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Polarized Plasmonic Enhancement by Au Nanostructures Probed through Raman Scattering of Suspended Graphene

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Supporting Information

ABSTRACT: We characterize plasmonic enhancement in a hotspot between two Au nanodisks using Raman scattering of graphene. Single layer graphene is suspended across the dimer cavity and provides an ideal two-dimensional test material for the local near-field distribution. We detect a Raman enhancement of the order of 10^3 originating from the cavity. Spatially resolved Raman measurements reveal a near-field localization one order of magnitude smaller than the wavelength of the excitation, which can be turned off by rotating the polarization of the excitation. The suspended graphene is under tensile strain. The resulting phonon mode softening allows for a clear identification of the enhanced signal compared to unperturbed graphene.



KEYWORDS: Raman spectroscopy, enhancement, plasmonic cavity, suspended graphene, strain

 \mathbf{F} or its fundamental physics and technological applications, graphene has attracted enormous interest since its experimental discovery.¹ It has become the model system for two-dimensional materials, and its ballistic conduction at room temperature² makes graphene a promising material for transistors, interconnects, and a variety of optoelectronic applications.^{1–3} Recently, the combination of graphene with plasmonic nanostructures has substantially improved the photo detection capabilities of graphene.^{4–6}

From a spectroscopic point of view, surface-enhanced Raman scattering (SERS) has become a spectacular application of plasmonics.⁷ It combines the generation of highly localized light fields at metal—dielectric interfaces with the variety of properties that can be obtained by Raman spectroscopy, such as strain,⁸ doping,^{9–12} or the nature of defects¹³ in the case of graphene. The 2D nature of graphene and its well-known Raman spectrum makes it a favorable test bed for investigating the mechanisms of SERS. A variety of nanoparticle geometries has proven to deliver considerable Raman enhancement factors, such as well-defined arrays of gold nanodisks on top of a graphene/SiO₂ system,¹⁴ densely packed gold-nanopyramids¹⁵ and a photonic crystal nanocavity¹⁶ covered with graphene. An alternative way to control the generation of highly enhanced electromagnetic fields is to create a nanoscale cavity formed by closely placed metallic nanoparticles of defined geometry, allowing for instance single-molecule detection.¹⁷

In this paper, we demonstrate a graphene Raman enhancement up to 10^3 arising from a nanoscale cavity between two closely spaced gold nanodisks. Graphene is suspended between the two disks and partially extends into the cavity. Spatially resolved Raman measurements reveal that the enhancement in the cavity is localized in an area one order of magnitude smaller than the wavelength of the excitation. Upon rotating the polarization, we decouple the two disks, which now act as two separated plasmonic particles. The enhancement factor drops by a factor of 20 and the localization is lifted. The enhanced Raman signal exclusively arises from suspended graphene under tensile strain, which is induced by the double structure partially elevating the graphene. This allows us to simultaneously probe strained and unstrained graphene. Raman enhancement in strained graphene can be used to characterize plasmonic enhancement arising from any variety of nanostructure geometries. We demonstrate this method and analysis on a double-dot structure, which can be applied to any other desired plasmonic structure.

An SEM picture of the double structure we investigate is shown in the inset of Figure 1a. It consists of two disks with a height of 45 nm (5 nm Cr + 40 nm Au) and diameter of ~ 100 nm with an interparticle distance of ~ 30 nm on a flat SiO₂

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Figure 1. (a) AFM image of graphene placed on top of the double structure. The colored arrows indicate the *y*-position of the height profiles shown in (b). Each height profile is offset by 10 nm for clarity. (c) Sketch of the sample configuration. (d) Experimental dark-field spectra (circles) and simulated scattering cross sections for P_X (solid) and P_Y (dashed). The excitation wavelengths employed in the Raman experiments are indicated as vertical lines, together with the corresponding wavelengths of the G and 2D modes of graphene.

surface of 300 nm thickness. Graphene is prepared by mechanical cleavage and transferred on top of the structures.¹⁸ Atomic force microscope measurements reveal the topography of the graphene layer deposited on top of the double dot structure as shown in Figure 1a. The graphene layer is suspended over the gap between the two particles and between the edge of the particles and the surrounding substrate over a length of around 150 nm in all directions. The colored arrows indicate height profiles at different topographic conditions shown in Figure 1b, such as crossing the particle centers and the gap (red), and crossing the edge of the particles and the gap (blue). The green arrow shows the graphene suspended at half the height of the antennas and the black arrow indicates graphene completely adsorbed on the substrate. Figure 1c shows a sketch of the sample configuration.

