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Enhanced light-matter interaction of aligned armchair graphene nanoribbons using arrays of plasmonic nanoantennas

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We couple photoluminescent semiconducting 7-atom wide armchair edge graphene nanoribbons to plasmonic nanoantenna arrays and demonstrate an enhancement of the photoluminescence and Raman scattering intensity of the nanoribbons by more than an order of magnitude averaged over large areas, and by three orders of magnitude in the hot spots of plasmonic antennas. The increase in signal allows us to study Raman spectra with high signal-to-noise ratio. Using plasmonic enhancement we are able to detect the off-resonant Raman scattering from the modified radial breathing-like mode (RBLM) due to physisorbed molecules, the 3rd order RBLM, and C-H vibrations. We find excellent agreement between experimental data and simulations describing the spectral dependence of the enhancement and modifications of the polarization anisotropy. The strong field gradients in the optical near-field further allow us to probe the subwavelength coherence properties of the phonon modes in the nanoribbons. We theoretically model this considering a finite phonon correlation length along the GNR direction. Our results allow estimating the correlation length in graphene nanoribbons.

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I. INTRODUCTION

Optical nanoantennas are plasmon resonant nanoparticles that enable converting propagating light fields into localized energy and vice versa^{1,2}. Optical antennas have found applications particularly in enhancing the light emission from subwavelength sources such as single molecules or quantum dots³⁻⁹, in modifying the radiation pattern¹⁰⁻¹², and in enhancing spectroscopic signals^{4,5,13-16}. For low quantum yield emitters optical antennas can be used to significantly increase the quantum yield by enhancing the radiative decay rate^{13,14}. Extreme field gradients near the nanoscale plasmonic structures even allow modifying the selection rules for optical transitions¹⁷⁻¹⁹. Plasmonic nanoantennas thus open up new domains in spectroscopy for weakly luminescent materials.

Graphene nanoribbons (GNRs) have attracted a lot of interest in recent years due to their remarkable electronic and optical properties²⁰⁻³¹. Various species of GNRs can selectively be grown with atomic precision and with a high degree of alignment using bottom-up fabrication³²⁻³⁶. Even atomically precise doping and heterostructures can be realized in this way³⁷⁻⁴². The properties of GNRs are strongly influenced by ribbon width and geometry of their edges^{29,43-45}. Here we focus on seven atom wide armchair edge GNRs (7-AGNRs), which are semiconducting. Recently, photoluminescence^{22,31} and electroluminescence⁴⁶ from AGNRs was observed. 7-AGNRs exhibit a broad fluorescence spectrum centered in the red-spectral domain, which for pristine nanoribbons is weak in intensity^{31,47}. The low quantum yield is attributed to dark excitons degenerate with the optically active state^{48,49}. It was recently shown that the degeneracy can be removed by introducing defects into the ribbon^{31,50}. To avoid deterioration of the electronic properties of GNRs due to a high density of defects, here we apply plasmonic nanoantennas to increase the quantum efficiency of GNRs. By placing the nanoribbons in the near-field of arrays of plasmon resonant gold nanoparticles we increase both the excitation and radiative decay rates. This results in more than three orders of magnitude increase in the Raman scattering and photoluminescence rate in the hot spots of the antennas. An enhancement factor of 20 is obtained when averaging over the unit cell of the array. The strong field gradients of the optical near field additionally result in modified Raman scattering and allow us to probe the phonon correlation length.

