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DNA-Templated Fabrication of Arbitrary-Structured Porous Carbon
Materials

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DNA-Templated Fabrication of Arbitrary-Structured Porous Carbon Materials

Grant number: FA9550-13-1-0083

Final Technical Report for 03/27/2013 – 03/31/2016

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Summary

The goal of this YIP project is to develop a toolset that will enable the fabrication of 2D and 3D porous carbon materials with arbitrary structures. The proposed synthetic approach is based on the shape-conserving carbonization of DNA nanostructures. The DNA nanostructure will be coated with a thin layer of SiO_2 and then carbonized at high temperature; the SiO_2 coating will ensure a shape-conserving transformation from the DNA nanostructure to the porous carbon material in this process.

We have achieved the original objective of the project. We have coated both 1D and 2D DNA nanostructures with a thin film of Al_2O_3 by atomic layer deposition (ALD) followed by heating the coated DNA nanostructure in low pressure H_2 atmosphere at 800 - 1000°C. Raman spectroscopy and atomic force microscopy (AFM) data showed that carbon nanostructures were produced and their shape were the same as the DNA nanostructure. Conductive AFM measurement shows that the carbon nanostructures are electrically conductive. To address this main objective, we have extensively investigated the interaction between DNA nanostructure with a solid substrate (*e.g.*, SiO_2 , graphite, graphene) and how that interaction can be impacted by surface chemistry. These research activities revealed a rich

These research activities have resulted in 24 peer reviewed journal articles (23 published and 1 in revision) acknowledging the support of the AFOSR YIP grant. In recognition of his research contributions, the PI was awarded a Young Investigator Award by the European Materials Research Society 2013 Spring Meeting (Symposium Q: Bionanomaterials for imaging, sensing and actuating)

1. Research goals

The goal of this project is to develop a toolset that will enable the fabrication of 2D and 3D porous carbon materials with arbitrary structures. Our synthetic approach will make it possible to design and synthesize a porous carbon material with an ‘ideal’ structure to achieve the ultimate performance in strength-to-density ratio, porosity, surface area, thermal conductivity, electrical conductivity, or a combination thereof.

Our synthetic approach is based on the shape-conserving carbonization of DNA nanostructures. This strategy is illustrated in **Fig. 1** where the fabrication of a 2D nano-porous carbon mesh is used as an example. Briefly, we will design and self-assemble a library of DNA strands to form a DNA super-lattice having the targeted structure for the porous carbon material. The DNA nanostructure will then be coated with a thin layer of SiO₂ and carbonized at high temperature; the SiO₂ coating will ensure a shape-conserving carbonization. After removing the SiO₂ coating, the synthesis will produce a 2D porous carbon film, the internal structure of which is entirely determined by that of the DNA template. The same concept will be extended to make 3D porous carbon materials. The specific aims of this project are: (1) to develop methods for the deposition of SiO₂ onto a DNA nanostructure; and (2) to develop a shape-conserving carbonization process to convert a SiO₂-coated DNA nanostructure into an amorphous or graphitic carbon nanostructure.

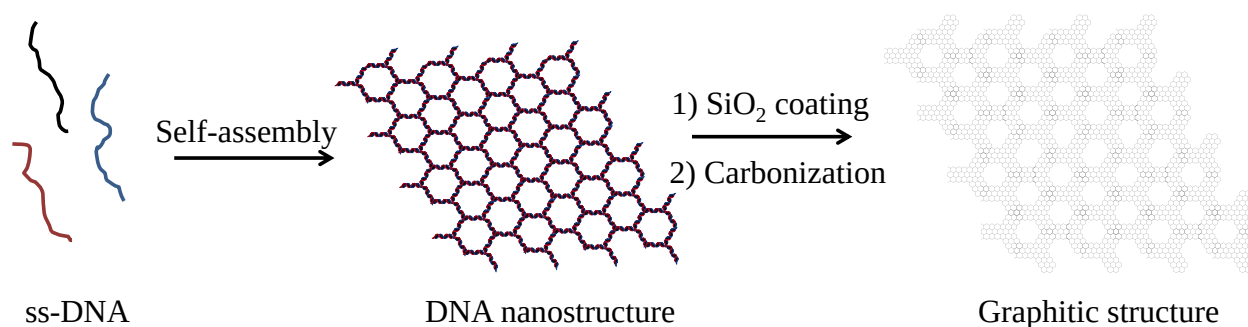


Fig. 1. Fabrication of porous carbon through shape-conserving carbonization of DNA nanostructures. Note that the structures are not drawn to scale.

