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Supporting Information

Bioinspired One-step Synthesis of Pomegranate-like Silica@Gold Nanoparticles with Surface-Enhanced Raman Scattering Activity

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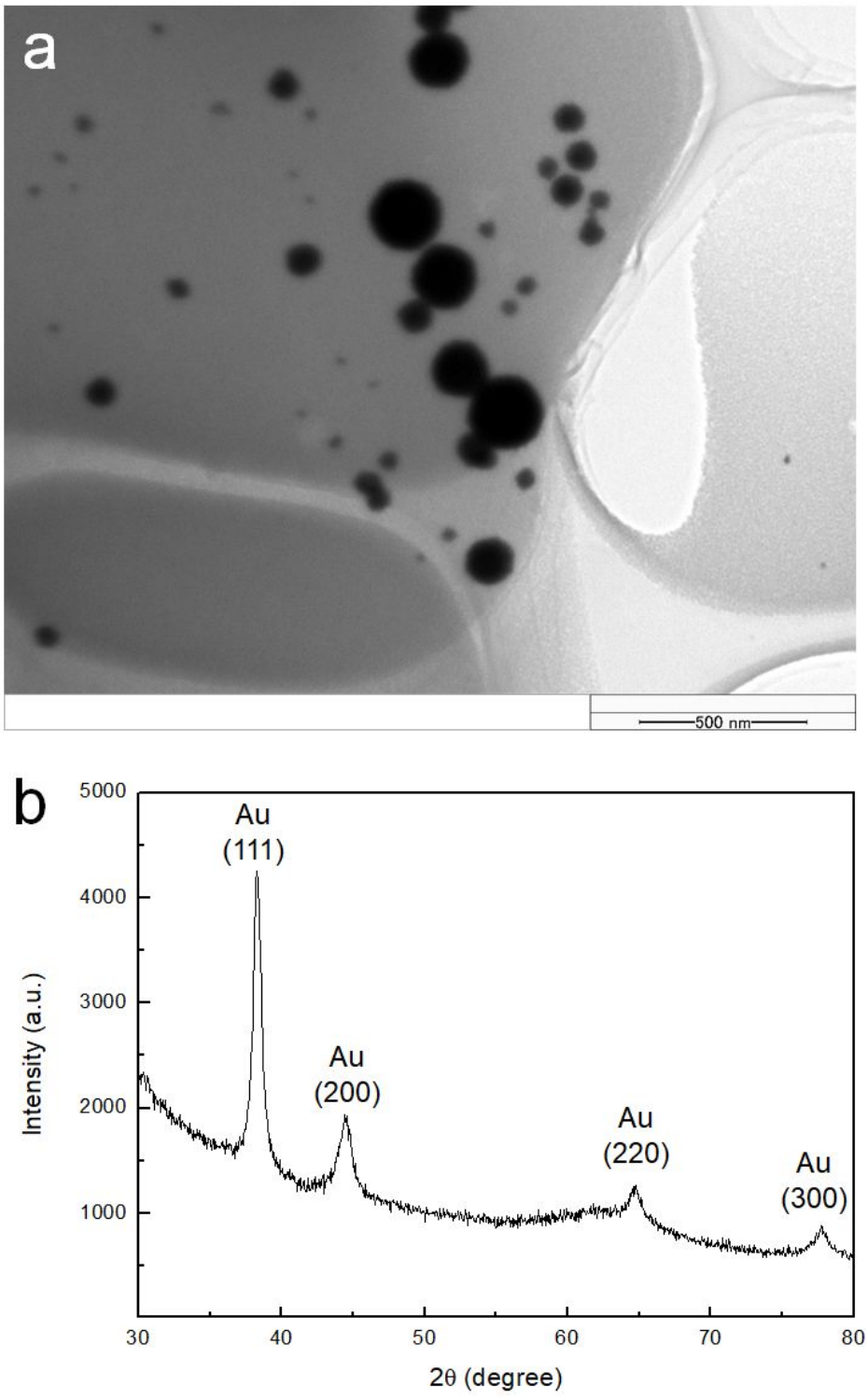

Figure S1. (a) TEM image of the P-SiO_2@Au NP suspension before washing; (b) powder XRD spectrum of the dried P-SiO_2@Au NP suspension.

