Supporting information

Vertically cross-linking silver nanoplate arrays with controllable density based on seed-assisted electrochemical growth and their structurally enhanced SERS activity

Guangqiang Liu, Weiping Cai,* Lingce Kong, Guotao, Duan, Fangjing Lü

Figure S1 G.Q. Liu et al

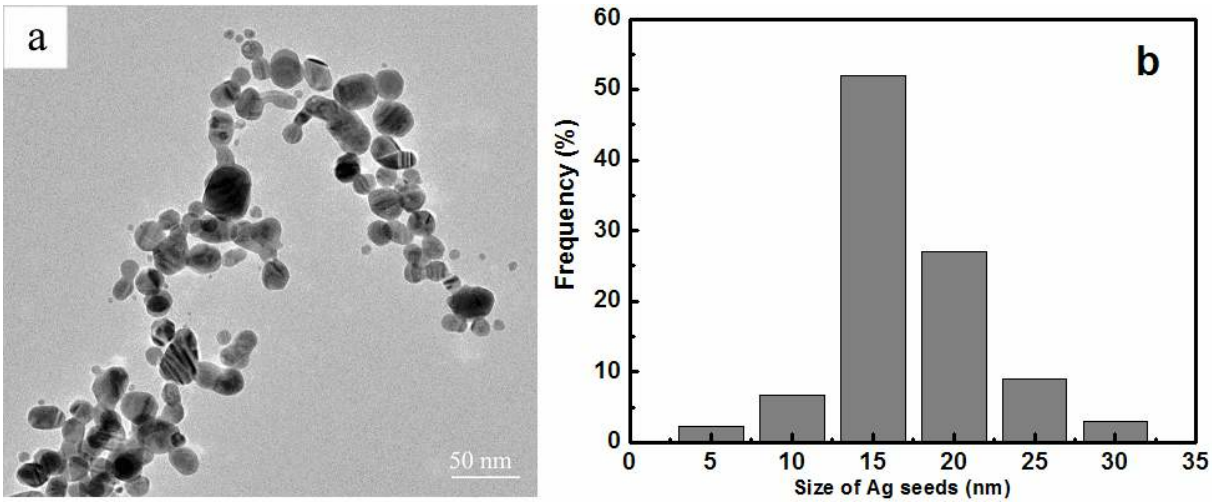

Figure S1 TEM image (a) and Size distribution (b) of the pre-prepared silver nanoparticles (seeds) in the colloidal solution

