Electronic Supplementary Information

Functionalized Gold Nanoparticles as Nanosensor for Sensitive and Selective Detection of Silver Ions and Silver Nanoparticles by Surface-enhanced Raman Scattering

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EXPERIMENTAL SECTION

Materials

2-mercaptoisonicotinic acid (2MNA) was purchased from J&K Chemical Co. (China); $FeCl_2$, $CoCl_2$, $CaCl_2$, $Cd(NO_3)_2$, $MgCl_2$, $NiCl_2$, $Zn(NO)_2$, $CuCl_2$, $Pb(NO_3)_2$, $HgCl_2$, $Na_2S_2O_3$, Na_2HPO_4, NaH_2PO_4 and trisodium citrate were bought from Beijing Chemical Reagent Co. (China); hydrogen tetrachloroaurate (III) tetrahydrate ($HAuCl_4{\cdot}4H_2O$) were purchased from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). All the chemicals were of analytical grade and used as obtained without further purification. Aqueous solutions were prepared using deionized (DI) water, except where noted in the text.

Apparatus

Raman spectra were recorded on JY HR800 Raman spectrometers (France) with excitation wavelength of 647 nm, 15mW power, 10x lens and 600 lines/mm gratings. The inductively-coupled plasma atomic mass (ICP-MS) spectroscopy measurements were operated at Thermo ICP-MS XII (Thermo Fisher, America) in a standard curve method. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al Kα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C_{1s} line at 284.8 eV from adventitious carbon.

Preparation of AuNPs

Gold nanoparticles (AuNPs) were prepared by trisodium citrate reduction of $HAuCl_4$ in aqueous solution. Typically, a total volume of 80 mL of $HAuCl_4$ (48μM) was brought to the boil with stirring. 1.6 mL of 1% trisodium citrate solution was then added into the mixture and the solution boiled for another 30 min. Then the colloidal solution cooled down to room temperature. The colloid was stored in refrigerator at 4 ℃. The average diameter of the as-prepared AuNPs was about 40nm.

Functionalization of AuNPs with 2MNA

2MNA-functionalized AuNPs were prepared by mixing 2MNA with the AuNPs under stirring. The mixture was incubated beyond 4 h at room temperature to make sure of the sufficient adsorption of 2MNA molecules onto Au surface. After that, the resulting mixture was collected by centrifugation and redispersed in phosphate buffer (2 mM NaH_2PO_4/Na_2HPO_4, PH =6.0) with masking agent (EDTA, 5mM) for further examinations.

Assay Measurements

The as-prepared 2MNA-AuNPs suspension (150μL) was added to different concentrations of Ag^+ ions (or other metal ions) solution (450μL) and incubated under ambient conditions for 20 minutes and then the SERS spectra were collected, unless otherwise illuminated specially. The intensity ratios of the selected bands (I_{1160}/I_{1125} and I_{847}/I_{815}; bands at 815 and 1125 cm^{-1} correspond to the coupling vibrations of the O-H bending and the C-S stretching, while the bands at 847 and 1160 cm^{-1} are assigned to the out-of-plane C-H wagging and the coupling vibration of the C-S stretching and the C-H bending. [1,2]) were taken for criterions of determination of these metal ions.

Computational Details

We adopted a cluster-model based DFT method to simulate structure of 2MNA adsorbed on gold nanoparticles and the bonding of the adsorbed molecule with silver. An Au atom is chosen to represent surface atoms of Au nanoparticles interacted with the molecule. A silver ion (Ag^+) is used to represent the analytes ($AgNO_3$ or Ag nanoparticles). The geometries of the 2MNA molecule, the 2MNA-Au and Ag^+-2MNA-Au complexes were fully optimized with the Becke three-parameter hybrid function combined with the Lee-Yang-Parr correlation functional (B3LYP),[3,4] and LanL2DZ[5] for Ag and Au atoms (Fig. S3B). The basis set for H, C, N, O, and S atoms of the 2MNA is 6-311+G(d, p), which includes a polarization function to all five kinds of atoms and a diffuse function to the C, N, O and S atoms.[6,7] The Raman scattering signals were calculated for the molecule and the complexes at the same computational level. All the quantum chemical calculation is performed using Gaussian09 Package.[8] The experimental and theoretical Raman spectra of solid 2MNA molecule and the SERS spectra of the 2MNA-Au and Ag^+-2MNA-Au complexes were shown in Fig. S3A and the assignments were given in Table S1.

