Van der Waals force-induced intralayer ferroelectric-to-antiferroelectric transition via interlayer sliding in bilayer group-IV monochalcogenides

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Two-dimensional materials with ferroelectric properties break the size effect of conventional ferroelectric materials and unlock unprecedented potentials of ferroelectric-related application at small length scales. Using first-principles calculations, a sliding-induced ferroelectric-to-antiferroelectric behavior in bilayer group-IV monochalcogenides (MX, with M = Ge, Sn and X = S, Se) is discovered. Upon this mechanism, the top layer exhibits a reversible intralayer ferroelectric switching, leading to a reversible transition between the ferroelectric and antiferroelectric states in the bilayer MXs. Further results show that the interlayer van der Waals interaction, which is usually considered to be weak, can actually generate an in-plane lattice distortion and thus cause the breaking/forming of intralayer covalent bonds in the top layer, leading to the observed anomalous phenomenon. This unique property has advantages for energy harvesting over existing piezoelectric and triboelectric nanogenerators. The interlayer sliding-induced big polarization change (40 μC cm⁻²) and ultrahigh polarization changing rate generate an open-circuit voltage two orders of magnitude higher than that of MoS₂-based nanogenerators. The theoretical prediction of power output for this bilayer MXs at a moderate sliding speed 1 m s⁻¹ is four orders of magnitude higher than the MoS₂ nanogenerator, indicating great potentials in energy harvesting applications.

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INTRODUCTION

Ferroelectric (FE) materials possessing stable and switchable spontaneous electric polarization are essential elements in many technology applications, including memories, field-effect transistors, solar cells, sensors, and actuators. Over the past decade, advances in two-dimensional (2D) functional materials have stimulated broad research interest in 2D ferroelectrics1. Compared with traditional FE materials, 2D ferroelectrics are more easily integrated as functional components in miniaturized electronic devices owing to their intrinsic nanoscale size and ferroelectricity without the limitation of the size effect1. Following extensive theoretical predictions of 2D FE materials in the past few years, ferroelectricity has been experimentally observed in some 2D materials with thicknesses as low as several unit cells and even one unit cell²⁻⁶. Similar to conventional ferroelectrics, the intrinsic intralayer polarization of 2D materials usually originates from an asymmetric crystal structure caused by atom displacement and/or asymmetric charge redistribution. For example, a distorted SnTe monolayer was experimentally detected, giving rise to a robust in-plane intralayer polarization⁷. The displacement of Mo atoms breaks the inversion symmetry of 1T-MoS₂ and results in an out-of-plane interlayer polarization⁸. A similar atomic displacement and lattice distortion-induced polarization has also been found in CuInP₂S₆, In₂Se₃⁹, and elemental group-V monolayer materials¹⁰. The interlayer electric polarization of 2D FE materials can be as high as 48 μC cm⁻², which is comparable with that of conventional FE materials¹¹.

Moreover, 2D materials offer new artificial designation approaches, e.g., interlayer sliding, to induce non-intrinsic ferroelectricity owing to their unique layered crystal structures. The relatively weak interlayer van der Waals (vdW) interaction allows 2D materials to stack freely without being limited by the directional atomic bonds or lattice mismatch and endows these materials with diverse stacking-dependent properties¹²⁻¹⁵. Tuning stacking order can break the centrosymmetric nature of the crystal and induce interlayer charge transfer in bilayers or few-layer 2D materials, such as WTe₂⁵, VS₂ bilayers⁶, and BN bilayers¹⁷⁻²⁰, which then leads to an out-of-plane interlayer electric polarization. Interlayer sliding is predicted to change the interlayer potential and switch the polarization from upward to downward¹¹,¹⁷,¹²,¹². This is an interesting phenomenon since it provides a new way to control the FE polarization in addition to the conventional electric field. Such unique properties could stimulate novel concepts for various applications, such as triboelectric nanogenerators (NGs) for energy harvesting. However, the interlayer charge transfer is weak, and the obtained FE polarization is less than 0.68 μC cm⁻², i.e., two orders of magnitude smaller than that of conventional FE BaTiO₃ (30 μC cm⁻²)²⁰,²³. The dilemma is the following: while, on one side, the weak interlayer interaction gives rise to interlayer sliding-controlled ferroelectrics, on the other side, it severely limits the polarization magnitude and thus the applications.

