Hyperbolic media have attracted much attention in the photonics community due to their ability to confine light to arbitrarily small volumes and their potential applications to super-resolution technologies. The two-dimensional counterparts of these media can be achieved with hyperbolic metasurfaces that support in-plane hyperbolic guided modes upon nanopatterning, which, however, poses notable fabrication challenges and limits the achievable confinement. We show that thin flakes of a van der Waals crystal, α-MoO$_3$, can support naturally in-plane hyperbolic polariton guided modes at mid-infrared frequencies without the need for patterning. This is possible because α-MoO$_3$ is a biaxial hyperbolic crystal with three different Reststrahlen bands, each corresponding to a different crystalline axis. These findings can pave the way toward a new paradigm to manipulate and confine light in planar photonic devices.

INTRODUCTION

Hyperbolic media are characterized by permittivity tensors that have a component along one axis with an opposite sign compared to the other two axes. They have been extensively studied for their unique optical properties, particularly their ability to support electromagnetic fields and, hence, achieve very strong light confinement (1–3). This concept can be directly generalized to two-dimensional (2D) media, where surface waves or guided waves are considered and implemented using hyperbolic metasurfaces (HMSs) (4–6). HMSs are flat photonic nanopatterned structures that support guided waves with in-plane hyperbolicity and can control 2D light propagation in an unconventional way, giving rise to a variety of intriguing optical phenomena including, for example, all-angle negative refraction (7), substantial enhancement of the photonic density of states (4, 8), and wavefronts with concave curvatures (9, 10). However, the required patterning typically leads to substantial optical losses and limits the confinement that can be practically achieved. Furthermore, the electromagnetic responses of the HMSs are governed by permittivity tensors as derived from the effective medium theory, which only holds below the long-wavelength limit where the structural periodicity is much smaller than the incident wavelength. Consequently, the hyperbolic dispersion is constrained to a very small region in the reciprocal space, thus limiting the electromagnetic wave vectors. In principle, this issue can be alleviated by reducing the structural periodicities of the metasurfaces down to the sub–10-nm scale. However, this must be done without introducing additional surface roughness or defects, which presents a notable challenge using existing nanofabrication techniques (11). Thus, there exists a need for a natural medium that can be used to achieve in-plane hyperbolicity without nanopatterning; this remains a very important problem in the field of nanophotonics.

3D hyperbolic responses can occur in specific types of naturally existing homogeneous materials with strong dielectric anisotropies (11–14). Unlike artificial hyperbolic materials, the structural periodicities of natural hyperbolic materials are those of the crystal lattice and, thus, are on an atomic scale. Because of this characteristic, the hyperbolic dispersion of a natural hyperbolic material extends into a much larger region in the reciprocal space than that of an artificial one (14–16). In particular, van der Waals (vdW) crystals, which can be exfoliated in a layer-by-layer manner down to a single atomic planar layer, have been shown to exhibit excellent hyperbolic properties in the wavelength range from ultraviolet to terahertz (16–19). However, to the best of our knowledge, all of the vdW materials reported so far are uniaxial crystals with negative (positive) and isotropic in-plane permittivity but positive (negative) out-of-plane permittivity. When these materials are exfoliated into 2D flakes, because the optical axis coincides with the direction of exfoliation, they cannot achieve in-plane hyperbolic responses unless they are patterned (such as HMSs) (20).

In a recent study, we demonstrated highly confined hyperbolic phonon polaritons (PhPs) in a new type of vdW semiconducting crystal, α-phase molybdenum trioxide (α-MoO$_3$), grown by the thermal physical deposition method (21). Here, we show that vdW α-MoO$_3$ is actually a type of natural biaxial hyperbolic crystal and that it exhibits pristine in-plane hyperbolic dispersion in the mid-infrared range. In addition, we use high-resolution optical scanning probe nanoinaging techniques to investigate PhP modes as they are launched, guided, and manipulated within the different hyperbolicity bands in thin α-MoO$_3$ crystal flakes. In particular, the concave wavefront of a polaritonic mode originating from the in-plane hyperbolicity of the flake is observed, which is an unmistakable signature of the preserved 3D hyperbolicity of this 2D material. Furthermore, potential applications of vdW α-MoO$_3$ in focusing and manipulating mid-infrared electromagnetic fields at the nanoscale are demonstrated. It should be pointed out that the in-plane anisotropic PhPs in α-MoO$_3$ have been demonstrated in a very recent study (22). In our current study, as discussed below, we move a step forward by proposing a universal 3D analytical dielectric and dispersion model, for describing the hyperbolic PhPs in the α-MoO$_3$, providing direct experimental real-space image of the concave wavefront of the in-plane hyperbolic PhPs, and measuring the whole dispersion relations of the hyperbolic PhPs corresponding to the three Reststrahlen bands by combining scattering-type near-field scanning optical microscopy (s-SNOM) and photo-induced force microscopy (PiFM) techniques. The model we proposed can provide a description closer to the practical situation, which will be beneficial for other types of vdW materials supporting PhPs.
RESULTS
The infrared spectrum of α-MoO$_3$ is governed by the phonon absorptions, as in other polar vdW crystal such as hexagonal boron nitride (h-BN). The lattice of α-MoO$_3$ is composed of octahedral unit cells with nonequivalent Mo—O bonds along the three principal crystalline axes (Fig. 1A, inset) (23, 24). This crystalline structure gives rise to rich phonon modes that are infrared-active along different crystalline directions (23). In each Reststrahlen band between the longitudinal optical (LO) and transverse optical (TO) phonon frequencies, the reflectivity is expected to be high and the real part of the permittivity, Re($\varepsilon$), is expected to be negative. In α-MoO$_3$, there are three Reststrahlen bands in the mid-infrared range of 545 to 1010 cm$^{-1}$. Band 1 in the range of 545 to 851 cm$^{-1}$, which originates from the in-plane phonon mode along the [001] crystalline (y-axis) direction, and Bands 2 and 3 in the ranges of 820 to 972 cm$^{-1}$ and 958 to 1010 cm$^{-1}$, which originate from the phonon modes along the [100] (x-axis) and [010] (z-axis) directions, respectively (19, 20). The optical response of the α-MoO$_3$ is dominated by the phonon absorption, thus its dielectric tensor can be calculated by using a Lorentz model: $\varepsilon_j = \varepsilon_{\infty}(1 + \frac{\omega_{\text{LO}}^2 - \omega^2}{\omega_{\text{LO}}^2 - \omega^2 - i\Gamma^2})$, $j = x, y, z$, where $\varepsilon_j$ denotes the principal components of the permittivity tensor. Parameter $\varepsilon_{\infty}$ is the high frequency dielectric constant, and $\omega_{\text{LO}}^j$ and $\omega_{\text{TO}}^j$ refer to the LO and TO phonon frequencies, respectively. Parameter $\Gamma$ is the broadening factor of the Lorentzian line shape. The x, y, and z denote the three principal axes of the crystal, which correspond to the crystalline directions [100], [001], and [010] of the α-MoO$_3$, respectively. The thicknesses of the α-MoO$_3$ flakes used in our study are 100 to 200 nm, where the quantum confinement effects can be ignored. Therefore, the phonon frequencies and lifetimes are independent of the thickness of the sample. To calculate the relative permittivities shown in Fig. 1A, the phonon frequencies are directly adopted from the literature (21, 23), while the $\Gamma$ and $\varepsilon_{\infty}$ are treated as fitting parameters to make the theoretical near-field distributions match with the experimental measurements (see table S1), as discussed below. An α-MoO$_3$ crystal can be exfoliated in the z direction to reduce it to thin flakes. α-MoO$_3$ exhibits different permittivity values in these three bands along