2. Research accomplishments

In the past three year, we have made significant progresses in three areas of research: (a) Developing methods for the deposition of SiO₂ onto a DNA nanostructure; (b) Fundamental understanding of the intrinsic wettability of graphitic materials; and (c) high temperature carbonization of DNA. These activities are detailed below (Note that some of the contents are taken from previous annual reports).

2.1 Selective deposition of inorganic oxides onto a DNA nanostructure template

We have developed a method to form custom-shaped inorganic oxide nanostructures by using DNA nanostructure templates.¹ Our results showed that a DNA nanostructure can modulate the rate of chemical vapor deposition (CVD) of SiO₂ and TiO₂ with nanometer scale spatial resolution.

The resulting oxide nanostructure inherits its shape from the DNA template. This method generates both positive-tone and negative-tone patterns on a wide range of substrates and is compatible with conventional silicon nanofabrication processes. In addition to fulfill our original goal, this result also opens the door to using DNA nanostructure as a general purpose template for high resolution nanofabrication.

Figure 1 summarizes the DNA-mediated CVD of oxide materials on various inorganic substrates. In a typical experiment, a DNA nanostructure was first deposited onto a substrate (e.g., Si wafer, mica, and gold). The CVD was carried out at room temperature in a closed glass chamber, inside which several liquid reservoirs delivered the CVD precursor and other required chemicals to the substrate through gas phase. Both positive-tone and negative-tone patterns can be obtained.

