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6. AUTHORS:

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

Missouri University of Science and Technol
300 W. 12th Street

Rolla, MO 65409 -1330

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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

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RPPR Final Report
as of 08-May-2019

Agency Code:

Proposal Number: 64828CH **Agreement Number: W911NF-14-1-0369**

INVESTIGATOR(S):

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Country: USA

DUNS Number: 804883767 EIN: 436003859
Report Date: 20-Oct-2018 Date Received: 17-Jan-2019
Final Report for Period Beginning 21-Jul-2014 and Ending 20-Jul-2018
Title: Fractal Assembly of Polymeric Nanoparticles into Fibers versus Globules: an Experimental and Computational Study
Begin Performance Period: 21-Jul-2014 **End Performance Period:** 20-Jul-2018
Report Term: 0-Other
Submitted By: Nicholas Leventis Email: leventis@mst.edu
Phone: (573) 341-4391
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STEM Degrees: 4 **STEM Participants:** 10

Major Goals: A.1.1 Overall Objective:
“Low-density solid monolithic macroscopic objects consisting of nanoporous 3D assemblies of nanoparticles are referred to as aerogels and are pursued mainly for their low thermal conductivity and high acoustic impedance. The overall objective of this effort is to learn how to control the 3D assembly of polymeric nanoparticles into nanofibrous aerogels, rather than allow them to form globular-cluster networks. The urgent need for research in that direction stems from the fact that with all other things being equal (chemical composition, density), nanofibrous aerogels are much stiffer, stronger and tougher materials, suitable for applications unrelated to aerogels before (e.g., armor). And, as preliminary results show, certain fibrous nanostructures are also superhydrophobic, thus adding multifunctionality and value.”

A.1.2 Specific Objective 1:
Understand the environmental parameters that favor nanofibers versus nanoglobules. For this, we will work experimentally with aerogels that have shown formation of both kinds of nanostructures (e.g., polyurea, polyimide and polydicyclopentadiene aerogels). We will vary the gelation solvent and temperature, monomer concentration, ionic strength, and catalyst concentration. Concurrently, our developing understanding will be applied onto highly promising emerging systems (e.g., polyurethane aerogels from small-molecule monomers).

A.1.3 Specific Objective 2:
Understand the role of the shape of the primary particles (e.g., ellipsoidal vs. spherical) upon their assembly into fibers versus globules. For this, we will design primary particles and trigger catalytically their assembly at a defined point in time. That task involves synthesis of large molecules that under the right conditions of solvent polarity (i.e., working just below their solubility limit) will behave, effectively, as primary particles. Those primary particles will be based on star or dendritic molecules built on symmetric or elongated cores. The catalyst-induced polymerization chemistry of choice will rely on ROMP.

A.1.4 Specific Objective 3:
Understand the role of the innate electro-static/dynamic properties of elementary nanoparticles that direct assembly

to fibers versus globules. This part will be a computational study whereas our basic premise is that in order for nanoparticles to assemble into fibers they need to posses a vectorial property (e.g., dipole moment, polarizability), and therefore display an angle-dependent sticking probability. As shown in Section IV, preliminary computational studies using the diffusion-limited cluster aggregation (DLCA) model with spheres provided with a phenomenological angle-dependent sticking probability, not only support this hypothesis, but they are also able to predict branching between fibers as observed by SEM. Working with real systems (e.g., polyurea), we will use a combination of ab initio / force-field methods to construct primary nanoparticles from the monomer up, thus knowing not only all their electrical properties, but also the functional group density on their surface. Introducing those computed nanoparticles in the DCLA model, and perhaps with the use of explicit solvation, we should be able to predict the exact experimental structures, thus identifying the important electrical parameters of the nanoparticles, which are responsible for the formation of nanofibers.

Accomplishments: A.1.1 Overall Objective
....learn how to control the 3D assembly of polymeric nanoparticles into nano fibrous aerogels.....

Status:
The overall objective was fully accomplished. Along the way it was discovered that sol-gel polymers demonstrate two types of fibers, associated with two different types of gelation mechanisms. We derived methodology by which we assign discrete nanomorphologies to specific index values and accordingly any nanomorphology, up to now a qualitative property, can be quantified and synthesized at will. We refer to that nanomorphology index as the K-index. The K-index has been presented in several conferences in 2018 and a manuscript has been submitted to ACS Nano.

A.1.2 Specific Objective 1
Understand the environmental parameters that favor nanofibers versus nanoglobules.

Status:
This specific objective is most intimately linked to our overall objective above. It was investigated with polyurea aerogels. It turned out to be a very large project, it involved several graduate students at different phases, and took the entire funding period to accomplish.

In parallel we worked with several other systems, like polyurethane aerogels as stated in Specific Objective 1. Along the way, we were ever surprised by the properties of those materials and we deviated away from the main objective that was left solely on polyureas. The most important discoveries along those promising leads were:
(a) Superelastic and shape memory aerogels based on polyurethanes, and the discovery of a Markus type kinetic thermodynamic relationship between the elastic modulus and shape recovery rate;
(b) Remarkable CO2 uptake from carbon aerogels derived from polyimide aerogels – that discovery has led to a re-investigation of the carbonization mechanism of phenolic aerogels, and the discovery of record-high CO2 uptake by carbons derived from low-density resorcinol-formaldehyde aerogels;
(c) New efficient carbon supported nanocatalysts derived from polyamides incorporating ferrocene as their polymer repeat unit;
(d) Discovered and carried out the complete mechanism elucidation of polyurea synthesis from isocyanates and mineral acids;
(e) Discovered a method of making ceramic and metallic aerogels from compacts of polymer crosslinked xerogel powders – reviewers characterized our method as "brilliant;" and,
(f) Demonstrated Co aerogel-based thermites fabricated via (e).

A.1.3 Specific Objective 2
Understand the role of the shape of the primary particles (e.g., ellipsoidal vs. spherical) upon their assembly into fibers versus globules.

Status:
After some initial experimentation with elongated cores derived from methylene p-diphenyldiisocyanate (MDI), we realized that the behavior of the sol and the properties of the derived aerogels were determined by the number of the polymerizable functional groups in the perimeter of the monomers, thus we did not pursue that Specific Objective further.

A.1.4 Specific Objective 3:
Understand the role of the innate electro-static/dynamic properties of elementary nanoparticles that direct assembly

to fibers versus globules.

Status:
We have developed a computational model for primary particles of polyurea formed by Van der Waals/H-bonding stacking of dendritic oligomers, and packing of those stacks again via the same kind of forces. The generation of the dendritic oligomers, the number of oligomers in the stacks and the number of oligomers in the packs was determined via Molecular Dynamics simulations stopped at the common cross-section of the calculated and experimental primary particle size, density and XRD pattern. A paper is in preparation.

In parallel, we established collaboration with Professor Changlin (Bob) Wu, a mechanical engineer of our Civil Engineering Department, and we are exploring computational aerogels as a means of elucidating the coupling of molecular and macroscopic properties over length scales (atomistic to meso to macro). A first paper was published in the fall of 2018 in Soft Matter and was selected for the cover of its issue.

Section B describes the technical results from our specific ARO-funded research activities above.

Training Opportunities: Trained / training nine (9) graduate students in polymer science, nanoscience / nanotechnology and a vast array of analytical techniques related to polymer and nanoporous polymer characterization and testing:

Shaheen Doulah	Ph.D. 2022	
Rushi U. Soni	Ph.D. 2021	
Chandana Mandal	Ph.D. 2019	(will join Intel Corp. at OR)
Parwani Rewatkar	Ph.D. 2019	(will return to India)
Tahereh Tagvahee	Ph.D. 2019	(will postdoc)
Suraj Donthula	Ph.D. 2018	(currently with Intel Corp. at OR)
Hojat Majedi Far	Ph.D. 2018	(will postdoc)
Adnan Malik Saeed	Ph.D. 2016	(currently with Intel Corp. at OR)
Tyler M. Fears	Ph.D. 1015	(currently stuff at the LLNL)

Trained in chemistry, polymers, nano composites two summer high school interns via the HSAP:

James Schisler	Summer 2015	(currently a Senior in chemistry at Washington U.)
Theodora Leventis	Summer 2015	(currently a Senior in chemistry at MU-Columbia)

and one visiting student from India (BOSH Scholar supported by the India Government):

T. K. Shruthi	Summer 2015	(currently a chemistry Ph.D. student at MSU)

Results Dissemination: Tutorials:

1. “Characterization of Nanoporous Materials,” N. Leventis, Pre-conference Tutorial - Spring 2017 MRS Meeting, Phoenix, AZ, April 17, 2017

2. “From Phenolic to Fe(0) Aerogels for Energetic Materials – An Integrated View,” N. Leventis, Pre-conference Tutorial - Spring 2017 MRS Meeting, Phoenix, AZ, April 17, 2017

3. “Isocyanate Derived Aerogels: Polyurethanes and Polyureas, but also Polyimides, Polyamides and Co-Polymers,” N. Leventis, Pre-conference Tutorial - Spring 2017 MRS Meeting, Phoenix, AZ, April 17, 2017

Presentations:
  Total: 40
  Invited & Keynotes: 9
  Invited for the SCI-Mix at ACS Meetings: 8
  Foreign: 5

In the News:

On the MS&T WEBSITE
Researchers create shape-memory aerogels with rubber-like elasticity
Posted by Peter Ehrhard
On May 2, 2017
https://news.mst.edu/2017/05/researchers-create-shape-memory-aerogels-with-rubber-like-elasticity/

Two days later in THE ROLLA DAILY NEWS
Breakthrough! MO S&T Researchers create shape-memory material that has great potential for high tech applications
Posted May 4, 2017 at 8:08 AM
https://www.therolladailynews.com/news/20170504/breakthrough-mo-st-researchers-create-shape-memory-material-that-has-great-potential-for-high-tech-applications

***********************Many other places around the world***********************

One year later in TECH BRIEFS

MAY 4, 2018 | MANUFACTURING & PROTOTYPING | MATERIALS
Shape-Memory Aerogels Created With Rubber-Like Elasticity
https://www.techbriefs.com/component/content/article/tb/stories/news/28935?m=1063

THE NEWS RELESE FROM ABOVE:

Nick Leventis and student Suraj Donthula demonstrate the flexibility of their super elastic aerogels.

Polymeric aerogels are nanoporous structures that combine some of the most desirable characteristics of materials, such as flexibility and mechanical strength. It is nearly impossible to improve on a substance considered the final frontier in lightweight materials. But chemists from Missouri University of Science and Technology have done just that by making aerogels that have rubber-like elasticity and can “remember” their original shapes.

Aerogels are created by replacing liquids with gases in a silica, metal oxide or polymer gel. They are used in a wide variety of products, from insulation of offshore oil pipelines to NASA space missions.

“The specific kind of polyurethane aerogels we have created are superelastic, meaning that they can be bent in any direction or be smashed flat and still return to their original shape,” says Dr. Nicholas Leventis, lead researcher on the project and Curators’ Distinguished Professor of chemistry at Missouri S&T. “Our superelastic aerogels are different from rubber in that they can on-command return to a specific form. That is, they also show a strong shape memory effect, meaning that they can be deformed and cooled and keep the deformed shape forever.

“However, when the temperature rises back to room temperature, they recover their original un-deformed shape,” Leventis explains. “The shape memory effect is not new. Shape memory metallic alloys and polymers are known for many years, however, shape memory aerogels are the last frontier in lightweight.”

Leventis and his group have demonstrated this unique property by shaping a “bionic hand” that is capable of mimicking coordinated muscle functions. When stimulated by heat, the aerogel and can close from its open-palm state and grab a pen.

IMAGE OF BIONIC HAND FROM:
Chem. Mater. 2017, 29, 4461-4477 (most visited article in May 2017)

Missouri S&T researchers created this “bionic hand” to demonstrate the biomimetic properties of new polymeric aerogel materials.

“We believe this work has produced one of the ‘holy grails’ in the field of aerogels,” says Leventis. “I see a lot of biomimetic applications for these aerogels in the future. Their flexibility, combined with elasticity, greatly enhance the range of possible uses.”

Leventis and his team’s work can be seen in the Chemistry of Materials journal published today, Tuesday, May 2, by the American Chemical Society. Working with Leventis at S&T are Dr. Chariklia Sotiriou-Leventis, professor of chemistry, and graduate students Suraj Donthula, Chandana Mandal, and Adnan Malik Saeed, and summer interns Theodora Leventis and James Schisler. The work was supported by the U.S. Army Research Office, and partial support was also provided by BASF Polyurethanes GmbH.

Honors and Awards: Midwest Regional Graduate Student Award: The purpose of this award is to recognize outstanding graduate students from the Midwest Region and allow them to deliver oral or poster presentations on their research. Award recipients were nominated by their home institutions, and provided a cash prize, certificate, complementary meeting registration, and complementary admission to the awards banquet. Note that funding for these awards was donated by the Wakarusa Valley Local Section. (Funding for the awards was provided directly out of section resources, and was not included in the meeting expenses.) Award Recipients:

? Suraj Donthula, South Central Missouri

For:

“Shape Memory Superelastic Poly(isocyanurate-urethane) Aerogels (PIR-PUR) for Deployable Panels and Biomimetic Applications,” S. Donthula, C. Mandal, T. Leventis, J. Schisler, M. A. Saeed, C. Sotiriou-Leventis, N. Leventis, 52nd ACS Midwest Regional Meeting, Lawrence, KS, October 19, 2017

Protocol Activity Status:

Technology Transfer: Patents Filed and issued in the funding period (3)

1. “Flexible to Rigid Nanoporous Polyurethane-Acrylate (PUAC) Type Materials for Structural and Thermal Insulation Applications,” N. Leventis, C. Sotiriou-Leventis, A. Bang, U.S. Patent No. 9,994,516 (06-12-2018; filed 10-31-2016).