![Fig. 1. Mid-infrared biaxial hyperbolic electromagnetic responses of a vdW α-MoO3 flake. (A) Real parts of the permittivities along the three principal axes. The different Reststrahlen bands are shaded in different colors. Inset: Schematic showing the crystalline unit cell of α-MoO$_3$. The three oxygen sites of the asymmetric Mo—O bonds along the different crystalline axes are labeled as O$_1$, O$_2$, and O$_3$. (B) 3D isofrequency surfaces observed in the three Reststrahlen bands, indicating that biaxial hyperbolic dispersion occurs in natural vdW α-MoO$_3$. (C) Isofrequency curves on the x-y plane at three typical frequencies, 623, 925, and 1000 cm$^{-1}$. The red and green arrows indicate the propagation directions of the hyperbolic PhPs modes arising at 623 and 925 cm$^{-1}$, respectively. (D) Schematic showing the launching of the PhPs on an α-MoO$_3$ surface with a z-polarized electric dipole. (E to G) Calculated magnitudes of the electric field distributions, $|E|$, on a natural α-MoO$_3$ surface at the same three frequencies as shown in (C). (H to J) Calculated real parts of z components of the electric field distributions, $\text{Re}(E_z)$, on a natural α-MoO$_3$ surface at the same three frequencies. (H) and (I) show two hyperbolic PhPs with in-plane concave wavefronts, while an elliptical wavefront is shown in (J). (K to M) Fourier transforms of (H) to (J), respectively. The white dashed lines delineate the corresponding isofrequency curves that are shown in (C).]
the three principal axes (i.e., $\varepsilon_x \neq \varepsilon_y \neq \varepsilon_z$); this is expected for a biaxial crystal. Furthermore, in the full range of 545 to 1010 cm$^{-1}$, there is always at least one component with a negative Re($\varepsilon$) value (Fig. 1A), making the crystal hyperbolic in the whole frequency range but along different directions for each of the Reststrahlen bands. Using the permittivity tensor, the isofrequency surfaces of $\alpha$-MoO$_3$ can be calculated by applying the general Fresnel equation:

$$\sum_{j=x,y,z} \frac{e_{ij}^2}{\varepsilon_j} = 0$$

(25). To simplify the description, we only used the Re($\varepsilon$) value in the calculations. Considering an $\alpha$-MoO$_3$ thin flake with a surface perpendicular to the [010] direction (z axis), as shown in Fig. 1B, the isofrequency surfaces for the PhPs in the three Reststrahlen bands are asymmetric hyperboloids, including two opening surfaces and a close surface near the center. The close surface can be ascribed to the transverse electric (TE) mode, that is, the ordinary electromagnetic wave in the crystal. Because of the closed topography, the maximum magnitude of TE mode wave vectors are finite, not allowing high electromagnetic field localizations. Therefore, in our current study, we only focus on the opening surfaces, which relate to PhPs with hyperbolic responses and therefore ultrahigh wave vectors. Specifically, in Band 1, where $\varepsilon_x < 0$ and $\varepsilon_y \neq \varepsilon_z > 0$, the polaritonic modes exhibit out-of-plane and in-plane hyperbolic dispersion simultaneously. A similar effect occurs when $\varepsilon_z$ is negative in Band 2. Thus, in Bands 1 and 2, strongly confined polaritonic modes exist in an $\alpha$-MoO$_3$ flake, with in-plane directional propagation depending on the specific hyperbolicity band. In Band 3, when $\varepsilon_x$ is negative and $\varepsilon_y$ and $\varepsilon_z$ are positive but not equal to each other, the out-of-plane dispersion is hyperbolic but the in-plane dispersion is elliptical (Fig. 1B); as a result, the polaritonic mode propagates anisotropically in the x-y plane. These complex isofrequency surface behaviors are distinctly different from those that have been previously reported for uniaxial hyperbolic media (e.g., h-BN and hyperbolic metamaterials), which exhibit negative (positive) and isotropic in-plane permittivity and positive (negative) out-of-plane permittivity. For this reason, while nanostructuring is required for in-plane hyperbolic responses to occur in these conventional media, it is expected that this property can be achieved in $\alpha$-MoO$_3$ flakes naturally without the need for nanostructuring (20, 26).

