Electronic Supplementary Information

Fabrication of a honeycomb-like bimetallic SERS substrate for detection of triphenyltin chloride

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S 1.1. AEF calculation

Analytical enhancement factor (AEF) which is defined as the ratio of SERS intensity and normal Raman intensity of a sample.

$$AEF = \frac{I_{SERS}}{I_{Raman}} \times \frac{N_{Raman}}{N_{SERS}} \qquad (1)$$

Where I_{SERS} and I_{Raman} are the Raman intensity of the sample under the corresponding detection mode. N_{SERS} and N_{Raman} are the numbers of adsorbed R6G molecules which are excited by the laser under SERS and normal Raman detection conditions, calculated by equation (2).[1, 2]

$$N = \pi\left(\frac{d}{2}\right)^2 h \cdot C \cdot N_A \qquad (2)$$

Where N_A is the Avogadro constant, 'd' and 'h' are the diameter and height of the laser spot, respectively. C is the concentration of R6G solution detected by SERS and normal Raman. Under the same laser conditions, the parameters 'd' and 'h' will remain the same, so the calculation formula of AEF can be simplified as equation (3):

$$AEF = \frac{I_{SERS}}{I_{RS}} \times \frac{C_{RS}}{C_{SERS}} \qquad (3)$$

Therefore, when the experimental conditions for measuring Raman spectrum and SERS spectrum are the same, the formula is valid.

The AEF value of the HC5-AgAu to R6G:

The Raman characteristic peak intensity at 610 cm^{-1} was used to obtain AEF for the HC5-AgAu substrate, using the clean SiO_2 as the reference substrate. The reference concentration of R6G was determined at 10^{-13} M for C_{SERS} and 10^{-3} M for C_{Raman}.

$$AEF = \frac{I_{SERS}}{I_{RS}} \times \frac{C_{RS}}{C_{SERS}} = 6.08 \times 10^9$$

The AEF value of the HC5-AgAu to TPhT:

The Raman characteristic peak intensity at 655 cm^{-1} was used to obtain AEF for the HC5-AgAu substrate, using the clean ITO as the reference substrate. The reference concentration of TPhT was determined at 10^{-10} M for C_{SERS} and 10^{-3} M for C_{Raman}.

$$AEF = \frac{I_{SERS}}{I_{RS}} \times \frac{C_{RS}}{C_{SERS}} = 3.38 \times 10^6$$

S 1.2. Reference substrate treatment process

The clean SiO_2 and ITO substrates were obtained by ultrasonically treatment with acetone, ethanol and deionized water in sequence. Then stored with deionized water, and dried with nitrogen before using.

S 1.3. DFT simulation

The initial structure diagram of TPhT molecule was drawn with GaussView6.0, then calculated and optimized under Density functional theory (DFT) theory. The basis set of Raman spectroscopy simulation was selected according to the structure and elements of TPhT. Among them, the non-metal elements C, H, Cl were at the B3LYP/6-311+G** level, and the main group metal element Sn used the SDD basis set for simulation calculation. The solvent model in the calculation process was set as the methanol solvent.[3] In addition, the frequency correction factor (0.9887)[4] were also considered in the calculation of Raman spectrum to obtain the accurate resonant frequency.

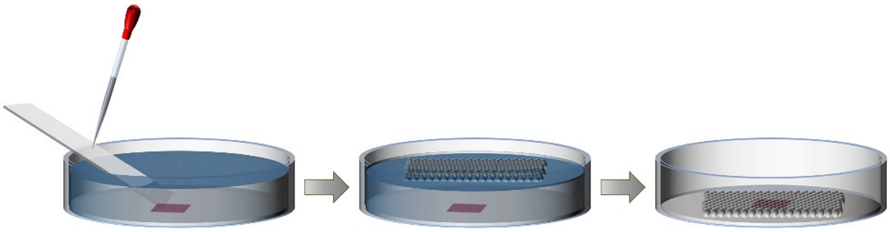


Figure S1. The schematic illustration of the PS array preparation.

