Towards compact phase-matched and waveguided nonlinear optics in atomically layered semiconductors

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Nonlinear frequency conversion provides essential tools for generating new colors and quantum states of light. Transition metal dichalcogenides possess huge nonlinear susceptibilities; further, 3R-stacked transition metal dichalcogenide crystals possess aligned layers with broken inversion symmetry, representing ideal candidates to boost the nonlinear optical gain with minimal footprint. Here we report the second-order nonlinear processes of 3R-MoS₂ along the ordinary and extraordinary directions. Along the ordinary axis, by measuring the thickness-dependent second-harmonic generation, we present the first measurement of the second-harmonic-generation coherence length of 3R-MoS₂, and achieve record nonlinear optical enhancement from a van der Waals material, >10⁴ stronger than a monolayer. It is found that 3R-MoS₂ slabs exhibit similar conversion efficiencies of lithium niobate, but within 100-fold shorter propagation lengths. Furthermore, along the extraordinary axis, we achieve broadly tunable second-harmonic generation from 3R-MoS₂ in a waveguide geometry, revealing the coherence length in such a structure. We characterize the full refractive-index spectrum and quantify its birefringence with near-field nanoimaging. Our results highlight the potential of 3R-stacked transition metal dichalcogenides for integrated photonics, providing critical parameters for designing highly efficient on-chip nonlinear optical devices including periodically poled structures, optical parametric oscillators and amplifiers, and quantum circuits.

Nonlinear optics lies at the heart of light generation and manipulation. Coherent frequency conversion, such as second-harmonic generation (SHG), third-harmonic generation, and parametric light amplification and down-conversion, enables a deterministic change in wavelength as well as control of temporal and polarization properties. When integrated within photonic chips, nonlinear optical materials constitute the basic building blocks for all-optical switching, light modulators, photon entanglement and optical quantum information processing. Conventional nonlinear optical crystals display moderate second-order nonlinear susceptibilities ($|\chi^{(2)}| \approx 1$–30 pm V⁻¹) and perform well in benchtop setups with discrete optical components. However, such crystals do not easily lend themselves to miniaturization and on-chip integration. Two-dimensional (2D) transition metal dichalcogenides (TMDs) possess huge nonlinear susceptibilities ($|\chi^{(2)}| \approx 100$–1,000 pm V⁻¹) and owing to their deeply sub-wavelength thickness, they offer a unique platform for on-chip nonlinear frequency conversion and light amplification. Furthermore, their semiconducting properties render TMDs superior for applications compared with opaque materials with exceptionally large $|\chi^{(2)}|$ such as Weyl semimetals.

In single- or few-layer TMD samples, SHG is extensively exploited for the characterization of structural properties such as crystal orientation or local strain. However, due to their atomic thickness, these samples display a notably lower SHG efficiency (η_SHG = I₂/Ι₀ ≈ 10⁻¹¹ at Ι₀ = 30 GW cm⁻²) compared with standard nonlinear crystals (η_SHG = I₂/Ι₀ ≈ 1–50%). The SHG efficiency can be written as η_SHG ∝ $|\chi^{(2)}|^2L^2$, where L is the thickness of the nonlinear medium (assuming perfect phase matching and non-depletion regime). The nonlinear conversion efficiency of a TMD could, thus, be scaled by increasing the propagation length L through the active medium. This is attainable by increasing the number of layers in the TMD sample. However, the nonlinear optical properties of multilayer TMDs critically depend on their crystallographic symmetry.

Group VI trigonal TMDs (for example, MoS₂) are stable in two crystallographic phases: polytype 2H (hexagonal) and polytype 3R (rhombohedral). 2H-MoS₂ is naturally centrosymmetric, giving an opposite dipole orientation among consecutive layers. This results in a vanishing nonlinear susceptibility ($|\chi^{(2)}| = 0$) for crystals with even number of layers and precludes efficient nonlinear conversion in multilayer 2H-TMDs. To circumvent this limitation—and restore the quadratic scaling of the nonlinear conversion efficiency with the number of layers N (Ι₂/Ι₀ ∝ N²)—one can artificially stack several monolayers in the AA configuration, aligning their dipole moments. Although the mechanically assembled stacks serve as a proof of concept for fundamental studies, their labour-intensive fabrication prevents massive large-scale production.

