Tunable plasmonic topological transitions in WTe$_2$ van der Waals films

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Naturally existing in-plane hyperbolic polaritons and the associated topological transitions, which avoid the nano-structuring to achieve hyperbolicity, can outperform their counterparts in artificial metasurfaces. Such polaritons based on plasmons are rare and only experimentally revealed recently in WTe$_2$ van der Waals thin films, though plasmons form the mainstream in nanophotonics. Different from phonon polaritons, hyperbolic plasmons originate from the interplay of free carrier Drude response and interband transitions, which promise good intrinsic tunability. However, tunable in-plane hyperbolic plasmon and its topological transition to elliptical regime in a natural material have not been realized. Here we demonstrate the tuning of the plasmonic topological transition through Mo doping and temperature. The topological transition is tuned in a wide range, with frequencies from 429 cm$^{-1}$ (23 microns) for pure WTe$_2$ to 270 cm$^{-1}$ (37 microns) at the 50% Mo-doping level at 10 K. Moreover, temperature-induced blueshift of the topological transition is also revealed, enabling active and reversible tuning. Surprisingly, the localized plasmon in skew ribbons shows unusual polarization dependence, accurately manifesting its topology, which renders a reliable means to track the topology with far-field techniques. Our results open an avenue for reconfigurable photonic devices capable of plasmon polariton steering, such as canaling, focusing and routing, and pave a way for low-symmetry plasmonic nanophotonics based on anisotropic natural materials.
Introduction

The recently discovered natural in-plane hyperbolic polaritons, such as phonon polaritons in MoO$_3$\textsuperscript{1,2} and V$_2$O$_3$\textsuperscript{3} and plasmon polaritons in WTe$_2$\textsuperscript{4}, open up a plethora of opportunities in reconfigurable on-chip integrated photonics\textsuperscript{5,6}. These findings have fueled an emerging research field termed low-symmetry nanophotonics\textsuperscript{7-15}. The tunability of the hyperbolic frequency range and the topological transition to the elliptical topology is highly desirable to fulfill the potential. However, phonon polaritons, which are based on polar lattice vibrations, intrinsically show rather fixed Reststrahlen bands and material-specific polariton dispersions. This certainly limits their tunability, although efforts have been devoted to extrinsic schemes, such as interfacing with suitable substrate\textsuperscript{16-19}, stacking with highly tunable graphene\textsuperscript{20-22}, and twisting bilayer structures\textsuperscript{23-26}. Progress has also been achieved through more disruptive measures, such as intercalation\textsuperscript{3,27}, but the phonon bands only shift a small amount\textsuperscript{3} (around 30 cm\textsuperscript{-1}), and hyperbolic polariton was not observed after intercalation. On the other hand, plasmon polaritons are easier to be tamed intrinsically, particularly in the 2-dimensional form\textsuperscript{28,29}, which has been exemplified by graphene plasmons\textsuperscript{30}. More crucially, with inherently strong coupling to light and the leniency to the electrical manipulation\textsuperscript{31}, plasmons have become the mainstream of modern nanophotonics, with other forms of polaritons as complements\textsuperscript{32}. Naturally existing in-plane hyperbolic plasmons are recently demonstrated only in WTe$_2$ thin films\textsuperscript{4} in the frequency range of 429 cm\textsuperscript{-1} to 632 cm\textsuperscript{-1}, with elliptical topology below 429 cm\textsuperscript{-1}. With limited choice of such materials, it’s even more imperative to tune the topological transition energy to suit various applications.

The plasmon dispersion in a natural hyperbolic plasmonic surface is typically governed
by the anisotropy of both free carrier response and bound interband transitions\textsuperscript{4,33}, with the former for inductive and the latter for capacitive optical responses. Any variation of electronic properties, such as carrier density, effective mass anisotropy, frequency and strength of interband transition resonance, will give rise to a modulation of the hyperbolicity\textsuperscript{33,34}. Though as promising as it sounds, however, the experimental modulation has not been realized up to date. Here, for the first time, we report the intrinsic tuning of the in-plane plasmonic topological transition in a broad frequency range in a natural material through chemical doping and temperature. We reveal such tunability in Mo-doped WTe\textsubscript{2} (Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2}) thin films, a recently discovered layered Type-II Weyl semimetal with composition-dependent band structure\textsuperscript{35,36} and electric transport\textsuperscript{37}. Meanwhile, an innovative technique to track the topology based on the far-field polarization dependence of the localized plasmon in skew ribbons has been developed. Our study not only extends the hyperbolic plasmon regime in natural materials, but also reveals the peculiar and informative polarization property of localized plasmons in microstructures made from an anisotropic material.