2. “Multifunctional Porous Aramids (Aerogels) and Fabrication Thereof,” N. Leventis, C. Sotiriou-Leventis, M. Adnan Saeed, U.S Patent No. 9,593,225 (03-14-2017; filed 10-31-2014).

3. “Multifunctional Porous Aramids (Aerogels) and Fabrication Thereof,” N. Leventis, C. Sotiriou-Leventis, M. Adnan Saeed, U.S Patent No. 9,260,581 (02-16-2016; filed 10-31-2014).

Patents Filed in the funding period and pending (4)

1. “Novel Highly Porous Ceramic and Metal Aerogels from Xerogel Powder Precursors, and Methods for their Production and Use,” N. Leventis, C. Sotiriou-Leventis, M. A. Saeed, P. Rewatkar, T. Taghvaee (filed 04-06-2018).

2. “Selective CO2 Sequestration with Monolithic Bimodal Micro/Macroporous Carbon Aerogels Derived from Polyamide-Polyimide-Polyurea Random Co-polymers,” N. Leventis, C. Sotiriou-Leventis, M. A. Saeed (filed 03-23-2017).

3. “Process for Producing Isocyanate-based Xerogels and Aerogels with Mineral Acids,” N. Leventis, C. Sotiriou-Leventis, A. M. Saeed, W. Loelsberg, M. Fricke, D. Weinrich, U.S. Patent Application (filed by BASF on 10-16-2015).

4. “Organic and Metallic Aerogels, Composition, for the Organic and Metallic Aerogels, and Method for Manufacturing the Organic and Metallic Aerogels,” N. Leventis, C. Sotiriou-Leventis, S. Mahadik-Khalnorkar, U.S. Patent Application (filed 04-08-2015).

Technology transfer to the labs of:
- Professor Hongbing Lu, Mechanical Engineering Department, UT-Dallas
Superplastic / shape-memory aerogels for acoustic attenuation applications

- Professor Firouzeh Sabri, Physics Department, U of Memphis
Superplastic / shape-memory aerogels for biomedical applications

PARTICIPANTS:

Participant Type: PD/PI
Participant: Nicholas Leventis
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co PD/PI
Participant: Chariklia Sotiriou-Leventis
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Suraj Donthula
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Tahereh Tagvahee
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Hojat Majedi Far
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Adnan Malik Saeed
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Chandana Mandal
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Parwani Rewatkar
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Rushi Soni
Person Months Worked: 2.00
Funding Support:
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Shaheen Doulah
Person Months Worked: 1.00
Funding Support:
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Tyler Fears
Person Months Worked: 1.00
Funding Support:
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: High School Student
Participant: James Schisler
Person Months Worked: 3.00
Funding Support:
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: High School Student
Participant: Theodora Leventis
Person Months Worked: 3.00
Funding Support:
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

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Journal: Journal of Non-Crystalline Solids
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Date Submitted: 1/17/19 12:00AM Date Published: 11/1/17 3:00PM
Publication Location: United States
Article Title: Sound insulation properties in low-density, mechanically strong and ductile nanoporous polyurea aerogels
Authors: Sadeq Malakooti, Habel Gitogo Churu, Alison Lee, Tingge Xu, Huiyang Luo, Ning Xiang, Chariklia Sotiri
Keywords: Polyurea, aerogel, Metamaterials, Porous materials, Acoustics Sound transmission loss Poroelasticity
Abstract: Aerogels are quasi-stable, nanoporous, low-density, three-dimensional assemblies of nanoparticles. In this paper,an extremely high sound transmission loss for a family of ductile polyurea aerogels (e.g., over 30 dB within 1 to4 kHz at bulk density 0.25 g/cm3 and 5 mm thickness) is reported. The fundamental mechanisms behind the aerogel acoustic attenuations are investigated. Sharing striking similarities with acoustic metamaterials, initially, aerogels are studied via a one-dimensional multi degree-of-freedom mass-spring system. Different effects such as spring constant disparity are investigated in regards to the structural vibration wave transmission loss. Results are given for different configurations consistent with the aerogel nano/microstructures. A significant wave attenuation is observed by considering a random spring distribution. In the next step towards modeling such a complex hierarchical and random structural material, the continuum Biot's dynamic theory of poroelasticit
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Volume: 7 Issue: 81 First Page #: 51104
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Article Title: Air-oxidation of phenolic resin aerogels: backbone reorganization, formation of ring-fused pyrylium cations, and the effect on microporous carbons with enhanced surface areas
Authors: Hojat Majedi Far, Suraj Donthula, Tahereh Taghvaee, Adnan Malik Saeed, Zachary Garr, Chariklia Soti
Keywords: silicon carbide, silicon nitride, aerogels, aerogels
Abstract: We report the carbothermal synthesis of sturdy, highly porous (>85%) SiC and Si3N4 monolithic aerogels from compressed polyurea-cross-linked silica xerogel powders. The high porosity in those articles was created via reaction of core silica nanoparticles with their carbonized polymer coating toward the new ceramic framework and CO that escaped. Sol?gel silica powder was obtained by disrupting gelation of a silica sol with vigorous agitation. The grains of the powder were ~50 ?m in size and consisted of 3D assemblies of typical silica nanoparticles. The individual silica nanoparticles within the grains of the powder were coated conformally with a nanothin layer of carbonizable polyurea derived from an aromatic triisocyanate,The wet-gel powder was dried at R.T, and was compressed to suitable shapes, were converted to same-shape SiC or Si3N4 artifacts at 1500 °C under Ar or N2, respectively. The overall synthesis was time-, energy-, and materials-efficient.
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Publication Location: United States
Article Title: Sturdy, Monolithic SiC and Si3N4 Aerogels from Compressed Polymer-Cross-Linked Silica Xerogel Powders
Authors: Parwani M. Rewatkar, Tahereh Taghvaee, Adnan Malik Saeed, Suraj Donthula, Chandana Mandal, Nav
Keywords: silicon carbide, silicon nitride, aerogels, aerogels, powders
Abstract: We report the carbothermal synthesis of sturdy, highly porous (>85%) SiC and Si3N4 monolithic aerogels from compressed polyurea-cross-linked silica xerogel powders. The high porosity in those articles was created via reaction of core silica nanoparticles with their carbonized polymer coating toward the new ceramic framework and CO that escaped. Sol?gel silica powder was obtained by disrupting gelation of a silica sol with vigorous agitation. The grains of the powder were about 50 ?m in size and irregular in shape and consisted of 3D assemblies of silica nanoparticles as in any typical silica gel. The individual elementary silica nanoparticles within the grains of the powder were coated conformally with a nanothin layer of carbonizable polyurea derived from the reaction of an aromatic triisocyanate (TIPM: triisocyanatophenyl methane) with the innate ?OH, deliberately added ?NH2 groups, and adsorbed water on the surface of silica nanoparticles.
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Date Submitted: 1/17/19 12:00AM Date Published: 5/31/18 3:00PM
Publication Location:
Article Title: Scalable, hydrophobic and highly-stretchable poly(isocyanurate–urethane) aerogels
Authors: Sadeq Malakooti, Saman Rostami, Habel Gitogo Churu, Huiyang Luo, Jenna Clark, Fabiola Casarez, O
Keywords: hydrophobic, superplastic, polyurethane, aerogel, PIR-PUR
Abstract: Scalable, low-density and flexible aerogels offer a unique combination of excellent mechanical properties and scalable manufacturability. Herein, we report the fabrication of a family of low-density, ambient-dried and hydrophobic poly(isocyanurate–urethane) aerogels derived from a triisocyanate precursor. The bulk densities ranged from 0.28 to 0.37 g cm ┌3 with porosities above 70% v/v. The aerogels exhibit a highly stretchable behavior with a rapid increase in the Young's modulus with bulk density (slope of log–log plot > 6.0). In addition, the aerogels are very compressible (more than 80% compressive strain) with high shape recovery rate (more than 80% recovery in 30 s). Under tension even at high strains (e.g., more than 100% tensile strain), the aerogels at lower densities do not display a significant lateral contraction and have a Poisson's ratio of only 0.22.
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Publication Location: United States
Article Title: Nanostructure-Dependent Marcus-Type Correlation of the Shape Recovery Rate and the Young's Modulus in Shape Memory Polymer Aerogels
Authors: Suraj Donthula, Chandana Mandal, James Schisler, Theodora Leventis, Mary Ann B. Meador, Chariklia
Keywords: aerogels, polyurethane, shape memory, fill factor, recovery rate, elastic modulus, Marcus theory
Abstract: Thermodynamic?kinetic relationships are not uncommon, but rigorous correlations are rare. On the basis of the parabolic free-energy profiles of elastic deformation, a generalized Marcus-type thermodynamic?kinetic relationship was identified between the shape recovery rate, Rt(N), and the elastic modulus, E, in poly (isocyanurate-urethane) shape memory aerogels. The latter were prepared with mixtures of diethylene, triethylene, and tetraethylene glycol and an aliphatic triisocyanate. Synthetic conditions were selected using a statistical design of experiments method. Microstructures obtained in each formulation could be put into two groups, one consisting of micron-size particles connected with large necks and a second one classified as bicontinuous. The two types of microstructures could be explained consistently by spinodal decomposition involving early versus late phase separation relative to the gel point. Irrespective of microstructure, all samples showed a shape memory effect
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Publication Location:
Article Title: Multi-scale progressive failure mechanism and mechanical properties of nanofibrous polyurea aerogels
Authors: Chenglin Wu, Tahereh Taghvaee, Congjie Wei, Arman Ghasemi, Genda Chen, Nicholas Leventis, Wei
Keywords: polyurea, aerogels, fibrous, multi-scale, nanoindentation, simulations
Abstract: The nonlinear mechanical properties, deformation and failure mechanisms of polyurea aerogels (PUAs) were investigated using a multi-scale approach that combines nanoindentation, analytical and computational modeling. The atomistic structure of primary particles of PUAs and their mechanical interactions were investigated with molecular dynamics simulations. From nanoindentation we identified four deformation and failure modes: free ligament buckling, cell ligament bending, stable cell collapsing, and ligament crush induced strain hardening. The corresponding structural evolution during indentation and strain hardening were analyzed and modeled. The material scaling properties were found to be dependent on both the relative density and the secondary particle size of PUAs. Using a porositydependent material constitutive model, a linear relationship was found between the strain hardening index and secondary particle size instead the conventional power-law relationship.
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Article Title: Exceptionally High CO2 Adsorption at 273 K by Microporous Carbons from Phenolic Aerogels: The Role of Heteroatoms in Comparison with Carbons from Polybenzoxazine and Other Organic Aerogels
Authors: Hojat Majedi Far, Parwani M. Rewatkar, Suraj Donthula, Tahereh Taghvaee, Adnan Malik Saeed, Chari
Keywords: aerogels, carbon dioxide, absorption, phenolic, polybenzoxazine,
Abstract: Phenolic aerogels containing oxygen and other polymeric aerogels containing both oxygen and nitrogen (polybenzoxazine and a polyamide-polyimidepolyurea co-polymer) are converted to carbon aerogels (800 °C/Ar), and are etched with CO2 (1000 °C). Etching opens closed pores and increases micropore volumes and size. Heteroatoms are retained in the etched samples. All carbon aerogels are evaluated as CO2 absorbers in terms of their capacity and selectivity toward CH4, H2, and N2. CO2 adsorption capacity is linked to microporosity. In most cases, monolayer coverage of micropore walls is enough to explain CO2 uptake quantitatively. The interaction of CO2 with micropore walls is evaluated via isosteric heats of adsorption, and is stronger with carbons containing only oxygen heteroatoms. The extremely high adsorption capacity of etched carbon aerogels from low-density RFaerogels (14.8 ± 3.9 mol of CO2 per g at 273 K, 1 bar) was attributed to a pore-filling process.
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Journal: ACS Nano
Publication Identifier Type: DOI Publication Identifier:
Volume: Issue: First Page #:
Date Submitted: 1/17/19 12:00AM Date Published:
Publication Location: United States
Article Title: K-index: A Descriptor, Predictor and Correlator of Complex Nanomorphology to Other Material Properties
Authors: Tahereh Taghvaee, Suraj Donthula, Parwani Rewatkar, Hojat Majedi Far, Chariklia Sotiriou-Leventis, Ni
Keywords: nano morphology, k-index, descriptor, predictor, correlation
Abstract: Morphology is a qualitative property of nanostructured matter, and is articulated by visual inspection of micrographs. For deterministic procedures that relate nanomorphology to synthetic conditions, it is necessary to express nano/micro-structure numerically. Selecting polyurea aerogels as a model system with demonstrated potential for rich nanomorphology, and guided by a statistical Design-of-Experiments model, we prepared a large array of materials (208) with identical chemical composition, but quite different nanostructures. By reflecting on SEM imaging it was realized that our first pre-verbal impression about a nanostructure is related to its openness and texture; the former is quantified by porosity (?), and the latter is oftentimes related to hydrophobicity, which in turn is quantified by the contact angle (?) of water droplets resting on the material. Nano morphology is described uniquely by the ? /? ratio, which is referred to as K-index.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
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CONFERENCE PAPERS:

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: 251st ACS National Meeting
Date Received: 27-Aug-2016 Conference Date: 16-Mar-2016 Date Published: 17-Jan-2016
Conference Location: San Diego, CA
Paper Title: Nanoporous Polyurea from Triisocyanates Reacting with Mineral Acids
Authors: Malik A. Saeed, Suraj Donthula, Hojat Majedi Far, Parwani M. Rewatkar, Chariklia Sotiriou-Leventis, Nic
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Conference Name: 251st National ACS Meeting
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Conference Location: San Diego, CA
Paper Title: One-step Synthesis of Highly Porous Silicon Nitride and Silicon Carbide from Polymer-Crosslinked Silica Aerogels
Authors: Malik A. Saeed, Parwani M. Rewatkar, Suraj Donthula, Chariklia Sotiriou-Leventis, Nicholas Leventis
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Conference Location: San Diego, CA
Paper Title: Multiscale Hierarchical Nanoporous Aerogels based on ?-Cyclodextrin for CO2 Sequestration
Authors: Parwani M. Rewatkar, Malik A. Saeed, Suraj Donthula, Hojat Majedi Far, Nicholas Leventis, Chariklia S
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Paper Title: Multiscale Hierarchical Nanoporous Aerogels based on ?-Cyclodextrin for CO2 Sequestration
Authors: Parwani M. Rewatkar, Malik A. Saeed, Suraj Donthula, Hojat Majedi Far, Nicholas Leventis, Chariklia S
Acknowledged Federal Support: **Y**

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Date Received: 27-Aug-2016 Conference Date: 24-Aug-2015 Date Published: 24-Aug-2015
Conference Location: Max Plank Institute, Dresden, Germany
Paper Title: Carbothermal Synthesis of Nanoporous Metals and Carbide Aerogels from Interpenetrating Networks of Polymer-Oxide Nanoparticles
Authors: Nicholas Leventis
Acknowledged Federal Support: **Y**

PATENTS:

Intellectual Property Type: Patent Date Received: **30-Aug-2017**
Patent Title: Flexible to rigid nanoporous polyurethane-acrylate (PUAC) type materials for structural and thermal insulation applications
Patent Abstract: Novel urethane-acrylate (UAC) Star monomers and polyurethane-acrylate (PUAC) aerogel poly
Patent Number: US 9,550,846 B2
Patent Country: USA
Application Date: 13-Mar-2014 Application Status: 3
Date Issued: 24-Jan-2017

Intellectual Property Type: Patent Date Received: **30-Aug-2017**

Patent Title: Multifunctional porous aramids (aerogels), fabrication thereof, and catalytic compositions derived therefrom
Patent Abstract: The present disclosure provides a series of new and improved porous polyamide aerogels deriv
Patent Number: US 9,593,225
Patent Country: USA
Application Date: 16-Dec-2015 Application Status: 3
Date Issued: 14-Mar-2017

Intellectual Property Type: Patent Date Received: **17-Jan-2019**
Patent Title: Flexible to rigid nanoporous polyurethane-acrylate (PUAC) type materials for structural and thermal insulation application
Patent Abstract: Novel urethane-acrylate (UAC) Star monomers and polyurethane-acrylate (PUAC) aerogel poly
Patent Number: US 9,994,516 B2
Patent Country: USA
Application Date: 31-Oct-2016 Application Status: 3
Date Issued: 12-Jun-2018

Fractal Assembly of Polymeric Nanoparticles into Fibers-*vs*-Globules: an Experimental and Computational Study

Final Report

to the

Army Research Office, Polymer Chemistry Division

January 14, 2019

Grant No.: W911NF-14-1-0369

P.I.s: N. Leventis (50%), C. Sotiriou-Leventis (50%)

Amount: $360,000

Initial Period: August 1, 2014 – July 31, 2017

Extended to: July 31, 2018

A. Executive Summary – Initial Objectives and Status

A.1 Objectives Set in the Original Proposal and their Status

A.1.1 *Overall Objective:*

> "Low-density solid monolithic macroscopic objects consisting of nanoporous 3D assemblies of nanoparticles are referred to as aerogels and are pursued mainly for their low thermal conductivity and high acoustic impedance. The overall objective of this effort is to ***learn how to control the 3D assembly of polymeric nanoparticles into nanofibrous aerogels***, rather than allow them to form globular-cluster networks. The urgent need for research in that direction stems from the fact that with all other things being equal (chemical composition, density), nanofibrous aerogels are much stiffer, stronger and tougher materials, suitable for applications unrelated to aerogels before (e.g., armor). And, as preliminary results show, certain fibrous nanostructures are also superhydrophobic, thus adding multifunctionality and value."

Status:

The overall objective was fully accomplished. Along the way it was discovered that sol-gel polymers demonstrate two types of fibers, associated with two different types of gelation mechanisms. We derived methodology by which we assign discrete nanomorphologies to specific index values and accordingly any nanomorphology, up to now a qualitative property, can be quantified and synthesized at will. We refer to that nanomorphology index as the *K*-index. The *K*-index has been presented in several conferences in 2018 and a manuscript has been submitted to *ACS Nano*.

A.1.2 *Specific Objective 1*:

> ***Understand the environmental parameters that favor nanofibers versus nanoglobules***. For this, we will work experimentally with aerogels that have shown formation of both kinds of nanostructures (e.g., polyurea, polyimide and polydicyclopentadiene aerogels). We will vary the gelation solvent and temperature, monomer concentration, ionic strength, and catalyst concentration. Concurrently, our developing understanding will be applied onto highly promising emerging systems (e.g., polyurethane aerogels from small-molecule monomers).

Status:

This specific objective is most intimately linked to our overall objective above. It was investigated with polyurea aerogels. It turned out to be a very large project, it involved several graduate students at different phases, and took the entire funding period to accomplish.

In parallel we worked with several other systems, like polyurethane aerogels as stated in *Specific Objective 1*. Along the way, we were ever surprised by the properties of those materials and we deviated away from the main objective that was left solely on polyureas. The most important discoveries along those promising leads were:

(a) Superelastic and shape memory aerogels based on polyurethanes, and the discovery of a Markus type kinetic thermodynamic relationship between the elastic modulus and shape recovery rate;
(b) Remarkable CO_2 uptake from carbon aerogels derived from polyimide aerogels – that discovery has led to a re-investigation of the carbonization mechanism of phenolic aerogels, and the discovery of record-high CO_2 uptake by carbons derived from low-density resorcinol-formaldehyde aerogels;
(c) New efficient carbon supported nanocatalysts derived from polyamides incorporating ferrocene as their polymer repeat unit;
(d) Discovered and carried out the complete mechanism elucidation of polyurea synthesis from isocyanates and mineral acids;
(e) Discovered a method of making ceramic and metallic aerogels from compacts of polymer crosslinked xerogel powders – reviewers characterized our method as "brilliant;" and,
(f) Demonstrated Co aerogel-based thermites fabricated via (e).

A.1.3 *Specific Objective 2*:

Understand the role of the shape of the primary particles (e.g., ellipsoidal vs. spherical) upon their assembly into fibers versus globules.

For this, we will design primary particles and trigger catalytically their assembly at a defined point in time. That task involves synthesis of large molecules that under the right conditions of solvent polarity (i.e., working just below their solubility limit) will behave, effectively, as primary particles. Those primary particles will be based on star or dendritic molecules built on symmetric or elongated cores. The catalyst-induced polymerization chemistry of choice will rely on ROMP.

Status:

After some initial experimentation with elongated cores derived from methylene *p*-diphenyldiisocyanate (MDI), we realized that the behavior of the sol and the properties of the derived aerogels were determined by the number of the polymerizable functional groups in the perimeter of the monomers, thus we did not pursue that *Specific Objective* further.

A.1.4 *Specific Objective 3*:

Understand the role of the innate electro-static/dynamic properties of elementary nanoparticles that direct assembly to fibers versus globules.

This part will be a computational study whereas our basic premise is that in order for nanoparticles to assemble into fibers they need to posses a vectorial property (e.g., dipole moment, polarizability), and therefore display an angle-dependent sticking probability. As shown in Section IV, preliminary computational studies using the diffusion-limited cluster aggregation (DLCA) model with spheres provided with a phenomenological angle-dependent sticking probability, not only support this hypothesis, but they are also able to predict branching between fibers as observed by SEM. Working with real systems (e.g., polyurea), we will use a combination of *ab initio* / force-field methods to construct primary nanoparticles from the monomer up, thus knowing not only all their electrical properties, but also the functional group density on their surface. Introducing those computed

> nanoparticles in the DCLA model, and perhaps with the use of explicit solvation, we should be able to predict the exact experimental structures, thus identifying the important electrical parameters of the nanoparticles, which are responsible for the formation of nanofibers.

Status:
We have developed a computational model for primary particles of polyurea formed by Van der Waals/H-bonding stacking of dendritic oligomers, and packing of those stacks again via the same kind of forces. The generation of the dendritic oligomers, the number of oligomers in the stacks and the number of oligomers in the packs was determined via Molecular Dynamics simulations stopped at the common cross-section of the calculated and experimental primary particle size, density and XRD pattern. A paper is in preparation.

In parallel, we established collaboration with Professor Changlin (Bob) Wu, a mechanical engineer of our Civil Engineering Department, and we are exploring computational aerogels as a means of elucidating the coupling of molecular and macroscopic properties over length scales (atomistic to meso to macro). A first paper was published in the fall of 2018 in *Soft Matter* and was selected for the cover of its issue.

Section B describes the technical results from our specific ARO-funded research activities above.

A.1.5 *Products*

Funding from W911NF-14-1-0369 supported 8 Ph.D. students. Additional funding in the summer of 2015 supported two high school students through the HSAP program. Funding from W911NF-14-1-0369 is acknowledged in 22 publications and 6 book chapters, resulted in 3 U.S. patents filed and issued within the funding period, 4 patent applications filed within the finding period and pending with the USPTO, 40 presentations in national and international meetings and 3 tutorials. Many of the posters presented in ACS National Meetings were selected for the SciMix Session.

B. Technical Results

B.1 The *K*-Index: A Quantifier, Descriptor, Predictor and Correlator of Nanomorphology to Other Material Properties

B.1.1. Summary of Prior Activities Leading to the *K*-index - Background

In 2010 we proposed that if polymeric aerogels could be made with the same nanostructure and nanomorphology as polymer-crosslinked aerogels, they should have similar mechanical properties. In the last 8 years that prediction has been confirmed with almost all mainstream polymers including phenolic aerogels and polybenzoxazines, isocyanate-derived aerogels (polyurethanes, polyureas, polyimides and polyamides), hydrocarbon aerogels (polydicyclopentadiene and polyacrylics) and molecular copolymers such as polyurethane-polyacrylonitrile, polyurethane-polyborbornene, polyurea-polyisocyanurate and polyurea-polyimide-polyamide random copolymers. All that activity was funded by W911NF-14-1-0369 (this grant) and ARO W911NF-10-1-0476 (our previous ARO grant).

Along those studies we noticed that depending on the synthetic conditions, several polymeric aerogels demonstrate a variety of nanomorphologies under the same chemical composition. The widest variety of nanostructures was noted with certain aliphatic polyureas. The new question that emerged at that point was whether those nanostructures could be prepared at will by predicting and using suitable synthetic conditions such as the monomer and catalyst concentration, and the solvent.

B.1.2. Summary of Findings (Abstract of paper submitted to *ACS Nano*)

Morphology is a qualitative property of nanostructured matter, and is articulated by visual inspection of micrographs. For deterministic procedures that relate nanomorphology to synthetic conditions, it is necessary to express nano/micro-structure numerically. Selecting polyurea aerogels as a model system with demonstrated potential for rich nanomorphology, and guided by a statistical Design-of-Experiments model, we prepared a very large array of polyurea aerogels with identical chemical composition, but quite different nanostructures. By reflecting on SEM imaging it was realized that our first pre-verbal impression about a nanostructure is related to its openness and texture; the former is quantified by porosity (Π), and the latter is oftentimes related to hydrophobicity, which in turn is quantified by the contact angle (θ) of water droplets resting on the material. Herewith, the θ/Π ratio is defined as *K*-index, and it was noticed that all polyurea samples of this study could be put in eight *K*-index groups (Figure 1) with unique nanomorphologies ranging from caterpillar-like assemblies of nanoparticles, to thin nanofibers, to cocoon-like structures, to large bald microspheres. A first validation of the *K*-index as a morphology descriptor was based on compressing samples to different strains: it was observed that as the porosity decreases, the water contact angle decreases proportionally, and the *K*-index remains constant. The predictive power of the *K*-index was demonstrated with 20 polyurea aerogels prepared in eight new binary solvent systems. Subsequently, several material properties were correlated to nanomorphology through the *K*-index and in turn, that provided insight about the origin of the diversity of the nanostructure in polyurea aerogels. Finally, using response surface methodology, *K*-indexes and other material properties of practical interest were correlated to the monomer, water and catalyst concentrations as well as the three Hansen Solubility Parameters of the sol. That enabled synthesis of materials with up to six prescribed properties at a time, including nanomorphology, bulk density, BET surface area, elastic modulus, ultimate compressive strength, and thermal conductivity.

