

Microcavity confinement of anisotropic phonon polaritons enabled by fabrication-ready monocrystalline α -V₂O₅ flakes

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Large-area growth of monocrystalline α -V₂O₅ flakes and tailored microcavity confinement of anisotropic phonon polaritons

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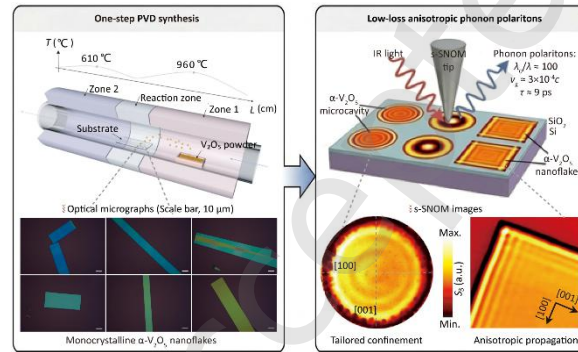
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This work demonstrates the scalable physical vapor deposition (PVD) growth of free-standing monocrystalline α -V₂O₅ flakes with lateral dimensions up to hundreds of micrometers and thicknesses down to a few nanometers, and reveals their low-loss in-plane anisotropic phonon polaritons (PhPs) featuring strong light confinement ($\lambda_0/\lambda \approx 100$), ultraslow group velocities ($\sim 3 \times 10^{-4} c$), and lifetimes up to 9 ps. We further achieve geometry-defined tailored manipulation of polaritonic near fields via patterned microdisk cavities, breaking the long-standing bottleneck of fabricable high-quality large-area α -V₂O₅ samples and establishing a promising new material platform beyond α -MoO₃ for infrared flat photonics and on-chip polaritonic devices.

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ABSTRACT: Van der Waals (vdW) crystals supporting in-plane anisotropic hyperbolic phonon polaritons (HPhPs) provide a promising route toward mid-infrared (MIR) and terahertz (THz) nanophotonics by enabling deep-subwavelength confinement, low-loss propagation, and directional control of light within the crystal plane. Although such anisotropic HPhPs have been reported in a few vdW crystals, most studies have relied on bulk crystals or mechanically exfoliated flakes, which limits scalability and compatibility with device fabrication. At present, α -MoO₃ is essentially the only vdW material available as large-area nanoflakes for fabrication-ready anisotropic polaritonic structures. Here, we demonstrate the scalable physical vapor deposition (PVD) growth of free-standing, monocrystalline α -V₂O₅ nanoflakes with lateral dimensions up to hundreds of micrometers and thicknesses down to a few nanometers. Using infrared nano-imaging together with theoretical analysis, we uncover low-loss in-plane anisotropic HPhPs in α -V₂O₅ with strong confinement ($\lambda_0/\lambda \approx 100$), ultraslow group velocities ($\sim 3 \times 10^{-4}c$), and lifetimes up to 9 ps. We further show that patterned microdisk cavities enable geometry-defined shaping of the polaritonic near field, allowing tailored in-plane electromagnetic confinement. Our results establish α -V₂O₅ as a large-area, monocrystalline, fabrication-ready vdW material for low-loss anisotropic polaritonics, and expand the materials basis for scalable infrared flat photonics and future on-chip polaritonic devices.

KEYWORDS: van der Waals crystals, monocrystalline α -V₂O₅ nanoflakes, phonon polaritons, in-plane anisotropy, subwavelength light confinement, polariton lifetime, microdisk cavities

1. Introduction

Polar vdW crystals have emerged as an important platform for nanophotonics due to their phonon polaritons, hybrid quasiparticles arising from the coupling of photons with optical phonons [1-6]. Owing to their deep-subwavelength confinement, low propagation loss, and long polariton lifetimes, phonon polaritons in vdW crystals provide a powerful route for manipulating infrared electromagnetic fields at the nanoscale [7-9]. In particular, hyperbolic PhPs (HPhPs) have attracted broad interest because their highly anisotropic dispersion enables unusual wavefront engineering [10, 11], directional energy transport [12-14], and extreme optical confinement [15], opening opportunities for applications in subdiffractional imaging [16-18], nanoscale waveguiding [19-21], sensing [22-24], controllable thermal radiation [25], and flat optical devices [26-28]. This field has expanded rapidly with the discovery of HPhPs in several vdW crystals with distinct symmetry and

dispersion characteristics. Hexagonal boron nitride (hBN), as a prototypical uniaxial vdW crystal, established the foundation for low-loss hyperbolic polaritonics in the mid-infrared [29, 30]. More recently, biaxial crystals such as α -MoO₃ have introduced in-plane hyperbolic propagation and directional polariton transport, greatly enriching the available degrees of freedom for near-field control [15, 31]. Beyond these representative systems, recently reported quaternary vdW crystals have further broadened the polaritonic materials family by offering additional forms of in-plane anisotropic dispersion and tunable polaritonic responses [32]. Despite this progress, a central materials bottleneck remains: although in-plane anisotropic polaritons have been reported in several vdW systems, most studies still rely on bulk crystals or mechanically exfoliated flakes [8, 21-34], which limits scalability, thickness control, and compatibility with device fabrication. At present, α -MoO₃ is essentially the only vdW material available as large-area nanoflakes suitable for fabrication-ready anisotropic polaritonic structures.

Developing fabrication-ready anisotropic polaritonic crystals is therefore essential for advancing the field from proof-of-concept studies toward practical nanophotonic devices [35]. Such materials must simultaneously provide low-loss polariton propagation, monocrystallinity, nanometer-scale thickness, large lateral dimensions, and compatibility with micro/nanofabrication. However, meeting all of these requirements in a single vdW material remains challenging, largely because suitable synthesis methods are still lacking [36]. Existing growth approaches often yield either bulk crystals or polycrystalline films with defects, grain boundaries, and interfacial disorder that increase optical loss and degrade polariton propagation [37, 38]. While bulk crystals may offer good crystallinity, they must still be exfoliated into nanometer-thick flakes for nanodevice fabrication, a process that is often poorly controllable in thickness, lateral size, and yield, and may introduce additional defects or contamination. Consequently, conventional vapor growth, chemical synthesis, and mechanical exfoliation generally fail to provide scalable access to high-quality ultrathin monocrystalline flakes for device-ready polaritonics.

Among low-symmetry vdW oxides, α -V₂O₅ is a particularly attractive candidate for anisotropic polaritonics. Its orthorhombic crystal structure and anisotropic V-O bonding give rise to strong in-plane optical anisotropy, and previous studies have shown that it supports in-plane anisotropic phonon polaritons in the mid-infrared [33]. However, progress in polaritonics of α -V₂O₅ has been limited by the lack of high-quality, large-area, nanometer-thick monocrystalline flakes suitable for both low-loss polariton studies and device patterning. Here, we address this challenge by developing a precisely temperature-controlled physical vapor deposition method for the scalable growth of free-standing, monocrystalline α -V₂O₅ nanoflakes with lateral dimensions up to hundreds of micrometers and thicknesses down to a few nanometers. Using theoretical analysis together with infrared nano-imaging, we show that these nanoflakes support low-loss in-plane anisotropic phonon polaritons with strong confinement ($\lambda_0/\lambda \approx 100$), ultraslow group velocities ($\sim 3 \times 10^{-4}c$), and long lifetimes of up to 9 ps. We further demonstrate that lithographically defined microdisk cavities enable geometry-controlled shaping of the in-plane polaritonic near field. These results establish α -V₂O₅ as a fabrication-ready vdW polaritonic material beyond α -MoO₃, thereby expanding the available material family for low-loss anisotropic polaritonics and scalable infrared flat photonics.

2. Results and Discussion

2.1 Preparation and characterizations of α -V₂O₅ monocrystalline nanoflakes

An improved PVD method was employed to synthesize high-quality monocrystalline α -V₂O₅ nanoflakes, as illustrated in **Fig. 1(a)**. High-purity α -V₂O₅ powder was

sublimed in the high-temperature zone at 960 °C, and the resulting vapor species were transported by a controlled oxygen flow to the low-temperature zone, where nucleation and crystallization occurred. **Figure 1(b)–1(g)** show the representative morphology of the as-grown α -V₂O₅ nanoflakes dispersed on SiO₂/Si substrates. The flakes exhibit well-defined rectangular shapes, consistent with the intrinsic structural anisotropy of the crystal. A gradual change in optical contrast, from dark blue to yellow, indicates the corresponding variation in flake thickness. Statistical analyses of the lateral dimensions are summarized in **Fig. 1(h) and 1(i)**, showing that the nanoflakes typically reach sizes exceeding 100 $\mu\text{m} \times 10 \mu\text{m}$, with some flakes longer than 100 μm , as also shown in **Fig. S1** (Supporting Information). Atomic force microscopy (AFM) measurements (**Fig. 1(k)**, **Fig. S2(a)**, Supporting Information) further reveal smooth surfaces and thicknesses ranging from 30 nm to about 100 nm, with mean roughness values between 0.26 and 0.94 nm and a root-mean-square (RMS) roughness between 0.33 and 1.15 nm (**Fig. S2(b) and S2(c)**, Supporting Information). Such large lateral dimensions combined with nanometer-scale thicknesses yield high-aspect-ratio flakes that are well suited for planar nanophotonic structures.

The crystal phase and structural quality were further examined by Raman spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy. The Raman spectrum in **Fig. 1(l)** confirms the α -V₂O₅ phase, with characteristic peaks at 146.4 cm^{-1} (skeleton bending vibration), 285.0 cm^{-1} (O2-V-O3 bond bending), and 701.8 cm^{-1} (V-O2 bond stretching). The strong peak at 995.9 cm^{-1} is assigned to the stretching vibration of terminal V=O bonds, which is a fingerprint of the layered structure [39]. Additionally, Raman spectral statistics collected from 20 nanoflakes from different batches show that the characteristic Raman peaks near 145 cm^{-1} and 995 cm^{-1} vary by only 2.19 cm^{-1} and 1.39 cm^{-1} , respectively (**Fig. S2(d) and S2(e)**, Supporting Information). These small peak-position variations across samples confirm the high phase purity and batch-to-batch uniformity of the nanoflakes.

As illustrated in the inset of **Fig. 1(j)**, α -V₂O₅ consists of stacked layers built from corner- and edge-sharing VO₅ polyhedra, forming zigzag (V2O4)_n chains along the [001] direction. XRD measurements (**Fig. 1(m)**) further verify the orthorhombic α -V₂O₅ phase (JCPDS No. 41-1426). The dominant (001) peak together with the series of (00*l*) reflections indicates strong preferential orientation along the [001] direction and high crystallinity, both characteristic of layered vdW crystals [40]. High-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) measurements on individual nanoflakes (**Fig. 1(n)–1(q)**) further confirm their monocrystalline nature. Clear lattice fringes with a spacing of 5.8 Å are assigned to the {001} planes, while the SAED pattern can be indexed to the [010] zone axis of orthorhombic V₂O₅, consistent with the {200} and {1 $\bar{1}$ 0} plane families (**Fig. 1(q)**, **Fig. S2(f)–S2(h)**, Supporting Information).