The observed topography suggests that the graphene is under tensile strain, which is defined by the corresponding relative elongation $\Delta L/L_0$ as $\varepsilon_x = \Delta L_x/L_x$ and $\varepsilon_y = \Delta L_y/L_y$ within our laboratory frame. The strain configuration (ε_x , ε_y) varies for different locations on and around the structure. We expect the strain components to be maximal on top of and in the very vicinity of the structures, decreasing outward. As we will show in the course of the data analysis, Raman spectroscopy limits the sum of ε_x and ε_y to <1%.

In comparison to a perfect graphene sheet of equal lateral dimensions, the height profiles crossing the particle centers yield maximal relative elongations/strains of ε_{xx} $\varepsilon_y > 2.5\%$, assuming zero elongation at the unsuspended parts. These values are about five times higher than the values deduced from Raman spectroscopy and seem to be unrealistically high; calculations on pressurized graphene balloons state that strains

of 5% require adhesion energies of 3 $J/m^{2,19}$ which is roughly ten times the experimentally obtained values of 0.45 J/m^{2} on SiO₂.²⁰ For strains derived from the topology only, one would therefore expect immediate delamination, resulting in an increase of the suspended parts and a reduction of the energy stored in strain.

The differences can be explained by two main mechanisms. First, during processing and transfer the graphene/PMMA sandwich is placed on top of the structures and bends slightly, partially reflecting their topology. Therefore, the reference for the geometric calculations is larger than the assumed flat graphene sheet, which as a result reduces the relative elongation. Second, the graphene shows wrinkles and undulation on the suspended parts and on SiO₂, which lessens the relative elongation further. While the topology fails to quantitatively deliver the true strain, we observe a dominating strain in *y*-direction, as the graphene is pulled ca. 4 nm into the gap between the two particles. Optical images, and topographic data on this and additional structures are presented in the Supporting Information.

Figure 1d shows the scattering cross section (dots) of the double structure obtained by polarized dark-field spectroscopy before graphene deposition. The polarization P_X of the illumination source is oriented along the *x*-axis defined in Figure 1a. In order to obtain the maximum SERS enhancement, the plasmonic antennas were designed in such a way that the P_X resonance matches the excitation laser of 638 nm. We simulate the scattering cross section of the double structure for P_X and P_Y , where P_Y is blue-shifted compared to P_X , using a commercially available finite-difference time-domain code (Lumerical FDTD). The polarization dependence of the



Figure 2. Raman spectra on the double structure for (a) $\lambda = 532$ nm and P_{χ_2} (b) $\lambda = 532$ nm and P_{γ_2} (c) $\lambda = 638$ nm and P_{χ_2} (d) $\lambda = 638$ nm and P_{γ_2} . The spectra are normalized to the 2D peak height measured on SiO₂ next to the structure for the corresponding excitation and polarization.

simulated scattering cross section is explained by near-field coupling. The localized plasmon resonance of a single metallic particle depends on its material, shape, and size. If the distance between two adjacent particle becomes small ($d \ll \lambda$), they interact via their near-field. This interaction leads to (i) a shift in the scattering cross section compared to single particles and (ii) a strong near-field localization in the cavity formed between the two particles. Using disks instead of rods as optical antennas allows us to quantify the coupling effect between the two particles by rotating the excitation polarization. In our case, P_X couples the particles and P_Y lets them act as two single particles. Geometrical deviations of the real particles, such as nonperfect edges, cause a blueshift of the experimental data compared to our simulation. In addition, the effect of the Cr adhesive layer may be underestimated in simulations.²¹

The wavelengths of the scattered light corresponding to the G and 2D peaks, which are the dominant phonons observed in graphene Raman spectra, are indicated in Figure 1d for the two laser lines employed. Especially the energy of the 2D phonon $E_{\rm ph}$ is of the same order of magnitude as the line width Γ of the plasmon. We are therefore able to distinguish rudimentarily between the regimes of enhanced absorption (red) and enhanced emission (green) and expect the SERS enhancement factor to scale with the square of the field enhancement factor $|E_{\rm Loc}|/|E|$ for both cases. This can be clearly distinguished from scaling with the fourth power of field enhancement, which is generally observed in SERS for $E_{\rm ph} \ll \Gamma.^{22,23}$