In contrast, 3R-MoS₂ is naturally non-centrosymmetric. The optical emission from consecutive in-plane nonlinear dipoles of 3R-MoS₂ results in constructive interference, prompting the $N^2$ enhancement of the nonlinear conversion efficiency for thin samples. Similar to 2H-MoS₂, bulk 3R-MoS₂ can be grown by chemical vapour transport and thin 3R-MoS₂ flakes can be obtained by dry mechanical exfoliation. The nonlinear optical response of 3R-MoS₂ has been explored in some recent pioneering studies, so far focusing on thinner crystals, reporting $N^2$ enhancement at the 2D limit, and showing a maximum SHG enhancement of ~10⁴ occurring within specific thickness windows. Pushing towards general application,
However, requires higher nonlinear enhancements and thus larger $N_i$, which, in turn, leads to more intricate interferences and interactions within the crystal. Specifically, for multilayer TMDs, the wavevector mismatch between the fundamental wavelength (FW) and second harmonic (SH) needs to be considered, as it limits the maximum propagation length for constructive interference. In addition, thick 3R-MoS$_2$ crystals act as Fabry–Pérot cavities, which modulate the FW power inside the sample. The combination of these effects determines the optimum thickness of 3R-MoS$_2$ for the highest SHG conversion efficiency. Due to their layered nature, 3R-stacked TMDs are also naturally anisotropic and thus birefringent—a key prerequisite for achieving perfect phase matching.

Here we measure SHG and difference-frequency generation (DFG) from multilayer 3R-MoS$_2$ crystals with variable thickness, using a custom transmittance microscope to determine the maximum enhancement in nonlinear conversion efficiency, revealing the intrinsic upper limits of the material. We provide a comprehensive model that explains the second-order nonlinearity of 3R-MoS$_2$ including phase mismatch and intrinsic interference effects. We report the first measurement of the coherence length $L_c$ of 3R-MoS$_2$, elucidating the role of phase matching at excitation photon energies close to the telecom band. In addition, we reveal that 3R-MoS$_2$ enables broadband SH conversion in waveguide geometries. On edge coupling of the FW, we detect and map both FW and SH emission from the opposite edge of the flake within our field of view. We observe the characteristic SHG signal modulation with increasing path length, allowing us to quantify the out-of-plane coherence length in 3R waveguide structures. Further, we also characterize the anisotropic linear optical properties by imaging the propagation of waveguide modes in real space using near-field nanoimaging, identifying the conditions for phase-matched SHG in waveguide geometries. Together, these findings pave the way for achieving birefringent phase matching in waveguides of van der Waals (vdW) semiconductors, directly impacting the field of vdW photonics by enabling future advances in conversion efficiencies and integration.

**Results**

We use a custom transmission microscope (Methods) (Fig. 1a) to measure SHG and DFG from the multilayer 3R-MoS$_2$ flakes with tunable thickness $h$. The 3R-MoS$_2$ microcrystals are mechanically exfoliated from a commercial chemical-vapour-transport-grown bulk 3R-MoS$_2$ crystal (HQ Graphene) onto a 200-μm-thick fused silica (SiO$_2$) substrate. The bulk sample has been characterized by energy-dispersive X-ray (EDX) and X-ray diffraction (XRD) analyses (Supplementary Fig. 1). The thickness of each exfoliated flake has been determined by atomic force microscopy (AFM) (Supplementary Note 1 and Supplementary Figs. 2 and 3). The detection objective has a larger numerical aperture (NA) than the excitation one to maximize signal collection from scattering at larger angles.

Figure 1b shows the power-dependent SHG measured on 119-nm-thick 3R-MoS$_2$ (dots) and the fitted power law (line). The pump wavelength is set to 1,520 nm (0.815 eV) yielding SHG centered at 760 nm (1.63 eV) (the inset shows a representative spectrum). The SHG emission follows the expected quadratic power dependence. The saturation regime is beyond the maximum excitation power that we can achieve at the focus in our setup, that is, ~45 mW, corresponding to an intensity of ~120 GW cm$^{-2}$. Moreover, since both FW and SH are tuned below the bandgap of 3R-MoS$_2$, the material is essentially transparent, and no appreciable degradation of the sample is detected (Supplementary Fig. 6). This highlights the potential to boost the nonlinear conversion efficiency at higher intensities. Due to damage considerations, such intensities are usually unattainable in the absorptive above-gap regime, where excitonic resonances are exploited to enhance the nonlinear response of TMDs$^{12,13}$. A representative six-lobed polarization-dependent SHG flower pattern$^{14}$ (Fig. 1b, inset), in which the pump polarization is rotated by a half-wave plate and the transmission axis of the detection polarizer is kept parallel to the pump, reflects the $D_{3h}$ point group of the 3R crystal with broken inversion symmetry. It shows two longer lobes along one of the armchair directions, attributable to the staggered stacking direction$^{26}$.

