

## Supporting Information

# Facile Interfacial Synthesis of Gold Roses and their Applications for Efficient Surface Enhanced Raman Scattering

*Xinying Li,<sup>a</sup> Kaisheng Yao,<sup>b</sup> Weiwei Lu<sup>b</sup> and Jianji Wang<sup>\*ab</sup>*

<sup>a</sup> School of Chemistry and Environmental Sciences, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xixiang, Henan 453007, P. R. China

<sup>b</sup> School of Chemical Engineering and Pharmaceutics, Henan University of Science and Technology, Luoyang, Henan 471003, P. R. China

\* Corresponding author

E-mail: [jwang@henannu.edu.cn](mailto:jwang@henannu.edu.cn) (Prof J. Wang)

Tel: +86-373-3325805

Fax: +86-373-3326445

## Experimental Section

**Chemicals:** *O*-ethoxyaniline (98%) and *P*-aminothiophenol (PAPT, 97%) were purchased from Aladdin Chem. Co.; Chloroauric acid tetrahydrate, tetrahydrofuran ( $\geq 99\%$ ) and ethanol were purchased from Sinopharm Chem. Reagent Co. These Chemicals were used without further purification. Double distilled water was used throughout the experiments.

**Synthesis:** In a typical synthesis of the Au nanostructures, 4 ml of aqueous  $\text{HAuCl}_4$  solution (5 mM) with pH 1.0, adjusted by 1 M HCl solution, was slowly added onto 4 ml of *o*-ethoxyaniline (OEA, 5.5 mM) in  $\text{CHCl}_3$  along glass wall of the vial (2.2 cm in diameter). The solutions were kept at room temperature for 72 h without disturbance. The Au nanostructures were formed at the  $\text{CHCl}_3$ - $\text{H}_2\text{O}$  interface and could be transferred to various substrates placed at the bottom of the vial by removing the solution with a syringe, and then the obtained products were immersed in THF for 6 h to remove the generated poly(*o*-ethoxyaniline) (POEA). Various morphologies can be obtained by employing different reaction conditions.

**Characterization:** Morphologies of the films, deposited on silicon wafer or glass slide, were observed by a JEOL JSM-6390LV scanning electron microscope (SEM). The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance X-ray diffractometer (Cu irradiation,  $\lambda = 0.154056$  nm) in  $2\theta$  ranging from  $10^\circ$  to  $90^\circ$ . The thermogravimetric (TG) measurements was performed using a Netzsch STA449C thermal analyzer in air atmosphere at a heating rate of  $20^\circ\text{C min}^{-1}$  within the temperature range of  $25$ - $800^\circ\text{C}$ . Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and selected-electron diffraction (SAED) were obtained on a JEOL 2100 transmission electron microscope at an acceleration voltage of 200 kV. The specimens for the TEM measurements were prepared by depositing a drop of dilute alcohol solution of the sample on a carbon-coated copper grid and drying at room temperature. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer in the wavelength range of  $200$ - $800$  nm. Raman scattering experiments were performed by using a

Renishaw Invia Reflex spectrometer equipped with a Peltier charge-coupled device (CCD) detector. A diode laser with a wavelength of 785 nm was utilized as an excitation source. The spot diameter of the laser beam is about 1  $\mu\text{m}$  and the power at the sample is about 0.12 mW.

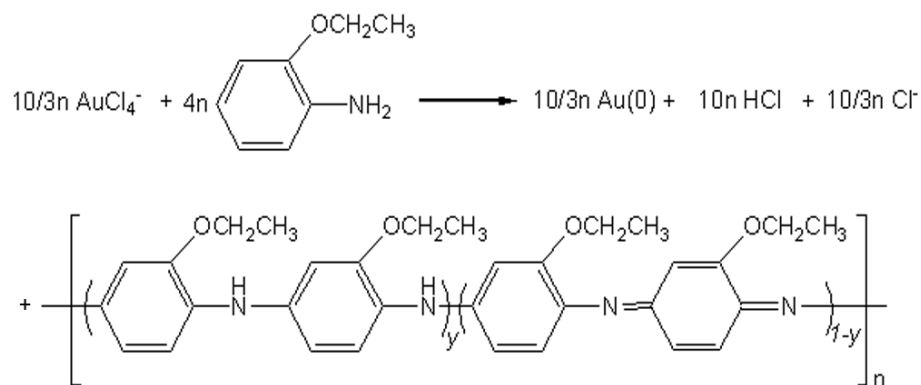
**SERS Measurements:** For SERS investigations, P-aminothiophenol (PATP) was used as a probe molecule. The purified samples deposited on the silicon wafers were immersed in  $10^{-5}$  M ethanol solution of PATP for 24 h. The samples were then taken out, rinsed with ethanol to remove the free PATP molecules and dried in air before Raman measurements.

