

Highly Confined and Tunable Hyperbolic Phonon Polaritons in Van Der Waals Semiconducting Transition Metal Oxides

Zebo Zheng, Jianing Chen, Yu Wang, Ximiao Wang, Xiaobo Chen, Pengyi Liu, Jianbin Xu, Weiguang Xie,* Huanjun Chen,* Shaozhi Deng,* and Ningsheng Xu*

2D van der Waals (vdW) layered polar crystals sustaining phonon polaritons (PhPs) have opened up new avenues for fundamental research and optoelectronic applications in the mid-infrared to terahertz ranges. To date, 2D vdW crystals with PhPs are only experimentally demonstrated in hexagonal boron nitride (hBN) slabs. For optoelectronic and active photonic applications, semiconductors with tunable charges, finite conductivity, and moderate bandgaps are preferred. Here, PhPs are demonstrated with low loss and ultrahigh electromagnetic field confinements in semiconducting vdW α -MoO₃. The α -MoO₃ supports strong hyperbolic PhPs in the mid-infrared range, with a damping rate as low as 0.08. The electromagnetic confinements can reach $\approx \lambda_0/120$, which can be tailored by altering the thicknesses of the α -MoO₃ 2D flakes. Furthermore, spatial control over the PhPs is achieved with a metal-ion-intercalation strategy. The results demonstrate α -MoO₃ as a new platform for studying hyperbolic PhPs with tunability, which enable switchable mid-infrared nanophotonic devices.

Phonon polaritons (PhPs), quasiparticles induced by coupling of electromagnetic fields with optical phonons in polar crystals, can strongly confine the free-space light field deeply below the incidence wavelength.^[1–3] In comparison with the well-documented metallic plasmon polaritons, the PhPs can achieve improved light confinements, significantly reduced optical losses, and much higher quality factors.^[4–7] These characteristics enable a wealth of potential applications, such as sensing,^[8] thermal management,^[9,10] and ultramicroscopy,^[11,12] especially in the mid-infrared and terahertz spectral ranges where most of the plasmon polaritons cannot access.^[13] For those reasons, the PhPs have been thoroughly explored in a variety of bulk polar

dielectric crystals, such as SiC,^[14] SiO₂,^[15] GaAs,^[16] InP,^[17] CaF₂,^[18] and hexagonal boron nitride (hBN).^[19]

In recent years, 2D vdW atomic crystals have attracted much attention due to the exotic optical and optoelectronic responses originated from their atomically thin thicknesses.^[20–22] In particular, the weak vdW forces between adjacent layers and strong covalent bonding within a specific layer can give rise to highly anisotropic lattice vibrations along the in- and out-of-plane directions of the crystals. As a result, the optical responses along these two directions are distinctly different, making the 2D vdW materials natural hyperbolic materials.^[6,7,23] The propagating waves within such crystals can have much high momentum which leads to PhPs with extremely high electromagnetic confine-

ments.^[6,7,24] For that reason, the 2D vdW polar crystals have been considered as promising platforms for studying nanoscale light-matter interactions involving the PhPs. To date, 2D vdW crystals sustaining PhPs have only been demonstrated in thin hBN slabs.^[24,25] In comparison with the insulating and wide-band-gap hBN, 2D materials with semiconducting characteristics are more preferred for practical optoelectronic device applications in terms of their rich electronic structures, excellent electrical transportation characteristics, tunable optoelectronic properties upon doping, strong light absorption and emission as well as high optical-to-electrical conversion efficacy. These properties can provide new opportunities for the PhPs in active

Dr. Z. Zheng, X. Wang, Prof. H. Chen, Prof. S. Deng, Prof. N. Xu
State Key Laboratory of Optoelectronic Materials and Technologies
Guangdong Province Key Laboratory of Display Material and Technology
School of Electronics and Information Technology
Sun Yat-sen University
Guangzhou 510275, China
E-mail: chenhj8@mail.sysu.edu.cn; stsdz@mail.sysu.edu.cn;
stxsns@mail.sysu.edu.cn

Prof. J. Chen
Institute of Physics
Chinese Academy of Science and Collaborative Innovation Center
of Quantum Matter
Beijing 100190, China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.201705318>.

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Prof. J. Chen
School of Physical Sciences
University of Chinese Academy of Science
Beijing 100049, China

Y. Wang, Prof. X. Chen, Prof. P. Liu, Prof. W. Xie
Siyan Laboratory
Guangzhou Key Laboratory of Vacuum Coating Technologies
and New Energy Materials
Department of Physics
Jinan University
Guangzhou 510632, China
E-mail: wgxie@email.jnu.edu.cn

Prof. J. Xu
Department of Electronic Engineering and Materials Science
and Technology Research Center
The Chinese University of Hong Kong
Hong Kong SAR 999077, China