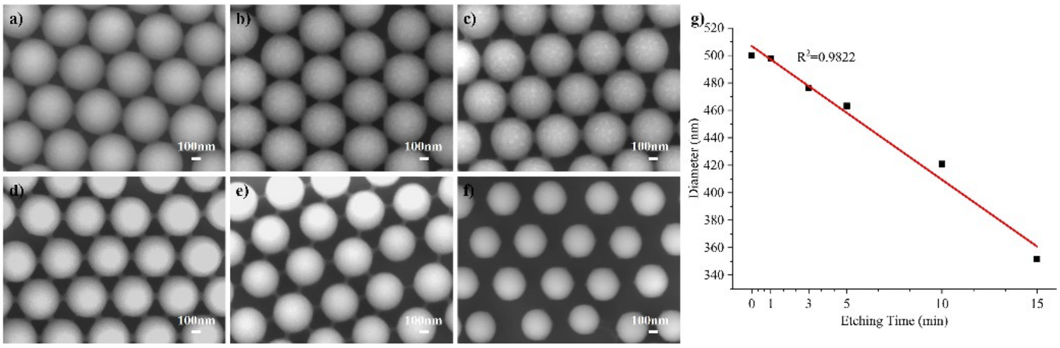


Figure S2. a-f) SEM images of PS at etching time of 0, 1, 3, 5, 10, 15 min, respectively, g).

Linear relation graph of PS particle size and etching time.

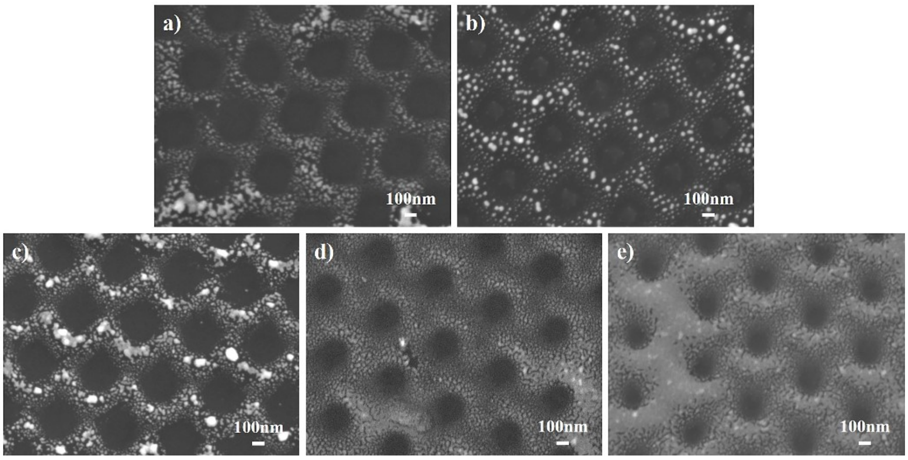


Figure S3. SEM images of honeycomb-like Ag arrayed structure at different etching time: a-e) 1, 3, 5, 10, 15 min, respectively.

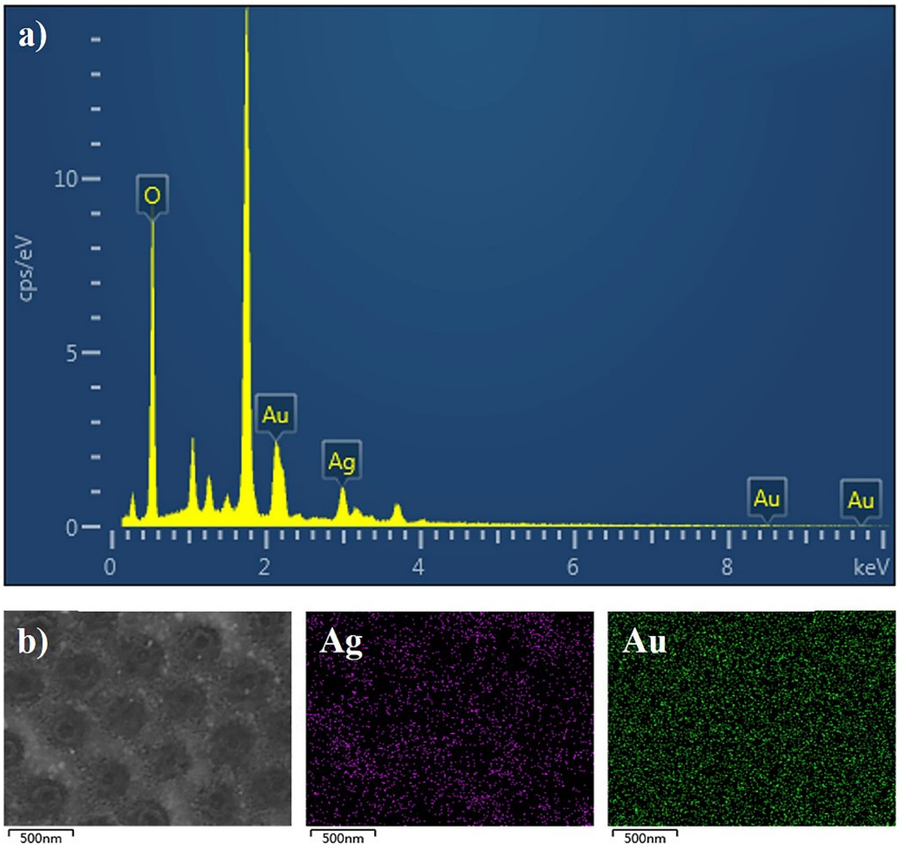


Figure S4. a) EDS analysis of HC5-AgAu substrates, b) EDS mapping results of HC5-AgAu substrates.