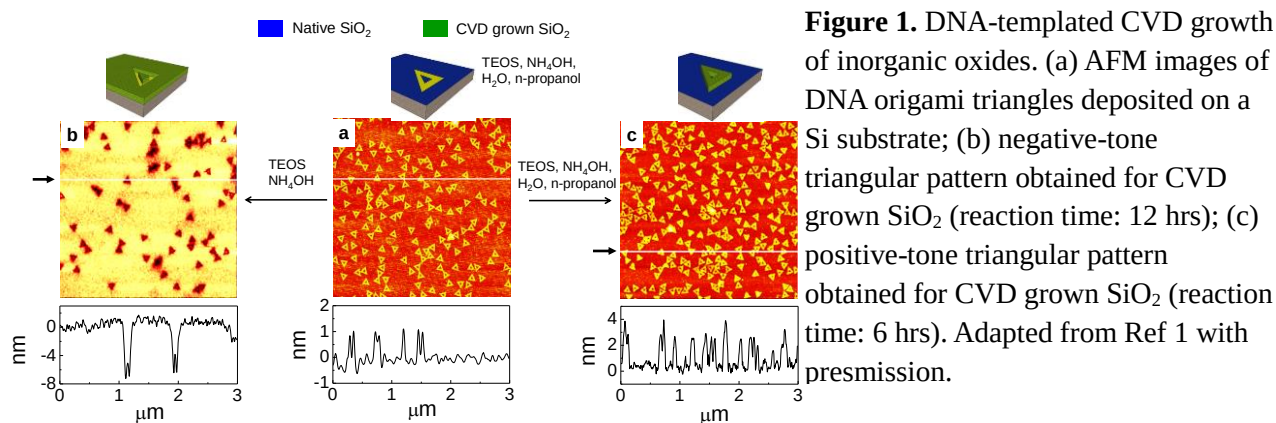


Figure 1a shows the atomic force microscope (AFM) image of DNA triangle templates deposited on a silicon wafer that has a thin layer (*ca.* 2 nm) of native oxide. The height and width of the edge of the DNA triangle was 1.2 ± 0.1 nm and 27 ± 1 nm, respectively (all reported width values are full width at half maximum). When this sample was exposed to a mixed vapor of Si(OEt)₄ (TEOS), H₂O, and NH₃, deposition of SiO₂ occurred selectively on the SiO₂ surface that was not covered by the DNA template, resulting in a negative-tone pattern of SiO₂ (Figure 1b). The width of the trenches in Figure 1b is 42 ± 5 nm while the depth is 7 ± 2 nm. The center void of the triangle template is retained in almost all the structures, although with a reduced height contrast. To reverse the area selectivity of the CVD, we introduced propanol vapor and increased the relative humidity of the reaction chamber. In this case, the CVD reaction selectively deposited SiO₂ onto DNA nanostructures to produce a positive-tone pattern (Figure 1c). After the CVD, the average height of the triangle structures increased from 1.2 ± 0.1 nm to 2.6 ± 0.5 nm while the width of the ridges increased from 27 ± 1 nm to 37 ± 3 nm. We note that the lateral dimension measured by AFM is likely limited by the tip-sample convolution effect and should be regarded as an upper limit. Nevertheless, faithful pattern transfer was clearly achieved for almost every DNA templates under both positive-tone and negative-tone conditions. Our result contrasts with previous work on

metallization of DNA nanostructures, in which case the metal plating process typically produced grainy and sometimes discontinuous metal nanostructures.²⁻⁸

This DNA-mediated CVD is a versatile tool for general purpose nanofabrication. First of all, the area selective deposition of oxide materials is not limited to silicon wafer and can be extended to pattern other substrates. For example, Figure 2a and 2b show the positive-tone CVD of SiO₂ onto DNA nanostructures deposited on a mica and a gold substrate, respectively. Second, oxide materials other than SiO₂ can also be deposited in a similar fashion by using suitable CVD precursors. For example, using titanium isopropoxide (Ti(OiPr)₄) as the precursor we have successfully produced positive-tone TiO₂ structures on a silicon wafer by using the same DNA triangle templates (Figure 2c). Finally, this CVD is compatible with custom-shaped DNA templates. Figure 2d shows high resolution AFM images of both positive-tone and negative-tone SiO₂ patterns templated by three different shapes of DNA nanostructures: triangle, rectangle, and L-shape; Figure 2e shows high resolution AFM images of positive-tone SiO₂ patterns templated by 26 letters constructed using the recently developed single-strand tiles (SST) approach.⁹

