

Molecular plasmonic cavities

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Abstract

Graphene-based photonic structures have emerged as fertile ground for the controlled manipulation of surface plasmon polaritons (SPPs), providing a two-dimensional platform with low optoelectronic losses. In principle, nanostructuring graphene can enable further confinement of nano-light – enhancing light-matter interactions in the form of SPP cavity modes. In this study, we engineer nano-scale plasmonic cavities composed of self-assembled C₆₀ arrays on graphene. Using scattering-type scanning near-field optical microscopy (s-SNOM) in conjunction with first-principles density functional theory (DFT) calculations, we show that C₆₀ assemblies behave as molecular plasmonic cavities, giving rise to precisely-defined hole-doped regions within continuous samples of graphene. By tuning the deposition conditions of C₆₀, the lateral dimensions of molecular cavities can be tailored to the SPP wavelength. Finite-element simulations verify the existence of SPP cavity modes, revealing a real-space pattern characteristic of confined SPPs. Thus, our study provides a straight-forward scheme for tailoring SPP mode volume by leveraging molecular self-assembly.

Keywords: cavities, plasmons, graphene, charge transfer, polaritons

Optical cavities are essential components of modern optics and form the foundation of technologies based on the interference of coherent light. Starting with the Fabry-Pérot interferometer,¹ optical cavities have served as a key element for enhancement of light-matter interactions – enabling lasing^{2,3} and other nonlinear optical phenomena,⁴ ultra-sensitive metrology and spectroscopy,^{5,6} and polariton excitation.⁷ In the context of near-field optics, cavity-based structures also provide a means of probing high-momentum polaritonic states existing at subdiffractional length scales.⁸ Here, the degree of optical confinement is limited by the minimum spatial resolution of nanopatterned structures, typically on the order of 10^2 nm.

Two-dimensional (2D) materials are natural platforms for studying confined light, as their reduced dimensionality provides the requisite conditions for supporting subdiffractional optical phenomena with little or no additional nanostructuring.^{9,10} Moreover, 2D materials such as hexagonal boron nitride (*h*BN),¹¹⁻¹⁴ graphene,¹⁵⁻¹⁸ transition metal dichalcogenides (TMDs),¹⁹⁻²¹ and others²²⁻²⁷ possess exceptional optical properties which enable long-range coherent propagation of polaritonic modes and enhanced light-matter coupling. In principle, nanostructuring of these 2D systems can be used to amplify light-matter interactions to create 2D cavities analogous to optical cavities in bulk materials. Indeed, some progress has been made using 2D cavities to tune the behavior of *h*BN phonon polaritons (PhP)^{28,29} and graphene surface plasmon polaritons (SPPs).³⁰⁻³⁴ However, such systems are subject to ubiquitous disorder during the lithographic process, and lack the ability to embed such nanostructures within continuous 2D sheets. In contrast, an ideal platform for 2D cavity optics would allow for arbitrarily small mode volume with well-defined, clean boundaries in an unadulterated 2D sheet.

Creating precise molecular/2D material interfaces is a promising route to engineer the properties of 2D materials at the nanoscale.³⁵⁻³⁸ Since the properties of graphene are highly

dependent on its chemical surroundings,^{39,40} one can precisely engineer its optoelectronic behavior using molecular functionalization. For example, previous work has established that C₆₀ acts to enrich the hole concentration in graphene, leading to enhanced electronic^{41,42} and optical⁴³ conductivity in C₆₀-coated graphene samples. To date, charge-transfer studies of C₆₀/graphene have focused on the gross behavior of fully-coated graphene samples. However, interfacial charge transfer is expected to be a localized phenomenon,^{44,45} and thus well-defined domains of C₆₀ heterostructured on graphene should increase the local conductivity. In principle, this controlled, local charge doping of graphene provides the ideal conditions for generating plasmonic cavities with clean boundaries and arbitrarily small mode volumes set by the size of the C₆₀ molecular islands.

