Van der Waals Phonon Polariton Microstructures for Configurable Infrared Electromagnetic Field Localizations

Wuchao Huang, Fengsheng Sun, Zebo Zheng, Thomas G. Folland, Xuexian Chen, Huizhen Liao, Ningsheng Xu, Joshua D. Caldwell, Huanjun Chen,* and Shaozhi Deng*
and square $\alpha$-MoO$_3$ microdisks.\textsuperscript{[8,9]} Nevertheless, configuring the near-field distributions associated with the in-plane anisotropic, and critically hyperbolic polaritons, via patterning and the associated design principles is still incomplete. As such developing these understandings of highly anisotropic polariton propagation and spatial confinement is anticipated to open new degrees of freedom for sub-diffraction-limit light focusing and manipulation.

Here, through the combination of theoretical calculations and real-space nanoimaging, we demonstrate the engineering of infrared electromagnetic field localization of HPhPs in microstructures constructed from biaxial $\alpha$-MoO$_3$ crystal. The polariton waves that propagate inside a specific microstructure will encounter and be reflected by boundaries, whereby polariton interference results, generating complex standing wave patterns. We show that such interference is governed by the orientation of the in-plane polaritonic isofrequency curve (IFC) relative to the microstructure edges. This is possible because the energy flow directions of the incident and reflected polariton waves are both normal to the IFC. Therefore, the electromagnetic field spatial distributions within a microstructure can be configured by tuning the size and shape, as well as the excitation frequency. The obtained localized fields are highly anisotropic, irrespective of the symmetric microstructure shapes that are supported within. Moreover, we show that the spatial near-field distributions of a wedge-shape microstructure are strongly dependent on the angles between the bisector of the vertex angle and the [001] axis of the $\alpha$-MoO$_3$ crystal. Such result further illustrates the combination of in-plane anisotropy and boundary manipulation as a paradigm for configuring electromagnetic fields at the nanoscale.

2. Results

$\alpha$-MoO$_3$ supports anisotropic HPhPs throughout the mid-infrared (545 to 1010 cm$^{-1}$) and THz (267 to 400 cm$^{-1}$) spectral range,\textsuperscript{[8,9,15,16]} over much of which these modes are hyperbolic in nature. These hyperbolic spectral bands originate from the opposite signed permittivities along different crystalline directions: $\text{Re}(\epsilon_x)\text{Re}(\epsilon_y) < 0$, with $i$ and $j$ representing the [100] ($x$-axis), [001] ($y$-axis), and [010] ($z$-axis) crystalline axes (Figure S1a,b, the Supporting Information).\textsuperscript{[8,9]} In the $x$–$y$ plane, the HPhPs exhibit open hyperbolic-shaped IFCs and propagate with concave wavefronts inside Rerstrahlen band 1 (545 to 851 cm$^{-1}$) and Band 2 (820 to 972 cm$^{-1}$) (Figure 1a,b,d,e; Figure S2b,c, Supporting Information). Even for Rerstrahlen Band 3 (958 to 1010 cm$^{-1}$) where the IFC is closed due to both in-plane permittivities being positive, the polaritons remain anisotropic featuring elliptical wavefronts (Figure 1g,h; Figure S2d, Supporting Information) as $\text{Re}(\epsilon_x) \neq \text{Re}(\epsilon_y)$. For ease of discussion, hereafter Bands 1, 2, and 3 will be named as negative-$\epsilon_x$-band, negative-$\epsilon_y$-band, and elliptical band, respectively. Every polariton wave launched into a microstructure will propagate with the energy flow in direction orthogonal to the IFC. This will be reflected by the boundaries of the microstructure and subsequently interfere with the reflected wave, thereby generating standing-waves of various spatially localized electromagnetic field distributions.\textsuperscript{[13]} Because the interference effects originate from the superpositions of the polariton wavefronts, the standing-waves are determined by the wavevector distributions, i.e., polariton IFC topology. Consequently, the anisotropic IFCs can bring a new degree of freedom for configuring the localized electromagnetic fields in $\alpha$-MoO$_3$ microstructures, which, otherwise is exclusively determined by the microstructure geometry fabricated from crystals with an isotropic IFCs (i.e., $\text{Re}(\epsilon_x) = \text{Re}(\epsilon_y)$, Figures S2a and S3a–c, Supporting Information).\textsuperscript{[13,44]}

