Supporting Information to:

Design of Anti-Aggregated SERS Sensing Platform for Metal Ions Detection Based on Bovine Serum Albumin-Mediated Metal Nanoparticles

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A. Experimental Section

Materials: PATP, R6G, BSA, AgNO₃, and Hg(NO₃)₂ were purchased from Sigma-Aldrich Co. Ltd. and used without further purification. All other chemicals were purchased from Beijing Chemical Reagent Factory. Ultrapure water (18 M cm) was used for all experiments. The mineral water was purchased from Hangzhou Nongfu Spring Co., Ltd..

Instruments: The UV-vis-NIR spectra were recorded on a Shimadzu UV-3600 spectrophotometer. The images of samples were measured on a JEM-2100F transmission electron microscope (TEM) operating at 200 kV. Dynamic light scattering (DLS) were measured using Malvern Zetasizer Nano-ZS. Surface-enhanced Raman scattering (SERS) spectra were measured on a system with excitation wavelength of 633 nm. A He/Ne laser of 17 mW was used as the excitation source, and the power at the sampling position was 7.1 mW. The data acquisition time was usually 60 seconds for each measurement. The Raman band of the silicon wafer at 520.7 cm⁻¹ was used to calibrate the spectrometer.

Preparation of BSA modified sensing platform: The 15 nm Au NPs were prepared using a conventional synthetic route that has been reported elsewhere.¹ An aliquot of the mixture solution (100 uL) consisted of PATP or R6G (10^{-5} M), BSA (1mg/mL), and phosphate buffer (0.01 M, pH 7.4) was added to Au NPs solution (3 mL). The solution was incubated at room temperature for 30 min. After modification, they were separated by centrifugal filtration (RCF 9500g, 20 min) and washed three times with phosphate buffer solution. The purified PATP-Au@BSA sample was resuspended separately in phosphate buffer solution and stored in a refrigerator (4 °C).

Metal detection using probe-Au@BSA sensing platform: A typical metal ions detection procedure was conducted as follows. Metal ions solution with different concentration was obtained by serial dilution of the stock solution. 100 uL metal ions solution with different concentration was mixed with 900 uL of the prepared probe-Au@BSA sensing platform. After mixture was shaken thoroughly, and then incubation for 30 min at room temperature, 50 uL of each sample was dripped into an aluminum pan for SERS measurement. The error bars represent standard deviations based on three independent measurements.

Electronic Supplementary Material (ESI) for Chemical Communications This journal is The Royal Society of Chemistry 2013

B. Additional Figures.



Fig. S1 TEM images of (A) Au NPs, (B) PATP-Au@BSA, and (C) R6G-Au@BSA. (D) Histogram of the distance between neighboring Au NPs (Left: PATP-Au@BSA; Right: R6G-Au@BSA).



Fig. S2 Dynamic light scattering (DLS) analysis of Au nanoparticles, probe-modified and BSA-modified Au nanoparticles at 25 °C. Note that the hydrodynamic diameters are shown on the corresponding profile.



Fig. S3 SERS spectra of (A) R6G-Au and (B) PATP-Au NPs before and after modification with BSA. As BSA is adsorbed on the surface of Au NPs, the surface area and active sites on the particle surface are decreased, thus resulting in the loss of SERS intensities of probe molecule. The SERS intensities both of R6G-Au@BSA and PATP-Au@BSA are decreased by almost 3-fold.



Fig. S4 UV-vis-NIR absorption spectra of Au NPs, PATP-Au, and R6G-Au in the absence and presence of 1 M NaCl. Inset shows the photographs of (a) Au NPs, (b) Au NPs+NaCl, (c) PATP-Au@BSA, (d) PATP-Au@BSA+NaCl, (e) PATP-Au@BSA, and (d)R6G-Au@BSA+NaCl.



Fig. S5 TEM images of (A) Au NPs, (B) PATP-Au@BSA, and (C) R6G-Au@BSA in the presence of 1 M NaCl. The strongest aggregates were observed upon the addition of 1M NaCl. This observation is consistent with the fact that the citrate-reduced Au NPs readily aggregated in metal halide salt solution. However, there are only a small number of overlap region, but no obvious aggregates are observed in PATP-Au@BSA (Fgire S1B) and (Figure S1C) R6G-Au@BSA, indicating that the introduction of BSA is an effective measure to inhibit the Au NPs aggregation.



Fig. S6 Variation in intensity of a typical band at 610 cm⁻¹ in a SERS spectrum of R6G-Au and R6G-Au@BSA measured at different concentrations of NaCl.



Fig. S7 Selectivity of R6G-Au@BSA sensing platform for Hg^{2+} ions (0.5 ppb, about 1.5 nM) over other metal ions, the concentration of each of the metal ion is 1 mM. It was clearly found that the R6G-Au@BSA sensing platform exhibited greater selectivity and lower interference toward Hg^{2+} ions, indicating that the present sensing platform is suitable for analyzing samples in various environments. The high selectivity probably arises from the specificity of Au⁺-Hg²⁺ interactions.²⁻⁵ Moreover, the formation of stable complexes between the phosphate ions in the buffer and heavy metal ions also causes a masking effect (The formation constants (p*K*_f) of PbHPO₄, CdHPO₄, and HgHPO₄ are 21.1, 13.47 and 8.8, respectively.).⁶



Fig. S8 The band intensity of R6G at 610 cm⁻¹ versus the concentration of Hg^{2+} ions. The error bars represent standard deviations based on three independent measurements. The detection limit is ~60 times lower than the maximum level (6 ppb) of Hg^{2+} in drinking water permitted by the World health Organization (WHO).



Fig. S9 Selectivity of PATP-Au@BSA sensing platform for Ag^+ ions over other metal ions, the concentration of each of the metal is 10^{-3} M. To evaluate the selectivity of the as prepared PATP-Au@BSA sensing platform towards Ag^+ , a wide range of common environment-related metal ions such as Mg^{2+} , Cr^{3+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} were tested as a control. As shown in Fig. S7, there are no obvious responses could be observed in the presence of other ions at the concentration of 1 mM, whereas only 0.4 ppm Ag^+ could effectively result in the increase in the relative SERS intensity between the bands at 1140 and 1077 cm⁻¹. This may be due to the interaction between PATP and Ag^+ ion give rise to matched energy level for charge transfer and subsequently selectively enhanced the b_2 mode of PATP through the Herzberg-Teller contribution. Moreover, neither of them would interfere with the Ag^+ assay when they were mixed. These results indicate that the as-prepared sensing platform display a remarkably high selectivity for Ag^+ ions.

Table 1 Recovery data for the determination of Ag^+ and Hg^{2+} in Ag^+ or Hg^{2+} spiked deionize water, mineral water, and tap water by using PATP-Au@BSA sensing platform, respectively. The calculated Ag^+ or Hg^{2+} concentration for each sample were determined from three independent measurements.

| Spiked concentration | deionize water | | mineral water | | tap water | |
|------------------------------------|----------------|----------|---------------|----------|-----------|----------|
| | Detected | recovery | detected | recovery | detected | recovery |
| 0.20 ppm Ag+ | 0.190 | 94.83% | 0.202 | 100.88% | 0.199 | 99.44% |
| $0.50 \text{ ppb } \text{Hg}^{2+}$ | 0.580 | 116.02% | 0.522 | 104.44% | 0.472 | 94.37% |

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