

Supporting Information for Electrochemically Created Highly Surface Roughened Ag Nanoplate Arrays for SERS Biosensing Applications

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Experimental Section:

Parameters for the preparation of the highly surface-roughened Ag nanoplates.

The electrolyte solution was prepared by dissolving an equal amount (10 g) of AgNO_3 and H_3BO_3 (boric acid) into 1 L deionized (DI) water. Electrochemical deposition was carried out in a double-electrode system under a potentiostatic mode. Two cleaned silicon wafers (resistivity: 0.2 $\Omega\cdot\text{cm}$, boron doped) were used as the electrodes with a working area of about 1 cm^2 . The voltage applied between these two electrodes was 10 V. The total deposition time was 10 min, unless otherwise noted. For the deposition of Pt nanoplates, an electrolyte solution prepared by dissolving 0.25 g HPtCl_4 and 10 g H_3BO_3 into 1 L DI water was used. The morphology of the deposited materials was observed using a scanning electron microscopy (SEM, NOVA NANO 630).

FDTD numerical simulations. Finite-difference time domain (FDTD) simulations were conducted to simulate the electromagnetic field distributions on the SERS substrates using a commercially available software package (FDTD Solutions, Lumerical Inc., Canada).

SERS detections. 10 μL of Rhodamine 6G (R6G) aqueous solution (10^{-6} M) was dropped onto the SERS substrate before Raman spectral detections. The Raman spectra were recorded with a confocal microprobe Raman system (WITec). The excitation wavelength was 532 nm (excitation using a 488 nm laser will generate strong photoluminescence from R6G molecules) with a power of about 0.5 mW. The

accumulation time was 10 s. The Raman detection was carried out 5 times at different sites and showed only a small deviation (less than 15%). The intensity of the Raman signal at each site was averaged for accuracy.

SERS enhancement factor. 4-aminothiophenol (4-ATP) is used as the probe molecule to evaluate the enhancement factor (EF) of the highly surface-roughened Ag nanoplates using the equation:

$$EF = (I_{SERS}/N_{ads})/(I_{bulk}/N_{bulk})$$

where I_{SERS} is the Raman signal intensity at a specific vibration mode (i.e., 1080 cm^{-1}) of the 4-ATP molecules attached on a highly surface-roughened Ag nanoplate array. I_{bulk} is the Raman signal intensity of solid 4-ATP powder. N_{ads} and N_{bulk} are the numbers of 4-ATP molecules adsorbed on the Ag nanoplates and in the powder exposed to the laser light, respectively. In the case of solid 4-ATP powder, N_{bulk} can be roughly calculated depending on the probe volume (a tube with a diameter of ~500 nm and depth of ~20 μm , according to the instruction manual of our Raman spectrometer) of the equipment. Taking into account of the density of 4-ATP powder (about 1.2 g/cm^3), N_{bulk} can be estimated to be about 2.5×10^{10} . Since 50 μl 4-ATP solutions (10^{-9} M) are spreaded on to the highly surface-roughened Ag nanoplate array surface (the area is about 0.5 cm^2), N_{ads} is estimated to be around 110. I_{SERS} and I_{bulk} at 1080 cm^{-1} are about 150 and 30, respectively (see Figure S9). Taken together, the EF of the highly surface-roughened Ag nanoplate array is estimated to be $\sim 1.1 \times 10^9$.

SERS biosensing. The power of the laser for the detection of DNA, protein, and viruses was kept at 100 μ W to avoid any possible thermal decomposition induced by laser exposure. The accumulation time was 5 s. A 10 μ L aqueous solution composed of DNA (single-strand or double-strand), Protein A/G, and viruses, respectively, at different concentrations of 1 μ M, 1 μ M, and 1 nM were dropped onto the SERS substrate and dried by natural convection before SERS measurements. For the SERS mapping of DNA and Protein A/G, the accumulation time was reduced to 1 s in order to reduce the mapping time.