**The Calculation of SERS Enhancement factor (EF):** The EF is defined as

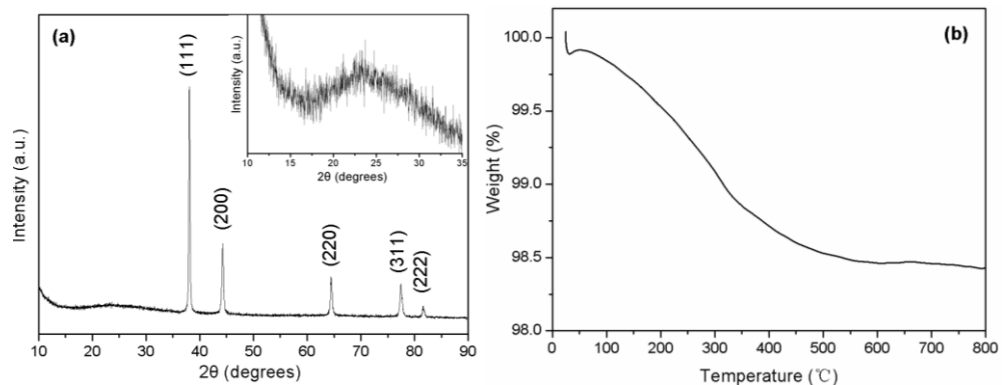
$$EF = (I_{surf}/N_{surf}) / (I_{bulk}/N_{bulk})$$

where  $I_{surf}$  and  $I_{bulk}$  are denote the intensity of PAPT obtained with Au thorned roses and solid bulk PAPT, respectively. For the calculation of EF values, the intensity of peaks at  $1592\text{ cm}^{-1}$  was used. The  $N_{surf}$  and  $N_{bulk}$  are the number of PAPT molecules adsorbed on the SERS substrate and bulk molecules within the SERS detecting spot, respectively.

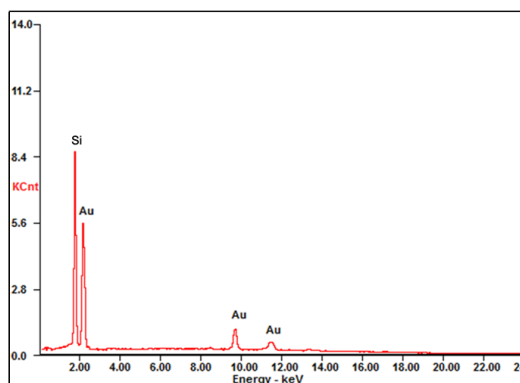
The spot diameter of the laser beam is about  $1\mu\text{m}$  and its penetration depth is about  $2\mu\text{m}$ . Therefore,  $N_{bulk}$  can be calculated to be  $8.9 \times 10^9$  considering the density of the solid PAPT ( $1.18\text{ g cm}^{-3}$ ).<sup>[1]</sup> On the other hand, each PAPT molecule occupies an area of  $\sim 0.2\text{ nm}^2$  on full coverage of Au,<sup>[1]</sup> we assumed dense monolayer coverage of PAPT molecules within the laser beam,<sup>[1b,c]</sup> thus,  $N_{surf}$  can be calculated to be about  $3.9 \times 10^6$ . According to the results of the SERS measurements, the intensity ratio of  $I_{surf}$  to  $I_{bulk}$  is  $4.6 \times 10^3$ , so the EF is calculated to be  $1.1 \times 10^7$ .



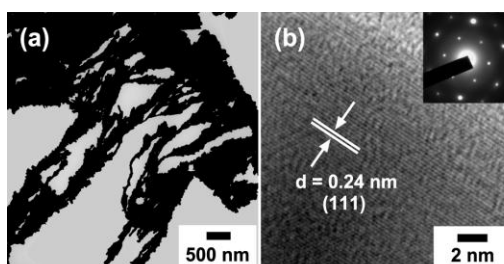
**Scheme 1** Reaction conversion for the preparation of Au thorned roses at the  $\text{CHCl}_3\text{-H}_2\text{O}$  interface.



**Fig. S1** XRD pattern (a) and TGA curve (b) of the Au micro/nanostructures under air atmosphere.

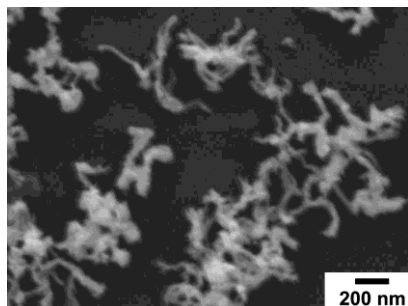


**Fig. S2** EDX spectra of the purified Au thorned roses.

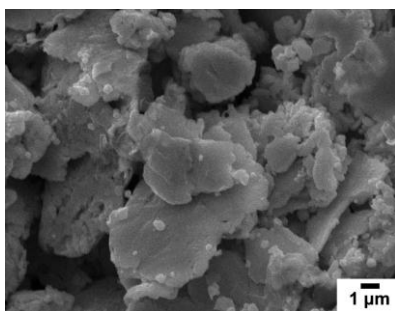


**Fig. S3** TEM and HRTEM images of the thorned roses: (a) TEM; (b) HRTEM; and the inset shows the corresponding SAED patterns.

