Strong coupling of carbon quantum dots in plasmonic nanocavities

Katzen, J., Tserkezis, C., Cai, Q., Li, L. H., Kim, J., Lee, G., Yi, G-R., Hendren, W. R., Santos, E. J. G., Bowman, R. M., & Huang, F. (2020). Strong coupling of carbon quantum dots in plasmonic nanocavities. *ACS Applied Materials and Interfaces*, 12(2020), 19866. <https://doi.org/10.1021/acsami.0c03312>

Published in:
ACS Applied Materials and Interfaces

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
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Nanopolaritons of single graphene quantum dots in plasmonic nanocavities

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KEYWORDS: nanopolariton, polariton, strong coupling, graphene quantum dot, plexciton, Rabi splitting, plasmonics

Nanopolaritons are magnificent examples of cavity quantum electrodynamics (QED) phenomena^{1,2}. They arise from extraordinarily strong light-matter interactions and are instrumental to modern optics, such as in lasers, single photon transistors, Bose-Einstein condensation and quantum information processing³⁻⁶. However, diffraction effects limit confinement of light to the wavelength scale in conventional photonic structures. Here we demonstrate the realization of nanopolaritons of single graphene quantum dots (GQDs) in plasmonic nanocavities. The extremely strong optical near-fields confined in plasmonic nanocavities facilitate the formation of single GQDs and empower the strong coupling between the localized surface plasmon and the excitons of the GQDs, forming nanopolariton quasiparticles that are half-matter, half-light. Significant Rabi-splitting up to 200 meV is observed at room temperature, which is also continuously tuneable. Realizing nanopolaritons of individual GQDs provides unique avenues for studying

cavity QED at the nanoscale and offers exciting opportunities to develop ultracompact, robust and high-performance optoelectronic devices.

Light emitters confined in a cavity form polaritons when the conditions for strong coupling (SC) are fulfilled¹⁻⁶. In this scenario, the spontaneous emission of quantum emitters couples strongly with cavity modes, hybridizing into polariton quasiparticles that are half-matter, half-light. Polaritons have been mostly achieved in high-Q cavities at cryogenic temperature due to the stringent requirements of extraordinarily strong light-matter interaction, however, due to the diffraction effect, conventional microcavities can only confine light in space at the wavelength scale of volume $V \sim \lambda^3$ ($1.25 \times 10^8 \text{ nm}^3$ for $\lambda = 500 \text{ nm}$). By contrast, plasmonic structures can concentrate light in nanocavities of volume $V \approx L^2 d$, (L is the lateral confinement of the optical fields and d is the gap size. For a typical plasmonic nanocavity, $L = 10 \text{ nm}$, $d = 1 \text{ nm}$, $V \approx 1 \times 10^2 \text{ nm}^3$), millions of times more compact than conventional photonic structures, which can enormously enhance the local optical fields. These have been at the core of a broad range of applications, including subwavelength imaging, single molecular sensing, ultrahigh density data storage and nonlinear optical effects⁷⁻¹⁰. While plasmonic materials usually are lossy, the extremely strong optical near-fields confined within the ultracompact cavity overwhelm the damping effects to facilitate SC within nanoscale cavities, as the coupling strength g is proportional to $\frac{1}{\sqrt{V}}$, where V is the cavity volume¹¹. As such, plasmonic nanostructures have emerged as excellent platforms for realizing nanopolaritons induced by the SC between spontaneous emission and localized surface plasmon, so called plexcitons^{1,11-14}, which have been demonstrated on a range of nanomaterials, including J-

aggregates¹¹, semiconductor quantum dots^{1,12}, single molecules¹³ and two-dimensional materials¹⁴.

