Supporting Information

Uniform gold spherical particles for single-particle surface-enhanced Raman spectroscopy

Hai-Xin Lin,[‡a] Jie-Ming Li,[‡a] Bi-Ju Liu,[a] De-Yu Liu,[a] Jinxuan Liu,[b] Andreas Terfort,[c] Zhao-Xiong Xie,[a] Zhong-Qun Tian[a] and Bin Ren*[a]

[a] *State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China. Fax: +86-592-2181906; Tel: +86-592-2186532; E-mail: bren@xmu.edu.cn.*
[b] *Institute of Functional Interfaces, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, B 330, Eggenstein-Leopoldshafen D-76344, Germany.*
[c] *Institute of Inorganic and Analytical Chemistry, Goethe-University Frankfurt am Main, Frankfurt 60438, Germany.*

Chemicals:

Chloroauric acid ($HAuCl_4 \cdot 3H_2O$, A.R.), cetyltrimethylammonium bromide (CTAB, A.R.), sodium borohydride ($NaBH_4$, A.R.), and ascorbic acid (AA, A.R.), peroxid (H_2O_2, 30%), ammonia ($NH_3 \cdot H_2O$, 25%), ethanol (C_2H_5OH, A.R.) were purchased from Shanghai Chemicals Co. Ltd. without furher purification. 4'-Pyridin-4-yl-biphenyl-4-thiol (PBT, A.R.) was synthesized according to ref. 1. High-purity water (18.2 MΩ·cm) produced with a Milli-Q apparatus was used in the all experiments. All solutions and reaction mixtures in this work are aqueous solution if without further specification.

Preparation of Au particles:

Au cubes

Au cubes were prepared through a modified reported seed-mediated method.[2] Firstly, 10 mL aqueous solution containing $HAuCl_4$ (0.25 mmol/L) and CTAB (75 mmol/L) was first prepared. Then, 0.6 mL ice-cold $NaBH_4$ (10 mmol/L) was rapidly injected to the mixture with vigorously stirring in 30 ºC. A brown solution was observed in a few seconds. The whole solution was kept stirring slowly for two hours at room temperature to promote the decomposition of the remaining $NaBH_4$ in the solution. Then, 1 mL of the above hydrosol was diluted to 100 mL with water, which was then used as a seed solution. Secondly, 25 mL of colorless mixture containing $HAuCl_4$ (0.15 mmol/L), CTAB (16 mmol/L) and ascorbic acid (AA, 6 mmol/L) was prepared. Then the 0.3 mL seed hydrosol was added to the mixture immediately and mixed them by a vortex-mixer. The reaction mixture was left undisturbed at 30 ºC overnight. A claret-red colloid was achieved indicating the formation of Au cube with 55 nm edge length. The colloidal solution was used as the seed solution for further growth of Au sphere without further treatment.

Au sphere

In a typical synthesis of Au sphere with diameter about 265 nm, 50 μL of the above cubic Au seed solution was added into a 10 mL mixture solution that contains 20 mmol/L CTAB and 0.5 mmol/L AA. Then, 1 mL $NH_3 \cdot H_2O$ (25%) and 100 μL H_2O_2 (1.5%) was added, followed by addition of 70 μL $HAuCl_4$ (25 mmol/L) immediately. The solution was mixed by a votex-mixer and left undisturbed for more than 3 hours for reaction. To prepare Au sphere with different roughness, the concentration of AA was increased from 0.5 mmol/L (Fig. 2a) to 1 mmol/L (Fig. 2b), 2 mmol/L (Fig. 2c) and finally to 5 mmol/L (Fig. 2d). To prepare Au sphere with different size, the amount of cubic Au seed solution was decreased from 100 μL (Fig. 4a) to 50 μL (Fig. 4b), 25 μL (Fig. 4c) and finally to 10 μL (Fig. 4d). For Au particles prepared by one-step method and by seed-mediated method without H_2O_2, the cubic seed and H_2O_2 were not added respectively.

Characterization:

For morphological and optical characterizations, all the samples were washed via centrifugation-dispersion cycles by water before characterization. The size and morphology of as-prepared samples were characterized by scanning electron microscopy (SEM, Hitachi-S4800). The optical absorption spectra were recorded using an AvaSpec-2048 fiber optic spectrometer. The dark field scattering spectra and SERS signal from single particle were recorded on Renishaw inVia Raman system equipped with a Leica DM2500 microscope. A tungsten halogen lamp was used as the light source, and dark field objective (NA 0.55) was used for collect the signal. The dark field image was taken by a color CCD (QImage).