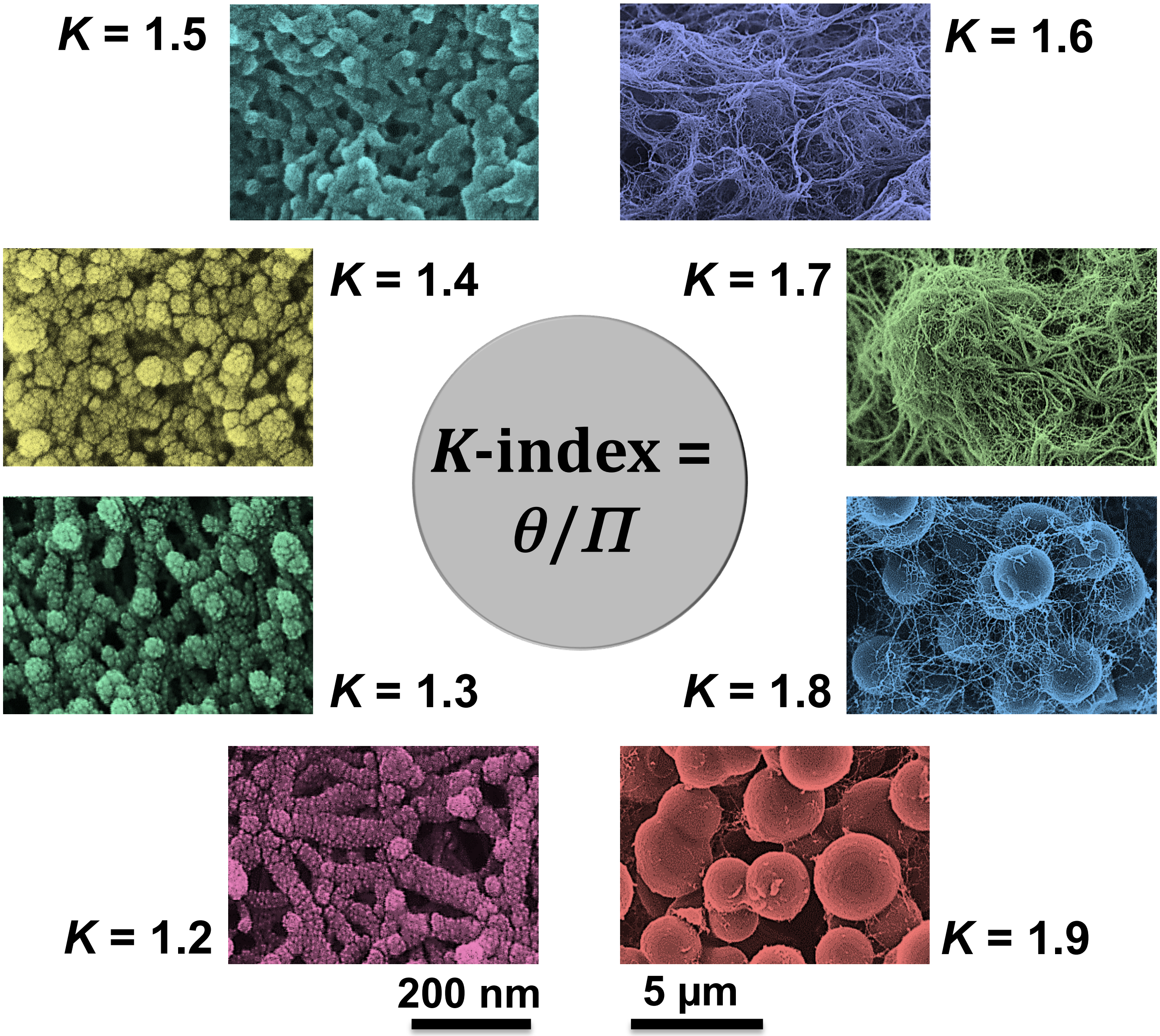


Figure 1. (Graphical Abstract of paper submitted to *ACS Nano*). Eight nanomorphology groups identified from 188 formulations prepared in 8 solvents. *K*-indexes were defined as the ratios of the water contact angles to the corresponding percent porosities (θ/Π).

B.1.3. Moving Forward

Quantification and prediction of the morphology of nanostructured polymers was the main objective of W911NF-14-1-0369. That objective has been fully accomplished. At this point, the concept of the *K*-index needs to be expanded to other nanoporous polymers. It will be particularly instructive to explore the effect of the chemical identity of the polymer, and whether the *K*-index that has been developed based on polyurea can be transferred to other materials. Prime candidates for those studies are sol-gel polymers that, depending on the synthetic conditions, show both fibrous and particulate nanostructures; those sol-gel polymers include certain polyimides and polydicyclopentadiene.

B.2 Superelastic and Shape Memory Poly(isocyanurate-urethane) Aerogels (PIR-PUR) and Fundamental Investigations of Mechanical Properties as a Function of Nanostructure

B.2.1. Summary of Findings

This project stemmed from *Specific Objective 1*, and was developed and carried out entirely within the funding period of ARO W911NF-14-1-0369. We demonstrated that aliphatic PIR-PUR aerogels show a robust shape memory effect and are suitable for deployable panels and as biomimetic devices (Figure 2). Our paper (*Chem. Mater*. **2017**, *29*, 4461-4477) was among the top 10 downloads in *Chem. Mater.* in May 2017, it was reviewed by the popular press around the world. A year later, in May 2018, NASA Tech Briefs wrote a surprising news item about those materials.

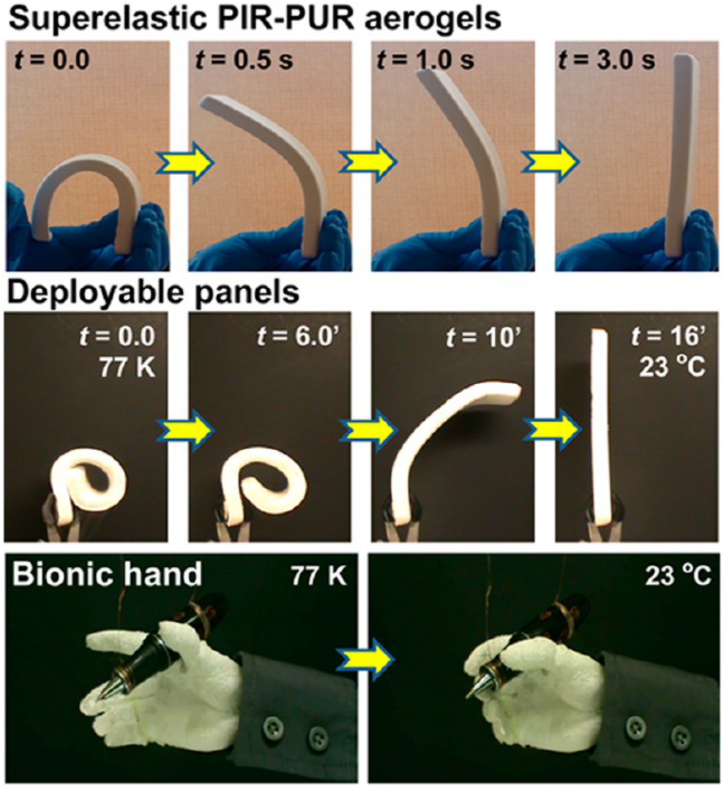
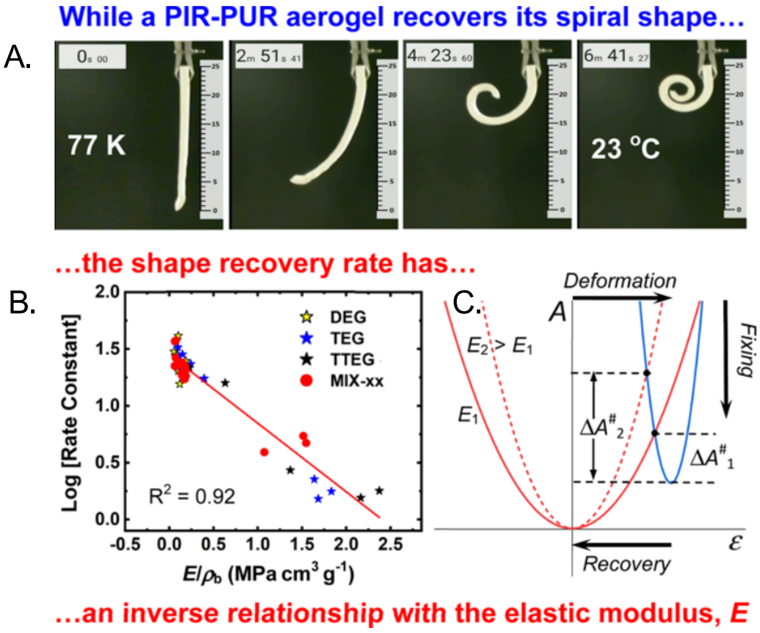


Figure 2. Superelastic PIR-PUR aerogels (top) show the shape-memory effect, and are suitable for deployable panels (middle) and biomedical applications (bottom).

Along those studies we noticed that the literature refers to the rate of shape recovery as an important parameter of the shape memory effect, however, we could not identify any means for quantifying said shape recovery rate. Thus we introduced an additional figure of merit for the shape memory effect, the shape recovery rate, and we noticed that it depends on the elastic modulus of the material in its deformable state (i.e., above its glass transition temperature – Figure 3B). Analysis of that behavior (Figure 3C) led to a fundamental Markus-type relationship between the activation free energy of the shape recovery rate ($A^{\#}$) and the density-normalized elastic modulus, $\mathcal{E}$ (Eq 1):

$$\Delta A^{\#} = \mathcal{E}\varepsilon_m^2\left(1-\frac{T_f}{2T_d}\right) \tag{1}$$


While a PIR-PUR aerogel recovers its spiral shape…

…the shape recovery rate has…

…an inverse relationship with the elastic modulus, *E*

Figure 3. (Graphical abstract of *ACS Appl. Mater. Interfaces* **2018**, 10, 23321-23334.) A. Shape recovery a PIR-PUR panel fabricated in a spiral form as its permanent shape. B. Shape recovery rate as a function of the elastic modulus. C. Parabolic profiles of the free energy (A) versus strain (ε) above (red) and below (blue) T_g. Marcus-type Eq. 1 that was derived from those profiles explains the thermodynamic-kinetic correlation of frame 3B.

Along those studies it was further noted that bicontinuous nanostrucures (Figure 4A) are stiffer than spheroidal morphologies (Figure 4B) and they recover their shape more slowly (right-hand side points in Figure 3C). That observation is at the cutting edge of research on the dependence of mechanical properties on nanomorphology.

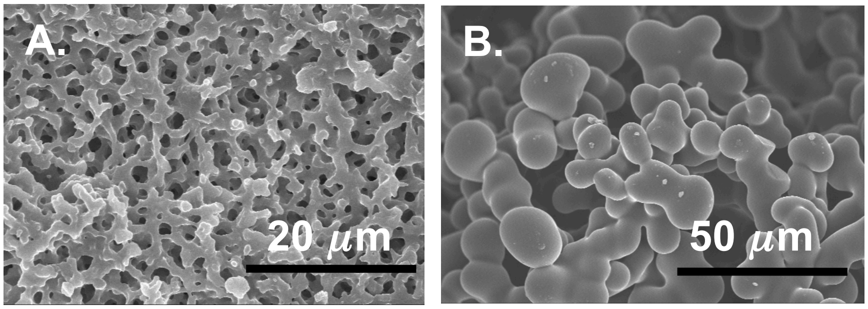


Figure 4. Bicontinuous (A) and spheroidal (B) microstructures of shape-memory PIR-PUR aerogels at the same composition, but different densities. The difference was attributed to gelation kinetics and triggered current activities described in section B.2.2. Preliminary results confirm that hypothesis.

The dependence of mechanical properties on nanomorphology is pursued further for its fundamental significance. To that end, it is important to prepare nanoporous polymers (not necessarily shape-memory) with the same chemical composition, same density, same porosity, but with radically different nanomorphologies (e.g., Figure 4). One way to bring about that effect is by working with polymers that gel via spinodal decomposition, and by accelerating or decelerating gelation with different catalysts. For this, we have developed new catalysts for polymerization of aliphatic alcohols with aliphatic isocyanates. Those catalysts are based on metal ions and bring gelation closer, or move it further away from the point of phase separation.

B.2.2 Moving Forward

(a) Other groups have already adopted our shape-memory polyurethane aerogels and are working towards applications. Most notably Professor H. Lu at UT-Dallas is exploring applications in acoustic insulation, while Professor F. Sabri at the University of Memphis is exploring biomedical applications, as for example casts in orthopedics.

(b) We have discovered that Cu^{2+} is at least 5 times more efficient catalyst for the polymerization of aliphatic alcohols and aliphatic isocyanates (such as those yields the morphologies of Figure 4) than conventional tin-based dibutyltindilaurate (DBTDL).

(c) We are in the process of quantifying the relative kinetics of our new metal-ion based catalysts using rheology.

