



Large Area Nanoplasmonic Architectures for Solar Applications

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Introduction

Background:

- Solar energy driven dye-based and polymer-based organic solar cells offer a promising and inexpensive alternative to crystalline Si solar cells
 - Efficiencies of these organic solar cells remain less than 10%
- Recent advances have demonstrated that plasmon resonances of metal nanostructures can be engineered to enhance charge carrier generation in adjacent semiconductors resulting in significant performance enhancement
 - Integration of plasmonic nanostructures for enhanced photon concentration in organic solar cells remains in its infancy due to the lack of conceptual understanding of plasmonic engineering

Direction:

- Design large area plasmonic architectures with various geometries, dimensions, and unique optical resonances enabling the capture of broadband solar radiation.
- These wafer scale nanoplasmonic architectures have ideal surface characteristics to directly integrate with organic and inorganic media for solar device fabrication.

Colloidal Lithography:

- Plasmonic architectures (nanoholes and Fischer patterns) were designed by nanosphere lithography (NL)

Nanosphere Lithography:

- close-packed monolayer of polystyrene or silica nanospheres are formed on a substrate via self-assembly
 - metal deposition is used to generate an array of plasmonic architectures

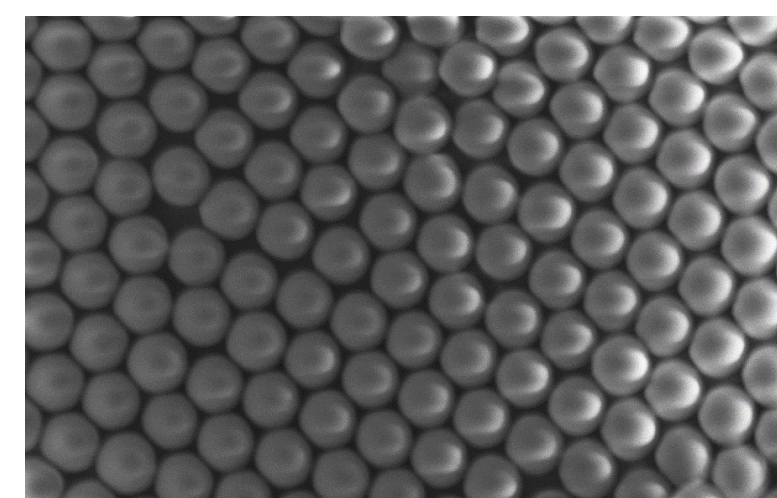


Figure 1: Close-packed array of 1.1 μm Polystyrene beads

Advantages of NL:

- moderately reproducible process
- relatively fast
- cost effective

Approach:

- cast a close-packed layer of nanospheres on the surface of water
- transfer the free-floating nanosphere mask on a solid substrate
 - forces that cause self-assembly:
 - electrostatic forces
 - van der Waals forces
 - steric interactions

Objectives:

- Design large area plasmonic architectures with various geometries, dimensions, and unique optical resonances enabling the capture of broadband solar radiation
- Construct routes to integrate large area architectures with standard dye-sensitized solar cells to achieve higher efficiency by plasmonic enhancement

Materials and Methods

Large-Scale Area Method:

- Solution A is 60 μl of polystyrene (PS) beads and solution B is made by mixing 54 μl of ethanol and 6 μl of 1% hexylamine in ethanol solution and placed in an ultrasonic bath for 10 s. The two solutions are mixed and shaken up.

- 120 μl of the mixed solution is put in the bent tip pipette and placed onto the surface of the water in a Petri dish. The process is carried out in a nearly closed plastic box with ethanol environment. Scoop the solution off of the surface of the water using a glass or silicon substrate.

- Dry the substrate in the ethanol environment to prevent drying effects

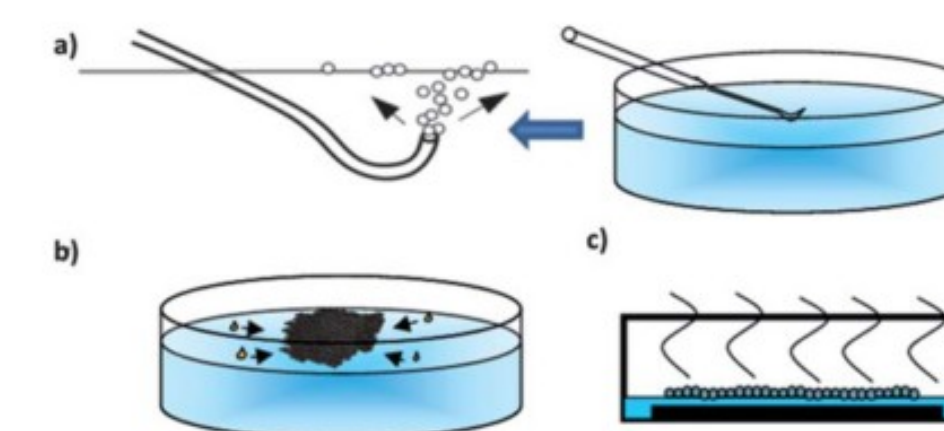


Figure 2: Schematic of large-scale area method
<http://pubs.rsc.org/en/content/articlepdf/2011/jm/c1jm11936b>

