Supplementary Information

Shadow Overlap of Ion-beam Lithography (SOIL) for Nanoarchitectures

Yeonho Choi[†], Soongweon Hong[†], and Luke P. Lee[*]

Biomolecular Nanotechnology Center, Berkeley Sensor & Actuator Center, Department of Bioengineering, University of California at Berkeley, Berkeley, California 94720, USA

[†]Equally contributed to this work.

* To whom correspondence should be addressed. E-mail: lplee@berkeley.edu

METHODS SUMMARY

Preparation of self-assembled polystyrene nanosphere array on a glass substrate

A glass slide was cut into ~1'' x 1''and cleaned in a piranha etch solution (30 %, 3:1 H_2SO_4:H_2O_2, *warning: strong acidic oxidant, very harmful to personal contact*) for 1 h. After rinsing with DI water, the substrate was dried with N_2 gas and exposed to oxygen plasma for 10 min to make a hydrophilic surface on glass. 10 μL polystyrene (PS) nanosphere (477 nm in diameter, Polyscience inc.) colloidal solution was dropped on the cleaned glass. After drying the solution, the oxygen plasma (March Plasmod inc.) for the isotropic dry etching was applied to the glass slide, and the final size of PS beads became 405 nm on average. The 20 nm gold layer and 1 nm titanium adhesion layer were deposited on the substrate placed on top of copper wedges to provide the inclinations of 10, 20, 30, and 40 deg. For the directional dry etching, ion-milling was applied to the samples on top of the copper wedges for 5 min. As a final step, the substrates were sonicated in acetone for 1 h to completely remove the PS beads.

The microscopy system for scattering spectroscopy depicted in Fig. 4a consisted of a Carl Zeiss Axiovert 200 inverted microscope (Carl Zeiss) equipped with a dark-field condenser (NA 1.2 ~ 1.4), a true-color digital camera (CoolSNAP cf, Roper Scientific), and monochromator (300 mm focal length and 300 grooves per mm, Acton Research) with a 1024 X 256 pixel cooled spectrograph CCD camera (Roper Scientific). A 2-μm-wide aperture was placed in front of the monochromator in the region of interest.

Numerical Simulation Analysis

In the numerical study of SOIL structures, electromagnetic simulations were done with a modified Drude model for the gold structures.[1] The thickness of the gold structures was defined from the angled deposition of 20 nm thickness as the experiments, while the structure was defined by the combination of angles expected in metal deposition and ion milling processes. To look into the trend of electric-field change, simulated structures were varied with 1° step deposition angle. The most highly enhanced spots as well as electric field distribution were searched on the middle cross section of structures.