(d) We are exploring the mechanical properties of superelastic polyurethane-polyisocyanurate aerogels as a function of the nanomorphology at exactly the same chemical composition, bulk density and porosity by employing the catalysts from (b). The only variable is the nanomorphology. Mechanical properties of interest include the elastic modulus, the ultimate strength and the energy absorption. We are working both under compression and under tension.

B.3 Carbon Aerogels as Catalyst Supports and Platform Materials for Gas Sorption and Separations

B.3.1 Background

Starting from the previous funding period (W911NF-10-1-0476), we have expended the list of carbon aerogel precursors well beyond the all-familiar phenolic resorcinol-formaldehyde aerogels. In this funding period (W911NF-14-1-0369) we have made several fundamental mechanistic discoveries on the carbonization process, and we have produced materials suitable for a number of diverse applications in catalysis and gas soprtion.

B.3.2 Fundamental Advances

- During the previous funding period (W911NF-10-1-0476) we discovered that "curing" polybenzoxazines (PBOs) in air causes oxidative ring-fusion aromatization, which in turn becomes responsible for increasing the carbonization yield from 27% to 62% w/w. In this funding period (W911NF-14-1-0369) we investigated whether ring-fusion aromatization plays a role in the carbonization of other main-stream phenolic resins (e.g., resorcinol-formaldehyde, phloroglucinol-formaldehyde, phloroglucinol-terephthaldehyde (abbreviated as TPOL), phenol-formaldehyde). We found out that oxidative ring-fusion aromatization takes place only in phloroglucinol–based phenolic resins (Figure 5), however, unlike in PBOs, it does not affect carbonization yields (at 800 ^{o}C under Ar); the only difference was that the resulting carbon aerogels from phloroglucinol-based phenolic aerogels had higher BET surface areas if before carbonization they were subjected to air oxidation at 240 ^{o}C. Along the way we also discovered that all oxygen that was retained in phenolic-resin derived carbons is exclusively in two forms: heteroaromatic O^+ (pyrylium) and charge-compensating O^- (phenoxide). That discovery was explored in gas sorption (see Section B.3.3 below).

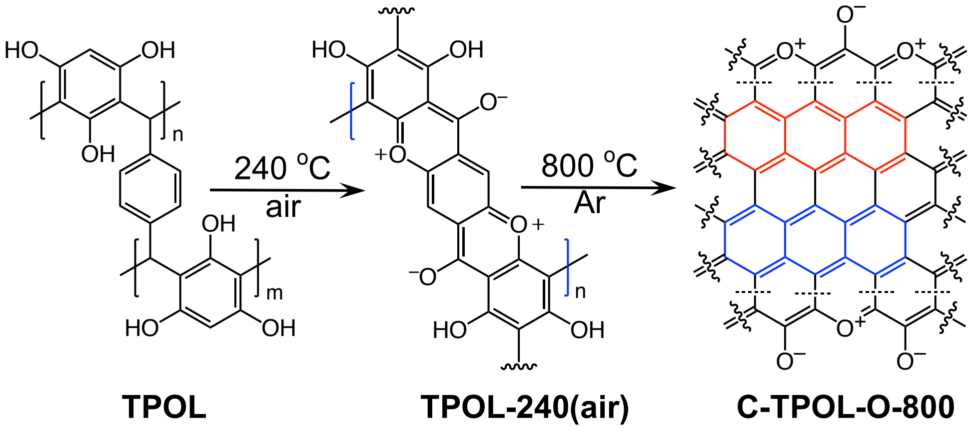


Figure 5. Air-oxidation of TPOL (see text) at 240 ^{o}C, followed by pyrolytic carbonization, revealed that carbons from phenolic resins contain fused pyrylium rings and phenoxides.

- During the previous funding period (W911NF-10-1-0476) we demonstrated polyamide aerogels from the reaction of triisocyanates and tricarboxylic acids. In this funding period (W911NF-14-1-0369) we attempted to expand those findings into inorganic polyamide aerogels prepared from triisocyanates and tribasic Brønsted mineral acids. Instead we discovered that that reaction does not yield inorganic polyamides, but rather polyureas (identical to those made via reaction of the same triisocyanates and water). The network remains doped with the side-product of that reaction, which is the oxide (or the element) of the mineral acid. Upon carbonization we obtained carbon aerogels doped with a network of Au, TeO_2, SeO_2 and As_2O_3 nanoparticles (Figure 6).
-

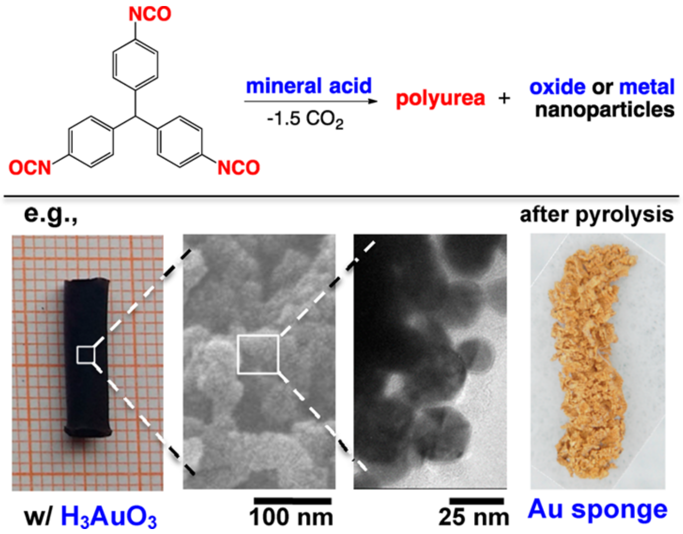
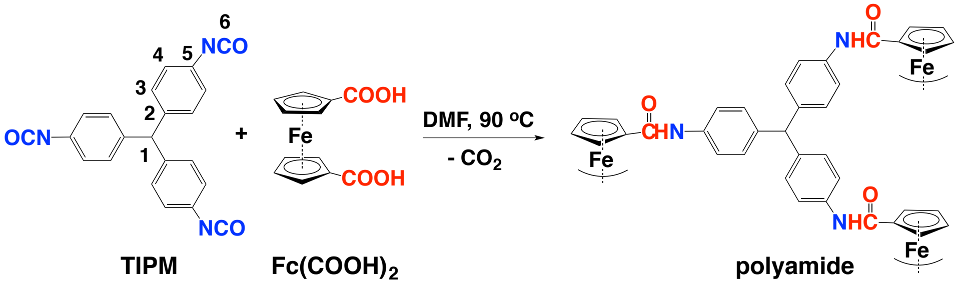


Figure 6. (Graphical abstract of *Chem. Mater.* **2016**, *28*, 67-78.) A triisocyanate reacting with a mineral acid yields polyurea aerogels doped with nanoparticles of the anhydride of the mineral acid (an oxide) or the element (case of precious metals). This is demonstrated with auric acid. After carbonization, the network is doped with a nanostructured Au sponge.

B.3.3 Applications

- We applied our patented method of synthesizing polyamide aerogels from isocyanates and carboxylic acids to a new type of monomer: ferrocene dicarboxylic acid ($Fc(COOH)_2$ – Eq 2).

 (2)

The resulting polyamide contains one ferrocene moiety in every polymer repeat unit. Pyrolysis of those materials yielded carbon aerogels doped with Fe(0) nanoparticles (Figure 7). Because Fe(0) is a good graphitization catalyst, Fe(0) nanoparticles were shrouded in graphitic ribbons. Fe(0) could be transmetallated galvanically with ions of various precious metals yielding carbon aerogels doped with Au, Pt, Pd nanoparticles. All those metal-doped monolithic carbon aerogels demonstrated excellent catalytic activity. They could be picked up with a pair of tweezers and redeployed immediately in a new reaction mixture. Remarkably, we were awarded a U.S. patent faster than the paper (*Chem. Mater.* **2016**, *28*, 4867-4877) was published.

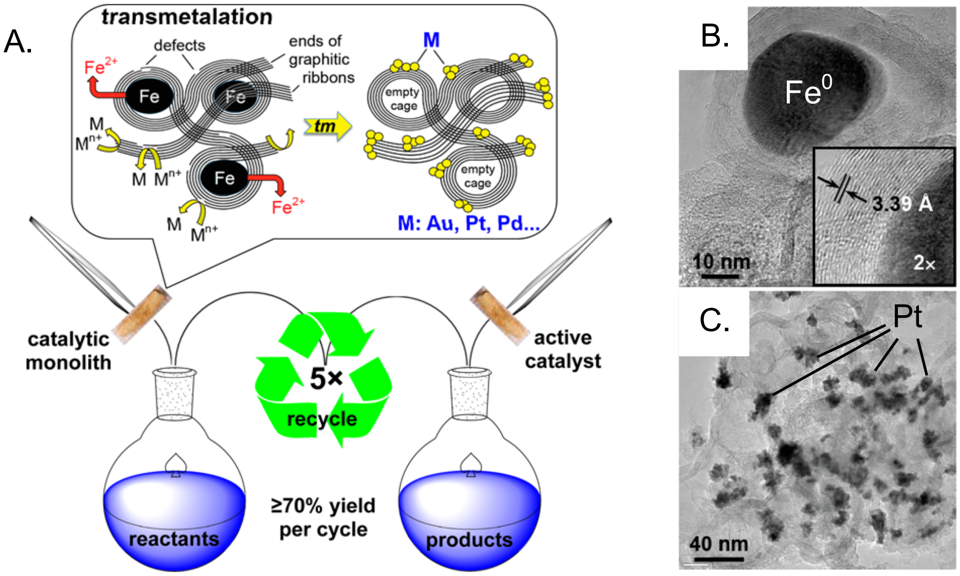
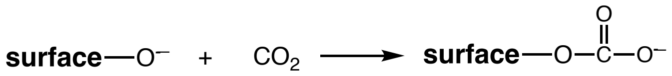
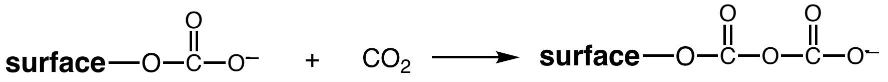


Figure 7. (A) Graphical abstract of *Chem. Mater.* **2016**, *28*, 4867-4877. (B) After pyrolysis of polyimide aerogels bearing one ferrocene moiety per polymer repeat unit, the resulting carbons contain Fe(0) nanoparticles shrouded in graphitic ribbons. (C) Galvanic transmetallation with precious metal ions replaces Fe(0) with much smaller precious metal nanoparticles (e.g., Au, Pt, Pd – case shown: Pt). All metal-doped monolithic carbon aerogels are efficient catalysts that can be reused by just picking them up with a pair of tweezers and placing them in a new reaction mixture as shown in frame 7A.

- We have investigated the CO_2 uptake capability of all our microporous carbon aerogels. Uniformly, the CO_2 uptake was among the best reported in the literature for all kinds of adsorbers including MOFs, COFs and other microporous materials. Blue bars in Figure 8 show the performance of our materials. Only-oxygen containing carbons (that is carbons from RF, TPOL, FPOL and PF) displayed higher CO_2 uptake capacity than those containing nitrogen (that is carbons from polybenzoxazines (PBOs) and polyamides (PA). That behavior has been attributed to an isoenthalpic reaction between surface $–O^-$ and CO_2 (Equations 3 and 4) that is entropically favorable only when it takes place within micropores, because in order to enter micropores CO_2 has already paid the entropic penalty associated with the loss of its degrees of freedom by condensing down to a surface.



$$\text{surface}{-}O^- + CO_2 \longrightarrow \text{surface}{-}O{-}\overset{\overset{O}{\parallel}}{C}{-}O^- \quad (3)$$



$$\text{surface}{-}O{-}\overset{\overset{O}{\parallel}}{C}{-}O^- + CO_2 \longrightarrow \text{surface}{-}O{-}\overset{\overset{O}{\parallel}}{C}{-}O{-}\overset{\overset{O}{\parallel}}{C}{-}O^- \quad \text{etc.} \quad (4)$$

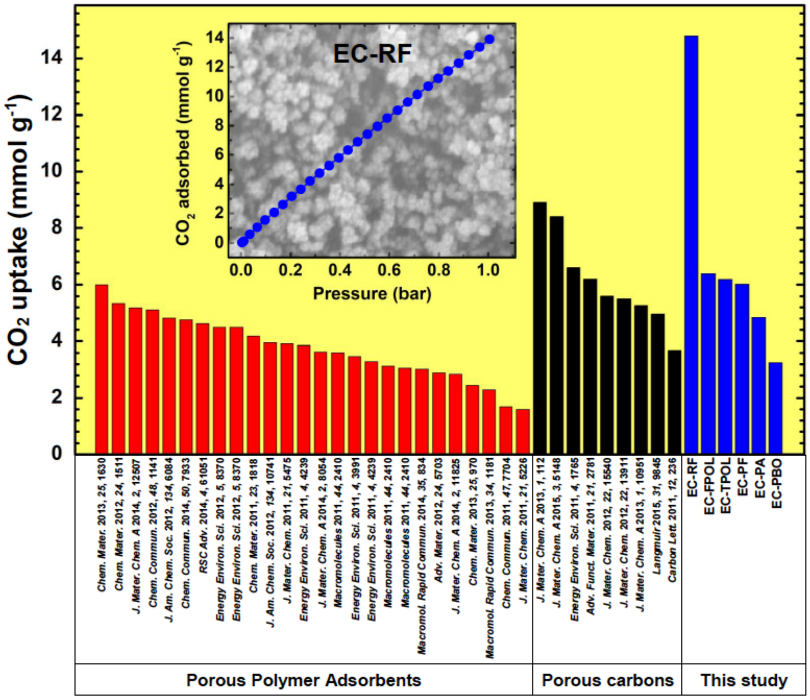


Figure 8. Comparison of CO_2 adsoprtion by our materials at 1 bar and 273 K with other superior CO_2 sorbents from the literature, including porous carbons. Inset: SEM and CO_2 adsorption isotherm at 273 K of the best performer: EC-RF carbon. (Other materials are identified with their bibliographic reference. Our materials are described in *Macromol. Chem. Phys.* **2019**, *220*, 1800333.)

