

Supplementary Information

"Enhanced light-matter interactions in graphene-covered gold nanovoid arrays"

Xiaolong Zhu,^{†,‡} Lei Shi,[¶] Michael S. Schmidt,[§] Anja Boisen,[§] Ole Hansen,^{§,||}
Jian Zi,[¶] Sanshui Xiao,^{*,†,‡} and N. Asger Mortensen^{*,†,‡}

Department of Photonics Engineering, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark, Center for Nanostructured Graphene (CNG), Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark, Department of Physics, Key Laboratory of Micro- and Nano-Photonic Structures (Ministry of Education) and State Key Laboratory of Surface Physics, Fudan University, Shanghai 200433, China, Department of Micro and Nanotechnology, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark, and Center for Individual Nanoparticle Functionality (CINF), Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

E-mail: saxi@fotonik.dtu.dk; asger@mailaps.org

*To whom correspondence should be addressed

[†]DTU Fotonik

[‡]CNG

[¶]Fudan University

[§]DTU Nanotech

^{||}CINF

Chemicals and Methods

Preparation of gold nanovoid arrays.

Glass substrates were firstly rinsed in an ultrasonic bath with deionized water and ethanol, and subsequently dried in a nitrogen gas flow. The colloidal crystals were made of monodispersed polystyrene latex spheres (ThermoFisher Scientific) supplied as a 1 wt.% water solution. Before usage, the suspensions were homogenized by successive and gentle inversions for 5 minutes followed by a sonication for 30 s. All solvents and chemicals here were of reagent quality and were used without further purification. The commercial cyanide free gold plating solution (TSG-250) was obtained from Transene Company, Inc. (Danvers, MA, USA). Evaporated gold electrodes used as substrates were prepared by evaporating a 10-nm-thick Cr adhesion layer, and then a 150 nm Au film onto the treated glass substrates. These gold coated substrates were thoroughly cleaned in ultrasonic bath with deionized water and ethanol for 0.5 h, and then dried under a gentle nitrogen gas flow. Two-dimensional colloidal monolayers of polystyrene spheres assembled on these substrates were prepared by a self-assembly method.¹ Electrochemical deposition was performed in a thermostatic cell at room temperature using a conventional three-electrode configuration controlled by an electro-chemical workstation (CHI-760C, CHI, US). The gold substrate with spheres array was used as the working electrode in addition to a large-area platinum counter electrode and a CHI saturated calomel reference electrode (SCE). Gold films were deposited under static potential conditions at 0.05 V vs. SCE. By controlling the amount of current passed through the system in the electrochemical deposition, gold structures shaped from open periodic dish arrays up to fully encapsulated spherical cavities can be obtained. After electro-chemical deposition, the samples were immersed in Tetrahydrofuran for 72 h to dissolve the polystyrene spheres.

SERS of Rhodamine 6G (R6G) solution.

To investigate the detection capabilities of our SERS substrates, we choose R6G as probe molecule. As the gold nanovoid arrays exhibit roughness, the resultant SERS substrates reveal unique surface

superhydrophobicity. In our experiment, a droplet of R6G ethanol (instead of water) solution with a concentration of 10 μM (10 mM for the reference substrates) was dropped on the SERS substrate, followed by the evaporation of ethanol solvent. The initial volume of the injected R6G solution is 1 μL . With the spreading of ethanol, the volume increases obviously. After the solvent was evaporated, a final spot area is measured to be a circle with a radius of about 1 cm. We randomly selected 5 different probe sites around the center of the drop to avoid coffee-ring effects² and averaged them to obtain the final result. The Raman spectrum of bulk R6G is taken by making a pile of powder, flattening it and doing the spectra directly on the flattened surface, which serves as a reference spectrum.

Optical characterization

The Raman signals displayed in Figure 5 were performed using a Thermo Scientific DXR Raman microscope with a 50X objective focusing a 532 nm laser on the samples. The laser power was kept at 1 mW for all measurements with an integration time of 1 s in Figure 5(a) and 5 s in Figure 5(b-e). Five spectra were collected at each point and the average spectra were plotted. Optical reflectance spectra under normal incident light were measured using UV-vis-NIR spectroscopy connected to a microscope and angle-resolved spectra (PG Pro and R1, Idea Optics Co., China) were measured by a fiber-coupled setup.

