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V-shaped active plasmonic meta-polymers

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We report the design and fabrication of V -shaped plasmonic meta-polymers on glass substrate or silicon wafer using a surface functionalization approach. The efficacy of the assembly method, is examined by analyzing the surface enhanced Raman scattering by individual V-shaped antenna experimentally and using computational simulations to determine the polarization dependence of local electromagnetic field enhancement.

Localized surface plasmon resonance (LSPR) of noble metal nanoparticles (NPs) enables many capabilities in optical devices and applications via large field enhancements and spectral selectivity.[1] These properties can be further enhanced by assembling NPs in ensembles that allow combination of their individual properties and/or generation of new properties using mutual interaction between particles. The size and shape of the particles, spacing and the overall geometry of the assembly together determine the near and far field properties of the NP assembly.[2] However, it is necessary to develop a facile and robust method to organize NPs in a predetermined structure to allow practical applications in electronics, photonics and sensing. A monolayer of metallic NPs arranged in a periodic manner allows the study of collective response (properties) of the array. Recently many advances have been made in nanophotonics using metasurfaces for enhanced light-matter interaction, highly efficient wavefront shaping, improved nonlinear effects, and multi-dimensional control on electromagnetic waves, thus paves way for designing of improved nanophotonic devices.[3-7] Researchers have started using top-down lithography techniques to construct meta-polymers for plasmonic applications[8-10] Some drawbacks of top down processes include tedious and time consuming processes for fabrication as well as polycrystallinity of nanostructures which has adverse effects on device performance.[11, 12] On the other hand, bottom up processes yield metallic NPs with tunable composition, geometry and surface functionality. In low loss and strongly coupled plasmonic systems which can tolerate a few variations in geometry and material compositions, colloidal metallic NPs and their assemblies prepared by bottom up process can provide good building blocks.[13-16] On the other hand, if specific positioning of colloidal plasmonic NPs in the target site is required, then top down and bottom up processes can be merged to overcome the limitations of each process. Optical tweezing[17] and dielectrophoretic[18,19] trapping have been used to place NPs in specified locations with high resolution but these techniques can only be used for very small areas. Capillary assembly method has been effective to assemble individual NPs in lithographically templated surfaces.[20-22] This method has been utilized to arrange Au nanowires, nanoprisms, nanocubes, etc. inside templated trenches. However, without chemical bonding between the substrate and NPs, it can be challenging to keep the NP assembly intact on the substrate after removal of the template. Moreover, both humidity and temperature affect the process. Some methods that have been demonstrated to retain ensemble structure are gravitational force,[23] electrostatic forces[24] or molecular recognition,[25] microcontact printing and surface functionalization[26] etc. Björn M. Reinhard et al demonstrated a template assisted approach and subsequent functionalization of substrate and Au NPs to assemble Au nanoclusters on the substrate. The number of Au NPs inside the trench was altered by changing dimensions of the trench.[27] The method used polylysine and –COOH terminated polyethylene glycol, both of which are expensive and require the use of buffer solutions of specific pH. In this paper, we show a facile, scalable, and robust method which utilizes both top down and bottom up processes to assemble NPs in a predetermined fashion. Assemblies of NPs can be used to study the collective plasmonic properties of NPs. Particularly, V-shaped nanoantennas are interesting since they can form asymmetric surface plasmon

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Electronic Supplementary Information (ESI) available: Experimental procedures, additional FESEM image (Figure S1). See DOI: 10.1039/x0xx00000x polariton (SPP) wavefronts and enhanced fields at the vertices.[28-30] By tuning the length of the antenna arms and angle between them, resonant frequency and scattering cross-section of both symmetric and asymmetric mode of SPP can be controlled. We show formation of periodic arrangement of V-shaped antennas comprising Au NPs on glass substrate/silicon wafer using silanization technique. Thus, the meta-polymer system is made of meta-molecules (V antenna) comprised of meta-atoms (Au NPs) arranged periodically in an array on a substrate. This method to assemble NPs on a substrate is very stable, scalable, cheap, and can be employed for other metallic NPs, making it ideal for use in optical devices and media. The V antenna assembly has unique polarization and electric field signatures which enhances molecular signatures in the near field. We therefore validate the efficacy of this method by reporting SERS signatures from molecules in close proximity of the assembled V antenna. We also study the dependence of SERS signals on input polarization using the polarization dependent electric field patterns. We corroborate our experimental results with full wave 3D Finite Difference Time Domain (FDTD) simulations.

