# Electronic supplementary information for

# Sub-5 nm nanobowl gaps electrochemically templated by SiO<sub>2</sub>-coated Au nanoparticles as surface-enhanced Raman scattering hot spots

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### 1. Experimental section

#### Materials

Sodium silicate solution ( $\geq 10\%$  NaOH,  $\geq 27\%$  SiO<sub>2</sub>) and 4-mercaptobenzoic acid (4-MBA, purity 90%), and 3-aminopropyltrimethoxysilane (APTS, 97%) were obtained from Sigma-Aldrich and Alfa Aesar, respectively. Sodium citrate, HAuCl<sub>4</sub>, hexadecyl trimethyl ammonium bromide (CTAB), chloroform, hydrochloric acid, isopropyl alcohol, ethanol, and methanol, all of analytical grade, were purchased from Sinopharm Chemical Reagent Ltd Co., Shanghai, China. All the materials were used as received without further purification. Sulfite-based gold plating solution TSG-250 was purchased from Transene company, Inc., Danvers, USA. Glass microscope slides coated with a 10 nm Cr adhesion layer and a 150 nm layer of evaporated gold (denoted as Au substrate hereafter) were ordered from JingRuiGuangDian Ltd Co., Changchun, China. Ultrapure water purified from a deionized water system (YZS-RO-S50) and doubly distilled was used throughout the experiments.

#### Synthesis of Au and Au@SiO<sub>2</sub> nanoparticles

55 nm Au nanoparticles (NPs) were synthesized following the method established by Frens.<sup>1</sup> Briefly, 200 mL of 0.01 wt% HAuCl<sub>4</sub> aqueous solution was heated to boiling under vigorously stirring. Then, 1.4 mL of 1 wt% sodium citrate solution was quickly added. The color of the mixtures turned from light yellow to red brown in a few minutes, indicating the formation of Au NPs. To accomplish the reaction completely, the Au colloids were continually stirred for another 40 minutes. Then, the heating was removed and the final Au colloids were cooled down and kept at room temperature.

Ultrathin (4 nm) silica-coated 55 nm Au (Au@SiO<sub>2</sub>) NPs were prepared following by the method established by Li et al.<sup>2</sup> First, 0.4 mL of freshly prepared 1 mM APTS aqueous solution was added to 30 mL of Au colloids under vigorous stirring in 15 minutes, thereby enabling APTS to be sufficiently adsorbed on the surfaces of the Au NPs. Silica coating was achieved using activated sodium silicate, prepared by diluting 2 mL of stock solution to 0.54 wt% in water and adjusting the pH to 10~11 with 0. 5 M HCl. Then, 3.2 mL of 0.54 wt% sodium silicate solution was added to the Au colloids, again under vigorous stirring for 3 minutes at room temperature. Finally, the Au colloids were transferred into a 90°C water bath and stirred at this temperature for 1 h to accelerate silica deposition on the surfaces of the Au NPs. The as synthesized Au@SiO<sub>2</sub> NPs were cleaned by two centrifugation/redispersion cycles and stored in ultrapure water.

#### Diagnosis of pinholes on the shell of the Au@SiO<sub>2</sub> NPs using electrochemical and SERS methods.

To ensure that the ultra-thin silica shells are really pinhole-free, cyclic voltammetry (CV) and SERS tests 2

were used to check the pinholes following the protocols reported in reference 2. As shown in Fig. S2, pure 55 nm Au NPs supported on a glass carbon electrode show typical electrochemical responses like those of polycrystalline Au. While the reduction peak for Au oxide at about 0.9 V was removed upon coating the Au NPs with a silica shell, thereby indicating the pinhole-free character for the silica shell. For SERS test, a drop of Au@SiO<sub>2</sub> colloids was dried on a smooth Si wafer. Then, a drop of 0.01 M pyridine aqueous solution was spread on the dried Au@SiO<sub>2</sub> NPs, followed by covering the solution with a cover glass to prevent evaporation. For Au@SiO<sub>2</sub> NPs whose shells exist pinholes, pyridine can adsorb on the Au core through the pinholes. Therefore, SERS peaks for pyridine are observed. In contrast, SERS peaks for pyridine will not be observed for Au@SiO<sub>2</sub> NPs without pinholes present in the shell.