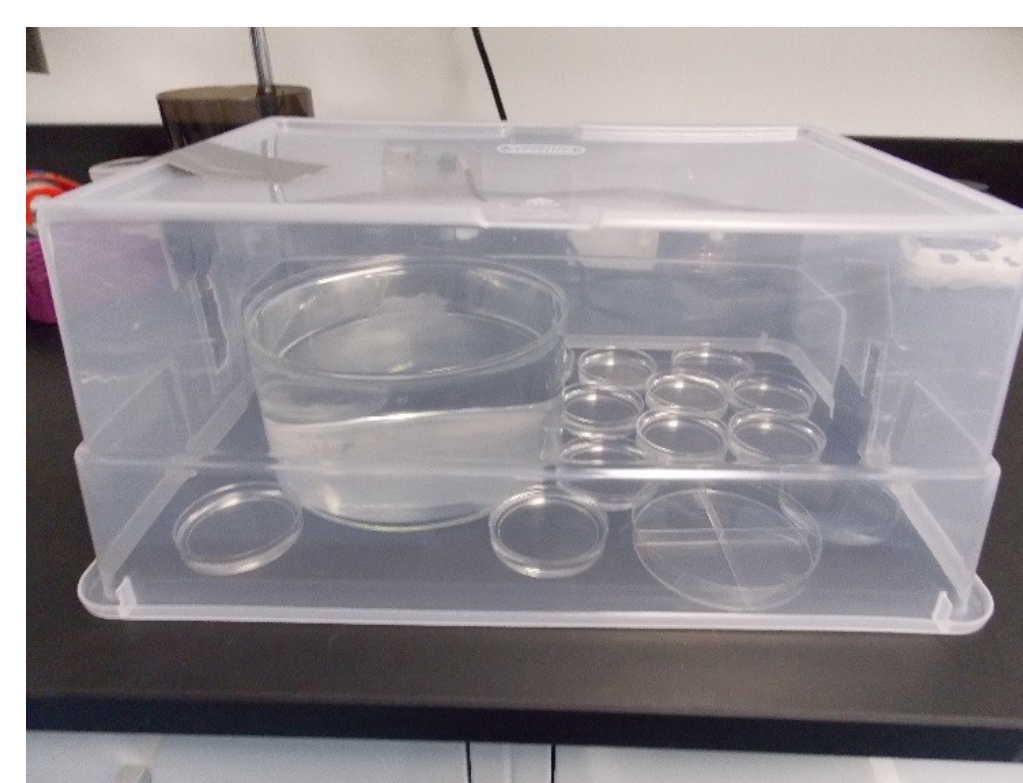


Figure 3: Ethanol environment with Petri dish for the large substrate

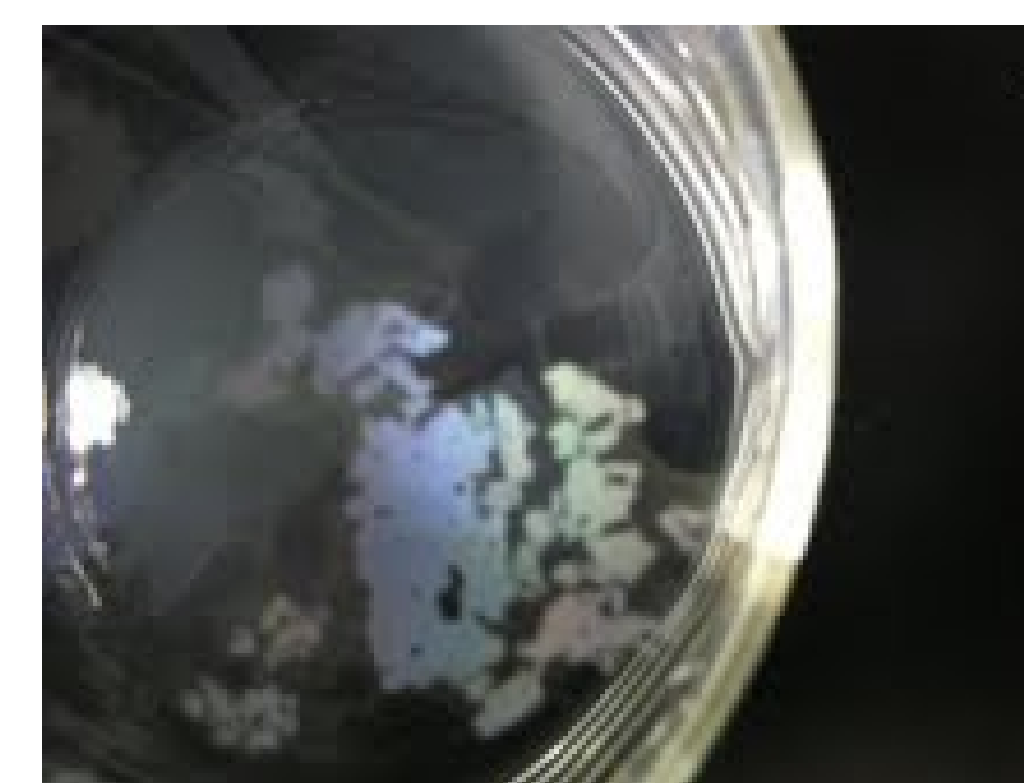


Figure 4: 1.1 μm PS bead solution on the surface of the water

Results

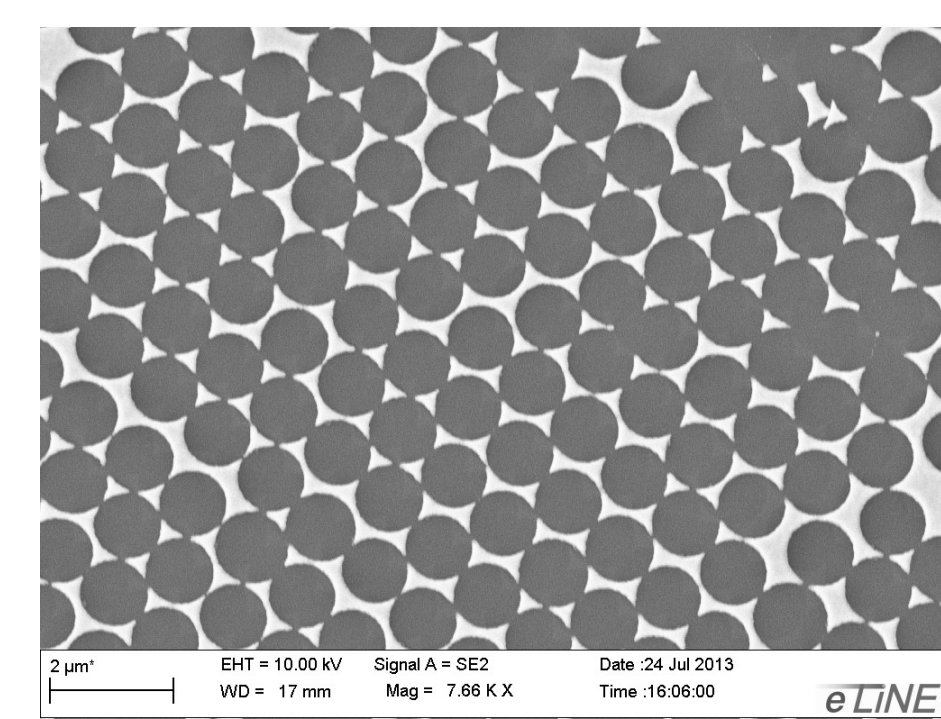


Figure 5: Nanohole Structure
