Non-synchronous bulk photovoltaic effect in two-dimensional interlayer-sliding ferroelectrics

Rui-Chun Xiao1, Yang Gao2✉, Hua Jiang3, Wei Gan1, Changjin Zhang4,14 and Hui Li3✉

Spontaneous polarization and bulk photovoltaic effect (BPVE) are two concomitant physical properties in ferroelectric materials. The flipping of ferroelectric order usually accompanies the switching of BPVE in all directions because both of them are reversed under the inversion symmetry. In this study, we report the non-synchronous BPVE in two-dimensional (2D) interlayer-sliding ferroelectric materials featuring unsynchronous in-plane BPVE (light-induced photocurrent in the xy plane) and switchable out-of-plane BPVE (light-induced polarization along the z-direction). Symmetry analysis within the abstract bilayer crystal model and first-principles calculations validate these BPVE properties. It is because the positive and negative ferroelectric states caused by interlayer sliding are related by mirror symmetry which cannot flip all the BPVE tensor elements. This finding extends the understanding of the relationship between ferroelectricity and BPVE. On one hand, the switchable out-of-plane BPVE can be used to design switchable photoelectric devices. On the other hand, the in-plane BPVE is robust against the ferroelectric flipping, and the unsynchronous character is beneficial to construct larger-scale photoelectric devices.

INTRODUCTION

Ferroelectricity and bulk photovoltaic effect (BPVE) are two basic physical phenomena that emerge in condensed matter materials due to symmetry breaking. Generally speaking, BPVE, an intrinsic optical rectification phenomenon, appears in materials without inversion symmetry which can convert light to electricity as solar cells, hence it is naturally fulfilled the symmetry requirement in ferroelectric materials. As a result, the ferroelectric materials with switchable electronic polarization are one of the most studied BPVE materials1–3, and the corresponding energy conversion efficiency can exceed the Shockley-Queisser limit3–5.

It is known to us that the BPVE usually switches with the ferroelectric order. Under the inversion operation, both ferroelectric order and BPVE in all directions switch signs, i.e., BPVE switches synchronously with the ferroelectric order. Therefore, the ferroelectric polarization is often taken as a handle to manipulate the direction of BPVE photocurrent in, e.g., perovskite oxides BiFeO3–8, Pt/BiFeO3/SrRuO3, 2D (two-dimensional) CuInP2Se5,6, charge-transfer complex7, SnTe monolayer12, MX (M = (Ge, Sn) and X = (Se, S))11,13 etc. However, from the aspect of symmetry, the ferroelectric polarization is a polar vector, while the BPVE coefficients form a rank-three tensor. They are hence subject to distinct symmetry transformation rules, and should not always synchronize. There should exist components of the BPVE tensor that do not switch with the ferroelectric order, which was visioned14, but has not been comprehensively studied before. For example, a mirror reflection perpendicular to the polarization will reverse the polarization just as the inversion operation does, while it cannot flip all the components of the BPVE. Thus, a precise understanding of the relationship between the ferroelectric order and the BPVE is of tremendous significance in both fundamental research and the design of photoelectric devices.

In this work, we think the exceptional case that non-synchronous BPVE with ferroelectric order can be found in 2D interlayer-sliding ferroelectric materials15. As demonstrated in recent experiments, the out-of-plane ferroelectricity can be achieved in bilayer WTe2,16–19, BN20,21, InSe22,23, MoS224,25 etc. by interlayer sliding, which effectively extends the family of 2D ferroelectric materials26–29. This ferroelectric flip mechanism may lead to the BPVE property beyond the switchable scenario.