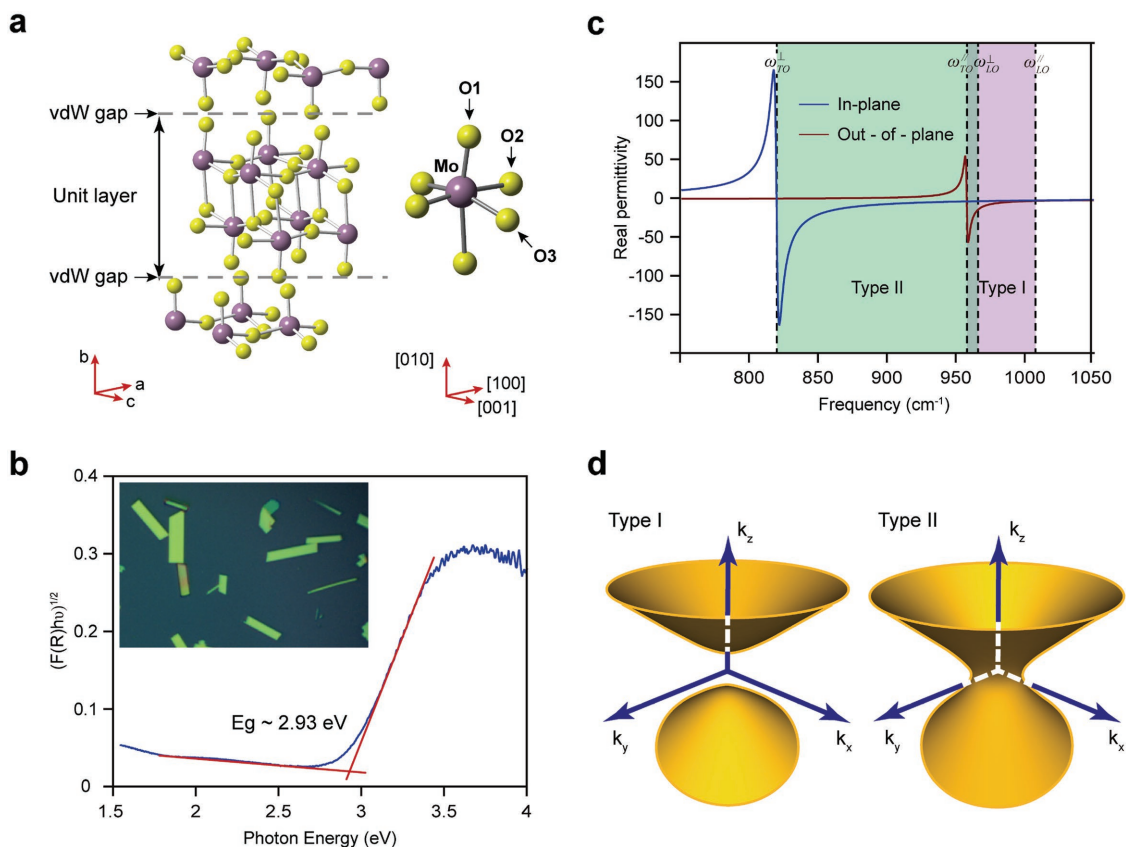


Figure 1. Crystalline structure and dispersion of the α - MoO_3 2D flake. a) Scheme of the crystalline structure of the α - MoO_3 . The three different oxygen sites are indicated by O1–O3, respectively. b) Kubelka–Munk transformed diffuse reflectance spectrum of the as-grown α - MoO_3 sample. The extracted energy bandgaps is ≈ 2.93 eV. Inset: Optical microscopy image of typical α - MoO_3 2D flakes. c) Real parts of the in- and out-of-plane permittivities of the α - MoO_3 . Types I and II Reststrahlen bands are shaded in purple and green, respectively. d) Schematic showing the isofrequency surfaces of a Type I (left) and II (right) hyperbolic material.

applications of nanophotonics and optoelectronic devices. However, to the best of our knowledge, experimental demonstration of the PhPs in semiconducting 2D vdW crystals remains unexplored.

As a typical vdW semiconductor, α - MoO_3 has drawn considerable attention in recent years due to its rich electronic and crystalline structures that are significant in various optoelectronic applications.^[26–28] The large separation between adjacent layers and large octahedron unit can greatly facilitate the injection/extraction of extrinsic atoms (Figure 1a, left), allowing the electronic band structure and phonon modes of the α - MoO_3 to be tailored in a wide range via ion intercalation.^[28–31] This tunability makes it very advantageous in tunable optoelectronic devices. Most importantly, the α - MoO_3 can exhibit negative permittivity in specific spectral ranges where different types of polaritons can exist. For example, MoO_3 flake with appropriate stoichiometry can sustain plasmon polaritons. On the other hand, the rich phonon modes in the α - MoO_3 can result in various “Reststrahlen” bands, spectral ranges bracketed by the longitudinal optical (LO) and transverse optical (TO) phonon frequencies.^[32–34] Within these bands the α - MoO_3 are foreseen to support PhPs at their surfaces. Moreover, in comparison with the most studied hBN and SiC, the significant difference in the masses of the Mo and oxygen atoms can lead to a large

frequency gap between the optical and acoustic phonons, which can significantly reduce the PhPs damping rates.^[33,34] Whereas the plasmon polaritons have been demonstrated in sub-stoichiometric 2D α - MoO_3 nanoflakes,^[35–37] the PhPs within this type of vdW crystals remain completely unexplored.

Here, with state-of-the-art real-space nanoimaging techniques, we for the first time unveil the hyperbolic PhPs with low loss and ultrahigh electromagnetic field confinements in the 2D vdW α - MoO_3 . The PhPs are strongly dependent on the thicknesses of the α - MoO_3 . Additionally, we demonstrated the spatial control of the α - MoO_3 PhPs through artificial boundaries, which were established by metal ion intercalations.

The α - MoO_3 samples used in our study are 2D flakes with orthorhombic crystalline structure (Figure 1b, inset, Section S1, Figures S1 and S2, Supporting Information). The longitudinal direction of a specific flake is along the [001] direction (Section S1 and Figure S3, Supporting Information). They are typical semiconductors with energy bandgap of ≈ 2.93 eV, which is extracted from the Kubelka–Munk transformed diffuse reflectance spectrum (Figure 1b). The semiconducting nature of the α - MoO_3 samples can also be manifested from the X-ray photoelectron spectroscopy (XPS) characterizations, which provide the information about their valance band electronic structures. The pristine α - MoO_3 samples show an electronic valance

band at -3.1 eV, which confirms that they are n-type semiconductors (Figure S4, Supporting Information).^[38] In addition, the pristine α -MoO₃ 2D flake exhibits a Schottky-type electrical transportation behavior (Figure S5, Supporting Information), which is due to the energy barrier formed at the interface between the semiconductor MoO₃ and metal electrodes. The current is relatively small due to the moderate bandgap of the 2D flake. The lattice of the α -MoO₃ is composed of octahedron unit cells with nonequivalent Mo–O bonds along the three principal crystalline axes (Figure 1a, right). Such a low-symmetry crystalline structure gives rise to asymmetric phonon modes that are infrared-active along different crystalline directions. In particular, in the spectral regime between 810 and 1010 cm^{-1} there are four infrared-active phonon modes.^[32,33] Two of them correspond to in-plane vibrations perpendicular to the b -axis of the α -MoO₃ (B_{3u} modes), which are respectively the TO and LO phonon modes with resonance frequencies of 818 cm^{-1} ($\omega_{\text{TO}}^{\perp}$) and 974 cm^{-1} ($\omega_{\text{LO}}^{\perp}$). The other two are the B_{2u} modes with resonances at 962 cm^{-1} ($\omega_{\text{TO}}^{\parallel}$) and 1010 cm^{-1} ($\omega_{\text{LO}}^{\parallel}$), which are associated with out-of-plane vibrations parallel to the b -axis. These phonon modes give rise to two Reststrahlen bands where the real parts of the in-plane ($\text{Re}\epsilon_{\parallel}$) and out-of-plane ($\text{Re}\epsilon_{\perp}$) permittivities exhibit opposite signs (Figure 1c and Section S2, Supporting Information), indicating that the layered α -MoO₃ is a type of material with intrinsic hyperbolic isofrequency surface (Figure 1d).^[23] Specifically, the upper band (962–1010 cm^{-1})

corresponds to Type I hyperbolic response with $\text{Re}\epsilon_{\parallel} < 0$ and $\text{Re}\epsilon_{\perp} > 0$, while the lower one (818–974 cm^{-1}) of Type II hyperbolic response exhibits $\text{Re}\epsilon_{\parallel} > 0$ and $\text{Re}\epsilon_{\perp} < 0$. In such a material with its surface normal to the b -axis, the PhPs waves can be restricted to a specific direction of angle $\theta = \arctan(i\sqrt{\epsilon_{\perp}}/\sqrt{\epsilon_{\parallel}})$ with respect to the b -axis, resulting in very-large-momentum extraordinary rays guided within the flake.