The in-plane propagation behavior of PhPs in $\alpha$-MoO$_3$ can be predicted by inspecting the isofrequency curves in the x-y plane, as shown in Fig. 1C, for the typical frequencies of the three Reststrahlen bands. For frequencies of 623 cm$^{-1}$ (Band 1) and 925 cm$^{-1}$ (Band 2), two-sheet dispersion curves can be observed. In contrast, the dispersion for a frequency of 1000 cm$^{-1}$ (Band 3) is elliptical (see also fig. S1). The in-plane hyperbolic responses can be revealed by calculating the polaritonic wave launched onto the surface of a 160-nm-thick $\alpha$-MoO$_3$ flake by an electric dipole source (Fig. 1D and see details in note S2 and fig. S2). Polaritonic waves with evident hyperbolic shapes can be seen in the electric field amplitude distributions at both 623 and 925 cm$^{-1}$ (Fig. 1, E and F, respectively). In addition, the real parts of the $E_y$ exhibit concave wavefronts, with opening directions along the y and x axes at 623 and 925 cm$^{-1}$, respectively (Fig. 1, H and I). On the other hand, we observed elliptically shaped radial propagation at 1000 cm$^{-1}$ (Fig. 1, G and J). These dispersive behaviors can be more visualized by plotting the Fourier transforms (FTs) of the Re($E_z$) images (Fig. 1, K to M). The FT distributions are consistent with the trajectories shown in Fig. 1C, except for bright spots located at the centers of the images, which originate from the background electric fields launched by the electric dipole. The FT results also reveal that the in-plane hyperbolic dispersions can result into very large wave vectors and large field confinements ($k_{\text{phs}}/k_0$), which enable focusing and manipulation of the mid-infrared electromagnetic waves at a subwavelength scale. To be more specific, the polaritonic mode will propagate preferentially along a cone with an axis coincident with the direction normal to the isofrequency curve shown in Fig. 1. This means that the polaritonic wave propagation direction at 623 cm$^{-1}$ (925 cm$^{-1}$) is at $\theta = 34^\circ$ ($\theta = 58^\circ$) with respect to the y axis (Fig. 1, E and F). These angles agree well with the theoretical values of 36$^\circ$ and 55$^\circ$ derived from the equation $\theta(\omega) = \frac{\pi}{2} - \arctan(\sqrt{\varepsilon_y(\omega)/\varepsilon_z(\omega)})$ (12).

According to the theoretical description above, the propagation angle, $\theta$, is very sensitive to the frequency, $\omega$, increasing as the frequency increases in Band 1 and decreasing as the frequency increases in Band 2 (fig. S3). Similar behavior occurs in the calculated electric field distributions (fig. S2, B to G). Specifically, as the frequency increases in Band 1, the hyperboloid progressively opens and flattens, while the hyperbolic polariton transforms into a polaritonic plane wave at 820 cm$^{-1}$. By further increasing the frequency in Band 2, the hyperboloid is reoriented from the y axis to the x axis; as the frequency is still further increased, a similar trend occurs as the hyperboloid progressively opens (fig. S2, E to G). These behaviors demonstrate how the hyperbolic polaritons in an $\alpha$-MoO$_3$ flake can be tuned by changing the excitation frequency.

To experimentally verify that $\alpha$-MoO$_3$ naturally exhibits in-plane hyperbolic responses, we used optical nano-imaging techniques to directly visualize the polaritonic modes supported on an $\alpha$-MoO$_3$ flake. In an initial experiment, we deposited a silver nanowire antenna (2.5 μm long and 60 nm wide) on the surface of the (010) crystalline plane (i.e., the x-y plane) of a 220-nm-thick $\alpha$-MoO$_3$ flake (Fig. 2A and note S3). Upon illumination with p-polarized light, the localized plasmons of the nanoantennas concentrated the optical fields to its extremities with sufficient momentum to launch a polaritonic wave onto the $\alpha$-MoO$_3$ surface. The polaritonic field, $E_p$ (specifically, the direct contribution, as described in (27, 28)) interferes with the local field due to the material polarizability, $E_{in}$ (i.e., the material contribution, as described in (27, 28)), giving rise to interference fringes on the sample surface. We mapped the interference patterns by measuring the scattered field from the metallic tip of an s-SNOM (Fig. 2B and note S4). Because of this interference, the near-field amplitude image closely matches the wavefronts of the polaritonic mode launched by the in-plane nanoantenna.

