

Supporting information

Au@Ag core-shell nanoparticles with hidden internal reference promoted quantitative solid phase microextraction-surface enhanced Raman spectroscopy detection

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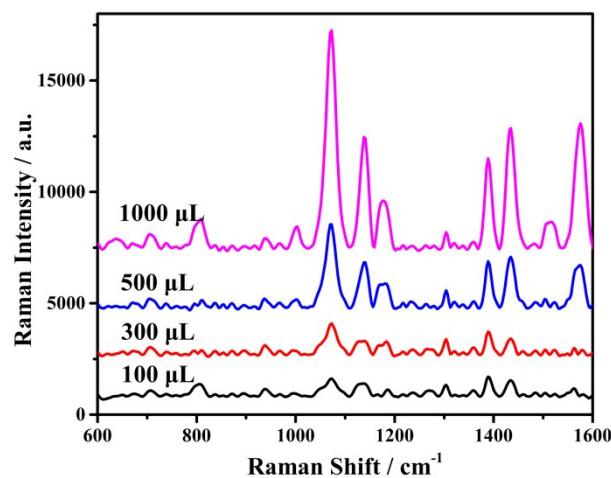


Fig. S1 Raman spectra of Au@4-ATP@Ag NPs with different volume of 4-ATP embedded. The concentration of 4-ATP is 0.01 mM.

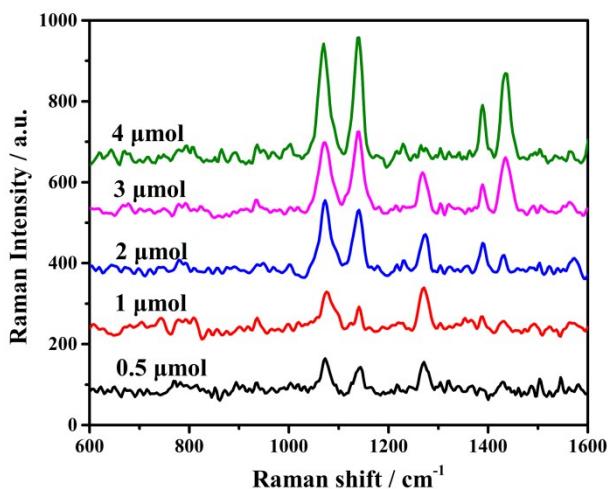


Fig. S2 Raman spectra of Au@4-ATP@Ag NPs prepared by adding different amount of AgNO₃ to form the shell.

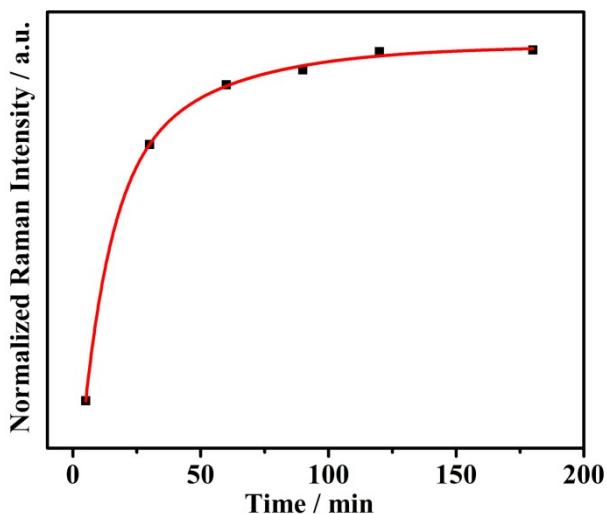


Fig. S3 The kinetic curve of MG adsorption.