Raman detection:

10 mL of the as-prepared Au sphere was washed and re-dispersed into a 4 mL aqueous suspension. For the detection of PBT, the washed Au colloid was dispersed into corresponding PET ethanol solution and left over night for adsorption equilibrium. 15 μL of the final mixture was dropped on a hydrophilic silicon wafer and dried before SERS detection.

All SERS signals were excited by a 632.8 nm laser with diameter of 2 μm on the sample. The laser power on the sample was 0.8 mW. The acquisition time is 30 s for each particle. The SERS signals of 30 random particles were collected for each sample. To avoid the data dispersion, the two strongest and the two weakest signals of each sample were removed. The remaining 26 spectra are sufficient for statistic purpose.

Supplemental result and discussion

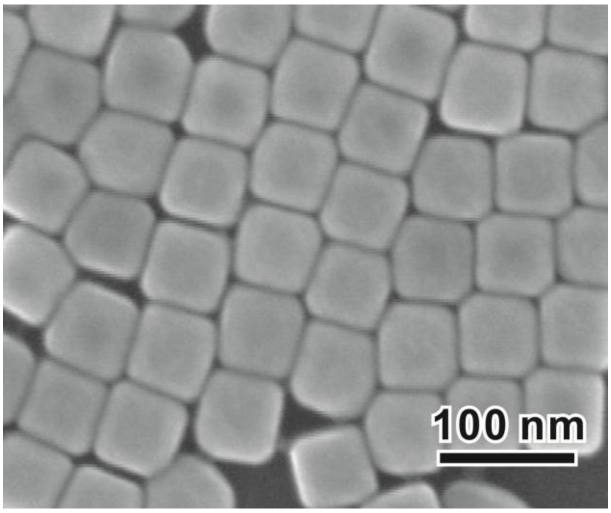

Fig. S1 High magnification SEM image of Au cubes as the seeds with a 55 nm edge length.

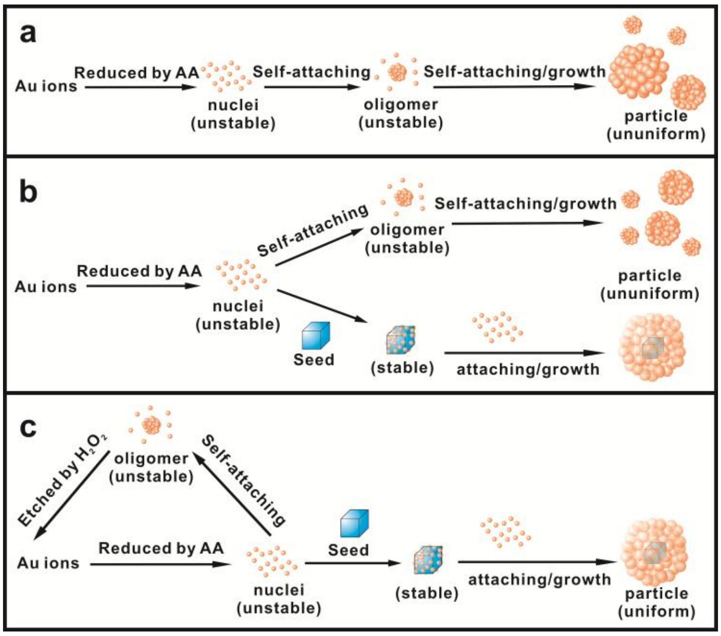

Fig. S2 Illustration of the proposed mechanism of **a)** one step method (OM); **b)** seed-mediated method (SM); and **c)** etching assisted seed-mediated method (EM).