SERS analysis of DNA. Briefly, in Figure 5a, the 810 cm^{-1} peak was assigned to the symmetric stretching mode from the phosphodiester bond. Deoxyribose-phosphate induced the appearance of the 1180 cm^{-1} peak. Vibrations of adenine emerged at 1300 cm^{-1} and 1440 cm^{-1} . The 1370 cm^{-1} peak can be assigned to vibrations from thymine, adenine, and guanine. The stretching vibrations from C=N and C=C bonds in adenine and guanine gave rise to the formation of the 1590 cm^{-1} band. The origin of the 1480 cm^{-1} peak was the stretching mode from N7=C8 bonds present in guanine and adenine. The peak situated at 1533 cm^{-1} had a strong association to guanine and cytosine. The C=O (in thymine) stretching vibrations resulted in the formation of 1620 cm^{-1} band.

Supporting Figures:

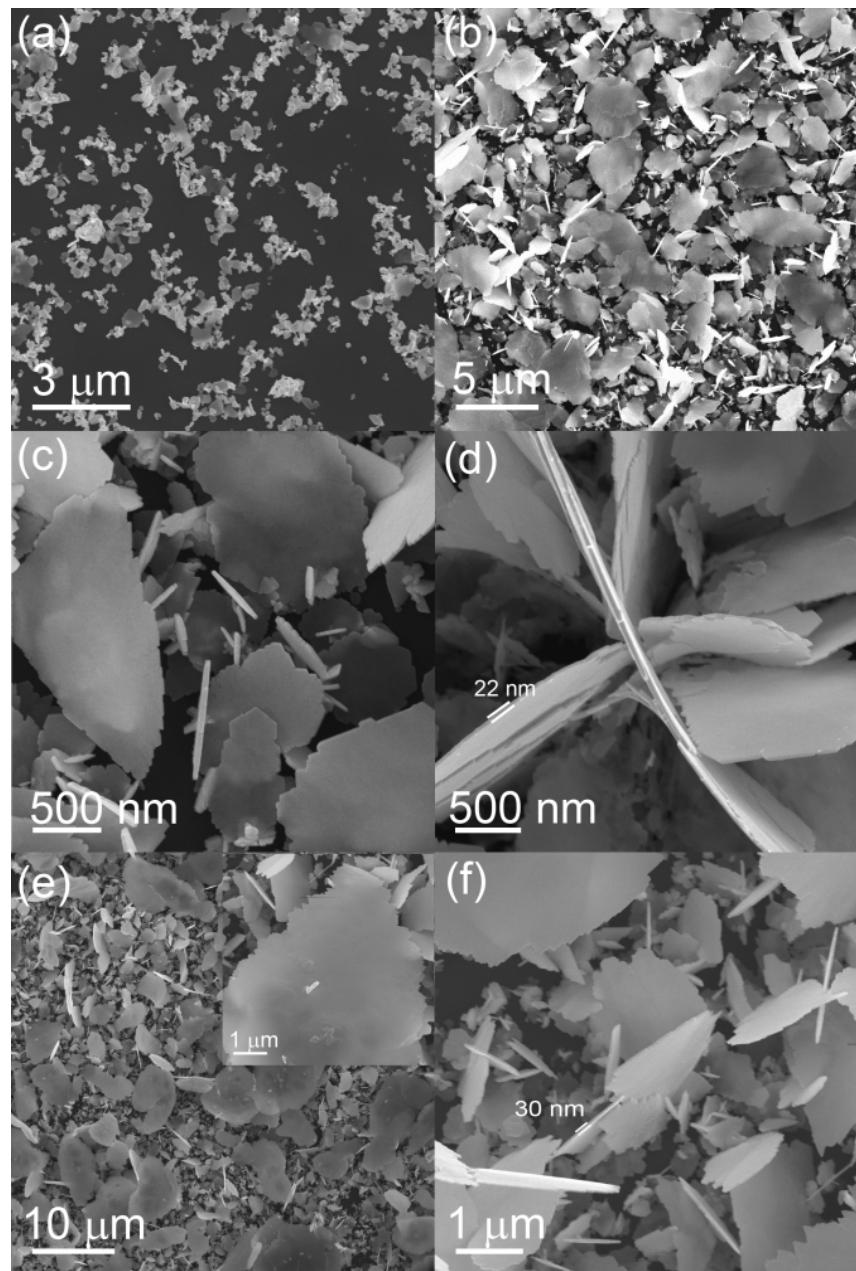


Figure S1. Morphological evolutions as electrochemical deposition proceeds at 10 V. (a) after 10 s; (b-d) after 1 min; (e) and (f) after 3 min.