B.3.4 Moving Forward

The mineral acid approach to metal- or oxide-doped carbon aerogels is pretty straightforward and can be expanded by using any kind of hydrated metal salt, $[M(H_2O)_6]^{n+}$, as the Brønsted acid in the reaction with the aromatic triisocyanates.

The entropic argument for the high uptake CO_2 by microporous carbons is very powerful. It implies that many other adsorbates can go in and out of micropores suitably lined to effect near-neutral enthalpic interactions with the adsorbates. That concept has been put to practice with polyurethane aerogels containing one cyclodextrin moiety in every polymer repeat unit. Cyclodextrin is a natural microcavity molecule decorated with many hydroxyl groups and develops H-bonding interactions with water. Cyclodextrin-based polyurethane aerogels can absorb water vapor, over 100% their weight, from moist environments. Desorption is affected by just changing the relative humidity of the environment – no heating is required. A publication is in preparation.

B.4 Monolithic Metal and Ceramic Aerogels

B.4.1 Summary of Findings

Starting in 2015, we have developed, published and filed for a patent on the synthesis of ceramic and metallic monolithic aerogels from xerogel powders, whose elementary primary particles are coated with a carbonizable polyurea derived from TIPM (Figure 9). Using xerogels as precursors has decoupled aerogel synthesis from drying with supercritical fluids; using xerogels in *powder* form has liberated us from handling delicate aerogels. Monoliths are created from compacts of powders compressed to shaped objects, while aerogel porosity is created when the carbonizable polymer reacts away with the underlying oxide. Our first paper (2018) demonstrated the method with ceramic aerogels (SiC and $S_{i3}N_4$) prepared from silica xerogel powders (Figure 9).

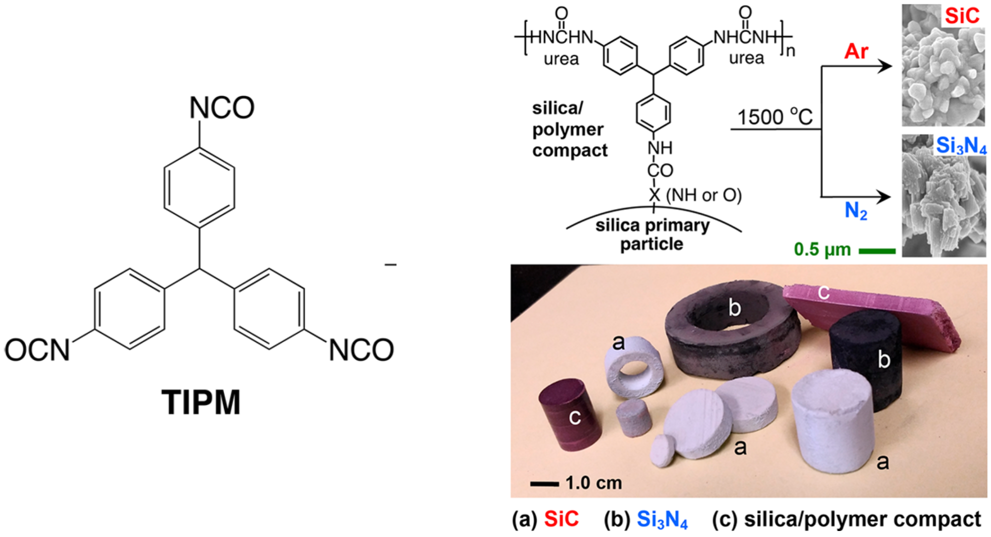


Figure 9. TIPM reacts with water adsorbed on the silica primary particles and produces a conformal polyurea coating around those particles. By 800 °C TIPM-derived polyurea yields carbon. By 1500 °C carbon reacts with underlying silica and yields SiC under Ar, and Si_3N_4 under N_2. (From Graphical Abstract of *Chem. Mater.* **2018**, *30*, 1635-1647.)

By employing polymer-coated cobaltia xerogel powders, we have obtained Co(0) aerogels. The porous space of those aerogels was filled completely with $LiClO_4$ uptaken from a melt of the salt. Figure 10 shows such a Co(0)/$LiClO_4$ disc after ignition with an electrical resistor. During reaction discs glow white, Co(0) is oxidized completely to Co(II), and the final object consists of CoO (by XRD) and had ~0% porosity suggesting that the temperature had reached at least the m.p. of Co (1495 °C).

Figure 10. ***The Cobalt Sun***: A Co(0)/$LiClO_4$ thermite disk (3 cm in diam.), after thermal ignition with an electrical resistor (wire) wrapped around it. (Still image captured from video 26 s after ignition: current to the wire is turned off and only part of the disc still glows white. The disc was glowing red for another 20 s.)

B.4.2 Moving Forward

B.4.2.1 Replacing isocyanate chemistry. The carbonizable polymer we have been using so far is a polyurea that is obtained from reaction of TIPM (Figure 9) with gelation water remaining adsorbed on the inorganic skeletal framework. The inorganic framework is engaged via reaction of N=C=O groups from TIPM with surface –OH.

That technology works very well and is generalizable. Nevertheless, as the technology becomes broadly accepted we seek to develop alternatives to the isocyanate chemistry. In that regard, we are developing free-radical chemistry in which an initiator (AIBN) is immobilized on the nanoparticle surface and is triggered thermally to induce polymerization of acrylonitrile. Being the industrial choice for the production of graphite fiber, polyacrylonitrile (PAN) is a reliable source of carbon.

B.4.2.2 Other porous metallic systems of interest. Carbothermal reduction works well with several oxides that produce carbides (of Si, Ti, Cr, Zr, Hf), nitrides (Si) and borides (Zr), and only a limited list of oxides that yield metals in the elemental form (Fe, Co, Ni, Ru, Sn, Cu). However, there is a long list of metals of interest that remain as oxides through a carbothermal process – those include all the rare earth elements. One of the reasons rare earths in elemental form are interesting is because they comprise the basis for rare earth magnets – most notably Sm-Co and Nd-Fe-B. Rare earth oxides are reduced either electrochemically, or with strongly reducing metals in what is referred to as metallothermic synthesis. Ca has been the most common reducing agent.

Co-gelation of samarium and cobalt salts yields Sm oxide / Co oxide xerogel powders according to the protocol of *Chem. Mater.* **2018**, *30*, 1635-1647. As it has turned out, the two oxides are intermingled at the atomic level. That is, we did not obtain an interpenetrating network of Sm oxide and Co oxide nanoparticles, but rather a mixed oxide network: Sm-O-Co-O-Sm etc. Similar results have been obtained with Nd-Fe-B.

We will implement all of the above in the metallothermic synthesis of porous rare earth magnets. One of the targeted applications is efficient magnetophoretic separation of rare earths from lower-yield ores along the quest for independence from foreign sources.

B.5 Experimental and Computational Bridging of Load Transfer Across Lengthscales: Multi-scale progressive failure mechanism and mechanical properties of nanofibrous polyurea aerogels (in collaboration with Dr. Chenglin Wu)

B.5.1 Abstract of *Soft Matter* 2018, *14*, 7801-7808. The nonlinear mechanical properties, deformation and failure mechanisms of polyurea aerogels (PUAs) were investigated using a multi-scale approach that combines nanoindentation, analytical and computational modeling. The atomistic structure of primary particles of PUAs and their mechanical interactions were investigated with molecular dynamics simulations. From nanoindentation we identified four deformation and failure modes: free ligament buckling, cell ligament bending, stable cell collapsing, and ligament crush induced strain hardening. The corresponding structural evolution during indentation and strain hardening were analyzed and modeled. The material scaling properties were found to be dependent on both the relative density and the secondary particle size of PUAs. Using a porositydependent material constitutive model, a linear relationship was found between the strain hardening index and secondary particle size instead the conventional power-law relationship. Finally, the structural efficiency of PUAs with respect to the capability for energy absorption is evaluated as a function of structural parameters and base polymeric material properties.

The cover of that issue emphasized the use of nanoindentation for the identification of the deformation and failure modes (Figure 11).

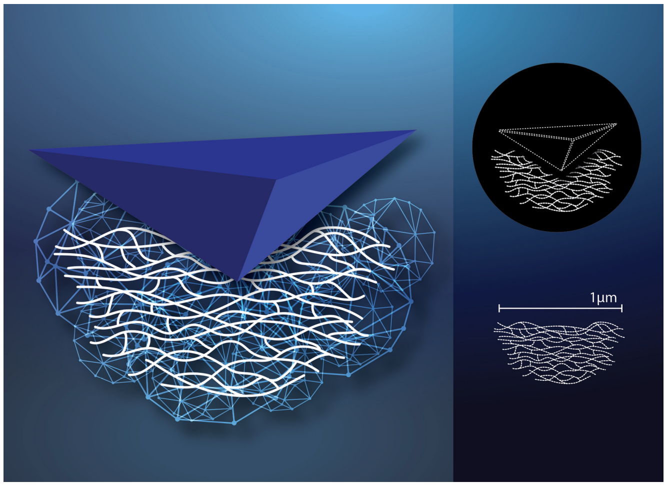


Figure 11. Cover the September 2018 issue of *Soft Matter* showing the use of a nanoindenter to probe the mechanical deformation and failure modes of polyurea aerogels.

C. Students Supported by W911NF-14-1-0369

C.1 *Graduate Students Involved and Supported (8)*

Shaheen Doulah	Ph.D. 2022	
Rushi U. Soni	Ph.D. 2021	
Chandana Mandal	Ph.D. 2019	(will join Intel Corp. at OR)
Parwani Rewatkar	Ph.D. 2019	(will return to India)
Tahereh Tagvahee	Ph.D. 2019	(will postdoc)
Suraj Donthula	Ph.D. 2018	(currently with Intel Corp. at OR)
Hojat Majedi Far	Ph.D. 2018	(will postdoc)
Adnan Malik Saeed	Ph.D. 2016	(currently with Intel Corp. at OR)

C.2 *Graduate Student Involved, not Supported (1)*

Tyler M. Fears	Ph.D. 1015	(currently stuff at the LLNL)

C.3 *Undergraduate Student Involved, not Supported (1)*

T. K. Shruthi	Summer 2015 BOSH Scholar supported by the India Government (currently a chemistry Ph.D. student at MSU)

C.4 *High School Students Involved and Supported via the ARO HSAP in 2015 (2)*

James Schisler	Summer 2015 (currently a Senior in chemistry at Washington U.)
Theodora Leventis	Summer 2015 (currently a Senior in chemistry at MU-Columbia)

D. Publications Acknowledging Support from W911NF-14-1-0369

(Total: 22; In Preparation: 3; Submitted: 1; In press: 18)

1. “Cobalt Sun: Thermites based on Metallic Cobalt Aerogels with Porosities completely filled with $LiClO_4$,” P. Rawetkar, R. Soni, C. Sotiriou-Leventis, N. Leventis (in preparation).

2. “High, Reversible Moisture Adsorption at Ambient Conditions by Multiscale Hierarchical Nanoporous Polyurethane Aerogels based on α- and β-Cyclodextrin,” P. Rawetkar, H. Majedi Far, C. Sotiriou-Leventis, N. Leventis (in preparation).

3. “The Internal Structure of Primary Particles in Polymeric (Polyurea) Aerogels via Bottom-up Molecular Dynamic Simulations,” T. Taghvaee, H. Yaghoobnejad, C. Wu, N. Leventis (in preparation).

4. “*K*-index: A Quantitative Correlator of Complex Nanomorphology, Synthetic Conditions and Material Properties,” T. Taghvaee, S. Donthula, P. Rewatkar, H. Majedi Far, C. Sotiriou-Leventis, N. Leventis, *ACS Nano* (submitted).

5. “Exceptionally High CO_2 Adsorption at 273 K by Microporous Carbons from Phenolic Aerogels: The Role of Heteroatoms in Comparison with Carbons from Polybenzoxazine and Other Organic Aerogels,” H. Majedi Far, P. M. Rewatkar, S. Donthula, T. Taghvaee, A. M. Saeed, C. Sotiriou-Leventis, N. Leventis, *Macromolecular Chem. Phys.* **2019**, *220*, 1800333 (Invited for special issue honoring Professor H. Ishida’s 70th birthday.)

