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Journal

ACS Photonics, 8(10)

ISSN

2330-4022

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Publication Date

2021-10-20

DOI

10.1021/acsp Photonics.1c00955

Peer reviewed

Ultrabroadband nanocavity of hyperbolic phonon polaritons in 1D-like α -MoO₃

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Abstract

The exploitation of phonon-polaritons in nanostructured materials offers a pathway to manipulate infrared (IR) light for nanophotonic applications. Notably, hyperbolic phonons polaritons (HP²) in polar bidimensional crystals have been used to demonstrate strong electromagnetic field confinement, ultraslow group velocities, and long lifetimes (~ up to 8 ps). Here we present nanobelts of α -phase molybdenum trioxide (α -MoO₃) as a low-dimensional medium supporting HP² modes in the mid- and far-IR ranges. By real-space nanoimaging, with IR illuminations provided by synchrotron and tunable lasers, we observe that such HP² response happens via formation of Fabry-Perot resonances. We remark an anisotropic propagation which critically depends on the frequency range. Our findings are supported by the convergence of experiment, theory, and numerical simulations. Our work shows that the low dimensionality of natural nanostructured crystals, like α -MoO₃ nanobelts, provides an attractive platform to study polaritonic light-matter interactions and offer appealing cavity properties that could be harnessed in future designs of compact nanophotonic devices.

Introduction

MoO₃ has received considerable attention in a wide range of applications including inorganic light-emitting diodes^[1], Li-ion batteries^[2–4], electrochemical supercapacitors^[5,6], electrochromic devices^[7] and others^[8,9]. The α -phase of this material (α -MoO₃) has been synthesized in a variety of nanostructures: nanowires^[10], nanobelts^[11,12], nanorods^[13], two-dimensional (2D) crystals^[14], among others^[15]. In particular, α -MoO₃, as a typical van der Waals (vdW) semiconductor, has shown an exquisite optical response^[16,17] caused by its crystalline anisotropy. This crystal has an orthorhombic layered oxide structure^[18,19] composed of distorted and edge-shared MoO₆ octahedra, wherein each octahedron contains three types of oxygen sites: the terminal O₁, which is doubly bonded with the Mo atom, the doubly coordinated and asymmetric bridging O₂, and the triply coordinated and symmetric bridging O₃, as shown in Figure 1a. The α -MoO₃ structural anisotropy can be described by a layered structure parallel to the (010) plane^[20,21]. Each layer is then composed of two sub-layers, each of which formed by corner-sharing octahedra along the [001] and [100] planes (Figure 1b).

Because of this atomic configuration, α -MoO₃ is optically biaxial, and in 2D shapes exhibits directional hyperbolic phonon-polariton (HP²) waves^[17,20–22] whose photonic properties depend on the crystal thickness and structural anisotropy. Fundamentally, HP² modes^[23–26] are quasi-particles formed by the coupling of electromagnetic field excitation to lattice vibrations of a polar medium with an anisotropic and phononic resonant electrical permittivity $\vec{\epsilon} = (\epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz})$, where $\vec{\epsilon}$ is a diagonal second-rank tensor valid for the α -MoO₃ case. A hyperbolic medium is defined within spectral regions where the real part of two components of the $\vec{\epsilon}$ have opposite sign. In general, this condition occurs inside a ‘Reststrahlen band (RB)’, which is the spectral window delimited between the transverse ω_{TO} and longitudinal ω_{LO} optical phonons^[26]. Therefore,

the HP² waves are characterized by modes of the frequencies (ω) inside the RBs of a hyperbolic medium. Forming open hyperboloidal-shaped isofrequency surfaces of type I ($\varepsilon_{zz} < 0$, but $\varepsilon_{xx} > 0$ and/or $\varepsilon_{yy} > 0$) or type II ($\varepsilon_{xx} < 0$ and/or $\varepsilon_{yy} < 0$, but $\varepsilon_{zz} > 0$) in the momenta space, the HP² possess high momentum (q). Their photonic properties is, typically, described in terms of the corresponding type I or II $\omega - q$ dispersion relations^[27]. In the case of 2D crystals of α -MoO₃, strong phonons^[18] enable HP² waves^[17,20,21,28,29] in an ultra-broadband frequency range spanning from 250 cm⁻¹, in the THz domain, to 1200 cm⁻¹ in the mid-IR.