• Si substrate
• 1.1 μm PS beads
• O₂ RIE etch for 20 s
• 5 nm Cr / 100 nm Au
• 30 min water sonication

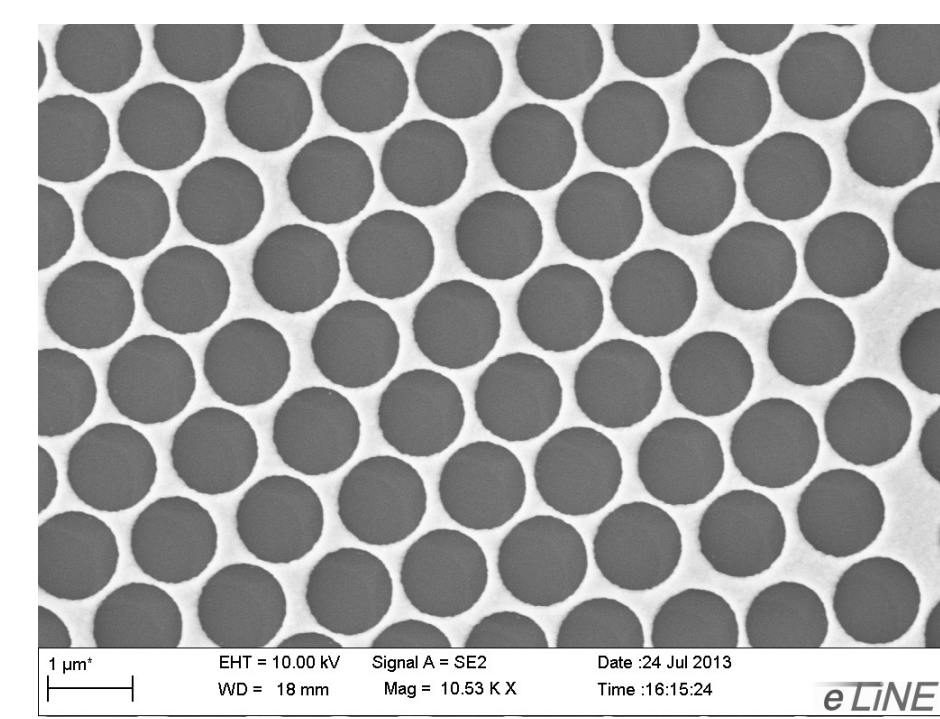


Figure 6: Nanohole Structure
• Si substrate
• 1.1 μm PS beads
• O₂ RIE etch for 40 s
• 5 nm Cr / 100 nm Au
• 30 min water sonication

