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Electronic Supplementary Information for

Strong Light-matter Interactions in Sub-nanometer Gaps Defined by Monolayer Graphene: Towards Highly Sensitive SERS Substrates

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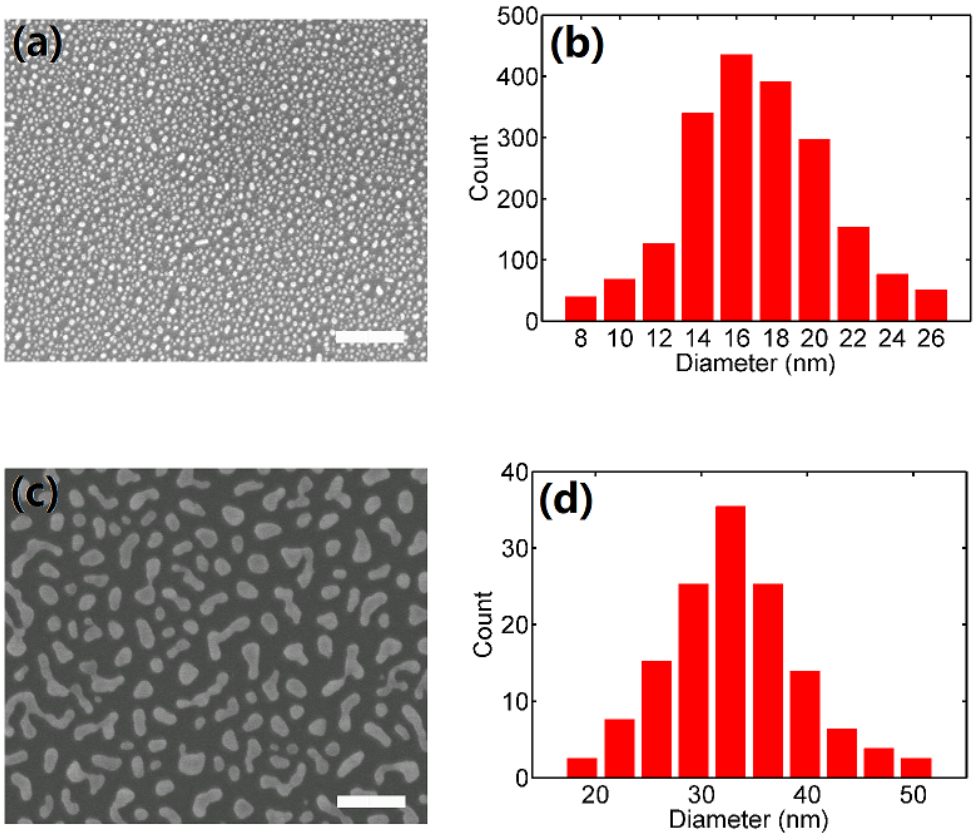

Fig. S1 SEM and size distribution histogram of Au NPs obtained by annealing (a) 4 nm- and (c) 8 nm-thick Au film, giving an diameter of (b) ~16 nm and a particle density 1980/μm^2 for 4 nm Au; (d) ~32 nm and a particle density 138/μm^2 for 8 nm Au, respectively. The scale bar in a and c is 200 nm.