#### Assembly of submonolayer and monolayer Au@SiO<sub>2</sub> NP arrays on Au substrate

Self-assembly of a submonolayer of Au@SiO<sub>2</sub> NP arrays was following the method established by Freeman et al.<sup>3</sup> with slight modification. Au substrates were cut into  $2 \times 1.5$  cm slides. The Au substrates were subsequently cleaned by sonication in isopropanol for 90 min, washed with water, and finally dried with N<sub>2</sub> blow. APTS-functionalization of the Au substrates was performed by immersing the substrates in a 0.05% (v/v) APTS ethanol solution for 8 h, followed by rinsing with ethanol and drying with N<sub>2</sub> blow. Then, the APTS-functionalized Au substrates were immersed in an Au@SiO<sub>2</sub> NP aqueous solution under gentle stirring for 6 h, followed by rinsing with ethanol and drying with N<sub>2</sub> blow. Finally, a submonolayer of Au@SiO2 NP arrays was assembled on the Au substrate.

Self-assembly of a monolayer of Au@SiO<sub>2</sub> NP arrays at a water-air interface was performed according to the reported method<sup>4-6</sup> with slight modification. Briefly, 10 mL of Au@SiO<sub>2</sub> NP aqueous solution was centrifuged at 4000 rpm for 25 minutes, the supernatant was removed, and the concentrated Au@SiO<sub>2</sub> colloids at the bottom of the centrifuge tube were redispersed in 10 mL of methanol. Then, 1 mL of 4 mM CTAB aqueous solution was added and stirred for 1 h. This resulted in modification of the NPs with a layer of CTAB, thereby conferring a relatively hydrophobic surface to the Au@SiO<sub>2</sub> NPs and enabling them to be easily assembled at the water-air interface. 2 volumes of CTAB-modified Au@SiO<sub>2</sub> colloids were mixed with 2 volumes of chloroform in a beaker, followed by quickly adding 5 volumes of water. As a result, white emulsions were formed upon quick addition of water. The emulsions completely broken in a few minutes and this led to a monolayer of Au@SiO<sub>2</sub> NP arrays were transferred onto the cleaned Au substrate by aslant immersing the substrate underlying the Au@SiO<sub>2</sub> arrays and then gently drawing it out.

#### Preparation of sub-5 nm nanobowl gaps around submonolayer and monolayer Au NP arrays

The preparation of reproducible sub-5 nm nanobowl gaps involved assembly of Au@SiO<sub>2</sub> NP arrays on the Au substrate, electrodeposition of Au through the arrays, and removal of the SiO<sub>2</sub> shells. To enable control of the height of the deposited Au, a rectangular area was defined on the Au substrate using nail varnish to insulate the other areas. Sulfite-based, cyanide-free gold plating solution TSG-250 was used for the electrodeposition of Au at a constant current of 10  $\mu$ A/cm<sup>2</sup>. The height of the deposited gold was controlled by monitoring the charge passed during electrodeposition and by employing 70% efficiency for the electrodeposition. After electrodeposition, SiO<sub>2</sub> shells were removed by immersing the Au substrate in a 5 M NaOH solution for 1 h, followed by washing with water and drying with N<sub>2</sub> blow.

#### **Characterizations**

UV-vis spectra were conducted on a Shimadzu UV-1800 spectrophotometer using 1-cm quarts cells. All electrochemical experiments were carried out using an Autolab PGSTAT 128N electrochemical workstation, using Pt plate and saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were obtained on a JEOL JEM-2100F microscope and a Hitachi S-4800 microscope, respectively. SERS spectra of 4-MBA were collected from a LabRam-010 Laser Raman spectrometer. A  $\times$  50 objective with 8-mm working distance was used to focus the laser beam into a 2  $\mu$ m spot at the sample and to collect the Raman signals in a back scattering geometry.