Focusing on the four most common stacking cases of 2D bilayers with interlayer sliding, we use an abstract bilayer crystal model to locate the available configurations and symmetries with nontrivial ferroelectric order. We find two cases (Case 1b and Case 2a) can have the possibility to achieve the interlayer-sliding ferroelectricity, moreover the opposite ferroelectric states in the two cases are all related by the mirror operator. Coincidently, the interlayer-sliding ferroelectric materials found in the experiments are attributed to these two cases. Using bilayer MoS2 and WTe2 as representative examples, we performed first-principles calculations and found that the in-plane BPVE does not change the sign with ferroelectric order, which is different from conventional ferroelectrics. In contrast to in-plane BPVE, out-of-plane BPVE switches with the reverse of the ferroelectric order. This non-synchronous character will lead to distinct photovoltaic phenomena in experiments.

RESULTS

Polarization flipping via interlayer sliding

Now we introduce the mechanism of the polarization flipping via interlayer sliding. Figure 1a shows the out-of-plane polarization \( P_z \) in bilayer vdW (van der Waals) material without inversion nor horizontal mirror symmetry. Because the in-plane polarization is usually annihilated by in-plane rotational symmetry in real materials, the \( P_z \) and \( -P_z \) polarization are denoted as \( +P \) and \( -P \) for short. The out-of-plane polarization can be flipped in two different ways: (i) intralayer movement, i.e., atomic relative

1Institute of Physical Science and Information Technology and Information Materials and Intelligent Sensing Laboratory of Anhui Province, Anhui University, Hefei 230601, China.
2Department of Physics, University of Science and Technology of China, Hefei 230026, China.
3School of Physical Science and Technology, Soochow University, Suzhou 215006, China.
4High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, China.
5email: ygao87@ustc.edu.cn; huili@ahu.edu.cn

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displacements in each monolayer [Fig. 1b], and (ii) interlayer sliding\textsuperscript{15} where the crystal structure of each monolayer is invariant [Fig. 1c]. Although polarization flipping can be achieved in both situations, the underlying symmetries of the switch of ferroelectric states are different. For situation (i), the $+P$ and $-P$ ferroelectric states are correlated by the inversion operator, as indicated in unit cells in Fig. 1a, b. While for situation (ii), the $+P$ and $-P$ ferroelectric states are correlated by the mirror symmetry $M_{iy}$, as seen in unit cells in Fig. 1a, c (detailed analyses are presented in the Symmetry analysis section for real materials). The interlayer sliding mechanism is feasible experimentally and has been observed in bilayer vdW materials\textsuperscript{16–19} as stated above, which further extends the family of 2D ferroelectric materials\textsuperscript{26}.\textsuperscript{27} Out-of-plane polarization via interlayer sliding in Fig. 1a, and the black arrows mean the interlayer sliding direction. The polarization is reversed to $b$ when the crystal structure of each monolayer is invariant with respect to the anions.

Next, we analyze how to design the bilayer vdW materials with interlayer sliding, and we can analyze their symmetries with an abstract bilayer crystal model which only considers the above crystal symmetries and ignores the specific crystal structures. The complete symmetry analysis for each case is summarized in Supplementary Note 1, and the corresponding results are shown in Table 1. As can be seen, Case 1b and Case 2a host the out-of-plane polarization, and the two opposite interlayer-sliding states are correlated by $M_{iy}$ operator, instead of inversion $i$ operator. In contrast, the crystal structures in Case 1a and Case 2b possess the inversion symmetry whatever the interlayer-sliding vector, which forbids the occurrence of ferroelectricity and BPVE.

With the abstract bilayer crystal model, the interlayer-sliding ferroelectric materials are further classified into two kinds (Case 1b and Cases 2a). Such classification outlines a potential roadmap to search for more 2D ferroelectric materials, which could greatly facilitate and advance the research and application of BPVE in 2D ferroelectric materials. Table 2 summarizes several bilayer candidates for the above four cases that can be experimentally realized by either simply mechanical exfoliation or tear-and-stack methods. In particular, the out-of-plane ferroelectricity of the bilayer WTe\textsubscript{2}–MoS\textsubscript{2} with Case 1b and BN\textsubscript{16,20,21} and InSe\textsubscript{22,23}–MoS\textsubscript{2} bilayer-TMD\textsuperscript{24,25} with Case 2a have been discovered in experiments recently. The abstract bilayer model is convenient and efficient in symmetry analysis for vdW materials with interlayer sliding because it does not rely on the specific crystal structure. The symmetry of trilayer vdW materials with interlayer sliding can also be obtained using a similar method, and the results are shown in Supplementary Note 7, where the transformations of ferroelectricity and BPVE are also discussed there.

