Gate-Tuning Hybrid Polaritons in Twisted α-MoO₃/Graphene Heterostructures

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ABSTRACT: Modulating anisotropic phonon polaritons (PhPs) can open new avenues in infrared nanophotonics. Promising PhP dispersion engineering through polariton hybridization has been demonstrated by coupling gated graphene to single-layer α-MoO₃. However, the mechanism underlying the gate-dependent modulation of hybridization has remained elusive. Here, using IR nanospectroscopic imaging, we demonstrate active modulation of the optical response function, quantified in measurements of gate dependence of wavelength, amplitude, and dissipation rate of the hybrid plasmon–phonon polaritons (HPPPs) in both single-layer and twisted bilayer α-MoO₃/graphene heterostructures. Intriguingly, while graphene doping leads to a monotonic increase in HPPP wavelength, amplitude and dissipation rate show transition from an initially anticorrelated decrease to a correlated increase. We attribute this behavior to the intricate interplay of gate-dependent components of the HPPP complex momentum. Our results provide the foundation for active polariton control of integrated α-MoO₃ nanophotonics devices.

KEYWORDS: gate-tuning, hybrid plasmon–phonon polaritons, twisted α-MoO₃, dispersion, s-SNOM

PhPs are quasiparticles formed by the hybridization of light and optical phonons in polar crystals.1,2 Their deeply subwavelength optical confinement and low loss, emerging in several polar crystals at infrared (IR) frequencies, have been laying the foundation of a new paradigm for IR nanophotonics technologies. When the principal elements of the in-plane permittivity tensor show opposite signs, highly confined in-plane hyperbolic PhPs emerge, with signature hyperbolic-shaped iso-frequency contours (IFCs), as demonstrated in the vdW materials α-MoO₃ and α-V₂O₅ as well as in polar crystals calcite and beta-phase Ga₅O₇ (bGO). In particular, PhPs in α-MoO₃ have demonstrated exciting opportunities for deeply subwavelength nanofocusing and negative refraction. Control of PhPs in α-MoO₃ through the modification of the dielectric environment, chemical intercalation, and isotope enrichment has been achieved and recently extended through the formation of hybrid polaritons in twisted bilayer α-MoO₃ and a single-layer α-MoO₃/graphene heterostructure. Particularly, gate tuning the resulting in-plane hybrid polaritons can give rise to active control of topological transitions in the IFCs and negative refraction.

Despite the demonstration of active modulation of polariton hybridization mentioned above, there is still an open question regarding the underlying mechanism behind the gate-dependent behavior. Therefore, it is crucial to comprehensively analyze the modulated variation behaviors of the fundamental parameters of hybrid polaritons: wavelength (λ), amplitude (A), and dissipation rate (γ). In this article, using infrared scattering-type scanning near-field optical microscopy (IR s-SNOM), we demonstrate the active modulation of hybrid plasmon–phonon polaritons (HPPPs) in both single-layer and twisted bilayer α-MoO₃/graphene heterostructures. Most

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notably, we unveil the underlying gate-dependent mechanism by probing the nanooptical response function, quantified in measurements of gate dependence of \( \lambda_p \), \( A_p \), and \( \gamma_p \) of HPPPs. Intriguingly, we observe a monotonic increase in \( \lambda_p \) and an initially anticorrelated decrease and then correlated increase of \( A_p \) and \( \gamma_p \) with the absolute value of graphene Fermi energy \( |E_F| \). This behavior is attributed to the distinct dependencies of \( \lambda_p \), \( A_p \), and \( \gamma_p \) on the HPPP real and imaginary parts of the complex momentum. Our work systematically establishes nontrivial correlations of the key optical parameters of HPPPs with the \( E_F \)-dependent complex optical conductivity of graphene, forming the basis for active hybrid polariton control in integrated IR nanophotonic technologies.