* To whom all correspondence should be addressed
E-mail: wpcai@issp.ac.cn

Figure S2 G.Q. Liu et al

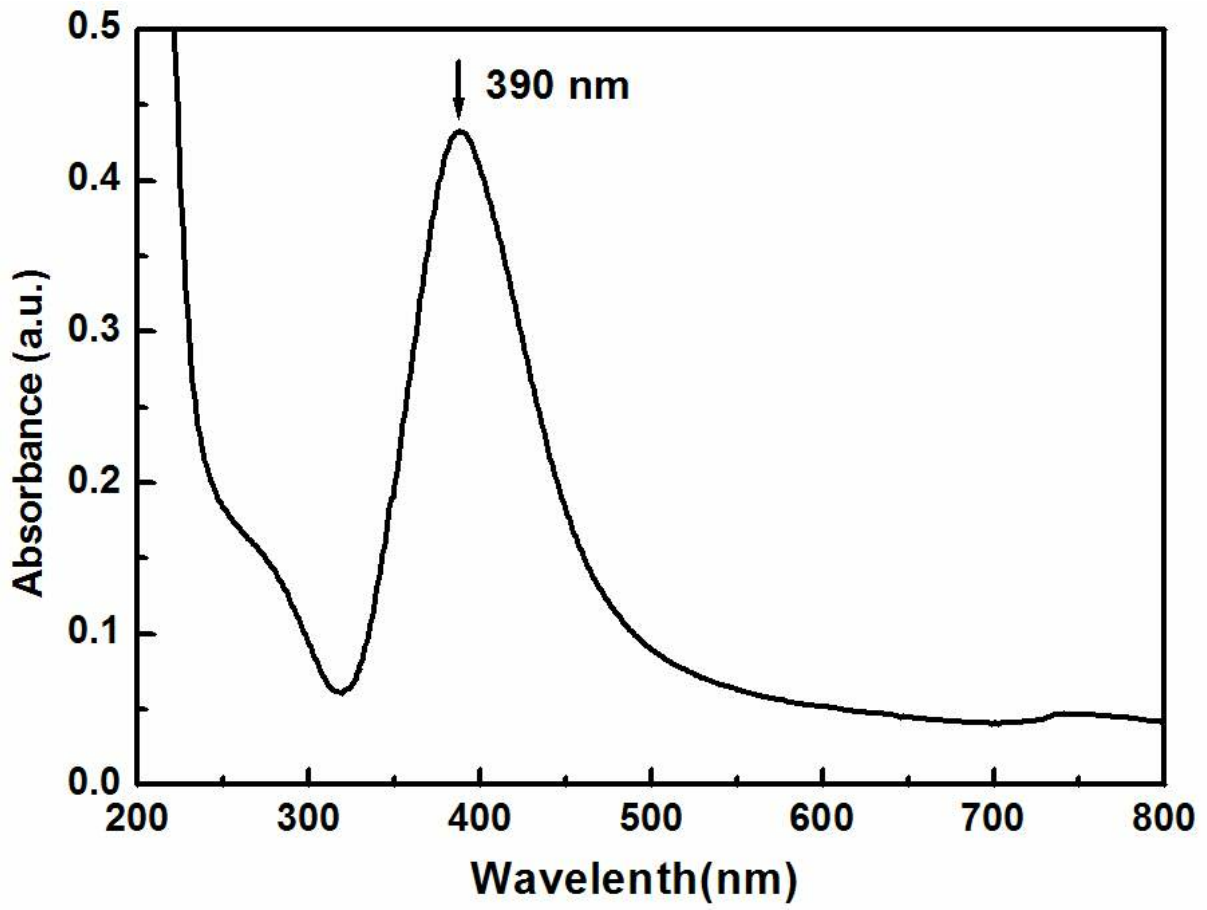

Figure. S2 Optical absorbance spectrum of the pre-prepared silver colloidal solution.

Figure S3 G.Q. Liu et al

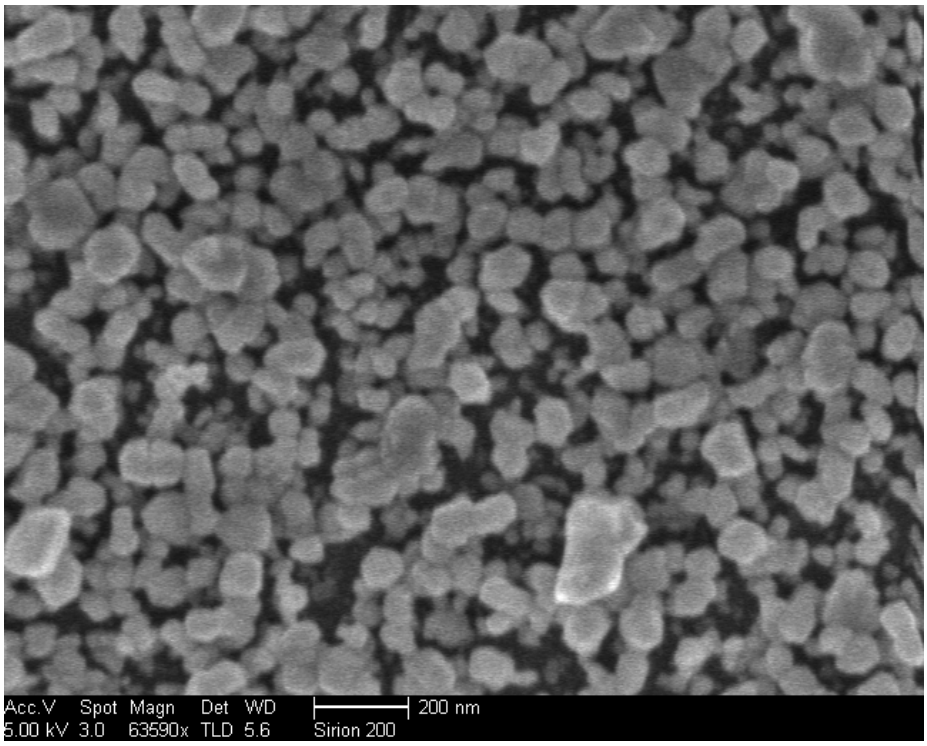

Figure S3 FESEM image of the sample obtained by usual silver mirror reaction. The particles are about 80nm in mean size.

