa_2)$ and $K = \kappa_1 \cdot \kappa_2$. To confirm that the models generated in Section 2.1 conform to this important signature of spinodal structures, we extract the principal curva-

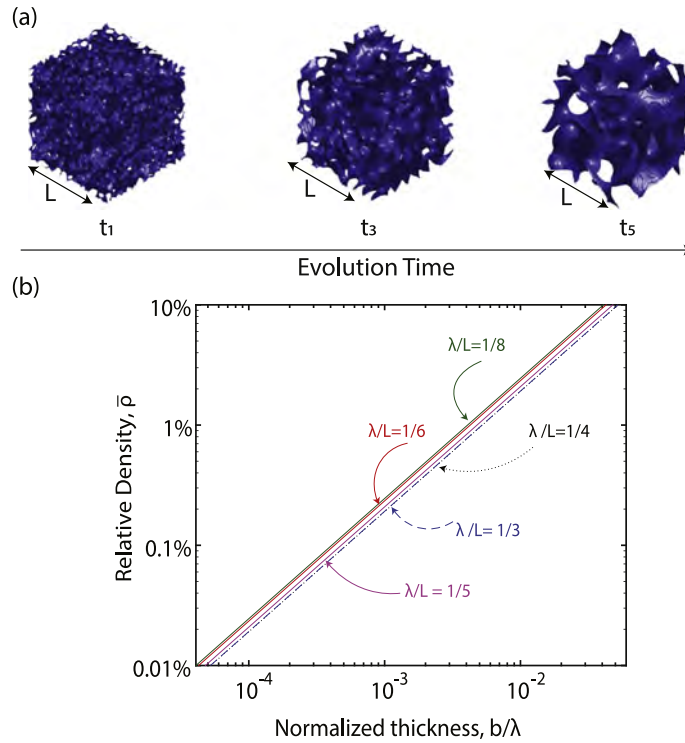


Fig. 5. (a) 3D spinodal shell models corresponding to the interfaces of spinodal solid models of $\bar{\rho} = 0.5$, extracted at three different evolution times (t_1 , t_3 , and t_5). (b) Relative density of shell spinodal cellular materials, as a function of the shell thickness, b , normalized by the characteristic feature size, λ . L denotes the cubic domain size.

tures at any location in each shell spinodal model with the algorithm described in Appendix 2. The results are plotted in Fig. 6. A number of important results clearly emerge: (i) for all topologies derived from 50% dense solid models (i.e., same amount of solid and void phases), $H \sim 0$ and $K < 0$, with most surface points within a very narrow range, as predicted by the theory of spinodal decomposition (Kwon et al., 2010); henceforth, we will use these models to construct shell spinodal topologies for mechanical characterization; (ii) for topologies derived from solid models with densities lower (higher) than 50%, $H < (>) 0$ and $K < 0$, with most surface points within a very narrow range; (iii) for all topologies, the magnitudes of the principal curvatures decrease with evolution time, remaining consistent with the trends mentioned above; this is clearly consistent with the characteristic feature size coarsening over time, as noticed above.

3. Mechanical performance of spinodal topologies

3.1. Numerical modeling of mechanical response

The finite element (FE) meshes of the solid and shell spinodal models, generated as described in Section 2, are imported in the commercial FE software package Abaqus Standard, and static simulations are performed to extract the mechanical response of these cellular materials under uniaxial loading, specifically the effective Young's modulus, E , and the effective yield strength, σ_y . The base material is modeled as isotropic elastic-perfectly plastic, with Young's modulus, $E_s = 210$ GPa and yield strength, $\sigma_{ys} = 235$ MPa (the actual values are immaterial, as the effective properties are normalized by these values). Geometric nonlinearity is allowed during deformation.

To simulate the uniaxial response of an infinite solid, the following boundary conditions are applied on the cubic domains (Fig. 7): (i) the nodes on the $-x$ face are restrained from moving in the x -direction but allowed to move freely in the y - and z -direction; (ii) a compressive displacement, $\delta_x = -6$, corresponding to a lattice level strain $\varepsilon_x = -6\%$, is applied to all the nodes on the $+x$ face, which are otherwise free to move in the y - or the z -direction; (iii) all the nodes on the $+y$ face are free to move in all directions, although their y -displacement is coupled to that of a reference node (and hence is the same for all nodes on the face); similarly, all the nodes on the $+z$ face are free to move in all directions, although their z -displacement is coupled to that of a reference node (and hence is the same for all nodes on the face); (iv) the nodes on the $-y$ face are constrained from moving in the y -direction but are free to move in the x - or z -direction, and the nodes on the $-z$ face are constrained from moving in z -direction but are free to move in the x - or y -direction. Although not as rigorous as periodic boundary conditions, these boundary conditions simulate the mechanical response of infinite spinodal structures, ensuring that all plane faces remain plane and allowing for Poisson's contraction upon uniaxial compression.

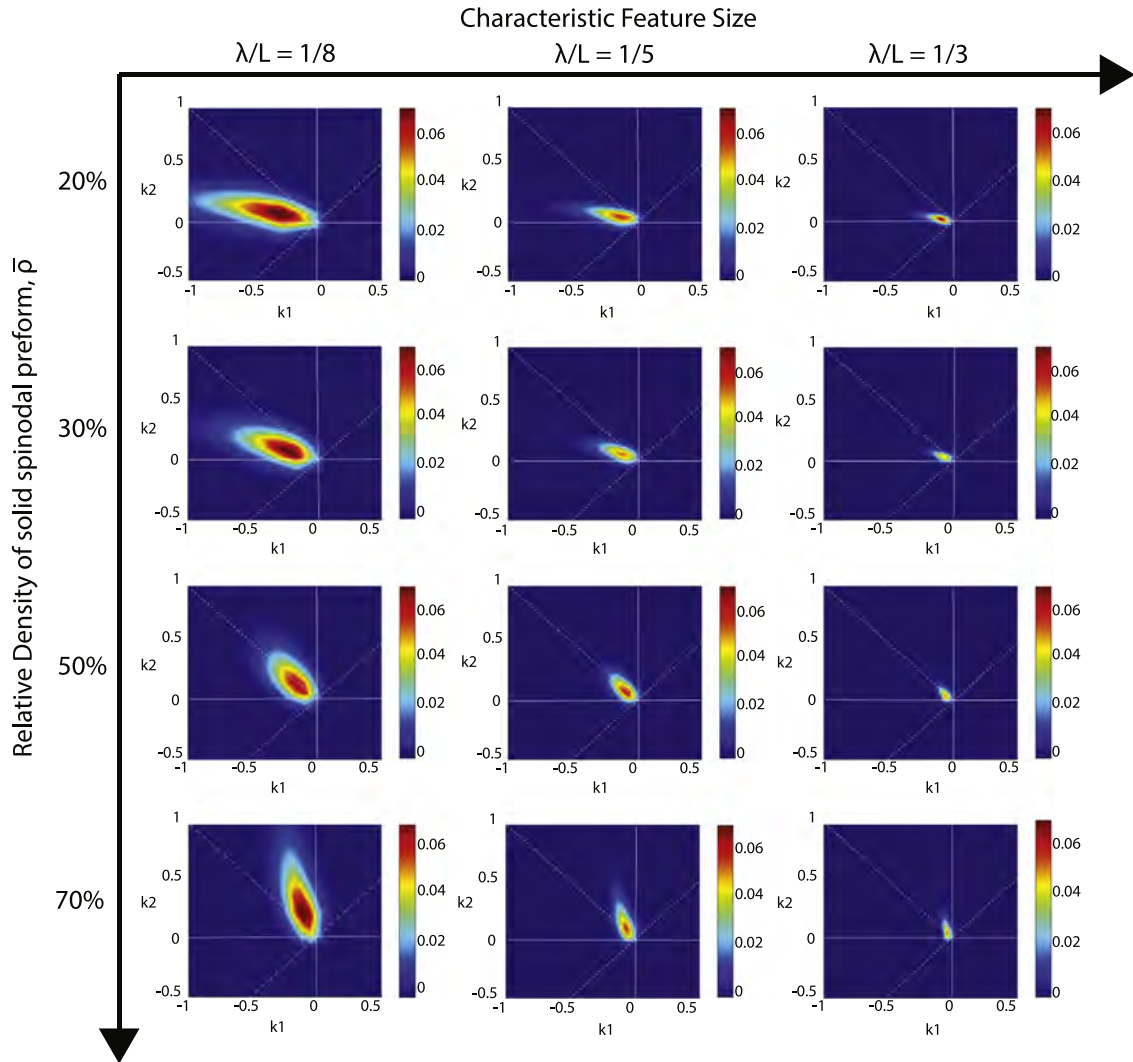


Fig. 6. Principal curvature maps of the surface of shell spinodal models, derived from different relative densities ($\bar{\rho} = 20\%$, 30% , 50% , and 70%) and different characteristic features sizes ($\lambda/L = 1/8, 1/5, 1/3$) of solid spinodal preforms. Notice that only the 50%-derived shell topology has near-zero mean curvature, $H = \frac{1}{2}(\kappa_1 + \kappa_2)$, throughout the surface.

The reaction force (F_R) integrated on all the nodes on the $-x$ face is extracted through the simulation. The stress-strain curve for the cellular material can then be generated, with stress and strain defined as $\sigma = F_R/L^2$ and $\varepsilon = \delta_x/L$, respectively, with L the cubic domain size. The effective Young's modulus of the cellular material, E , is calculated as the slope of the linear region in the stress-strain curve, and the effective yield strength, σ_y , is extracted as the 0.2% offset strength.

3.2. Imperfection sensitivity analysis

Thin shells (and by extension thin shell-based architected materials) are known to be stiff and strong but significantly sensitive to geometric imperfections (Hutchinson and Thompson, 2018), a characteristic that significantly limits their load carrying potential in practical applications. To quantify this effect in spinodal shell models, an imperfection sensitivity analysis is performed.

First, linear eigenvalue (elastic buckling) analyses are performed on the original meshes and the first ten eigenmodes with positive eigenvalues are extracted from each mesh. Second, imperfections are introduced in the original meshes as linear combinations of the first ten eigenmodes with equal weights; the magnitude of the imperfection parameter, $\psi = h_{\max}/b$, with $h_{\max}$ the largest displacement from the original mesh and b the shell thickness, is systematically increased in order to probe the imperfection sensitivity. Finally, post-buckling non-linear quasi-static Riks analyses are performed in uniaxial compression, subject to same boundary conditions described above, in order to capture the deformation evolution in imperfect meshes. Figs. 8 and 9 show meshes and stress-strain curves for two different 10% dense shell spinodal topologies,

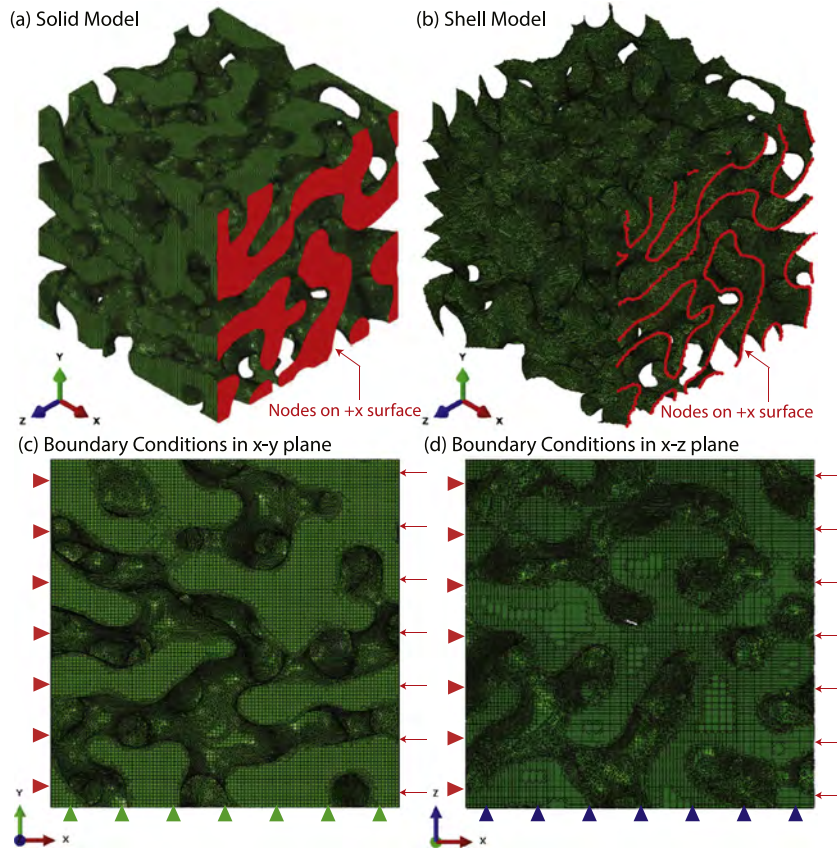


Fig. 7. Finite element model of (a) a solid spinodal model ($\bar{\rho} = 50\%$) and (b) the corresponding shell spinodal model. The nodes on the positive x surface are highlighted in red indicating how the boundary conditions are applied to the models. (c and d) Boundary conditions applied to a spinodal solid model in the x-y and x-z planes. Red, green and blue triangles indicate that translations are constrained along the x, y, and x directions, respectively. The sides opposite to those indicated with red, green and blue triangles are allowed to displace in the x, y, and z directions, respectively, but with the condition that all nodes on the side displace by the same amount. The same boundary conditions are applied to spinodal shell models. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

differing by the size of the characteristic feature, λ , relative to the domain size ((a) $\lambda/L = 1/8$, (b) $\lambda/L = 1/3$). For each topology, the response of the perfect structure ($\psi = 0$) is compared to the responses of the same topology with increasing amounts of imperfection. A very notable conclusion emerges: the topology with $8 \times 8 \times 8$ ‘unit cells’ in the domain (Fig. 9a) is absolutely imperfection insensitive, with imperfection magnitudes as large as 20 times the shell thickness showing no effect on the mechanical response. Even for very coarse topologies, with only $3 \times 3 \times 3$ ‘unit cells’ in the domain (Fig. 9b), the imperfection sensitivity becomes appreciable only when $\psi \sim 10$. (To further emphasize the imperfection insensitivity of these topologies, notice that the topology with characteristic feature size, $\lambda/L = 1/3$ (Fig. 8c, d and Fig. 9b) has much smaller surface area per unit volume than the topology with $\lambda/L = 1/8$ (Fig. 8a, b and Fig. 9a), and hence larger shell thickness; hence, in absolute terms, the imperfection magnitudes displayed in Fig. 9b are much larger than those in Fig. 9a (as evident from comparing Fig. 8a and b with Fig. 8c and d), explaining the emergence of some degree of imperfection sensitivity). Overall, the remarkable conclusion is that, unlike regular shell-based architected materials, spinodal shell based architected materials are remarkably imperfection insensitive; this important characteristic is attributed to the stochastic nature of the spinodal shell topologies. With this conclusion, all subsequent finite element analyses are performed on perfect meshed, without loss of conservatism.

3.3. Experimental verification

The accuracy of the finite element simulations is verified with a selected set of uniaxial compression experiments. Solid and shell spinodal samples were fabricated at the micro-scale via two-photon polymerization Direct Laser Writing (DLW), using a Nanoscribe Photonic Professional GT and a negative tone photoresist (IP-Dip, produced by Nanoscribe GmbH). All samples were fabricated using the Galvo mode with the 63X, N.A. 1.4 objective lens. Printing parameters were 35 mW and 17,000 $\mu\text{m/s}$ for laser power and scan speed, respectively. Cubic samples with edge length, $L = 140 \mu\text{m}$, are generated, using the solid and shell spinodal geometries calculated in Section 2. A characteristic feature size, $\lambda/L = 1/5$, is used for all sam-

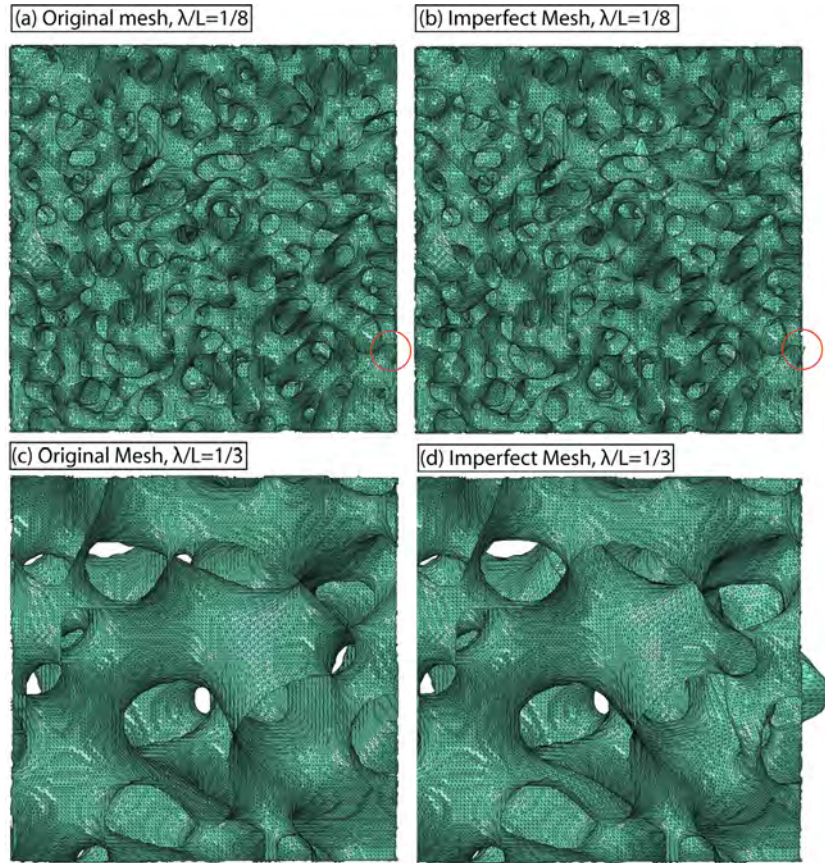


Fig. 8. Comparisons of perfect (a,c) and perturbed (c,d) meshes for spinodal shell topologies with characteristic feature size, $\lambda/L = 1/8$ (a,b) and $\lambda/L = 1/3$ (c,d). The magnitude of the imperfection is equal to $\psi = 20$ (b) and $\psi = 9.3$ (d), respectively. The small circles in (a,b) represent examples of subtle imperfections.

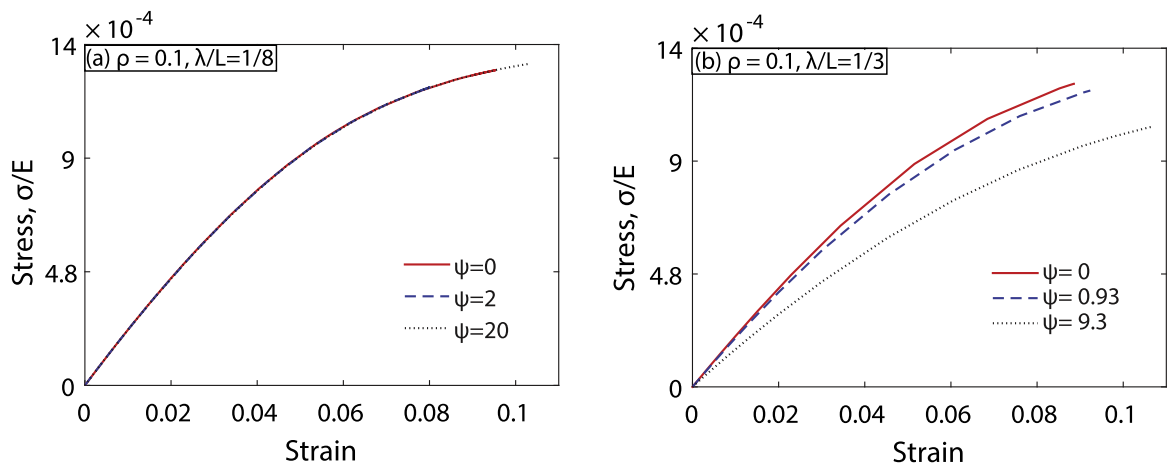


Fig. 9. Imperfection insensitivity of shell spinodal models. The non-dimensional imperfection magnitude, ψ , is defined as the largest displacement from a perfect mesh normalized by the shell thickness. Comparison of post-buckling stress-strain curves of 10% dense spinodal shells with characteristic feature size, $\lambda/L = 1/8$ (a) and for $\lambda/L = 1/3$ (b), with three different magnitudes of imperfection. The constituent material has Young's modulus, $E_s = 210$ GPa and yield strength, $\sigma_{ys} = 235$ MPa.

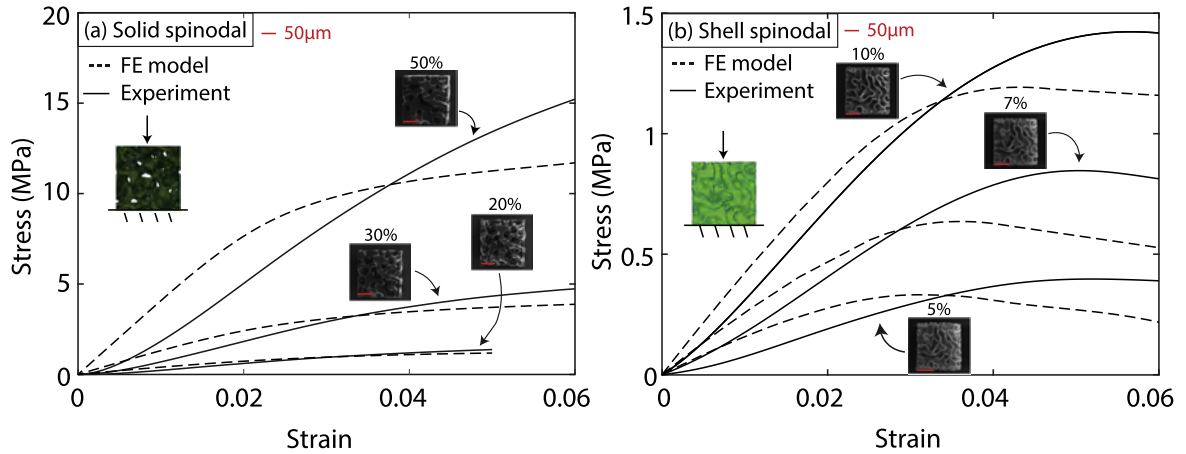


Fig. 10. Comparison of numerical and experimental stress-strain curves for (a) solid and (b) shell spinodal topologies at different relative densities, loaded in uniaxial compression. The characteristic feature size, $\lambda/L = 1/5$ is used for all models. The insets depict SEM images of the samples, fabricated by two-photon polymerization Direct Laser Writing in IP-Dip, with a Nanoscribe GT Photonics Professional, and tested with an Alemnis Nanoindenter. Higher resolution SEM images of all samples are shown in Fig. S1. The properties of IP-Dip were measured by micropillar compression tests, and input in the simulations as an elastic-perfectly plastic solid with $E_s = 2$ GPa, and yield strength $\sigma_{ys} = 60$ MPa.

ples. Solid spinodal samples with relative densities of 20%, 30% and 50%, and shell spinodal samples with relative densities of 5%, 7% and 10% were fabricated, respectively (all shell spinodal topologies were extracted from a 50% dense solid spinodal, as explained in Section 2). After DLW, samples were first immersed in propylene glycol monomethyl ether acetate (PGMEA) for 20 min to dissolve the remaining liquid resin, and subsequently in isopropanol for 2 min for final cleaning. See Fig. S1 for SEM images of all samples.

The mechanical response of all spinodal structures was characterized by displacement-controlled uniaxial compression tests with a maximum strain of 15%, performed at a constant strain rate of 0.005/s. All tests were performed with an Alemnis Nanoindenter. Load-displacement curves were recorded and extracted, and converted to stress-strain curves as explained in Section 3.1. To compare experimental results with numerical predictions, finite element models of the same topologies were generated and loaded in uniaxial compression, as explained in Section 3.1. In order to best approximate the experimental conditions, FE simulations are performed with the bottom face fully constrained, the lateral faces free and the top face subjected to uniform vertical displacement but unconstrained laterally. In order to extract the base material properties for the numerical analyses, a number of IP-Dip cylinders with diameters between 12.5 and 50 μm and aspect ratios of four were DLW printed with the same parameters as the spinodal samples and tested in uniaxial compression (see Supplementary Material Fig. S2) (ASTM D695-15, 2008). As the mechanical properties of this DLW acrylate resin are affected by the printing conditions and feature size (which cannot be kept identical for all the structures being printed), extracting an accurate stress-strain curve for the base material is challenging. To simplify the model, and in agreement with the results in Fig. S2, the base material was modeled as elastic-perfectly plastic, with Young's modulus, $E_s = 2$ GPa, and yield strength $\sigma_{ys} = 60$ MPa. While this simplification will slightly under-predict the ultimate strength of the structures, it is appropriate for the scope of this section.

Experimental and numerical stress-strain curves are compared in Fig. 10a and b, for solid and shell spinodal models, respectively. With the caveat on ultimate strength mentioned above, the agreement is very good throughout, thus validating all the finite element results presented in this work.

3.4. Scaling laws and mechanical performance

Effective Young's modulus and yield strength were extracted from finite element calculations (performed as described in Section 3.1) for solid and shell spinodal models, for a range of relative densities, $\bar{\rho}$ and characteristic feature size, λ/L . In all simulations the constituent material was modeled as isotropic elastic-perfectly plastic, with Young's modulus, $E_s = 210$ GPa and yield strength, $\sigma_{ys} = 235$ MPa. These values are representative of a relatively low yield strain metal, with yield strain $\epsilon_y \sim 0.001$. Most results presented here are general and independent on the choice of base material.

The effective Young's modulus and yield strength of solid spinodal models depending on $\bar{\rho}$ are depicted in Fig. 11. Notice that $E \sim (\bar{\rho})^{2.0-2.6}$ and $\sigma_y \sim (\bar{\rho})^{1.7-2.3}$, with the lower exponents corresponding to topologies with larger characteristic feature size to domain size ratios. We excluded the 20% dense samples from the scaling calculations, as the 20% dense spinodal topologies displayed isolated islands on the inside of the models that depressed the mechanical properties and unrealistically steepened the slopes. While these large exponents are not unexpected at such large relative densities, this likely indicates that the solid spinodal topologies are bending dominated and the spinodal arrangement of matter is not

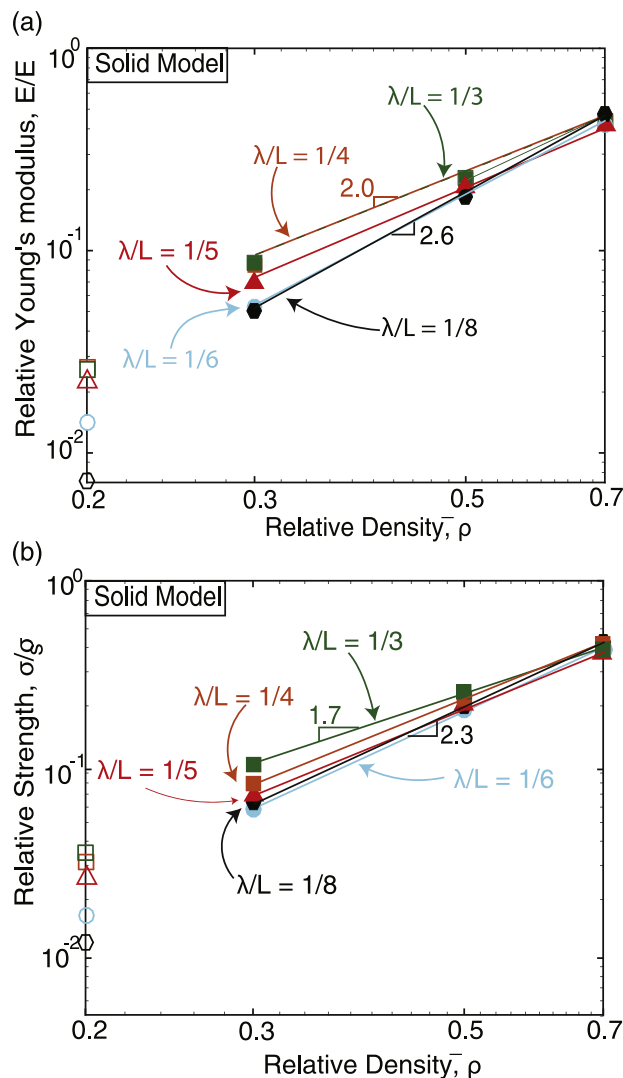


Fig. 11. Numerical predictions of (a) Relative Young's modulus and (b) relative yield strength of spinodal solid models, as a function of their relative density, $\bar{\rho}$. Hollow markers indicate models with isolated internal islands, which have been excluded from the scaling calculations. The constituent material has Young's modulus, $E_s = 210$ GPa and yield strength, $\sigma_{ys} = 235$ MPa. Different curves refer to models with different characteristic feature size, λ . L denotes the domain size.

very mechanically efficient. The numerical simulations indicate that solid spinodal models are yielding-limited (as opposed to elastic buckling-limited) for all relative densities of interest, 20–70%.

Remarkably, these conclusions change dramatically for shell spinodal topologies (Fig. 12). Here, $E \sim \sigma_y \sim (\bar{\rho})^{1.2-1.3}$, a scaling that is very similar to that of the best stretching dominated lattice materials. We attribute this exceptional performance to the deformation behavior of doubly curved surfaces, which cannot be readily bent without the introduction of significant membrane stresses – and hence deform in a stretching-dominated manner. For the base material yield strain used in the calculation, shell spinodal topologies remain yielding-limited down to relative densities in the order of 0.1%. Once the failure mechanism switches to buckling, the scaling worsens somewhat (as expected), but remains reasonably close to one. Interestingly, the relationship between scaling law exponent and characteristic feature size to domain size ratio, λ/L , is inverted compared to the case of solid spinodal topologies. In shell spinodal topologies, a larger λ/L corresponds to a steeper scaling exponent for both stiffness and strength.

The exceptional mechanical efficiency of shell spinodal topologies is attributed to its uniform surface curvature (see Section 2.2), which results in a very uniform local stress distribution upon loading, avoiding areas of substantial stress intensification. To confirm this hypothesis, we contrast the local stress distribution upon uniaxial loading of a shell spinodal sample and a hollow microlattice material of the same relative densities, reproduced from (Valdevit et al., 2013) (Fig. 13); the difference in Mises stress uniformity is clearly evident. In other words, shell spinodal topologies are extremely efficient

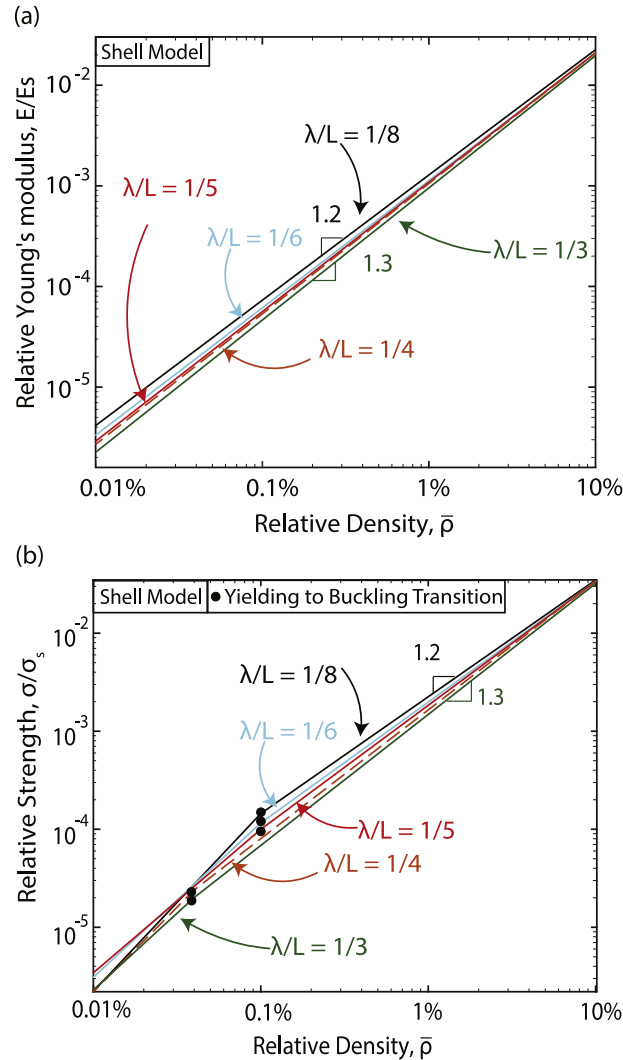


Fig. 12. Numerical predictions of (a) Relative Young's modulus and (b) relative yield strength of spinodal shell models, as a function of their relative density, $\bar{\rho}$. The constituent material has Young's modulus, $E_s = 210$ GPa and yield strength, $\sigma_{ys} = 235$ MPa. Different curves refer to models with different characteristic feature size, λ . L denotes the domain size. The black dots mark the transition from yielding to buckling failure.

in terms of material utilization, with the entire structure failing nearly simultaneously, rather than localizing failure at the nodes (a well-known shortcoming of hollow lattice materials (Meza et al., 2015, 2014; Schaedler et al., 2011; Torrents et al., 2012; Valdevit et al., 2013)).

An obvious question emerges regarding the role of near-zero mean curvature on the uniformity of the stress distribution and hence the mechanical efficiency of shell spinodal topologies. As clearly illustrated in Fig. 6, all 50%-derived spinodal shell topologies possess the characteristics of minimal surfaces (i.e., $\kappa_1 = -\kappa_2$ almost everywhere on the surface), while the same is not true for shell spinodal topologies derived from solid spinodals with densities different from 50%. To quantitatively ascertain the impact of zero mean curvature on the mechanical properties of spinodal shell topologies, we generated finite element models of 20% and 70%-derived spinodal shell topologies at two different characteristic feature sizes ($\lambda/L = 1/8$ and $\lambda/L = 1/3$), and compared their stress-strain curve to those of 50%-derived topologies. All shell thicknesses were chosen so that all shell topologies had a 10% relative density. The results are reported in Fig. 14. Two interesting results emerge: (i) 50%-derived shell spinodal topologies outperform both the 20% and the 70%-derived topologies, at both characteristic length scales, confirming that the minimal surface characteristics of 50%-derived spinodal structures are partly responsible for their mechanical efficiency. This is attributed to a more homogeneous stress distribution (see insets). (ii) The mechanical performance of topologies derived from solid spinodal structures with densities significantly different from 50% seem to be largely unaffected by the characteristic feature size, in contrast with 50%-derived spinodal topologies.