**Results**

**Sample fabrication and polarized infrared spectra.** We grew Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} crystals (\(x \leq 0.5\)) in semi-metallic orthorhombic \(T_d\)-phase using a chemical vapor transport technique with iodine as the transport agent (Methods). The zigzag W-W chains are along \(a\)-axis, with W atoms partially substituted by Mo after Mo-doping\textsuperscript{38}, as displayed in Fig. 1a. Figure 1b shows the schematic illustration of a skew ribbon array patterned from an exfoliated single crystal film of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} with a skew angle of \(\theta = -33^\circ\) with respect to \(a\)-axis (Methods), and illuminated by the normal incident light with polarization angle \(\phi\). It should be noted that all
of the studied skew ribbons in this paper have the same -33° skew angle. Localized plasmons can be excited in such ribbon arrays with far-field incident light. Figures 1c and d display two typical extinction spectra (characterized by $1 - T/T_0$, where $T$ and $T_0$ are the transmission of light through the sample and the bare substrate, respectively) of such skew ribbon arrays with composition ratio $x = 0.278$ but different ribbon widths $L$ (corresponding to the effective plasmon wavevector of $\pi/L$). The light polarization ($\phi = -14.8^\circ$, 24.5°) was chosen to most efficiently excite the plasmon, with resonance frequencies (219 cm$^{-1}$, 462 cm$^{-1}$) in the elliptic and the hyperbolic regimes respectively (to be discussed below). Besides the plasmon resonance, the spectrum in Fig. 1d exhibits evident Drude response, in sharp contrast to that in Fig. 1c, suggesting that the polarization for maximal plasmon intensity in the hyperbolic regime deviates significantly from the perpendicular direction of ribbons. Such deviation was first reported in self-assembled carbon nanotubes$^{39}$. However, the implication on plasmon topology has not been revealed. Here, we show that such optimal polarization is fully dictated by the ratio of the imaginary parts of the anisotropic conductivities, and in turn can be utilized to determine the plasmon topology.

**Polarization dependence of the plasmon in skew ribbon arrays.** When a skew ribbon array is illuminated, the plasmon resonance is most intense when the polarization of the incident light $E_{\text{ext}}$ is parallel to the polarization current density $J_{\text{polar}}$ ($J_{\text{polar}} = \partial P/\partial t$, with $P$ as the polarization vector), which is associated with the depolarization field $E_{\text{depol}}$ induced by the polarization charge. Note that $E_{\text{depol}}$ is always perpendicular to the ribbon edge due to the translation-invariance of the polarization charge distribution along the edge (Figs. 1e-f), and $J_{\text{polar}}$ is not the conduction current related to the real part of the conductivity, which is
responsible for the energy dissipation in the material. In an isotropic 2D material, the incident light with polarization perpendicular to the ribbon leads to the maximal plasmon resonance, since \( P \) and hence \( J_{polar} \) are parallel to \( E_{depot} \) due to the isotropic polarizability (conductivity) tensor. In ribbons made from an anisotropic film, however, \( P \) and \( J_{polar} \) are not necessarily parallel to \( E_{depot} \). Thus, as shown in Figs. 1e-f, the optimal polarization \( \phi_{max} \) for plasmon excitation deviates from the perpendicular direction of the ribbon, the value of which is determined by the ratio of the imaginary parts of conductivities (\( \sigma_{aa}'' \) and \( \sigma_{bb}'' \)) and the skew angle \( \theta \) (Supplementary Note 1):

\[
\tan \phi_{max}(\omega) = \frac{\sigma_{bb}''(\omega)}{\sigma_{aa}''(\omega)} \tan \theta
\]

where \( \phi_{max} \) can be restricted in the range of -90° to 90°. Therefore, \( \phi_{max} \) has the same sign as \( \theta \) in the elliptic regime since \( \sigma_{aa}'' \sigma_{bb}'' > 0 \) (Fig. 1e), but opposite sign in the hyperbolic regime, for which \( \sigma_{aa}'' \sigma_{bb}'' < 0 \) (Fig. 1f). Particularly, for the plasmon at the topological transition energy (\( \sigma_{bb}'' = 0 \)), the optimal light polarization coincides with \( a \)-axis.

To benchmark this scheme, we firstly use equation (1) to reexamine the plasmonic topology in WTe\(_2\) films, for which a topological transition has been reported at about 429 cm\(^{-1}\) (23 microns in wavelength). Skew ribbon arrays as in Fig. 1b with the same skew angle of \( \theta = -33^\circ \) but different ribbon widths were fabricated from WTe\(_2\) films. The polarization-resolved extinction spectra for two representative samples at 10 K are shown in Figs. 2a-b (Methods). Resonance peaks of plasmons can be observed at frequencies of 308 cm\(^{-1}\) in the elliptic regime (Fig. 2a) and 510 cm\(^{-1}\) in the hyperbolic regime (Fig. 2b), thus expected to have maximal plasmon intensity at polarization angles of different signs, according to equation (1). Note that, in Fig. 2b, spectra with polarization at around -33°
(perpendicular to the ribbon) are nearly flat, indicating almost no plasmon absorption, in striking contrast to ribbons patterned from isotropic films. To see the polarization dependence more clearly, the extinction spectra in Figs. 2a-b are plotted as pseudo color maps in Figs. 2c-d. The maximal plasmon intensity in Fig. 2c can be found below the zero line (red dashed line), while the plasmon in Fig. 2d exhibits strongest absorption at an angle well above zero. The feature below 200 cm\(^{-1}\) comes from the Drude response of free carriers, whose maximum is always along the ribbon direction (\(\phi = 57^\circ\)), a common scenario for both isotropic and anisotropic ribbons (Supplementary Note 2). To extract the plasmon weight, spectra were fitted with the Drude-Lorentz model (Methods, Supplementary Note 3), with the fitted plasmon weight plotted in Figs. 2e-f as a function of the polarization angle. As shown in Fig. 2e (Fig. 2f), the polar angle \(\phi_{\text{max}}\) is -11.7° (40.0°), which has the same (opposite) sign as the skew angle (-33°), consistent with the elliptic (hyperbolic) topology of the plasmon.