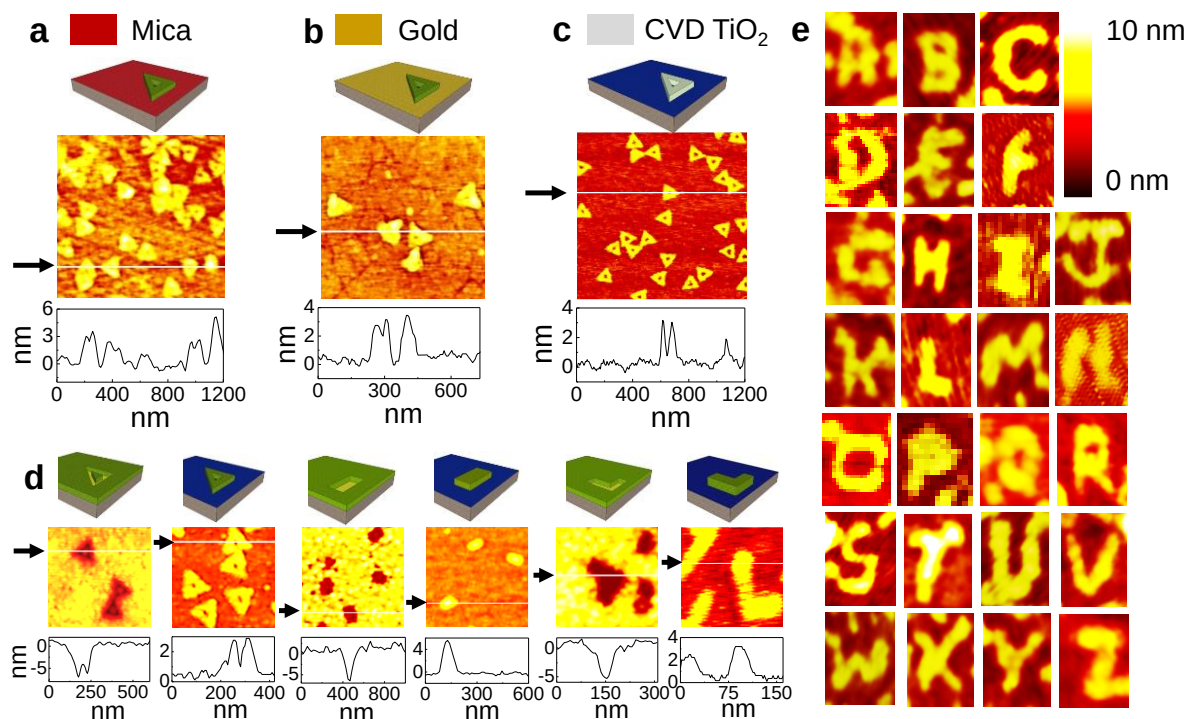


Figure 2. DNA-templated CVD growth of inorganic oxides of different shapes and substrates. Cartoon representation and AFM image of positive-tone triangular pattern of (a) CVD grown SiO₂ obtained on mica substrate, (b) CVD grown SiO₂ obtained on gold substrate, and (c) CVD grown TiO₂ on a Si substrate. (d) High resolution AFM images of both positive-tone and negative-tone SiO₂ patterns templated by three different shapes of DNA nanostructure on silicon wafer: triangle, rectangle, and L-shape. (e) High resolution AFM images (140 nm by 160 nm) of 26 (A to Z) positive-tone SiO₂ letters obtained using the corresponding DNA letters as templates. The arrows and white lines in (a) - (e) indicate the locations of cross section. Adapted from Ref 1 with permission.

2.2 Intrinsic wettability of graphitic surfaces

Our study on the wettability of graphitic materials was motivated by the possibility to use graphitic substrates (*e.g.*, graphene and graphite) to improve the area selectivity of DNA-mediate CVD reaction. We hypothesized that the absence of dangling bonds on graphitic surface will allow a much wider range of CVD reactions to be implemented. The wettability of the graphitic substrate is important because many of the CVD reactions are sensitive to surface adsorbed water, as we showed in **section 2.1**.

Since experiments by Fowkes and Harkins in 1940,¹⁰ extensive studies have concluded that graphitic surfaces are hydrophobic with water contact angles (WCAs) within the 75° - 95° range.¹⁰⁻²² Hydrophobicity has also been observed on other graphitic materials. Aligned carbon nanotubes have shown superhydrophobic behavior where WCAs of 163.4°²³ and 158.5°²⁴ were observed. Additionally, as-grown carbon nanotube forests exhibit WCA of 161°.¹² Raj *et al.* reported advancing WCA of monolayer graphene on SiO₂ substrate of *ca.* 90°, similar to that of graphite.

*Surprisingly, our results showed that graphitic surfaces are much more hydrophilic than previously believed and exposure to ambient air has a drastic impact on their water wettability.*²⁵ Shown in Figure 3a, within 10 seconds of taking a graphene/copper sample out of the CVD chamber, its WCA was found to be only 44°. The WCA quickly reached *ca.* 60° within 20 minutes, after which the rate of increase drastically slowed down. The WCA eventually plateaued at 80° after 1 day. Similar increase of WCA was also observed in HOPG and graphene/Ni samples; in both cases, a freshly prepared sample showed much lower WCA than those previously reported in the literature.

