Final Technical Report

Award Title: **A DNA-based 3D Nanofabrication for Surface Engineering**
ONR Award Number: **N00014-18-1-2555**
Reporting period: **July 1st 2018 to June 30th, 2021**
Principal Investigator Name: **Professor Haitao Liu**
Organization: **University of Pittsburgh**

Distribution Statement

The goal of this project is to develop a general approach to fabricate nanoscale 3D textured surfaces using 3D DNA nanostructure templates. With a coating of 3D nanostructure, a surface can exhibit favorable interfacial properties, such as super-hydrophobicity, anti-fouling, and drag reduction. However, current approaches to produce such 3D nanostructures require multistep nanofabrication and often specific substrates (*e.g.*, silicon). The proposed approach will produce complex 3D nanoscale patterns on surfaces in a single step and will be of low cost and scalable to large areas (> m^2). Due to COVID-related disruptions, the project objective has since been slightly modified to include a broader range of DNA-based patterning techinques and their applications in surface engineering.

1. Significance and Naval Relevance

While conventional nanofabrication excels at producing high quality 2D patterns, using it to produce 3D nanostructures is still a time-consuming process that typically involves multiple steps of 2D lithography patterning. In this regard, there are inherent advantages in using 3D DNA nanostructure as template for 3D nanofabrication. DNA nanostructures can be easily made into well-defined 3D shapes. DNA nanostructures are made by self-assembly and amendable to mass production. However, the weak chemical and mechanical stability of DNA has long been a bottleneck in the use of DNA nanostructure in 3D nanofabrication. This proposal will address such challenges by developing new chemistry-based methods to convert 3D DNA nanostructures into 3D inorganic nanostructure of the same topography. This work could enable new applications of DNA nanostructure in a wide range of research and engineering applications. This proposal will explore the use of DNA-templated nanoscale texture for controlling the wettability of surfaces and enhance their anti-fouling properties.

Controlling the solid-water interfacial interaction is of fundamental importance to many areas of Navy interests, such as wetting, biofouling, and drag reduction. Robust super-hydrophobicity is key to high performance water repellant and anti-icing coatings. Biofouling is a major concern to fleet operation because it increases drag and fuel consumption. Current commercial antifouling coatings rely on releasing toxic compounds to kill fouling organisms, releasing large amount of toxin into the environment during its life cycle. The proposed research will offer a new approach to mass produce super-hydrophobic and anti-fouling surfaces using DNA nanostructure templates.

2. Major Research Accomplishments

During the funding period, we have made significant progress in DNA-based patterning of a variety of substrate and characterization of their properties arising from the nanostructured surface. The most significant accomplishments are:

1. Antifouling properties of DNA-patterned SiO_2 substrates.

2. DNA-mediated area-selective atomic layer deposition (ALD) and its application in antireflection.

In addition to these major accomplishments, we have also investigated silica coating of DNA nanostructure in solution in an effort to enhance the stability of DNA nanostructure for 3D patterning; developed a DNA-based area-selective deposition of metals and area-selective doping for Si substrate for potential use in the fabrication of 2D and 3D electronics; developed a bacteria-imprinted chip for selective capture and kill of bacteria in solution, and identified polymer substrates that DNA nanostructure can deposit onto.

The details of these accomplishments have already been described the interim reports submitted in the past three years. Below we will provide a succinct summary of the major accomplishments.

2.1. Antifouling properties of DNA-patterned SiO_2 substrates.

DNA-based nanofabrication can produce high resolution designer patterns but aligning these patterns is a major technical challenge. The lack of pattern alignment has severely limited the real-world application of DNA-based nanofabrication. This project demonstrates antifouling as a new application for DNA-based nanofabrication that does not require precise pattern alignment. We used DNA triangle nanostructures as template to produce nanoscale triangular-shaped trenches on SiO_2. Using *B.subtilis* as a bacterial model, we found that such nanopatterned surface showed a 75% reduction in bacterial adhesion and 74% reduction in biofilm density at only 35% surface coverage of nanoscale triangle trenches (Fig. 1). Our work demonstrates the potential of DNA-based nanofabrication in antifouling and other surface engineering applications.