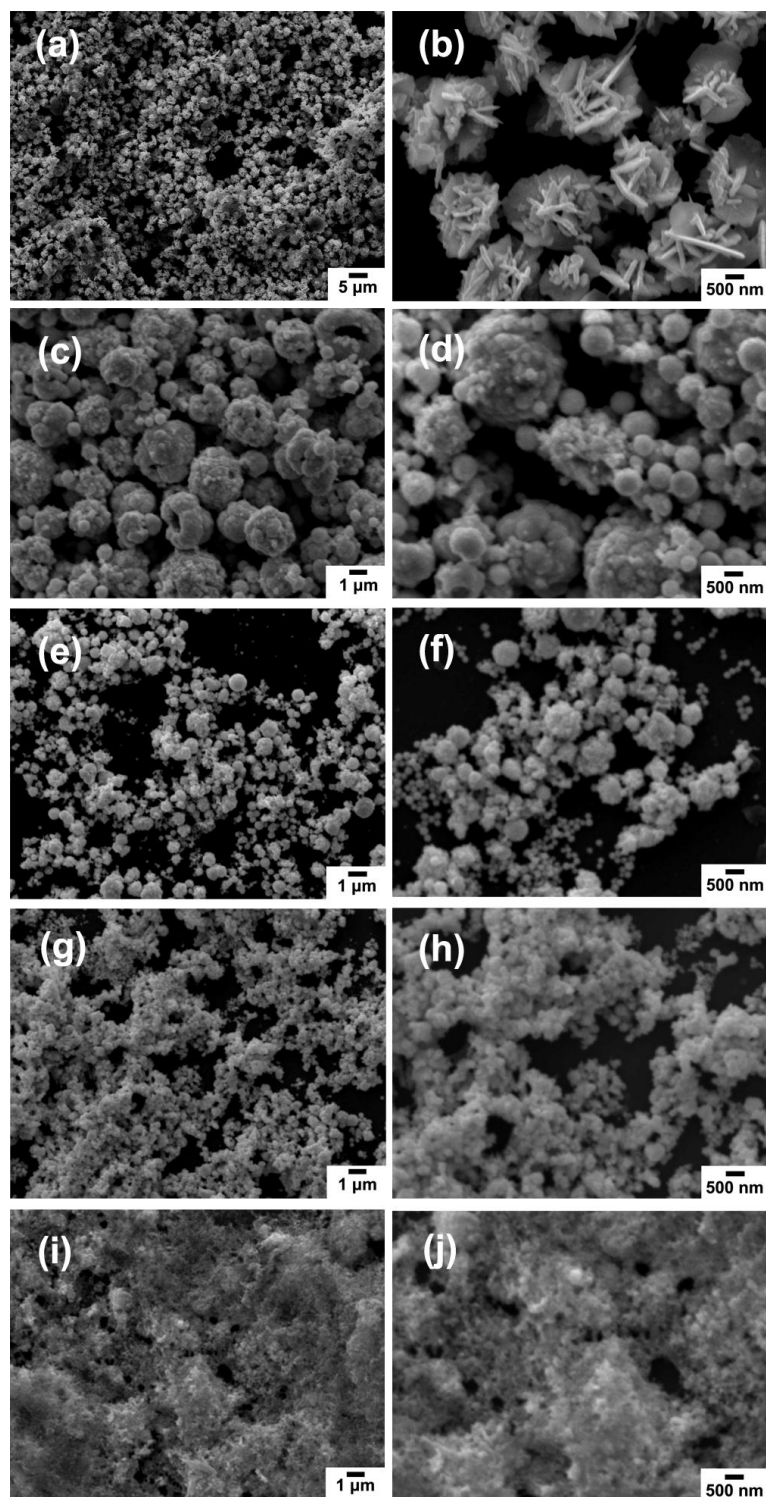
From the Fig. S3a, the thorned rose can be clearly seen, in good agreement with the SEM observations (Fig. 1 and 2). The HRTEM (Fig. S3b) indicates lattice fringes of a nanopetal from a flower of the thorned rose. The lattice spacing of 0.24 nm agrees well the (111) lattice plane of the face-centered cubic (fcc) structure of Au. The corresponding SAED patterns (inset of Fig. S3b) of the nanopetal show the hexagonal symmetry of the pattern spots. This also indicates that the nanopetal is fcc single-crystal growing along the (111) plane.<sup>[2]</sup>