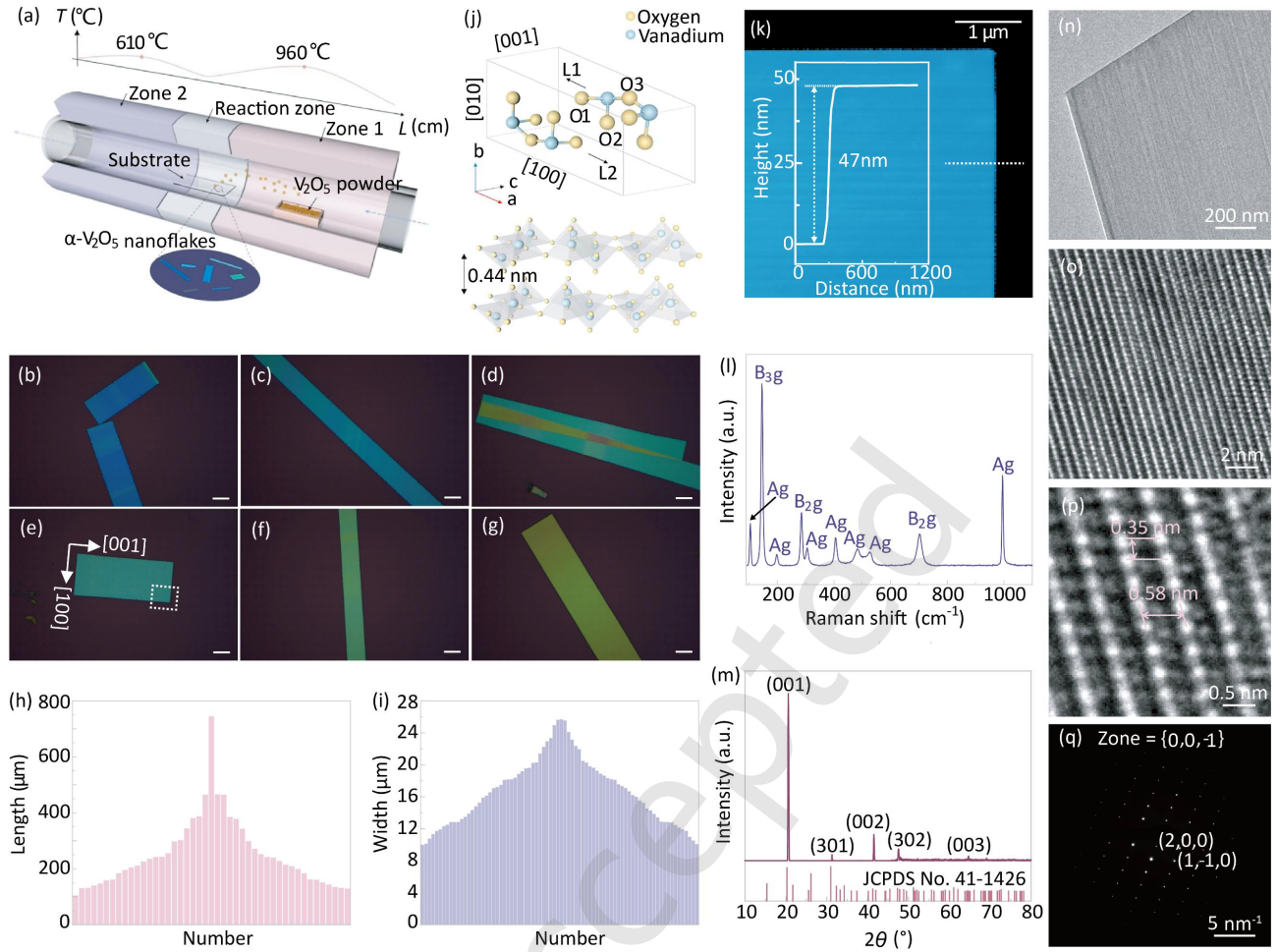


Figure 1. Growth and structural characterization of monocrystalline α - V_2O_5 nanoflakes. (a) Schematic of the PVD setup for the growth of monocrystalline α - V_2O_5 nanoflakes. (b-g) Optical micrographs of representative α - V_2O_5 nanoflakes. Arrows mark the [100] and [001] crystallographic directions. Scale bar: 10 μm . (h) Length distribution of the α - V_2O_5 nanoflakes, showing that most flakes exceed 100 μm . (i) Width distribution of the α - V_2O_5 nanoflakes. (j) Schematic crystal structure of α - V_2O_5 , with lattice constants $a = 1.15$ nm, $b = 0.36$ nm, and $c = 0.44$ nm. Blue and yellow spheres denote V and O atoms, respectively. The three nonequivalent oxygen sites are labeled O1-O3. The weakly coupled vdW layers along the [010] direction are denoted as L1 and L2. (k) AFM topography of the region outlined by the white dashed box in panel (e), together with the corresponding height profile taken along the white dashed line. (l) Raman spectrum of the α - V_2O_5 nanoflakes. (m) XRD pattern of the α - V_2O_5 nanoflakes. (n) Low-magnification bright-field TEM image of an individual α - V_2O_5 nanoflake on a lacey carbon grid. (o, p) HRTEM images of the same nanoflake at different magnifications, showing the lattice spacing and high crystallinity. (q) SAED pattern of the corresponding nanoflake.

Importantly, this synthesis strategy enables direct growth of well-dispersed monocrystalline nanoflakes with controllable geometry, including lengths of 50-1000 μm , widths of 10-30 μm , and thicknesses below 100 nm. Unlike approaches that require post-growth exfoliation or ultrasonication [33, 39, 41], this one-step process avoids additional handling that can compromise flake uniformity and introduce structural defects. The resulting combination of large lateral size, nanometer thickness, and high crystalline quality is particularly important for polaritonic nanophotonics, where defects strongly increase optical loss and polariton scattering. Therefore, beyond demonstrating a reliable growth route, this PVD method provides a scalable way to obtain fabrication-ready α - V_2O_5 nanoflakes for low-loss polariton studies and subsequent device patterning. A comparison with alternative synthesis routes is provided in **Table S1** (Supporting Information), showing that our method features a concise process flow without post-

synthesis separation steps, thereby reducing operational complexity and equipment cost while offering high process integration and controllability. The as-grown products combine phase purity, high crystallinity, good dispersion, nanoscale thickness, large lateral dimensions, and regular morphology, achieving an excellent balance between scalable production and structural uniformity. Notably, although a previously reported method was able to grow large crystalline α - V_2O_5 [39], the resulting material was obtained in bulk form and therefore still required mechanical exfoliation to produce nanometer-thick flakes for polariton studies and device fabrication. Such an approach is not truly fabrication-ready, because exfoliation is inherently less controllable and can introduce defects, contamination, and sample-to-sample variability. In contrast, our method directly yields large quantities of ultrathin, large-area monocrystalline nanoflakes with ultralow surface roughness in a single step, without requiring post-growth separation.

The nanoflakes can be transferred through direct adsorption onto clean target substrates, enabling efficient and damage-free deposition with near-unity yield. This capability renders the method inherently suitable for fabrication-ready polaritonics and device integration. In addition, this method operates at moderate temperatures (high-temperature zone below 1000 °C) and under low vacuum (0.1-10 Torr), without metal catalysts or organic additives, and produces no liquid chemical waste. It is fully compatible with silicon-based substrate processing, underscoring its strong process compatibility and environmental friendliness.

At present, the growth substrate contains densely distributed and partially stacked nanoflakes, so transfer and dispersion onto clean SiO₂/Si or quartz substrates remain necessary for detailed characterization and device fabrication. However, transfer is not intrinsically required. Direct growth on device-compatible substrates should be feasible if the substrate can tolerate the PVD growth temperature, but position-controlled growth will require further optimization of substrate placement, precursor flux, nucleation density, and growth kinetics to suppress stacking and define flake locations. For this reason, transfer currently provides a more practical and reproducible route for integrating high-quality α -V₂O₅ nanoflakes with target device substrates.

Overall, our proposed method shows a growth success rate of nearly 100%, meaning that α -V₂O₅ nanoflakes with comparable thicknesses and lateral dimensions can be reproducibly obtained in every batch using the same growth recipe. Statistical AFM measurements confirm smooth surfaces, good thickness uniformity, and high flake-to-flake reproducibility. In addition, each PVD growth run produces a large quantity of α -V₂O₅ nanoflakes on the growth substrate, ensuring a high production yield. Flakes with suitable lateral size and thickness can then be selected and transferred onto target substrates. The transfer process relies on direct adsorption onto clean target substrates, enabling efficient and damage-free deposition with a high success rate. Together with optimized lithography and etching conditions, this enables reliable and reproducible fabrication of α -V₂O₅ micro/nanostructures.

2.2 Temperature-dependent growth mechanism of large-lateral-size α -V₂O₅ nanoflakes

The formation of large-lateral-size α -V₂O₅ nanoflakes is governed by the temperature-dependent growth kinetics in the dual-zone tube furnace (**Fig. 1(a)**). Because V₂O₅ exhibits strong temperature-sensitive crystallization and diffusion behavior [42, 43], the thermal gradient between the source zone and the growth zone plays a decisive role in determining the final crystal morphology. In our growth scheme, the source-zone temperature (Zone 1) was fixed at 960 °C to ensure a stable supply of vapor species, while the growth-zone temperature (T_2 , Zone 2) was systematically varied to regulate nucleation, surface diffusion, and anisotropic crystal growth. The temperature-dependent

products are summarized in **Fig. S3** (Supporting Information). Specifically, at high T_2 (≥ 860 °C), the large thermal budget provides sufficient adatom mobility for crystal growth along multiple crystallographic directions, leading to bulk α -V₂O₅ crystals with millimeter-scale dimensions. In this regime, rapid diffusion and efficient atomic incorporation reduce the kinetic selectivity between different directions, favoring three-dimensional (3D) growth. As T_2 decreases to around 760 °C, the overall growth rate is reduced, and the bulk crystals shrink into smaller crystalline islands. In the range 660 °C $< T_2 \leq 760$ °C, the products evolve into densely packed microflakes, indicating the onset of kinetically anisotropic growth. However, the relatively high local supersaturation and still-limited directional selectivity in this regime lead to dense nucleation and clustered flake formation, rather than isolated large-area nanoflakes.

A more distinct transition occurs when T_2 is lowered below the melting point of V₂O₅ (~ 670 °C). In this regime, the reduced thermal energy increasingly suppresses out-of-plane crystal thickening [44, 45], while lateral growth within the basal plane remains favorable. As a result, the crystal morphology evolves from bulk-like structures toward 2D nanoflakes. In the intermediate range 610 °C $< T_2 \leq 660$ °C, the thickness decreases sharply to below 300 nm, while lateral extension becomes increasingly pronounced. The emergence of edge protrusions along the [100] direction suggests that the growth kinetics become strongly anisotropic, with the specific in-plane directions remaining active even as vertical growth is suppressed.

This temperature-dependent evolution can be understood from the intrinsically anisotropic crystal structure of α -V₂O₅. The crystal is composed of corner- and edge-sharing VO₅ square pyramids, forming layered networks with strong in-plane bonding and comparatively weak interlayer coupling. Such bonding anisotropy naturally leads to direction-dependent growth barriers. At high temperatures, these barriers can all be overcome, so crystal growth proceeds along both in-plane and out-of-plane directions, resulting in thick bulk crystals. As the temperature decreases, the available thermal energy is no longer sufficient to sustain comparable growth rates in all directions. The more weakly favored directions, especially out-of-plane stacking, are suppressed first, whereas in-plane growth remains operative. This selective suppression is the key reason why the morphology progressively shifts from 3D crystals to 2D flakes. The optimized condition at $T_2 = 610$ °C corresponds to a critical kinetic balance among precursor supply, nucleation density, and anisotropic surface diffusion. At this temperature, out-of-plane growth is sufficiently inhibited to prevent excessive thickening, while in-plane diffusion is still active enough to sustain substantial lateral expansion before growth terminates. Meanwhile, the nucleation density is moderated compared with that at higher T_2 , which helps avoid the formation of densely packed microflake domains and instead promotes the growth of isolated flakes with large lateral dimensions.

When T_2 is further reduced below 560 °C, the thermal energy becomes insufficient even for sustained lateral diffusion and step-edge propagation. Under these conditions, crystal growth is confined to narrow preferential pathways, producing slender nanobelts and eventually quasi-one-dimensional (1D) nanowires (**Fig. S4**, Supporting Information). The accompanying color change to dark blue is consistent with the pronounced reduction in thickness. Raman measurements confirm that all of these temperature-derived structures remain in the α -V₂O₅ phase (**Fig. S5**, Supporting Information), indicating that the temperature mainly regulates crystal morphology rather than phase purity.

Overall, the unusually large lateral size of the α -V₂O₅ nanoflakes arises from an optimized growth window rather than from thickness reduction alone. Temperature-dependent experiments show that their formation is governed by the interplay of multidirectional crystal growth, anisotropic bonding, surface diffusion, and nucleation density. Near 610 °C, this balance suppresses vertical growth, preserves lateral expansion, and avoids excessive nucleation, thereby enabling the direct growth of ultrathin, large-area monocrystalline nanoflakes.