In light of the large intralayer FE polarization of some 2D materials¹¹,²⁴⁻²⁶, a natural question arises: is it possible to use interlayer sliding to switch the intralayer polarization and thus solve the dilemma? Intuitively, this sounds very unlikely since the interlayer vdW interaction is very weak, whereas intralayer atom displacement is usually constrained by strong chemical bonds. In this work, using density functional theory (DFT) calculations, we prove this hypothesis for bilayer group-IV monochalcogenides, namely MX (M = Ge, Sn; X = S, Se), thus revealing a huge potential for 2D ferroelectrics. MXs have a distorted puckered structure that generates a considerably large intralayer FE polarization in all...
predicted 2D ferroelectrics. Our results show that a mechanical interlayer sliding can trigger a direction change of the electric polarization of the top layer, leading to a reversible transition between the FE and antiferroelectric (AFE) states of bilayer MXs. Our in-depth analysis shows that, under different stacking orders of bilayer MXs, the out-of-plane interlayer vdW interaction can induce an in-plane lattice distortion and thus promote intralayer covalent bond breaking/forming in the top layer. This new sliding-induced FE-to-AFE phenomenon shows that the robust intralayer FE polarization in 2D materials can be switched not only by external fields, as is traditionally done, but also by this unique interlayer sliding mechanism. Under a sliding speed of 1 m s⁻¹, the large polarization switching occurring within the nanoscale atomic lattice leads to an alternating displacement current with ultrahigh frequency. For example, a bilayer MX flake with a length of 10 nm can in principle generate a short-circuit current of 35 nA and a maximum power output of 107 nW, which is four orders of magnitude higher than the state-of-the-art MoS₂-based NGs.

The superior electrical performance renders bilayer MXs promising candidates for potential application as NGs and energy harvesting devices. Through the recently obtained advances in 2D material tribology, many techniques have been developed to precisely manipulate interlayer sliding. Therefore, it is of great relevance to implement these findings in real-world applications.

RESULTS AND DISCUSSION

Stacking order of bilayer MX and FE/AFE state

Monolayer group-IV monochalcogenides, namely MX (M = Ge, Sn; X = S, Se), have a hinge-like crystal structure similar to that of black phosphorene. Due to the broken centrosymmetry in the monolayer, a considerable spontaneous electric polarization, ranging from 18 to 48 μC cm⁻², exists along the x (armchair) direction (Fig. 1a) and is retained at room temperature. For bilayer MXs stacked together by two monolayers, as shown in Fig. 1b, there are four high-symmetry stacking orders (8 atoms per unitcell). The AA stacking order refers to the top layer being precisely matched with the bottom layer in the x–y plane. Compared with the AA stacking, the AB stacking corresponds to the top layer being shifted by a half lattice constant along the x-direction, i.e., by 0.5a (where a is the lattice constant in the armchair direction). Shifting the top layer by a half lattice constant 0.5b along the y-direction (where b is the lattice constant in the zigzag direction) yields the AC stacking. Finally, moving the top layer by a half lattice constant along both the x- and y-direction results in the AD stacking. As each monolayer exhibits intrinsic FE polarization, bilayer MX can be constructed with either parallel or anti-parallel polarization coupling between the two layers for a given stacking order. Consequently, a specific stacking order exhibits either an FE state or an AFE state (Fig. 1c).

The energetic orders of these bilayer MXs for these four stacking orders and corresponding two electric polarization states were investigated via DFT calculations. In these DFT calculations, the relative position of the two layers was fixed, while the lattice constants and interlayer spacing were allowed to relax. Supplementary Table 1 summarized the results. For bilayer MXs under the FE state, the AC stacking order, here denoted by $A_{CFE}$, is the most stable. The general energetic order trend is as follows: $A_{CFE} < A_{BE} < A_{AEFE} < A_{DE}$. By contrast, for the AFE state, bilayer MXs with the $A_{BE}$ stacking order are the most stable, and $A_{CFE}$ is the second most stable stacking order structure. GeSe, SnS, and SnSe bilayers have $A_{AEFE} < A_{DE}$, which is similar to the FE state. However, the opposite is true for GeS bilayers.

Figure 1c shows the energy difference between the FE and AFE states for each stacking order. For all these bilayer MXs, the AA and AC stacking orders prefer the FE state, while the AB and AD stacking orders prefer the AFE state. Although the bulk allotrope of these four MX materials has an AFE configuration, both the FE and AFE states in 2D nanoscale materials have been successfully fabricated and characterized in experiments. Based on these results, we speculate that the change of stacking order via mechanical interlayer sliding can lead to the intralayer polarization switching of the top layer, thus, for bilayer MXs, corresponding to a phase transition between the FE and AFE states. Such a phase transition and resultant polarization change/switch has not yet been reported.