II. RESULTS AND DISCUSSION

A. Plasmonic enhancement

We synthesized densely lying aligned 7-AGNRs on a Au(788) surface by on-surface assembly from molecular precursors. The obtained single layer of GNRs is transferred by so-called "bubbling" technique onto arrays of plasmonic antennas on a glass substrate preserving the ribbon alignment^{31,51,52}. The ribbons are aligned along one of the arrays' main axes as schematically illustrated in Fig. 1a. The plasmonic structures are square arrays of square disk gold nanoantennas. We consider arrays with periods smaller than the emission wavelength in the substrate (and thus also superstrate). In this case there is no coupling of the exciton in the nanoribbon to long-range grating plasmons. Figure 1b shows an optical micrograph of a section of an array with transferred ribbons. The array shown here consists of square-shaped nanoantennas with a side length of 100 nm and a period of 350 nm. The spectral position of the surface plasmon resonance of the individual array element is approximately 680 nm based on simulations (see Fig. S1a in supplementary material). The edge of the nanoribbon coverage is indicated by the dashed white line. The individual array elements can be resolved in the magnified image shown in the inset of Fig. 1b. Figure 1c shows a micrograph of the spectrally integrated emission or scattering consisting of spectrally broad photoluminescence and Raman scattering for the sample region shown in Fig. 1b. Here the excitation wavelength is 595 nm and light with wavelengths longer than 645 nm are collected. The excitation is thus detuned from the plasmon resonance and mainly the emission or scattering processes are enhanced. We identify four regions with different brightness levels. These regions are in ascending order of brightness: the clean substrate (empty), regions beside the plasmonic nanostructures covered by a homogeneous layer of nanoribbons (GNRs), regions where the array is not covered by GNRs (array), and the array covered with a homogeneous layer of GNRs (GNRs on array). From the comparison of regions (GNRs) and (GNRs on array) we can deduce a (spatially averaged) brightness increase of about one order of magnitude due to coupling to the array. The collected light is characterized by measuring spectra in these four regions. The presence of characteristic Raman features, which originate from nanoribbons, in regions (GNRs) and (GNRs on array), and their absence in regions (empty) and (array) confirms the attribution of the sample regions. Figure 1d

Figure 1. a) Sketch of GNRs on a plasmonic nanoantenna array. b) The region of the plasmonic array covered with nanoribbons is clearly visible in a reflection micrograph. c) Photoluminescence micrograph shows that photoluminescence (PL) and Raman scattering (D- and G- like modes) from the same sample region as in (b) are increased by an order of magnitude. d) Raman spectra for aligned GNRs for 532 nm and e) 633 nm excitation wavelength with incident polarization along (red) and perpendicular (blue) to the ribbons. Spectra for GNRs and GNRs on array are shown in the left and right half, respectively. From the magnified acoustic region (gray), we observe a second peak (*) for the RBLM in the off-resonant Raman spectrum. Spectra for polarization along ribbon for 532 nm are offsetted by 2, spectra for 633 nm by 3 and 60, for GNRs and GNRs on array, respectively.

shows the spectrum for GNRs on and next to the array for 532 nm excitation wavelength. The spectra from the uncovered regions on and besides the array were used for background subtraction.

B. Raman scattering

Figure 1d and e display the Raman spectra for 532 nm (Fig. 1d) and 633 nm (Fig. 1e) excitation wavelength for polarization along and perpendicular to the alignment direction

of the GNRs. For 532 nm (2.327 eV) we excite the GNRs resonantly around the E_{22} excitonic transition and thus observe strong Raman scattering. For 633 nm (1.959 eV) the energy is smaller than the lowest energy exciton E_{11} and thus Raman scattering for the off-resonant illumination wavelength is weaker than in the resonant case. The measurements were performed on the same spots on the sample. We observe that the enhancement due to the plasmonic nanostructure for GNRs on array for 532 nm wavelength is negligible. For 633 nm wavelength we obtain an enhancement of the signal by a factor of approximately 20 for incident light polarized along the ribbons. We remark that the enhancement factor represents a spatial average over the unit cell of the array. This is different than the enhancement factors obtained for, e.g., a single emitter placed in the hot spot of a single nanoantenna. Within the unit cell we expect there to exist hot spots around the antenna where the signal is enhanced much more than on average. The observed wavelength dependence is consistent with the extinction spectrum of the plasmonic array (see Fig. 2a and S1). The 532 nm is far away from the plasmon resonance and no significant enhancement of the Raman signal is expected.

Surprisingly, for 633 nm wavelength incident light we observe that the Raman signal on the plasmonic array is stronger for incident light polarized perpendicular to the ribbon (see Fig. 1e). In the absence of the plasmonic nanostructure the scattering for polarization along the ribbon is significantly stronger than for the orthogonal polarization as evidenced by the Raman spectra collected besides the array and reported earlier³¹. Based on additional polarization-resolved measurements (see Fig. S3 in supplementary material), where the polarization state of the emission is analyzed, we conclude, that the observed polarization dependence of the enhancement is predominantly explained by a change of the polarization state of the incident light in the vicinity of the plasmonic nanoantennas. The scattered light is in this case still strongly polarized along the ribbons. Using finite element simulations (see supplementary material for details about simulations) we find, that for perpendicular polarization, there are hot-spots in the near field with a noticeable enhancement of the local field along the ribbons. These hot-spots of the incident field overlap with the regions of enhanced scattering of the y -oriented dipole at the Raman scattering wavelength. Due to this we observe the change of the polarization anisotropy.