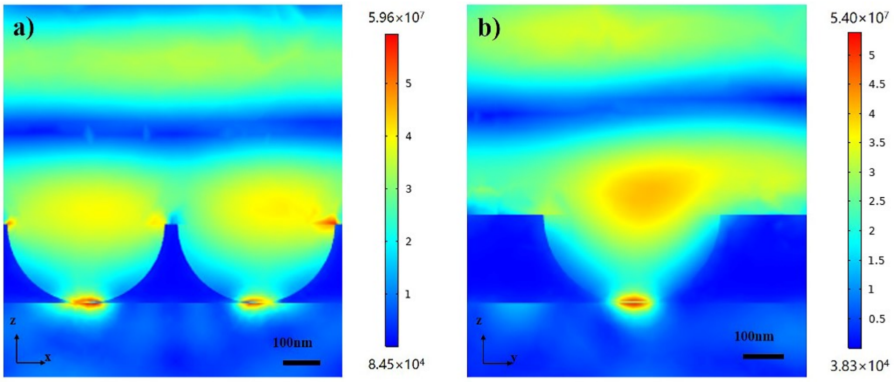


Figure S5. a). Electromagnetic field distribution of the substrate HC5-Ag: the x-z longitudinal section, b). Electromagnetic field distribution of the substrate HC5-Ag: the y-z longitudinal section.

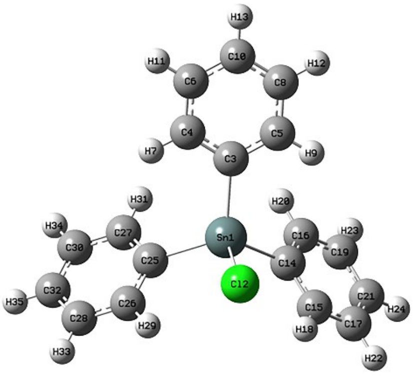
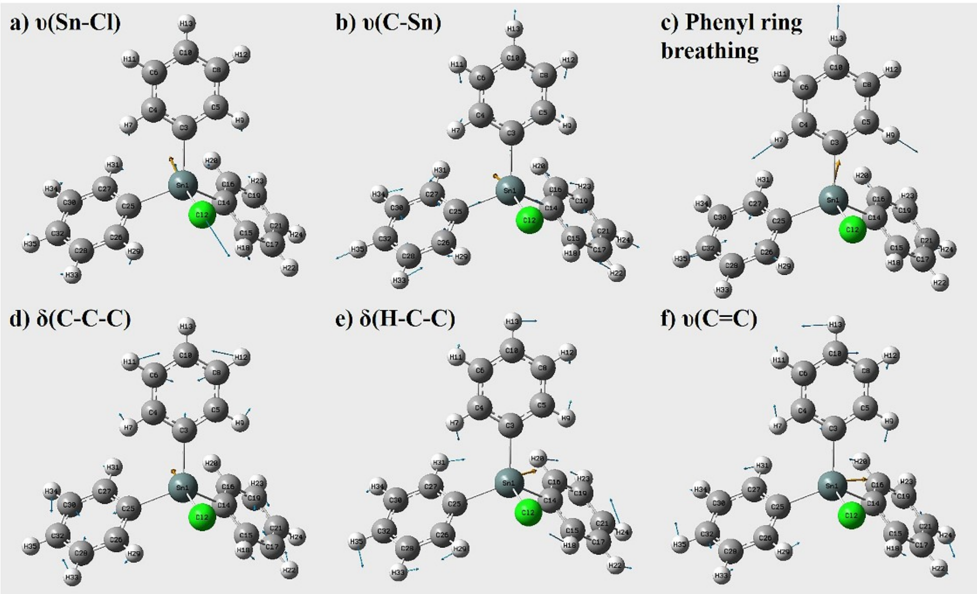


Figure S6. Optimization structure of TPhT molecule by DFT theory.


a) υ(Sn-Cl)

b) υ(C-Sn)

c) Phenyl ring breathing

d) δ(C-C-C)

e) δ(H-C-C)

f) υ(C=C)

Figure S7. Schematic atomic displacements of the main Raman vibration modes of TPhT.