It is instructive to compare the mechanical efficiency of solid and shell spinodal topologies to that of a wide range of strut-based and shell-based architected materials, in particular solid strut metallic nanolattices (Khaderi et al., 2017), solid

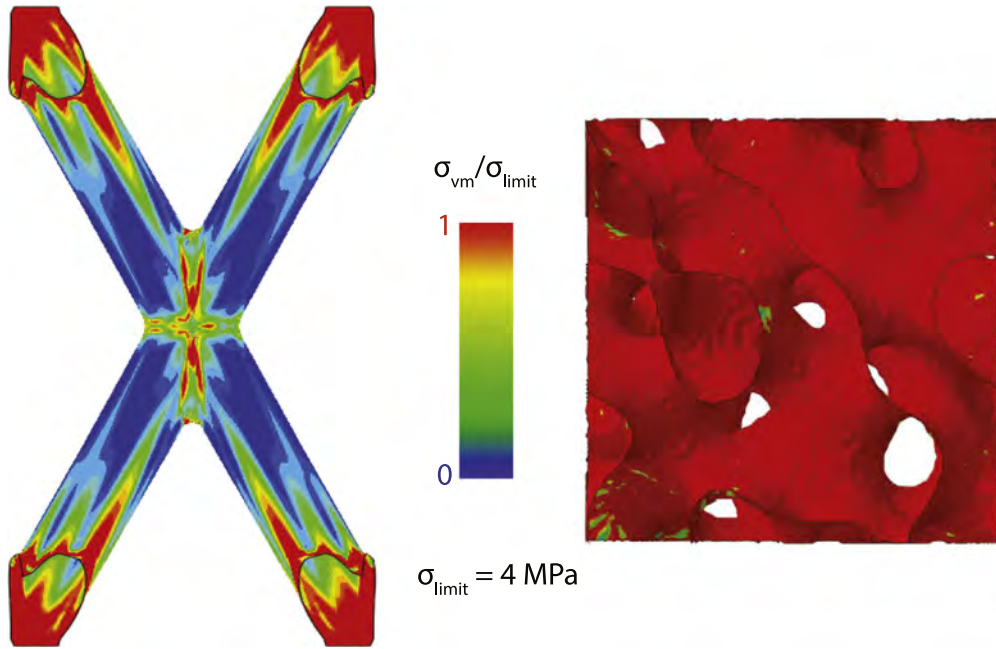


Fig. 13. Comparison of von Mises stress distribution in a hollow microlattice unit cell with bar aspect ratio ~ 6 , and angle $\theta = 60^\circ$ (Valdevit et al., 2013) and a spinodal shell model with characteristic feature size, $\lambda/L = 1/3$, both at relative density of 0.01%, and under a compressive strain of 0.1%. The constituent material has Young's modulus, $E_s = 210$ GPa and yield strength, $\sigma_{ys} = 235$ MPa. The stress limits (used to distinguish stress contours where $\sigma_{vm}/\sigma_{limit} \geq 1$) are colored "red", with $\sigma_{limit} = 4$ MPa. Notice that the spinodal shell topology has a much more uniform stress distribution, yielding excellent mechanical efficiency. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

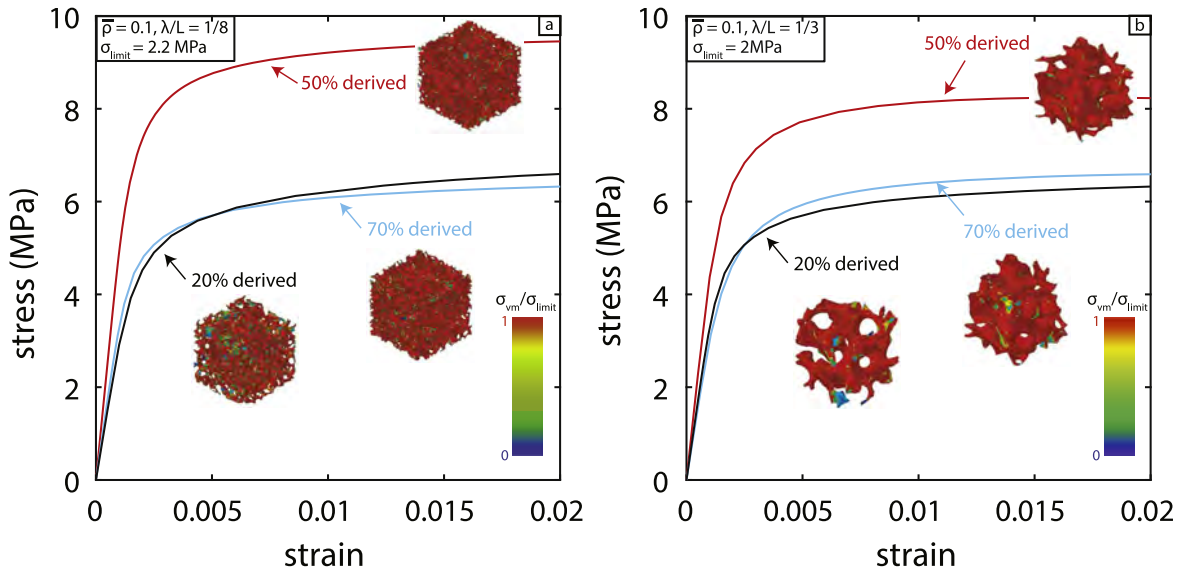


Fig. 14. The effect of mean surface curvature, H , on the mechanical efficiency of shell spinodal topologies. The insets display contours of von Mises stress. Notice that spinodal shell topologies derived from 50%-dense spinodal solids (and hence exhibiting near-zero mean curvature everywhere on the surface) are more efficient than spinodal shell topologies of equal relative density but derived from 20% and 70% solid spinodals (and hence having non-zero mean curvatures throughout the surface). The constituent material has Young's modulus, $E_s = 210$ GPa and yield strength, $\sigma_{ys} = 235$ MPa. The stress limits (used to distinguish stress contours where $\sigma_{vm}/\sigma_{limit} \geq 1$) are colored "red", with (a) $\sigma_{limit} = 2.2$ MPa and (b) $\sigma_{limit} = 2$ MPa. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

strut carbon nanolattices (Bauer et al., 2016b), hollow strut metallic microlattices (Schaedler et al., 2011; Zheng et al., 2014), hollow strut ceramic nanolattices (Meza et al., 2015, 2014), and two mechanically efficient metallic shell-based architected materials, the P-surface material (Han et al., 2015) and the D-surface material (Han et al., 2017). These comparisons are presented in Fig. 15 in terms of relative Young's modulus, E/E_s , and relative yield strength, σ_y/σ_{ys} , versus relative density, $\bar{\rho}$. Only spinodal topologies with $\lambda/L = 1/5$ are depicted for clarity, for two different values of the base material yield strain: $\epsilon_{ys} = 0.01$ (representative of IP-Dip, thus allowing direct comparison with experimental results) and $\epsilon_{ys} = 0.001$ (repre-

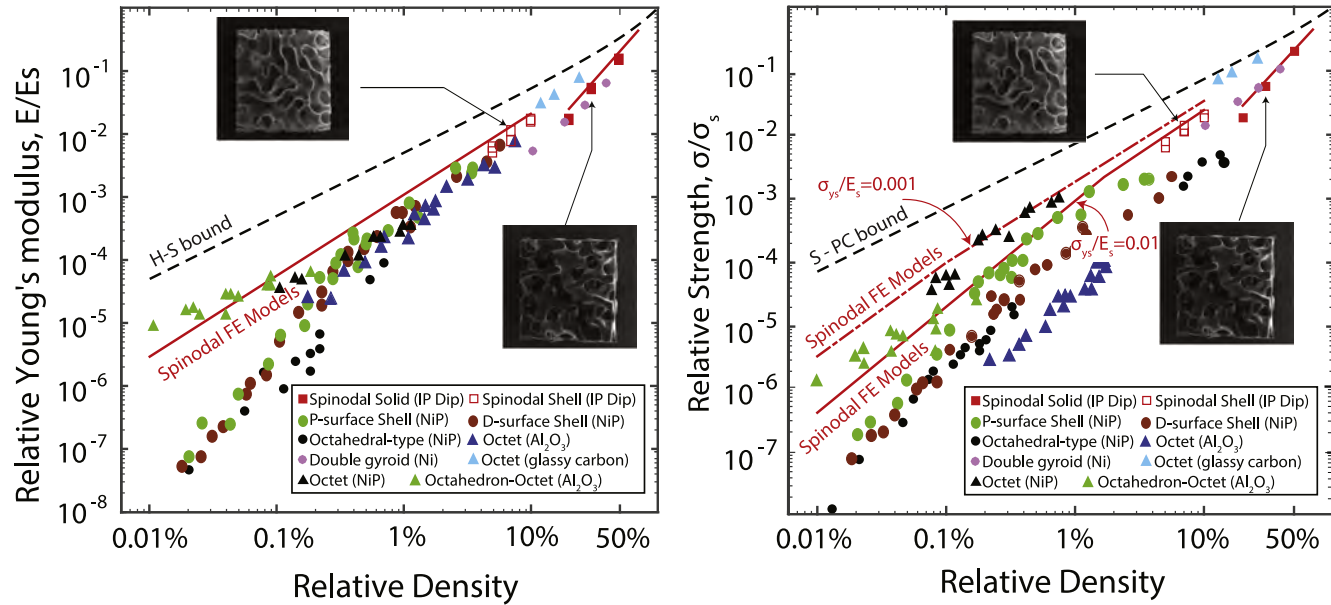


Fig. 15. Comparison of the mechanical performance of solid and shell spinodal topologies and well-established strut-based and shell-based architected materials: hollow octahedral-type metallic microlattices (Schaedler et al., 2011), hollow octet ceramic nanolattices (Meza et al., 2014), hollow octet metallic microlattices (Zheng et al., 2014), hollow octahedron-octet nanolattices (Meza et al., 2015), solid glassy carbon nanolattices (Bauer et al., 2016b), double gyroid nanolattices (Khaderi et al., 2017), P-surface (Han et al., 2015) and D-surface (Han et al., 2017) architected materials. Only spinodal topologies with characteristic feature size, $\lambda/L = 1/5$ are depicted for clarity, for two different values of the base material yield strain: $\varepsilon_{ys} = 0.01$ (representative of IP-Dip, thus allowing direct comparison with experimental results) and $\varepsilon_{ys} = 0.001$ (representative of a metal). Also depicted are the Hashin-Shtrikman upper bound for stiffness (Hashin and Shtrikman, 1963; Khaderi et al., 2017) and the Suquet-Ponte-Castaneda nonlinear upper bound for strength (Castaneda and Debotton, 1992; Suquet, 1993), which represent theoretical limits for the mechanical performance of isotropic cellular materials.

sentative of a metal). As all the results depicted in Fig. 15 for the 10 comparison structures are obtained experimentally, experimental results for solid and shell spinodal topologies (obtained as described in Section 3.2) are depicted as well. Also plotted on Fig. 15 are the Hashin-Shtrikman upper bound for stiffness (Hashin and Shtrikman, 1963; Khaderi et al., 2017) and the Suquet - Ponte-Castaneda nonlinear upper bound for strength (Castaneda and Debotton, 1992; Suquet, 1993), which represent theoretical limits for the mechanical performance of isotropic cellular materials. We emphasize that solid and shell spinodal architectures are the only isotropic topologies in Fig. 15. Notice that while spinodal solid topologies are worse than double gyroid materials and glassy carbon lattices at high relative densities, shell spinodal topologies are on par with or better than all referenced ultralight topologies across a relative density range covering 3 orders of magnitude, clearly demonstrating their exceptional mechanical efficiency.

While the model predictions for spinodal shell topologies at ultra-low density (i.e., in the buckling-limited regime) are not verified experimentally due to fabrication challenges, the remarkable imperfection insensitivity of spinodal shell topologies demonstrated in Section 3.2 strongly suggest that very small knock-down factors will apply, providing confidence in the numerical results.

4. Conclusions

The mechanical performance of spinodal topologies was numerically investigated and experimentally verified. Cellular materials with spinodal architectures were numerically generated by solving the Cahn-Hilliard evolution equation with a Finite Difference numerical scheme. Topologies were extracted at different evolution times, corresponding to different characteristic feature size to domain size ratios, and different relative densities, i.e., different ratios of solid to void phase. We refer to these topologies as solid spinodal models. Another class of spinodal topologies was generated by retaining the interface between the solid and void phases of solid spinodal models and eliminating both volumetric phases: we refer to these topologies as shell spinodal models. The characteristic feature size of spinodal models was calculated by Fast Fourier Transform analysis, and used as a metric for 'unit cell size' of these stochastic cellular materials. This feature size was shown to scale with the cubic root of the evolution time, in agreement with the theory of spinodal decomposition. The distribution of principal curvatures of all spinodal models was also extracted, and verified to be representative of naturally occurring spinodal systems. The mechanical performance of solid and shell spinodal topologies was investigated numerically by finite element analysis. The numerical models, verified by mechanical experiments performed on solid and shell spinodal samples fabricated at the microscale by two-photon polymerization Direct Laser Writing (DLW), showed three key results: (i) shell spinodal topologies are remarkably efficient, displaying stretching dominated behavior over a very wide range of relative densities; (ii) whereas shell-based architected materials are generally imperfection sensitive, shell spinodal topologies display remarkable imperfection insensitivity, which is expected to result in superior mechanical response at ultra-low relative densities, where buckling knock-down effects plague the response of most architected materials; (iii) in the low-relative density regime ($\bar{\rho} < 1\%$) architected materials with shell spinodal topologies outperform most strut and shell-based architected materials in terms of specific stiffness and strength, while displaying complete isotropy in three dimensions.

These remarkable properties are entirely due to the topological characteristics of the architecture, and are attributed to the very uniform double curvature across the entire surface of the material, which avoids stress intensifications and prevents local bending deformations of the surface without the introduction of membrane stresses, thus imparting stretching dominated behavior to the cellular material. Importantly, base material effects have not been considered in this analysis: if emerging nano-scale fabrication techniques are used to exploit size effects in metallic and ceramic base materials (Khaderi et al., 2017; Mallory and Hajdu, 1990; Schwartzberg and Olynick, 2015), unprecedented specific strength can be achieved. These opportunities are currently under investigation.

Finally, we emphasize that the true potential of these topologies stems from the fact that they can be self-assembled, using a variety of physical processes at multiple length scales. While the experiments in this article are performed on 3D printed samples to facilitate fabrication of samples of controlled size and shape and application of mechanical loads, macroscale samples can be produced by selective etching of a metallic solid solution (Hodge et al., 2007) or by phase separation of a colloidal suspension (bijel technology) (Lee and Mohraz, 2010), resulting in nanoscale and microscale characteristic feature size, respectively. These self-assembly methodologies can be combined with additive manufacturing at a larger scale to create macroscale architected materials with unprecedented structural hierarchy, vastly improving the scalability of micro/nano-architected materials processing.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.jmps.2019.01.002](https://doi.org/10.1016/j.jmps.2019.01.002).

Appendix 1. Synopsis of algorithm for spinodal decomposition

The spinodal decomposition equation (Eq. (1)) is solved numerically with a Finite Difference scheme, as described in detail in Sun et al., 2013. Here we report the key details of the algorithm for completeness.

Eq. (1) is solved on a cubic volume with edge length, $L = 100$, which is discretized into a lattice of mesh size, $\ell = L/100 = 1$. Let u_{ijk}^m denote the discrete value of the phase field variable $u(i, j, k, m\tau)$ at nodal point (i, j, k) , where τ is the integration time step ($\tau = 0.005$ is chosen as a good compromise between solution accuracy and computational cost, as suggested by Sun et al., 2013) and m is the number of time steps.

A finite difference scheme is used to discretize Eq. (1) as:

$$\frac{u_{ijk}^{m+1} - u_{ijk}^m}{\tau} = \Delta \left[(u_{ijk}^m)^3 - u_{ijk}^m - \theta^2 \Delta u_{ijk}^m \right] \quad (\text{A1})$$

where again θ represents the thickness of the phase A / phase B interface (here chosen as 1.1) and Δ is the Laplacian operator. Eq. (2) is solved with periodic boundary conditions:

$$u(i, j, k, m\tau) = u(i + L, j, k, m\tau) \quad (\text{A2.1})$$

$$u(i, j, k, m\tau) = u(i, j + L, k, m\tau) \quad (\text{A2.2})$$

$$u(i, j, k, m\tau) = u(i, j, k + L, m\tau) \quad (\text{A2.3})$$

and a randomly generated initial condition, $u(i, j, k, 0) = u_0(i, j, k, 0) \in [-5, 5] \cdot 10^{-4} \neq 0$.

Here, phase A ($u = -1$) represents void space, and phase B ($u = 1$) represents solid material. As the solution progresses, the system phase separates at relative early times, and subsequently continues to coarsen; during the coarsening phase, the curvature of the interface between solid and void decreases and the size of the single-phase domains increases.

To enforce a specific relative density (i.e., a prescribed ratio of phase A and phase B regions), the threshold method with the cutoff u_c^m is used. The phase value of point (i, j, k) at time $m\tau$ is defined as:

$$PV_{ijk}^m = H(u_{ijk}^m - u_c^m) \quad (\text{A3})$$

where $H(u_{ijk}^m - u_c^m)$ is the Heaviside function. When $u_{ijk}^m - u_c^m > 0$, then $PV_{ijk}^m = 1$, indicating the space is occupied by material. When $u_{ijk}^m - u_c^m < 0$ then $PV_{ijk}^m = 0$ indicating void space. For a desired relative density $\bar{\rho}$, the cutoff u_c^m is adjusted such that:

$$\bar{\rho} = \frac{1}{L^3} \sum_1^L \sum_1^L \sum_1^L PV_{ijk}^m = \frac{1}{L^3} \sum_1^L \sum_1^L \sum_1^L H(u_{ijk}^m - u_c^m) \quad (\text{A4})$$

With this approach, dense spinodal topologies with arbitrary relative densities are generated.

Appendix 2. Algorithm for extraction of curvature probability maps

The principal curvatures of a surface at a point P , κ_1 and κ_2 , are defined as the minimum and maximum curvatures at that point, respectively. A paraboloid fitting method can be used to extract these curvatures at each point of the shell spinodal meshes, as proposed in (Gatzke and Grimm, 2006; Surazhsky et al., 2003). The following procedure is implemented: (i) The triangular shell mesh (generated as described in Section 2.1) is imported in Matlab. (ii) For any node P in the surface mesh, a number J of elements is identified as the set of elements belonging to the three neighboring rings of node P , with the first neighboring ring defined as all the elements sharing node P , and the next two rings as the elements sharing the boundary nodes of the previous ring. (iii) Unit normal vector to each element in the set J is constructed by normalizing the cross product of two edges of the element. (iv) The unit normal of the surface at node P , $\mathbf{n}_P$, is obtained as the average of the unit normals of all the elements in the first three neighboring rings of the point P as follows

$$\mathbf{n}_P = \frac{1}{J} \sum_1^J \mathbf{n}_e \quad (\text{A5})$$

where $\mathbf{n}_e$ is the unit normal of element “e”. (v) All the nodes in the first three rings of P , along with P , are transformed using a rotation matrix such that $\mathbf{n}_P$ align with the z-axis of the global coordinate system. (vi) The transformed coordinates of these nodes are used to least-square fit the coefficients a_0 to a_5 of the biquadratic polynomial surface:

$$z_v = a_0 + a_1x + a_2y + a_3xy + a_4x^2 + a_5y^2 \quad (\text{A6})$$

(vii) The Hessian matrix of the polynomial surface is calculated as:

$$\begin{bmatrix} 2a_4 & a_3 \\ a_3 & 2a_5 \end{bmatrix} \quad (\text{A7})$$

(viii) The pairs of minimum and maximum principal curvatures, κ_1 and κ_2 , at P are extracted as the eigenvalues of the Hessian matrix. (ix) The process above is repeated to find the principal curvatures at every single node of the spinodal shell mesh. Outliers in κ_1 and κ_2 are determined based on a median absolute deviation method (Leys et al., 2013), and any (κ_1 , κ_2) pair that has an outlier is removed. (x) Principal curvature density function maps are generated as contour plots of the probability density function $P(\kappa_1, \kappa_2)$, defined as:

$$P(\kappa_1, \kappa_2) = \frac{N(\kappa_1, \kappa_2)}{\sum N(\kappa_1, \kappa_2)} \quad (\text{A8})$$

where $N(\kappa_1, \kappa_2)$ is the number of (κ_1, κ_2) pairs having curvatures in the range $[(\kappa_1, \kappa_2), (\kappa_1 + \Delta\kappa_1, \kappa_2 + \Delta\kappa_2)]$. Here, $\Delta\kappa_1 = \frac{\max(\kappa_1) - \min(\kappa_1)}{N_1}$ and $\Delta\kappa_2 = \frac{\max(\kappa_2) - \min(\kappa_2)}{N_2}$, with N_1 and N_2 the number of intervals in κ_1 and κ_2 , respectively.

This procedure was used to generate the contour plots in Fig. 6.

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Programmable Mechanical Properties of Two-Photon Polymerized Materials: From Nanowires to Bulk

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Two-photon polymerization direct laser writing (TPP-DLW) is the most promising technology for additive manufacturing of geometrically complex parts with nanoscale features, and could dramatically accelerate the development of a wide range of engineering micro/nanosystems. However, a major obstacle to TPP-DLW's widespread industrial adoption is the lack of systematic data on material properties and limited knowledge on their correlation with processing parameters. These correlations for the acrylate-based resin IP-Dip are experimentally established over a large range of process parameters and length scales ranging from nanometers to centimeters. Universal characteristic relations between mechanical properties and process parameters are identified, which enable the tailoring of the material strength and stiffness over half an order of magnitude from rubbery soft to hard and strong. With a threshold-based optics model presented herein, the mechanical properties of the two-photon polymerized material can be accurately captured as a function of the applied process parameters, laying the foundation for a universal quantitative predictability of two-photon polymerization with programmable mechanical properties. This knowledge enables fabrication of microscale components with tailored local gradients in their mechanical properties, with significant implications for the development of novel mechanical, photonic, and photonic metamaterials.

direct laser writing (TPP-DLW) being the most versatile technology for fabricating 3D meso, micro, and nanoscale parts.^[1–3] Some of the most prominent research fields accelerated by TPP are photonic and mechanical metamaterials,^[4–6] microactuators,^[7,8] microrobots,^[9–11] bioscience,^[12–14] and biomimetics.^[15–17] Microfluidic and biomedical devices,^[18–22] microoptical elements on fiber-tips,^[23–25] and chip-to-chip interconnects,^[26,27] may soon become the first industrial applications.

While TPP technology is rapidly progressing,^[3] fabrication is still largely empirical, hindered by the lack of systematic data on material properties (e.g., strength and stiffness), and limited knowledge on their dependence on the process parameters. A small number of studies have reported certain properties of two-photon polymerized materials.^[28–32] However, most studies were specific to particular, application-relevant specimen geometries and sizes, with limited general implication on the establishment of TPP processing-structure-properties relations.

Mechanical properties like strength and stiffness have not been studied, or were estimated from indirect measurements, respectively.^[29–31] By contrast, for additive manufacturing processes which have experienced wide-spread industrial adoption (e.g., fused deposition modeling and direct metal laser sintering), processing-microstructure-properties relationships have been studied extensively,^[33–36] with the overarching goal of understanding all the underlying physical mechanisms. Clearly, TPP will not reach significant industrial penetration until precise and reliable specification and control of material properties are established.

TPP uses a focused ultrafast pulsed laser beam to locally expose a photosensitive material by two- or multi-photon absorption.^[1] Polymerization only occurs within a confined ellipsoid-shaped volume in the focal point of the laser beam. This volume element, or voxel, is the most elemental TPP feature. Smallest reported voxels dimensions are below 100 nm,^[1,3] while typical widths and heights are ≥ 200 nm and ≥ 600 nm, respectively. TPP-derived parts are generally hatched from multiple voxel-lines, i.e., continua of voxels, in a line-by-line fashion, using galvanometric mirrors and 3-axis stages.

1. Introduction

Additive manufacturing is rapidly advancing toward wide-spread industrial usability, with two-photon polymerization

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The most common TPP materials are negative-tone acrylate-based resins,^[37,38] due to their processing ease and the wide assortment of functionalities and monomer sizes.^[39] Other successfully employed materials include epoxies, most notably SU-8,^[40] hydrogels,^[41] organic–inorganic hybrids,^[42] proteins,^[43] and elastomers like PDMS.^[44] In the simplest case, acrylate resins consist of a monomer, which will be cross-linked, and a photoinitiator, which absorbs light and cleaves into free radicals which then start the polymerization reaction. During polymerization via radical chain growth, several initiation, propagation, and termination reactions, each with their own different rates, occur simultaneously. Monomers react only with the propagating reactive center, not with other monomers, and chain addition ceases when the concentration of radicals is depleted by a number of termination reactions. Although reaction kinetics differ,^[45] the fundamental mechanisms which impact mechanical properties are often similar,^[46,47] and comparable dependencies on TPP process parameters may be expected.

The mechanical properties of acrylate-based resins are related to the degree of conversion (DC), i.e., the extent of cross-linking between polymer chains, which itself correlates with the exposure dose of light (D) during fabrication. The DC can be assumed proportional to the number of radicals generated within a volume element.^[48] Neglecting diffusion mechanisms,^[49] the density of radicals (ρ) is given by the two-photon absorption rate equation

$$\frac{d\rho}{dt} = (\rho_0 - \rho) \delta_{2,\text{eff}} I^2 \quad (1)$$

with the photoinitiator concentration in the uncured photoresist (ρ_0), the effective two-photon cross section ($\delta_{2,\text{eff}}$) and the spatial photon flux intensity distribution (I), corresponding to the typically Gaussian spatial laser beam profile at the focal point.^[46] Integration of Equation (1) gives the dependency of ρ on D as

$$\rho = \rho_0 \left(1 - e^{-\delta_{2,\text{eff}} D}\right) \quad (2)$$

where D is the integral of I^2 over the exposure time (t). The solubility of negative-tone photoresists is a highly nonlinear function of the exposure dose, causing a distinct threshold behavior, whereby a polymerized photoresist network remains soluble below a threshold exposure dose (D_{th}). This means that sustainable polymerization able to withstand a solvent bath requires $D \geq D_{\text{th}}$. Conversely, above a certain damage threshold, the photoresist may boil. The ratio of damage to polymerization threshold is the dynamic range of the photoresist. Equivalent relations are valid for cationic polymerization of epoxies.^[47]

Three key TPP process parameters determining the exposure dose, as well as the fabrication duration and accuracy, are the laser average power (P), the writing speed (v), and the writing density, which can be quantified by the hatching distance (d_h) and the slicing distance (d_s) between neighboring voxel-lines.^[50] Based on the TPP model discussed above, D can be expressed as

$$D = D_0 D_v \propto \frac{P^2}{v} D_v \quad (3)$$

with the spatial exposure dose distribution (D_v), relative to the peak value (D_0).^[47,51] D_0 can be expressed in terms of P , v , and D_v correlates with the spatial intensity profile of the laser beam. For a hatched material, D_v is a function of d_h and d_s .

Development of meaningful and reliable mechanical property data of two-photon polymerized materials requires the systematic characterization across the entire dynamic range, on all relevant length-scales. The size of a solitary voxel-line feature and its mechanical properties correspond to the above-threshold portion of the Gaussian intensity profile of the laser beam. Surrounding polymerized material corresponding to the below-threshold wings of the profile is dissolved during development. When several voxel-lines are printed with the same process parameters in sufficient proximity, the doses of the sequential exposures accumulate, with the photoresist “remembering” previous below- and above-threshold exposures. Depending on the applied process parameters, this “memory effect” may further cross-link already insoluble material, or form new, less cross-linked material by the overlap of below-threshold Gaussian wings.^[52] Enclosed minima may permanently remain below threshold, resulting in weak regions within a polymerized part. In practice, this ideal memory effect is superimposed to time-dependent processes, such as molecular diffusion.^[45] Thus, the effective properties of TPP-derived parts are a nontrivial function of the properties of the corresponding constituent features.

In this paper, we systematically characterize the mechanical properties of the two-photon polymerized acrylate-based resin IP-Dip. We report the direct measurement of the mechanical properties of individual voxel-line features and derive the mechanisms controlling the effective mechanical properties of TPP-derived hatched parts. Specimens spanned multiple length-scales, from 190 nm to centimeters (**Figure 1a**), including nanowires consisting of individual voxel-lines, multi-voxel-line bars and conventionally cured bulk samples. We measure Young’s modulus (E), yield strength (σ_y), ultimate tensile strength (σ_{UTS}), and degree of conversion by uniaxial compression and tension experiments and Raman microspectroscopy, respectively (**Figure 1b–d**). We find that the mechanical properties of solitary voxel-lines are largely independent on their size and the applied TPP process parameters, suggesting the existence of a mobility threshold which counterbalances the expected process parameter-sensitivity. In contrast, multi-voxel-line hatched parts can be vastly tailored from rubbery soft to hard and strong, depending on the degree of “overlap” of constituent voxel-line features. We identify universal characteristic trends for the mechanical properties, which hold over a large range of process parameter combinations. We quantify the observed behavior with a threshold-based optical model, which accurately captures the mechanical properties of the two-photon polymerized material as a function of the applied process parameters. This study provides a database to systematically tailor process parameters depending on the required mechanical properties, precision and process time for IP-Dip and lays the foundation for a universal quantitative predictability of the mechanical properties of TPP-derived parts. While IP-Dip is one of the most commonly used TPP materials, the fundamental physics unveiled in this work will apply to a wide range of photosensitive material systems.

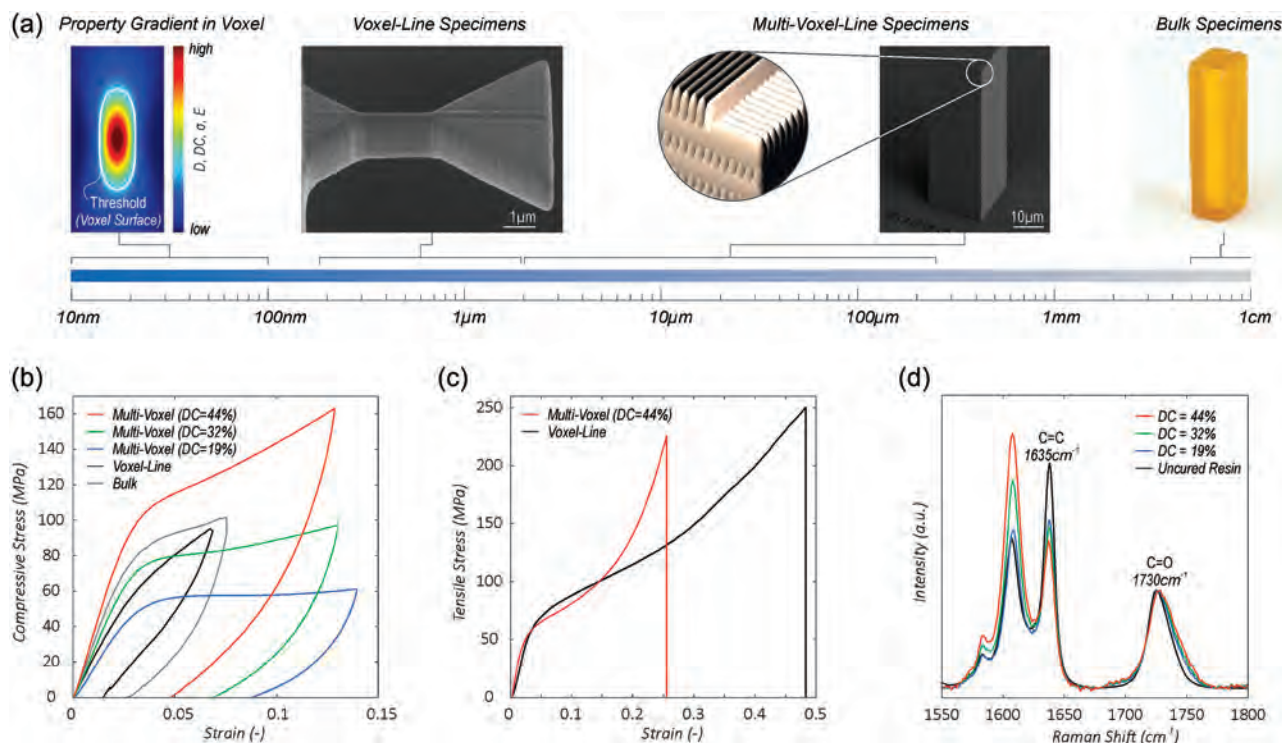


Figure 1. Mechanical characterization of the triacrylate TPP resin IP-Dip from nanowires to bulk, from polymerization to damage threshold. a) The investigated length scale ranges from sub-voxel gradients over individual voxel-lines and multi-voxel-line hatched specimens to conventionally cured bulk material. Representative b) compressive and c) tensile stress–strain curves and d) Raman spectra show the large tailorability of strength, stiffness and degree of conversion (DC) of multi-voxel-line hatched specimens compared to solitary voxel-lines and bulk specimens.

2. Results

2.1. Single Voxel-Line Specimens

Two-photon polymerized nanowire specimens are designed as dumbbell-shaped cantilever bars with one voxel-line in the gauge section, allowing for the direct measurement of the material strength and stiffness at the most elemental TPP level. Single voxel-line cantilevers are printed onto previously formed support blocks, and dumbbell sections are subsequently added by alternately printing additional lines on both sides. This symmetric printing strategy with sufficiently low writing speeds overcomes the typical warping of unsupported slender TPP features due to close-by exposures, resulting in high-quality specimens over the entire dynamic range of the photoresist. Customized support blocks provide easy accessibility without the need of additional specimen preparation. Figure 1b,c includes compressive and tensile stress–strain curves of specimens with ≈ 400 nm wide voxel-lines (Movies S1 and S2, Supporting Information). We find elasto-plastic behavior, with almost identical yield strength and stiffness under compression and tension. The material is remarkably tough, considering the high ultimate tensile strength of 255 ± 7 MPa with failure strains over 40%.

The mechanical properties of voxel-lines are found to be largely insensitive to their size and applied TPP process parameters (Figure 2). We manufacture 190–640 nm wide compression specimens, by varying the combination of laser average power and writing speed (Figure 2a). For a first set of

specimens, we keep ν constant at $10 \mu\text{m s}^{-1}$ and vary P across the entire dynamic range of the photoresist, with the smallest and the largest specimens at the polymerization and the damage threshold, respectively. A second set of specimens is manufactured with ν spanning four orders of magnitude from 100 to $10\,000 \mu\text{m s}^{-1}$, where P was adjusted to yield ≈ 300 nm wide voxel-lines. Figure 2b shows the mechanical properties of both specimen sets as a function of the voxel-line size, while Figure 2c shows the mechanical properties as a function of P for specimens printed with $\nu = 10 \mu\text{m s}^{-1}$. Toward the polymerization threshold our data indicate a certain decrease in the Young's Moduli as well as to some extent in the compressive yield strengths. However, both E and σ_y plateau in a narrow range with average values of 48 ± 6 MPa and 2.4 ± 0.3 GPa, respectively.