The preparation details are as follows. One gram of solid $AgNO_3$ was first dissolved in 5 ml of deionized water in a 150-ml beaker and triethanolamine was added slowly with stirring until the brownish solution became clear. Then deionized water was added to make a total volume of 80 ml. A cleaned glass slide substrate was vertically placed into the beaker and kept at 45–50 ^{O}C in a water bath for one hour, the substrate was removed and washed with deionized water and dried in air. Ag particle film on the substrate is thus obtained.

Estimation of enhancement factor

Further, taking 4-aminothiophenol (4-ATP) as test molecules, the enhancement factor (EF) of the samples was estimated, in order of magnitude, by the equation:

$$EF = (I_{SERS}/N_{ads})/(I_{bulk}/N_{bulk}) \qquad (S1)$$

Where I_{SERS} and I_{bulk} are the Raman signals at a certain vibration for the 4-ATP molecules adsorbed on a substrate with SERS effect and solid 4-ATP molecules, respectively. N_{ads} and N_{bulk} are the numbers of the adsorbed and the solid 4-ATP molecules within the laser spot, respectively. In our experimental condition for solid 4-ATP, the probe volume could be considered to be a tube with a waist diameter of ~ 1.0μm and a depth of ~ 20μm. So we can calculate the N_{bulk} value, about 9.41×10^{10} 4-ATP molecules. Fig.S4(a) gives the Raman spectrum of the sold 4-ATP molecules. For the vibration at 1075 cm^{-1}, $I_{bulk}/N_{bulk}= 9.0\times10^{-9}$. So Eq.(S1) can be written

$$EF=1.1\times10^{8} (I_{SERS}/N_{ads}) \qquad (S2)$$

For the Ag nanoparticles film prepared by usual mirror reaction, we immersed substrate into 10^{-3} M 4-ATP solution (such concentration is high enough for 4-ATP molecules to fully cover the nanoparticles film) for over one night, rinsed with de-ionized water, and dried with high-purity flowing nitrogen. N_{ads} can be obainted according to the method proposed by Orendorff et al [S1], that is:

$$N_{abs}= N_d A_{laser} A_N/\sigma \qquad (S3)$$

Where N_d is the number density of the Ag nanoparticles, A_{laser} the area (0.25π μm^2) of the focal laser spot, A_N is the average footprint area of a nanoparticle, and σ is the surface area ocuupied by one 4-ATP molecule. N_d and A_N can be obtained from Fig S3, 132 nanoparticles μm^{-2} and 2.8×10^{-3} μm^2. Kim et al[S2] have reported that each 4-ATP molecule occupies 0.2 nm^2. So the N_{abs} is about 1.5×10^{6}. Fig.S4(b) shows the corresponding Raman spectrum. We can thus obtain the EF value, for the vibration at 1075 cm^{-1}, about 5×10^{3}.

For the Ag nanoplate array, however, it is difficult to determine the value of A_N because of the nanoplates standing on the substrate. We can use a new method to estimate the EF.

The Ag nanoplate array with 1 cm^2 was immersed into 1ml of 10^{-6} M 4-ATP solution for over one night. Even if all molecules (about 6×10^{14} molecules cm^{-2}) in the solution absorb on the surface of the nanoplates, the nanoplates in the array can not be fully covered since full

coverage of 1cm^2 flat surface needs 5×10^{14} 4-ATP molecules. Fig.S4(c) gives a Raman spectrum for the the Ag nanoplates array with 1cm^2 after immersion into 1ml of 10^{-6} M 4-ATP solution for over one night and drying. Correspondingly, we can take the value of absorbed molecules within the laser spot N_{ads} upto 4.7×10^6. The EF value is thus obtained, for the vibration at 1075 cm^{-1}, about 2×10^5. Obviously, the EF value by such estimation is under-evaluated and the real one should be higher.