Assembling NPs in predetermined geometries over large areas is a much researched at challenging problem. In this paper, we demonstrate the processes required to assemble and adhere NPs on substrate with specified geometry and periodicity over a large area with high yield. NPs remain intact upon removal of the template. Further, we demonstrate the efficacy of the fabrication method by constructing V-shaped antennas made of Au NPs. These arrays show enhancement of Raman scattering. Figure 1 schematically shows the fabrication process to build periodic arrangements of V-shaped NP arrays (meta-polymer) on Si wafer. Piranha solution treatment of the substrates gives rise to surface -OH groups and the surface becomes hydrophilic. The hydrophilic surface facilitates the functionalization process required to adhere the Au NPs. Here electron beam lithography was used to create periodic trenches by etching the PMMA polymer on the substrate. Then the substrate surface is functionalized using APTES. Both silicon wafer and glass slides have silanol (Si–OH) groups on their surface which react readily with APTES yielding a monolayer of APTES on the surface of the substrate. Washing the substrate with water removes excess APTES. The APTES modified substrates were immersed into an aqueous solution of citrate-stabilized Au NPs for 6 hours. Strong electrostatic interaction between the negatively-charged Au NP surrounded by ionic double layer and positively-charged amino groups immobilize Au NPs on the silanized glass and silicon wafer surface. They were thoroughly washed with water, and dried with N_2. Two approaches were taken for the APTES modification of the substrate. First, the hydrophilic substrate was chemically functionalized using 2% aqueous solution of APTES to form monolayer of APTES and in the next step EBL was performed on that substrate. In the other attempt, first EBL was performed on the substrate to form trenches and then it was treated with 2% aqueous solution of APTES. As PMMA is inert towards silanization due to the unavailability of surface –OH groups, only monolayer by APTES should form in the trenches because of exposed silanol groups. For the former case, repeatedly it was found that NPs are adhering in the trenches in an irregular pattern which indicates that the homogeneity of APTES monolayer is lost after EBL, as depicted in Figure S1. The second approach of functionalizing the trenches after EBL yielded regular array of NPs. Here we implement a V-shaped structure to execute a V-shaped nanoantenna that could find applications in sensing and wavefront engineering. It should be noted that the coating speed and concentration of PMMA was adjusted such that the thickness of PMMA layer was around 120 nm. While keeping thickness of the PMMA layer too high, around 200 nm, irregular patches of Au NPs were found throughout the trench implying poor functionalization of the surface. The radius of the Au NPs is ~60 nm, therefore the width of the trench was set at 75 nm to ensure single line of NP in the trench arms. These substrates were dipped overnight in a stirring aqueous solution of citrate functionalized Au NPs. Only a few NPs were deposited in the trench in a random fashion. Next, two trenches of width 100 nm and 200 nm were made and most regularized array of Au NPs was obtained using the trench with 100 nm width (Figure 2). 200 nm trench width resulted in multiple NPs deposited across the width (Figure S1). In all the samples, outside length of both axes of V-shaped trench was 500-600 nm and the angle between two axes was~80°. Optimization of the trench dimension and the concentration of Au NP were done simultaneously. Optimum concentration of Au solution was found to be 1/5th of the concentration of as-prepared Au NP solution. Very concentrated (as prepared) Au NP solution resulted in unwanted aggregated Au patches on the surface in a few places but after one-third dilution, formation of patches

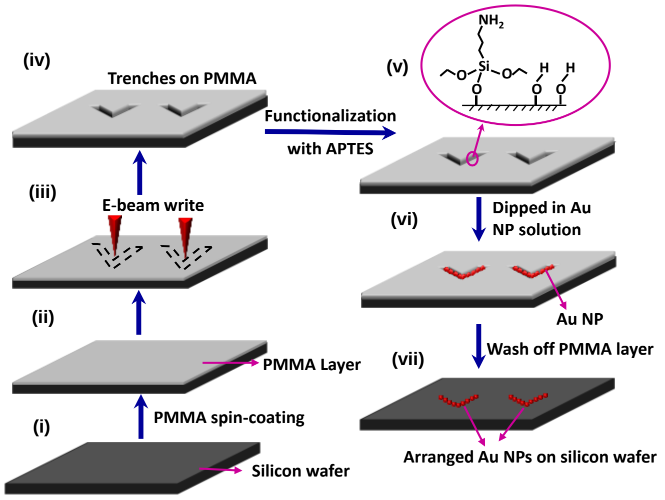

Figure 1. Step by step schematic illustration showing the formation of periodic pattern of ‘V’ antennas comprised of Au NPs on silicon wafer. (i, ii) PMMA layer spin-coated on silicon wafer, (iii, iv) formation of trenches on PMMA by e-beam lithography, (v) functionalization of trenches by APTES, (vi, vii) adhesion of Au NPs on functionalized trenches.