2.2. Hatched Multi-Voxel-Line Specimens

In contrast to individual voxel-lines, the mechanical properties of hatched multi-voxel-line specimens show a pronounced dependency on the TPP process parameters (Figure 3), consistent with previously reported data.^[28,31] We examine the impact of different combinations of laser average power, writing speed and writing density. E , σ_y , and DC are measured by uniaxial compression and by Raman spectroscopy of bars with nominal dimensions of $20 \times 20 \times 65 \mu\text{m}$, with a constant hatching-to-slicing-distance ratio ($d_s/d_h = 2$).

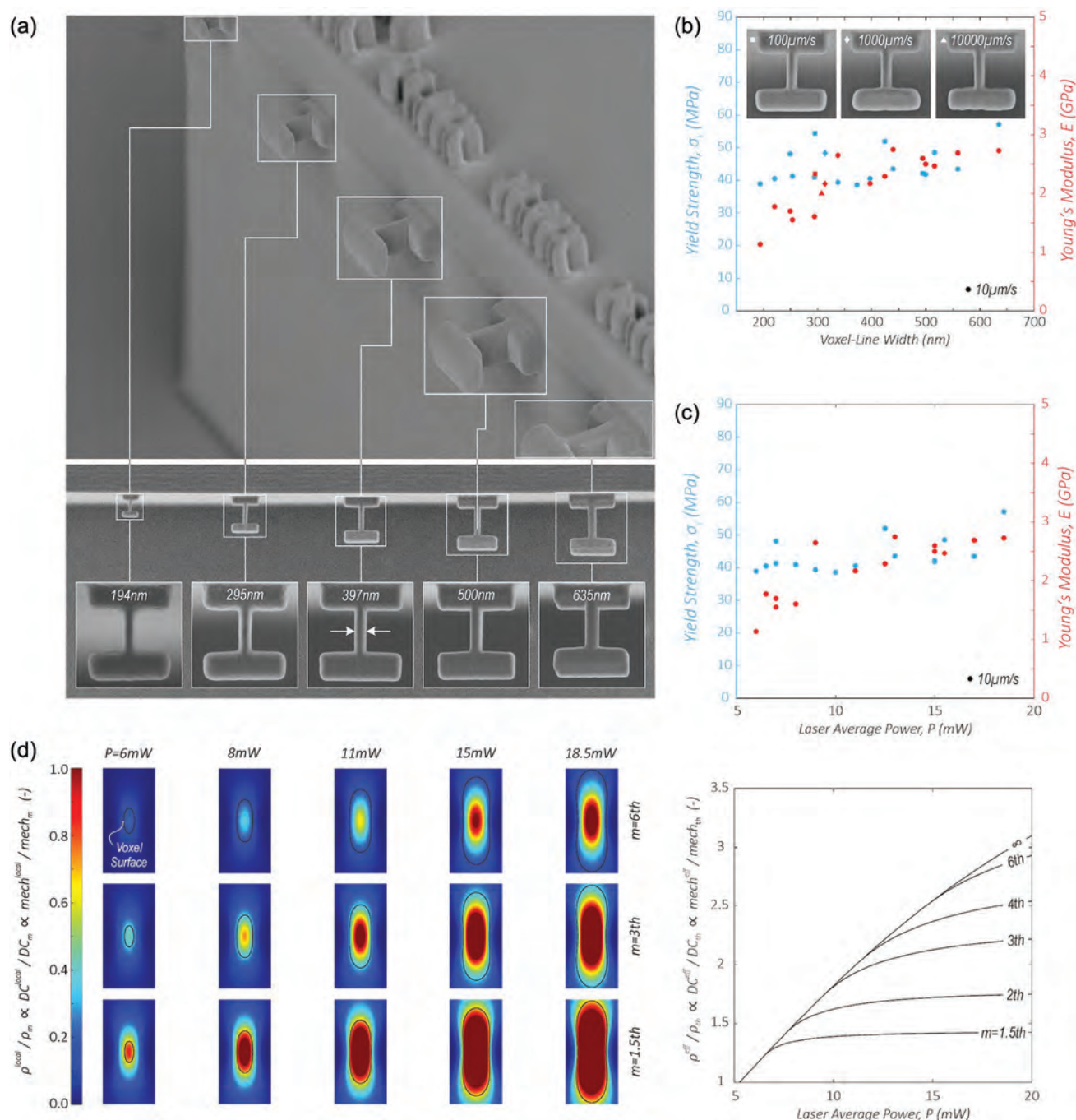


Figure 2. Mechanical properties of voxel-line features are found size and TPP process parameters independent. a) Varying the combination of laser average power (P) and writing speed (v) across the dynamic range of IP-Dip manufactures compression specimens with 195–660 nm wide voxel-lines. Compressive yield strength and Young's modulus versus b) voxel-line size and c) P (only specimens with $v = 10 \mu\text{m s}^{-1}$). d) Simulated radical density (ρ) in voxel-line cross-section depending on P ($v = 10 \mu\text{m s}^{-1}$); local gradients (left) and corresponding effective properties (right) considering a mobility threshold (m) which limits ρ , compared to a mobility threshold free material ($m = \infty$). Increasing (m) with respect to the polymerization threshold (th) reduces process-parameter sensitivity of ρ , degree of conversion (DC) and mechanical properties (mech).

P , v , and d_h each show a characteristic impact on the mechanical properties, allowing to tune E and σ_y across half an order of magnitude, from 0.6 to 3.6 GPa and from 20 to 70 MPa, respectively (Figure 3a). E , σ_y and DC increase with P and decrease with v and d_h . In all cases, specimens start to fully form with a DC above $\approx 20\%$; by comparison, the

damage threshold is just below $\approx 45\%$ (Figure 3b). Decreasing mechanical properties are thereby accompanied by increasing shrinkage with respect to the nominal dimensions (Figure 3c and Figure S1, Supporting Information). Correlating with emerging porosity for $d_h \geq 0.45 \mu\text{m}$, the DC plateaus above $\approx 20\%$, whereas the mechanical properties drop. For

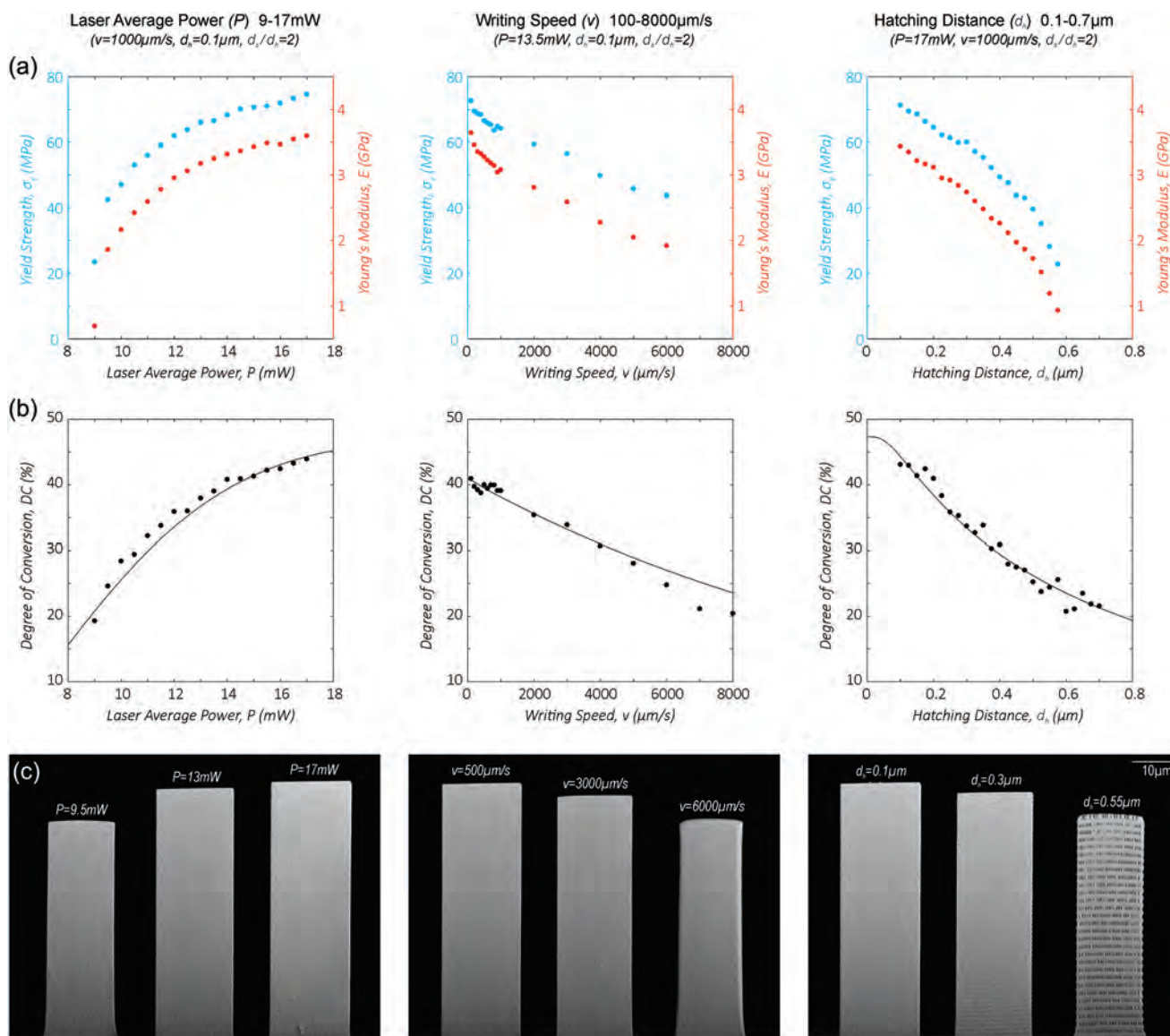


Figure 3. TPP process parameters tailor the mechanical properties of hatched multi-voxel-line specimens. Laser average power (P), writing speed (v) and hatching distance (d_h) (left to right column) have a characteristic impact on a) compressive yield strength (σ_y), Young's modulus (E) and b) degree of conversion (DC). Measured DC values are complemented by analytical predictions (Equation (6)). c) SEM images of selected specimens.

$v > 6000 \mu\text{m s}^{-1}$ and $d_h \geq 0.6 \mu\text{m}$, specimen quality starts to significantly degrade, making mechanical tests unfeasible. The found dependencies well translate to other ratios d_s/d_h (Figure S2, Supporting Information), whereby the effective properties slightly shift corresponding to the varying writing density.

Combining all experimental results from Figure 3, shows a linear dependency of E and σ_y with the DC (Figure 4). Independent from specific process parameters, specimens with the same DC roughly have the same mechanical properties. E and σ_y approximately increase with the DC as

$$E = (9.52 \text{ DC} - 0.56) \text{ GPa} \quad (4)$$

$$\sigma_y = (170.36 \text{ DC} - 0.84) \text{ MPa} \quad (5)$$

Conversely, the above equations allow estimation of the DC of individual voxel-lines, which may hardly be measured directly due to their small dimensions. With the average voxel-line strength and stiffness, Equations (4) and (5) estimate a DC of $\approx 30\%$.

The tensile properties of hatched multi-voxel-lines specimens well correspond to the compressive properties and their process parameter dependency. Under tension (Figure S3, Supporting Information), increasing P from 9.5 to 17 mW, with $v = 1000 \mu\text{m s}^{-1}$, $d_h = 0.1 \mu\text{m}$ and $d_s/d_h = 2$, increases E from 1.5 to 3.5 GPa, the same as under compression (Figure 3). At

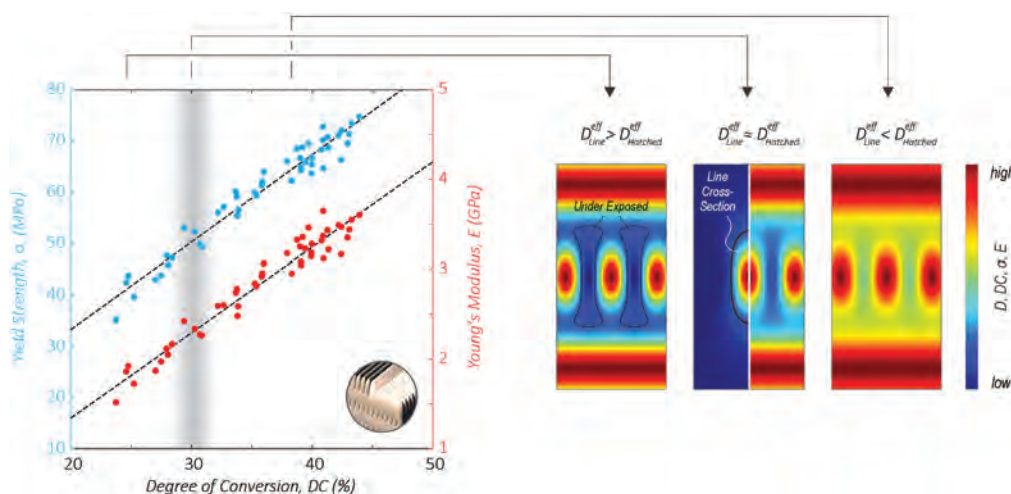


Figure 4. Combining the mechanical property data of hatched specimens from Figure 3 shows linear scaling with the degree of conversion (DC), independent from specific process parameters. With increasing laser average power (P), decreasing writing speed (v) or decreasing hatching distance (d_h) the dose distributions of neighboring exposures increasingly overlap. Depending on the extent of overlap, the “memory effect” creates additional, weaker cross-linked material (effective properties reduced with respect to solitary voxel-lines) or further cross-links previously formed above threshold material (effective properties increased with respect to solitary voxel-lines). Data points of nonporous, fully formed specimens are shown.

the same time, the ultimate tensile strength varies between 115 and 230 MPa.

The measured relations between TPP process parameters and mechanical properties (Figures 3 and 4) are found to be universal for a large range of process parameter combinations. **Figure 5a** shows the dependency of the DC of hatched multi-voxel-line specimens on both P and v over a range of 5–50 mW and 400–100 000 $\mu\text{m s}^{-1}$, respectively, with $d_h = 0.1 \mu\text{m}$ and $d_s/d_h = 2$. While trends remain similar, they become milder with increasing v . Over a large field of combinations of P and v , the accessible DC range of roughly 20–45% corresponds to the results of Figures 3 and 4. For $v > 50\,000 \mu\text{m s}^{-1}$, the maximum DC before overexposure starts to drop and is below 35% for $v = 100\,000 \mu\text{m s}^{-1}$.

With increasing dimensions of hatched multi-voxel-line specimens, the mechanical properties decrease. Increasing the edge length of square-shaped compression bars from 2 to 80 μm decreases the DC from 41% to 33%; similarly, E and σ_y decrease from 3 to 2.3 GPa and from 64 to 56 MPa, respectively (Figure S4, Supporting Information). Bulk specimens of $0.4 \times 0.4 \times 1.2 \text{ cm}$ nominal size are cured by single-photon flood exposure. Compressive yield strength and Young's Moduli of up to 65 MPa and 3.3 GPa are measured, respectively. In contrast to TPP-derived microbars, the bulk specimens are affected by spalling and hairline cracks, which are present prior to testing (Figure S5, Supporting Information). We measure the density of bulk specimens as $1.25 \pm 0.01 \text{ g cm}^{-3}$, which is about 6% higher than the density of the liquid resin.^[53]

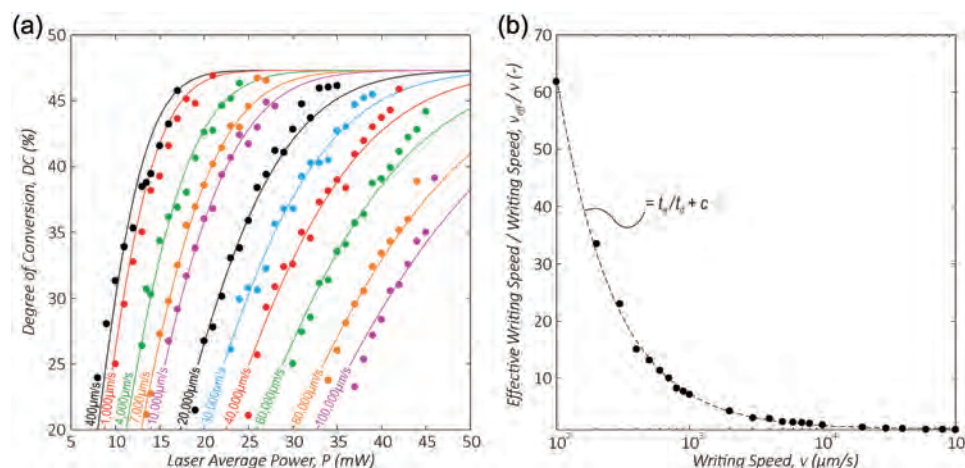


Figure 5. A threshold-based model predicts the degree of conversion (DC) depending on the TPP process parameters. a) Experimental data and predictions (Equation (6)) for a range of combinations of laser average power (P) and writing speed (v). b) With the effective writing speed (v_{eff}) the predictive model accounts for diffusion afflicted polymerization; values of v_{eff} determined based on all conducted experiments (Figures 3 and 5a) are proportional to the ratio of writing to diffusion time (t_w/t_d).

3. Discussion

3.1. Single Voxel-Line Specimens

Knowledge of the mechanical properties of individual TPP features is key for a thorough understanding of the mechanisms determining the mechanical behavior of TPP-derived parts. However, difficulties in reliable fabrication of nanoscale specimens, in combination with strain measurement challenges (due to charging of the polymer inside the SEM) and low stiffness and strength of the material (resulting in very small loads) make mechanical experiments challenging. The limited number of existing studies are based on indirect, error-prone measurements, reporting the nanomechanical behavior of TPP materials to be subjected to pronounced size effects, with properties orders of magnitudes lower than bulk counterparts.^[30,54,55] By providing the first direct measurement of the mechanical properties of individual TPP features, our study in contrast shows good agreement with typical bulk values of IP-Dip and other common TPP polymers,^[56–59] and the absence of pronounced size effects.

The dynamic range of TPP resins is thought to be limited by the solubility and the damage threshold; however, our observed size and process parameter insensitivity of the mechanical properties of voxel-lines may suggest the presence of a third, mobility threshold (m) (Figure 2d). Above a mobility threshold radical density (ρ_m), steric hindrance may inhibit polymerization, “trapping” active species in the already solidified polymer and thus preventing further cross-linking.^[60,61] Ideally, the mechanical properties of two-photon polymerized voxel-lines may be assumed to gradually decrease from the inside to the outside, correlating with the spatial laser beam profile.^[48] As the process parameters are varied, the corresponding exposure dose distribution shifts relative to the polymerization threshold, changing both the size of the voxel-line and the effective value of the above-threshold portion of the exposure dose distribution in the voxel-line volume. Assuming the mechanical properties proportional to ρ , and solving Equation (2) for the cross-sectional plane of a solitary voxel-line (see the Experimental Section), gives a pronounced process parameter dependency of the effective mechanical properties ($m = \infty$). Figure 2d shows the spatial distributions and effective values of ρ . Without a mobility threshold, one may expect a pronounced increase of the effective ρ across the range of laser average powers applied to form voxel-line specimens printed with $v = 10 \mu\text{m s}^{-1}$. Although this trend may not transfer exactly to the degree of conversion and the mechanical properties, it nonetheless disagrees with the found plateau in E and σ_y (Figure 2c). By contrast, assuming that polymerization is limited by ρ_m cuts the maximum mechanical properties in the voxel-line core corresponding to $\rho = \rho_m$. Depending on the ratio of m/th this yields a much milder dependency of the effective properties on the process parameters (Figure 2d), which correlates well with our experimental data. As ρ_m approaches ρ_{th} , property gradients in the voxel-line cross-section disappear, whereby $\rho_m = \rho_{\text{th}}$ itself may not be reached as it implies ideal threshold behavior. Our experimental data (Figure 2c) suggest $m \approx 3\text{th}$. With $m = 3$ and $\text{DC}^{\text{eff}} \approx 30\%$, Figure 2d estimates $\text{DC}_{\text{th}} \approx 14\%$ and $\text{DC}_m \approx 42\%$, which is in good agreement

with the accessible DC range measured for multi voxel-line specimens.

3.2. Hatched Multi-Voxel-Line Specimens

The pronounced tailorability of the mechanical properties of hatched two-photon-polymerized material compared to solitary voxel-lines may primarily be caused by the “memory effect.” Depending on the combination of P , v , d_h , and d_s , the dose distributions of neighboring exposures overlap to different extents. Simply speaking, neighboring voxel-lines increasingly overlap as they become “larger” (with increasing P and decreasing v) and as d_h and d_s are reduced, thus creating a bandwidth of effective properties even if those of corresponding solitary voxel-lines would be identical. Thereby, existing insoluble material with relatively low DC, like the surface region of previously solitary voxel-lines, is further cross-linked, producing an increase in the effective properties relative to those of solitary voxel-lines. Conversely, “smaller” constituent voxel-lines (produced by decreasing P and increasing v) and larger d_h and d_s limit overlap to the below-threshold Gaussian wings of neighboring exposures, thus introducing less cross-linked material between constituent voxel-lines and reducing the effective properties of hatched structures. Examples of property distributions with lower, equivalent and higher effective values than individual voxel-lines are qualitatively sketched in Figure 4. For d_h and d_s above the resolution limit, below-threshold Gaussian tails can be dissolved during development, yielding a porous material as shown in Figure 3c. Hatched specimens with a DC of $\approx 30\%$ have the same strength and stiffness as solitary voxel-lines, suggesting that formation of less cross-linked material and further cross-linking of previously formed above-threshold material cancel each other out, yielding a composite hatched material that is on average mechanically equivalent to a single line.

In contrast to solitary voxel-lines, the impact of a mobility threshold on multi-voxel-line materials is uncertain. With the mobility threshold, the maximum effective properties of a hatched material may be reached once the entire material volume approaches $\text{DC}_m \approx 42\%$; this well agrees with the maximum DC from Figures 3 and 4. However, the same DC values are also found to approach the damage threshold. Compared to a hatched material, an individual line exposure can have a significantly higher dose before the damage threshold is reached. In a hatched material the damage threshold may be reached before a mobility threshold can have a notable effect. The somewhat lower tensile strength of hatched specimens (loaded perpendicular to printing direction) with respect to voxel-line specimens (loaded parallel to printing direction) (Figure 1c), indicates that hatching, even in a high DC material, may still yield anisotropic composite-like behavior.

To reduce the process time, shell-scaffold printing strategies leave certain enclosed material volumes in the liquid state and cross-link those by single-photon flood-exposure subsequently to TPP.^[62] Compared to point-by-point TPP exposure, single-photon flood exposure simultaneously cross-links a large material volume. With increasing part size, this may notably reduce the radical mobility and hence the maximally achievable DC

and mechanical properties. At the same time, we have observed increasing flaw nucleation. Yield strengths and Young's Moduli of the presented, several millimeter-size flood-exposed specimens are 7% and 8% lower than the respective maximum values of TPP-derived specimens. For sufficiently small volumes, the mechanical properties of the enclosed material may be similar to the maximum values obtained via TPP.

With decreasing writing speed, TPP of hatched materials increasingly deviates from the ideal "memory effect"-based model.^[45] As the time between the exposures of neighboring lines increases, below-threshold active species of a first exposure diffuse away before the next exposure would increase their concentration to a high enough level to form insoluble material. Typical specimens in this study had an edge length (a) of 20 μm and were printed with $d_h = 0.1 \mu\text{m}$ and $d_s = 0.2 \mu\text{m}$. The average time which elapses between the writing of two neighboring lines (t_w) can be approximated as $(a + a^2/d_h)/2\nu \approx 2000 \mu\text{m}/\nu$. The critical diffusion path length (d) for an active species not to be affected by a subsequent exposure can be estimated as the distance between neighboring lines plus the TPP resolution (r). With Abbe's diffraction limit providing $r = \lambda/(2 \text{ NA})$,^[63] $d \geq 0.6 \mu\text{m}$ may be obtained. Fick's second law approximates the diffusion time (t_d) as $t_d \approx 2\delta/d^2$,^[64] with the diffusion coefficient (δ). For photoinitiator molecules in liquid solution, δ is on the order of 10^{-1} – $10^2 \mu\text{m}^2 \text{ s}^{-1}$.^[49,65] These estimates provide a critical writing speed $\nu_{\text{crit}} \approx (a + a^2/d_h)\delta/d^2 \approx 10^3$ – $10^5 \mu\text{m s}^{-1}$. Below ν_{crit} , diffusion reduces the DC with respect to an ideal, diffusion-free polymerization. Writing speeds in this study range from 10^1 – $10^5 \mu\text{m s}^{-1}$, indicating that the measured properties are diffusion affected at the lower writing speeds.

A simple threshold-based model predicts the experimentally measured dependencies of the mechanical properties on P , ν , and d_h . Assuming a linear correlation between ρ and DC, Equations (2) and (3) provide

$$\text{DC} = c_1 \rho_0 \left(1 - e^{-\delta_{2,\text{eff}} c_0 \frac{p^2}{\nu_{\text{eff}}} D_V} \right) + c_2 \quad (6)$$

with the constant (c_0) comprising the relevant optical parameters of the TPP process (see the Experimental Section) and the proportionality constants (c_1) and (c_2). To account for molecular diffusion, the actual writing speed (ν) is replaced by an effective writing speed (ν_{eff}).^[66] Other effects, such as temperature-dependent diffusion are not accounted for but may need to be considered for higher laser pulse widths than used here.^[67] Nonlinear least square fitting of all presented DC data provides the explicit dependency of ν_{eff} on ν (Figure 5b), and gives $c_1 \rho_0 = 0.62$, $c_2 = -0.15$, and $D_V = c_3 / d_h^n$ with $c_3 = 1.5\text{e}4 \mu\text{m}^{-2.36}$ and $n = 0.64$. With ν replaced by ν_{eff} , the presented TPP model well predicts diffusion-affected polymerization (Figures 3b and 5a), whereas it would drastically overestimate properties with the actual writing speed (ν) instead.^[28] Combining Equation (6) with Equations (4) and (5) provides the relationships between strength and stiffness and the process parameters. This allows to individually program a large range of mechanical properties of TPP-derived parts by simple process parameter adjustment.

Whereas the effective writing speed has been introduced as a simple fudge factor,^[66] our data shows that it may be derived

from molecular diffusion physics. The ratio ν_{eff}/ν is proportional to t_w/t_d and, for a diffusion coefficient of $0.55 \mu\text{m}^2 \text{ s}^{-1}$, can be closely approximated by $\nu_{\text{eff}}/\nu = t_w/t_d + c$, with $c = 1.13$ (Figure 5b). For low writing speeds, ν_{eff} substantially exceeds ν , while in the $10^4 \mu\text{m s}^{-1}$ range the difference between ν_{eff} and ν drops below 10%. Notice that $\nu_{\text{eff}} \rightarrow \nu$ as the writing speed increases (e.g., as $t_w/t_d \rightarrow 0$), supporting the argument that molecular diffusion becomes negligible at high writing speeds. At the same time though, those high writing speeds seem to increase the local heat influx, potentially causing the decrease of the damage threshold that we observe (Figure 5a), which lowers the achievable maximum mechanical properties.

The above diffusion considerations are consistent with the measured size-dependence on the mechanical properties of hatched pillars (Figure S4, Supporting Information). The critical writing speed below which diffusion needs to be considered is proportional to the part size. For a given writing speed, parts become increasingly diffusion affected as their dimensions increase, resulting in a decrease of their mechanical properties. Similarly, the toolpath can be expected to have an influence. To maximize the mechanical properties, optimized toolpath strategies could reduce the average time in between the exposure of neighboring lines, e.g., by consecutive instead of parallel printing of individual features, by breaking large features down into several smaller ones, or by decreased writing density of volumes without high surface finish requirements (Figure S6, Supporting Information).

The observed dependencies may be expected to transfer to different resin systems, processing conditions, and printing strategies, however, it is emphasized that specific quantitative relations may differ. A full understanding of all polymerization-relevant processes, and their dependency on printing patterns, part geometry, and resin chemistry will require further in-depth experimental characterization and combined photonics- and molecular dynamics-based modeling. The model presented in this work is an approximation based on a paraxial Gaussian light intensity distribution. While this condition is not rigorously justified at the high numerical apertures used here, it is sufficient as i) the highest intensity part of the light distribution at the focal point can be described by a Gaussian envelope, and ii) the laser pulse width encompasses many optical cycles.^[46,52,68] If desired, higher degree of precision could be achieved by a photonics model based on Debye vectorial diffraction theory.^[69,70] Beyond the printing parameters, other process conditions, such as the details of the development strategy, may also affect some properties of TPP-derived materials and would need to be considered.^[32]

4. Conclusion

This study provides insight into the mechanical behavior of two-photon-polymerized individual voxel-line features and derives the mechanisms controlling the effective properties of parts which are hatched from multiple voxel-lines. We systematically show that the mechanical properties, precision and process time of the acrylate-based resin IP-Dip can be vastly tailored via corresponding TPP process parameter selection. With a threshold-based model we accurately predict the

processing-structure-properties relation, laying the foundation for a universal quantitative predictability of the mechanical properties of TPP-derived materials.

The characterization methodology presented herein may serve as general framework to establish a standardized knowledge base for TPP material systems. In future studies, the dependencies found herein may thereby enable substantial reduction of experimental characterization. Our findings may be expected to transfer to different acrylate-based and other resins systems, and provide meaningful knowledge for ongoing effort to overcome major technological challenges of TPP, including increasing the resolution,^[63,71] and developing novel printable materials.^[72–74] In particular, this study may help to understand and optimize the properties of TPP-derived ceramics and metals.^[74,75] The demonstrated broad bandwidth of properties furthermore opens up vistas for novel concepts of pseudo-multi-material design with locally tailorable properties and optimized response to complex external loads.

5. Experimental Section

Fabrication: All specimens were manufactured from the photoresist Ip-Dip (Nanoscribe GmbH). TPP was performed using a Photonic Professional GT (Nanoscribe GmbH) DLW system equipped with a Plan-Apochromat 63 × 1.4 Oil DIC M27 (Carl Zeiss AG) objective and a FemtoFiber pro NIR (TOPTICA Photonics AG) laser, with a center wave length (λ) of 780 nm, a pulse width (τ) of ≈ 100 fs, and a repetition rate (f) of 80 MHz.^[76] The laser average power (P) is the mean power value at the aperture of the objective, with 100% corresponding to 50 mW.^[76] A transmittance of the objective (T) of 65% was measured.

Specimens were printed on fused silica substrates in a layer-by-layer sequence using the system's galvanometric mirror scanning mode. After DLW, samples were submerged in propylene glycol monomethyl ether acetate (PGMEA) for 20 min, to dissolve uncured photoresist, followed by a 5 min long isopropanol bath for further cleaning. Subsequently, specimens were dried using an Autosamdri-931 (Tousimis Research Corp. Inc.) critical point dryer operated in the auto mode. To minimize effects of varying process conditions on the measured properties, the experimental routines were precisely kept consistent and were carried out in a climate-controlled environment.

Voxel-line specimens were manufactured as dumbbell-shaped compression and tensile bars with gauge sections consisting of one individual voxel-line of uniform elliptical cross section. Widths and heights of the gauge sections of 190–640 nm and 670–1850 nm, respectively, were realized by different combinations of P and the writing speed (v). The dumbbell-shape of compression bars was chosen to increase the contact area between the test bar and the measurement system. Gauge sections of compression bars had slenderness ratios of 11 to 15:1.^[77] Hatched multi-voxel-line specimens were manufactured in a [0/90] laminate manner from unidirectional layers with a hatching distance (d_h) between the axes of neighboring voxel-lines and a slicing distance (d_s) between neighboring layers. Compression bars were designed as uniform square-shaped bars with a height-to-edge length ratio of 3.25 and nominal edge lengths of 2–80 μm . Tensile specimens were designed as push-to-pull mechanisms.^[78] The gauge section of dumbbell-shaped tensile bars had a uniform rectangular shape of $4 \times 3.2 \times 9.5 \mu\text{m}$. Bulk samples of $4 \times 4 \times 12$ mm nominal size were cured for 60 min via single-photon flood exposure, using a LQ-Box (Rolence Enterprise Inc.) UV-lamp with a peak wavelength of 405 nm and an average light intensity of 150 mW cm^{-2} .

Experimental Characterization: Specimen dimensions were optically measured using a FEI Magellan 400XHR (Thermo Fisher Scientific Inc.) SEM. To determine E , σ_y , and σ_{UTS} , uniaxial compression and tension

experiments were performed at a constant strain rate of 0.001 s^{-1} . Voxel-line experiments were carried out with a FT-NMT03 (FemtoTools AG) nanomechanical testing system equipped with a FT-S200 sensor. Focused ion beam (FIB) milling was used to cut tensile grippers into the FT-S200 sensor in a FEI Quanta 3D FEG (Thermo Fisher Scientific Inc.) dual beam (SEM/FIB). For multi-voxel-line specimens an Alemnis Nanoindenter (Alemnis AG) equipped with a flat punch diamond tips, $400 \mu\text{m}$ in diameter, was used. Bulk specimens were compressed with the Universal testing frame Instron 8800 (Instron, ITW Inc.). Load–displacement curves were recorded. For the voxel-line and multi-voxel-line tensile specimens, the displacement was corrected for equipment and substrate compliances via a digital image correlation (DIC) algorithm developed in house. Applying the measured dimensions, engineering stress and strain were determined. E was extracted as the maximum slope of the linear elastic regime and σ_y as the 0.2% yield offset of the corresponding stress–strain curve.^[77,79] σ_{UTS} was the maximum engineering tensile stress at specimen rupture. The density of bulk specimens was determined with the nominal dimensions and the weight, measured with a M-prove scale (Sartorius AG).

Raman spectroscopy was used to determine the DC of multi-voxel line compression specimens. Raman spectra were acquired using an inVia (Renishaw plc) confocal Raman microscope with a 50× objective, operated at an excitation wavelength of 785 nm, with a laser intensity of 50% and an exposure time of 1.5–2 s averaged over 15 acquisitions. DC values were extrapolated from Raman spectra as

$$DC = 1 - \left(\frac{A_{C=C}/A_{C=O}}{A_{C=C}/A_{C=O}} \right) \quad (7)$$

with the integrated intensities of carbon–carbon and carbon–oxygen double bond peaks $A_{C=C}$ and $A_{C=O}$ in the polymerized resin, and $A'_{C=C}$ and $A'_{C=O}$ the integrated intensities of the same peaks in the unpolymerized resin.^[28] $A_{C=C}$ and $A_{C=O}$ were determined by fitting Lorentzian and Voigt functions to the respective peaks.