More systematically, a series of samples with the same skew angle (\(\theta = -33^\circ\)) and incremental plasmon frequencies from 185 cm\(^{-1}\) to 510 cm\(^{-1}\) were fabricated by changing the ribbon width. The polarization-resolved absorption spectra due to the plasmon are plotted as pseudo color maps for several plasmon frequencies in Fig. 2g (Methods). The angle for maximal plasmon intensity gradually evolves from negative to positive, crossing the zero line (\(a\)-axis) when the plasmon frequency coincides with the elliptic/hyperbolic boundary (429 cm\(^{-1}\), determined by the plasmon dispersion in previous work\(^4\)). The measured frequency-dependent polarization angle for the maximal plasmon intensity (\(\phi_{\text{max}}\)) is displayed in Fig. 3a. The topological transition from the elliptic to the hyperbolic can be directly manifested by the sign change of the angle, which agrees well with the calculations.
by equation (1) (blue solid line) using the conductivities extracted from the plasmon dispersion in previous work\textsuperscript{\textit{a}} (Supplementary Note 4), validating the capability of tracking the topological transition both qualitatively and quantitatively. Note that when the skew angle is fixed, $\phi_{max}$ is solely determined by $\frac{\sigma_{bb}(\omega)}{\sigma_{aa}(\omega)}$ at the plasmon frequency, and will not be affected by the ribbon width or film thickness (assuming an unchanged band structure with sample thickness), enabling it a superior method to determine the topology of the plasmon at individual frequencies.

As a matter of fact, to determine the plasmon topology in far-IR range is a daunting task without the aforementioned polarization-based method. In principle, both near- and far-field techniques can probe the plasmon topology in WTe\textsubscript{2}. However, the near-field scheme is not mature in the far-IR range, especially with samples in the cryogenic conditions, even though it is widely and successfully employed in the mid-IR to image in-plane hyperbolic phonon polaritons\textsuperscript{1-3,8,12-14,16-18,20,21,23-27}. As a consequence, up to now, there is no near-field imaging of hyperbolic plasmons in WTe\textsubscript{2}. As for the far-field technique, previously we determined the WTe\textsubscript{2} plasmon topology through mapping the plasmon dispersion in the whole 2-dimensional momentum space\textsuperscript{4}, which was laborious and required numerous samples (each momentum $q$ needs a ribbon array). Fortunately, now in our far-field method based on the polarization dependence, we can determine the plasmon topology at individual plasmon frequencies, without invoking the whole plasmon dispersion, which is truly advantageous.

**Mo-doping-dependent plasmonic topological transition.** With the convenient toolkit in hand, now we can proceed to investigate the tuning of the plasmon topology. Ribbon arrays with the same configuration as in Fig. 1b were fabricated on Mo-doped WTe\textsubscript{2} films with
various ribbon width, hence exhibit different plasmon frequencies (Supplementary Note 5). The polarization dependence of plasmons was measured and the fitted $\phi_{\text{max}}$ are summarized in Figs. 3b-c for 27.8% and 50% doping levels, respectively. A sign change for $\phi_{\text{max}}$ can be observed in Figs. 3b-c as the plasmon frequency increases, suggesting a topological transition for doped samples as well. A large redshift of the zero-crossing point or the topological transition frequency (indicated by the vertical black dashed line) occurs. It changes from 429 cm$^{-1}$ (23 microns) for WTe$_2$ to about 270 cm$^{-1}$ (37 microns) for Mo$_{0.5}$W$_{0.5}$Te$_2$. This corresponds to 38% redshift in frequency or 1.6 times of increase in wavelength for the topological transition.

To further manifest the doping effect on the topological transition, as an example, we compare the polarization dependence of the plasmon with similar resonance frequency of 345 ± 15 cm$^{-1}$ for different doping levels. As shown in Figs. 3d-f, the polarization angle for the maximal plasmon intensity increases from negative to positive upon doping. This can be seen even more clearly in Figs. 3g-i, which shows that the angle $\phi_{\text{max}}$ increases from $-9.5^\circ$ for WTe$_2$ films to $23.9^\circ$ at 50% Mo-doping, suggesting the transition of the topology from the elliptical to the hyperbolic by Mo-doping. Note that the plasmon linewidth of these samples increases with doping (72 cm$^{-1}$ of WTe$_2$, 112 cm$^{-1}$ at 27.8% doping and 250 cm$^{-1}$ at 50% doping). The increasing linewidth is primarily due to the stronger coupling between plasmons and interband transitions, which have lower energy at larger doping level and hence are closer to the plasmon mode, as shown in Fig. 4g. Such coupling induced broadening is manifested in WTe$_2$ as well$^4$. As shown in Fig. 2g, the plasmon linewidth increases as the frequency approaches that of the interband transition. The linewidth of intrinsic plasmons at lower
frequencies, hence largely free of interband coupling, is more similar for all Mo$_x$W$_{1-x}$Te$_2$ samples (with resonance frequencies of 295.0, 291.7, 214.3 cm$^{-1}$ and quality factors of 3.4, 3.1, 2.1 along a-axis at different doping levels respectively, Supplementary Note 6).