To experimentally investigate the gate-tuning properties of HPPPs, we designed and fabricated two types of \( \alpha \)-MoO\(_3\)/graphene devices. For single-layer \( \alpha \)-MoO\(_3\)/graphene devices, we dry transferred single-layer \( \alpha \)-MoO\(_3\) with 140 nm thickness on top of a monolayer graphene on a silicon substrate (with a 285 nm silica dielectric layer). For twisted bilayer \( \alpha \)-MoO\(_3\)/graphene devices, the bottom and top \( \alpha \)-MoO\(_3\) layers, with thicknesses of 134 and 46 nm, respectively, were sequentially stacked on top of a monolayer graphene with a relative 47° twist angle between the [100] crystal direction of two \( \alpha \)-MoO\(_3\) layers (see Methods for details). We modified \( E_F \) by applying a gate voltage to the silicon substrate. The graphene charge neutral point (CNP) is determined by two independent methods: gate-dependent electronic transport measurements and third-harmonic generation (THG) intensity measurements, showing consistent results (see Supporting Information, section 1 for details).
IR s-SNOM HPPP nanoimaging was performed at the frequency of 931 cm⁻¹ with homodyne near-field detection, as illustrated in Figure 1a (see Methods for details). HPPPs are launched by a gold-coated tip, propagating and interfering with the reflected wave by the α-MoO₃ edge. From line profiles of the resulting interference fringes, we retrieve the $\lambda_p$, $A_p$, and $\gamma_p$ of HPPPs, as shown in Figure 1b. Additionally, we conducted two-phase homodyne near-field detection on the twisted bilayer α-MoO₃/graphene device, showing consistent results with the homodyne measurements and providing further confirmation of the accuracy and validity of our experimental findings (see Supporting Information, section 5 for details).

In terms of numerical simulations, we used the finite-difference time-domain (FDTD) method to simulate the HPPP fringes as measured in experiments. The optical response of α-MoO₃ and graphene was modeled by a Lorentz oscillator and the Kubo formula, respectively. The real part of the out-of-plane electric field $\text{Re}(E)$ of the HPPP wave was retrieved from the simulations (see Supporting Information, section 2 for details).

The gate tunability of the emerging HPPPs is illustrated in Figure 1c and d. The level of graphene $E_g$ significantly modifies the dispersion and dissipation rate of the graphene surface plasmon polaritons (SPPs), and consequently influencing the dispersion of HPPPs in the twisted bilayer α-MoO₃/graphene heterostructure, for low (Figure 1c) and high (Figure 1d) doping levels.

We first characterized HPPPs in single-layer α-MoO₃/graphene devices as a reference. Figure 2a shows near-field images for three values of $E_g$, 0 eV (top), −0.20 eV (middle), and −0.36 eV (bottom), showcasing remarkable variations in $\lambda_p$, $A_p$, and $\gamma_p$ of polariton interference fringes as a function of $E_g$. We then performed sweeps of back-gate voltage $V_g$ from 70 to −70 V ($E_g$: from 0.23 to −0.36 eV) in increments of 5 V. Figure 2b shows the corresponding IR s-SNOM line profile of near-field images with 10 V increments of $V_g$ (see Figure S6 for line profiles at other $V_g$ values).

We fit the line profile intensity $I_{NP}$ of HPPPs using a model that accounts for geometric spread and interference between tip-launched and edge-reflected polariton waves (see Supporting Information, section 6 for more details)

$$I_{NP} = A_p \frac{e^{-2x_{ps}/\lambda_p^x}}{\sqrt{x}} \sin \left(2\pi \frac{x - x_c}{\lambda_p} \right) + B \frac{e^{-4x_{ps}/\lambda_p^x}}{x} + I_0,$$

