Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Material

Improving LSPR Sensing Performance by Multilayered Composition Graded AgCu Nanotriangle Arrays

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Experimental section:

Materials

500 nm diameter polystyrene nanospheres (PSNS) (Polyscience, Lot # 679675) were used to form the colloid monolayer onto clean glass slides (Gold Seal, Part# 301) and silicon wafers (University Wafer). Sulfuric acid (Fisher Scientific, 98%), ammonium hydroxide (Fisher Scientific, 98%), and hydrogen peroxide (Fisher Scientific, 30%) were acquired to clean the glass and silicon. Silver and copper pellets (Plasmaterials, 99.99% and Alfa Aesar, 99.9%) were purchased as the evaporation materials. Ethanol (Sigma-Aldrich, 98%), toluene (Fisher Scientific, 99.8%), acetone (Fisher Scientific, 99.8%), and isopropanol (Fisher Scientific, 99.8%) were used for the colloid monolayer preparation and to remove residual PSNS from the substrates after the Ag and Cu deposition. Deionized (DI) water (18 MΩ) was used throughout all the experiments. All chemicals and materials were used without further purification.

Fabrication of the Ag-Ti Composite Nanostructures

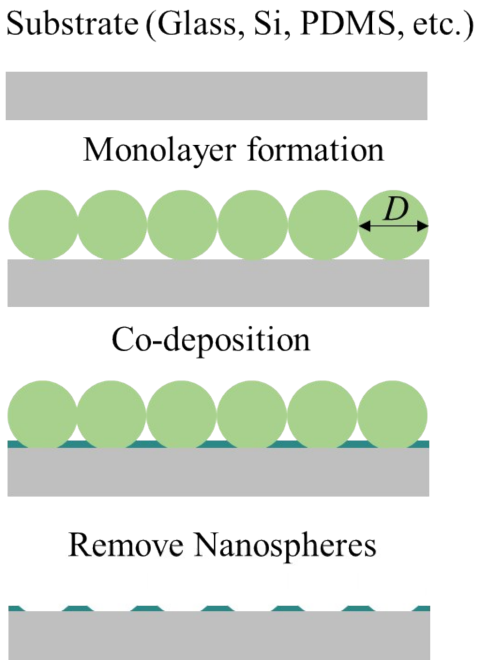

Figure S1:A diagram of the nanosphere lithography process showing the formation of the monolayer, co-deposition, and removal of the nanospheres.

Figure S1 summarizes the fabrication steps for making the nanotriangle and nanohole arrays. First, glass slides and silicon wafers were cut into small pieces with dimensions of 1 cm × 2.5 cm and 1 cm × 1 cm, respectively. Glass substrates were washed in a heated piranha solution, 4:1 volume ratio of concentrated sulfuric acid to 30% hydrogen peroxide, for 20 min. Silicon substrates were cleaned using the first step of the RCA method, heated in a 5:1:1 ratio of DI water, ammonium hydroxide, and hydrogen peroxide, for 20 min. All substrates were then thoroughly rinsed in DI water; substrates that were not coated with monolayers were then dried under a N_2 gas flow.

Then the D = 500 nm PSNS monolayers were prepared on different substrates using an air-water interface method as previously reported.[1] Briefly, the PSNS suspension was first diluted in DI water to a concentration of 0.01 w/v % and then washed several times *via* centrifugation. Next, the suspension was further diluted with ethanol to a 2:1 volume ratio of PSNS. The resulting suspension was loaded into a syringe and droplets of PSNS suspension were dispensed at a rate of 0.015 mL/min onto the surface of a tilted cleaned glass Petri dish (diameter of 10 cm) containing approximately 24 mL of DI water via a syringe pump. This process continued until a monolayer was formed and covered the entire water surface. A Teflon ring was placed gently on the surface of the water to protect the monolayer film against adhering to the side wall of the glass Petri dish. The water level then was raised. Glass and silicon substrates were carefully slid below the monolayer film. Finally, the monolayer was lowered on the substrates by slowly pumping out the water with a peristaltic pump, followed by drying in the air overnight.

The Ag-Cu nanostructures were then fabricated using a custom-built dual source electron deposition system (Pascal Technology). The Ag and Cu crucibles were 17.8 cm apart from each other inside the chamber. The PSNS monolayer coated and uncoated substrates were mounted 53 cm above the crucibles and centered horizontally relative to the two crucibles. With respect to the substrates normal, the vapor incident angle of the Ag and Cu were, $\theta = -10°$ and 10°, respectively. After loading the samples, the deposition chamber was pumped down to a base pressure of $< 1 \times 10^{-6}$ Torr. The deposition rate and total thickness of each evaporation source were monitored by two quartz crystal microbalances (QCM) independently, such that the total deposition thickness, *i.e.*, the sum of Ag and Cu thickness, was fixed to be 50 nm, while keeping the total deposition rate $R_{\mathrm{Ag}} + R_{\mathrm{Cu}} = 0.1$ nm/s. The relative deposition rates of Ag (R_{Ag}) and Cu (R_{Cu}) were varied to achieve the graded and layered structures. During the deposition, the chamber pressure was kept below 1×10^{-5} Torr, and the substrates were rotated azimuthally at a speed of 15 rpm to ensure even mixing of Ag and Cu. After the co-deposition, the substrates were allowed to cool down to room temperature in vacuum before being taken out. Then, as shown in Figure 1, the colloid template was removed from the substrate using Scotch tape, and any remaining PSNS residue was removed by rinsing in toluene, acetone, and isopropanol successively.