In this study, we realize nanoscale plasmonic cavities in arrays of C₆₀ on graphene (Fig. 1A). Using a combination of atomic force microscopy (AFM) and scattering-type scanning near-field optical microscopy (s-SNOM), we are able to simultaneously characterize and correlate local molecular morphology with its associated charge transfer-induced nano-optical response. Here, charge transfer-enabled SPPs in graphene are confined within C₆₀ islands. Since the size of C₆₀ islands can be tailored to the dimensions of the SPP wavelength, the boundary conditions imposed by this local charge transfer lead to SPP cavity modes. We verify the existence of cavity modes by measuring the near-field response, whose real-space pattern diverges significantly from that of freely propagating modes. Our experimental results agree well with finite-element simulations, verifying the plasmonic origin of our near-field observations. Furthermore, this analysis together with the expected ω -dependent SPP dispersion enable quantitative extraction of the magnitude of local charge transfer in the vicinity of molecular clusters: $n \sim 6 \times 10^{12} \text{ cm}^{-2}$. The conclusions drawn from our nano-optical measurements are well-supported by first-

principles density functional theory (DFT) calculations, which reveal comparable levels of interfacial charge transfer in heterostructures composed of 2D arrays of C₆₀ on graphene. Our results provide a proof-of-concept for molecular plasmonic cavities, and demonstrate significant advances in experimental benchmarks for lateral confinement of graphene SPPs.

The C₆₀/graphene samples used in this study were fabricated in a two-step process starting with assembly of the van der Waals (vdW) heterostructure followed by thermal deposition of C₆₀ (see supplemental methods). The appearance of C₆₀ islands is verified using AFM imaging (Fig. 1B). Depending on the choice of deposition conditions, the typical cluster dimensions can vary from ~50 – 300 nm in diameter. In addition, C₆₀ clusters present with approximate circular, elliptical, and triangular morphologies (Figures 1, S1). For the purposes of our plasmonic study, we focus on clusters possessing a high degree of spatial symmetry (e.g., ellipses).

Typical mid-infrared (MIR, $\omega = 920 \text{ cm}^{-1}$) s-SNOM images of C₆₀ clusters on graphene are displayed in Fig. 1C showing the near-field phase (Φ_5), demodulated at the fifth harmonic of the tip tapping frequency (see supplemental methods). The near-field contrast is observed to be significantly enhanced in the location of clusters compared to the surrounding bare graphene. Moreover, Φ_5 shows nodal structures with a characteristic length scale of $\sim 10^2 \text{ nm}$. For the fixed wavelength of incident light in Fig. 1C, the number of observable nodes increases with the size of the associated C₆₀ island. This near-field pattern suggests the presence of electromagnetic standing waves confined within C₆₀ islands. Since graphene SPPs typically possess a characteristic length of $\sim 10^2 \text{ nm}$ at MIR frequencies, the molecular cavity scenario is a natural candidate for the behavior depicted in Fig. 1C. However, quantitatively verifying this

interpretation necessitates additional energy-dependent measurements and optical modelling of graphene-supported C₆₀ clusters.

The wavelength of freestanding graphene SPPs (λ_p) has a well-known frequency dependence given by the SPP energy-momentum dispersion:¹⁵

$$\mathbf{q}(\omega) = q_1 + iq_2 = \frac{i\omega}{2\pi\sigma(\omega)} \quad (1)$$

where $\sigma(\omega)$ is the graphene conductivity and $\mathbf{q}(\omega)$ is the complex-valued SPP wavevector whose real component (the SPP momentum q_1) is inversely proportional to the wavelength: $\lambda_p = \frac{2\pi}{q_1}$. Here, the graphene conductivity $\sigma(\omega) \sim \mu_{\text{gr}} \sim \sqrt{n}$, where μ_{gr} is the graphene chemical potential and n is the charge density. Thus, if the near-field contrast of C₆₀/graphene is primarily plasmonic in origin, the nodal structure observed on molecular clusters should depend on the incident laser frequency in correspondence with the SPP dispersion and the degree of interfacial charge transfer.

To test this hypothesis, we perform a series of frequency-dependent measurements on a C₆₀ island with an elliptical geometry (Fig. 2A). Fig. 2B-D shows the near-field amplitude S_5 (left panels) and Φ_5 (right panels) with increasing frequency ($\omega = 870 \text{ cm}^{-1}$, 920 cm^{-1} , and 1020 cm^{-1} , respectively). Focusing first on S_5 , it is clear that as the frequency increases, the contrast within the C₆₀ cluster evolves from displaying a single antinode at 870 cm^{-1} to two antinodes at 1020 cm^{-1} . On the other hand, Φ_5 shows contrast maxima around the outside of the cavity at 870 cm^{-1} which develops into two nodes at 920 cm^{-1} and a single antinode at 1020 cm^{-1} . The behavior observed in both near-field channels is consistent with the expected reduction in the SPP wavelength with increasing frequency, with the SPP field being confined within the