# 2. Three-dimensional finite-difference time-domain simulation of electromagnetic field distribution

A three-dimensional finite-difference time-domain (3D-FDTD) method, whose basic principle is to numerically solve the Maxwell's differential equations, was employed to simulate the electromagnetic (EM) field distribution on the three types of nanostructures. The simulations were performed using a commercial software, FDTD Solutions (version 7.5), purchased from Lumerical Solutions, Inc. (Vancouver, Canada). According to the SEM images show in Fig. 2 and Fig. S4, a single, isolated Au@SiO<sub>2</sub> NP on an Au surface and a closely packed (111) array of Au@SiO<sub>2</sub> NPs on an Au surface were used as the geometric models for the simulations of EM field distribution on the submonolayer and monolayer Au@SiO<sub>2</sub> NP arrays, respectively. The 632.8 nm excitation was defined as propagating along the negative *z*-axis direction with linear polarization along *x*-axis direction, and its electric field amplitude is chosen to be 1.0 V/m. Perfectly  $\mathbf{4}$ 

matched layer boundary conditions were used for all simulations. To ensure accuracy for the simulations, the Yee cell was set to be  $0.25 \times 0.25 \times 0.25$  nm, which automatically met the conditions of "ten cells per wavelength", required for a FDTD simulation. Because smaller Yee cell size requires more simulation time and memory resources, non-uniform FDTD mesh method was used for the simulations. Time domain monitor was added to ensure the convergence of simulations. Optical constants for gold and silica were taken from references.<sup>7,8</sup>



## 3. Calculation of the averaged enhancement factors

Fig. S-EF1. Cartoon model showing how to determine the probe molecules adsorbed on the nanostructure of a single Au particle around with a sub-5 nm nanobowl gap (i.e., particle-in-nanobowl).



Fig. S-EF2. Raman intensity-depth profile of the integrated intensity of 520.6 cm<sup>-1</sup> band for a silicon slide. The pinhole and slit for the Raman instrument were set at 1000 and 100  $\mu$ m, respectively, and a 50× long working-length (8 mm) objective with numerical number 0.50 was used.



Fig. S-EF3. Normal Raman spectrum for 0.5 M 4-MBA in NaOH solution (4-MBA is difficult to dissolve in pure water, so that it was transferred to water-soluble sodium salt by dissolving it in NaOH solution). Accumulation time: 30 s. The laser power was attenuated to the same extent that was employed for measuring the SERS spectra shown in Fig. 3 and Fig. S6.

Fig. S-EF1 shows the carton model which we used to calculate the EFs for the Au nanoparticles around with sub-5 nm nanobowl gaps. The averaged enhancement factor (EF) is defined as the ratio of the intensity of the analyte on the surface to a non-surface adsorbed molecule, expressed as below<sup>8</sup>:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{NRS}/N_{NRS}} \quad (1)$$

where  $I_{\text{SERS}}$  and  $I_{\text{NRS}}$  are the SERS and normal Raman intensities, and  $N_{\text{SERS}}$  and  $N_{\text{NRS}}$  are the number of molecules contributing to the SERS and normal Raman intensities, respectively. The peak at 1077 cm<sup>-1</sup> was chosen for the calculation of the averaged EF factors. To insure that the SERS intensity 6

is solely contributed by the molecules adsorbed on the Au nanoparticles around with sub-5 nm nanobowl gaps, the SERS intensity contributed from the non-uniform surface morphology or imperfections (curves b in Fig. 3 and Fig. S6) were deducted from the SERS intensity for the peak 1077 cm<sup>-1</sup> (curves c in Fig. 3 and Fig. S6). From the SEM images (Fig. 2 and Fig. S4, or Fig. S5), the number of the nanostructure of particle-in-nanobowl for their submonolayer and monolayer arrays are determined to be 38.5 and 292.5/ $\mu$ m<sup>2</sup>, respectively. Assuming a monolayer adsorption for 4-MBA and knowing its occupied area on a surface (~0.2 nm<sup>2</sup>),<sup>9</sup> the number of molecules in the laser spot,  $N_{\text{SERS}}$ , can be calculated from the the total surface for the particle-in-nanobowl arrays. Because the confocal Raman microscope posses a sensitive depth resolution, the term,  $N_{\text{NRS}}$ , has to be calculated based on the confocal feature of the microscope. A so-called confocal depth *h* is then determined from the Raman intensity-depth profile of the integrated intensity of 520 cm<sup>-1</sup> band for a silicon slide (Fig. S-EF2) following the reported method<sup>10</sup>:

$$h = \frac{\int_{-\infty}^{\infty} I(z) dz}{I_{\max}} \qquad (2)$$

In the present study, *h* is calculated to be 28.2  $\mu$ m from Fig. S-EF2. The value of *h* can be considered as the key parameter of the confocal characteristic: with the aid of *h*, the real probed volume in a solution, which is difficult to be directly measured, can be represented by an equivalent volume defined as *Ah* (*A*, the area of the focal spot of the laser). Therefore,  $N_{\text{NRS}}$  in the probed volume in the aqueous solution can be determined:

$$N_{\rm NRS} = AhcN_{\rm A} \quad (3)$$

where, *c* is the concentration of 4-MBA and  $N_A$  the Avogadro constant. Therefore, the averaged EFs experimentally determined for submonolayer and monolayer Au NP arrays around with sub-5 nm nanobowl gaps are  $2.25 \times 10^5$  and  $1.94 \times 10^5$ , respectively.

## 4. Supplementary Figures

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Fig. S1. UV-vis spectra for 55 nm Au NPs and Au@SiO2 NPs with a 55 nm core and a 4 nm-thick SiO2 shell.



Fig. S2. Cyclic voltammograms of the synthesized Au NPs and Au@SiO<sub>2</sub> NPs deposited on glassy carbon electrodes in  $0.5 \text{ M H}_2\text{SO}_4$  solution. Scan rate: 0.1 V/s.



**Fig. S3.** SERS spectra of pyridine from Au@ SiO<sub>2</sub> NPs on Si wafer with (black curve) and without (red curve) pinholes on the shells. The SERS spectra were obtained for a single 10-s accumulation.



**Fig. S4.** SEM images (A-C) and corresponding EM field distribution (D-F) of monolayer Au@SiO<sub>2</sub> NP arrays on an Au surface before electrodeposition (A, D), after electrodeposition of a 32 nm-thick Au film (B, E), and upon removal of the silica shells (C, F). Note that the calculated distribution of  $|E|^4$  is normalized by the fourth power of the electric field of the incident wave at the position of the molecule and is shown under logarithmic coordinates. Scale bars are 100 nm.



Fig. S5. Lower magnified SEM images of submonolayer and monolayer  $Au@SiO_2$  NP arrays that are partially embedded in Au deposit film before (A, C) and after removal of the silica shells (B, D). Scale bars are 100 nm.



**Fig. S6.** SERS spectra of 4-MBA adsorbed on monolayer  $Au@SiO_2$  NP arrays before electrodeposition (a), after electrodeposition of a 32 nm-thick Au film (b), and upon removal of the silica shells (c). Excitation line: 632.8 nm; accumulation time: 10 s. To avoid laser burning the molecule, its intensity is attenuated to an extent that the intensity of the 520 cm<sup>-1</sup> peak of silicon for a single 1-s accumulation is 423 cps.



Fig. S7. Spectral sequence of SERS spectra of 4-MBA adsorbed on submonolayer  $Au@SiO_2$  NP arrays around with sub-5 nm nanobowl gaps. Excitation line: 632.8 nm; accumulation time: 10 s. To avoid laser burning the probe molecule, the laser power is attenuated using a D0.6 filter.



Fig. S8. Spectral sequence of SERS spectra of 4-MBA adsorbed on monolayer Au@SiO<sub>2</sub> NP arrays around with sub-5 10

nm nanobowl gaps. Excitation line: 632.8 nm; accumulation time: 10 s. To avoid laser burning the probe molecule, the laser power is attenuated using a D0.6 filter.



**Fig. S9.** Simulated EM field distribution for submonolayer Au NP arrays around with sub-5 nm nanobowl gaps templated from the Au@SiO<sub>2</sub> NPs with a shell thickness of (A) 1, (B) 2, (C) 3, and (D) 4 nm, respectively. Note that the calculated distribution of  $|E|^4$  is normalized by the fourth power of the electric field of the incident wave at the position of the molecule and is shown under logarithmic coordinates. (We also tried to template Au NP arrays around with nanobowl gaps using Au@SiO<sub>2</sub> nanoparticles with a shell thickness of ~8 and ~12 nm, and found that upon removal of the thicker SiO<sub>2</sub> shell in alkaline solution, some Au nanoparticles detached from the nanobowl gaps to quantitatively correlate the experimental and simulated results so that only simulated results are present here).

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