To unveil the hyperbolic PhPs of the α -MoO₃, we utilized the scattering-type scanning near-field optical microscope (s-SNOM) to excite and image the sample in the mid-infrared regime. Briefly, a sharp metal-coated probe (curvature radius $r \approx 20$ nm) was employed as a nanoantenna to focus the free-space infrared light into the gap between the tip and sample. The strongly confined electromagnetic field thereafter provided sufficient momentum to launch the propagating PhPs wave with wavelength of λ_{PhPs} along the surface of the α -MoO₃. The PhPs can subsequently form standing waves due to the interference with the reflected waves by the sample edges (Figure 2a), with the period of the standing-wave corresponding to $\lambda_{\text{PhPs}}/2$. The near-field distributions associated with the PhPs can be readily imaged by scanning the probe across the edges of a 2D α -MoO₃ flake.^[39,40]

Figure 2b shows the s-SNOM image of a typical 2D α -MoO₃ flake (thickness $t = 102$ nm) upon the illumination with frequency ω_0 of 986 cm^{-1} (wavelength $\lambda_0 = 10.14$ μm). The normalized near-field amplitudes $S(\omega) = S_{\text{MO}}(\omega)/S_{\text{SiO}_2}(\omega)$ are monitored to accurately study the pristine near-field properties

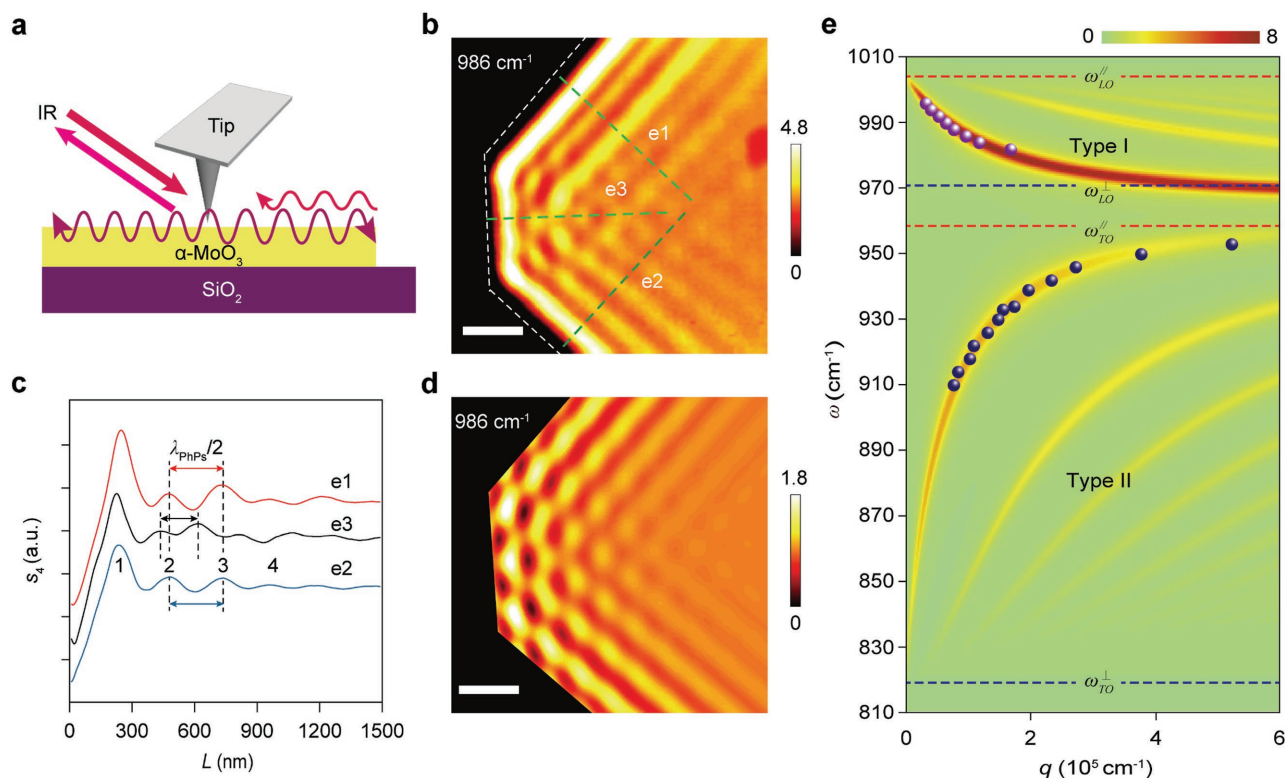


Figure 2. PhPs in the layered α -MoO₃ 2D flake. a) Scheme of the s-SNOM experiments. b) Real-space near-field optical image of a typical α -MoO₃. The sample is illuminated by an incidence frequency of 986 cm^{-1} . The thickness of the flake is 102 nm. The white dashed lines mark the edges of the flake. c) Extracted profiles of the scattering amplitudes along the e1, e2, and e3 lines indicated in (b). d) Simulated near-field optical image of the α -MoO₃ flake corresponded to (b). The scale bars are 500 nm. e) Dispersion of the PhPs in the α -MoO₃. Symbols indicate experimental data extracted from the e2 profiles under varied excitation frequencies. The false color image delegates the imaginary part of the complex reflectivity, $\text{Im}r_p(q, \omega)$, of the air/ α -MoO₃/SiO₂ multilayer structure obtained from theoretical calculations.

of the PhPs, with S_{MO} and S_{SiO_2} the scattering amplitudes of the $\alpha\text{-MoO}_3$ and SiO_2 substrate, respectively. Evident periodic fringes parallel to the sample edges can be observed from the image. In addition, a variety of bright and dark spots can be clearly found at the intersects of the fringes, which are originated from the multibeam interferences of the PhPs reflected from the edges.^[25,41]

To analyze the fringes in detail, line profiles of the near-field amplitudes were extracted along the directions perpendicular to the two identical flake edges (dashed green lines e1 and e2 in Figure 2b). As shown in Figure 2c, the profiles are strongest close to the edges, followed by a series of annihilated peaks away from the edges. The degradation of the fringes suggests dissipation of the PhPs along with their propagation. The polariton wavelength can therefore be determined as $\lambda_{\text{PhPs}} = 470$ nm, which is $\approx 1/21$ of the incidence wavelength ($\lambda_0 = 10.14$ μm). In addition, the propagation lengths of the PhPs can also be estimated according to the near-field profiles as $\approx 7\lambda_{\text{PhPs}}$, which is twice that of the plasmon polariton reported in graphene at similar operation frequencies.^[39,40] This result suggests that the $\alpha\text{-MoO}_3$ flake can sustain PhPs with very low dissipation.

An interesting observation is that “even–odd” oscillations appear in all of the extracted profiles from the s-SNOM image (Figure 2b,c). Instead of a monotonic decay behavior, the intensities of the annihilated peaks exhibit consecutive oscillations, with the odd peaks in the fringe profiles larger than the adjacent even ones. To separate the harmonic components in these profiles, we performed 2D Fourier transformation analysis on the near-field optical image. The result indicated that the total near-field image is constructed by two harmonic components entangled with each other, which are respectively the fundamental oscillation with momentum q_1 and high-order one with momentum $q_2 = 2q_1$ (Figure S6, Supporting Information). This interesting phenomenon has also been observed previously in the near-field images of plasmon polariton in graphene sandwiched between the hBN flakes, where the even–odd peak oscillations could be ascribed to interference between the polariton and evanescent waves reflected at the sample edge.^[42]

Another observation one should pay attention to is that the fringe spacings along the e1 and e2 directions are the same, while those along the e3 direction (perpendicular to the short edge) exhibit smaller values (Figure 2b,c). We owe such a discrepancy to two origins. The first one is the geometry of the 2D flake used in our measurement. As shown in Figure 2b, in the region enclosed by the three edges the PhPs waves reflected from the long edges can interact with that reflected by the short edge. Such an interaction will disturb the intrinsic standing-waves formed by interference between the tip-launched PhPs and that reflected by the short edge. As a result, the fringe spacings perpendicular to the short edge can be different from those perpendicular to the long edges, which are due to the interference between the tip-launched and edge-reflected waves exclusively.