molecular island. Thus, we have ostensibly traversed energies associated with neighboring cavity modes, with additional SPP oscillations fitting within the elliptical cluster at 1020 cm^{-1} compared to 870 cm^{-1} . Similar frequency-dependent nodal patterns are also observed in other C_{60} islands, including those displaying approximate three-fold symmetry (Fig. S1). Therefore, frequency-dependent s-SNOM data supports the interpretation that near-field contrast within C_{60} islands is derived from confined SPPs.

Verification of the plasmonic origin of s-SNOM data can be obtained through extraction of the experimental SPP dispersion. For freely propagating SPPs, this is typically achieved by fitting a multi-component damped oscillator to the near-field line profile.⁴⁶ However, for the present scenario the conditions for constructive and destructive interference of cluster-confined SPPs are more complex than in the freely-propagating case. This precludes the use of these traditional methods for analyzing SPP fringes within molecular cavities. Analysis of our experimental data thus requires judicious accounting of SPP propagation within a finite region whose dimensions closely match those of our C_{60} islands.

In order to provide quantitative comparison to our experimental data, we perform finite-element simulations of S_5 and Φ_5 (Figs. 2E-H). Here, we model the C_{60} cluster/graphene heterostructure as an elliptical region of doped graphene with some non-zero optical conductivity ($\sigma > 0$) surrounded by a region of undoped graphene ($\sigma = 0$). In addition, the reflection coefficient of the substrate $\beta = \frac{\epsilon-1}{\epsilon+1}$ is defined in terms of the permittivity of the underlying substrate ϵ . Since C_{60} /graphene resides on a thick slab of hBN ($> 50\text{ nm}$), β is taken to be that of hBN (i.e., $\epsilon = \epsilon_{hBN}$), causing additional SPP confinement compared to free-standing graphene or graphene on few-layer hBN . On the other hand, no explicit coupling to hBN phonon ($760\text{--}825\text{ cm}^{-1}$ and $1360\text{--}1614\text{ cm}^{-1}$)⁴⁷ is expected within our experimental frequency window ($860\text{--}1080$

cm^{-1}). Here, a non-trivial β results in SPP screening, modifying the plasmon wavelength λ_p compared to its value in free-standing graphene $\lambda_{p,0}$:

$$\lambda_p = (1 - \beta)\lambda_{p,0} \quad (2)$$

Due to the out-of-plane component of the SPP field, the thin layer of C_{60} (≤ 3 nm) is expected to cause small additional confinement (see Fig. S2), but is excluded from our finite element simulations for the sake of simplicity. We estimate that this simplification results in at most an $\sim 11\%$ underestimation of μ_{gr} in the following discussion (see eq. 1), which does not impact the overall interpretation of our experimental results. To simulate s-SNOM images, we model the tip as a local dipole that raster scans along the model elliptical cavity shown in Fig. 2E, where the local complex electric field is computed at each pixel. The 2D map of this complex electric field is defined as the model near-field scattering signal $\boldsymbol{\rho} = \rho_1 + i\rho_2$, where the magnitude $|\boldsymbol{\rho}|$ and phase $\tan^{-1}(\rho_2/\rho_1)$ of $\boldsymbol{\rho}$ act as good proxies for S_5 and Φ_5 , respectively. This finite element approach has been used previously to faithfully reproduce near-field images associated with graphene SPPs^{30,44,48} and other conducting 2D materials⁴⁹ (see methods).

Figs. 2F-H show the simulated nearfield amplitude (left panels) and phase (right panels) corresponding to the frequencies shown in Figs. 2B-D. Here, the frequency-dependent conductivity within the elliptical cavity is non-zero, and depends on the graphene chemical potential (μ_{gr}) due to charge transfer with C_{60} (discussed in detail in the following section). For the data shown in Figs. 2F-H, the conductivity within the elliptical cavity is set by the associated value of λ_p , as indicated in each panel. For the select values of λ_p , it is clear that many of the experimental features are mirrored in our simulations. For instance, the evolution of the nodal structure in the simulation follows that of the experiment, where a single antinode in the

simulated amplitude at 870 cm^{-1} ($\lambda_p = 206 \text{ nm}$) is seen to progressively split into two antinodes at 1020 cm^{-1} ($\lambda_p = 112 \text{ nm}$). A similar progression is also seen in both experimental and simulated phase images, where the overall intensity is highest on and just outside the perimeter of the cluster at 870 cm^{-1} ($\lambda_p = 206 \text{ nm}$), and evolves into two nodes at 920 cm^{-1} ($\lambda_p = 157 \text{ nm}$) and a single antinode at 1020 cm^{-1} ($\lambda_p = 112 \text{ nm}$).