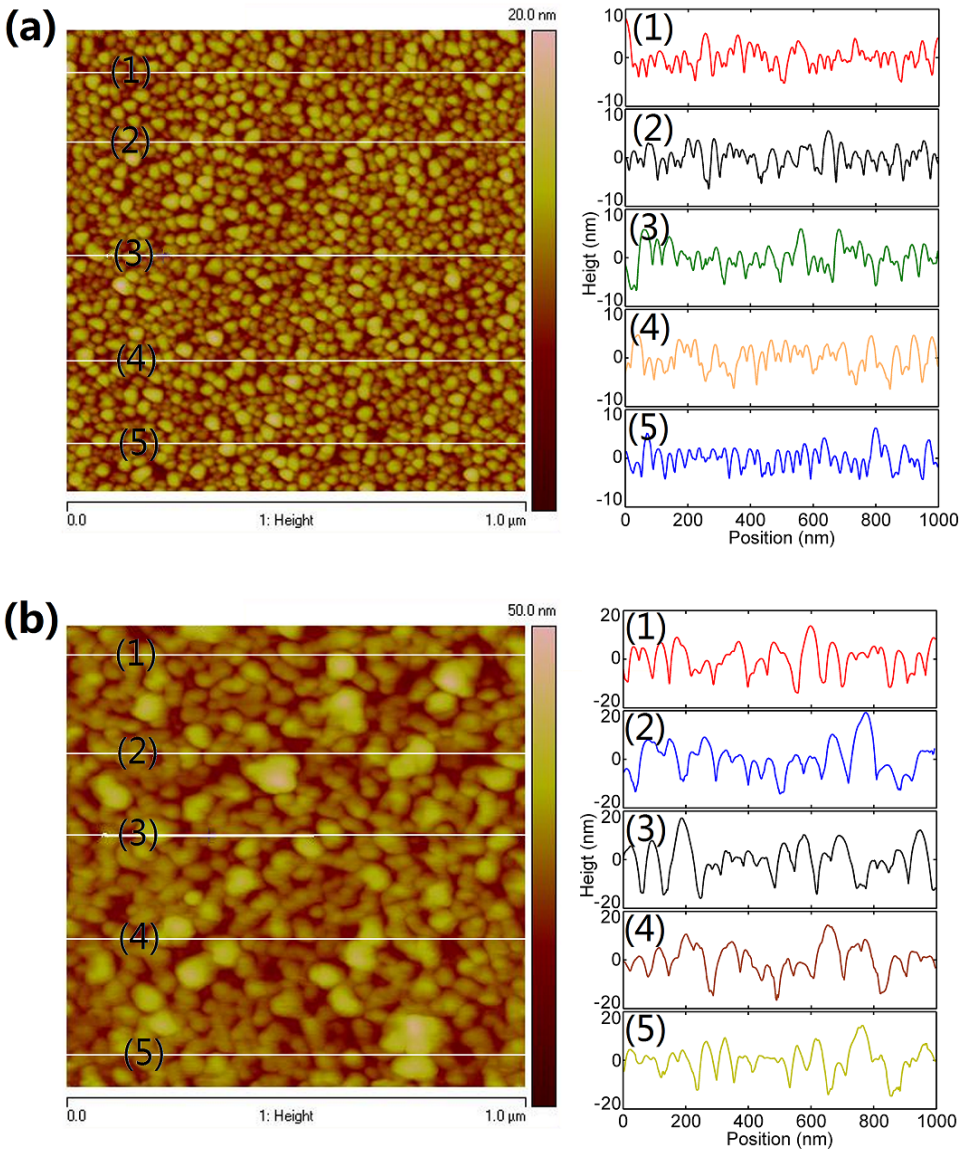

Fig. S2 AFM images and cross-sections along the white lines marked by numbers for (a) 4 nm Au and (b) 8 nm Au, respectively.

