Ordered Ag and Cu Nanorod Arrays for Enhanced Raman Scattering Created via Guided Oblique Angle Deposition on Polymer

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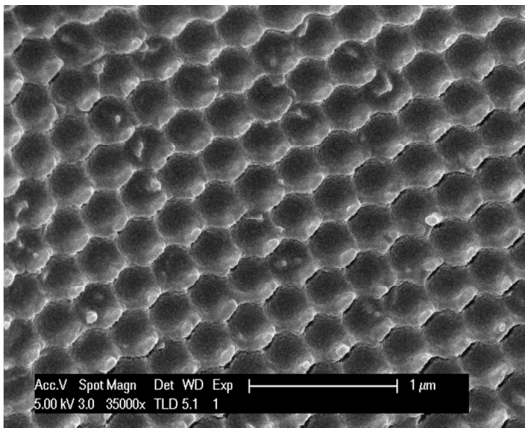
SERS

For point-to-point collection of SERS spectra, all spectra were recorded using a Leica DM/LM microscope equipped with an Olympus 20×/N.A. 0.4 long-working distance objective to collect 180^0 backscattered light. The spectrometer system was a Renishaw Ramascope System 2000 with a 632.8 nm laser as the excitation source. The unfocussed output power was measured to be approximately 3.2, 3.5 and 3.7 mW at the Ag-polymer/silica, Cu and Ag-silicon substrates respectively. All spectra were normalised to a silicon standard. Dielectric edge filters were used to reject the Rayleigh scattered light. All substrates were left overnight in an aqueous solution of trans-1, 2-bis-(4-pyridyl) ethylene (BPE). BPE concentrations were 10^{-5} and 10^{-4} M for the Ag and the Cu nanorods arrays respectively. For Ag substrates, SERS intensity of BPE was recorded by averaging the height of the 1200 cm^{-1} peak after baseline correction from 10 spectra collected over an area of

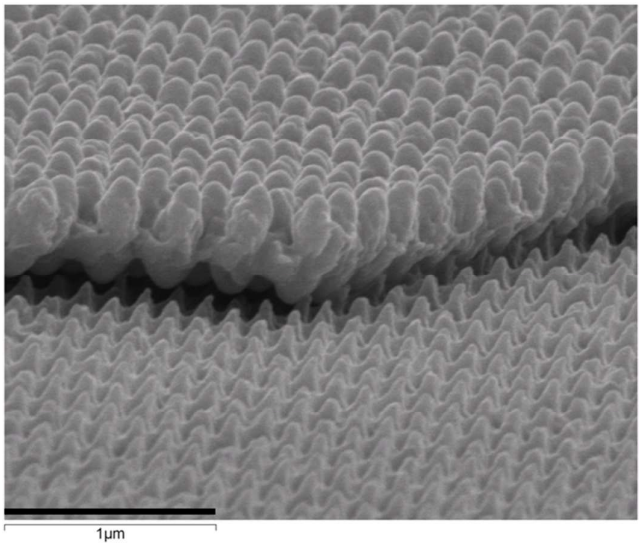
about 1 cm^2 of the substrate. The 1636 cm^{-1} peak height averaged from 20 spectra was used for Cu with the same area under interrogation and OriginPro 8.6 software was used for data analysis. Spectra were acquired during a collection time of 0.1s for the Ag-silica control, 85 and $85:85^0$ Ag polymers and 1s for the 0:85 and 0:85:85 polymers which were corrected to 0.1s for comparison. A collection time of 30s was used for the Cu substrates. SERS mapping of 10^{-5} M BPE on Ag polymer and silica arrays was performed using 632.8 and 785 nm laser lines as excitation sources and a Witec Confocal Raman Microscope alpha300 R. Five maps from each sample, each consisting of 100 spectra, were collected over an area of 10 μm x 10 μm (10 points per line, 10 lines per image), using a 100 × 0.9 objective and 50 ms collection time. The unfocussed power at each sample was 1.5 mW. SERS mapping of Cu + 1.156×10^{-5} M (aq) rhodamine B ITC was conducted on the same machine with 632.8 nm excitation and a 10 × 0.25 objective, during a 2.5 s collection time with an unfocussed power at the sample of 24.3 mW. Each of two maps per sample corresponded to an area of 100 × 100 μm^2 with 400 spectra per map and the height of the band near 1200 cm^{-1}. Mapping of Cu polymer and Si arrays + 10^{-5} M methanolic BPE was carried out on a DXR Raman Microscope (Thermo Scientific) using 780 nm excitation and a 50× objective with a 1 s collection time. Each of five maps corresponded to an area of 90×140 μm^2, and the height of the 1636 cm^{-1} peak with 150 spectra collected.