Selection of Incubation Time

To optimize the detecting process, we investigated the influence of incubation time in Ag^+ detection experiment. When Ag^+ was added into the testing system, the intensity ratios of the related Raman bands changed in different manners with incubation time increasing in the presence of different concentrations of Ag^+ (Fig. S5). However, the intensity ratios reached a plateau and changed less after the addition of Ag^+ to the solution over 20 min. So the 20min incubation time was appointed in detection experiment except for extra illustration.

Tunableness of LOD

In our experiments, the change of SERS spectra of 2MNA is originated from the coordination between 2MNA and Ag^+. So the relative amount of 2MNA and Ag^+ is the main factor which affects the change of SERS spectra. Thus, the detection range of the sensor can be easily tuned by adjusting the relative amount of 2MNA and Ag^+ in the probing system, namely changing the LOD. As shown in Fig. S6, the intensity ratios of the corresponding SERS bands selected from two systems (SERS spectra of 150μL of 2MNA-Au upon addition of 450μL of 5.0×10^{-8} M Ag^+ and 75μL of 2MNA-Au upon addition of 450μL of 2.5×10^{-8} M Ag^+) are nearly same. The result shown that the LOD of our sensor can be tuned and pushed down further (for example, 2.5×10^{-8} M).

Influence of H_2O_2 and Determination of AgNPs

We try to detect AgNPs in solution using our proposed sensor. For this end, we investigated the response of the probes in the presence and absence of 1mM H_2O_2 in detection solution. The results show that H_2O_2 has no obvious effect on the SERS spectrum of probes in the presence and absence of Ag^+ in solution (Fig.S7). We prepared silver nanopartilces (AgNPs) according to Lee's method[9] and the average diameter of AgNPs is about 40 nm. The as-obtained AgNPs suspension was diluted and the final concentration of Ag was adjusted to 1.0×10^{-4} M. Then the Ag sol was incubated in the mixed solution of 1mM H_2O_2 and 1mM NaH_2PO_4 for more than 1h at room temperature. The Ag^+ by oxidation was separated and diluted to different concentrations ranging from 5.0×10^{-8} to 1.7×10^{-5} M and determined using the same method as above. It was found that dependence between the values of I_{1160}/I_{1125} and I_{847}/I_{815} and concentrations of Ag^+ for Ag^+ from $AgNO_3$ and Ag^+ from AgNPs are the nearly same (Fig.3).

Detection of AgNPs in the Fabric by Our Proposed Sensor

We determined the concentration of AgNPs in commercial fabric using the sensor. A portion of fabric was immersed into the mixed aqueous solution of H_2O_2 (1mM) and NaH_2PO_4 (1mM). After 30min, the dissolved solution was diluted with DI water and immediately used to the quantitative analysis by our proposed sensor. The concentration of the AgNPs, about 2.9×10^{-7} M, can be obtained by comparison the result with the standard curve of $AgNO_3$ solutions (Fig. S8).

Detection of AgNPs in the Fabric by the Inductively-Coupled Plasma Atomic Mass Spectroscopy (ICP-MS)

ICP-MS spectroscopy measurements were operated at Thermo ICP-MS XII (ThermoFisher, America) and sample preparation were followed by the standard test method for elements in water by this instrument. The Ag^+ ions solution was as same as sample used in the determination of AgNPs in the fabric by our proposed SERS sensor. And the result shown that silver concentration in the sample was about 3.06×10^{-7} M. Compared to the concentration obtained using our sensor, the relative error was less than 10%, which shown that our proposed sensor can be used in real samples' assay.

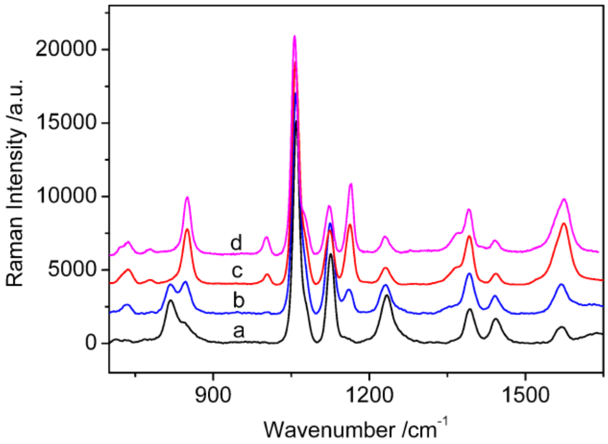

Fig. S1 SERS spectra of 2MNA-AuNPs (a) in the absence of Ag^+; (b) in the presence of 5.0×10^{-7} M Ag^+; (c) in the presence of 1.7×10^{-5} M Ag^+; (d) SERS spectrum of 2MNA in Ag colloid. Peak intensities were calibrated according to intensity of 1060 cm^{-1}, following baseline correction and a smoothing filter.

