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Supplementary

Engineering Branched Au@Ag Nanostar Plasmonic Array for Coupling Electromagnetic Enhancement and SERS Trace Detection of Polystyrene in Aquatic Environments

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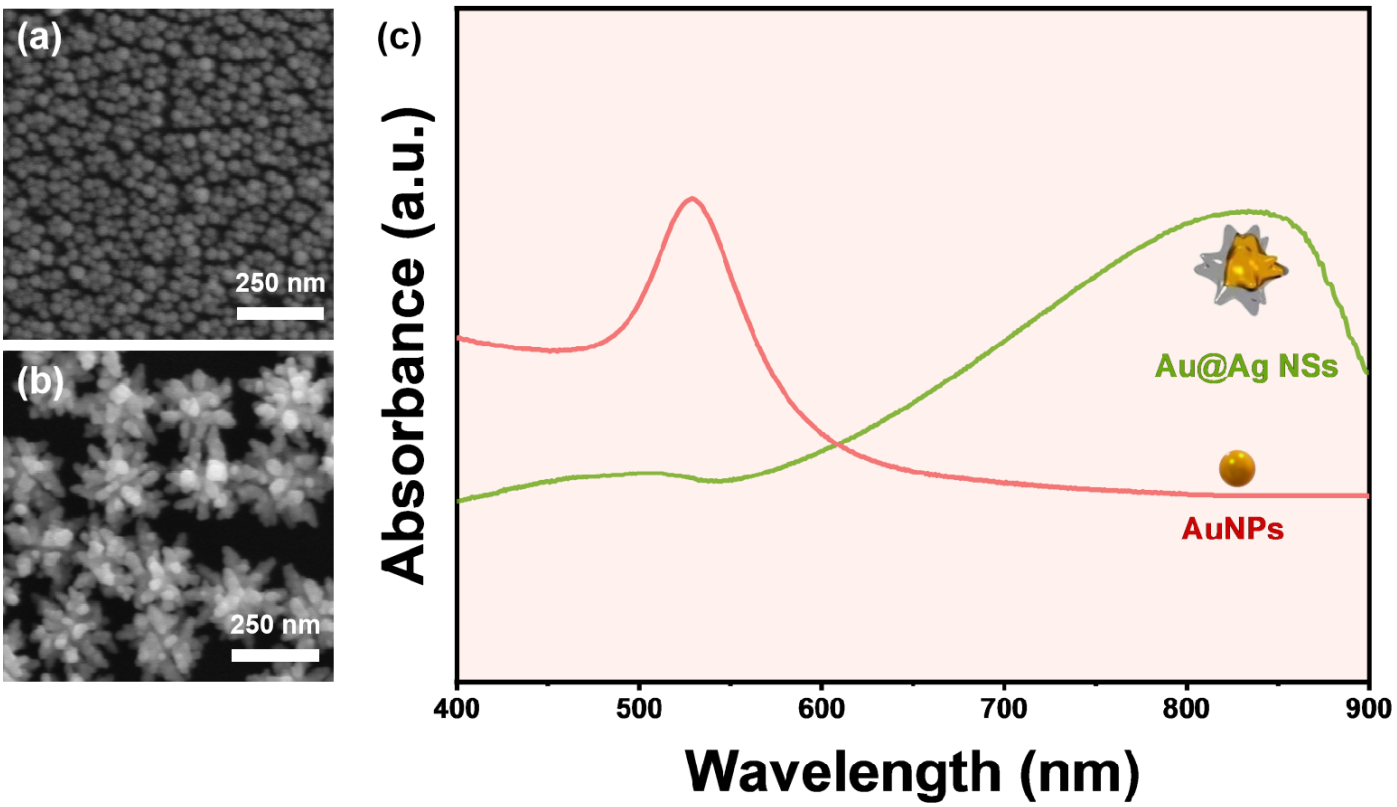

Figure S1. SEM images of (**a**) AuNPs; (**b**) Au@AgNSs; (**c**) UV/VIS spectra of AuNPs and Au@AgNSs.