**Hyperbolic regime determined by the optical absorption in Mo$_x$W$_{1-x}$Te$_2$ thin films.** To delve into the physical mechanism of the tunable topological transitions, polarization-resolved extinction spectra of pristine films of Mo$_x$W$_{1-x}$Te$_2$ ($x = 0, 0.278, 0.5$, with thicknesses of 110, 80, 42 nm respectively) were examined. The measured spectra (far- and mid-IR ranges) and their fitting curves (Supplementary Note 7) are plotted in Figs. 4a-c. The corresponding extracted sheet optical conductivity (imaginary part) is displayed in Figs. 4d-f, with the generally expanding hyperbolic regime marked by the shaded area based on their signs. The lower boundary of the hyperbolic regime redshifts upon doping, consistent with the polarization behavior of the plasmons in skew ribbon arrays. In general, the plasmon topology is determined by the optical response of both the intraband (Drude response) and interband transitions of carriers. The transition energy and oscillator strength of the interband transition resonance are determined by the specific band structure and the Fermi level, and the free carrier Drude response depends on the carrier density and effective mass. In our experiment, the extinction spectra in Figs. 4a-c share similar qualitative profiles. The primary difference in the far-IR spectra is quantitative in nature, such as the peak position of the first interband transition resonance, as shown in Fig. 4g. The transition energy decreases from 726 cm$^{-1}$ for WTe$_2$ to about 488 cm$^{-1}$ at 50% doping (Supplementary Note 7), as indicated by blue arrows for the spectra of $b$-axis polarization in Figs. 4a-c, which brings the whole interband transition feature to lower frequencies. This salient doping dependence governs the redshift of the
hyperbolic lower boundary, as the dielectric (capacitive) part of the optical conductivity at long wavelength is primarily attributed to interband transitions. It is also worth noting that the fitted Drude weight (normalized with thickness) along $b$-axis slightly decreases upon Mo-doping (Supplementary Note 7), playing a minor role in the redshift of the topological transition.

Furthermore, by substituting $\text{Im}(\sigma)$ in Figs. 4d-f into equation (1), the calculated frequency dependence of $\phi_{max}$ is plotted as gray dashed lines in Figs. 3a-c, which are consistent with the directly measured angles (brown dots) in skew ribbon arrays. Hyperbolic boundary frequencies derived from the polarization dependence of skew ribbons (red dots), film extinction measurements (black right-pointing triangles) and the plasmon dispersion in Ref. [4] (blue pentagrams) are summarized in Fig. 4h. All these procedures show consistent doping dependence of the lower boundary, substantiating the redshift of the topological transition.

**Temperature-dependent plasmonic topological transition.** As a typical semimetal, the electronic properties of WTe$_2$ exhibit strong temperature dependence$^{4,40}$, enabling an active tuning of plasmonic topological transitions. To fulfill this potential, the polarization-resolved extinction spectra of one WTe$_2$ bare film (with thickness of 35 nm) at different temperature (78 K, 130 K, 155 K, 180 K, 230 K 300 K) was measured. The corresponding spectra (far- and mid-IR ranges) and fitting curves are plotted in Figs. 5a-c. The anisotropy of interband transitions (between 700 and 1100 cm$^{-1}$) along two axes decreases, whereas the Drude weights increase due to more thermal carriers at higher temperature. As a result, the lower boundary of the hyperbolic regime blueshifts from 428 cm$^{-1}$ at 78 K to 553 cm$^{-1}$ at 180K
(inset of Fig. 5d), which is manifested by the extracted sheet optical conductivity. The hyperbolic topology in the far-IR regime vanishes above 230 K. A kink appears in the temperature dependence of the hyperbolic regime at about 130 K, which also exists in the temperature dependence for the plasmon frequency and Drude weight in WTe$_2$\textsuperscript{4}. This is probably attributed to the temperature-induced Lifshitz transition at about 147 ~ 160 K, where the two hole pockets move down in energy with respect to the Fermi surface and finally disappear, resulting in no hole carriers at higher temperatures\textsuperscript{41,42}. Further, the polarization dependence of plasmons of the same devices as in Fig. 3a at corresponding temperature was measured. The polarization angle $\phi_{max}$ was extracted in the same way, which agrees well with the calculation of equation (1) as shown in Fig. 5d, demonstrating the temperature-induced shifts of topological transitions. The details are summarized in Supplementary Note 8. Compared to nearly temperature-independent phonon polaritons, the hyperbolic regime in WTe$_2$ shifts in a wide range with temperature.