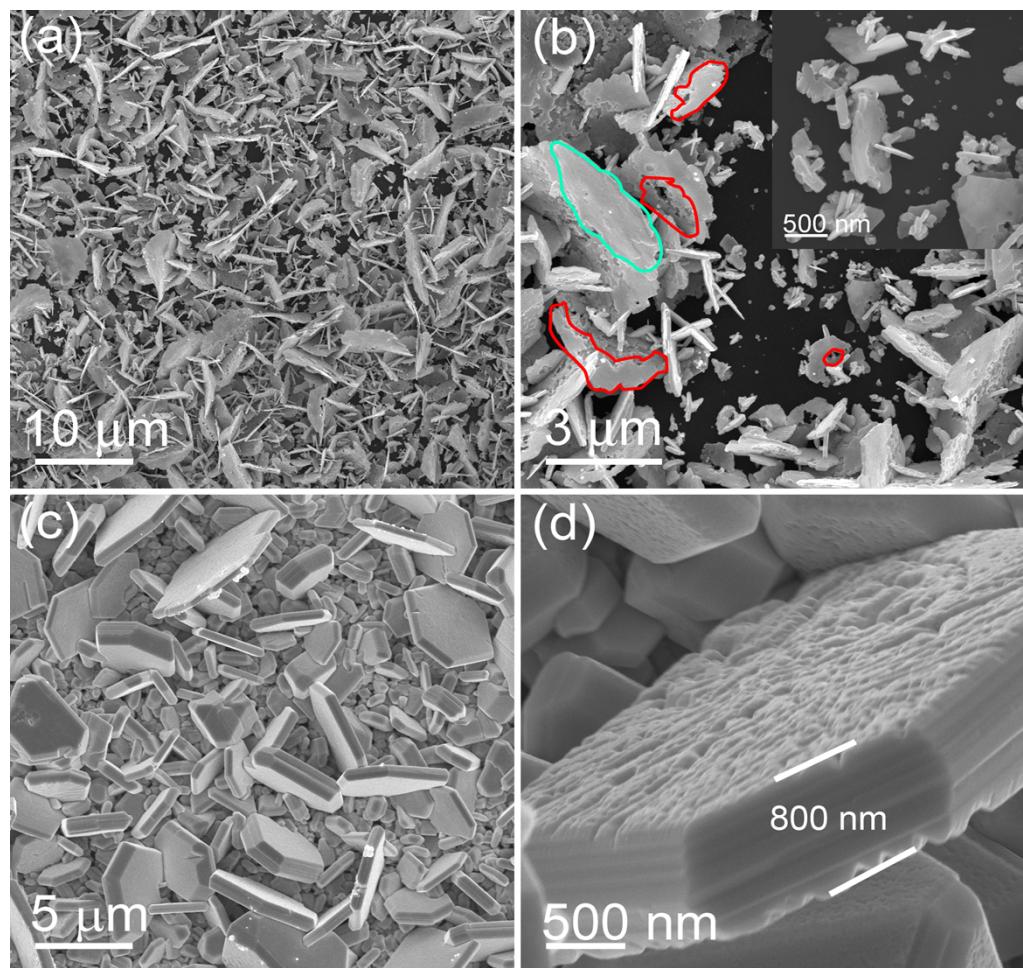


Figure S2. SEM images of Ag nanoplates prepared at 10 V (a and b) for 30 min and (c and d) for 10 h. Inset in (b) is the magnified image. Colored curves in (b) marked the boundaries between the smooth and the coarse areas on the same nanoplate.