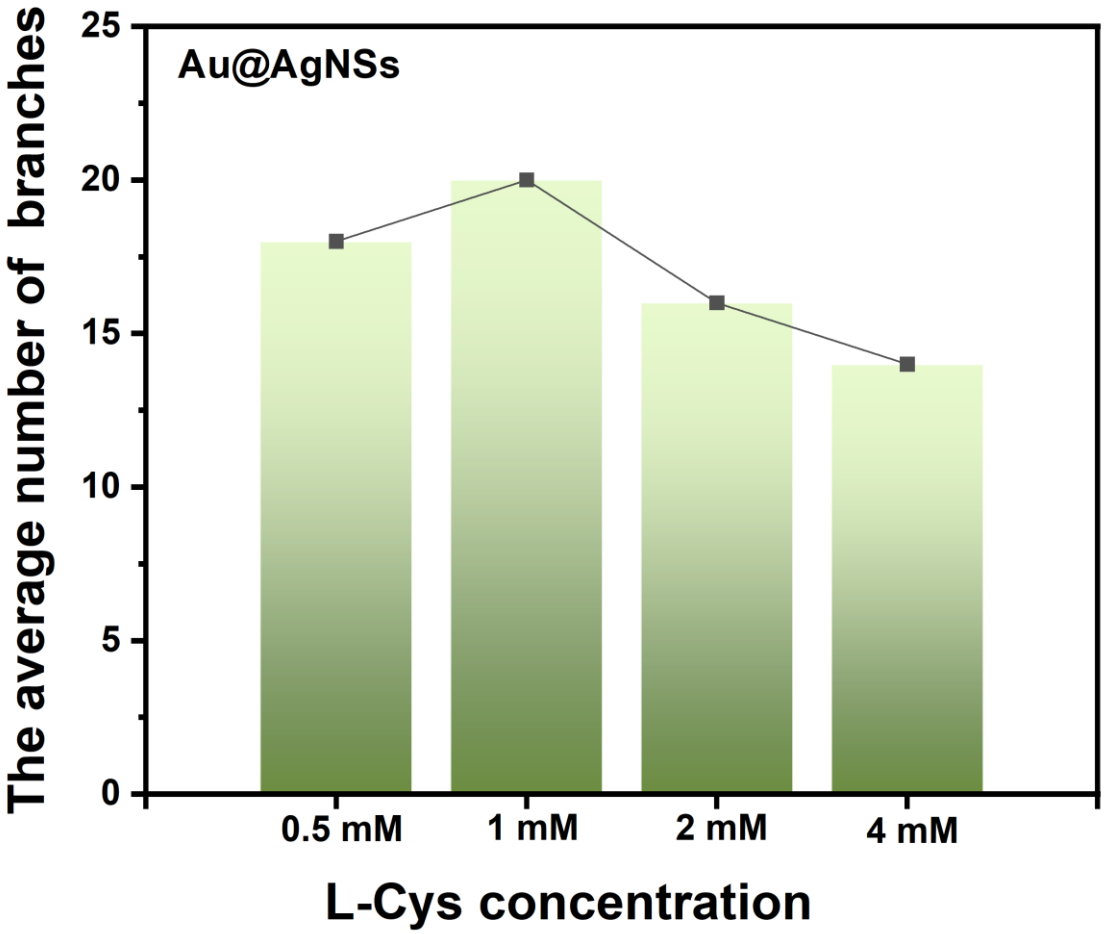

Figure S2. The plot between the average number of branches of Au@AgNSs and L-Cys concentration.