Here we report the realization of nanopolaritons of single graphene quantum dots (GQDs) in plasmonic nanocavities. GQDs are nanometer-sized graphene fragments, which are fascinating fluorescent nanomaterials^{15,16}. Unlike conventional graphene, GQDs have a non-zero bandgap due to quantum confinement effects, which span from deep ultraviolet to near infrared and can be tuned with a plethora of means, including size, shape, edge configuration, functional groups, doping, defects, reduction and oxidization processes¹⁷⁻¹⁹. Compared to other luminescent materials, such as semiconductor quantum dots, dye molecules and up-conversion nanoparticles (NPs), GQDs have superior properties such as chemically stable, biocompatible, nontoxic and robustly photo-stable, as such, they have emerged as wonderful alternative biolabeling nanomaterials and important building blocks in photovoltaics, display and sensing¹⁵⁻¹⁹. Realizing nanopolaritons on single GQDs will pave the way to develop robust, bright and broadly tuneable quantum emitters central to many applications¹⁵⁻¹⁷, however, this has not been demonstrated. Fabricating and manipulating individual GQDs are remarkably challenging. Conventional fabrication technologies, either the top-down or the bottom-up methods, produce assemblies of GQDs^{20,21}. Single GQDs were only demonstrated to be fabricated by unconventional techniques like transforming fullerene molecules such as C₆₀ under elevated temperatures²², which is not scalable and extremely difficult to precisely deposit in a plasmonic cavity.

We demonstrate the realization of both the synthesis and SC of single GQDs in plasmonic nanocavities. Employing a nanoparticle-on-mirror (NPoM) plasmonic structure and using monolayer graphene films as the spacing layer (Figure 1), we fabricated ultracompact nanocavities with massive enhancement of the local optical fields up to ~ 320 folds in magnitude. The extremely strong and tightly confined optical near-fields facilitate the formation of single GQDs (see Graphene quantum dots section for details) and empower the SC between the localized surface plasmon and the excitons of the formed GQDs, manifested as distinctive double-peak profiles in the optical scattering spectra of the hybrid plasmonic system. The two split scattering modes exhibit typical anti-crossing behaviour with magnificent Rabi splitting energy of ~ 200 meV, which is extraordinary for a single quantum emitter at room temperature, much higher than those reported in the literature¹¹⁻¹⁴. We further proceeded to demonstrate a continuously tuneable SC on a single NPoM/GQD structure, which shows anti-crossing behaviour superbly match that measured on assemblies of individual NPs. The synthesized GQDs are characterized by Raman and photoluminescence (PL) spectroscopies. The results are compared to theoretical simulations, which match excellently.

Results

Figure 1a shows the schematic of the NPoM structure. A Au NP is placed on top of a reflective thick Au film of 100 nm, separated by a graphene layer, forming a sub-nanometer-sized cavity of volume $V \approx L^2 d$ (Figure 1a). Such a NPoM structure can produce extraordinarily strong field enhancements in the gap, making it one of the most popular plasmonic structures widely adopted in plexciton studies and applications^{12,14,23-26}. To minimize the impacts of NP geometry variance, we used ultra-smooth and near-perfect spherical Au NPs with a nominal diameter of 93 ± 3 nm, as shown in the transmission electron microscopy (TEM) image (Figure 1b). Au NPs deposited on a clean Au substrate look identically green and uniform under dark-

field optical microscope (Figure 1c), confirming the excellent uniformness of the NP geometry. Graphene films were exfoliated onto Au substrates using traditional scotch tape methods^{27,28}. Film thickness was characterized by optical contrast spectroscopy, atomic force microscopy (AFM) and Raman spectroscopy (see Supplementary Figures 1 and 2 for details). Au NPs were drop-cast on top (see Method for details). Dispersed individual NPs are clearly visible in the dark-field (Figure 2a) and bright-field (Figure 2b, converted to grey scale for better contrast. True-colour image see Supplementary Figure 1) optical images which show notably different colours in different regions. Particles in region I (bare Au surface) are mostly green, consistent with Figure 1c. The variance of some NP colours is due to the tape residuals on the Au surface after exfoliation and/or NP clusters (the bright ones). Particles in region II (on monolayer graphene) and region III (on multilayer graphene films) appear red/yellowish, much different to the green ones on clean bare Au surfaces (Figure 1c).

