

Supplementary Information

Self-Assembly of noble metallic spherical aggregates from monodisperse nanoparticles: synthesis and their pronounced SERS and catalytic properties

Yanyan Liu, Yunxia Zhang*, Hualin Ding, Sichao Xu, Ming Li, Fengyu Kong, Yuanyuan Luo and Guanghai Li*

Phase transfer of Au nanoparticles (NPs) from the organic to the aqueous phase.

CTAB (or SDS) used to be the phase-transfer reagent when the oil-in-water emulsion experiment was carried at low concentration of hydrophobic NPs or high concentration of surfactant aqueous solution.¹ In a typical experiment, 0.5 ml of Au NPs (10.7 nm) in cyclohexane (~ 0.1 M) was added to 5 mL of SDS (5 mM) aqueous solution. The above solution was stirred vigorously and a homogeneous oil-in-water microemulsion was obtained. After heated at 70 °C for 10 min, cyclohexane in the microemulsion was removed and the aqueous-phase dispersed Au NPs was finally generated.

Preparation of Ag-Citrate NPs.

AgNO₃ (18 mg) was dissolved in 100 mL of H₂O and brought to boiling. Then 0.5 mL of sodium citrate (0.02 g) was added while stirring. The solution was kept under refluxing temperature for an additional 30 min².

Calculations of enhancement factor.

The enhancement factor (EF) is calculated using the following expression^{3,4},

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{Raman} / N_{Raman}}$$

I and *N* represent the intensity of peak and the number of molecules absorbed on the substrate within the laser spot, where the subscripts SERS and Raman stand for measurements performed with SERS or non-SERS substrate. For SERS examination, a volume (50 μL) of 4-ATP ethanol solution was dispersed to an area of 5×5 mm² wafer at certain concentration (*C*). The Raman (non-SERS) was measured by dispersing 50 μL of 0.1 M 4-ATP ethanol solution on the 5×5 mm² wafer at varying laser wavelength and during time. Since the identical area of Si wafer, the isometric analyst solution and identical experimental conditions (laser wavelength, laser power, microscope lenses, spectrometer, etc.), the above mentioned equation thus becomes⁵

$$EF = \frac{I_{SERS}}{I_{Raman}} \cdot \frac{C_{Raman}}{C_{SERS}}$$

* Address correspondence to Email: yxzhang@issp.ac.cn, ghli@issp.ac.cn

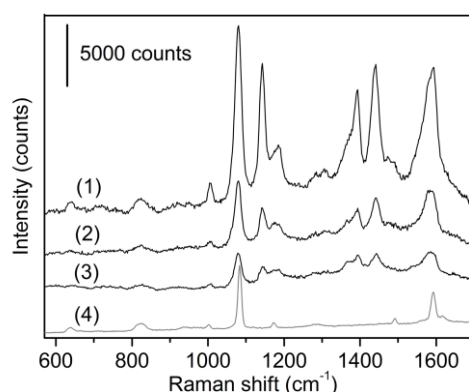


Fig.S1 Comparison of SERS spectra and the normal Raman spectrum of 4-ATP: (1-3) SERS spectra of 4-ATP on Au spherical aggregates at concentrations of 10^{-3} , 10^{-5} and 10^{-7} M, respectively; (4) the Raman spectrum of 4-ATP (0.1 M) with the intensity of decreased twice times. The above spectra were excited at 633 nm laser wavelength for 10 s.

Reproducibility of the SERS Substrate.

To test the uniformity of the as-produced substrates, we take Ag spherical aggregates for an example. Ten random points on the same substrate were applied for SERS signals as shown in Fig.S2 (a). And the intensities of three peaks at 1510, 1363 and 614 cm^{-1} in these spectra are shown in Fig.S2 (b).

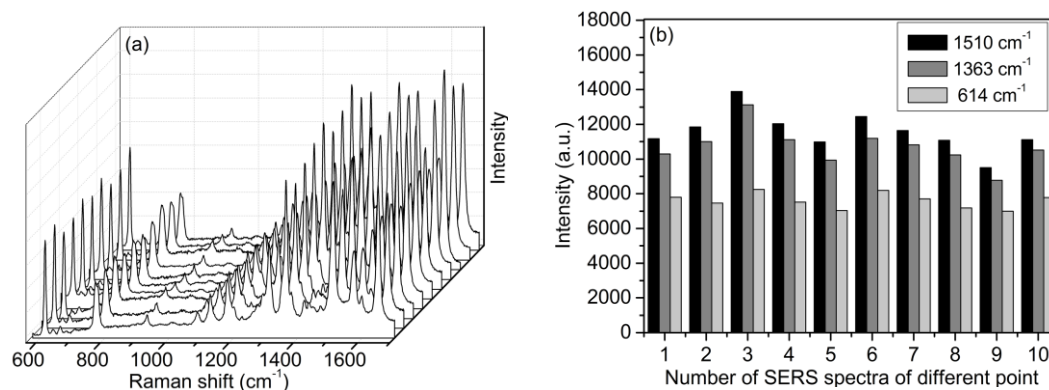


Fig.S2 (a) SERS spectra of 10^{-6} M R6G aqueous solution on ten random points of the Ag spherical aggregates. The integration time was 5 s for each point with a 532 nm laser; (b) the intensities of three characteristic peaks at the ten random points.

Reference

1. J. Kim, J. E. Lee, J. Lee, J. H. Yu, B. C. Kim, K. An, Y. Hwang, C. H. Shin, J. G. Park, J. Kim and T. Hyeon, *J. Am. Chem. Soc.*, 2006, **128**, 688.
2. P. C. Lee and D. Meisel, *J. Phys. Chem.*, 1982, **86**, 3391.
3. S. Abalde-Cela, S. Ho, B. Rodriguez-Gonzalez, M. A. Correa-Duarte, R. A. Alvarez-Puebla, L. M. Liz-Marzan and N. A. Kotov, *Angew. Chem. Int. Ed. Engl.*, 2009, **48**, 5326.
4. M. Chirumamilla, G. Das, A. Toma, A. Gopalakrishnan, R. P. Zaccaria, C. Liberale, F. De Angelis and E. Di Fabrizio, *Microelectron. Eng.*, 2012, **97**, 189.
5. E. C. Le Ru, E. Blackie, M. Meyer and P. G. Etchegoin, *J. Phys. Chem. C*, 2007, **111**, 13794.