The second origin is that the propagation of the PhPs in the $\alpha\text{-MoO}_3$ 2D flake is orientation dependent. We suggest that such dependence might stem from the anisotropic crystal structure of the $\alpha\text{-MoO}_3$. As shown in Figure 1a, due to the nonequivalent Mo–O bonds along the two in-plane principal crystalline axes, i.e., the [001] and [100] directions, the phonon

vibrations along these two axes exhibit different modes.^[32] These in-plane phonon modes will give rise to distinct dielectric responses along these two in-plane principal directions. From this point of view, to precisely calculate the PhPs characteristics of the $\alpha\text{-MoO}_3$, one needs to employ an anisotropic dielectric function, i.e., a dielectric tensor, rather than the isotropic scalar. In such circumstance, the anisotropic dielectric functions of the $\alpha\text{-MoO}_3$ will result in the anisotropic PhPs dispersion along different directions. As a result, the wavevector values of the PhPs vary along different directions within the a – c plane, giving rise to the orientation-dependent fringe spacings observed in our experiments (Figure 2b,c). The anisotropic PhPs in the $\alpha\text{-MoO}_3$ 2D flake is a very interesting topic that deserved further study, which is out of the scope of the current study and will be reported later. Our main purpose here is to demonstrate the PhPs in a semiconductor. Therefore to simplify the analysis, we choose to employ the isotropic dielectric function for calculating the PhPs near-field patterns as well as dispersions. In the specific calculations, the parameters in the dielectric function were adjusted to make the theoretical near-field profile matching with the experimental one along the e2 line indicated in Figure 2b. The same dielectric function was then utilized for the subsequent analyses.

With the isotropic dielectric function, the near-field distributions can be readily simulated by calculating the interference patterns of the PhPs wave using a phenomenological cavity model (Figure 2c and Section S3, Supporting Information),^[41,43] which further corroborates the propagating nature of the PhPs in the 2D $\alpha\text{-MoO}_3$ flake. More insights of the PhPs can be obtained from its dispersion, which can be readily derived and visualized via the 2D false color plot of the imaginary part of the complex reflectivity $\text{Im}r_p(q, \omega)$ (Section S5 and Figure S7, Supporting Information).^[25] As shown in Figure 2e, series of bands with strong reflection appear in the spectral range of 810–1010 cm^{-1} , indicating that multimode PhPs waves can be guided by the $\alpha\text{-MoO}_3$ flake. The dispersion of the PhPs in the upper (Type I) Reststrahlen band is flatter than that in the lower one (Type II), suggesting a wider tuning range for the PhPs wavelengths of the former upon varying the incidence frequencies. More interestingly, the slope $(\partial\omega/\partial k)$ in the Type I Reststrahlen band is negative, while that in the Type II band is positive. Similar Type I hyperbolic PhPs bands with negative slopes have previously been reported in the hBN slabs.^[24,44,45] With time-domain interferometry and near-field data processing, it was demonstrated that the negative dispersion could give rise to hyperbolic PhPs propagating with negative phase velocity, rather than the negative group velocity.^[45] We therefore reason that the negative slope of the dispersion in the Type I band observed in our current study suggests a negative phase velocity to occur. To experimentally verify this issue one needs to perform time-resolved nanoimaging on the PhPs to measure the sign of the phase velocity. However, at present such a technique is beyond the capability of our s-SNOM microscope. The calculated dispersions can be further verified by the s-SNOM imagings upon illuminations with different frequencies (Figure S8, Supporting Information). The extracted dispersions from the experimental measurements along the e2 line are overlaid on the false color map, which agree very well with the lowest-order branch of both of the upper and lower bands

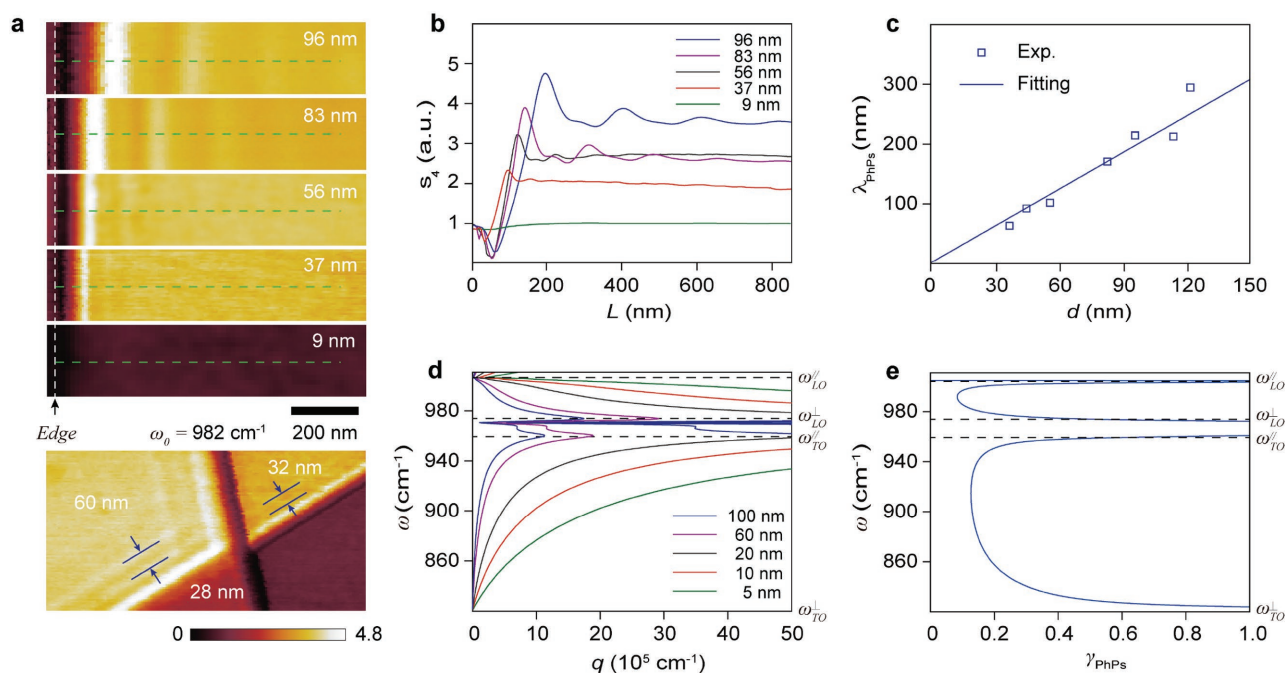


Figure 3. Thickness-dependent PhPs in the α -MoO₃ flakes. a) s-SNOM images of the α -MoO₃ flakes with different thicknesses. The thicknesses of the samples were controlled during the growth processes (upper) or by stacking together two thin flakes (lower). The illumination frequency was 982 cm⁻¹. b) Line profiles of the scattering amplitudes along the green dash lines indicated in (a). c) PhPs wavelengths in the α -MoO₃ flakes with different thicknesses. Squares are obtained from the experimental measurements and solid line is the theoretical fitting. d) Calculated dispersion relation of the PhPs (mode $l = 0$) in the α -MoO₃ with different thicknesses. e) Calculated loss factor γ of the PhPs.