In this work we exploit the polaritonic response of α -MoO₃ nanobelts, with reduced dimensionality approaching “1D-like” (Figure 1c), using synchrotron infrared nano-spectroscopy (SINS)^[30–33] and scattering-scanning near-field optical microscopy (s-SNOM). As reported^[34], such nanoscopy techniques (see details in supplementary material) possess a high spatial resolution and momentum nanoprobe allowing for full characterization of HP² waves. The polaritons in α -MoO₃ nanobelts feature Fabry-Perot (FP) resonances, primarily, from type I HP²s^[20,22] in the 970-1100 cm⁻¹ range. The modes show dependence on the geometric form factor (thickness and width) of the nanobelt and propagate along the [100] crystal direction. In the same crystalline axis, we also show the first infrared nanoimages of type I polaritonic modes in the far-IR band extending from 440 to 490 cm⁻¹. Those analyses are confirmed by a robust convergence among experiment and numerical simulations. Hence, α -MoO₃ nanobelts are presented as an HP² nanocavity directly synthesized without the need of lithography or other post-synthetic sculpting processes. This low-dimensional polaritonic material opens new avenues for integrated planar IR photonics^[35], dictating polaritons control^[36] and nanoresonators for phonon-enhanced molecular vibrational spectroscopy^[37].

Figure 1 | Overview of α - MoO_3 nanobelts crystal structure and morphology. (a) Scheme of the three oxygen sites of asymmetric Mo–O bonds along the different crystalline axes labeled as O_1 , O_2 , and O_3 of α - MoO_3 . (b) The unit cell of α - MoO_3 shown by the dashed lines with the lattice constants: $a = 0.396$ nm, $b = 1.385$ nm and $c = 0.369$ nm. Green/gray spheres represent molybdenum/oxygen atoms. The principal axes of the crystal, x , y , and z coincide with the crystalline directions $[100]$, $[001]$, and $[010]$, respectively. (c) SEM images of α - MoO_3 nanobelts (scale bar: 1 mm) on the substrate. (d) Corresponding XRD patterns: nanobelts (black) and bulk (green). (e) Raman spectra of α - MoO_3 nanobelts and bulk crystal on a glass substrate.

Results

The α -MoO₃ nanobelts were synthesized by the hydrothermal method^[12] that yields an orthorhombic crystalline structure in which all three lattice parameters (a , b and c) are different as shown in Figure 1b. Representative scanning electron microscopy (SEM) images of the α -MoO₃ nanobelts (Figure 1c) reveal well-defined rectangular-like shapes for the synthesized crystals in which the long-axis corresponds to the [001] direction, as already reported^[38–41]. The synthesis produced nanobelts of widths (w) varying between 150 and 400 nm and lengths, from 10 to 30 μ m. X-ray diffraction (XRD) reveals the predominance of the α -phase as confirmed by the good correspondence with MoO₃ bulk crystals (Figure 1d). The diffraction peaks of the XRD pattern for both species can be readily indexed to be orthorhombic with lattice parameters $a = 0.396$ nm, $b = 1.385$ nm and $c = 0.369$ nm according to the JCPDS database number 05-0508^[39,42]. The more intense peaks are identified in the family planes ($0\ k\ 0$), with $k = 2, 4$ and 6 , which suggests an anisotropic structure. It is well known that α -MoO₃ has a lamellar structure along the [010] axis, formed by layers of MoO₆ octahedra with preferential growth along the [001] axis^[42]. No peaks of other phases were detected, indicating a high crystalline purity of the nanobelts.

The α -MoO₃ orthorhombic type has three oxygen species (O₁₋₃) along different crystallographic directions giving rise to the various Mo–O bonding types (Figure 1a). Such a complex structure leads to a great variety of phonon modes in the mid- to far-IR as depicted by the nearly coincident Raman spectra of the bulk crystal and nanobelts in Figure 1e. The peaks at 994, 814, 663, 473, 373, 332, and 286 cm⁻¹ are assigned to vibrational modes of the orthorhombic α -MoO₃ phase^{[43,44],[18]}. The 286 cm⁻¹ peak is attributed to O=Mo=O wagging vibrations. The peaks at 332 and 373 cm⁻¹ are assigned to O₃-Mo-O₃ bending mode and O-Mo-O scissoring, respectively. The peak at 473 cm⁻¹ corresponds to the Mo–O–Mo stretching and bending vibration. The peak at 663 cm⁻¹ stems from triple-coordinated oxygen stretching mode and the peak at 814

cm^{-1} , from the O–Mo–O stretching along the [100] direction. The peak at 994 cm^{-1} is due to the oxygen stretching vibration of Mo–O₁ bond along the [010] direction.