Discussion

It should be noted that the lower and higher boundaries of the hyperbolic regime here correspond to the sigma-near-zero points along $b$- and $a$-axis respectively. When a material exhibits near-zero effective permittivity (conductivity), novel physical effects arise, such as field enhancement, tunneling through anomalous waveguides and transmission with small phase variation, which are also known as epsilon-near-zero photonics\textsuperscript{43}. Thus, Mo$_x$W$_{1-x}$Te$_2$ naturally serves as an in-plane tunable anisotropic sigma-near-zero material for functional photonic devices. Particularly, at the lower hyperbolic boundary, the iso-frequency contour comprises two almost straight lines parallel to $b$-axis in momentum space, analogous to the
so-called canalization regime in hyperbolic phonon polaritons (PhPs)\textsuperscript{12,23,25}. The tunability of the lower boundary not only enables us to manipulate the energy flow through doping and temperature, but also expands the intrinsic hyperbolic regime (Figs. 4h and 5d), with the latter hardly realizable for hyperbolic PhPs. Through twisting of two $\alpha$-MoO$_3$ flakes, the topological transition of PhPs has been demonstrated, but the long-sought hyperbolic regime shrinks in that case.

In conclusion, our work demonstrates the inherent tunability of hyperbolic plasmons and the topological transition in vdW surfaces by chemical doping and temperature in a wide range. The tuning mechanism involves both bound states and free carriers, which offers more dimensions for the manipulation of topology. Our experiments take advantage of a peculiar feature in the polarization-resolved extinction spectra of skew ribbons to determine the topology, which can be of great use to other anisotropic 2D materials as well.
Methods

**Mo,W\textsubscript{1-x}Te\textsubscript{2} crystal growth.** Mo,W\textsubscript{1-x}Te\textsubscript{2} single crystals were grown by a chemical vapor transport technique with iodine as the transport agent. Stoichiometric Mo, W and Te mixed powders were loaded into a quartz tube with a small amount of iodine, which was subsequently sealed in vacuum and placed in a two-zone furnace. The hot zone was maintained at 850 °C for two weeks while the cold zone was maintained at 750 °C. The composition of the final crystal was characterized through an energy dispersive spectroscopy with a scanning electron microscope.

**Sample preparation and fabrication.** Single crystal WTe\textsubscript{2} was bought from HQ Graphene. Bare films of Mo,W\textsubscript{1-x}Te\textsubscript{2} (\(x \leq 0.5\)) with thickness about 40-120 nm through the standard exfoliation technique were transferred to polycrystalline diamond substrates. The substrate has no polar phonon absorption and the transmission is about 70% in the far-IR range. The thickness of the sample was determined by a stylus profiler (Bruker DektakXT) in conjunction with the optical contrast. Preferred sample size is 200 by 200 \(\mu\text{m}^2\), with the side length longer than the far-IR wavelength (~100 \(\mu\text{m}\)). Skew ribbon arrays were patterned using electron beam lithography (Zeiss Sigma SEM with Raith Elphy Plus), with the uncertainty in skew angle of less than 0.5 degree. An intermediate skew angle of \(-33^\circ\) was chosen in our study, because a too small angle results in a small \(\phi_{max}\) as shown in equation (1), and a too large one leads to a more dramatic reduction of the maximal plasmon frequency achievable in that wavevector direction. Reactive ion etching (RIE) with SF\textsubscript{6} gas was used to define the ribbons. If necessary, the surroundings of the sample were further etched away using the director writer UPG501 and RIE to ensure IR response only from the targeted
sample.

**Far-IR optical spectroscopy.** For the polarized far-IR extinction spectra, we used a Bruker FTIR spectrometer (Vertex 70v) integrated with a Hyperion 2000 microscope and a cryogen-free silicon bolometer system as the detector. The incident light was focused on Mo$_x$W$_{1-x}$Te$_2$ samples with a 15× IR objective. A THz polarizer was used to control the light polarization. The samples were cooled to 10 K in a helium-flow cryostat (Janis Research ST-300) with vacuum at about $5 \times 10^{-5}$ mbar. Throughout the entire measurements, compressed dry air with dew point below -70 °C was purged to an enclosed space housing the cryostat. This procedure minimized the absorption of IR light by moisture in air and effectively increased the signal/noise ratio. The polarization dependence of plasmons in skew ribbon arrays was studied by rotating the polarizer with a step size of 11° from -90° to 90°. Hence, a total of 16 spectra were collected to extract each $\phi_{\text{max}}$.