Materials

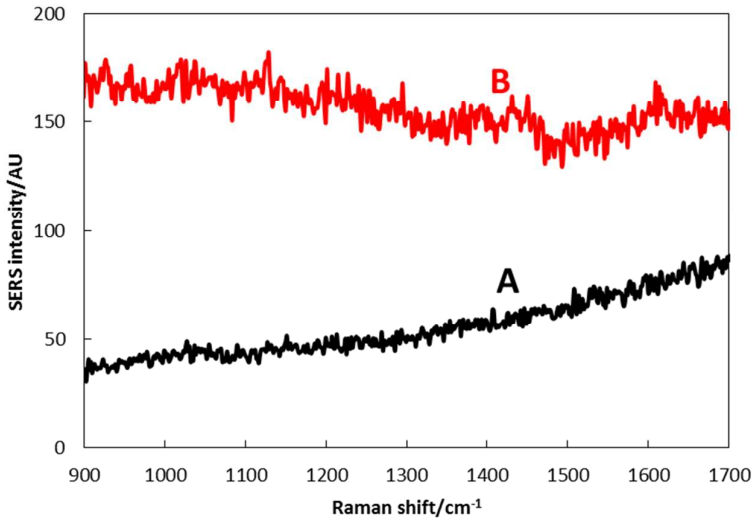
Silver and copper, 99.99%, Kurt J. Lesker and Company; BPE (Sigma Aldrich assay 97%), RBITC (Sigma Aldrich).



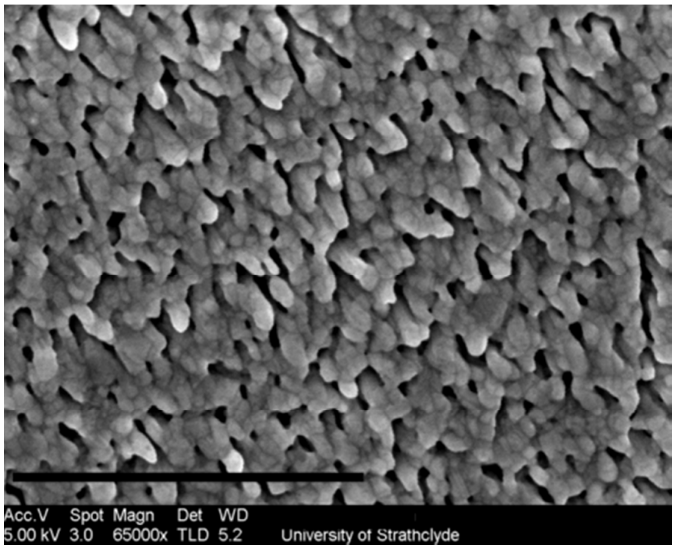
S1. SEM image of polycarbonate sheet (underside) with an inverted structure of nanosphere assembly in closely packed hexagonal arrangement.



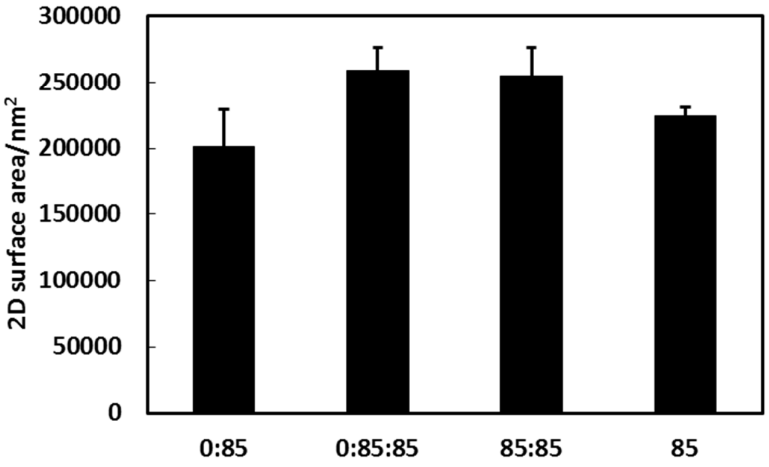
S2. Ag nanorod arrays on polymer created by 0^0 Ag deposition. Lower part shows bare polymer.