A near-field optical image obtained with a 944-cm$^{-1}$ incident light (Band 2) is shown in Fig. 2C ($\varepsilon_x = -0.98 + 0.08i$, $\varepsilon_y = 1.12 + 0.018i$, and $\varepsilon_z = 10.49 + 0.57i$ at this excitation frequency). Interference fringes with concave shapes are observed, originating from the tip of the nanoantenna. The anomalous wavefront has an opening direction along the [100] direction (x axis). In addition, the FT of the s-SNOM image (Fig. 2D) shows a dispersion of the hyperbolic shape, which is consistent with the isofrequency curves calculated using the Fresnel equation without any adjustable parameters (Fig. 1). When the illumination frequency is changed to 980 cm$^{-1}$ (Band 3) such that the real parts of the in-plane permittivities are positive ($\varepsilon_x = 0.67 + 0.04i$, $\varepsilon_y = 1.56 + 0.014i$, and $\varepsilon_z = -0.23 + 0.064i$), the polariton wavefront changes from concave to convex (Fig. 2E). This occurs because the polaritons in Band 3 have no in-plane hyperbolic responses as evidenced by the elliptically shaped FT distribution (Fig. 2F). The experimentally obtained s-SNOM images can be further corroborated by numerical simulations based on the permittivities at these two frequencies (see details in note S5). As shown in Fig. 2 (G and I), the simulated near-field distributions are consistent with the experimentally obtained

Zheng et al., Sci. Adv. 2019;5: eaav8690 24 May 2019
s-SNOM images in terms of both the fringe separations and curvatures. In addition, the opening angles and separations of the fringes change with the illumination frequency (see theoretical calculations in fig. S4).

An additional polaritonic feature that can be observed from the s-SNOM images shown in Fig. 2 (C and E) is fringes close to the flake edge with twice the periodicity of those close to the antenna (Fig. 2, H and J). These fringes result from polaritonic modes coupled into the flake by the s-SNOM tip (i.e., round-trip components): The polaritons are launched by the tip, reflected by the edge, and again sampled by the tip (27).

In another experiment, the in-plane polaritonic dispersion relations, $\omega(\vec{q})$, where $\vec{q}$ is the wave number, were derived. To that end, we performed s-SNOM imaging on a carefully selected $\alpha$-MoO$_3$ flake that had two orthogonal natural edges, one along the [001] (y-axis) direction (edge I) and the other along the [100] (x-axis) direction (edge II), as determined using micro-Raman spectroscopy (Fig. 3A, note S6, and fig. S5). Under excitation frequencies of 910 and 926 cm$^{-1}$ (Band 2), we observed the only fringes parallel to the [001] direction at edge I. This is consistent with the directional propagation of the polaritonic mode, resulting from the in-plane hyperbolic dispersion in this band, which shows that the isofrequency curve opens toward the [100] direction (Fig. 1C). This topology causes the polaritons to propagate perpendicularly to edge I instead of edge II (fig. S6, A to E). As a result, we obtained only fringes associated with the polariton waves launched by the s-SNOM tip and reflected from edge I (top panels in Fig. 3, D and F).

In contrast, under frequencies in Band 1, only type II PhPs propagating along the [001] direction were observed using PiFM (27, 28), as shown in Fig 3 (C, E, and G). Last, in Band 3, where $\varepsilon_x \neq \varepsilon_y > 0 > \varepsilon_z$, the in-plane elliptical isofrequency curve allows polaritons to propagate in all directions, unlike in the other two bands. This results in fringes parallel to both edges I and II, as shown in Fig. 3D (bottom panel), under illumination at 986 and 992 cm$^{-1}$. In addition, the lack of circular symmetry in the isofrequency curve resulted in a different periodicity for the fringes orthogonal to edges I and II at the same illuminating wavelength (Fig. 3F). We also observed this effect in the simulation, as shown in Fig. 3B (see also note S7 and fig. S7).

Next, the polaritonic fringe periodicity was used to calculate the polariton wavelengths, $\lambda_p$, corresponding to the illumination frequency, $\omega$ (fig. S6 and movies S1 and S2), and the polaritonic wave vector ($|\vec{q}| = 2\pi/\lambda_p$) (13, 15). As shown in Fig. 3H, the dispersion relation for the PhPs in $\alpha$-MoO$_3$ exhibits obvious in-plane anisotropic behaviors. Type I (type II) hyperbolic responses with positive (negative) real part of the in-plane permittivities are observed in the $\alpha$-MoO$_3$ flake. Specifically, for illumination frequencies between 780 and 800 cm$^{-1}$, only type II PhPs propagating along the [001] direction were observed with decreasing (increasing) $\lambda_p$ ($q$) values as $\omega$ was increased (fig. S9 and movie S1). A similar trend was observed in the frequency range of 820 to 950 cm$^{-1}$, but the PhPs instead propagated toward the [100] direction (fig. S9 and movie S2). However, if $\omega$ is varied in the range of 820 to 950 cm$^{-1}$, then type I PhPs were observed along both the [001] and [100] directions (movies S1 and S2) with decreasing $q$ values as $\omega$ was increased. These experimental results agree well with the theoretical predictions shown as a 2D pseudocolored plot of the complex reflectivity (Fig. 3H, note S6, and fig. S8). In addition, the electromagnetic confinement (defined as $q/\kappa$) of the PhPs calculated according to the dispersion relation was as high as about 87 at 953 cm$^{-1}$, corresponding to an effective refractive index of 87; this measurement agrees closely with the theoretically predicted value. In particular, a larger electromagnetic field confinement can be achieved in a flake with smaller thickness (21). For a monolayer $\alpha$-MoO$_3$ with a thickness of 1.4 nm, the maximum possible confinement that can be achieved would be
Fig. 3. In-plane PhP dispersion relations for a 160 nm-thick α-MoO₃ flake. (A) Schematic showing real-space s-SNOM imaging of the PhPs reflected by the sample edges. (B) Numerical simulation of the PhP near-field distributions. (C) Schematic of PIFM imaging of the PhPs. Light is modulated at the difference between the frequencies of the two first cantilever modes. (D) s-SNOM images obtained with varied illumination frequencies. (E) PIFM images obtained in Band 1 at 790 and 798 cm⁻¹ (left and right, respectively). (F) Near-field optical-amplitude profiles along the [100] (solid) and [001] (dashed) directions extracted from (D). (G) PIFM profiles along the [001] direction extracted from (E). (H) Dispersion relation for the PhPs in the α-MoO₃ flake. The blue and red dots indicate experimental data extracted from s-SNOM and PIFM images, respectively, with different excitation frequencies. The pseudocolored image represents the calculated imaginary part of the complex reflectivity, Im[τ(q,ω)], of the air/α-MoO₃/SiO₂ multilayered structure.