Supplementary discussions

Graphene thickness in simulation

Graphene is a monolayer of sp² carbon atoms with a thickness about 0.34 nm. In our numerical simulations, we treated graphene as an effective medium with a thickness of 1 nm. This value is reasonable for CVD-grown graphene if we consider the inhomogeneities, which can lead to a thicker graphene layer. In order to verify the impact of this assumption on the final results, we

performed simulations with different graphene thickness on the structure #1, as shown in Figure S3. We found that the simulated resonance shifts with an effective graphene thickness of 1 nm fit quite well with the experimental results in Figure 3(a). Besides, the simulated resonance for the graphene-covered GNVA becomes weaker and broader too when compared with that for the bare GNVA, which is as expected in agreement with the experiments.

Absorption and resonances shift with multilayered graphene

Absorption and resonances shift of GNVA covered with multilayered graphene enables easy detection of the graphene sheet and an unambiguous quantification of the number of layers in the short-range region, which is governed by the fact that electric field for surface plasmons on a planar metal surface decays exponentially over a length scale of around 50-100 nm in the different dielectric materials.³ From Eq. (1) and (2) in this Letter, we find that the optical absorption and resonances shift are strongly correlated with the EM field. In order to clarify the statements in the context, we calculated the vertical field distribution which is shown in Figure S4(a). From Figure S4(a), we find that the field at the opening of the nanovoid decays exponentially to the free space. However, for $Z \sim$ several nanometers (several layers of graphene), the change of the EM field is neglectable, while for larger Z , the EM field decays a lot.

From the context we know that the resonance in graphene-covered GNVA shifts towards longer wavelength and becomes broader with lower reflectance (higher absorption) when compared with that for the bare GNVA. In our simulations for multilayered graphene, the wavelength shift per layer decreases exponentially when increasing the number of graphene layers and the total shift saturates when approaching 10 layers of graphene.⁴ At the same time, the resonance will smear out and be undistinguishable in the end (e.g. 10 layers of graphene, as show in Figure S4(b)). An empirical equation reported in Refs. 2 and 3 that describes the peak wavelength shift versus the thickness of the refractive index change is written as $\Delta\lambda = m\Delta n[1 - \exp(-d/L_d)]$, where Δn is the difference between the refractive index of the sensing material and the surrounding medium; m is the refractive index sensitivity; d is the thickness of graphene; and L_d is the characteristic

decay length of the electromagnetic field surrounding the plasmonic nanostructures. According to the real part of the refractive index, $n = 3$, for varying layers of graphene, a curve with $m\Delta n = 67$ nm and an electric field decay length of $L_d = 6$ nm gives a good fit to the data as shown in Figure S4(b). For $d < 3$ nm, the exponential equation can be reduced to a linear one, which agrees well with our case in the Letter. Owing to strong light-graphene interaction in our case, a relatively high refractive index sensitivity ($m \approx 22$ nm) and broadband resonance tunability (~ 60 nm) can be achieved.

Rough gold substrate

Surface-enhanced Raman scattering (SERS) has been proved to be one of the most sensitive spectroscopic techniques for chemical analysis. This technique can be easily achieved with the presence of metallic nanoparticles, mainly gold or silver. The SERS mechanism is partly attributed to electromagnetic field enhancement by surface plasmons of metallic nanoparticles. A rough Au substrate with aggregates of Au nanoparticles has been easily obtained on glass substrates by physical sputtering under primary vacuum⁵ and is used as a reference for graphene Raman measurements in our work. The SEM picture of the rough Au substrate covered with a monolayer graphene is shown in Figure S5, where the roughness smaller than 100 nm can be distinguished.

References

- (1) Sun, J.; Tang, C.; Zhan, P.; Han, Z.; Cao, Z.; Wang, Z. *Langmuir* **2010**, *26*, 7859–7864.
- (2) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Nature* **1997**, *389*, 827–829.
- (3) Malinsky, M. D.; Kelly, K. L.; Schatz, G. C.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2001**, *123*, 1471–1482.
- (4) Chen, H.-A.; Hsin, C.-L.; Huang, Y.-T.; Tang, M. L.; Dhuey, S.; Cabrini, S.; Wu, W.-W.; Leone, S. R. *J. Phys. Chem. C* **2013**, dx.doi.org/10.1021/jp312363x.

(5) Merlen, A.; Gadenne, V.; Romann, J.; Chevallier, V.; Patrone, L.; Valmalette, J. C. *Nanotechnology* **2009**, *20*, 215705.