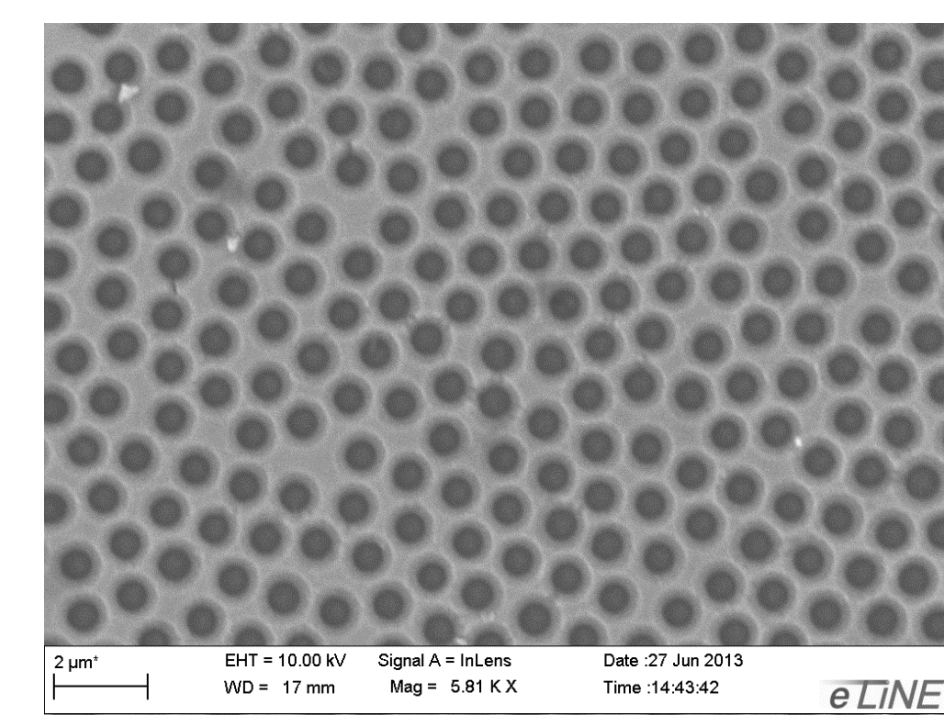


Figure 7: Nanohole Structure
• Glass substrate
• 1.1 μm PS beads
• O₂ RIE etch for 90 s
• 5 nm Cr / 100 nm Au
• 30 min water sonication

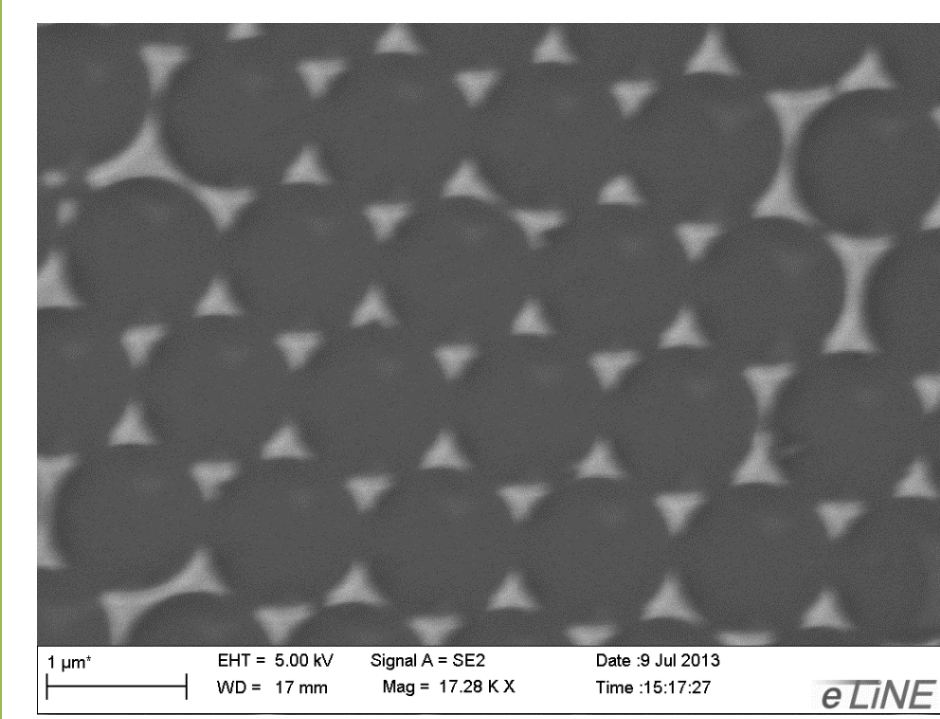


Figure 8: Fischer Pattern
• Glass Substrate
• 1.1 μm PS beads
• 5 nm Cr / 40 nm Au
• 10 min sonication in dichloromethane

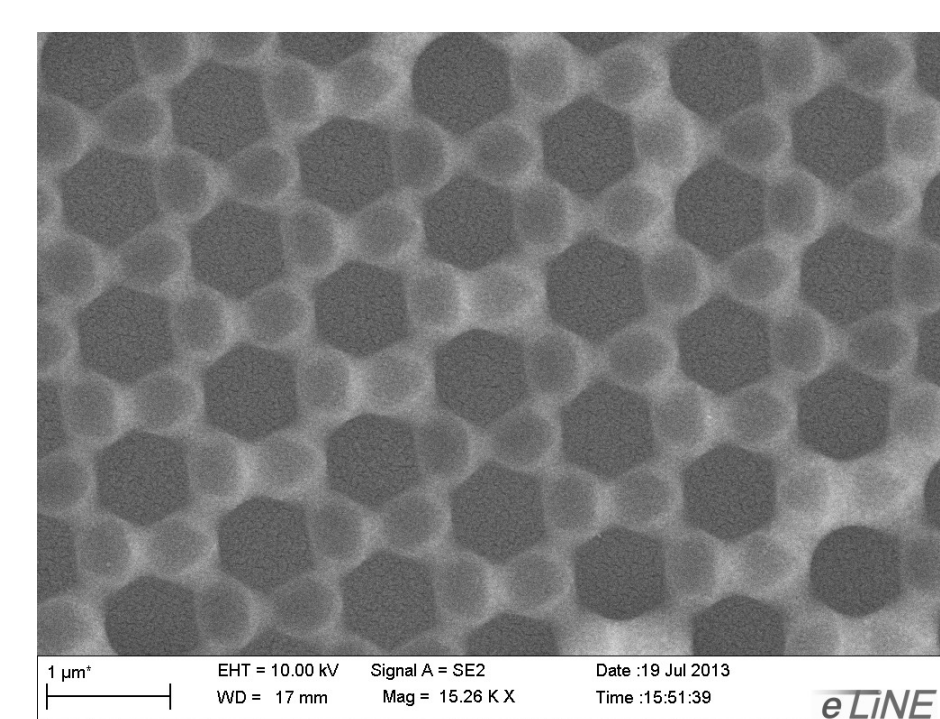


Figure 9: Fischer Pattern
• 1.1 μm PS beads
• 5 nm Cr / 100 nm Au
• 30 min water sonication
• Substrate rotation speed: about 10.6 rpm