Analytical Model: The photon flux intensity distribution (I) during exposure in the cross-sectional plane of an infinite voxel-line in a Cartesian system, with its length along the x -axis, is the superimposition of a train of femtosecond laser pulses, scanned in x -direction with v . For the writing speeds used here the transit time across an observation point is much longer than the duration of a laser pulse and the photon flux intensity is effectively static. Assuming a Gaussian laser beam, $I(x, y, z, t)$, where the y – z plane corresponds to the voxel-line cross-section, can be written as^[47,51]

$$I(x, y, z, t) = I_0 \left(\frac{w_0^2}{w(z)^2} \right) e^{-\frac{2((x+vt)^2 + y^2)}{w(z)^2}} \quad (8)$$

with the peak photon flux intensity (I_0), the beam radius ($w(z)$) along the propagation direction (z) and the beam waist ($w_0 = w(0)$). vt accounts for the position of the center of the beam at the time (t). The beam radius is defined as $w(z) = w_0 \sqrt{1 + (z/z_R)^2}$ with the Rayleigh length ($z_R = (\pi w_0^2)/\lambda$) and the excitation wavelength (λ). w_0 can be approximated by the radius of the central airy disk ($0.61 \lambda/\text{NA}$),^[52,68] with the numerical aperture of the focusing optics (NA).

Evaluation of Equation (1) with Equation (8), at an observation plane $x = 0$ which the beam passes at $t = 0$ gives

$$\int_0^P \frac{d\rho}{(\rho_0 - \rho)} = \delta_{2,\text{eff}} I_0^2 \left(\frac{w_0^4}{w(z)^4} \right) \int_{-\infty}^{\infty} e^{-\frac{4(y^2 + y^2)}{w(z)^2}} dt \quad (9)$$

which after integration yields the radical density distribution $\rho(y, z)$ in the cross-sectional plane of the voxel-line

$$\rho(y, z) = \rho_0 \left(1 - \exp \left[-\delta_{2,\text{eff}} I_0^2 \left(\frac{w_0^4}{w(z)^4} \right) \sqrt{\frac{\pi}{4}} \frac{f\tau}{v} e^{-\frac{y^2}{w(z)^2}} \right] \right) \quad (10)$$

with the laser repetition rate (f), and the pulse width (τ). I_0 can be expressed in terms of the laser average power (P) as

$$I_0 = \frac{2e^2}{e^2 - 1} \left(\frac{TP\lambda}{\pi\omega_0^2\tau\hbar c} \right) \quad (11)$$

with the fraction of light transmitted through the magnification optics (T), Planck's constant ($\hbar$) and the speed of light in vacuum (c).^[80,81] With Equation (11), the effective radical density in the voxel-line cross-section can be expressed in terms of P and ν as

$$\rho = \rho_0 \left(1 - \exp \left[-\delta_{2,\text{eff}} c_0 \frac{P^2}{\nu} D_V \right] \right) \quad (12)$$

where (c_0) comprises the optical parameters and numerical factors and with the mean value of the term $\exp((-4y^2)/(\omega(z)^2))/\omega(z)^3$ over the voxel-line cross-section (D_V). Equation (12) is also valid for a hatched material with ideal memory effect behavior, however, D_V may only be determined numerically. $\delta_{2,\text{eff}}$ has been taken as $3 \times 10^{-55} \text{ cm}^4 \text{ s}$.^[46] Although a constant τ was used, it is noted that $\delta_{2,\text{eff}}$ and therefore the radical density are sensitive to the pulse width.^[67] Voxel-line dimensions are given by $\rho(y, z) = \rho_{\text{th}}$, nonlinear least square fitting of the measured voxel-line dimensions with Equation (10) gave a ratio of ρ_{th} to ρ_0 of 0.0793, which agrees with reported values of other TPP photoresists.^[46]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

direct laser writing, Ip-Dip, mechanical properties, Young's Modulus

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Evaluating sputter deposited metal coatings on 3D printed polymer micro-truss structures

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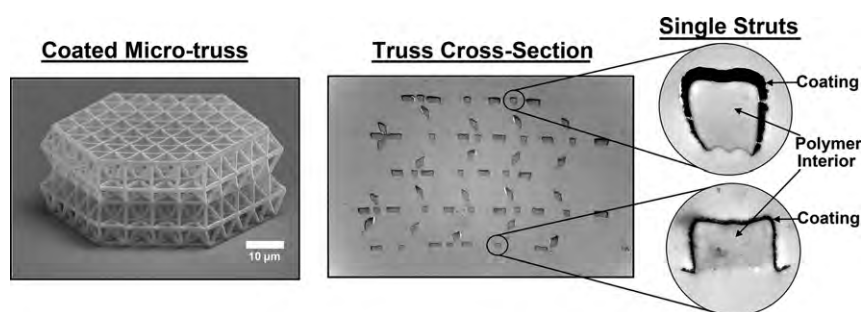
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HIGHLIGHTS

- A method for coating micro-trusses with metal alloys via sputtering is proposed.
- Microtome sectioning is used to accurately measure layer thickness of coated trusses.
- Compression tests reveal mechanical properties can be tuned with coating material.

GRAPHICAL ABSTRACT



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ABSTRACT

As the capabilities of additive manufacturing (AM) further advance, researchers can design materials and structures without traditional constraints on manufacturability, such as implementing structural features on the order of nanometers. While polymer AM is most mature, especially for producing features on smaller length scales, complex metal structures are also desirable because they provide enhanced strength, conductivity, and electrochemical properties. Here we explore a method to produce metal-polymer lattices by coating epoxy-based micro-trusses via magnetron sputtering. Unlike other deposition methods that are limited to single elements and a few alloys, sputtering enables the use of various metals and alloys such as Aluminum, Inconel 600, and Ti 6Al-4V, which were used in this study. Two sputtering configurations were applied: a stationary and a rotating substrate holder. Microtome sectioning was used to evaluate the cross-section of individual struts to measure coating thicknesses. Compression of the coated structures reveals the range of achievable mechanical properties when different metal coatings are used. Overall, the work here demonstrates that sputtering can be leveraged to impart favorable metallic properties on polymer microlattices with coatings in nearly any alloy combination, expanding the potential applications of polymer micro-trusses functionalized with metal films.

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1. Introduction

Improvements in additive manufacturing (AM) techniques, including the reduction of minimum achievable feature sizes and the expansion of the number of materials that can be printed, have altered the

structure optimization component of design. Rather than developing materials or structures based on manufacturability, they can be designed based on function with virtually no limits on configuration [1–3]. Advances in metal printing, the fastest growing sector of AM [4], have shown particular promise for aerospace applications, where metallic structures can be built in configurations that are not amenable to traditional machining. This means that components that were previously too costly or physically impossible for production can now be

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produced in a manner that reduces the overall amount of material, yielding a significant reduction in mass, which is critical in payload oriented industries [5,6]. However, to date, only a few alloys can be reliably printed out of about 5500 commercial metal alloys in existence [7]. Therefore, there is a critical need for improvements to metal additive manufacturing or alternative methods in order to generate arbitrary metal shapes from any desired alloy.

Compared to 3D polymer printing, where numerous printing systems exist, metal additive technology still has several major areas for growth, such as improving surface finishes [8] and reducing the internal stresses in printed parts [9]. One relevant area to this study is the reduction of the achievable minimum feature size for metal materials with arbitrary structures. Currently, metal microscale devices with feature sizes as small as 10 μm can be generated by using an electrochemical fabrication (EFAB) process, which is essentially electrodeposition of fine layers [10]. For other metal printing systems, such as selective laser melting (SLM), the minimum feature size is about 150 μm [11]. The ability to produce materials with fine feature sizes is important when generating structures such as hierarchical materials which can be used for a wider range of applications, from photonics to catalysis.

As an alternative, functional coatings on microscale polymer scaffolds can be used when the preferred ceramic or metal structures cannot be directly printed in complex hierarchical configurations. Two previously used deposition methods include atomic layer deposition (ALD) and electroless deposition, which apply uniform and conformal coatings on the structures [12–14]. However, these methods, are limited to materials that undergo specific chemical reactions, such as in the case of ALD which produces mainly oxide films like Al_2O_3 or TiO_2 [15]. Electrodeposition of metals is likewise restricted to single elements or to alloy systems such as CuNi and CuZn, where overlapping deposition voltage windows can be achieved with the addition of cyanide as a complexing agent [16]. These constraints limit the materials that can be used to coat lattice structures and eliminates commercially relevant structural materials such as Al or Ti alloys, which cannot be plated through ALD or electrodeposition.

In this work, composite microcellular structures were produced with 3D direct laser writing (3D-DLW) and then coated with three different metals via magnetron sputtering, a physical vapor deposition (PVD) process. By using this deposition method, nearly any metallic target material can be sputtered, including commercial alloys. Pairing this material selection independence with the technology to print polymer structures at microscale dimensions, is an innovative approach to develop microcellular structures with both arbitrary shapes and metal coatings. This allows researchers to move beyond the limited technology to print metals at the microscale and achieve a previously unattainable range of material functionality. While other studies have explored sputtering to coat microlattice structures for mechanical or functional purposes, this work focuses on an in-depth evaluation of coating quality and multiple types of coatings on several sizes of structures. The metals used in this study, which are Al, Inconel 600, and Ti 6Al-4V, were purposefully selected to extend across a range of characteristic material properties, such as strength, thermal stability, and crystalline structure, so that the broad application and impact of this technique can be established. By leveraging the versatility of magnetron sputtering and 3D-DLW to synthesize metal-polymer composite microcellular truss structures, tailorable complex architected metallic structures at the microscale could be fully realized.

2. Experimental methods

The sequential protocol for developing metal-polymer tetrahedral trusses is shown in Fig. 1. The structures were designed and produced using 3D-DLW with a Nanoscribe Photonic Professional as shown in Fig. 1a and b. The proprietary, epoxy based resist IP-Dip (Nanoscribe GmbH) was used as the base material for all of the structures used in this study. Further details on 3D-DLW can be found in an article by Valdevit and Bauer [17].

Four different sizes of tetrahedral truss structures [18,19] (A–D) were printed on glass substrates in the configuration shown in Fig. 2a. Sample dimensions are shown in Table 1, where strut length refers to each individual lattice member that makes up the truss.

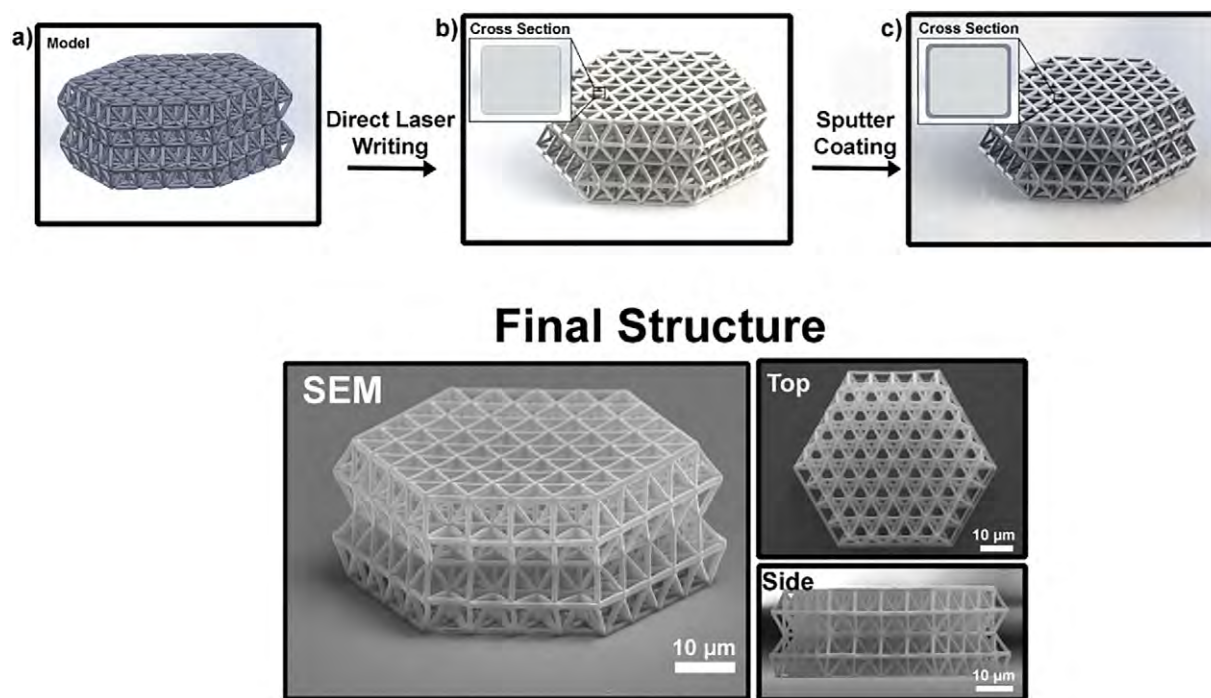


Fig. 1. Schematic showing the design and development of polymer-metal truss structures. a)–b) A tetrahedral truss structure model is designed and subsequently fabricated using 3D direct laser writing. c) After being written, the structures are coated with a metal film using magnetron sputtering. Inset shows schematic of a strut cross section. (d) SEM images of the actual structures after processing.

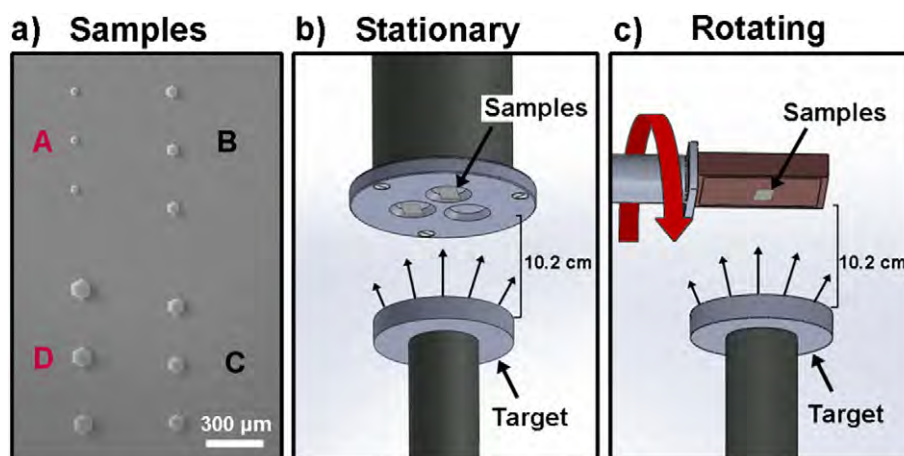


Fig. 2. Sputtering setup: a) shows SEM image of sample layout on the glass slide. The samples are labeled according to their increasing strut length; A (5 μm), B (7.5 μm), C (10 μm), and D (12.5 μm) b) shows the representative sputtering schematic for stationary sputtering. c) Shows schematic for rotating sputtering setup with samples mounted in the center of the rotating holder. Sample is rotated once every 54 seconds.

All samples were sputtered in a vacuum chamber evacuated to at least 4.5×10^{-6} Torr. Prior to sputtering the chamber was filled with Argon. Each metal coating was sputtered using a working Ar pressure of 4 mTorr and a power of 65 W, only the sputtering times were adjusted to compensate for differences in sputtering rates. The structures were placed 10.2 cm away from a 7.6 cm diameter sputtering target of the selected source material. Three different target materials were used in this study; Aluminum (99.95%, Plasma Materials), Ti-6Al-4V (Plasma Materials), and Inconel 600 (prepared in-house). Two sputtering configurations were employed and are shown in Fig. 2b and c. In one configuration, samples were sputtered using a stationary setup, where the sample holder is in direct line-of-sight of the target and actively cooled from the backside using flowing water at 16 °C (Fig. 2b). The second setup uses a holder that rotates once every 54 seconds throughout sputtering (Fig. 2c) without cooling. Consequently, the structures are not in line-of-sight of the target for half the sputtering time. These sputtering parameters were used to minimize excessive heating in the polymer structures, which were measured to be less 105 °C. Additionally, literature has shown that they are capable of surviving heat treatments of 200 °C [18] and maintaining shape during pyrolysis at 900 °C [20]. For both configuration, the samples were attached to the substrate holder using Kapton tape (Ted Pella). Nominal thickness is defined as the expected thickness of a film on a flat surface based on calculated sputtering rates. An example of a coated microtruss structure is shown in the SEM images in Fig. 2d. Additionally, 1 μm thick films were sputtered in the stationary configuration on either glass or unetched Si wafers from each target for material characterization.

The metal films were characterized by scanning electron microscopy, electron dispersive spectroscopy (EDS) and X-ray diffraction (XRD). XRD scans were acquired using a Rigaku Ultima-IV X-Ray diffraction machine. A series of 2 θ scans from 30° to 100° with the rate of 3°/min were performed. EDS scans were performed using an EDAX Element Silicon Drift Detector for characteristic X-ray detection and EDAX Genesis software for data processing and elemental determination on both the 1 μm thick samples and directly on the structures. For EDS on the structures, lower accelerating voltages were used to reduce the elemental peaks from the epoxy based sample. SEM was performed using a JSM-7001F-LV field-emission SEM, moreover, images of tested truss structures were taken with a helium ion microscope (ORION Nanofab, Zeiss). TEM images were taken on an FEI Morgagni 268 at an accelerating voltage of 80 kV.

Film thicknesses were measured using aligned truss struts like that shown in Fig. 6 below. Measurements were made using a MATLAB script that opens the images and makes measurements by detecting contrast in the images between the dark film and light epoxy. A hundred

measurements were made along each side of the strut. Average thickness measurements are shown in the Results and discussion section.

A JEOL JIB-4500 FIB was used in this study to explore the cross sections of micron thick sputter deposited films as well as for the FIB milling of coated truss structures to expose their cross section. The samples were also sectioned using microtome, where the samples are embedded in an epoxy resin (Epon), heat polymerized, and removed from the glass slide using thermal cycling in liquid nitrogen. The bottom of the sample, where the structures were removed from the glass slide was then covered with the same epoxy. Once embedded in epoxy, the samples were cut into 100 nm thin sections with a diamond knife. The sections were floated on water and picked up using a formvar film slot grid. Structures A and D with Al and Inconel 600 coatings were sectioned using this method.

Uniaxial compression tests were performed using a G200 XP nanoindenter (Agilent Technologies) with a diamond flat punch of 100 μm in diameter for structures A and B and 200 μm for C and D, respectively. Compression tests were carried out for truss structures with 81 nm Al, 205 nm Al, 35 nm Inconel 600, and 35 nm Ti 6Al-4V coatings. The tests were carried out at a constant displacement rate of 100 nm/s on 3 trusses of each type of sample. Except for sample type A with 81 nm Al coating and sample type D with 35 nm Inconel 600 coating for which only 2 samples were tested. The structures in this study were not loaded until full densification, but to a fixed maximum displacement. The stress and strain of the samples were analyzed using the nominal hexagonal cross-sectional area of the trusses and the nominal height of the samples, respectively.

3. Results and discussion

3.1. Film synthesis

Table 2 shows a summary of the metals used to coat the structures and their corresponding nominal thickness, which is defined as the thickness of the coating on a flat surface for a given sputtering time.

Table 1
Summary of polymer tetrahedral truss dimensions per type of structure.

Structure	Nominal strut length (μm)	Nominal height (μm)	Strut length-to-equivalent diameter ratio	Relative density
A	5.0	17.3	5.7	15.5%
B	7.5	26.0	6.9	11.0%
C	10.0	34.6	7.5	9.7%
D	12.5	43.3	8.1	8.5%

Table 2

Summary of sputtering targets and deposition parameters. Note that all the structures are coated simultaneously in each sputtering procedure.

Type of coating	Setup	Sputtering time	Nominal thickness
Al	Stationary	6 min	81 nm
Al	Rotating	40 min	205 nm
Inconel 600	Stationary	3 min	35 nm
Inconel 600	Stationary	8.5 min	100 nm
Inconel 600	Rotating	80 min	305 nm
Ti 6Al-4V	Stationary	6 min	35 nm

Fig. 3a–c shows images of the structures coated with their respective metal films including respective XRD and EDS measurements. Visually, the coatings for pure Al are significantly rougher than Inconel 600 or Ti 6Al-4V, which is typical for PVD Al deposition.

For the Al coatings, EDS measurements showed that the coatings are deposited without any contaminant elements and the XRD data showed that the deposited material is textured along the (111) growth direction. The textured microstructure has been observed in other sputtered Al films [21] and was also present in the Inconel 600. The elemental composition of the as-sputtered alloys, Inconel 600 and Ti 6Al-4V, matches closely to the expected values with a slight deviation of the Cr and Al content, respectively. However, the deviations in composition are expected from the multielement detection used in qualitative EDS analysis [22].

XRD data of the Ti alloy reveals that sputtering of the commercial alloy results in a textured β -phase Ti microstructure, where corresponding peaks were observed at 38.7° (110) and 82.9° (220) with no α -phase peaks detected. The presence of a β -phase dominated microstructure is unusual since the β transus of Ti 6Al-4V is about 980°C [23]. However, the formation of β -phase in sputtered Ti alloys has been previously observed and attributed to the non-equilibrium sputtering process [24]. Essentially, the energy of the condensing atoms is sufficiently high to form the high-temperature phase, but the structure is “quenched” as the atoms arrive at the cool substrate, thus forming the metastable phase [24]. The α -phase could form by changing conditions such as temperature, as has been shown for other sputtered materials [25].

Compared to sputtering, the electrodeposition of Ti and Al, for example, is only accomplished with non-aqueous solutions. Plating Ti can be done using a molten salt bath [26,27], whereas the most common method for Al plating is with ionic liquid plating solutions [28,29], which require oxygen free environments for optimal performance. Electrodeposition of any kind requires the optimization and balance of several influencing factors. In contrast, the sputtering process presented here uses the same experimental setup for three completely different metals, where only the source material or target is altered. Furthermore, the sputtering rate of metals can be easily increased by increasing the power input (target polarity) of the sputtering system [30,31]. However, since the magnetron sputtering deposition process is moment driven

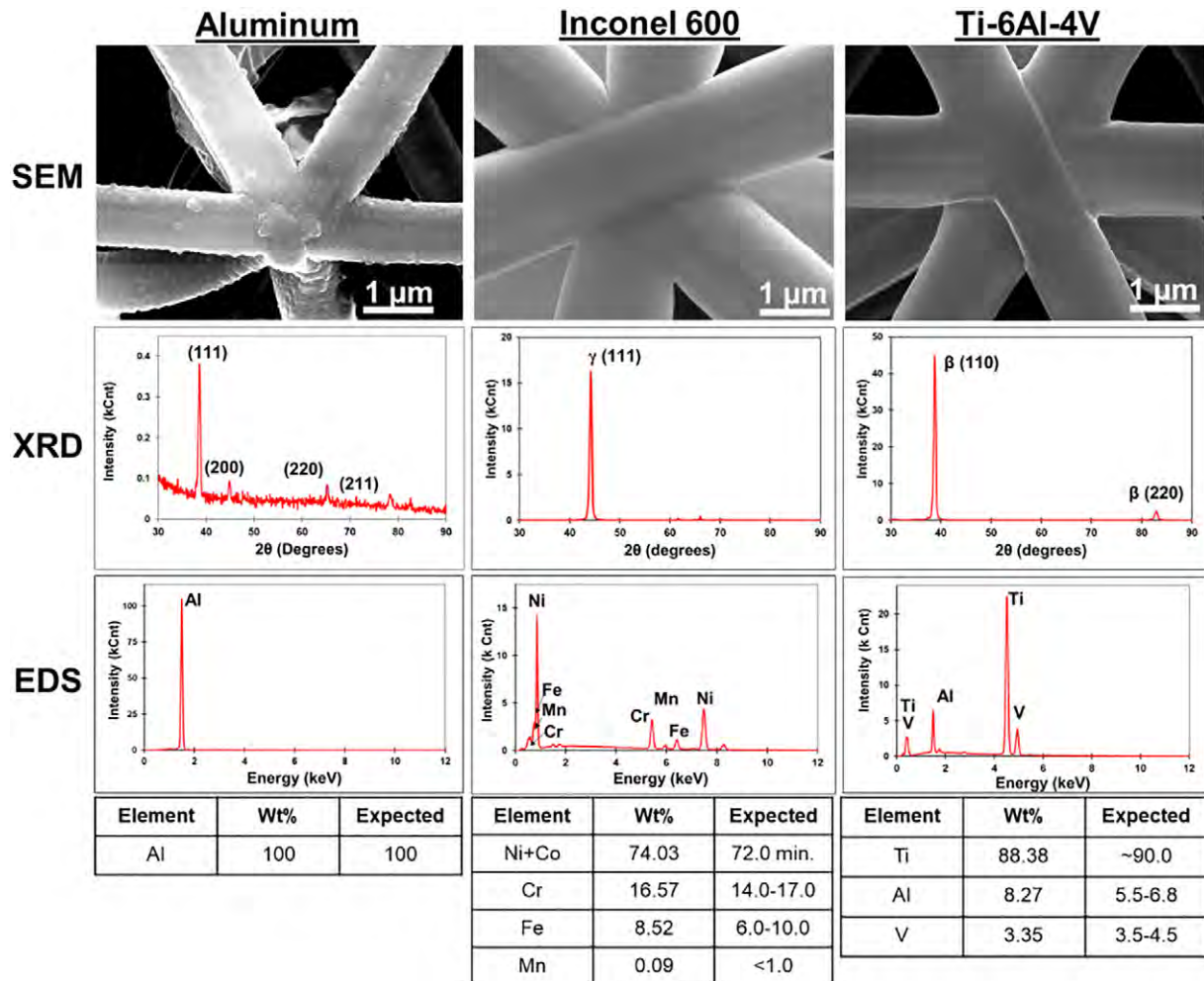


Fig. 3. a–c) SEM images of sputtered coatings on tetrahedral truss structures: Aluminum, Inconel 600, and Ti 6Al-4V. Below each image is a corresponding XRD scan and EDS spectra for each type of coating from a 1 μm thick film sputtered in the same conditions. Note that the sputtered alloys have maintained stoichiometry.

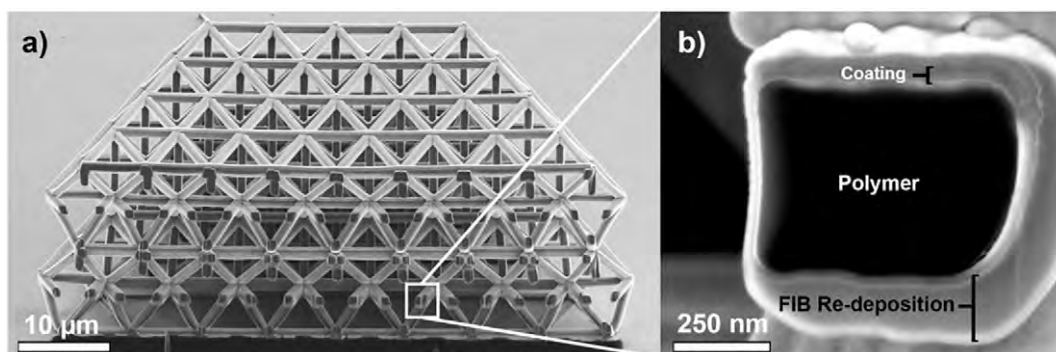


Fig. 4. a) FIB image of a tetrahedral truss structure milled in half to expose the coating cross section. b) SEM image of a strut cross section exposed with FIB milling. The actual coating material is obscured by material redeposition from the part of the truss structure that was eroded during FIB milling.

and line of sight sensitive, surface coverage of the metal coatings needs to be addressed. The effect of sputtering on coating uniformity is addressed in the next section, where the coatings are assessed with imaging techniques.

3.2. Cross-section evaluation

To closely evaluate the coatings, especially the film thickness, FIB cuts were made across the center of the structure so that half of the sample was removed and the entire cross section revealed (Fig. 4a). This allowed for observation of the coating variation from the top to the bottom of the structure as well as from the interior to the exterior. Closer evaluation of the ligament cross sections with SEM, in Fig. 4b, showed that FIB milling of the tetrahedral trusses resulted in significant FIB redeposition of the eroded material inside the structure. The redeposition layer becomes more pronounced towards the bottom of the structure, which is the area nearest the glass surface. It is apparent that the ligament cross-sections and the deposited layer of material is obscured by FIB damage and cannot be easily measured. The redeposition layer is visible for all structure sizes and material combinations. However, the layer is most prevalent in structure size A, which has the smallest strut length and highest density.

The effect of FIB redeposition on sample preparation has been observed for solid samples, where redeposited material lands in the area to be sputtered [32]. However, the effect is exacerbated for 3D materials because the material lands within the area that will be evaluated. While several studies have used FIB milling as a method to section microlattice materials or to expose the polymer core for etching [33–36], to the author's knowledge, only one study has mentioned the possibility of FIB milling redeposition obscuring the cross-sectional evaluation [37], although the issue was not further investigated. A recent study suggests that the thicker films on the bottom side of the struts are the result of redeposition from atoms during film growth and not from FIB milling [38]. Several factors may be contributing to FIB redeposition, such as the FIB instrument quality or the structure density, which is an indicator of how “open” the cellular material is to penetration from the metal atoms during sputtering. Another factor may be the strut geometry; our study employs rectangular cross-sections while others have circular or oval cross sections [33,38]. However, our results indicate that FIB redeposition from micromachining of 3D parts will result in some degree of redeposition that is more prevalent at the bottom of the struts. Therefore, special care must be taken when evaluating the coatings on 3D materials, particularly for methods that are known to yield non-uniform coatings (i.e. electrodeposition and sputtering).

In order to mitigate artifacts from FIB and accurately measure the coating thickness, microtome was used to embed the structures in epoxy so that the metal coating is preserved during sectioning. Microtome has been shown to be a reliable method for sectioning biological samples thin enough for electron microscopy [39,40]. The sectioning

method can be difficult for hard samples because there is separation between the embedded epoxy from the sample as well as damage incurred by the sectioning knife. However, since the metal layers in this study are thin, and the core of the structure is epoxy based, the samples can be sectioned. An example of the cross sections that can be obtained from this method are shown in Fig. 5, where both a structure coated with the stationary setup (Fig. 5a) and rotating setup (Fig. 5b) are shown for Al coated structures with dimensions corresponding to structure size D. The nominal Al coating corresponding to the stationary and rotating setup are 81 nm and 205 nm, respectively. For both samples, the coating thickness is highest on the top side of the structure (red arrows), which directly face the sputtering target during the coating process. The rotated sample also shows a dark and thicker coating on the outer edges of the samples (white arrows), which are exposed to the sputtering target upon rotation.

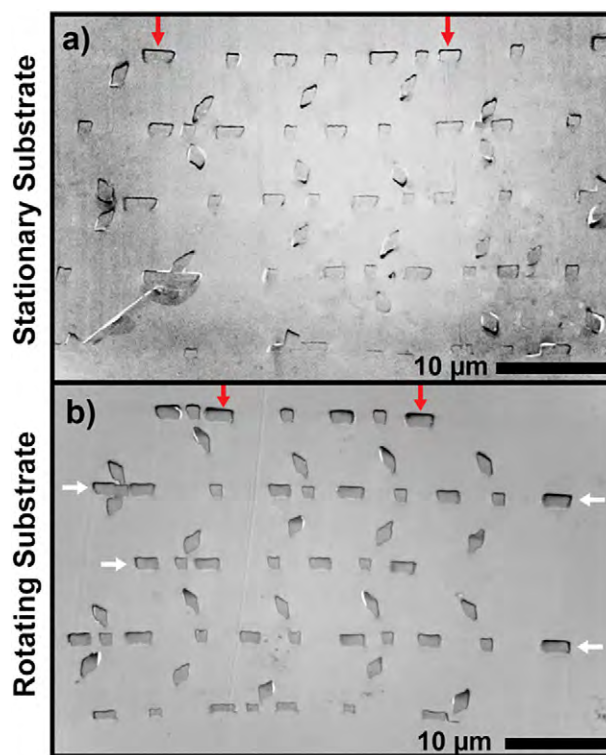


Fig. 5. Microtome prepared cross sections of Al coated structures with either the stationary (a) or rotating (b) configurations. Images shown are for structure size D with 12.5 μm strut length. The red arrows for both images show the thicker top side coatings, while the white arrows show the thicker outer coatings generated with the rotating sample.

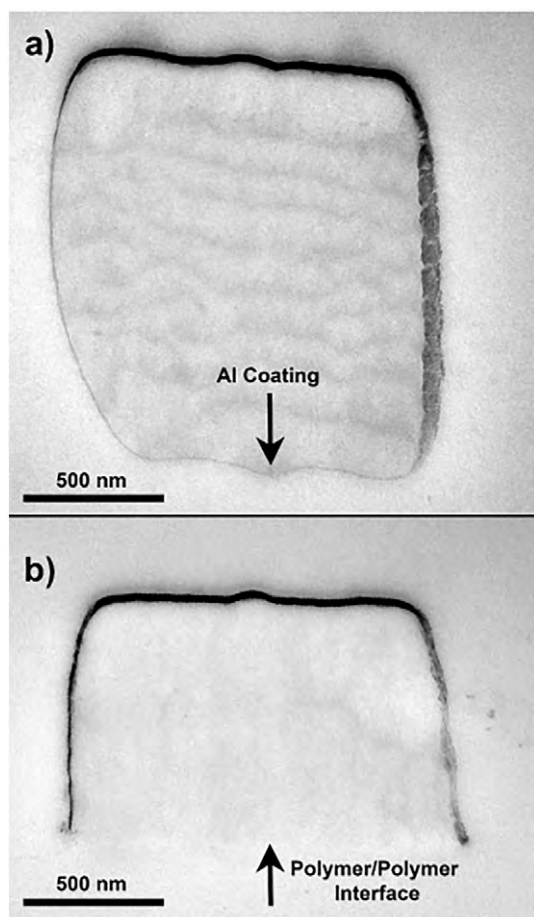


Fig. 6. TEM micrographs of strut cross-sections coated in the stationary setup from center of the structure (a) and from the bottom of the structure (b), which was masked during sputtering.

The coatings were further assessed by imaging the aligned truss ligaments at higher magnification, like the TEM images in Fig. 6, which was coated in a stationary configuration. A coating thickness variation is present along the metal/polymer interface when comparing the left side of the strut in Fig. 6a to the right side. This variation is not uncommon with magnetron sputtering, a PVD process, which relies on atoms being ejected from a source material as a result of bombardment from ionized gas particles. The process is inherently momentum driven and therefore, the coating of complex geometries is challenging due to a line-of-sight dependency [41–43].

One method to improve the coating uniformity of the film is to rotate the substrate during sputtering in order to increase the angles of exposure from the sputtering target to the cellular structure. Rotation of the substrate in this study confirmed that the coating thickness can be influenced; demonstrated by the increase in the outer edge coating thickness, which was periodically exposed to the target upon rotation. In our study, the samples were rotated along one axis during sputtering, as shown in Fig. 2. The coating variation could potentially be improved by rotating the cellular structures on multiple axes, by rotating the sample layout by 90° or by mounting the glass slide perpendicular to the current experimental setup.