Now we analyze the characters of in-plane and out-of-plane BPVE of the interlayer-sliding ferroelectric materials in Case 1b and Case 2a under the normal incidence of light. The in-plane BPVE current density is

$$J_x = \sum_{bc} \sigma_{bc}^{\mathrm{ee}} E_b(\omega) E_c(-\omega).$$ \hfill (1)

where $a, b, c \in \{x, y\}$, $E_b$ and $E_c$ are electric fields of light along $b$ and $c$ direction, $\omega$ is the frequency of light, and $\sigma_{bc}^{\mathrm{ee}}$ is the BPVE coefficient. In contrast to $x$ and $y$ directions, the photo-excited shift of the wave package along the out-of-plane direction induces a static electric polarization instead of an electric current along the $z$-direction because the $z$-direction of 2D materials is discontinuous. The out-of-plane BPVE polarization is

$$P_z = \sum_{bc} \sigma_{bc}^{\mathrm{ee}} E_b(\omega) E_c(-\omega).$$ \hfill (2)

where $P_z$ is $z$-component polarizability. Similar to other nonlinear optics tensors, the BPVE tensor $[\sigma_{ab}^{\mathrm{ee}}]_{3 \times 3 \times 3}$ in Eq. (1) [or Eq. (2)] obeys

$$\sigma_{jk}^{\mathrm{ee}} = \sum_{abc} R_{ia} R_{jb} R_{kc} \sigma_{bc}^{\mathrm{ee}}.$$ \hfill (3)

where $[R_{ij}]$ is the $3 \times 3$ matrix of the symmetry operator $R$. As shown in Fig. 1f, $M_{y}$ will result in the reverse of the out-of-plane vector with invariant in-plane vectors, and the corresponding

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**Fig. 1** Polarization flipping in a 2D vdW bilayer material via intralayer movement or interlayer sliding, and related symmetries. a A 2D system with positive out-of-plane polarization $+P$. b The polarization is reversed to $-P$ by atom displacements in each monolayer, and the black arrow means the movement of the cations relative to the anions. c The polarization is reversed by interlayer sliding and the black arrows mean the interlayer sliding direction. d The basis vectors and their transformations under $i$ inversion symmetry $f$ horizontal mirror symmetry. The black rectangles denote the bilayer unit cells in (a)-(c), and the gray rectangles denote the monolayer unit cells.
The operator matrix is

$$[M_{xy}] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}.$$ (4)

The opposite states are connected by the mirror operator $[M_{xy}(+P) = -P]$ in interlayer-sliding ferroelectric materials. Therefore, the in-plane BPVE coefficient is invariant with the change of ferroelectric orders, i.e., $\sigma_{bc}^x(+P) = \sigma_{bc}^x(-P)$, $a, b, c \in \{x, y\}$, according to Eq. (3). This is strikingly different from the out-of-plane case where the BPVE coefficient is reversed with the switch of ferroelectric orders, as indicated by $\sigma_{bc}^z(+P) = -\sigma_{bc}^z(-P)$ ($b, c \in \{x, y\}$). The calculated BPVE characters in Fig. 1a, c by a 1D effective model are also consistent with our symmetry analysis (see Supplementary Note 2).

In contrast, for the ferroelectric states correlated by inversion symmetry $[^I(+P) = -P]$, the inversion operator $[^I]$ will lead to the reverse of all the vectors (Fig. 1d), i.e., $\sigma_{ab}^c(+P) = -\sigma_{ab}^c(-P)$ ($a, b, c \in \{x, y, z\}$) according to Eq. (3). It is the reason why the BPVE coefficients reverse with ferroelectric orders in the conventional ferroelectric materials.

