Supporting Information

Silver nanoparticle based surface enhanced resonance Raman scattering (SERRS) probe for ultra sensitive and selective detection of formaldehyde

Wen-Gang Qu, Li-Qiang Lu, Ling Lin and An-Wu Xu*

Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China

* *Address correspondence to this author. E-mail: anwuxu@ustc.edu.cn*

Experimental Section

Chemical. Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$), acetylacetone, formaldehyde and ammonia were obtained from the Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Synthesis of Ag nanoparticle. 0.4 ml of 0.01 M sodium citrate in water was added to 40 ml $AgNO_3$ aqueous solution (0.5 mM) and stirred. Then, 0.05 ml of freshly prepared aqueous $NaBH_4$ solution (0.1 M) was added. The resulting solution was mixed by stirring for 10 min and left undisturbed at least four hours. The resulting Ag nanoparticles were ~30 nm in diameter.

Preparation of product DDL solutions. To a flask were added 1mL acetylacetone (0.2 M), 0.05 mL ammonia (2 M) and a series of standard formaldehyde solutions, and then the mixtures were diluted to 10 mL with purified water. After refluxing in 60 ºC water bath for 10 min, the reaction to form DDL is completed.

Fabrication of the SERRS-active substrate. All glass slides were thoroughly cleaned with aqua regia, followed by rigorously washing with ultrapure water and air-dried in an oven. To prepare the SERS substrate, 20 μL of colloidal Ag nanoparticles was dropped onto a clean glass slide. After air-drying under ambient conditions, a spot of ~5 mm in diameter was formed on the slide. Then, minute amounts (10 μL) of DDL aqueous solution at different concentrations were carefully dropped onto the printed spot and dried in air for SERRS measurements.

Instrumentation. UV-Vis spectra were recorded on a HITACHI U-3900 spectrophotometer. Transmission electron microscopic (TEM) images were taken with a JEOL-2010 microscopic operating at 200 KV. Scanning electron microscopy (SEM) images were obtained with a field emission scanning microscopy (FESEM, Philips Model XL30 S FEG). The dark-field photograph was taken by an Olympus BX51 inverted research microscope and a DP72 CCD. The SERS and SERRS measurements were recorded on a Renishaw System 2000 spectrometer using ~2 mW 457 nm excitation laser lines. Spectra were collected in high-resolution mode with an accumulation time of 5 s. The SERS signal intensities were an average of five randomly selected points.

Calculation of enhancement factor

The average enhancement factor (EF) value is calculated according to the following formula:

$$\mathrm{EF} = \frac{I_{\mathrm{SERRS}} / N_{\mathrm{SERRS}}}{I_{\mathrm{RS}} / N_{\mathrm{RS}}}$$

where I_{SERRS} and I_{RS} are the signal intensities of SERRS and normal Raman spectra of DDL at the same band (~1647 cm^{-1}), and N_{SERRS} and N_{RS} represent the corresponding number of molecules in the focused incident laser spot. We assume the DDL molecules distributed evenly on the substrates. N_{SERRS} and $\mathrm{N_{RS}}$ can be calculated according to $N_{\mathrm{RS}} = C_{\mathrm{RS}} \bullet V_{\mathrm{probe}}$, where $\mathrm{C_{RS}}$ is the concentration of DDL in solution and V_{probe} is the probe volume of the laser. In the normal Raman characterization, 10 μL of 1.0×10^{-2} M DDL aqueous solution is dispersed on a piece of clean glass slide. The V_{probe} is calculated to be 5.97×10^{-5} mm^3 according to the diameter of laser spot (~10 μm). Hence, $\mathrm{N_{RS}}$ is approximately equal to 3.59×10^{10}. In our SERRS experiment, silver nanoparticle aggregates are confined to an area with a diameter of ~5 mm where the DDL solution is dropped on. So, 10 μL of 1.0×10^{-11} M DDL aqueous solution is dispersed on the substrate. Calculated in a similar manner above, N_{SERRS} is estimated to be 27.2. Herein, we can get that the I_{SERRS} and I_{RS} are 357 unites and 421 unites at the Raman band of ~1647 cm^{-1}, respectively, leading to an overall EF expression

$$\mathrm{EF} = \frac{357 / 28.2}{421 / \left(4.69 \times 10^{10}\right)} = 1.08 \times 10^{9}$$