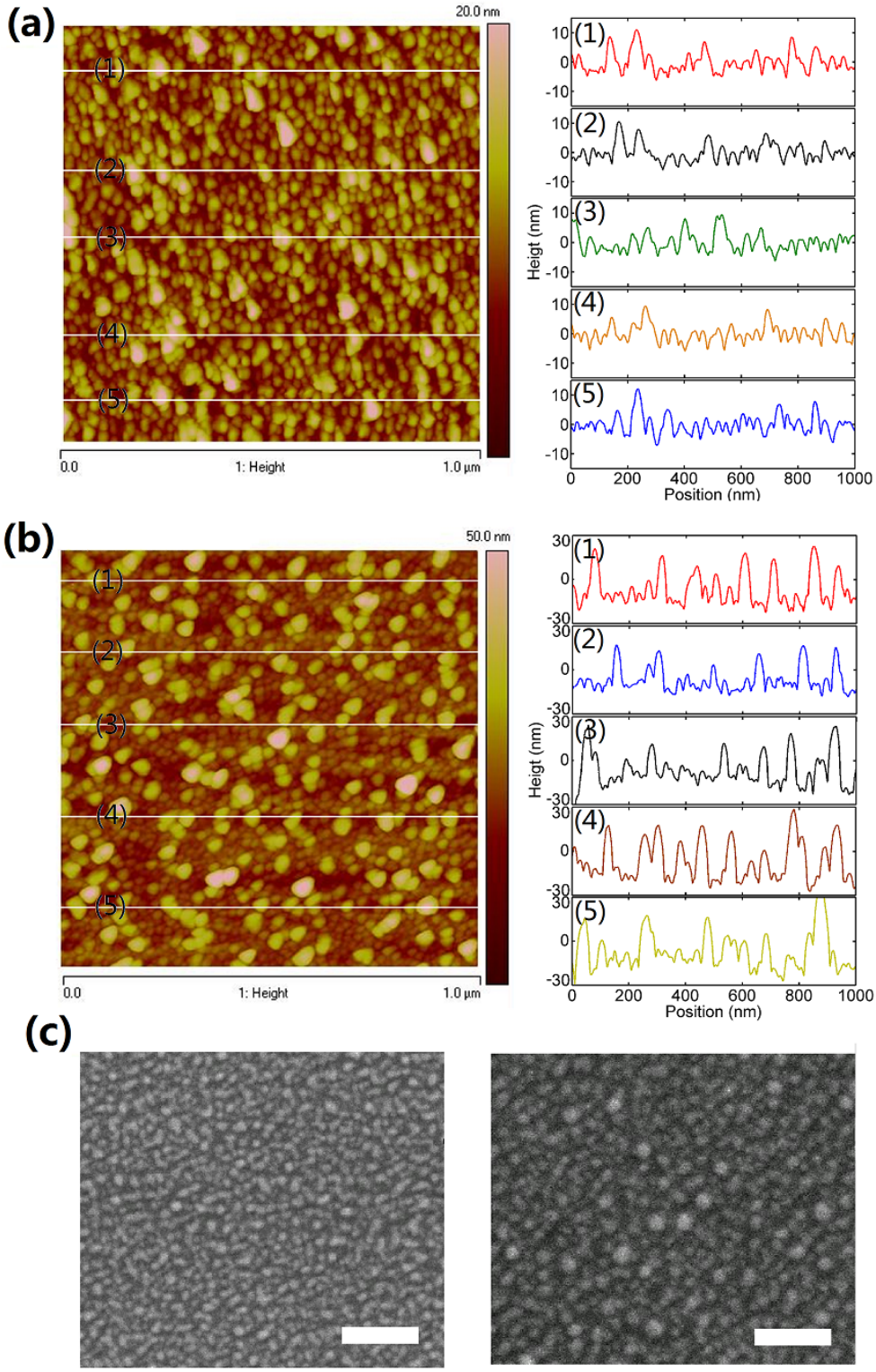

Fig. S3 AFM images and cross-sections along the white lines marked by numbers for (a) 4 nm Au/1LG/4 nm Au and (b) 8 nm Au/1LG/8 nm Au, respectively. (c) SEM images of 4 nm Au/1LG/4 nm Au and 8 nm Au/1LG/8 nm Au hybrid structures. The scale bar is 200 nm.

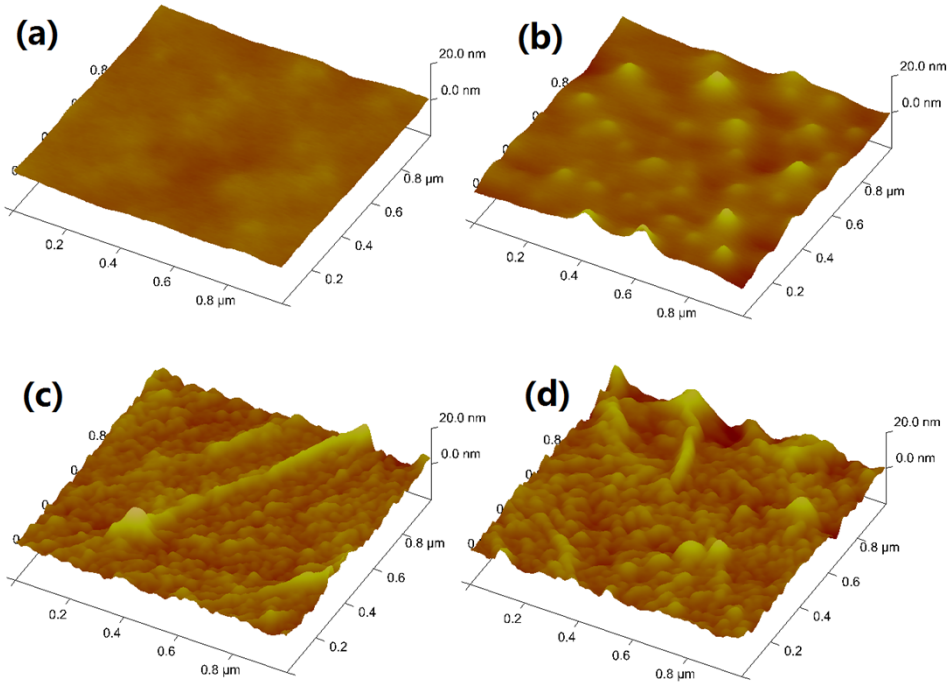

Fig. S4 AFM images of 1LG-covered (a, c) 4 nm Au and (b, d) 8 nm Au (a, b) before and (c, d) after annealing the whole structure again when graphene is transferred onto the first layer of Au NPs, respectively.

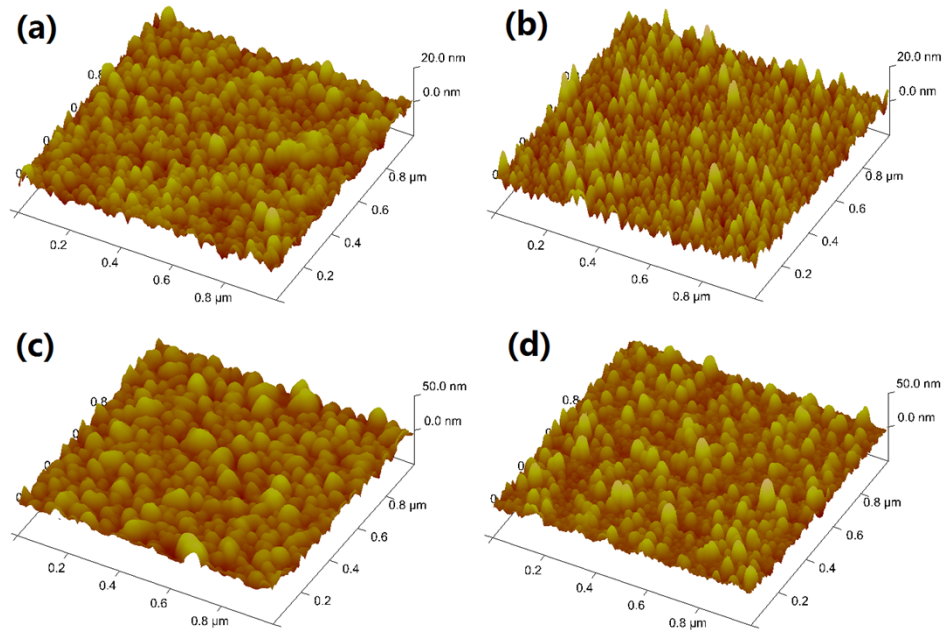

Fig. S5 AFM images of (a) 4 nm Au/4 nm Au, (b) 4 nm Au/1LG/4 nm Au, (c) 8 nm Au/8 nm Au and (d) 8 nm Au/1LG/8 nm Au, respectively.