Four hyperbolic RBs are predicted for $\alpha\text{-MoO}_3$ crystals according to the plot of $Re(\epsilon_{xx})$, $Re(\epsilon_{yy})$ and $Re(\epsilon_{zz})$ in Figure 2a. These permittivity components are expressed by the Lorentz model using input parameters from previous reports^{[18,20,28],37}. As illustrated, in a wide IR range, the signs of permittivities along three directions can achieve many different combinations, showing different types and directions of hyperbolicity. Specifically, in RB₁ and RB₄, where $\epsilon_{xx}, \epsilon_{yy} > 0$ ($\epsilon_{xx} \neq \epsilon_{yy}$) and $\epsilon_{zz} < 0$, the out-of-plane dispersion is hyperbolic while the in-plane dispersion is elliptical, and the modes propagate anisotropically in the x-y plane. In RB₂, $\epsilon_{yy} < 0$ and $\epsilon_{xx}, \epsilon_{zz} > 0$ ($\epsilon_{xx} \neq \epsilon_{zz}$), and in RB₃, $\epsilon_{xx} < 0$ and $\epsilon_{yy}, \epsilon_{zz} > 0$ ($\epsilon_{yy} \neq \epsilon_{zz}$), the polaritonic modes show in-plane and out-of-plane hyperbolic dispersion with directional propagating depending on the RB.

Accordingly, such anisotropy determines different field distributions and polariton propagation in each RB as shown by the simulations in Figure 2b. The simulations employed finite-difference time-domain (FDTD) numerical method, where a dipole source was used to excite the polaritons in a semi-infinite nanobelt of $w=1 \text{ }\mu\text{m}$, and $t=100 \text{ nm}$. The polariton response was obtained by monitoring the real value of the electric field in the z-direction ($Re(E_z)$) on a plane above the crystal surface (see Methods for more details). As one may observe, the polaritons fringes are approximately isotropically distributed in RB₁ and RB₄, while in RB₂ and RB₃ the propagation is restricted to [001] and [100] directions, respectively. Thus, the simulations confirm the in-plane elliptical dispersion in RB₁ and RB₄ and demonstrates the extreme in-plane anisotropy in RB₂ and RB₃.

The in-plane anisotropy ($\epsilon_{xx} \neq \epsilon_{yy}$) of the $\alpha\text{-MoO}_3$ crystal leads to different $\omega - q$'s for the [100] and [001] crystalline directions as revealed from the poles of the reflectivity coefficient $r_p(\omega, q)$, visualized by the false color plot of the imaginary part of $r_p(\omega, q)$ in Figure 2c for a 2D flake of $\alpha\text{-MoO}_3/\text{Au}$. From those

calculations, we remark type I (type II) hyperbolic response with positive (negative) real part of the in-plane permittivities in the α -MoO₃ flake. The RB₁ and RB₄ present type I $\omega - q$ for both crystalline directions. Type II $\omega - q$'s are found in the RB₂ along [001] and in the RB₃ along [100].

Figure 2: Polaritonic response of α -MoO₃ | (a) Spectral dependence of the real part of ϵ_{xx} , ϵ_{yy} and ϵ_{zz} of an α -MoO₃ crystal. The x , y and z axes are coincident with the crystallographic axes [100], [001] and [010], respectively. Shaded regions indicate the four Reststrahlen bands (RB₁, RB₂, RB₃, and RB₄). (b) Simulated $\text{Re}(E_z)$ field distributions of polaritons on a α -MoO₃ nanobelt of $w = 1 \text{ }\mu\text{m}$ and $t = 100 \text{ nm}$ on top of gold for: $\omega = 476 \text{ cm}^{-1}$ in RB₁, $\omega = 609 \text{ cm}^{-1}$ in RB₂, $\omega = 880 \text{ cm}^{-1}$ in RB₃ and $\omega = 990 \text{ cm}^{-1}$ in RB₄. The scale bar represents 500 nm. (c) Calculated false-color map of the imaginary part of $r_p(\omega, q)$, $\text{Im}[r_p(\omega, q)]$, for the air/(2D) α -MoO₃/Au structure along the [100] and [001] crystallographic directions. (d) Normalized SINS amplitude and corresponding simulation spectra of α -MoO₃ nanobelt ($w = 1 \text{ }\mu\text{m}$ and $t = 100 \text{ nm}$) on Au.

To verify how such anisotropy influences the polaritonic response, we analyze by SINS (Figure 3a) different α -MoO₃ nanobelts. The SINS point spectrum, in Figure 2e, taken in the center of an isolated nanobelt with $w = 490$ nm and $t = 107$ nm on a Au substrate, reveals optical phonon resonances^[18]: the stronger peak at 989 cm^{-1} is attributed to stretching mode of Mo-terminal oxygen (O_1) with an indicator of the layered orthorhombic MoO₃ phase; and two smaller ones at 810 and 475 cm^{-1} ascribed to the stretching mode of oxygen, in Mo–O–Mo bonds, O_3 and O_2 atoms linked to two or three molybdenum atoms, respectively^[18]. These phononic resonances are reproduced in the simulated point-spectrum for an analogous nanobelt (see Methods for more details). We note the overall correspondence in lineshape with the main phonon resonances appearing at approximate spectral positions either in the experiment and the modeling. Small divergences can be attributed to (i) shape inhomogeneities of the real materials (like the rough Au surface) compared with the idealized rectangular nanobelt and fully plane Au surface used in the modeling and (ii) differences between the theoretical and experimental values of permittivity of α -MoO₃. Such good agreement between experiment and simulations confirms that our simulation results provide good support to interpret the experimental data in the following.