[S1] Orendorff C J, Gole A, Say T K and Murphy C J, *Anal. Chem* 2005, **77**, 3261

[S2] Kim K and Yoon J K, J. Phys. Chem. B, 2005, **109**, 20731

Figure S4 G.Q. Liu et al

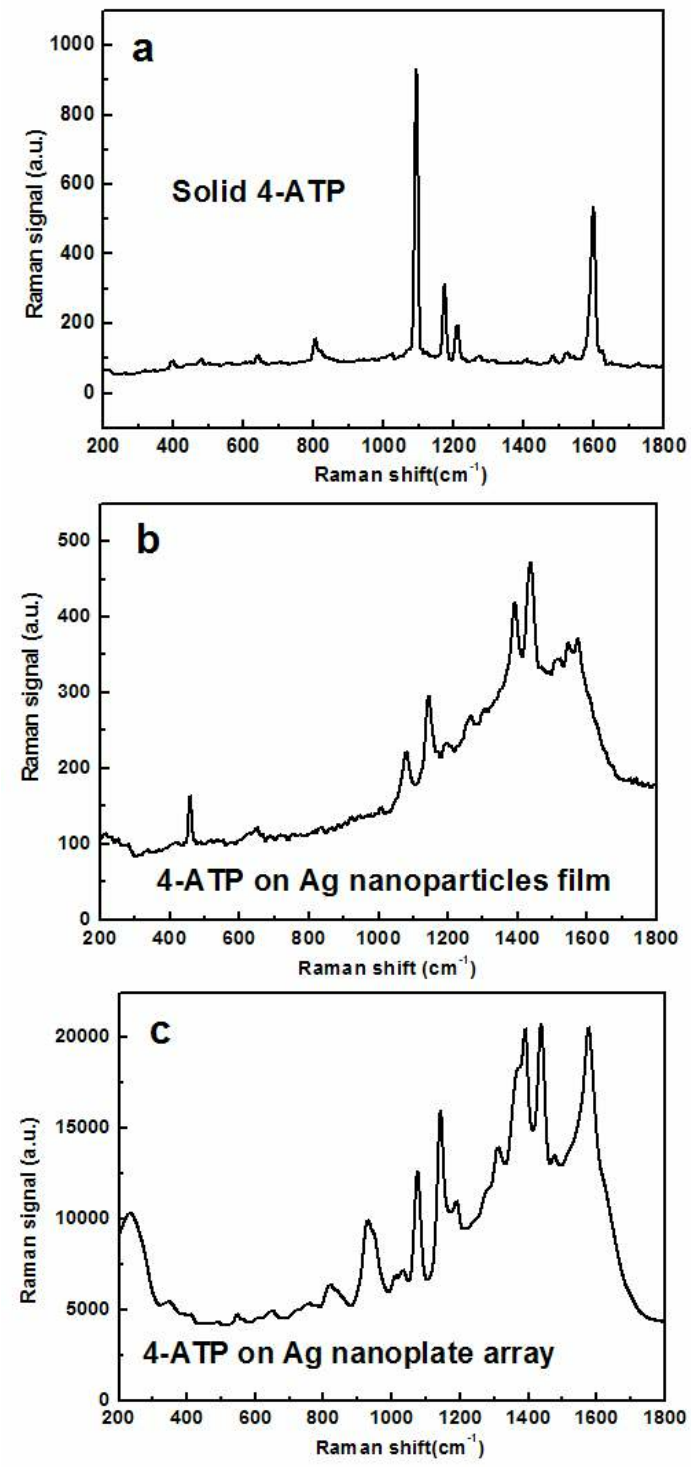

Figure S4 Raman spectra for different samples (Integral time: 10s). (a): solid 4-ATP. (b): the Ag nanoparticles film after immersion into 10^{-3} M 4-ATP solution for over one night , rinsing with de-ionized water, and dring with high-purity flowing nitrogen. (c): the Ag nanoplate array after immersion into 10^{-6} M 4-ATP solution for over one night, rinsing and drying.