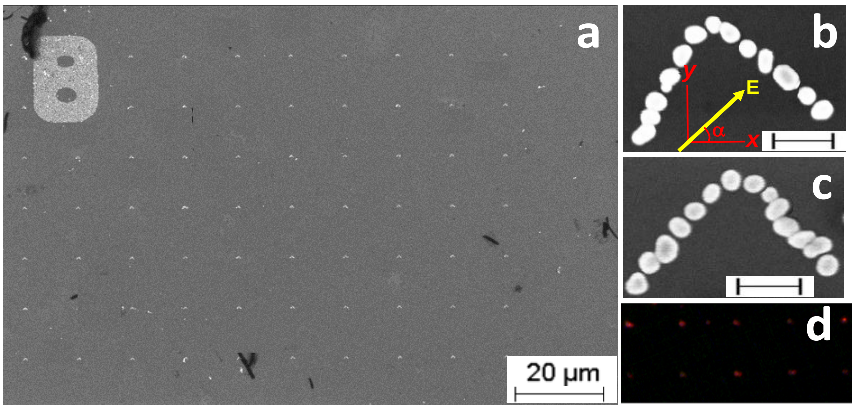

Figure 2. (a) FESEM image of a 100 x 60 μm periodic arrangement of V-shaped antennas, letter B has been fabricated in the corner for the ease of correlation study, (b) and (c) Two V-shaped antennas under high magnification showing the monolayer arrangement of Au NPs. Scale bar is 200 nm. For SERS experiment, single V antenna was illuminated using a focused LASER of 633 nm wavelength. Inset of (b) shows the direction of incident light where a is the polarization angle, (d) Dark field image of two rows of periodic arrangement, showing the red bright dots as the V antennas.

was significantly reduced. After the formation of meta-polymer, the substrate was cleaned with N-methyl pyrrolidone, which removes the PMMA only, leaving behind the meta-polymer on the bare substrate. Formation of this periodic pattern can be seen from the FESEM image (Figure 2a). Au NPs were also immobilized in the 'B' shaped fiducial marker in the corner of the sample. Distance from one V-shaped NP array to other was maintained at 10 μm in both sides. Representative magnified images of arrays are shown in Figures 2b and c. Figures 2b and c show that the Au NPs form a monolayer along the two axes of V antenna. The sample was visualized in dark field configuration which is shown in Figure 2d. Thus, from the images it can be seen that the process enables placing of multiple Au NPs inside a single trench in a continuous manner without having any rigid lithographically made layer to spatially differentiate them. Random placement of few Au NPs on the surface can be seen from Figure 2a. To our understanding, maximum probability of the abovementioned defect occurs during washing off the PMMA layer. Beside the APTES functionalized trenches, some Au NPs may sit on the PMMA layer randomly (though the layer is not functionalized). N-methyl pyrrolidone is expected to wash off the PMMA layer as well as the Au NPs sitting on PMMA, but in practice, some NPs may still stick randomly on the substrate surface. In the next step, washing the substrate with DI water couple of times, should be helpful to minimize random Au NP sticking. Accomplishment of whole process depends on optimization of two factors: firstly, getting desired trench on polymer by EBL and secondly, functionalization of the bare substrate in the trench portion so that nanoparticles can adhere. If these two processes can be done efficiently, then patterns of different shape/geometry can be achieved.

Polarized SERS measurements were carried on one V antenna, with the Raman marker molecule Nile blue chloride Here, we describe the polarized SERS response of a single. The distance between two V-shaped antennas is set as 10 μm to mitigate interference from coupling with adjacent antennas. Typical SERS spectra of Nile blue from a V antenna under different polarizations (0° to 90° polarization angle) are shown in Figure 3a. Change of polarization on the V antenna is depicted pictorially by the inset of Figure 2b. Peak amplitudes were noted for different polarizations at 587 cm^{-1} and plotted against the polarization angles. Maximum intensity was obtained at 45° polarization angle, see Figure 3b. Figure 4a shows the schematic of the NP antenna in the simulations. The samples were placed on glass substrate and excited using a plane wave source at 656 nm wavelength (wavelength at which the

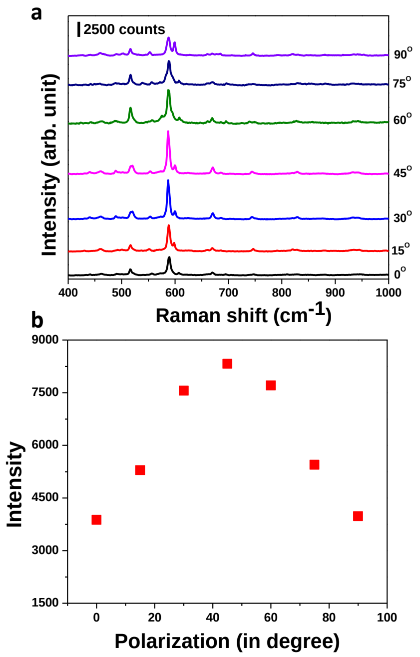

Figure 3. (a) Polarization dependent SERS spectra of a V antenna and (b) corresponding intensity versus polarization angle plot.