Aside from rotation, modified PVD processes have been previously used to coat macro-cellular materials with metals, including coating carbon foams with titanium [44] or coating polymer foams with a nickel-based super alloy [45]. Both of these studies manipulated the flow of the metal vapor to coat the structures more uniformly. Additional techniques to coat complex shapes with PVD include the use of cylindrical sputtering targets, which completely surround the substrate and

help prevent material waste by localizing the sputtered material inside the target [42]. The use of directed gas flow and pressure can also be used to mitigate uniformity issues without substrate rotation [41,43].

To investigate the line-of-sight coating issues for the bottom side of the struts, a comparison was made between a strut from the interior of the structure (Fig. 6a) and a strut that was attached to the glass slide during sputtering. The strut attached to the glass slide is completely masked during sputtering and cannot be coated (Fig. 6b). Fig. 6a shows that the sample is coated on the bottom side of the structure facing away from the sputtering source, while Fig. 6b shows the embedded polymer-polymer interface. By comparing the two images, it was concluded that the bottom sides of the samples are coated with a thin layer of material, which was true for all materials sectioned with microtome. This observation also indicates that the film growth rate at the top side of struts is higher than the bottom, which could lead to greater film thickness inhomogeneity with longer sputtering times.

A collection of individual cross-section images for structure A from the rotated Al sample is shown in Fig. 7, where the images are placed relative to their locations within the full structure cross section. From this visual perspective, it is apparent that the use of a rotating substrate increases the coating thickness variation, as previously mentioned. If the center images are compared across each level of the structure, the coating is thickest along the top side of the structure and the top side thickness decreases with each level of the structure, moving from top to bottom. The exterior facing sides of the ligaments are also thicker than the interior facing sides. This can be clearly seen in the right side image in the second level, where the outer side has a coating that is considerably thicker. As the structures are rotated, the edges of the material are directly in sight of the sputtering target, producing the thicker exterior coating. This variation is more pronounced in structure size A,

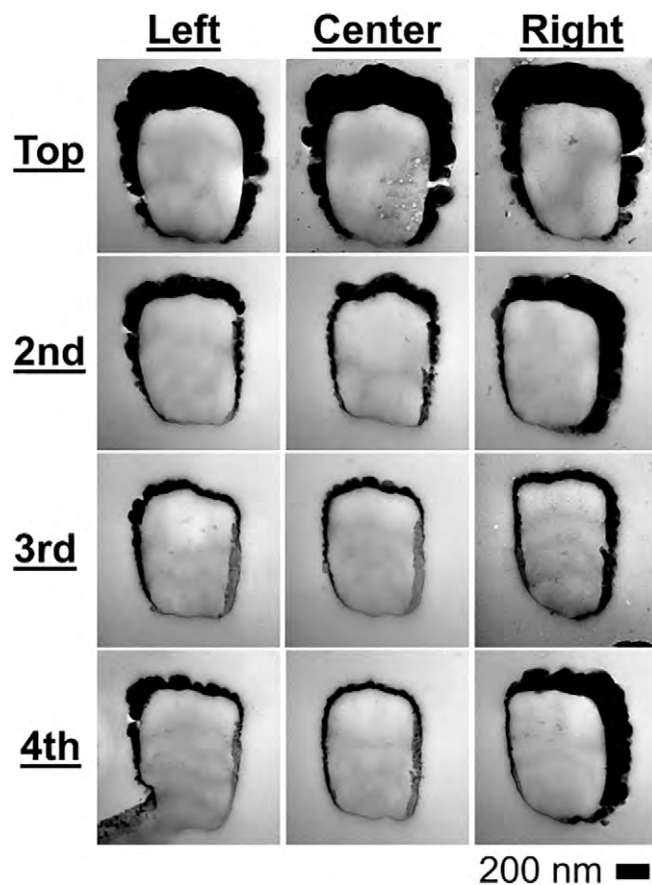


Fig. 7. TEM images of strut cross sections of structure A rotated and coated with Al. The zoomed in images of the struts are arranged according to the cross section and exhibit a decreasing top surface thickness of the coating at the lower levels of the truss structure.

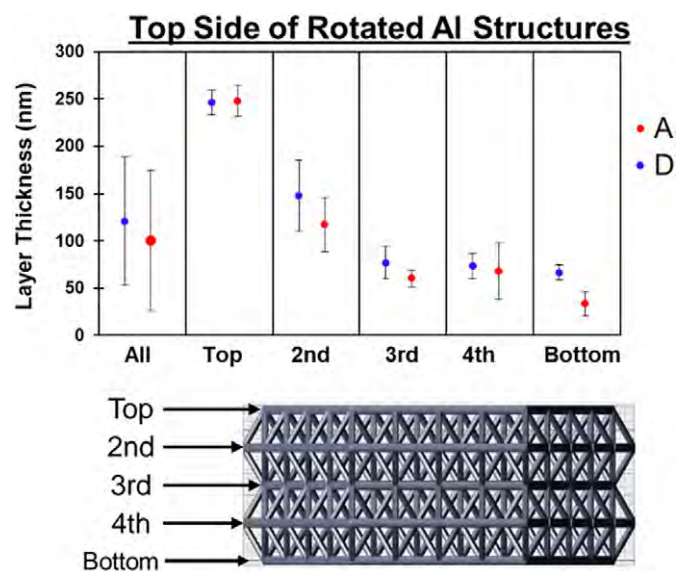


Fig. 8. Measurements of the top side of the struts and the corresponding area of the structure for the rotated Al structure corresponding to the level of structure where the measurement was taken. In both samples, the thickness of the top layer becomes smaller as the measurements are taken at lower levels in the samples.

which is the denser structure. This suggests that structure density or “openness” should be a factor in selecting materials for magnetron sputtering of complex shaped materials.

In Fig. 8, the thickness of the top side coating is shown relative to the level or depth into the sample the measurements were taken. Values were measured on rotated structure sizes A and D coated in Al. The average coating of the top surface is around 250 nm for both sizes of the structures, which is expected since both are equally exposed to the sputtering target. Measurements made on the 2nd level on the top side of the struts were ~100 nm less than the top layer for structure size D and almost half for structure size A. The coating thickness for both structures is also reduced from the 2nd to 3rd level, but then remains about the same in the 4th and bottom levels. The drop off in thickness is observed for the top side measurements for all structures measured in this work; Al rotated ~205 nm, Al stationary ~81 nm, Inconel 600 rotated ~305 nm, and Inconel 600 stationary ~100 nm. This indicates that the sputtering process yields a characteristic coating on the structures explored in this study. It should be noted that the top side thicknesses, rather than the sides or bottom, were presented here

because these measurements provided the clearest comparison of the variation that is apparent from the images shown in Fig. 7.

For the stationary coated samples, the interior facing strut side has a similar coating thickness to the center region struts. However, for the rotated samples, the exterior facing side of the struts has a thicker coating compared to the interior and exterior struts; consider the bottom right image in Fig. 7. This is explained by considering that the outer facing struts are directly exposed to the sputtering target as the sample is rotated during coating. The difference in interior and outer facing side thickness is not observed in the samples coated with the stationary sputtering setup. Alternate rotating axes, for example, could be used to more uniformly distribute the coating. Another idea, would be to sputter the structures with a low vacuum chamber so that the mean free path of ejected metal atoms is reduced and scattering of the film is encouraged [46].

3.3. Mechanical testing

In addition to the coatings evaluation, the mechanical properties of the coated trusses were investigated using uniaxial microcompression tests. Representative stress-strain curves for structure type A are shown in Fig. 9a. As expected, the fracture strength for all coating materials and thicknesses is higher than the uncoated polymer structures (Curve 1), which is a result of the lower stiffness and strength of the polymer material compared to the metals. The highest failure stress and stiffness are measured for the truss structure with an Al coating of ~205 nm (Curve 3), followed by the ~35 nm Inconel 600 coated truss structure (Curve 4). The failure stress and stiffness associated with a thinner Al coating (~81 nm, Curve 2) and the ~35 nm thick Ti 6Al-4V coating (Curve 5), are between curves 4, and the pure polymeric truss structure. Theoretically, the only difference between the Inconel 600 and the Ti 6Al-4V coated structures is the coating material, since all other experimental parameters are identical. Therefore, it follows that for a given nominal thickness the Inconel 600 coated structures have a higher compressive strength than the Ti 6Al-4V coated structures. Compared to the uncoated scaffold, Inconel has more than double the compressive strength with only minimal coating. For reference, the coating time for this structure was only 3 min. Overall, the highest failure stress was achieved by a ~205 nm thick coating of Al in the rotating coating configuration.

Fig. 9b depicts the data of the same compression tests, but with the stress values normalized by the density of the truss structures so that specific stress values are plotted. The calculated effective density values of the truss structures are listed in the Supplementary Material in Table S.1. These calculated values can be interpreted as an upper limit

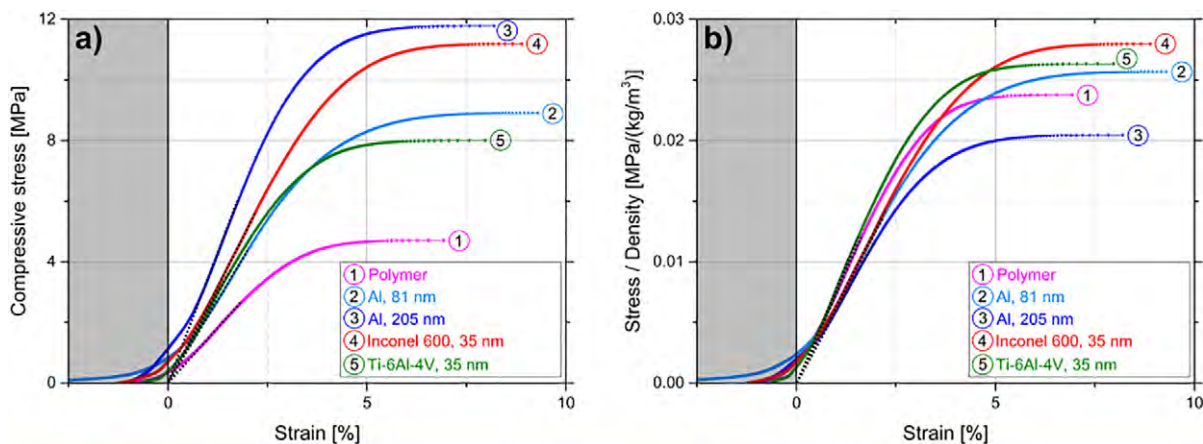


Fig. 9. Representative curves of uniaxial compression tests showing the range of mechanical behavior observed for tetrahedral truss structures of type A coated with different metals. a) Absolute stress values as a function of strain, b) stress values normalized by the density of the structures as a function of strain. The curves are shifted to account for misalignment between tip and sample surface or roughness effects (gray region in the graph).

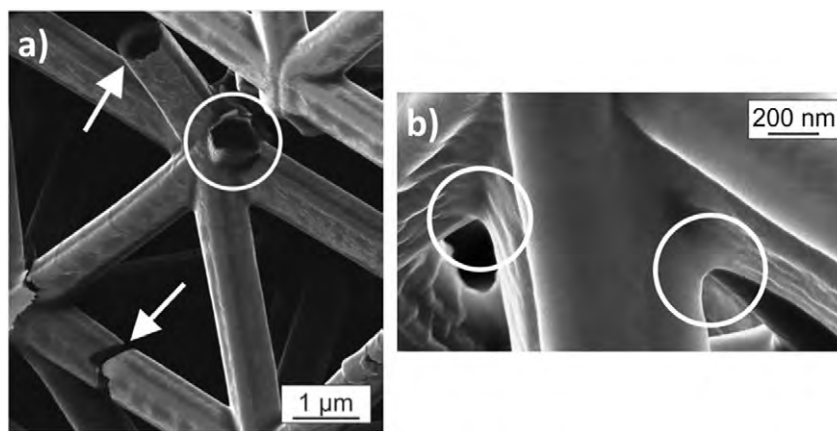


Fig. 10. Helium ion microscopy (HIM) images of compressed truss structures of type A coated with ~ 35 nm Inconel 600 in stationary configuration. a) Structure failure at a truss node is shown and marked with circle. The arrows note failure along the ligaments. b) Close up image of structure node where the coating is non-conformal and forms a webbed structural feature.

due to the nominal coating thicknesses being thicker than the real coating thicknesses in the inner part of the truss structures (compare Section 3.2). The specific fracture strengths of the different truss structures differ less than the absolute values (see also Supplementary Material, Table S.1), resulting from the increased density due to the coatings. The ~ 35 nm thick Inconel 600 coating still increases the specific strength compared to the polymeric truss structure. However, the specific strength of the 205 nm Al coated truss structure is even lower than the specific strength of the polymeric one. Moreover, for the specific stiffness, the metal coating is also disadvantageous, since only for the Ti 6Al-4V coated truss structure the specific stiffness is higher than the one of the pure polymeric truss structure. This may be explained by the high stiffness of the titanium alloy. Nevertheless, one must keep in mind that the calculated density values may be overestimated, which may result in an underestimation of the specific strength and stiffness values for the coated truss structures.

Analyzing the influence of different coating thicknesses of the same material (Curves 2 and 3, Al coated structures), it is observed that the absolute values of strength and stiffness increase due to a thicker metal coating supporting the polymeric core. In contrast, the specific fracture strength of the structures decreases with increasing Al thickness which may be related to the mechanical size effect, as also observed for alumina hard coatings [19]. The specific stiffness is approximately the same for both coating thicknesses, confirming the measurements and calculations. By comparing truss structures with the same coating thickness of technologically more relevant coating materials (Curves 4 and 5, ~ 35 nm Inconel 600 and Ti 6Al-4V), the influence of the coatings' material properties can be observed. The stiff Ti 6Al-4V coating increases the specific stiffness of the polymeric truss structures, whereas the Inconel 600 coating increases the specific strength, regardless of the high density of Inconel 600 [47]. The specific strength due to the ~ 35 nm thick Ti 6Al-4V coating is the same as for the truss structures with the ~ 81 nm Aluminum coating (compare Table S.1), showing the superior specific material properties of the titanium alloy in comparison to Aluminum.

Closer inspection of the Inconel coated structure in Fig. 10b shows possible shape optimization of the truss nodes due to the sputtered metal developing a webbed coating (white circles). This coating morphology may be the source of a shift in fracture behavior from nodal failure to fracture at both the nodes and along the struts. Fig. 10a shows points of fracture observed at the truss nodes, shown by the circles, and regions of fracture along the ligaments are also present (noted by the arrows). This is significant since nodal failure, not ligament failure, is a common occurrence for microscale architected materials under compression [12,18,19,48–50]. As discussed earlier and depicted in Fig. 9b, the influence of the metal coating on the specific strength values of the truss structures is only to a minor extent. However, the nodal

features added by the coating are possibly enhancing the mechanical efficiency of the trusses, regarding long term loading and energy dissipation. A simulation by Valdevit et al. showed that the strength of a hollow lattice structure can increase when the volume of material around the node is thickened relative to the strut regions [51]. However, a comprehensive mechanical study would be needed to determine the contribution of this coating technique to mechanical performance.

4. Outlook and conclusion

The commercialization of 3D-DLW has sparked several studies in a wide range of research areas including in-depth investigations into the relationship between hierarchical structure and the mechanics of lattices. Novel microdevices are also being developed, such as sputter coated microlattices for battery applications [52] and silver deposition on 3D structures for photonic metamaterials [14,53]. Advancements in coating capabilities, especially new setups that would mitigate line-of-sight effects, would expand these applications so that tailormade structural features could be accompanied by the unparalleled materials selection offered by magnetron sputtering.

This endeavor is explored in this study, where microlattice metal-polymer composites were generated using a combination of 3D direct laser writing (3D-DLW) and metal coating via magnetron sputtering. Using magnetron sputtering, a variety of metal coatings, including Aluminum, Inconel 600, and Ti 6Al-4V, were deposited onto microlattice structures. The inclusion of alloy coatings is significant because traditional deposition methods for metals are limited to a few systems. Therefore, using sputtering as a metal deposition method has the potential to expand the achievable properties of composite microtruss structures to include unique combinations of strength, conductivity, and chemical activity. Uniaxial compression of the samples revealed that, by applying metal coatings, the deformation mode of the composite structures can be shifted from node-dominated failure towards a ligament dominated failure. This realization, which needs to be studied in more detail, may lead to improved lattice structure and nodal design for future microlattice structures.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matdes.2017.12.005>.

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Nanoporous Metals with Structural Hierarchy: A Review

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Nanoporous (np) metals have generated much interest since they combine several desirable material characteristics, such as high surface area, mechanical size effects, and high conductivity. Most of the research has been focused on np Au due to its relatively straightforward synthesis, chemical stability, and many promising applications in the fields of catalysis and actuation. Other materials, such as np-Cu, Ag, and Pd have also been studied. This review discusses recent advances in the field of np metals, focusing on new research areas that implement and leverage structural hierarchy while using np metals as their base structural constituents. First, we focus on single-element porous metals that are made of np metals at the fundamental level, but synthesized with additional levels of porosity. Second, we discuss the fabrication of composite structures, which use auxiliary materials to enhance the properties of np metals. Important applications of these hierarchical materials, especially in the fields of catalysis and electrochemistry, are also reviewed. Finally, we conclude with a discussion about future opportunities for the advancement and application of np metals.

1. Introduction

The concept of hierarchical organization is ubiquitous, encompassing both deliberately designed structures and natural materials. Examples of ordered hierarchy are most evident in biological systems, where pore networks in trees and bones reduce the density of the structure and provide channels for fluid and nutrient flow, enhancing mechanical properties while adding functionality.^[1] Biological systems exploit hierarchy from the nanometer up to the macroscale, with a complex architecture in which the structural elements themselves have structure on a smaller scale.^[2] Humans have attempted to mimic

advanced biological systems by designing frame structures like the Eiffel Tower, but the complexity that can be found in natural materials, such as bamboo, has yet to be realized.^[3] There may be opportunities in reproducing these types of geometries in man-made materials, where hierarchy is found in the length scales occupied by structural features, such as tiered porosity in single element materials or the spatial distribution of elements in composites. However, this requires the development of new strategies for advanced materials design, specifically the appropriate preparation procedures and an understanding of the effects of hierarchical structure on functional properties.

Advances in metal or ceramic deposition methods, templating, and dealloying methods, have made it possible to produce hierarchical structures in a variety of elements and configurations. This review focuses on hierarchy in porous materials

that include characteristic pore sizes down to the nanoscale. Specifically, we consider materials in which the smallest and definitive length scale is occupied by nanoporous (np) metal made by dealloying. Examples of as-dealloyed np topologies are shown at the center of **Figure 1**. Alternative processing methods that can produce additional levels of tunable structure in single-phase materials (left of Figure 1) or in composites (right of Figure 1) are also reviewed.

2. Background

2.1. Materials with Multiple Length Scales, Stochastic versus Periodic

Metals with pore sizes on the order of nanometers to millimeters are used in a variety of structural and functional applications such as heat exchangers,^[4,5] filters,^[6,7] energy absorbers,^[8,9] and catalysts.^[10,11] Their key benefits include a large amount of internal surface area and high thermal and electrical conductivity.^[12,13] In particular, the automotive, construction, and aerospace industries are interested in foams as lightweight structural components to maximize strength to weight ratios, impact absorption, and vibrational damping.^[14,15]

Incorporating additional length scales or architectures can significantly improve the performance of materials. A prime example is the design of sandwich panels and their core structure to improve both mechanical properties and heat transfer properties when a fluid flows through the panel.^[16–18]

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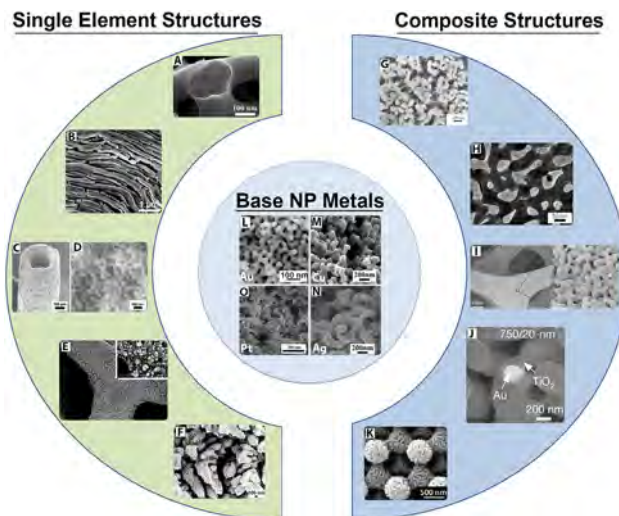


Figure 1. Schematic representing various hierarchical structures in single element np materials (a–f) and composite structures (g–k) that are based on np metal morphologies (l–o) produced by dealloying. f, b, and j) reproduced from ref.^[105,122,206] respectively. Copyright 2009, 2012, 2015 American Chemical Society. m, l, and c & d) reproduced with permission from ref.^[68,74,85] respectively. Copyright 2011, 2006, 2015, John Wiley and Sons. e) adapted from ref.^[105] with permission from Springer. Copyright 2016. n, i, and g) reprinted from ref.^[70,138,213] respectively, with permission from Elsevier. h) adapted with permission from Macmillan Publishers Ltd: Nature Nanotechnology, ref.^[126] copyright 2011. k and o) reproduced from ref.^[137,214] with permission of The Royal Society of Chemistry.

Examples of different core architectures include traditional foam core, honeycombs, or truss structures with periodic architecture. The variety of available core designs and numerous material options allows for the optimization of these metal cellular structures for applications in the aerospace and automotive industry.^[16,19]

Cellular materials can be classified into two broad categories, stochastic and periodic, see the examples in **Figure 2**. Stochastic materials (Figure 2a–c) have random pore distributions, where various degrees of short-range order and pores size distribution can be found. Periodic structures (Figure 2d–f) have a base cell that is repeated in two dimensions, such as the honeycomb in Figure 2f, or in three dimensions, such as the trusses in Figure 2e.^[14,15,20] Each category is associated with distinct mechanical properties as well as differences in relative density and production effort or cost. The use of various synthesis methods can also yield characteristic pore and ligament sizes from the macroscale down to the nanoscale. Both stochastic and periodic materials can be fabricated with a wide variety of base metals, from aluminum to titanium, and with closed or open porosity. The distinction between closed and open porosity is crucial. For instance, the latter implies permeability to fluids, typically along with a lower density.^[14,21]

When evaluating the mechanical properties of stochastic and periodic structures, one finds that for a given relative density, ordered porous structures have superior load-bearing properties when compared to their stochastic counterparts.^[22]

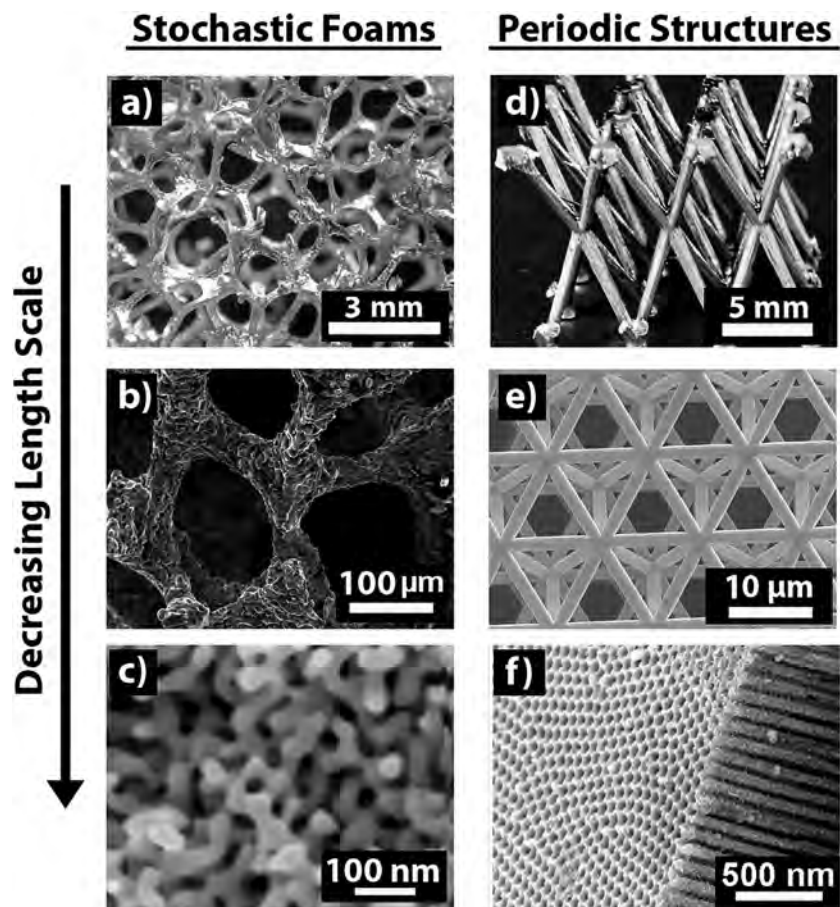


Figure 2. Classifications of cellular materials as either stochastic a–c) or periodic d–f), with cellular features from the macroscale down to the nanoscale for each type of cellular structure. f) adapted with permission from ref.^[215] Copyright 2015 American Chemical Society.

This is because periodic trusses or networks are typically stretch-dominated materials when loaded, whereas random networks are bending-dominated.^[23] Additionally, closed-cell materials usually have an increased relative modulus for a given relative density, making them more desirable for load bearing applications.^[15,22] Key advantages of using open porous structures for practical applications include mass reduction and the large accessible surface area.^[14,15] This, for example, is important for catalysis^[24] or applications requiring cooling, since both the rate of product formation and heat transfer increase with the available surface area.^[25,26] For the purposes of this review, we are only interested in open cell structures, since their large accessible surface area enhances the potential for the added functional applications, such as catalysis and energy storage, that are discussed in Section 4.

The mechanical behavior of stochastic porous solids, as well as ordered cellular materials such as truss structures, are described in the seminal work on the mechanics of cellular solids by Gibson and Ashby.^[27] This work shows that the strength of porous solids is fundamentally governed by the relative density of the material. By contrast, the Gibson–Ashby approach predicts that mechanical properties do not depend

on the cell size, except for a certain sensitivity of strength to the ratio of the cell wall thickness to cell length.^[27] It is therefore unexpected that the properties of the np metals discussed in this review do not scale according to the Gibson and Ashby equations.^[28–30] The interest in this issue can be traced back to early experiments revealing drastic changes in strength when the struts or ligaments of np gold are varied while maintaining the same relative density.^[29–40] Studies on the mechanical behavior of np metals are numerous and suggest interesting size effects. Still, the influence of structural hierarchy on the plastic yield and flow behavior in these materials remains to be clarified. By contrast, hierarchy from the nm scale up has been thoroughly addressed by theory analyzing the fracture strength of biological materials.^[41,42] Therefore, this review will instead focus on the relevance of hierarchy for functional applications and on emerging preparation techniques.

2.2. Fabrication of Macro-Foams to Nanoporous Materials: Basic Concepts

The origins of the earliest made porous metals for commercial use can be traced back to the 1920s, when French scientist De Meller described a process of injecting gas into molten metals, now common practice for producing metallic foams.^[43] The injected gases develop into bubbles that become pores.^[9] Alternative processing

methods use powder sintering, where fine metal powders are compacted with a metal hydride and heat-treated near the melting temperature of the metal. This releases gas from the hydride and forms pores in the soft metal.^[9] One approach to enhance the properties of metal foams includes careful selection of the base metal alloy to produce strengthening intermetallics.^[44]

It is important to note that these foaming techniques form mm sized pores and are thus generally limited to macroscale porosity (Figure 2a). Furthermore, these techniques offer limited ability to impart additional levels of structural hierarchy other than material characteristics such as grain size and dispersed particles. An established technique to create microscale porous foams involves the deposition of metal onto a polymer scaffold and subsequent etching or burning out of the polymer, which results in a hollow strut metal foam (Figure 2b). Unlike the foaming methods, this approach can be tailored by using engineered microlattice polymer scaffolds and controlling the amount of metal deposited onto the scaffold, allowing some influence on the wall thickness.^[45,46] Thus far, traditional preparation methods for metal foams have not been able to achieve cell sizes below the micron scale.

Recent fundamental work on the synthesis, properties, and applications of nanoporous metals with feature sizes in the tens of nanometers, has started a research field focusing on a new class of porous metals. As a key advancement, dealloying has emerged as a synthesis route toward monolithic np metals. Dealloying combines high structural definition and morphological control with compositional flexibility and a high level of reproducibility. Np metals made by dealloying lack the cell structure that is characteristic of materials produced by foaming. Instead, this new class of materials is characterized by an interconnected network of nano- or microscale ligaments interpenetrated by a contiguous (open) array of pore channels. Like their macroporous counterparts, nanoscale networks exhibit high stiffness. However, a distinctive feature of np metals is their drastically increased surface area. The specific surface area (per volume or per mass) scales inversely with the feature size. The large surface area that can be achieved with nanoscale pores makes dealloyed np metals highly attractive when function derives from properties or processes at the material surface, for instance in catalysis,^[11,47–50] sensing,^[11,51,52] and actuation.^[53,54]

The fundamental mechanisms of dealloying to produce np metals have been explored since the early 20th century.^[55,56] Examples for more recent studies can be found in the work by Pickering and Swan,^[57,58] Forty,^[59] as well as Newman and Sieradzki.^[60,61] The present understanding of dealloying was established when Sieradzki, Erlebacher and coworkers reproduced key experimental observations in a simple atomistic simulation scenario.^[62–64] Essentially, dealloying is the selective electrolytic corrosion of a master alloy that is a solid solution or compound of a more noble element (MNE) and a less noble element (LNE). Its central process is the corrosive dissolution of the LNE in free-corrosion dealloying, through the immersion of the alloy in a corrosive medium, or in electrochemical dealloying, by the combined action of chemical and electric driving forces for dissolution.^[32] In the latter case, the electrode potential affords control of the rate of LNE removal.^[61,62] More recently, liquid metal dealloying has been employed where one or more components of the starting alloy selectively dissolve in molten metal.^[65]

It is important to realize that the characteristic pore/ligament structure of np metals made by dealloying is not related to any similar structure in the master alloy. Instead, the nanoscale structure is formed by self-organization during the corrosion process. The underlying atomic-scale processes are the dissolution of the LNE and surface diffusion of one or both elements along the metal-solution interface. This results in monolithic bodies with a bicontinuous structure of pore and solid. The uniform 3D morphology is shown in **Figure 3**. The interpenetrating networks of pore channels and ligaments are not periodic, yet each individually exhibits a high connectivity and

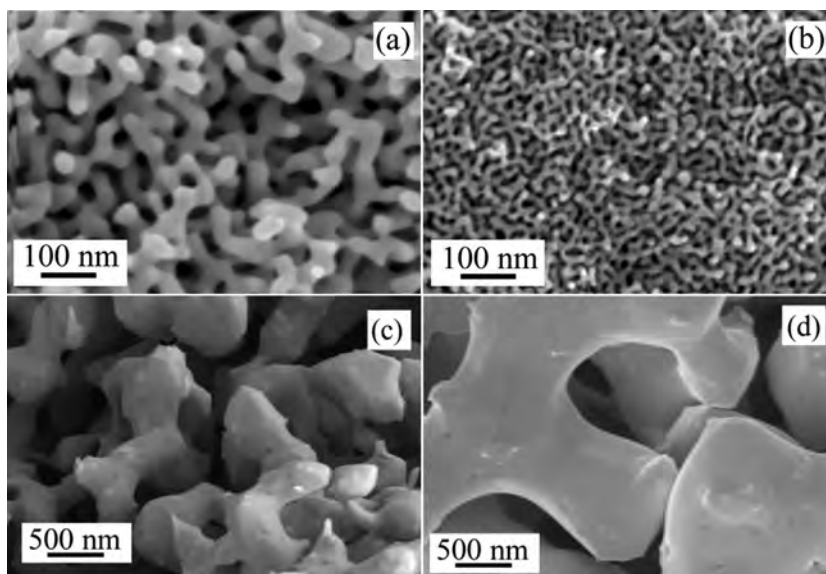


Figure 3. SEM images of np-Au foam prepared by a) free corrosion and b) electrochemically driven corrosion. SEM images of free corrosion samples after 2 h heat treatments at c) 400 °C and d) 600 °C. Reprinted with permission from ref.^[74] Copyright 2006 John Wiley and Sons.

well-defined characteristic feature size and spacing between neighboring elements.

Important parameters in dealloying are the parting limit and the critical potential for dealloying.^[66,67] The parting limit marks the minimum concentration of LNE (or maximum concentration of MNE) which is required for corrosion to proceed throughout the bulk of an alloy rather than being arrested by passivation. For example, studies suggest a parting limit of approximately 45 at% Au for Ag–Au alloy.^[66] In electrochemical dealloying, the critical electrode potential, E_c , again refers to a criterion for achieving bulk corrosion. This parameter is composition dependent. For example, in Ag–Au alloys, E_c increases with increasing Au content.

The dealloying process can be applied to other solid solutions for the synthesis of np-Cu,^[68] Ni,^[69] Ag,^[70] Pd,^[71] and Pt.^[72] Au is most studied as the material of choice due to its chemical stability and the availability of established dealloying protocols for control and reproducibility of the nanoscale morphology. For a detailed overview of the present understanding of dealloying and porosity evolution, we point the interested reader to a recent review by McCue and Erlebacher.^[73]

The length-scale most typically associated with as-dealloyed np gold is about 40–50 nm, but these dimensions depend on the metal and they can be altered by adjusting master alloy composition or dealloying parameters to reduce the ligament size to ≈ 5 nm.^[74–76] The scanning electron microscope (SEM) image in Figure 3a shows a np-Au foam made by free corrosion in nitric acid while Figure 3b shows the structure produced from the same alloy but using electrochemically driven dealloying in 1 M HNO₃ and 0.01 M AgNO₃. The impact of different popular dealloying scenarios in aqueous solutions – free corrosion in HNO₃ versus electrochemically assisted corrosion in HNO₃ or electrochemical corrosion in HClO₄ – is explored in the comparative study in ref.^[77]

Coarsening heat treatments afford increased ligament sizes, up to the micron scale.^[74] For instance, a 2 h heat treatment at 400 °C can double the ligament size (Figure 3c). Higher temperatures and longer heat treatments can yield substantially larger ligaments, such as those in Figure 3d, after 2 h at 600 °C. Heat treatment protocols by other authors differ, see for instance ref.^[78] The ease with which one can alter the ligament size is advantageous since it allows for tuning of properties that depend on size or specific surface area, such as the mechanical strength.^[28,35,40,74]

Thus far, the field of np metals has grown to encompass a wide range of materials and functionalities or prospective applications. Key aspects of the properties and applications of np gold, as the most intensely studied np metal, are treated in the book edited by Wittstock et al.^[79] The more recent and detailed literature is extensive, therefore only a fraction of it can be referenced in this work. Here, special attention is given to studies that have expanded the achievable configurations and applications of np metals by adding structural hierarchy.

