NDnano
Center for Nano Science and Technology

ND*nano* Undergraduate Research Fellowship (NURF)

2019 Project Summary

1. Student name & home university:

Zijuan Liang

University of Notre Dame

2. ND faculty name & department:

Svetlana Neretina

Karel Matous

3. Summer project title:

Fabrication of Gold Nanoplates Using Substrate-Immobilized Seeds Lined with Planar Defects via a Directed-Shock Wave

4. Briefly describe new skills you acquired during your summer research:

The course *Science of Engineering Materials*, which I took in the Spring Semester of my sophomore year, aroused my interest in the science of nanomaterials, but I have not had the opportunity to witness, experience, and apply the knowledge I acquired in this class until this summer. In the Nanomaterial Fabrication Research Lab, I studied in-depth crystalline structures and crystallographic defects through research journals, atomic models, and supercomputing simulations. However, the most significant leap in this studying process is carrying out nanoscale experiments. I had plentiful opportunities to apply nanoimprint lithography to fabricate Au seed arrays, synthesize substrate-immobilized Au nanoplates, and examined the results in a Scanning Electron Microscope (SEM). Through such experiences, I gained firsthand insights into the field of nanomaterials and novel nanotechnology. Majoring in mechanical engineering, I also obtained valuable experience as a chemist, as I used pipettes, diluted solutions, calculated pH, and manipulated nano-samples on a daily basis.

5. Briefly share a practical application/end use of your research:

Gold nanoplates can act as a nanoantenna on a photonic chip, which could prompt the development of on-chip photonics through miniaturization and sensitivity enhancements.

6. 50- to 75-word abstract of your project:

We present a novel method for the solution-based synthesis of substrate-immobilized hexagonal Au nanoplates using the block copolymer Brij® 700 and $HAuCl_4$. The growth mode has been optimized with respect to the copolymer and Au salt concentrations, pH, temperature, and growth time. Planar defects are needed for nanoplates growth, but the high crystallinity of Au seeds limits the number of defects formed. We, therefore, prototyped a device to induce planar defects in single-crystal Au by a manually generated shockwave in water. Preliminary spectroscopic data and simulations show that the shockwaves altered the Au morphology.

7. References for papers, posters, or presentations of your research:

Nair, Resmi V. **2018**. Gold nanorods decorated with a cancer drug for multimodal imaging and therapy. *The Royal Society of Chemistry 2018 Faraday Discuss*, 207, 423–435.

Huang, Yang. **2018**. Creating a Nanoscale “Black Hole” to Trap Light by a Single Au Nanosphere in an All-DIelectric Nanocavity. *Adv. Optical Mater*, 6, 1800366.

Lofton, Charles. **2005**. Mechanics Controlling Crystal Habits of Gold and Silver Colloids. *Adv. Funct. Mater*, 15, 1197-1208.

Zhai Yueming. **2016**. Polyvinylpyrrolidone-induced anisotropic growth of gold nanoprisms in plasmon-driven synthesis. *Nature Materials*, 15, 889. DOI: 10.1038/NMAT4683

S. D. Golze, R. A. Hughes, S. Rouvimov, R. D. Neal, T. B. Demille, S. Neretina. **2019**. Submitted

Numerous applications of Au nanostructures, such as surface-enhanced Raman scattering (SERS) and photovoltaics, require that they be immobilized on a substrate surface. Specifically, planar structures such as hexagonal Au nanoplates generate a plasmonic resonance that is tunable from visible to infrared frequencies, giving it potential applications that are not readily realizable using other plasmonic structures. However, the synthesis of substrate-immobilized hexagonal Au nanoplates remains a challenge due to the severe restrictions placed on the seeds used to promote growth and in adapting colloidal syntheses to the substrate surface. As part of this project, we devised a novel method for the solution-based synthesis of substrate-immobilized hexagonal Au nanoplates on sapphire using only the block copolymer Brij® 700, a Au^{3+} source, i.e., $HAuCl_4$, and NaOH.

The initial fabrication of Au seeds is achieved through the nanoimprint lithography process which includes solid-state dewetting of ultrathin Au films on [0001]-oriented sapphire substrate and a sacrificial antimony layer. Brij® 700 acts as both the capping agent and the reducing agent. It is added on the sample foremost to coat the surface of the Au seeds. Following the addition of $HAuCl_4$, the hydrophilic ends of the Brij® 700 reduce Au^{3+} to Au neutral atoms, which subsequently deposit onto the Au seeds in the lateral direction. $HAuCl_4$ provides Au^{3+}, while NaOH controls the pH, and thus controls the plate growth kinetics. The higher concentration the NaOH is, the higher the pH, the faster the plate growth. The growth mode observed is kinetically driven and has been optimized with respect to the copolymer and Au salt concentrations, pH, temperature, and growth time. The optimal conditions for hexagonal gold plate growth have been determined to be the following: 5 mM 2mL Brij® 700, 10 mM 0.2 mL NaOH, and 10 mM 0.2 mL $HAuCl_4$. Growth time is optimized to be 6 h and the temperature to be 20 ℃. This novel fabrication method has significantly reduced the 3-dimensional structures from the previous synthesis and therefore improved the yield. Figure 1 shows an SEM image of hexagonal Au nanoplates produced using the optimized conditions.