with physical fit parameters $A_p$, $\gamma_p$, $\lambda_p$, $x_c$, $B$, and $I_0$. Figure 2c shows the derived values of $\lambda_p$, increasing monotonically with $E_g$ and $\lambda_p$. $A_p$, $\gamma_p$, and $\lambda_p$, shown in Figure 2d and e, respectively, are correlated and initially decrease, yet then increase with increasing $|E_g|$, with a turning point at ~0.2 eV. The experimental data for another device with a single-layer α-MoO₃ thickness of 175 nm are shown in Figure S14. We
Figure 4. Gate-tuning mechanism of hybrid plasmon–phonon polaritons. (a,b) Theoretically calculated \( E_p \) dependence of \( \lambda_p \), \( \gamma_p \), and \( \text{Re}(q_||^p) \) (red lines) and \( \text{Im}(q_\perp^p) \) (black lines) for a twisted bilayer \( \alpha\text{-MoO}_3 \)/graphene heterostructure, which has the same \( \alpha\text{-MoO}_3 \) thicknesses and twist angle as the device shown in Figure 3. The direction of the in-plane momentum \( q_\perp^p \) is along the [100] crystal direction of the bottom \( \alpha\text{-MoO}_3 \) layer. The calculated dispersion (color plots) of HPPPs in the twisted bilayer \(\alpha\text{-MoO}_3 \)/graphene heterostructure with \( E_p = 0 \) eV (left panel) and \( E_p = -0.34 \) eV (right panel). The direction of in-plane momentum \( q_\perp^p \) is along the [100] crystal direction of the top \( \alpha\text{-MoO}_3 \) layer. The black dots represent experimental data extracted from Figure 3d. (d) Numerically simulated \( E_p \) dependence of \( A_p \) at heights of \( z = 0 \), 50, and 100 nm, indicated by brown, light green, and light blue dots, respectively. The error bars represent the 95% confidence intervals. Color solid lines are guides for the eye.

compare these experimental observations with numerical simulations of the near-field fringes (see Supporting Information, section 6 for more details). The derived values for \( \lambda_p \), \( A_p \), and \( \gamma_p \) and predicted variations with \( E_p \), are in good agreement with our experimental results.

Next, we performed corresponding experiments on the twisted bilayer \( \alpha\text{-MoO}_3 \)/graphene device, as shown in Figure 3. Figure 3b and c shows near-field images taken in the area marked by the yellow dashed square in Figure 3a, for \( E_p = 0 \) and \(-0.43 \) eV, respectively. In this area, two sets of polariton interference fringes are observed due to the interference between tip-launched polariton waves and their reflections from the edges of the top and bottom \( \alpha\text{-MoO}_3 \) layers.

Applying the same analysis as above, we retrieve two sets of \( \lambda_p \), \( A_p \), and \( \gamma_p \) as a function of \( E_p \) along the [100] crystal direction of the top and bottom \( \alpha\text{-MoO}_3 \) layers, as shown in Figure 3d–i (see Figure S5 for additional data for a similar device). Analogous to the single-layer \( \alpha\text{-MoO}_3 \)/graphene device, both \( \lambda_{p\text{-top}} \) (Figure 3d) and \( \lambda_{p\text{-bot}} \) (Figure 3g) increase monotonically with \( |E_p| \). Simultaneously, the amplitude \( (A_{p\text{-top}} \) in Figure 3e and \( A_{p\text{-bot}} \) in Figure 3h) and dissipation rate \( (\gamma_{p\text{-top}} \) in Figure 3f and \( \gamma_{p\text{-bot}} \) in Figure 3i) exhibit an inflection point at \( |E_p| \approx 0.2 \) eV. We attribute the slight differences in the variation of \( A_{p\text{-top}} \) and \( A_{p\text{-bot}} \) to the difference in the real part of the HPPP complex in-plane momentum along the edges of the top and bottom \( \alpha\text{-MoO}_3 \) layers. We also performed simulations analogous to the single-layer \( \alpha\text{-MoO}_3 \)/graphene device, which also shows good agreement with experiments. Additional simulations exploring various twist angles and \( \alpha\text{-MoO}_3 \) thicknesses are shown in Figures S7–9.

The mechanism underlying the demonstrated gate-dependence behavior of HPPPs can be explained based on the variation of the complex momentum with \( E_p \). The quantities \( \lambda_p \), \( A_p \), and \( \gamma_p \) are associated with the in-plane \( q_\parallel^p \) and out-of-plane \( q_\perp^p \) momentum components through:

\[
\lambda_p = 1/\text{Re}(q_\parallel^p) \tag{2}
\]

\[
\gamma_p = \text{Im}(q_\parallel^p)/\text{Re}(q_\parallel^p) \tag{3}
\]

\[
A_p = A_0 e^{-|q_\parallel^p|z} \tag{4}
\]