Figure 1c shows the AFM image of a representative 3R-MoS$_2$ flake, along with a line cut of the height profile (Fig. 1d), in which we can distinguish two flat regions of 20 and 119 nm thickness. A sample-scanning confocal modality is used for mapping the spatially dependent SHG and DFG intensities over the flake (Fig. 1e,f, respectively). The SHG (FW at 1,520 nm, 0.815 eV) is measured with pump polarization and the collection analyser directions parallel to the armchair direction with the largest nonlinear response. In Fig. 1e, the 20-nm-thick region displays an SHG intensity twice as large as the one obtained on a 119-nm-thick flake. In other words, by increasing the thickness of the 3R-MoS$_2$ flake, the emitted SHG decreases. Since both FW and SH photon energies lie below the optical bandgap (~1.85 eV), this effect cannot be attributed to absorption (indirect absorption losses are negligible for these wavelengths and thicknesses; Fig. 2c).

The DFG map at 574 nm (~2.16 eV) (Fig. 1f) is recorded on the same flake using a pump wavelength of 400 nm (~3.11 eV) and a signal at 1,300 nm (~0.95 eV). The pump and signal beams have parallel polarizations, whereas the collection is unpolarized. Note that as with SHG, the thicker area has a weaker DFG signal than the thinner area. Considering that both pump and idler photon energies lie above the optical gap, we estimate that the absorption is the main reason for the measured weaker idler intensity in this case. Indeed, we cannot detect any idler signal through a 622-nm-thick 3R-MoS$_2$ flake.

To understand the thickness dependence of SHG efficiency, we must take into account both interference and phase-matching effects. We analyse light propagation in the nonlinear medium using the transfer matrix method, modelling our structure as a three-layer system (SiO$_2$/MoS$_2$/air) with refractive indexes $n_i/n_{i+1}$. The transmissivity of FW light changes periodically with sample thickness $h$ (Supplementary Note 2 provides an extended calculation) as

$$T_w(h) = \frac{\text{Re}(n_j)}{\text{Re}(n_i)} \frac{t_{01} t_{12}}{r_{01} r_{12} e^{-i k_i h}}^2,$$  

where $n_i$ is the refractive index of layer $i$; $t_{ij}$ and $r_{ij}$ are the transmissivity and reflectivity coefficients from layer $i$ to layer $j$, respectively; $k$ is the wavevector; and $h$ is the thickness of the 3R-MoS$_2$ layer. The effective FW intensity at the sample is $I_{w} = T_w(h) I_{w0}$, where $I_{w0}$ is the FW intensity after the focusing objective, which is kept fixed during the experiment. Due to interference effects, the effective power flux across the sample changes periodically along the thickness (Fig. 2a, black curve).

The discrepancy in refractive index for FW at frequency $\omega$ and SH at frequency $2\omega$ sets further constraints on conversion. Efficient frequency conversion in bulk nonlinear crystals is achieved by fulfilling the phase-matching condition, that is, by coherently adding the signals generated at different longitudinal coordinates of the crystal. Due to frequency dependence of the refractive index, after a certain propagation length, the locally generated SH will be out of phase with the SH from previous planes of the crystal. The overall SH intensity continues to grow until the so-called coherence length $L_c$ is reached and then begins to decrease due to destructive interference$^{21}$. The SH intensity under phase-mismatched conditions can be written as

$$I_{2\omega} \propto \left| \mathcal{K}^{(2)} \right|^2 \frac{1}{\Delta k^2} I_{w0} \sin^2 \left( \frac{\Delta k h}{2} \right),$$  

where $\mathcal{K}^{(2)}$ is the second-order susceptibility tensor and $\Delta k$ is the wavevector mismatch.

**Conclusion**

In conclusion, we have demonstrated a novel route for multilayer TMDs by exploiting the effect of thickness on SHG efficiency. Our results provide a comprehensive understanding of the nonlinear properties of 3R-MoS$_2$, which can be exploited for various applications in THz and mid-IR quantum photonics.
where $\Delta k = k_{\omega} - 2k_{\omega} = 2\omega c (n_{s\omega} - n_{s})$ is the wavevector mismatch between the SH and FW (Fig. 2a, red curve) and $c$ is the speed of light. Equation (2) shows that the maximum efficiency is reached for a thickness of the nonlinear crystal corresponding to coherence length $L_c = \pi/\Delta k$. Combining thickness-dependent FW transmission $T_c(h)$ and the phase-matching relationship, one can see that the SHG efficiency is modulated by both multilayer interference effects and phase mismatch, giving the optimal thickness of the nonlinear crystal.

