Supporting Information

Galvanic Replacement Mediated Growth of Dendritic Gold Nanostructures with a Three-Fold Symmetry and Their Applications to SERS

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The calculation of EF:[S1]

The enhancement factor (EF) values of R6G on the gold dendrites 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 nd 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 gold dendrites are densely packed and then N_d and 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 1.96×10^5. 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 613 cm^{-1} was about 14573 and 259 for SERS and ordinary Raman, respectively. Finally, the EF for the band located at 613 cm^{-1} can be calculated to be about 7.15×10^5. Beside, the EF for the band located at 1365 cm^{-1} is about 2.24×10^5, which is comparable with that of 613 cm^{-1}.
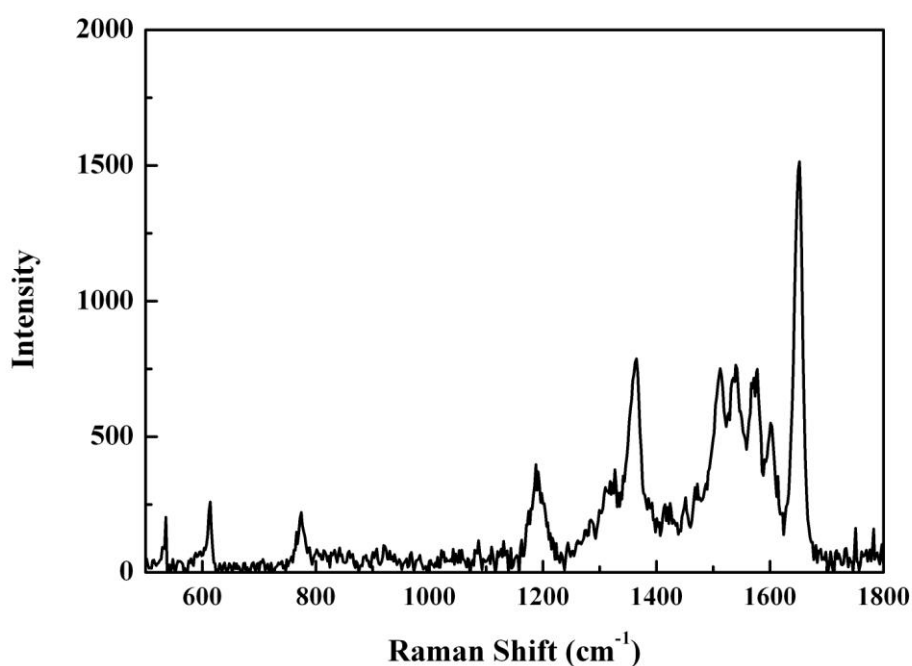

Figure S1 Normal Raman spectrum of solid R6G

References

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

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

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