Figure 2 shows the Raman spectra taken on the structures for 532 nm (green, panels a,b) and 638 nm excitation (red, panels c,d) for P_X (panels a,c) and P_Y (panels b,d). In all Raman measurements, the analyzer in the spectrometer is set parallel to the polarization of the excitation. For comparison, the spectrum of graphene on SiO₂ (black) under the same experimental conditions but 1.5 μ m away from the structure is shown. All spectra are normalized to the 2D peak height on SiO₂. The position and the full width at half-maximum (fwhm) of the G

peak (~ 1580/11 cm⁻¹) and the 2D peak (~ 2670/25 cm⁻¹) on SiO₂, extracted from Figure 2(a), confirm the presence of single layer graphene.⁹ This is supported by the peak height ratio 2D/G of 2.8, which is in agreement with single-layer graphene for an excitation of 532 nm and an oxide layer thickness of 300 nm.^{24,25} We relate the intensity drop on top of the dimer to the partial reduction of constructive interference (see Supporting Information). Note that we concentrate on the 2D peak when evaluating the enhancement, as the G peak is not suitable for two reasons: the gold nanostructures exhibit a luminescence,²⁶ whose shoulder overlaps with the G peak (negligibly with 2D) and generally causes noisier spectra. In addition, we observe peaks at 1450 and 1530 cm⁻¹ on top of the structure and next to it for 638 nm excitation, which we assign to remainders of the glue used in graphene exfoliation.

Neglecting the shape and the position of the peaks observed on the structure at this stage, we find a good qualitative agreement between the observed signal intensities and scattering cross sections in Figure 1d with respect to enhanced absorption. The highest 2D intensity occurs for 638 nm and P_{Xy} where the excitation is closest to the experimentally observed scattering cross section. Combining the lower simulated scattering cross section with the blueshift for P_{Yy} shifting the maximum further away from the excitation of 638 nm, leads to the enhancement we observe for P_{Yy} . It is present but less pronounced than for P_{Xy} .

Interestingly, we do not observe a notable enhancement for 532 nm with either polarization; while the scattered light is off the plasmon resonance for 638 nm, it is in resonance for 532 nm, yet no enhancement occurs. While this observation is not decisive regarding the conclusions of this work, the apparent lack of enhanced emission is certainly of interest regarding the mechanism of cavity induced SERS of graphene and is currently being studied. In the following, the term enhancement refers to enhanced absorption only.

In Figure 2a, the 2D peak observed on top of the structures shifts down 9 to 2661 cm⁻¹ compared to the spectrum on SiO₂. Its width increases from 26 to 37 cm^{-1} . While we do not observe a downshift of the G peak within the resolution of our spectrometer, the fwhm increases from 11 cm⁻¹ on SiO₂ to 17 cm⁻¹ on the structure. Strain modifies crystal phonons; tensile strain results in a phonon mode softening. We expect a frequency downshift from the graphene topology discussed earlier. In general, the 2D peak is more sensitive to strain than the G peak, 8,27,28 which explains that we do not observe a downshift of the G peak in the presence of peak broadening. The broadening itself reflects the spatial variations of the strain configurations on and around the structure. A similar behavior of the 2D peak has been observed by Tomori et al.,²⁹ when they deposited graphene on pillars made of e-beam resist and arrived at a comparable type of topography. The broadened G and 2D peaks and the downshifted 2D peak on the structures represents the sum of all locations in the laser focus.

Peak positions and widths change drastically when plasmonic enhancement comes into play. In Figure 2c, the 2D peak consists of three components; the two lower components arise from local hot spots where the enhanced near-field from the particles interacts with strained graphene. The same mechanism applies to the now dominating G peak component at 1558 cm⁻¹. The uppermost 2D and G components approximately match the peaks measured on SiO₂ in intensity and frequency. They stem from scattering in the laser focus which is not subject to plasmonic enhancement.

