Large-area nanoengineering of graphene corrugations for visible-frequency graphene plasmons

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Quantum confinement of the charge carriers of graphene is an effective way to engineer its properties. This is commonly realized through physical edges that are associated with the deterioration of mobility and strong suppression of plasmon resonances. Here, we demonstrate a simple, large-area, edge-free nanostructuring technique, based on amplifying random nanoscale structural corrugations to a level where they efficiently confine charge carriers, without inducing significant inter-valley scattering. This soft confinement allows the low-loss lateral ultra-confinement of graphene plasmons, scaling up their resonance frequency from the native terahertz to the commercially relevant visible range. Visible graphene plasmons localized into nanocorrugations mediate much stronger light–matter interactions (Raman enhancement) than previously achieved with graphene, enabling the detection of specific molecules from femtometer solutions or ambient air. Moreover, nanocorrugated graphene sheets also support propagating visible plasmon modes, as revealed by scanning near-field optical microscopy observation of their interference patterns.

The nanoscale confinement of its charge carriers is an effective approach for engineering the properties of graphene, for example, through opening sizeable band gaps, or tuning its plasmon resonance frequencies. While transverse confinement—at the origin of the unique properties of 2D crystals—can easily be achieved by isolating single layers, an efficient in-plane confinement usually requires much harsher modifications, such as defining physical edges or employing covalent chemistry. Such hard potentials, acting through strong inter-valley scattering of charge carriers, significantly reduce charge carrier mobility and they also strongly damp plasmon resonances. While these adverse effects can be tolerated in larger structures, they become increasingly prohibitive in the sub-10 nm range. Softer (smoother) potentials, avoiding inter-valley scattering, are usually not effective for confinement, since intra-valley backscattering is pseudospin-suppressed in graphene. Nevertheless, this suppression can be lifted by pseudo-magnetic fields emerging from mechanical strain. Edge-free confinement has previously been achieved in graphene by creating local $p-n$ junction resonators. However, downsizing the confining structure size into the sub-10 nm range, as well as defining macroscopic arrays of such $p-n$ resonators, is highly challenging. Here, we achieved the sub-5 nm edge-free confinement of charge carriers by employing strong nanoscale corrugations. Random nanocorrugations are characteristic of 2D crystals, conferring them mechanical stability. However, the associated relatively weak distortions only slightly perturb the atomic and electronic structure and are primarily regarded as a source of disorder. By increasing their amplitude, one only expects to amplify the disorder. By contrast, we found that increasing the corrugation beyond a critical level ($<5$ nm lateral size, $>0.4$ aspect ratio) enables an efficient modification of the electronic structure, through nanoscale confinement of charge carriers, while largely avoiding their inter-valley scattering. Graphene plasmonics is a prominent field that can benefit from such soft nanostructuring. Graphene plasmons possess many intriguing properties, outperforming conventional metal nanoparticles in terms of mode volume confinement, environmental stability and biocompatibility. However, exploiting graphene plasmons in the commercially relevant visible range is hindered by their significantly lower (THz) native resonance frequency. In the classical Drude approximation, the resonance frequency of graphene plasmons scales as $\omega \propto D^{-1/2}$, where $D$ is the confining structure size. Experiments employing arrays of graphene nanoribbons and quantum dots confirmed that, by decreasing the nanostructure size, the plasmon resonance frequency can be increased. Graphene nanoribbons of widths below 100 nm hosting infrared plasmons have been employed to enhance the detection of various gas molecules with infrared spectroscopy. However, further decreasing the size of nanostructures substantially increases losses that become prohibitive before plasmon frequencies could reach the visible range. Charge carrier scattering on graphene edges was identified as one of the main reasons for damping graphene plasmon resonances. In this Article, we show that the simple and scalable soft nanoengineering technique, based on amplifying random nanoscale corrugations, allows the edge-free lateral confinement of graphene plasmons into ultra-small (sub-5 nm) areas, scaling up their resonance frequency into the visible range.

