Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Two-step-route to Ag-Au nanoparticles grafted on Ge wafer for extra-uniform SERS substrates

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1. Finite difference time domain (FDTD) simulations

The 3D FDTD method was used to calculate the electric field by the Lumerical FDTD Solutions software. A schematic illustration of the model was showed in Figure S1. In Figure S1a, Ag NPs with a diameter of 50 nm were placed on a Ge substrate, with a gap of 25 nm between them. The model of Ag-Au NPs was showed in Figure S1b, Au NPs with a diameter of 10 nm were placed between the Ag NPs, in which the gap between Au NPs is 8.75nm. A linearly polarized plane wave of a certain wavelength (633 nm) was incident perpendicularly to the substrate from the top of the dimeric noble metal spheres. A non-uniform grid size was used for the overall simulation volume, which varies with the refractive index of each material. In order to best capture the electric field in the vicinity of noble metal-dielectric material interfaces, a small region of 75 nm × 75 nm × 70 nm containing part of the substrate and a Ag sphere or a Ag sphere plus seven Au ones was set with a grid of 0.5 nm. The simulation time was set at 500 fs to ensure the fields to decay completely before termination of the simulation. To obtain the electric field distribution, a plane monitor was placed parallel to the substrate with the same height of the centre of the noble metal spheres.

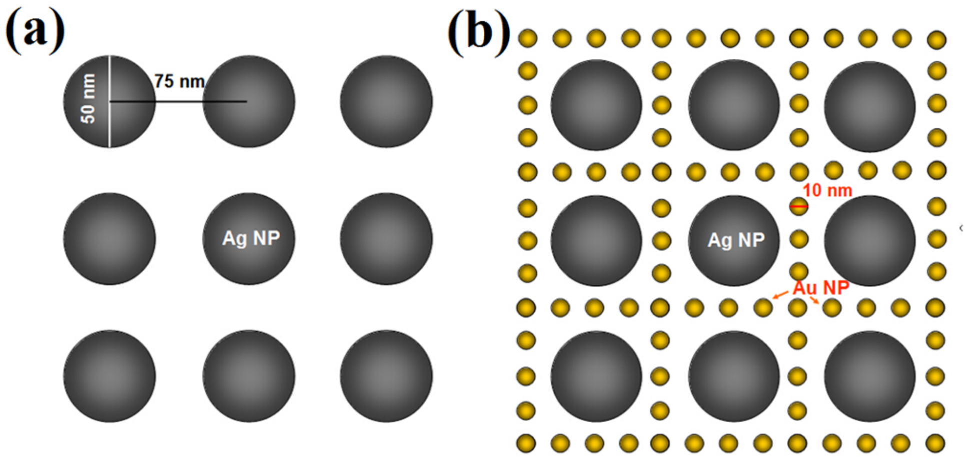
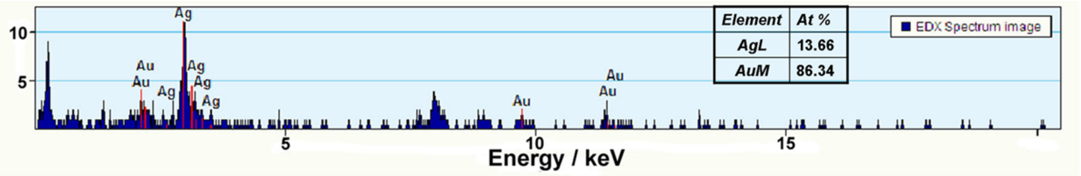


Figure S1. Schematic representation of Ag NPs (a) and Ag-Au NPs (b) substrate in the FDTD calculation.

2. **The EDS spectra of the Ag nanoparticle in the Ag-Au NPs/Ge substrate**



Element	*At %*
AgL	13.66
AuM	86.34

Figure S2. The EDS spectra of the Ag nanoparticle in the Ag-Au NPs/Ge substrate.

3. The UV-vis spectrum of Ag and Ag-Ag nanoparticles

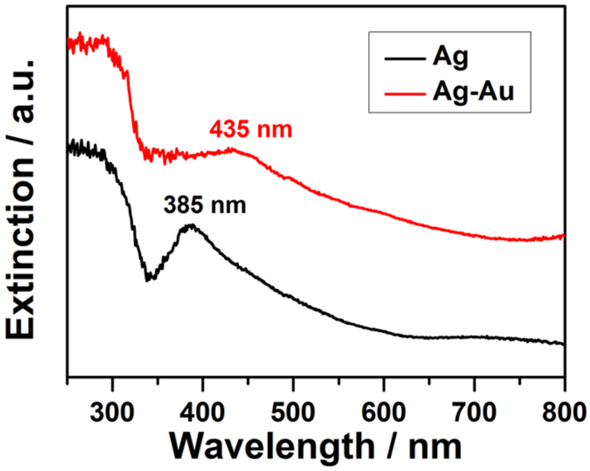


Figure S3 The UV-vis spectrum of Ag and Ag-Ag nanoparticles (deduct background of Ge substrate).

4. The normal Raman spectrum of 0.01 M R6G methanol solution

Figure S2 shows the characteristics of the Raman spectra of 0.01 M R6G methanol solution. The C-C stretching vibration bending mode is 1181 cm^{-1}. The bands at 1366, 1511, 1580, and 1654 cm^{-1} are assigned to the aromatic C-C stretching modes.