8100. This is an exciting value, although rigorous theoretical analysis taking into account the quantum confinement effect should be performed to give a more precise value.

The unique in-plane anisotropic hyperbolicity observed from α-MoO₃ flakes can be combined with artificial confinement of the polaritonic modes imposed by structuring the flake into specific geometric shapes (29, 30). As a simple demonstration, we fabricated an α-MoO₃ disk (1.6 μm in diameter, 160 nm thick) using a focused ion beam (FIB) and characterized its near-field optical properties (note S3) using s-SNOM. At an excitation frequency within Band 3 (992 cm⁻¹), the polaritonic modes launched by the SNOM tip and reflected from the disk edges produce an elliptical interference pattern (Fig. 4A, top panel). Although the flake has cylindrical symmetry, the ellipticity of the isofrequency curve dominates all the way to the center of the disk. The polaritonic anisotropy (defined as λₚₓ/λₚᵧ) was measured to be 1.47, which is comparable to the value of 1.25 reported in a recent study, although the previous study required a sample with a rather complex artificial heterostructure (31). In contrast, for the same structure, when the illumination frequency was in Band 2 (900 cm⁻¹), the interference pattern comprised fringes that were deformed along the x axis (Fig. 4B, top panel). Notably, the absence of interference fringes at the direction along the y axis ([001] direction) can be observed, which arises from the previous observation that the in-plane hyperbolic iso-frequency curves open toward the x axis (Fig. 1C). The interference patterns can be further controlled by structuring the α-MoO₃ flake into other shapes, for example, a square slab with edges along the [001] and [100] direction of α-MoO₃ (Fig. 4, A and B, bottom panels). For the PhPs excited in Band 3, we observed fringes along both of the [001] and [100] directions, while for Band 2, only straight fringes parallel to the [001] direction can be seen. These results indicate the geometry of the α-MoO₃ flake as an additional degree of freedom for tailoring the electromagnetic waves.

One of the most promising applications for hyperbolic media is subdiffraction optical focusing, by taking advantage of their highly directional polariton waves (2, 4). However, in artificial HMSs, the degree of focusing is usually limited by the relatively small maximum wave vector they can provide. This limitation can be overcome by using natural hyperbolic materials because they have atomic-scale unit cells (12, 14, 15). Furthermore, in contrast to other natural hyperbolic materials, α-MoO₃ is expected to exhibit anomalous optical focusing behavior due to its in-plane hyperbolicity. Specifically, in the uniaxial natural hyperbolic materials (e.g., h-BN), the in-plane isotropic dielectric tensor gives rise to PhP waves with isotropic wavefronts. Consequently, a point emitter placed on their surface will excite guided PhP waves with circular in-plane wavefront propagating on the surface. To focus these PhP waves, a circular gold nanodisk with a sharp edge is usually used (12, 15), which results in a focusing spot of circular shape. In contrast to the h-BN, the in-plane hyperbolic PhPs in α-MoO₃ exhibit wavefronts of concave shapes. The opening directions of these concave waves are strongly dependent on the operation frequency. For the PhPs in Band 1, the opening directions of their wavefronts are along the [001] direction (y axis), whereas for those in Band 2, the opening directions for the wavefronts are aligned the [001] direction (x axis). These concave wavefronts can lead to interesting focusing spots of anisotropic shapes. To better demonstrate subdiffraction focusing of these concave waves, we used a square metal disk instead of a circular one. As shown in Fig. 4 (C and D), we simulated the guiding and focusing of mid-infrared light by a 300-nm-thick α-MoO₃ flake as a proof-of-concept demonstration. To
Subsequently propagate at a fixed angle with respect to the two slab edges that are parallel to the \( \alpha \)-MoO\(_3\) flakes. These strips are approximately 80 nm wide (Fig. 4E), which is about \( 1/136 \) of the incident wavelength. In contrast, when the sample is excited (400 nm by 400 nm) underneath the MoO\(_3\) flake; it was intended to visualize the focusing spot, we placed a 20-nm-thick metallic slab (400 nm by 400 nm) underneath the MoO\(_3\) flake; it was intended to function as a nanoantenna to launch the polaritonic mode. Because of the in-plane anisotropic hyperbolic dispersion, the mid-infrared light can be guided and subsequently focused by controlling the frequency and polarization of the incident light. For example, if the MoO\(_3\) flake is illuminated with an \( x \)-polarized plane wave that has a frequency of 914 cm\(^{-1}\) such that the opening direction of the hyperboloid is along the [100] direction (\( x \) axis), then polaritonic waves are launched from the two slab edges that are parallel to the \( y \) axis (Fig. 4F). These waves subsequently propagate at a fixed angle with respect to the \( x \) axis, giving rise to narrow stripes that are oriented parallel to the [001] axis (\( y \) axis). These strips are approximately 80 nm wide (Fig. 4E), which is about \( 1/136 \) of the incident wavelength. In contrast, when the sample is excited with \( y \)-polarized light at 776 cm\(^{-1}\), the incident light is focused into stripes running parallel to the \( x \) axis (Fig. 4G and 4H). This subdiffraction focusing behavior can be attributed to the biaxial hyperbolic response of \( \alpha \)-MoO\(_3\) and can be leveraged for polarization optics in the mid-infrared range and efficient light trapping in energy-harvesting and photo-detecting device applications.