**Fitting of IR extinction spectra and plotting pseudo color maps for plasmon spectra.** The extinction spectrum is determined by the sheet optical conductivity $\sigma(\omega)$ as follows:

$$1 - \frac{T}{T_0} = 1 - \frac{1}{|1 + Z_0 \sigma(\omega)/(1 + n_s)|^2}$$  \hspace{1cm} (2)

where $Z_0$ is the vacuum impedance, $\omega$ is the frequency of light, and $n_s$ is the refractive index of the substrate. The conductivity of the sample is expressed by the Drude-Lorentz model, where the Drude model describes free carriers and the Lorentz model accounts for the bound states such as plasmon resonance or interband transitions in our system:

$$\sigma(\omega) = \frac{i}{\pi} \frac{D}{\omega + i\Gamma} + \sum_k \frac{i}{\pi} \frac{\omega S_k}{\omega^2 - \omega_k^2 + i\omega \Gamma_k}$$  \hspace{1cm} (3)

In (3), $D$ and $S_k$ represent the spectrum weights, $\omega_k$ represents the resonance frequency of the plasmon or interband transitions, $\Gamma$ and $\Gamma_k$ are the corresponding FWHMs. The
polarization angle $\phi_{max}$ was extracted by fitting the whole set of 16 polarization spectra with one Drude component and two Lorentz components (plasmon, interband transitions respectively). The spectral weights were fitting parameters and the Drude scattering rate, plasmon frequency and interband transition resonance frequency were kept the same for all spectra. Pseudo color maps in Fig. 2g and Figs. 3d-f were plotted by substituting the fitted conductivities of plasmons into equation (2) in turn. The plasmon weights $S_{\text{plasmon}}$ extracted above were fitted as $\cos^2 \phi$ to obtain $\phi_{max}$. The fitting details of the extinction spectra of Mo$_x$W$_{1-x}$Te$_2$ bare films in Figs. 4a-c are discussed in Supplementary Note 7.
Reference:

1. Ma, W. et al. In-plane anisotropic and ultra-low-loss polaritons in a natural van der Waals crystal. *Nature* **562**, 557-562 (2018).
2. Zheng, Z. et al. A mid-infrared biaxial hyperbolic van der Waals crystal. *Sci. Adv.* **5**, eaav8690 (2019).
3. Taboada-Gutiérrez, J. et al. Broad spectral tuning of ultra-low-loss polaritons in a van der Waals crystal by intercalation. *Nat. Mater.* **19**, 964-968 (2020).
4. Wang, C. et al. Van der Waals thin films of WTe$_2$ for natural hyperbolic plasmonic surfaces. *Nat. Commun.* **11**, 1158 (2020).
5. Zhang, Q. et al. Interface nano-optics with van der Waals polaritons. *Nature* **597**, 187-195 (2021).
6. Hu, G. et al. Phonon Polaritons and Hyperbolic Response in van der Waals Materials. *Adv. Opt. Mater.* **8**, 1901393 (2020).
7. High, A. A. et al. Visible-frequency hyperbolic metasurface. *Nature* **522**, 192-196 (2015).
8. Li, P. et al. Infrared hyperbolic metasurface based on nanostructured van der Waals materials. *Science* **359**, 892-896 (2018).
9. Yang, Y. et al. Hyperbolic spoof plasmonic metasurfaces. *NPG Asia Mater.* **9**, e428-e428 (2017).
10. Dai, Z. et al. Artificial Metaphotonics Born Naturally in Two Dimensions. *Chem. Rev.* **120**, 6197-6246 (2020).
11. Lee, D. et al. Hyperbolic metamaterials: fusing artificial structures to natural 2D materials. *eLight* **2**, 1 (2022).
12. Li, P. et al. Collective near-field coupling and nonlocal phenomena in infrared-phononic metasurfaces for nano-light canalization. *Nature Communications* **11**, 3663 (2020).
13. Martín-Sánchez, J. et al. Focusing of in-plane hyperbolic polaritons in van der Waals crystals with tailored infrared nanoantennas. *Science Advances* **7**, eabj0127 (2021).
14. Zheng, Z. et al. Controlling and Focusing In-Plane Hyperbolic Phonon Polaritons in $\alpha$-MoO$_3$ with a Curved Plasmonic Antenna. *Advanced Materials* **34**, 2104164 (2022).
15. Krasnok, A. & Alù, A. Low-Symmetry Nanophotonics. *ACS Photonics* **9**, 2-24 (2022).
16. Zhang, Q. et al. Hybridized Hyperbolic Surface Phonon Polaritons at $\alpha$-MoO$_3$ and Polar Dielectric Interfaces. *Nano Letters* **21**, 3112-3119 (2021).
17. Duan, J. et al. Enabling propagation of anisotropic polaritons along forbidden directions via a topological transition. *Science Advances* **7**, eabf2690 (2021).
18. Folland, T. G. et al. Reconfigurable infrared hyperbolic metasurfaces using phase change materials. *Nat. Commun.* **9**, 4371 (2018).
19. Dai, S. et al. Phase-Change Hyperbolic Heterostructures for Nanopolaritonics: A Case Study of hBN/VO$_2$. *Adv. Mater.* **31**, 1900251 (2019).
20. Zeng, Y. et al. Tailoring Topological Transitions of Anisotropic Polaritons by Interface Engineering in Biaxial Crystals. *Nano Lett.* (2022).
21. Ruta, F. L. et al. Surface plasmons induce topological transition in graphene/$\alpha$-MoO$_3$ heterostructures. *Nature Communications* **13**, 3719 (2022).
22. Dai, S. et al. Graphene on hexagonal boron nitride as a tunable hyperbolic metamaterial. *Nat. Nanotechnol.* **10**, 682-686 (2015).
Hu, G. et al. Topological polaritons and photonic magic angles in twisted $\alpha$-MoO$_3$ bilayers. *Nature* **582**, 209-213 (2020).