An analytical model was first developed to calculate the in-plane IFC $q(\omega, \alpha, \theta, \delta)$, of the HPhPs propagating inside a vdW slab of finite thickness (see Note S1, Supporting Information).\textsuperscript{[36,37]} To simplify the discussion, $\epsilon$ denotes the real part of the permittivity in our following discussion. According to the model calculations, the electromagnetic waves in the hyperbolic vdW slab are dominated by the TM polariton modes with a dispersion relation

$$\sqrt{\frac{\varepsilon_x}{\varepsilon_z} k_0^2 \varepsilon_z - q^2 \varepsilon_x} = \arctan \left( \frac{\sqrt{\varepsilon_x \varepsilon_z} \sqrt{q^2 - k_0^2 \varepsilon_x}}{\varepsilon_x \sqrt{k_0^2 \varepsilon_z - q^2}} \right) + M \pi$$

where $\varepsilon_x = \varepsilon_x \cos^2 \theta + \varepsilon_y \cos^2 \theta$; $d$ is the slab thickness; $k_0$ is the free-space wavevector; $\theta$ denotes the angle of the propagation direction relative to the $x$-axis, $M$ represents the order of the different TM modes, and $\epsilon_x$ and $\epsilon_y$ are the dielectric constants for air and the substrate, respectively. Using the permittivity of $\alpha$-MoO$_3$ as the input parameter (see Note S1 and Table S1, Supporting Information), the in-plane IFCs of the slabs were calculated according to Equation (1) at representative frequencies, which agree well with the numerical results (Figure 1c,f,i). Specifically, for an $\alpha$-MoO$_3$ slab, the IFCs in negative-$\epsilon_x$-band are hyperbolas opening toward the $x$-axis (Figure 2a). The polariton wave vectors are restricted inside the opening angle of $\phi = 2\arctan(\sqrt{\varepsilon_x/\varepsilon_0}/\sqrt{\varepsilon_x/\varepsilon_0})$ bisected by $x$-axis. As a result, polaritons within the Rerstrahlen band are forbidden to propagate along $y$-axis. Similar calculation results can be obtained for the negative-$\epsilon_y$-band (see Note S2 and Figure S4a, Supporting Information). In elliptical band, the IFCs are ellipses (Figure 2b), resulting in polaritons spreading along all directions in the $x$–$y$ plane, but with orientation-dependent wavevectors.

Having established the IFC, the interference patterns of $\alpha$-MoO$_3$ microstructures can be readily calculated using the phenomenological cavity model (see Note S3, Supporting Information).\textsuperscript{[15,20,36,38]} Only the boundary perpendicular to the polariton wavevector is considered in our calculations to simplify the discussion and correlate the model calculations directly with near-field measurements performed using scattering-type scanning near-field optical microscopy (s-SNOM).\textsuperscript{[38]} In other words, the interference effects are dominated by those between a polariton wave and its antiparallel back-reflected wave. As will be shown in the following discussion, this approximation already captures the main physics of the polariton interference in $\alpha$-MoO$_3$ microstructures. To demonstrate the impacts of IFCs on the interference patterns, we first consider the polariton waves launched into a circular microdisk of rotational symmetry (radius
Figure 1. HPhPs in biaxial vdW crystals. a,d,g) Calculated 3D isofrequency contours in the $\alpha$-MoO$_3$ slab. The calculations were performed at 700 cm$^{-1}$ (negative-$\epsilon_x$-band), 937 cm$^{-1}$ (negative-$\epsilon_y$-band), and 980 cm$^{-1}$ (elliptical band), respectively. b,e,h) Calculated Re($E_z$) above the $\alpha$-MoO$_3$ slab surface at the same three frequencies. Green arrows indicate the propagation directions of the polariton waves. c,f,i) Isofrequency curves of the $\alpha$-MoO$_3$ slab at the same three frequencies. The Re($E_z$) distributions were calculated by launching the HPhPs on the sample surfaces using $z$-polarized electric dipoles. The isofrequency curves shown in (c,f,i) were obtained as Fourier transforms of (b,e,h), respectively. The dashed lines represent the in-plane dispersions obtained from the analytical electromagnetic waveguide model calculations. The $\alpha$-MoO$_3$ slab is 170 nm thick.