To evaluate the strain, we use the G mode and the 2D' mode (~ 3200 cm⁻¹). The frequency of these Raman lines under strain depends only on changes in the force constants and is independent of the electronic structure.³⁰ For both the G and the D' modes, the change in frequency under strain $\Delta \omega_{E_{2G}}^{\pm}$ is given by^{27,31,32}

$$\Delta \omega_{E_{2G}}^{\pm} = \Delta \omega_{E_{2G}}^{h} \pm \frac{1}{2} \Delta \omega_{E_{2G}}^{S}$$
$$= -\omega_{E_{2G}}^{0} \gamma_{E_{2G}} \varepsilon_{h} \pm \frac{1}{2} \omega_{E_{2G}}^{0} \beta_{E_{2G}} \varepsilon_{s}$$
(1)

where E_{2G} denotes the phonon symmetry, $\Delta \omega_{E_{2G}}^{h}$ is the shift due to the hydrostatic component of the strain $\varepsilon_{h} = \varepsilon_{y} + \varepsilon_{x}$ and $\Delta \omega_{E_{2G}}^{S}$ is the phonon splitting due to the shear component of the strain $\varepsilon_{s} = \varepsilon_{y} - \varepsilon_{x}^{33}$ The peak position at zero strain is given by $\Delta \omega_{E_{2G}}^{0}$ while $\gamma_{E_{2G}}$ denotes the Grüneisen parameter and $\beta_{E_{2G}}$ denotes the shear deformation potential of the corresponding vibration.

Averaged spectra from a line scan (step size 100 nm) are shown for the G and 2D' mode in Figure 3a,b, respectively. The G-mode shifts down 23 cm⁻¹ and its fwhm increases from 17^{34} to 23 cm⁻¹. For 2D', we observe a downshift of 44 cm⁻¹ and an increase in the fwhm from 15 to 20 cm⁻¹. Neglecting the shear strain component, we insert the Grüneisen parameters $\gamma_{\rm G} = 1.8$ and $\gamma_{\rm 2D'} = 1.6^{35}$ in eq 1 and obtain an excellent agreement between the hydrostatic strain components $\varepsilon_y + \varepsilon_x$ derived from G (0.82%) and 2D' (0.81%). The broadening of the modes under strain indicates a nonvanishing shear strain. This is supported by the splitting of the 2D mode and the presumably dominant y-strain determined from the topology. For uniaxialy strained graphene, a G peak splitting is recognizable at shear strains >0.4%.²⁷ We conclude that in the areas of plasmonic enhancement the graphene is under strain Letter



Figure 3. Sum of Raman spectra of (a) G mode and (b) 2D' mode obtained from a line scan over the structure with $\lambda = 638$ nm and P_{x} . The peaks corresponding to strained graphene (red) are downshifted and broadened compared to the peaks arising from unstrained graphene (blue).

with a hydrostatic component $\approx\!0.8\%$ and shear component <0.4%.

The 2D mode cannot be used for strain evaluation because of the nonstandard strain configuration (i.e., graphene bending on a nm scale at the particle edges). In addition, the nature of the 2D peak splitting in the presence of shear strain is currently under debate in the literature.^{28,36–38} While the overall intensity is assumed to be independent of polarization, the relative intensities and shift rates for each subpeak depend on the polarization of each excitation and emission, the orientation of the strain, the crystallographic axis and their combined relative orientations. Therefore we use the 2D peak only for evaluating the plasmonic enhancement via its intensity. Peak fits for P_X are provided in the Supporting Information. For polarization in y-direction, a comparable strain analysis is impossible, as the low signal intensities hamper the clear identification of a shifted G and 2D' mode.

By investigating the signal intensities and the strain configuration we have so far established that (i) the enhanced Raman peaks arise from areas under strain, indicating that (ii) the enhancement is localized around the particles and that (iii) the enhancement depends on the polarization. In the following, we show how the polarization dependence can be directly related to near-field coupling for P_X and the corresponding strong localization in the cavity and the lack thereof for P_Y . In Figure 4a, we depict a Raman line scan over the structure for 638 nm excitation and P_X taken in x-direction with a step size of 100 nm. The spatial position of the laser focus relative to the antenna center is plotted versus the sum of the integrated intensity of the three 2D components. The intensity is



Figure 4. Raman line scan over the antenna structure where the sum of all 2D peak components is plotted versus the spatial position of the laser focus for P_X (a) and P_Y (b) with $\lambda = 638$ nm. The corresponding Gaussian fits including fwhm are shown.

normalized to the integrated 2D intensity on SiO₂ away from the structure. As expected, the signal enhancement is maximal when the laser focus is centered on the structure. The profile represents the convolution of the laser spot, which has a fwhm of \approx 570 nm and the sites of localized enhancement. Raw data of the line scan and laser spot size are given in the Supporting Information. A Gaussian fit delivers an enhancement factor of 12.8 with a fwhm of 610 nm for P_{X} , exceeding the fwhm of the laser spot by less than 10%. Figure 5a depicts the corresponding simulated near-field enhancement $|E/E_0|^2$ at a height of 40 nm. Because of the near-field coupling of the particles, the enhancement is concentrated in the area between the particles and acts approximately like a pointlike source.

