

SUPPLEMENTARY INFORMATION

Giant Second-Harmonic Generation in Ferroelectric NbOI₂

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Table S1 | Crystal data and structure refinement for NbOI₂ at 298K and 100K.

Temperature	298 K	100 K
Chemical formula	I ₂ NbO	I ₂ NbO
Molecular weight	362.71 g/mol	362.71 g/mol
Crystal system	monoclinic	monoclinic
Space group	C 1 2 1	C 1 2 1
Unit cell dimensions	$a = 15.1882(15) \text{ \AA}$ $b = 3.9329(4) \text{ \AA}$ $c = 7.5232(8) \text{ \AA}$ $\alpha = 90^\circ$ $\beta = 105.404(4)^\circ$ $\gamma = 90^\circ$	$a = 15.1243(14) \text{ \AA}$ $b = 3.9296(4) \text{ \AA}$ $c = 7.5061(7) \text{ \AA}$ $\alpha = 90^\circ$ $\beta = 105.420(4)^\circ$ $\gamma = 90^\circ$
Volume	433.24(8) Å ³	430.05(7) Å ³
<i>Z</i>	4	4
Density (calculated)	5.561 g/cm ³	5.602 g/cm ³
Absorption coefficient	16.824 mm ⁻¹	16.949 mm ⁻¹
Theta range for data collection	2.78 to 29.56°	2.81 to 29.58°
Reflections collected	679	3424
Independent reflections	679 [$R_{\text{int}} = 0.0390$]	1201 [$R_{\text{int}} = 0.0379$]
Coverage of independent reflections	99.3 %	99.6 %
Goodness-of-fit on F^2	1.247	1.145
Final R indices		
$R_1, wR_2 [I > 2\sigma(I)]$	0.0390, 0.1147	0.0305, 0.0888
R_1, wR_2 (all data)	0.0411, 0.1212	0.0307, 0.0892

Note S1: Importance of the Peierls distortions for stabilizing the structure of NbOI₂

The Peierls distortions are energetically favorable as they lower the total electronic energy of the NbOI₂ system. In essence, the Nb–Nb dimerization doubles the size of the repeating unit cell from NbOI₂ to (NbOI₂)₂ and splits each folded d-block band (for instance, the Nb $d_{x^2-y^2}$ and Nb d_{xy} bands split into low-energy valence bands and high-energy conduction bands). The splitting of the bands in the vicinity of the Fermi level lowers the energy of the highest occupied band (v_1), and therefore acts as a driving force towards pairing distortion. In addition, the Nb polar displacement leads to the hybridization of Nb d_{xy} (d_{yz}) orbitals, thereby allowing orbital mixing between the Nb d_{xy} (d_{yz}) and O p_x (p_z) orbitals at the high-symmetry Γ point of the first Brillouin zone. Therefore, the bonding interaction of the O p -block orbitals and the antibonding interaction of the Nb d -block orbitals become more effective for an Nb–O bond than the adjacent O···Nb bonds. This stabilizes the system further by lowering the O p_x (p_z) bands and raising the Nb d_{xy} (d_{yz}) bands.