We attribute the change of wettability to hydrocarbon accumulation on the graphene/copper substrate upon its exposure to air. Shown in Figure 3b are ATR-FTIR spectra taken on the same location of a graphene/copper sample as a function of its exposure time in ambient air. Two major peaks were observed at 2850 cm⁻¹ and 2930 cm⁻¹, which can be assigned to the symmetric and asymmetry stretching of methylene group (-CH₂-), respectively.²⁶ Both peaks showed a monotonic increase with increasing air exposure (Figure 2b inset). At longer times, a much weaker peak can be observed at 2950 cm⁻¹ that can be assigned to the asymmetric stretching of -CH₃ group.²⁶ The same hydrocarbon accumulation on graphene/copper sample was also observed with X-ray photoelectron spectroscopy (XPS, see Methods for details). In Figure 3c we compare two C1s XPS spectra of the same graphene/copper sample, one collected within 10 minutes after taking out of the CVD chamber and the other after 2 weeks of storage in air. The difference spectrum showed a positive peak near 285.7 eV with a shoulder at 287.6 eV. This peak is consistent with the adsorption of hydrocarbon onto graphene.

These data showed that a clean graphitic surface absorbs hydrocarbon from ambient air and becomes more hydrophobic as a result. Significant hydrocarbon contamination could occur within

several minutes of air exposure and as a result, this effect could be easily overlooked if the WCA measurement was not done immediately after the synthesis of graphene. The much smaller WCA we observed here also suggest a much stronger water – graphene interaction and calls for a revisit of the wetting models developed for graphitic surfaces.

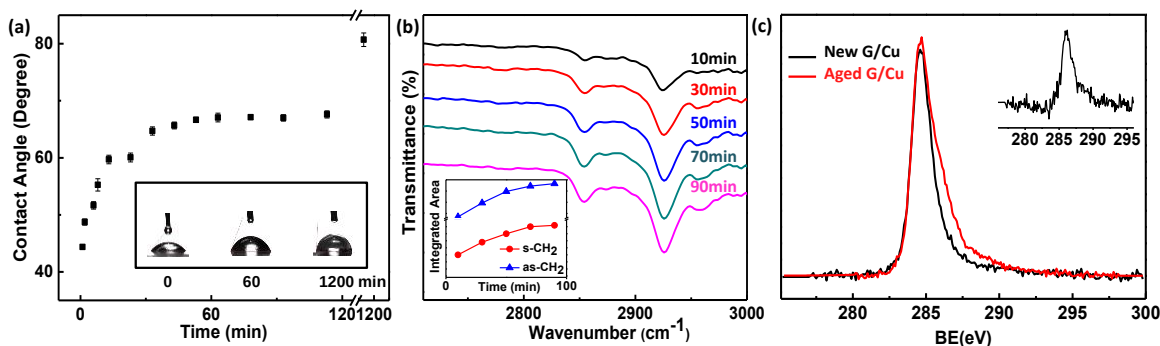


Figure 3 (a) Temporal evolution of the WCA measured on a graphene/copper sample. The sample was taken out of the CVD chamber at time 0. The three photographs show the water drops captured at 1 min, 60 min, and 1200 min. (b) ATR-FTIR spectrum of a graphene/copper sample. The spectra were shift vertically for clarity. The sample was taken out of the CVD chamber at time 0. The inset shows the integrated peak area vs time for the peaks at 2930 cm^{-1} (asymmetric CH_2 stretching, blue) and 2850 cm^{-1} (symmetric CH_2 stretching, red). (c) Carbon 1s XPS peak of an as-prepared graphene/copper sample and the same sample after exposed to air for 2 weeks. Inset: difference between new and aged Cu/G sample, BE: binding energy. Adapted from ref 25 with permission.

2.3. High temperature carbonization of DNA nanostructures.

We tested the high temperature carbonization of DNA that are covered by the CVD-grown SiO_2 . However, the results showed that the SiO_2 is not thermally stable enough at $>800^\circ\text{C}$. Subsequently, it was found that Al_2O_3 is a better coating material for this purpose.

Shown in Figure 4A, there are four steps in the carbonization process. First, DNA nanostructure was deposited onto a Si wafer substrate. Then, *ca.* 20 nm of Al_2O_3 was conformally coated onto the DNA nanostructure using atomic layer deposition (ALD). To convert the DNA to carbon nanostructures, the Al_2O_3 -coated DNA nanostructure was heated in a low pressure H_2 atmosphere at $800\text{-}1000^\circ\text{C}$ for 3 - 5 min. For characterizations, the Al_2O_3 coating can be removed by a H_3PO_4 etch to expose the carbon material, if needed.

