Supplementary Information:

Surface-Enhanced Raman Scattering Study on Graphene-Coated Metallic Nanostructure Substrates

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Abstract

Graphene, which has a linear electronic band structure, is widely considered as a semimetal. In the present study, we combine graphene with conventional metallic surface-enhanced Raman scattering (SERS) substrates to achieve higher sensitivity of SERS detection. We synthesize high-quality, single-layer graphene sheets by chemical vapor deposition (CVD) and transfer them from copper foils to gold nanostructures, *i.e.*, nanoparticle or nanohole arrays. SERS measurements are carried out on methylene blue (MB) molecules. The combined graphene nanostructure substrates show about threefold or ninefold enhancement in the Raman signal of MB, compared with the bare nanohole or nanoparticle substrates, respectively. The difference in the enhancement factors is explained by the different morphologies of graphene on the two substrates with the aid of numerical simulations. Our study indicates that applying graphene to SERS substrates can be an effective way to improve the sensitivity of conventional metallic SERS substrates.

Keywords: Graphene, SERS, Plasmonics, Nanostructure

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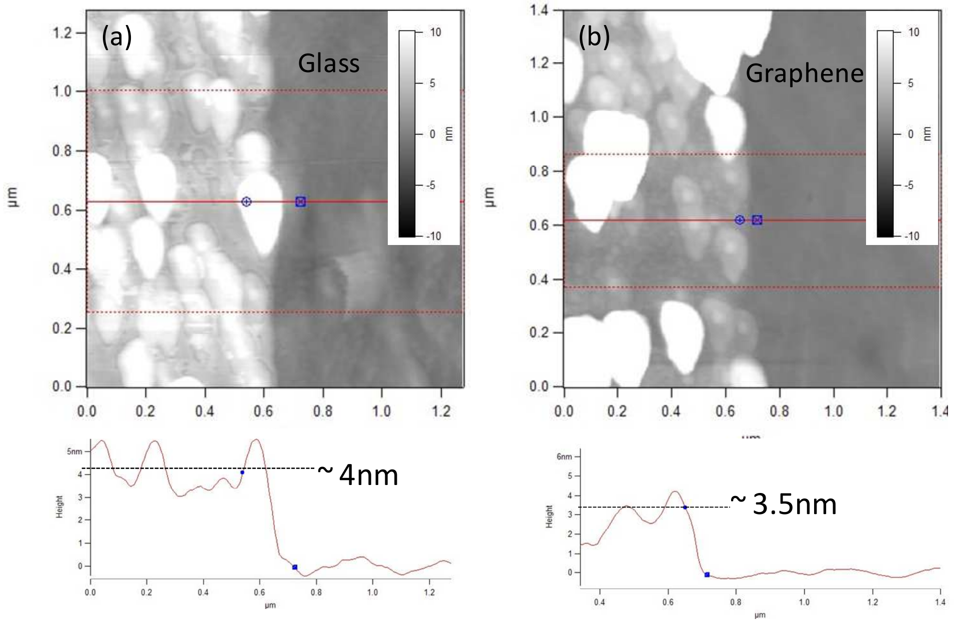

Figure S1. Atomic Force Microscope (AFM) measurement of the coverage of methylene blue molecules (a) on glass and (b) on graphene. Molecules on the right part of each image were first scratched away by an AFM tip in contact mode. A second scan was used to image the thickness of the molecular layer. For both substrates, a molecular layer of ~ 4 nm is adsorbed onto the substrates.

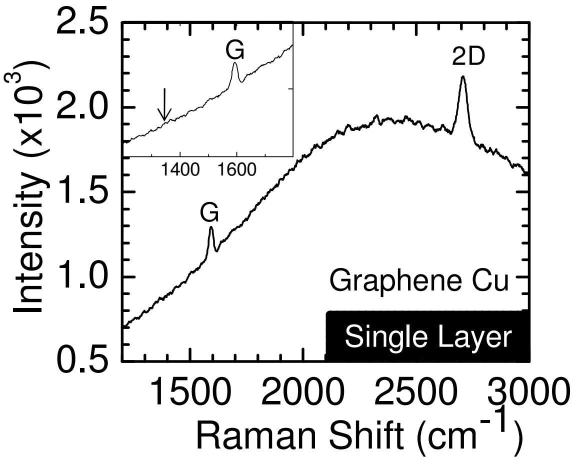

Figure S2. Raman spectrum of as-grown graphene on copper foil. Laser excitation of 514 nm is used. No observation of an apparent D band suggests that we have high graphene quality.