2.3 Simulations on mid-infrared hyperbolic phonon polaritons of α -V₂O₅ nanoflakes

As a biaxial crystal, α -V₂O₅ exhibits distinct permittivity components along its three principal axes, $\epsilon_x \neq \epsilon_y \neq \epsilon_z$, which gives rise to strongly anisotropic phonon polaritonic responses in the mid-infrared regime. In the spectral range of 506-1050 cm⁻¹, α -V₂O₅ supports three Reststrahlen bands (RBs), associated with infrared-active phonon modes polarized along different crystallographic directions. The frequency-dependent dielectric tensor is described by the Lorentz oscillator model [33],

$$\epsilon_j = \epsilon_j^\infty \left(1 + \frac{(\omega_{LO}^j)^2 - (\omega_{TO}^j)^2}{(\omega_{TO}^j)^2 - \omega^2 - i\Gamma_j} \right), (j = x, y, z) \quad (1)$$

Where ϵ_j^∞ is the high-frequency dielectric constant, ω_{LO}^j and ω_{TO}^j are the longitudinal and transverse optical phonon frequencies, and Γ_j is the damping factor. For the tens-of-nanometer thick α -V₂O₅ nanoflakes studied here, quantum-confinement effects are negligible, so the phonon frequencies and lifetimes can be treated as thickness-independent. The dielectric parameters for Bands 1 and 2 were taken from previous work [33], while those for Band 3 were fitted to match the experimental results discussed below (**Table S2**, Supporting Information). Band 1 (506-842 cm⁻¹) originates from phonon modes polarized along [001] (y -axis), Band 2 (765-952 cm⁻¹) from modes polarized along [100] (x -axis), and Band 3 (994-1050 cm⁻¹) from modes polarized along [010] (z -axis). As shown in **Fig. 2(a) and 2(b)**, at least one principal permittivity component becomes negative across the 506-1050 cm⁻¹ range, enabling hyperbolic polaritonic responses in all three RBs, with the

hyperbolic axis depending on the band. Each sign reversal of $\text{Re}(\epsilon)$ is accompanied by enhanced $\text{Im}(\epsilon)$ in the same spectral region, consistent with the underlying phonon resonance. Based on the calculated dielectric tensor, the PhP isofrequency surfaces were obtained from the characteristic equation for wave propagation in anisotropic media [46]. For clarity, only $\text{Re}(\epsilon)$ was used in these calculations. For an α -V₂O₅ nanoflake with surface normal along [010] (z -axis), the calculated isofrequency surfaces in the three RBs consist of one closed surface near the origin and two open lobes (**Fig. 2(c)-2(e)**). These open lobes correspond to highly confined polaritonic modes and determine the in-plane propagation characteristics. In Bands 1 and 2, where the in-plane permittivity components have opposite signs, the projected in-plane isofrequency contours exhibit hyperbolic shapes (**Fig. 2(f) and 2(g)**), indicating hyperbolic in-plane propagation. The propagation direction of the polaritons is determined by the local normal to the isofrequency contour (**Fig. 2(f) and 2(g), red arrows**). In contrast, Band 3 shows an elliptical in-plane contour (**Fig. 2(h)**), because both in-plane permittivity components are positive, although unequal. Thus, owing to its biaxial dielectric response, α -V₂O₅ supports band-dependent in-plane polariton propagation, changing from hyperbolic in Bands 1 and 2 to elliptical in Band 3.

To further describe the guided PhP modes in realistic nanoflakes, we calculated the frequency-dependent in-plane dispersion, $\omega[\text{Re}(q_x), \text{Re}(q_y)]$, for a 44 nm-thick α -V₂O₅ slab on SiO₂ with air cladding. In Bands 1 and 2, the open contours confirm hyperbolic in-plane PhP dispersion (**Fig. 2(j) and 2(k)**), arising from the opposite signs of the in-plane permittivity components. In Band 3, the contour becomes elliptical (**Fig. 2(l)**) because both in-plane permittivities are positive but anisotropic. These calculations establish the band-dependent in-plane polaritonic topology of biaxial α -V₂O₅, providing the basis for understanding the propagation patterns and near-field distributions observed experimentally in the following sections.

The dispersion relation, ω - $\vec{q}$ relation, along a given propagation direction is obtained from the intersection of the corresponding isofrequency contour with a plane passing through the origin and oriented along the wavevector $\vec{q}$ [46]. **Figure 2(i)** shows the calculated dispersion relations for polaritons propagating along the [100] and [001] directions, revealing pronounced in-plane anisotropy. Specifically, in Band 1, only HPhPs propagating along the [001] direction are supported, with the wavevector $\vec{q}$ increasing monotonically with frequency ω . A similar positive correlation between $\vec{q}$ and ω is found in Band 2, where the polaritons propagate exclusively along the [100] direction. In contrast, in Band 3 type I HPhPs propagate along both the [001] and [100] directions, and $\vec{q}$ decreases as ω increases. The group velocity, $v_g = \partial\omega/\partial q$, is obtained by numerically differentiating the dispersion curves along a specific direction. Bands 1 and 2 exhibit normal dispersion with $v_g > 0$, whereas Band 3 shows anomalous dispersion with $v_g < 0$ (**Fig. 2(i)**).

To further examine the in-plane anisotropic response of HPhPs in α -V₂O₅ under spatial confinement, we carried out numerical simulations of the near-field distributions in patterned micro-/nanostructures. This allows us to directly connect the intrinsic polariton dispersion to the propagation and confinement behavior in realistic device geometries.

Such analysis is particularly important for assessing the suitability of nanoscale α -V₂O₅ flakes for structured polaritonic devices, a direction that has remained largely unexplored because fabrication-ready vdW α -V₂O₅ flakes with sufficiently large

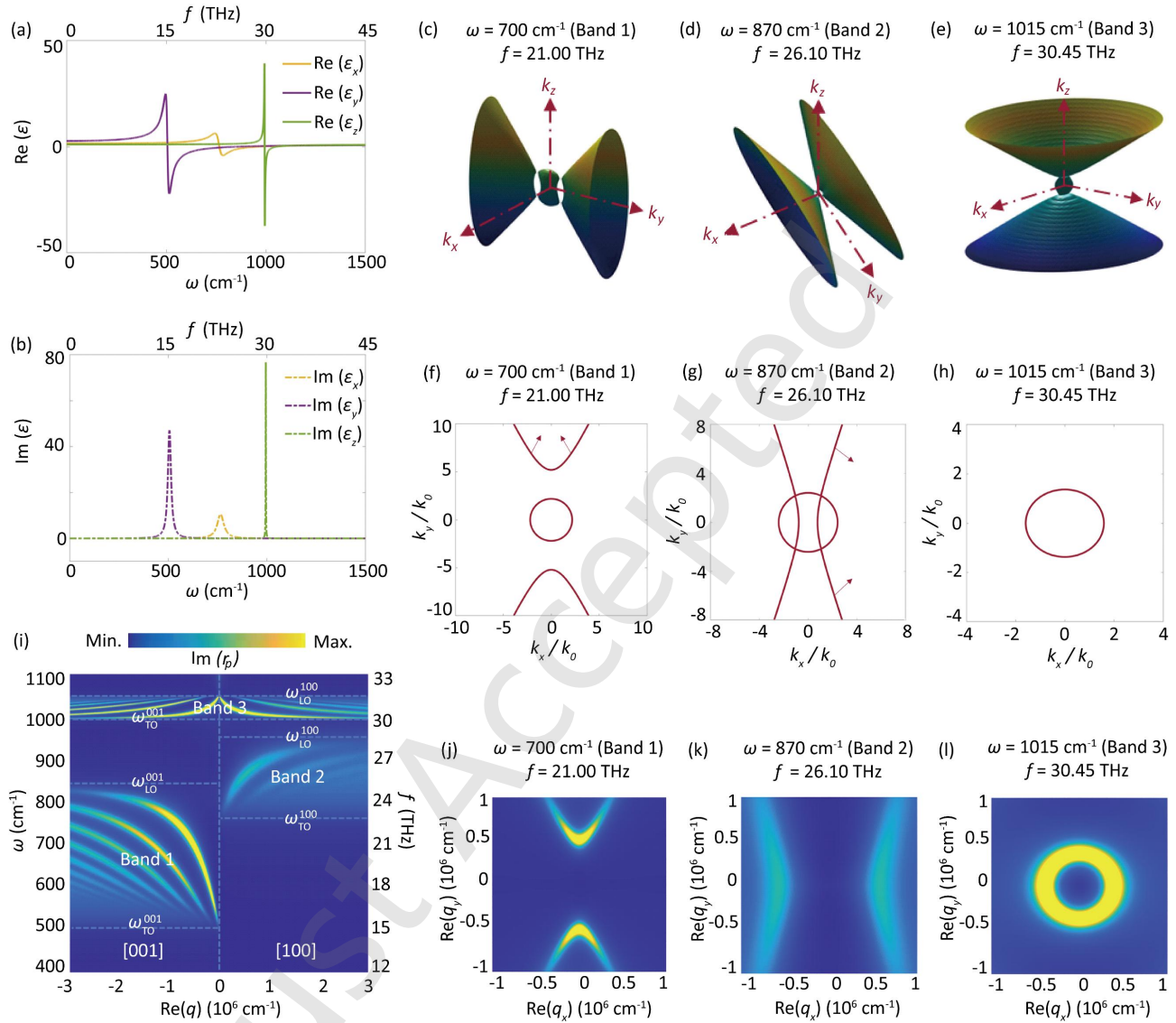


Figure 2. Simulated mid-infrared hyperbolic polariton responses of α -V₂O₅. (a, b) Real (a) and imaginary (b) parts of the permittivity components along the three principal axes, respectively. (c-e) Simulated 3D isofrequency surfaces in the three Reststrahlen bands, showing the biaxial hyperbolic dispersion of bulk α -V₂O₅. (f-h) In-plane isofrequency contours in the x - y plane at representative frequencies of 700, 870, and 1015 cm⁻¹, respectively. Red arrows indicate the propagation directions of the hyperbolic PhP modes at 700 and 870 cm⁻¹. (i) Calculated PhP dispersion relations along the [001] and [100] crystalline directions of the α -V₂O₅ nanoflake. The pseudocolor map shows the imaginary part of the complex reflectivity, $\text{Im}[r_p(q, \omega)]$, for the air/ α -V₂O₅/SiO₂ multilayer structure. (j-l) Simulated in-plane dispersion contours of the PhP modes at 700 cm⁻¹ (Band 1) (j), 870 cm⁻¹ (Band 2) (k), and 1015 cm⁻¹ (Band 3) (l), respectively. The thickness of the nanoflake corresponding to (i-l) is 44 nm.

lateral size have not previously been available for micropatterning. We chose circular α -V₂O₅ microdisks as a model system because their symmetric boundaries provide a simple and robust platform for revealing anisotropic polariton propagation under confinement. In such a geometry, polariton waves launched inside the disk are reflected back toward the interior, generating clear interference patterns that sensitively encode the underlying in-plane anisotropy. Rather than relying solely on full

numerical simulations, we describe these patterns using a phenomenological multi-beam interference model [47]. To capture the essential physics while keeping the analysis transparent, the model considers only reflections from boundaries locally perpendicular to the polariton wavevector, so that the dominant interference arises from the superposition of a forward-propagating polariton wave and its antiparallel back-reflected counterpart.

Distinct from the concentric rings of isotropic polaritons,

HPhPs in α -V₂O₅ microdisks produce strongly anisotropic frequency-dependent interference patterns. In Bands 1 and 2 with in-plane hyperbolicity, the calculated near fields show bright and dark curved fringes aligned along the y - and x -axes, respectively (**Fig. 3(a)-3(d)**, **3(j)-3(m)**). This behavior reflects the highly directional propagation of HPhPs in these two bands. By contrast, in Band 3, the simulations reveal

concentric elliptical fringes (**Fig. 3(e)**, **3(f)**, **3(n)**, and **3(o)**), indicating that polariton propagation is allowed over all in-plane azimuthal directions. The fringe ellipticity directly reflects the in-plane elliptical dispersion. For a fixed disk size, the interference pattern evolves systematically with frequency. In Bands 1 and 2, increasing frequency leads to narrower fringes, smaller fringe spacing, and a more

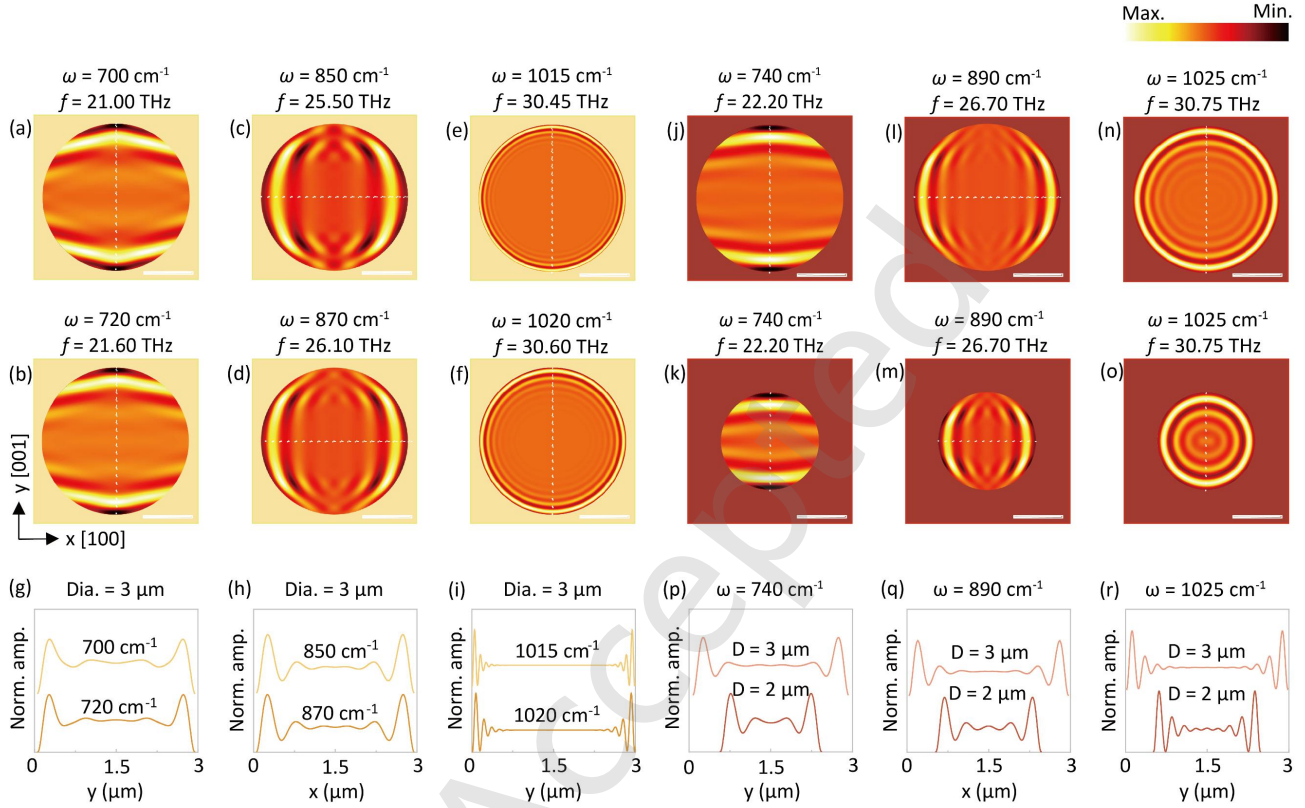


Figure 3. Calculated interference patterns and corresponding normalized amplitude profiles of α -V₂O₅ microdisks obtained using the phenomenological model. (a-f) Interference patterns of a 3 μ m-diameter, 44 nm-thick α -V₂O₅ microdisk at different excitation frequencies. Scale bars: 1 μ m. **(g-i)** Normalized amplitude profiles extracted along the white dashed lines in **(a-f)**. **(j-o)** Interference patterns of α -V₂O₅ microdisks of different diameters. Scale bars: 1 μ m. **(p-r)** Normalized amplitude profiles extracted along the white dashed lines in **(j-o)**.