Graphene with strongly enhanced nanoscale corrugation

Graphene sheets with unprecedentedly strong nanoscale corrugations were prepared by cyclic thermal annealing (typically 2–4 cycles between room temperature and ~400°C) of mechanically exfoliated graphene flakes on standard SiO$_2$/Si substrates (see Supplementary Section I for details). Figure 1a,b shows the nanoscale topography obtained from scanning tunnelling microscopy (STM) investigations of electrically contacted flakes, revealing a heavily nanocorrugated graphene structure.
The root mean square roughness value extracted from topographic STM images is about 0.5 nm. This is almost double the root mean square value measured in graphene on SiO₂ (0.27–0.35 nm)¹⁹. The characteristic aspect ratios \( h_{\text{max}}/R \), where \( h_{\text{max}} \) stands for the maximum height of the corrugation and \( R \) stands for the in-plane radius of the corrugation) of graphene nanocorrugations are typically 0.4–0.5 (Fig. 1c). To ensure that the topography obtained by STM is not strongly influenced by the electronic structure, we also performed atomic force microscopy (AFM) investigations (Supplementary Fig. 2). The results clearly highlight the extreme nature of the nanoscale deformations (corrugation) of graphene sheets, especially as scanning probe techniques tend to underestimate the aspect ratio of nanoscale features due to tip convolution effects²⁰. The ability to create heavily nanocorrugated graphene originates from the interplay of two strong, but antagonistic, effects. These are the large strains emerging in supported graphene during thermal processing (owing to its negative thermal expansion coefficient²¹) and its strong adhesion to the SiO₂ substrate²². Although nanoscale deformations of graphene can be quite different from those of classical membranes²³, molecular dynamics simulations (see Methods for details) of graphene reproduce surprisingly well the characteristic nanoscale lateral size and high aspect ratio of the experimentally observed corrugations, upon compressing the Si substrate (Fig. 1d).

Raman spectroscopy investigations of heavily nanocorrugated graphene samples using 532 nm wavelength excitation reveal no significant disorder (D) peak (Supplementary Fig. 3a), providing evidence for the absence of inter-valley scattering in spite of the heavily deformed nanoscale structure. Further details of the Raman analysis are given in Supplementary Section III.

To investigate the influence of nanoscale deformations on the electronic structure of graphene, we performed tunnelling spectroscopy measurements (Fig. 2a). Tunnelling spectra acquired on nanocorrugations display distinctive features (peaks/shoulders) around ±450 mV compared to spectra measured on quasi-flat areas of the same sample. From the peak positions, one can estimate the characteristic confinement size to be about 3–4 nm (ref. ²⁴). For further tunnelling spectra, see Extended Data Fig. 1. To confirm our interpretation of the observed features in the tunnelling spectra, we performed density functional theory (DFT) calculations on a model graphene corrugation of similar geometry (see Methods for details). The calculated density of states averaged over the graphene nanocorrugation (Fig. 2b) displays good agreement with the experimental tunnelling spectra. Plotting the spatial distribution of the calculated local density of states (LDOS) at energies near the LDOS peak clearly provides evidence for electronic states localized on the graphene nanoprotrusion (Fig. 2b inset). The ability of structural deformations (mechanical strain) to spatially confine charge carriers has already been shown both theoretically²⁵,²⁶ and experimentally²⁷,²⁸. The confinement is enabled by the large pseudo-magnetic fields emerging from nanoscale graphene corrugations (Supplementary Fig. 4) that curve the classical trajectories of...
charge carriers into closed orbits around the peaks of the inhomogeneous pseudo-magnetic field\(^26,27\).