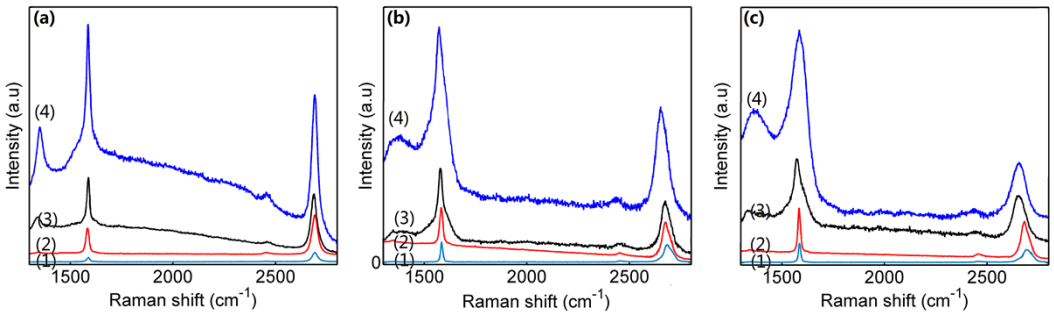

Fig. S6 Raman spectra of (a) one layer, (b) two layers and (c) three layers of graphene on quartz (curve 1), on 4 nm Au before (curve 2) and after (curve 3) annealing the whole structure when graphene is transferred onto the first layer of Au NPs and embedded in between two layers of vertically stacked 4 nm Au (curve 4), respectively. In each picture, the Raman spectra are measured under the same conditions and shown on the same intensity scale.

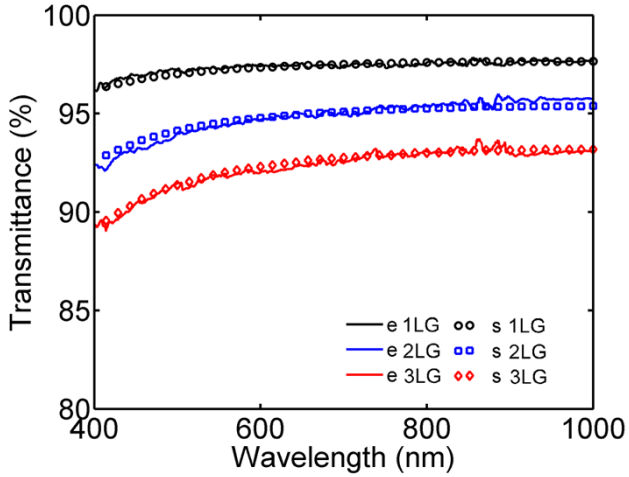

Fig. S7. Measured (lines) and simulated (dots) transmission spectra for one layer, two layers and three layers of graphene on quartz substrate, 'e' stands for experimentally measured results and 's' for the simulation, respectively.

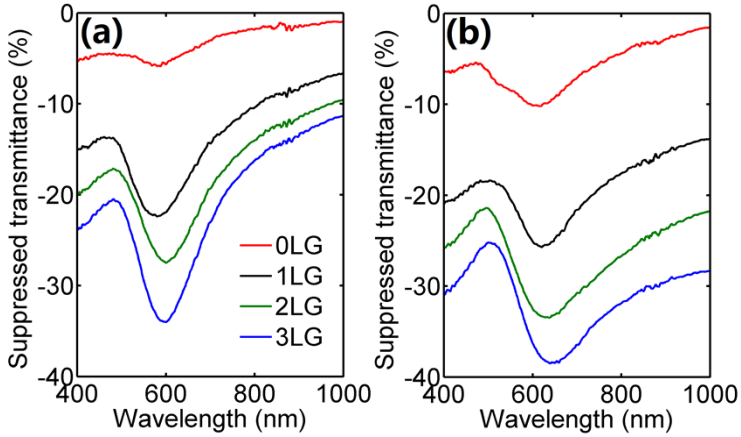

Fig. S8. Suppressed transmittance for (a) 4 nm Au/graphene/4 nm Au relative to 4 nm Au and (b) 8 nm Au/graphene/8 nm Au relative to 8 nm Au when having different number of graphene layers sandwiched.