The in-plane BPVE coefficients can be calculated by the standard second-order Kubo formalism theory$^{33,34}$, and the out-of-plane BPVE coefficients can be obtained by a modified second-order Kubo formalism theory$^{12}$ that was proposed recently. BPVE coefficients are calculated by the Wannier function (see Method for details)$^{35–37}$. Recently, theory works indicate that$^{38,39}$ BPVE coefficients are highly related to the geometry theory of electron band. In the following part, we choose a representative material for each case: bilayer MoS$_2$ (Case 2a) and bilayer WTe$_2$ (Case 1b) to perform the numerical first-principles calculations (see Methods section for calculation details).

**First-principles calculation results**

**Bilayer MoS$_2$** Bilayer MoS$_2$ (Case 2a) that is consisted of two identical non-ferroelectric monolayers shows out-of-plane ferroelectricity$^{15}$, which has been confirmed in experiments recently$^{24,15}$. Noting that conventional bilayer MoS$_2$ is stacked in A/B form (Case...
try24,25, which is consistent with the above symmetry analysis. Moreover, the out-of-plane BPVE coefficients switch with the ferroelectric orders due to the mirror image of light (see Supplementary Note 3). It is noted that this unswitchable in-plane BPVE character of interlayer-sliding ferroelectric materials is different from those of conventional ferroelectric materials6,12,40 and antiferromagnets41,42, where the BPVE is switched with the ferroelectric/ferromagnetic order. The in-plane BPVE photocurrent as a function of the polarization direction of light is shown in Fig. 3d, which shows the in-plane BPVE coefficients are the same in two opposite ferroelectric states, as shown in Fig. 2f. Similarly, experimentally prepared bilayer BH4,20,21, InSe22,23, GaSe, etc, possess similar interlayer-sliding ferroelectricity (Case 2a) and the same symmetry. Therefore, similar in-plane and out-of-plane BPVE features are also expected to exhibit in these materials.

**Fig. 2** Calculated results of ferroelectric bilayer MoS2. a Crystal structures of ferroelectric states (upper panel: side view, lower panel: top view). The arrows denote the transformation of the +P and −P states by interlayer rotation. The definitions of +P and −P states are adopted from ref. 24. b Band structure of +P and −P states. c In-plane and out-of-plane BPVE coefficients. d In-plane BPVE photocurrent and f out-of-plane BPVE polarization (in arbitrary unit) with the direction of normal-incidence polarization of light in the +P states. 0 in d and f is the azimuthal angular direction of the polarization of light relative to the x axis, and the dash lines mean the vertical mirror planes.

As shown in Fig. 2c, the calculated in-plane BPVE coefficients with +P and −P states are equal. The in-plane BPVE is invariant with the change of the ferroelectric order as predicted. In addition, σxx = σyx = −σyy, and σxx = σyx = 0 for each ferroelectric state due to the C3v symmetry (see Supplementary Note 3). It is noted that this unswitchable in-plane BPVE character of interlayer-sliding ferroelectric materials is different from those of conventional ferroelectric materials6,12,40 and antiferromagnets41,42, where the BPVE is switched with the ferroelectric/ferromagnetic order. The in-plane BPVE photocurrent as a function of the polarization direction of light is shown in Fig. 3d, which shows the in-plane BPVE coefficients are the same in two opposite ferroelectric states, as shown in Fig. 2f. Similarly, experimentally prepared bilayer BH4,20,21, InSe22,23, GaSe, etc, possess similar interlayer-sliding ferroelectricity (Case 2a) and the same symmetry. Therefore, similar in-plane and out-of-plane BPVE features are also expected to exhibit in these materials.