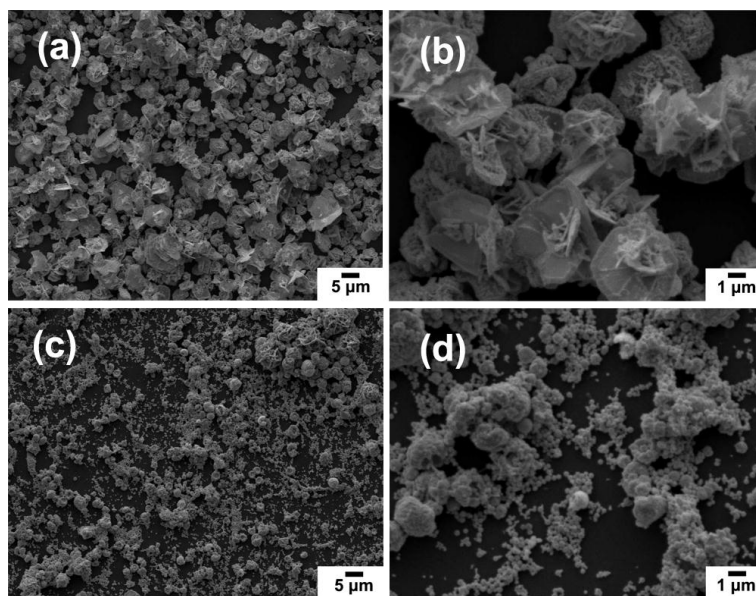
**Fig. S4** SEM image of the samples prepared at the  $\text{CHCl}_3\text{-H}_2\text{O}$  interface at 1 h.



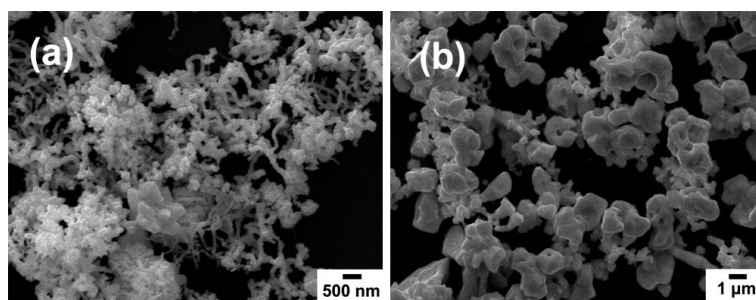
**Fig. S5** SEM image of the sample prepared under stirring without changing other conditions.



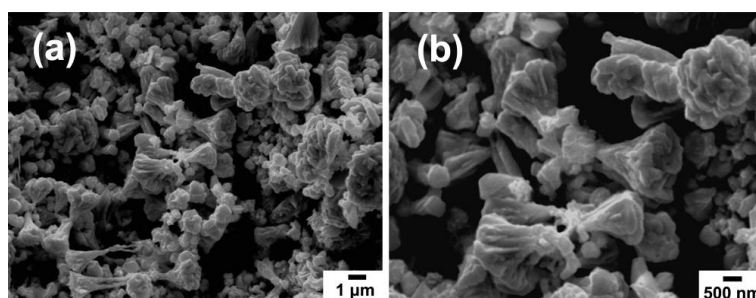
**Fig. S6** SEM images of the samples prepared at  $\text{CHCl}_3\text{-H}_2\text{O}$  interface with different pH values of aqueous chlorauric acid solution: (a, b), 0.5; (c, d), 4.0; (e, f), 7.0; (g, h), 10.0; (i, j), 12.5.



**Fig. S7** SEM images of the samples prepared at the  $\text{CHCl}_3\text{-H}_2\text{O}$  interface with different OEA concentrations in  $\text{CHCl}_3$ : (a, b), 25.0 mM; (c, d), 100.0 mM.



**Fig. S8** SEM images of the samples prepared at the  $\text{CHCl}_3\text{-H}_2\text{O}$  interface with different heights of aqueous column: (a), 1.58 cm; (b), 2.11 cm.



**Fig. S9** SEM images of the samples prepared at the toluene- $\text{H}_2\text{O}$  interface.



## References

- [1] (a) K. Kim and J. K. Yoon, *J. Phys. Chem. B*, 2005, **109**, 20731; (b) G. Lu, C. Li and G. Shi, *Chem. Mater.*, 2007, **19**, 3433; (c) S. Guo, L. Wang and E. Wang, *Chem. Commun.*, 2007, 3163.
- [2] (a) Z. Li, Z. Liu, J. Zhang, B. Han, J. Du and Y. Gao, *J. Phys. Chem. B.*, 2005, **109**, 14445; (b) Y. Qin, Y. Song, N. Sun, N. Zhao, M. Li and L. Qi, *Chem. Mater.*, 2008, **20**, 3965.