Interlayer sliding-induced reversible FE-to-AFE transition and polarization switching

Using DFT calculations, the total energies and the polarization variation (in the x-direction) of bilayer MX were examined through a progressive mechanical sliding of the top layer with respect to the bottom layer. The $A_{CFE}$ state was taken as the starting point. Note that, owing to the significant advances obtained in 2D material tribology in the past few years, precise control of mechanical interlayer sliding in various 2D materials has been achieved.

Bilayer SnSe is here taken as an example to demonstrate the variation of atomic structure in Fig. 2a and the polarization variation along two sliding pathways that connect two high-symmetry stacking orders: from AC to AD in Fig. 2b and from AC to AB in Fig. 2c. Note that bilayer SnSe exhibits a stable FE state for the AC stacking and a stable AFE state for both AD and AB stackings (Fig. 1c). As the top layer moves toward the AD stacking along the x-direction (Fig. 1b), the horizontal Sn–Se bonds in the top layer break and reconnect with another neighbor. At the same time, the vertical Sn–Se bonds gradually tend to perpendicular with the x–y plane and finally rotate into the opposite direction. Figure 2b shows a gradual reduction of $P_x$ from 40 to ~30 μC cm⁻² followed by an abrupt drop to nearly zero at a sliding distance of 0.128a. After careful inspection of the crystal structure (Supplementary Fig. 1), it was found that the top layer had switched the polarization direction via breaking and forming of Sn–Se covalent bonds. The anti-parallel polarization of the two layers forms an AFE state. This AFE state remains unchanged until the top layer continues to slide into the ADAFE state. The reverse sliding direction (starting from the ADAFE state) changes the Metades in the AFE state until the relative sliding distance reaches 0.021a. At this critical point, a sharp increase of $P_x$ from zero to ~40 μC cm⁻² is observed, indicating a phase transition back to the FE state. Indeed, the analysis of the crystal structures shows that the polarization of the top layer switches back to the initial state during this backward sliding process (Supplementary Fig. 1). Therefore, the observed phase transition between $A_{CFE}$ and $A_{DAFE}$ is reversible and occurs spontaneously. The different critical phase transition points in these two opposite sliding directions result in a hysteresis loop, as shown in Fig. 2b. Similarly, Fig. 2c shows the pathway from AC to AB, $P_x$ decreases slightly to 35 μC cm⁻² and then drops abruptly to nearly zero at a sliding distance of 0.115a in the x-direction. Again, via inspection of the atomic structures (Supplementary Fig. 1), a crystal structure change of the top layer similar to that of the AC–AD case is observed, i.e., breaking and subsequent forming of Sn–Se covalent bonds. A backward mechanical sliding results in a sudden increase of $P_x$ to 40 μC cm⁻² at 0.06a, indicating a spontaneous reverse phase transition to the FE state.

Moreover, the relative total energy change versus interlayer sliding was investigated. The bottom plot of Fig. 2b shows the case of the corresponding path from AC to AD. The total energy of $A_{CFE}$ is here taken as reference. Starting from $A_{CFE}$, the relative energy shows a parabolic-like increase until a sliding distance of 0.128a, at which point the energy suddenly drops, corresponding to the FE-to-AFE phase transition. The energy then increases following another smooth curve till the AD stacking is reached. It
should be noted that ADAFE is at the top of the energy curve and is thus mechanically unstable. Once the mechanical sliding constraints applied to the top layer are released, the top layer slides spontaneously in the backward direction. In the backward sliding process, the bilayer SnSe energy follows the second smooth energy curve till 0.021\(a\), at which point the energy drops, corresponding to the AFE-to-FE phase transition in the curve of polarization. These two smooth energy curves clearly correspond to the FE (black) and AFE (red) states, respectively. They have a crossing point at ~0.08\(a\), which separates the stable FE and AFE regions. Note that the two observed spontaneous phase transitions do not take place at this crossing point. This can be attributed to the presence of an energy barrier that will be discussed later. The bottom plot of Fig. 2c shows the variation of the relative total energy along the AC-AB sliding pathway. In contrast to ADAFE in Fig. 2b, ABAFE is a metastable structure with an energy barrier of 18 meV per atom (i.e., 144 meV per cell) that separates it from the ground state ACFE. Upon releasing the sliding constraints, bilayer SnSe remains in the ABAFE stacking order. This phenomenon could be used in information storage applications.