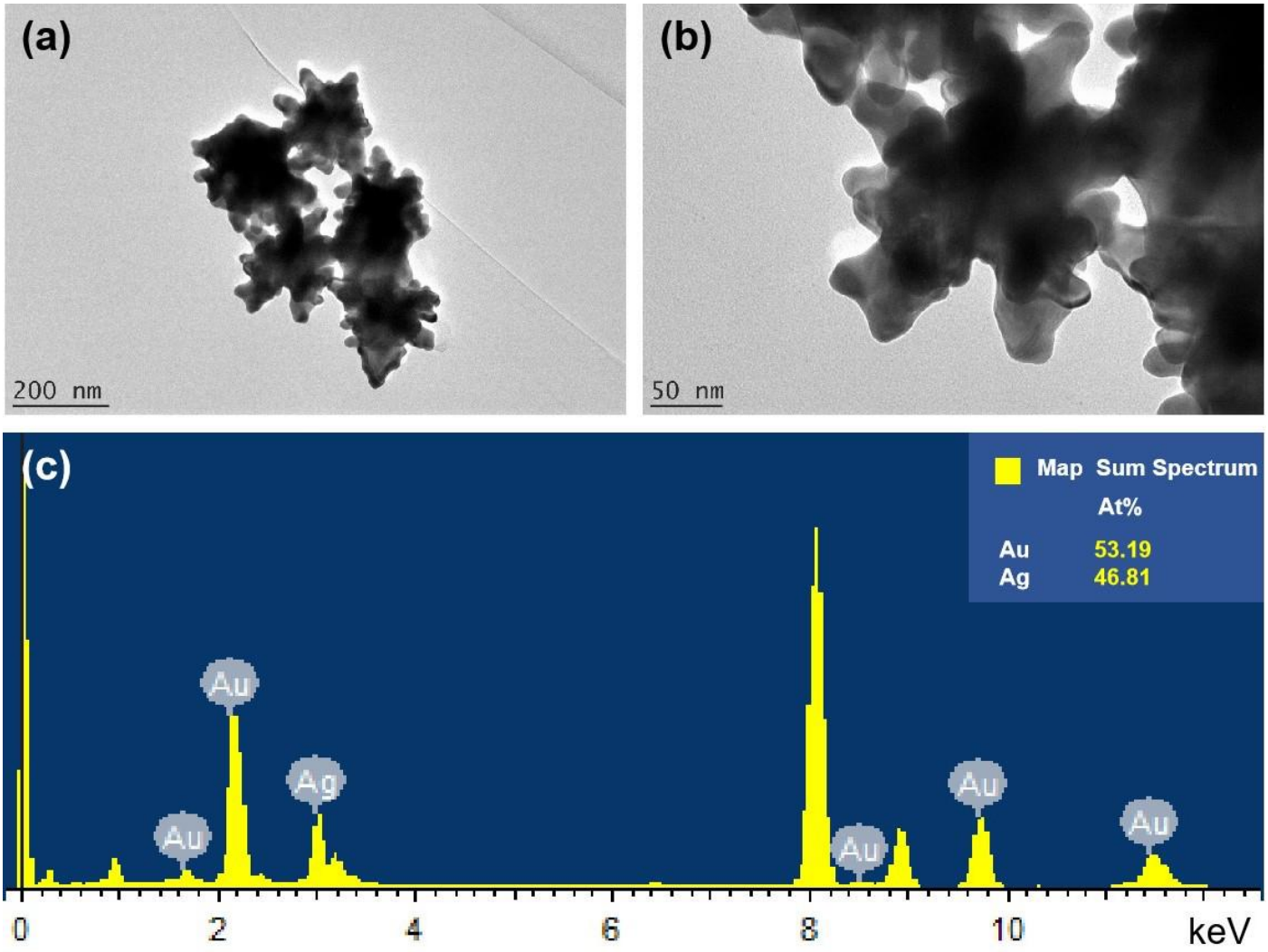

Figure S3. (**a**) and (**b**) TEM of Au@AgNSs; (**c**) Energy dispersive spectroscopy image.