Chen, M. et al. Configurable phonon polaritons in twisted $\alpha$-MoO$_3$. *Nature Materials* **19**, 1307-1311 (2020).

Duan, J. et al. Twisted Nano-Optics: Manipulating Light at the Nanoscale with Twisted Phonon Polaritonic Slabs. *Nano Letters* **20**, 5323-5329 (2020).

Zheng, Z. et al. Phonon Polaritons in Twisted Double-Layers of Hyperbolic van der Waals Crystals. *Nano Letters* **20**, 5301-5308 (2020).

Wu, Y. et al. Chemical switching of low-loss phonon polaritons in $\alpha$-MoO$_3$ by hydrogen intercalation. *Nat. Commun.* **11**, 2646 (2020).

Basov, D. N., Fogler, M. M. & García de Abajo, F. J. Polaritons in van der Waals materials. *Science* **354**, aag1992 (2016).

Low, T. et al. Polaritons in layered two-dimensional materials. *Nat. Mater.* **16**, 182-194 (2017).

Ju, L. et al. Graphene plasmonics for tunable terahertz metamaterials. *Nat. Nanotechnol.* **6**, 630-634 (2011).

Bharadwaj, P., Bouhelier, A. & Novotny, L. Electrical Excitation of Surface Plasmons. *Phys. Rev. Lett.* **106**, 226802 (2011).

Maier, S. *Plasmonics: Fundamentals and Applications* (Springer, 2007).

Nemilentsau, A., Low, T. & Hanson, G. Anisotropic 2D Materials for Tunable Hyperbolic Plasmonics. *Phys. Rev. Lett.* **116**, 066804 (2016).

Torbatian, Z., Novko, D. & Asgari, R. Tunable Low-Loss Hyperbolic Plasmon Polaritons in a $\mathrm{T\delta}$$\mathrm{e}$WTe$_2$ Single Layer. *Phys. Rev. Appl.* **14**, 044014 (2020).

Belopolski, I. et al. Discovery of a new type of topological Weyl fermion semimetal state in Mo$_x$W$_{1-x}$Te$_2$. *Nat. Commun.* **7**, 13643 (2016).

Chang, T.-R. et al. Prediction of an arc-tunable Weyl Fermion metallic state in Mo$_{0.5}$Te$_2$. *Nat. Commun.* **7**, 10639 (2016).

Fu, D. et al. Tuning the electrical transport of type II Weyl semimetal WTe$_2$ nanodevices by Mo doping. *Nanotechnology* **29**, 135705 (2018).

Rhodes, D. et al. Engineering the Structural and Electronic Phases of MoTe$_2$ through W Substitution. *Nano Lett.* **17**, 1616-1622 (2017).

Roberts, J. A. et al. Tunable Hyperbolic Metamaterials Based on Self-Assembled Carbon Nanotubes. *Nano Lett.* **19**, 3131-3137 (2019).

Frenzel, A. J. et al. Anisotropic electrodynamics of type-II Weyl semimetal candidate WTe$_2$. *Phys. Rev. B* **95**, 245140 (2017).

Wu, Y. et al. Temperature-Induced Lifshitz Transition in WTe$_2$. *Phys. Rev. Lett.* **115**, 166602 (2015).

S, S. et al. Interband scattering across the Lifshitz transition in WTe$_2$. *Phys. Rev. B* **106**, 115421 (2022).

Niu, X., Hu, X., Chu, S. & Gong, Q. Epsilon-Near-Zero Photonics: A New Platform for Integrated Devices. *Adv. Opt. Mater.* **6**, 1701292 (2018).

Yan, H. et al. Tunable infrared plasmonic devices using graphene/insulator stacks. *Nat. Nanotechnol.* **7**, 330-334 (2012).
Acknowledgments

H.Y. is grateful to the financial support from the National Natural Science Foundation of China (Grant Nos. 12074085 and 11734007), the National Key Research and Development Program of China (Grant Nos. 2021YFA1400100 and 2017YFA0303504), the Natural Science Foundation of Shanghai (Grant No.20JC1414601), and the Strategic Priority Research Program of Chinese Academy of Sciences (XDB30000000). C.W. is grateful to the financial support from the National Natural Science Foundation of China (Grant No. 12274030, 11704075). F.S. acknowledges the financial support from the National Key Research and Development Program of China (Grant No. 2017YFA0303203), the National Natural Science Foundation of China (Grant Nos. 92161201, 12025404, and 11904165), the Natural Science Foundation of Jiangsu Province (Grant No. BK20190286). S.H. is grateful to the financial support from the China Postdoctoral Science Foundation (Grant No. 2020TQ0078). Part of the experimental work was carried out in Fudan Nanofabrication Lab.