**DISCUSSION**

The homogeneous biaxial hyperbolic vdW \( \alpha \)-MoO\(_3\) crystal investigated here offers the prospect of planar photonics without the need for complex nanopatterning, which is unavoidable in 2D artificial counterparts. The unique biaxial hyperbolicity can provide an opportunity for controlling the nanoscale interactions in a direction-dependent manner. One example is the control and manipulation of dipole-dipole interactions that are important for photovoltaic and photodetection technologies (32). Previous study using uniaxial hyperbolic h-BN has indicated that, by taking advantage of the broadband hyperbolic dispersion, the nonradiative near fields can be engineered to give long-range dipole-dipole interactions (33). In comparison with the h-BN with uniaxial hyperbolicity, the in-plane permittivity of the biaxial \( \alpha \)-MoO\(_3\) is highly anisotropic, the interaction ranges between two dipoles orientating along \( x \) and \( y \) axes should therefore be expected to be different. Such a characteristic can provide more freedom for controlling the dipole-dipole interaction at nanoscale. On the other hand, in principle, the wave vectors of the guided electromagnetic waves that can be attained within \( \alpha \)-MoO\(_3\) are only limited by the atomic crystalline periodicity; thus, very strong electromagnetic confinement can be reached. In addition, the confinement and manipulation of electromagnetic fields at the nanoscale can be further enriched by introducing sophisticated nanostructures (Fig. 4). Moreover, \( \alpha \)-MoO\(_3\) is also a semiconductor, which demonstrates the potential for applications of hyperbolic media in active optoelectronic devices because of their excellent electrical transportation characteristics, the tunability of their physical characteristics by external doping, and their high optical-to-electrical conversion efficacy.

Another important potential application we want to mention is the thermal emission manipulation. Because of the high photonic density of states that can be achieved in hyperbolic materials, a broadband super-Planck thermal emission can be realized (34, 35). This effect can pave the way for engineering the thermal emission at nanoscale. The super-Planck thermal emission behavior has been demonstrated using hyperbolic metamaterials, which are consisted of stacked layers of SiC and other dielectric materials. However, one should note that the photonic density of states in these hyperbolic metamaterials is limited by the relatively large size of the structure unit cell. Such a limitation can be overcome by using the natural hyperbolic materials, such as \( \alpha \)-MoO\(_3\) and h-BN. Because of their atomic-scale unit cells, a much higher photonic density of state can be achieved, which therefore gives rise to a much larger enhancement of the thermal emission. Furthermore, in comparison with the uniaxial hyperbolic h-BN, the unique in-plane hyperbolicity of \( \alpha \)-MoO\(_3\) can give rise to highly anisotropic photonic density of states at its surface. Therefore, the thermal emission is expected to be dependent on the polarization states. For example, the enhancements of thermal emission should vary for polarizations along [001] and [100] crystalline directions. Such a characteristic can further enrich the manipulation of the thermal radiation at nanoscale.
The biaxial hyperbolic characteristics described in this study can, in principle, be generalized to other types of layered materials with different Reststrahlen bands associated with the three optical axes; thus, a broad range of applications are possible by choosing materials with appropriate hyperbolic bands. Therefore, these results are expected to pave the way toward a new paradigm in manipulating and confining light in planar photonic devices.

**MATERIALS AND METHODS**

**Sample preparation**

**Growth of the α-MoO₃ vdW crystal flakes**

The α-MoO₃ vdW flakes were synthesized by thermal physical deposition method (36) using a tube furnace. The MoO₃ powder with a purity of 99.9% (0.1 g) as source was placed at the center of a quartz tube. The cleaned SiO₂ substrate was placed at the low temperature zone 13.0 to 14.5 cm away from the source. The tube was heated up to 780°C in 70 min and then kept at that temperature for 120 min. During the thermal treatment, the MoO₃ powder was sublimated and recrystallized onto the low-temperature regions of the SiO₂ substrate. Subsequently, the quartz tube was cooled down naturally to room temperature, whereby the α-MoO₃ vdW flakes with various thicknesses (tens to hundreds of nanometers) could be found on the SiO₂ substrate.

**Deposition of the nanoantenna onto the α-MoO₃ surface**

The high aspect ratio silver nanowires (with a diameter of 50 to 60 nm and length of 2 to 3 μm) were synthesized using the overgrowth method, with the gold nanobipyramids as seeds (37). The longitudinal plasmon resonance frequency of the silver nanoantenna can be precisely tuned by controlling their aspect ratios. In our current study, the plasmon frequency of the silver nanoantenna was ~1000 cm⁻¹. To integrate the nanoantenna onto the α-MoO₃ surface, an aqueous solution of the silver nanowires was drop-casted onto the SiO₂/Si substrate with randomly distributed α-MoO₃ flakes. Various nanoantennas were found on the α-MoO₃ surfaces after the droplet was dried naturally under ambient conditions.

**Fabrication of the α-MoO₃ disk**

To fabricate the α-MoO₃ disk, we used a 30-keV FIB etching system (AURIGA, Zeiss). The beam diameter was kept at ~10 nm, and the ion current was 5 pA. A piece of 150-nm-thick α-MoO₃ flake was chosen. The dose of the Ga⁺ beam for the etching was set at 0.6 nC/μm², with a dwell time of 0.3 μs. After the FIB fabrication, the sample was annealed at 300°C for 2 hours under ambient conditions to eliminate the intercalated Ga³⁺ inside the α-MoO₃, whereby the PhPs characteristics could be recovered.