As noted above, to avoid absorption losses, we choose FW and SH photon energies below the optical gap of MoS$_2$. The experimental data of the measured nonlinear emission and fitting curve $I_{SH}(h)$ are shown in Fig. 2b, with the amplitude as the only free-fitting parameter. The ~10% fluctuation of the nonlinear signal originates from the sample spatial inhomogeneity. The measured refractive indices of 3R-MoS$_2$ are $n_s = 3.795$ at 0.815 eV and $n_p = 4.512$ at 1.630 eV, and the corresponding refractive-index mismatch is $n_p - n_s = 0.717$, which is in agreement with previously reported values for bulk 2H-MoS$_2$ (refs. 28,29). These values give, for a pump photon energy of 0.815 eV, a coherence length of $L_c \approx 530$ nm and transmittance period of 182 nm for 3R-MoS$_2$, in excellent agreement with experimental results (Fig. 2b). In the low-thickness regime, the deviation in the experimental data from the model calculated with the transfer matrix method is due to the evolution of the band structure. The refractive index of mono- and few-layer TMDs differs from the refractive index of bulk MoS$_2$ (ref. 34), with thinner films having a smaller refractive index and larger overall transmissivity. In our model, we estimate the thickness-dependent SHG using the bulk refractive index. Therefore, at lower thicknesses, the SHG intensity is higher than the calculated one.

The largest experimental SHG enhancement with respect to a monolayer, obtained for a 622-nm-thick 3R-MoS$_2$ crystal, is approximately $1.5 \times 10^5$ times with respect to monolayer MoS$_2$ within one coherence length at the pump photon energy of 0.815 eV. Considering that the reported conversion efficiency of monolayer MoS$_2$ at FW = 1,560 nm is $\sim 7 \times 10^{-11}$ at 30 GW cm$^{-2}$ (ref. 24), the overall conversion efficiency of MoS$_2$ at the coherence length thickness will be $\sim 10^{-8} \div 10^{-5}$. Our results show that to realize an optimal nonlinear conversion efficiency, one needs to choose a material thickness close to the coherence length that simultaneously guarantees constructive interference for the FW. Further enhancement can then be achieved by regularly structuring or poling larger crystals or waveguides with a periodicity on this length scale or by exploiting birefringence.

The advantage of 3R-MoS$_2$ for nonlinear frequency conversion becomes particularly striking when one compares its conversion efficiency density $\eta := P_{SH}/(P_{FW} L^2)$ with that of state-of-the-art LiNbO$_3$ devices at the telecom wavelength. Utilizing our measured material parameters, we calculate $\eta = 71,800$ W$^{-1}$ cm$^{-2}$ in 3R-MoS$_2$ for $L = 622$ nm, whereas $\eta = 460$ W$^{-1}$ cm$^{-2}$ for LiNbO$_3$ on an insulator waveguide with a propagation length of 50 μm (ref. 13). The coherence length $L_c$ of LiNbO$_3$ at FW of 1,545 nm is 9.5 μm (ref. 32), and
Fig. 2 | In-plane SHG coherence length. a, Calculated pump transmissivity (black) and phase-mismatch curve (red) as a function of 3R-MoS2 thickness. b, Measured thickness-dependent SHG enhancement of 3R-MoS2 with respect to the monolayer (circles) and calculated theoretical enhancement (line). FW and SH photon energies are 0.815 and 1.630 eV, respectively. The pump power is kept constant at 5.4 mW and the linear pump polarization is parallel to the armchair direction. The error bars represent the variance of the nonlinear signal over 25 spectra corresponding to a flake area of 5 μm × 5 μm (25 pixels). The error originates from sample inhomogeneity, which induces a fluctuation in the nonlinear signal of ~10%.

c, Real (n) and imaginary (κ) parts of the refractive index of bulk 3R-MoS2 (n = n + iκ). Here n and κ are extracted from the transmittance and reflectance spectra (Supplementary Note 3) of a representative 94-nm-thick 3R-MoS2 on a fused silica substrate. The peaks in κ at 675 and 624 nm are attributed to A and B exciton resonances. The circles and triangles represent the ordinary (n) and extraordinary (κ) refractive indexes determined by s-SNOM (Fig. 5). The dashed line indicates the average n, in the low-energy range, expected to be nearly constant. d, SHG excitation spectrum measured on a 4.2-nm-thick 3R-MoS2, with a constant pump power of 1.35 mW and tunable FW (0.78–1.55 eV). The inset shows a comparison between the SHG spectrum and imaginary refractive index κ (grey line) (a zoomed-in view with regard to the excitonic resonance absorption energy range).

The conversion efficiency at coherence length Lc is Ic/I0 ≈ 3 × 10−4. Notably, 3R-MoS2 achieves similar conversion efficiencies with two orders of magnitude shorter propagation lengths.