($l = 0$). The strong electromagnetic confinement, $\beta = \lambda_0/\lambda_{\text{PhPs}}$, of the PhPs in the α -MoO₃ can be clearly revealed from the dispersion of the Type II band, with a value as high as 87 at 953 cm⁻¹.

Due to the long-range vdW interactions between different layers, the electronic and photonic properties of the vdW materials are strongly dependent on their thicknesses.^[21,22] This merit allows the PhPs to be tailored by controlling the sample thicknesses. The s-SNOM images and corresponding line profiles of the α -MoO₃ flakes with different thicknesses are displayed in Figure 3a,b, which show similar spatial evolutions of the near-field intensities under illumination of 982 cm⁻¹. In addition, the extracted PhPs wavelengths monotonically decrease upon reducing the flake thicknesses (Figure 3c). These results clearly demonstrate that the PhPs waves can persist in the α -MoO₃ down to tens of nanometers thick, whereby the electromagnetic confinements can be tailored by precisely controlling the thicknesses of the 2D α -MoO₃ flake. One should note that for the flake thinner than 10 nm, the PhPs interference patterns are very weak in comparison with those of the thicker ones. This can be ascribed to two aspects. On the one hand, the phonons from the SiO₂ substrate can scatter and smear out the PhPs waves for α -MoO₃ flakes with small thicknesses. On the other hand, as the thickness of the α -MoO₃ flakes is reduced, the lattice vibrations become weak and therefore the PhPs intensity is lower.

The PhPs can be tailored not only by controlling the thicknesses of the α -MoO₃ via manipulating the growth conditions but also by stacking individual thin flakes into multilayer structures. For example, in a stacked α -MoO₃ double-layer with a 28 nm thick flake on top of a 32 nm thick one, the PhPs is

distinctly modified from the two individual ones (Figure 3a, lower panel). Such a property can open new avenues for studying and tuning of the PhPs by stacking vdW crystals with different PhPs characteristics.

The thickness dependence of the PhPs can be manifested from their dispersion relationships. Instead of calculating the 2D plots of the $\text{Im}r_p(q, \omega)$, we referred to a simplified yet analytical dispersion model, whereby more physical insights of the PhPs can be revealed. Specifically, under the approximation of $\lambda_{\text{PhPs}} \ll \lambda_0$, the dispersion can be expressed as^[4,25]

$$q(\omega) + iq'(\omega) = \frac{2}{d \tan \theta} (l\pi + \Delta\varphi) \quad (1)$$

where l , d , and θ respectively delegate the PhPs mode order ($l = 0$ in this study), flake thickness, and the angle between the PhPs propagation direction and the b -axis. The factor $\Delta\varphi = \arctan(\varepsilon_0/(\varepsilon_{\perp} \tan \theta)) + \arctan(\varepsilon_{\text{sub}}/(\varepsilon_{\perp} \tan \theta))$ is the phase shift associated with total internal reflection of the PhPs waves at the two interfaces of the α -MoO₃ flake. The parameters ε_0 , ε_{sub} , and $\varepsilon_{\perp}$ are the permittivities of air, substrate, and the α -MoO₃ (for direction perpendicular to the b -axis), respectively. As shown in Figure 3d, the α -MoO₃ with different thicknesses all exhibit similar dispersions with Types I and II Reststrahlen bands, which are similar to the $l = 0$ mode shown in Figure 2e. Additionally, for a fixed illumination frequency, the Equation (1) clearly indicates that the PhPs wavelength (proportional to $1/q$) scales linearly with the flake thickness, which agrees well with the experimental measurements (Figure 3c). Such a behavior corroborates that strong electromagnetic confinements can be

achieved with thin α -MoO₃ flakes. For example, the β can be up to ≈ 120 for a 10 nm thick α -MoO₃, which has been verified experimentally with an excitation of 996 cm⁻¹ (Figure S9, Supporting Information). This value is comparable and even better than the thin hBN slabs can offer, where a maximum confinement of ≈ 50 is expected for monolayer sample.^[25] From the analytical dispersion model one can also evaluate the polariton damping rates, which is defined as $\gamma = |q'/q|$. The calculation shows that considerable low damping rate ($\gamma \approx 0.08$) can be achieved for Type I PhPs, while for the Type II ones, their losses are relatively larger (Figure 3e).

Active control over the polaritons is very important for their applications in switchable nanophotonic devices. Usually this is challenging for the PhPs because the lattice vibrations of the polar crystals are inert to external stimulus. A very recent study has shown that reversible tailoring of the PhPs in the SiO₂ can be realized by switching the dielectric environment via tuning the structure of a phase-change material coated onto the SiO₂ surface.^[46] To preserve the pristine characteristics of the PhPs, tuning strategies without introducing extraneous coating are preferred.

For the vdW α -MoO₃, the relatively large interlayer separation makes it ideal host for extrinsic metal ions. The lattice structure of the MoO₃ can be distorted through metal ion intercalation. Furthermore, more charge carriers will also be injected into the crystalline matrix. Both of these two mechanisms can modify the phonon structures of the MoO₃ and thereafter provide opportunity for tuning of its PhPs. To this end, the α -MoO₃ flake was subjected to Sn ion intercalation via chemical approaches. Upon the intercalation, two regions of different colors can be observed in a typical α -MoO₃ flake. They are separated by a clear boundary of $\approx 47^\circ$ with respect to the [001] direction (Figure S10, inset, Supporting Information). These two regions exhibit distinctly different Raman spectra, indicating

that the lattice vibrations of the intercalated region were altered (Figure S10, Supporting Information). In contrast, the intercalated ions will not deteriorate the surface morphology of the sample (Figure 4a), which guarantee the subsequent optical characterizations. The semiconducting nature of the flake will not be deteriorated. Upon the Sn-intercalation, a gap state centering at ≈ 1 eV appears (Figure S4, Supporting Information), which can contribute more electrons to the flake. In addition, due to these doped electrons, the conductance of the sample is strongly improved (Figure S5, Supporting Information).