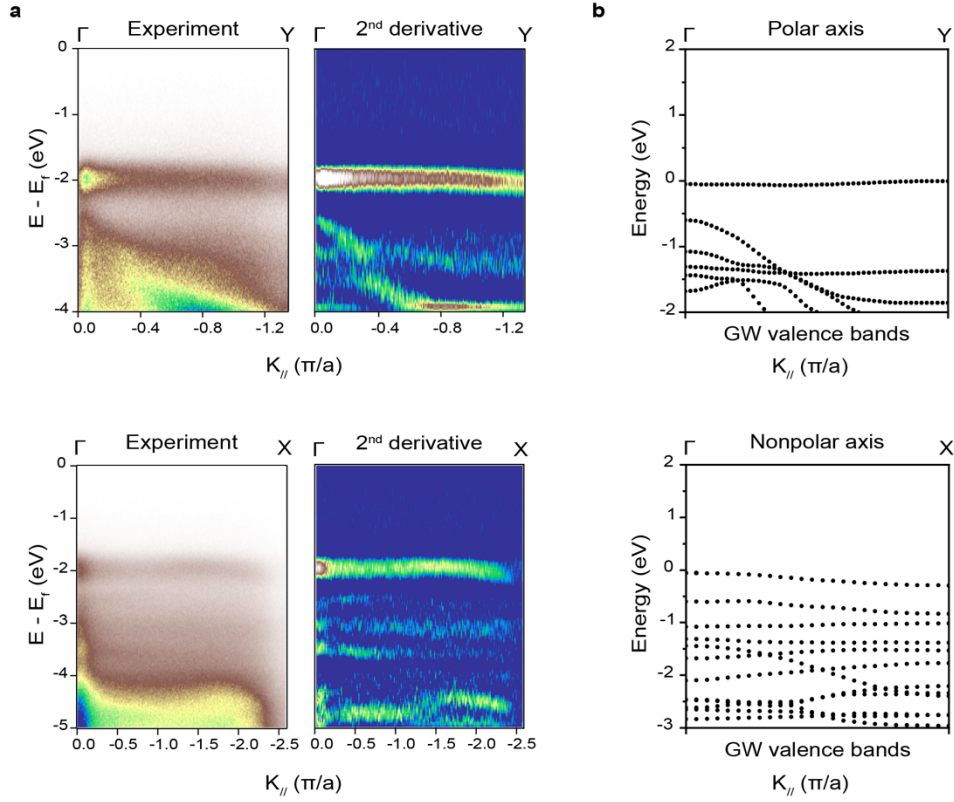


Fig. S1 | Comparison between experimental and theoretical band structures of NbOI₂. **a**, ARPES intensity plots and their corresponding second-derivative plots of bulk NbOI₂ along the polar (top) and nonpolar (bottom) directions, where $k_{||}$ is the in-plane component of electron momentum. Fermi level is at zero energy. **b**, GW calculated band structure of NbOI₂ monolayer in the polar (top) and nonpolar (bottom) directions. The valence band maximum is set to zero energy. It can be observed that the highest energy valence band is broadened in the experiment, particularly at Γ . This can be attributed to interlayer interactions (*see* Fig. S2).

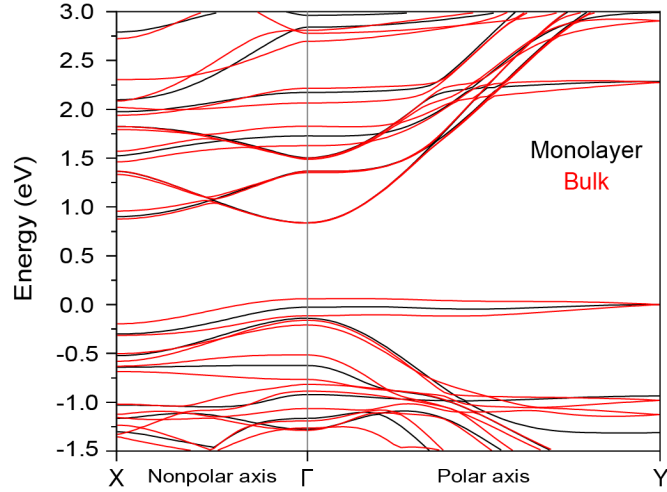


Fig. S2 | Comparison between the DFT monolayer and bulk band structures of NbOI₂. Interlayer interactions in bulk NbOI₂ induce band splitting for the bands that arise from out-of-plane orbitals. This can explain the broadening observed for some bands in the ARPES band structure. The DFT band structures provide qualitative information but should not be used for quantitative comparison with ARPES. The GW band structure (Fig. S1b) includes electron self-energy effects and provides a quantitative description of the band structure.

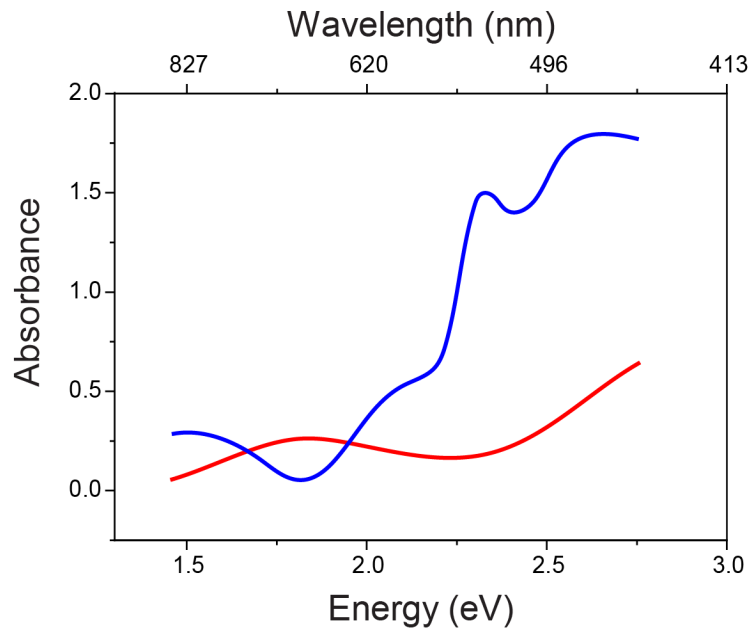


Fig. S3 | Linear absorbance measurements on a NbOI₂ nanosheet. Linear absorbance spectra of a NbOI₂ nanosheet collected with incident white light polarized along the polar and nonpolar directions. Blue (red) line: nonpolar (polar) axis.

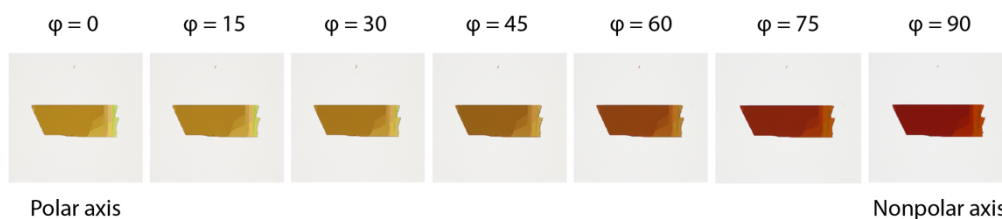


Fig. S4 | A series of optical images of a NbOI₂ nanosheet captured in transmitted light mode under different incident polarizations. ϕ is the polarization angle (relative to the polar axis) of the incident white light. The increase of the absorbance as the linear polarization varies from the polar to the nonpolar direction is due to the large oscillator strength of the nonpolar excitons in the visible region.