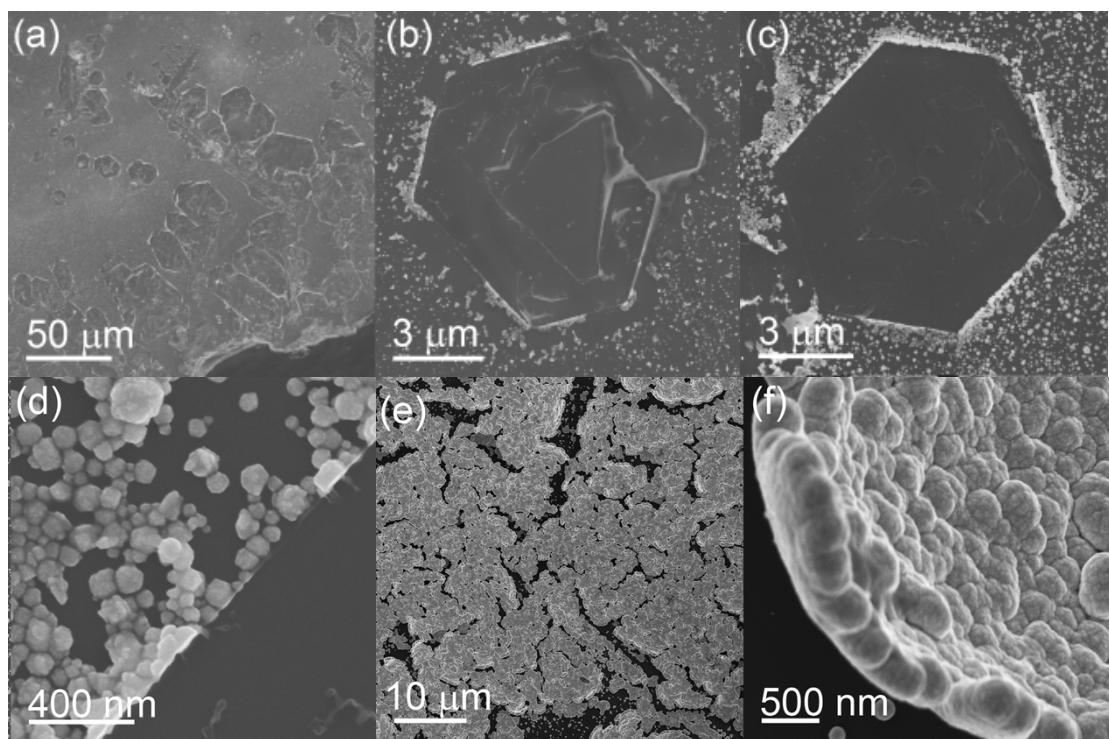


Figure S3. SEM images of Pt nanostructures deposited on the cathode Si wafer. (a) Low magnification of the deposited Pt nanoplates. (b) and (c) An irregularly shaped and a hexagonally shaped Pt nanoplate. (d) Enlarged image at the edge area in (c). (e) and (f) Pt particle film formed after 6 h deposition.