To demonstrate the switching of the PhPs by the metal intercalation, we imaged and compared the near-field optical distributions of the pristine and intercalated regions of the MoO₃ flake. As shown in Figure 4b, the near-field intensity becomes much weaker upon intercalation. The bright fringes can be hardly found in the intercalated region, while in the pristine region, strong bright fringes can be observed not only at the sample edges but also at the boundary between the pristine and colored regions. Because there are no distinct morphology changes during the intercalation, we can ascribe these boundary fringes to the interferences of the tip-launched polariton waves with those reflected by the boundary. The near-field characteristics can be more clearly seen by extracting the profiles from the SNOM images (Figure 4c). The PhPs waves propagating along the [100] direction (profile associated with e1) in the pristine region show long propagation length, which is consistent with the results shown in Figure 2b,c. However, the PhPs waves in the intercalated region exhibit much shorter propagation lengths (profiles along e2). Only one interference maximum can be found, indicating that the damping of the PhPs is higher than that in the pristine region. On the other hand, the PhPs dispersions are also modified. The wavelengths of the PhPs in the intercalated α -MoO₃ are a little shorter (209 nm) than those of the pristine one (212 nm). Moreover,

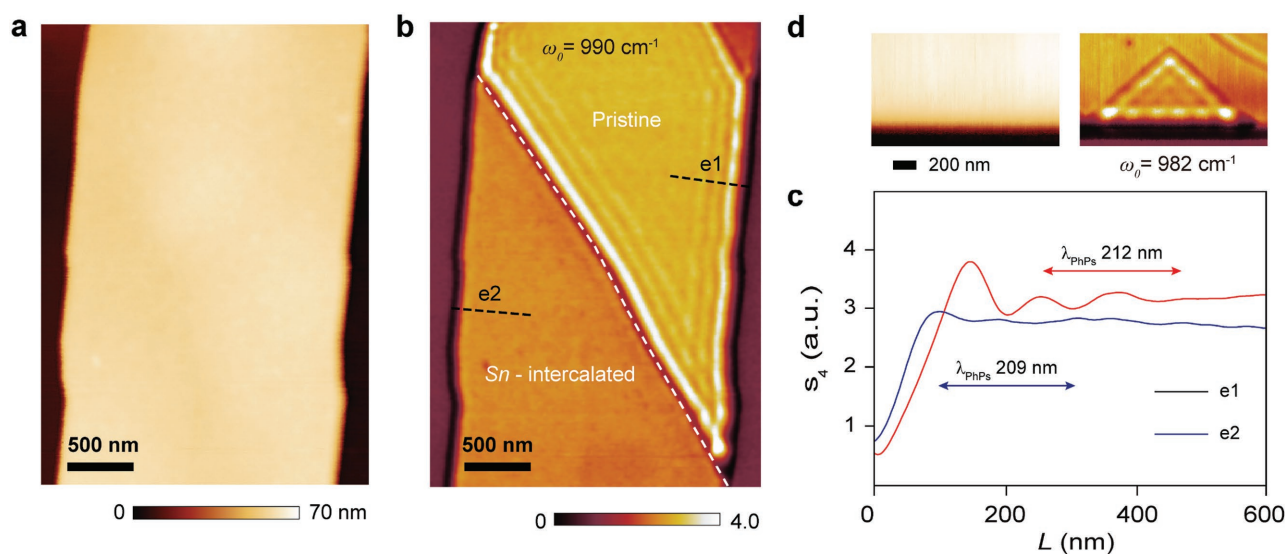


Figure 4. Spatial control on the PhPs upon metal ion intercalations. a) Atomic force microscopy (AFM) image of a typical Sn-intercalated α -MoO₃ 2D flake. The thickness of the flake is 56 nm. b) s-SNOM image of the Sn-intercalated α -MoO₃ flake corresponded to (a). The incidence frequency was 990 cm⁻¹. The boundary between the pristine and intercalated regions was indicated by the white dashed line. c) Near-field profiles extracted along the e1 and e2 dashed lines shown in (b). d) Interference pattern of the PhPs in an MoO₃ triangular cavity formed by the metal ion intercalation. Left: AFM image showing no morphological features. Right: s-SNOM image with strong interference patterns inside the triangular cavity. The incidence frequency was 982 cm⁻¹.

with increased illumination frequencies, the near-field intensity and fringe spacings in the intercalated region were respectively enhanced (Figure S11, Supporting Information). In particular, the PhPs can even exist above 1004 cm^{-1} , which is out of the upper “Reststrahlen band” of the pristine $\alpha\text{-MoO}_3$. These results clearly reveal the capability of metal ion intercalation on tuning the intensities and wavelengths of the MoO_3 PhPs.

The intercalated metal ions can affect the PhPs from two aspects. First, the Sn ions can lead to expansion of the Mo–O1 bond and distortion of the MoO_3 lattice, which can therefore modify the phonon frequencies associated with the PhPs. As a result, the dispersion of the PhPs will be modulated accordingly. The discontinuity of the crystalline structure across the two regions can lead to reflection of the PhPs waves and therefore produce the fringes observed near the boundary (Figure 4b). Second, the Sn ions can also act as scattering centers for the PhPs waves, giving rise to stronger damping rates in the intercalated region. To quantitatively compare the damping rates of the pristine and intercalated MoO_3 , we employed the ratio R between the first maximum of their interference fringes (S_m) and near-field amplitudes (S_{in}) in the inner part of the flake.^[47] For the PhPs in the pristine region, $R \approx 1.19$. In contrast, the R decreases to ≈ 1.04 in the intercalated region, indicating a higher damping rate of the PhPs there. On the other hand, it is possible that the strong doping of the MoO_3 can lead to plasmon resonances, which could damp the PhPs by plasmon–phonon coupling. According to previous studies, the doped MoO_3 with a carrier density as high as 10^{21} cm^{-3} can generate plasmons in the visible and infrared regions.^[35,37] Although it is difficult to precisely determine the carrier density in the intercalated region, we can still get some preliminary insights on the plasmons in it. We measured the near-field distributions of the pristine and intercalated regions using 1550 nm excitation (Figure S12, Supporting Information). Upon the Sn-intercalation, the near-field intensity of the MoO_3 was significantly enhanced. We owe such an enhancement to the excitation of the plasmons, which can induce stronger polarization and thereafter the light scattering intensity. This result suggests that the operation wavelengths of the plasmons in the intercalated MoO_3 should locate in the near-infrared region. In contrast, the excitation wavelengths of the PhPs are in the mid-infrared regions, which are far away from that of the plasmons. In view of this, the coupling between the plasmons and PhPs should be very small due to such a discrepancy in their respective operation wavelength. Therefore we believe that the damping of the PhPs in the intercalated region should be governed by scattering from the Sn ions but not the plasmon–phonon coupling.

The spatial control over the PhPs can be further manifested by investigating the near-field distribution of a “cavity structure,” where a specific pristine region was enclosed by the metal-intercalated ones. The PhPs waves will experience multiple reflections at the cavity boundaries. The interferences between the reflected waves and tip-launched one can produce standing-wave patterns with bright and dark spots, which correspond to the constructive and destructive superposition of the polariton waves.^[41,48]

The β and γ of the PhPs in the $\alpha\text{-MoO}_3$ are comparable to the state-of-the-art 2D vdW materials with polaritonic

properties.^[6,7] In particular, the γ is among the lowest values in polar materials with hyperbolicity that is phonon in origin.^[7] These characteristics can significantly benefit the light–matter interactions at the nanometer scale. The large β is associated with the in- and out-of-plane permittivities of the $\alpha\text{-MoO}_3$, which lead to a small propagating angle θ for the PhPs waves within the flake and therefore a short PhPs wavelength. The small γ can be ascribed to two mechanisms. First, the pristine MoO_3 samples used in our study were single crystalline of very high quality.^[49] There are few defects or impurities that can scatter the PhPs waves. Second, the mass differences between the Mo and oxygen atoms are relatively large, which can induce a large frequency gap between the optical and acoustic phonons. Such a gap will greatly suppress the intrinsic phonon–phonon scattering in the MoO_3 , which therefore give rise to the low damping rate of the PhPs waves.

