Supplementary Information

# The Direct and Reliable Patterning of Plasmonic Nanostructures with Sub-10-nm Gaps

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## Figure S1: TEM image of HSQ structures with ~ 5 nm feature size

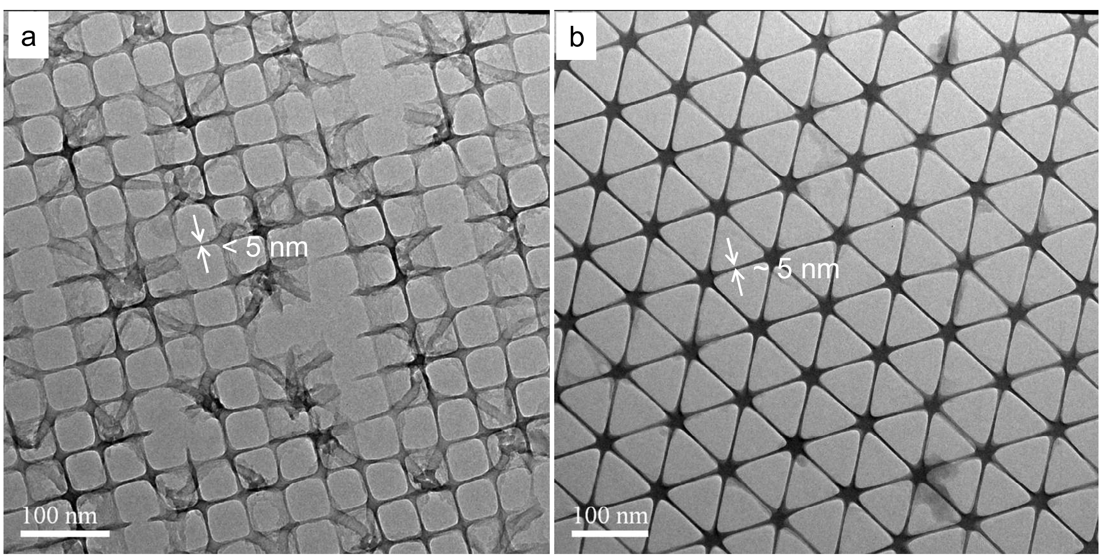


**Figure S1.** Bright-field transmission electron microscopy (TEM) images of HSQ structures fabricated by high-resolution electron-beam lithography. (a) High-aspect ratio HSQ structures with sub-5-nm feature size. Some of them collapsed due to the capillary force during the evaporation-drying process. (b) HSQ structures with feature size of ~ 5 nm. The thickness of HSQ was ~ 80 nm. TEM was used here to confirm that the HSQ structures we fabricated for lift-off were as small as 5 nm.

**Figure S2: A representative pattern achieved using HSQ-based lift-off**

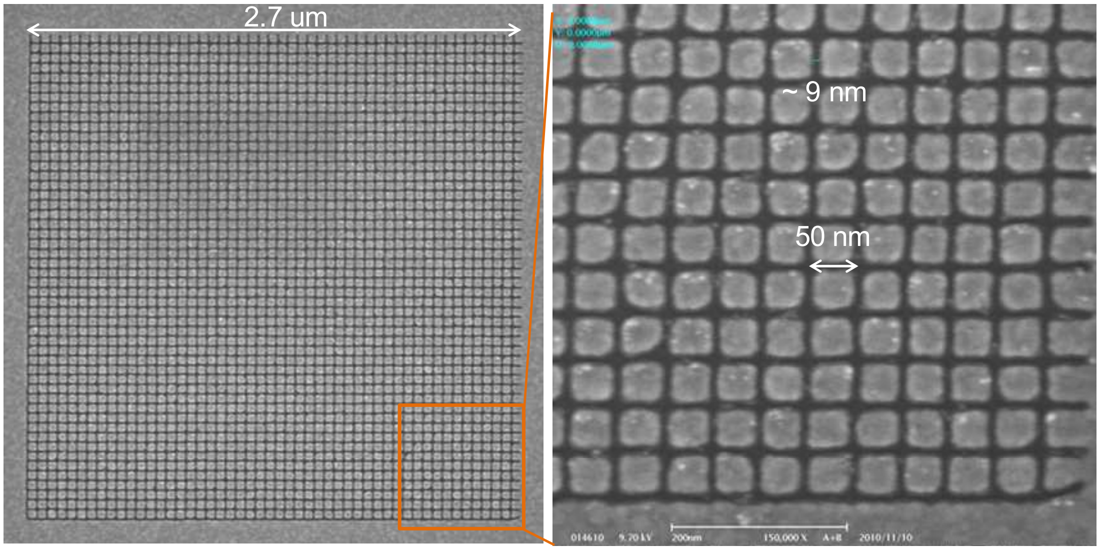


**Figure S2.** SEM images of gold nanostructures fabricated using HSQ-based lift-off process. Left image shows that the entire area of HSQ structures was removed. Right image shows that sub-10-nm gaps were obtained with this process. The pitch of structures was 50 nm and the thickness of gold was 15 nm.