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Bilayer WTe2. Bilayer WTe2 is composed of two 180°-rotated two monolayers (Case 1b), as shown in Fig. 3a. Even though each monolayer (with C2v = {E, I, Cxx, Myy} symmetry) has the inversion i symmetry, the bilayer breaks this symmetry. Besides, the interlayer-sliding vector along b axis further breaks Mxx and in-plane C2v symmetry. Thereby the bilayer has the C3v = {E, I, Cxx, Myy} symmetry (C3v = C3v + MxxC3v).

Interlayer sliding43,44 induced out-of-plane ferroelectricity in bilayer WTe2 has been verified experimentally18–19. The −P state is the mirror image of +P state, as shown in Fig. 3a. Figure 3b shows the band structures of +P and −P states, where the valence and conduction bands overlap in our calculation. The calculated in-plane BPVE coefficients are shown in Fig. 3c. There are three independent tensor elements σzz, σxx, and σyy, and σzz = σxx = 0 due to the C3v symmetry. The calculated in-plane BPVE coefficients are the same in two opposite ferroelectric orders:

σzz(+P) = σzz(−P), σxx(+P) = σxx(−P), σyy(+P) = σyy(−P), which is consistent with the above symmetry analysis. The in-plane BPVE photocurrent with the direction of polarization of light is shown in Fig. 3d, which shows Mxx symmetry, and its magnitude is dependent on the light (see Supplementary Note 4 for details). Recently, it was shown that bilayer WTe2 exhibits unswitchable in-plane nonlinear anomalous Hall effect18,19. On the contrary, the out-of-plane BPVE coefficients switch with the change of ferroelectric order, σzz(+P) = −σzz(−P), σyy(+P) = −σyy(−P) [Fig. 3e]. Unlike the bilayer MoS2, the out-of-plane BPVE coefficients show anisotropy σxx ≠ σyy, which is consistent with our symmetry analysis. The calculated out-of-plane BPVE coefficients are shown in Fig. 2e. For each ferroelectric state, σzz = σyy, and σxx = 0. Moreover, the out-of-plane BPVE coefficients switch with the ferroelectric order, as following σzz(+P) = σzz(−P), which is consistent with our symmetry analysis. The out-of-plane BPVE is isotropic, and photo-induced polarization is independent of the polarization direction of light due to C3v symmetry, as shown in Fig. 2f.
ferroelectric state due to the absence of in-plane $C_3$ symmetry, leading to the out-of-plane BPVE polarization is dependent on the polarization of light as shown in Fig. 3f. Recently, ZrI$_2$, a sister material of polar semimetals WTe$_2$, is also demonstrated\cite{45} to have interlayer-sliding ferroelectricity. Similar BPVE behaviors with bilayer WTe$_2$ are expected to be observed due to the same symmetry and interlayer-stacking way (Case 1b).

The calculated values of the in-plane BPVE coefficient of bilayer MoS$_2$ and bilayer WTe$_2$ are comparable to the reported monolayer MX ($M = (\text{Ge, Sn})$ and $X = (\text{Se, S})$)\cite{13,48} and larger than 3D conventional ferroelectric materials (such as BiFeO$_3$\cite{49}, BiTiO$_3$, and PbTiO$_3$\cite{58}). The out-of-plane BPVE coefficients are comparable to twisted bilayers graphene\cite{32}, which induces voltage are detectable experimentally. We can distinguish the photo-induced polarization and intrinsic polarization of interlayer-sliding ferroelectric materials in two subsequent detections with/without light in experiments.