To conclude, we have successfully revealed the mid-infrared PhPs in the semiconducting vdW $\alpha\text{-MoO}_3$ flakes with the help of nanoimaging technique. The strong longitudinal and transverse phonon resonances in the $\alpha\text{-MoO}_3$ can give rise to two Reststrahlen bands in the frequency range of $818\text{--}1010\text{ cm}^{-1}$, where low-loss hyperbolic PhPs with strong electromagnetic confinements can be sustained. The electromagnetic confinements can reach as high as $\lambda_0/120$, which is strongly dependent on the thicknesses of the $\alpha\text{-MoO}_3$ flakes. We further show that by taking advantage of the crystalline structure of the semiconducting $\alpha\text{-MoO}_3$, the PhPs characteristics can be switched off by the metal-ion-intercalation approach. We believe that these results have provided a new natural platform for studying the hyperbolic PhPs, which constitutes potential candidate for future optoelectronic devices operating in the mid-infrared regime.

Experimental Section

Growth of the $\alpha\text{-MoO}_3$ 2D Flakes: The $\alpha\text{-MoO}_3$ 2D flakes were synthesized by thermal physical deposition method.^[49] Briefly, an alumina crucible with MoO_3 powder (0.1 g) as source was placed at the center of a quartz tube. The SiO_2 substrate was cleaned and placed at the low temperature region of $580\text{ }^\circ\text{C}$. The separation between the source and substrate was $13.0\text{--}14.5\text{ cm}$. The source was heated up to $780\text{ }^\circ\text{C}$ in 70 min and then kept at that temperature for another 120 min . During the thermal treatment the MoO_3 powder was sublimated and recrystallized onto the SiO_2 substrate. Subsequently the quartz tube was cooled down naturally to room temperature, whereby numerous $\alpha\text{-MoO}_3$ 2D flakes with different thicknesses were found on the SiO_2 substrate.

Intercalation of Sn Ions into the $\alpha\text{-MoO}_3$ 2D Flakes: Metal ion intercalation was performed under a microscope integrated with a hotplate.^[30] Specifically, the SiO_2 substrate with the 2D $\alpha\text{-MoO}_3$ flakes was put into a quartz groove that was kept onto the hotplate. Afterward, SnCl_2 aqueous solution ($10 \times 10^{-3}\text{ M}$) was mixed with tartaric acid ($100 \times 10^{-3}\text{ M}$) and then dropped onto the MoO_3 sample. A cover glass was placed onto the groove to form a liquid layer of $\approx 1\text{ mm}$ thick. The hotplate was subsequently heated up to $65\text{ }^\circ\text{C}$ to allow the diffusion of the Sn ions into the MoO_3 . The intercalation process was monitored in situ from the optical microscope. Once the metal intercalation was initiated, vivid color changes from both sides of a specific MoO_3 flake along the $[001]$ direction can be readily observed from the microscope. The sample was washed with deionized water and dried in air to stop the intercalation.

Characterizations: The Raman spectra of the $\alpha\text{-MoO}_3$ flakes were collected using a Renishaw inVia Reflex system with a microscope

(Leica). The excitation laser (532 nm) was focused onto the samples with a diameter of $\approx 1 \mu\text{m}$ through a $50\times$ objective (numerical aperture 0.8). The back-scattered Raman signals were collected by the same objective and transferred to a spectrometer with grating of 1800 lines mm^{-1} .

The diffuse reflectance spectra were measured using a Shimadzu UV 2550 UV/visible/near-infrared spectrophotometer equipped with an integrating sphere. The as-grown MoO_3 flakes were dissolved in isopropanol and then subjected to vacuum filtration, whereby a compact solid film was formed on the filter membrane. The solid thin film was then peeled off and cut into $1\times 1 \text{ cm}^2$ for the reflectance measurements. A BaSiO_4 flake was used as reference. The XPS characterizations on the pristine and metal ion-intercalated $\alpha\text{-MoO}_3$ flakes were performed on an ESCALAB 250Xi (Thermo-VG) X-ray photoelectron spectrometer.

The s-SNOM nanoimaging was conducted using a scattering-type near-field optical microscope (NeaSNOM, Neaspec GmbH). To image the PhPs in real-space, a mid-infrared laser (Access Laser) with tunable wavelengths from 9.20 to 10.99 μm ($910\text{--}1087 \text{ cm}^{-1}$) was focused onto the sample with a metal-coated AFM tip (Arrow-IrPt, Nanoworld). During the measurements, the tip was vibrated vertically with a frequency around 280 kHz. The back-scattered light from the tip was demodulated and detected at a fourth harmonic of the tip vibration frequency.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

hyperbolicity, mid-infrared, phonon polaritons, transition metal oxides, vdW materials

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- [1] K. Huang, *Nature* **1951**, 167, 79.
- [2] M. Born, K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford University Press, Oxford **1954**.
- [3] L. Novotny, B. Hecht, *Principles of Nano-Optics*, Cambridge University Press, Cambridge, UK **2012**.
- [4] J. D. Caldwell, O. J. Glembocki, Y. Francescato, N. Sharac, V. Giannini, F. J. Bezares, J. P. Long, J. C. Owrutsky, I. Vurgaftman,