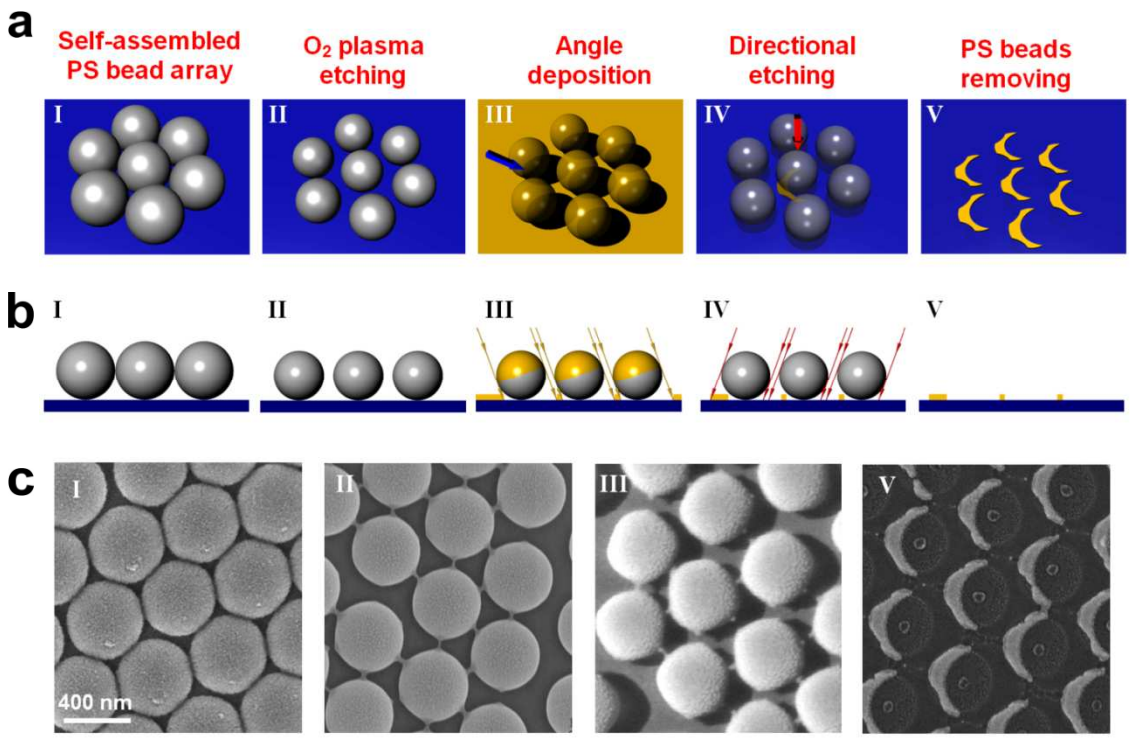

Figure S1. The fabrication steps and corresponding SEM images of Shadow Overlap of Ion-beam Lithography (SOIL) a. Perspective and **b.** cross-section view of schematic diagram. **c.** Representative SEM images of each fabrication step. I Self-assembly of polystyrene (PS) beads → II O_2 plasma etching → III Directional gold deposition → IV Fixed angle dry etching → V Final nanoplasmonic pattern array. The arrows in schematic diagram (III and IV) indicate the directions of gold deposition and ion-milling, respectively.

Figure S1.

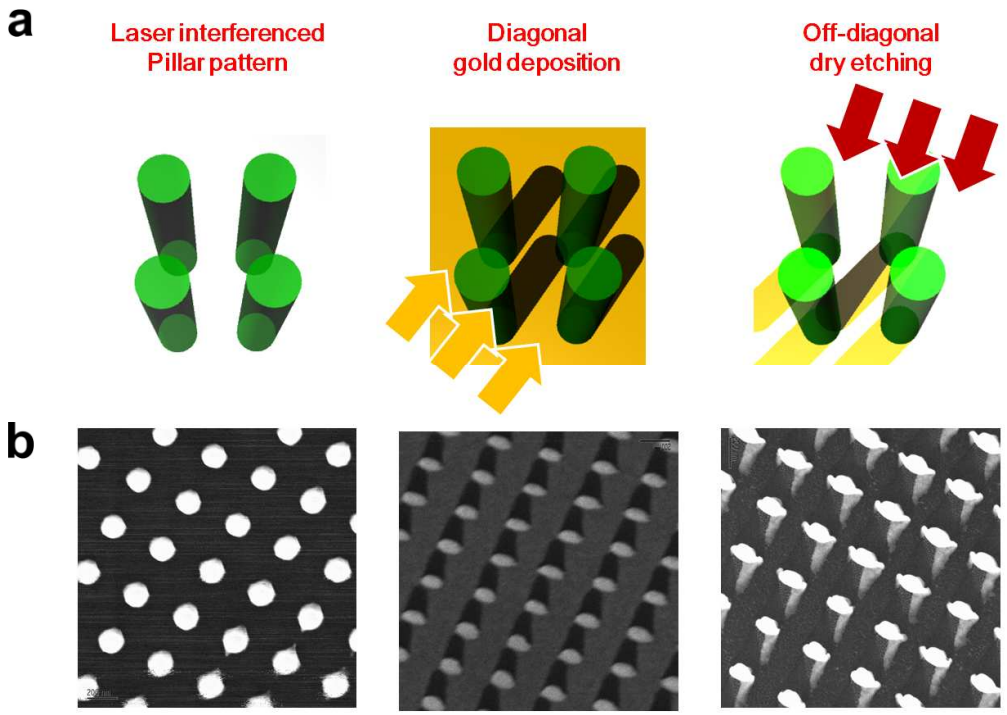

Figure S2. a. The illustration and **b.** corresponding SEM images of nanoneedle array fabricated by SOIL assisted by Laser interference Lithography (LIL). As a pre-pattern, 100 nm in diameter and 300 nm height cylinder arrays were fabricated on top of 4" quartz wafer using LIL. 20 nm gold was deposited with a 10 deg azimuth angle and 45 deg zenith angle. As a final step, ion-milling was applied for selectively removing the gold film with a 0 deg azimuth angle and 45 deg zenith angle.

Figure S2.