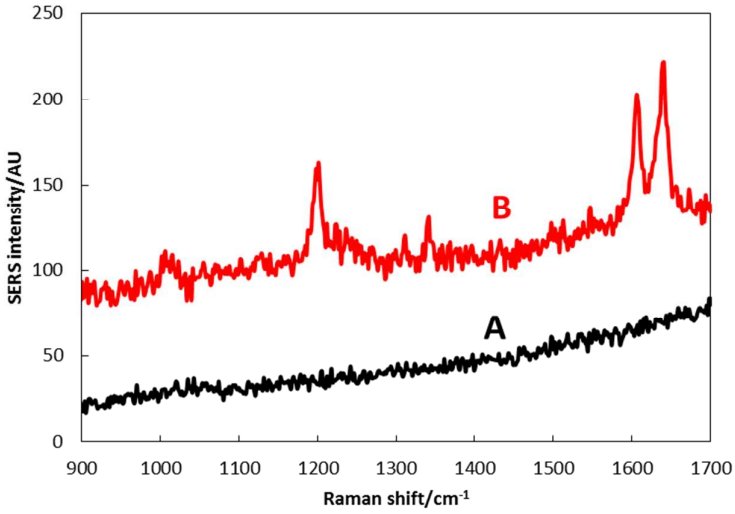
S3. Background SERS spectra of bare Ag nanorods arrays deposited at 0^0 on (A) silicon and (B) polymer substrate.



S4. SEM image of OAD Ag nanorod array grown on silicon showing random distribution.



S5. 2-D surface areas of Ag nanorods on polymer as measured from SEM images.

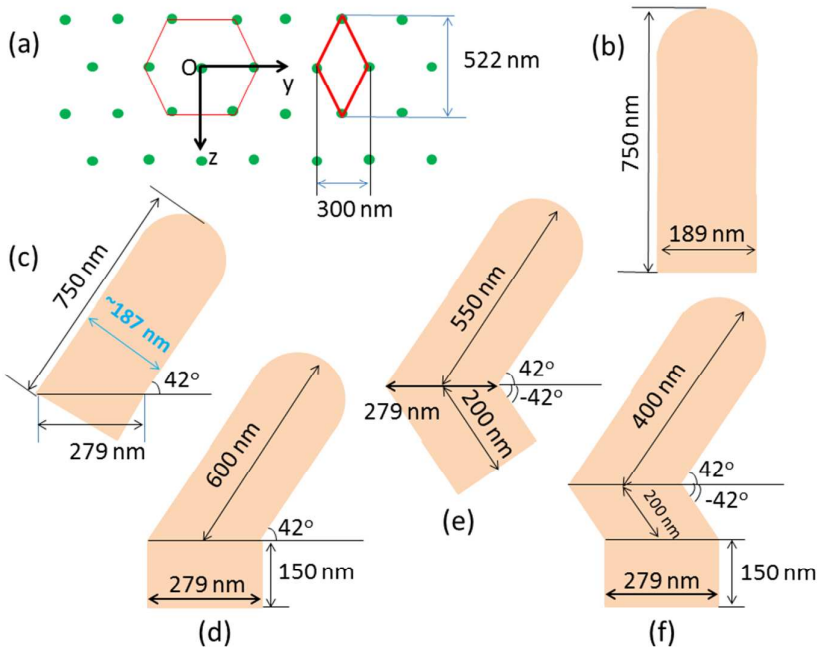


S6. SERS spectra of BPE on Ag nanorod arrays deposited at 0^0 on (A) silicon and (B) polymer substrate.