6. “Multi-scale Progressive Failure Mechanism and Mechanical Properties of Nanofibrous Polyurea Aerogels,” C. Wu, T. Taghvaee, C. Wei, A. Ghasemi, G. Chen, N. Leventis, Wei Gao, *Soft Matter* **2018**, *14*, 7801-7808 (Selected for Cover Page - DOI: 10.1039/c8sm01546e)

7. “Nanostructure-Dependent Marcus-Type Correlation of the Shape Recovery Rate and the Young’s Modulus in Shape Memory Polymer Aerogels,” S. Donthula, C. Mandal, J. Schisler, T. Leventis, M. A. B. Meador, C. Sotiriou-Leventis, N. Leventis, *ACS Appl. Mater. Interfaces* **2018**, *10*, 23321-23334.

8. “Scalable, Hydrophobic and Highly-stretchable Poly(isocyanurate–urethane) Aerogels,” S. Malakooti, S. Rostami, H. G. Churu, H. Luo, J. Clark, F. Casarez, O. Rettenmaier, S. Daryadel, M. Minary-Jolandan, C. Sotiriou-Leventis, N. Leventis, H. Lu, *RSC Adv.* **2018**, *8*, 21214-21223.

9. “Sturdy, Monolithic SiC and Si_3N_4 Aerogels from Compressed Polymer-Cross-Linked Silica Xerogel Powders,” P. M. Rewatkar, T. Taghvaee, A. M. Saeed, S. Donthula, C. Mandal, N. Chandrasekaran, T. Leventis, T. K. Shruthi, C. Sotiriou-Leventis, N. Leventis, *Chem. Mater.* **2018**, *30*, 1635-1647.

10. “Sound Insulation Properties in Low-Density, Mechanically Strong and Ductile Nanoporous Polyurea Aerogels,” Malakooti, S.; Churu, H. G.; Lee, A.; Xu, T.; Luo, H.; Xiang, N.; Sotiriou-Leventis, C.; Leventis, N.; Lu, H. *J. Non-Cryst. Solids* **2017**, *476*, 36-45.

11. “Air-oxidation of Phenolic Resin Aerogels: Backbone Reorganization, Formation of Ring-Fused Pyrylium Cations, and the Effect on Microporous Carbons with Enhanced Surface Areas,” H. Majedi Far, S. Donthula, T. Taghvaee, A. M. Saeed, Z. Garr, C. Sotiriou-Leventis, N. Leventis *RSC Advances* **2017**, *7*, 51104–51120.

12. “Shape-Memory Poly(isocyanurate-urethane) (PIR-PUR) Aerogels for Deployable Panels and Biomimetic Applications,” S. Donthula, C. Mandal, T. Leventis, J. Schisler, A. M. Saeed, C. Sotiriou-Leventis, N. Leventis, *Chem. Mater.* **2017**, *29*, 4461-4477 (most visited in May 2017).

13. “Selective CO_2 Sequestration with Monolithic Bimodal Micro/Macroporous Carbon Aerogels Derived from Stepwise Pyrolytic Decomposition of Polyamide-Polyimide-Polyurea Random Co-polymers,” A. M. Saeed, P. M. Rewatkar, H. Majedi Far, T. Taghvaee, S. Donthula, C. Mandal, C. Sotiriou-Leventis, N. Leventis, *ACS Appl. Mater. Interfaces* **2017**, *9*, 13520-13536.

14. “Reusable Monolithic Nanoporous Graphite-supported Nanocatalysts (Fe, Au, Pt, Pd, Ni and Rh) from Pyrolysis and Galvanic Transmetalation of Ferrocene-Based Polyamide Aerogels,” A. M. Saeed, C. A. Wisner, S. Donthula, H. Majedi Far, C. Sotiriou-Leventis, N. Leventis, *Chem. Mater.* **2016**, *28*, 4867-4877.

15. “Economical Synthesis of Vanadia Aerogels via Epoxide-Assisted Gelation of $VOCl_3$,” T. M. Fears, C. Sotiriou-Leventis, J. G. Winiarz, N. Leventis, *J. Sol-Gel Sci. Technol.* **2016**, *77 (1)*, 244-256.

16. “Nanoporous Polyurea from a Triisocyanate and Boric Acid: A Paradigm of a General Reaction Pathway for Isocyanates and Mineral Acids,” N. Leventis, C. Sotiriou-Leventis, A. M. Saeed, S. Donthula, H. Majedi Far, P. M. Rewatkar, H. Kaiser, J. D. Robertson, H. Lu, G. Churu *Chem. Mater.* **2016**, *28*, 67-78.

17. “Ferrocene-Based Polyamide Aerogels: Graphitization, Transmetalation, and Use in Heterogeneous Catalysis,” M. A. Saeed, C. A. Wisner, S. Donthula, A. Mumtaz, C. Sotiriou-Leventis, N. Leventis *PMSE Preprints* **2015**, Vol. *112*.

18. “Shape Memory Polyurethane Aerogels,” S. Donthula, F. Zheng, C. Sotiriou-Leventis, N. Leventis *PMSE Preprints* **2015**, Vol. *112*.

19. “Synthesis and Characterization of Robust Terephthalaldehyde-Phloroglucinol (TPOL) Aerogels as Precursors for Nanoporous Carbons,” H. M. Far, A. M. Saeed, N. Leventis, C. Sotiriou-Leventis *PMSE Preprints* **2015**, Vol. *112*.

20. “Synthesis and Mechanical Characterization of Mechanically Strong, Polyurea-Crosslinked, Ordered Mesoporous Silica Aerogels,” G. Churu, B. Zupančič, D. Mohite, C. Wisner, H. Luo, I. Emri, C. Sotiriou-Leventis, N. Leventis, H. Lu *J. Sol-Gel Sci Technol.* **2015**, *75*, 98-123.

21. “Polydicyclopentadiene Aerogels from 1st *vs* 2nd Generation Grubbs’ Catalysts: A Molecular *vs* a Nanoscopic Perspective,” A. Bang, D. Mohite, A. M. Saeed, N. Leventis, C. Sotiriou-Leventis *J. Sol-Gel Sci Technol.* **2015**, *75*, 460-474.

22. “Flexible Aerogels from Hyperbranched Polyurethanes: Probing the Role of Molecular Rigidity with Poly(urethane acrylates) versus Poly(urethane norbornenes),” A. Bang, C. Buback, C. Sotiriou-Leventis, N. Leventis *Chem. Mater.* **2014**, *26*, 6979-6993.

E. Book Chapters Acknowledging Support from W911NF-14-1-0369

E.1 *Published (1)*

1. “HCl-Catalyzed Polymerization of Benzoxazine and Chemical Transformations along Carbonization,” N. Leventis, S. Donthula in *Advanced and Emerging Polybenzoxazine Science and Technology*, Ishida, H.; Froimowicz, P. Eds. Elsevier: Amsterdam, 2016, Chapter 34.

E.2 *Submitted (5)*

1. “Polymer Crosslinked Aerogels,” N. Leventis, C. Sotiriou-Leventis, C. Mandal, H. Lu in *Springer Handbook of Aerogels*, M. Aegerter, N. Leventis, M. Koebel, S. S. Steiner Eds. Springer: New York, N.Y. 2019.

2. “Isocyanate-derived Aerogels,” N. Leventis in *Springer Handbook of Aerogels*, M. Aegerter, N. Leventis, M. Koebel, S. S. Steiner Eds. Springer: New York, N.Y. 2019.

3. “Interpenetrating Phenolic/Oxide Networks and Carbothermal Synthesis of Metallic Aerogels as Energetic Materials,” N. Leventis, C. Sotiriou-Leventis, S. Donthula in *Springer Handbook of Aerogels*, M. Aegerter, N. Leventis, M. Koebel, S. S. Steiner Eds. Springer: New York, N.Y. 2019.

4. “Phenolic-type Aerogels and Derived Carbons: The Paradigms of Resorcinol-Formaldehyde and Polybenzoxazine Chemistries, C. Sotiriou-Leventis, N. Leventis, S. Mulik in *Springer Handbook of Aerogels*, M. Aegerter, N. Leventis, M. Koebel, S. S. Steiner Eds. Springer: New York, N.Y. 2019.

5. “Mechanical Characterization of Aerogels,” H. Luo, S. Malakooti, H. G. Churu, N. Leventis, H. Lu in *Springer Handbook of Aerogels*, M. Aegerter, N. Leventis, M. Koebel, S. S. Steiner Eds. Springer: New York, N.Y. 2019.

F. Patents from W911NF-14-1-0369

F.1 *Filed and issued in the funding period (3)*

1. "Flexible to Rigid Nanoporous Polyurethane-Acrylate (PUAC) Type Materials for Structural and Thermal Insulation Applications," N. Leventis, C. Sotiriou-Leventis, A. Bang, U.S. Patent No. 9,994,516 (06-12-2018; filed 10-31-2016).

2. "Multifunctional Porous Aramids (Aerogels) and Fabrication Thereof," N. Leventis, C. Sotiriou-Leventis, M. Adnan Saeed, U.S Patent No. 9,593,225 (03-14-2017; filed 10-31-2014).

3. "Multifunctional Porous Aramids (Aerogels) and Fabrication Thereof," N. Leventis, C. Sotiriou-Leventis, M. Adnan Saeed, U.S Patent No. 9,260,581 (02-16-2016; filed 10-31-2014).

F.2 *Filed in the funding period and pending (4)*

1. "Novel Highly Porous Ceramic and Metal Aerogels from Xerogel Powder Precursors, and Methods for their Production and Use," N. Leventis, C. Sotiriou-Leventis, M. A. Saeed, P. Rewatkar, T. Taghvaee (filed 04-06-2018).

2. "Selective CO_2 Sequestration with Monolithic Bimodal Micro/Macroporous Carbon Aerogels Derived from Polyamide-Polyimide-Polyurea Random Co-polymers," N. Leventis, C. Sotiriou-Leventis, M. A. Saeed (filed 03-23-2017).

3. "Process for Producing Isocyanate-based Xerogels and Aerogels with Mineral Acids," N. Leventis, C. Sotiriou-Leventis, A. M. Saeed, W. Loelsberg, M. Fricke, D. Weinrich, U.S. Patent Application (filed by BASF on 10-16-2015).

4. "Organic and Metallic Aerogels, Composition, for the Organic and Metallic Aerogels, and Method for Manufacturing the Organic and Metallic Aerogels," N. Leventis, C. Sotiriou-Leventis, S. Mahadik-Khalnorkar, U.S. Patent Application (filed 04-08-2015).

G. Tutorials Acknowledging Support from W911NF-14-1-0369

1. “Characterization of Nanoporous Materials,” N. Leventis, Pre-conference Tutorial - Spring 2017 MRS Meeting, Phoenix, AZ, April 17, 2017 (13:15-13:40 pm).

2. “From Phenolic to Fe(0) Aerogels for Energetic Materials – An Integrated View,” N. Leventis, Pre-conference Tutorial - Spring 2017 MRS Meeting, Phoenix, AZ, April 17, 2017 (9:00-9:20 am).

3. “Isocyanate Derived Aerogels: Polyurethanes and Polyureas, but also Polyimides, Polyamides and Co-Polymers,” N. Leventis, Pre-conference Tutorial - Spring 2017 MRS Meeting, Phoenix, AZ, April 17, 2017 (8:35-9:00 am).

H. Presentations Acknowledging Support from W911NF-14-1-0369

Total: 40
Invited & Keynotes: 9
Invited for the SCI-Mix at ACS Meetings: 8
Foreign: 5

1. "*K*-index: A Quantitative Correlator of Complex Nanomorphology, Synthetic Conditions and Material Properties," N. Leventus, T. Taghvaee, S. Donthula, C. Sotiriou-Leventis, ACAC2018, National and Kapodistrian University of Athens (NKUA), Greece, October 30, 2018 (Conference celebrating the 100th Anniversary of the Chemistry Department at the NKUA – Invited Keynote Lecture.)

2. "*K*-index: A Quantitative Tool that Correlates Complex Polymeric Nanomorphologies with Synthetic Conditions," N. Leventis, T. Taghvaee, S. Donthula, C. Sotiriou-Leventis, 256th ACS National Meeting, Boston, MA, Wednesday, August 22, 2018 (Porous Polymer Symposium - PMSE 679).

3. "Sturdy, Monolithic SiC and Si_3N_4 Aerogels from Compressed Polymer-Crosslinked Silica Xerogel Powders," P. Rewatkar, T. Taghvaee, A. M. Saeed, S. Donthula, C. Mandal, N. Chandrasekaran, T. Leventis, T. K. Shruthi, C. Sotiriou-Leventis, N. Leventis, 256th ACS National Meeting, Boston, MA, Wednesday, August 22, 2018 (INOR 748)

4. "Nanomaterials in 3D: A 20-Year Adventure from Mechanically Strong Polymer-Crosslinked Aerogels to Porous Metals and Ceramics," N. Leventis, 255th ACS National Meeting, New Orleans, LA, Monday, March 19, 2018 (PMSE 168 – Advances in Macromolecular Science & Engineering: Symposium in honor of David Schiraldi – Invited).

5. "Oxidative Ring-fusion Aromatization and its Role to Pyrolytic Carbonization of Polybenzoxazines and Other Phenolic Resins," N. Leventis, S. Donthula, H. Majedi Far, S. Mahadik-Khanolkar, C. Mandal, A. M. Saeed, C. Sotiriou-Leventis, 255th ACS National Meeting, New Orleans, LA, Monday, March 19, 2018 (PMSE 137 – Third International Symposium on Polybenzoxazines: Towards Diamond Jubilee of Benzoxazine Chemistry).