Table S1. Attribution of Raman vibration mode of TPhT characteristic peaks.

Raman (cm^{-1})	SERS (cm^{-1})	DFT (cm^{-1})	Vibration Mode
216	209	196	τ(C-C-C-C)
	235	212	δ(C-C-Sn)
333	334	276	υ(Sn-Cl)
620	617	620	δ(C-C-C)
657	655	652	υ(C-Sn)
	696	700	τ(H-C-C-C), τ(C-C-C-C)
	734	740	
	854	852	τ(H-C-C-C)
	913	916	
998	999	996	symmetric and asymmetric phenyl ring breathing
1022	1022	1012	δ(C-C-C)
	1075	1068	δ(H-C-C)
1157	1158	1156	
1192	1191	1188	
	1332	1332	
	1431	1428	υ(C-C)
	1481	1476	
	1569		υ(C=C), δ(H-C-C)
1577	1579	1580	
3047	3046	3124	υ(C-H)

Notation: υ, stretching vibrations; δ, in-plane deformational vibrations; τ, out-of-plane vibrations.

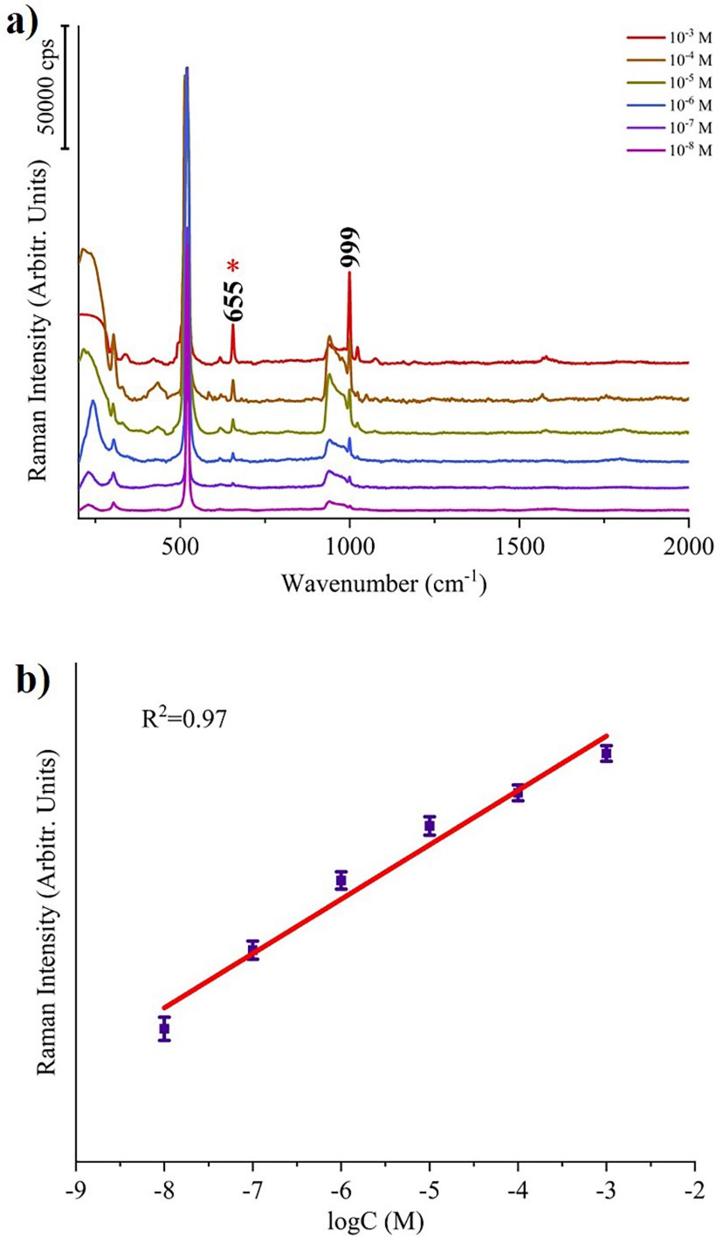


Figure S8. a). SERS spectra of TPhT of varying concentrations from 10^{-3} to 10^{-8} M by HC5-Ag substrate; b). Log-log correlation graph of the intensity at 655 cm^{-1} and TPhT concentrations. The error bar was obtained by three replicated determinations.

References

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4. J. P. Merrick, D. Moran, L. Radom, *J. Phys. Chem. A*, **2007**, *111*, 11683-11700.