Electronic Supplementary Material (ESI) for Analyst

Supplementary Information

Fabrication of a Bowl-shaped Silver Cavity Substrate for SERS-based Immunoassay

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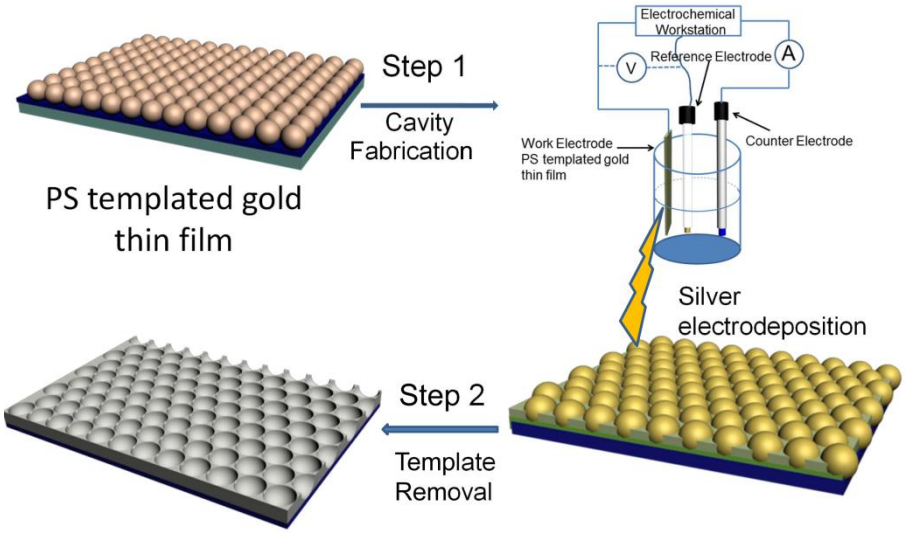

Figure S1. Schematic illustration of the procedures for fabricating bowl-shaped silver cavity thin film.

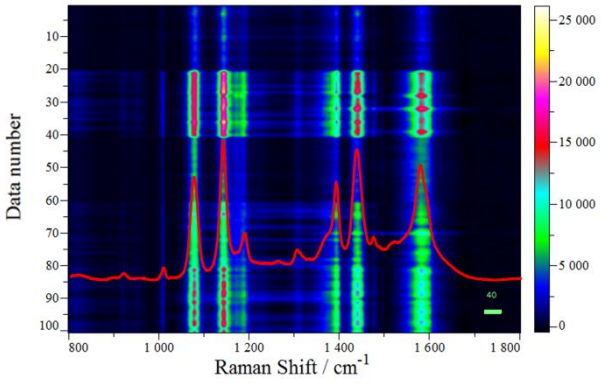

Figure S2. Thickness-dependent spectral trajectory of PATP on BSSC thin film with 633 nm excitation. The vertical axis is different points on 5 different substrates, 1~20 represent 0.7 *R* thickness, 21~ 40 for 0.9 *R*, 41~60 for 1.2 *R*, 61~80 for 1.4 R, 81~100 for 1.6 *R*. Also shown in red curve is the SERS spectrum of PATP.

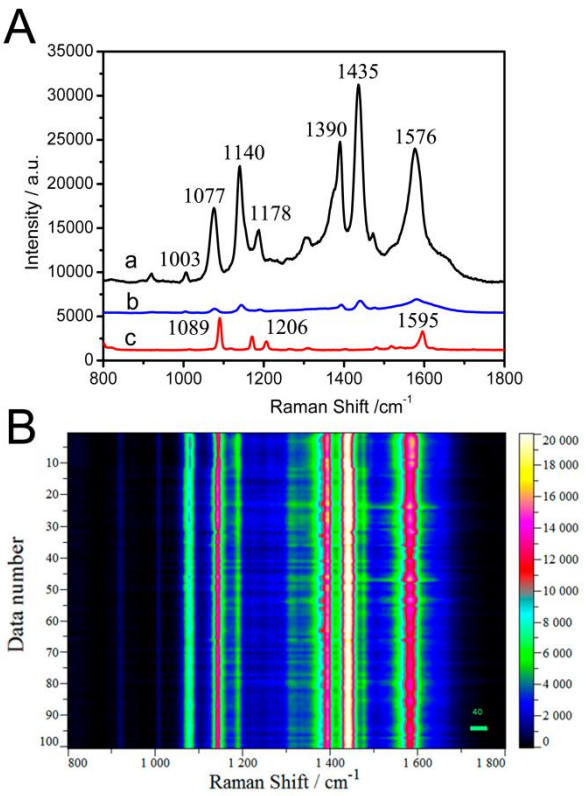

Figure S3. (A) The comparison of Raman spectra of PATP (a) in the solid state, and SERS spectra obtained on (b) flat Ag and (c) BSSC thin film. (B) Spectral intensities of PATP on BSSC thin film with 514 nm excitation. The spectra were collected from 5 different substrates with 20 random points each substrate.