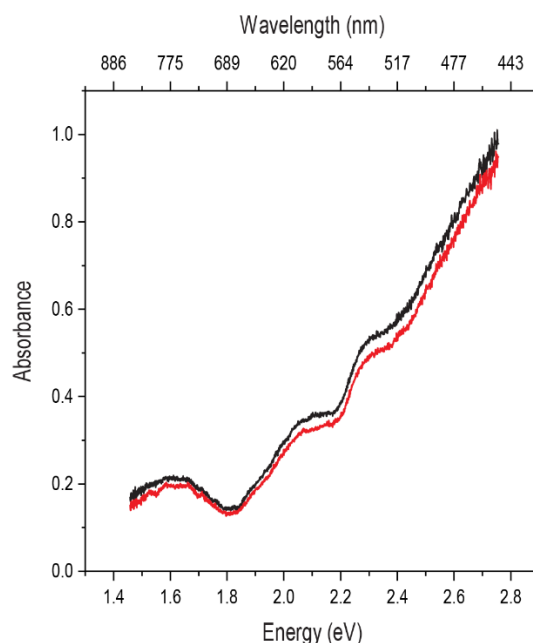


Fig. S5 | Circular absorbance measurements on a NbOI₂ nanosheet. Typical absorbance spectra of a NbOI₂ nanosheet illuminated with right (σ^- , black curve)- and left (σ^+ , red curve)-handed circularly polarized light.

Note S2: Nonlinear optical tensor for the crystallographic $C2$ point group of NbOI_2

For monoclinic $C2$ symmetry with twofold rotation axis about y ($2 \parallel y$), the optical second-order NL polarization ($P^{2\omega}$) has a tensorial form of

$$P^{2\omega} = \begin{pmatrix} P_1 \\ P_2 \\ P_3 \end{pmatrix} = d_{ij} (E^\omega)^2 = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{21} & d_{22} & d_{23} & 0 & d_{25} & 0 \\ 0 & 0 & 0 & d_{34} & 0 & d_{36} \end{pmatrix} \begin{pmatrix} E_1^2 \\ E_2^2 \\ E_3^2 \\ 2E_2E_3 \\ 2E_1E_3 \\ 2E_1E_2 \end{pmatrix}$$

Here, the electric fields E_i are at frequency ω and the P_i is at frequency 2ω . The d_{ij} tensor is the SHG susceptibility tensor. With Kleinman symmetry conditions

$$P^{2\omega} = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{16} & d_{22} & d_{23} & 0 & d_{14} & 0 \\ 0 & 0 & 0 & d_{23} & 0 & d_{14} \end{pmatrix} \begin{pmatrix} E_1^2 \\ E_2^2 \\ E_3^2 \\ 2E_2E_3 \\ 2E_1E_3 \\ 2E_1E_2 \end{pmatrix}$$

where subscripts

1 = x (nonpolar axis),

2 = y (polar axis),

3 = z (the out-of-plane direction / fundamental beam propagation axis),

4 = 23 = 32 = yz = zy,

5 = 13 = 31 = xz = zx, and

6 = 12 = 21 = xy = yx

From the 2D approximation, $d_{14} = d_{23} = 0$; $E_3 = 0$.

$$P_1 = 2d_{16} E_1 E_2$$

$$P_2 = d_{16} E_1^2 + d_{22} E_2^2$$

Thus, the relation between the generated SHG intensity (I) and the polarization angle (φ) of incident fundamental light can be expressed as:

$$I \propto (2d_{16} \cos \varphi \sin \varphi)^2 + (d_{16} \cos^2 \varphi + d_{22} \sin^2 \varphi)^2$$

It is possible to use this equation to fit the experimental data and extract the relative value of d_{22}/d_{16} ($d_{22} \gg d_{16}$).

Using the fact that $(\cos \varphi \sin \varphi) \ll \cos^2 \varphi + \sin^2 \varphi$, we further simplify the intensity by neglecting the mixed component to

$$I \propto (d_{16} \cos^2 \varphi + d_{22} \sin^2 \varphi)^2$$

By this, we can extract the relative value of $\left(\frac{d_{22}}{d_{16}}\right)^2$ by measuring the SHG signal in dependence of the incident angle.

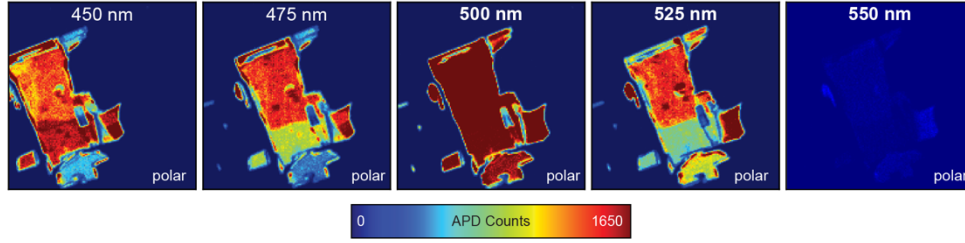


Fig. S6 | The intensity dependence of SHG on the fundamental wavelength. SHG maps of the sample in Fig. 3a at $\lambda_{\text{pump}} = 900, 950, 1000, 1050,$ and 1100 nm. The sample is excited by equally intense excitation pulses linearly polarized along the polar axis. The enhancement of the SHG signal around $\lambda_{\text{pump}} = 1000$ nm is attributed to the combined effect of ferroelectricity and two-photon resonance at the nonpolar exciton states (Note S5 and Fig. S13a).