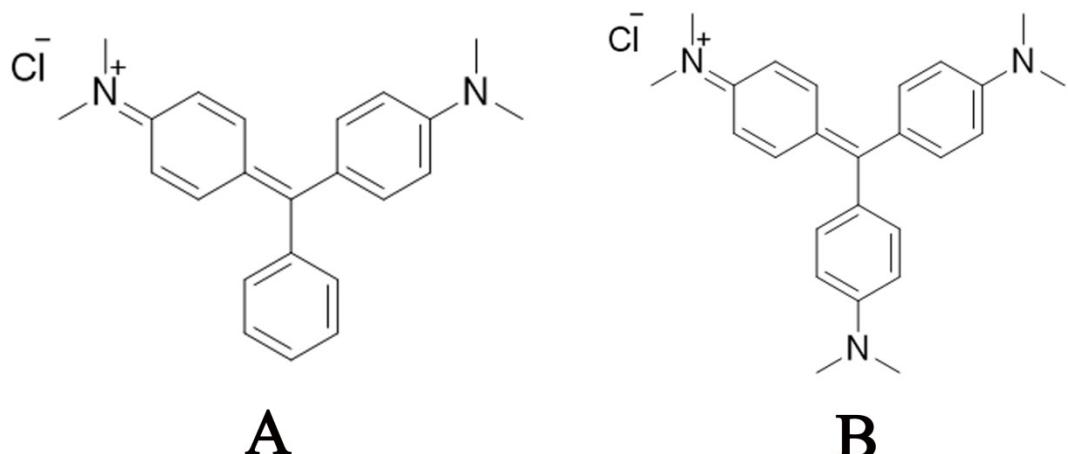


Fig. S4 Chemical structure of MG (A) and CV (B).

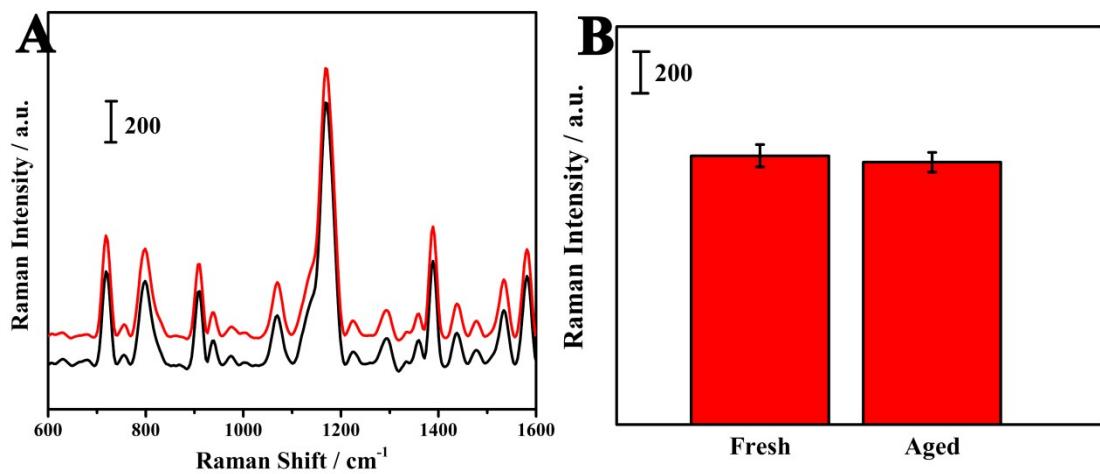


Fig. S5 (A) The SERS spectra of MG on the fresh prepared and aged fibers. (B) The SERS intensity of MG at 1174 cm^{-1} on fresh prepared SPME fibers and on SPME fibers aged for 2 months. The error bars were obtain from five parallel experiments.

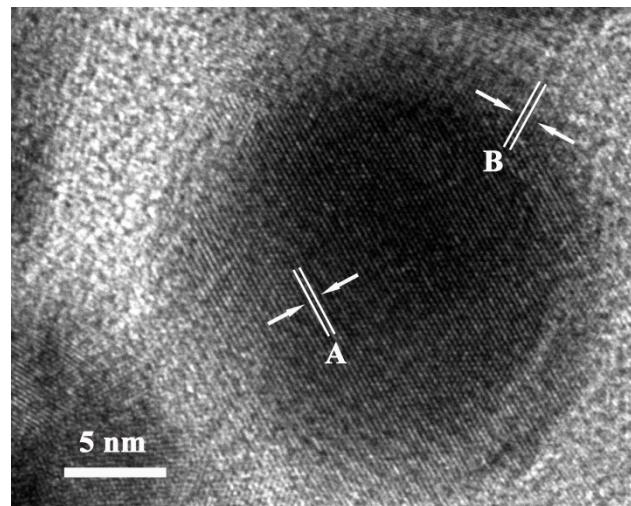


Fig. S6 HRTEM image of the Au@4-ATP@Ag NPs. (A) interplanar distance of gold; (B) interplanar distance of silver.