The agreement between simulation and experiment further evidences the interpretation that C_{60} clusters on graphene host SPP cavity modes, with the C_{60} acting as a charge reservoir to imprint conductivity features on the underlying graphene. Moreover, the lateral profile of this interfacial charge transfer must decay abruptly at the cluster boundary to enable SPP reflection and confinement – behavior consistent with nanometer-scale conductivity features achieved through similar charge-transfer heterostructures.⁴⁴ The salient input parameters in our simulation are λ_p and the quality factor $Q = \frac{q_1}{q_2}$, allowing us to extract the SPP dispersion and plasmonic damping from experimental data. This parameter extraction is achieved by fitting simulated line-profiles along high-symmetry axes of the elliptical cavity to the associated experimental data at each frequency. In so doing, we can use the results of our finite-element simulation to measure the charge density within C_{60} clusters (i.e., the charge transfer between graphene and C_{60}), and quantify the lateral confinement of SPPs.

In order to extract the SPP dispersion using our simulation-based fitting approach, we first perform a series of closely-spaced frequency dependent measurements of the cavity shown in Fig. 2A over the range $\omega = 860\text{--}1080 \text{ cm}^{-1}$. We then extract the line profiles of S_5 and Φ_5 along the major (Fig. 3A,C; lefts panels) and minor (Fig. 3B,D; lefts panels) axes of the elliptical structure and plot them as a function of frequency. We repeat this process with our finite element simulation, noting that the ω -dependence of λ_p depends on the as yet unknown shift in the

graphene chemical potential μ_{gr} due to charge transfer with C_{60} . We find that the goodness-of-fit between our experimental and simulated line profiles in Fig. 3 depends sensitively on both μ_{gr} and Q , with a global minimum in the RMS deviation occurring at $\mu_{\text{gr}} = 0.28$ eV and $Q = 5$ (Fig. S3A). We also evaluate the best-fit Q at each experimental frequency, and observe a slight frequency dependence with nominal Q -factors falling in the range $Q = 5 \pm 2$ (Fig. S3B). These values of Q fall within the expected range for SPPs in unencapsulated graphene,^{50,51} and can likely be improved with the introduction of interstitial and/or encapsulating layers of hBN .⁴⁶

The best-fit value of $\mu_{\text{gr}} = 0.28$ eV corresponds to a hole density of $n \sim 6 \times 10^{12} \text{ cm}^{-2}$ in graphene due to charge transfer with C_{60} , which falls in the range of values observed previously in similar systems⁴³ and equates to 0.05 electrons per C_{60} in a face-centered cubic (FCC) array. The right panels of Figs. 3A-D show the corresponding frequency-dependent linecuts from our simulations with $\mu_{\text{gr}} = 0.28$ eV and $Q = 5$. Most notably, the overall progression of the cavity modes matches that of experiment, with branching in the nodal pattern of the simulated amplitude and phase occurring at similar energies to their experimental counterparts. Moreover, the real-space pattern within simulated cavities displays an energy-dependence that deviates significantly from that of freely propagating modes (Fig. S4), underscoring the critical role of the molecular cavity in confining and amplifying of the SPP field. We note that some features appear to broaden or merge within the experimental images compared to simulation. We attribute this to the finite measurement resolution, where the real-space pattern is expected to convolve with the non-zero radius of our probe ($R_{\text{tip}} \sim 20\text{--}50$ nm). Nevertheless, the agreement between simulation and experiment demonstrates that C_{60} islands on graphene act as molecular plasmonic cavities.

