Supplementary Information

Metal-Dielectric-Graphene Sandwich for Surface Enhanced Raman Spectroscopy

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Experimental Section

Single-layer graphene was prepared by mechanical exfoliation of Kish graphite (Graphene supermarket) on SiO2/Si (285nm thick oxide) wafer. Optical imaging and Raman spectrum were employed to identify monolayer graphene and its quality [1]. Hafnia coating was deposited by ALD (Cambridge Nanotech), the chamber was kept at room temperature before graphene samples were put inside, and then increase to 270 °C at low vaccum level. One single cycle of an ALD is composed of 1s pulse of TEMAH (tetrakis (ethylmethylamido) hefnium) and successive 1s pulse of water vapor followed by nitrogen purge of 5s. Different thicknesses of hafnia were controlled by using 10, 20, 30 and 40 cycles. In all the experiments with or without hafnia, gold was deposited by E-beam evaporation. Average thickness of the deposited gold film was measured by an in-situ crystal in the chamber. Then the gold films were annealed at 300 ℃ in H_2/Ar atmosphere (ratio 1:9) for 60 min. The films were transformed into a distribution of nanoislands and were characterized by SEM and AFM.

Rhodamine B (RhB), a widely used dye in surface enhanced Raman spectroscopy, was employed as a probe molecule because it is usually very difficult to be detected by conventional Raman spectroscopy at low concentrations. RhB (Rhodamine B) solutions with different concentrations were made by dissolving RhB powder in methanol at room temperature. The gold-dielectric-graphene substrates were immerged in the solution and dried gradually at ambient.

Both the Raman and SERS measurement were carried out with a 633 Raman system (WITec CRM200), the Raman band of a Si wafer at 520 cm^{-1} was used as a reference to calibrate the spectrometer.

FDTD simulations:

Three-dimensional FDTD simulations were performed by commercial software. In the simulations, the graphene sheet is treated as an anisotropic material with a thickness of 0.5 nm. The out plane dielectric constant of graphene is set as 2.5 based on the dielectric constant of graphite. The in-plane optical conductivity is derived from radom-phase approximation (RPA) in the local limit[S2]. The optical constants of Au, HfO_2 were taken from Ref. 2 in the spectrum range of 200 nm to 1000 nm[S3]. Perfectly matched layer boundary condition was applied in the z-direction, while periodic boundary condition was set in the x and y directions.

References

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S2. L. A. Falkovsky,S. S. Pershoguba, *Phys. Rev. B,* **2007,** *76* (15), 153410.

S3. E. D. Palik, Handbook of Optical Constants of Solids. Academic: **1985**.