Figure 1 | Nanoparticle-on-mirror plasmonic structure (a) Diagram of a gold nanoparticle on top of a reflective thick Au film, separated by a graphene spacing layer, forming a nanocavity of volume $V \approx L^2 d$. (b) TEM image of an ultra-smooth spherical gold particle of 95 nm diameter. (c) Optical dark-field images of gold NPs directly (without graphene spacer) deposited on a clean gold surface of 100 nm thickness. Scale bar, 5 μm .

Figure 2 | Optical images and scattering spectra of NPoM structures (a) Dark-field and (b) bright-field (grey scale) optical images of Au NPs deposited on bare 100 nm Au film (region I), on monolayer graphene spacers (region II) and on multilayer graphene spacers (region III). Borders are marked by dashed lines. Scale bar, 10 μm . (c) Measured scattering spectra of Au NPs spaced by 0 (bare Au), 1, 2 and 3-layer graphene films. (d) Measured scattering spectra of a number of Au NPs on monolayer graphene spacers.

The different appearance in colour was confirmed by optical scattering spectra. Au NPs on bare Au substrates (0L, Figure 2c) show two scattering peaks in the green spectral region at 2.15 eV and 2.32 eV, respectively. The 2.32 eV peak is the transverse mode of isolated Au NPs, whereas the 2.15 eV low-energy mode is the remnant of a weak charge transfer plasmon due to the contact between the NP and substrate²⁶. By contrast, the scattering spectra of NPs on 1-3L graphene films show strong scattering peaks between 1.8-2.1 eV (Figure 2c), which are absent in the spectra of NPs on bare Au surfaces. These modes are the bonding dimer modes due to the coupling between the NP and its image particle in the substrate²⁶. More intriguingly, for Au NPs spaced by monolayer graphene (for simplicity, hereafter this structure is referred as NPoM1LG), the scattering spectrum exhibits split double peaks (1L, Figure 2c), whereas those

spaced by 2-3L films only show a single peak. We measured the scattering spectra of a number of NPoM1LGs, which universally show split two peaks between 1.8-2.1 eV with varying profiles (Figure 2d). These are characteristic features of plexciton, frequently observed in experiments¹¹⁻¹⁴.

Strong coupling

The SC between exciton and plasmon can be described by a semi-classical coupled oscillator model, with the frequency of the two splitting modes given by^{2,29}:

$$\omega_{\pm} = \frac{(\omega_{sp} + \omega_0)}{2} \pm \sqrt{g^2 + \frac{\delta^2}{4}} \quad (1)$$

ω_{sp} , ω_0 are the frequencies of plasmon and exciton, respectively; $\delta = \omega_{sp} - \omega_0$; $g \propto \frac{1}{\sqrt{V}}$ is the coupling strength.

The Rabi splitting energy Ω is the difference between the upper branch (ω_+) and the lower branch (ω_-),

$$\Omega \equiv \omega_+ - \omega_- = 2\sqrt{g^2 + \frac{\delta^2}{4}} \quad (2)$$

$\omega_{\pm}$ can be obtained by fitting the scattering spectra with two Lorentzian peaks. The results obtained from a number of individual NPoM1LGs are shown in Figure 3a (large symbols of pentagons and hexagons), which show typical anti-crossing behaviour and a plasmonic mode of $\omega_{sp} = 1.82 \pm 0.1$ eV. The exciton energy is obtained from $\omega_0 = \omega_+ + \omega_- - \omega_{sp}$ (eq.1). The minimum Rabi splitting energy at the resonant condition ($\omega_0 = \omega_p = 1.82$ eV) is ~ 140 meV and the maximum is ~ 200 meV, which are magnificent for a single quantum emitter observed at room temperature, almost twice as large as those reported in the literature¹¹⁻¹⁴. For

SC to occur, a stringent condition of $\Omega > \frac{\gamma_{sp} + \gamma_0}{2}$ must be matched^{2,29}, γ_{sp} and γ_0 are the decay rates of plasmon and exciton, respectively. As $\gamma_{sp} + \gamma_0 = \gamma_+ + \gamma_-$, where γ_+ and γ_- are the full-width-at-half-maximum (FWHMs) of ω_+ and ω_- , respectively², from the experimental results it is inferred that $\frac{\gamma_+ + \gamma_-}{2} \approx 130$ meV, which is smaller than the minimum Rabi splitting energy (140 meV), hence the condition of SC is adequately fulfilled.