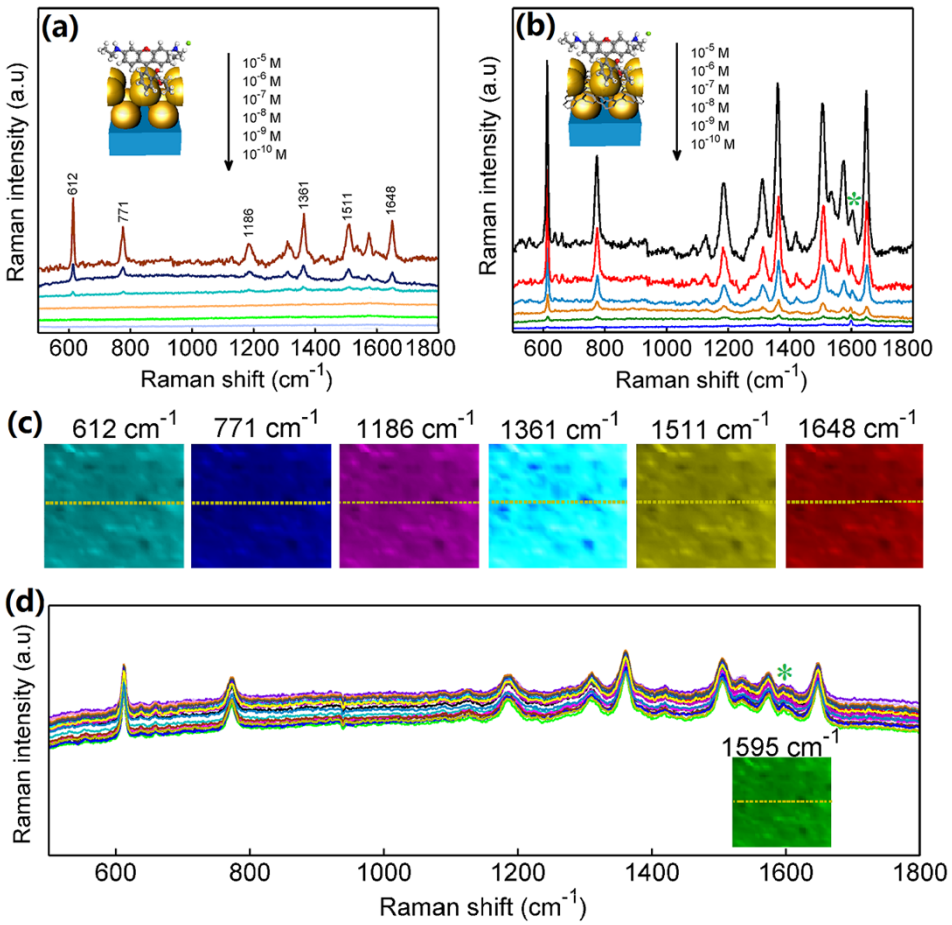

Fig. S9. SERS spectra of R6G on (a) 4 nm Au/4 nm Au and (b) 4 nm Au/1LG/4 nm Au with 6 different molecular concentrations. The insets show the schematic of sample structures. (c) Spatial resolved Raman intensity mappings of 10^{-7} M R6G on 4 nm Au/1LG/4 nm Au with Raman peaks at 612 cm^{-1} (cyan), 771 cm^{-1} (blue), 1186 cm^{-1} (magenta), 1361 cm^{-1} (light blue), 1511 cm^{-1} (yellow) and 1648 cm^{-1} (red) on the same area. (d) Raman spectra taken from the mappings of (c) along the yellow dotted lines. The inset shows the G-band mapping of graphene at 1595 cm^{-1} (green). * in (b) and (d) marks the G-band of graphene. The Raman spectra are obtained on the same conditions for all figures.