contracted overall pattern, consistent with the increase in polariton wavevector and stronger field confinement. In Band 3, the opposite trend is observed: as frequency increases, the fringes broaden and the pattern expands, reflecting the decrease in wavevector and weaker confinement. These trends are consistent with the anomalous dispersion in this band and are quantitatively confirmed by the line profiles in **Fig. 3(g)-3(i)**.

The disk size also strongly affects the confined field distribution. Reducing the disk diameter from 3 μ m to 2 μ m preserves the fringe orientation but compresses the overall pattern, decreases the number of fringes, and reduces their spacing (**Fig. 3(j)-3(o)**), indicating enhanced confinement. At frequencies of 890 cm⁻¹ and 1025 cm⁻¹, respectively, the interference fringes in the 2 μ m-diameter disks collapse into an elongated bright spot and an elliptical bright spot at the center due to their finite size (**Fig. 3(m)** and **3(o)**). **Figure 3(p)-3(r)** show the normalized amplitude profiles extracted along the white dashed lines in **Fig. 3(j)-3(o)**, which quantitatively corroborate the aforementioned pattern

evolution. As the disk diameter decreases from 3 μ m to 2 μ m, increased peak amplitude, decreased full-width at half-maximum (FWHM), and reduced peak separation are observed at all frequencies, indicating enhanced electromagnetic field confinement. In **Fig. 3(q)** and **3(r)**, the central peak corresponds to the interference bright spot at the disk center. If the disk size is further reduced so that the round-trip path of the boundary-reflected HPhPs falls within their propagation length, strong interference can build up at the disk center. As the disk size decreases, the central intensity is expected to oscillate between a dark and a bright spot, such that the entire disk effectively behaves as a Fabry-Pérot cavity (**Fig. S6**, Supporting Information). These results clarify how spatial confinement reshapes the propagation and interference of anisotropic HPhPs in α -V₂O₅, and show that both excitation frequency and disk size provide effective means to tailor the local near-field distribution in patterned structures.

2.4 Nano-imaging of low-loss anisotropic phonon

polaritons in α -V₂O₅ nanoflakes and microdisks

As discussed above, the intrinsic in-plane anisotropic polaritonic response of α -V₂O₅ nanoflakes, predicted by theoretical analysis and numerical simulations, was experimentally examined by scattering-type scanning near-field optical microscopy (s-SNOM). To this end, a sharp metal-coated AFM tip with curvature radius $r \approx 20$ nm acts

as a nano-antenna that concentrates the incident mid-infrared light into the nanoscale gap at the tip-sample junction. This highly confined near field supplies the large in-plane momentum required to launch propagating HPhPs with wavelength λ_p on the α -V₂O₅ surface. The launched HPhPs propagate until they are reflected by the flake edges, and the interference between the forward and reflected waves generates standing-wave fringes with a period of $\lambda_p/2$. By raster-scanning the tip across

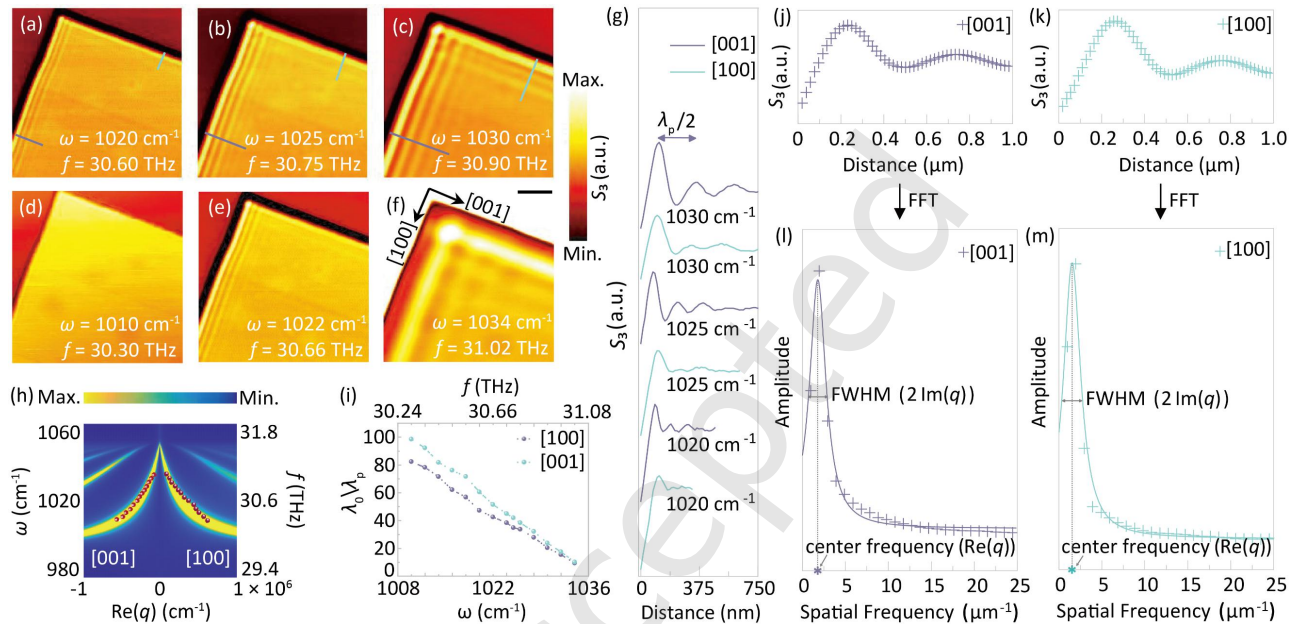


Figure 4. Real-space imaging of the HPhPs on the surface of a natural 44 nm-thick α -V₂O₅ nanoflake. (a–f) s-SNOM images acquired under different illumination frequencies ω . (g) Near-field optical amplitude profiles along the [100] (cyan) and [001] (purple) directions, extracted from (a–c). (h) Dispersion relation for the HPhPs in Band 3. The red and brown data points correspond to the wavevectors extracted from s-SNOM measurements along the [001] and [100] directions, respectively, at multiple excitation frequencies. (i) Electromagnetic confinement of the HPhPs across the range of illumination frequencies ω . (j, k) Near-field optical amplitude profiles along the [100] (cyan) and [001] (purple) directions at an illumination frequency ω of 1034 cm⁻¹. (l, m) Fourier transforms of profiles (j) and (k), respectively. Solid lines represent Lorentzian function fits.

the flake, we directly mapped the near-field amplitude distributions of these standing-wave patterns, thereby imaging the polaritonic modes in real space. All measurements were performed on a high-quality monocrystalline α -V₂O₅ nanoflake synthesized by the PVD method described above. The s-SNOM study focused on a 44 nm-thick flake with two orthogonal natural cleavage edges aligned along the [100] (Edge I) and [001] (Edge II) crystallographic directions, respectively. These two edges are naturally present in typical as-grown α -V₂O₅ nanoflakes, enabling direct and quantitative comparison of PhP propagation along the two principal in-plane crystallographic axes.

Because the available quantum cascade laser (QCL) source (Methods) used in our current study only covers the spectral range of Band 3, our experimental study focuses on this band rather than Bands 1 and 2. Under excitation within Band 3 (1010–1034 cm⁻¹), clear polaritonic interference fringes are observed parallel to both the [100] and [001] edges (Fig. 4(a)–4(f)). This behavior is consistent with the in-plane elliptical dispersion of HPhPs in α -V₂O₅: the elliptical isofrequency contour allows propagation in all in-

plane azimuthal directions, but with direction-dependent wavelengths. As a result, at the same excitation frequency, the fringe periods measured perpendicular to Edge I and Edge II are different. To quantify this anisotropy, near-field amplitude line profiles were extracted perpendicular to each edge (solid cyan and purple lines in Fig. 4(a)–4(c)). As shown in Fig. 4(g), the profiles exhibit maxima near the edges followed by series of damped oscillations with increasing distance, characteristic of lossy PhP propagation. The polariton wavelength λ_p at each frequency was determined as twice the peak-to-peak spacing of the interference fringes. The extracted wavelengths for propagation along the [100] and [001] directions over the 1010–1034 cm⁻¹ range are summarized in Fig. S7(a).

The polaritonic dispersion relation is determined as $\omega(\mathbf{q})$, where $\mathbf{q}$ is the polariton wavevector with magnitude $|\mathbf{q}| = 2\pi/\lambda_p$ [46]. The experimentally extracted dispersion of the α -V₂O₅ nanoflake agrees well with the theoretical prediction, as shown by the two-dimensional pseudocolor map of the complex reflectivity in Fig. 4(h) (Supplementary Section S9). The low-loss propagation and long polariton lifetime are further supported by the exceptionally small

group velocities, v_g , derived from the dispersion curves. Linear fitting yields $v_g[001] \approx 0.00032c$ and $v_g[100] \approx 0.00027c$ in Band 3. These values are substantially smaller than those reported for HPhPs in natural hBN ($v_g \approx 0.027c$) and α -MoO₃ in Band 3 ($v_g[001] \approx 0.0015c$, $v_g[100] \approx 0.0011c$) (Table 1) [30, 31]. In addition, the electromagnetic field confinement factor, defined as q/q_0 and obtained from the dispersion relation, reaches ~ 98 at 1010 cm^{-1} (Fig. 4(i)), indicating deep-subwavelength confinement.

Beyond the group velocity, the propagation quality factor Q , defined as $\text{Re}(q)/\text{Im}(q)$, provides another useful metric for evaluating phonon polariton propagation. For the α -V₂O₅ nanoflake, Q values were extracted from amplitude profiles obtained from s-SNOM images over the 1012 - 1034 cm^{-1} range. As shown in Fig. 4(j) and 4(k), these spatial profiles were transformed into the spatial-frequency domain by fast Fourier transform (FFT) (Fig. 4(l) and 4(m)), and the resulting spectra were fitted with Lorentzian functions (solid

Table 1. Comparative summary of phonon polariton properties in representative van der Waals materials.