Au (III) is firstly reduced by AA and nucleates in the solution or on the seed. The nuclei on the cubic seed are stable due to lower surface energy compared with which disperse in the solution. The ongoing nucleation continues to form nuclei and assemble to oligomers without seed to reduce the surface energy. In the absence of seeds (Fig. S2a) and H_2O_2 (Fig. S2b), the oligomers continue self-attaching and growth into stable particles. However, the nucleation is a fast process, so that the self-attaching is difficult to be controlled. It will cause a wide size distribution. With H_2O_2 (Fig. S2c), the nuclei and the oligomers will be etched to Au ions before growing to stable particles. Au ions are reduced by AA again and the cycles continue. Meanwhile, the nuclei on the cubic seeds and the seeds themselves are well crystallized and have a lower surface energy, they are stable and will not be etched by H_2O_2. The attachment the nuclei in the solution and further growth to big particles will continue till the end of reaction. As all the particles are grown starting from uniform Au cubes, and the same amount of Au atoms were further grown on the cubes, the size distribution should be very narrow.

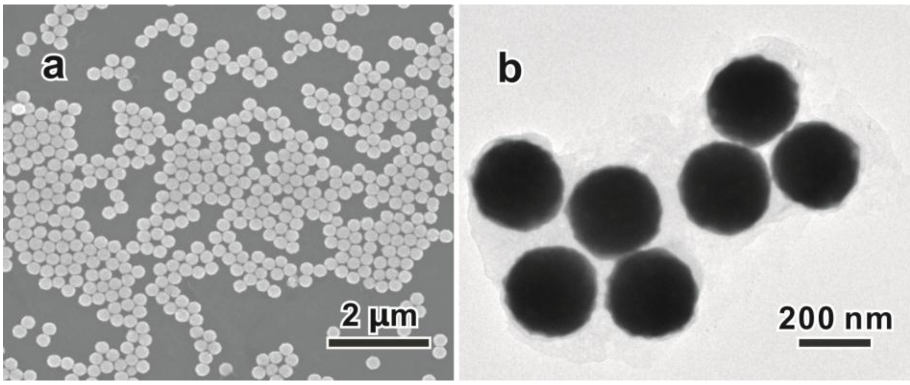

Fig. S3 a) Low magnification SEM image and **b)** HR-TEM image of Au microspheres prepared by EM with a diameter about 265± 11 nm.

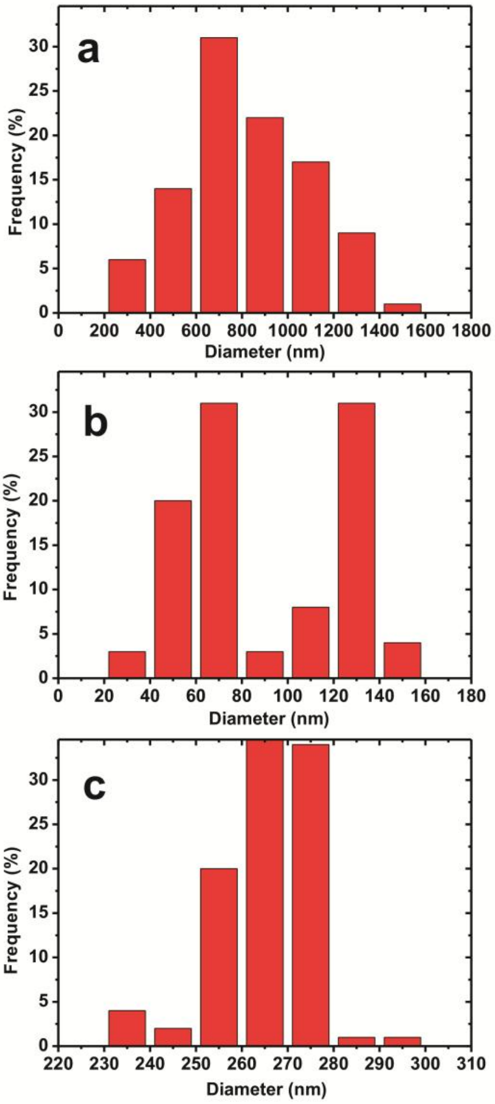

Fig. S4 Diameter statistical diagram of Au spheres prepared by **a)** OM; **b)** SM; and **c)** EM.

All the diameter statistical diagrams were achieved by measuring the sizes of 100 particles under SEM in non coffee ring regions to avoid the size-selecting effect.

References

1. B. Schuepbach and A. Terfort, *Org. Biomol. Chem*., 2010, **8**, 3552-3562.
2. T. K. Sau and C. J. Murphy, *J. Am. Chem. Soc.*, 2004, **126**, 8648-8649.