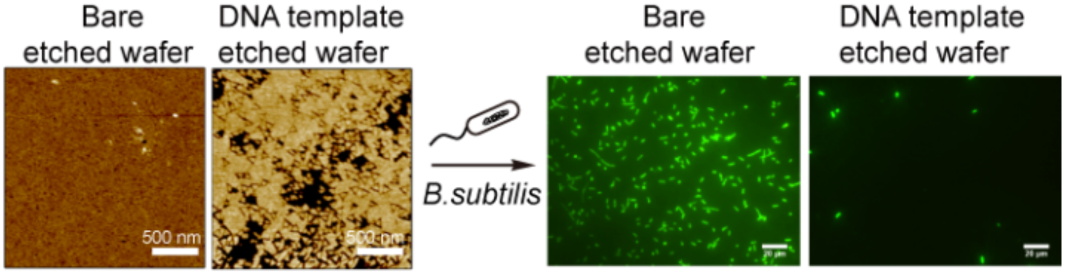

Fig 1. AFM images (left) and fluorescence images (right) of SiO_2 without and with DNA-patterned nanotrenches. Upon exposure to *B. subtilis*, the DNA-tempalted sample showed much reduced attachment of bacteria on the surface.

2.2 DNA-mediated area-selective ALD and its application in antireflection.

In this project we demonstrate area-selective ALD of oxides on DNA nanostructures. Area selective ALD of Al_2O_3, TiO_2 and HfO_2 were successfully achieved on both 2D and 3D DNA nanostructures deposited on a polystyrene substrate. The resulting DNA-inorganic hybrid structure was used as a hard mask to achieve deep etching of Si wafer for antireflection applications (Fig 2a). Shown in Fig 2b, DNA nanostructure alone cannot survive the harsh plasma etching environment and no nanostructure was produced. However, after an ALD coating of metal oxides, these structures can be used as masks to produce high-aspect ratio hollow triangle column on the Si surface (Fig 2c-d). The nanostructured surface show much reduced reflection (Fig 2e). ALD is a widely used process in coating and thin film deposition; our work established to a new way to pattern oxide materials using DNA template and to enhance the chemical/physical stability of DNA nanostructure for applications in surface engineering.

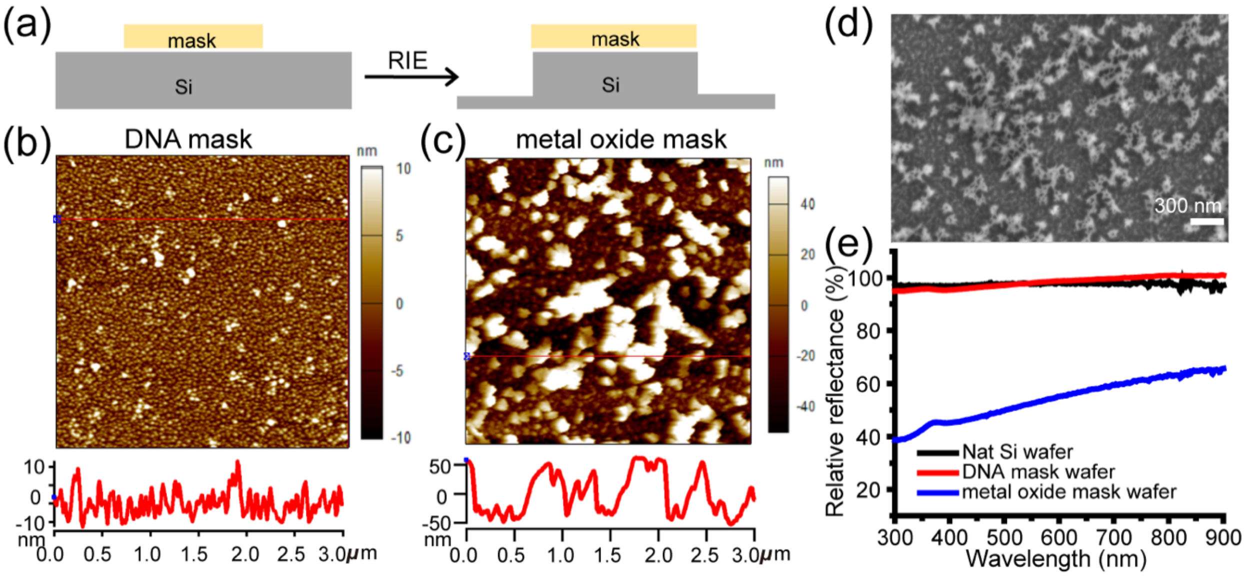

Fig 2. DNA-mediated etching of Si. (a) Schematics of RIE of Si wafer. AFM images and height profiles of etched wafer using (b) unmodified DNA nanostructure as a mask, and (c) DNA-metal oxide hybrid nanostructure as a mask. (d) SEM images of the Si wafer patterned using the DNA-metal oxide hybrid nanostructure. (e) Antireflection property of Si wafer surface measured by microspectrophotometer (MSP), including native oxide Si wafer, DNA itself-templated etched Si wafer and DNA-metal oxide hybrid templated etched Si wafer. A piece of bare Si wafer surface was used as reference with reflectance of 100% across the wavelength of 300 – 900 nm to calibrate the setup. Each line was reported as the average of reflection spectra on the center of two different samples.