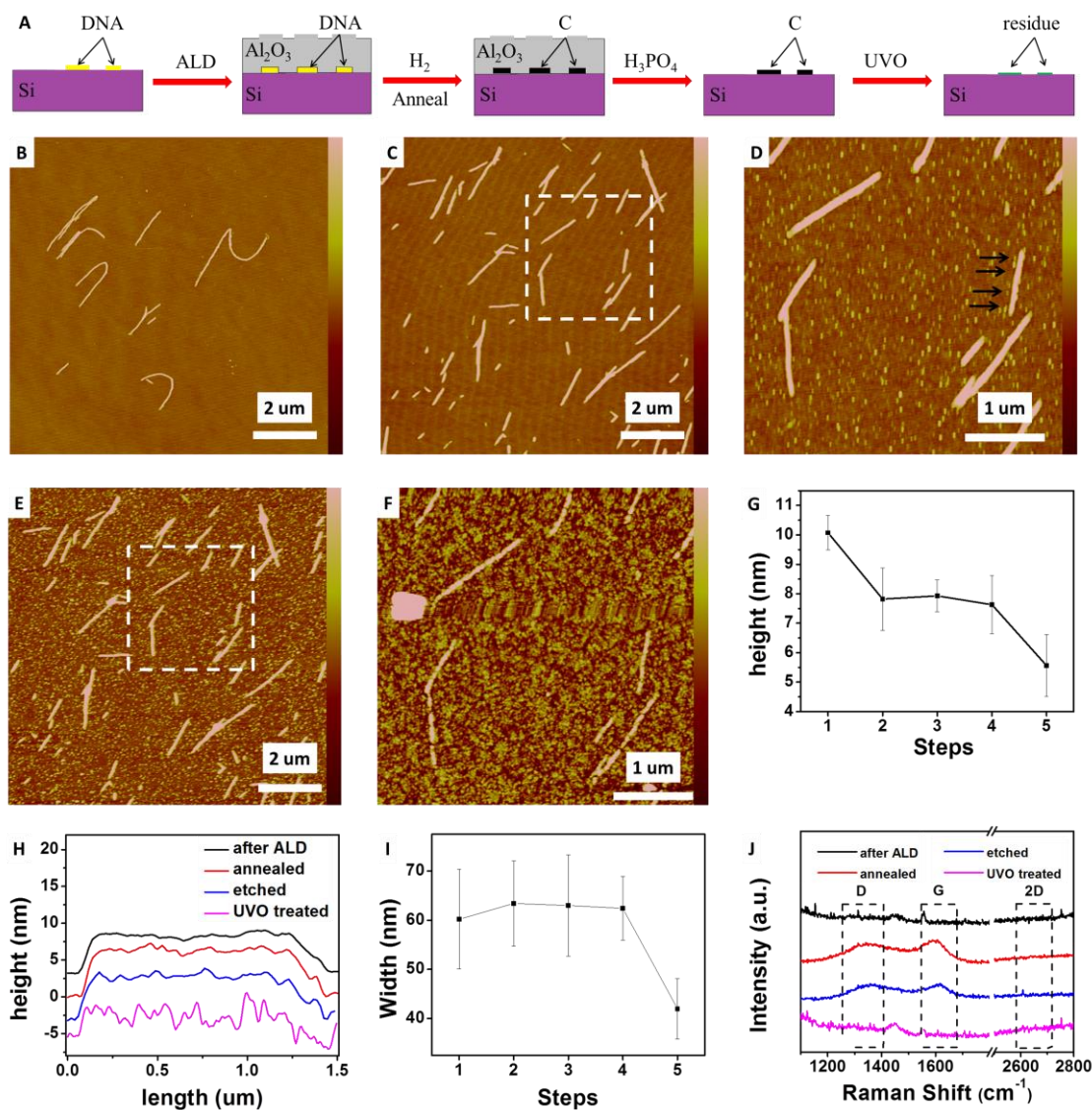


Figure 4. (A) Schematic of shape conserving carbonization of 1D DNA structure and the corresponding AFM topographic images of 1D DNA structure (B) after deposition on top of Si substrate, (C) after ALD of Al_2O_3 film, (D) after annealing at 800°C for 5 min, (E) after removal of Al_2O_3 film and (F) after UV/Ozone (UVO) treatment. (G) Average height of 1-D DNA at each step. (H) Height profile of the same 1D-DNA structure, marked by arrows in Figure 1D. The traces were shifted in the vertical axis for clarity. (I) Average width of 1-D DNA at each step. (J) Raman spectra of 1D-DNA. The AFM height scale bars for 1D DNA (A-E) are 10 nm. Note: C-F were AFM images taken on the same location; in G and I, the horizontal axis represents the 5 steps of the fabrication process: (1) after deposition on top of Si substrate, (2) after ALD of Al_2O_3 film, (3) after annealing, (4) after removal of Al_2O_3 film and (5) after UV/Ozone treatment.

The 1D DNA brick crystal was constructed using the DNA brick approach developed by Yin and co-workers. Figure 4B shows an AFM image of the DNA nanostructure. The structures are several micrometers in length, 10.1 ± 0.6 nm in height and about 60 ± 10 nm in width (measured from 10 different samples). After the ALD coating of 20 nm of Al_2O_3 , the AFM image of the Al_2O_3 surface still showed the characteristic shape of the DNA nanostructure, as one would expect for a conformal coating process (*i.e.*, the topography of the DNA is propagated to the Al_2O_3 surface). We then thermally annealed the Al_2O_3 -coated sample at 800 °C for 5 min. As can be seen from Figure 4C and Figure 4D, there was not change in the shape and relative position of the nanostructures. We attribute this observation to the high melting point of Al_2O_3 (2072 °C). After etching of H_3PO_4 , the sample was again imaged by AFM at the same location and the image is shown in Figure 4E. It can be seen that the overall shape of the nanostructure is identical to that of the DNA template (Figure 4C).