Material	Conductivity	Bandgap	Reststrahlen bands	PhP dispersion	Confinement factor	PhP group velocities	PhP lifetime
hBN (Natural abundance) [30]	Insulator	$\sim 6.0 \text{ eV}$	Type I RB: 760 - 825 cm^{-1} Type II RB: 1360 - 1610 cm^{-1}	In-plane isotropic; hyperbolic out-of-plane	25	$v_g \approx 0.027c$	$\tau[\text{type II}] \approx 0.8 \text{ ps}$
α-MoO₃ (Natural abundance)	n-type semiconductor [15]	Indirect, $\sim 3.0 \text{ eV}$ [15]	Band 1: 545 - 851 cm^{-1} ; Band 2: 820 - 972 cm^{-1} ; Band 3: 958 - 1010 cm^{-1} [46]	Band 1: in-plane hyperbolic Band 2: in-plane hyperbolic Band 3: in-plane elliptical [46]	~ 87 at 953 cm^{-1} [46]	Band 3: $v_g[001] \approx 0.0015c$; $v_g[100] \approx 0.0011c$ [31]	Band 3: $\tau[100] \approx 8 \text{ ps}$ [31]
α-V₂O₅ (natural abundance, this work)	n-type semiconductor [41]	Direct, 2.2 - 2.7 eV [41]	Band 1: 506 - 842 cm^{-1} ; Band 2: 765 - 952 cm^{-1} ; Band 3: 994 - 1050 cm^{-1}	Band 1: in-plane hyperbolic Band 2: in-plane hyperbolic Band 3: in-plane elliptical	~ 98 at 1010 cm^{-1}	Band 3: $v_g[001] \approx 0.0003c$; $v_g[100] \approx 0.0003c$	Band 3: $\tau[100] \approx 9 \text{ ps}$; $\tau[001] \approx 8 \text{ ps}$

curves). This analysis yields the central peak position, corresponding to $\text{Re}(q)$, and the FWHM, corresponding to double $\text{Im}(q)$. The extracted Q factors range from 1.3 to 1.6 for HPhPs propagating along the $[100]$ direction and from 1.5 to 1.8 along the $[001]$ direction. These values are much smaller than those reported for HPhPs in hBN ($Q \sim 20$) [30]. To further quantify the propagation dynamics, the PhP lifetime τ was estimated from $\tau = L_p/v_g$, where $L_p = 1/\text{Im}(q)$ is the propagation length and v_g is the group velocity obtained from the dispersion analysis (Supplementary Section S9) [33]. The calculated lifetimes reach up to $\sim 8 \text{ ps}$ for HPhPs propagating along $[001]$ and $\sim 9 \text{ ps}$ along $[100]$ within Band 3. These picosecond-scale lifetimes are a clear signature of the low-loss character of HPhPs in α -V₂O₅. Notably, they are comparable to the reported value for high-quality natural α -MoO₃ ($\sim 8 \text{ ps}$) [31], and about seven times longer than that of hBN ($\sim 0.8 \text{ ps}$) (Table 1) [30]. In particular, the lifetime along $[001]$ in our α -V₂O₅ nanoflakes reaches 8 ps , representing an approximately 33% increase over the $\sim 6 \text{ ps}$ reported for mechanically exfoliated α -V₂O₅ flakes [33]. This improvement further reflects the high crystalline quality and purity of the nanoflakes grown by our method, which avoids the impurities and defects that can be introduced during mechanical exfoliation and may degrade

polariton oscillations. It should be noted that although the extracted Q factors are lower than those of hBN, this does not contradict the longer lifetimes observed here, because the markedly reduced group velocity in α -V₂O₅ prolongs the time required for polaritons to decay during propagation. To summarize (Table 1), compared with hBN and α -MoO₃, α -V₂O₅ not only supports in-plane anisotropic and low-loss HPhPs, but also exhibits a higher confinement factor (~ 98), slower polariton group velocities ($\sim 0.0003c$), and longer polariton lifetimes of up to 9 ps . Furthermore, as an n-type semiconductor with a bandgap of 2.2 - 2.7 eV , α -V₂O₅ offers more favorable electrical functionality than wide-bandgap insulating hBN and indirect-bandgap α -MoO₃, thereby extending its potential applicability to active polaritonic and optoelectronic devices.

The microstructures discussed above provide an effective route for spatial confinement and tailoring of the electromagnetic field. However, such functionality has remained largely unexplored in α -V₂O₅, mainly because previously reported studies relied on mechanically exfoliated flakes, which typically suffer from limited lateral size, irregular geometry, and poor controllability for micro-/nanopatterning. As a result, earlier work could only implement metallic antennas on α -V₂O₅ surfaces to locally

launch and visualize in-plane polariton modes, rather than directly patterning the crystal itself into functional polaritonic structures [32]. In contrast, the α -V₂O₅ nanoflakes synthesized by our method are intrinsically fabrication-ready. The products are large-area, free-standing, atomically flat, and monocrystalline, and can therefore be directly patterned into designed microstructures. This capability allows us, for the first time, to directly observe geometrically confined PhP modes in intrinsic α -V₂O₅ microstructures. Specifically, the α -V₂O₅ microdisks were

fabricated by reactive ion etching (RIE) (**Fig. 5(a)**; detailed procedures are described in the Methods). The resulting structure consists of a 39 nm-thick α -V₂O₅ layer on a 300 nm-thick SiO₂ substrate. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images (**Fig. 5(b)** and **5(c)**) confirm that the fabricated microdisks have well-defined circular geometries. The mean surface roughness in the central region of the microdisk, measured within the white dashed box in **Fig. 5(c)**, is approximately 3.8 nm. This value corresponds to only 1.12%

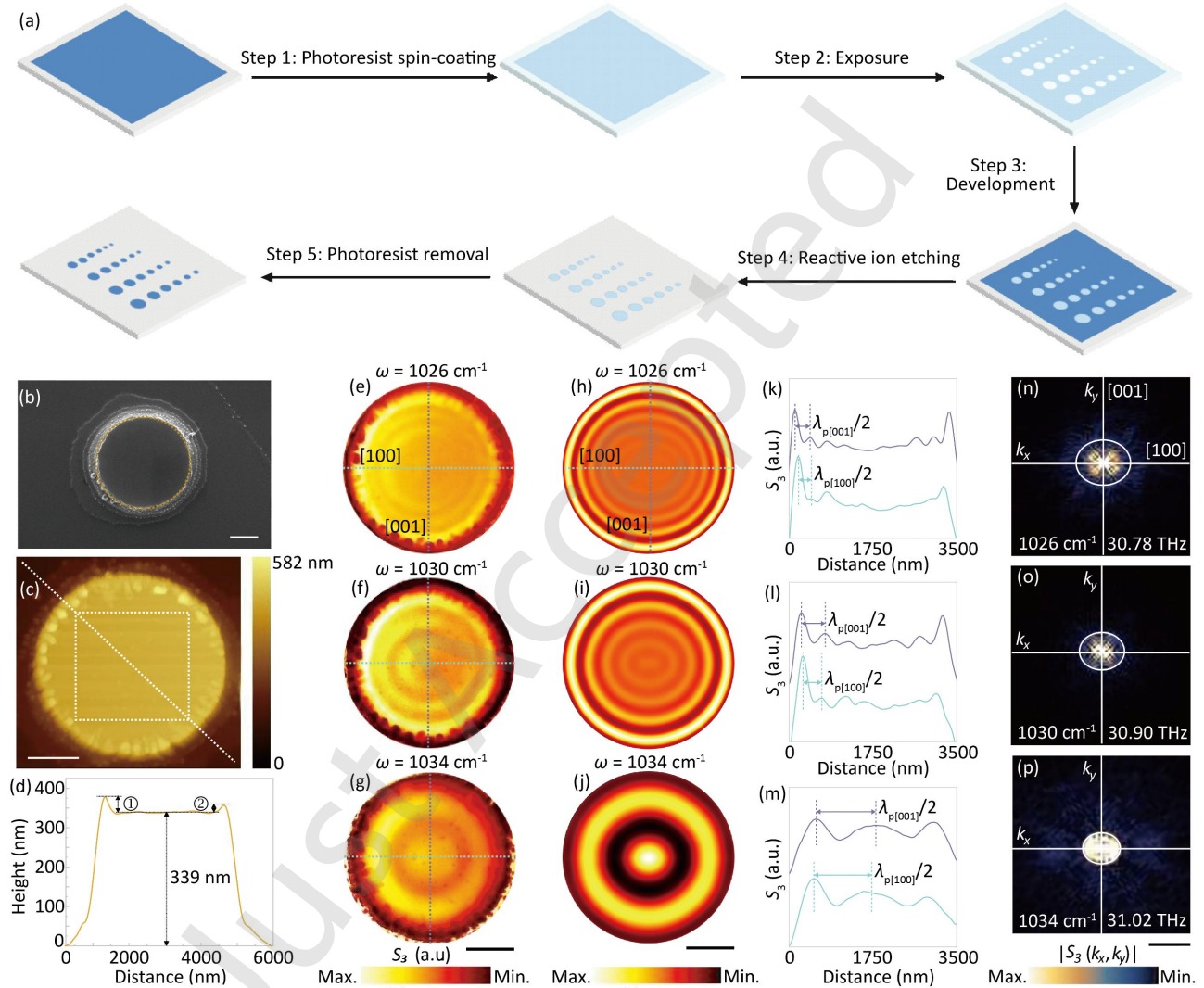


Figure 5. The fabrication process, structural morphology, and anisotropic PhP interference characteristics of α -V₂O₅ microdisk cavities. (a) Schematic illustration of the fabrication process for α -V₂O₅ microdisk cavities. (b) SEM image of an α -V₂O₅ microdisk on a Si substrate. The disk structure consists of an upper α -V₂O₅ layer overlying a SiO₂ layer. The α -V₂O₅ boundaries are marked with yellow dashed circles. Scale bar: 1 μ m. (c) AFM morphology of the α -V₂O₅ microdisk shown in (b). The mean roughness in the central region of the microdisk (within the white dashed box in (c)) is measured to be approximately 3.8 nm. Scale bar: 1 μ m. (d) Height profile along the white dashed line in the corresponding AFM image (c). The total height of 339 nm, indicated by the dashed arrow, is composed of 300 nm SiO₂ and 39 nm α -V₂O₅. Region ① exhibits a height of 40 nm, while Region ② exhibits a height of 18 nm. (e-g) s-SNOM images of the α -V₂O₅ microdisk (radius = 1.5 μ m; thickness = 39 nm) acquired at different excitation frequencies. The dashed lines indicate the [100] and [001] directions. Scale bar: 1 μ m. (h-j) Calculated interference patterns of a 1.5 μ m-radius, 39 nm-thick microdisk at different excitation frequencies using the phenomenological model. (k-m) Experimental amplitude profiles extracted along the cyan and purple dashed lines indicated in (e-g). (n-p) Absolute values of the Fourier transforms of the near-field images corresponding to (e-g). The white dashed lines depict the isofrequency curves. The scale bar represents $5k_0$, where k_0 is the momentum of light in free space.

of the total etch depth of 339 nm, indicating good surface uniformity after etching. Together with the well-preserved circular boundary, these results demonstrate the reliability

of the fabrication process.

The edge profile extracted along the dashed line in the AFM image (**Fig. 5(c)** and **5(d)**) shows a sidewall roughness

of approximately 18-40 nm. This topographic fluctuation is smaller than the measured polariton wavelength range of 1010-1040 nm, and is therefore unlikely to significantly perturb the overall polariton reflection at the microdisk boundary. The local edge protrusions visible in the AFM topography are therefore expected to have only a minor influence on the global interference pattern. The relatively sharp etched boundaries provide effective reflection of propagating phonon polaritons. The real-space polaritonic interference patterns within these microcavities were subsequently visualized by s-SNOM. In Band 3, the near-field amplitude maps display distinct concentric elliptical fringes (**Fig. 5(e)-5(g)**), directly evidencing anisotropic phonon polariton propagation over all in-plane azimuthal directions. As the excitation frequency increases, both the fringe width and fringe spacing increase, indicating a corresponding increase in polariton wavelength. Because of the finite disk size, the innermost fringe gradually collapses into a central elliptical bright spot at 1030 and 1034 cm^{-1} . The experimentally observed near-field patterns agree well with the calculated results (**Fig. 5(h)-5(j)**), supporting the reliability of both the measurements and the model. **Figure 5(k)-5(m)** shows the normalized amplitude profiles extracted along the purple and cyan dashed lines in **Fig. 5(e)-5(g)**, which quantitatively confirm this evolution. The longer fringe period along the vertical axis indicates a larger λ_p in that direction, identifying the vertical minor axis of the ellipse as the crystallographic [001] direction, and the horizontal major axis as the [100] direction. Fourier transformation of the s-SNOM images yields the corresponding momentum-space maps (**Fig. 5(n)-5(p)**), which display clear elliptical isofrequency contours. These contours provide direct experimental evidence that the supported HPhPs in $\alpha\text{-V}_2\text{O}_5$ possess elliptical dispersion, in full agreement with the calculated in-plane isofrequency contours in the x - y plane (**Fig. 2(h)**). Moreover, the contours contract as the excitation frequency increases, consistent with the anomalous dispersion of $\alpha\text{-V}_2\text{O}_5$ in Band 3. The successful patterning of these high-quality $\alpha\text{-V}_2\text{O}_5$ microdisks, together with the precise experimental verification of their anisotropic polaritonic response, highlights the value of our fabrication-ready $\alpha\text{-V}_2\text{O}_5$ platform. More broadly, the ability to directly pattern large-area, monocrystalline $\alpha\text{-V}_2\text{O}_5$ nanoflakes into well-defined microstructures that sustain low-loss, anisotropic phonon polaritons establishes this material as a promising platform for infrared flat photonics with versatile subwavelength field manipulations.