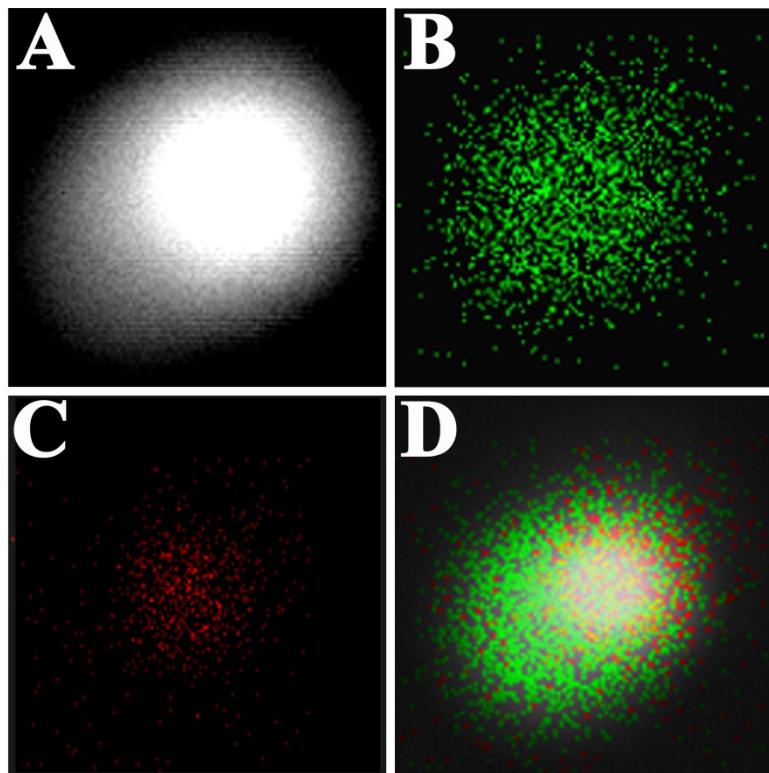


Fig. S7 STEM-HAADF image (A) and EDS elemental mapping images of the Au@4-ATP@Ag NP for Ag map (B), Au map (C) and an overlay of the Au and Ag maps (D).

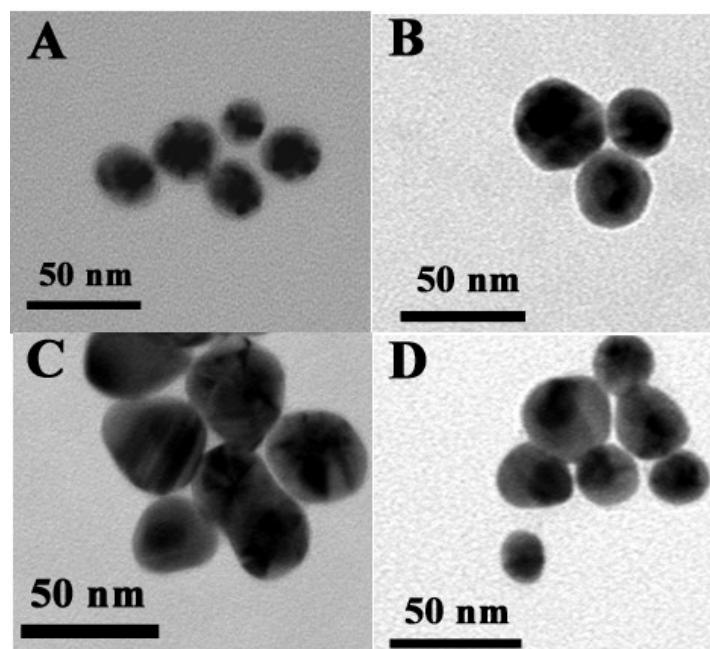


Fig. S8 TEM images of Au@4-ATP@Ag nanoparticles.

Table. S1 The detection of CV compared with other SERS sensor

| SERS Substrate s | Au sol ¹ | Au-Ag core- shell sol ² | Au/ZnO nanostructure ³ | Our fiber In this work |
|------------------------|---------------------|---------------------------------------|--------------------------------------|--|
| Linear range (M) | Not Mentioned | Not Mentioned | 10 ⁻⁶ -10 ⁻⁹ | 5 × 10 ⁻⁸ to 5 × 10 ⁻⁶ |
| R ² | Not Mentioned | Not Mentioned | 0.978 | 0.990 |
| LOD (nM) | 1000 | 100 | 0.103 | 1.9 |

Table. S2 The detection of CV compared with other methods

| Methods | LC-MS ⁴ | HPLC ⁵ | LC-MS-MS ⁶ | Our fiber In this work |
|--------------------------|--------------------|-------------------|-----------------------|---------------------------|
| LOD ($\mu\text{g/kg}$) | 0.18 | 0.20 | 0.35 | 0.78 |

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