To quantify the degree of shape conservations, we measured the average height (Figure 4G) of the nanostructures at each stage of the fabrication. A minor decrease of the height was observed after ALD coating (step 1 to step 2), likely due to the shrinkage of DNA lattice interspace under Al_2O_3 film. Cross sections were measured on a piece of linear DNA crystal, as marked by arrows in Figure 4D. The cross sections showed a high degree of similarity (Figure 4H) showing that the shape of DNA nanostructure is conserved in this carbonization process. Finally, Figure 4I shows that there was no change in the width of the nanostructures after carbonization and removal of Al_2O_3 .

To identify the chemical nature of the nanostructures, Micro-Raman spectroscopy was used. Due to its small Raman cross section and low surface coverage, DNA nanostructure do not produce detectable Raman signal. As can be seen in Figure 4J, the sample became Raman active after thermal annealing. Both D band (1339 cm^{-1}) and G band (1611 cm^{-1}) were observed, characteristic of carbon nanomaterials. Removal of Al_2O_3 layer does not affect the Raman signal, indicating that the Raman signal was from DNA nanostructures underneath the Al_2O_3 film. We note that the absence of 2D band at *ca.* 2700 cm^{-1} suggests the lack of large scale conjugated sp^2 carbon structure. It might be possible to increase the sp^2 domain by incorporating metal-ions to catalyze the carbonization. However, due to time and resource limitation, this experiment will be planned in the future.

We used XPS to further confirm the graphitic nature of the nanostructure product. We found that after annealing, the XPS data showed a significant decrease in nitrogen content and the sp^2 C=C species increased from 22% to 70%, confirming that the shape-conserving carbonization produced graphitize carbon nanostructures.

4. Publications, presentations, and awards

4.1. Peer reviewed publications acknowledging AFOSR support (all as corresponding author. _ indicates undergraduate coauthors; * indicates corresponding author).