3. Conclusion

In summary, we have developed a facile PVD method for the growth of large-area, high-quality monocrystalline $\alpha\text{-V}_2\text{O}_5$ nanoflakes, and clarified the underlying anisotropic growth mechanism arising from their layered crystal structure. Under the optimized growth condition of 610 $^\circ\text{C}$, the nanoflakes exhibit large lateral dimensions, uniform

thickness, and low defect density, making them well suited for low-loss PhP propagation. A key advantage of this method is that it directly yields fabrication-ready $\alpha\text{-V}_2\text{O}_5$ nanoflakes without post-growth exfoliation, thereby avoiding the limited controllability, defect generation, and contamination often associated with mechanical exfoliation.

Through theoretical analysis, numerical simulations, and infrared s-SNOM measurements, we reveal in-plane anisotropic polaritonic responses in these nanoflakes. The calculations predict hyperbolic and elliptical PhP dispersions across the three Reststrahlen bands of biaxial $\alpha\text{-V}_2\text{O}_5$, while simulations capture the confined interference patterns in microdisk cavities. Experimentally, the HPhPs in $\alpha\text{-V}_2\text{O}_5$ exhibit deep-subwavelength confinement, slow group velocities, and long lifetimes of up to 9 ps, highlighting the low-loss nature of this material platform. Furthermore, by directly patterning high-quality $\alpha\text{-V}_2\text{O}_5$ flakes into microstructures, we demonstrate deterministic control of anisotropic mid-infrared field localization through geometric confinement, in excellent agreement with simulations.

Our work advances the understanding of anisotropic growth in vdW oxides and expands the family of fabrication-ready low-loss PhP materials beyond hBN and $\alpha\text{-MoO}_3$. By bridging scalable synthesis, direct patterning, and low-loss anisotropic polaritonics, our work highlights $\alpha\text{-V}_2\text{O}_5$ as a compelling vdW material platform for next-generation infrared planar nanophotonics.

4. Methods

4.1 Growth of the $\alpha\text{-V}_2\text{O}_5$ vdW monocrystalline nanoflakes

The $\alpha\text{-V}_2\text{O}_5$ vdW monocrystalline nanoflakes were synthesized via PVD in a tube furnace. High-purity V_2O_5 powder (99.99%, 1 g) as the source material was positioned at the center of the high-temperature zone, while a cleaned quartz or SiO_2/Si substrate was placed in the transition region between the high- and low-temperature zones. The high-temperature zone was heated to 960 $^\circ\text{C}$ and maintained at this temperature for 3 h, and the low-temperature zone was followed by heating to 610 $^\circ\text{C}$ with an identical holding duration. During this process, V_2O_5 sublimed from the source and recrystallized onto the substrate. Subsequent natural cooling to room temperature yielded $\alpha\text{-V}_2\text{O}_5$ nanoflakes with thicknesses ranging from ~ 10 to 100 nm on the substrate (**Fig. 1(a)**).

4.2 Near-field optical imaging

Near-field optical measurements were performed using an s-SNOM (NeaSNOM, Neaspec GmbH) combined with an atomic force microscope. This setup enables the simultaneous mapping of the near-field optical response and topography. A tunable mid-infrared quantum cascade laser (Daylight Solutions) covering 860-1200 cm^{-1} was focused onto the sample via a metallized AFM probe tip (Arrow-IrPt,

NanoWorld; apex radius ~ 25 nm) to image the HPhPs in real space. The AFM operated in tapping mode, with the tip oscillating vertically at its resonance frequency $f = 260$ kHz. The backscattered light was collected using a mercury cadmium telluride (MCT) detector (Kolmar Technologies). The near-field optical signal $E_s(x, y)$ was extracted from the background scattering using pseudo-heterodyne interferometry and demodulated at a higher harmonic of the tip oscillation frequency f_n (typically $n \geq 3$). Both the amplitude and phase of $E_s(x, y)$ were recorded. Specifically, the figures presented herein depict the magnitude $|E_s(x, y)|$.

4.3 Fabrication of α -V₂O₅ microdisks

The as-synthesized α -V₂O₅ nanoflakes were transferred onto a highly resistive silicon substrate with a 300 nm-thick thermal oxide layer. Selected nanoflakes were then patterned into microdisks with a diameter of 3 μ m using a combination of maskless ultraviolet lithography (TTT-07-UV Litho-ACA system) and RIE (Oxford System 100 Cluster). For the lithography step, AR-P 5350 photoresist was used and developed in AR 300-26 developer. The subsequent RIE process was performed using a gas mixture of CF₄ (70 vol.%), O₂ (18 vol.%), and Ar (12 vol.%) at an RF power of 100 W for 25 min.

Electronic Supplementary Material: Supplementary material (Optical image of α -V₂O₅ monocrystalline nanoflakes with lengths exceeding one hundred micrometers; Summary of different synthesis approaches for α -V₂O₅ micro/nanocrystals; The batch-to-batch uniformity of α -V₂O₅ nanoflakes; Optical microscopy images of α -V₂O₅ crystals synthesized at different Zone 2 temperatures; Evolution behavior of α -V₂O₅ from nanobelts to nanowires; Raman spectra of α -V₂O₅ structures synthesized at varied Zone 2 temperatures; Description of principal axis dielectric function parameters for α -V₂O₅ used in theoretical calculations; Calculated interference patterns of α -V₂O₅ nanodisks; Calculation of group velocity and lifetime for HPhPs propagating along the [100] and [001] directions in α -V₂O₅ nanoflakes under Excitation at Band 3) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909117>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic SupplementaryMaterial. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Ying Wu: Investigation, Methodology, Visualization, Writing - original draft, Writing - review & editing, Data curation.

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Wuchao Huang: Formal analysis, Investigation, Data curation.

Ertao Hu: Investigation, Formal analysis.

Huanjun Chen: Conceptualization, Methodology, Project administration, Writing - review & editing, Resources, Funding acquisition, Investigation.

Shaozhi Deng: Conceptualization, Investigation, Funding acquisition, Methodology, Writing - review & editing, Project administration, Resources.

Ningsheng Xu: Conceptualization, Investigation, Funding acquisition, Writing - review & editing, Methodology, Project administration, Resources.

All the authors have approved the final manuscript.

Use of AI statement

None.

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Microcavity confinement of anisotropic phonon polaritons enabled by fabrication-ready monocrystalline α -V₂O₅ flakes

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Section 1. Optical image of α -V₂O₅ monocrystalline nanoflakes with lengths exceeding one hundred micrometers

Figure S1 presents several α -V₂O₅ monocrystalline nanoflakes with lengths exceeding one hundred micrometers. A series of observations and statistical analyses revealed that the as-synthesized α -V₂O₅ monocrystalline nanoflakes exhibit lateral dimensions of 50-1000 μm in length and 10-30 μm in width, with a thickness of ≤ 100 nm. Their large lateral sizes and ultrathin characteristics make them an ideal intrinsic material platform for exploring low-dimensional physical properties and developing high-performance devices. Moreover, the nanoflakes demonstrate exceptional dispersibility, enabling the direct acquisition of discrete single-crystalline entities without the need for additional processing. This unique attribute facilitates fundamental investigations into the intrinsic properties of individual α -V₂O₅ nanostructures.

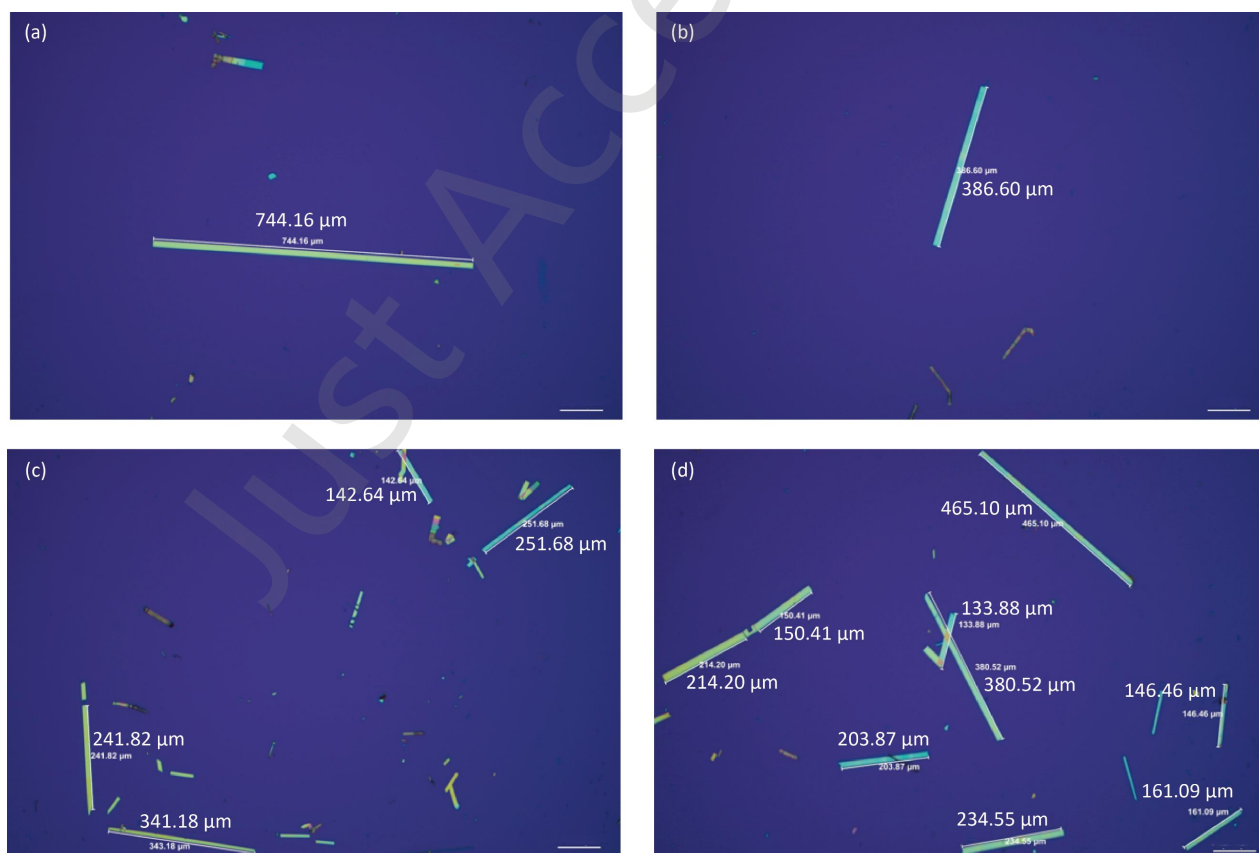


Figure S1. Optical image of α -V₂O₅ monocrystalline nanoflakes. The scale bar corresponds to 100 μm .

Section 2. Summary of different synthesis approaches for α -V₂O₅ micro/nanocrystals

Table S1. Summary of different synthesis approaches for α -V₂O₅ micro/nanocrystals

Sample	Synthesis	Crystallinity	Dimensions (L×W×T)	Separation	Transfer	Roughness	Micro/nano fabrication
α -V ₂ O ₅ bulk crystals[1]	Purification	High-purity	L: 5 cm; W: 1 cm; T: 1 mm	Exfoliation	N/A	N/A	Exfoliation: Partial
α -V ₂ O ₅ bundled nanowires[2]	Hydrothermal	Single-crystal line	L: cm; Dia.: 80-120 nm	Ultrasonication	Ethanol-dispersed	3D stacking	Poor
α -V ₂ O ₅ dispersed nanobelts[3]	CVD	Single-crystal line	L: cm; W: 20-500 nm; T: N/A	N/A	N/A	N/A	Poor
α -V ₂ O ₅ stacked nanoflakes[4]	Solvothermal	Single-crystal line	L: ~100 μ m; W: ~100 μ m; T: ~2-5 nm	Inseparable	Ethanol-dispersed	Locally smooth	Partially
α -V ₂ O ₅ stacked nanoflakes/nanorods[5]	Hydrothermal	N/A	N/A	Inseparable	Cellulose paper-grown	3D stacking	Poor
α -V ₂ O ₅ grass-like nanowires/microwires [6]	PVD	Single-crystal line	L: mm-cm; W: $\leq$ 1 μ m; T: $\leq$ 10 μ m	Ultrasonication	Ethanol-dispersed	Smooth	Partially
V ₂ O ₅ bulk crystals[7]	VLS	Single-crystal line	L: cm; T: N/A	Exfoliation	Scotch tape-assisted	Uneven	Exfoliation: Partial
V ₂ O ₅ film[7]	VLS	Near-single-crystalline	Dia.: 2 inch T: N/A	Inseparable	TRT/PMMA-assisted	0.5-2 nm (avg.)	Compatible
α -V ₂ O ₅ dispersed nanoflakes (this work)	PVD	Single-crystalline	L: 10-1000 μ m; W: 10-30 μ m; T: $\leq$ 100 nm	Separation-free	Direct absorption	0.2-0.9 nm (avg.)	Compatible

NA indicates data not available in the referenced literature.