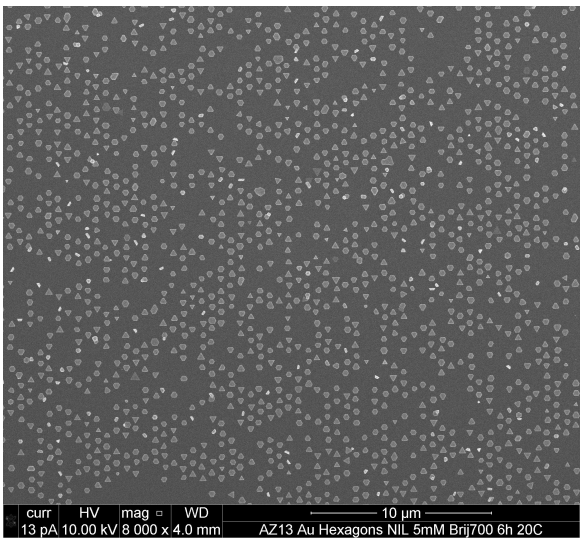

Figure 1. Au Nanoplates Growth Using Brij® 700

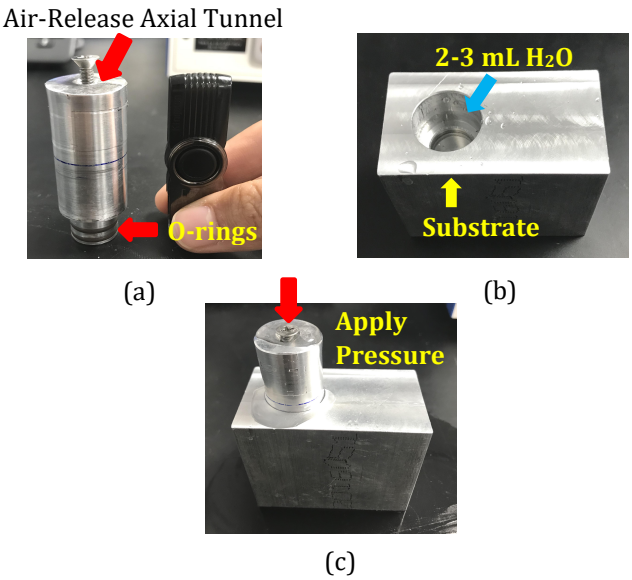

Figure 2. Aluminum Device for creating Shockwave-Induced Defects

Nevertheless, the unavoidably high crystallinity of Au seeds achieved via solid-state dewetting schemes constrains the yield of structures containing the planar defects needed to promote nanoplate growth. In an attempt to remedy this deficiency, we prototyped a device designed to induce planar defects in single crystal Au structures by means of a manually generated shockwave through an aqueous environment. The device consists of two parts, a piston (Figure 2a) and an aluminum block with an extruded hole whose diameter matches that of the piston (Figure 2b). The piston has two O-rings at the bottom for the purpose of sealing and an air-release tunnel in the axial direction. We first place the Au sample at the bottom of the hole and fill the hole with 2-3 mL of H_2O. We then insert the piston to seal the hole, creating a water-filled chamber inside the hole with the substrate at the bottom. The tunnel is sealed by tightening the screw on top after all air is released. We then apply a pressure to the piston to generate shock waves (Figure 2c). We hypothesize that the shock waves will transfer from the water onto the Au seeds, thus inducing defects in the Au lattice.

Preliminary Ultraviolet-Visible Spectroscopy, as shown in Figure 3, demonstrates an 8 nm continuous red shift, indicating a flattening of Au seeds morphology; however, the SEM images of the seeds indicate that the overall morphology of the seeds has been preserved. To obtain more insights into the Au lattices after exposure to pressure, we build a computing model to simulate the Au seeds morphology before and after exposure to the shockwaves. We examined a specific condition where concentrated pressure is applied on the crest of the pseudo-spherical Au seeds. The simulations results indicate that 500 MPa of pressure deforms Au atom on the top of the seeds for a maximum displacement of 0.5 nm, which is approximately one gold lattice constant. <111> pole figures generated from the simulations also indicate that plastic deformation by dislocation motion grows as applied pressure increases from 100 MPa to 700 MPa.

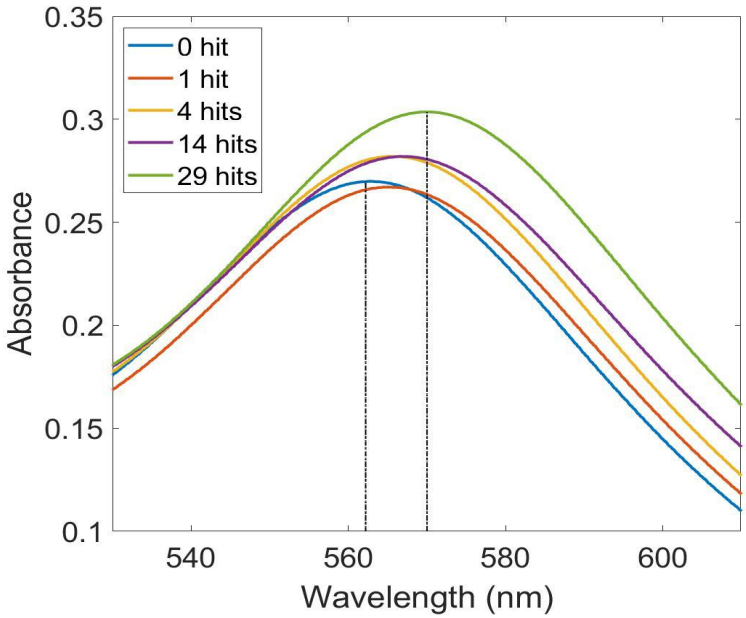

Figure 3. LSPR Peak Transformation Resulting from Shockwave-Induced Defects