Furthermore, comprehensive DFT calculations were conducted to obtain the variation of the electric polarization and total energy as a function of the interlayer sliding in the whole \(x-y\) plane. Fig. 2d, e shows the polarization-sliding map for SnS and SnSe, respectively. Supplementary Fig. 2 shows the total energy landscape. Note that these two maps are obtained by progressively sliding the top layer along various sliding pathways (starting from the ACFE state) in DFT calculations. For SnS and SnSe, neither FE nor AFE has a complete energy landscape across the whole \(x-y\) sliding plane due to the spontaneous phase transition. Therefore, the FE and AFE energy landscapes were combined together (Supplementary Fig. 2), and the phase boundary is depicted with a dotted line in Fig. 2d, e. At the boundary, the FE and AFE states have equal total energy values. The middle region of the \(x-y\) sliding plane represents the stable AFE state. ACFE and ABAFE are stable states for SnS and SnSe, whereas AAFE and ADAFE are unstable states. Across the phase boundary, there is a significant \(P_s\) drop from 40–60 \(\mu\)C cm\(^{-2}\) to zero (Fig. 2d, e).

Similarly, Fig. 2f, g show the polarization-sliding map of GeS and GeSe, and Supplementary Fig. 3 illustrates the corresponding energy landscapes. Through DFT calculations, one energy landscape is obtained for the FE state and another one for the AFE states across the whole \(x-y\) sliding plane. The energy differences between the states are shown in Supplementary Fig. 3 c, f for GeS and GeSe, respectively. The intersection curves of the two energy landscapes are projected onto the \(x-y\) plane and indicated by dashed lines. They represent the theoretical phase boundaries that separate the stable FE and AFE regions. Combining the phase diagram (Supplementary Fig. 3) and polarization contour map (Supplementary Fig. 4), the theoretical polarization phase diagrams for GeS and GeSe can be obtained, as shown in Fig. 2f, g, respectively. A sharp change of \(P_s\) takes place across the boundary. Due to the energy barrier, the FE-to-AFE phase...
transitions cannot spontaneously take place during mechanical sliding, but can occur at a specific finite temperature.

The nudged elastic band (NEB) method was adopted in the DFT calculations to determine the energy barrier (Supplementary Fig. 5). In the vicinity of the phase boundary, the energy barriers of bilayer GeS and GeSe are about 78 and 33 meV per atom, respectively. They are comparable with the thermal excitation energy at ambient conditions (–26 meV per atom at 300 K). Thus, GeS could exhibit the phase transition near room temperature, whereas GeSe might need an elevated temperature for the phase transition to occur. From a thermodynamics perspective, mechanical sliding across the boundaries would lead to a reversible FE-to-AFE phase transition. In contrast, SnS and SnSe have an almost vanishing energy barrier near their phase boundary, which is consistent with the observed spontaneous phase transition.

Fig. 2 FE-to-AFE phase transition upon tribological mechanical interlayer sliding. a The variation of atomic structures in the sliding process. FE polarization $P_s$, and total energy difference as functions of the sliding distance (along the x-direction) of the top layer from the AC to the AD stacking order for bilayer SnSe. The sudden drop in the increase of $P_s$ at the critical sliding distance of 0.128a or 0.021a indicates the spontaneous FE-to-AFE or AFE-to-FE phase transition, respectively. A hysteresis loop can be observed, which is analogous to that of the traditional FE materials under external electric field stimulus. At the two critical transition points, bilayer SnSe suddenly releases energy and transforms into the more stable phase. The energy crossing point is between the two critical points. $P_s$ and total energy difference as functions of the sliding distance (along the diagonal direction in the x-y plane) from the AC stacking to the AB stacking. Similar phase transitions and hysteresis loop can be observed. A double-well-like curve due to the metastable AB stacking is shown (different from the unstable AD stacking). d-g Contour plots of $P_s$ as a function of the mechanical sliding distance (leading to different stacking orders) for SnS, SnSe, GeS, and GeSe, respectively. The color bar denotes the $P_s$ magnitude of bilayer MX. The black dotted lines represent the phase boundary between the FE and AFE states. The tribological mechanical sliding of the top layer across the boundary leads to the reversible FE-to-AFE phase transition, i.e., reversible switching of the FE polarization. This new phenomenon is here referred to as tribo induced FE-to-AFE behavior.

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Physical origins of the observed tribo induced FE-to-AFE phenomena

The FE-to-AFE phase transition of the discovered phenomenon involves covalent bonds breaking and forming within the MX layer (Supplementary Fig. 1). This is surprising as conventional knowledge suggests that interlayer vdW interactions are much weaker than intralayer chemical bonds. In the past, to change the intralayer crystal structure and thus achieve polarization switching, either an external stress or an electric field had to be directly applied to the given layer. Note that some recent studies have shown that the interlayer vdW interaction could stabilize stacked crystal structures in some few-layer vdW materials (e.g., the AA stacking of few-layer SnS and the AFE state of CuInP2S6 group) contrary to their bulk counterparts. However, the reversible intralayer chemical bonds reconfiguration caused by interlayer interactions has not been reported before. It is thus
relevant to investigate the physical origins of this anomalous phenomenon.