To probe the effects of excitonic and interband transitions on χ(2) of 3R-MoS2, we extracted the full refractive-index spectrum of a bulk crystal using a combination of transmission and reflection experiments and compared the results with SHG frequency dependence. We report the full refractive-index spectrum for in-plane polarization in Fig. 2c (Supplementary Information provides details for the wide-range spectrum). The real and imaginary components of the index, namely, n and κ, respectively, are retrieved from the complex dielectric function ε, which is extracted from the transmittance (T) and reflectance (R) spectra measured on an ~94-nm-thick 3R-MoS2 crystal on a fused silica substrate (Supplementary Information). The absorption resonances of the κ(λ) spectrum (Fig. 2d, inset) are attributed to excitonic effects. In particular, the peaks at 675 and 624 nm are A and B excitons, respectively. The onset of the transparency region of 3R-MoS2 lies at ~750 nm.

Figure 2d shows the SHG spectrum measured on a 4.2-nm-thick 3R-MoS2 flake on 200-μm-thick SiO2, revealing the wavelength dependence of χ(2) of 3R-MoS2 along the armchair direction. The response of our system has been calibrated with a standard alpha-quartz sample. The error in the measurement is negligible, as it mainly originates from laser-power fluctuations, inducing a change in the nonlinear signal of ~0.1%. Here each point results from the average of ten integrated spectra measured on a single spot of the flake. The main peaks at ~670 and 620 nm are consistent with the A- and B-exciton absorption resonances, respectively, measured on bulk 3R-MoS2 (Fig. 2c, κ spectrum in grey), whereas the peak at 470 nm originates from high-energy transitions at the band-nesting region between the K and Γ points of the Brillouin zone. The slight energy deviation from the excitonic resonances in 2H-MoS2 can be attributed to the different crystal structure of the 3R polytype, affecting the band structure and optical absorption.

Increasing the nonlinear conversion efficiency of 3R-MoS2 for propagation lengths beyond the coherence length requires phase matching, that is, Δk = 0. Phase-matched nonlinear interactions can exploit the optical anisotropy (birefringence) of non-centrosymmetric nonlinear crystals. Notably, perfect phase matching achieved in waveguides lies at the heart of on-chip integrated nonlinear optics. To explore the birefringence of 3R crystals, in the following, we show that far-field edge coupling of the FW
into a 3R-MoS₂ flake enables broadband SH emission in waveguide geometries; then, we employ near-field imaging to visualize the waveguided modes.

We use a confocal microscope in reflection geometry (Fig. 3a) to probe the nonlinear frequency conversion in a waveguiding flake of 3R-MoS₂. The FW beam is displaced to the side of the objective (NA = 0.95) to achieve edge coupling on one side of the flake. By tuning the polarization of the FW, we launch both transverse-electric (TE)-like and transverse-magnetic (TM)-like modes. The SH generated inside the 3R-MoS₂ waveguide over a propagation length of ~30 μm is detected from the opposite side of the flake with the same objective. Both output FW and SH intensities depend on the FW polarization (Fig. 3b). Although the most efficient FW edge coupling inside the waveguide is achieved for p-polarized light, that is, TM modes, the conversion efficiency of SHG is the maximum when the FW is s polarized, that is, when we launch the TE modes. We ascribe this result to the asymmetry of the FW electric field in the TE mode. The field is aligned to MoS₂ sheets, specifically to the armchair direction whose dipole moment is also asymmetric.

Figure 3c reports the AFM map of the flake in which we achieve broadly tunable waveguided SHG. The micrographs of the edge coupling of a representative FW at 1,020 nm and SH at 510, 530, 580, 590, 620 and 660 nm are shown in Fig. 3d. Here the FW polarization is set parallel to the a.c. direction, which is aligned to the input edge of the flake (a.c. directions are shown in the AFM map and Fig. 3d (leftmost panel)).

In Fig. 4, we further investigate the mechanism of edge coupling and the out-of-plane SH coherence length in 3R-MoS₂ waveguides. By vertically displacing the excitation spot across the input edge (Fig. 4a), the SH fringe pattern changes accordingly, indicating that the FW coupling efficiency sensitively depends on the relative position of the input edge. In this case, the overall intensity of the output SH fringe pattern as a function of the FW vertical displacement is fitted with a Gaussian profile, which is consistent with the approximate profile of the focused excitation.