3. Publications

This grant has produced 13 peer reviewed publications and another two manuscripts are in preparation.

1. Wang, R.; Zhang, G.*; **Liu, H.*** "DNA-based Nanofabrication" *Curr. Opin. Colloid Interface Sci.* **2018**, *38*, 88-99.

2. Ricardo, K. B.; **Liu, H.*** "Graphene-encapsulated DNA Nanostructure: Preservation of Topographic Features at High Temperature and Site-specific Oxidation of Graphene" *Langmuir* **2018**, *34*, 15045-15054.

3. Hui, L.; Zhang, Q.; Deng, W.; **Liu, H.*** "DNA-Based Nanofabrication: Pathway to Applications in Surface Engineering" *Small* **2019** DOI: 10.1002/smll.201805428

4. Salim, M.; Hurst, J.; Montgomery, M.; Tolman, N.; **Liu, H.*** "Airborne Contamination of Graphite as Analyzed by Ultra-Violet Photoelectron Spectroscopy" *J. Electron Spec. Rel. Phenom.* DOI: 10.1016/j.elspec.2019.06.001

5. Tolman, N. L.; Mukai, J. M.; Wang, S.*; Zito, A.; Luo, T.; and Liu, H.* "The Effect of Physical Adsorption on the Capacitance of Activated Carbon Electrodes." *Carbon* **2019**. DOI: 10.1016/j.carbon.2019.05.005

6. Hui, L.; Xu, A.; **Liu, H.*** "DNA-based Nanofabrication for Antifouling Applications" *Langmuir* **2019**, *35*, 12543-12549.

7. Hurst, J.; Kim, A.; Peng, Z.; Li, L.*; **Liu, H.*** "Assessing and Mitigating Airborne Hydrocarbon Contamination of Carbon Electrode Materials" *Chem. Mater.* **2019**, *31*, 7133-7142.

8. Hui, L.; **Liu, H.*** "DNA-based Nanofabrication for Low-cost, High-resolution Patterning" *Proc. SPIE* **2019** DOI: 10.1117/12.2532934.

9. Kim, M.; Qiu, N.; Li, Z.; Huang, Q.; Chai, Z.; Du, S.*; **Liu, H.*** "Electric Field Effect on the Reactivity of Solid State Materials: The Case of Single Layer Graphene" *Adv. Func. Mater.* **2020**, *30*, 1909269.

10. Zhou, F.; Sun, W.; Zhang, C.; Shen, J.; Yin, P.*; **Liu, H.*** "3D Freestanding DNA Nanostructure as a Low-Density High-Strength Material". *ACS Nano.* **2020**, *14*, 6582-6588

11. Hui, L.; Nixon, R.; Tolman, N.; Mukai, J.; Bai, R.; Wang, R.; **Liu, H.*** "Area-Selective Atomic Layer Deposition of Metal Oxides on DNA Nanostructures and Its Applications" *ACS Nano* **2020**, 14, 13047-13055.

12. Bai, R.; Du, Y.; Xu, A.; Erikson, J. R.; Hui, L.; Chen, J.; Xiong, F.*; **Liu, H.***; "DNA-based Strategies for Site-specific Doping" *Adv. Func. Mater.* **2020**, 2005940

13. Hui, L.; Chen. J.; Kafley P.; **Liu, H**.* "Capture and Kill: Selective Eradication of Target Bacteria by a Flexible Bacteria-Imprinted Chip" *ACS Biomater. Sci. Eng.* **2021**, *7*, 90-95

4. Patent Application

We have applied one patent that mentioned this grant as support:

1. Salim, M.; Liu, H.; Thimons L.; Kim, M.; Jacobs, T. "Carbon Fibers and Method of Fabrication Thereof" US Patent application 62/969,964

There is no technical transfer activity to report.

5. Honors and Awards

The PI was awarded the **Early-Career Award in Experimental Physical Chemistry** by American Chemical Society in 2019.

5. Student Support

This grant has provided partial support for 1 postdoctoral scholar (Liwei Hui, 6 month effort each year) and 5 graduate students (Anqin Xu, Nathan Tolman, Justin Hurst, Ruobing Bai, Min Kim) with 3 – 6 months effort each year each student. These 5 graduate students have all obtained their Ph.D. in the last three years.

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14. ABSTRACT
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