Supporting Information

Plasmonic-enhanced Raman scattering of graphene on growth substrate and its application in SERS

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Calculation of enhancement factor

The SERS enhancement factors (EFs) were estimated by \( \text{EF} = \frac{I_{\text{SERS}}}{I_{\text{bulk}}} \times \frac{N_{\text{bulk}}}{N_{\text{SERS}}} \),\(^1\) where \( I_{\text{SERS}} \) is the peak intensity of the specific Raman band for the probe molecules with \( 10^{-9} \) M on the SERS substrate, \( I_{\text{bulk}} \) is the intensity of the same Raman band from \( 10^{-2} \) M analyte. \( N_{\text{SERS}} \) and \( N_{\text{bulk}} \) are the number of molecules contributing to \( I_{\text{SERS}} \) and \( I_{\text{bulk}} \). Here, \( 1649 \text{ cm}^{-1} \) Raman peak of RhB and \( 612 \text{ cm}^{-1} \) Raman peak of R6G are selected for EFs calculation. The SERS substrate containing analyte was 4 nm Au/analyte/graphene/Cu foils and the substrate for reference was analyte/graphene/Cu foils, respectively. For two substrates, the analytes were both deposited on the surface of graphene/Cu foils, thus the number of molecules contributing to Raman signals was only related to the concentration of the analyte and \( N_{\text{bulk}}/N_{\text{SERS}} = 10^7 \). For RhB, the peak intensities \( I_{\text{SERS}} \) and \( I_{\text{bulk}} \) at \( 1649 \text{ cm}^{-1} \) were 645 (a.u) and 1255 (a.u). The EF for RhB is estimated to be \( \sim 5.14 \times 10^6 \). For R6G, the peak intensities \( I_{\text{SERS}} \) and \( I_{\text{bulk}} \) at \( 612 \text{ cm}^{-1} \) were 452 (a.u) and 534 (a.u). The EF for R6G is calculated to be \( \sim 8.46 \times 10^6 \). In fact, the EFs should be higher than the values calculated as the Au nanoislands could cover a part of molecules and much less molecules contribute to the Raman intensity \( I_{\text{SERS}} \).

The effective diameter of Au nanoislands is estimated as the diameter of a circle surrounding the nanoisland. The average inter-island distance was 18.1 nm, 6.2 nm, 7.0 nm, 9.0 nm, 10.6 nm and 11.3 nm for 2 nm, 4 nm, 6 nm, 8 nm, 10 nm and 18 nm Au, respectively.
Supporting figures

Fig. S1 SEM images for (a) 2 nm, (b) 4 nm, (c) 6 nm, (d) 8 nm, (e) 10 nm and (f) 18 nm Au on graphene/Cu substrates, giving an effective diameter of (g) ~15.5 nm and a particle density of $828/\mu m^2$ for 2 nm Au, (h) ~24.2 nm and a particle density of $1071/\mu m^2$ for 4 nm Au, (i) ~32.7 nm and a particle density of $604/\mu m^2$ for 6 nm Au, (j) ~44.1 nm and a particle density of $357/\mu m^2$ for 8 nm Au, (k) ~55.6 nm and a particle density of $225/\mu m^2$ for 10 nm Au, (l) ~78.3 nm and a particle density of $127/\mu m^2$ for 18 nm Au, respectively. The scale bar in (a-f) is 500 nm.
Fig. S2 Simulated electric field intensity distribution of Au/graphene/Cu hybrid system at 1100 nm in the x-z plane for Au particle diameter $d$ and period $p$ to be (a) $d=70$ nm, $p=60$ nm and (b) $d=80$ nm, $p=60$ nm. The gray dot lines are 1 nm-thick graphene. The scale bar is 10 nm.

Fig. S3 The intensity of SERS signal at 1649 cm$^{-1}$ versus 11 different molecule concentration of RhB.
**Fig. S4** (a) SERS spectra of R6G (4 nm Au/R6G/graphene/Cu) with six different molecular concentrations. * marks the G band of graphene. (b) The intensity of SERS signal at 612 cm\(^{-1}\) versus the concentration of R6G.

**Fig. S5** Raman spectra of (a) RhB and (b) R6G on different substrates with different concentrations. Raman spectra of \(10^{-9}\) M in 4 nm Au/analyte/graphene/Cu structure (dark green lines) and \(10^{-2}\) M on graphene/Cu substrate (rose lines), respectively.
Fig. S6 The intensity of SERS signal versus the concentration of (a) Sudan III at 1345 cm$^{-1}$ and (b) Sudan IV at 1344 cm$^{-1}$.

Notes and references