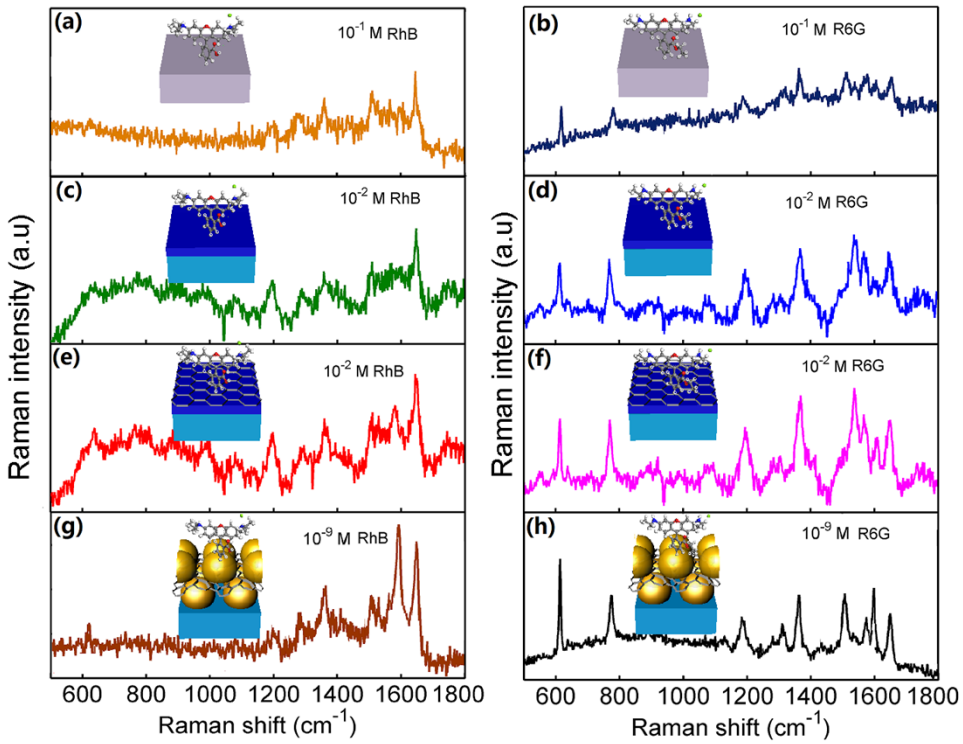

Fig. S10 Raman spectra of (a, c, e, g) RhB and (b, d, f, h) R6G on different substrates with different concentrations. Raman spectra of (a, b) 10^{-1} M on quartz substrate, (c, d) 10^{-2} M on SiO_2/Si substrate, (e, f) 10^{-2} M on 1LG/SiO_2/Si substrate and (g, h) 10^{-9} M on 4 nm Au/1LG/4 nm Au sandwich structure, respectively. All Raman spectra are measured under the same conditions and are shown on the same intensity scale. Inset pictures are the schematically sample structures.