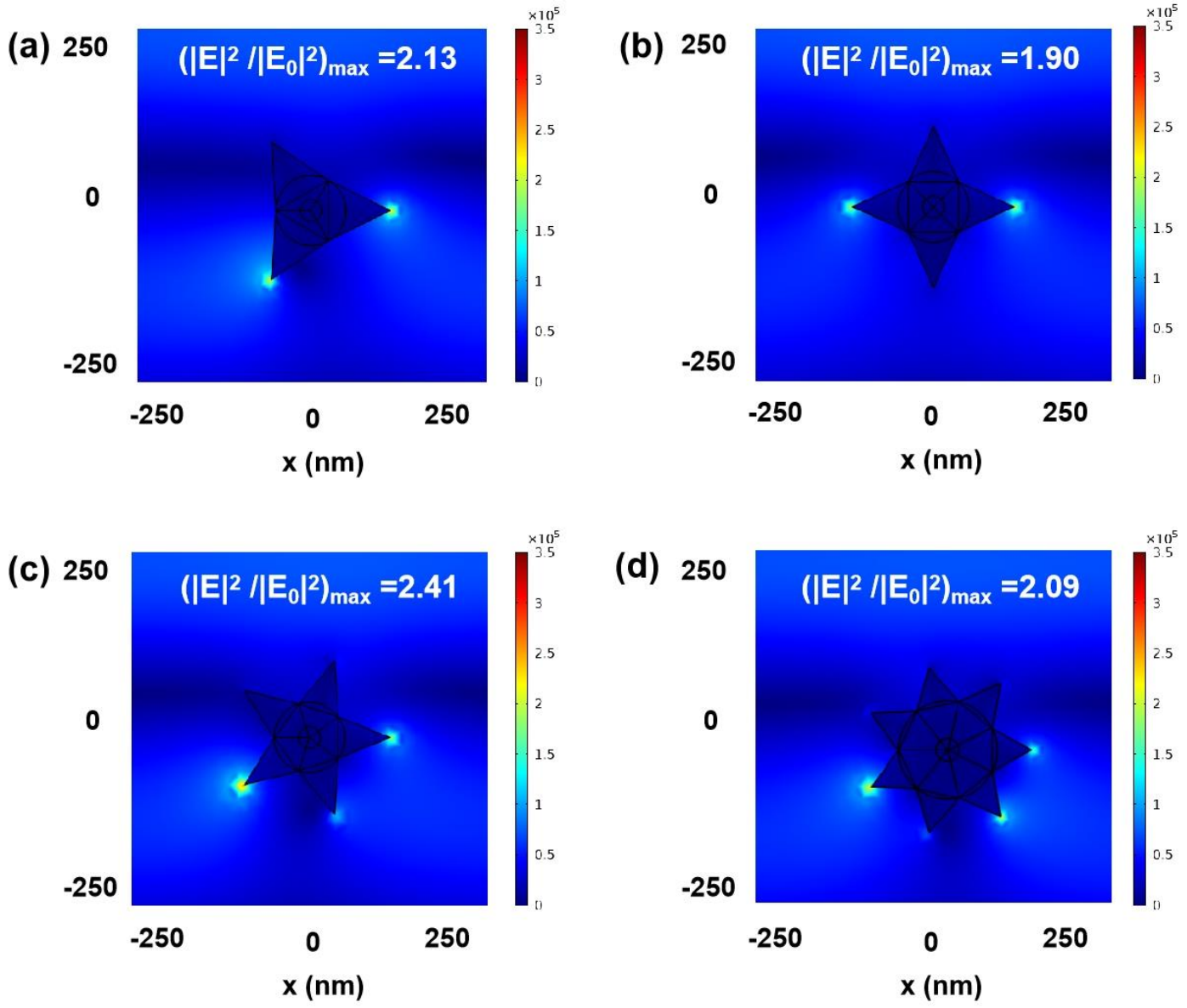

Figure S4. FDTD simulation of nanostars with different branch numbers (**a**) 3, (**b**) 4, (**c**) 5, (**d**) 7.