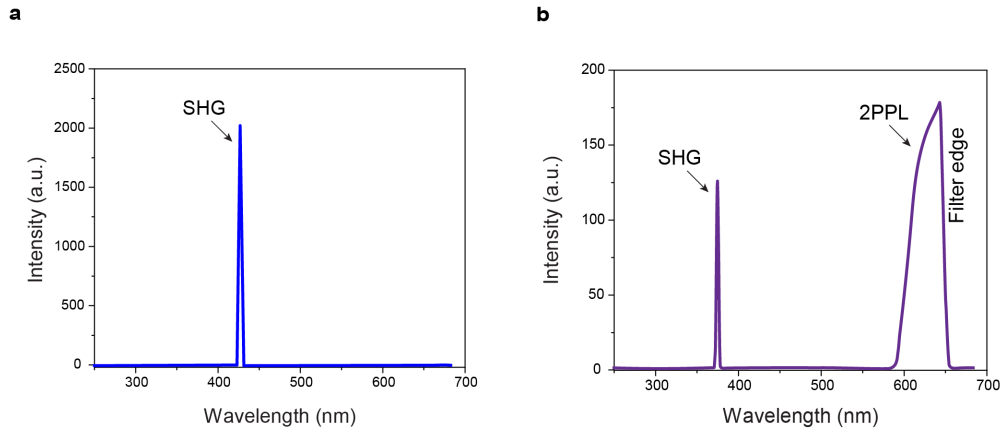


Fig. S7 | Nonlinear optical processes in NbOI₂. Nonlinear spectra for the excitation wavelengths of $\lambda_{\text{pump}} = 850$ nm (a) and 750 nm (b). 2PPL: two-photon photoluminescence.

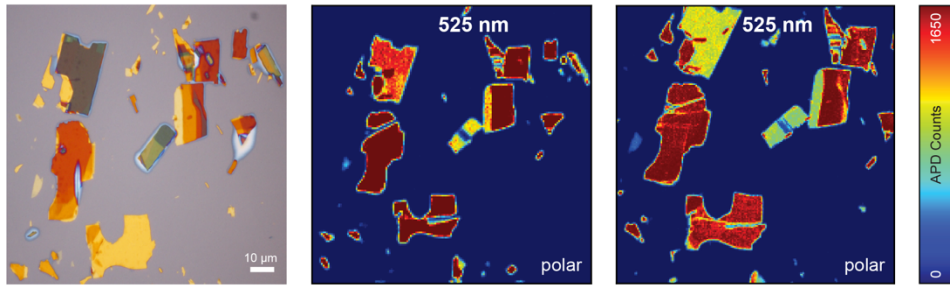


Fig. S8 | Nonlinear optical performance over time. Optical image of NbOI₂ flakes on quartz substrate (left panel) and corresponding SHG maps acquired with the as-prepared sample (center panel) and twelve months after preparation (right panel), excited at $\lambda_{\text{pump}} = 1050$ nm. No significant difference in the NL optical properties is observed between the fresh and aged samples.

Table S2 | Second-harmonic generation susceptibility ($\chi^{(2)}$) and absolute conversion efficiency (η_{SHG}) of different nonlinear materials at room temperature.

Material	Thickness (t)	$ d_{ij} $	$\chi^{(2)}$ ($\times 10^{-11} \text{ m V}^{-1}$)	η_{SHG} (%) [*]	Fundamental wavelength (nm)	Reference
NbOI ₂	monolayer	d_{eff}	19	3×10^{-4}	1050 ^R	This work
NbOI ₂ (3.1% strain)	monolayer	d_{eff}	113	1×10^{-2}	1050 ^R	This work
MoS ₂	monolayer	d_{eff}	0.6	3×10^{-9}	1600	Ref. ¹
			2.9		1560	Ref. ²
			0.2		1560	Ref. ³
			7.8		1400 ^R	Ref. ⁴
			4.5	$\sim 10^{-8}$	1350 ^R	Ref. ¹
			3.1		1210 ^R	Ref. ¹
			10		884 ^R	Ref. ⁵
			32		810 ^R	Ref. ⁶
MoSe ₂	monolayer	d_{eff}	5		1620 ^R	Ref. ⁷
WSe ₂	monolayer	d_{eff}	6	2.7×10^{-8}	1500 ^R	Ref. ⁸
<i>h</i> -BN	monolayer	d_{eff}	0.1		810	Ref. ⁶
GaSe	monolayer	d_{eff}	1.8	6×10^{-8}	1560	Ref. ⁹
GaTe	monolayer	d_{eff}	0.115	1.3×10^{-9}	1560	Ref. ¹⁰
TaAs	bulk	d_{33}	720		800	Ref. ¹¹
GaAs	bulk	d_{14}	70		810	Ref. ¹²
LiNbO ₃	bulk	d_{33}	5.2		852	Ref. ¹³
β -BaB ₂ O ₄	bulk	d_{22}	10.2		880	Ref. ¹⁴
Quartz	bulk	d_{11}	0.08		884	Ref. ¹⁵