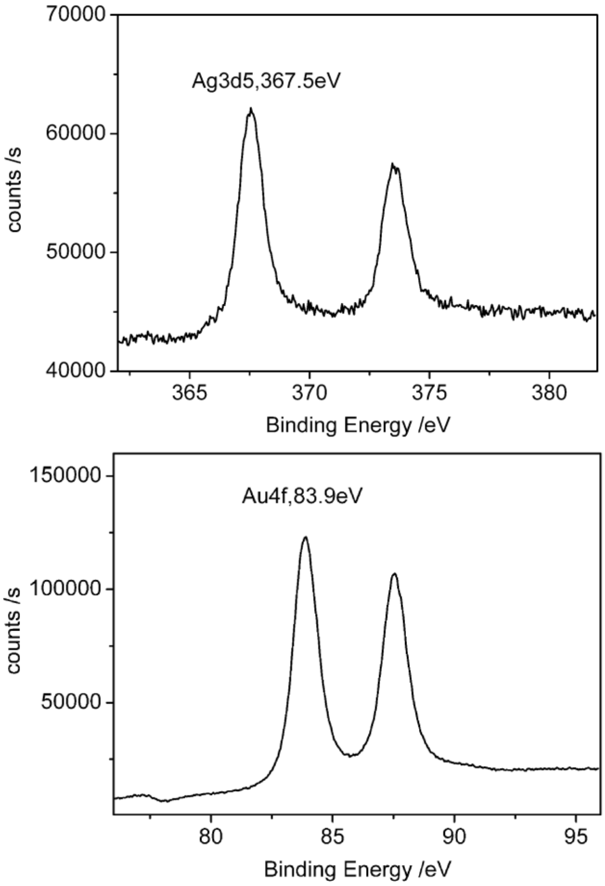

Fig. S2 The XPS spectra of (A) Ag 3d and (B) Au 4f.

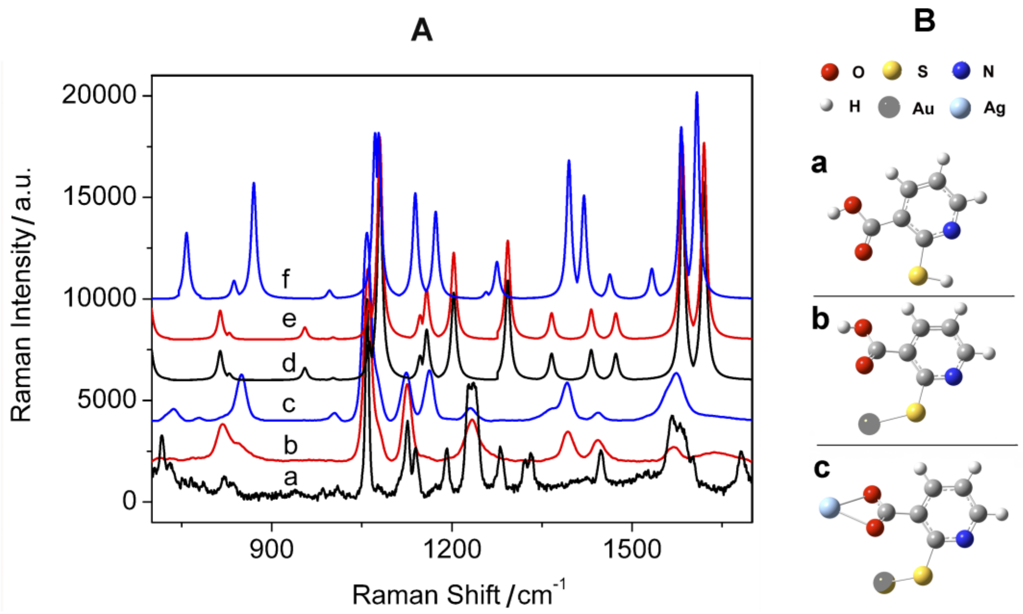

Fig. S3 (A) (a-c) Experimental Raman spectra of solid 2MNA molecule and the SERS spectra of the 2MNA-Au and Ag$^+$-2MNA-Au complexes, (d-f) theoretical Raman spectra of solid 2MNA molecule and the SERS spectra of the 2MNA-Au and Ag$^+$-2MNA-Au complexes. (B) The optimized geometries of the 2MNA molecule (a), the 2MNA-Au (b) and Ag$^+$-2MNA-Au complexes (c).

