Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

V-shaped active plasmonic meta-polymers

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Experimental procedures

Fabrication of V-shaped meta-polymers

Glass cover slips and silicon wafers were cleaned using piranha solution (70/30, v/v, concentrated H_2SO_4/30% H_2O_2) heated to 75 °C for 20 minutes and then washed thoroughly with distilled water and dried with N_2. (Warning: *"piranha" solutions are strong oxidant, reacts violently with organic materials. Appropriate safety precautions should be utilized including the use of acid resistant gloves and adequate shielding).* This process also hydroxylates most surfaces and makes the surface extremely hydrophilic. The substrates were then heat treated at 170 °C for 5 mins to remove any remnant solvent. Next, a 4% (w/v) 950 kD PMMA solution in anisole was spin-coated (10000 rpm for 60 seconds) onto the substrates and then substrates were baked on a hot plate at 190 °C for 20 minutes. Trenches were fabricated using e-beam lithography in the PMMA at 3 different intervals- 10 μm along both the row and column, 10 μm along the column and 2 μm along the row, and finally 2 μm along both the row and column. Developer (mixture of isopropyl alcohol and methyl isobutyl ketone in 3:1 ratio) was used to remove the etched polymer in the trench. The samples were then washed with isopropyl alcohol and dried with N_2. The trenches were functionalized using the following method. First, the substrates were kept in a 2 wt% aqueous solution of APTES for 10 minutes. Then they were washed thoroughly twice with DI and dried with N_2. The substrates were kept over a hot plate at 120 °C. Thus, only the trenches are expected to be functionalized by APTES (Scheme 1). The samples were then immersed in sonicated aqueous solution of Au NPs (2.49×10^{-4} M) kept in stirring condition for 6 hours. Au NPs were synthesized using a citrate reduction method.[1] Finally the substrates were cleaned with water. N-methyl pyrrolidone was used to remove the polymer from the surface of the glass substrates leaving behind only the Au NPs. The substrates were then dipped into 10^{-4} M Nile blue chloride aqueous solution for 30 minutes followed by a DI water rinse for the SERS study.

Instrumentation

Patterning was carried out using EBL with a Zeiss Supra scanning electron microscope equipped with an e-beam instrument provided by RAITH (LP plus-GDSII software). A letter 'B'

was etched using EBL as a fiducial marker for optical and electronic microscopic correlation and orientation of the pattern. The trenches and patterned NP arrays were imaged using SEM. The NP arrays were also inspected using dark field microscopy. The sample was visualized in dark field configuration illuminating the substrate at slant angle using super-continuum white light source and collecting the scattered light using a 100x 0.8 NA objective lens. A high-resolution confocal Raman microscope (LabRam HR, Horiba Jobin Yvon) with 100X, 0.8NA objective lens was used for the SERS measurements. A 633 nm He-Ne laser was utilized as excitation source. A half wave plate was introduced in the illumination path to analyze dependence on polarization. The collected light was then dispersed using a grating with 1800 grooves per mm.

Simulation methodology

Numerical simulations were performed using Finite Difference Time Domain (FDTD) method using commercially available solver Lumerical. The simulation consisted of a plasmonic V-shaped antenna comprised of nanospheres (diameter~60nm) with inter-arm angle of 80^{o} on a glass substrate to emulate the experimental setup (Figure 4). The antenna was illuminated using a plane wave with λ=656 nm and the near field electric field was recorded at the metal –glass interface. Wavelength dependent refractive indices of gold and glass were taken from literature. [2,3] The polarization of the input wave was varied in steps of 15^{o}. Maximum value of electric field was plotted against the input polarization angle.

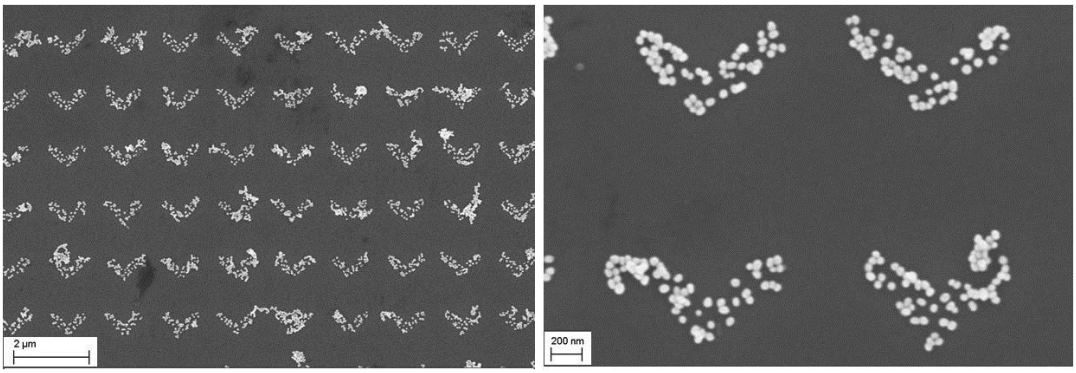

Figure S1. FESEM image of a periodic arrangement of 'V' shaped Au NP arrays with different trench width and surface functionalization condition. Here width of the trench was kept at 200 nm and functionalization of the substrate with APTES was done before EBL. FESEM image depicts random fixation of NPs on the substrate which is probably the result of inadequate functionalization of the substrate surface. Also, as the trench width is much larger than the average NP size, multiple NPs can be observed across the width.

References

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3 E. D. Palik, *Handbook of Optical Constants of Solids*, Elsevier, 1997.