A careful inspection of the crystal structures reveals that interlayer sliding leads to structural distortions. When two fully relaxed monolayers stack together, the interlayer interaction lowers the total energy of the bilayer system, which is directly correlated to the interlayer vertical distance in the sliding process (Supplementary Fig. 6). It should be noted that one stacked layer is slightly different from the previous fully relaxed monolayer because the intralayer bonds and lattice constants are slightly changed by the interlayer interaction (Supplementary Fig. 7). As listed in Supplementary Table 1, the lattice strain in the x-direction became as large as 2%. The strain here is calculated related to the lattice constants of the corresponding ground state, \( \Delta C_{\text{GS}} \) stacking. For quantitative analysis, the total energy of bilayer MX was split into three components:

\[
E_{\text{tot}}^{\text{bi-MX}} = E_{\text{MX}} + E_{\text{e}} + E_{\text{inter}}
\]

where \( E_{\text{tot}}^{\text{bi-MX}} \) is the total energy of the fully relaxed monolayer MX, \( E_{\text{e}} \) is the strain energy of the top and bottom layers, and \( E_{\text{inter}} \) is the interlayer interaction between the slightly deformed layers. The observed lattice distortion \( (E_{\text{inter}}) \) should be attributed to the sliding-induced interlayer interaction changes \( (E_{\text{inter}}) \). Taking SnSe as an example, we calculated the total energy of the rigid bilayer SnSe during its transition from the AC to the AD stacking and compared it with those of the relaxed cases (Supplementary Fig. 8). Figure 3a shows the \( E_{\text{inter}} \) and \( E_{\text{e}} \) results separately. Comparing the relaxed curve (with lattice distortion) with the rigid case (no lattice distortion), it is noticed that the lattice distortion significantly reduces \( E_{\text{inter}} \) while only slightly increasing \( E_{\text{e}} \).

To explore the driving force of the FE-to-AFE transition, an energy analysis for the FE and AFE phases was conducted for SnSe transitioning from the AC to the AD stacking. In principle, the drop of total energy is the driving force for phase transition. At the critical points, it is consisted of two parts, the interlayer interaction energy \( (E_{\text{inter}}) \) and the structural strain energy \( (E_{\text{e}}) \). Figure 3b, c summarizes the variation of them, although their absolute value is comparable, their changes at the critical points are quite different. The former lower drop but slightly rises at critical points, while the latter drops clearly, and the value of this energy drop is comparable with that of total energy in Fig. 2b, indicating that \( E_{\text{e}} \) is the driving force behind the transition. Specifically, it can be observed from Fig. 3c that \( E_{\text{e}} \) increases as the top layer slides away from the \( AC_{\text{FE}} \) state and then exhibits a sudden drop of 4.2 meV per atom to the AFE state at the phase transition point. In the reverse sliding process, \( E_{\text{e}} \) gradually increases till the phase transition returns to the FE state, at which point an energy drop of 4.1 meV per atom is observed. The magnitude of the \( E_{\text{e}} \) change is close to that of \( E_{\text{tot}} \), indicating that the lattice strain energy relaxation is a key driving force for the tribo induced FE-to-AFE phase transition of bilayer SnSe. By further splitting \( E_{\text{e}} \) into the two different contributions from the top and bottom layers (Supplementary Fig. 9), the top layer strain energy undergoes a minor drop during the phase transition. The observed \( E_{\text{e}} \) change in Fig. 3c for bilayer SnSe originates from the bottom layer, indicating that the release of strain energy in the bottom layer contributes
more to the FE-to-AFE phase transition. In the reverse AD_{AFE}→AC_{FE} process (Supplementary Fig. 9), the strain energy of the top and bottom layers decreases by 2.47 and 1.66 meV per atom, respectively, revealing that the release of strain energy for both layers contributes to the reverse phase transition. The \( E_z \) can be further split into the part from cell deformation (\( E_{\text{cell}} \)) and another part from internal degree of freedom (\( E_{\text{internal}} \)), which are defined in Supplementary Note 2. Within the AC-to-AD sliding process, the \( E_{\text{internal}} \) is dominant to release the strain energy, while during the backward sliding process, the \( E_{\text{cell}} \) becomes dominant to relax the system.