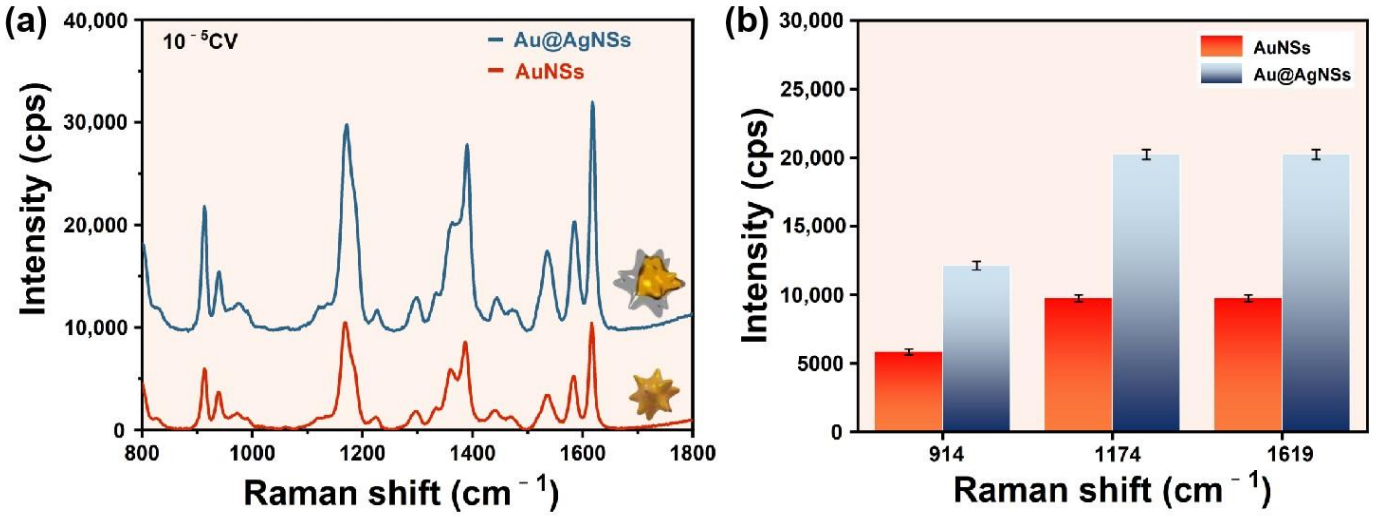

Figure S5. (**a**) The average SERS spectrum of CV (10^{-5} M) on the Au@AgNSs and AuNSs; (**b**) SERS intensity variation of 914 cm^{-1}, 1174 cm^{-1} and 1619 cm^{-1} peaks.

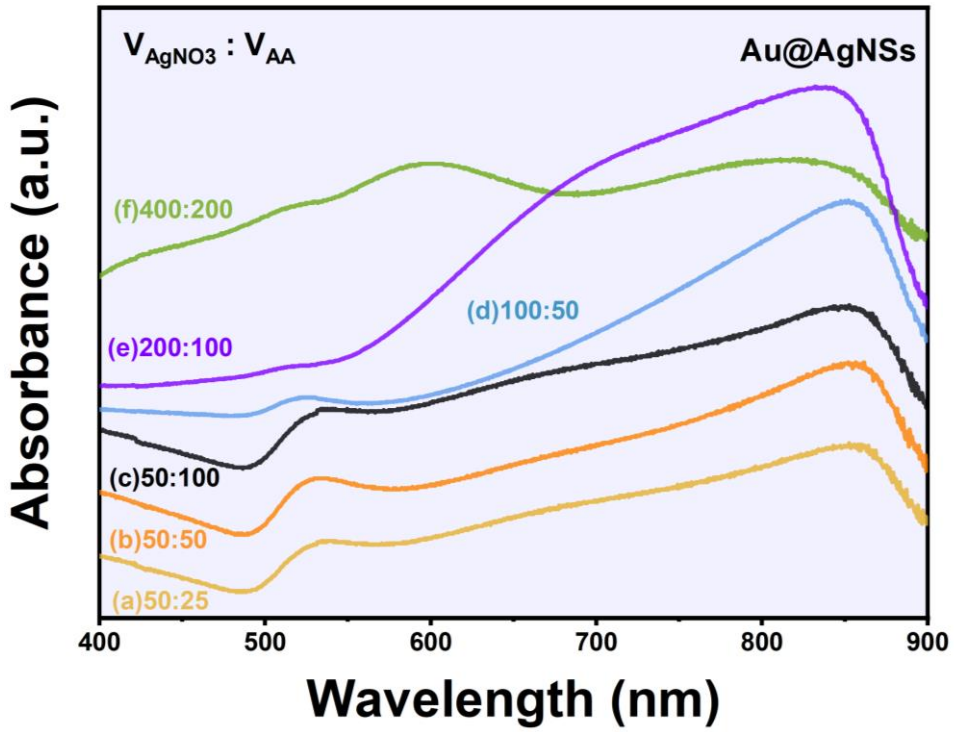

Figure S6. UV-vis spectra of the Au@AgNSs with different volume ratio of $AgNO_3$ to AA: (**a**) 50:25, (**b**) 50:50, (**c**) 50:100; and (**d**) 100:50, (**e**) 200:100, (**f**) 400:200.