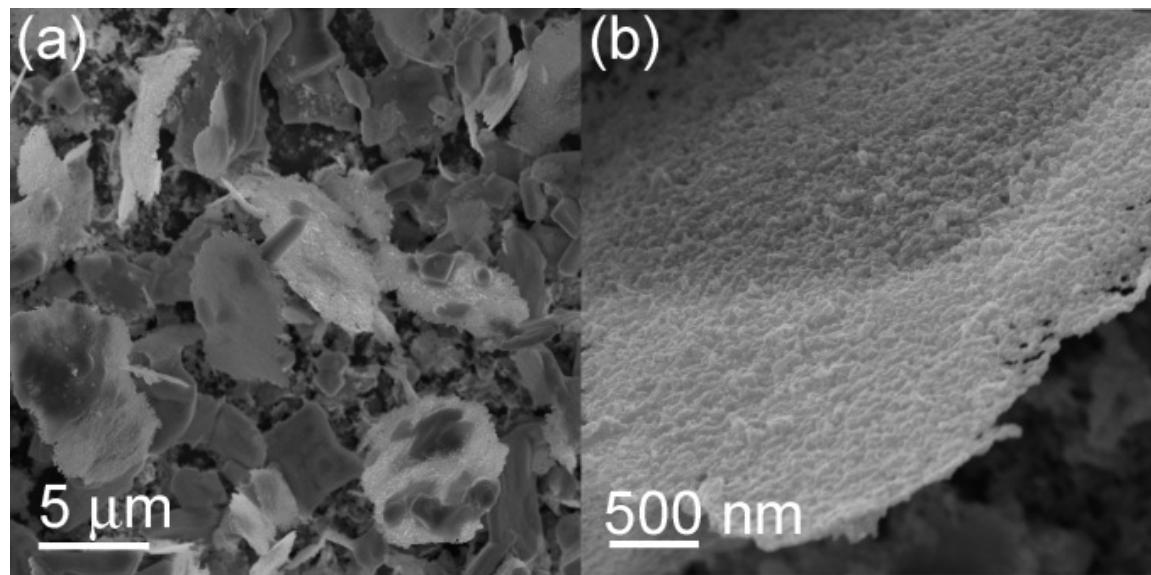


Figure S4. SEM images of Pt nanoplates prepared by etching the smooth-surfaced Ag nanoplates with Pt^{3+} ions.

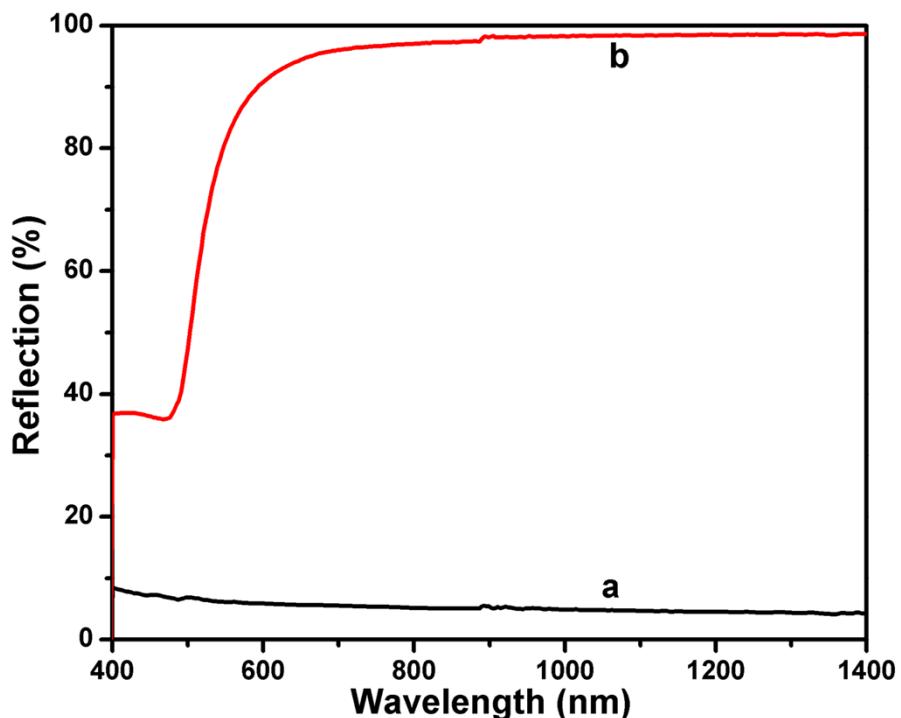


Figure S5. Reflection spectrum of a 3D highly surface-roughened Ag nanoplate array (curve a) compared with a thermally evaporated gold film (30 nm) on a silicon wafer (curve b).