^{*} denotes maximum attainable efficiencies measured at input powers above which the SHG power begins to deviate from the quadratic behavior due to thermal effects. The $\chi_s^{(2)}$ and η_{SHG} of NbOI₂ scale with thickness, as shown in Fig. S10. The effective SHG efficiency of monolayer NbOI₂ in Table S2 is obtained by dividing the SHG sheet efficiency by its thickness. ^R indicates that the SHG energy is in resonance with the excitonic states of the material system. The off-resonance efficiency of NbOI₂ at $\lambda_{\text{pump}} = 800 \text{ nm}$ is lower by a factor of 5 compared to its on-resonance efficiency at $\lambda_{\text{pump}} = 1050 \text{ nm}$ (Fig. 3f). Since there are large discrepancies in the experimentally reported $\chi_{eff}^{(2)}$ values for 2D materials due to the different formalisms^{1, 5, 6, 9, 16-19} adopted in literature (for instance, ~ 3 orders of magnitude variation in $\chi_{eff}^{(2)}$ was reported for monolayer MoS₂ at 810 nm)^{5, 19}, the conversion efficiency would be a better figure of merit to evaluate the NL response. Yet, η_{SHG} may strongly depend on the experimental conditions, thickness, and pump and SHG self-absorption. This can result in difficulties in comparing the SHG efficiency across bulk and monolayer materials, and therefore, caution should be taken when making comparisons of different sets of data in reports.

Note S3: Calculated single particle SHG susceptibility ($|\chi_{yyy}^{(2)}|$) for unstrained monolayer NbOI₂

The single particle SHG susceptibility is defined according to Eq. 35 in Ref. 20:

$$\chi_{ijk}^{(2)}(-2\omega, \omega, \omega) = \frac{e^3}{\tilde{\omega}^3 \hbar^2 m^3 V} \sum_{\mathbf{k}nml} \frac{G_{nml}^{ijk}}{\omega_{mn}(\mathbf{k}) - 2\tilde{\omega}} \left[\frac{f_{nl}(\mathbf{k})}{\omega_{ln}(\mathbf{k}) - \tilde{\omega}} + \frac{f_{ml}(\mathbf{k})}{\omega_{ml}(\mathbf{k}) - \tilde{\omega}} \right] \quad (\text{S1})$$

where $G_{nml}^{ijk} = \frac{1}{2} \text{Im}\{p_{nm}^i(\mathbf{k})[p_{ml}^j(\mathbf{k})p_{ln}^k(\mathbf{k}) + p_{ml}^k(\mathbf{k})p_{ln}^j(\mathbf{k})]\}$, $p_{nm}^i(\mathbf{k}) = \langle u_{n\mathbf{k}} | p^i | u_{m\mathbf{k}} \rangle$ is the momentum matrix element, $f_{nl}(\mathbf{k}) = f_n(\mathbf{k}) - f_l(\mathbf{k})$ is the occupation function difference, $\hbar\omega_{mn}(\mathbf{k}) = \epsilon_{m\mathbf{k}} - \epsilon_{n\mathbf{k}}$ is the single particle energies difference, which can be obtained by solving the mean field single particle Hamiltonian $H_{\mathbf{k}}u_{n\mathbf{k}} = \epsilon_{n\mathbf{k}}u_{n\mathbf{k}}$.

The single particle SHG susceptibility for unstrained monolayer NbOI₂ is calculated within DFT on a $48 \times 24 \times 1$ k-grid with 33 valence and 33 conduction bands. The monolayer cell volume (V) in the above expression is defined using the thickness (0.73 nm) for monolayer NbOI₂. The energy denominator in Eq. 35 of Ref. 20 contains a small imaginary part $\tilde{\omega} = \omega + i\eta$, which we choose to be the same as the energy step in ω (0.01 eV). Numerical results are shown in Supplementary Fig. S9 and Table S3. This approach ignores electron self-energy effects and excitonic effects.

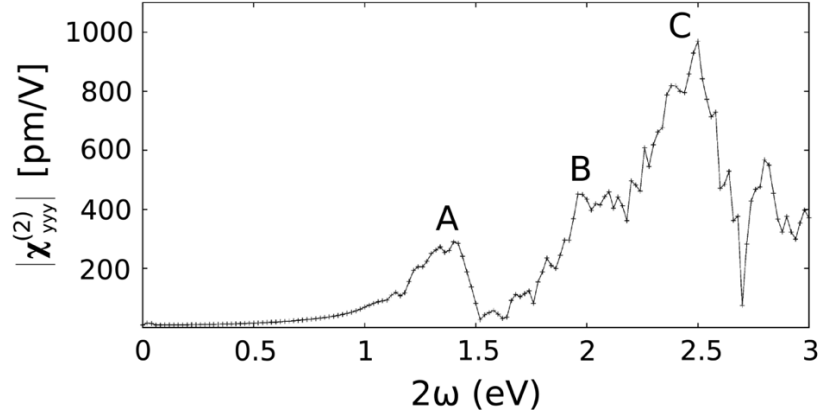


Fig. S9 | Calculated single particle SHG susceptibility ($|\chi_{yyy}^{(2)}|$) for unstrained monolayer NbOI₂. Calculated absolute value of $|\chi_{yyy}^{(2)}|$ as a function of the energy of the out-going photon (2ω), where y is the polar direction. Supplementary Table S3 provides information on the origin of the A, B and C peaks marked in the figure.

Table S3 | Analysis for the first three lowest energy peaks in the single particle SHG susceptibility ($|\chi_{yyy}^{(2)}|$). These peaks arise from the poles in Eq. S1, which correspond to the transitions shown in the table. ‘ $v_4 \rightarrow c_2$ ’ refers to the transition between the 4th highest-energy valence band and the 2nd lowest-energy conduction band. X and Γ are defined in Fig. 2a of the main text.