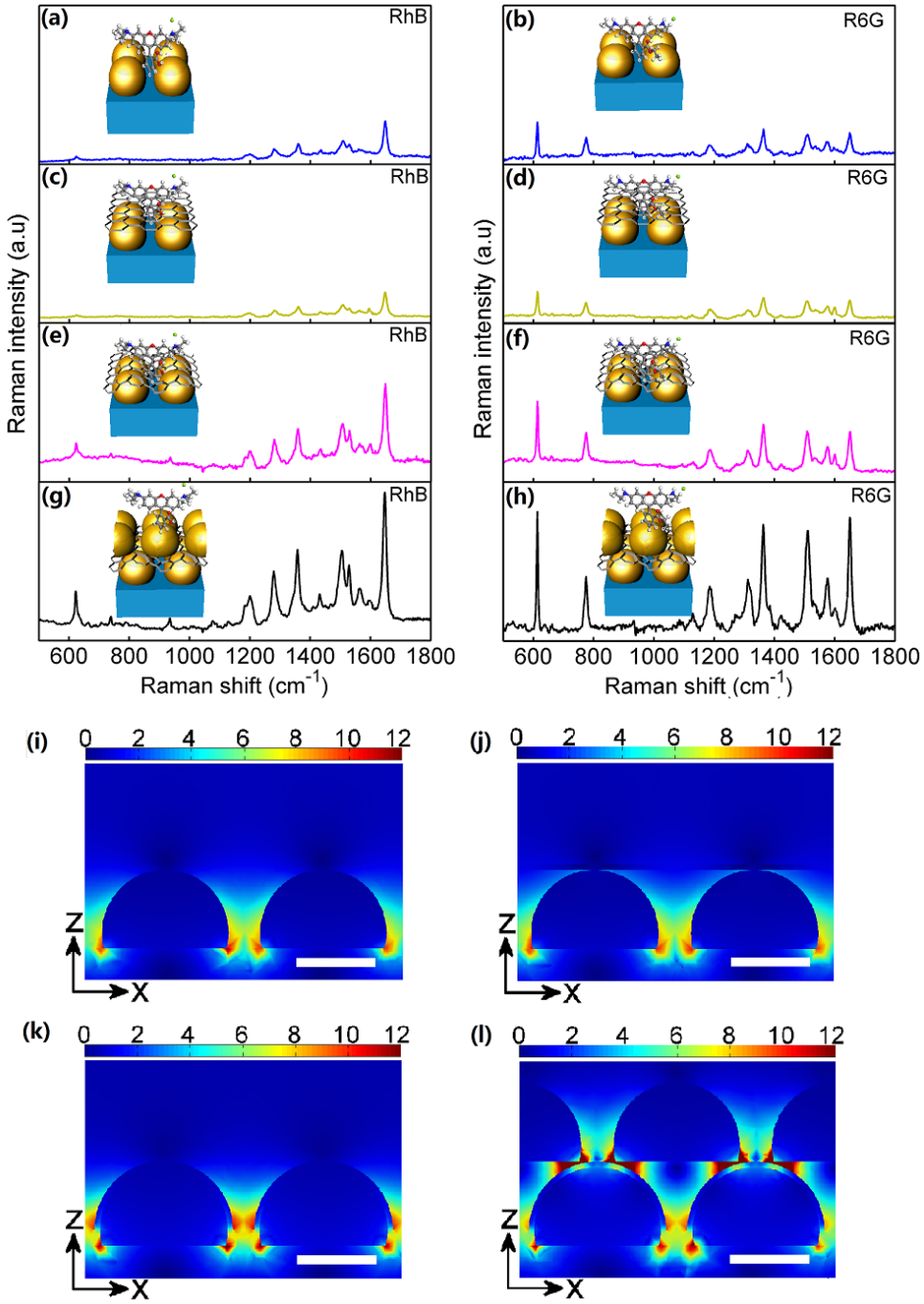

Fig. S11 Comparison of the Raman spectra of RhB and R6G with different substrates. Raman spectra of 10^{-5} M (a, c, e, g) RhB and (b, d, f, h) R6G on (a, b) 4 nm Au, 1LG-covered 4 nm Au (c, d) before and (e, f) after annealing the whole structure when graphene is transferred onto Au NPs and (g, h) 4 nm Au/1LG/4 nm Au sandwich structure, respectively. All Raman spectra are measured under the same conditions and are shown on the same intensity scale. The insets are the schematically sample structures. Simulated electrical field intensity distributions in the xz plane at 532 nm for (i) Au NPs, (j) 1LG suspending on Au NPs, (k) 1LG-veiled Au NPs and (l) Au NPs/1LG/Au NPs, respectively. The scale bar is 10 nm.

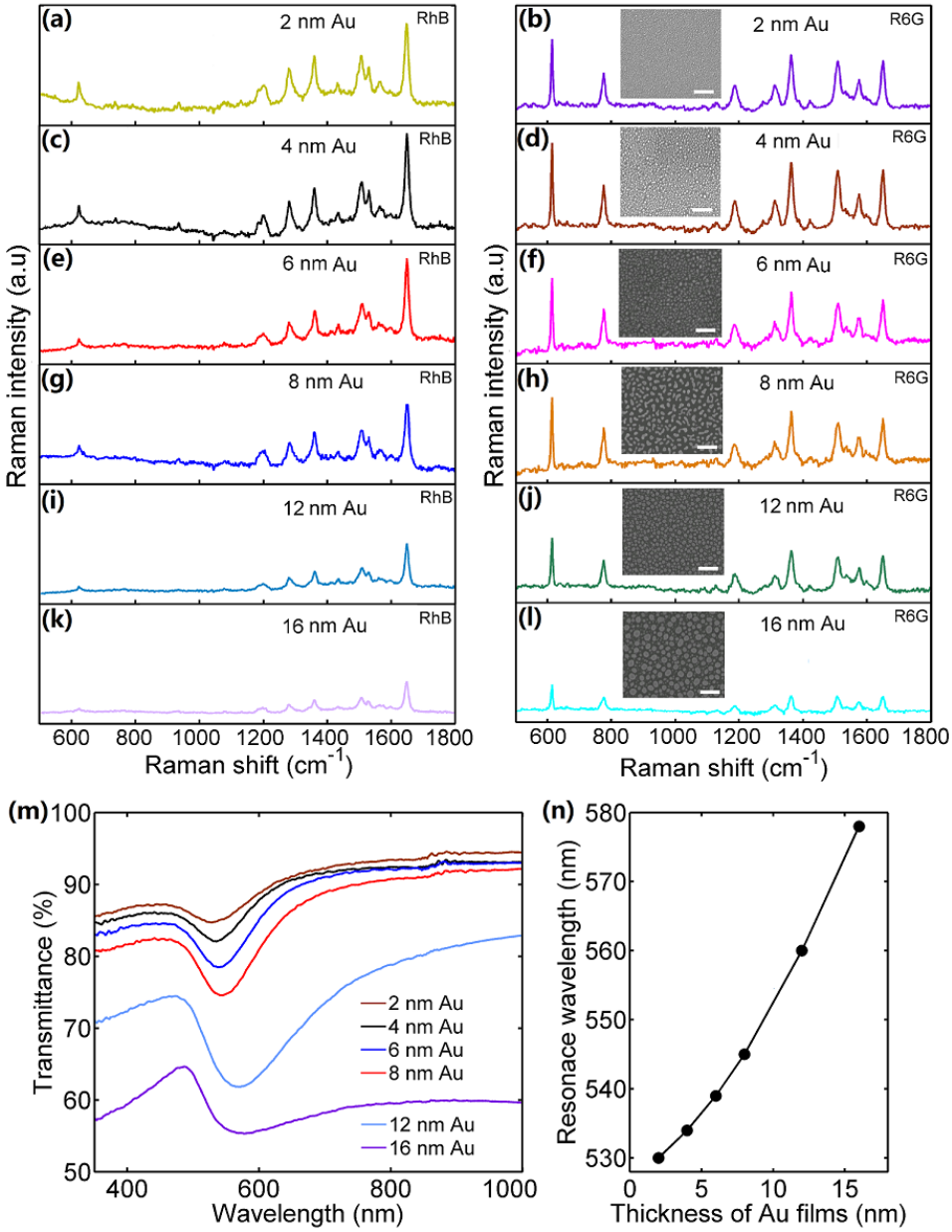

Fig. S12 Raman spectra of 10^{-5} M (a, c, e, g, i, k) RhB and (b, d, f, h, j, l) R6G on (a, b) 2 nm, (c, d) 4 nm, (e, f) 6 nm, (g, h) 8 nm, (i, j) 12 nm and (k, l) 16 nm Au, respectively. All Raman spectra are measured under the same conditions and are shown on the same intensity scale. The insets in (b, d, f, h, j, l) present the SEM images of Au NPs after annealing different thicknesses of Au film. The scale bar is 200 nm. (m) The measured transmission spectra for 2 nm, 4 nm, 6 nm, 8 nm, 12 nm and 16 nm Au, respectively. (n) The resonance wavelength shifts with respect to the original Au film thickness.