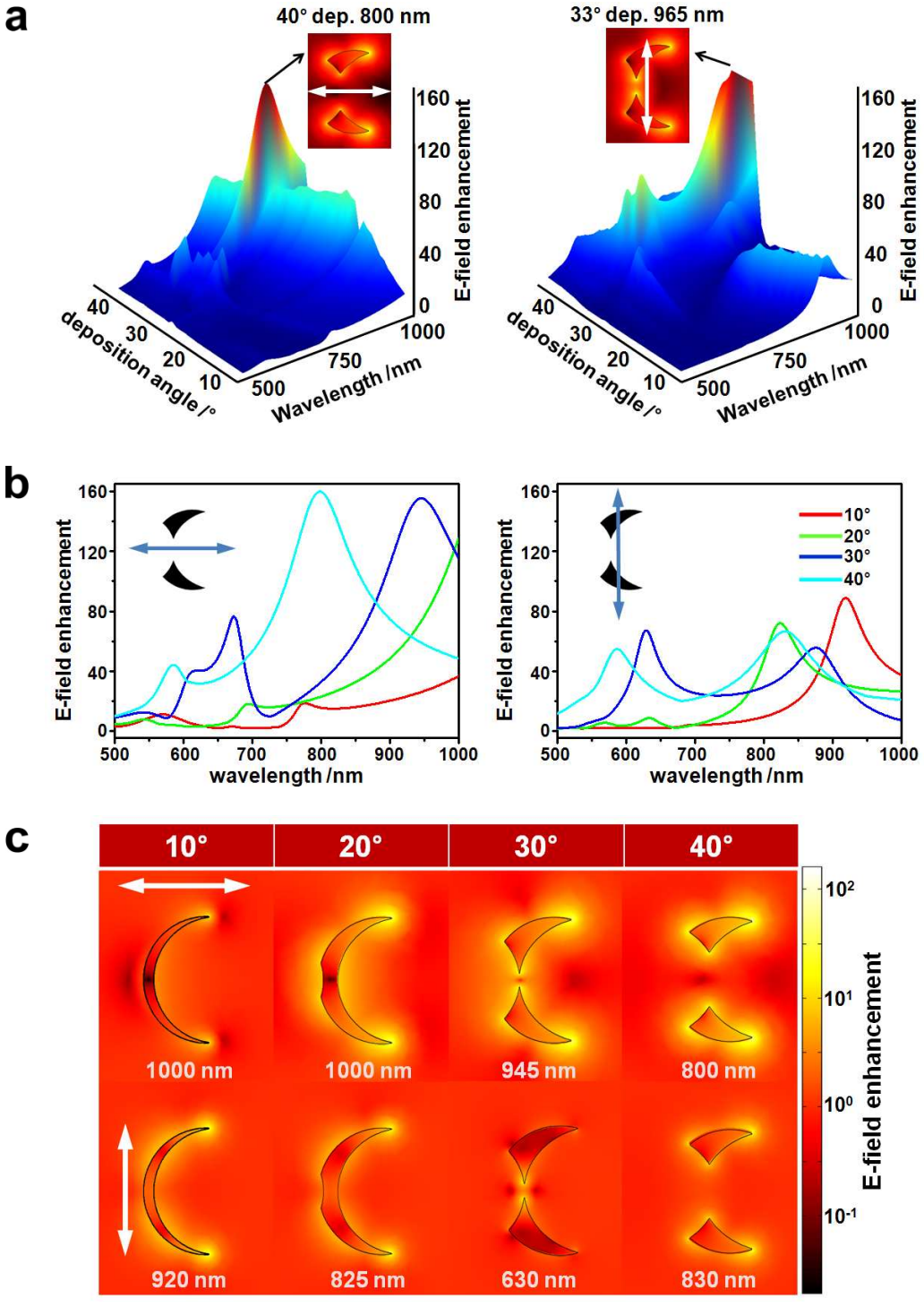
a
40° dep. 800 nm
33° dep. 965 nm
E-field enhancement
deposition angle /°
Wavelength /nm
b
E-field enhancement
wavelength /nm
10°
20°
30°
40°
c
10°
20°
30°
40°
1000 nm
1000 nm
945 nm
800 nm
920 nm
825 nm
630 nm
830 nm
E-field enhancement

Figure S3.

Figure S3. The near-field optical characterization of the nano-axes array fabricated by SOIL **based on simulation a.** Electromagnetic field amplitude enhancement profile as functions of gold deposition angle and wavelength **b.** The representative polarization dependent EM amplitude enhancement spectrum and **c.** EM distribution at 10°, 20°, 30°, and 40° gold deposition angle.