To better understand the physical origin of molecular plasmonic cavities, we model C_{60} clusters on graphene from first-principles using a series of model systems within a DFT

framework (Figure 4). Here, an FCC array of C₆₀ on graphene is employed in the so-called dimer-hole orientation.⁴¹ In this configuration, the band structure displays characteristic features of both graphene and C₆₀ (Fig. 4B). Most notably, the Dirac-point energy (E_{Dirac}) of graphene is evident, with an overall positive shift of ~ 0.3 eV. This shift corresponds well with the value of μ_{gr} extracted from our nano-optical measurements. Indeed, within the Dirac cone model ($n = \frac{1}{\pi} \left(\frac{E_{\text{Dirac}}}{\hbar v_F} \right)^2$), this shift in E_{Dirac} equates to $n = 6.6 \times 10^{12} \text{ cm}^{-2}$ holes residing in the graphene layer. Dispersive conduction bands (CBs) derived from the C₆₀ lowest unoccupied molecular orbital (LUMO) can also be found extending from 0.5 eV to just below E_F – indicating electron doping of the C₆₀ CB due to charge transfer with graphene. We note that calculations consisting of C₆₀ single- and multi-layers exhibit similar degrees of charge transfer, consistent with the observed independence of SPP behavior on C₆₀ thickness.

While the magnitude of interfacial charge transfer computed in Fig. 4 matches well with experiment, we find that the expected charge transfer can be significantly reduced by modifying the orientation of the C₆₀ relative to the underlying graphene (Fig. S5), as reported previously.⁴¹ This reduced charge transfer occurs because the hopping strength between neighboring C₆₀ molecules decreases for the different model structures shown in Fig. S5, causing the CB bandwidth to be commensurately reduced. Reduction of the CB bandwidth causes the lowest energy unoccupied states to increase in energy, decreasing the overall driving force for charge transfer. This is also evident when computing the charge transfer between a single C₆₀ molecule and graphene, which shows that the dispersionless LUMO of C₆₀ is not low enough in energy to accept charge from graphene (Fig. S5). Ultimately, the dimer-hole structure shown in Fig. 4 is predicted to have the most dispersive CB, and thus exhibits the most charge transfer with graphene. Given that the observed SPP behavior implies uniform and theoretically maximal

doping within our molecular cavities, it is possible that our C_{60} clusters form well-ordered arrays on graphene. While we were not able to verify orientational alignment with our experimental probe, previous high-resolution studies have demonstrated that C_{60} can have preferred orientational alignment with respect to the crystallographic axes of underlying graphene, HOPG, and metallic substrates.⁵²⁻⁵⁵ Thus, our DFT calculations support the interpretation that local hole-doping of graphene in the vicinity of molecular clusters enables the formation of plasmonic cavities.

We have presented a joint experimental and theoretical study of molecular plasmonic cavities achieved through local charge transfer between C_{60} clusters and graphene. By exploiting the electron-accepting behavior of C_{60} and its tunable self-assembly properties on graphene, we were able to tailor the local conductivity of graphene at plasmonic length scales. The resulting C_{60} clusters act as potential wells for graphene SPPs, enabling control of SPP confinement. Insights from first-principles calculations underscore the potential role of adsorption geometry on interlayer charge transfer. Together, our experimental and theoretical results provide foundational understanding of the limits of polaritonic confinement made achievable using molecular plasmonic cavities.

Our realization of molecular plasmonic cavities represents a significant step forward in the control of light-matter interactions at the nanoscale. The ability to reproducibly generate high-quality, nanoscale plasmonic cavities using existing methods is fundamentally restricted by lithography-induced defects, uncontrolled interfacial disorder in 2D heterostructures, and fringing electric fields associated with a non-trivial gate dielectric thickness. Molecular plasmonic cavities suffer none of these drawbacks, allowing sub-wavelength confinement of the SPP field. In principle, reproducible ordered assembly of molecular islands can be controlled

using electromigration,⁵⁶ substrate-templating,⁵⁷ or gate-tunable molecular assembly.^{58,59} In addition, C₆₀/graphene heterostructures are promising candidates for strong light-matter coupling between SPPs and molecular vibrational modes, as observed previously between *h*BN phonon polaritons and organic adsorbates.⁶⁰ This approach can be extended to a wide range of donor/acceptor adsorbates, providing control over the magnitude of local charge transfer and enabling additional tunable proximate interactions (e.g., magnetism, ferroelectricity). Finally, the use of molecular cavities is general to 2D materials, and can be used as a basis for charge-mediated optical confinement within the growing library of polaritonic vdW materials.