Complementary, we employed IR SINS (Figure 3a) and pseudo-heterodyne (PH) s-SNOM nanoimaging (Figure 3b) to experimentally access the real-space visualization of HP^2 in α -MoO₃ nanobelts. In both techniques, the IR radiation is strongly confined at the apex of a metallic AFM tip allowing the launching and detection of HP^2 s waves due to the momentum match between the nanoprobe and these quasiparticles. With the IR SINS experiment, one can access the broadband response of the nanobelt in a single-shot-like fashion across the mid to far-IR ranges at once. In this case, hyperspectral imaging are necessary for a narrowband analysis (Figure 3c,d). Yet the PH s-SNOM, despite it is not possible to access the full spectral response of SINS, the modality allows fast and highly sensitive narrowband nanoimaging at selected frequencies (Fig. 3e). Polariton fringes at different frequencies over the RB_1 and RB_4 , can be visualized in Figure

3c from nanoimaging reconstructed from SINS hyperspectral measurement on a α -MoO₃ nanobelt ($w = 667\text{nm}$, $t = 129\text{nm}$). The fringes result from the interference among type I polaritons waves travelling inside the crystal with strong dependence on the excitation frequency. Similar measurements at RB₄ and RB₃ for an α -MoO₃ nanobelt ($w = 1.3\text{ }\mu\text{m}$, $t = 149\text{ nm}$) are presented in Figure 3d. Additionally, using a tunable mid-IR s-SNOM, we present in Figure 3e near-field images of α -MoO₃ nanobelt with $w = 590\text{ nm}$, $t = 113\text{ nm}$ taken at frequencies residing inside the RB₄.

Figure 3 | Far- and mid-IR real-space imaging of HP² modes in α -MoO₃ nanobelt | Schematics of the (a) SINS experiment for ultrabroadband hyperspectral imaging and (b) QCL s-SNOM experiment for narrowband imaging. (c, d) AFM topography and SINS amplitude ($|S_2|$) narrowband maps reconstructed from a hyperspectral image of α -MoO₃

nanobelts/Au in all RBs. Nanobelts dimensions in (c) $w = 667$ nm, $t = 129$ nm and, (d), $w = 1.3$ μ m, $t = 149$ nm. The horizontal, blue-dashed lines indicate the nanobelts edges in correspondence with the topographies. (e) AFM topography and s-SNOM $|S_3|$ on a α -MoO₃ nanobelt/Au ($w = 590$ nm, $t = 113$ nm) for different ω s in the RB₄. Scale bars: 400 nm in (c), 1 μ m in (d) and 500nm in (e).

The experimental data (Figures 3c-e) demonstrate spectral bands exhibiting a series of amplitude maxima along the [100] crystal direction (indicated by the arrows). The mechanism that regulates the waves patterns observed in Figures 3c-e is described by tip-launched HP² waves, which travels across the x-axis of the nanobelts and are reflected by the side edges acquired a round-trip phase. The overlapping of all leads to the formation of standing waves, a FP cavity. The number of maxima (n is the FP resonance order) is related to the excitation ω within the RBs, indicating a clear dependence of the near-field distribution with the polariton dispersion. Due to the asymmetrical shape of the nanobelts, as seen from AFM topography, the near-field peaks are dislocated from the nanobelt center. Yet, we observe the formation of higher n , especially in Figure 3e, in which the s-SNOM nanoimaging presents higher optical contrast due to the superior output power of the laser in comparison to the synchrotron in narrowband experiments.

For a comprehensive assessment of the phenomena observed and as supplementary evidence of nanocavity modes in α -MoO₃ nanobelts, we show in Figure 4a the simulated (see Methods for numerical simulation details) and experimental SINS spectral linescan of $w = 490$ nm and $t = 107$ nm nanobelt fully covering all RBs. From the experiment, we note the formation of different standing waves patterns along the crystalline axis [100] for each RB due to multiple reflection of HP² waves at the nanobelt edges. In both simulated and experimental results, the polaritonic activity is not observed in the [001] direction since the measurements are performed far from the extremities of the nanobelt. Such close agreements between experiments and simulations confirm the nanobelt crystalline orientation with respect to the substrate plane

and give valuable insights into the HP² modes ruled by the cavity geometry formed between the nanobelt edges.