Why do we choose to evaluate the near-field at a height of 40 nm instead of the 45 nm, the nominal height of the particles? A near-field cross section in the (x,z) plane is shown in Figure 5b. The hot spots on the particles edges are caused by the lightning rod effect, which describes field enhancement as a purely geometrical phenomenon of electromagnetic field line crowding at sharp edges. While the assumption of perfect edges does not hold for real structures, the evaluation of the enhancement in the cavity is a very valid approximation. The height profiles shown in Figure 1b confirm that the graphene is suspended at a height of 41 nm in the gap center. Over the range of gap in the *y*-direction, the height drops to about 37 nm (see blue profile). Therefore we achieve the best correspondence between simulation and experiment by examining the near-field at a height of 40 nm instead of 45 nm. A spatial profile of the near-



Figure 5. Near-field enhancement $|E/E_0|^2$ for P_X is shown in the (x,y) plane at z = 40 nm (a) and in the (x,z) plane at y = 0 (b). The area considered contributing to the enhancement is indicated by the dashed line in (a). The corresponding data for P_Y is shown in (d,e). Cross sections of the near-field enhancement relevant for the enhancement factor are given in (c) for P_X and (f) for P_Y .

field enhancement at z = 40 nm and y = 0 is given in Figure 5c, where the cavity is indicated by the gray square.

In Figure 4b, we depict a comparable Raman line scan for $P_{\rm V}$. A Gaussian fit yields a maximal enhancement factor of 3.2 and a fwhm of 840 nm. Here, the particles approximately act as two isolated particles. The near-field, shown in Figure 5d, extends predominantly in the y-direction for each of the particles and no cavity enhancement is present. Scanning in the x-direction, the simulation predicts two spatially separated scattering centers, which lead to the observed broadening of the intensity profile. As explained in the previous paragraph, we evaluate the near-field at a height of 40 nm to avoid edge effects. A potential contribution of the particle top surface to the enhancement is negligible, as it does not depend on the polarization. If significant, it would smear the difference in the width of the intensity profiles of P_X and P_Y . To verify the correlation between polarization and near-field coupling, we conduct similar line scans for 532 nm excitation and both polarizations. While we do not observe a notable enhancement, the effects of the structure can be transformed into a spatial profile which yields a width of around 710 nm for both polarizations (see Supporting Information).

As the field is localized in a very small area compared to the laser spot, the actual enhancement is significantly higher than the observed factor of 12.8 for P_X . In Figure 5a, the dashed line encircles the area relevant for the enhancement. It includes 90% of the calculated integrated near-field intensity within the cavity. Comparing this area with the size of the laser spot yields an overall enhancement of 4×10^3 . Figure 6 shows how the



Figure 6. Percentage of total near-field intensity in the cavity plotted versus the resulting enhancement factor. Taking into account 90% of the near-field intensity yields an overall enhancement factor of ca. 4×10^3 .

enhancement depends on the near-field intensity in the cavity considered to be relevant. Applying a similar analysis for P_Y yields an enhancement factor of 2.2×10^2 . The area taken into account is indicated in Figure 5d,f. Again, the cutoff is set to 90% of the integrated near-field intensity.

A comparison between the experimental enhancement factors for P_X and P_Y allows us to estimate the contribution from the outer particle edges to the cavity enhancement. Upon a 90° rotation, the near-field at the outer particle edges for P_X approximately matches the near-field for P_Y in shape and magnitude. This can be easily seen by comparing Figure 5c and (f). Therefore, 50% of experimentally observed enhanced intensity for P_Y represents the enhancement we expect from the outer particle edges for *x*-polarization. Inserting these values yields a contribution of around 12% with each edge contributing 6% and confirms that the observed enhancement

predominantly arises from the cavity. This estimate appears reliable, as it is independent of the real near-field distribution, factors in geometrical deviations of the particles compared to the simulation, and agrees well with localization observed in the intensity profile for P_X .