**Near-field optical imaging**

The near-field optical measurements were conducted using s-SNOM (NeaSNOM, Neaspec GmbH), which was built on the basis of an atomic force microscope (AFM). The near-field optical distributions of the sample can be mapped simultaneously with its topography. To image the PhPs in real space, a mid-infrared laser (quantum cascade laser, Daylight Solutions) with tunable frequencies from 900 to 1240 cm⁻¹ was focused onto the sample through a metal-coated AFM tip (Arrow-IrPt, NanoWorld). During the measurements, the AFM was operated in tapping mode, where the tip vibrated vertically with a frequency of f = 280 kHz. The back-scattered light from the tip was collected by an MCT detector (HgCdTe, Kolmar Technologies). The near-field signal was extracted by applying the pseudo-heterodyne interferometric method, and the detected signal was demodulated at high harmonic nf (n ≥ 3) of the tip vibration frequency.

PiFM detects localized near-field features of the investigated material as forced oscillations of an AFM cantilever, illuminated with infrared light. PiFM measurements were performed using a commercial Molecular Vista setup equipped with a pulsed quantum cascade laser from Block Engineering, whose emission frequency can be tuned between 795 and 1900 cm⁻¹. The p-polarized light from the laser was focused on a metallic-coated AFM tip (with a resonant frequency of ~300 kHz) operating in tapping mode. The laser was modulated at the frequency difference between the first and second flexural modes (eigenmodes) of the cantilever. The second mechanical eigenmode was used in the AFM feedback loop to control the tip-sample distance, with typical tapping modulation amplitude of 2 nm and typical set point of 85%. The amplitude of the light-induced oscillations of the first cantilever eigenmode was recorded as PiFM signal. PiFM measurements were performed in hyperspectral mode, in which the laser was swept in the 795- to 1000-cm⁻¹ frequency range for each position of the sample scan. The hyperspectral dataset was then elaborated to build PiFM images at single frequency or PiFM hyperspectral movies.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/8/eaav8690/DC1

Note S1. Theoretical model for calculating the isofrequency surface of the PhPs

Note S2. Simulation of the dipole-launched PH waves on the α-MoO₃ surface

Note S3. Simulation of the nanoantenna launched PHPs on the α-MoO₃ surface

Note S4. Determination of the crystalline direction of a typical α-MoO₃ flake

Note S5. Simulation of the s-SNOM image using the phenomenological cavity model

Note S6. Calculations on the complex reflectivity of the multilayer structure α-MoO₃/SiO₂

Fig. S1. Schematic showing the isofrequency curves of the PHPs in the biaxial α-MoO₃ flake

Fig. S2. Simulations of the dipole-launched hyperbolic PHPs on the α-MoO₃ surface

Fig. S3. Propagation directions of the in-plane hyperbolic PHPs

Fig. S4. Silver nanoantenna-launched PHPs at various incidence frequencies

Fig. S5. Determination of the crystalline directions of the α-MoO₃ by Raman spectroscopy

Fig. S6. Near-field optical images showing in-plane anisotropic PHPs characteristics of the α-MoO₃

Fig. S7. Comparison of the experiment and simulation near-field images of the PHPs distributions illuminated by 986 cm⁻¹ (Band 3)

Fig. S8. Scheme of the multi-layered structure consisted of air/α-MoO₃/SiO₂

Fig. S9. Optical image of the α-MoO₃ flake used for conducting the hyperspectral PiFM movies

Movie S1. Hyperspectral PiFM movie of the edge perpendicular to the [100] direction, which is adjacent to the corner 1 shown in fig. S9

Movie S2. Hyperspectral PiFM movie of the edge perpendicular to the [001] direction, which is in proximity of the corner 1 shown in fig. S9

Table S1. Parameters used in calculating the relative permittivities (Eq. S1)

**REFERENCES AND NOTES**

1. D. R. Smith, D. Schurig, Electromagnetic wave propagation in media with indefinite permittivity and permeability tensors. Phys. Rev. Lett. 90, 077405 (2003).

2. A. Podolsky, I. Iorsh, P. Belov, Y. Kivshar, Hyperbolic metamaterials. Nat. Photonics 7, 958–967 (2013).

3. V. P. Drachev, V. A. Podolsky, A. V. Kilishev, Hyperbolic metamaterials: New physics behind a classical problem. Opt. Express 21, 15048–15064 (2013).

4. A. V. Kilishev, A. Boltasseva, V. M. Shalaev, Planar photonics with metasurfaces. Science 339, 132309 (2013).

5. N. Yu, F. Capasso, Flat optics with designer metasurfaces. Light propagation with phase discontinuities: Generalized laws of reflection and refraction. Science 334, 333–337 (2011).