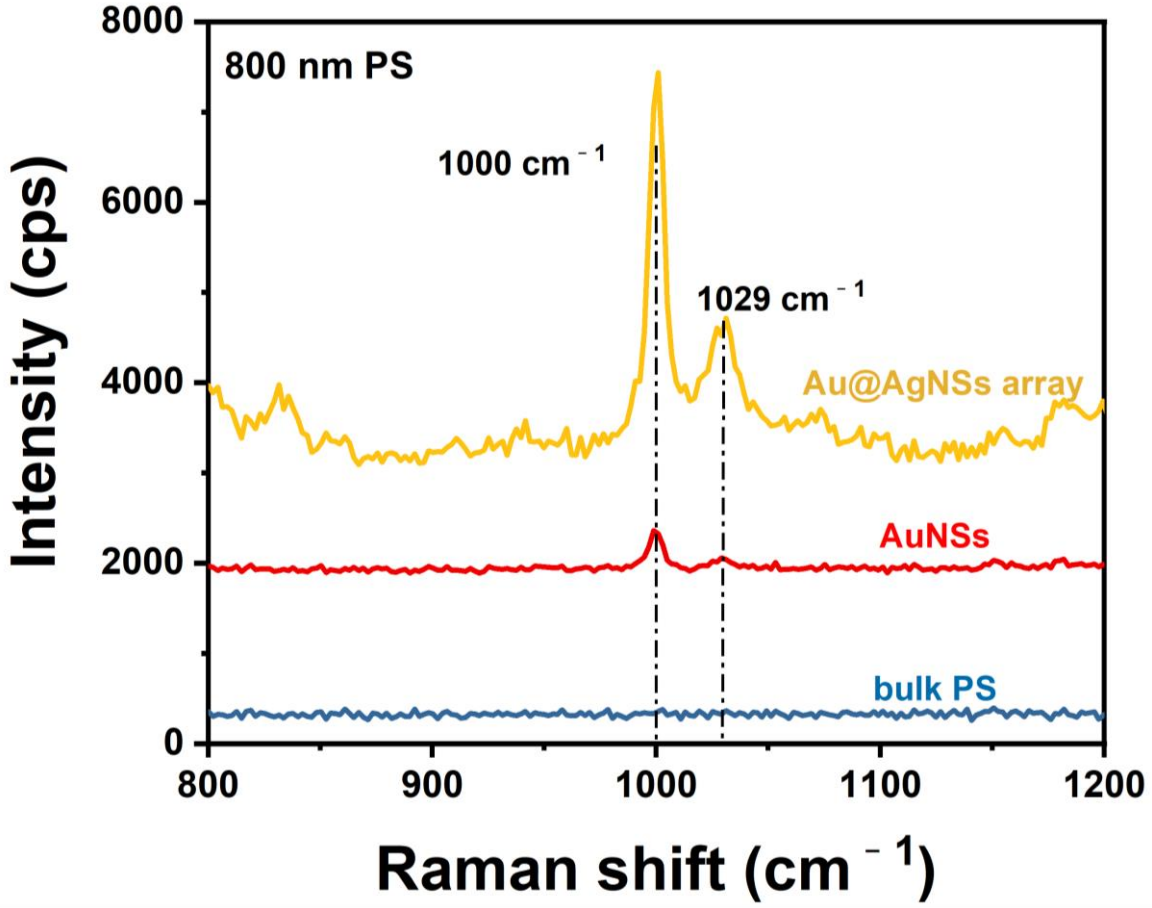

Figure S7. SERS spectrum of 800 nm PS on different substrates, (**a**) Au@AgNSs array, (**b**) AuNSs, (**c**) bulk PS.

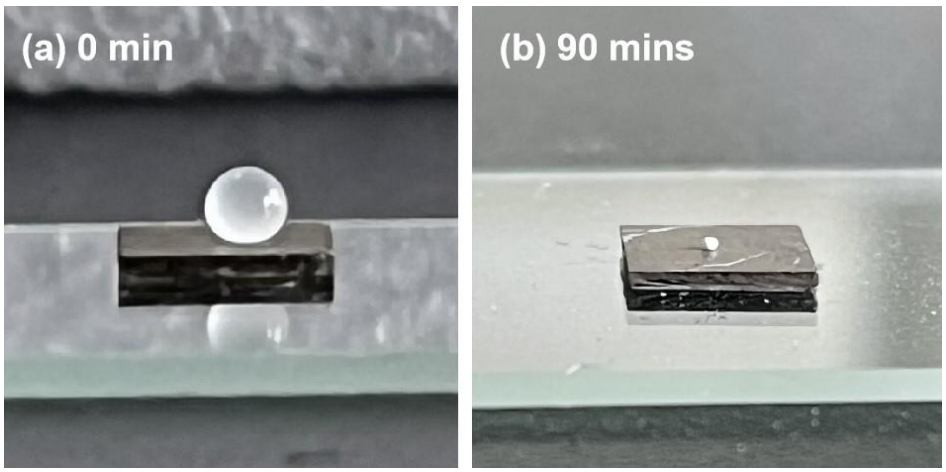

Figure S8. Change of PS solution with time (**a**) 0 min, (**b**) 90 min.