where \( A_0 \) is the HPPP amplitude at the surface of \( \alpha\text{-MoO}_3 \), and \( z \) is the height above the \( \alpha\text{-MoO}_3 \) surface where the near-field signal is detected. Note that we consider only \( q_\parallel^p \) along the [100] crystal direction of \( \alpha\text{-MoO}_3 \) consistent with our experiments. The dependence of \( \text{Re}(q_\parallel^p) \) and \( \text{Im}(q_\parallel^p) \) with \( E_p \), as predicted from the theory (see Supporting Information, section 4), is shown in Figure 4a and b, respectively. Our theory indeed confirms the observed dependence of \( \lambda_p \), \( A_p \), and \( \gamma_p \) as a function of \( E_p \) along the [100] crystal direction of \( \alpha\text{-MoO}_3 \). Furthermore, due to the interplay between \( \gamma_p \) and \( |E_p| \), in determining the damping rate, following eq 3, \( \gamma_p \) initially decreases with \( |E_p| \), reaching an inflection point at \(-0.2 \) eV, and then increases (Figure 4b).

The derived variations of \( \lambda_p \) and \( \gamma_p \) are in good agreement with the experimental and numerical simulation results shown in the previous section. Despite the dependence on both \( \text{Re}(q_\parallel^p) \) and \( \text{Im}(q_\parallel^p) \), due to the weaker variation of \( \text{Re}(q_\parallel^p) \) with \( E_p \) (Figure 4a), \( \gamma_p \) follows the variation of \( \text{Im}(q_\parallel^p)/|E_p| \) to first order. For illustration, Figure 4c shows the underlying calculated dispersion of the HPPPs (see Supporting Information, section 3) for two selected values of \( E_p \) (see Figures S15–18 for other values of \( E_p \)). With increasing \( |E_p| \), \( \text{Re}(q_\parallel^p) \) becomes smaller at a given frequency, and the
experimental data (black dots in Figure 4c) are in good agreement with the calculations. At last, apart from the expected general decrease of $A_p$ with distance $z$, $A_p$ varies nontrivially with $E_p$ and differently as the distance from the sample varies (Figure 4d). Based on the dependence of the evanescent $q_p$ with $E_p$ (Figure S12), for larger distances $z$, the term $e^{-\kappa z}$ in eq 4 dominates the behavior of $A_p$, giving rise to an overall increase of $A_p$ with $E_p$. However, when $z$ is close to 0, $A_p$ scales similarly to $A_{00}$, which is affected by the propagation length of HPPPs, showing the same inflection point as $\gamma_p$. In contrast, $\gamma_p$ is solely associated with the in-plane complex momentum $q_p^\parallel$. Therefore, the variation of $\gamma_p$ remains independent of $z$, as shown in Figure S13b. We attribute the slight deviation in inflection points between theoretically calculated and experimental trends to the inaccuracies introduced by the infinite conductor model used in our calculations. It is worth noting that while the twist angle and the thickness of $\alpha$-MoO$_3$ would influence the absolute values of $\text{Re}(q_p^\parallel)$ and $\text{Im}(q_p^\parallel)$ our observations regarding the gate-tuning behaviors of HPPPs remain consistent and broadly applicable across different twist angles and $\alpha$-MoO$_3$ thicknesses, as detailed in the Supporting Information, section 7.

In summary, we investigated the gate dependence of HPPPs stemming from the coupling between PhPs in $\alpha$-MoO$_3$ and SPPs in graphene. By modulating the graphene $E_p$, we demonstrated gate tunability of the optical response in IR s-SNOM measurements, retrieving the dependence of three key parameters, i.e., wavelength, amplitude, and dissipation rate, in heterostructure devices composed of single-layer and twisted bilayer $\alpha$-MoO$_3$/graphene. Combined with numerical simulations and theoretical calculations, we showed how gate tunability is fundamentally controlled by the $E_p$-dependent optical conductivity of monolayer graphene. Our work highlights how $\lambda_p$, $A_p$, and $\gamma_p$ can be tailored by the real and imaginary parts of the momentum associated with the gate-tunable polaritons. Their complex dependence originates from the intricate interplay of gate-dependent in-plane and out-of-plane components of the HPPP complex momentum. The elucidation of the gate-dependent mechanism of hybrid polaritons, along with its successful implementation in twisted bilayer $\alpha$-MoO$_3$/graphene devices, establishes the foundation for harnessing the full potential of gate tuning of hybrid polariton systems for nanophotonic devices in the infrared regime, yielding reprogrammable polaritronics and real-time control over nanoscale light routing and confinement. Coupled with localized quantum emitters, the demonstrated platform may modulate in real-time light–matter coupling and emission features, paving the way for a range of opportunities for nanophotonics.

