Hollow Au Nanoparticles for Single-Molecule Raman Spectroscopy via Synergic Electromagnetic and Chemical Enhancement Strategy

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S1. EM of hollow gold nanoparticles

As shown in **Figure S1**, the nanostructure is modeled as a hollow gold sphere with a diameter of 160 nm and a wall thickness of 5 nm. This sphere is positioned on a cubic gold substrate with dimensions of 1500 nm × 1500 nm × 300 nm. A 2 nm thick silicon dioxide (SiO_2) layer acts as the separation layer between the gold sphere and the gold cube, maintaining a 2 nm gap between the two nanostructures. The excitation source is

uniformly set to p-polarized light with a wavelength of 785 nm, as p-polarization is most effective in enhancing the electromagnetic field [1].

According to Equation 1, the EF in the EM can be expressed as $\frac{|E(r_0,\omega)|^4}{|E_0(r_0,\omega)|^4}$, which is the ratio of the fourth power of the scattered light to the incident light. EM originates from the excitation of LSPR, which can significantly enhance the local optical field on the metal surface to amplify the Raman signal. **Figure S1a** shows that with the same diameter of the gold sphere, the solid sphere only has an EF of 10^6. Meanwhile, as shown in **Figure S1b**, the enhanced electric field is distributed at the edge of the sphere, reducing the probability of the molecule's position experiencing an enhanced electric field. After changing from a solid gold sphere to a gold nanoshell, the EF reaches a value of 1.5×10^9, as illustrated in **Figure S1c**. Additionally, combining **Figure S1b** and **Figure S1d**, it can be observed that the electric field distribution in the gap of the nanoshell has a higher intensity, increasing the probability of the molecule's position experiencing an enhanced electric field.

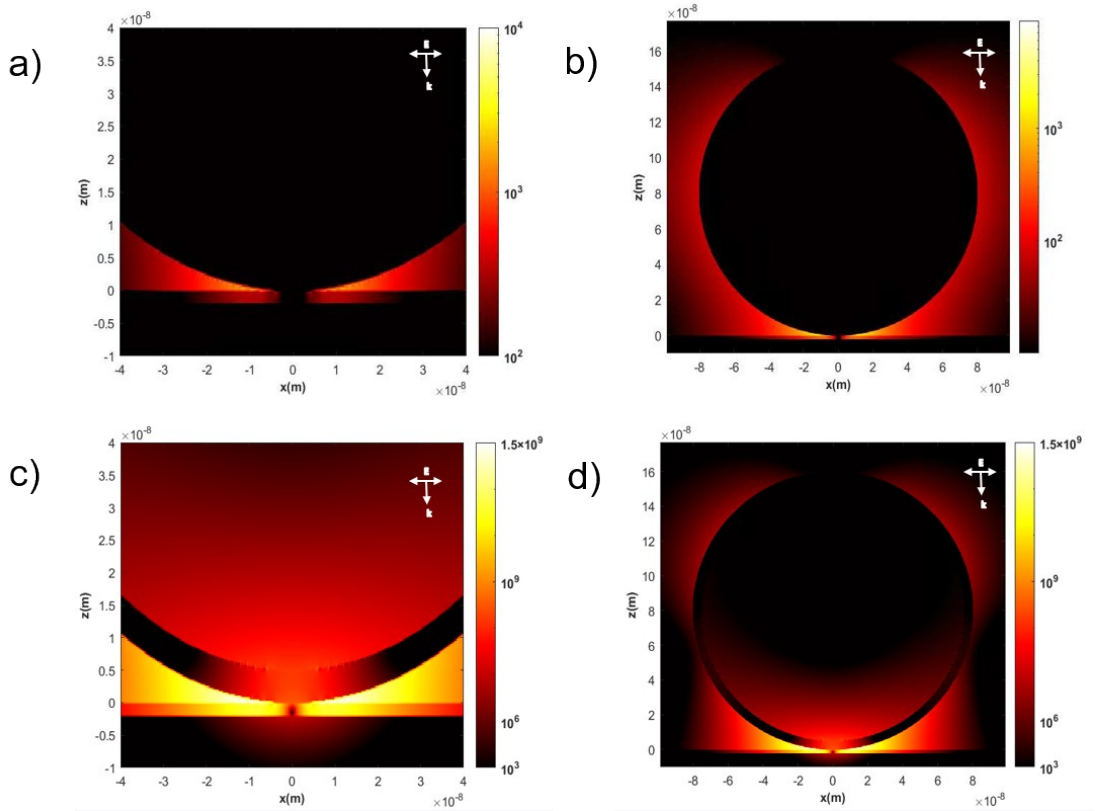

Figure S1 The electromagnetic enhancement of two different single-molecule Raman substrate which using the 3D-FDTD method, with incident light at a wavelength of 785 nm and vertically incident. **a.** Results of simulating the EF for an 80-nm radius gold sphere. **b.** Electromagnetic field distribution simulation for an 80-nm radius gold sphere. **c.** Results of simulating the EF for an 80-nm radius gold nanoshell with a 5-nm thickness. **d.** Electromagnetic field distribution simulation for an 80-nm radius gold nanoshell with a 5-nm thickness.