Focusing on the Raman modes for GNRs on the array (Fig. 1d and e), we observe an enhancement of the radial breathing-like mode (RBLM), which, due to its resonant nature,

is not typically well visible with high signal-to-noise ratio for off-resonant Raman scattering (633 nm). Here we observe a broadened peak (in comparison to the spectrum obtained with 532 nm excitation), which can be resolved as two peaks in the plasmonically enhanced spectrum. Fitting the spectrum with two Lorentzian functions and assuming the RBLM of pristine GNRs at 396.0 cm^{-1} , we obtain a sideband at 363.9 cm^{-1} (see Fig. S4a in supplementary material). The shift to smaller wavenumbers indicates a broader effective width of the GNRs. As the polarization anisotropy of the sideband is not modified we attribute it to the physisorption of atoms or small molecules or, e.g., oxidation at the GNRs edges^{53,54}. Besides the two narrow bands at 750 cm^{-1} and 889 cm^{-1} , which we identify as C-H modes⁵⁵, we observe a broader peak at 953 cm^{-1} (see Fig. S4c of the supplementary material) in the plasmonically enhanced Raman scattering (Fig. 1e). This mode is attributed to the next odd higher-order transverse acoustic 3-RBLM mode as theoretically predicted^{56,57}.

C. Photoluminescence

We now move to the enhancement of photoluminescence. When we look at the emission spectrum for 630 nm wavelength incident light on a broader spectral range than in the Raman spectroscopy experiments we observe a broad emission peak at 700 nm, which is the photoluminescence of GNRs³¹ (see upper panel in Fig. 2a). Here strong Raman signals from D- and G- like modes are superposed on the PL signal. The enhancement of the PL due to the plasmonic array is obtained as the ratio of the spectra on and away from the array. The total enhancement, which is an average over a large area compared to the unit cell of the array, has a maximum value of 16 at a wavelength of 680 nm (Fig. 2a). The PL spectra are collected from an area with a diameter of approximately $6\text{ }\mu\text{m}$.

We now want to relate the spectral enhancement (upper panel in Fig. 2a) to the optical properties of the antenna array. Due to the large size of the single array elements, scattering dominates in comparison to absorption (see Fig. S1 in supplementary material). The extinction [defined here as $1 - \text{transmission}$ (1-T)] spectrum hence reflects the scattering properties. The lower panel in Fig. 2a shows the extinction spectrum (black) for the antenna array from Fig. 1b (period 350 nm). When we compare the measured extinction and enhancement spectra we notice that they are similar in shape but that there is an approximately 13 nm red-shift of the peak of the enhancement from the spectral position of the

peak of the extinction spectrum. This shift can be explained as the spectral deviation of the maximum enhancement in the near-field from the plasmon resonance observed in far-field scattering^{58–60}.

For a quantitative comparison between experiment and model we use finite element simulations to calculate the increase in the collected emission from the GNRs. Here we apply the Lorentz reciprocity theorem to deduce the modification in far-field fluorescence due to a local source near the plasmonic structure^{61–64}. The nanoribbons are modeled as electric point dipoles oriented along the y -axis (see Fig. 2b) and we consider emission only along the surface normal direction. Due to the absence of long-range grating plasmons the angular distribution of emission is not strongly modified due to the array. The calculated and measured enhancement and extinction spectra are in good agreement (see Fig. 2a). The calculated spectra are sharper and the maximum enhancement is larger than the data from experiment. We attribute these to defects in the structures, inhomogeneous broadening, and uncertainty in the exact position of the ribbons. We expect the layer of ribbons to bend around the antennas. In the simulations we assume that they form a flat layer (see inset in Fig. 2a).