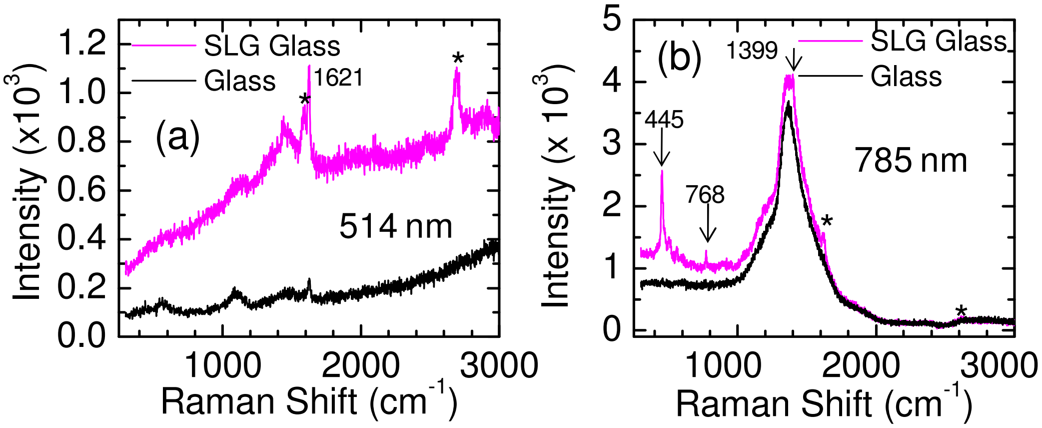

Figure S3. Raman spectra of methylene blue on glass and single layer graphene (SLG) substrates with (a) 514 nm excitation, and (b) 647 nm excitation. 2D and G bands of graphene are marked by *.

Even though far from the absorption peak of methylene blue (~ 665 nm), Raman measurements with 514 nm and 785 nm laser excitation still show the SERS enhancement from graphene. Interestingly, SERS enhancement for methylene blue is sensitively dependent on the excitation laser wavelength: For 514 nm excitation, it seems that only the 1621 cm^{-1} Raman peak is enhanced, while for 785 nm excitation, the 445 cm^{-1} peak is strongly enhanced. SERS enhancement from graphene is chemically mechanized, thus the enhancement for a certain Raman peak depends on the laser excitation energy and the relative electronic energy level where the phonon is generated with respect to the Fermi level of graphene.

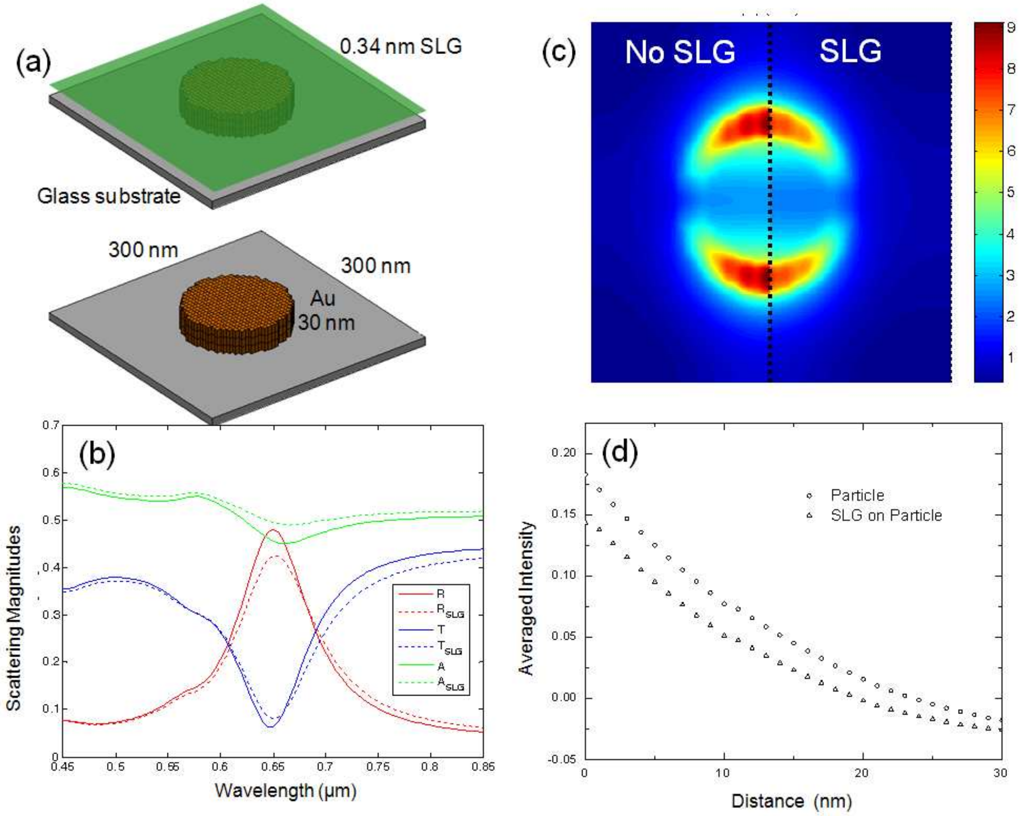

Figure S4. Comparative simulations of nanoparticle array with and without graphene. (a) The simulated nanoparticle geometry. (b) Simulated scattering magnitudes: reflection (R), transmission (T) and absorption (A). (c) Electric field intensity distributions 1 nm above the Au surface under a 660 nm incident wave. The left half, without graphene, and right half, with graphene. (d) Distance dependent averaged electric field intensity in a unit cell away from the structure surface (distance = 0 nm at the Au surface) into the air. Intensity is plotted on a logarithmic scale.