For clarity, the following definitions are followed in this review. *Structural hierarchy* is considered to imply organized features on distinct length scales, especially when the elements of the structure at one scale themselves have structure at a smaller scale. Some materials discussed in this review have hierarchical porosity and others have hierarchy that is related to the spatial distribution of the solid phase. *Bimodal* refers to the presence of two distinct characteristic length scales. When applying the term to hierarchical structures in this review, we imply self-similarity of the pore structures on two distinct length scales. *Networks* are interconnected arrays of linear features, forming continuous pore or solid pathways. *Single element* materials are composed of only one element or base np material. Finally, *composites* are named in the traditional sense, where materials incorporate a combination of constituent materials or elements that are not alloys.

3. Synthesis of Nanoporous Materials with Hierarchy

3.1. Hierarchical and Multimodal Structures

Materials with multiple levels of porosity or hierarchal elements can be achieved by numerous methods, including the use of 3D-printed polymer structures as scaffolds for material deposition, generating more complex architected structures.^[45] Etching (or retention) of the polymer after the coating extends the achievable properties of the overall structure, based on the intrinsic properties of the base materials.^[80] In a similar manner, using np materials as a base constituent has its own advantages, namely the scalability and the enhancement in surface area. These two main methods (dealloying and templating) for achieving np materials with multimodal porosity are explored below with consideration for the nuanced approaches toward realizing these unique materials in multiple configurations.

3.1.1. Templating

While Ding et al.^[81] developed the first bimodal np-Au in thin foil form, Nyce et al.^[82] developed the first 3D hierarchical bulk

np-Au samples with two distinct length scales of porosity using a combination of templating and dealloying. Ag/Au polystyrene (PS) core-shell particles were first prepared by electroless deposition of Ag and Au on PS spheres followed by casting to obtain a monolithic 3D bulk sample, which was then heat treated to remove the PS template while simultaneously alloying the Ag/Au layers. Finally, dealloying transformed the hollow Ag–Au alloy shells of the structure into hollow np shells showing the typical bicontinuous morphology of np Au. The 200 nm thick shell wall survived dealloying without crack formation despite the low pre-dealloying Au content of only 15 at%. In general, hierarchical structures^[83] and low-dimensional nanoscale objects^[84] seem to be more resistant to stress induced cracking than uniform bulk samples that tend to disintegrate during dealloying of low Au content alloys.

This type of templating and homogenization of the structures was expanded upon in a study by Juarez and Hodge, where the overall higher order structure was in the form of hollow tubes approaching the centimeter length scale in the largest dimension.^[85] The processing steps for this method are shown in **Figure 4**. First, a hollow Au tube is coated with Ag followed by a heat treatment to form the alloy. The np morphology was then introduced by free corrosion in concentrated nitric acid, resulting in a structurally stable fully np-Au tube.

Alternatively, templating can be achieved through electrodeposition of metal into predetermined areas defined by masking. In this sense, Ag–Au nanowires can be made by electroplating the alloy into the nanopores of a suitable template. The alloy nanowires are stripped from the template and dispersed on a substrate, then dealloyed to form np wires (**Figure 5a**).^[86,87] The same idea was applied to develop arrays of nanotubes with np walls, as shown in **Figure 5b**, and porous Pt-Co nanowires.^[88,89] Still, the fabrication of these rods through mesh templating limits the length of the nanowires to the thickness of the resist used to mask the plating channels. The length of the potential nanoarrays was increased by a method for the electrodeposition of Au–Cu onto a patterned silicon substrate. The substrate was made conductive by a vapor-deposited Au seed layer.^[90] The resulting patterned structure consists of one-dimensional lines with np structure.

More recent work has demonstrated centimeter long np nanowires developed by first sputtering Au–Cu on a rotating silicon substrate with 120 nm wide nano-patterned grates and a length of a few centimeters. Rotating the structure with the grates perpendicular to the target throughout sputtering develops the circular cross-section of the rod. The sputtering was followed by electrochemical dealloying of the patterned nanowires resulting in the structures shown in **Figure 5c** and **d**.^[91]

Aside from 2D nanowire arrays, it is also possible to fabricate hierarchically structured 2D np-Au opal films by electrodepositing a Au–Ag alloy into a silica inverse-opal template. The final np-Au opal structure (**Figure 6**) is obtained by removing the silica template with an HF etch, followed by free corrosion dealloying in nitric acid.^[92] The overall structure of the hierarchical film is displayed in **Figure 6c**; the smallest pore spacing inside the opals was approximately 10 nm. The opals themselves were approximately 400 nm in diameter with an interstitial spacing of 40–100 nm, where the larger gaps in the

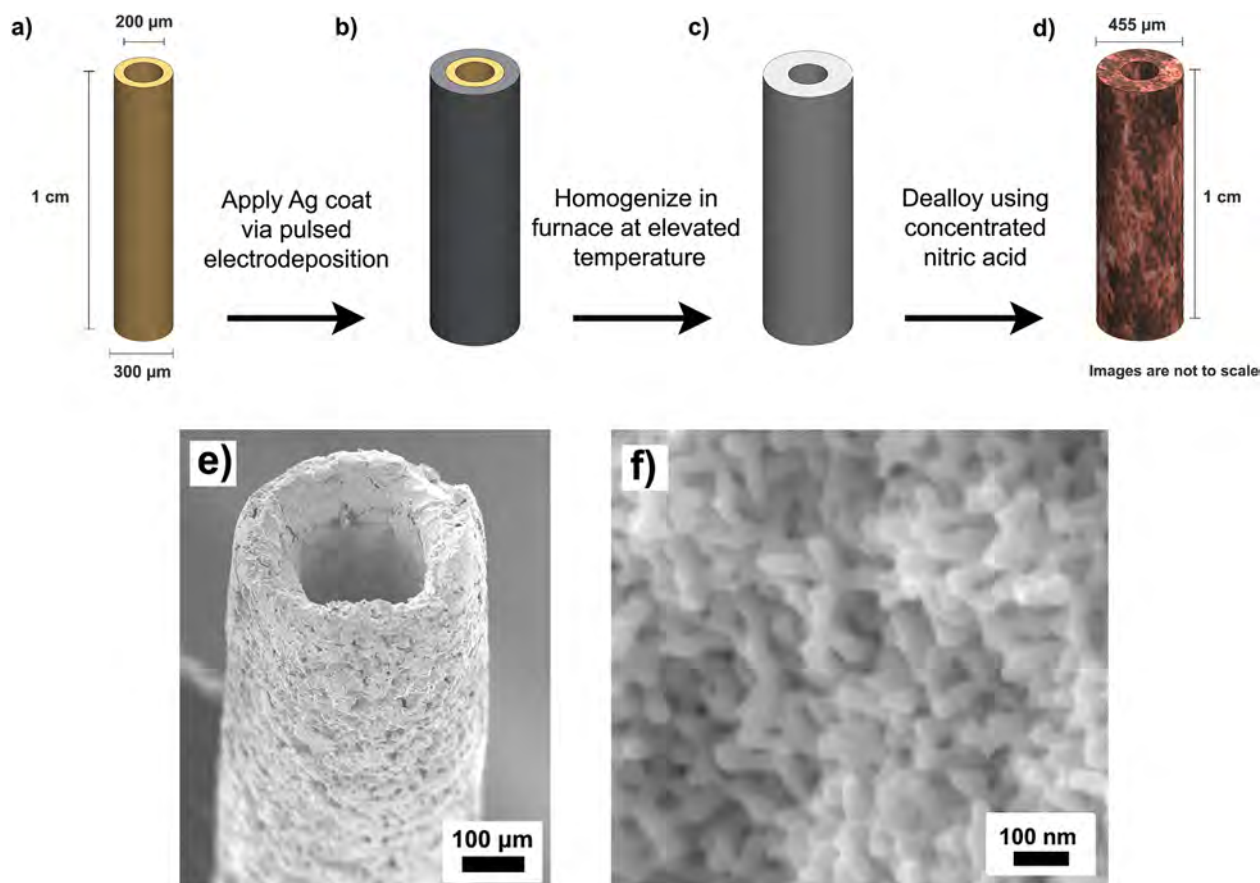


Figure 4. Schematic representation and cross-sectional images for the processing of nanoporous gold tubes. Fabrication begins with a base Au tube a) that is coated with a layer of Ag via electrodeposition b). The layered tube is then homogenized in a furnace c) and then dealloyed to produce a nanoporous Au tube d). SEM images for the tube and the embedded np ligaments are shown in e and f). Adapted with permission from ref.^[85] Copyright 2015 John Wiley and Sons.

structure are a result of opal shrinkage during dealloying. Overall, the film is about 2 μm thick and attached to a substrate. Thus far, this type of material, like the shorter nanowires, has not been synthesized in bulk quantities.

Templating and dealloying are methods that can be used in combination to incorporate porosity and control of the overall structure of the final material, such as the 1D nanowires, 2D opal structures, and the 3D bulk materials discussed in this section. The use of templates, however, increases the number of synthesis steps required to produce these intricate structures. While templating is necessary when a specific shape is desired, multiple length scales can also be implemented by other methods relying on electrochemistry or the initial microstructure of the precursor alloy which will be discussed in the next section.

3.1.2. Dealloying

The earliest example of a hierarchical structure based on np metals, with distinct length scales of self-similar porosity, is from Ding and Erlebacher.^[81] The ligaments of this material are composed of smaller ligaments with the same characteristic

shape. This architecture was realized by depositing Ag onto a previously dealloyed and subsequently annealed 1 μm thick Au–Ag leaf, with ligament diameters in the range of 100 nm. After Ag deposition and annealing to form an alloy, another dealloying step is performed, resulting in formation of the bimodal pore size structure shown in **Figure 7a**.^[81] The uniform deposition of Ag inside the np-Au structure was achieved by the development of a new gas-liquid interface electroless plating technique that takes advantage of the tendency of np-Au leafs to float on aqueous solutions and therefore requires the film to be thin.

While the above concept is limited to the preparation of hierarchical structures in the form of thin films, Qi and Weissmüller demonstrated a dealloying protocol that yields self-similar nested networks on different length scales in the form of three-dimensional bodies.^[83] They developed a method to electrochemically dealloy a high LNE alloy ($\text{Ag}_{95}\text{Au}_5$), while retaining enough Ag content to approach the parting limit of the Au–Ag alloy and produce the characteristic np-Au ligament morphology. Coarsening of the initial dealloyed materials increased the ligament size from ~ 16 to ~ 200 nm, similar to the case of np-Au. The key finding in this study is that the characteristic porous structure can be achieved without fully

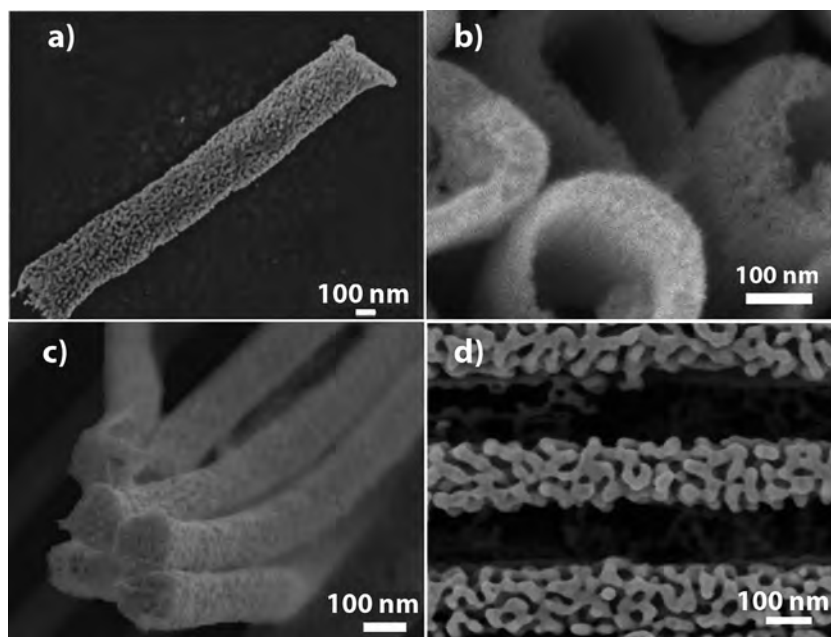


Figure 5. Various nanowire structures ranging from short np wires^[86] a) to np nanotubes^[88] b) to long nanowires fabricated on silicon patterned substrates c and d).^[91] Adapted with permission from ref.^[86,88,91] Copyright 2003, 2008, 2016 American Chemical Society.

leaching out the Ag, allowing for annealing and a second dealloying step, producing a nested structure like that shown in Figure 7b, with both a higher and lower level of porosity. This sequential dealloying process was later applied to porous sheets of a Ag–Au alloy to generate tri-modal porous structures.^[93]

Another example of multiphase precursors is demonstrated by the dealloying of Pd–Al alloys produced by spark plasma sintering to make hierarchical np-Pd. A bimodal porous structure is developed in regions where the microstructure is heterogeneous due to the different chemical activities for Al and PdAl₃ phases.^[96] In regions where both phases are present, a bimodal structure is formed, whereas in regions with only PdAl₃, a monolithic porous structure is formed. The regions rich in Pd produce ligaments as small as 7 nm, and the regions rich in Al produce larger pores (≈ 200 nm) with embedded smaller pores due to the PdAl₃ phase.^[96] Note that doping a precursor alloy with a more noble and low mobility element, such as Pt or Pd, can be used to reduce the size of the np ligaments in single or bimodal materials because of the slower surface diffusion of the more noble element.^[75,97–99] Hierarchical np-Pd has also been generated by the electrochemical dealloying of a Pd–Ni–P metallic glass.^[100]

An early study that showed clear evidence for the benefits of using two-phase starting alloys was by Jin et al.^[101] In their study, the solidification of a Pt–Ag master alloy led to Pt-rich dendrites, which resisted corrosion during later dealloying. The dendrites that remained embedded in the nanoporous matrix acted as efficient crack stoppers, substantially enhancing the toughness.

In addition to the studies discussed in detail above, several Al alloys, where the Al

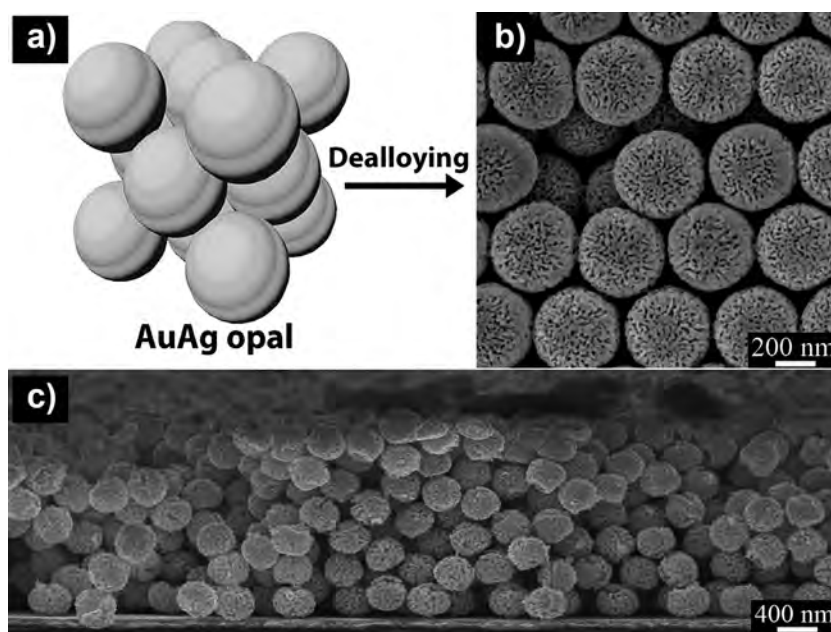


Figure 6. Alloy opal structures a) are dealloyed in nitric acid to develop a porous opal structure b). The overall film structure c) is about 2 μ m thick. Adapted with permission from ref.^[92] Copyright 2012 American Chemical Society.

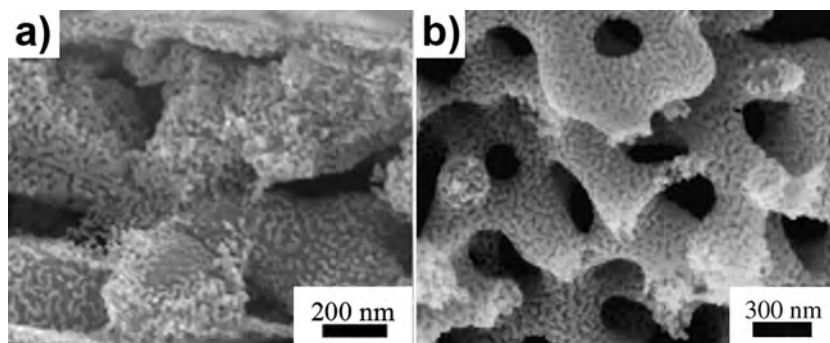


Figure 7. a) Nested np structure generated by depositing an alloying element into a np metal followed by diffusion and dealloying.^[81] b) Nested np metal by two-step dealloying of an alloy with abnormally high LNE content.^[83] Reproduced with permission from ref.^[81] Copyright 2003 American Chemical Society.

is removed during dealloying, have been exploited to generate bimodal materials. These include multiphase alloys, including Ni–Al,^[102] Al–Cu,^[103,104] and Al–Au,^[105,106] as well as ternary alloys such as Al–Pd–Au^[107] and Pt–Ti–Al^[108] that generate binary alloy np materials. In the two latter studies, Al was first dealloyed in NaOH or NaOH/HCl and the more noble elements were removed with nitric acid. Further studies, using multiphase or multi-element alloys for dealloying multimodal porosities can be found in the following references.^[109–112]

Hierarchical foams can also be made by dealloying preformed, multiphase grain structures within percolation thresholds. Cox and Dunand formed macro/microporous Au–Ag foam by mixing salt into a metal powder pack before compression and sintering.^[113] The salt was dissolved in water, which produced large block-shaped macropores, while micropores were developed from the gas expansion of water vapor trapped in the powder compact. This structure is shown in **Figure 8**. The sintering process alloyed the Au and Ag powders, resulting in a Au₁₉Ag₈₁ at% alloy with graded porosity. The final tier of structure, nanoporosity, was added by dealloying in nitric acid.

Preexisting commercial macroscopic foams can also be manipulated to exhibit nanoporosity. Roughening the surface of commercial Cu foams using electrodeposition and

electrochemical dealloying develops a nanoporous layer on the foam surface.^[114] This is accomplished using a single aqueous electrolyte solution, where a Ni–Cu alloy is deposited onto a macroporous Cu foam and the Cu is selectively etched during dealloying from both the alloy coating and the pure Cu cell walls underneath. Undercutting of the Ni–Cu film results in the removal of the Ni components, leaving a roughened np layer of Cu on the surface of the walls. Both the number of deposition/dealloying cycles, as well as the time duration for the dealloying pulse can control roughness.^[114]

In other studies, a combined Gasar and dealloying process fabricated np Cu rods. The Gasar process, that consists of melting a material in a gas atmosphere to saturate

it with hydrogen followed by directional solidifying under strictly controlled thermodynamic and kinetic conditions, generates rods with tubular pores oriented along the length of the cylinder.^[115] The method was used to develop Gasar Cu–34.5 wt% Mn alloys that then were dealloyed under free corrosion conditions. The resulting bulk samples exhibited both the longitudinal pores from the Gasar process, but also lower level nanoporosity from dealloying of the constituent alloy.^[116,117] The material is shown in **Figure 9**.

The initial microstructure of the alloy before selective dissolution can also impact the overall structure of the material. Channeling contrast in focused ion beam imaging^[118] and later electron backscatter diffraction imaging,^[40,119] showed that nanoporous gold inherits the polycrystalline microstructure of the master alloy, with perfectly coherent crystallites tens of micron in size, in spite of the underlying nanoporosity. Depending on the processing of the master alloy, its grain boundaries can either be completely dissolved to form a gap or can be continuous across the boundary.^[120,121] Obviously, mechanical integrity and, even more so, good mechanical behavior under load makes it mandatory to avoid weakening of the porous structure at grain boundaries. Dealloying protocols for Ag–Au and Cu–Au can be tailored to achieve this, as is evidenced by transgranular fracture, as opposed to intergranular fracture along grain boundaries.^[33,121]

In some instances, it was deemed advantageous to accept the extreme brittleness that comes from preformed cracks at grain boundaries to achieve multiphase microstructures. Thus, Detsi et al.^[122] found that a combination of rolling, from 5 mm to sub-millimeter material thickness, and heat treatment of the master alloy can generate features in the microstructure (**Figure 10a**) that lead to de-cohesion along planar faults during dealloying. Stacked microlayers of np-Au resulted (**Figure 10b**), where a length scale is described by the layer thickness and another by the ligament size.

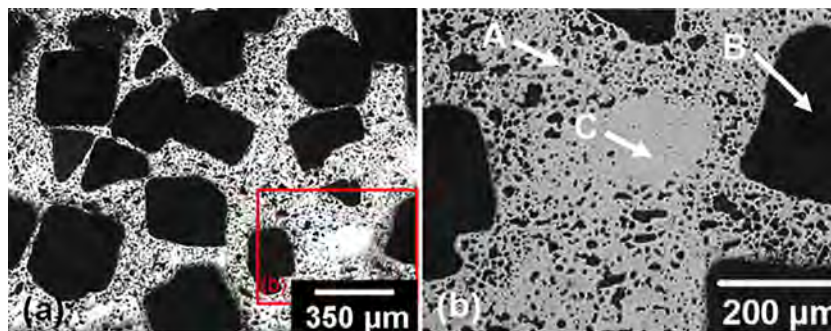


Figure 8. Cross-section of alloy foam before dealloying. a) Large block shaped macropores from salt removal. b) Enlarged area showing micropores from gas expansion. Reprinted from ref.^[113] with permission from Elsevier.

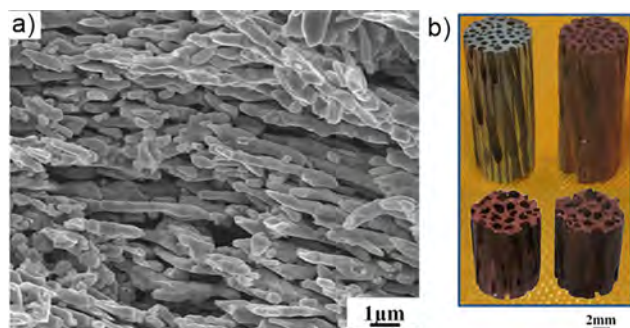


Figure 9. Bimodal Cu rods developed by a combination of the Gasar and dealloying processes to produce nanopores a) within longitudinal pores b). Adapted from ref.^[116] with permission from Elsevier.

3.2. Composite Structures Based on Nanoporous Metals

In this section, synthesis methods for incorporating secondary or tertiary materials for auxiliary hierarchy are reviewed, particularly deposition methods that add an additional layer of material onto a np metal surface. Synthesis techniques to develop functional np metal films on larger structures, as well as hierarchical alloy materials, are discussed.

3.2.1. Film Deposition on np Ligaments

The challenge of material deposition onto the ligaments of np metals is to achieve uniform coatings on these ultrahigh aspect ratio materials (where aspect ratio is defined as the ratio between the pore length and the pore diameter). This is specifically true for bulk np metals regardless if they have nonhierarchical or hierarchical porosities. Deposition requires mass transport of some sort (for example via ion diffusion in electrodeposition) through the porous network. Concurrent deposition leads to depletion of the species to be deposited, which results in inhomogeneous coatings. Achieving truly homogeneous coatings in bulk np materials thus requires a deposition technique that is self-limiting, that is, after deposition of a certain amount

of material the surface becomes passivated against further deposition.

One technique that fulfills this requirement is atomic layer deposition (ALD), a chemical vapor deposition process that relies on two sequential, self-limiting surface reactions. The technique has been successfully used to deposit extremely thin (as thin as 0.25 nm per cycle) and conformal layers of both metals and metal oxides on np bulk materials.^[123] The layer thickness is controlled by the number of ALD cycles. Biener et al.^[123] used this technique to coat np-Au samples with either Al₂O₃, chosen for its thermal stability, or TiO₂, targeted for catalytic properties.

Liquid impregnation with a metal salt solution followed by freeze drying and reduction has also been successfully applied to uniformly deposit sub-monolayer amounts of Ni on the ligaments of bulk np-Cu.^[124] Here, the amount of deposited metal/metal oxide is controlled by the metal salt concentration of the solution used for impregnation; freeze drying then preserves the uniformity of the metal ion distribution during drying.^[124] Air drying of the impregnated sample has also been used for applications where the uniformity of the deposited material is not a critical issue.

Electroless deposition, underpotential deposition (upd), and galvanic exchange/replacement are other frequently used techniques to deposit metals or metal oxides on np metals. However, all of these techniques have limitations with respect to the sample thickness that can still be uniformly coated (typically 100 nm up to a few microns). The underlying causes of this limitation include mass transport limitations (electroless deposition), voltage drop across the sample (upd), and non-local reactions (galvanic exchange/replacement). To overcome the diffusion limitation of conventional electroless plating that results in non-uniform coatings with the interior of the sample uncoated, Ding et al.^[125] developed a gas-liquid interphase electroless plating technique to uniformly coat np-Au leaf with Pt.

The same gas-liquid (N₂H₄-KMnO₄) interphase electroless plating technique was later used by Lang et al.^[126] to fabricate a np-Au leaf/MnO₂ composite material. This is an interesting electrode material for electrochemical supercapacitors as it combines the high electrical conductivity on np-Au with the high charge storage capacitance of MnO₂. The material and its

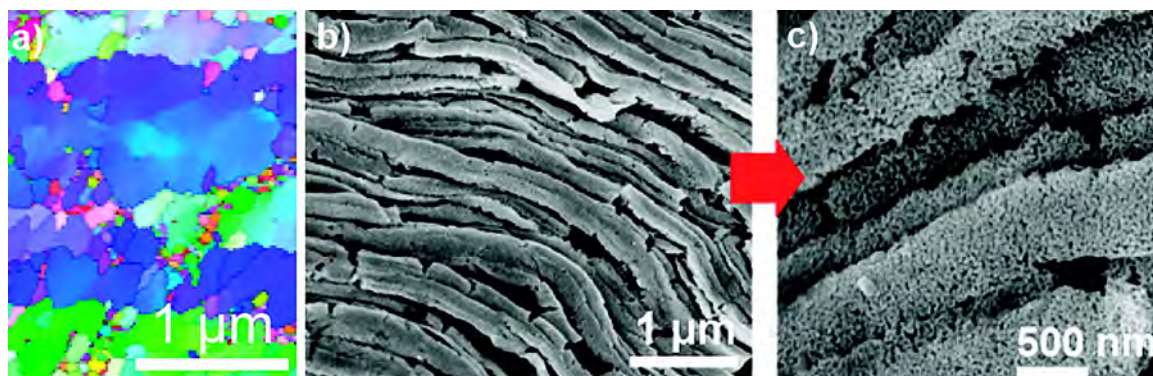


Figure 10. a) EBSD map showing the grains of a textured alloy after cold rolling. b) Low-magnification SEM image of layered structure after dealloying. c) Higher magnification SEM image showing the layered structure with embedded nanoporosity. Adapted with permission from ref.^[122] Copyright 2012 American Chemical Society.

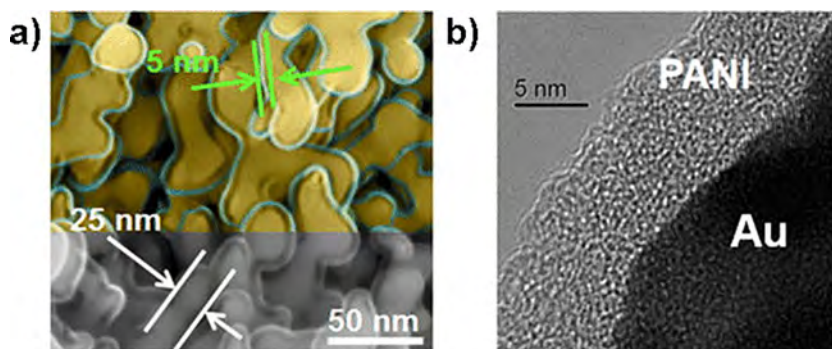


Figure 11. Left; color enhanced SEM image of PANI coated np-Au. Right; TEM image of PANI layer on the surface of np-Au. Reprinted from ref.^[136] with the permission of AIP Publishing.

performance will be discussed in more detail in Section 4, which is dedicated to functional properties and applications.

In another example, upd was used to deposit an ultra-thin and conformal Cu layer onto the np-Au wire arrays discussed in Section 3.2.1.^[88,127] The Cu coated arrays are subsequently submerged in an aqueous solution containing Pt ions where the Cu is replaced by Pt in a spontaneous displacement reaction, resulting in a Au/Pt bimetallic material.^[128] The same technique was used for Pt deposition on bulk np-Au.^[129] Thicker coatings can be achieved by repeating the upd and ion displacement reaction process, as demonstrated for the deposition of Pd on np-Au.^[130–132] Displacement reactions of Cu with Au and Pd/Pt, respectively, have also been exploited to decorate np-Cu with Au or Pt metals to generate inexpensive, core-shell nanostructures.^[133,134]

Finally, polymer/np-Au leaf composites have been fabricated by electrochemical oxidative polymerization of aniline in 0.5 M sulfuric acid.^[135,136] The resulting polyaniline (PANI) layer shows excellent coverage and uniformity, and can be grown up to a thickness of 5–10 nm (Figure 11). The PANI/np-Au composite is an interesting material for electrical energy storage as it combines the high conductivity of np-Au (high power density) with the high electrical charge capacitance of PANI (high energy density).^[135]

3.2.2. Nanoporous Metals as Coatings

In contrast to composite materials where np metal ligaments have been coated by supplemental elements, this section

discusses np metals being used as a coating on preexisting porous structures. A schematic representation for one way to generate this type of material is shown in Figure 12: A template is coated by an alloy film, which is then dealloyed to remove the less noble element and reveal a np coating. Hierarchical np-Au–C or Ag–C composite structures have been produced in this manner, where Au–Ag or Al–Ag binary alloys are placed on macroporous carbon (Figure 13a).^[137] After coating by sputtering or electrodeposition, the film is dealloyed to generate the np film shown in Figure 13b. The multimodal porosity is described by a pore diameter of about 800 nm, from the coated carbon, and the np

film ligaments, which are as small as 10 nm for np-Au and 70 nm for np-Ag.

The same principles were used to develop a bimetallic electrode of np-Au mounted on a macroporous Ni foam (Figure 13c–d), which was made by electrodepositing a Au–Sn alloy film followed by dealloying in 5 M NaOH and 1 M H₂O₂. The pore size of the Ni foam is between 100 and 200 μm, while the nanopores are between 30 and 90 nm.^[138] A follow-up study on these materials involved an additional electrodeposition step to coat the surface with Pd for enhanced H₂O₂ electroreduction.^[139] Additional application-based benefits from the hierarchical structures are discussed in detail in Section 4.

4. Properties and Applications

Many promising opportunities for using np metals as functional materials exploit the large specific surface area in the pore space. Local processes at the surface of the pores or at their interface with a fluid are exploited for applications in fields such as catalysis,^[11,47–50] sensing,^[11,51,52] actuation (see below), optical switching,^[140–142] electropumping for microfluidic devices,^[143] integrated circuit contacting,^[144] biological implants,^[145–148] and as electrodes where a large surface area is needed.^[149–151]

In most instances, the function exploits the transport of mass and/or of electric signals in the form of ions through the open pore space. Non-hierarchical nanoporosity, however, restricts mass transport and thus response time.^[24] It has been pointed



Figure 12. Schematic representation of the general process of depositing np metal films onto cellular structures. First, an alloy is deposited or sputtered onto a porous template. The alloy is then dealloyed so that the remaining material is a macroporous foam with a nanoporous coating. Reproduced from ref.^[137] with permission of The Royal Society of Chemistry.

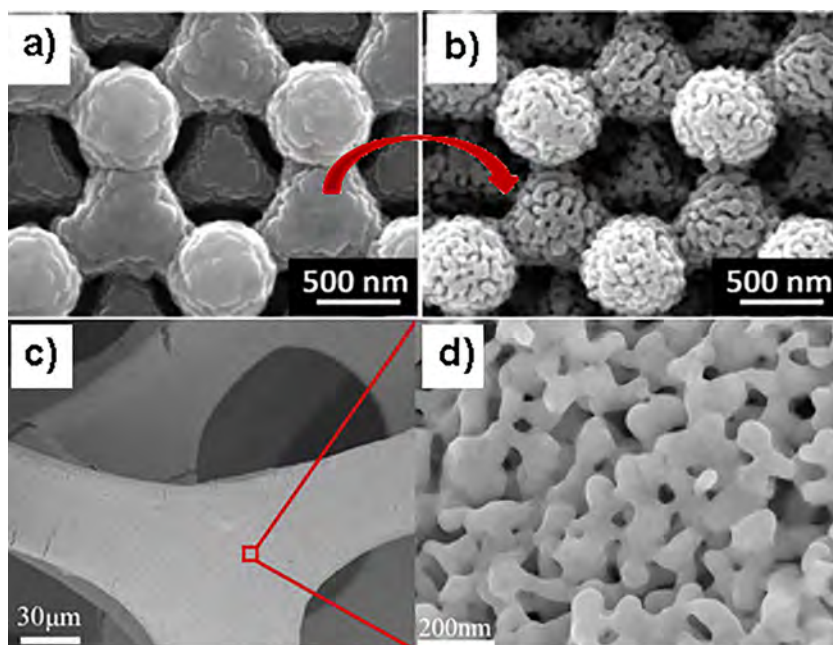


Figure 13. Examples of np metals mounted on cellular scaffolds. a and b) np Ag on porous carbon produced by sputtering of AlAg then dealloying.^[137] c and d) np-Au on commercial Ni foams produced by electrodeposition of AuSn then dealloying.^[138] a and b) reproduced from ref.^[137] with permission of The Royal Society of Chemistry. c and d) reprinted from ref.^[138] with permission from Elsevier.

out that many of the applications listed above therefore entail conflicting requirements on the material structure.^[97,152] Function requires high surface area with many active surface sites and, hence, small pores. On the other hand, fast response to external signals requires a network of interconnected

macropores that act as a “highway” system enabling fast mass transport. Structural hierarchy is the obvious approach toward reconciling these conflicting requirements. A simple hierarchical structure will contain small pores at the lower hierarchy level to achieve local function, combined with large pores at an upper hierarchy level in order to achieve fast mass transport.