The experiment gives only spatially averaged quantities. These are well reproduced by the simulations. Therefore, we now turn to the spatial distribution of the emission enhancement around the plasmonic nanoantennas using simulations. Figure 2b shows the simulated emission enhancement in a plane 2 nm above the array (green layer in inset of Fig. 2a) for the plasmon resonance wavelength (680 nm). We observe that on resonance the emission enhancement reaches values of approximately 100, which is comparable to the enhancement factors obtained for single emitters^{7,9}. Surprisingly, the emitters on top of the plasmonic nanoantennas are strongly enhanced. For an emitter oriented along the metal surface the induced image dipole $\mathbf{p}_{\text{ind}}$ is out-of-phase with the emitting dipole $\mathbf{p}$ and one expects suppression due to destructive interference⁶⁵. Here the increased radiation is a result of the collected emission coming dominantly via the antenna. This can be qualitatively described by treating the antenna as a polarizable oblate ellipsoid. The ratio of the total dipole moment with and without antenna can be expressed as

$$\frac{|\mathbf{p} + \mathbf{p}_{\text{ind}}|^2}{|\mathbf{p}|^2} = \left| 1 - \frac{1}{4\pi\epsilon_0} \alpha_{yy} \frac{\exp(ikR)}{R^3} \right|^2, \quad (1)$$

where α_{yy} is the relevant component of the polarizability tensor of the nanoantenna, R is

Figure 2. a) Upper panel: Photoluminescence spectra spectra on and beside the array (blue and gray, respectively) for 630 nm excitation wavelength. The measured enhancement spectrum (orange solid line) is obtained as the ratio of the two spectra. Finite element simulations are in good agreement with experiment for the enhancement spectrum (red solid line). The enhancement is obtained by spatial averaging in a plane above the substrate (green line in the inset in lower panel). Lower panel: Measured and simulated extinction spectra (black and gray solid line, respectively). b) Enhancement of collected emission from emitters in a plane above the array [green layer in inset in (a)] at the resonance wavelength 680 nm. The regions of suppression are due to destructive interference between direct and array-coupled emission pathways. c) Excitation enhancement in the unit cell of the array for the illumination wavelength 630 nm [marked with an arrow in panel (d)]. d) The spectrally averaged measured enhancement as a function of the excitation wavelength (orange circles) follows the extinction spectrum (solid line). e) The total enhancement at the peak of the enhancement for illumination (630 nm) and emission (680 nm). In the hot spots enhancement factors of up to 2000 are obtained.

the distance between the antenna and emitter dipoles, and $k = 2\pi/\lambda$. Due to the geome-

try here only the transverse component of the emitter's near-field is relevant. The induced and primary dipoles are indeed out of phase (negative sign in Eq. 1). However, the resonantly induced dipole in the antenna significantly exceeds the primary dipole, resulting in enhancement. We remark here that for a spherical antenna or a continuous metal film the enhancement turns to a suppression of emission as intuitively expected.

To disentangle the enhancement of the excitation and emission processes we simulate the intensity distribution in the unit cell of the array for one of the excitation wavelengths (630 nm) used in the experiments. As seen in Fig. 2c, the largest enhancement region is localized on top of the antenna. The wavelength dependence of the excitation process is shown in Fig. 2d. Here the measured spectrally averaged enhancement (see Fig. 2a for spectral enhancement) for the array considered in Fig. 2a–c is shown as a function of the excitation wavelength. We point out that the spectrally averaged enhancement is approximately 50 % of the maximum enhancement, which occurs at a wavelength of about 680 nm. The enhancement as a function of excitation wavelength closely follows the far-field resonance (extinction spectrum). The total enhancement pattern that is probed in the experiment is given by the product of excitation and emission enhancement. This is shown in Fig. 2e for the excitation wavelength (630 nm) marked in Fig. 2d and for emission at 680 nm wavelength (green arrow in Fig. 2a), i.e. at the maximum of the spectral enhancement. The overlap of the regions of enhancement in emission and excitation occur only in regions above the antenna or very close to it. Double-resonant antennas could thus be very useful to match the regions of enhancement⁶⁶. From the simulated field distributions of Fig. 2e a maximum of about 2000 close to the antenna is obtained. The spatially averaged enhancement factor is 21. For comparison, the maximum average enhancement for Raman scattering is about 20 for this wavelength (see Fig. 1e). The calculated average enhancement is thus in good agreement with the experimental data and (indirectly) confirms the large enhancement factors in the antennas hot-spots.

D. Difference in enhancement of Raman scattering and photoluminescence

Figure 3a shows the emission spectra for GNRs and GNRs on the array (black and red, respectively) for an excitation wavelength of 615 nm. Here we identify the PL as a broad background and the D- and G-like Raman bands at ≈ 670 nm and ≈ 680 nm, respectively.