To obtain the out-of-plane coherence length, we measure the waveguide SH as a function of propagation length. We select a 775-nm-thick 3R-MoS₂ flake (Supplementary Fig. 3 shows the AFM map) with a sharp horizontal input edge and a diagonal output edge (Fig. 4b, c). In this way, by scanning the FW beam along the input edge over an ~50 μm distance, we can collect the output FW and SH as a function of propagation length within the slab. The intensity maps of FW and SH at different wavelengths are shown in Fig. 4d. On scanning the FW beam along the input edge, at each point, we collect the total transmitted FW and generated SH from the other side of the flake. The intensity of each pixel, thus, represents the total intensity coupled into the flake, which can be affected by spatial inhomogeneities of the input edge. To quantify the thickness-dependent SHG with constant FW power, we normalize the SH intensity maps by the FW maps as SH/FW². The normalized SH intensity profiles
at the three different wavelengths as a function of the propagation length (that is, the distance between the input and output edges) are reported in Fig. 4c. The SH intensity profiles are fitted to equation (2), with constant $I_\omega$. As expected, the region highlighted in red changes irregularly due to the presence of a defect at the output edge (a zoomed-in view of a spatial defect is shown in Fig. 4c (red box)). The fitting profile of the oscillating phase-mismatched SHG provides the out-of-plane coherence lengths $L_c$, which are 1.54, 1.57 and 1.60 $\mu$m at SH wavelengths of 510, 520 and 530 nm, respectively. Considering the multimode capacity of 3R-MoS$_2$ in this thickness, the extracted $\Delta k$ here is probably related to the primary modes of FW and SH, with the mode dispersion relationship discussed in more detail below. Although in-depth optimization lies beyond the scope of this work, the waveguide frequency conversion and quantification of coherence lengths established here allow for future device fabrication, structuring and $\chi^{(2)}$-mode engineering in next-generation compact TMD platforms.

To further identify the conditions for phase matching, we characterize the birefringence of 3R-MoS$_2$ by imaging the propagation of waveguide modes (WMs) in real space using near-field nano-imaging. Due to their layered nature, vdW crystals exhibit vastly different dielectric properties along the in-plane and out-of-plane directions. Since the far-field experiments described above are mostly sensitive to the in-plane optical properties of thin 3R-MoS$_2$ flakes, to access the full dielectric tensor of 3R-MoS$_2$, we investigate the propagation of WMs featuring in-plane and out-of-plane electric-field components using scattering-type scanning near-field optical microscopy (s-SNOM; Fig. 5a).
In maps of the scattered amplitudes $s_n$ (Methods) at near-infrared photon energies, WMs manifest as periodic modulations. Figure 5b shows the interference fringes close to the edge of an ~215-nm-thick flake recorded with an incident wavelength of 760 nm. The wavevectors of the contributing modes are shown in Fig. 5b (inset) and were extracted with an established procedure (Methods). Here the wavevectors are given in units of the free-space wavevector $k_0$ of incident light. In this case, the interference pattern comprises two transverse-magnetic (TM) and two transverse-electric (TE) modes, mostly characterized by out-of-plane and in-plane electric fields, respectively. Since the fields at the apex of the near-field tip are dominated by out-of-plane components, the TM modes can be excited more efficiently and consequently have larger spectral amplitudes than the TE counterparts. An analogous map of $s_n$ for an incident wavelength of 1,520 nm is shown in Fig. 5c.

To obtain the full refractive-index tensor of 3R-MoS$_2$ for 760 and 1,520 nm, we systematically vary the sample thickness (Fig. 5d,e) and trace the evolution of the TM and TE modes, thereby determining the in-plane and out-of-plane refractive indexes, namely, $n_s$ and $n_p$, respectively. We model the WM dispersion via the imaginary part of Fresnel reflection coefficients for s-polarized ($r_s$) and p-polarized ($r_p$) light.
part of the Fresnel reflection coefficients for s-polarized \( r_s \) and p-polarized \( r_p \) light calculated with the code provided elsewhere\(^4^4\). We obtain the best agreement with our experimental data for \((n_x, n_y) = (4.60, 3.03) \) (\( \lambda = 760 \text{ nm} \); Fig. 5d) and \((n_x, n_y) = (4.12, 3.15) \) (\( \lambda = 1.520 \text{ mm} \); Fig. 5e). When the finite NA of the objective lens in the far-field experiment is considered, the near-field measurement of the in-plane dielectric response \( n_x \) is consistent with the refractive index \( n \) shown in Fig. 2c. Due to the similar crystal structure, the in-plane properties of 3R-MoS\(_2\) match previous reports on the 2H polytype\(^3^6\). These results verify that infrared nanoimaging is a sensitive probe of anisotropic optical properties.

The full WM dispersion of a representative flake (\( h \approx 215 \text{ nm} \)) derived from the anisotropic model is provided in Fig. 5f. Here \( n_x \) plotted in Fig. 2c was used as an input and \( n_z \) was kept constant—a reasonable assumption for the range of photon energies below the exciton resonances\(^3^7\) (Fig. 3c). For this particular thickness \( h \), the wavevector difference \( \Delta k \), previously visualized in the phase-mismatch plot of Fig. 5d) between WMs at the FW and SH is sizeable. Due to the birefringence of the crystal, TM and TE branches exhibit substantially different dispersions. Therefore, by tailoring the thickness of the 3R-MoS\(_2\) slab, the TE \( 0 \) modes at the FW and selected higher-order modes at the SH can be phase matched in a waveguide geometry (Fig. 5f, inset). Different FWs or other nonlinear processes can be analyzed in a similar fashion.