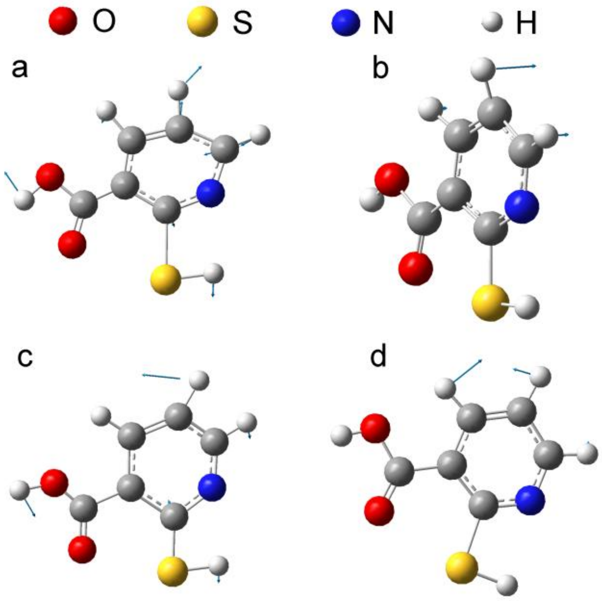

Fig. S4 The vibration motions of the bands at (a) 817, (b) 834, (c) 1128 and (d) 1140 cm^{-1} in the normal Raman spectrum of solid 2MNA.

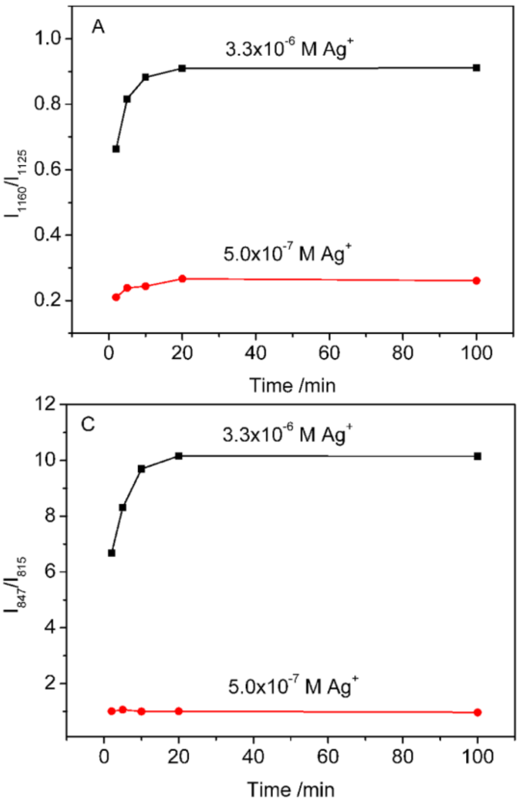

Fig. S5 Time dependent intensity ratios of the selected SERS bands change when different concentrations of Ag^+ ions were added into the 2MNA-AuNPs system.

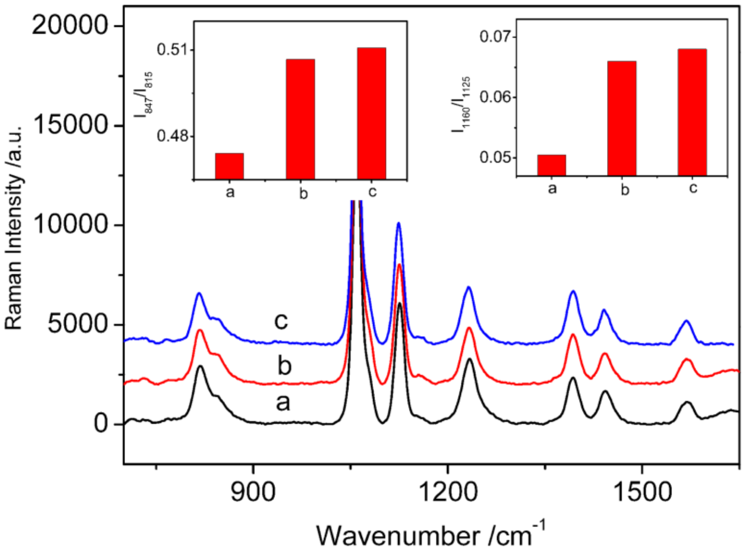

Fig. S6 (a) SERS spectrum of 2MNA-AuNPs in absence of Ag^+, (b) SERS spectrum of 150μL 2MNA-AuNPs upon addition of 450μL 5.0×10^{-8} M Ag^+, (c) SERS spectrum of 75μL 2MNA-AuNPs upon addition of 450μL 2.5×10^{-8} M Ag^+, peak intensities were calibrated according to intensity of 1060 cm^{-1}, following baseline correction and a smoothing filter; the insets are the corresponding histograms according to the intensity ratios of I_{1160}/I_{1125} and I_{847}/I_{815}, respectively.