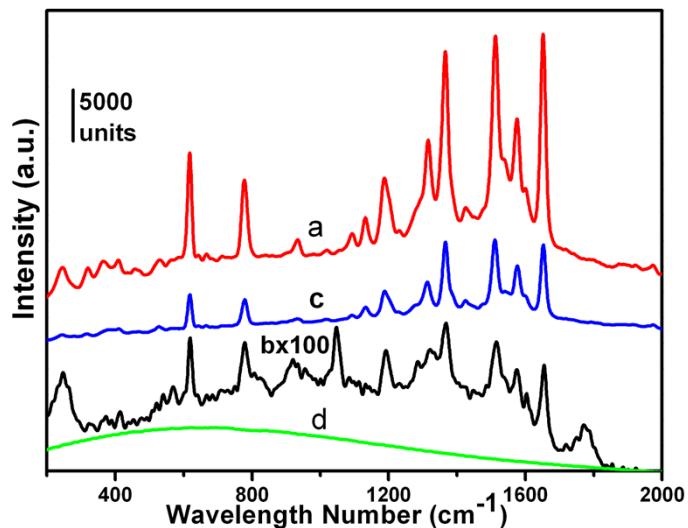


Figure S6. Raman signal of the R6G molecules adsorbed on the highly surface-roughened Ag nanoplates (curve a), smooth and thick Ag nanoplates (curve b), thin Ag nanoplates (curve c), and thermally evaporated Au film (curve d). The typical morphologies corresponding to curves a, b, and c are shown in Figures 1, S6, and 3, respectively.

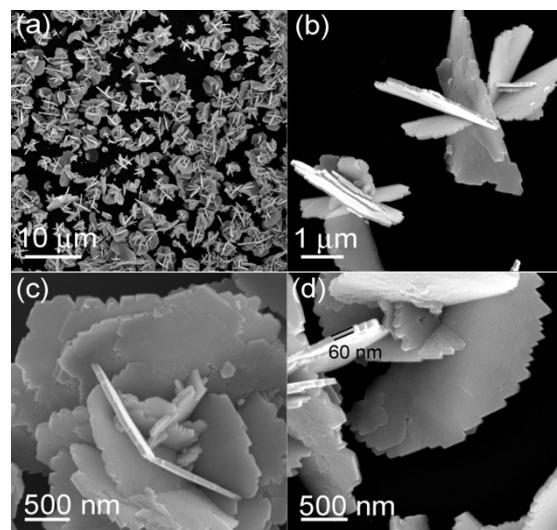


Figure S7. (a–d) Morphology of the Ag substrate corresponding to curve b in **Figure S6** (electrodeposited at 10 V for 10 min).

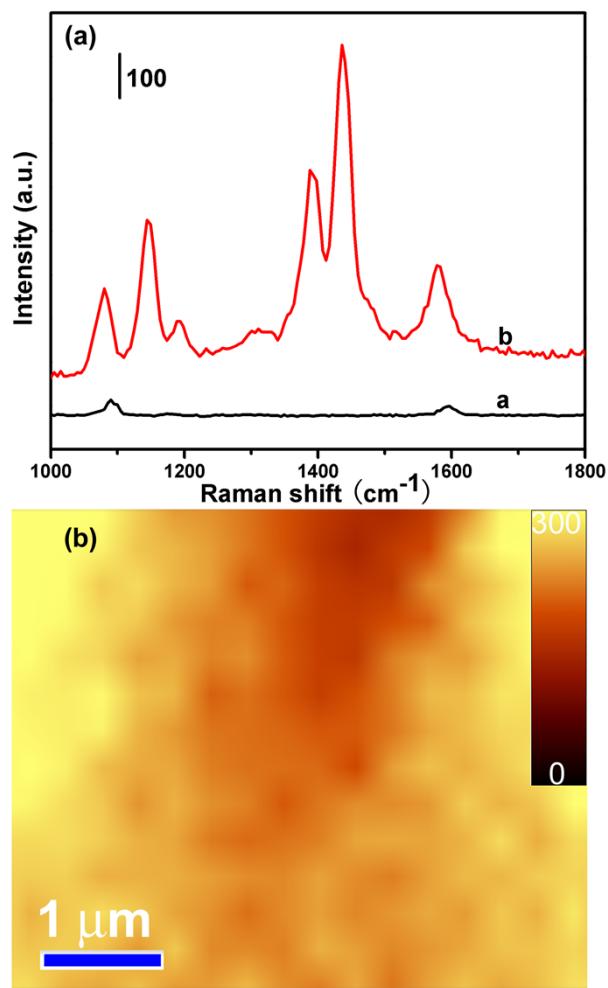


Figure S8. (a) Raman spectra of solid 4-ATP (curve a) and after drying 50 μ l 4-aminothiophenol (10^{-9} M) on the highly surface-roughened Ag nanoplate array. (b) SERS mapping result of 4-ATP at 1080 cm^{-1} .