Author contributions

H.Y. and C.W. initiated the project and conceived the experiments. Y.X. prepared the samples, performed the measurements and data analysis with assistance from C.W., Y.D., L.Y., Q.X., C.S., S.H., F.W., Y.L., L.M. and J.Z.. F.F. and F.S. grew and characterized the bulk single crystals of Mo$_x$W$_{1-x}$Te$_2$. H.Y. and C.W. and Y.X. co-wrote the manuscript. H.Y. supervised the whole project. All authors commented on the manuscript.

Competing financial interests

The authors declare no competing financial interests.

Additional information
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Fig. 1 | Polarization $\phi_{\text{max}}$ for the maximal plasmon intensity. a, A sketch of Mo-doped WTe$_2$ in $T_d$-phase. Brown/green represents Mo/W atoms, gray represents Te atoms. b, Schematic illustration of skew ribbon arrays under illumination. Counter clockwise rotation
with respect to $a$-axis is defined as positive. The polarization of normal incident light is $\phi$ and the perpendicular direction of the ribbon edge is $\theta = -33^\circ$. c, d, The typical extinction spectra of skew ribbon arrays (composition ratio $x = 0.278$, ribbon widths of 4.5 and 1.9 $\mu$m) along the polarization ($\phi = -14.8^\circ, 24.5^\circ$) in the elliptic/hyperbolic regime respectively. Right inset in c shows the SEM image of the skew ribbon array. Scale bar is 10 $\mu$m. Top left insets in c and d are schematics of the iso-frequency contours of plasmon mode in the elliptic and hyperbolic regimes respectively. Red arrows labelled by $q$ are the corresponding wave vector direction (related to the $-33^\circ$ skew angle). e, f, The configuration of polarization current density $J_{polar}$ and depolarization field $E_{depol}$ in elliptic and hyperbolic regimes respectively. $\phi_{max}$ has the same sign as $\theta$ in the elliptic regime, but opposite sign in the hyperbolic regime.
Fig. 2 | Polarization-resolved plasmons in skew ribbon arrays of WTe₂. a, b, Polarization dependence of raw extinction spectra at plasmon frequencies of 308 cm⁻¹ and 510 cm⁻¹ respectively. Degrees in black indicate the polarization of incident light. Angles of 57° and −33° in red represent the parallel and perpendicular directions of ribbon edges. 0° denotes \(a\)-axis of WTe₂. For clarity, spectra are shifted vertically. c, d, The corresponding pseudo color maps of a and b. e, f, Polarization dependence of the corresponding normalized plasmon weights of a and b. Blue solid lines are fitting results of \(\cos^2 \phi\). g, The pseudo color maps of the plasmon absorption spectra at different resonance frequencies. In c, d and g, black dashed lines denote the parallel (57°) and perpendicular (−33°) directions with respect to the ribbon edge and the red dashed lines denote \(a\)-axis.
Fig. 3 | Tunable topological transition by doping. a-c, The polarization $\phi_{\text{max}}$ as a function of the plasmon frequency at different doping levels. Brown dots are fitted results of polarization experiments with errors about 3° from both angle measurements and fitting. Vertical black dashed line highlights the lower boundary of the hyperbolic regime. Blue solid curve in a is based on the conductivity from the plasmon dispersion in Ref. [4]. Gray dashed lines in a, b and c are calculated using the fitted conductivities from the extinction spectra of unpatterned films in Figs. 4a-c. d-f, The pseudo color maps of the plasmon spectra with similar resonance frequency ($345 \pm 15$ cm$^{-1}$) at different Mo-doping (0, 0.278, 0.5 from top to bottom). g-i, The corresponding normalized plasmon weights of d-f versus the polarization.
Fig. 4 | The mechanism of tunable topological transition. a-c, The experimental and fitting results of anisotropic extinction spectra of bare films of Mo$_x$W$_{1-x}$Te$_2$. Blue downward arrows represent the first interband transition resonances along $b$-axis. d-f, The imaginary parts of conductivities along two crystal axes. Shaded areas denote the corresponding hyperbolic regimes. g, Doping dependence of the frequency of the first interband transition resonance. h, Doping dependence of the hyperbolic regime. Black right-pointing triangles are determined by fitted conductivities from d-f and shaded areas are the corresponding hyperbolic regimes. Red dots are determined by the polarization $\phi_{\text{max}} = 0$. Azure pentagrams are from the plasmon dispersion in Ref. [4].
Fig. 5 | Temperature-induced shifts of topological transitions in WTe$_2$. a-c, The anisotropic extinction spectra and fitting curves of bare films of WTe$_2$ at 78, 155, 230 K respectively. d, The optimal polarization $\phi_{\text{max}}$ as a function of the plasmon frequency at different temperature. Dashed line is the same as the gray dashed line in Fig. 3a. Solid lines are calculated using the fitted optical conductivities from the extinction spectra (in a-c or Supplementary Note 8) at the corresponding temperature. Inset shows the temperature dependence of the hyperbolic regime determined by the corresponding extracted imaginary part of the optical conductivity.