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Author Contributions

D.J.R. and M.R. performed all s-SNOM measurements. M.R. performed all device fabrication, including assembly of vdW heterostructures and deposition of C₆₀ clusters. D.J.R. performed finite-element simulations of molecular cavities. H.L., D.S., and A.R. performed DFT calculations of the C₆₀/graphene heterostructures. K.W. and T.T. performed growth and

characterization of *h*BN single crystals. A.V. and D.N.B. advised and participated in experimental design and interpretation. The manuscript was written with input from all authors.

Competing Interests

The authors declare no competing financial interests.

Data Availability

All data presented in the manuscript are available upon request.

Supporting Information Available

Supporting Information contains experimental and theoretical methods, additional AFM and s-SNOM measurements on C₆₀ clusters, calculations of the loss function for the experimental device, details regarding parameter extraction from the experimental cavity data, finite-element simulations of freely propagating graphene SPPs, and additional DFT calculations.

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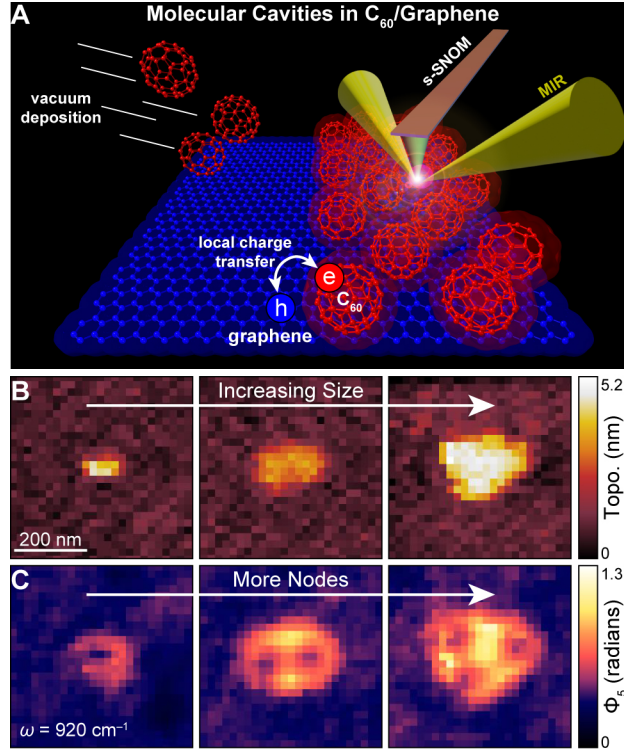


Figure 1. Realizing molecular plasmonic cavities in C₆₀/graphene heterostructures. (A) Overview of C₆₀/graphene molecular plasmonic cavity experiments. Vacuum deposition of C₆₀ on graphene leads to the formation of self-assembled islands that locally transfer charge to the underlying graphene. The graphene charge puddles in the vicinity of C₆₀ islands form the basis of plasmonic cavities, which are interrogating using s-SNOM with MIR light. (B) AFM topographic maps showing self-assembled C₆₀ islands with increasing size. (C) Co-located measurement of the near-field phase Φ_5 ($\omega = 920 \text{ cm}^{-1}$) showing an increase in the number of nodes with island size.