Finally, we note that edge coupling (Figs. 3 and 4) occurs at a natural edge of the flake. To achieve a more efficient in-plane momentum propagation through the waveguide, prism or grating couplers (Fig. 5a, right) directly placed on top of the waveguide would be beneficial. Further fabrication and structure engineering in this direction can allow for tailored mode excitations that can boost the conversion efficiencies of the SHG in waveguides of vdW semiconductors.

**Outlook and conclusions**

We have fully characterized the second-order nonlinear frequency conversion from 3R-MoS\(_2\), a naturally non-centrosymmetric layered material, as a function of the propagation length, both along the in-plane and out-of-plane directions. In-plane SHG is generated by far-field normal incidence, whereas out-of-plane SHG is enabled by edge coupling in a waveguide geometry. We report both in-plane and out-of-plane SH coherence lengths, achieving a record value for nonlinear conversion efficiency in TMDs, exceeding the monolayer value by more than four orders of magnitude. For nonlinear integrated photonics, our demonstration of waveguide SHG in 3R-MoS\(_2\) slabs promises the same conversion efficiencies associated with LiNbO\(_3\) but within propagation lengths that are two orders of magnitude shorter at telecom wavelengths\(^1^1^4\). In addition, waveguiding in vdW semiconductors enables top-down fabrication compatibility and straightforward integration with Si-based platforms.

These results are fully corroborated by transfer matrix calculations including both multilayer interference effects and phase-matching constraints. Furthermore, the full dielectric tensor of 3R-MoS\(_2\), is accessed using waveguide-mode nanoimaging. The determined birefringence along in-plane and out-of-plane directions, as supported by numerical models, allows one to evaluate phase-matching conditions via mode dispersion relationship for any nonlinear process in waveguide geometry as a function of sample thickness. Moreover, due to the larger transparency window along the out-of-plane direction of TMDs\(^3^7\), it should be possible to harness the TM \( 0 \) modes, thereby partially circumventing the losses of in-plane dielectric response close to the exciton resonances. This scheme provides a viable handle to design and evaluate integratable nonlinear photonic devices based on 3R-TMD systems.

In addition, due to the weak interlayer vdW forces, TMDs offer the key advantage of being easily stackable into vertical heterostructures with nearly arbitrary relative orientation or twist angle\(^2^7\) due to their atomically flat interfaces free of lattice mismatch limitations. This capability can be exploited to extend the concept of quasi-phase matching to non-centrosymmetric layered semiconductors using periodically poled TMD structures, achieved by stacking multilayer 3R-TMDs plates, each with a thickness corresponding to the coherence length determined in the present work—suitably rotated to introduce a \( \pi \)-phase shift between the consecutives layers. Periodic poling in 3R-TMDs promises macroscopic nonlinear gain with values achieved in millimetre-thick crystals of standard materials, but with thicknesses that are more than 100-fold smaller. Thus, by virtue of the exceptional nonlinear properties and possibility of cavity integration and phase matching in waveguide geometries, we foresee ultracompact devices with extremely high nonlinear conversion efficiency—even exceeding multipass state-of-the-art photonic resonators of aluminium nitride\(^2^9\)—opening new frontiers for engineering on-chip integrated nonlinear optical devices including periodically poled structures, photonic resonators and optical quantum circuits.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41566-022-01053-4.

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Methods

Transmission spectroscopy. The custom-designed transmission microscope (Fig. 2a) is assembled with a cage system (Thorlabs). The excitation laser is focused by a ×40 reflective objective (Thorlabs) with NA = 0.5. The emitted SHG and DFG are detected by a ×50 objective (Nikon) with NA = 0.95. The sample is loaded on a three-axis piezo-stage (PI)/two-axis manual stage (Thorlabs). The best focus of each flake is adjusted with the z axis of the piezo-stage, whereas the position of the top/bottom objectives is fixed. The laser source (Coherent) is a Ti:sapphire oscillator emitting 120 fs pulses at 1.55 eV with a repetition rate of 80 MHz. The oscillator pumps an optical parametric oscillator emitting pulses tunable from 0.83 to 1.21 eV. The excitation-spot diameter on the sample is ~1 μm, corresponding to a peak intensity of ~2.7 GW cm−2 for an average power of 1 mW impinging on the sample. Nonlinear emission is detected with a silicon electron-multiplying charge-coupled device camera. Accounting for all the transmissive optical elements of the setup, both pump and signal pulses have a duration of ~250 fs at the sample plane; in DFG mapping, they are temporally synchronized by means of a mechanical delay stage before the excitation objective.