**Strong Raman enhancement on nanocorrugated graphene**

An intriguing question is: how can the modifications discussed above of the atomic and electronic structure impart novel functionality to graphene? The edge-free nature of the confinement can allow localized plasmons to persist at such ultra-high confinement levels. This is required to scale up their resonance frequency into the visible region. A key signature of plasmons is their strong local electric field, enabling a particularly strong enhancement of light–matter interaction, leading to applications such as surface-enhanced Raman scattering (SERS) or plasmon-enhanced emission\(^1\). Graphene is already known to provide moderate Raman enhancements, often referred to as graphene-enhanced Raman scattering (GERS), and this is due to chemical enhancement mechanisms (charge transfer). GERS is characterized by enhancement factors of the order of tens as demonstrated for several molecules including copper phthalocyanine (CuPc), zinc phthalocyanine (ZnPc) and rhodamine 6G (Rh6G)\(^29–31\). Here, we performed Raman spectroscopy investigations of such molecules on strongly nanocorrugated graphene sheets. The most striking findings were observed when measuring the Raman spectra of nanocorrugated graphene sheets using 633 nm wavelength excitation. Such measurements revealed high-intensity Raman peaks without subjecting the corrugated samples to any solution, only exposing them to laboratory air (Fig. 3b). Such features were highly reproducible with different corrugated graphene samples and substrates (Supplementary Fig. 5), excluding the possibility of local contamination. The strong Raman signal picked up from air (Fig. 3b) with nanocorrugated substrates can be attributed to CuPc molecules\(^30\). While its concentration in the environment is unknown, CuPc is the synthetic dye molecule produced in the largest quantity in the world\(^32\). Using AFM and STM investigations, we ensured that no unusual contamination could be observed on the surface of nanocorrugated graphene (Supplementary Section VII). Atomic resolution STM investigations revealed features that most likely correspond to CuPc molecules present at a very low density (Supplementary Fig. 6). Consequently, the observation of Raman peaks up to 20 times higher than the graphene G peak must originate from an exceptionally strong enhancement mechanism rather than a large quantity of adsorbed molecules. As expected, exposing quasi-flat graphene sheets to the same conditions does not result in any detectable CuPc signal (Fig. 3a). Based on the comparison (of G peaks) with quasi-flat graphene, we can estimate the lowest limit of the enhancement factor for CuPc on corrugated graphene to be of the order of \(10^5\). This is clearly beyond the range of chemical enhancement (below \(10^3\) on flat graphene)\(^29,30\), indicating plasmonic activity. The highly selective detection of phthalocyanine molecules from air is truly remarkable and provides evidence for the exceptional enhancement provided by nanocorrugated graphene for such molecules. However, the overall control of the process is quite limited. To overcome this, we performed controlled experiments using ZnPc molecules. We prepared solutions of very low concentrations by serial dilution of ZnPc in isopropanol. Then, using the soaking technique\(^33\), we investigated the detection limit of nanocorrugated graphene substrates for ZnPc. The results are summarized in Fig. 3c,d. Besides ZnPc Raman peaks, CuPc peaks can also be clearly detected since Raman spectroscopy measurements were performed under ambient conditions using 633 nm wavelength excitation. We chose ZnPc as the test molecule, because two of its most intense Raman peaks are clearly distinguishable from those of CuPc (Fig. 3d). Our results reveal that ZnPc can be clearly detected from \(10^{-14}\) M solutions, while its strongest peak is still detectable from \(10^{-15}\) M solutions. This is a remarkable sensitivity, providing evidence for a three orders of magnitude lower detection limit than previously achieved with graphene (\(10^{-11}\) M)\(^31\). We also observed strong Raman enhancement on nanocorrugated graphene for a different type of molecule (R6G) at a different excitation wavelength (533 nm) (Supplementary Section VIII). Various approaches for tuning the corrugation morphology and the corresponding plasmon resonance frequency are discussed in Supplementary Section IX.