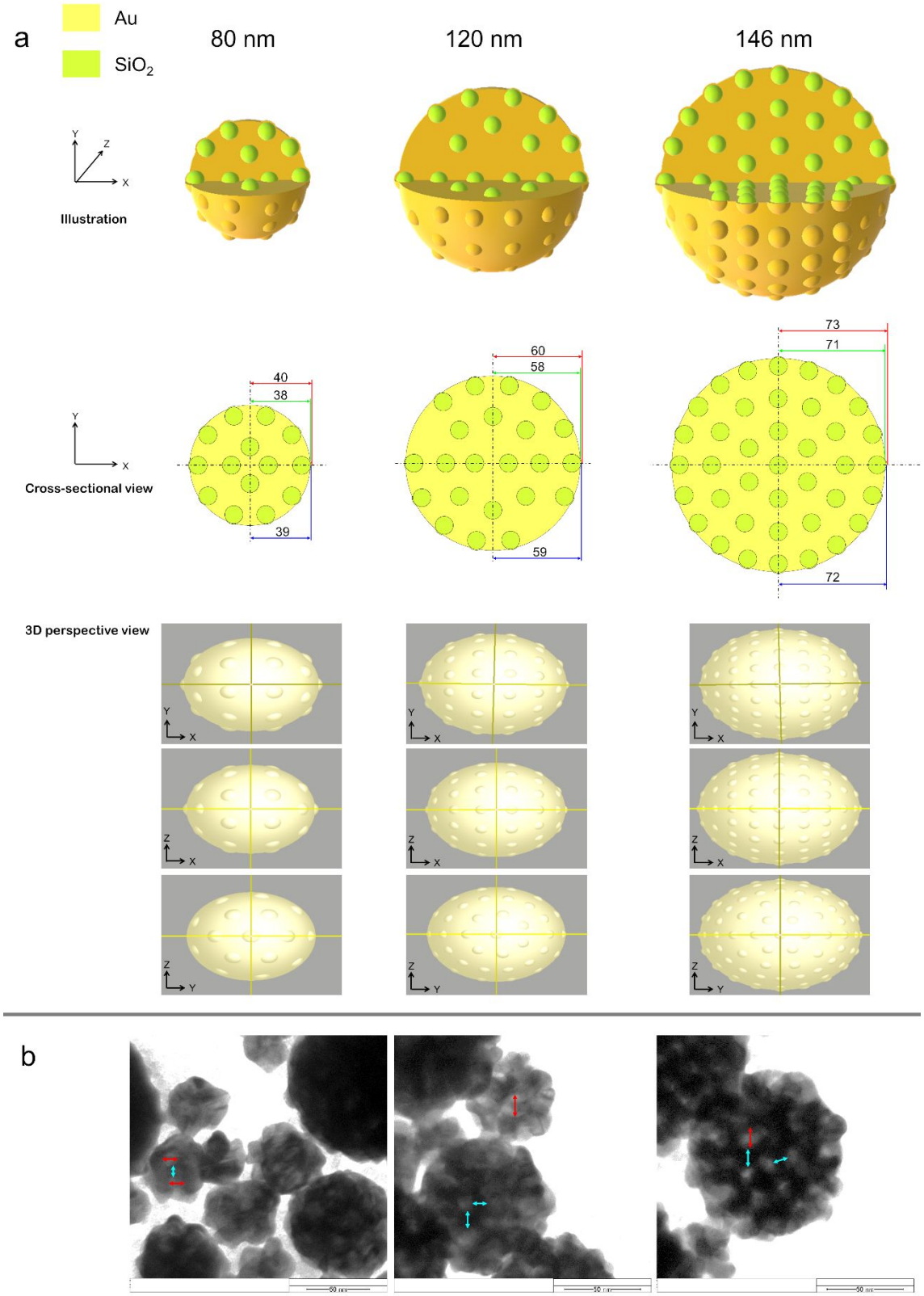

Figure S2. (a) Illustration, cross-sectional views, and 3D perspective views of the models of P-SiO_2@Au NPs for simulation. (b) Examples of TEM images used for estimation of the parameters

of the interior structure. The image contrast is adjusted for better imaging of the inner boundaries. Red arrows indicates the size of the embedded SNPs; blue arrows indicates the Au "wall" thickness between neighboring SNPs to derive the inter-SNP distances.