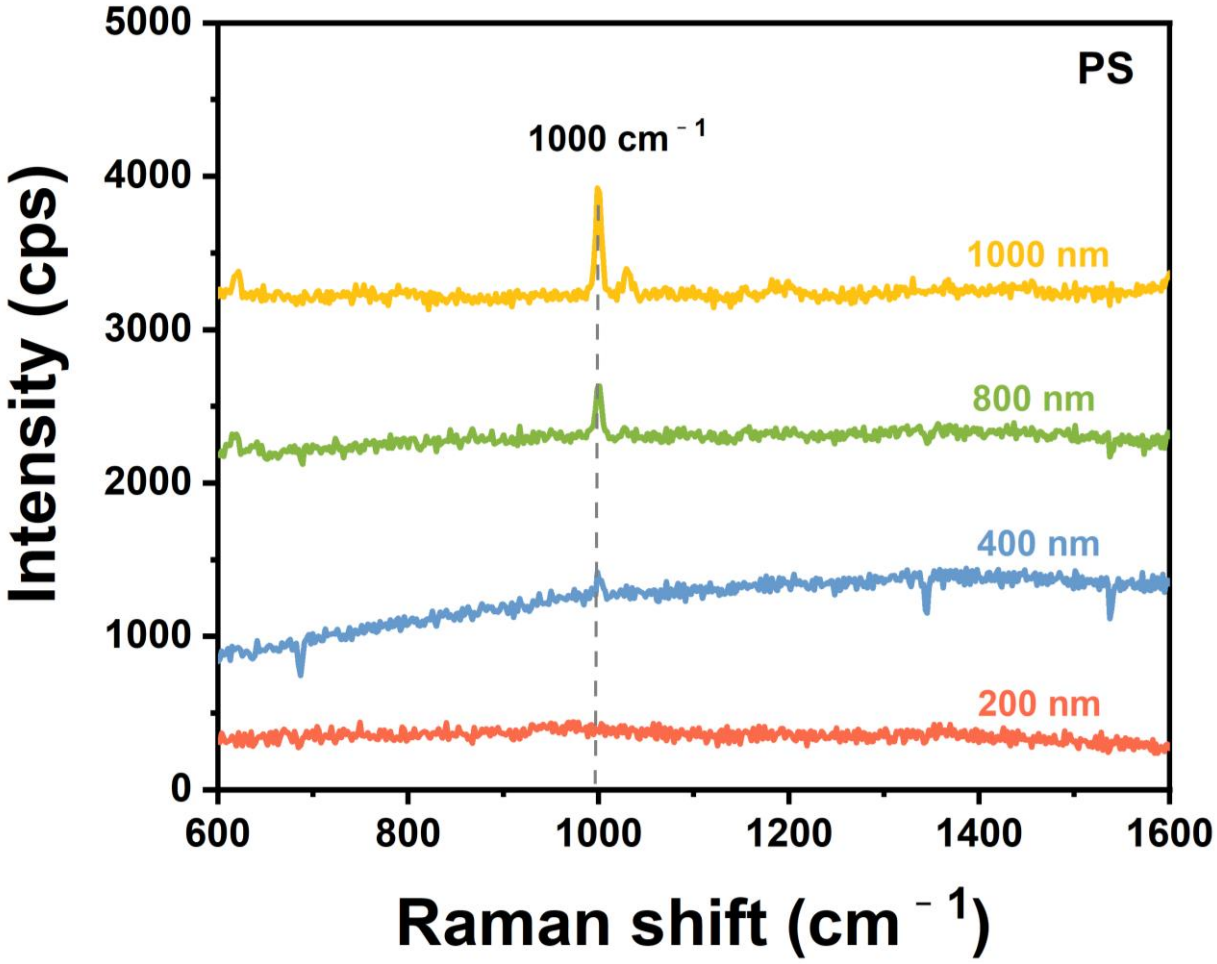

Figure S9. SERS spectra of PS standard solution (2.5 mg/mL) with different particle size on the silicon substrate.