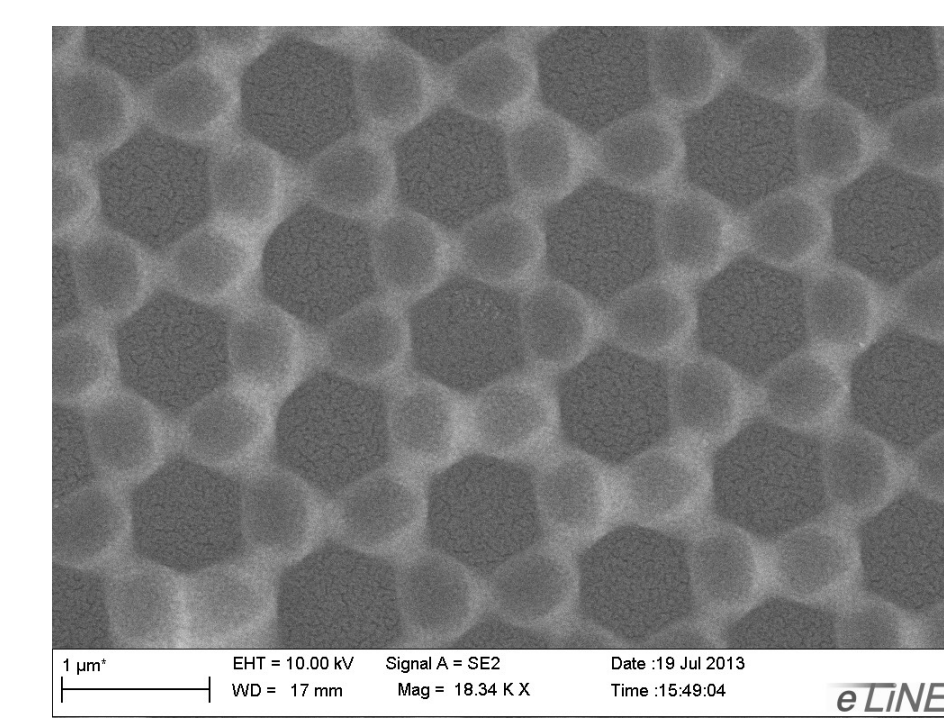


Figure 10: Fischer Pattern
• 1.1 μm PS beads
• 5 nm Cr / 100 nm Au
• 30 min water sonication
• Substrate rotation speed: about 26.5 rpm

Absorbance over wavelength for nanohole structures compared to the solar spectrum