Figure 3. a) We observe dips in the enhancement spectrum at the positions of the Raman modes. From the spectra we deduce different enhancement factors for PL and Raman scattering. b) Calculated relative suppression of the enhancement factor for Raman scattering as a function of phonon correlation length (black squares). The measured values for the suppression are shown with orange circles. The curve is a guide to the eye.

We notice that we observe dips in the enhancement at the spectral positions of the Raman bands indicating that the enhancement process for PL and Raman are different. The illumination and the detection wavelengths are the same for both processes. As photoluminescence at room temperature for the nanoribbons is a purely incoherent process, the total emission is equal to the incoherent sum of the radiation from the individual emitters. The total (measured) enhancement is the product of the enhancements for excitation and emission, as discussed above. For plasmonic near-field enhancement of Raman scattering the process is partially coherent. This was recently predicted and experimentally confirmed for tip-enhanced Raman scattering of the D, G, and 2D Raman modes of graphene^{67,68}.

In these works a phonon correlation length of about 30 nm explained the experimental results. The partially coherent nature of the scattering process leads to a difference of the enhancement of the Raman scattering from photoluminescence due to interference. From the experimental data presented in Fig. 3a we can extract the contributions of photoluminescence and Raman scattering by fitting these with Gaussian functions. From this we obtain enhancement factors of 11.8 and 13.8 for Raman scattering and photoluminescence, respectively. The reduction of the Raman enhancement could be due to correlation effects on the length scale of the ribbons. Scanning tunneling microscopy images suggest GNR lengths of approximately 30 nm³¹. For a propagating electromagnetic wave interference effects on this scale would not be observable. However, for evanescent fields around optical antennas the phase changes on a much shorter length scale than the wavelength (see Fig. 2b and c). This enables (destructive) interference for scattering from points with separations shorter than the correlation length that could result in a decrease in the enhancement for Raman scattering.

We apply the theory of Ref. 67 to the geometry of Fig. 2c to study the influence of coherence on the observed difference in enhancement for Raman scattering and PL. Briefly, using full field simulations at the incident and scattered wavelength λ_i and λ_s , respectively, we calculate the average total enhancement $S(\lambda_s)$ including a finite correlation length L_c in the direction of the ribbons (y -direction). This is performed by introducing the one-dimensional correlation function

$$f_c(y_1, y_2) = \frac{\exp\left(-\frac{|y_1 - y_2|}{L_c}\right)}{\sqrt{\pi}L_c} \quad (2)$$

between two points (x_1, y_1, z_1) and (x_2, y_2, z_2) . We obtain the average enhancement signal $S(\lambda_s)$ for y -polarized light following the model in Ref. 67 as

$$S(\lambda_s) = A \int_{A_{\text{unit}}} \int_{A_{\text{unit}}} dA_1 dA_2 f_c(y_1, y_2) G^*(\mathbf{r}_0, x_1, y_1; \lambda_s)_{yy} G_{yy}(\mathbf{r}_0, x_2, y_2; \lambda_s) \\ \times \alpha_{yy} \alpha_{yy} E_y^*(x_1, y_1; \lambda_i) E_y(x_2, y_2; \lambda_i), \quad (3)$$

where A is a proportionality constant and $G_{yy}(\mathbf{r}_0, x_i, y_i; \lambda_s)$ with $i = 1, 2$ is the yy -component of the dyadic Green's function evaluated at the field point $\mathbf{r}_0$, which here corresponds to the detector, and for the source point (x_i, y_i) . In Eq. 3 $E_y(x_i, y_i; \lambda_i)$ is the electric field at the position (x_i, y_i) and α_{yy} is the polarizability of the ribbon. Using the reciprocity

theorem, we can replace the Green's function by the numerically calculated value for the electric field when a y -polarized plane wave is incident on the structure. Figure 3b shows the suppression of the enhancement factor for Raman scattering relative to the PL enhancement factor as a function of the correlation length L_c . The experimental values are obtained from measurements on different sample positions. Comparing the mean reduction of 14 % found in the experiment with the calculated reduction for the detected Raman scattering intensity from the fully incoherent situation as a function of the correlation length, we deduce a correlation length along the GNRs of 15 nm. We thus conclude that the Raman correlation length seems to mainly be limited by the length of the ribbons and not by defects in the material.