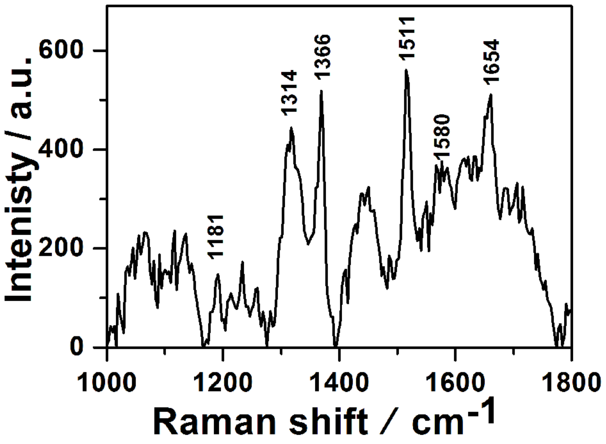


Figure S4. The normal Raman spectrum of 0.01 M R6G methanol solution.

5. Histograms of normalized Raman intensities of R6G (1 × 10^{-9} M) on Ag-Au NPs/Ge SERS substrate

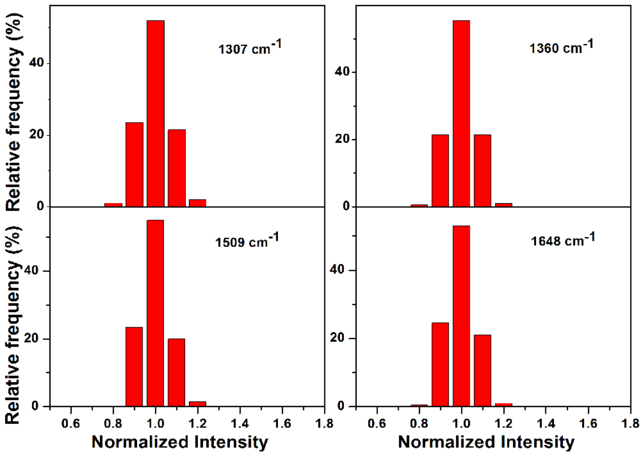


Figure S5. Histograms of normalized Raman intensities of R6G (1 × 10^{-9} M) on **Ag-Au NPs/Ge** SERS substrate.

6. EF calculation of the as-prepared Ag-Au NPs/Ge substrate:

The average SERS EF was calculated according to the formula:

$$\mathrm{EF}=\frac{I_{\mathrm{SERS}}N_{0}}{I_{0}N_{\mathrm{SERS}}}$$

where I_0 and I_{SERS} are the peak intensity of the Raman measurement with 0.01 M R6G solution and SERS measurement with 1×10^{-9} M R6G solution, respectively; N_0 and N_{SERS} are the number of R6G molecules in the scattering volume for the Raman measurement and SERS measurement, respectively.

$$N_0 = n_0 N_A = C_0 V_0 N_A;$$

$$N_{SERS} = n_{SERS} N_A = C_{SERS} V_{SERS} N_A;$$

So, $EF = \dfrac{I_{SERS}N_0}{I_0 N_{SERS}} = \dfrac{I_{SERS}C_0 V_0 N_A}{I_0 C_{SERS} V_{SERS} N_A} = \dfrac{I_{SERS}C_0}{I_0 C_{SERS}} = \dfrac{2124\times1\times10^{-2}}{560\times1\times10^{-9}} = 3.8\times10^{7}$;

where n_0 and n_{SERS} are the amount substance of R6G molecules in the scattering volume; V_0 and V_{SERS} are the scattering volume ($V_0 = V_{\mathrm{SERS}}$); C_0 and C_{SERS} are the concentration of R6G solution. The subscripts 0 and SERS represent Raman measurement and SERS measurement, respectively. A is the area of laser spot; h is the laser spot depth of focus; N_{A} is Avogadro constant.

7. Histograms of normalized Raman intensities of CV (1×10^{-8} M) on Ag-Au NPs/Ge SERS substrate

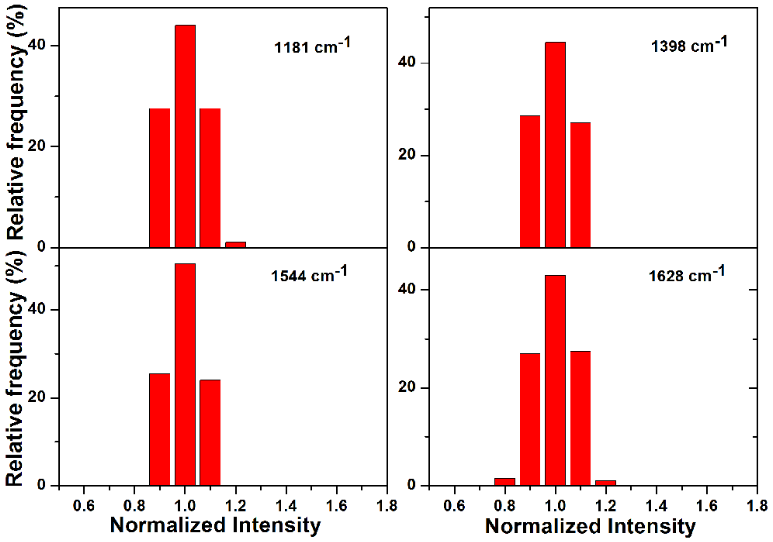


Figure S6. Histograms of normalized Raman intensities of CV (1 × 10^{-8} M) on **Ag-Au NPs/Ge** SERS substrate.