Peak label	Band transitions	Brillouin zone
A	$v_1 \rightarrow c_1, v_1 \rightarrow c_2$	Γ
B	$v_4 \rightarrow c_1, v_5 \rightarrow c_1, v_2 \rightarrow c_2, v_3 \rightarrow c_2$	X
C	$v_4 \rightarrow c_2, v_6 \rightarrow c_2$	Γ

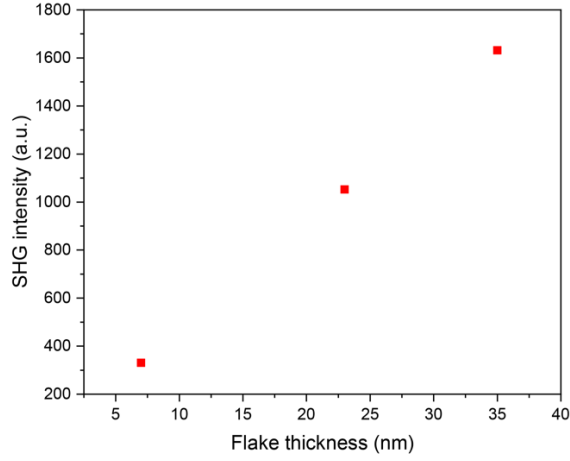


Fig. S10 | Nonlinear optical response of NbOI₂ as a function of thickness. The SHG intensity of NbOI₂ flakes of different thicknesses at $\lambda_{\text{pump}} = 900$ nm. The samples are excited by equally intense excitation pulses linearly polarized along the polar axis. The deviation from the quadratic dependence of SHG intensity on the layer number, usually observed for ultrathin 2D films, can be attributed to the interference effects between the surface and bulk SHG contributions, which result in high-contrast oscillations in the overall nonlinear signal²¹. These SHG contributions are influenced by the absorption of the pump beam, the partial reabsorption of the emitted signal, the system's resonant energy, and the complex refractive index and associated phase mismatch effects, which vary with thickness²²⁻²⁴.

Note S4: Ferroelectric domain walls in NbOI₂

Due to the one-dimensional (1D) FE nature of NbOI₂, only 180° domain walls are permissible. Energetically, the side-by-side 180° domain walls between domains polarized in antiparallel directions are more favorable than the head-to-head (tail-to-tail) walls²⁵. Although the antiparallel FE domains yield the same SHG intensity, their Ising-type 180° domain walls can still be seen as dark lines in the 2D SHG intensity maps. This happens because the SHG fields generated in the different domains are exactly 180° out-of-phase with each other, causing them to interfere destructively at the domain–domain interface.

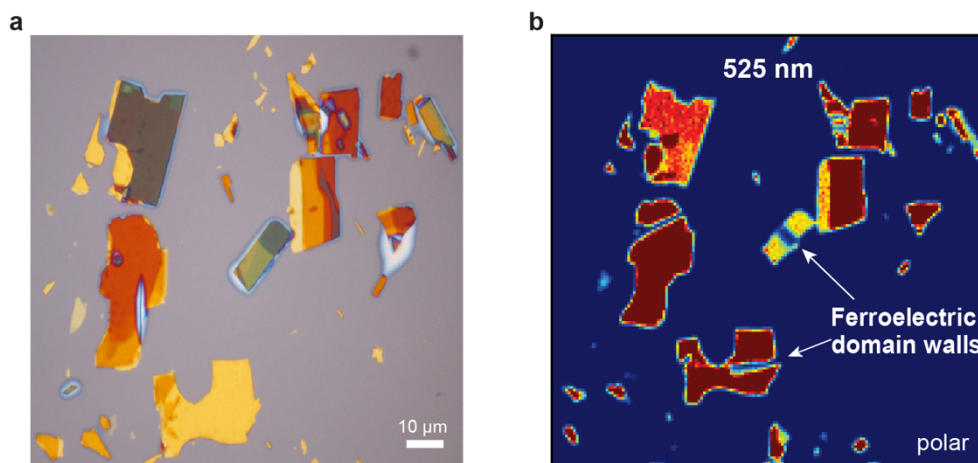


Fig. S11 | Ferroelectric domain walls in NbOI₂. Optical image of NbOI₂ flakes on quartz substrate (a) and the corresponding SHG map at $\lambda_{\text{pump}} = 1050$ nm (b) (same as in Fig. S8). The dark lines in the 2D SHG map point out 180° domain walls separating oppositely polarized FE domains.

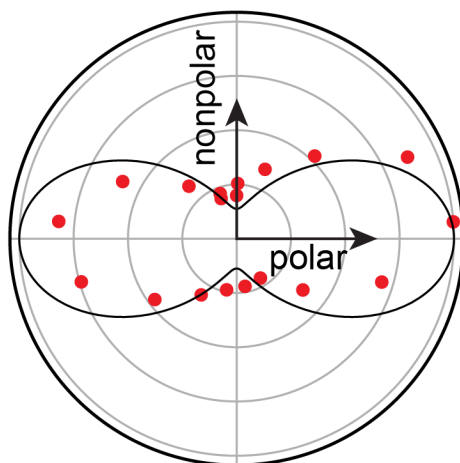


Fig. S12 | Polar plot of the SHG intensity as a function of the polarization angle of the incident beam at $\lambda_{\text{pump}} = 1500 \text{ nm}$. Experimental data (red circles) and theoretical model prediction (black line).