In Figure 4b, we zoom in the RB₁ (440-500 cm⁻¹), RB₃ (821-963 cm⁻¹) and RB₄ (957-1007 cm⁻¹) from the experimental linescan in Figure 4a with HP² profiles extracted at selected frequencies. Standing waves patterns are noteworthy with well-defined number of amplitude maxima, mainly in the RB₃ and RB₄, indicating different resonant orders of a FP cavity. As a consequence of the different hyperbolicities of each band (Figure 2c), in type I band, the distance between maxima of the spectral linescan increases as we can see in RB₄ band. However, in type II band, the opposite trend happens was observed in the RB₃ band. Inside the RB₁, although standing wave patterns were not observed, we detected polariton activity within the band.

Figure 4 | SINS spectral linescan of α -MoO₃ nanobelt with $w = 490$ nm and $t = 107$ nm | (a) Simulated and Experimental spectral linescan and AFM line profile in nanobelt. The RB₁, RB₃ and RB₄ predicted by the theory along the [100] direction are observed. (b) Magnified portions from the experimental linescan in (a) highlighting RB₄, RB₃ and RB₁ from which profiles (black curves) for selected ω s were extracted. For each peak n we observed oscillations ($n = 1, 2$, and 3) yielding the Fabry–Perot resonances.

In Figure 5a, as a supplementary evidence for the formation of FP resonances in α -MoO₃ nanobelts, we show a simulated spectrum obtained for a nanobelt with $w = 1.3 \mu\text{m}$ and $t = 267\text{nm}$ and, therefore, for different cavity parameters (See section S4 in the supplementary information for the comparison with experimental result). Figure 5b presents the amplitude profile for selected frequencies inside all RBs shown in Figure 5a. The different resonant FP orders n are clearly distinguishable, occurring within all RBs, except for RB₂ for the reasons already mentioned. The cavity modes are qualitatively explained in terms of FP resonances, where M_0 mode (defined as the mode accessed experimentally in this work - see supporting information) travel across the nanobelt and reflects at the side edges, giving rise to standing waves patterns. The polariton M_0 wavelength (λ_{M_0}) for each resonant frequency were calculated, in good approximation, through $\lambda_{M_0} = \frac{\delta}{2}$, where δ is the distance between adjacent near-field maxima at the center of the nanobelt^[35]. The extracted correspondent momentum values (q) for the frequencies are plotted (black circles) in Figure 5c, along the (ω - q) dispersion relation for the M_0 modes, calculated for an infinite α -MoO₃ 2D slab of thickness $t = 267\text{nm}$. We note a reasonable agreement between the theoretical dispersion and the q extracted from the simulations, leading to the conclusion that the FP cavity theory explain the modes transversal to the nanobelt axis.

Figure 5 | Simulated visualization of FP cavity modes in α -MoO₃ nanobelt of $w = 1.3 \mu\text{m}$ and $t = 267 \text{ nm}$ (a) Simulated spectral linescan across the nanobelt a top of Au showing the RB₁, RB₃ and RB₄. (b) Polariton profiles for selected ω s acquired in (a). (c) Dispersion curve of HP² modes M_0 calculated analytically, see supporting information, (solid curve) at mid to far wavelengths along the [100] direction. Black circles are the values of q of the profiles in (b).

Finally, we estimated a confinement factor ($\lambda_{Ir}/\lambda_{M_0}$) of approximately 80 times that of the light in free space ($\lambda_{Ir} = 1/\omega$) at $\omega = 990 \text{ cm}^{-1}$ excitation frequency, which is comparable to ultimate values found in other layered 2D materials^[34,45,46]. Therefore, our analysis provides a direct experimental evidence of that α -MoO₃ nanobelts form a Fabry-Perot cavity for HP² modes. We emphasize that whilst type I and II HP² waves have been imaged by s-SNOM using narrow-band lasers in the Mid-IR range^[20,22,28] and using free-electron laser^[47] in the THz-IR^[29], images for type I HP² shown here by SINS in far-IR range are unprecedented.

Conclusion

In summary, we used SINS and s-SNOM to map the dispersion of HP² modes in α -MoO₃ nanobelts at mid to far-IR wavelengths. Comparing such nanoimaging with a detailed FDTD-simulation, we conclude that α -MoO₃ nanobelts exhibit Fabry-Perot resonances which are dependent of the sample dimensions.

Additionally, we estimated a confinement factor of about 80 times for the M_0 modes. As a further step into applications, we studied the ultrabroadband nanocavity properties of as-grown α - MoO_3 nanobelts exploring their lithography-free advantage. For these reasons, we believe that this work offers new prospects to the field of nanophotonics, whereby one may incorporate a single material for resonator applications. The knowledge about the vibrational and optical properties of this low-dimensional material brings insights into new opportunities for studying enhanced light-matter interaction in the mid- to far-IR range.