Calculation of SERS Enhancement Factor (EF)

To quantify the enhancement contribution from Au@AgNSs arrays substrates, we calculated it enhancement factor (EF) based on the following formula:

$$EF = \frac{I_{SERS}}{I_{BULK}} \times \frac{N_{BULK}}{N_{SERS}} \quad (1)$$

where I_{SERS} and I_{BULK} are the integrated intensities of SERS signals and the normal Raman of the analyte solution at characteristic peaks 1174 cm^{-1} (Figure S10), respectively. N_{SERS} and N_{BULK}, denote the numbers of corresponding CV molecules effectively excited by a laser beam in SERS measurement and normal Raman measurement, respectively. According to the above formula, the EF for the Au@AgNSs arrays substrate is calculated to be 3.80×10^7.

N_{BULK} = (Laser spot area/Diffusion area) × (N_A × Volume $_{BULK}$ × Concentration $_{BULK}$)

N_{SERS} = (Laser spot area/Substrate area) × (N_A × Volume $_{SERS}$ × Concentration $_{SERS}$)

Diffusion area = $\pi(d/2)^2 = 0.5027$ cm^2, which means that a drop of 10^{-1} CV (200 μL) is spread on a slide on the glass.

Substrate area = 0.25 cm^2, which means that the substrate deposited on a fixed size of silicon (0.5 cm × 0.5 cm)

Volume $_{BULK}$ = Volume $_{SERS}$, in order to simplified calculation.

Concentration $_{BULK}$ = 10^7 × Concentration $_{SERS}$, according to Figure.S10(a).

$N_{BULK}/N_{SERS} = (0.25/0.5027) \times 10^7 = 5 \times 10^6$

I = intensity of the 1174 cm^{-1} peak

I_{BULK} = 46957.42

I_{SERS}, Au@AgNSs array = 35734.03, according to Figure.S10(a).

$EF = (I_{SERS}/I_{BULK}) \times (N_{BULK}/N_{SERS}) = 3.80 \times 10^7$

I_{SERS}, Au@AgNSs = 974.27401, according to Figure.S10(b).

$EF = (I_{SERS}/I_{BULK}) \times (N_{BULK}/N_{SERS}) = 1.04 \times 10^5$

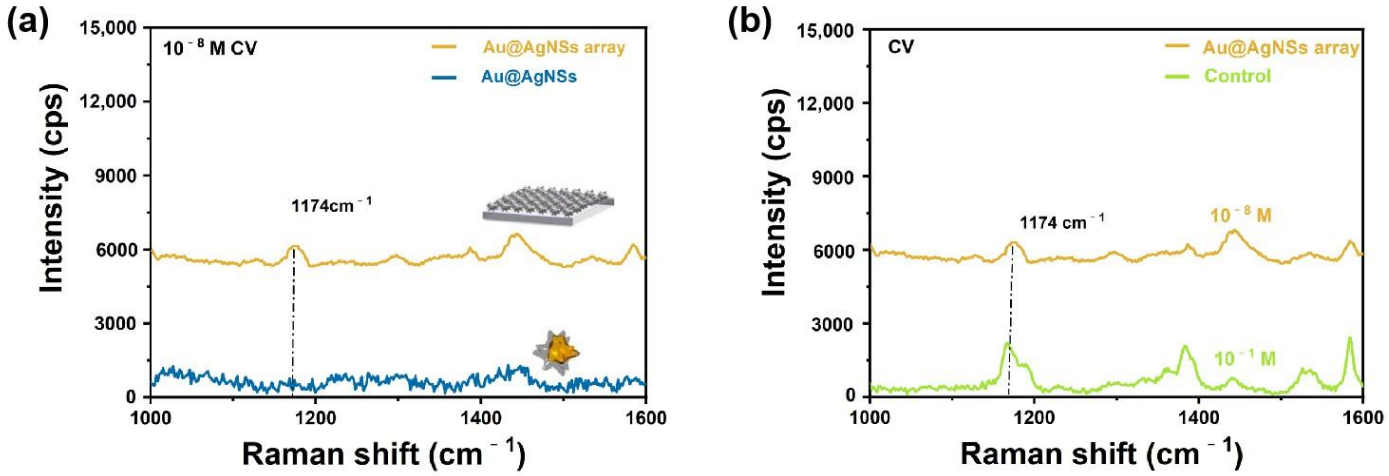

Figure S10. (**a**,**b**) SERS spectra used to calculate EF. The spectrum labelled as "control" is the normal Raman spectrum of CV (10^{-1} M) spread on the glass.