Note S5: Polarization state of the generated SHG signal in NbOI₂

The polarization of the detected SHG signal is analyzed along the two in-plane crystallographic axes of the sample. In doing so, linear polarizers were used in the excitation and detection channels^{26, 27}. The excitation and detection polarizations were co-linearly (YY, ZZ) or cross-linearly (YZ, XY) polarized along either the *b* or *c* axis, giving a total of four different configurations (Fig. S13a). In accord with the theoretical model, the emitted SHG light is found to be strongly polarized along the nonpolar direction, regardless of the excitation polarization. Furthermore, polarization-resolved SHG spectra taken with circularly polarized light ($\sigma = \pm 1$) are shown in Fig. S13b. As expected from a monoclinic system under circular optical excitation perpendicular to the two-fold rotational axis²⁸, the cross-circularly polarized SHG component (σ^+/σ^- or σ^-/σ^+) of NbOI₂ is always stronger than the co-circularly polarized SHG component (σ^+/σ^+ or σ^-/σ^-).

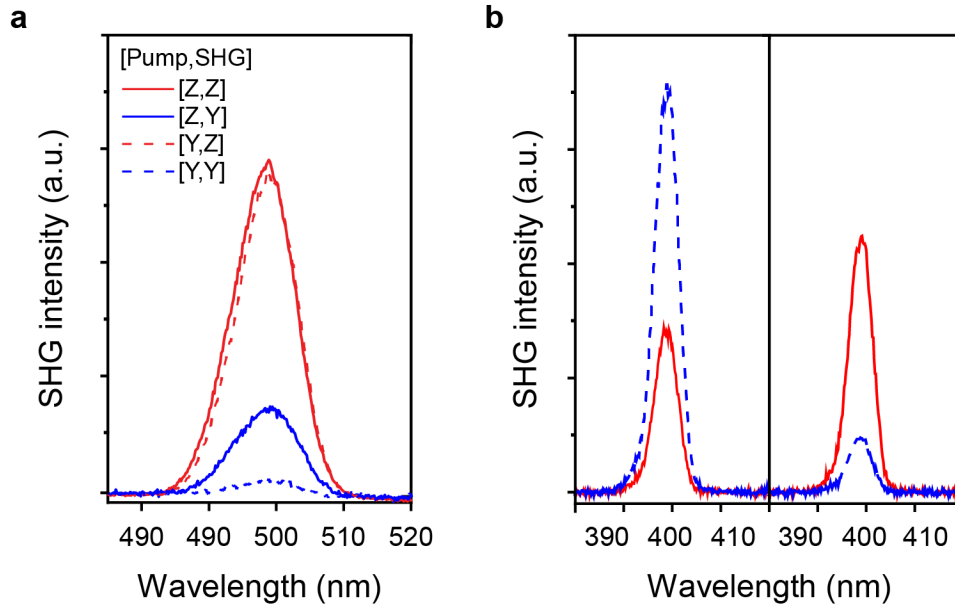


Fig. S13 | Polarization-resolved SHG in NbOI₂. **a**, Polarization-resolved SHG spectra obtained with co-linearly (YY, ZZ) and cross-linearly (YZ, XY) polarized excitation and detection. The fundamental wavelength is 1000 nm. Y indicates the polarization along the polar *b* axis of NbOI₂ while Z indicates the polarization along the nonpolar *c* axis. **b**, Polarization-

resolved SHG spectra obtained with co-circularly (σ^+/σ^+ , σ^-/σ^-) and cross-circularly (σ^+/σ^- , σ^-/σ^+) polarization configurations with a fundamental wavelength of 800 nm. Solid red (dashed blue) line: σ^+ (σ^-) excitation. Left (right) panel: σ^+ (σ^-) detection.

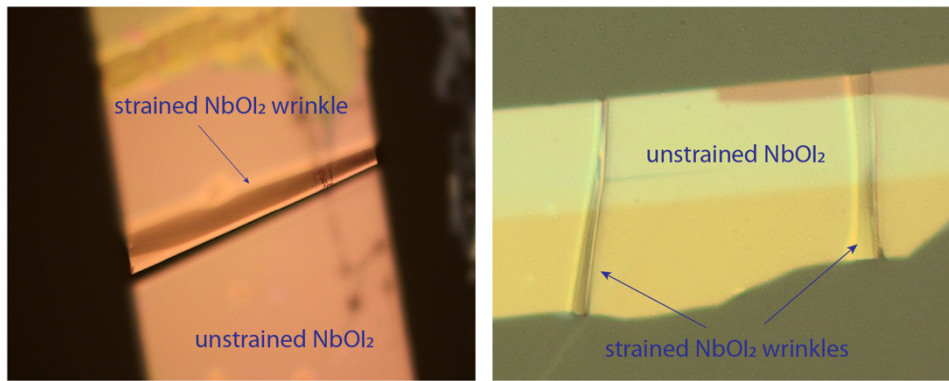


Fig. S14 | Optical images of wrinkled NbOI₂ flakes. The NbOI₂ wrinkles are generated via the buckling-induced delamination process.

Note S6: Estimation of the tensile strain magnitude of the NbOI₂ wrinkles

The maximum tensile strain (ε) accumulated on top of the wrinkles can be estimated from the geometry of the wrinkles as²⁹:

$$\varepsilon \sim \frac{\pi^2 h t}{(1 - \tilde{\nu}^2) w^2}$$

where h and w are the height and width of the wrinkle, t is the thickness of the flake, and $\tilde{\nu}$ is the NbOI₂ Poisson's ratio (0.087). The h , w , and t are determined by atomic force microscopy (AFM).