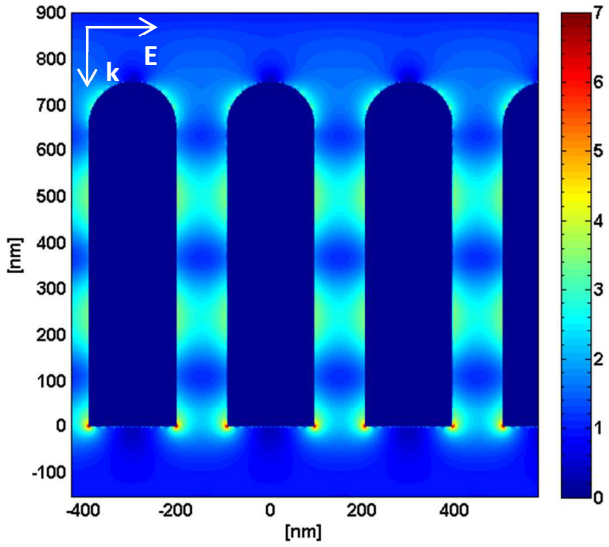
Numerical Calculations

The discrete dipole approximation (DDA) method was used to simulate the local field enhancements of infinite Ag nanorod arrays in vacuum by employing DDSCAT 7.2 code. The cubic grid spacing was 3 nm in all calculations. The dielectric constants of Ag were obtained from the experimental data of Johnson and Christy[5] without size corrections, as the size dependence can be neglected in our studies. The incident wavelength used in calculations was 632.8 nm, which was the excitation wavelength in our SERS measurements. The value of the interaction cutoff parameter γ was taken to be 0.01.

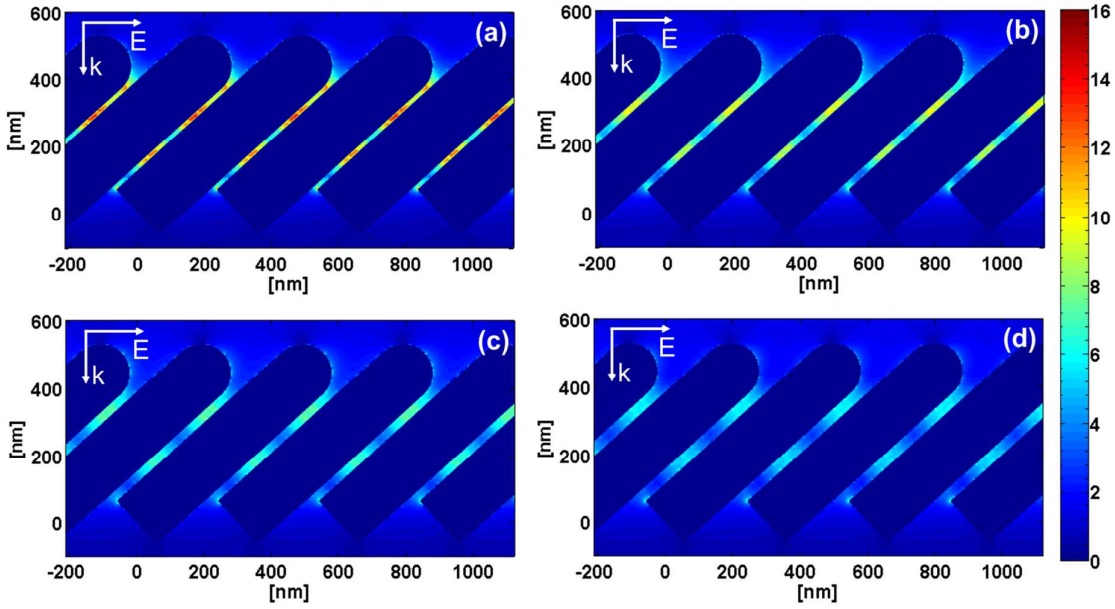
The hexagonal pattern substrate and five different target units used in this calculation are depicted below in S7 with parameters shown. The nanorods were arranged in the hexagonal lattice with a periodicity of 300 nm, the same as the hexagonal pattern templates used in the sample fabrications. The orientation of the oblique nanorods was chosen to be along y-direction, and the tilted angle was set to 42 degrees. The upper oblique parts of the nanorods were all modelled as titled cylinders with a hemispherical cap at each end, in order to avoid the 'lightening rod effect' at the top edges of the nanorods in the electrodynamics simulations. The gaps between adjacent nanorods were fixed to be 21 nm along y-direction, resulting in a cylinder with diameter ~187 nm. The total lengths of the individual nanorods were all fixed to be 750 nm in order to investigate the structural effect on the near-field properties. The polarizations of incident light studied in all calculations were parallel to y-direction.