Several tens of particles were estimated to give the following results for P-SiO_2@Au NPs synthesized with different amounts of $HAuCl_4$.

$HAuCl_4$ (μ mol)	SNP size (nm)	Au "wall" thickness (nm)
12.1	12	10
24.3	7.5	10
36.4	10	10

Simplified models are constructed for simulation with the following considerations.

(1) Diameter of the embedded SNPs is set to be 12 nm.

(2) The structure is simplified through arranging the SNPs in a manner as shown in Figure S2a. The SNPs are away from each other at certain inter-SNP distance (center-to-center). The inter-SNP distance cannot be fixed to a constant value because the symmetry of the whole structure has to be considered. The inter-SNP distances are varied around 22 nm according to the above estimation results.

(3) Surface of the P-SiO_2@Au NP is Au, as is confirmed by HR-TEM. Because the Au-SNP interface at the surface has not been clearly imaged, the thickness of the surface Au layer should be very thin. In the model, the SNPs at the surface are covered by an Au shell with 1 nm thickness.

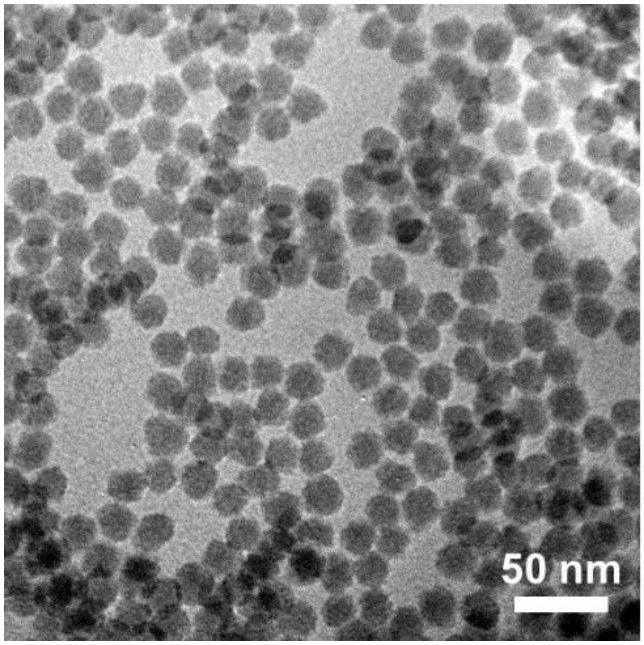

Figure S3. TEM image of the preformed SNP sol.

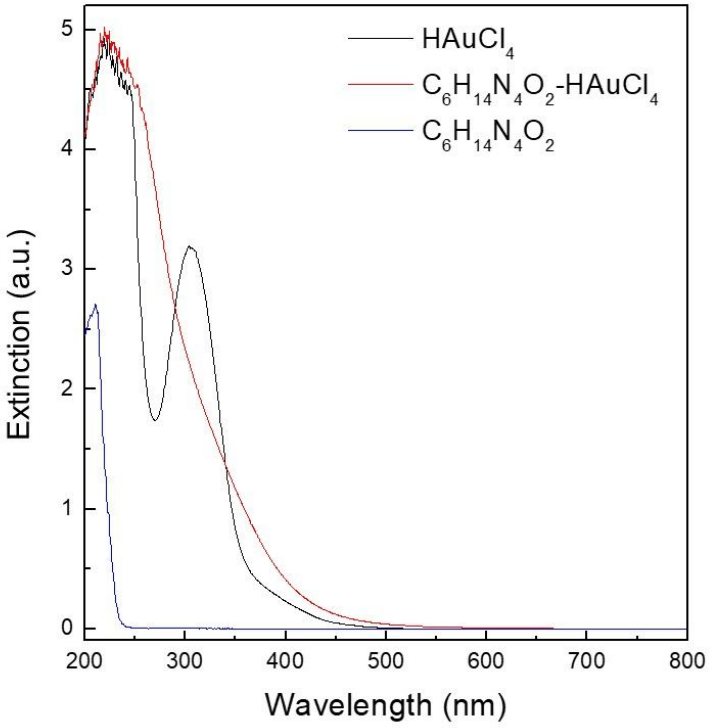

Figure S4. UV-Vis extinction spectra of the $HAuCl_4$ (0.69 mM), $C_6H_{14}N_4O_2$ (8 mM), and $C_6H_{14}N_4O_2$ (8 mM)–$HAuCl_4$ (0.69 mM) aqueous solutions.