Supplementary figures

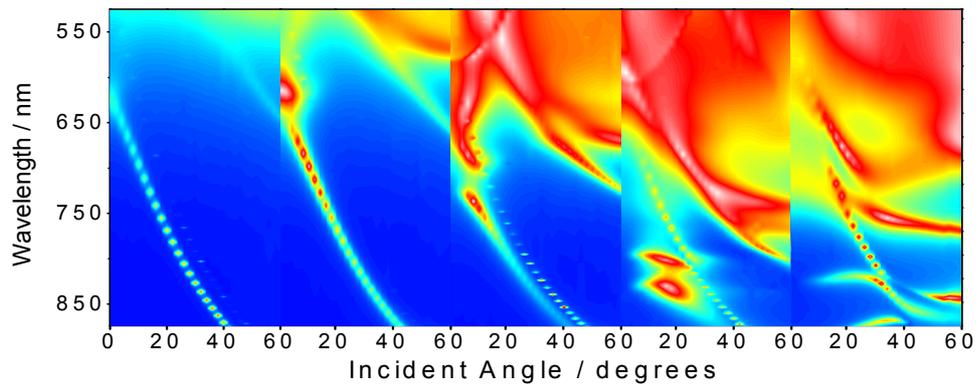


Figure S1: Simulated reflection spectra of the corresponding GNVA in Fig. 1(b) at different incident angles.

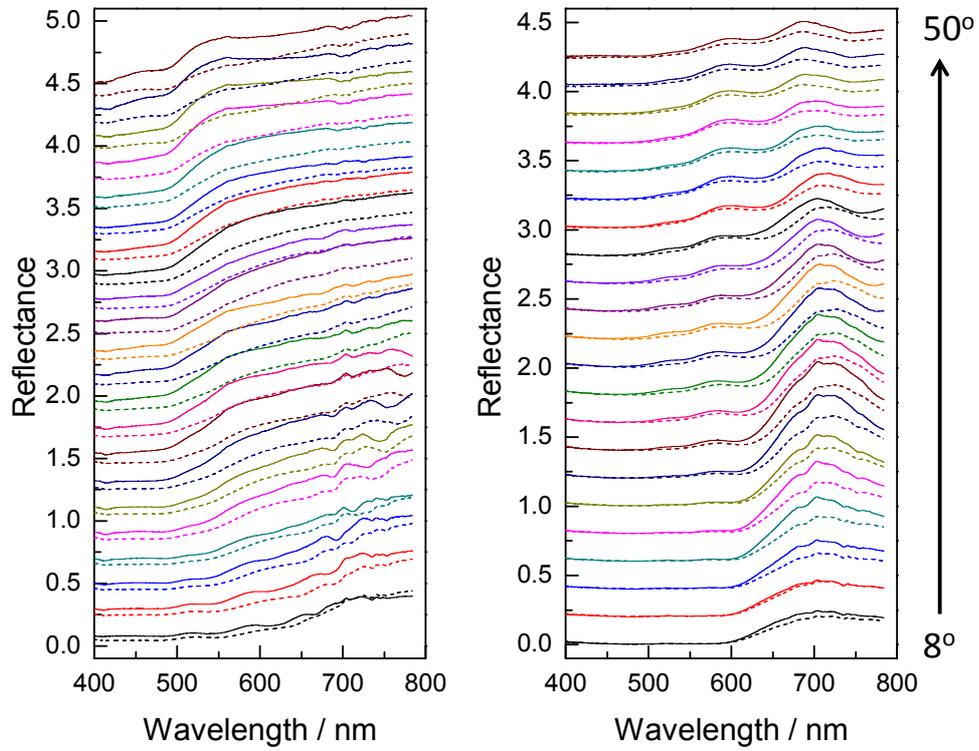


Figure S2: Measured reflection spectra of the GNVA #2 (left) and #3 (right) with (the dashed line) and without (the solid lines) monolayer graphene under oblique incidence. For the sake of clarity, each curve is shifted vertically by 0.2 unit with respect to the previous one.