$L = 1.0 \mu$m, thickness $t = 170$ nm). The circular edge guarantees that all polariton waves propagating through the center can be back-reflected. For two typical frequencies in negative-$\epsilon_x$-band, i.e., $\omega = 900$ and 930 cm$^{-1}$, the calculation indicates deformed bright (dark) fringes along the $\gamma$-axis due to constructive (destructive) interference that results (Figure 2c,d). These features result from reduction of polariton wavelength $\lambda_p$ (corresponding to the fringe spacing) along the $\gamma$-axis, which are consistent with previous results.\cite{8,9} For the polaritons in elliptical band, the interference fringes are a series of ellipses (Figure 2e,f, Figure S5a–S5e, Supporting Information).

In addition to the fringe shapes, the anisotropic IFCs can modulate the interference patterns in three aspects. First, in negative-$\epsilon_x$-band, the IFCs exhibit a larger $\varphi$ at a smaller $\omega$ (Figure 2a; Figure S4b, Supporting Information). Therefore, as $\omega$ is reduced, interference fringes contributed by polaritons with wavevectors close to the IFC asymptotes will extend toward the two disk end points along the $\gamma$-axis (Figure 2c,d; Figure S5f–j, Supporting Information). Second, in both negative-$\epsilon_x$-band and elliptical band, the fringe spacings are smaller for excitation frequencies corresponding to IFCs with larger wavevectors (Figure 2e–f,k,m; Figure S5f–j,p, Supporting Information). As the fringe spacings are reduced, the widths of the bright fringes become smaller, indicating stronger electric field confinements. To quantitatively evaluate the field localization, a confinement factor defined as $\text{CF} = \lambda_0/W$ is employed, with $\lambda_0$ and $W$ as the free-space excitation wavelength and full width at half maximum (FWHM) of the outermost bright fringe to the edge, respectively. CF clearly increases as the excitation frequency is increased for negative-$\epsilon_x$-band (Figure 2l; Figure S5q, Supporting Information), whereas a reverse evolution is observed in elliptical band (Figure 2n; Figure S5r, Supporting Information). Third, the field confinements are nonuniform within an individual bright fringe. In negative-$\epsilon_x$-band, the CF of the outermost fringe increases as the angle
Figure 2. HPhP interferences in a α-MoO₃ microdisk. a,b) In-plane IFCs at two representative frequencies in negative-εₓ-band a) and elliptical band b). The dashed lines in (a) denote the asymptotes of the IFCs. c–f) Calculated interference patterns of a 1.0 µm radius, 170 nm thick microdisk at different excitation frequencies using the phenomenological model (see Note S3, Supporting Information). The two dashed white lines in (c,d) indicate the extent of the outmost bright fringes. g–j) Real-space nanoimaging of the corresponding microdisks. The boundaries are marked with white dashed circles. k,m) Experimental (dashed) and calculated (solid) amplitude profiles extracted along the horizontal dashed lines marked in (c–f). The amplitudes are normalized by those from the substrate next to the disk. l,n) Field confinement factors of the microdisk at different excitation frequencies. The symbols are the experimental values, and the solid lines are the calculation results. The error bars in (l,n) are obtained based on the two symmetrical points along the y-axis on the outmost fringes. Angle γ is defined as the angle with respect to x-axis along the center of the outmost fringe. Scale bars: 500 nm.