In the present section, we will follow our earlier theme and first explore single element materials, followed by a discussion on composite materials that exploit the symbiotic relationship of base np metals and their composite counterparts. As the key areas of functionality we identify actuation, catalysis, sensing, and applications as capacitors and battery components; see the schematic representation **Figure 14**. Since large surface area combined with fast mass transport are the drivers for implementing structural hierarchy, we start out with a brief inspection of this topic.

4.1. Specific Surface Area and Transport Rates

Many of the reviewed applications, especially catalysis, and batteries, are dependent on a combination of large surface area and fast transport. Since the pore space in nanoporous metals is open, the concept of “electrochemically active surface area” (EASA), which is relevant to electrochemical energy storage designs, is identical to the net surface area.

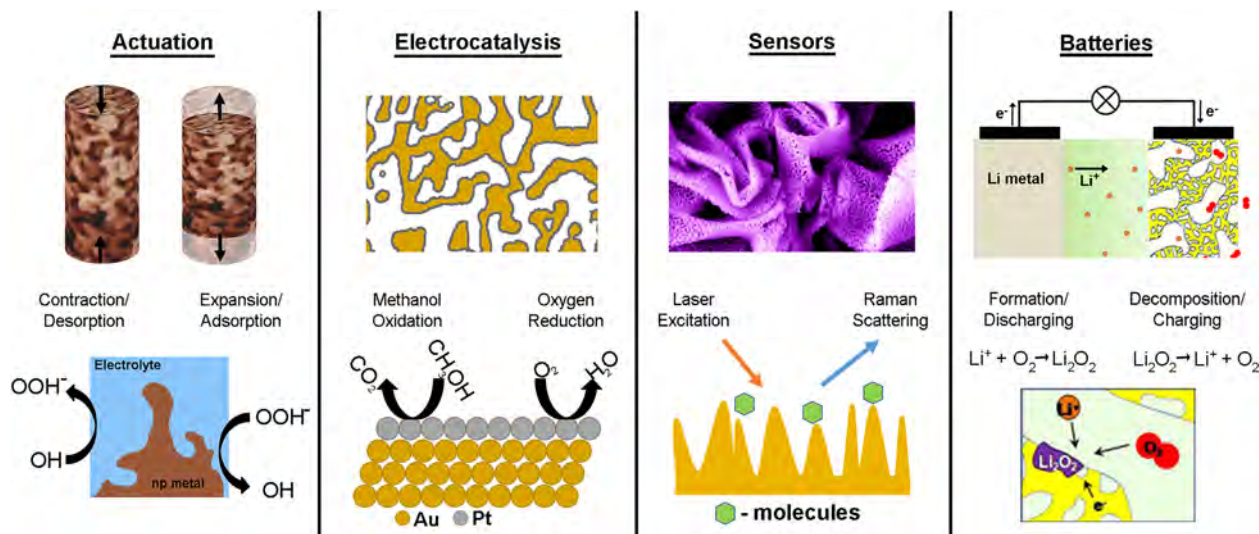


Figure 14. Schematics showing potential applications for hierarchical nanoporous materials. Actuation: np sample contraction and expansion when OH is adsorbed or desorbed from the np surface. Catalysis: electrooxidation of methanol and oxygen reduction by nanoporous metal surface. Sensors: enhanced Raman scattering of incident light from roughened np films. Top image adapted with permission from ref.^[172] Copyright 2011 American Chemical Society. Batteries: hierarchical Li–O₂ np electrode batteries. Adapted from ref.^[201]

Table 1 lists specific surface area values for a selection of materials. Also listed are measures for the reported “peak currents,” which may provide an indication of transport rates. The compilation in Table 1 prefers values from the areas of energy storage and catalysis; more values can be found in studies of porous metals linked to other areas.

Many technological processes are standardized to work with the specific base solid, for instance carbon, and it is then of interest to classify materials by mass specific surface area. This parameter is also reported in many scientific publications.

However, this is often impractical since mass-specific surface areas are of little meaning when the Archimedes density of the solid phase changes. By contrast, the volume-specific area of surface (*per volume of the solid phase*) scales inversely with characteristic structure size. Therefore, this parameter is linked to the defining microstructural length scale. It is therefore stipulated to report volume-specific surface areas as a matter of routine in scientific studies of porous materials.

Table 1 also provides catalytic benchmark information, such as peak current densities, grouped by catalytic reaction for

Table 1. Voltammetry parameters for methanol and ethanol oxidation on hierarchical nanoporous materials. Key parameters include the electrochemically active surface area (EASA) and the forward peak current density. The ratio between the forward and reverse peak current densities, which indicates tolerance to poisonous species, is also presented. Note that the data is grouped by reference.

Reaction	Material	EASA [$\text{m}^2 \text{g}^{-1}$]	Sweep Rate [mV s^{-1}]	Onset Potential [V]	f-Peak Current Density [mA cm^{-2}]	j-f/j-b	Source
Methanol	np-Pd rods	20.5 ^{a)}	50	−0.401	223.52 ^{d)}	1.53 ^{b)}	[181]
	np-Au	–	10	−0.5 V	0.0884	–	[189]
	np-Au w/Pt coating	–	10	−0.7 V	0.14 ^{b)}	1.55 ^{b)}	“
	np-Au w/porous Pt coating	48.3 ^{c)}	50	–	0.65 ^{b)}	1.44 ^{b)}	[196]
	np-Au w/porous Pt coating	67.04 ^{c)}	50	–	0.68 ^{b)}	1.42 ^{b)}	“
	np-Au w/porous Pt coating	70.4 (264.07 ^{c)})	50	–	1.1 ^{b)}	1.1 ^{b)}	“
	Pt-plate	–	50	–	0.15 ^{b)}	1 ^{b)}	“
	Tubular Mesoporous Pt/Cu	32.4	20	–	2.49 ^{b)}	1.55	[134]
	Commercial Pt Catalyst	–	20	–	0.7 ^{b)}	0.81	“
	np-Au w/Pt coating	150	10	–	650 ^{b,d)}	2.3	[195]
	Pt-Ru	–	10	–	450 ^{b,d)}	1.1	“
	np-Cu w/Au coating	–	20	−0.05	18.9 ^{d)}	–	[133]
	np-PtNi nanowire	40.4	50	–	5.31	0.8 ^{b)}	[197]
	np-PtCo nanowire	31.1	50	–	5.43	0.9 ^{b)}	“
	Pt/C E-TEK	36.5	50	–	1.36	0.78 ^{b)}	“
	PtRu/C E-TEK	13.3	50	–	3.77	1.15 ^{b)}	“
	np-PtCo nanowire	37.6	50	–	2.38	0.90	[89]
	np-PtCo nanowire	46.4	50	–	5.57	0.88	“
	Pt/C 30 E-TEK	53.3	50	–	1.26	0.76	“
	PtCo/C E-TEK	48.7	50	–	1.70	1.32	“
Ethanol	Hierarchical np-Au-Cu	–	20	−0.08	25	–	[216]
	Hierarchical np-PdAl	8.9 ^{a)}	10	−0.307	53.41	1.57 ^{b)}	[49]
	Hierarchical np-PdAl	10.8 ^{a)}	10	−0.366	105.16	1.17 ^{b)}	“
	Pt decorated np-Au	10.6	50	–	1.21	1.23	[217]
	Pt/C Catalyst	–	50	–	0.95	0.77	“
	Hierarchical np-Pd	70	50	−0.552 ^{c)}	221.2	1.27	[96]
	Hierarchical np-Pd	50.47	50	−0.519 ^{c)}	255.1	1.37	“
	Pd plate	–	50	−0.37 ^{e)}	–	–	“
	Hierarchical np-PdAl	8.9 ^{a)}	10	−0.461	52.66	0.72 ^{b)}	[49]
	Hierarchical np-PdAl	10.8 ^{a)}	10	−0.501	90.64	0.71 ^{b)}	“
	Hierarchical np-AgPd alloy	30.74 cm^{-2}	50	–	1.17	3.74	[184]
	np-Pd	25.56 cm^{-2}	50	–	0.65	0.99	“

^{a)} Determined by CO stripping method.

^{b)} Values approximated from figures in the corresponding reference.

^{c)} Units are in $\text{m}^2 \text{cm}^{-3}$.

^{d)} Units are in mA mg^{-1} .

^{e)} Units are in mV.

readers interested in a direct comparison of electrocatalytic performance.

4.2. Actuation and Active Strain Sensing

One of the consequences of the extremely large specific surface area of np metals is that the interior of their ligaments experiences large elastic strain. The strain originates in the stress that is required for compensating the capillary forces acting along the many surfaces.^[153] As it turns out, these forces can be controlled through externally imposed electric^[53,154] or chemical^[155] potentials. Np metal bodies can then be made to expand or contract on demand. In other words, they can function as actuators. The surface-induced mean stress and, therefore, the macroscopic strain are linear functions of surface area per volume of the solid phase.^[153]

Functionalizing np metals to become electrochemical actuators uses a materials design strategy that converts the porous metal into a hybrid nanomaterial by filling the pore space with an ionic conductor, typically water. The metal–water hybrid material is distinguished by its two separate and interpenetrating conduction paths: the metal skeleton conducts electrons while the water conducts ions. Since the two pathways are capacitively coupled along the internal surface, superficial space charge layers can be set up under the control of a potential difference between the pathways. The space charge controls the interatomic bond forces in the metal and, thereby, the surface stress.^[156,157] In this way reversible effective mean strains of the metal network, or relative changes of the external dimensions of nanoporous bodies, have been demonstrated in Au,^[53] Ag,^[158] Pd,^[159] Pt,^[154] with strain amplitudes reaching up to 0.65%.^[76] The macroscopic strain of the network is isotropic, so that 0.65% linear strain imply 2.0% reversible volume change.

In a phenomenological description of electrochemical np metal actuators, the stresses and strains can be derived from free energy functions that include the superficial charge density at pore surfaces as a state variable.^[160] A Maxwell relation relates the local surface-stress charge coupling to the response of the local electrode potential to strain^[161] and has been precisely verified in experiments.^[162] The relation implies that the same phenomena that give rise to the actuation behavior can be exploited for inverting the operation principle; np metals can afford active strain sensing because they react to external loads by generating electric signals. Stenner et al.^[52] have shown that the sensing and actuation behavior of np-Au are quantitatively consistent with a common thermodynamic framework. This implies that a gold–water hybrid nanomaterial effectively exhibits piezoelectric behavior.^[52] Because of the many active sites at internal surfaces, the charge-load response of np-Au is unusually robust.

The electrical modification of the stress state at the surface may be amplified when pseudo-capacitive processes are incorporated. This has been demonstrated for Ni (Figure 15b), where surface layers of nickel hydroxide, several molecules in thickness, can undergo cycles of the oxidation state.^[102,163] Strain amplitudes up to 2% have been achieved in this way.^[102]

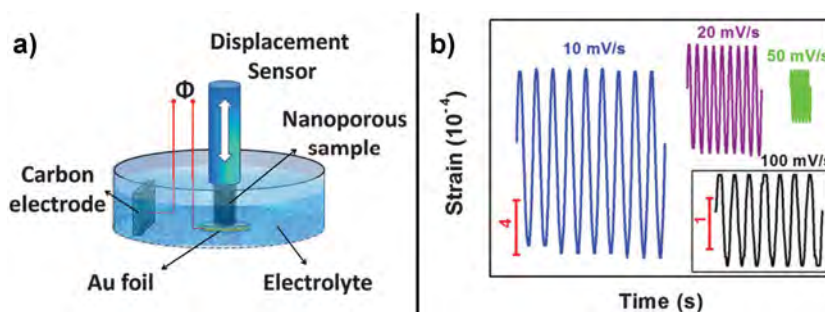


Figure 15. a) Schematic of the model actuator and a displacement sensor for strain amplitude measurement. b) Reversible strain amplitudes of the np-Ni sample during CV cycling for different scan rates. Reproduced from ref.^[102] with permission of The Royal Society of Chemistry.

The strain amplitude may be amplified in microstructures with multiple length-scales. Maximum strain amplitudes of up to 6% have been reported for layer structures of np-Au in which loosely connected layers buckle and thereby achieve large displacements in the direction of their normal.^[122]

Thin films of nanoporous metal can actuate with switching times well below one second.^[164] Yet, the switching time for actuation with larger nanoporous metal bodies is limited by the time required for the electrical migration of ions into the pore space. This is another instance where hierarchical structuring may be beneficial, since small pores at the lower hierarchy level may afford the required large specific surface area while larger pores at an upper hierarchy level may accelerate the transport.

Examples for the above strategy have recently been provided by studies of actuation with np-Pd.^[71,165,166] These studies highlight yet another opportunity by demonstrating that the actuation strain can be enhanced by exploiting the reversible absorption of interstitials into the bulk of the ligaments rather than capacitive or pseudo-capacitive processes at their surface. The samples of refs.^[52,162] inherited their multiscale structure from the multiphase microstructure of the master alloy, as generated during solidification. Nanoporous metal made in this way typically exhibits an abundance of native cracks at the scale (microns) of the features from solidification. The cracks imply brittleness even in compression, raising the question if the material has the load-bearing capability that is required for actuation.

Shi et al.^[71] have shown that dealloying single-phase solid solutions of Cu-Pd may lead to hierarchical np-Pd with a uniform microstructure, somewhat similar to the nested-network structure of ref.^[152] This material is highly deformable in compression without failure. It exhibits hydrogen-enhanced actuation with amplitudes up to 4%, stable actuation over >1000 cycles and switching times of 10 s of seconds.

Systematic studies of the impact of structural hierarchy on actuation, specifically on the rate of switching, or on active strain sensing remain to be reported.

4.3. Surface-Enhanced Raman Scattering

Np metals are excellent substrates for surface enhanced Raman scattering (SERS) sensing of low concentration analytes due to nanoscale roughness and gaps on the surface from nanoporosity.

Gold, silver, and copper, which can all be synthesized in np morphologies, are typically used for SERS-based sensing, which detects amplified Raman signals from active analyte molecules that have been adsorbed onto metal surfaces.^[167] Furthermore, several groups have demonstrated that various SERS enhancement factors can be achieved by tuning the pore size of np-Au.^[168–170] More recent efforts have aimed to increase SERS response by incorporating supplemental surface features. For example, Qian et al.^[171] decorated np-Au with Au nanoparticles by infiltrating the nanopores. The addition of the nanoparticles significantly enhanced the Raman scattering when compared to np-Au. Zhang et al.^[172] also demonstrated improved Raman scattering for wrinkled np-Au films, which are produced by the thermal shrinkage of the film substrate. A hundred-fold increase in the SERS enhancement was observed for the wrinkled np-Au films when compared to flat np films. A hierarchical porous gold structure with aligned arrays of ~100 nm holes and evenly distributed mesopores also exhibited superior SERS activities compared to commercial materials, see **Figure 16**.^[173]

In addition to np-Au, np-Cu has also been investigated for SERS applications. Most notably, Chen et al.^[174] showed that the SERS response of nanostructured Cu could be tailored by altering ligament sizes. At the optimum pore size, np-Cu achieved SERS enhancement factors ($\approx 1.85 \times 10^{-5}$) that are comparable to np-Au.

Although not extensively studied, other hierarchical np materials have also been developed for alternative sensing applications. One such study used np-Au nanowires for sensing the adsorption of octadecanethiol, which resulted in detection sensitivities comparable to ultrathin films.^[84] np-Au films mounted on commercial Ni foams were shown to detect

hydrazine gas and hydrogen peroxide.^[175] Finally, bimodal np-Pt–Ti have been explored for the sensing of ascorbic acid, dopamine, and uric acid.^[176]

4.4. Catalytic Applications

To date, the most studied and viable application of np metals is catalysis. Raney nickel, first developed in 1926, is used for a variety of industrially important hydrogenation reactions, and Raney copper is a widely-used catalyst for the water-gas shift reaction.^[177] Recent advancements in synthetic methods, paired with high electrical conductivity, high surface area, and a high density of reactive sites make np metals highly efficient heterogeneous catalysts and electrocatalysts. Examples include the electrooxidation of methanol and ethanol, as well as the electroreduction of oxygen, carbon monoxide, and carbon dioxide. For fuel cell applications, Pt remains to be the preferred catalyst material despite its high cost due to its superior catalytic activity. By contrast, the production and conversion of many important platform chemicals requires more selective and thus less reactive metals than Pt. Here, recent developments in the field of noble metal based dilute alloy np catalysts have been very promising.^[178] The idea behind this development is that the noble metal majority alloy component provides the desired selectivity while the minority alloy component provides reactive sites for critical reaction steps.

It is also important to understand that the catalytic properties of these materials also strongly depend on the surface chemical composition *under reaction condition*. This can be very different from the surface composition present when the material was initially prepared and characterized. A good example is np-Au prepared from Ag–Au alloys, which is actually a dilute alloy bimetallic system. As recently demonstrated by in situ microscopy and spectroscopy, activation by ozone enriches the surface in Ag and leads to the formation of active sites for O₂ activation.^[179]

For this section, np metals are discussed first, followed by a section on np composite catalysts. Keeping with the format of this review, materials are discussed by structure type but categorized by catalytic reaction in Table 1.

4.4.1. Metal Catalysts

A 2003 study revealed that np-Pt has improved methanol oxidation activity compared to polycrystalline Pt, suggesting that material architecture can play a role in promoting catalytic activity.^[180] Furthermore, the same material shows reduced oxygen reduction capabilities since approximately three quarters of the internal pore surface area is inaccessible.^[180] This is likely due to poor ion penetration of the sample because the small pore size obstructs fluid flow.^[12] Utilization of the inner surface area could be improved by a multimodal pore distribution or architecture where larger pores make the smaller pores more accessible for ions.

Hierarchical np-Pd, synthesized by dealloying of Pd–Al alloys with multiple phases, is also an effective catalyst for alcohol oxidation.^[96,181] In the former study, nested bimodal np-Pd

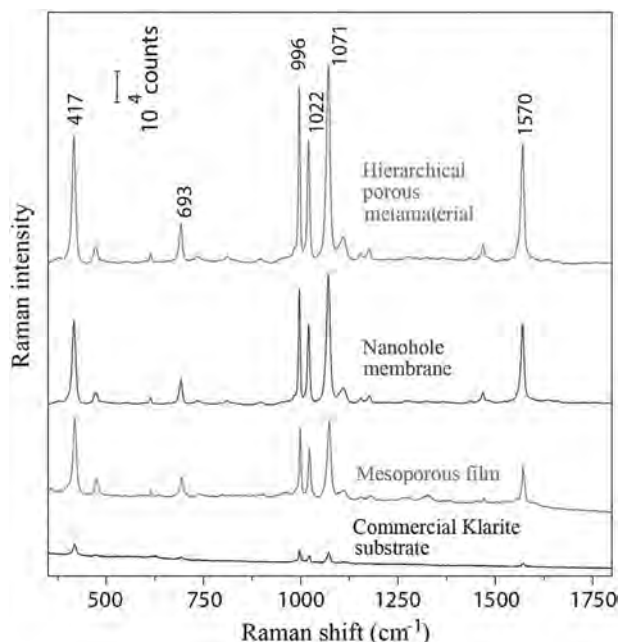


Figure 16. SERS spectra on (from bottom to top) a commercial Klarite substrate, mesoporous film, nanohole membrane, and a hierarchical structure with a nanohole membrane and mesoporous film. Adapted with permission from ref.^[173] Copyright 2014 John Wiley and Sons.

exhibited improved reaction kinetics for ethanol oxidation when compared to a Pd plate electrode and nonhierarchical np-Pd.^[96] In the same study, two bimodal structures, one with larger pores than the other, were compared for catalytic activity. Interestingly, the nested structure with larger pore sizes, but with lower surface area, showed a higher reactivity for ethanol oxidation.

Aside from bimodal single element catalysts, bimodal np alloys have also shown intriguing catalytic activity for several desirable reactions. Compared to np-Pt and commercial Pt/C catalysts, hierarchical np-Pt-Fe retains more EASA after 5000 cycles and also shows significantly decreased CO poisoning during methanol oxidation.^[111] np-Pt-Au is another example of an alloy that has shown superior catalytic activity, particularly for formic acid oxidation, with higher current densities in both forward and reverse voltage scans when compared to Pt/C.^[182] Oxygen reduction was studied on bimodal Pt-Al intermetallics with an atomic layer of Pt at the surface. The specific activity was about five times higher than that of Pt/C catalysts.^[183] Finally, ethanol oxidation was explored using bimodal np-Ag-Pd alloys. Although not compared against a commercial catalyst, np-Ag-Pd showed a higher ratio of anodic peaks, indicating better poisoning tolerance, and a lower peak potential, indicating more favorable ethanol oxidation, than np-Pd.^[184]

Nanoporous nanoparticles, which are inherently hierarchical, have also been studied for their catalytic properties since they have a higher surface-to-volume ratio than bulk np metals or nanoparticles.^[185] In one study, np-Pt-Cu and np-Pt-Co nanoparticles were investigated for their particle size dependent np morphology and catalytic activity for oxygen reduction.^[186] It was found that both types of alloy np nanoparticles showed enhanced surface activity compared to a commercial Pt/C catalyst. A study on np-Pt-Ni nanoparticles, yielded similar results, where the mass specific activity for oxygen reduction was about four times higher than the compared commercial catalyst.^[187] A separate investigation of np-Pt-Ni nanoparticles showed that the EASA of the np particle is about 2.5 times greater than that of Pt-Ni nanoparticles.^[188] While the increase in EASA surface area of nanoparticles is advantageous, several other factors influencing the catalytic activity must be addressed, including particle size distribution, particle agglomeration, and the choice of particle dispersion support.

Previously, pure Au has shown catalytic activity in the form of supported nanoparticles (<5 nm), but several studies found that larger np-Au samples with ligaments between 12 and 30 nm can be effective catalysts for both methanol and CO oxidation,^[50,189,190] as well as oxygen and hydrogen peroxide reduction.^[48,191] Reproducible catalyst activation of these np-Au catalysts is critical but can be achieved through an ozone treatment at atmospheric pressure.^[192]

Similar to the previously mentioned np-Pt, there are mass transport limitations due to the tortuous porosity of the material, which become more severe with decreasing pore size.^[24] The importance of the material architecture is illustrated by the results of a recent study that evaluated the reactivity of np-Au catalysts in three different forms: ingots, foils, and hollow shells.^[192] The study revealed that the conversion rates of methanol to methylformate are five times higher for the hollow shell and foil morphology when compared to the ingot.^[192] The higher conversion rates for foils and porous shells reveal that

these morphologies can mitigate the mass transport limitations that are inherent to non-hierarchical bulk np materials. As pointed out before, hierarchical pore morphologies are ideally suited for applications such as catalysis that benefit from the combination of high surface area (provided by nanopores) and fast mass transport (provided by macropores).

Further insight into mass transport for catalysis in nanoporous materials is given in a study by Snyder et al.,^[193] where quantitative measurements of EASA are given as a function of both overpotential and the dealloyed volume of similarly sized np-NiPt samples. It was found that for samples with a larger dealloyed volume or roughness factor (i.e., longer dealloying times), the EASA increases with decreasing overpotential. This is related to the diffusion of oxygen molecules into the porous structure, where the molecules will diffuse further into the np network at lower overpotentials, but will reduce at the exterior surfaces at high overpotentials.^[193] Therefore, the active surface area during oxygen reduction is a balance between the applied overpotential and the depth molecules must travel to utilize all the np ligament surfaces.

4.4.2. Composite Catalysts

Coating of np metals with additional materials provides another avenue for tailoring catalytic activity and selectivity of these materials. As discussed in detail in Section 3.3.1, achieving uniform coatings on these ultrahigh aspect ratio materials remains to be very challenging, and only a few techniques are suited to generate deposits of the desired spatial uniformity. However, if successful, the coating approach can result in large performance improvements. For example, coating the ligaments of np-Au with Pt or Pd (for synthesis details, refer to Section 3.3.1)^[194] creates a bimetallic np material that, if used as an electrode in fuel cells, performs as well as conventional Pt/C catalysts but with much lower Pt loading. Other work has shown that Pt coated np-Au (referred to as NPG-Pt) has enhanced structural stability with better catalytic activity for methanol reduction and resistance to catalyst poisoning from CO than commercial Pt/Ru catalysts.^[195] In a similar study, the long-term formic acid oxidation stability of the bimetallic structures was improved by depositing a layer of Au clusters on top of the Pt so that areas of the Pt layer are still exposed (referred to as NPG-Pt-Au).^[129] The Au clusters disrupt the continuous Pt layer and are believed to shorten the reaction path of formic acid by preventing CO poisoning. These materials also retained a significant amount of EASA, where the EASA loss of NPG-Pt-Au was 45% compared to a 75% loss for NPG-Pt.^[129] An analogous study explored the methanol oxidation of np-Au coated with porous Pt deposits, which are characterized as small islands rather than a conformal layer (**Figure 17a**).^[196] These samples exhibited activity for methanol oxidation, while bare NPG showed none (**Figure 17b**). Furthermore, higher Pt content increases catalytic activity from the availability of additional Pt sites.^[196]

Another example demonstrating the catalytic improvements that can be achieved by Pt deposition on np metal surfaces is a study by Shin et al.,^[88] which showed that np tubes (**Figure 5b**) with a thin Pt layer exhibited better methanol reduction activity compared to smooth-walled tube arrays and carbon-supported Pt

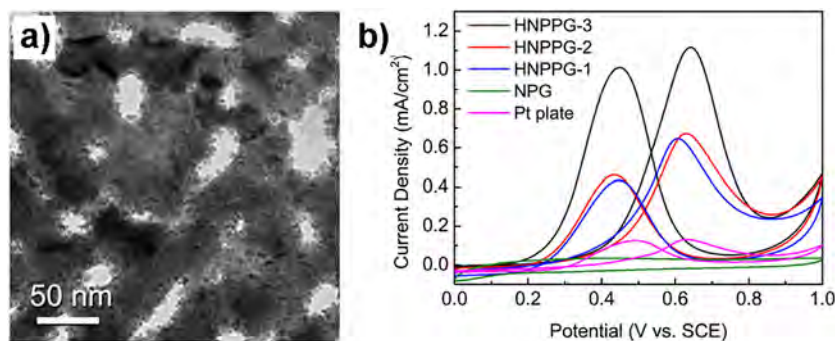


Figure 17. a) TEM image of HNPPG-2 showing non-conformal Pt islands forming a porous film. b) CV curves for methanol oxidation for a Pt plate, bare NPG and NPG coated with various amounts of porous Pt. As the Pt content increases, the current density increases. Reproduced by permission from Macmillan Publishers Ltd: Scientific Report, ref.^[196] Copyright 2014.

nanoparticles. This is likely due to a higher CO poisoning tolerance that has been established for these types of bimetallic materials.^[88]

So far we have discussed the effect of Pt coatings on the catalytic performance of np metals. Another metal that is frequently used to tailor the reactivity of np metals is Pd. For example, Kiani and Fard showed that a Pd monolayer coating, comparable to the Pt coatings discussed above, increased the oxygen reduction activity of np-Au when compared to both a bare np-Au or a flat Pd-decorated electrode.^[130] In another study, the Zhang group showed that the hydrogen storage capability of Pd-coated np-Au increases with increasing number of monolayer Pd deposition cycles, suggesting potential applications as an electrocatalyst.^[132] More recent work specifically investigated the electrocatalytic activity for oxygen reduction, and revealed that Pd coated np-Au shows a higher oxygen reduction activity than np-Au or a commercial Pt/C catalyst. The highest specific oxygen reduction activity was found when only a single layer of Pd was deposited on the np-Au surface.^[131]

Another potential substrate for thin layer depositions is np-Cu, which is economical, highly conductive, and easily coated with Au via a spontaneous replacement reaction. Chen et al.^[133]

showed that a Au on np-Cu composite (Au np-Cu) exhibits significant electrocatalytic activity for the oxidation of methanol as judged by both higher peak current and lower onset potential for methanol oxidation as compared to np-Au. That material also showed good electrochemical stability, retaining over 90% of its activity after 100 cycles compared to 57% for np-Au. It is important to note that even very small loading levels can dramatically affect the reactivity of np-metals. For example, it has recently been shown that deposition of as little as 0.3 at% Ni on np-Cu dramatically lowers the activation barrier for selective dehydrogenation of ethanol to acetaldehyde, from $\sim 70 \text{ kJ mol}^{-1}$ for np-Cu to $\sim 45 \text{ kJ mol}^{-1}$ for np-Ni_{0.003}Cu.^[124]

Nanowire arrays generated from a variety of np metals have also been studied as catalytic supports because such structures combine an open morphology to facilitate fluid flow and high surface area for activity. For example, mesoporous nanotubular Pt-Cu alloys (Figure 18a) have three times higher specific activity and higher CO poisoning tolerance than that of commercial Pt/C.^[134] Several other types of alloy np nanowires have been generated through mild or incomplete dealloying by Liu et al.,^[89,197,198] including np-Pt-Co, Pt-Ni, Pt-Co-Ni, Pt-Co-Au, and Pt-Ru-Co-Ni. These nanowires showed enhanced catalytic activity for methanol oxidation when compared to commercially available catalysts. In addition to catalytic activity, the ternary (and quaternary) alloy nanowires were investigated for durability, where the Pt-Ru-Co-Ni nanowires retained over 90% of their active surface area after 1000 cycles. For further comparison, the np-Pt-Ni nanowires shown in Figure 18b and c exhibited higher activity than Pt-Co with similar Pt content. Other np wires synthesized by mild dealloying include interwoven Pt-Fe nanowires, which also demonstrate better oxygen reduction and durability than Pt/C.^[199]

Up to this point only np metallic catalytic structures have been discussed, however np metal-metal oxide composites have also shown promise as future catalytic materials. The use of TiO₂ to

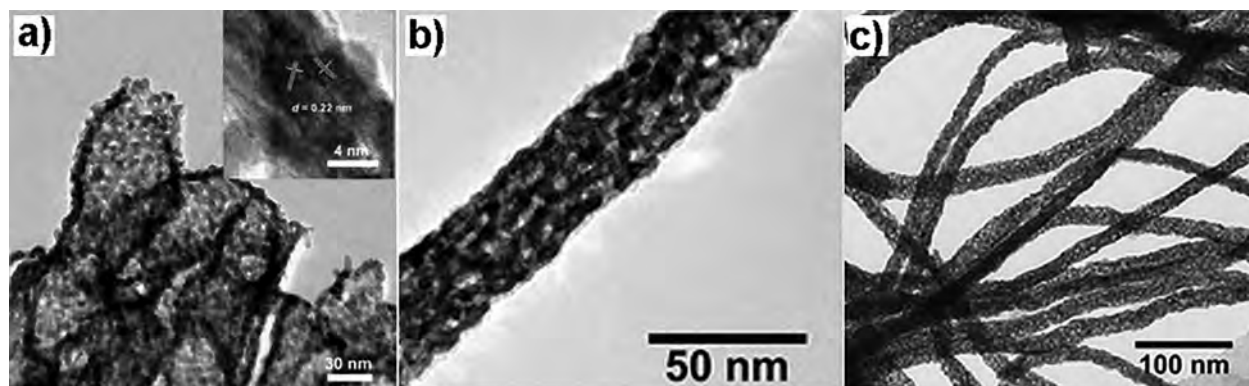


Figure 18. a) Mesoporous nanotubular PtCu structures with core-shell shapes.^[134] b) Single PtNi nanoporous nanowire showing pore sizes below 5 nm.^[197] c) bundle of np-PtNi nanowires.^[134] a) adapted with permission from.^[134] Copyright 2009 John Wiley and Sons. b and c) reproduced from ref.^[197] with permission of The Royal Society of Chemistry.

functionalize the surface of np-Au has also been explored. Jia et al.^[200] used np-Au decorated with TiO₂ nanoparticles to develop a photocatalytic electrode for methanol oxidation. In a later study, Biener et al.^[123] demonstrated that highly dispersed TiO₂ particles on np-Au improve the thermal and morphological stability of the metal, which has a tendency to coarsen, and also increases CO oxidation activity by 300%. The presence of TiO₂ nanocrystals on the surface of np-Au increases the efficiency for O₂ dissociation, which is the rate limiting step for CO oxidation with gold based catalysts, and stabilizes the high surface area of np-Au.^[123]

In the synthesis section, emphasis was placed on the multimodal structures fabricated from dealloying multiphase or multi-element alloys in two-step dealloying processes. These types of materials were also investigated for their catalytic activity. Unlike the coated np materials, these hierarchical structures provide large pores for unobstructed transport of molecules and smaller pores for increased surface area and a high density of reactive sites.^[108] Similar to the majority of materials discussed in this section, bimodal np structures with Pt and Pd content were studied, including hierarchical np-PtTi alloys. Compared to commercial Pt/C catalysts and similar np-Pt samples, hierarchical np-PtTi showed 3 and 2.5 times higher mass activity for oxygen reduction, respectively. Additionally, the hierarchical structure was stable, without significant feature changes, and also showed less current degradation over time, signaling higher retention of active site availability.^[108]

Hierarchical Pd-Al structures were studied for methanol and ethanol reduction, and showed enhanced activity when compared to a flat Pd electrode.^[49] While no comparison was made to a commercial catalyst, the key feature of this study is the comparison between similar hierarchical structures with different feature sizes. Compared to a structure with smaller pores, the more open structure with larger pores (15–25 nm vs. 3–6 nm) has a higher electrochemically active surface area. This suggests that a smaller pore size, and therefore higher geometrical surface area, may not lead to increased activity since mass transport will be more difficult with finer pore channels.^[49]

General trends from this section show that Pt group metals are still relied on for catalytic function, however increased surfaced area and surface access can reduce the Pt loading necessary for high catalytic activity. Additionally, np metal materials provide structurally stable catalysts that resist agglomeration of nanoparticles and CO poisoning more effectively than commercially available catalysts. However, viable np catalysts, like those discussed here, have yet to become commercially available.

4.5. Energy Applications

4.5.1. Lithium Ion Battery Systems

Hierarchical np metals have been explored for rechargeable energy storage devices such as supercapacitors and electrodes for new battery technologies. Similar to the electrocatalysis application discussed above, these applications also benefit from the high electrical conductivity of np metals in general and the

large electrochemically active surface area of hierarchical np metals in particular. Both are necessary for energy storage and fast electron/ion transport, making np metals worthwhile materials to investigate for these applications. Recently, Guo et al.^[201] developed a hierarchical np-Au electrode for use in a Li–O₂ battery system. Compared to non-hierarchical as-prepared np metals, the hierarchical structure increased the reversible capacity and lead to longer cycling lifetimes at low overpotentials. The high reversible capacity of about 1000 mA g^{−1} is only reached for low overpotentials, however with a redox mediator, the capacity and cyclic retention are improved.