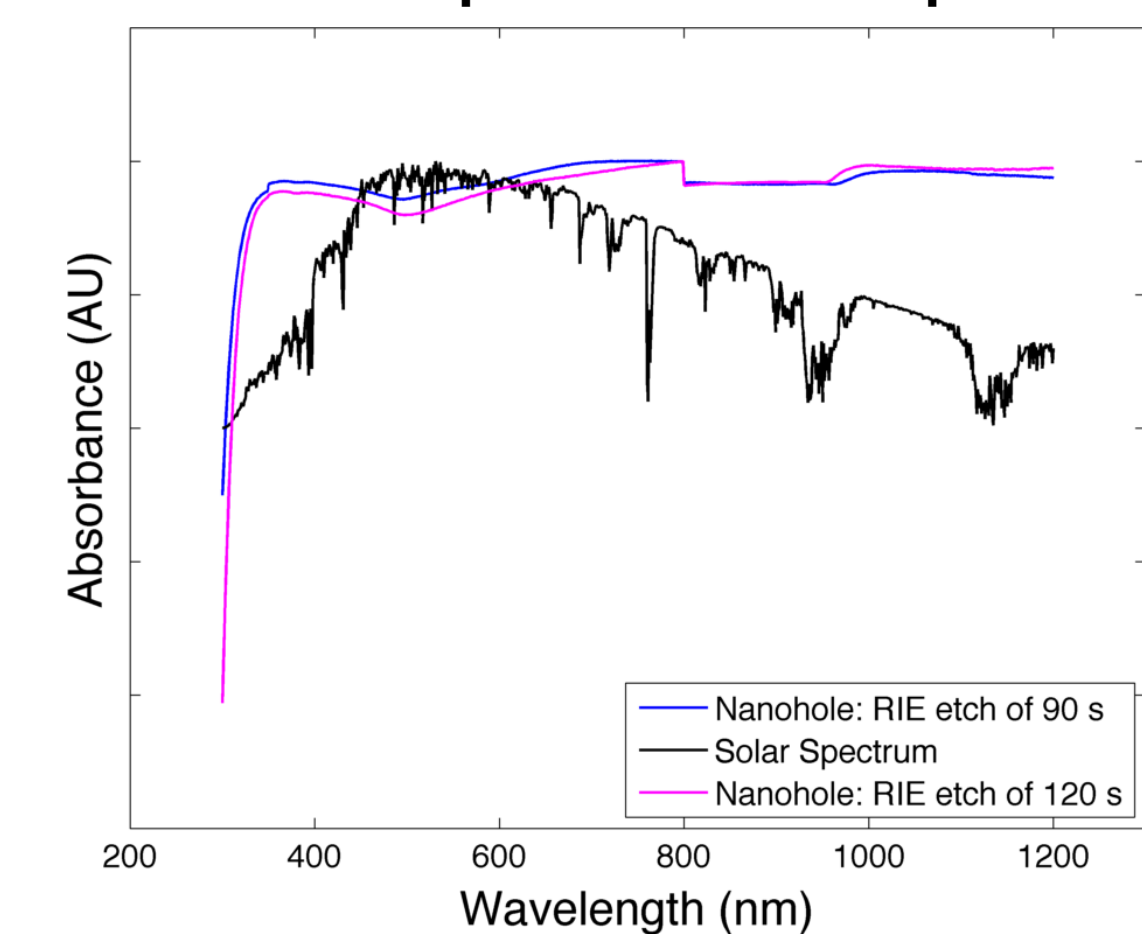


Figure 11: UV-Vis spectrum of nanohole structures

Absorbance over wavelength for Fischer Patterns compared to the solar spectrum

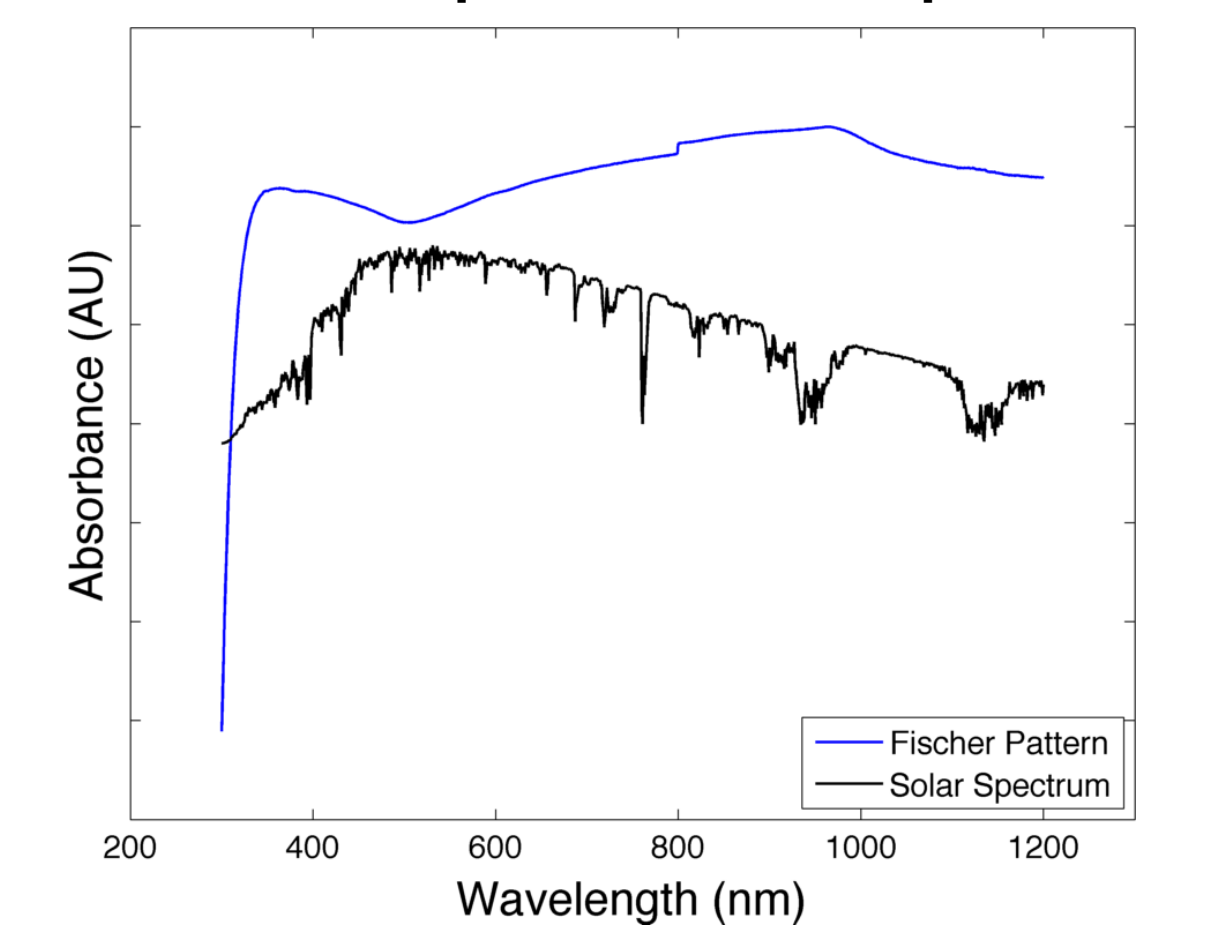