Optical and Morphological Characterization

The optical transmission spectra of the Ag-Cu nanostructures were measured by an ultraviolet-visible spectrophotometer (UV-Vis, Jasco-750). Atomic force microscopy (AFM) images of the samples were taken with a Park Systems NX-10 AFM. Scanning electron microscopy images and energy dispersive X-ray spectroscopy (EDX) measurements of the nanostructures were taken by a field emission scanning electron microscope (SEM, FEI Inspect F). The crystal structures of the thin films and nanostructures were characterized by a PANalytical X'Pert PRO MRD X-ray diffractometer (XRD) with a fixed incidence angle of 0.5°. The XRD scans of the thin films were recorded with a Cu Kα1 radiation ($\lambda = 1.541$ Å) in the 2α range from 20° - 80° with a step size of

0.010°. Ellipsometry measurements of the thin films were taken by a spectroscopic ellipsometer (M-2000, J.A Woollam Co., Inc.) at incident angles of 65°, 70°, 75°, and 80°, respectively, over a wavelength range of 370 - 1000 nm.

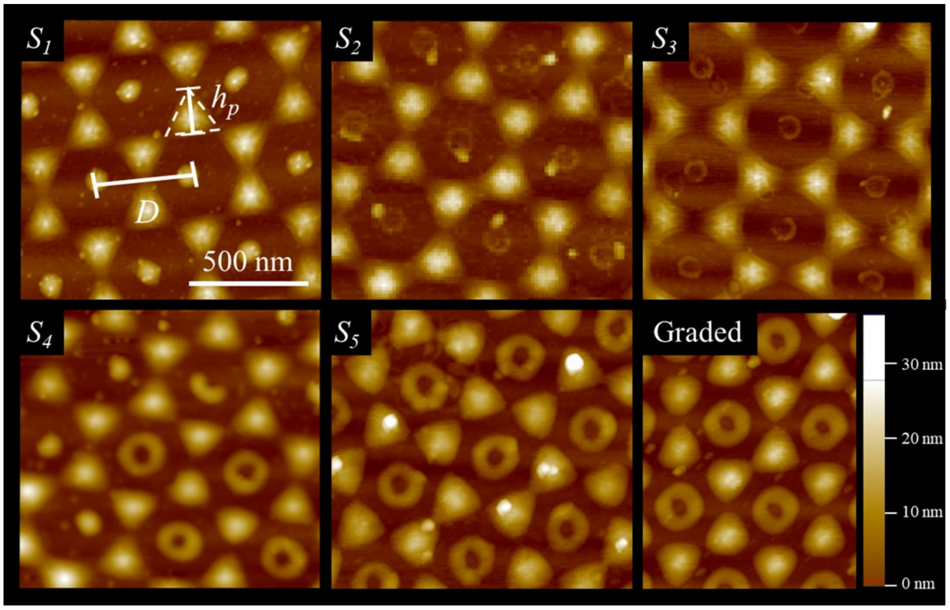

Figure S2: Representative AFM images of different NT samples. The donut shaped or doom shaped patterns are PS residue.

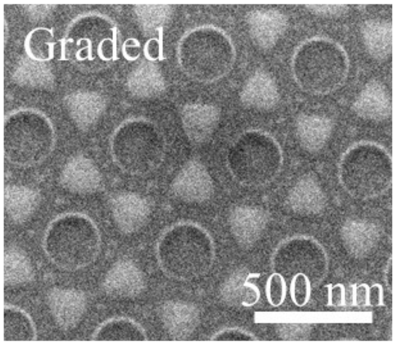

Fig S3: Representative SEM image of the graded NT sample.