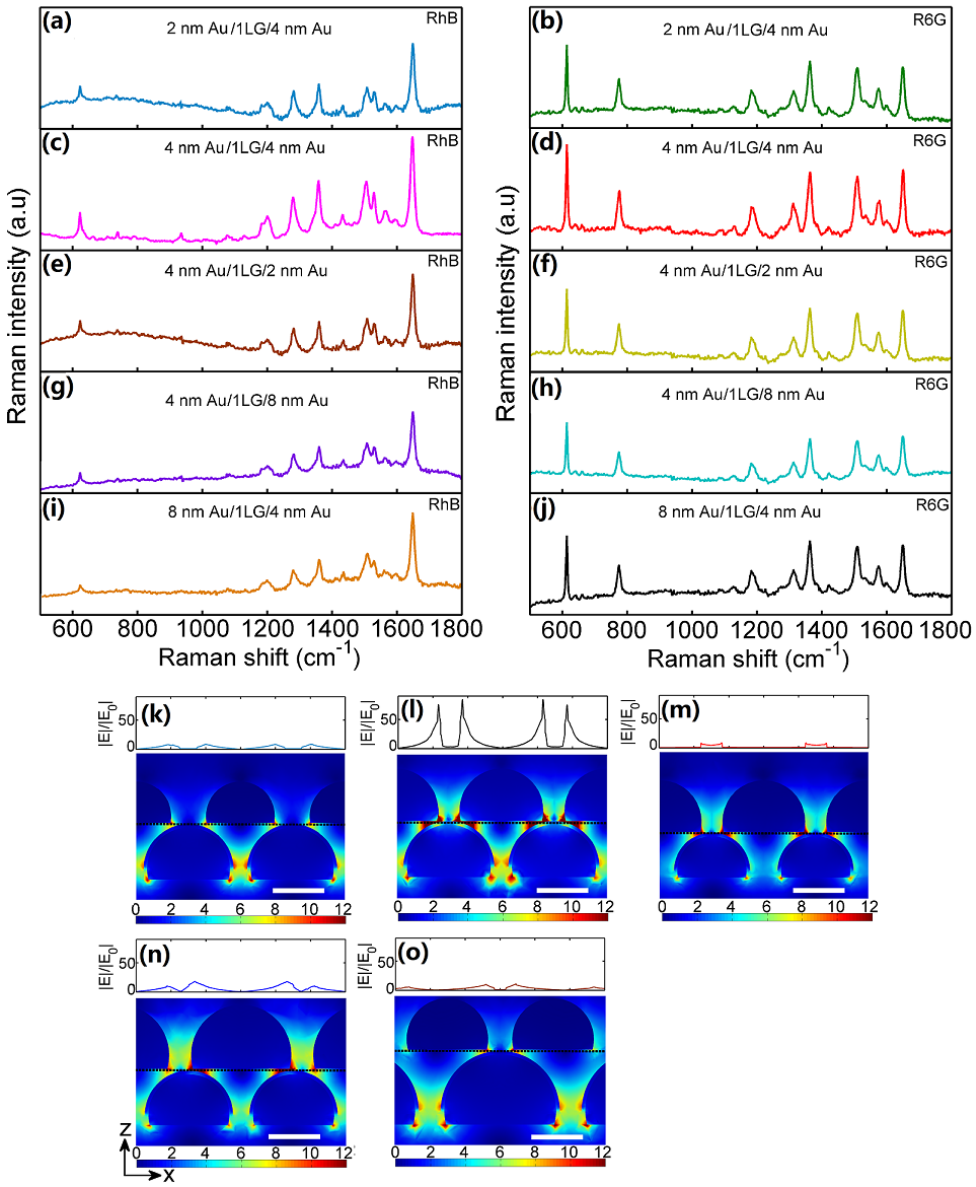

Fig. S13 Raman spectra of 10^{-5} M (a, c, e, k, g, i) RhB and (b, d, f, h, j) R6G on (a b) 2 nm Au/1LG/4 nm Au, (c, d) 4 nm Au/1LG/4 nm Au, (e, f) 4 nm Au/1LG/2 nm Au, (g, h) 4 nm Au/1LG/8 nm Au and (i, j) 8 nm Au/1LG/4 nm Au, respectively. All Raman spectra are measured under the same conditions and are shown on the same intensity scale. Simulated electrical field intensity distributions in the xz plane at 532 nm for (k) 12 nm-diameter Au NPs/1LG/16 nm-diameter Au NPs, (l) 16 nm-diameter Au NPs/1LG/16 nm-diameter Au NPs, (m) 16 nm-diameter Au NPs/1LG/12 nm-diameter Au NPs, (n) 22 nm-diameter Au NPs/1LG/16 nm-diameter Au NPs and (o) 16 nm-diameter Au NPs/1LG/22 nm-diameter Au NPs structure, respectively. The scale bar is 10 nm. The top of each picture shows the normalized electrical field intensity magnitude along the black dot lines.