γ with respect to x-axis becomes larger (Figure 2l; Figure S5q, Supporting Information). In contrast, in elliptical band, the CF weakens as γ is increased (Figure 2n; Figure S5r, Supporting Information). These behaviors can be understood by considering that the evolution of q as a function of γ in negative-εₓ-band is opposite with those in elliptical band (Figure 2a,b). It should be noted that polariton interferences behaviors in negative-εᵧ-band are similar to those in negative-εₓ-band, where the calculated fringes deform along the x-axis (see Note S2, Figure S5k–p,s, Supporting Information).
The above model calculation results can be verified experimentally. To that end, α-MoO3 microstructures of various sizes and shapes are fabricated by employing the focus-ion beam (FIB) technique (Figures S6a and S7, Supporting Information). The interference patterns are visualized using a real-space nanoimaging approach based on s-SNOM (Figure S6b, Supporting Information). As shown in Figure 2g–j, the measured near-field distributions agree with the calculated interference features, showing similar deformed and elliptical fringes for the excitation frequencies in negative-εx-band and elliptical band. By extracting the respective amplitude profiles crossing the disk center along the x- and y-axes (Figure 2k,m; Figure S8, Supporting Information), it is observed that both numbers of the oscillating maxima and their dependence on the excitation frequency are consistent between the experimental and calculation results. Additionally, the s-SNOM characterizations and model calculations are in good quantitative agreement in terms of CF dependence on γ (Figure 2l,n). Note the differences between the experimental and calculated amplitudes close to the disk center, where the nanoimages show small fluctuations. We attribute these discrepancies to the defects and impurities introduced during the microdisk fabrication.

We further corroborate the model calculation results and reveal the complex interference fields by calculating the near-field distributions, Re(Ez), above the microdisks launched by a z-polarized electric dipole. Such a simulation configuration ensures that all reflected waves, and not just the back-reflected ones, are included in the interference fields. The simulations are performed using finite element method (FEM, Comsol). The results indicate that unlike other polaritons generating isotropic concentric patterns,[33,39] the localized fields in the microdisk clearly reveal highly anisotropic frequency-dependent spatial distributions. Cross-shape fringes that stem from the directional polariton propagation associated with the in-plane hyperbolic response of the α-MoO3, can be observed near the disk center at ω = 900 cm\(^{-1}\) (negative-εx-band) (Figures 1e and 3a). Meanwhile, elongated concentric fringes that originate from the in-plane elliptical response can be observed for excitation at 994 cm\(^{-1}\) (elliptical band) (Figures 1h and 3d). These anisotropic HPhPs will be reflected by the circular edge and generate deformed fringes close to the edge (Figure 3a,d). The phase difference between two adjacent bright fringes is approximately π, which is a typical characteristic of wave interference. Accordingly, the polariton wavelengths can be readily quantified by measuring the separations between the near-field maxima and minima (as indicated in Figure 3a,d) yielding λp/2. The extracted polariton wavelengths are consistent with the model calculations and s-SNOM measurements (Figure 3f). For a more direct comparison with the s-SNOM measurements, near-field images are simulated by recording the |Ez| as a function of the dipole position. The obtained |Ez(x, y)| corroborates with the experimental results in terms of fringe shapes and spacings (Figures 2j and 3b,c,e,f; Figure S8a,b, Supporting Information). It should be noted that the polariton field decays faster at 994 cm\(^{-1}\) outside the disk than that at 900 cm\(^{-1}\) (Figure 3a,b,d,e). Such a difference can be understood from two aspects. First, polaritons excited by 900 cm\(^{-1}\) exhibit in-plane hyperbolicity. The energy density within the IFC cone at 900 cm\(^{-1}\) will be larger than that at 994 cm\(^{-1}\). This can lead to stronger polariton reflection and transmission at the disk edge, which will result in longer decay length of the polariton field outside the disk. Second, the diameter of the disk excited at 900 cm\(^{-1}\) (1.5 µm) is smaller than that excited by 994 cm\(^{-1}\) (2.0 µm). A larger disk diameter will lead to a longer polariton propagation length and therefore a stronger damping. This will also make the polariton field decay fast outside the disk at 994 cm\(^{-1}\).