We can calculate the light-induced out-of-plane electric dipole moment and voltage caused by the out-of-plane BPVE, and estimate the possibility to flip the ferroelectric order. With light power of $2.65 \times 10^{11}$ W/cm$^2$ (equivalent electric field $E = 1$ V/nm) and a typical value of $\sigma_{\text{xx}} = \sigma_{\text{yy}} = 1$ eV$^2$ for the out-of-plane BPVE coefficients, the light-induced polarization $p_{\text{dr}} = 1$ e/nm$^2$, meanwhile the light-induced voltage difference between the two layers ($V = p_{\text{dr}} d / \varepsilon_0$, $d = 1$ nm) is found to be 1.8 V. The photo-induced polarization is already bigger than intrinsic polarization of interlayer-sliding ferroelectric materials (about 0.01 e/nm$^2$)\cite{15}, and the photo-induced out-of-plane voltage is also bigger than the flipping voltage (about 0.1 V/nm) in experiments\cite{16-25}. Therefore, we think the photo-induced polarization can flip the ferroelectric order when the laser intensity is larger enough. Recently, experiment\cite{50} shows that the stacking order in bulk WTe$_2$ can be manipulated by ultrafast optical excitation, which indicates the possibility for the flip the ferroelectric order by optical irradiation. The kinetic process of ferroelectric phase transition under light is beyond the scope of current work, which needs to be further studied.

In our work, we only studied BPVE caused by the electronic shift current mechanism. While recently studies\cite{51-53} showed that excitons can enhance BPVE even above the band gap. The excition effect on the BPVE in interlayer-sliding ferroelectric materials is deserved further study, however, the BPVE behavior with the ferroelectric order should not be changed because it is constrained by symmetry.

**DISCUSSION**

According to the above two specific examples, the in-plane BPVE is invariant, while the out-of-plane BPVE reverses with the change of ferroelectric order in interlayer-sliding ferroelectric materials. The ferroelectric order and BPVE in bilayer interlayer sliding ferroelectric materials are subject to different symmetry transformation rules, and do not always synchronize. The study of non-synchronous BPVE with the ferroelectric order in mirror symmetry-related ferroelectric materials allows the comprehension of the relationship between them in another view.

Moreover, these BPVE characters in 2D interlayer-sliding ferroelectric materials will lead to distinctive photovoltaic phenomena and applications in photoelectric devices. The in-plane BPVE photocurrents in a single crystal of interlayer-sliding ferroelectric materials are invariant with two opposite ferroelectric domains, thus the photovoltaic currents between different domains superimpose rather than cancel, as shown in Fig. 4. Since ferroelectric domains are often unavoidable in real materials, especially for the interlayer-sliding ferroelectric materials fabricated via the tear-and-stack method\cite{20,21,25,54}. Therefore, this unswitchable BPVE feature boosts the development of large-scale photovoltaic devices that are immune to the polarization of ferroelectric domains. Nevertheless, the out-of-plane BPVE inverses between
the opposite ferroelectric orders (Fig. 4), which can be utilized to construct switchable photoelectric devices.

In conclusion, we use the abstract bilayer crystal model to analyze the symmetries of the four most common cases of bilayer vdW materials with interlayer sliding and found two cases (Case 1b and Case 2a) can have the possibility to achieve the interlayer-sliding ferroelectricity, which the interlayer-sliding ferroelectric materials found in experiments fall into. We revealed that the opposite ferroelectric states in the interlayer-sliding ferroelectric materials are linked by the horizontal mirror symmetry, leading to the in-plane BPVE being invariant while the out-of-plane BPVE switches with opposite ferroelectric states. BPVE in all directions of interlayer-sliding ferroelectric materials are not flipped synchronously with the ferroelectric order, which is different from the scenario occurs in traditional ferroelectric materials. Our theoretical study provides a strategy for a comprehensive understanding of the relationship between the ferroelectric order and BPVE in 2D interlayer-sliding ferroelectric materials. Moreover, the switchable out-of-plane BPVE can be used to design switchable photoelectric devices. On the other hand, the in-plane BPVE is robust against the ferroelectric order, and the unswitchable character is beneficial to construct larger-scale photoelectric devices.

