Supplementary Material (ESI) for Chemical Communications

Templateless, Surfactantless, Simple Electrochemical Route to Rapid Synthesis of Diameter-controlled 3D Flowerlike Gold Microstructure with "Clean" Surface

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Experimental Section

Synthesis of ~25 nm gold nanoparticles. Au nanoparticles (~25 nm) were prepared by reduction of $HAuCl_4$ aqueous solution with trisodium citrate according to Frens's method.[1] Briefly, 100 mL of 0.01% $HAuCl_4$ solution was heated to boiling, and 1.5 mL of 1% trisodium citrate was added. The solution was kept boiling for 5 min, and allowed to cool at room temperature.

SERS measurements. The Raman instrument includes a FT-Raman spectrometer (Thermo Nicolet 960) equipped with an InGaAs detector and a Nd/VO_4 laser (1064nm) as an excitation source. The laser power used was about 380 mW. All spectra are obtained with 512 scans and 4 cm^{-1} resolutions. For FT-SERS studies, 20 μl of 1.0×10^{-4} M 4-ATP ethanol solution was dropped on the hierarchical flowerlike gold microstructure (The electrodeposition time is 30 min) film for drying. After washing the ITO with ethanol and drying by N_2, FT-SERS spectra were recorded under the ambient conditions. In comparison, 20 μl of 1.0×10^{-4} M 4-ATP ethanol solution was directly dropped on the gold nanoparticle modified ITO substrate. After drying, the FT-SERS spectrum was measured.

The calculation of EF value. The EF was defined as

$$EF = (I_{SERS}/N_{ads}) / (I_{bulk}/N_{bulk})$$

Where I_{SERS} stand for the intensity of a vibrational mode in the SERS spectrum of 4-ATP and I_{bulk} for that of the solution or solid sample. For the calculation of EF values, the intensity of the υ_{8a} (a_1) at ~1583 cm^{-1} was used. N_{abs} and N_{bulk} are the number of 4-ATP molecules adsorbed on the SERS substrate and bulk molecules illuminated by the laser light to obtain the corresponding FT-SERS and ordinary Raman spectra, respectively. N_{abs} can be obtained according to the method proposed by Orendorff et al. [2] which is

$$N_{ads} = N_d A_{laser} A_N/\sigma,$$

Where N_d is the number density of the nanoparticles, A_{laser} is the area of the focal spot of laser, A_N is the nanoparticles footprint area, and σ is the surface area occupied by an adsorbed 4-ATP molecule. N_d and A_N can be obtained from the SEM images in Figure 1A, and A_{laser} can be obtained from the diameter of the laser spot (~100 μm). According to the report by Kim, [3] each 4-ATP molecule occupies ~0.20 nm^2 on full coverage of Au, indicating that σ can be adopted as ~0.20 nm^2/ molecule. Then the total number of surface adsorbed molecules (N_{ads}) on the HFGMs located on ITO substrate within the illuminated laser spot can be obtained at 1.75×10^{10}. N_{bulk} is the molecule number of the solid 4-ATP in the laser illumination volume. In our experiment, the laser spot of 100 μm in diameter and the penetration depth (~180 μm) of the focused laser beam are used. Taking the density of the solid 4-ATP (1.18 g/cm^3) into account, N_{bulk} was calculated to be about 8.03×10^{15} within the illuminated laser light. Considering the intensity ratio of the υ_{8a} (a_1) bands at ~1589 cm^{-1} in Figure 3B (b) and Figure S3 were measured to be 5.7 and 11.7 for SERS and ordinary Raman, respectively. The EF at the HFGMs for the υ_{8a} (a_1) bands can be calculated to be as large as 2.2×10^5 at 1064 nm excitation. Correspondingly, the EF value of gold

nanoparticles (~25 nm) located on the ITO substrate was also calculated. Figure S2 shows the SEM image of gold nanoparticles located at the ITO glass. From the image, the surface coverage of gold nanoparticles is about 1600 particles/μm. The EF value could be calculated via the similar way. Briefly, the N_{ads} was approximated to be 3.89×10^{10} and the EF values for υ_{8a} (a_1) vibrational mode was calculated to be about 1×10^4, 22 times lower than that on the HFGMs.

Reference

1 Frens, G. Nature (Phys. Sci.) 1973, 241, 20.
2 C. J. Orendorff, A. Gole, T. K. Sau, C. J. Murphy, Anal. Chem. 2005, 77, 3261.
3. K. Kim, J. K. Yoon J. Phys. Chem. B. 2005, 109, 20731.