**METHODS**

Device Fabrication and Characterization. Monolayer graphene was mechanically exfoliated from graphite crystals (Shanghai Onray Technology Co., Ltd.) onto a plasma-treated (SUNJUNE PLASMA VP-R3) SiO$_2$ (288 nm)/Si substrate. $\alpha$-MoO$_3$ flakes were exfoliated from bulk materials (SixCarbon technology, Shenzhen) onto polydimethylsiloxane (PDMS). The desired thickness of $\alpha$-MoO$_3$ was checked and selected under optical microscopy before being stacked onto graphene via all-dry transfer methods to prevent any chemical contamination. To fabricate twisted bilayer $\alpha$-MoO$_3$/graphene devices, top and bottom $\alpha$-MoO$_3$ flakes with selected thicknesses were separately exfoliated onto PDMS and dry transferred onto monolayer graphene sequentially, with the desired twist angle achieved using a micromanipulator. Drain and source electrodes (50 nm Au/5 nm Cr) were evaporated onto the graphene through a prepatterned shadow mask using thermal deposition. The sample was then mounted on a compact chip carrier, with all electrodes wire-bonded to it for electrical gating and doping.

**IR s-SNOM Measurements.** Near-field images were obtained using a commercially available IR s-SNOM system (Bruker nanoIR3s) operating in tapping mode AFM. An IR beam with a frequency of 931 cm$^{-1}$ was generated by a CO$_2$ laser (Access Laser, L4SL-13CO2) and focused on the apex of a gold-coated AFM tip (160AC-GG, OPUS) with tapping frequency $\Omega \approx 270$ kHz. The backscattered light from the tip was collected with an off-axis parabolic mirror and directed to a HgCdTe (MCT) photodetector to extract the near-field signal from the device. Detected signals were demodulated at the second harmonic to suppress the background.

**Electric Transport and THG Measurements.** The back-gate voltage was applied using a SourceMeter (Keithley, 2450), and the graphene resistance was recorded by a lock-in amplifier (Ametek, 7270). For THG measurement, a mid-IR femtosecond laser beam (Carmina, APE GmbH) with a center wavelength at 2850 nm (0.44 eV) was focused on the $\alpha$-MoO$_3$/graphene heterostructure through a 0.5 NA reflective objective (Thorlabs, LMM40X-P01). The back-reflected THG signal was gathered and guided to a spectrometer (HRS-500MS, Teledyne Princeton Instruments). In-situ recording of the gate-dependent THG signal was performed while sweeping the back-gate voltage. Throughout the electric transport and THG measurements, devices were maintained in a dry air environment to avoid the effects of atmospheric moisture on the devices.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.3c03769.

Determination of graphene CNP and $E_p$, numerical simulations, calculation of polariton dispersion, theoretical calculation of relation between HPPP complex momentum and graphene conductivity, two-phase homodyne near-field detection of the twisted bilayer $\alpha$-MoO$_3$/graphene device, derivation of fitting equations, gate-tuning behavior of HPPPs in twisted bilayer $\alpha$-MoO$_3$/graphene across varying twist angles and $\alpha$-MoO$_3$ thicknesses, gate tuning of topological transition in twisted bilayer $\alpha$-MoO$_3$/graphene heterostructures (PDF)

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Author Contributions
△Z.Z., R.S., and J.X. contributed equally to this work; T.J. conceived and designed the experiments; Z.Z. conducted the near-field and electric transport measurements with guidance from T.J. and M.B.R.; A.A. suggested the model and supervised the development of the theory; R.S. fabricated devices with the help of S.D. and support from W.H., X.C., and Z.W.; R.S. performed the THG measurements; J.X. and Z.D. performed the simulations with guidance from X.N. and K.C.; J.X. and X.N. contributed to the theory with guidance from A.A.; Z.Z. and J.X. contributed to the data fitting and analysis with guidance from T.J. and D.H.; Z.Z. wrote the manuscript with the help of all authors. All authors discussed and interpreted the results.

Notes
The authors declare no competing financial interest.

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