Figure 12: UV-Vis spectrum of a Fischer Pattern

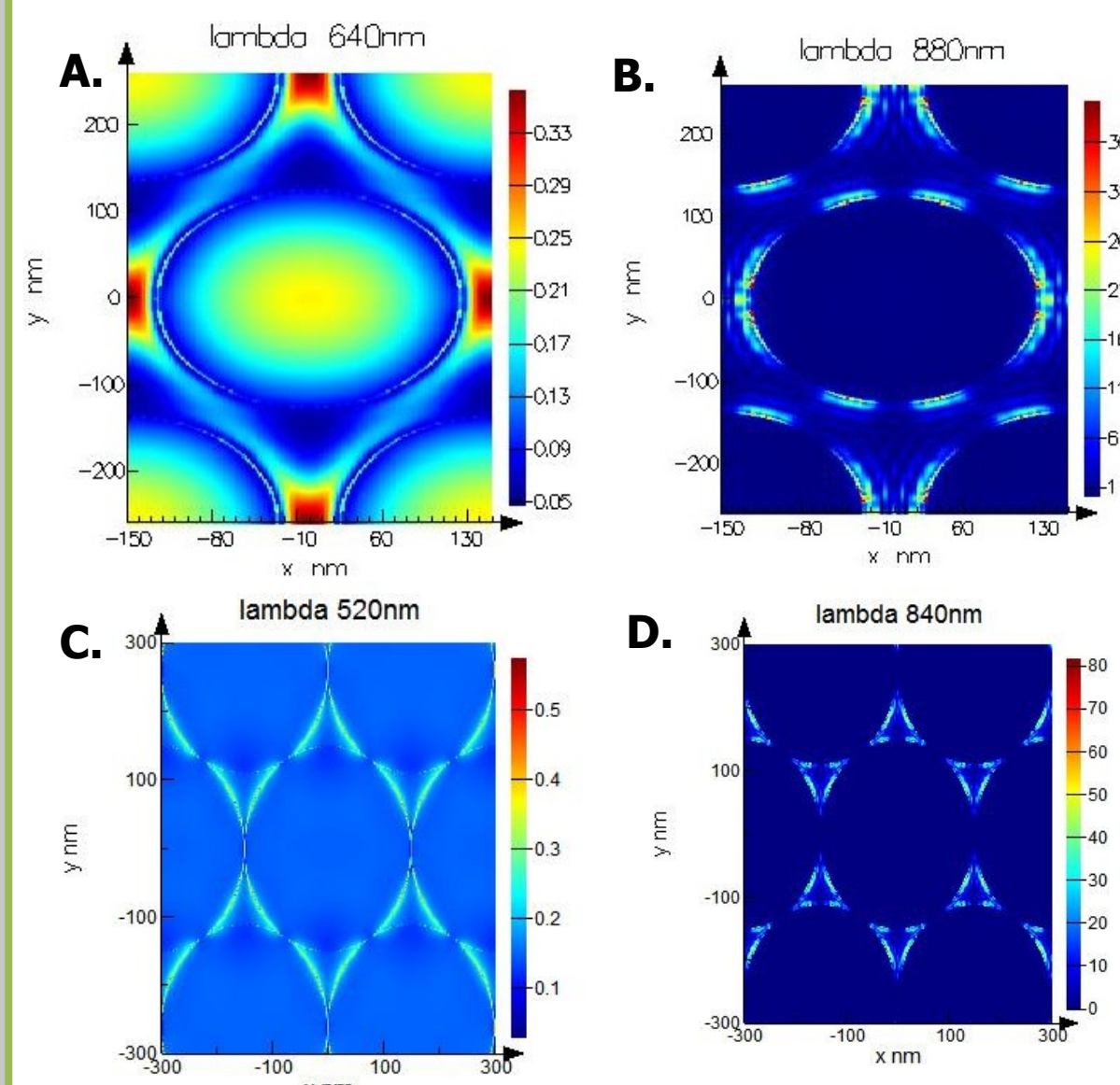


Figure 13: FDTD of A: nanohole at 640 nm, B: nanohole at 880 nm, C: Fischer Pattern at 520 nm, and D: Fischer Pattern at 840 nm
<http://redc.nrel.gov/solar/spectra/am1.5/>