Section 3. The batch-to-batch uniformity of α -V₂O₅ nanoflakes

Twenty nanoflakes are randomly selected from different growth batches and dispersed on SiO₂/Si substrates for AFM characterization. The nanoflake thicknesses range from 30 to 100 nm, with mean roughness values between 0.26 and 0.94 nm and corresponding RMS roughness between 0.33 and 1.15 nm, as plotted in **Figure S2(a)-S2(c)**. These results demonstrate excellent surface smoothness and high structural uniformity across different samples and batches.

Additionally, Raman spectra are collected from 20 nanoflakes from different batches dispersed on quartz substrates over the spectral range of 90-1100 cm⁻¹. Statistical analysis of the characteristic Raman peaks near 145 cm⁻¹ and 995 cm⁻¹ reveals peak position variations of only 2.19 cm⁻¹ and 1.39 cm⁻¹, respectively (**Figure S2(d)-S2(e)**). The small peak position shift across samples confirms high phase purity and uniformity from batch to batch.

To further verify the single-crystal characteristics of the samples, SAED patterns from two additional independent nanoflakes are added in **Figure S2(f)-S2(i)**. All patterns exhibit well-defined single-crystal diffraction spots, further corroborating the high crystalline uniformity of the as-grown nanoflakes.

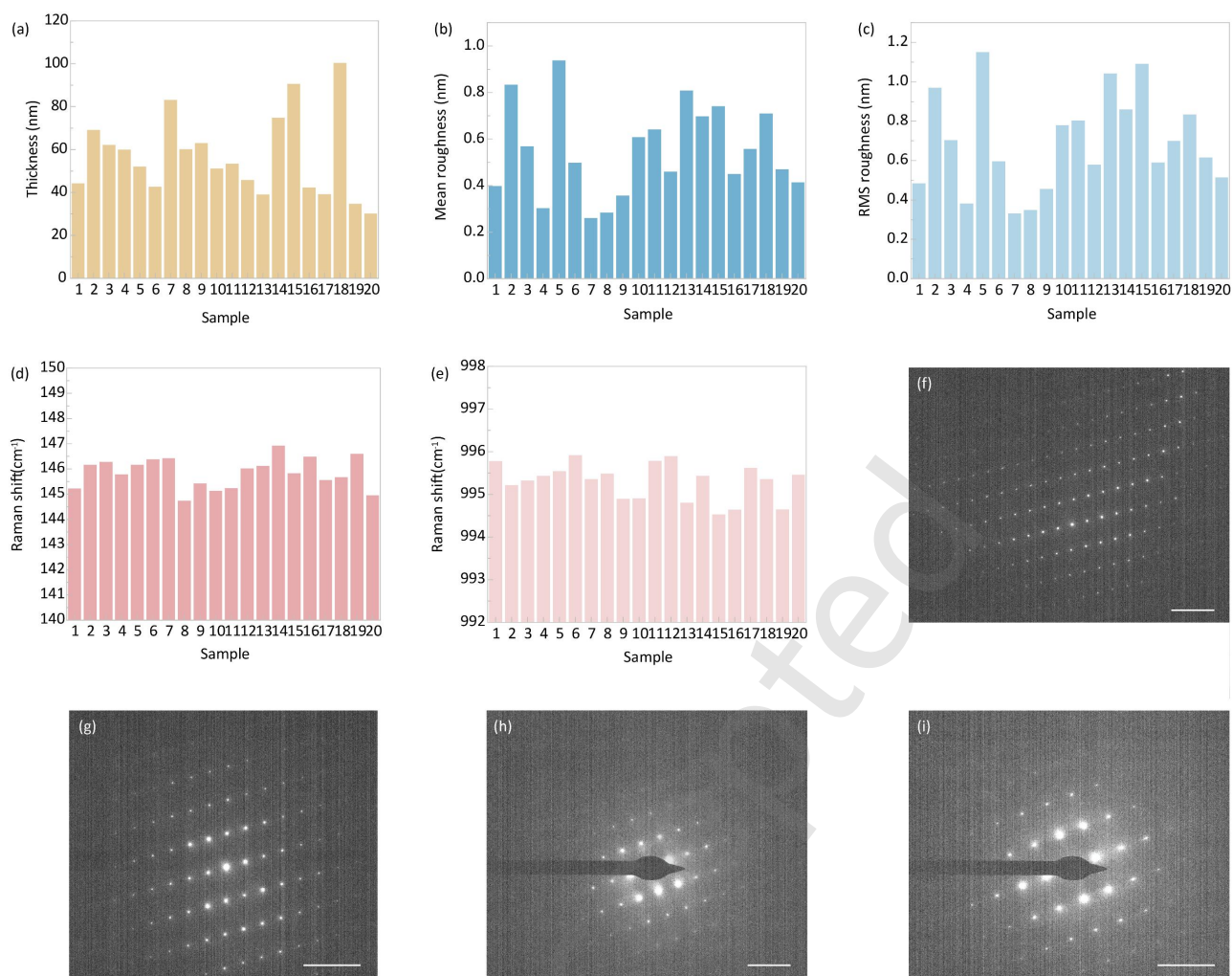


Figure S2. (a) Statistical distribution of thickness for 20 α -V₂O₅ nanoflakes from different growth batches. (b) Statistical distribution of mean roughness for the same set of 20 nanoflakes. (c) Statistical distribution of RMS roughness for the same set of 20 nanoflakes. (d) Statistical distribution of the Raman peak position near 145 cm⁻¹. (e) Statistical distribution of the Raman peak position near 995 cm⁻¹. (f-i) SAED patterns of two additional α -V₂O₅ nanoflakes at different magnifications. Scale bar: 5 nm⁻¹. Panels (f) and (g) correspond to one nanoflake, while panels (h) and (i) correspond to a second nanoflake.

Section4. Optical microscopy images of α -V₂O₅ crystals synthesized at different Zone 2 temperatures

As a temperature-sensitive phase-transition material, the crystallization of V₂O₅ is governed by thermal conditions. With Zone 1 (Fig. 1(a)) fixed at 960 °C, varying Zone 2 (Fig. 1(a)) temperatures directly modulated the morphology and crystallinity of the products.

When the temperature of Zone 2 was set above the melting point of V₂O₅ (670 °C), the resulting products manifested as α -V₂O₅ bulk crystals with diverse morphologies and thicknesses ranging from micrometers to millimeters. At a Zone 2 temperature of 860 °C, the elevated thermal energy provided sufficient driving force for crystal growth in multiple directions, leading to the formation of bulk products visible to the naked eye. As the temperature of Zone 2 was progressively lowered to 760 °C, the available energy for bulk crystal growth diminished considerably, resulting in a marked reduction in crystal size and the eventual formation of discrete islands interconnected by undeformed "tentacles". When the temperature of Zone 2 falls within the range of 660 °C to 760 °C, the morphology of the resulting products undergoes an abrupt transition. A distinct gap in product formation is observed between these two morphological types. Within this temperature window, the primary products are densely packed α -V₂O₅ microflakes. As the temperature of Zone 2 decreases, the available thermal energy for the growth of α -V₂O₅ microflakes diminishes, leading to a progressive reduction in both the lateral dimensions and the packing density of the flakes.

With continued decrease in temperature, these microflakes eventually evolve into aggregated, grass-like α -V₂O₅ crystals — a morphology aligned with previously reported structures [6] (see **Table S1, row 6**).

When the temperature of Zone 2 was set below the melting point of V₂O₅ (670 °C), the growth along the [010] crystallographic direction was significantly suppressed, leading to a morphological transition toward the formation of nanoflakes. Within the temperature range of 610 °C < $T_{\text{Zone 2}} \leq 660$ °C, the α -V₂O₅ crystals exhibited a sharp reduction in flake thickness accompanied by non-uniform size distribution (<300 nm). Concurrently, the crystals developed a pronounced growth tendency along the [100] direction, resulting in the emergence of outward protrusions at the edges, which can be regarded as an intermediate state during the transition from microplates to nanoflakes. At $T_{\text{Zone 2}} = 610$ °C, the products evolved into α -V₂O₅ nanoflakes with flat surfaces, uniform thickness, and well-defined edges (see **Fig. 1(a)**). As the temperature of Zone 2 was further decreased below 560 °C, the limited thermal energy restricted the extended growth along both the [010] and [100] directions. This led to a continuous reduction in the width of the nanoflakes, ultimately resulting in the formation of nanobelts and nanowires.

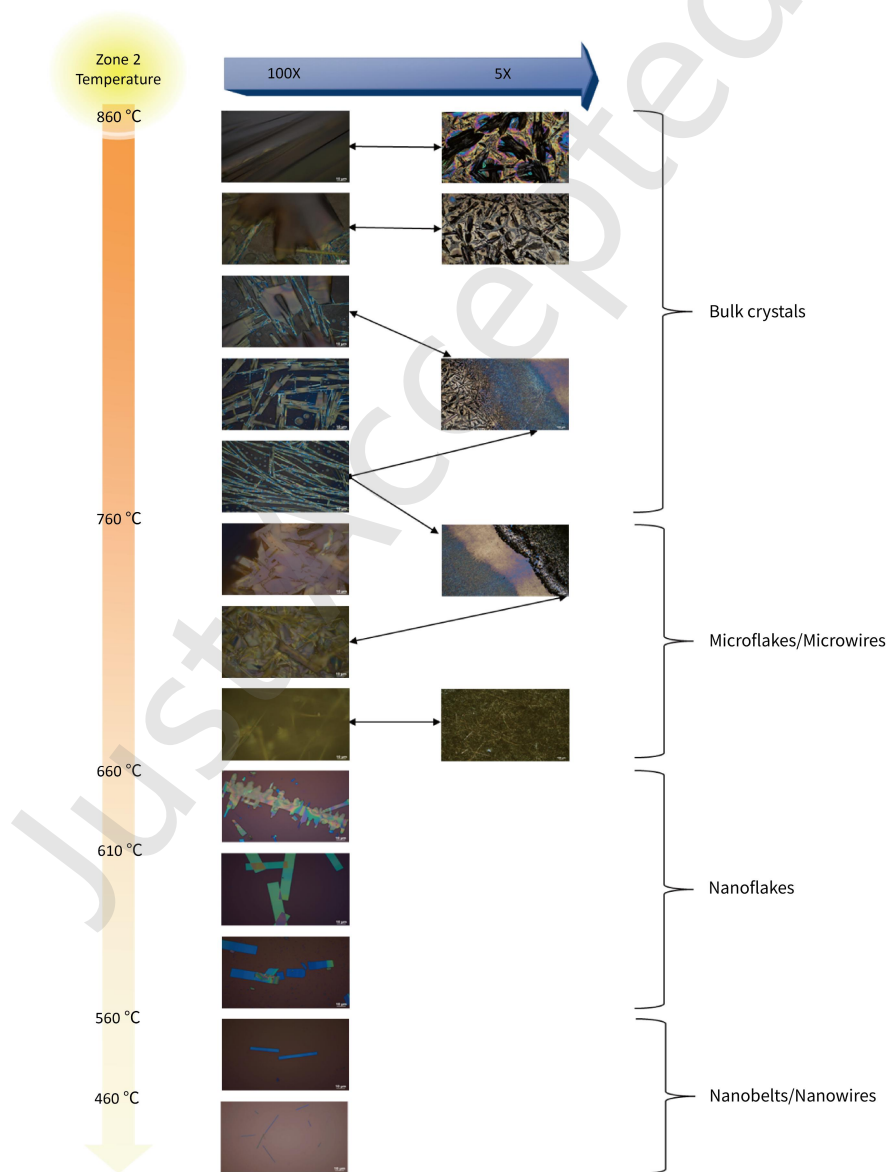


Figure S3. Optical microscopy images of α -V₂O₅ crystals synthesized at different Zone 2 temperatures. The left panel (scale bar: 10 μ m) and right panel (scale bar: 100 μ m) reveal the temperature-dependent morphological evolution from bulk crystals to nanoflakes.

Section 5. Evolution behavior of α -V₂O₅ from nanobelts to nanowires

To investigate the evolution from two-dimensional α -V₂O₅ nanobelts to quasi-one-dimensional nanowires, crystal growth is performed on elongated substrates that contain a continuous temperature gradient. The temperature at the substrate end extending into Zone 2 (**Fig. 1(a)**) is defined as the set Zone 2 temperature ($T_{\text{Zone 2}}$). Sample 1 is grown at a set $T_{\text{Zone 2}} = 560$ °C, while Sample 2 is grown at a set $T_{\text{Zone 2}} = 460$ °C. Extensive statistical analysis of the dimensions of α -V₂O₅ crystals grown on both samples is conducted, with results presented in **Fig. S3**. Numerous blue belt-shaped crystals are observed on Sample 1 (**Fig. S3**), with thicknesses ranging from 10 to 30 nm and widths ranging from 1.33 to 5.13 μm . In contrast, numerous blue wire-shaped crystals are formed on Sample 2 (**Fig. S3**), with identical thicknesses of 10-30 nm but significantly reduced widths ranging from 767 to 70 nm. The crystal width exhibits a temperature-dependent distribution as illustrated by the curves in **Fig. S4**: at $T_{\text{Zone 2}} = 560$ °C, the width of α -V₂O₅ nanobelts decreases rapidly from 5.13 μm to 1.33 μm ; at $T_{\text{Zone 2}} = 460$ °C, the width of α -V₂O₅ crystals deposited on Sample 2 decreases gradually from 767 nm to 70 nm, corresponding to a morphological transition from slender belt-like to wire-like structures.