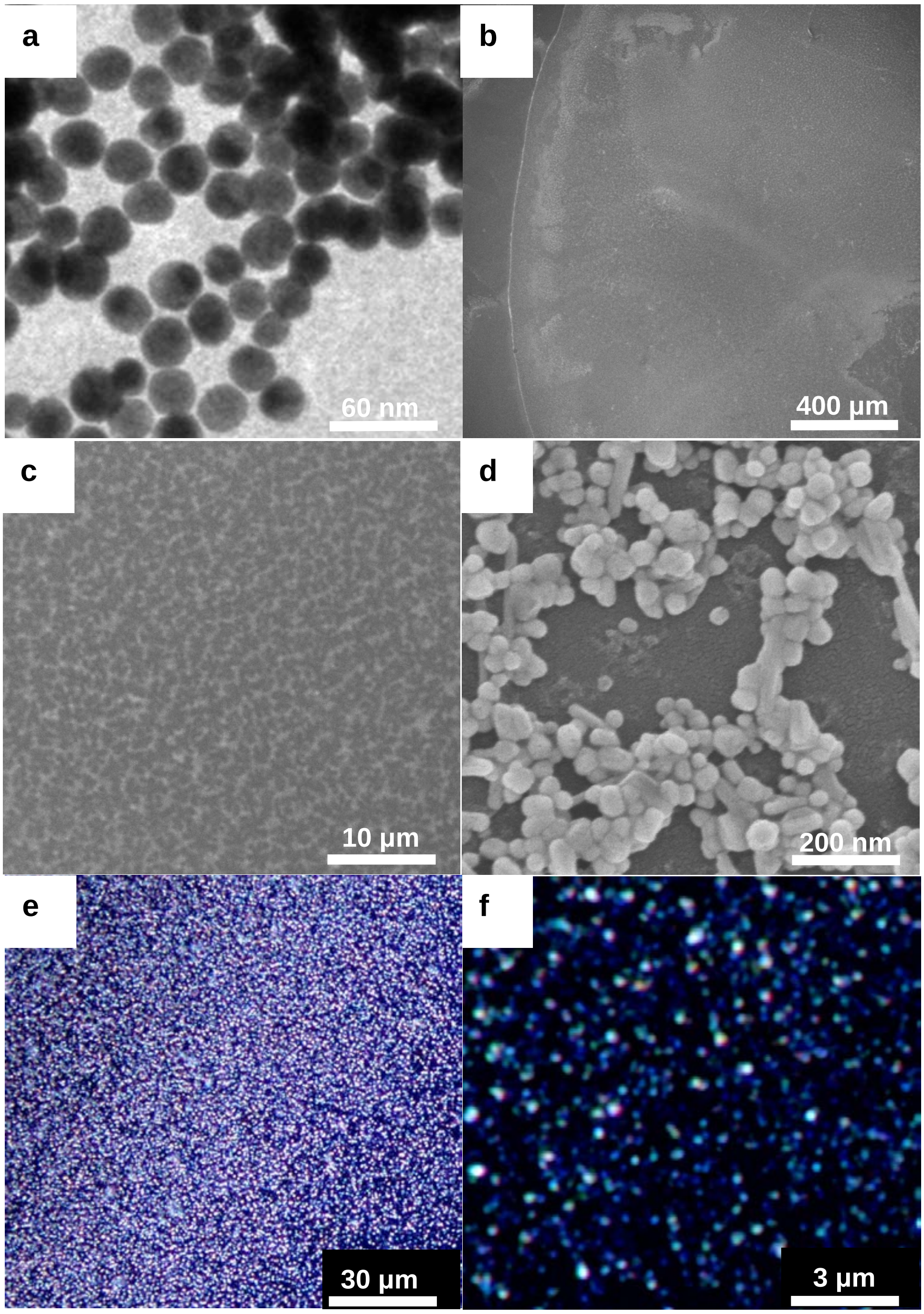

Fig. S1 (a) TEM image of the prepared Ag nanoparticles. (b), (c), (d) SEM images of the prepared Ag nanoparticles film by dropping casting. The large area of Ag nanoparticle film contains a dense collection of Ag aggregates consisting of many Ag-NPs. (e), (f) Dark-field photographs of the prepared Ag nanoparticles on a glass slide obtained under optical microscopy. Each bright spot represents the Ag aggregate.