Materials and Methods

Growth. The nanobelts of molybdenum trioxide were synthesized by the hydrothermal method proposed by Zhang^[12], using Heterocyclic ammonium tetrahydrate CRQ and Nitric Acid (HNO_3 65%) brand Dynamics Química Contemporânea e Ltda. Ammonium heptamolybdate tetrahydrate (AHM) was used as a source of molybdenum. All the chemical reagents were used without further purification, as follows: Initially, 0.4 mmol of AHM was diluted in 20 ml of distilled water. After 30 min of stirring, was obtaining a clear and colorless solution. Then, 10 mL of HNO_3 was added and again, the solution has stirred for 30 min. The solution was placed in a sealed autoclave and oven-heated at 180 °C for 20 hours at rate 10 °C / min. After 20 hours, the autoclave was removed from the oven and allowed to cool naturally until reaches room temperature. The product was centrifuged at 5000 rpm for 15 min. After centrifuge time, the solid part remains at the bottom of the tubes, and the supernatant liquid was removed. In this way, the material was washed (repeating the centrifugation procedure and withdrawing the supernatant) for 20 times. The first 10 washes were carried out with distilled water, and the other 10 with ethyl alcohol. The resulting material was oven-dried at 70 °C for 24 hours.

Scanning electron microscopy (SEM) images of the nanobelts were performed in performed in a JEOL model JSM6380-LV microscope. The SEM image of the nanobelts shows rectangular cross-section shape, in Figures 2a and 2b with lateral sizes between 50 and 500 nm, and length up to 50 mm.

Raman. A table Raman spectrometer was used, Advantage 532 model from SciAps with green laser (532 nm). The synthesized (powdered) material and the commercial molybdenum trioxide (Vitec brand) was characterized. In this way, a comparative analysis can be carried out between the two materials. The material (powder) was placed in cylindrical metal support with a diameter of 6.50 mm and compacted. The spectra were taken with power laser of 0.2 W during 25 s.

Synchrotron Infrared Nanospectroscopy (SINS). SINS experiments were performed at the Advanced Light Source (ALS)^[30] and at the Brazilian Synchrotron Light Laboratory (LNLS)^{[31],[32]}. Both beamlines use a similar optical setup comprising of an asymmetric Michelson interferometer within a commercial s-SNOM microscope (neaSNOM, Neaspec GmbH). The s-SNOM microscope is an atomic force microscope (AFM) that usually operates in non-contact (tapping) mode with suitable optics to focus and collect the incident and scattered light, respectively. In SINS, broadband IR synchrotron light illuminates the tip oscillating at its fundamental mechanical frequency Ω (~ 250 kHz) and induces an effective polarization of the tip that enhances light interaction with the sample. The optical near-field signal (S_m), which originates from a sample area comparable to the tip radius (around 25 nm in our case), is extracted from the detected back-scattered light by demodulating the signal at harmonics (m) of Ω , with $m \geq 2$ with a lock-in amplifier. In SINS, the backscattered light interferes with a reference IR synchrotron beam from a scanning mirror. The Fourier transform of the resultant interferogram yields the IR amplitude $|S_m(\omega)|$ and phase $\Phi_m(\omega)$ spectra of the complex optical near-field signal $S_m(\omega) = |S_m(\omega)|e^{i\Phi_m(\omega)}$. All SINS spectra here are measured with second harmonic demodulation, $m = 2$ to yield $S_2(\omega)$. For the mid-IR measurements, we used a ZnSe beamsplitter and a mercury cadmium telluride detector (MCT, IR Associates) for the interferometric setup, whereas for

the far-IR measurements, we used a KRS-5 beamsplitter and a custom, helium-cooled Ge:Cu photoconductor, which provides broadband spectral detection down to 320 cm^{-1} .

Infrared nanoimaging. The infrared nanoimaging of polaritons in $\alpha\text{-MoO}_3$ was performed by s-SNOM (Neasnom, Neaspec GmbH) illuminated by a tunable narrowband mid-infrared quantum cascade laser (Daylight Solutions MirCat) with frequency coverage from 930 to 1730 cm^{-1} (minimum frequency step of 1 cm^{-1}), in Figure 3e, and broadband IR synchrotron light coverage 320 to 3000 cm^{-1} (Fourier Transform processing with 10 cm^{-1} spectral resolution), in Figures 3c and 3d. For more detail about SINS data acquisition and data processing (hyperspectral images and spectral linescan) see the Supplementary Information.