Figure S5. Photograph of the suspension by reacting $HAuCl_4$ (24.3 μ mol) with lysine (8 mM) in water (35.2 ml) at 80 ° C for 24 hrs.

Table S1. The pH values of the reaction system before heating.

	pH (18 °C)
Arginine (8 mM) *aq.* solution	10.4
Arginine (8 mM) and chloroauric acid (0.69 mM) *aq.* solution	9.5

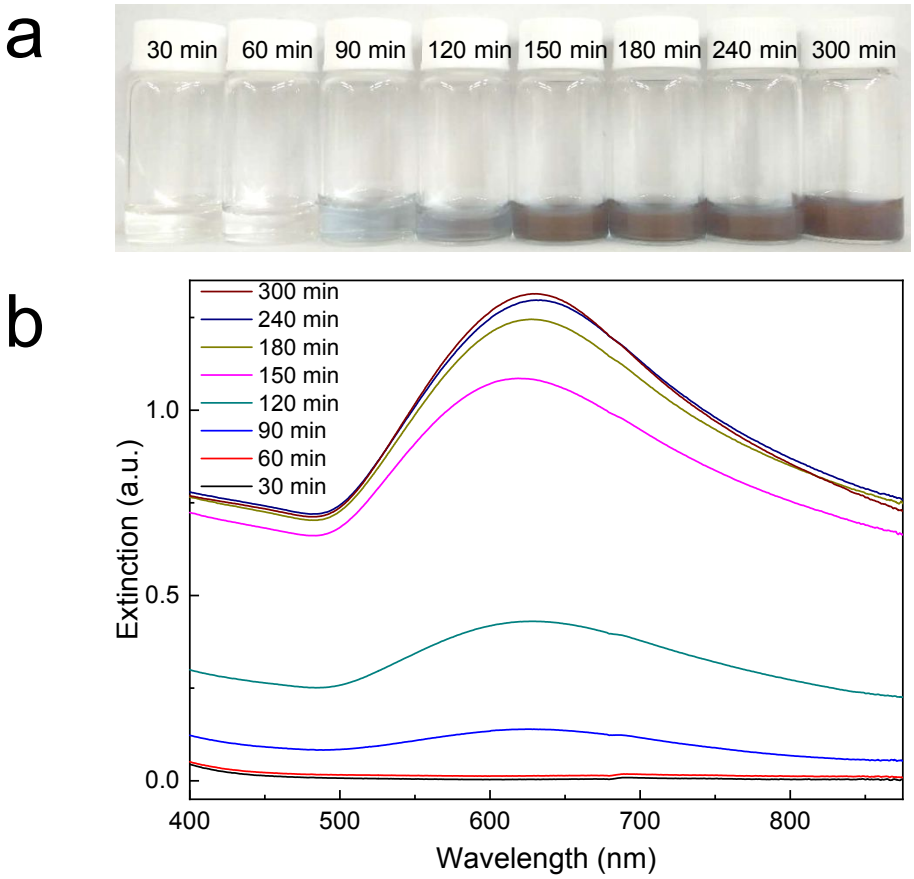

Figure S6. (a) Photograph and (b) UV-Vis extinction spectra of the suspension after different reaction time. The synthetic parameters were 24.3 μmol of $HAuCl_4$, 2.40 mmol of TEOS, 8 mM of arginine in 35.2 ml of water at 80 ° C with magnetic stirring.

Table S2. The pH values of the suspension measured at different time during reaction. (Reaction parameters were the same as those in Figure S6).

Reaction time (hr)	pH (70 °C*)
0.5	8.0
1	7.9
3	7.8
5	7.8
8	7.8
24	7.9

*Note: pH values were measured in-situ during reaction and this temperature (70 ° C) was indicated by the pH meter. The reaction temperature was set to 80 ° C with the oil bath. The difference may be caused by the slow equilibrium of the pH meter's temperature sensor.