S2. UV-Vis spectra of the hollow gold nanoparticles

As **Figure S2** shown, the hollow gold nanoparticles exhibit strong absorption at 785 nm, which typically indicates that the nanoparticles undergo LSPR at this wavelength. This can generate strong EME, thereby enhancing the Raman signal.

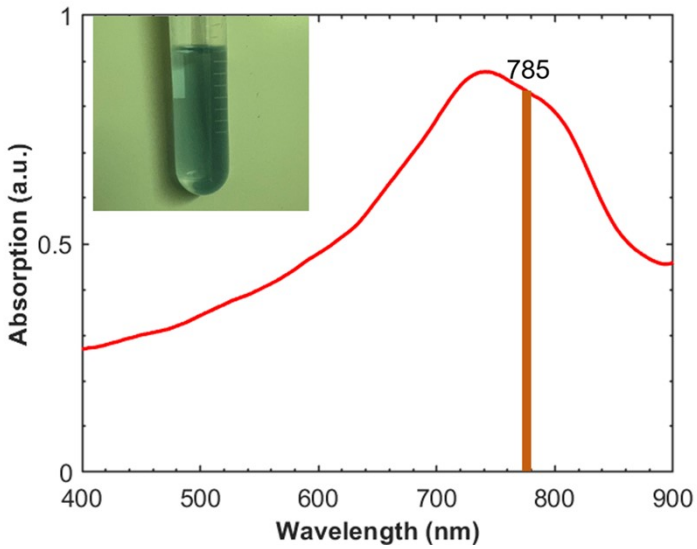

Figure S2 UV-Vis spectra of the hollow gold nanoparticles

S3. Simulation of target molecule Raman spectra

Figure S3 shows the Raman spectra of three target molecules calculated using Gaussian and plotted with Multiwfn. First, the target molecular geometry is optimized using Gaussian software to obtain the lowest energy conformation. This is typically done by Density Functional Theory (DFT) to ensure the molecule is in its most stable state. After that, based on the optimized molecular structure, vibrational frequencies are calculated. Last, providing temperature as well as incident wavenumber, it is easy to translate the vibrational mode's Raman activity into spectral features on Multiwfn [2], including peak intensities and positions. The simulated results correspond well with the experimental data.

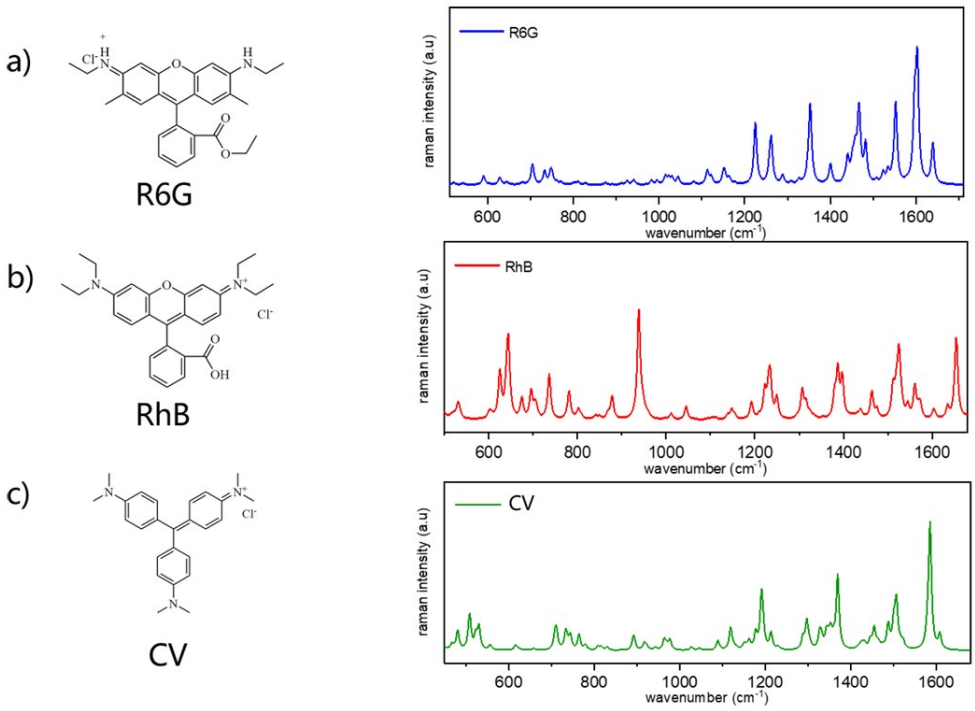

Figure S3 Molecular Schematics and Raman spectrum of the target molecule calculated using Gaussian. **a.** Simulation of R6G excited by 785 nm light in vacuum. **b.** Simulation of RhB excited by 785 nm light in vacuum. **c.** Simulation of CV excited by 785 nm light in vacuum.

Reference

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