**Figure S3: Large-area nanotriangle structures with ultrasmall gaps fabricated using HSQ-based lift-off**

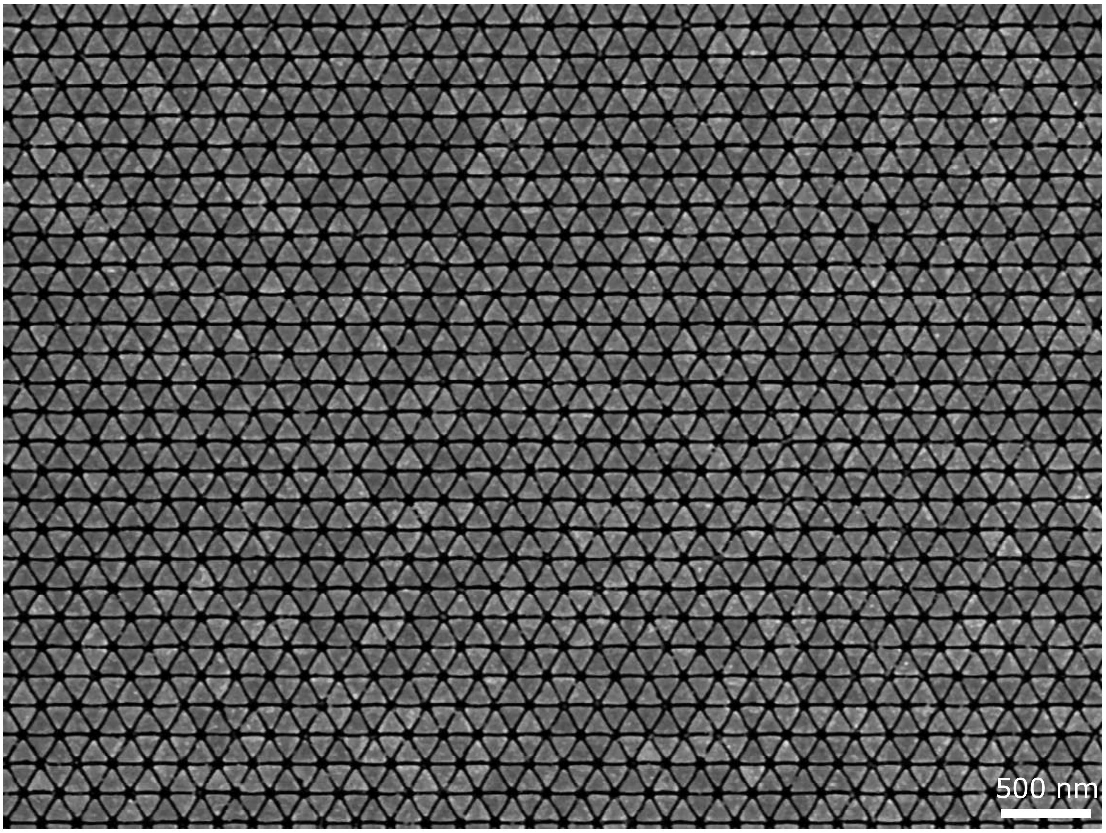


**Figure S3.** A SEM image of gold nanotriangles with 200 nm pitch and 30 nm thickness, showing that large-area gold plasmonic structures could be fabricated reliably.