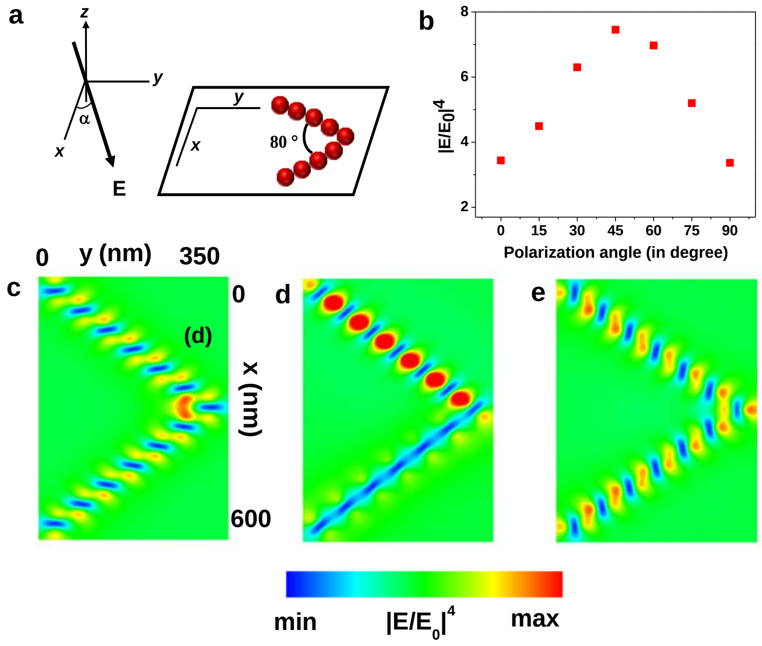

Figure 4. (a) Schematic of the simulation geometry. V-shaped antenna of NPs was formed with inter-arm angle of 80°. α is the angle between polarization of incoming light and x- axis. (b) Graph showing variation of electromagnetic enhancement ($|E/E_0|^4$) with polarization angle α. (c)-(e) Near field electric field maps of the V-antenna at the metal-air interface for polarization angles α=0,45 and 90° respectively.

prominent Raman mode of Nile blue molecules exist), polarized at an angle α with respect to the x –axis. The electric field enhancement was calculated ($|E/E_0|^4$) for input polarizations. Figure 4b shows the electric field enhancement calculated at the glass – NP interface for different polarizations of the input beam. The local field enhancement is largest at input angle 45°, which corresponds close to half of the inter-arm angle. At this angle the electric field vector is along the axis of the chain of NPs and excites them efficiently which creates a large local field enhancement and hence provides a platform for enhanced molecular emission (see Figure 4d). Figures 4c–e show the local electric field profile along glass–gold particle interface. For input polarization α=45°, we see largest electric field distribution when compared to that for 0° and 90° respectively. It should be mentioned that, the enhancement of SERS signals depends on the particle size as well as interparticle spacing, spacing between consecutive antennas. The polarization response, per se, depends on the inter-arm angle of the V-antenna. We corroborate the polarization dependence of SERS enhancement with 3D FDTD numerical simulations.

In this work, we have demonstrated a facile, scalable and robust approach to fabricate V-shaped meta-polymers on substrates combining both top down and bottom up approach. Proper chemical functionalization of the lithographically made trenches and Au NPs enable periodic arrangement of NP junction arrays. This process utilizes simple silanol chemistry to adhere the NPs on substrate. Further the efficacy of the method is demonstrated using V-shaped periodic nanoantenna combined with SERS signatures from molecules in close proximity of assembled V-antenna. Polarized SERS response from a single V-antenna reveals that the maximum electromagnetic field enhancement occurs along the half of the inter-arm angle. This straight forward method to prepare NP assemblies will find importance in various structure and provide a path to exploration of a variety of subwavelength assemblies for plasmonics and optical metamaterials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Table of Contents:

Facile, cheap, scalable method for fabrication of V shaped plasmonic meta-polymer on glass substrate/silicon wafer has been reported. This V shaped antenna shows unique polarization and electric field signatures which enhances molecular signatures in the near field.