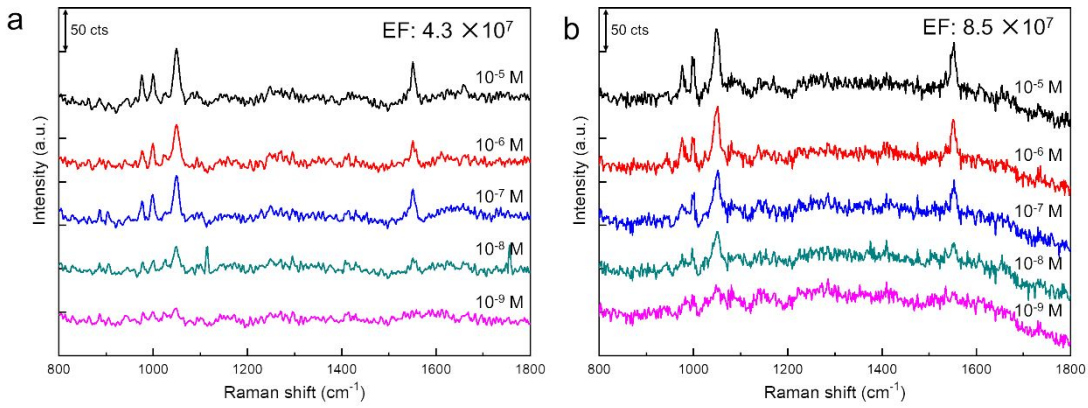

Figure S7. SERS spectra of trace amounts of TP in aqueous solution with P-SiO_2@Au NPs synthesized with (a) 12.1 and (b) 36.4 μmol of $HAuCl_4$. The spectra were off-set for clarity.

Calculation details of the enhancement factor (EF)

EF is calculated with the formula

$$\mathrm{EF} = \frac{I_{SERS}}{C_{SERS}} \times \frac{C_{Raman}}{I_{Raman}}$$

- Neat TP is a liquid matter. Its concentration C_{Raman} is calculated to be 9.77 M according to its density (1.08 g/cm³) and molecular weight (110.19 g/mol).

  I_{Raman} is the integrated peak area (9779) of the 1068 cm^{-1} peak in Figure 8a. The peak area is calculated with the peak integration function in the Origin software.

- TP can be detected down to 10^{-8} M (Figure 8b and Figure S7), hence C_{SERS} is 10^{-8} M.

  I_{SERS} is the integrated peak area of the 1049 cm^{-1} peak at 10^{-8} M in the SERS spectra. It is obtained with the peak integration function in the Origin software. I_{SERS} and the calculated EF of the P-SiO_2@Au NPs synthesized with varying amounts of $HAuCl_4$ are shown as follows.

$HAuCl_4$ (μ mol)	SERS spectra	I_{SERS} (1049 cm^{-1})	EF
12.1	Figure S7a	434	4.3×10^7
24.3	Figure 8b	568	5.7×10^7
36.4	Figure S7b	852	8.5×10^7

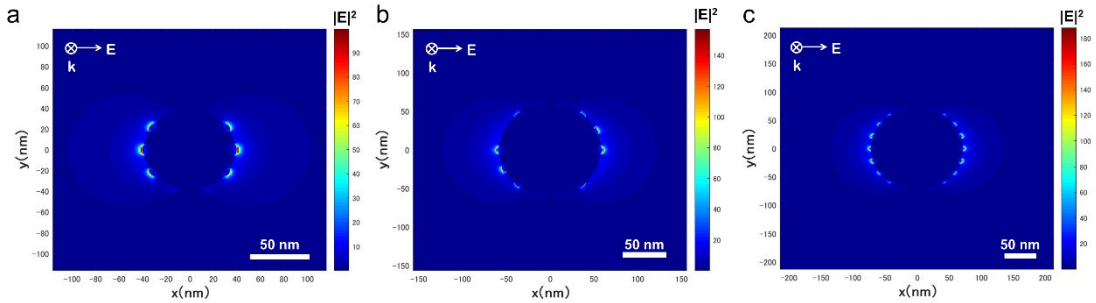

Figure S8. Calculated distribution of EM field intensity around P-SiO_2@Au NP with a size of (a) 80 nm, (b) 120 nm, and (c) 146 nm under light irradiation (785 nm). The models in Figure S2 are used for simulation. 785 nm is the laser wavelength used in the SERS measurements.