Previously, the detuning of plexcitons was mainly established from ensembles of plasmonic systems^{11,12,14}, which could have ambiguity caused by the variance in NP geometry and the number and orientations of molecules. In this investigation, we have significantly mitigated the variance of NP geometry by using uniform and near-perfect spherical NPs. We took a step further to tune the Rabi splitting on a single NPoM1LG. To achieve this, we irradiated a NPoM1LG with 532 nm laser of low power (75 μ W, focused by a 100 $\times$ magnification objective, NA= 0.9) for 10 seconds, then immediately measured the scattering spectrum (with laser off) on the NPoM1LG. This process was repeated successively. Figure 3b shows the successively measured scattering spectra after the N-th irradiation (0th refers to the spectrum prior to laser irradiation). Initially the two split peaks are distinctly separated, but they evolve continuously and gradually merge into a single broad profile after the 9th irradiation (the top spectrum, Figure 3b). The two split scattering modes are extracted through best fits of two Lorentzian peaks and plotted in Figure 3a (the small pentagons and hexagons, redshifting with irradiation as indicated by the arrows), which superbly follow the same trends of the anti-crossing curves measured from various individual NPoM1LGs (large pentagons and hexagons). This unambiguously confirms that nanopolaritons have been achieved on individual NPoM1LGs in the plasmonic nanocavity at ambient conditions. The detuning of

the SC is caused by enhanced carbon solubility in heated Au NPs under laser irradiation (details will be discussed in Graphene quantum dots Section).

Figure 3 | Strong coupling observed on the scattering spectra of NPoM1LGs (a)

Dependence of the Rabi splitting modes $\omega_{\pm}$ on the exciton energy of GQDs. Large and small symbols represent the results from individual NPoM1LGs and a single NPoM1LG tuned by laser irradiation, respectively; circles are from simulations shown in **d**. **(b)** Ten consecutive scattering spectra of a single NPoM1LG, measured (with laser off) immediately after the N-th irradiation by a $75 \mu\text{W}$ 532 nm laser for ten seconds. **(c)** Simulated near-field distribution of a NPoM1LG structure, excited by 685 nm . Dashed circle marks the NP geometry. Bottom: profile of field enhancement in the cavity along the horizontal dashed line, indicating a 320-folds enhancement at the cavity centre, with a FWHM $L = 14 \text{ nm}$. **(d)** Simulated scattering spectra of NPoM1LG as a function of exciton energy between 1.76 and 1.90 eV , increment by 0.02 eV . The Rabi splitting modes $\omega_{\pm}$ are shown in **a** (circles). The top spectrum is the scattering spectrum of NPoM1LG at $\omega_0 = 0$ without the coupling effect, showing an intrinsic plasmonic mode at 1.82 eV .

For better understanding the SC in the plasmonic nanocavity, Figure 3c shows simulated near-field distribution inside the nanocavity of a NPoM1LG (details see Method). Massive field enhancement of ~ 320 folds is concentrated in the cavity of $V \approx (0.6 - 6) \times 10^2 \text{ nm}^3$ ($V \approx L^2 d$, $L = 14 \text{ nm}$, $d: 0.3 - 3 \text{ nm}$, dependent on the thickness of GQDs), which is about two orders smaller than those reported in the literature^{11,14}. The simulated scattering spectra of NPoM1LGs of varying exciton energies show evolving profiles closely resembling those of the measured ones (Figures 3b, 3d). The energies of the two split modes are plotted in Figure 3a (circles), in excellent agreement with the experimental results. The calculated scattering spectrum of NPoM1LG without coupling with excitons ($\omega_0 = 0$) is shown at the top of Figure 3d, indicating an intrinsic plasmonic mode at $\omega_{sp} = 1.82 \text{ eV}$, consistent with the experimental result (Figure 3a).