The lattice distortion also has a critical role in setting the energy barrier separating the FE from the AFE state. Figure 3d presents the energy barrier results between the FE and AFE states for bilayer SnSe at different sliding distances from AC_{FE} to AD_{AFE}. When the sliding distance is far from the transition point, e.g., 0.05a, the FE state needs to overcome an energy barrier of 1.2 meV per atom to transform into the AFE state. Upon further sliding, the FE state gradually becomes metastable compared with the AFE state, and the energy barrier keeps decreasing. Upon reaching 0.127a (close to the critical point of 0.128a), the energy barrier is nearly zero. The phase transition thus happens spontaneously, which is consistent with Fig. 2b. In our energy barrier calculations, it was noticed that the transition state has a unit cell with an \( a/b \) ratio much closer to one (cubic-like) than those of the initial FE state and final AFE state. To quantitively investigate the influence of the unit cell shape, the unit cell rectangularity is defined as:

\[
\text{Rectangularity} = \frac{a}{b} - 1
\]

where \( a \) and \( b \) are the lattice parameters in the armchair and zigzag direction, respectively. Figure 3e shows the rectangularity of bilayer SnSe during mechanical sliding. Upon sliding, the rectangularity continuously decreases from about 0.04 to a minimum value of about 0.02 and then shows a sudden jump at the FE-to-AFE phase transition (black line in Fig. 3e). The reverse process is similar, and the rectangularity in this case reaches a minimum value \( <0.01 \) at the phase transition (red line in Fig. 3e). The results indicate that a small rectangularity strongly correlates with the disappearance of the energy barrier. Indeed, Fig. 3f shows the quantitative confirmation of such correlation. This figure demonstrates that the energy barrier decreases with decreasing rectangularity. A near-zero energy barrier is achieved when the rectangularity becomes smaller than 0.025. Moreover, the energy barriers of bilayer SnSe (hollow symbols) were compared with those of monolayer SnSe (solid symbols) for the same lattice constants (thus, for the same rectangularity). The comparable energy barrier values clearly indicate that lattice strain is the physical origin behind the energy barrier change rather than the interlayer interaction.

Through the mechanical sliding process, the vdW force leads to a significant lattice strain for bilayer SnS and SnSe, drastically reducing their rectangularity. This gives rise to a vanishing energy barrier and, consequently, to a spontaneous phase transition. On the contrary, the AC_{FE} states of bilayer GeS and GeSe have a large rectangularity, 0.20 and 0.12, respectively (Supplementary Fig. 10). These rectangularity values did not reduce, but instead increased to 0.22 and 0.13, upon sliding close to the phase boundary (Fig. 2). The relatively high rectangularity values are likely the reason for the calculated non-zero energy barrier in the vicinity of the phase boundary (Supplementary Fig. 5). For the FE-to-AFE phase transition to take place, some external stimulus, such as

Fig. 4 NG using the tribo induced FE-to-AFE phenomenon—theoretical model prediction. a Schematic illustration of a FE-to-AFE-based NG in connection with an external load resistor. The theoretical models were adopted from ref.47 (see the main text and the SI for details). b Variation of polarization, source voltage (\( V_{\text{source}} \)) and short-circuit current (\( I_{\text{sc}} \)) of a 10×10 nm NG under a 1 m s\(^{-1}\) sliding speed. Three sliding periods are shown. The considerably large values of \( V_{\text{source}} \) and \( I_{\text{sc}} \) benefit from the large polarization change and large polarization rate during the interlayer sliding process (see the main text for details). The voltage exhibits a linear relation with the polarization change and is simplified as a sinusoidal alternating voltage in subsequent modeling and discussion. c Dependence of \( V_{\text{oc}} \) and \( I_{\text{sc}} \) on the interlayer sliding speed. The voltage is independent of the sliding speed because of the constant polarization change (see the main text). \( I_{\text{sc}} \) is linearly related to the sliding speed because of its linear relation with the rate of polarization change. d Dependence of the voltage and current output under a 1 m s\(^{-1}\) sliding speed as a function of the load resistance. The inset is the equivalent circuit of the FE-to-AFE-based NG. e Power output as a function of the load resistance at different sliding speeds. f Maximum power at different sliding speeds obtained from the theoretical prediction.
temperature, electric field, or applied stress, is required to assist the interlayer sliding for bilayer GeS and GeSe.

The above shows that vdW interaction is robust in layered MX materials. The presence of vdW interaction reduced the energy barrier of polarization switching, implying the low cost of intralayer bonds breaking. In fact, recent studies also demonstrated that the vdW forces are not weak at interfaces. In some cases, the vdW interactions may dominate the interfacial interactions, and lead to an equal stability (bistable) phenomenon as compared to the chemical bonds.\(^{50,51}\) These findings present a breakthrough understanding of vdW interaction in condensed matter physics, offering strong support for our discovery.