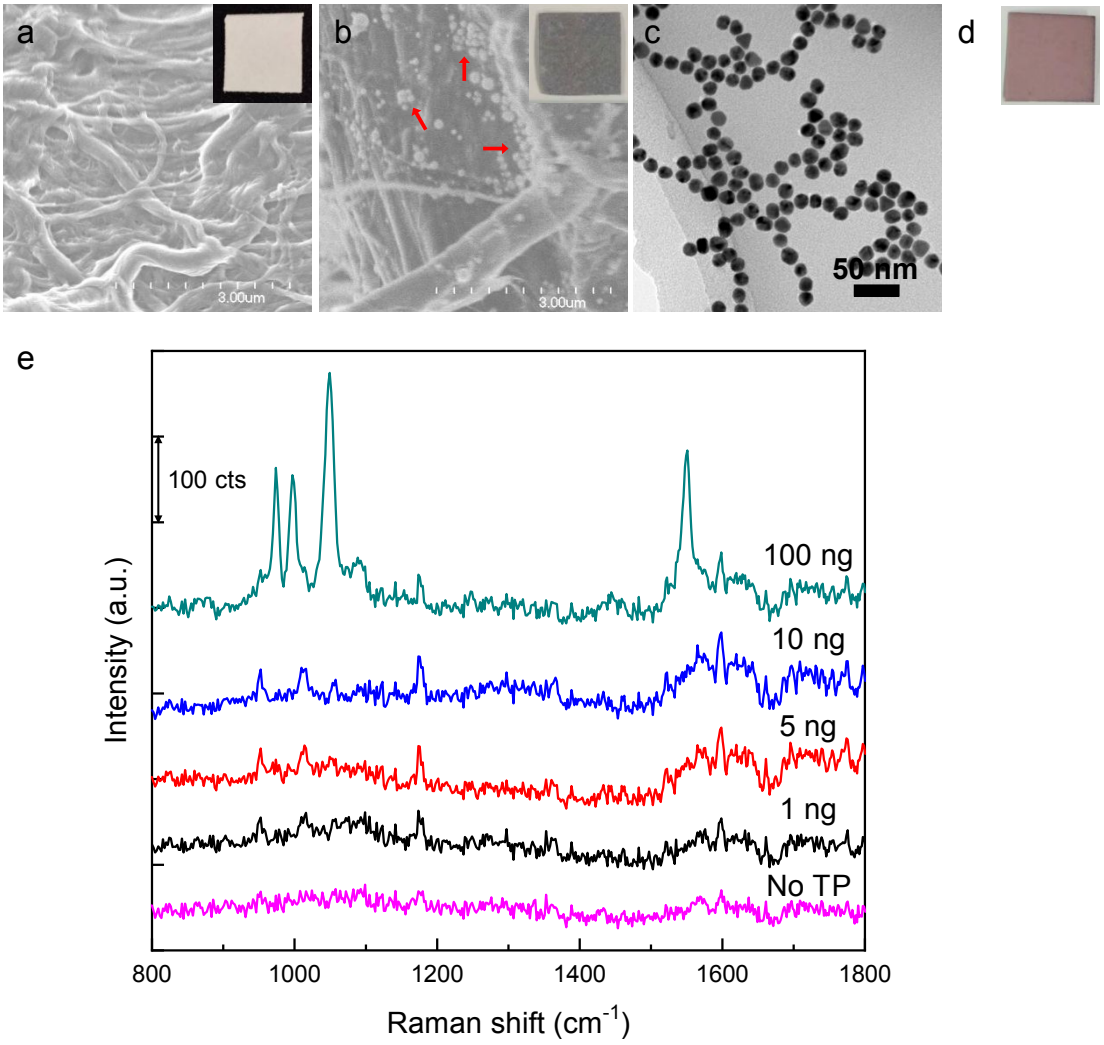

Figure S9. SEM images of the filter paper (a) before and (b) after impregnation with the P-SiO_2@Au NPs. Insets show photographs of the substrates. Red arrows in (b) indicate the P-SiO_2@Au NPs. The P-SiO_2@Au NPs were synthesized with the same parameters as those in Figure S6. (c) TEM image of the spherical Au NPs (*ca.* 17 nm). (d) Photograph of the Au-FP substrate. (e) SERS spectra of trace amounts of TP detected with the Au-FP substrates.