24. Tian, C.; Kim, H.; Sun W.; Yin, P.; Liu, H.* “DNA nanostructures mediated molecular imprinting lithography” *ACS Nano*, Revision and resubmit.
23. Zhou, F.; Sun, W.; Ricardo, K. B.; Shen, J.; Yin, P.; **Liu, H.*** “Programmable-shaped Carbon Nanostructure from Shape-conserving Carbonization of DNA” *ACS Nano*, **2016**, *10*, 3069.
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- Highlighted by *Nature Materials*, *Science Daily*, *Materials360*, etc.

1. Surwade, S. P.; Zhou F.; Wei, B.; Sun, W.; Powell, A.; O'Donnell, C.; Yin, P.*; **Liu, H.***; “Nanoscale growth and patterning of inorganic oxides using DNA nanostructure templates” *J. Am. Chem. Soc.* **2013**, 135, 6778-6781

- Highlighted by Faculty 1000 Prime.

4.2. Invited conference presentations and department seminars acknowledging AFOSR support (not listed here: > 30 departmental seminars and contributed talks at conferences)

6. “Water-graphite interaction” Telluride workshop on *Hydrophobicity: From Theory, Simulation, to Experiment*, July 2016

5. “Airborne contamination of 2D materials” AmeriMech Symposium on *Mechanical Behavior of 2D Materials – Graphene and Beyond*, Austin, TX, April, 2016

4. “DNA-based nanofabrication under extreme chemical environments” FNano 2015, Snowbird, UT, April, 2015

3. “Intrinsic wettability of graphene” UK-China Summer School Tribology & Surface Engineering, Qingdao, China. July, 2013

2. “DNA nanostructure meets nanofabrication” e-MRS spring 2013 meeting, Strasbourg, France

1. “Graphene as an ultra-thin coating material: corrosion, friction, and wetting”, International Conference on Metallurgical Coatings and Thin Films, Sand Diego, May 2013

4.3. Awards and recognitions

The PI was awarded a Young Investigator Award during the European Materials Research Society 2013 Spring Meeting (Symposium Q: Bionanomaterials for imaging, sensing and actuating).

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Organization / Institution name

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Grant/Contract Title**The full title of the funded effort.**

(YIP) DNA-Templated Fabrication of Arbitrary-Structured Porous Carbon Materials

Grant/Contract Number**AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".**

FA9550-13-1-0083

Principal Investigator Name**The full name of the principal investigator on the grant or contract.**

Haitao Liu

Program Manager**The AFOSR Program Manager currently assigned to the award**

Ali Sayir

Reporting Period Start Date

03/27/2013

Reporting Period End Date

03/31/2016

Abstract

The goal of this YIP project is to develop a toolset that will enable the fabrication of 2D and 3D porous carbon materials with arbitrary structures. The proposed synthetic approach is based on the shape-conserving carbonization of DNA nanostructures. The DNA nanostructure will be coated with a thin layer of SiO₂ and then carbonized at high temperature; the SiO₂ coating will ensure a shape-conserving transformation from the DNA nanostructure to the porous carbon material in this process.

We have achieved the original objective of the project. We have coated both 1D and 2D DNA nanostructures with a thin film of Al₂O₃ by atomic layer deposition (ALD) followed by heating the coated DNA nanostructure in low pressure H₂ atmosphere at 800 - 1000 °C. Raman spectroscopy and atomic force microscopy (AFM) data showed that carbon nanostructures were produced and their shape were the same as the DNA nanostructure. Conductive AFM measurement shows that the carbon nanostructures are electrically conductive. To address this main objective, we have extensively investigated the interaction between DNA nanostructure with a solid substrate (e.g., SiO₂, graphite, graphene) and how that interaction can be impacted by surface chemistry.

These research activities have resulted in 24 peer reviewed journal articles (23 published and 1 in revision) acknowledging the support of the AFOSR YIP grant. In recognition of his research contributions, the PI was awarded a Young Investigator Award by the European Materials Research Society 2013 Spring

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Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, \$K)

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