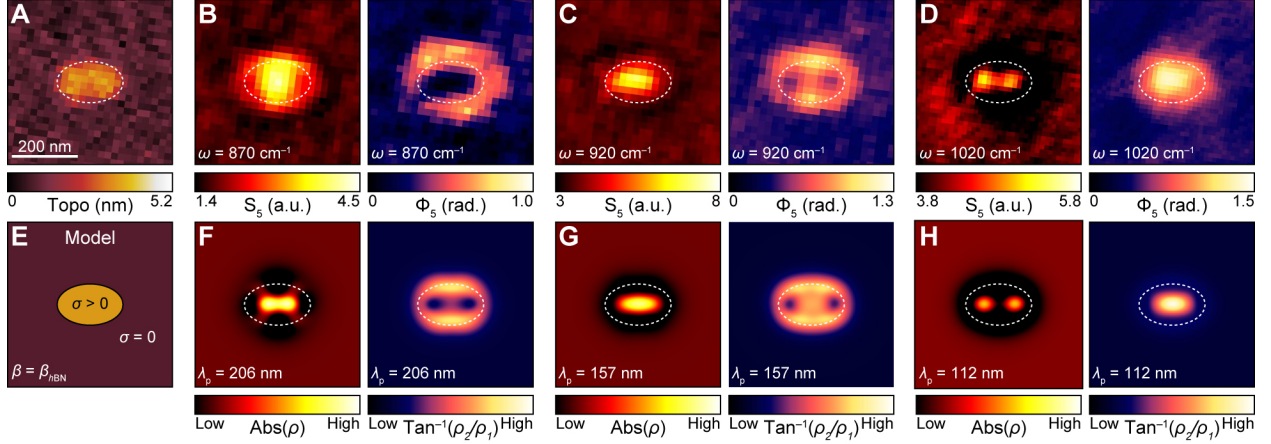


Figure 2. Visualizing cavity modes in an elliptical C_{60} island. (A) AFM topography of an elliptical C_{60} island with nominal major and minor axes equal to 200 nm and 125 nm, respectively. (B–D) Near-field amplitude S_5 (left panels) and phase Φ_5 (right panels) of the C_{60} island shown in (A) measured for $\omega = 870 \text{ cm}^{-1}$, 920 cm^{-1} , and 1020 cm^{-1} , respectively. The dashed lines indicate the physical boundary of the molecular island. The number of visible nodes and antinodes increases with ω , a hallmark of dispersing plasmonic cavity modes. (E) Model conductivity for graphene sheet with ideal elliptical charge region ($\sigma > 0$) surrounded by uncharged graphene ($\sigma = 0$) supported by an $h\text{BN}$ substrate with reflection coefficient $\beta = \beta_{h\text{BN}}$. (F–H) Model of the complex-valued near-field scattering signal $\boldsymbol{\rho} = \rho_1 + i\rho_2$ given by the complex electric field of a raster-scanned dipole over the conductivity profile in (E) for $\lambda_p = 206 \text{ nm}$, 157 nm , and 112 nm , respectively. The dashed lines indicate the physical boundary of the simulated molecular island. For all simulations $Q = 5$. The magnitude of $\boldsymbol{\rho}$ (left panel) acts as a good approximation to S_5 , while the complex phase of $\boldsymbol{\rho}$ (right panel) simulates Φ_5 . It is evident that the salient features of the experimental maps in (B–D) are reproduced in (F–H) for the values of σ within the model ellipse that correspond to the indicated λ_p .