**Optical excitations of nanocorrugated graphene**

The corrugation of graphene induces a nanoscale strain inhomogeneity that affects the chemical bonding and the local electronic structure, as also seen by tunnelling spectroscopy and by DFT calculations (Fig. 2). In this case, the electromagnetic field enhancement should be modelled by first-principles approaches to take into account such local effects. To maintain reasonable calculation times, we restricted our calculations to corrugated graphene with small unit cells (50 atoms, Supplementary Fig. 9). However, the
in our case the interference patterns are observed at visible frequencies in nanocorrugated graphene, while quasi-flat graphene on doped quasi-flat graphene at infrared frequencies. However, very similar to the SNOM images of plasmon interference patterns in the proximity of edges, as well as fainter ~400 nm oscillations nanocorrugated graphene samples, with 488 nm wavelength excitation of visible graphene plasmons propagating in nanocorrugated graphene. This is a surprising finding, since localized plasmons were primarily expected. However, localized and propagating plasmons are not mutually exclusive. It has been theoretically predicted and experimentally confirmed that when separated nanostructures, hosting localized plasmons, are located in the close vicinity of each other (<λexc, where λexc stands for excitation wavelength), their interaction can give rise to propagating plasmon modes. In nanocorrugated graphene, the corrugations are typically located at least an order of magnitude closer than the excitation wavelength, enabling the interaction of localized plasmons to give rise to propagating modes, observed in our SNOM measurements (Fig. 4b and Supplementary Fig. 15). Furthermore, in such systems, the dispersion of transversal propagating modes crosses the light line, enabling the existence of plasmon wavelengths larger than the excitation wavelength. This can account for the oscillations of about 400 nm observed in SNOM images. Propagating modes with significantly smaller wavelength might also be present, but they cannot be resolved by our SNOM setup. Furthermore, propagating plasmon modes emerging from interaction of localized plasmons are predicted to persist even when disorder is present, which is clearly the experimental case. A more detailed understanding of visible graphene plasmons propagating in nanocorrugated samples requires further experimental and theoretical investigations. Confocal microscopy measurements with the same excitation wavelength show no interference patterns on nanocorrugated samples (Supplementary Figs. 14b and 15).

Our computational results clearly confirm the ability of graphene nanocorrugations with high aspect ratio to host localized graphene plasmons of visible frequencies, supporting the plasmonic origin of the observed strong Raman enhancements in nanocorrugated graphene.

Scanning near-field optical microscopy

Scanning near-field optical microscopy (SNOM) measurements of nanocorrugated graphene samples, with 488 nm wavelength excitation (see Methods for details), reveal clear interference maxima in the proximity of edges, as well as fainter ~400 nm oscillations inward from edges and defects (Fig. 4b). The observed patterns are very similar to the SNOM images of plasmon interference patterns on doped quasi-flat graphene at infrared frequencies. However, in our case the interference patterns are observed at visible frequencies in nanocorrugated graphene, while quasi-flat graphene samples imaged under the very same conditions show no signs of plasmon interference (Fig. 4c). Detecting interference patterns clearly indicates the presence of propagating visible plasmons in nanocorrugated graphene. Main features reported for larger supercells are still captured (that is the localisation of the electronic states manifested in LDOS peaks, Supplementary Fig. 10). Our calculations showed that nanoscale corrugations of high aspect ratio significantly modify the in-plane conductivity of graphene in the visible range compared to the constant value for flat sheets (Supplementary Fig. 11). To understand the origin of these resonances, we simulated the corresponding electron energy loss spectroscopy (EELS) spectrum that reveals well-defined peaks, associated with plasmon-like excitation in the visible range, in contrast to the featureless loss spectrum of flat graphene (Fig. 4a). We also calculated and plotted the real-space charge distributions corresponding to various peaks; some of them shown as insets of Fig. 4a.

Fig. 3 | Large Raman enhancement on nanocorrugated graphene sheets. a, b, Raman spectra (633 nm) of quasi-flat (a) and nanocorrugated (b) graphene sheets subjected to air, the latter detecting high intensity CuPc contamination peaks from nominally clean laboratory air. c, Raman signature of ZnPc molecules detected from down to femtomerol (10⁻¹⁵ M) ZnPc solutions. CuPc peaks originate from air contamination. d, Enlargement of c on the region displaying distinct ZnPc (highlighted) and CuPc peak positions.
We have also found signatures of plasmon activity in nanocorrugated graphene by EELS, spectroscopic ellipsometry and optical reflectance measurements. The results are presented in Supplementary Sections XII, XIII and XIV, respectively.

Conclusions
We have shown that amplifying the random nanoscale corrugation of graphene allows the edge-free lateral confinement of plasmons into ultra-small (sub-5 nm) areas, scaling up their resonance frequency into the commercially relevant visible range. Visible frequency graphene plasmons can host both localized and propagating graphene plasmons. The observation of propagating plasmons in nanocorrugated graphene provides evidence for its unique potential as a versatile platform for strong light–matter interactions.