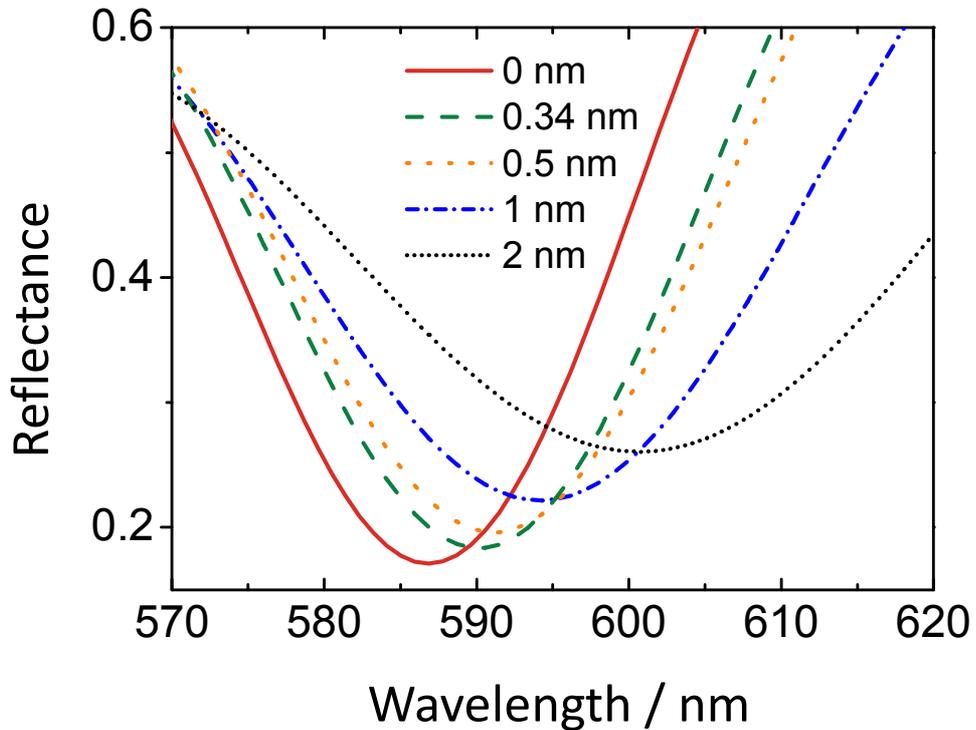


Figure S3: Simulated spectra of the GNVA #1 covered by graphene with different thickness.

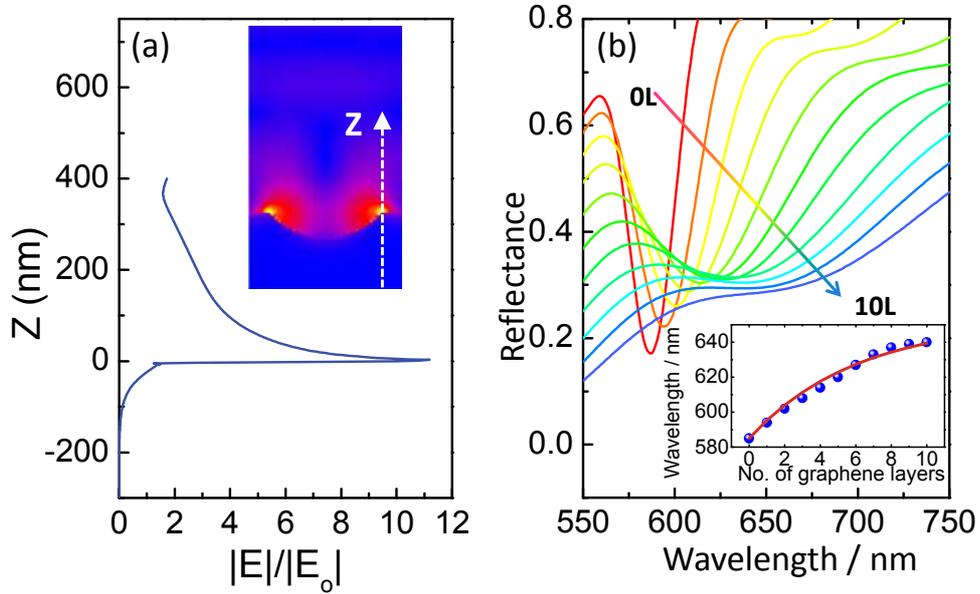


Figure S4: (a) The simulated vertical electrical field values at the positions indicated by the dashed line in the inset. Inset is the simulated field distribution for the mode m_2 of bare GNVAs #2. It should be noted that the kink at the far end of the $z > 0$ branch comes from the interference of the reflected evanescent wave with the incident wave. (b) Simulated resonance shift of the GNVAs #1 covered with 0-10 layers of graphene. The inset shows the resonance peak shift versus the corresponding graphene layers with a fitting curve by using the empirical equation.

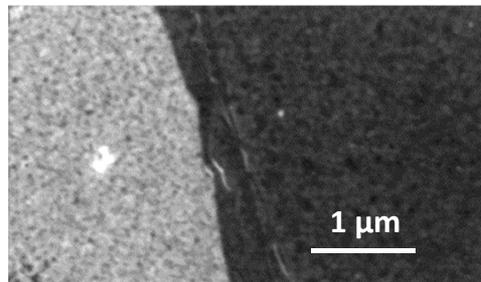


Figure S5: SEM picture of the gold rough substrate covered with a monolayer graphene. The dark part indicates the region where a monolayer CVD-graphene has been transferred.