Interference is governed by the phase factor \(e^{i\Delta}\), where \(\Delta\) denotes the polariton propagation lengths that can be controlled by tuning the microdisk size. We then perform nanoimaging on a set of microdisks with varied radii (L = 0.75, 1.0, and 1.26 µm) and fixed thicknesses (t = 170 nm). Near-field images are recorded at two representative frequencies at 900 cm\(^{-1}\) (negative-εx-band) and 986 cm\(^{-1}\) (elliptical band) (Figure 4a–c). Figure 4e–g depicts that all of the microdisks, irrespective of their sizes, exhibit highly anisotropic fringe shapes. The number of bright fringes particularly decreases as the disk size is reduced. These results can be validated by the corresponding cavity model calculations (Figure S9, Supporting Information). To quantify the dependence of field
localizations on the disk radius, we examine the near-field amplitudes at three different positions inside each disk as typical examples (indicated by letters “a,” “b,” and “c” in Figure 4a, e). For the two excitation frequencies, the experimental and calculated near-field amplitudes at these three exemplary positions all exhibit oscillations against \( L \) (Figure 4d, h). In addition, a bright fringe periodically appears at the center of the disk with a decreasing \( L \), providing clear evidence of the phase factor modulations. Another interesting observation is that the oscillation periods at \( b \) and \( c \) are different and can be seen more clearly from the model calculation results (solid lines in Figure 4d, h). For \( \omega = 900 \text{ cm}^{-1} \), the period at \( b \) (452 nm) is smaller than that at \( c \) (458 nm), while for \( \omega = 986 \text{ cm}^{-1} \), an opposite result is obtained (i.e., the period at \( b \) (283 nm) is a bit larger than that at \( c \) (280 nm)). These behaviors can be understood by considering the phase factor \( e^{i\Delta} \) and the highly anisotropic in-plane polariton wavevectors in these two bands. In negative-\( e_x \)-band, the polariton interference at positions \( b \) and \( c \) are contributed by the polaritons with a large \( q \) near the IFC asymptotes and a relatively small \( q \) near the \( q_x \)-axis (Figure 2a). Accordingly, a smaller oscillation period against the disk size is observed at position \( b \). In contrast, in elliptical band, the interference at position \( b \) is caused by the superposition of the polariton waves with smaller wavevectors (Figure 2b) giving rise to a larger oscillation period. These results clearly indicate that the microdisk radius is an important parameter for configuring the spatial localization field distributions.

As discussed before, the HPhP interferences are dominated by the boundaries perpendicular to the wavevectors of the polariton waves. Consequently, the interference fields can be tailored by modifying the shapes (i.e., boundary numbers and types) of the \( \alpha\text{-MoO}_3 \) microstructures. Figure 5 illustrates the spatial near-field distributions obtained by the model calculations and the experimental measurements in three typical microstructures (Figure S7c, e, f, Supporting Information). For ease of discussion, the left most boundary of each microstructure is kept parallel to the \( y \)-axis (\([001]\) crystalline direction). In contrast to the highly symmetric standing wave patterns formed by isotropic polariton superpositions,\(^{[33,39]} \) the in-plane anisotropic HPhPs will lead to abnormal asymmetric interference patterns in each microstructure. Specifically, for excitations in elliptical band (986 cm\(^{-1}\)), where the HPhPs can spread along all directions with orientation-dependent wavevectors, all boundaries can act as reflectors and generate polariton interferences that are strongly dependent on the microstructure shapes. For square (Figure 5a, g), regular pentagon (Figure 5b, h), and regular hexagon (Figure 5c, i), the bright spots formed by constructive interferences generally exhibit spatial distributions distorted from the geometrical symmetries of the microstructures. This can be more directly observed on the near-field profiles crossing the microstructure centers along the \( x \)- and \( y \)-axes (solid and dashed lines, respectively, in Figure 5m–o). In the square and regular hexagonal, the bright spots particularly follow elongated distributions along the \( x \)-axis (\([100]\) crystalline direction). Thus, the fringe spacings along the \( x \)-axis are smaller than those along the \( y \)-axis (solid and dashed lines, respectively, in Figure 5m, o) due to the larger wavevector of the HPhPs parallel to the \( x \)-axis (Figure 2b).