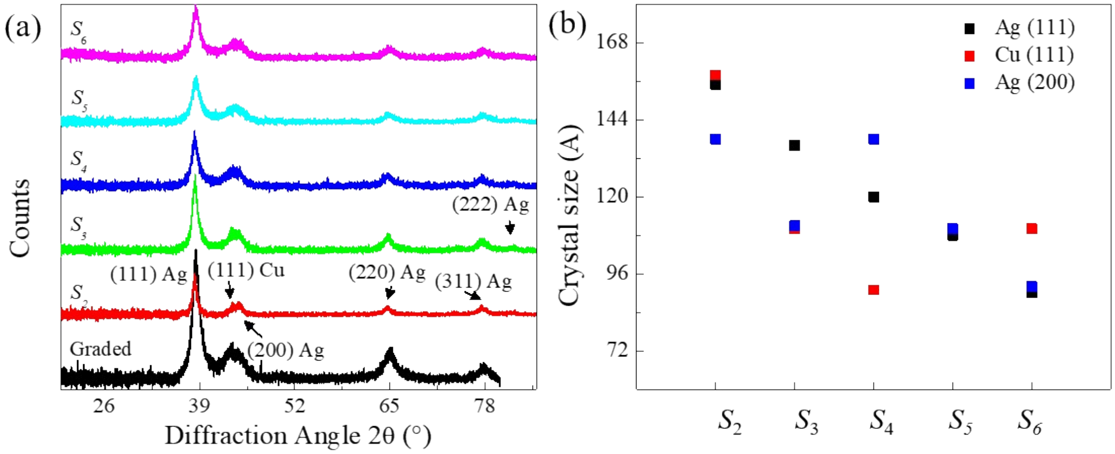

Figure S4: XRD patterns for different thin films of the corresponding NT samples and (b) Scherrer's equation crystal size analysis for the main Ag and Cu peaks.

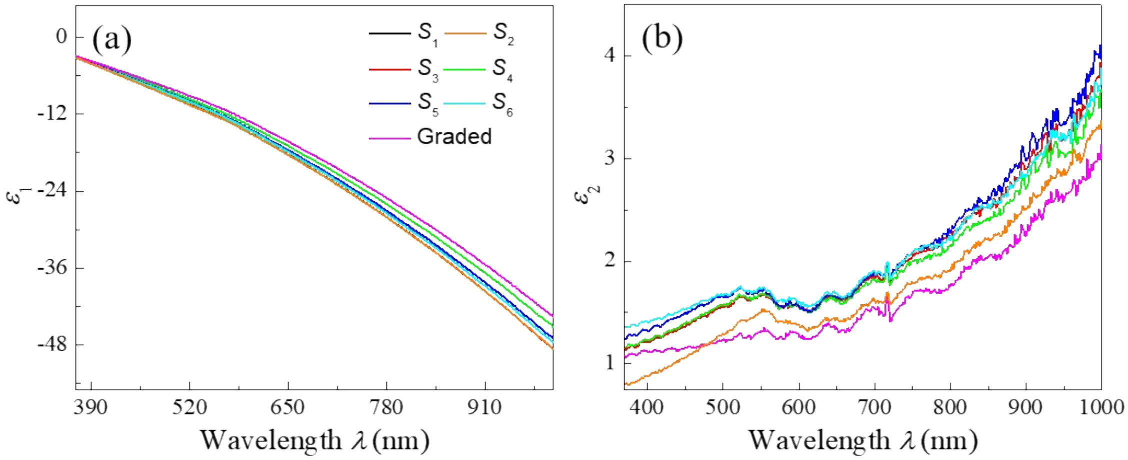

Figure S5: (a) Real ε_1 and (b) imaginary ε_2 parts of the complex dielectric functions from ellipsometry measurements from different thin films of the corresponding NT samples.

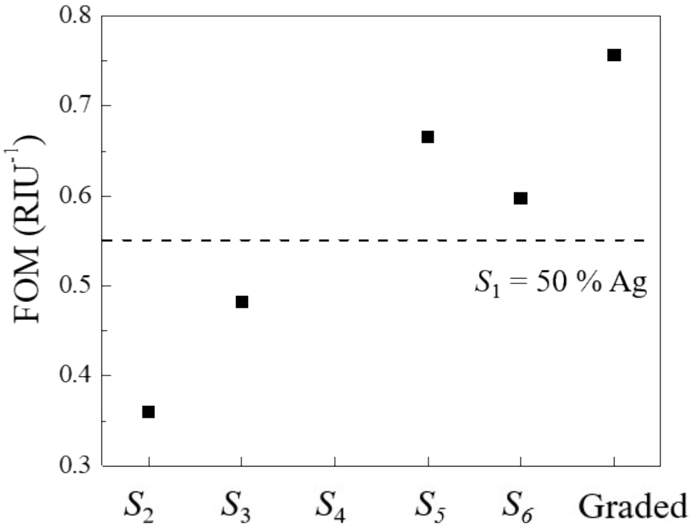

Figure S6: The FOM of the different NT samples as compared to that of the 50 at.% Ag-Cu NT sample.

References

1. W. Ingram, Y. He, K. Stone, W. Dennis, D. Ye and Y. Zhao, *Nanotechnology*, 2016, **27**, 385301.