Graphene quantum dots

The observed nanopolaritons are generated through the SC between the localized surface plasmon and the excitons of GQDs. Graphene fragments readily form on the surface of Au NPs supported on carbon films at elevated temperature³⁰⁻³². This also could happen by carbonizing the adsorbed hydrocarbon molecules on Au in the absence of the supporting carbon films^{21,33,34}. Carbon has very little solubility in bulk Au³⁰, however, heated Au NPs can take giant solubility of carbon³⁰, several orders higher than that in bulk Au. Upon cooling the over-saturated carbon atoms diffuse to the surface and form fragments of graphene or even complete graphene shells, which have been frequently observed in TEM³⁰⁻³². We observed thin graphene shells of $\sim 2 \text{ nm}$ thickness formed on the surface of Au NPs deposited on carbon films of TEM grids (Supplementary Figure 3). The NPoM1LG experiments are similar cases. Au NPs were

supported by graphene films in analogy to the TEM carbon film. The intense optical near-fields in the cavity heated up Au NPs, which absorbed a large concentration of carbon atoms. Upon cooling, carbon atoms precipitated and formed GQDs on the NP surfaces in the plasmonic cavity. When GQD-coated NPs were irradiated by laser, carbon atoms diffused from GQDs into Au NPs, which tuned the SC. In the experiments, the power of irradiation laser is low (75 μW), which did not cause permanent damages to the NPoM1LG system, such as deforming Au NPs or breaking graphene films. This is confirmed by the complete recovery of the scattering spectra of Au NPs after being irradiated by laser or heated on a hot plate to 160°C (Supplementary Figure 4). The recovery is a relatively slow process, usually taking a few or tens of hours. This rules out the possibility of doping, thermal expansion and strain as the possible major causes for the observed spectral evolution in the scattering spectra, as these effects would recover rather quickly after measurements. The long recovery time is a result of the slow diffusion process of carbon atoms in the solid of Au.

To confirm the existence of GQDs, we measured the Raman spectra on individual Au NPs deposited on 100 nm Au surface spaced by 1-4L graphene films (Figure 4a), which show strong *D*-modes ($\sim 1314\text{ cm}^{-1}$) and *G*-modes ($\sim 1589\text{ cm}^{-1}$) of carbon. These are not from the underlying graphene films, which show the typical *G*-modes ($\sim 1585\text{ cm}^{-1}$) and 2*D* modes ($\sim 2703\text{ cm}^{-1}$), but without the *D*-modes (Supplementary Figure 5). The *D*-mode is a characteristic Raman peak of carbon nanomaterials. The FWHM of *D*-mode is inversely linked to the size of carbon nanocrystals³⁵, for example, the *D*-modes of nano graphite and nano diamond films are narrow while those of amorphous carbons are very broad³⁵⁻³⁷. The Raman spectra shown in Figure 4a are the typical Raman spectra of GQDs^{18,20,38}, with a narrow *D*-modes (FWHM $\sim 183\text{ cm}^{-1}$) reflecting the nanometer-sized graphene crystals. The intensities

of the *D*-modes and the *G*-modes increase exponentially with decreasing graphene layers (Figure 4b, plotted in logarithmic scale). This is why SC is only observed on NPoM1LGs, not on structures with thick graphene spacers. Only the NPoM structures of the smallest cavity provide the massive field enhancements that are able to match the stringent conditions of SC.