6. N. Yu, F. Capasso, Flat optics with designer metasurfaces. Nat. Mater. 13, 139–150 (2014).

7. R. A. Shelby, D. R. Smith, S. Schultz, Experimental verification of a negative index of refraction. Science 292, 77–79 (2001).
8. Z. Jacob, I. I. Smolyaninov, E. E. Narimanov, Broadband purcell effect: Radiative decay engineering with metamaterials. Appl. Phys. Lett. 100, 181105 (2012).
9. J. S. Gomez-Diaz, A. Ali, Flatland optics with hyperbolic metasurfaces. ACS Photonics 3, 2211–2224 (2016).
10. Y. Liu, X. Zhang, Metasurfaces for manipulating surface plasmons. Appl. Phys. Lett. 103, 141101 (2013).
11. M. N. Gjerding, R. Petersen, T. G. Pedersen, N. A. Mortensen, K. S. Thygesen, Layered van der Waals crystals with hyperbolic light dispersion. Nat. Commun. 8, 320 (2017).
12. P. Li, M. Lewin, A. V. Kretinin, J. D. Caldwell, K. S. Novoselov, T. Taniguchi, K. Watanabe, F. Gaussianmann, T. Taubner, Hyperbolic phonon-polaritons in boron nitride for near-field optical imaging and focusing. Nat. Commun. 6, 7507 (2015).
13. S. Dai, Q. Fei, Q. Ma, A. S. Rodin, M. Wagner, A. S. Acleod, M. K. Liu, W. Gannett, W. Regan, K. Watanabe, T. Taniguchi, M. Thienners, G. Dominguez, A. H. C. Neto, A. Zettl, F. Keilmann, P. Jarillo-Herrero, M. M. Fogler, D. N. Basov, Tunable phonon polaritons in atomically thin van der Waals crystals of boron nitride. Science 343, 1125–1129 (2014).
14. J. D. Caldwell, A. V. Kretinin, Y. G. Chen, V. Giannini, M. M. Fogler, 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, Sub-diffractional volume-confined polaritons in the natural hyperbolic material hexagonal boron nitride. Nat. Commun. 5, 5221 (2014).
15. S. Dai, Q. Ma, T. Andersen, A. S. Acleoed, Z. Fei, M. K. Liu, M. Wagner, K. Watanabe, T. Taniguchi, M. Thienners, F. Keilmann, P. Jarillo-Herrero, M. M. Fogler, D. N. Basov, Subdiffractional focusing and guiding of polaritonic rays in a natural hyperbolic material. Nat. Commun. 6, 6963 (2015).
16. K. Korzecb, M. Gacj, D. A. Pawlak, Compendium of natural hyperbolic materials. Opt. Express 23, 25406–25424 (2015).
17. J. Sun, N. M. Litchinitser, J. Zhou, Indefinite by nature: From ultraviolet to terahertz. ACS Photonics 1, 293–303 (2014).
18. D. N. Basov, M. M. Fogler, F. J. García de Abajo, Polaritons in van der Waals materials. Science 354, aag1992 (2016).
19. T. Low, A. Chaves, D. V. Kretinin, A. Kumar, N. X. Fang, P. Avarious, T. F. Heinz, F. Guinea, L. Martin-Moreno, F. Koppens, Polaritons in layered two-dimensional materials. Nat. Mater. 16, 182–194 (2017).
20. P. Li, I. Dolado, F. J. Alfaro-Mozaz, F. Casanova, L. E. Hueso, S. Liu, J. H. Edgar, A. Y. Nikitin, S. Velez, R. Hillenbrand. Infrared hyperbolic metasurface based on nanostructured van der Waals materials. Science 359, 892–896 (2018).
21. Z. Zheng, J. Chen, Y. Wang, X. Wang, X. Chen, P. Liu, J. Xu, W. Xie, H. Chen, S. Deng, N. Xu, Highly confined and tunable hyperbolic phonon polaritons in van der Waals semiconducting transition metal oxides. Adv. Mater. 30, 1705318 (2018).
22. W. Ma, P. Alonso-González, S. Li, A. Y. Nikitin, J. Yuan, J. Martín-Sánchez, J. Taboada-Gutiérrez, I. Amanabar, P. Li, S. Vélez, C. T. Ellis, Z. Dai, Y. Zhang, S. Siram, K. Kalantar-Zadeh, S.-T. Lee, R. Hillenbrand, Q. Bao, In-plane anisotropic and ultra-low-loss polaritons in a natural van der Waals crystal. Nature 562, 557–562 (2018).
23. K. Eda, Longitudinal-transverse splitting effects in IR absorption spectra of MoO3. J. Solid State Chem. 95, 64–73 (1991).
24. M. A. Py, P. E. Schmid, J. T. Vallin, Raman scattering and structural properties of MoO3, Il Nuovo Cimento B 38, 271–279 (1977).
25. K. E. Ballantine, J. F. Donegan, P. R. Eastham, Conical diffraction and the dispersion surface of hyperbolic metamaterials. Phys. Rev. A 90, 013803 (2014).
26. A. A. High, R. C. Devlin, A. Dibos, M. Polking, D. S. Wild, J. Perczel, N. P. de Leon, M. D. Lukin, H. Park, Visible-frequency hyperbolic metasurface. Nature 522, 192–196 (2015).
27. A. Ambrosio, M. Tamagnone, T. Chaudhary, L. A. Laeugere, P. Kim, W. L. Wilson, F. Capasso, Selective excitation and imaging of ultralow phonon polaritons in thin hexagonal boron nitride crystals. Light Sci. Appl. 7, 27 (2018).
28. M. Tamagnone, A. Ambrosio, K. Chaudhary, L. A. Laeugere, P. Kim, W. L. Wilson, F. Capasso, Ultra-confined mid-infrared resonant phonon polaritons in van der Waals nanostructures. Sci. Adv. 4, eaat7189 (2018).
A mid-infrared biaxial hyperbolic van der Waals crystal
Zebo Zheng, Ningsheng Xu, Stefano L. Oscurato, Michele Tamagnone, Fengsheng Sun, Yinzhu Jiang, Yanlin Ke, Jianing Chen, Wuchao Huang, William L. Wilson, Antonio Ambrosio, Shaozhi Deng and Huanjun Chen

Sci Adv 5 (5), eaav8690.
DOI: 10.1126/sciadv.aav8690

ARTICLE TOOLS http://advances.sciencemag.org/content/5/5/eaav8690
SUPPLEMENTARY MATERIALS http://advances.sciencemag.org/content/suppl/2019/05/20/5.5.eaav8690.DC1
REFERENCES This article cites 36 articles, 8 of which you can access for free http://advances.sciencemag.org/content/5/5/eaav8690#BIBL
PERMISSIONS http://www.sciencemag.org/help/reprints-and-permissions

Use of this article is subject to the Terms of Service

Science Advances (ISSN 2375-2548) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. The title Science Advances is a registered trademark of AAAS.

Copyright © 2019 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).