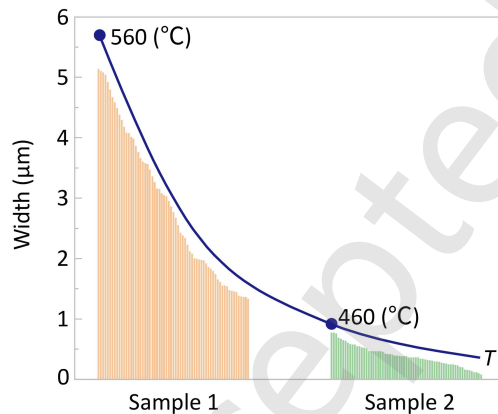


Figure S4. Statistical width distribution of α -V₂O₅ nanobelts and nanowires.

Section 6. Raman spectra of α -V₂O₅ structures synthesized at varied Zone 2 temperatures

Raman spectra of the α -V₂O₅ structures—including bulk crystals, microflakes, microwires, nanoflakes, nanobelts, and nanowires—synthesized at different Zone 2 temperatures are presented in **Fig. S3**, with corresponding spectra provided in **Fig. S5**. Although the relative intensity of the Raman characteristic peaks gradually decreases as the morphology evolves from three-dimensional bulk to one-dimensional wire-like structures, all peaks consistently match the standard spectrum of orthorhombic α -V₂O₅ without any detectable impurity phases. This confirms the phase purity of all synthesized α -V₂O₅ structures.

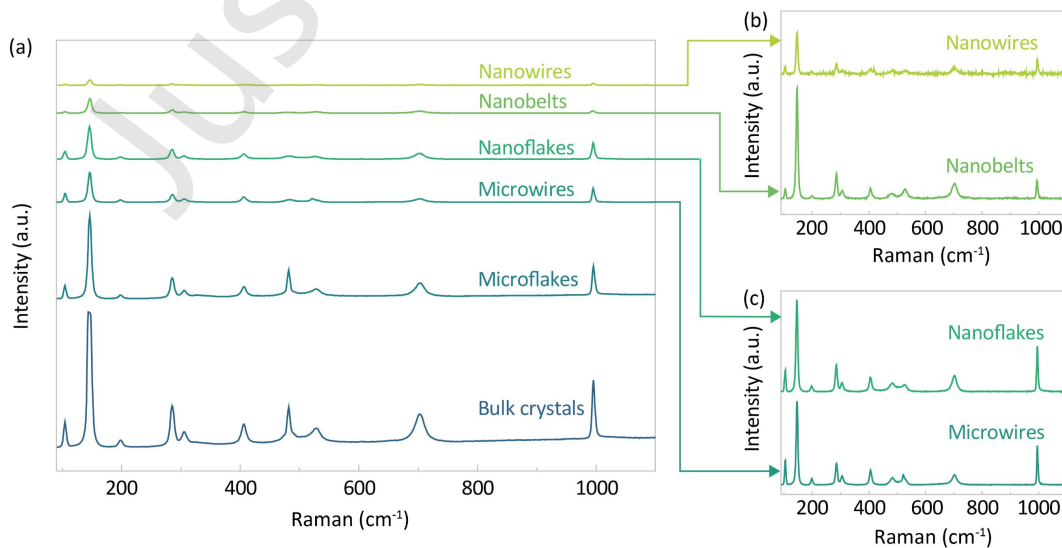


Figure S5. Raman spectra of α -V₂O₅ structures synthesized at varied Zone 2 temperatures.

Section 7. Description of principal axis dielectric function parameters for α -V₂O₅ used in theoretical calculations

It should be noted that while the parameters for the dielectric function of α -V₂O₅ crystals in our theoretical modeling of the electromagnetic response primarily reference Ref. [8], slight deviations in phonon frequencies can arise due to variations in fabrication methods, sample thickness, and substrate materials. Moreover, the parameters provided in Ref. [8] (which employed BaF₂ substrates) were themselves adjusted to match their experimental data. In the present study, substrates consist of high-resistivity silicon wafers coated with a 300-nm SiO₂ layer. Consequently, based on our experimental results, slight modifications were introduced to the ω_{LO} and ω_{TO} for Band 3, as detailed in **Table S3**. Specifically, ω_{TO} underwent a 1% adjustment (a 10 cm⁻¹ downshift from 1004 cm⁻¹ to 994 cm⁻¹), and ω_{LO} was adjusted by 1.3% (a 13 cm⁻¹ upshift from 1037 cm⁻¹ to 1050 cm⁻¹). Theoretical dispersion relations for PhPs propagating along the [100] and [001] directions, calculated using these final parameters, are presented in **Fig. 4(h)**. Importantly, the dispersion relations for intrinsic α -V₂O₅ PhPs propagating along [100] and [001] directions, statistically processed from our near-field optical experiments, show good agreement with the lowest-order (smallest-momentum) guided-wave modes identified in the multilayer Fresnel reflectometry calculations.

Table S2. Specified parameters for the principal axis dielectric function of α -V₂O₅ utilized in theoretical calculations.

ϵ (α -V ₂ O ₅)	ω_{TO} (cm ⁻¹)	ω_{LO} (cm ⁻¹)	ϵ^∞	Γ (cm ⁻¹)
ϵ_x [100] [8]	765	952	6.6	40
ϵ_y [001] [8]	506	842	6.1	19
ϵ_z [010]	994	1050	3.9 [8]	1.5 [8]

Table S3. Comparison between the parameters employed in this work for the α -V₂O₅ principal axis dielectric function during dispersion relation calculations and those reported in Ref. [8].

ϵ (α -V ₂ O ₅)	ω_{TO} (cm ⁻¹)	ω_{LO} (cm ⁻¹)	ϵ^∞	Γ (cm ⁻¹)
ϵ_x [100] (Ref. [8])	765	952	6.6	40
ϵ_x [100] (This work)	765	952	6.6	40
ϵ_y [001] (Ref. [8])	506	842	6.1	19
ϵ_y [001] (This work)	506	842	6.1	19
ϵ_z [010] (Ref. [8])	1004	1037	3.9	1.5
ϵ_z [010] (This work)	994	1050	3.9	1.5

Section 8. Calculated interference patterns of α -V₂O₅ nanodisks

A phenomenological model is employed to further investigate the interference patterns of α -V₂O₅ nanodisks (**Fig. S6**). For sufficiently small disk sizes, the round-trip propagation path of boundary-reflected phonon polaritons lies within their propagation length, allowing strong interference to develop at the disk center. With decreasing disk diameter down to 500 nm, the central intensity oscillates between a dark and a bright spot, such that the entire nanodisk functions effectively as a Fabry-Pérot cavity (**Fig. S6(d)-S6(f)**).

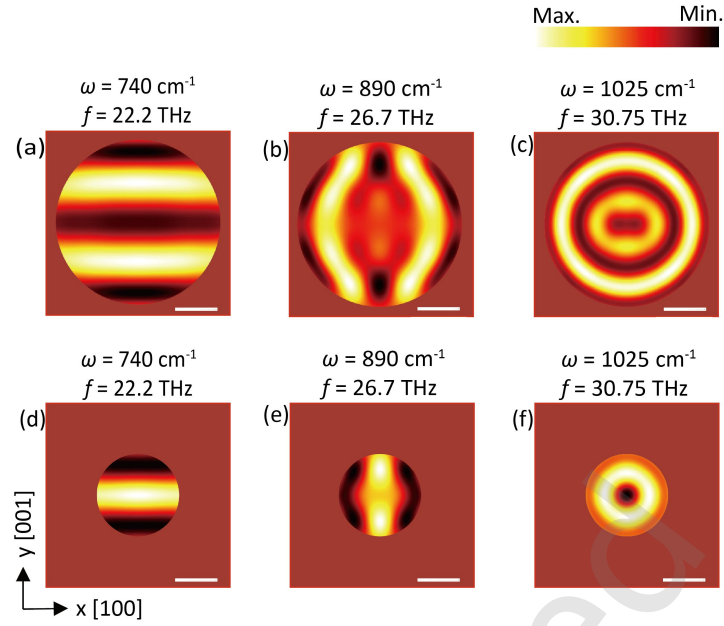


Figure S6. Calculated interference patterns of a 44 nm-thick α -V₂O₅ nanodisk at different excitation frequencies. Scale bars: 250 nm.

Section 9. Calculation of group velocity and lifetime for PhPs propagating along the [100] and [001] directions in α -V₂O₅ nanoflakes under excitation at Band 3

The dispersion relation of waveguide modes along an arbitrary in-plane propagation direction reflects the dependence of the group velocity v_g of electromagnetic waves on the frequency ω . By differentiating this relation, the group velocity v_g for a specific propagation direction can be derived as [8]:

$$v_g = \frac{d\omega}{dq} \quad (S1)$$

Where ω denotes the angular frequency of the PhPs waveguide, and q is the wave vector. When the ω lies within Band 3 of the intrinsic α -V₂O₅ nanoflakes, the group velocity $v_{g[001]}$ for PhPs propagating along the [001] direction is 9.681×10^4 m/s ($\sim 0.00032c$), while that along the [100] direction ($v_{g[100]}$) is 8.014×10^4 m/s ($\sim 0.00027c$).

The lifetime of PhPs (τ) is intrinsically linked to their propagation length (L_p) and group velocity (v_g) [8]:

$$\tau = \frac{L_p}{v_g} \quad (S2)$$

where the propagation length $L_p = 1/\text{Im}(q)$ [8]. By applying the Fourier transform to the near-field optical profiles and mapping them into the spatial-frequency domain, the spatial spectral curve can be fitted with a Lorentzian function. The central frequency of this curve corresponds to $\text{Re}(q)$, while its half-width at half-maximum (HWHM) equals $\text{Im}(q)$. Through this method, the propagation lengths of PhPs along the [001] and [100] crystallographic directions were computed across various frequencies, and the corresponding group velocities were extracted. The results reveal that in a 44 nm-thick α -V₂O₅ monocrystalline nanoflake, PhPs propagating along the [001] and [100] directions exhibit maximum lifetimes of ~ 8 ps and ~ 9 ps, respectively.

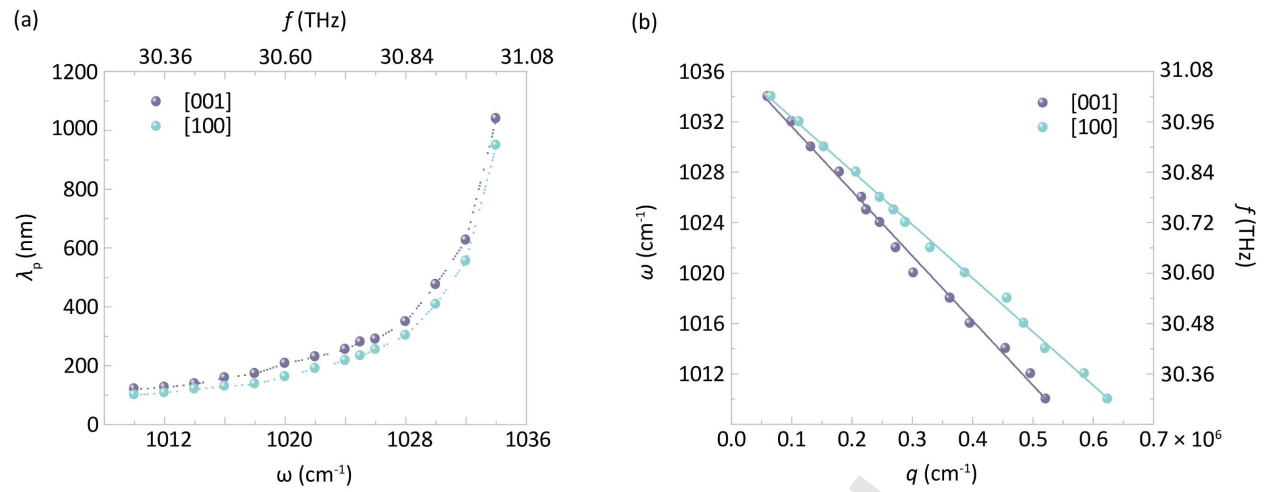


Figure S7. (a) Experimental wavelengths of phonon polaritons propagating along the [100] and [001] crystallographic directions in α - V_2O_5 nanoflakes, measured at an excitation frequency ω within Band 3. **(b)** Experimental dispersion of PhPs along these directions at the same frequency ω . Solid lines are fits by a potential function.

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