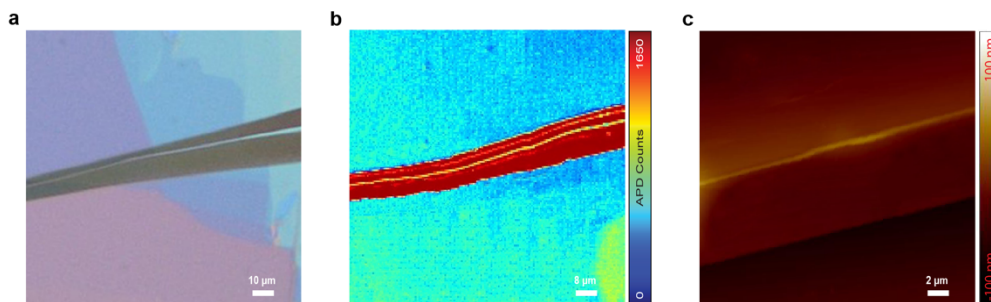


Fig. S15 | Characterization of wrinkled NbOI₂ flake. **a**, Optical image, **b**, SHG map, and **c**, Topography image of a wrinkled NbOI₂ flake. The SHG map is collected at $\lambda_{\text{pump}} = 1050$ nm.

Note S7: NbOI₂ polar switching

Applying an external electric field $E = (0, E_2, 0)$ along the polar direction can elongate or shorten the polar vector by an amount $\Delta P = (0, \Delta P_2, 0)$, where $\Delta P_2 = \varepsilon_0 \chi_{22}^{(1)} E_2 + \Delta P_s$ with ε_0 = the vacuum permittivity and $\chi_{22}^{(1)}$ is the linear electric susceptibility. Unlike the linear dielectric response ($\varepsilon_0 \chi_{22}^{(1)} E_2$), the history-dependent P_s scales nonlinearly with the electric field and is responsible for the hysteretic nature of the $P - E$ characteristic. At low electric fields, the sample behaves like an ordinary dielectric. However, when the electric field is increased to a critical value (so-called coercive field E_c), ferroelectric domains with oppositely oriented polarization begin to switch and align themselves along the electric field direction, resulting in the rapid increase of current and polarization. Under higher electric fields, the polarization is restored to linear and eventually reaches a saturation state due to the complete switch of the ferroelectric domains. When the field strength is swept backward, some domains would back-switch, however, a nonzero net polarization (remnant polarization P_r) persists even after the electric field is removed. To obtain a zero polarization, an opposite-pointing coercive field is needed. With further increasing the opposite field strength, a similar polarization profile with the reverse sign is observed, indicative of polarization reversal. The deviation of the $P - E$ curve in Fig. 4d (in the main text) from ideal rectangular-like hysteresis is due to the relatively small bandgap of NbOI₂ and associated leakage issues³⁰. The leakage current broadens the current peaks and yields a more rounded $P - E$ hysteresis. It has also been shown that both the magnitude of polarization (P_s) and the ferroelectric switching barrier (E_c) can be controlled by strain³¹. This implies that the field dependent SHG response can also be largely modulated by strain.

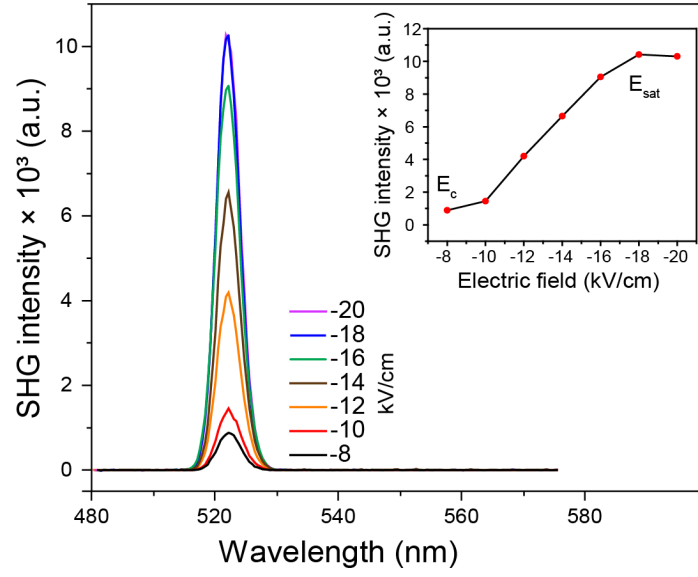


Fig. S16 | Electric field dependent SHG of NbOI₂ nanosheet. SHG spectra as a function of the external electric field strength. The electric field is applied along the polar direction of NbOI₂. The fundamental wavelength is 1050 nm. The inset shows the peak SHG intensity as a function of external electric field strength. The SHG intensity is not zero at the coercive field due to the incomplete cross cancellation of the SHG intensity between antiparallel domains in the area of the sample being probed.

The SHG intensity (I_{SHG}) of NbOI₂ can be expressed in terms of P_s as:

$$I_{SHG} \propto d_{22}^2 \propto (\chi^{(n)} P_s)^2$$

where $\chi^{(n)}$ is a nonlinear optical susceptibility tensor of a higher rank^{32, 33}.

References

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