**Performance of the tribo induced FE-to-AFE device as NG**

NGs are an emerging technology: they harvest energy from the ambient environment for self-powered micro/nanosystems. It is well established that the energy harvesting performance of NGs depends on the polarization-related displacement current:

\[
J_0 = \frac{\partial P_t}{\partial t} \tag{3}
\]

Polarization change is the key factor for the electrical output\(^{52}\). In piezoelectric nanogenerators (PENGs), such as monolayer MoS\(_2\), polarization change is obtained by applying an external strain, a phenomenon that is known as piezoelectricity.\(^{32,53}\) Triboelectric nanogenerators (TENGs) obtain polarized charges through contact electrification (triboelectricity) and convert mechanical energy into electricity via electrostatic induction\(^{54}\). Note that the polarization change (\(-40 \mu\text{C}\text{cm}^{-2}\)) induced by the FE-to-AFE phase transition herein is two orders of magnitude higher than that of PENGs (\(-0.27 \mu\text{C}\text{cm}^{-2}\) for monolayer MoS\(_2\)), which should lead to a much higher open-circuit voltage (proportional to the polarization change). The time during which the polarization change occurs is only \(-0.5 \text{ ns}\) under a moderate interlayer sliding speed of \(1 \text{ m}\text{s}^{-1}\). In other words, the rate of polarization change of this behavior is ultrahigh and can generate a considerable displacement current in principle. Such an intrinsic superiority motivates us to propose a FE-to-AFE-based NG and estimate its potential electrical performance. For simplicity, bilayer SnSe flakes with an in-plane size of \(10 \times 10 \text{ nm}\) were employed in this work (see the details in the Supplementary Information).

Taking bilayer SnSe as an example, Fig. 4a shows the schematic illustration of this mechanism-based NG in connection with an external load resistor, which is analogous to the previous model\(^{32,54,55}\). The tribo induced FE-to-AFE phenomenon in bilayer SnSe results in multiple repeated bursts of a significant electrical polarization change upon continuous interlayer sliding (over distances of several unit cells in Fig. 4a). Figure 4b illustrates the variation of polarization, source voltage, and short-circuit current of the proposed NG device in three sliding periods. The polarization \(P_t\) repeatedly changes between \(-40\) and \(0 \mu\text{Ccm}^{-2}\) during sliding periods. Using a well-established theoretical model\(^{52}\), the source voltage can be estimated for the \(10 \times 10 \text{ nm}\) bilayer MX device in the middle of Fig. 4b, showing an alternating change between \(-25\) and \(0 \text{V}\), as indicated by the dotted line. For simplicity, the source voltage is approximated as a simple sinusoidal alternating curve (the blue curve). The open-circuit voltage \(V_{oc}\) can be obtained from this curve (see details in the Supplementary Information).

The considerable output voltage benefits from the significant polarization change (\(-40 \mu\text{Ccm}^{-2}\)) during the interlayer sliding process. For monolayer MoS\(_2\)-based PENGs with the same size\(^{55}\), the polarization change is only \(-0.27 \mu\text{Ccm}^{-2}\), and the voltage is only \(-0.24 \text{ V}\). The voltage of the proposed NG (\(-25 \text{ V}\)) is thus two orders of magnitude higher.

For the proposed FE-to-AFE bilayer device, the polarization change rate depends on the sliding speed \(v\):

\[
\frac{dP}{dt} = \frac{dP}{dx} \cdot \frac{dx}{dv} = \frac{dP}{dx} \cdot v \tag{4}
\]

The bottom plot of Fig. 4b shows the calculated sinusoidal short-circuit current \(I_{sc}\) with an amplitude of \(-35\) and \(-17 \text{ nA}\) at a moderate sliding speed of \(0.5\) and \(1 \text{ m}\text{s}^{-1}\), respectively. A small phase difference in the source voltage can be observed (see details in the Supplementary Information). Note that the weak interlayer vdW interaction enables the ultralow friction and even the super lubricity in 2D materials. In the experiments, an interlayer sliding speed of \(25–294 \text{ m}\text{s}^{-1}\) has been achieved\(^{56,57}\). Fig. 4c summarizes the \(V_{oc}\) and \(I_{sc}\) outputs as a function of the sliding speed over a wide range, from 0.001 to \(10 \text{ m}\text{s}^{-1}\). \(V_{oc}\) is independent of the sliding speed, while \(I_{sc}\) depends linearly on the sliding speed. The electrical output of this NG can be tuned in a wide range by changing the sliding speed.