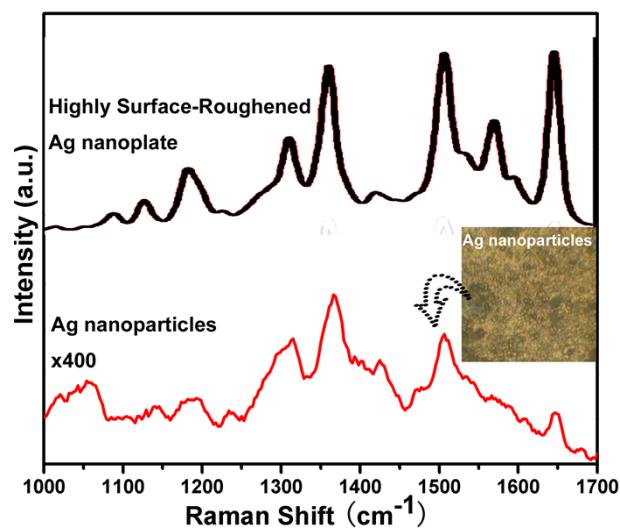


Figure S9. Comparison of the SERS performance between the highly surface roughened Ag nanoplates and Ag nanoparticles. Inset: an optical image of the Ag nanoparticle film.

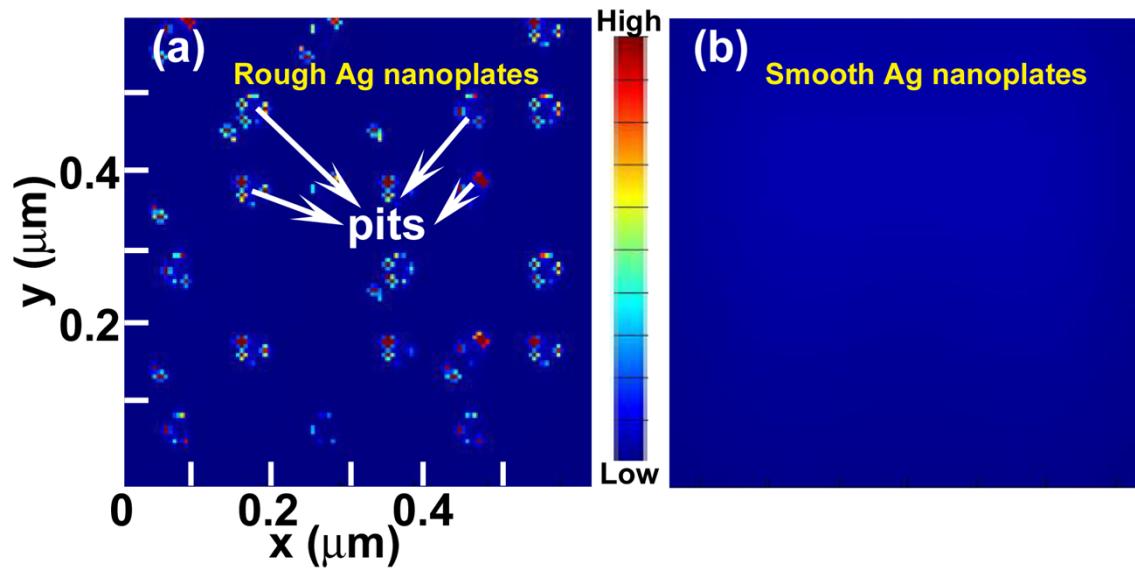


Figure S10. Electromagnetic field amplitude patterns from FDTD calculations for (a) highly surface-roughened Ag nanoplate and (b) smooth Ag nanoplate. To accelerate the simulation process, the density of the pits on the simulated model was greatly reduced relative to the experimentally prepared rough Ag nanoplates.