Electronic Supplementary Information

Siloxane Surfactant Induced Self-Assembly of Gold Nanoparticles and Their Application to SERS

Han Jia[a], Xiangtao Bai[a], Na Li[b], Li Yu[a], and Liqiang Zheng[a]*

a. Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan, 250100, China.

b. College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan, 250014, China.

Tel.: +86 531 88366062

Fax: +86 531 88564750

E-mail address: lqzheng@sdu.edu.cn

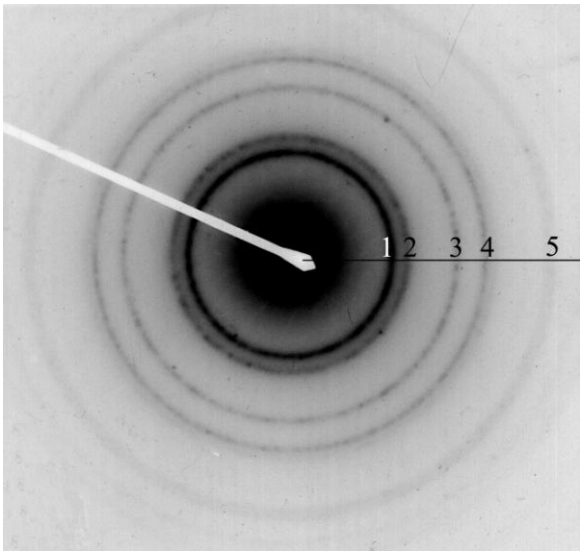

Figure S1. The corresponding electron diffraction pattern of the gold nanoparticle

(1 to 5 corresponding to {111} {200} {220} {311} and {331}).

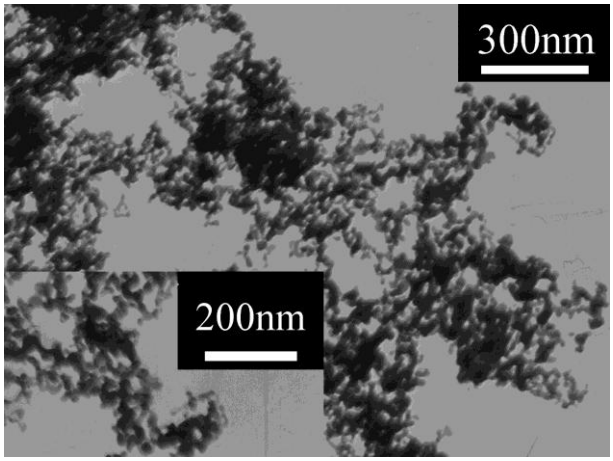

Figure S2. TEM image of aggregates formed when ascorbic acid was replaced by sodium borohydride.

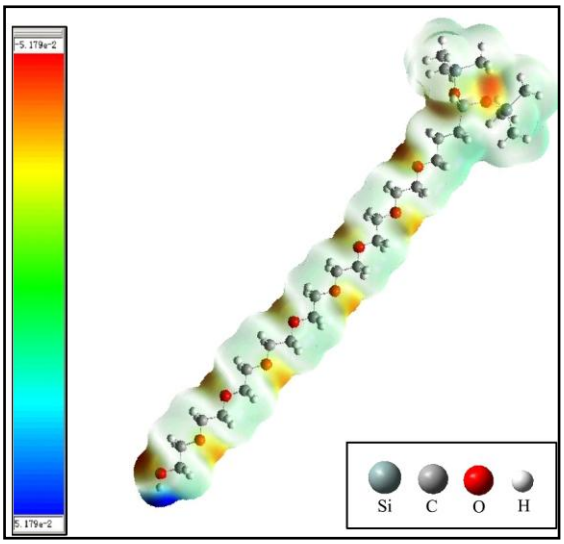

Figure S3. The configuration and electron density of Q2-5211.

The calculation of EF is followed:[S1]

In order to determine the enhancement effect of R6G on the assembling film, the enhancement factor (EF) values of R6G in the assembling film are determined using the following expression:

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

where I_{SERS} is the intensity of a vibrational mode in the surface-enhanced spectrum, I_{bulk} is the intensity of the same mode in the Raman spectrum, N_{ads} is the number of molecules adsorbed and sampled on the SERS-active substrate, and N_{bulk} is the number of molecules sampled in the bulk. *N*abs can be obtained according to the method proposed by Orendorff *et al.* [S2] which is

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

where N_d is the number density of the gold nanoparticles, A_{laser} is the area of the focal spot of laser, A_N is the footprint area of the gold nanoparticles, and σ is the surface area occupied by an adsorbed R6G molecule. In order to simplify the model, we assume that patterns of gold nanoparticles are densely packed and then N_d can be obtained. From the TEM we find that the mean diameter of the gold nanoparticles is about 20 nm and then A_N can be obtained. A_{laser} can be obtained from the diameter of the laser spot (~1 μm). The long-axis length of an R6G molecule is ca. 1.4 nm.[S3] Therefore, one can assume that in the densely packed R6G monolayer a single R6G molecule should take no more than 4 nm^2 in area, indicating that σ can be adopted as ~ 4 nm^2/molecule.[S4] Then the total number of surface adsorbed molecules (N_{ads}) within the illuminated laser spot can be obtained at 1.54×10^5. N_{bulk} is the molecule

number of the solid R6G in the laser illumination volume. In our experiment, the laser spot is about 1 μm in diameter and the penetration depth is about 2 μm. Taking the density of the solid R6G (1.26 g/cm^3) into account, N_{bulk} was calculated to be about 2.49×10^9 within the illuminated laser light. The intensity of the measured light at 1315 cm^{-1} was about 27000 and 146 for SERS and ordinary Raman, respectively. Finally, the EF at the assembled film for the band located at 1315 cm^{-1} can be calculated to be about 2.41×10^6.

References

[S1] S. J. Guo, S. J. Dong and E. K. Wang, *Cryst. Growth Des.* 2009, **9**, 372.

[S2] C. J. Orendorff, L. N. Gearheart, R. Jana and C. J. Murphy, *Phys. Chem. Chem. Phys.* 2006, **8**, 165.

[S3] R. Sasai, T. Fujita, N. Iyi, H. Itoh and K. Takagi, *Langmuir* 2002, **18**, 6578.

[S4] A. Kudelski, *Chem. Phys. Lett.* 2005, **414**, 271.