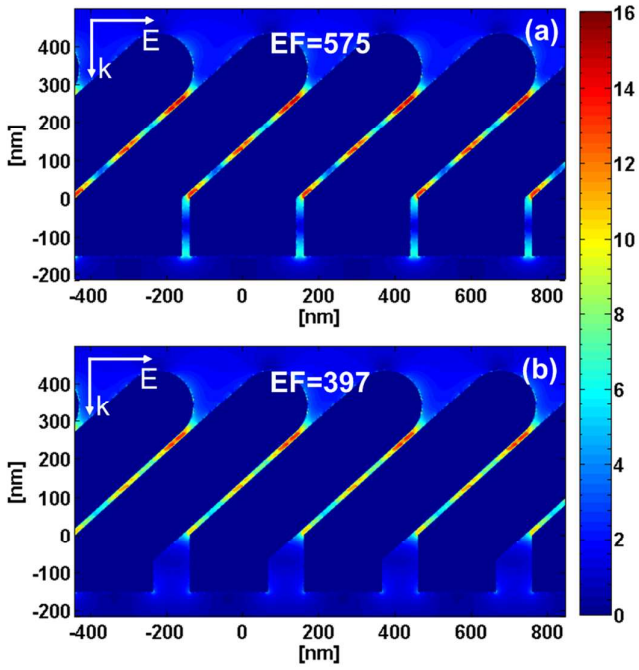
S7. Schematics of hexagonal pattern substrate and five different target units used in the simulations.



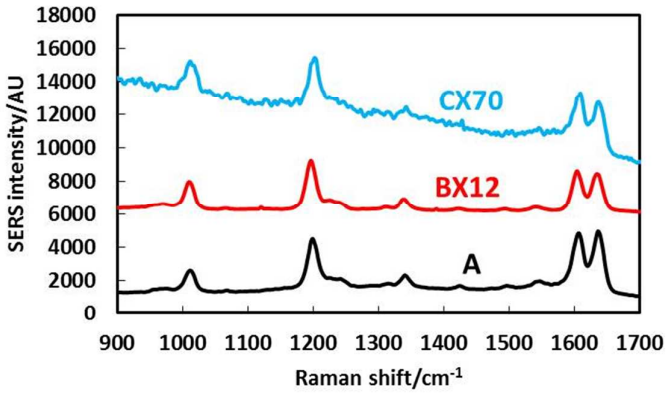
S8. Magnitude of normalized electric field, $g = |E|/|E_0|$, where E and E_0 are the local and incident fields respectively, of Ag nanorod array deposited at 0^0 on polymer. Enhancement factor (EF) of 29. All internal fields were set to zero for clarity.



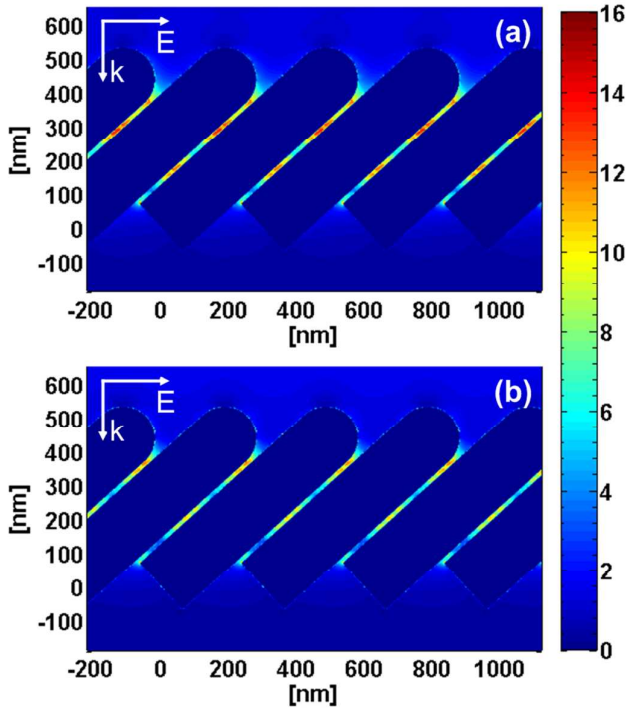
S9. Magnitude of normalized electric field, $g = |E|/|E_0|$, where E and E_0 are the local and incident fields respectively, of Ag nanorod arrays with (a) 21, (b) 27, (c) 39 and (d) 51 nm gaps. All internal fields were set to zero for clarity.



S10. Magnitude of normalized electric field of $0{:}85^0$ Ag nanorod arrays with different vertical pillar sizes. All internal fields were set to zero for clarity.



S11. SERS of BPE on 85^0 Ag nanorod arrays (A) on polymer under 633 nm excitation, (B) on polymer under 785 nm excitation, and (C) on silica under 633 nm excitation. Spectra are averages of the 1200 cm^{-1} peak height from 500 mapping spectra (100 spectra taken from 5 different locations on each sample).



S12. Magnitude of normalized electric field, $g = |E|/|E_0|$, where E and E_0 are the local and incident fields respectively, of Ag nanorod arrays under (a) 633nm and (b) 785nm excitation. All internal fields were set to zero for clarity.