**Figure S4: Nanogaps fabricated using PMMA-based lift-off**

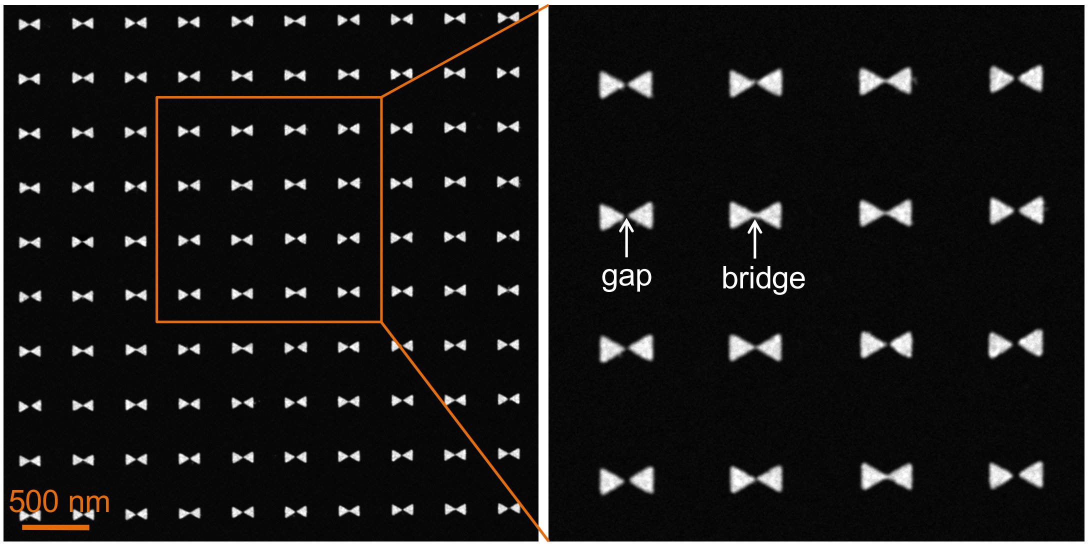


**Figure S4.** Scanning transmission electron microscopy (STEM) images of bowtie gold nanostructures fabricated using a high-resolution PMMA-based lift-off process. The thickness of gold here was 15 nm. This image shows that the nanogaps in these structures fabricated using PMMA-based lift-off process were not uniform compared to those fabricated by HSQ-based lift-off process. For example, in the PMMA-based lift-off process, we always observe ~ 50% connected structures when we want to push the gap size to ~ 10 nm, as shown in the right image. With HSQ-based lift-off technique, the yield to obtain ~ 10 nm gap size can be as high as 98%, as shown in the Figure 4 in the manuscript.

**Figure S5: Gold plasmonic nanostructures with different gap sizes**

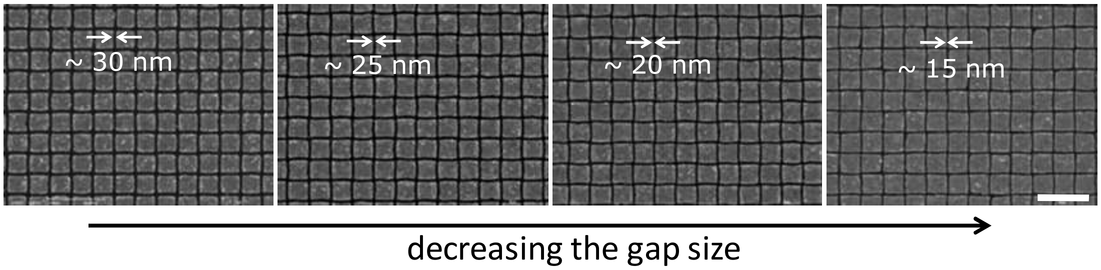


**Figure S5.** SEM images of gold plasmonic structures with different gap sizes fabricated by HSQ-based lift-off technique. The pitch of the structures was kept constant at 200 nm. The gap size was controlled by varying the feature size of initial HSQ structures, which was easily done by exposing HSQ with different dose. The thickness of gold here was 30 nm.