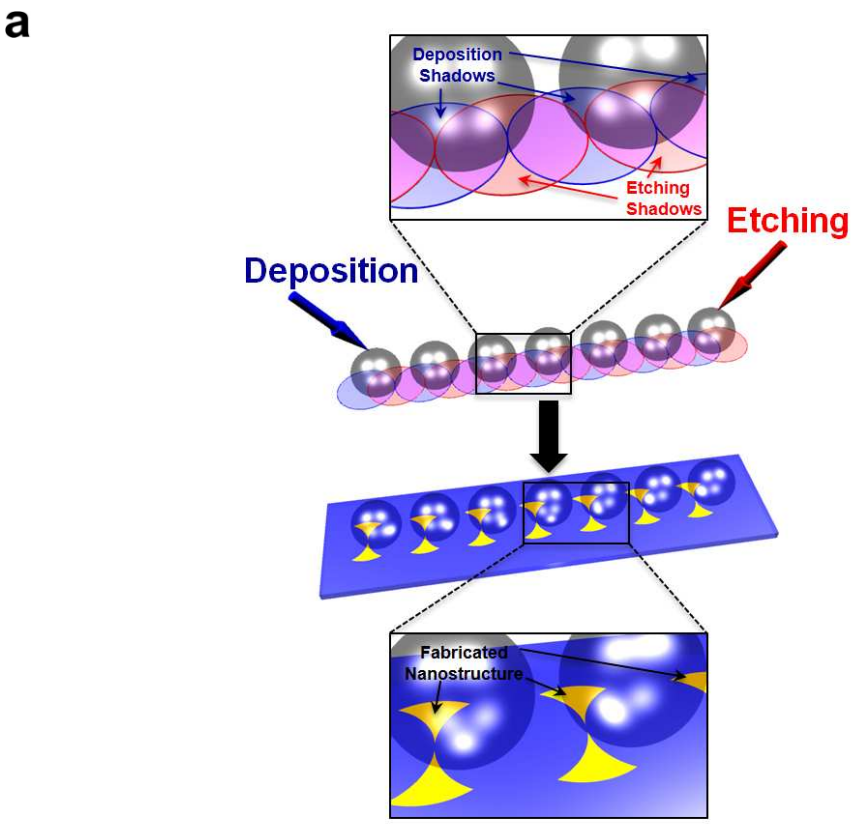
a
Deposition
Shadows
Etching
Shadows
Etching
Deposition
Fabricated
Nanostructure
b

Figure S4.

Figure S4. The representative nanostructure array fabricated by shadow overlap a. illustration and **b.** corresponded SEM images of nanoarchitectures created by SOIL. The bar corresponds to 200 nm.

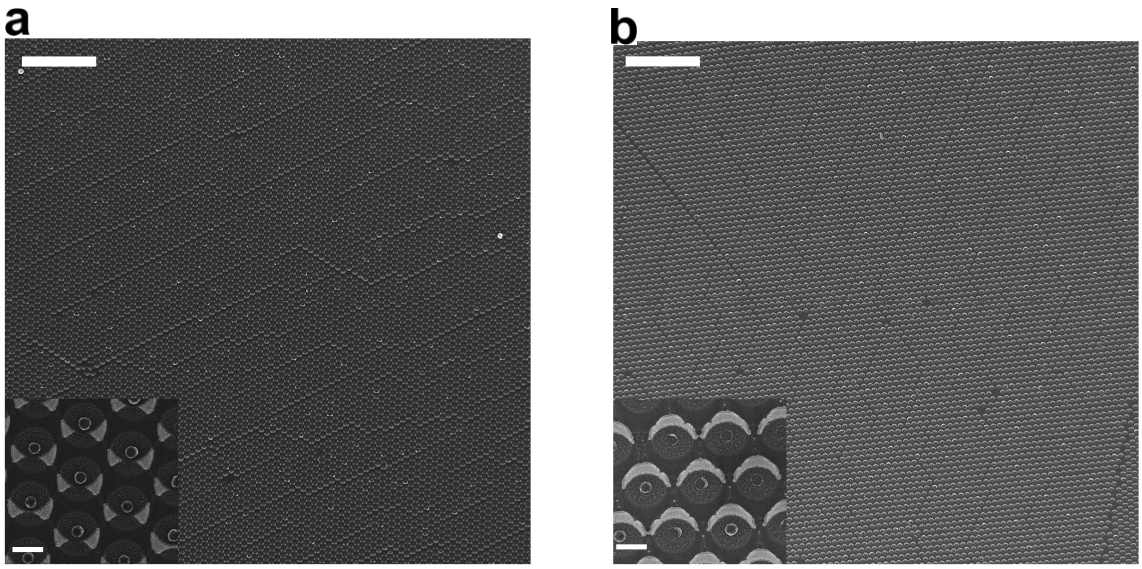

Figure S5. The uniformity of the nanoarchitectures by SOIL SEM images of SOIL patterns with **a.** 40 deg and **b.** 10 deg deposition angle. Insets are enlarged SEM images. The scale bar in main and inset SEM images correspond 5 μm and 250 nm, respectively

Figure S5

Reference

1. Hsu, C. M. *et al. Appl. Phys. Lett.* **2008,** 93, 133109.