- J. G. Tischler, V. D. Wheeler, N. D. Bassim, L. M. Shirey, R. Kasica, S. A. Maier, *Nano Lett.* **2013**, 13, 3690.
- [5] T. Wang, P. Li, B. Hauer, D. N. Chigrin, T. Taubner, *Nano Lett.* **2013**, 13, 5051.
- [6] D. N. Basov, M. M. Fogler, F. J. García de Abajo, *Science* **2016**, 354, aag1992.
- [7] T. Low, A. Chaves, J. D. Caldwell, A. Kumar, N. X. Fang, P. Avouris, T. F. Heinz, F. Guinea, L. Martin-Moreno, F. Koppens, *Nat. Mater.* **2016**, 16, 182.
- [8] B. Neuner III, D. Korobkin, C. Fietz, D. Carole, G. Ferro, G. Shvets, *J. Phys. Chem. C* **2010**, 114, 7489.
- [9] J. J. Greffet, R. Carminati, K. Joulain, J. P. Mulet, S. Mainguy, Y. Chen, *Nature* **2002**, 416, 61.
- [10] S. Shen, A. Narayanaswamy, G. Chen, *Nano Lett.* **2009**, 9, 2909.
- [11] T. Taubner, D. Korobkin, Y. Urzhumov, G. Shvets, R. Hillenbrand, *Science* **2006**, 313, 1595.
- [12] P. Li, M. Lewin, A. V. Kretinin, J. D. Caldwell, K. S. Novoselov, T. Taniguchi, K. Watanabe, F. Gaussmann, T. Taubner, *Nat. Commun.* **2015**, 6, 7507.
- [13] A. Boltasseva, H. A. Atwater, *Science* **2011**, 331, 290.
- [14] R. Hillenbrand, T. Taubner, F. Keilmann, *Nature* **2002**, 418, 159.
- [15] D. Z. A. Chen, G. Chen, *Appl. Phys. Lett.* **2007**, 91, 121906.
- [16] T. Dekorsy, V. A. Yakovlev, W. Seidel, M. Helm, F. Keilmann, *Phys. Rev. Lett.* **2003**, 90, 055508.
- [17] F. Ganikhanov, F. Vallee, *Phys. Rev. B* **1997**, 55, 15614.
- [18] P. Halevi, *Surf. Sci.* **1978**, 76, 64.
- [19] R. Geick, C. H. Perry, G. Rupprecht, *Phys. Rev.* **1966**, 146, 543.
- [20] K. S. Novoselov, V. I. Fal, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, 490, 192.
- [21] G. Fiori, F. Bonaccorso, G. Iannaccone, T. Palacios, D. Neumaier, A. Seabaugh, S. K. Banerjee, L. Colombo, *Nat. Nanotechnol.* **2014**, 9, 768.
- [22] F. Xia, H. Wang, D. Xiao, M. Dubey, A. Ramasubramaniam, *Nat. Photonics* **2014**, 8, 899.
- [23] E. E. Narimanov, A. V. Kildishev, *Nat. Photonics* **2015**, 9, 214.
- [24] 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, *Nat. Commun.* **2014**, 5, 5221.
- [25] 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. Dominguez, A. H. Castro Neto, A. Zettl, F. Keilmann, P. Jarillo-Herrero, M. M. Fogler, D. N. Basov, *Science* **2014**, 343, 1125.
- [26] M. B. Rahmani, S. H. Keshmiri, J. Yu, A. Z. Sadek, L. Al-Mashat, A. Moafi, K. Latham, Y. X. Li, W. Wlodarski, K. Kalantar-Zadeh, *Sens. Actuators, B* **2010**, 145, 13.
- [27] S. Balendhran, S. Walia, M. Alsaif, E. P. Nguyen, J. Z. Ou, S. Zhuikov, S. Sriram, M. Bhaskaran, K. Kalantar-zadeh, *ACS Nano* **2013**, 7, 9753.
- [28] S. Balendhran, J. Deng, J. Z. Ou, S. Walia, J. Scott, J. Tang, K. L. Wang, M. R. Field, S. Russo, S. Zhuikov, M. S. Strano, N. Medhekar, S. Sriram, M. Bhaskaran, K. Kalantar-Zadeh, *Adv. Mater.* **2013**, 25, 109.
- [29] P. R. Huang, Y. He, C. Cao, Z. H. Lu, *Sci. Rep.* **2014**, 4, 7131.
- [30] M. Wang, K. J. Koski, *ACS Nano* **2015**, 9, 3226.
- [31] W. G. Xie, M. Z. Su, Z. B. Zheng, Y. Wang, L. Gong, F. Y. Xie, W. H. Zhang, Z. Luo, J. Y. Luo, P. Y. Liu, N. S. Xu, S. Z. Deng, H. J. Chen, J. Chen, *ACS Nano* **2015**, 10, 1662.
- [32] K. Eda, *J. Solid State Chem.* **1991**, 95, 64.
- [33] M. A. Py, P. E. Schmid, J. T. Vallin, *Il Nuovo Cimento B* **1977**, 38, 271.
- [34] J. D. Caldwell, L. Lindsay, V. Giannini, I. Vurgaftman, T. L. Reinecke, S. A. Maier, O. J. Glembocki, *Nanophotonics* **2015**, 4, 44.
- [35] M. M. Alsaif, K. Latham, M. R. Field, D. D. Yao, N. V. Medehkar, G. A. Beane, R. B. Kaner, S. P. Russo, J. Z. Ou, K. Kalantar-Zadeh, *Adv. Mater.* **2014**, 26, 3931.

- [36] Q. Huang, S. Hu, J. Zhuang, X. Wang, *Chem. Eur. J.* **2012**, *18*, 15283.
- [37] H. F. Cheng, X. F. Qian, Y. Kuwahara, K. Mori, H. Yamashita, *Adv. Mater.* **2015**, *27*, 4616.
- [38] M. T. Greiner, L. Chai, M. G. Helander, W.-M. Tang, Z.-H. Lu, *Adv. Funct. Mater.* **2012**, *22*, 4557.
- [39] Z. Fei, A. S. Rodin, G. O. Andreev, W. Bao, A. S. McLeod, M. Wagner, L. Zhang, Z. Zhao, M. Thiemens, G. Dominguez, M. M. Fogler, A. H. Castro Neto, C. N. Lau, F. Keilmann, D. N. Basov, *Nature* **2012**, *487*, 82.
- [40] J. Chen, M. Badioli, P. Alonso-González, S. Thongrattanasiri, F. Huth, J. Osmond, M. Spasenovi, A. Centeno, A. Pesquera, P. Godignon, A. Z. Elorza, N. Camara, F. J. García de Abajo, R. Hillenbrand, F. H. L. Koppens, *Nature* **2012**, *487*, 77.
- [41] Z. B. Zheng, J. T. Li, T. Ma, H. L. Fang, W. C. Ren, J. Chen, J. C. She, Y. Zhang, F. Liu, H. J. Chen, S. Z. Deng, N. S. Xu, *Light: Sci. Appl.* **2017**, *6*, e17057.
- [42] J.-H. Kang, S. Wang, Z. Shi, W. Zhao, E. Yablonovitch, F. Wang, *Nano Lett.* **2017**, *17*, 1768.
- [43] J. A. Gerber, S. Berweger, B. T. O'Callahan, M. B. Raschke, *Phys. Rev. Lett.* **2014**, *113*, 055502.
- [44] 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.
- [45] E. Yoxall, M. Schnell, A. Y. Nikitin, O. Txoperena, A. Woessner, M. B. Lundberg, F. Casanova, L. E. Hueso, F. H. L. Koppens, R. Hillenbrand, *Nat. Photonics* **2015**, *9*, 674.
- [46] P. Li, X. Yang, T. W. W. Mass, J. Hanss, M. Lewin, A. K. U. Michel, M. Wuttig, T. Taubner, *Nat. Mater.* **2016**, *15*, 870.
- [47] A. M. Dubrovkin, J. Tao, X. C. Yu, N. I. Zheludev, Q. Wang, *Sci. Rep.* **2015**, *5*, 09837.
- [48] A. Y. Nikitin, P. Alonso-González, S. Velez, S. Mastel, A. Centeno, A. Pesquera, A. F. Casanova, L. E. Hueso, F. H. L. Koppens, R. Hillenbrand, *Nat. Photonics* **2016**, *10*, 239.
- [49] Y. Wang, X. Du, J. Wang, M. Su, X. Wan, H. Meng, W. Xie, J. Xu, P. Liu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 5543.