METHODS

In-plane and out-of-plane BPVE theory

According to the second-order Kubo formalism theory33,34, $\sigma_{bc}$ in the Eq. (1) of the main text can be expressed as

$$\sigma_{bc} = \frac{1}{2} \sigma(\omega) \equiv \frac{1}{2} \text{Re}\left(\chi_{bc}^\varphi + \chi_{cb}^\varphi\right),$$

where $\chi_{bc}^\varphi(\omega) = -\frac{e^2}{(2\pi)^2} \int \frac{d\mathbf{k}}{\hbar^2} \sum_{\mathbf{m}} f_{m\mathbf{k}} v_{m\mathbf{k}}^p \left(\frac{\partial f_{m\mathbf{k}}^\varphi}{\partial E_m} \delta(E_m - \hbar \omega + i\delta) - \frac{\partial v_{m\mathbf{k}}^p}{\partial E_m} \right)$

and $\chi_{cb}^\varphi(\omega) = \frac{e^2}{(2\pi)^2} \int \frac{d\mathbf{k}}{\hbar^2} \sum_{\mathbf{m}} f_{m\mathbf{k}} v_{m\mathbf{k}}^p \left(\frac{\partial f_{m\mathbf{k}}^\varphi}{\partial E_m} \delta(E_m - \hbar \omega + i\delta) - \frac{\partial v_{m\mathbf{k}}^p}{\partial E_m} \right)$.

where $v_{m\mathbf{k}}^p$ is the velocity operator.

Only has nonzero diagonal components which can be expressed as

$$\hat{p}_z = -e \left[ \begin{array}{ccc} r_{1z} & 0 & \cdots \\ 0 & r_{2z} & \cdots \\ \vdots & \vdots & \ddots \end{array} \right]$$

where $r_{ij}$ is the i-component position of the j-th atom. We define the middle of the 2D materials as the origin: $\sum_{j} r_{ij} = 0$. Equation (6) is very similar to Eq. (8), except for the position operator $\hat{p}_z$ instead of the velocity operator.

First-principles calculations

The first-principles calculations based on density functional theory (DFT) are performed by using the VASP package. General gradient approximation (GGA) according to the Perdew–Burke–Ernzerhof (PBE) functional is used. The energy cutoff of the plane wave basis is set to 400 eV. The Brillouin zone is sampled with a $12 \times 12 \times 1$ mesh of k-points for MoS2 (WTe2). To simulate the monolayers, vacuum layers (~15 Å) are introduced. The vdW force with DFT-D2 correction is considered in the main text. The calculation results and corresponding discussions using vdW force with DFT-D3 correction are shown in Supplementary Note 6. Spin-orbital coupling effects are considered for bilayer MoS2 and WTe2 in the band structure and BPVE calculations.

The DFT Bloch wave functions are iteratively transformed into maximally localized Wannier functions by the Wannier90 code55,56. Mo-d and S-p (W-d and Te-p) orbitals are used to construct the Wannier functions for MoS2 (WTe2). The in-plane and out-of-plane BPVE coefficients are calculated by our own program WNLOP (Wannier Nonlinear Optics Package) based on effective tight-binding (TB) Hamiltonian. A convergence test of k-mesh is performed, and 500 × 500 × 1 (600 × 300 × 1) k-mesh is sufficient in BPVE calculations of MoS2 (WTe2). We adopt $\delta = 0.02$ eV for Eq. (6) and Eq. (8) in our calculation to take into account various relaxation processes.

The 3D-like BPVE coefficients are obtained assuming an active single-layer with a thickness of $L_{\text{active}}$.

$$\sigma_{bc} = \frac{L_{\text{slab}}}{L_{\text{active}}} \sigma_{\text{lab}} - \sigma_{\text{slab}},$$

where $\sigma_{\text{lab}}$ is the calculated BPVE coefficient, and $L_{\text{slab}}$ ($L_{\text{active}} < L_{\text{slab}}$) is the effective thickness slab.

DATA AVAILABILITY

The authors declare that all source data supporting the findings of this study are available within the article and the Supplementary Information file.

CODE AVAILABILITY

The calculating codes are available from the corresponding authors upon reasonable request.

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