Composite materials have been successfully used to improve battery performance, such as Goodenough's layered electrodes, which were used in commercial batteries.^[202] A np-Au–Sn composite electrode made by the electroless deposition of Sn on np-Au leaf was investigated as an anode for rechargeable lithium ion batteries, and was shown to effectively accommodate the volume changes that occur during charge cycling.^[203] The electrode achieves a reversible capacity of 515 mAh g^{−1} in a voltage window of 0.005–1.0 V, and has a charge capacity retention of about 90% after 100 charge-discharge cycles. Sn-coated bimodal np-Cu films have also shown high charge capacity retention (95%) when cycled between 0.01 and 1.5 V.^[204] However, this is only achieved after the first 10–15 charge-discharge cycles, when the initial reversible capacity has already been reduced by half. The facile plating of Sn, along with its high electronic conductivity and large capacity for storage, make it an ideal element for bimetallic anodes.

Nanoporous Cu with oxide coatings have also been investigated as Li-ion battery anodes. In one study, np-Cu/MnO₂ electrodes were integrated with a solid Cu film to form anodes with a stable reversible capacity of ≈1100 mAh g^{−1} for 100 cycles. This was accomplished at a current density of 8.4 A g^{−1} after initial cycling at half that current density.^[205] Other np-Cu anodes with a cuprous oxide surface demonstrated a high reversible capacity of 1.45 mAh cm^{−2} after 120 cycles, where the initial capacity was 2.35 mAh cm^{−2}.^[151] Unlike the other anodes discussed in this section, these anodes are not freestanding films. Instead, the np-Cu is mixed in slurries and used as a coating on Ni foams.

Another noteworthy composite material is TiO₂-coated np-Au, previously discussed for its electrocatalytic properties. This particular material is also an effective electrode due to the symbiotic relationship between the Au scaffold, which is a current collector, and the TiO₂ coating, which acts to stabilize the structure and store Li.^[206] Theoretically, this type of structure can be fabricated from any np scaffold, such as Cu or Ni, to make the composite more economical. By providing the opportunity to independently vary both pore size and TiO₂ layer thickness, the porous electrode can be optimized for Li ion diffusivity for a given electrode thickness.^[206]

4.5.2. Supercapacitors

Supercapacitors can be classified as either electric double layer capacitors (EDLC), which store charge electrostatically (non-Faradaic) by polarization of the electrode–electrolyte interface, or

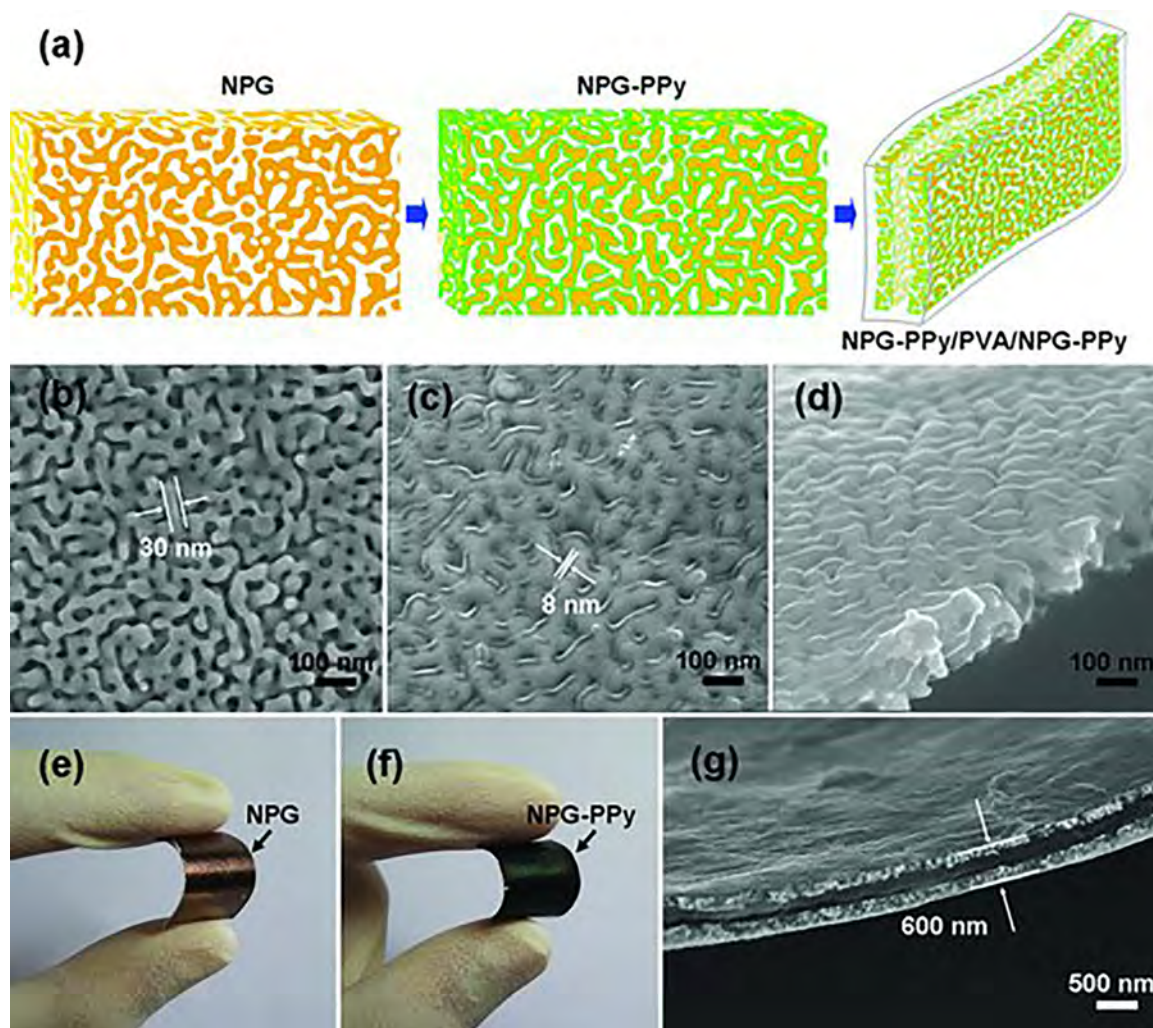


Figure 19. a) Schematic of the fabrication for polypyrrole coated np-Au. b–d) SEM images of bare and coated np-Au. e and f) Optical images of bare and coated np-Au membranes. g) SEM image of assembled supercapacitor device. Reproduced with permission from ref.^[211] Copyright 2011 John Wiley and Sons.

pseudocapacitors, which store charge Faradaically¹ by involving surface redox reactions.^[207] Assuming constant density, the volumetric capacitance (F cm^{-3}) of an EDLC increases with increasing surface area of the electrode material (see Table 1). The combination of high surface area and high conductivity thus makes np metals viable materials as supercapacitors. Lang et al.^[208] developed a supercapacitor device based on np-Au and tested it in both ionic liquid and alkaline solutions. With decreasing discharge current density, the volumetric capacitance increased from 9.6 to 21.6 F cm^{-3} in the ionic liquid and from 17.1 to 24 F cm^{-3} in an alkaline solution. The energy densities of the devices were found to be between 16.5 and 21.7 mWh cm^{-3} in the ionic liquid and 4.89–8.31 mWh cm^{-3} in KOH. For

¹Electrode processes in which the charge can be recovered while chemical bonding or oxidation states change are properly termed “pseudocapacitive.” The same processes are often also termed “Faradaic,” yet that term applies equally to processes where the charge cannot be recovered, such as electrocatalytic reactions.

comparison, novel graphene/hydrogel capacitors have achieved an exceptionally high energy density of 60 mWh cm^{-3} ,^[209] whereas commercially available supercapacitors have an approximate energy density of 5–8 mWh cm^{-3} .^[210]

Bimodal np-Ni alloys were also studied for their capacitive properties. A comparison of the specific areal capacitance, which was calculated from discharge curves and the electrode sheet area, at different current densities (1.25 vs. 20 mA cm^{-2}) showed similar values (≈ 1.05 vs. 1.11 F cm^{-2}). The volumetric capacitance was also evaluated and determined to be 317 F cm^{-3} in 1 M KOH.^[94] This value is large in comparison to those achieved by np-Au in the previous example. However, it should be noted that the redox reactions in nickel-hydroxide layers bring a very high capacitance at Ni surfaces. Therefore, the higher capacitance of nanoporous Ni structures are likely not the result of their hierarchical structure. A direct comparison between np-Ni and bimodal np-Ni would be necessary to ascertain the influence of hierarchy on capacitance.

Additionally, the coating of np metals with materials that exhibit high pseudocapacitance, such as transition metal oxides and conductive polymers, could provide symbiotic material relationships. The pseudocapacitive coating can efficiently store charge by undergoing fast surface redox reactions; the low conductivity of the material is overcome by supporting it on high conductivity np metals, which also act as double layer capacitors. Two studies by Lang et al.^[126,135] have capitalized on this design principle by coating np-Au with thin MnO₂ and polyaniline films.^[126,135] In the first study, the reaction kinetics of the poorly conductive metal oxide are mitigated by the conductive gold substrate, resulting in a high specific capacitance of 1145 F g⁻¹ for the MnO₂ and 601 F g⁻¹ for the combined Au/MnO₂ material. When used as electrodes in a supercapacitor, the metal/oxide composite material reaches an energy density of 57 Wh kg⁻¹ and a power density of 16 kW kg⁻¹.^[126] In a subsequent study, polyaniline (PANI), a conductive polymer, was used as a pseudocapacitive shell on np-Au. Np-Au/PANI based supercapacitors exhibited a volumetric capacitance of 1500 F cm⁻³, an energy density of 78 mWh cm⁻³, and a power density of 190 W cm⁻³.^[135]

Similarly, Meng and Ding developed a supercapacitor electrode by coating np-Au with a polypyrrole (PPy) film.^[211] A schematic representation of the fabrication process is shown in **Figure 19a**, along with SEM images of the bare (Figure 19b) and coated (Figure 19c) np-Au. The solid gel electrolyte used in this study also improved the flexibility of the np-Au electrode (Figure 19g). The evaluated capacitance reaches a maximum of 270 F g⁻¹ (per PPy mass) at a current density of 0.6 A g⁻¹. The volumetric power and energy of the entire supercapacitor device is estimated to be 56.7 W cm⁻³ and 2.8 mWh cm⁻³, respectively, while for a single electrode these values are much higher (283 W cm⁻³ and 19 mWh cm⁻³).^[211] When considering the entire device, the performance of the PPy coated np-Au has substantially lower power and energy densities.

An asymmetric supercapacitor was developed using two of the previously discussed electrode films; np-Au with a PPy film as the negative electrode and np-Au with MnO₂ as the positive electrode.^[212] These films can be used in combination due to their similar specific capacitances and overlapping voltage operation windows. The energy and power densities of the assembly were reported as 86 Wh kg⁻¹ and 25 Wh kg⁻¹, respectively, with a device capacitance of 193 F g⁻¹. The capacitance compared to a PPy/PPy capacitor is enhanced, but this value is reduced compared to a MnO₂/MnO₂ capacitor. Furthermore, the influence of the core np-Au is excluded since its specific capacitance is less than 1% of the composite films.^[212]

While the reported energy densities for these devices are several times higher than those reported for uncoated np-Au and possibly several orders of magnitude higher than commercial capacitors, these devices have a critical issue. The overall electrode volume, which ultimately determines the device storage capacity, is restricted by processing limitations requiring the electrodes to be thin (≈ 100 nm).

5. Conclusions and Future Outlook

In this review, several synthesis strategies for the development of np materials with structural hierarchy have been presented.

These include templating and dealloying methods, as well as multistep approaches that combine more than one processing technique. Strategies have also been demonstrated for a wide range of metals such as Au and more economical materials like Cu or Ni. In particular, hierarchical porosities can be realized by selecting suitable multi-element precursor alloys, alloy compositions, and multi-step dealloying protocols. For example, the sequential removal of different LNEs from a multi-element precursor alloy in combination with heat treatments can generate bimodal porosity. We also discussed examples for fabricating hierarchical np metal structures from binary alloys by using multiphase starting alloys (Cu–Al system) or by using alloy compositions that allow for sequential dealloying (Ag–Au system). Materials with multimodal porosity are intriguing because they help to overcome mass transport limitations in small pore networks by supporting fast transport through their macroporous system while providing the high surface area desired for catalysis through their nanoscale porosity. In particular, noble metal based materials, like np-Au and np-Pt, have been extensively explored as electrochemical catalysts because they exhibit high catalytic activity toward methanol and ethanol oxidation as well as oxygen reduction.

Additionally, the fabrication of hierarchical composites, where the hierarchy comes from the spatial distribution of the elements, were also included. Synthesis methods for these hierarchical composite materials include coating of np metal surfaces with films composed of metal oxides, polymers, or other metals to enhance their chemical, thermal, and mechanical properties. Np metals can also act as functional coatings on other porous materials by depositing precursor alloys on macroporous foams and dealloying the film.

In some instances, the symbiotic properties of two base materials make hierarchical composite structures viable for energy storage applications, including electrodes for Li batteries, or supercapacitors. It is important to note that the area-specific capacitance is an electrode material/electrolyte characteristic number and is independent of the microstructure of a porous material. Thus, the energy density of a supercapacitor with hierarchical structure does not change if the porosity stays the same, but the power performance will improve. The enhanced abilities of these materials for a wide variety of applications is in part due to the large surface area of np metals and their conductivity. The addition of hierarchy and other materials has expanded the working space of np metals by improving their specific properties.

Much progress has been made toward developing enhanced np materials through leveraging structure or symbiotic composites, and several applications are being explored. One particular area that deserves attention is the use of np structures to reduce the need of precious metals such as Pt or Pd for electrocatalysis. With the increased surface area and enhanced transport offered by hierarchical materials, cheaper materials may be able to replace precious metal systems. Alternatively, alloying materials can also enhance the material properties of Pt, Pd, or Au alloys.

Future studies on hierarchical materials should also explore structural size effects, optimum pore sizes, and surface area on catalytic behavior to further improve our ability to tailor superior

catalytic electrodes for specific system or material requirements. In this regard, the use of additively manufactured structures as base materials would be beneficial since they have known geometry and thus more predictable mass transport properties. Additionally, stability during cycling or exposure to elevated temperatures must be addressed since as the material coarsens, it loses surface area and therefore its specific catalytic activity towards the desired reaction.

In the area of supercapacitors, the reviewed studies developed promising proof of principle structures that demonstrate additional layers of carefully chosen materials can result in combined high double layer capacitance and pseudocapacitance from improved electron and ion transport. Subsequent work could involve the coating of multimodal structures and the subsequent tailoring of such structures, both in feature size and material composition, for further enhanced capacitive materials. Another intriguing approach would be to apply these designs to large scale production and supercapacitor fabrication techniques that are powder based.

Finally, scaling up and streamlining synthesis procedures must be on the forefront of experimental work. While new hierarchical materials show promise toward particular applications, their usefulness in practice is linked to their size and straightforward production. This is necessary in applications such as energy storage since the capacity of a supercapacitor depends on both the specific capacitance and the volume of the device. Thus, despite their excellent performance, thin film electrodes remain compromised by their volume limitations.

The potential practical applications of np metals with structural hierarchy are vast. The combination of control over the pore feature sizes and surface/interface composition may be the key to thoroughly understanding the influence of material structure and composition of materials on electrochemical behavior, which has repercussions in both catalysis and energy systems. It is the purpose of this review to consolidate recent work on hierarchical structures and guide researchers towards newer unexplored synthesis procedures that may lead to substantial insight on structure and functionality.

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Conflict of Interest

Authors declare no conflict of interest.

Keywords

dealloying; hierarchical materials; nanoporous metals; structural hierarchy; templating

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Synthesis of Nanoporous Gold Tubes**

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Hierarchical materials with tailored features provide promising structures for applications requiring light-weight, yet strong, materials. In this study, a method for synthesizing nanoporous gold tubes as a hierarchical structure is presented. Samples are fabricated via electrodeposition, homogenization, and dealloying to generate a random porous network in the tube wall. Electrodeposition parameters are optimized by using a reverse pulse current setup. As-prepared tubes exhibit a ligament diameter of approximately 45 nm and the hierarchy of the tubes is further altered by controlling the ligament size through heat treatments.

1. Introduction

Cellular metal structures offer favorable mechanical properties such as low-density, high stiffness, and high surface area. These materials provide several design advantages due to their high tailorability for specific applications. This enables their use as multifunctional materials for a variety of engineering applications such as sandwich panels,^[1] energy absorbers,^[2] and catalytic supports.^[3] Hierarchical materials with controlled periodic architecture exhibit improved stiffness and strength for a given relative density when compared to stochastic cellular structures such as foams.^[4,5] This superior performance has led to the development of cellular topologies such as hollow metallic microlattices, which are made through an additive manufacturing process that controls structural elements on multiple length scales.^[6–9] Numerical studies by Valdevit et al. indicate that significant strengthening of the overall structure can be achieved by modifying the thickness of the cell walls.^[10] Mechanical improvement of the wall may also be achieved through hybridization with additional layers of different materials or composite structures. Thus, an opportunity remains to increase

strength by introducing new morphological features in these materials. In particular, nanosized features could improve deformation behavior, several examples of this include ceramic lattices with nanometers thick walls that display ductility when compressed,^[11] microlattices with nanocrystalline Ni walls that recover after deformation,^[6] and collagen fiber, the nanosized building block of bone, that provides toughness in the otherwise brittle bone composition.^[12]

In this study, the authors use nanoporous (np) gold foam as the nanosized base material in hierarchical structures, where the ligaments and pores of the foam are the smallest structural constituents. Np foams are used as the walls of tubular structures in order to implement another level of hierarchy. The np Au network is generated through a multi-step process that uses a combination of synthesis techniques such as electrodeposition and dealloying. Ligament size of the np foam can be adjusted, allowing an additional controllable parameter in the hierarchical material. The main challenges are expanding the processing space from basic geometries such as films and creating complex ordered np structures. Here, the authors suggest one method to synthesize tubular np gold structures using established techniques that can be scaled up and applied to custom structures in future studies.

2. Experimental Section

A 1 cm long gold tube (Goodfellow, 99.99%) with an outer diameter of 0.3 mm and inner diameter of 0.2 mm was coated with a silver layer via electrodeposition in a silver nitrate (AgNO₃)-based commercial plating solution (Caswell). The electrochemical setup was placed in a beaker and used a conventional cell with a cylindrical Ag anode (Caswell, 99.97%), the previously mentioned gold tube as the cathode, and a Ag/AgCl reference electrode. The cylindrical anode

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completely surrounded the gold cathode and had a small slit along the vertical length. The surface of the gold tube was prepared for plating by submersion in 17.5% sulfuric acid and then rinsed in deionized (DI) water. The electrolyte bath was maintained at room temperature and a pH of 9.0. Electrolyte solutions were mechanically stirred with a magnetic stir rod at 400 revolutions per minute and actively filtered during electroplating. Plating was conducted with direct current and then later changed to a reverse pulsed current for other samples. The initial current density used was $20 \text{ mA} \cdot \text{cm}^{-2}$. This was later reduced to $10 \text{ mA} \cdot \text{cm}^{-2}$ for both DC and reversed pulse current conditions. The applied wave form for the pulsed current was square with a controlled forward and reverse alternating current of the same magnitude. Each cycle was a total of 1 s with the forward (positive) current active for 0.85 s and the reverse (negative) current for 0.15 s. Total plating time was determined by the desired thickness based on the dimensions and mass of the starting material. The electrolyte was replenished with a proprietary brightener (Caswell) and the pH of the solution was readjusted to 9.0 with KOH before each plating cycle.

After the tubes were coated in Ag, they were placed in a furnace for 24 h at 900°C under flowing argon. Energy dispersive spectroscopy (EDS) was used to confirm a uniform composition along the cross-section of each sample, indicating complete homogenization of the alloy tube. The outer diameter of the tube was polished to reduce surface roughness and the tube was subsequently dealloyed by free corrosion in 70% nitric acid for 24 h. After the samples were removed from the acid, they were rinsed in DI water and air dried. Additional heat treatments were performed on select samples at 200 or 400°C for 2 h in air. A schematic of the synthesis

procedure and a representative cross-section for each processing step is given in Figure 1.

The np tubes were characterized using a field emission scanning electron microscope (SEM JSM-7001 from JEOL) at 10 and 15 kV. SEM was used to confirm that the tubes were dealloyed with a np network embedded in the tube walls and to characterize ligament size. Final composition of the dealloyed samples was determined by EDS.

3. Results and Discussion

Several structures with hierarchical topography and optimized density, geometry, and material selection have been recently synthesized.^[7,13,14] For example, metallic sandwich panels have been made into bifunctional open cell structures by controlling core density and wall architecture.^[14–16] In the present study, the final wall thickness is dictated by the size of initial gold layer, where the final outer diameter is greater than the initial. A gold tube (Figure 1a) was selected as the starting material because its hollow cross-section represents typical ligaments found in hierarchical structures such as lattices. Figure 1b shows the Au tube plated with a Ag layer. Once the layers are diffused, the alloy composition is approximately Au₃₀Ag₇₀ at% (see experimental procedures). The AuAg dealloying system was used to confirm the feasibility of this processing method because it is a well-established starting alloy for the synthesis of np foams.^[17] Other np metals can be synthesized from different alloys such as np copper from CuZn^[18] or np silver from AgAl.^[19] However, the current synthesis procedure is not feasible using these alloys since large differences in the melting temperatures of the elements could cause sample distortion during diffusion of the metal layers.

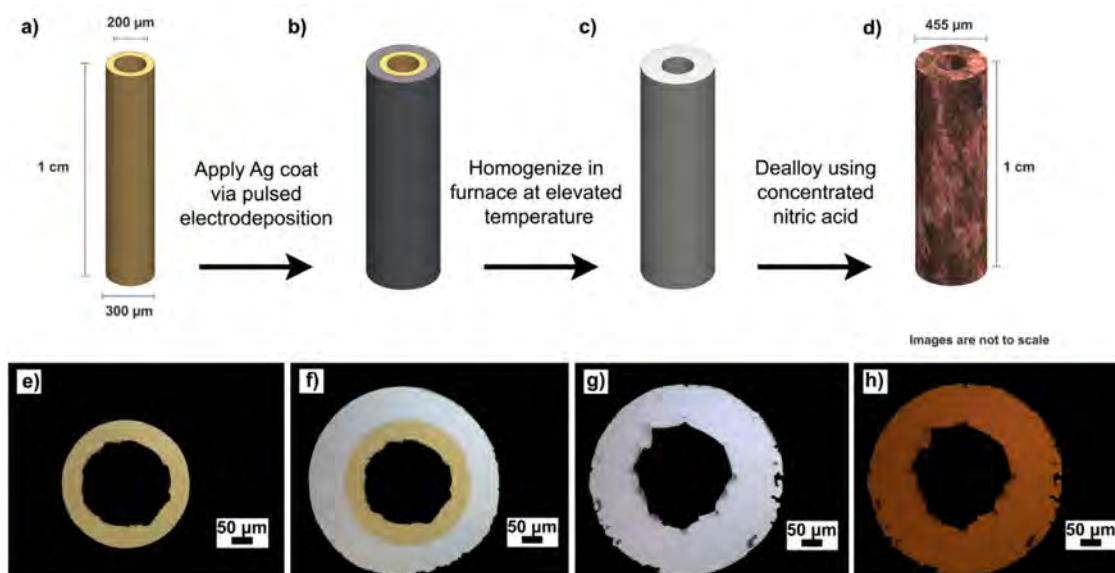


Fig. 1. Schematic representation and cross-sectional images for the processing of nanoporous gold tubes. Fabrication begins with a base Au tube (a) that is coated with a layer of Ag via electrodeposition (b). The layered tube is homogenized in a furnace (c) and then dealloyed to produce a nanoporous Au tube (d).

The result of homogenization of the AuAg alloy is illustrated in Figure 1c, where the distinction between the two metal layers no longer exists. Cross-sectional micrographs of coated and homogenized tubes are presented in Figures 1f and g, respectively. Figure 1f indicates that the electrodeposited silver layer adheres well to the gold tube. This is attributed to the inherently contaminant-free gold surface and the similar atomic size and crystal structure of the two metals, which are both key factors in uniform surface adhesion. The homogenized layer is uniform and has slight Kirkendall porosity. Alloy composition determined by EDS further confirmed the complete diffusion of the layers. Homogenized tubes were subsequently dealloyed through a chemical dissolution process.^[20,21] After dealloying, a structurally stable np Au tube was produced (Figure 1d). The embedded np network can be seen in Figure 2f and is discussed further in a later section.

The main challenge in developing the processing method was determining critical electrodeposition parameters. Figure 2 demonstrates the impact of plating conditions on the morphology of the plated layer. For DC current plating at $20 \text{ mA} \cdot \text{cm}^{-2}$, the silver layer grew radially from the surface of the tube with round hills at the exposed surface of the silver layer (Figure 2a). Voids are present in the less densely packed areas of the deposited silver. Reducing the current density to $10 \text{ mA} \cdot \text{cm}^{-2}$ during plating did not improve the roughness of the silver surface or the density of the deposit. Homogenization and dealloying were performed on the DC plated

samples plated at $20 \text{ mA} \cdot \text{cm}^{-2}$. Dealloying of the tube successfully created a np network (Figure 2c). Large voids were formed during the diffusion process in the region where the silver layer was deposited, while the inner section is free of large voids.

To further improve the coating quality, a reverse pulse current was used during the electrodeposition of silver. Using this type of current signal, silver deposition occurs in the cathodic (forward) pulse, while a small amount of the metal is stripped away in the shorter anodic (reverse) pulse. Figure 2d shows a cross-sectional image of a tube after reverse pulse electrodeposition at $10 \text{ mA} \cdot \text{cm}^{-2}$. Compared to the DC plated tube in Figure 2a, the surface of the silver layer was significantly improved by use of the reverse pulse conditions. The two important differences between the coatings in Figures 2a and d are the large roughness at the top surface and the non-uniform thickness of the silver layer around the tube. Using the reverse pulse plating, both of these issues were mitigated (Figure 2d). During DC plating, a negatively charged diffusion layer builds around the cathode as ions are depleted near the part limiting the diffusion of metal ions to reach the deposition surface. By reversing the polarity of the current, this layer is discharged, increasing the silver ion concentration near the tube surface.^[22] This also reduces the variance in the local current densities of the wire that tend to promote inconsistencies in the layer thickness. Finally, silver was removed from the top surface during the reverse pulses, limiting the continued growth of silver on

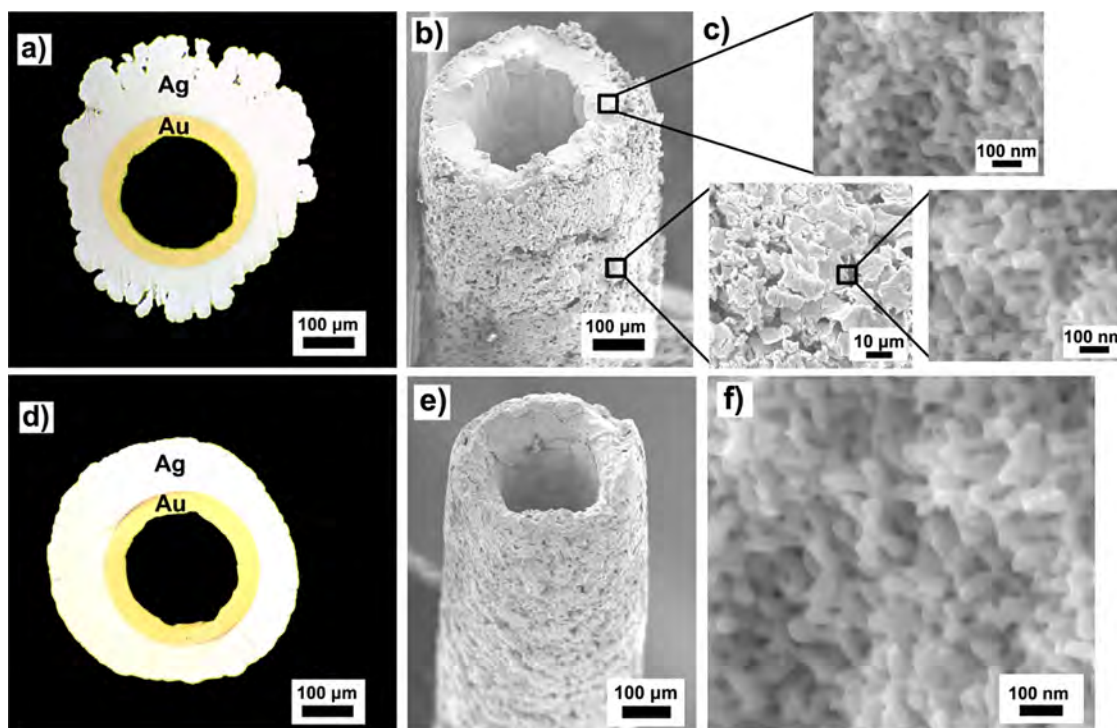


Fig. 2. Electrodeposition with direct current and a current density of $20 \text{ A} \cdot \text{cm}^{-2}$ showing a rough silver top surface (a). Homogenization and dealloying led to a bimodal tubular structure with an inner nanoporous network (b) and an outer macroporous region (c) that also contained a nanoporous network inside larger ligaments. Pulsed current with polarity reversal at a current density of $10 \text{ mA} \cdot \text{cm}^{-2}$ promoted even plating (d). SEM images of an optimized nanoporous Au tube (e) with np morphology inside structure walls (f).

protruding surface features and reducing the top surface roughness, resulting in a much smoother deposit than previously observed.

Improvement in coating quality carried over to the subsequent processing steps where the tubes were homogenized at elevated temperatures and dealloyed. This was accomplished using the same conditions as were used for the DC plated samples. Figure 2e illustrates the typical structure of tubes synthesized with optimized plating conditions. These samples presented a single tubular region without the large voids that were generated during homogenization in the DC plated samples. The average ligament size of the dealloyed samples was ≈ 45 nm (Figure 2f), similar to np Au films synthesized through free corrosion in nitric acid.^[20] EDS scans after dealloying revealed trace amounts of Ag (<4 at%) in the samples.

The key advancement toward improving the mechanical behavior of lattice structures has been the optimization of wall thickness to strut radius ratio,^[6,11] where both of these parameters can be controlled through the method presented here. For example, Shaedler et al. have demonstrated that nanocrystalline nickel microlattices, with the smallest feature being wall thicknesses of hundreds of nanometers, exhibits dimensional recovery from 50% compression.^[6] Similar results have also been achieved with ceramic lattices at an even smaller scale with wall thicknesses below 100 nm.^[11] In both studies, the main cause of failure in the lattices has been high stress concentration at the nodes, which leads to node cracking. Node failure is expected, since they are only supported by hollow strut walls. To realize the potential strength of these ultralight materials, the critical factor is improving nodal strength.^[10] Additional levels of structural hierarchy may be the key to solving the nodal issue and implementing a new parameter which may improve the nodal strength of the structures. Np structures can potentially provide this added strength. Mechanical studies on np Au and np Cu demonstrate higher than expected yield strengths under compressions but exhibit brittle failure in tension.^[23,24] Np Au follows scaling laws developed for macroporous foams, while the individual ligaments behave similarly to single nanowires.^[25,26] As a bulk material, np metals exhibit densification under uniaxial compression, which promotes macroscopic work hardening.^[18,27] A study by Hodge et al. also showed that the strength of np gold increases with decreasing ligament size.^[24,28] Therefore, the strength of the tube can be controlled by coarsening, although the strength of np Au is accompanied by limited ductility and brittle failure modes of the material. Recent studies have demonstrated that adjustments to dealloying conditions and impregnation of the pores with a polymer can significantly improve the ductility of the foam.^[29] Further hybridization of the np Au may impart ductility in both tension and compression of the walls.

The np tubes in this study were synthesized with three different ligament sizes (Figure 3). It has been shown that by adjusting the pore size of the foam, the material can be optimized for applications in catalytic materials,^[30,31]

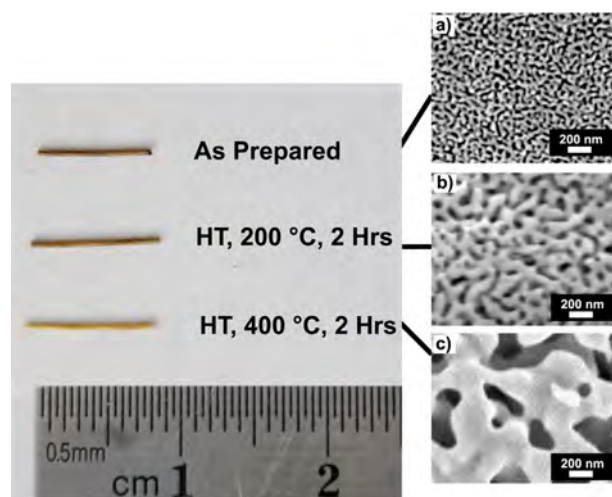


Fig. 3. Tunable ligament sizes for nanoporous Au tubes (a) as-prepared and after 2 h heat treatments at (b) 200 and (c) 400 °C.

microfluidic devices,^[32] and as structures for hybrid electrodes where a large surface area is needed.^[33,34] The SEM image in Figure 3a shows a typical as prepared sample with an average ligament diameter of 45 nm. Annealing treatments were used to coarsen the ligament diameter and morphology of the np Au; thermal conditions and resulting ligament diameters are summarized in Table 1. SEM images of the coarsened samples display ligaments that were grown to ≈ 80 nm at 200 °C in Figure 3b and ≈ 450 nm at 400 °C in Figure 3c. These results agree well with other studies exploring np foams with coarsened ligaments.^[24] Overall, the samples maintained their tubular shape and structural integrity after the heat treatments.

The step-by-step method described in Section 2 was designed for the future application of this technique to custom template structures. New synthesis techniques will facilitate the development of materials with high degrees of optimization for multiple properties. For example, one can tune mechanical properties from the micro-scale architecture and catalytic properties from the available surface area. The processing method presented is similar to template techniques where a layer of material is placed on structures of a predetermined shape.^[6] However, those methods only allow for the wall thickness to be modified. In this manuscript, the fabrication method involves further modification of the material once it has been deposited on the template, allowing for nanopores to be implemented in the overall structure. This process also introduces another parameter for structure optimization.

Table 1. Ligament sizes of heat treated nanoporous tubes.

Sample Type	Heat Treatment	Ligament Size [nm]
Au ₃₀ Ag ₇₀	As-prepared	≈ 45
Au ₃₀ Ag ₇₀	200 °C, 2 h	≈ 80
Au ₃₀ Ag ₇₀	400 °C, 2 h	≈ 450

Furthermore, the tubular np structures are unique because they combine both periodic and stochastic structures.

In summary, the authors have demonstrated a protocol for the synthesis of np Au tubes using a combination of electrodeposition, homogenization, and free-corrosion dealloying. The tubes maintained their structure throughout the processing sequence and yielded a np network within the macro tube structure. Heat treatments were used to further modify the ligament sizes and give another level of dimensional control. Future work will focus on expanding the processing space, in order to synthesize more complex hierarchical structures which can be used for a wide range of applications including sensors and nano-devices.

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