Note that the observed enhancement factor is inversely proportional to the estimated area of near-field localization. As indicated in Figure 6, variations in the analytical approach may therefore leverage the same experimental data into enhancement factors that differ by orders of magnitude. For this reason, it is difficult to relate our results to enhancement factors in the literature. For instance, in ref 14 an experimental enhancement factor of 35 is observed for gold nanodisks placed on top of graphene. The distance between the particles is too large to allow near-field coupling but is too small to observe the signal from isolated particles. In addition, the authors chose not to factor in the area of near-field localization, which would significantly increase the enhancement factor. Wang et. al¹⁵ measure graphene placed on top of closely spaced gold nanopyramids, observing an enhancement factor of the order of 10^4 in the experiment; by assigning the enhancement to a narrow area of 5×5 nm, corresponding to a low percentage in Figure 6, they arrive at an enhancement of 10^7 . In addition, to our knowledge no surface-enhanced Raman study on a single, isolated plasmonic dimer structure interfaced with graphene has been reported.

While we use the signal on SiO_2 as a reference, plasmonic enhancement occurs mainly at a height around ~40 nm. Therefore the interference effect due to the substrate has to be taken into account. Here, reflection and transmission at multiple interfaces (Si, SiO₂, graphene, and air) of the excitation as well as the scattered light may lead to constructive or destructive interference, depending on the wavelengths of excitation, emission, and the oxide layer thickness.^{24,25,39,40} Following the approach of ref 40, we arrive at a factor of 0.52 for 638 nm excitation on 300 nm SiO₂. An in-depth treatment of the interplay between interference and the cavity is beyond the scope of this work. In addition, it is doubtful that the picture of stratified media holds for the graphene topography in our sample configuration. We therefore neglect the interference effect for the suspended graphene and correct for the destructive interference on SiO₂, leading to an estimate of the enhancement $\geq 2 \times 10^3$.

The graphene suspended around and between the double structure serves two distinct purposes. From a purely plasmonics point of view, the graphene is a Raman active, two-dimensional membrane that serves as a detection channel of the near-field distribution. In the areas of enhancement, its Raman signals are shifted and therefore allow a clear assignment. From the perspective of Raman scattering on graphene, the double structures suspend the graphene, induce local strain and simultaneously provide the means of local detection. The induced strain represents a configuration of hydrostatic and shear strain ($\varepsilon_{\rm s} > \varepsilon_{\rm h} > 0$), which can neither be achieved by uniaxial strain ($\varepsilon_{\rm s} > \varepsilon_{\rm h} > 0$) nor biaxial strain ($\varepsilon_{\rm h} > 0$, $\varepsilon_{\rm s} = 0$).

In conclusion, we probe with surface-enhanced Raman scattering the plasmonic properties of an isolated Au double disk nanostructure interfaced with suspended graphene. By rotating the polarization of the excitation, we switch between the dots acting as single plasmonic particles and a coupling regime, realizing a plasmonic cavity. In the cavity, we observe a plasmonic enhancement of the order of 10³, where graphene

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serves as a two-dimensional, Raman active integrator of the local near field. The enhanced signal arises from an area one order of magnitude smaller than the wavelength of the excitation and probes suspended graphene under strain. The combination of phonon softening and local enhancement will allow studying the impact of high electric fields on the electrical transport in graphene. Our approach may allow the induction of different types of local strain configurations via the shape, size, number, and arrangement of plasmonic nanoparticles, and simultaneously provide the means to locally probe them by surface enhanced Raman scattering. This approach can be extended to using silver, which is the preferred material in plasmonics due to low losses and resonances toward lower wavelengths; Reed et al⁴¹ recently demonstrated that single layer graphene placed on top of silver nanostructures passivates their surface and maintains their performance by preventing sulfidation.

ASSOCIATED CONTENT

S Supporting Information

Fabrication and structural characterization; optical characterization; simulations; AFM data on dimers before and after graphene deposition; microscope images of graphene flake; AFM data and graphene topography on different structure; 2D peak fits for P_X ; Raman line scan raw data for 638 nm excitation; laser spot profile; intensity drop for 532 nm excitation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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