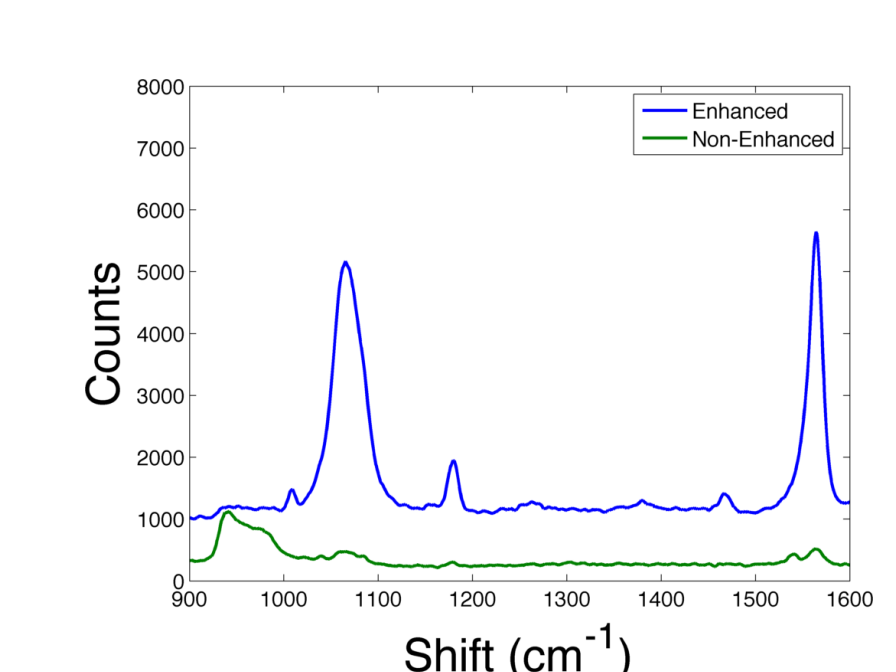


Figure 14: SERS spectra of benzenedithiol bound to a Fischer Pattern structure

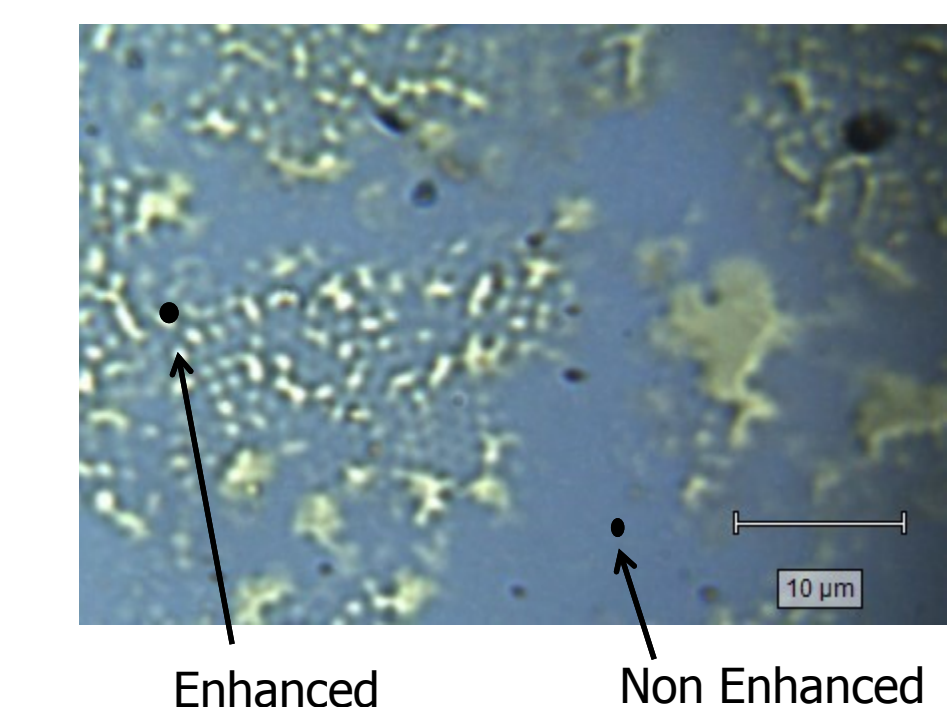


Figure 15: Image of enhanced and non enhanced area of a Fischer pattern

Future Work

Applications:

- Plasmonic Enhancement of solar devices
 - Incorporate nanohole arrays and Fischer patterns into solar cells
 - Construct other large-area architectures such as bimetallic nanostructures and metal-insulator-metal (MIM) structures
- Biomimetic: construct nanoscale designs in order to mimic structures in nature
 - Mimic the color of butterfly wings in order to obtain optical properties of nature

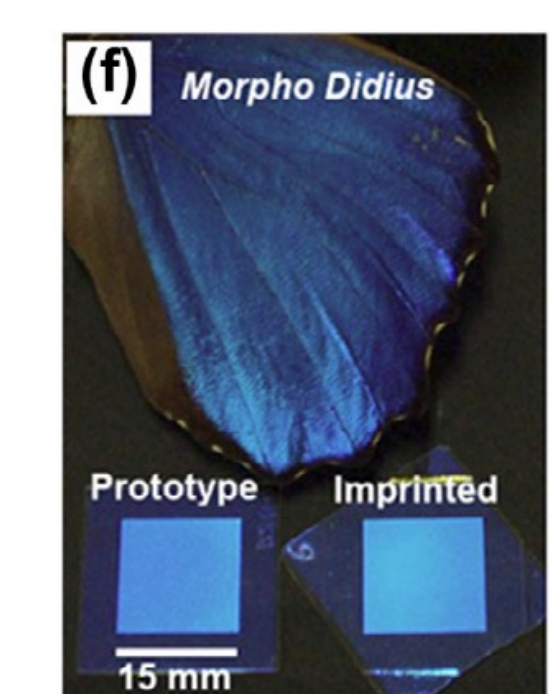


Figure 16: Morpho didius butterfly wing and fabricated Morpho - blue

Conclusions

We can generate plasmonic Fischer patterns by depositing various amounts of Cr/Au and lifting off the PS beads through water sonication. Nanoholes of various diameters and pitch length can be produced by decreasing the PS bead size with reactive ion etch, depositing layers of Cr/Au, and removing PS beads. The plasmon resonances of these large area architectures are highly tunable by simply altering the nanosphere size. Also these structures show enhancement and broadly match the UV-Vis solar spectrum.

References

- J. Zhao, B. Frank, S. Burger, H. Giessen, "Large-Area High-Quality Plasmonic Oligomers Fabricated by Angle Controlled Colloidal Nanolithography," ACS Nano 5, 11, (2011) 9009-9016.
- K. Yu, T. Fan, S. Lou, D. Zhang, "Biomimetic optical materials: Integration of nature's design for manipulation of light," Progress in Materials Science 58 (2013) 825-873.