To further confirm the formation of GQDs, we measured PL spectra on NPoM1LGs. The emission energy of most fluorescent materials is independent on the wavelength of the excitation laser. By contrast, the PL of GQDs is extremely sensitive to the excitation wavelength. Their emission peaks usually redshift and the intensities diminish with the excitation wavelength^{18,20,38}. Figure 4c shows the measured PL spectra on a NPoM1LG under excitation wavelengths of 532, 543, and 594 nm, respectively. As expected, the PL intensity excited by 594 nm is much weaker than that excited by 532 nm laser. The extraordinarily strong PL intensity excited by 543 nm is caused by the resonant absorption due to the $S_0 \rightarrow S_3$ transition^{19,21}. Each PL spectrum is composed of three peaks (as an example, the Lorentzian fitting of the PL spectrum excited by 543 nm is shown in Figure 4c. Results of all spectra are shown in Supplementary Figure 6), corresponding to the triplet electronic states of GQDs^{19,39}, which are not obvious on GQD assemblies due to the average of large numbers of molecules, but are pronounced on individual GQDs. The three PL emission peaks are presented in Figure 4d, which clearly redshift with the excitation wavelength, consistent with the literature^{18,20,38}. The long wavelength mode at 727 nm is a phosphorescent mode^{19,39}, whereas the one at 674 nm (black dashed line, Figure 4c) is a fluorescent mode, which couples strongly with the localized surface plasmon of the NPoM system, generating the nanopolaritons. The observation of PL is strong evidence of SC. Normally, PL is not observable in the NPoM structure, as it

would be quenched by the nearby metal surfaces. However, when SC happens, quenching can be overtaken by the SC effect and strong light emission becomes possible^{2,40}.

Figure 4 | Graphene quantum dots (a) Raman spectra measured from individual Au nanoparticles on 100 nm Au film, with 1-4L graphene film spacers. For better clarity, spectra are vertically offset and the spectra of 2-4L are magnified by the indicated factors. All Raman spectra were taken at 100x magnification with a 633 nm laser of 1.1 mW. (b) Raman intensity of the D-peaks and G-peaks of the spectra in a against the number of graphene layers, indicating an exponential dependence (natural log scale) on the number of graphene layers. (c) Photoluminescence spectra measured on a NPoM1LG excited by 532, 543 and 594 nm lasers, respectively, showing typical excitation-dependent behaviour. Dotted lines indicate three Lorentzian fitting curves of the 543 nm-excited PL spectrum with the combined fitting curve shown in red solid line. The middle peak at 674 nm is a fluorescent peak responsible for the SC. (d) Three emission peaks of the PL spectra in c.

Conclusion

Here we demonstrate the realization of nanopolaritons of single GQDs in plasmonic nanocavities. By adopting a NPoM plasmonic structure with monolayer graphene as the spacing layer, extraordinarily strong optical near fields are produced and tightly concentrated in the gap of the NPoM1LG structure, facilitating the formation of individual GQDs and empower the strong coupling between localized surface plasmon and the spontaneous emission of the formed GQDs. These are manifested in the optical scattering spectra as distinctive splitting peaks. The energies of the split scattering modes show typical anti-crossing behaviour with magnificent Rabi splitting up to 200 meV at room temperature. In addition, the GQD nanopolaritons are tuneable with laser irradiation and recoverable at ambient conditions. GQDs are excellent fluorescent nanomaterials, hugely important in a broad variety of areas. Exploring nanopolaritons of individual GQDs provides unique avenues to facilitate a range of important fundamental research, such as nanocavity QED, single GQD fluorescence and tuneable plexcitons, which are instrumental to a wide range of applications, such as in nanolasers, low-energy optical transistors and quantum computing.

Method

Sample fabrication

Gold substrates are fabricated by UHV magnetron sputtering. A 10 nm Ti adhesion layer was sputtered on top of substrates of 93 nm SiO₂/bulk Si, then followed by sputtering of 100 nm Au. Graphene and MoS₂ spacings were directly mechanically exfoliated from synthetic highly oriented pyrolytic graphite (HOPG) using Scotch tape. Gold NPs are prepared by slow reduction of chloroauric acid in ethylene glycol. PolyDADMAC stabilises the particles, while the reduction rate is maintained by phosphoric acid. An oxidizing agent (chloroauric acid) is

then added to the solution, forming ultrasmooth, spherical particles⁴¹. The particle solution was diluted by ten times in deionized water and 1-10 μL drop cast onto the sample with a micropipette. After the solution was allowed to dry in ambient conditions, the samples were cleaned with deionized water and dried with compressed air to remove excess particles.