Online content
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Methods

Raman spectroscopy and SNOM measurements were carried out using a Witec 300RS+ confocal system, with 488, 532 and 633 nm wavelength excitation lasers. Single Raman spectra were acquired using 0.5 mW laser power and exposure times between 60 and 180 s, ensuring that the Raman signal did not change significantly during the measurement. SNOM measurements were performed in reflection mode, with the SNOM sensor consisting of a Si cantilever and a hollow aluminium pyramid tip with an aperture of 150 nm.

STM, AFM and tunnelling spectroscopy measurements were performed on a Nanoscope Multimode 8 setup operating under ambient conditions. Some STM and tunnelling spectroscopy measurements were performed in an RHK Pan Scan ultra-high vacuum setup. AFM measurements were conducted in tapping mode.

For STM measurements, the graphene flakes on insulating SiO2/Si substrates were prepared in an ultra-high vacuum setup. AFM measurements were conducted in tapping mode. For STM measurements, the graphene flakes on insulating SiO2/Si substrates were electrically contacted and identified under an optical microscope, enabling a guided landing of the Pt–Ir STM tip.

Molecular dynamics simulations. The corrugation of periodic 400 × 400 graphene (roughly 640,000 atoms) was obtained on a Si(111) substrate by applying 0.75 GPa lateral pressure to the substrate at 300 K using Nose–Hoover NPT molecular dynamics simulations with the LAMMPS code (bcp carbon potential42, Lennard–Jones for carbon–Si interaction: ε = 0.025, r0 = 3.5 Å, cutoff = 6.0 Å, Tersoff–88 for Si43, adaptive time stepping).

Graphene nanocorruption model geometries. Gaussian nanowrinkles were generated and subsequently optimized using the LAMMPS code (conjugated gradient minimization together with the relaxation of the simulation cell vectors). In order to avoid the collapse of the protrusions, a pulling force along the z-axis perpendicular to the protrusion of the base sheet was utilized. Using this approach, we were able to stabilize the dome height and relax the buckled structure to the possible minimum strain level.

DFT band structure. The fully periodic SIESTA code44 was used for fully self-consistent electronic structure calculations (double zeta + polarization (DZP) basis set, 400 Ry mesh cutoff, 15 × 15 Monkhorst–Pack k-mesh, PBE exchange–correlation functional). A diffusion function was added to the standard DZP basis set in order to improve the long-range behaviour of the wavefunction for high-quality LDOS maps. The SIESTA-generated wavefunction file was used for post-processing the LDOS using the Denchar utility code. We ensured that the resulting peaks did not originate from the superlattice effect, but were characteristic of nanoscale graphene protrusions, by performing calculations with different supercell sizes.

Optical calculations. First-principles simulations of the conductivity, EELS spectra and associated maps of the induced potential were obtained using the GPAW code45. The local density approximation (LDA)46 for the exchange–correlation of electrons with a plane-wave basis set and an energy cutoff of 400 eV was employed. The Brillouin zone was sampled with a 32 × 32 × 1 Monkhorst–Pack mesh. For the calculation of the dielectric matrix we used an energy cutoff of 20 eV for the reciprocal lattice vectors G and G’ and a smearing of 0.025 eV. We note that the maxima of the conductivity do not perfectly match those of the EELS spectra, since EELS is more sensitive to collective excitations with high electromagnetic response and dipolar selection rules break down in EELS (ref. 47).

Data availability

Source data are provided with this paper. The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions

L.T. conceived and designed the experiments. G.D. and P.N.-I. performed the sample preparation and the Raman and SNOM measurements. G.D. performed the STM and AFM investigations. P.S. performed molecular dynamics, geometry optimization and DFT LDOS calculations. B.M., P.V. and L.H. performed the optical calculations. P.P. and B.K. performed the spectroscopic ellipsometry measurements. M.M. measured the EELS spectra. G.P. and G.D. conducted the reflectance spectroscopy measurements. L.T. wrote the paper. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Extended Data Fig. 1 | Tunneling spectra of graphene nanocorrugations. Additional tunneling spectra acquired under UHV conditions near the top of high aspect ratio ($h_{\text{max}}/R > 0.4$) graphene nanocorrugations. Inset shows the $dI/dV$ spectra acquired on quasi-flat areas of the sample. b) DFT calculated local density of stated at the apex of a graphene nanocorrugation with $h_{\text{max}}/R \sim 0.4$. 