The interference patterns become even more asymmetrical for the excitation frequency in negative-\( e_x \)-band (915 cm\(^{-1}\)). Both the square and regular hexagon microstructures only exhibit fringes parallel to the \( y \)-axis, with the two strongest located next to the edges (Figure 5d, j, f, l). This result can be understood by considering that the IFC at 915 cm\(^{-1}\) is a hyperbola opening toward the \( x \)-axis. The opening angle between the two asymptotes is \( \psi = 108^\circ \). Therefore, for polaritons with wavevectors confined by the two
asymptotes, only the two boundaries parallel to the y-axis can reflect the polariton waves, leading to the observed fringes along the y-axis. The polariton wavelengths extracted from the near-field profiles of these two microstructures are 475 and 480 nm (Figure 5p,r), respectively. These values match well with $\lambda_p = 2\pi/q_{[100]} = 480$ nm, where $q_{[100]}$ is the wavevector determined from the IFC for the HPhPs propagating along the x-axis. However, for a regular pentagon microstructure, the angle between the two edges intersecting with the x-axis is 108°. Two polariton waves can always be back-reflected by these two edges because $\pi - 108° = 72° < \phi$. As a result, additional fringes parallel to the two edges can be observed (Figure 5e,k). Moreover, due to the forbidden of polariton propagation, no fringes emanating from the rotated edges can be observed in all of the three microstructures (Figure 5d–f,j–l). Most interestingly, according to the IFC, the $q$ associated with the polariton waves propagating toward the two oblique edges is much larger than $q_{[100]}$ (Figure 2a), thereby rendering much shorter polariton wavelengths ($\lambda_p = 190$ nm) (Figure 5q) and indicating much stronger electric field confinements near the oblique edges. Another feature should be noted is that slightly deformed fringes can be observed experimentally at corners of square microstructure, while they are absent in the calculated image (Figure 5d,j). These deformed fringes are due to interference between high-wavevector polaritons, which are similar to those observed in the circular microdisk (Figure 2c–j). As mentioned before, in our calculations only the boundary perpendicular to the polariton wavevector is considered. Therefore, in the square microstructure, the contributions from polaritons with high wavevectors are neglected, giving rise to discrepancy of interference fringes at the corners between calculation and experimental results.

The results above unambiguously demonstrate that the electromagnetic field localizations can be configured by controlling the shape and the size of an $\alpha$-MoO$_3$ microstructure, and the excitation frequency. We further demonstrate the configurability by fabricating and imaging a set of $\alpha$-MoO$_3$ microwedges with fixed vertex angles at 30° and varied skew angles ($\beta$) from 0° to 90°, which is defined by the angle between the wedge bisector and the y-axis (upper panel, Figure 6a). The near-field distributions were first examined at an excitation frequency of 990 cm$^{-1}$, where the IFC is an ellipse (Figure 2b). Two polariton waves that can be back-reflected by the two edges always exist, leading to the interference fringes parallel to the wedge boundaries (Figure 6a). In particular, the orientations of the two edges relative to the major axes of the IFC will be adjusted by rotating the wedge around the z-axis (i.e., changing the $\beta$). Therefore, the two reflected polariton waves will exhibit different wavevectors, enabling modifications of their interference fields (see Note S4 and Figure S10, Supporting Information). For ease of discussion, the edge above (below) the x-axis is labeled as Edge I (Edge II) (as indicated in Figure 6a). For $\beta = 0$ and 90°, the wedges exhibit lateral symmetries relative to the y- and x-axes, respectively. The polariton waves perpendicularly reflected by the two edges exhibit the same $q$ (Figure S10, Supporting Information), making the two sets of fringes close to the edges equivalent (Figure S11, Supporting Information). The $q$ of the polariton wave reflected by Edge I will first be reduced and then increased as $\beta$ is steadily decreased from 90°. This is
Figure 6. HPhP interference effects in α-MoO₃ microwedges of varied skew angles and fixed vertex angles. a,c) Calculated and experimental HPhP interference patterns in a representative microwedge. Left panels: schemes of typical microwedges. The skew angle is defined by the angle between the bisector of the wedge and the y-axis. The two edges are labeled as Edge I and Edge II, respectively. Right panels: typical near-field image of the microwedge. The excitation frequency is 990 cm⁻¹ (elliptical band). b,d) Dependence of the HPhP wavelength on the skew angle of the wedge. The wavelengths are extracted from the fringes parallel to Edge I and Edge II. The solid lines and symbols in (b,d) denote the calculation and experimental results, respectively. Error bars in (b,d) are based on analyses of five typical amplitude line profiles perpendicular to Edge I and Edge II, respectively, in each experimental near-field image. The microwedge thickness is 170 nm. The excitation frequencies are 990 cm⁻¹ a,b) and 915 cm⁻¹ c,d). Scale bars: 1.0 μm.