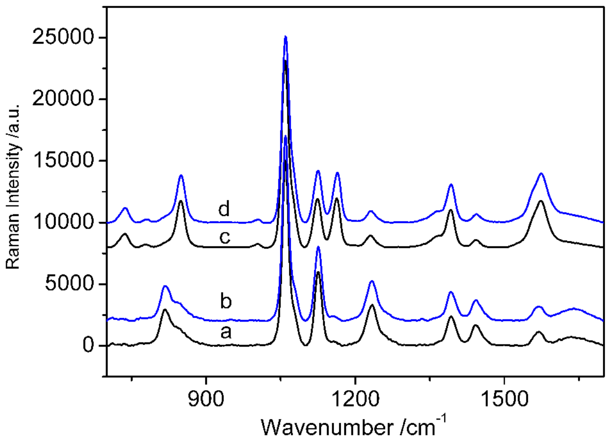

Fig. S7 Influence of H_2O_2 to SERS spectra of 2MNA-AuNPs (a) in the absence of Ag^+ and H_2O_2; (b) in the presence of 1.0×10^{-3} M H_2O_2 but absence of Ag^+; (c) in the presence of 3.3×10^{-6} M Ag^+ but absence of H_2O_2; (d) in the presence of 3.3×10^{-6} M Ag^+ and 1.0×10^{-3} M H_2O_2. Peak intensities were calibrated according to intensity of 1060 cm^{-1}, following baseline correction and a smoothing filter.

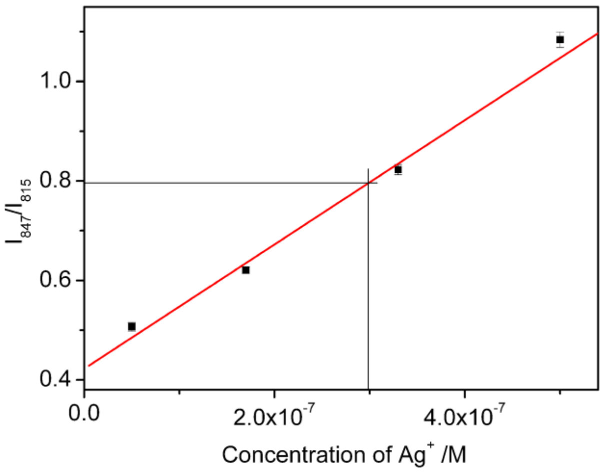

Fig. S8 Determination of the concentration of Ag^+ obtained from commercial fabric. The standard curve was obtained according to known concentrations of $AgNO_3$ solutions.

Table S1 Experimental and theoretical vibrational frequencies (cm^{-1}), and modes assignments of 2MNA calculated at the level of B3LYP/6-311+G**.

Experiment (cm^{-1})			Theory (cm^{-1})			Assignment^c
Solid	SERS^a	SERS^b	2MNA	2MNA-Au	2MNA-Au-Ag^+	
719	732	731	728	733	745	τCC
817	818	815	814	815	870	δOH+αring
834	845	847	830	830	837	πCH
1061	1060	1057	1080	1075	1072	νCS
1128	1123	1125	1147	1129		νCS+δOH+δCH
1140	1158	1160	1158	1154	1140	νCS+δCH

1194			1203	1195	1173	νCC
1236	1231	1225	1276	1258	1257	δCH
1285			1293	1286	1275	νCC, νCN
1337			1366	1352	1395	νCO, νCC
1397	1389	1390	1432	1424	1420	νCC, νCN
1451	1439	1442	1473	1463	1463	νCC+νCN+δCH
1568	1566	1555	1584	1573	1582	νCC
1603		1570	1620	1615	1608	νCC

[a] The vibrational frequencies of 2MNA adsorbed on the Au nanoparticles. [b] The vibrational frequencies of 2MNA interacting with Au nanoparticles and Ag^+. [c] Approximate description of the modes (ν, stretching; δ, in-plane bending; α, deforming; π, out-of-plane wagging).

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