FDTD simulations. The simulations presented in this paper were performed in the commercial software Lumerical FDTD v8.23. The dielectric function of the gold substrate was obtained from Olman *et al*^[48], while the dielectric function of $\alpha\text{-MoO}_3$ was calculated through the Lorentz model (See supplementary). The $\text{Re}(E_z)$ fields in figure 2d were excited by a dipole of height $H = 100\text{ nm}$ and monitored by a frequency-power plane monitor located at a height $h = 20\text{ nm}$ above the crystal surface. The far-fields of the dipole were filtered by applying a starting apodization located at a timeframe of $t = 500\text{ fs}$ with time-width of 200 fs . Standard PML boundaries were utilized to absorb the fields outside the simulation region and the simulations were early terminated at $t = 3250\text{ fs}$ to prevent simulation instabilities. The simulated point- and line-spectra presented in figures 2e, 4a, and 5a, were performed by approximating the near-field behavior of the s-SNOM tip to a dipole source^[49]. Since the dipole moment of the source is constant, tip-sampling coupling effects are not considered in our model. The simulated point-spectrum was obtained by measuring the $|E_z|_{\text{MoO}_3}$ with frequency-power point monitor located between the dipole and the crystal surface. These values were normalized by the simulated $|E_z|_{\text{Au}}$ fields, calculated on the Au substrate without the crystal. The simulated line-spectra were calculated by obtaining equally spaced point-spectra along the nanobelts x-direction. The height of the monitors, h , and the dipole source, H , in respect to the crystal surface were, respectively: (39 nm, 200 nm) for figures 2e and 4a, and (19 nm, 300 nm).

Acknowledgements

All authors thank the Brazilian Synchrotron Light Laboratory (LNLS) and Advanced Light Source (ALS) for providing beamtime for the experiments. NeaSpec GmbH is acknowledged for the technical assistance. Angelo L. Gobbi and Maria H. de Oliveira Piazzetta, from the Brazilian Nanotechnology National Laboratory. I.D.B, T.A.C, E.G.O, A.M.B.G, and D.C.B.A acknowledges the financial support from the Brazilian Nanocarbon Institute of Science and Technology (INCT/Nanocarbono). I.D.B. acknowledges the support from CNPq through the research grant 311327/2020-6. R.O.F. and R.A.M. acknowledge the FAPESP project 2019/08818-9. R.O.F. acknowledges the support from CNPq through the research grant 311564/2018-6 and FAPESP Young Investigator grant 2019/14017-9. T.A.C, E.G.O, A.M.B.G, and D.C.B.A also like to thank the support of the Universidade Federal de Mato Grosso do Sul - UFMS / MEC – Brazil. F.C.B.M. and F.H.F acknowledge the CNPq project 140594/2020-5. The authors acknowledge CNPq for financial support. The Electron Microscopy Center at UFMG and MULTILAM-UFMS is also greatly acknowledged. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001. This research used resources of the Advanced Light Source, a U.S. DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

Competing interests

The authors declare no competing interests.

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Supplementary Information

Ultrabroadband nanocavity of hyperbolic phonon polaritons in 1D-like α -MoO₃

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Section 1 (S1): SINS broadband imaging of α -MoO₃

Complementarily, SINS broadband imaging unveils morphology (AFM topography) and broadband local reflectivity of α -MoO₃ nanobelt transferred to Au substrate, a standard configuration for all samples analyzed in this work. The AFM topography corroborates the SEM morphological analysis while the s-SNOM amplitude maps highlight broadband reflectivity indicating a preliminary and qualitative view of optical confinement in the nanobelts. $|S_2|$ and $|S_3|$ represent the 2nd and 3rd harmonics of the s-SNOM tip demodulation, respectively, and confirm the high signal-to-noise ratio and background free quality of the analysis.

Figure S1: (a) Morphology (AFM topography) and broadband reflectivity, (b) $|S_2|$ and (c) $|S_3|$, nanoscale images of an isolated α -MoO₃ nanobelt/Au simultaneously measured by SINS. All scale bars represent 1 μ m.

Section 2 (S2): Dielectric function of α -MoO₃

In the infrared region, the optical response of α -MoO₃ is dominated by the phonon absorption. The components of the tensor $\vec{\epsilon}$ are defined in relation to the uniaxial optical axis of the crystal (z -axis).

$$\vec{\epsilon} = \begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{yy} & 0 \\ 0 & 0 & \epsilon_{zz} \end{pmatrix}; \epsilon_{xx} \neq \epsilon_{yy} \neq \epsilon_{zz} \quad 1$$

in which the in-plane and out-of-plane components are defined as: orthogonal to the z -axis $\epsilon_{xx} = \epsilon_{yy}$ and parallel to the z -axis ϵ_{zz} .