3. Conclusion

The patterning of photonic materials into micro- and nanostructures has been well established for controlling electromagnetic waves at the nanoscale. Our study demonstrates that by combining in-plane anisotropic polaritons with high spatial confinement, that polariton interference effects inside an α-MoO₃ microstructure can be controlled by tuning the excitation frequency (IFC topology), shape (number and type of the boundary), and size (polariton propagation length) of the microstructure. Thus, the configurability of the nanoscale electromagnetic fields can be extended in terms of anisotropic spatial distributions and orientation dependence, which, otherwise, usually requires the design and patterning of complex architectures in isotropic counterparts. It should be noted that very recently two in-plane THz polaritonic bands have been discovered in α-MoO₃.¹⁶ The results obtained in the current study can therefore also be applied to the
THz spectral region, which can help design of nanophotonic devices for THz applications. In principle, this rationale can also be generalized to other types of vdW crystals and artificial meta-surfaces with in-plane optical responses, which is expected to open up a new paradigm for confining and manipulating light flow in planar photonics. From a fundamental point of view, the \( \alpha \)-Mo\(_3\) microstructures sustaining highly anisotropic localized electromagnetic fields can provide a testing platform for studying light-matter interactions in complex spatially confined electromagnetic environments.

During submission of our manuscript, we became aware of a very recent publication reporting similar studies.\(^{[40]}\) Our work was conducted independently. In addition, in our present study, we further demonstrated configuring the electromagnetic field localizations in \( \alpha \)-Mo\(_3\) microstructures of different sizes and shapes.

4. Experimental Section

Fabrication of \( \alpha \)-Mo\(_3\) Microstructures: \( \alpha \)-Mo\(_3\) single crystal slabs were prepared using thermal physical vapor deposition method.\(^{[41]}\) The crystals were directly synthesized on silicon substrate grown with 300 nm thick SiO\(_2\) layer. The various \( \alpha \)-Mo\(_3\) microstructures were fabricated using the FIB technique. Specifically, Ga\(^+\) ions were used as ion sources in the FIB etching system (AURIGA, Zeiss). The acceleration voltage and current of Ga\(^+\) beam were respectively set as 30 kV and 10 pA, with a Ga\(^+\) beam dose of 1 nC \( \mu \text{m}^2\). The dwell time was 0.5 \( \mu \text{s} \). After the microstructures were constructed, they were annealed at 300 °C for 2 h in O\(_2\) ambient condition to eliminate the Ga\(^+\) embedded in the \( \alpha \)-Mo\(_3\).

Numerical Simulations: Numerical simulations were performed using the FEM (Comsol). To generate the near-field spatial distributions above the various 2D slabs and microstructures, HPHPs were launched using a z-polarized electric dipole source. Specifically, in each simulation, the dipole was located 200 nm above the sample surface. The near-field distributions, \( R(E_x) \), were obtained on the plane 20 nm above the sample surface. The dipole was scanned across the sample at a step of 5 nm. The thicknesses of the slabs and \( \alpha \)-Mo\(_3\) microstructures were set as 170 nm. Permittivities of the samples were modeled by fitting their respective experimental data using Lorentz dielectric models.\(^{[3,15]}\)

Nanoimaging of Various \( \alpha \)-Mo\(_3\) Microstructures: Real-space nanoimaging was performed using an s-SNOM (NeaSNOM, NeaSpec GmbH), which was built based on an atomic force microscope (AFM). In a specific measurement, the metal-coated tip (Arrow-IrPt, spec GmbH), which was built based on an atomic force microscope (AFM), was illuminated by a mid-infrared laser source with tunable frequencies from 900 to 1240 cm\(^{-1}\) (quantum cascade laser, Daylight Solutions). The tip was vibrated at a frequency of \( \approx 270 \text{ kHz} \). The back-scattered light from the tip was directed to an MCT detector (HgCdTe, Kolmar Technologies). The near-field signal was then extracted using a pseudo-heterodyne interferometric method, and the detected signal was demodulated at a third harmonic of the tip vibration frequency.