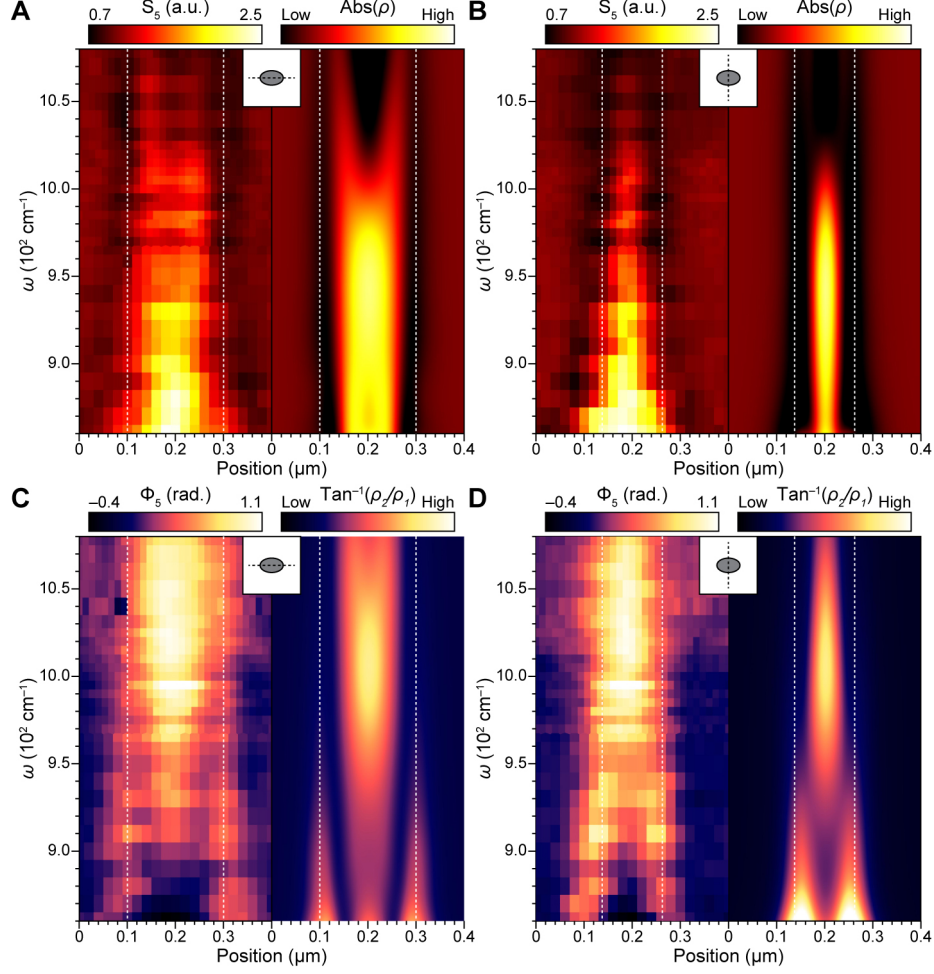


Figure 3. Plasmonic cavity dispersion in elliptical C_{60} /graphene islands. (A) Left Panel: Map of the frequency-dependence of the S_5 line profiles taken along the major axis of an elliptical C_{60} island (see inset). Right panel: Frequency-dependence of the major-axis line profiles of $Abs(\rho)$ for a graphene chemical potential μ_{gr} of 0.28 eV with $Q = 5$. The white dashed lines indicate the boundary of the elliptical cavity. (B) Same as (A) but for experimental S_5 (left panel) and model $Abs(\rho)$ (right panel) taken along the minor axis of the elliptical cluster. (C) and (D) same as (A) and (B) but for the experimental Φ_5 (left panels) and model near-field phase (right panels).

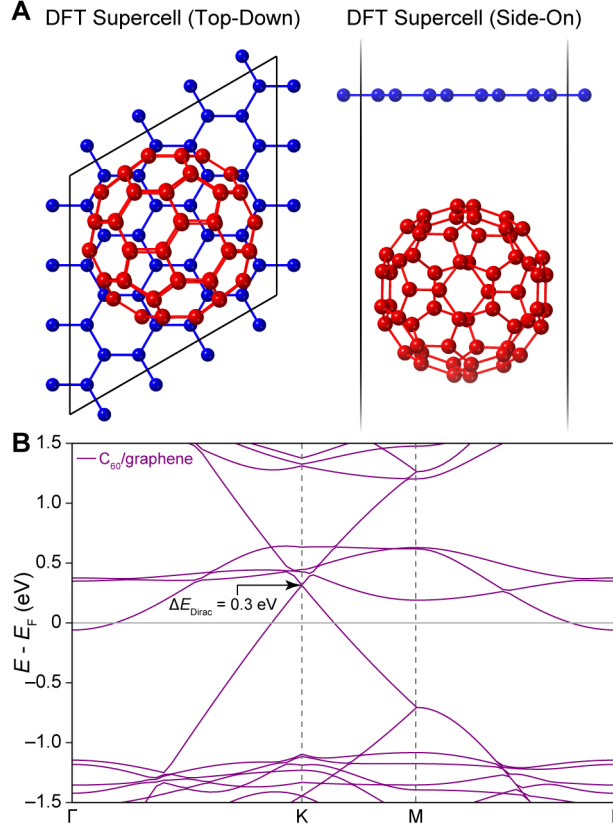


Figure 4. First-principles calculation of C₆₀/graphene heterostructure. (A) DFT supercell of C₆₀/graphene in the dimer-hole configuration as viewed from the top-down (left panel) and side-on (right panel) perspectives. The black solid line indicates the boundary of the supercell, which extends more than 15 Å out of the plane to avoid interaction of the 2D system with its periodic image (see methods). (B) DFT band structure associated with the supercell shown in (A). In the dimer-hole configuration, significant charge transfer is observed between the C₆₀ and graphene, leading to a positive shift of 0.3 eV in E_{Dirac} of graphene. Within the Dirac cone model ($n = \frac{1}{\pi} \left(\frac{E_{\text{Dirac}}}{\hbar v_F} \right)^2$), this corresponds to $n = 6.6 \times 10^{12} \text{ cm}^{-2}$ holes residing in the graphene layer.