**Figure S6: Nanorectangular structures and the polarization dependence of their plasmon resonance**

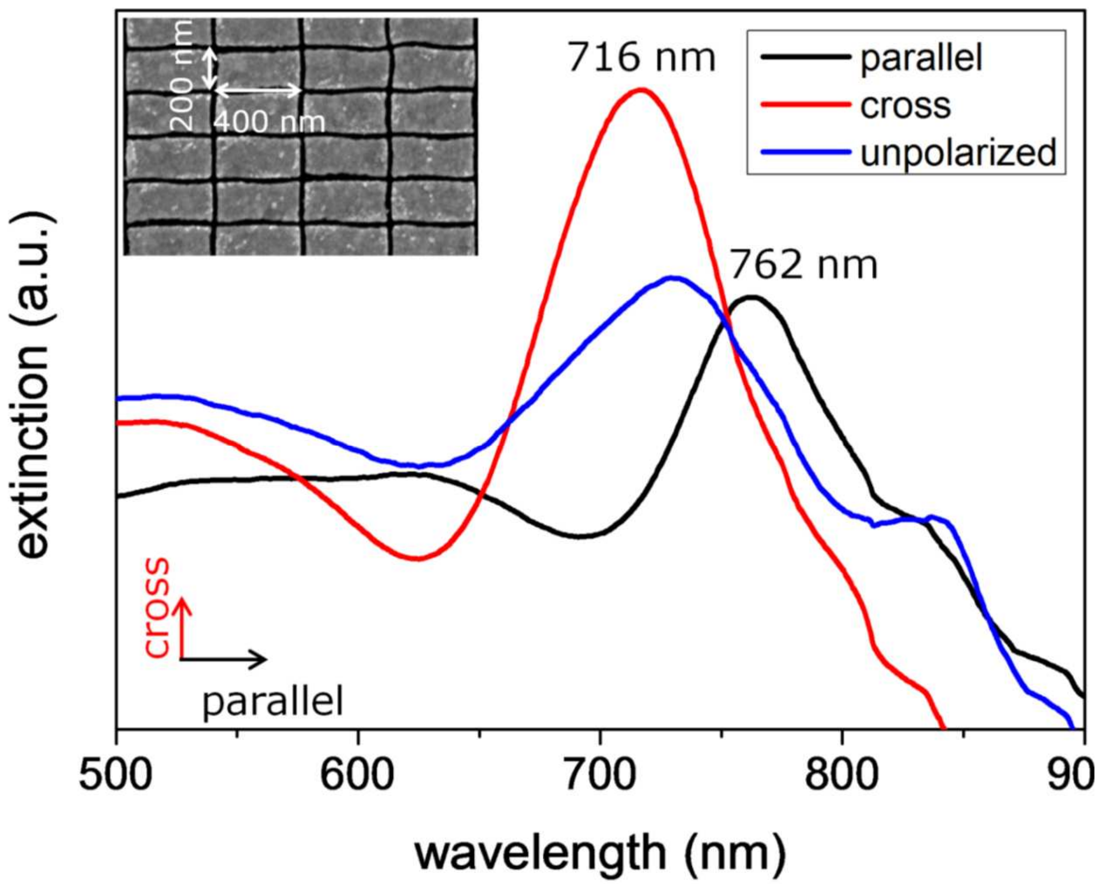


**Figure S6.** Experimental extinction spectra of densely-packed gold nanorectangles on the silicon substrate fabricated with HSQ-based lift-off process, showing two distinct plasmon resonance modes: longitudinal mode with lower resonance energy (black line) and transverse mode with higher energy (red line). The blue line shows the extinction spectrum measured with unpolarized light, whose profile approximately equals to the superposition of longitudinal mode and transverse mode. The thickness of the gold nanostructures was 30 nm with 1 nm Cr adhesion layer. The horizontal and vertical pitches were 400 nm and 200 nm respectively.

**Figure S7:** Comparison of the electric-field-distribution patterns of nanohexagons, nanosquares, and nanotriangles

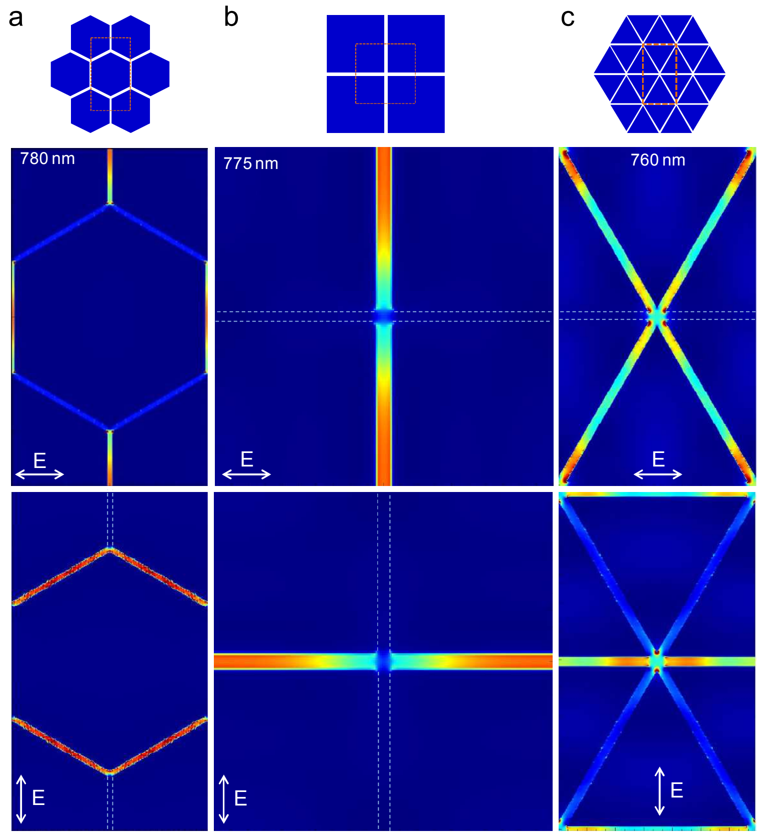


**Figure S7.** Comparison of the electric-field-distribution patterns at plasmon resonance for nanohexagons (a), nanosquares (b), and nanotriangles (c), showing that electric field distribution was more localized in nanotriangle array than that in nanohexagon and nanosquare arrays. The red color represents higher electric field, and blue color represents lower electric field. The sharp corners of the nanotriangles with highly-localized electric field may serve as the hot spots for SERS. The numbers in the field plots were the resonance wavelengths for the structures. The unit cells in the simulations for these structures are indicated by the dashed rectangles in the layout. The dashed lines in the field plots show the boundary of the structures. Note that the gap sizes in these structures were same (10 nm). To make the figures more readable, they were made at different magnifications.