Waveguide nanoimaging. Near-field experiments are performed with an s-SNOM instrument (neaspec). The AFM instrument operates in the tapping mode with a frequency of ~70 kHz and a tapping amplitude of ~50 nm. The scattered light is detected using a photodiode and a pseudo-heterodyne scheme47. To suppress any higher harmonics of the tip tapping frequency.

To further enhance the image contrast, we use a parallel-plate waveguide (PPWG) in transmission mode. An PPWG is fabricated by depositing a SiO2 layer on a glass substrate. The thickness of the waveguide is ~285 nm. The PPWG is excited by a femtosecond laser, which is focused onto the sample by a ×50 objective (Nikon) with NA = 0.95. The PPWG is illuminated with a linearly polarized laser beam, and the scattered light is collected by a charge-coupled device camera. Accounting for all the transmissive optical elements of the setup, both pump and signal pulses have a duration of ~250 fs at the sample plane; in DFG mapping, they are temporally synchronized by means of a mechanical delay stage before the excitation objective.

Waveguide extraction and WM dispersion. In line traces of the scattered amplitude $s_n$ (Fig. 4b,c), the wavevectors of the WMs forming the interference pattern can be extracted via a Fourier transform. To this end, the spectral components generated by the step-like increase in $s_n$ at the sample edge need to be suppressed and the relative positions of the tip, sample edge and detector need to be taken into account. For the former, a Parzen window is used (the procedure is introduced elsewhere38), whereas the geometrical correction derived in another study37 is used for the latter. In short, wavevector $k_{\text{WG}}$ of the WM is related to the observed wavevector $k_{\text{obs}}$ given by the periodicity of the interference fringes via the following relation:

$$k_{\text{WG}} = k_{\text{obs}} \cos(\beta) + k_{0} \cos(\gamma) \sin(\beta + \delta).$$

Here $\beta = \sin^{-1}(\frac{\lambda}{2 \mu} \cos(\gamma) \cos(\delta))$, $k_{0}$ denotes the wavevector of free-space radiation; and $\gamma$ and $\delta$ are the out-of-plane and in-plane angles of incidence of light with respect to the sample edge, respectively.39 When considering the relative wavevectors $k_{\text{TM}}$ for the TM, and TE, modes, the dispersions in Fig. 4d, approach the out-of-plane ($\eta_\perp$) and in-plane ($\eta_\parallel$) refractive indices, respectively, in the limit of infinitely thick samples30,31. As a result, the smaller values of $\eta_\perp$ for $\lambda = 1.52$ nm (Fig. 4d) compared with the values for $\lambda = 760$ nm (Fig. 4c) highlight a difference in refractive index even without further modelling.

For a quantitative analysis of WM dispersion, the matrix formalism provided in another study37 was adapted to calculate the Fresnel reflection coefficients $r_s$ and $r_p$ for anisotropic multilayered structures. For the data shown in Fig. 4f (inset), the transcendental equations provided in another study37 were solved instead. This analogous procedure essentially yields curves that trace the maxima of Im$(r_s + r_p)$ (for example, Fig. 4d–f) as the finite thickness of SiO2 (~285 nm) is neglected and hence the Si chip underneath.

Broadband reflectance and transmittance measurements. The near-infrared and visible reflectance and transmittance spectra of 3R-MoS2 flakes were measured using a Hyperion 2000 microscope coupled with a Bruker Fourier-transform infrared spectrometer (Vertex 80V). A tungsten halogen lamp was used as a light source covering a frequency range of 0.5 to ~2.5 eV. Unpolarized light was focused on the sample using a ×15 objective and the aperture size was set to be smaller than the sample dimensions. The reflectance and transmittance spectra are normalized to the bare substrate region. A mercury–cadmium–telluride detector and a silicon detector were used for the near-infrared and visible range, respectively.

Data availability

Source data are provided with this paper. The rest of the data is available from the corresponding authors upon reasonable request.

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Author contributions

X.X. and C.T. conceived the experiment and built the custom transmission microscope. X.X. prepared the samples and performed the nonlinear measurements. F.M. and S.Z. performed the near-field measurements. E.M. analysed the near-field data and implemented the corresponding numerical models. Y.S. and X.X. determined the dielectric function from transmission/reflection experiments. G.C., D.N.B. and P.J.S. supervised the study. X.X., C.T., F.M., G.C., D.N.B. and P.J.S. wrote the article with input from all the authors.

Competing interests

The authors declare no competing interests.

Additional information

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