The Ag aggregates with blue color can be clearly identified on the glass slide, which is consistent with the extinction spectrum.

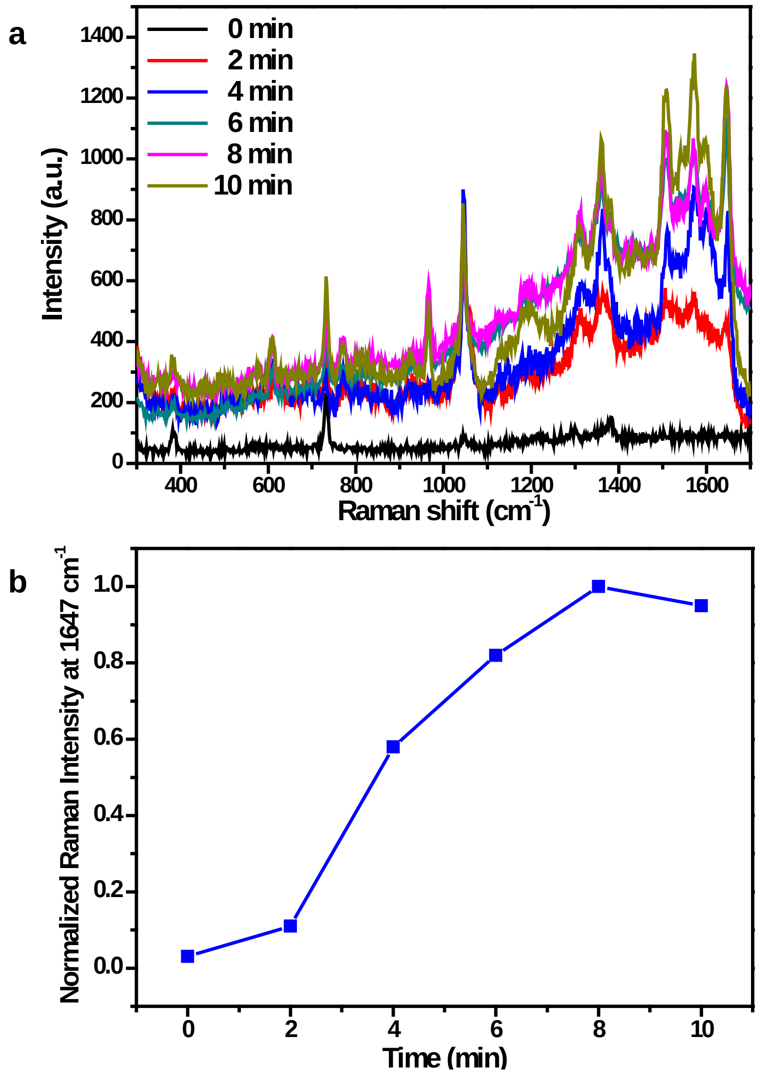

Fig. S2 (a) Time-dependent SERS measurement of the Hantzsch reaction of formaldehyde**,** taken every 2 min at 457 nm. (b) Temporal evolution of SERS intensity at 1647 cm^{-1} of DDL. The mixture was refluxed at 60 ºC in water bath. All of the concentration is 1 nM. The Raman intensity increased during the first few minutes and reached its maximum at about 8 min. Accordingly, to obtain the maximum SERS efficiency, all of the formaldehyde aqueous solutions in this work were refluxed with acetylacetone and ammonia in water bath at 60 ºC for 10 min to ensure that the Hantzsch reaction was completed.