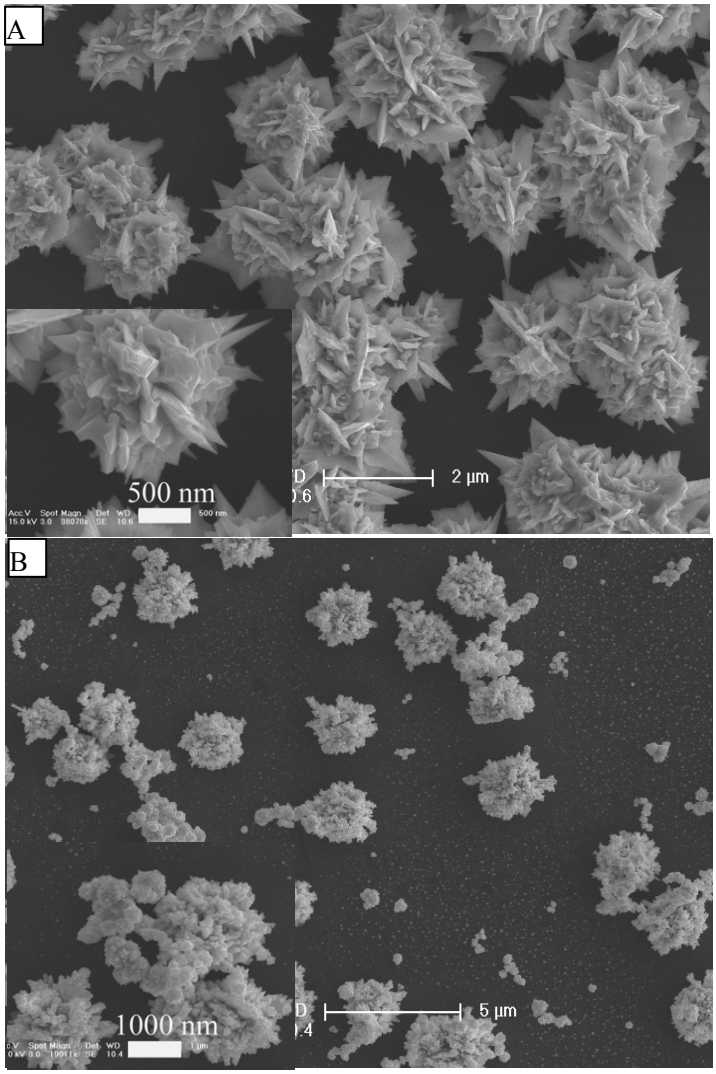

Figure S1 Typical FE-SEM images of the HFGMs located at ITO substrate. The deposition time for A and B is 30 min. The concentration of $HAuCl_4$ is 24.3 mM for A (potential under 0.7 V); The concentration of $HAuCl_4$ is 5 mM for B (potential under 0.5 V).

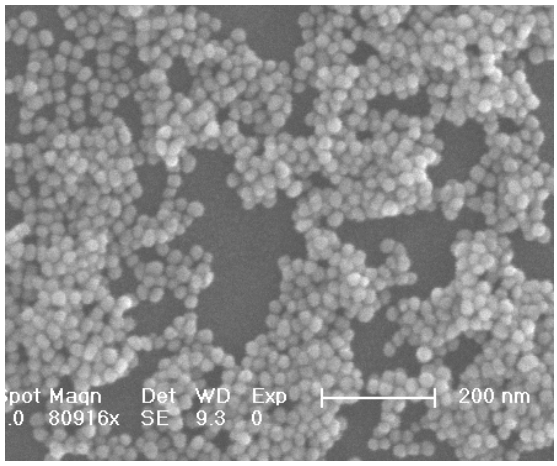

Figure S2 Typical SEM image of gold nanoparticles used for the calculation of the EF values.

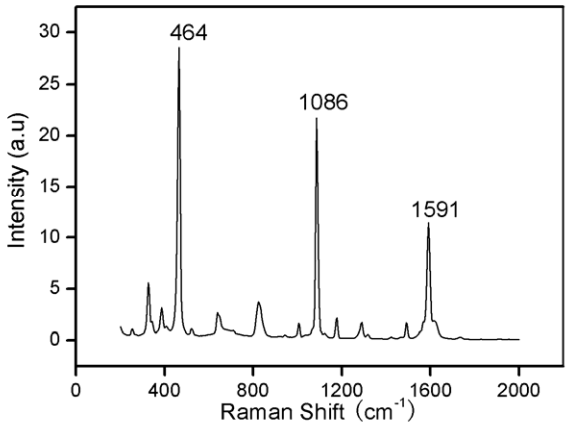

Figure S3 FT-Raman spectrum of solid 4-ATP sample.