Optical characterization and laser irradiation

Graphene flakes were first identified optically. Their thickness was then characterized through tapping mode AFM. Subsequently, Raman spectra were taken from the flakes, using a 532 nm laser (1 mW). Raman signals were measured with a Jobin Yvon HR640 spectrometer. The same apparatus is used to irradiate the particles, with a laser of power 75 μW . All measurements were taken with a 100 $\times$ objective (MPlan N, Olympus, NA=0.9).

Theoretical simulations

Numerical calculations were performed using the finite-element method (FEM). We employed the RF module of the commercial software Comsol Multiphysics 5.1. A plane wave impinging at 64° (corresponding to 0.9 numerical aperture) was used as the source, and Maxwell's equations were solved for the scattered field. The scattered energy was obtained by integrating the scattered contribution to the energy flow over a square surface containing the nanoparticle with side length 200 nm. The nanoparticle was separated from a 100-nm thick gold film by a graphene monolayer. 600-nm thick perfectly matched layers were employed to ensure minimum reflection at the simulation domain boundaries for the entire range of wavelengths of interest. The nanoparticle was meshed with triangular elements of minimum size 2 nm, while a minimum element size of 0.5 nm was used for meshing the graphene spacer. The gold particle was covered by a 2-nm-thick homogeneous excitonic shell to mimic the effect of GQD film. Gold was described by the experimental dielectric function

of Johnson and Christy⁴², while the excitonic shell was described by a Lorentzian permittivity:

$$\varepsilon = \varepsilon_{\infty} - \frac{f\omega_{\text{exc}}^2}{\omega^2 - \omega_{\text{exc}}^2 + i\omega\gamma_{\text{exc}}} \quad (3)$$

where $f = 0.05$ is the reduced oscillator strength, $\varepsilon_{\infty} = 2.5$ the background contribution to the permittivity, $\hbar\gamma_{\text{exc}} = 0.1$ eV the damping rate, and $\hbar\omega_{\text{exc}}$ the exciton energy which was modified during illumination. For graphene we used the anisotropic permittivity tensor obtained from density functional theory (DFT) calculation (Supplementary Figure 7), while we accounted for nonlocal screening in an effective way by simulating a layer of double the monolayer thickness, *i.e.* 0.68 nm^{43,44}.

Acknowledgements

FH acknowledges the support from the UK EPSRC (grant No. EP/N025938/1). CT acknowledges support from VILLUM FONDEN (grant no. 16498), and simulation support from the DeIC National HPC Centre, SDU. E.J.G.S. acknowledges the use of computational resources from the UK national high-performance computing service (ARCHER) for which access was obtained via the UKCP consortium (EPSRC grant ref EP/P022626/1); the UK Materials and Molecular Modelling Hub for access to THOMAS supercluster, which is partially funded by EPSRC (EP/P020194/1). The Queen's Fellow Award through the grant number M8407MPH, and the Department for the Economy (USI 097) are also acknowledged. RMB & WH acknowledge the support of Seagate Technology (Ireland) under SOW #00077300.0. RMB contribution to project was supported by the Royal Academy of Engineering under the Research Chairs and Senior Research Fellowships Scheme.

Author contributions

F.H. conceived and supervised the project. J.M.K. carried out experimental measurements, including scattering, Raman, TEM, PL and laser-irradiated tuning. W.R.H. fabricated Au substrates. Q.C., and L.H.L. exfoliated graphene films. G.R.Y. prepared spherical Au NPs. C.T. performed simulations. E.J.G.S provided the optical constants of graphene used in simulations. J.M.K. and F.H. wrote the manuscript. All authors contributed to the discussion and interpretation of the results.

Competing financial interests

The authors declare no competing financial interests.

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