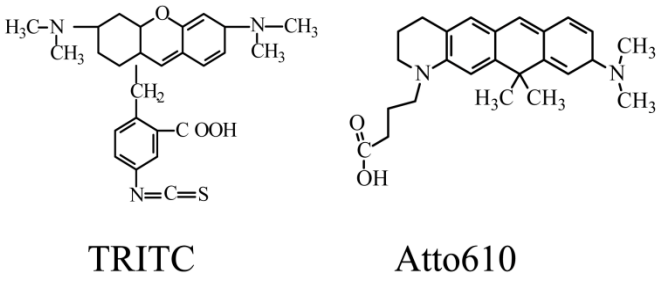

Figure S4 The chemical structure of TRITC and Atto610.

Calculation of ASEF values for BSSC thin films

Averaged surface enhancement factor (ASEF) of the BSSC thin films can be calculated using the following:[1]

$$ASEF = \frac{N_{bulk} I_{surf}}{N_{surf} I_{bulk} R} \qquad (1)$$

where I_{surf} and I_{bulk} denote the integrated intensities for the strongest band of the PATP adsorbed on the surface of BSSC thin films and the solid PATP, respectively. N_{surf} and N_{bulk} represent the numbers of the corresponding surface and solid molecules effectively excited by the laser beam, respectively. *R* is the surface roughness which can be obtained from AFM and should be taken into account during calculating (in this study, *R* was 1.3).

Calculation of N_{bulk}

The number of PATP molecules excited in the bulk solid, N_{bulk}, can be calculated as following equation (2):

$$N_{\text{bulk}} = \frac{\pi\left(\frac{d_{spot}}{2}\right)^2 D\rho_{PATP} N_A}{M_{r,PATP}} \qquad (2)$$

where $d$spot is the diameter of circular laser spot, *D* is the depth of the incident laser beneath the surface of PATP solid, ρ_{PATP} and $M_{r,\,PATP}$ are the density and molecular weight of PATP, respectively, N_A represents the Avogadro constant. In this study, the laser spot was a circle with diameter of ~2 μm, and the depth the laser could reach was about 19 μm, the density (1.18 g/cm^3) and molecular weight (125.19 g/mol) of solid PATP. The calculated value of N_{bulk} equals to 3.39×10^{11}.

Calculation of N_{surf}

For the PATP molecules adsorbed on the surface of BSSC thin films, assuming that the PATP molecules are fully adsorbed and adopt a standing-up orientation on Ag surface, then the area occupied by one PATP molecule is considered to be equal to the cross-sectional area of the molecule. The numbers of the PATP molecules effectively excited by the laser beam on the surface of the BSSC thin films, $N_{surf,}$ could be calculated as following equation (3):[2]

$$N_{\text{surf}} = \frac{1.91\pi\left(\frac{d_{spot}}{2}\right)^2}{A_{cs,PATP}} \qquad (3)$$

where d_{spot} has the same definition as equation (2), $A_{CS,PATP}$ is the cross-sectional area of the PATP molecule diameter of circular laser spot, which is ~0.22 nm^2. The calculated value of N_{bulk} equals to 2.73×10^7.

ASEF calculation

Raman intensity at 1587 cm^{-1} and 1435 cm^{-1} were used to calculate the ASEFs for a_1 and b_2 vibrational modes, respectively. A baseline correction was conducted for ASEF value calculation at each spectrum. The I_{surf} and I_{bulk} at 1576 cm^{-1} were 16453 and 337, the I_{surf} and I_{bulk} at 1435 cm^{-1} were 57888 and 58. Thus, the ASEFs for a_1 and b_2 vibrational modes were calculated to be 1.0×10^6 and 1.1×10^7, respectively.

S1 X.-M. Lin, Y. Cui, Y.-H. Xu, B. Ren, Z.-Q. Tian, Anal. Bioanal. Chemistry, 2009, 394, 1729.

S2 G. Hong, C. Li, Q. Limin, Adv. Funct. Mater., 2010, 20, 3774.