6. "Oxidative Ring-fusion Aromatization and its Role to Pyrolytic Carbonization of Polybenzoxazines and Other Phenolic Resins," N. Leventis, S. Donthula, H. Majedi Far, S. Mahadik-Khanolkar, C. Mandal, A. M. Saeed, C. Sotiriou-Leventis, 255th ACS National Meeting, New Orleans, LA, Monday, March 19, 2018 (SCI-MIX PMSE 137 - Invited).

7. "Nanotechnology in 3D: From Mechanically Strong Polymer-Crosslinked Aerogels to Nanoporous Shape-Memory Polyurethanes, Metals and Ceramics," N. Leventis, Department of Macromolecular Science and Engineering, Case Western Reserve University, 02-23-2018.

8. “Multiscale Hierarchical Nanoporous Polyurethane Aerogels Based on α- and β-Cyclodextrin for CO_2 Sequestration, Water Vapor Uptake and Cationic Dye Separation,” P. M. Rewatkar, M. A. Saeed, S. Donthula, H. Majedi Far, N. Leventis, C. Sotiriou-Leventis, 52nd ACS Midwest Regional Meeting, Lawrence, KS, October 18, 2017 (SCI-MIX - Invited).

9. “Highly Porous SiC & Si_3N_4 Monoliths via Carbothermal Reduction of Polymer-Crosslinked Sol-gel Silica Powder Compacts,” P. M. Rewatkar, T. Taghvaee, M. A. Saeed, S. Donthula, T. Leventis, J. Schisler, C. Sotiriou-Leventis, N. Leventis, 52nd ACS Midwest Regional Meeting, Lawrence, KS, October 20, 2017 (Materials Chemistry 514).

10. “Multiscale Hierarchical Nanoporous Polyurethane Aerogels Based on α- and β-Cyclodextrin for CO_2 Sequestration, Water Vapor Uptake and Cationic Dye Separation,” P. M. Rewatkar; M. A. Saeed, S. Donthula, H. Majedi Far, N. Leventis, C. Sotiriou-Leventis, 52nd ACS Midwest Regional Meeting, Lawrence, KS, October 20, 2017 (Materials Chemistry 525).

11. “*K*-Index: A Quantitative Tool that Describes Complex Soft-matter Nanomorphology and Correlates It to Synthetic Conditions,” T. Yazdeli, S. Donthula, C. Sotiriou-Leventis, N. Leventis, 52nd ACS Midwest Regional Meeting, Lawrence, KS, October 20, 2017 (Materials Chemistry 434).

12. “Significance of Inserting an Oxidative Ring-fusion Aromatization Step at the Early Stages of Pyrolytic Carbonization of Polybenzoxazines and Other Phenolic Resins,” H. Majedi Far, S. Donthula, S. Mahadik, T. Yazdeli, M. A. Saeed, N. Leventis, C. Sotiriou-Leventis, 52nd ACS Midwest Regional Meeting, Lawrence, KS, October 20, 2017 (Materials Chemistry 320).

13. “Shape Memory Superelastic Poly(isocyanurate-urethane) Aerogels (PIR-PUR) for Deployable Panels and Biomimetic Applications,” S. Donthula, C. Mandal, T. Leventis, J. Schisler, M. A. Saeed, C. Sotiriou-Leventis, N. Leventis, 52nd ACS Midwest Regional Meeting, Lawrence, KS, October 19, 2017 (Midwest ACS Graduate Awards Symposium 174).

14. “Polymeric Aerogels as a Point of Departure for Fundamental Mechanistic Studies – The Case of Polybenzoxazine and Other Phenolic Type Aerogels,” N. Leventis, S. Donthula, S. Mahadic-Khanolkar, H. Majedi Far, A. M. Saeed, C. Sotiriou-Leventis, Spring 2017 MRS Meeting, Phoenix, AZ, April 20, 2017 (NM3.10.03).

15. “Shape Memory Polyurethane Aerogels for Deployable Panels and Biomimetic Applications,” N. Leventis, S. Donthula, C. Mandal, J. Schisler, T. Leventis, C. Sotiriou-Leventis, Spring 2017 MRS Meeting, Phoenix, AZ, April 18, 2017 (NM3.3.02).

16. "Aerogel-Wise: Making Novel Heat Source Materials for Thermal Batteries," N. Leventis, The Future of Munitions Batteries Workshop, ARL-ALC, Adelphi, MD, December 8, 2016 (Invited)

17. "Reuseable Monolithic Nanoporous Graphite-Supported Nanocatalysts (Fe, Au, Pt, Pd, Ni, and Rh) from Pyrolysis and Galvanic Transmetalation of Ferrocene-Based Polyamide Aerogels," N**.** Leventis, M. A. Saeed, C. A. Wisner, S. Donthula, C. Sotiriou-Leventis, Athens International Catalysis Symposium, University of Athens, Greece, November 4, 2016 (Invited).

18. "Nanoporous Polyurea from Triisocyanates Reacting with Mineral Acids," M. A. Saeed, S. Donthula, H. Majedi Far, P. M. Rewatkar, C. Sotiriou-Leventis, N. Leventis, 251st ACS National Meeting, San Diego, CA, March 16, 2016 (PMSE 541)
https://ep70.eventpilotadmin.com/web/page.php?page=IntHtml&project=ACS16spring&id=2396362.

19. "One-step Synthesis of Highly Porous Silicon Nitride and Silicon Carbide from Polymer-Crosslinked Silica Aerogels," M. A. Saeed, P. M. Rewatkar, S. Donthula, C. Sotiriou-Leventis, N. Leventis, 251st ACS National Meeting, San Diego, CA, March 15, 2016 (PMSE 392)
https://ep70.eventpilotadmin.com/web/page.php?page=IntHtml&project=ACS16spring&id=2400259

20. "Multiscale Hierarchical Nanoporous Aerogels based on β-Cyclodextrin for CO_2 Sequestration," P. M. Rewatkar, M. A. Saeed, S. Donthula, H. Majedi Far, N. Leventis, C. Sotiriou-Leventis, 251st ACS National Meeting, San Diego, CA, March 15, 2016 (PMSE 393)
https://ep70.eventpilotadmin.com/web/page.php?page=IntHtml&project=ACS16spring&id=2400304

21. "Multiscale Hierarchical Nanoporous Aerogels based on β-Cyclodextrin for CO_2 Sequestration," P. M. Rewatkar, M. A. Saeed, S. Donthula, H. Majedi Far, N. Leventis, C. Sotiriou-Leventis, 251st ACS National Meeting, San Diego, CA, March 14, 2016 (SCI-MIX PMSE 393 – Invited)
https://ep70.eventpilotadmin.com/web/page.php?page=IntHtml&project=ACS16spring&id=2400304

22. "Carbothermal Synthesis of Nanoporous Metals and Carbide Aerogels from Interpenetrating Networks of Polymer-Oxide Nanoparticles," N. Leventis, NANOSA15, Max Plank Institute, Dresden, Germany, August 24, 2015.

23. "Ferrocene-based Polyamide Aerogels: Graphitization, Transmetalation and Use in Heterogeneous Catalysis," A. M. Saeed, C. Wisner, S. Donthula, A. Mumtaz, C. Sotiriou-Leventis, N. Leventis, Organic Chemistry Day, U. of Missouri-Columbia, Columbia, MO, April 11, 2015 (Paper No. 45).

24. “Multiscale Hierarchical Nanoporous Aerogels Based on β-Cyclodextrin,” P. M. Rewatkar, M. A. Saeed, S. Donthula, H. Majedi Far, N. Leventis, C. Sotiriou-Leventis, Organic Chemistry Day, U. of Missouri-Columbia, Columbia, MO, April 11, 2015 (Paper No. 44).

25. “Factors that Affect the Assembly of Organic Nanoparticles into Fibers vs. Clusters,” T. T. Yazdeli, S. Donthula, C. Sotiriou-Leventis, N. Leventis, Organic Chemistry Day, U. of Missouri-Columbia, Columbia, MO, April 11, 2015 (Paper No. 43).

26. “Shape-Memory Polyurethane Aerogels,” S. Donthula, F. Zheng, C. Sotiriou-Leventis, N. Leventis, Organic Chemistry Day, U. of Missouri-Columbia, Columbia, MO, April 11, 2015 (Paper No. 14).

27. “Synthesis and Characterization of Robust Terephthalaldehyde-Phloroglucinol (TPOL) Aerogels as Precursors for Nanoporous Carbons,” H. Majedi Far, A. M. Saeed, S. Donthula, N. Leventis, C. Sotiriou-Leventis, Organic Chemistry Day, U. of Missouri-Columbia, Columbia, MO, April 11, 2015 (Paper No. 03).

28. “Ferrocene-based Polyamide Aerogels: Graphitization, Transmetalation and Use in Heterogeneous Catalysis,” A. M. Saeed, C. Wisner, S. Donthula, A. Mumtaz, C. Sotiriou-Leventis, N. Leventis, 249th ACS National Meeting, Denver, CO, March 24, 2015 (PMSE 392).

29. “Synthesis and Characterization of Robust Terephthalaldehyde-phloroglucinol (TPOL) Aerogels as Precursors for Nanoporous Carbons,” H. Majedi Far, A. M. Saeed, S. Donthula, N. Leventis, C. Sotiriou-Leventis, 249th ACS National Meeting, Denver, CO, March 24, 2015 (PMSE 383).

30. “Shape-Memory Polyurethane Aerogels,” S. Donthula, F. Zheng, C. Sotiriou-Leventis, N. Leventis, 249th ACS National Meeting, Denver, CO, March 24, 2015 (PMSE 361).

31. “Ferrocene-based Polyamide Aerogels: Graphitization, Transmetalation and Use in Heterogeneous Catalysis,” A. M. Saeed, C. Wisner, S. Donthula, A. Mumtaz, C. Sotiriou-Leventis, N. Leventis, 249th ACS National Meeting, Denver, CO, March 23, 2015 (SCI-MIX-PMSE 392 - Invited).

32. “Synthesis and Characterization of Robust Terephthalaldehyde-Phloroglucinol (TPOL) Aerogels as Precursors for Nanoporous Carbons,” H. Majedi Far, A. M. Saeed, S. Donthula, N. Leventis, C. Sotiriou-Leventis, 249th ACS National Meeting, Denver, CO, March 23, 2015 (SCI-MIX-PMSE 383 – Invited).

33. “Shape-Memory Polyurethane Aerogels,” S. Donthula, F. Zheng, C. Sotiriou-Leventis, N. Leventis, 249th ACS National Meeting, Denver, CO, March 23, 2015 (SCI-MIX-PMSE 361 – Invited).

34. “3D Assemblies of Nanoparticles as Scaffolds for New Materials: from Mechanically Strong Polymer-Crosslinked Aerogels to Porous Metals and Ceramics,” Invited Seminar Speaker, Department of Chemistry, U. of Missouri-Columbia, Columbia, MO, March 3, 2015.

35. “Shape-Memory Polyurethane Aerogels,” S. Donthula, F. Zheng, C. Sotiriou-Leventis, N. Leventis, 49th Regional ACS Meeting, U. of Missouri-Columbia, Columbia, MO, November 13, 2014, Polymer and Materials Chemistry Session No. 290.

36. “Ferrocene-based Polyamide Aerogels: Graphitization, Transmetalation and Use in Heterogeneous Catalysis,” A. M. Saeed, C. Wisner, S. Donthula, A. Mumtaz, C. Sotiriou-Leventis, N. Leventis, 49th Regional ACS Meeting, U. of Missouri-Columbia, Columbia, MO, November 12, 2014 (SCI-MIX No. 17 – Invited).

37. “Synthesis and Characterization of Robust Terephthalaldehyde-phloroglucinol (TPOL) Aerogels as Precursors for Nanoporous Carbons,” H. Majedi Far, A. M. Saeed, S. Donthula, N. Leventis, C. Sotiriou-Leventis, 49th Regional ACS Meeting, U. of Missouri-Columbia, Columbia, MO, November 12, 2014 (SCI-MIX No. 24 – Invited).

38. “Polybenzoxazine Aerogels: Synthesis, Characterization and Use in the Carbothermal Synthesis of Nanoporous Metal and Alloy Aerogels,” S. Donthula, S. Mahadik-Khanolkar, C. Sotiriou-Leventis, N. Leventis, 49th Regional ACS Meeting, U. of Missouri-Columbia, Columbia, MO, November 13, 2014, Polymer & Materials Chemistry Session No. 287.

39. “Polybenzoxazine Aerogels: Synthesis, Characterization and Use in the Carbothermal Synthesis of Nanoporous Metal and Alloy Aerogels,” N. Leventis, C. Sotiriou-Leventis, S. Mahadik-Khanolkar, S. Donthula, International Society for Advancement of Supercritical Fluids, Seminar on Aerogels, Hamburg University of Technology (TUHH), October 6, 2014, Hamburg, Germany (Poster Presentation – P1).

40. “Isocyanate Derived Aerogels: Convenient Inexpensive Synthesis not only of Polyurethanes and Polyureas, but also of Polyimides and Polyamides,” N. Leventis, C. Sotiriou-Leventis, International Society for Advancement of Supercritical Fluids, Seminar on Aerogels, Hamburg University of Technology (TUHH), October 6, 2014, Hamburg, Germany (Invited Keynote Lecture).