Statistical Analysis: The error bars in Figure 2l,n were obtained based on the two symmetrical points along the \( \gamma \)-axis on the outmost fringes in Figure 2h,i. To obtain the error bars in Figure 4d,h, five points closest to positions \( a, b, \) and \( c \) in Figure 4a,e were analyzed. Error bars in Figure 6d,b are based on analyses of five typical amplitude line profiles perpendicular to Edge I and Edge II, respectively, in each experimental near-field image. All of the data were represented in form of average ± standard deviations.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

W.H., F.S., and Z.Z. contributed equally to this work. The support from the National Key Basic Research Program of China (Grant No. 2019YFA0210203), the National Natural Science Foundation of China (Grant Nos. 91963205 and 11904420), Guangdong Basic and Applied Basic Research Foundation (Grant Nos. 2019A1515011355 and 2020A1515011329) is acknowledged. H.C. acknowledges the support from Changjiang Young Scholar Program. Z.Z. acknowledges the project funded by China Postdoctoral Science Foundation (Grant No. 2019M663199). J.D.C. acknowledges support from the National Science Foundation, Division of Materials Research (Grant No. 1904793), while support for T.G.F. was provided by Vanderbilt University through the startup package of J.D.C.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electromagnetic field localizations, microstructures, nanoimaging, phonon polaritons, van der Waals crystals

Received: December 17, 2020
Revised: February 26, 2021
Published online: May 1, 2021

[1] R. Hillenbrand, T. Taubner, F. Keilmann, Nature 2002, 418, 159.
[2] T. Dekorsy, V. A. Yakovlev, W. Seidel, M. Helm, F. Keilmann, Phys. Rev. Lett. 2003, 90, 055508.
[3] J. D. Caldwell, A. V. Kretinin, Y. G. Chen, V. Giannini, M. M. Fowler, Y. Francescato, C. T. Ellis, J. G. Tischler, C. R. Woods, A. J. Giles, M. Hong, K. Watanabe, T. Taniguchi, S. A. Maier, K. S. Novoselov, Nat. Commun. 2014, 5, 5221.
[4] S. Dai, Z. Fei, Q. Ma, A. S. Rodin, M. Wagner, A. S. McLeod, M. K. Liu, W. Gannett, W. Regan, K. Watanabe, T. Taniguchi, M. Thiemens, G. Domínguez, A. H. C. Neto, A. Zettl, F. Keilmann, P. Jarillo-Herrero, M. M. Fogler, D. N. Basov, Science 2014, 343, 1125.
[5] J. D. Caldwell, L. Lindsay, V. Giannini, I. Vurgaftman, T. L. Reinecke, S. A. Maier, O. J. Glombecki, Nanophotonics 2015, 4, 44.
[6] T. Low, A. Chaves, J. D. Caldwell, A. Kumar, N. X. Fang, P. Avouris, T. F. Heinz, F. Guinea, L. Martin-Moreno, F. Koppen, Nat. Mater. 2017, 16, 182.
[7] D. N. Basov, M. M. Fogler, F. J. García de Abajo, Science 2016, 354, aag1992.
[8] W. Ma, P. Alonso-González, S. Li, A. Y. Nikitin, J. Yuan, J. Martín-Sánchez, J. Taboada-Gutiérrez, I. Amenabar, P. Li, S. Vélez, C. Tollan, Z. Dai, Y. Zhang, S. Sinram, K. Kalantar-Zadeh, S.-T. Lee, R. Hillenbrand, Q. Bao, Nature 2018, 562, 557.
[9] Z. Zheng, N. Xu, S. L. Ossicuro, M. Tamagnone, F. Sun, Y. Jiang, Y. Ke, J. Chen, W. Huang, W. L. Williams, A. Ambrosio, S. Deng, H. Chen, Sci. Adv. 2019, 5, eaay8690.
[10] S. Dai, Q. Ma, T. Andersen, A. S. McLeod, Z. Fei, M. K. Liu, M. Wagner, K. Watanabe, T. Taniguchi, M. Thiemens, F. Keilmann, P. Jarillo-Herrero, M. M. Fogler, D. N. Basov, Nat. Commun. 2015, 6, 6963.