The dielectric function, ϵ , can be described by a Lorentz oscillator model according to

$$\epsilon_a = \epsilon_{a,\infty} \left(1 + \sum_j \frac{(\omega_{Lo,j}^a)^2 - (\omega_{To,j}^a)^2}{(\omega_{To,j}^a)^2 - \omega^2 - i\omega\Gamma_j} \right), \quad 2$$

where a denotes the $\vec{\epsilon}$ component, with $a = xx, yy$ or zz , having a number j of active optical phonons. $\epsilon_{a,\infty}$ is the high-frequency term, ω is the excitation frequency and Γ_j , the dielectric damping factor, extracted from experimental results in Ref. ^{1,2}.

Main axis $\mathbf{a}$	Mode index $\mathbf{j}$	$\epsilon_{x,\infty}$	$\omega_{To} \text{ (cm}^{-1}\text{)}$	$\omega_{Lo} \text{ (cm}^{-1}\text{)}$	$\Gamma \text{ (cm}^{-1}\text{)}$
x	1	5.86	506.7	534.3	49.1
x	2		821.4	963	6

x	3		998.7	999.2	0.35
		$\epsilon_{y,\infty}$	$\omega_{TO} \text{ (cm}^{-1}\text{)}$	$\omega_{LO} \text{ (cm}^{-1}\text{)}$	$\Gamma \text{ (cm}^{-1}\text{)}$
y	1	6.59	544.6	850.1	9.5
		$\epsilon_{z,\infty}$	$\omega_{TO} \text{ (cm}^{-1}\text{)}$	$\omega_{LO} \text{ (cm}^{-1}\text{)}$	$\Gamma \text{ (cm}^{-1}\text{)}$
z	1	4.47	444	508	1.5
z	2		956.7	1006.9	1.5

Table S1. The experimental value of the parameters used in calculating permittivity.

Using the parameters of the normal oscillation modes, from table S1, we obtained the real part of the components of electrical permittivity shown in Figure 3a in the main text.

The dispersion relation of the α -MoO₃ can be described by reflectivity coefficient $r_p(\omega, q)$, considering a multilayer system comprising the Au substrate, α -MoO₃ hyperbolic medium and air. The false-color maps, shown in Figure 2c, feature the imaginary part of the Fresnel through the following equations:

$$r_p = \frac{r_1 - r_3 e^{i2k_2^b t}}{1 + r_1 r_3 e^{i2k_2^b t}}, \quad (3)$$

Where t represents the thickness of the α -MoO₃ slab, $r_a = \frac{\epsilon_{\perp} k_1^b - \epsilon_1 k_2^b}{\epsilon_{\perp} k_1^b + \epsilon_1 k_2^b}$, and $r_s = \frac{\epsilon_3 k_2^b - \epsilon_1 k_3^b}{\epsilon_3 k_2^b + \epsilon_1 k_3^b}$ represent the reflectivity coefficients at the interfaces Air and Au substrate, respectively. The subscripts 1, 2 and 3 denotes air, α -MoO₃ and Au. ϵ_1 , ϵ_3 and $\epsilon_{\perp}$ are the relative permittivities of air, Au and components perpendicular to the z-axis. In order to calculate the dispersion relation along the other propagation direction, $\epsilon_{\perp}$ can be changed by ϵ_x or ϵ_y in r_a .

Section 3 (S3): SINS data acquisition and data processing

In our SINS experiment, we collected point spectra with 10 cm⁻¹ spectral resolution; the spectra acquisition was done by integrating over 2048 points with 20.1 ms integration time per point. All spectrum are normalized by a reference spectrum acquired from a clean gold surface (100 nm thick Au sputtered on a silicon substrate). The images shown in Figure S1 were taken with 150 pixels × 200 pixels with an 11ms integration time per pixel. The spectral linescan in Figure 3c was performed along a line 1 μ m length segmented in 50 pixels, with 10 cm⁻¹ spectral resolution for each spectrum; 1024 acquisition points with 20 ms integration time per point. The hyperspectral images are recorded at each pixel over a 2.5 μ m (1.1 μ m) ×

2.0 μm (1.1 μm) area segmented in 50 (30) $\times$ 40 (30) pixels. Each spectrum in the hyperspectral map resulted from 1 (2) averages over the Fourier transform of an interferogram acquired with 600 μm optical path difference length, yielding 16.6 cm^{-1} spectral resolution, with 10 (5) ms integration time per point. The post-processing of the hyperspectral images data produces a narrow-band map shown in Figure S3 obtained by extracting the amplitude.

Section 4 (S4): Magnification portion of Far- and mid-IR real-space polaritonic imaging in $\alpha\text{-MoO}_3$ nanobelt

Figure S2| Experimental and Simulated visualization of FP cavity modes in $\alpha\text{-MoO}_3$ nanobelt of $w = 1.3 \mu\text{m}$ and $t = 267 \text{ nm}$ |(a) Experimental and (b) Simulated spectral linescan across the nanobelt showing the Reststrahlen bands RB_1 , RB_3 and RB_4 .

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