III. CONCLUSION

We have demonstrated a spatially averaged enhancement of the Raman scattering and photoluminescence from 7-AGNRs by a factor of 20 using arrays of plasmonic nanoantennas. Considering the field localization in the unit cell we deduce an enhancement of the optical signals by more than three orders of magnitude in the hot spots of the antennas. The increased signal allows us to perform Raman spectroscopy even for non-resonant excitation. We observe that for plasmonically enhanced off-resonant Raman, the RBLM consists of two spectral lines, which we attribute to the attachment of molecules on the ribbons. The field localization around the nanoantennas results in differences in the enhancement of Raman scattering and photoluminescence due to their different coherence properties. Using a theoretical model we analyze our experimental data and conclude that the phonon correlation length is approximately 15 nm.

Our work shows how to enhance light-matter interaction of graphene nanoribbons on a large scale using plasmonic gratings. Plasmonic enhancement allows Raman spectroscopy even using non-resonant excitation and creating field gradients on the nanoscale. This enables selective excitation of modes with different symmetry and exploring their wavelength dependence. The extreme field-confinement around plasmonic nanoantennas may even allow modifying the selection rules of optical transitions. Plasmonic arrays are thus a valuable addition to the spectroscopist's toolbox in the study of novel atomically thin materials. Finally, the performance of devices such as photovoltaic or light emitting devices can be

boosted using plasmonic arrays. For example, the absorption efficiency of atomically thin materials can be increased by coupling them to arrays.

IV. METHODS

A. Array fabrication

The plasmonic structures were designed using full-field simulations using a finite element solver (Comsol Multiphysics) and fabricated using electron beam lithography on glass substrates. The patterns of plasmonic nanoantenna arrays were exposed on a 200 nm thick double layer poly-methyl methacrylate (PMMA) resist on a glass substrate. The bottom layer (molecular weight 250000) is more sensitive than the top layer (molecular weight 950000), resulting in an undercut that facilitates lift-off processing. A 30 nm thick layer of conductive polymer (eSpacer 300Z) was spin coated on top of the resist to prevent charging of the sample. The sample was developed after exposure and 3 nm of chromium and 30 nm of gold were deposited by thermal evaporation from resistively heated sources. After a lift-off process the metal remains on the substrate only in the exposed regions.

B. Growth and transfer of GNRs

Seven atom wide armchair-edge graphene nanoribbons were grown on a single crystalline Au (788) surface as described earlier³¹. The ribbons are aligned along the crystal edges of the gold crystal on a macroscopic scale. We transferred the ribbons from the gold crystal to the plasmonic structures using bubbling transfer as described earlier^{31,51,52}. The nanoribbons were placed on the plasmonic arrays with their orientation aligned along one of the arrays' main axis.

C. Optical characterization

Photoluminescence and low-resolution Raman spectroscopy measurements were carried out in a sample-scanning micro-photoluminescence setup. The excitation was performed with a super-continuum source (NKT, SuperK EXTREME) in combination with a variable optical bandpass filter (NKT SuperK VARIA). To be able to perform tunable Raman spec-

troscopy, the spectral bandwidth of the incident light was further narrowed down to below 1 nm using a home-built optical filter based on a diffraction grating and slit assembly. The sample illumination was performed through a microscope objective with a numerical aperture of 0.8 (MPlanFl, Olympus). Emitted light was collected with the same objective and separated from the incident light using a beam splitter and long-pass filters. The incident laser light was weakly focused in the back focal plane of the microscope objective. With this the illumination spot size was increased to approximately 6 μm . This narrows down the angular spectrum of the illumination and improves the comparability to simulation, where we consider excitation by a plane wave (at normal incidence). All spectrally integrated signals were recorded with a single photon counting module. Spectra were acquired using a grating spectrometer equipped with a deep-cooled charge-coupled device (CCD) camera. The high-resolution Raman spectroscopy investigations (Figs. 1d and e) were performed in backscattering geometry under ambient conditions using a commercial Raman system (Renishaw). The laser power on the sample was kept below 0.1 mW (532 nm) or 0.2 mW (633 nm). Raman spectra were calibrated using Si peak at 520.5 cm^{-1} . A half-wave plate was used to rotate the polarization of the laser beam. To collect a certain polarization of the Raman light, a polarizer and a half-wave plate were inserted before the detector

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