To quantitatively estimate the power output of the FE-to-AFE-based NG, the NG device is regarded as a simple resistor-capacitor (RC) circuit, as was done in previous works\(^{5,24}\). It is necessary to investigate the voltage and current outputs as a function of the load resistance, as shown in Fig. 4d. Taking the sliding speed of \(1 \text{ m}\text{s}^{-1}\) as an example, the output current is unchanged for a load resistance of up to \(-10 \text{ M}\Omega\), and then decreases with increasing the load. On the other hand, the output voltage remains \(-0 \text{V}\) initially and starts to increase at the same point. As such, the maximum delivered power of \(107 \text{ nW}\) is achieved at an intermediate load of \(-350 \text{ M}\Omega\). Regarding other sliding speeds, the RC circuit model predicts a similar behavior for the voltage and current outputs. Figure 4e summarizes the power output as a function of the load resistance at different sliding speeds. For sliding speeds of \(1 \text{ m}\text{s}^{-1}\), \(5 \text{ m}\text{s}^{-1}\), and \(10 \text{ m}\text{s}^{-1}\), the power outputs are \(107 \text{ nW}, 533 \text{nW}, \text{and } 1057 \text{nW}\), respectively. Furthermore, the derived optimal load resistances are about \(350 \text{ M}\Omega, 70 \text{ M}\Omega, \text{and } 35 \text{ M}\Omega\), respectively. The optimized maximum power output is found to be linearly related to the sliding speed, as shown in Fig. 4f. The difference in electrical output between bilayer SnSe and monolayer MoS\(_2\) can be found in Supplementary Table 2. For monolayer MoS\(_2\), a mechanical deformation of \(0.5 \text{ GHz}\) can generate an alternating current with the same frequency and a power output of \(0.016 \text{nW}\), while a moderate mechanical sliding speed of \(1 \text{ m}\text{s}^{-1}\) can generate a current of \(2.29 \text{ GHz}\) and a power of \(106.6 \text{nW}\) for bilayer SnSe.

It is worth to make a further comparison between the proposed FE-to-AFE-based NG and the well-known PENGs/TENGs. In addition to the high polarization change and charging rate, for the FE-to-AFE-based NGs, a moderate mechanical sliding speed can generate high-frequency alternating electrical output without the need for any high-frequency input signal. For example, a sliding speed of \(1 \text{ m}\text{s}^{-1}\) theoretically corresponds to a current of \(35 \text{ nA}\) and a frequency of \(-2.29 \text{ GHz}\), which is nearly impossible for PENGs. Note that, in TENGs, increasing the number of grating units of dielectrics is a popular method to generate multiple electric outputs in one directional motion cycle\(^{35}\). However, these grating units requires sophisticated microfabrication techniques, and their sizes are of several micrometers. In the proposed NG, every unit cell (length of several angstroms) can be viewed as a grating unit. Moreover, the fragile grating units in TENGs may suffer mechanical failure (e.g., wear) under high-speed sliding and consequently a short lifetime\(^{44}\). The proposed FE-to-AFE-based NG clearly does not have these issues. The ultralow friction between vdW layers can enhance its lifetime\(^{58}\).

Here we propose this promising phenomenon in present bilayer MX materials and its potential application with the idealized condition. In practice, the effects of defects and intrinsic ripples in 2D materials are nonnegligible, which can be further investigated in future works.
In summary, a sliding-induced FE-to-AFE phenomenon was discovered in bilayer MX (M = Ge, Sn; X = S, Se) using DFT calculations. Among the four possible types of high-symmetry stacking order for bilayer MX, the AA and AC stacking orders favor an FE state with a parallel arrangement of the polarization, while the AB and AD stacking orders favor an AFE state with an anti-parallel arrangement of the polarization. Changing the stacking order through tribological interlayer sliding results in a reversible and hysteretic phase transition between the FE and AFE states. An in-depth analysis revealed that the lattice distortion caused by the interlayer vdW force plays a dominant role in the phase transition, which is surprising. Inspired by the intrinsically high magnitude of the electric polarization change and ultrahigh changing rate, we propose a bilayer MX-based energy harvesting NG. The performance predicted using a well-established theoretical model is superior compared with those of the widely studied PENG and TENG devices. This bilayer MX-based device is a promising candidate for future NGs.

**METHODS**

The DFT calculations in this work were performed using the Vienna ab initio simulation package (VASP)[50,51]. The projector-augmented wave (PAW) potentials with the generalized gradient approximation[52,53] in the Perdew-Burke-Ernzerhof (GGA-PBE) formulation[54] were used with a cutoff energy of 600 eV. The Brillouin zone integration for structure relaxation was obtained using a 25 × 25 × 1 Monkhorst-Pack[66] k-point grid. For the total energy calculations, among the four possible types of high-symmetry stacking orders for bilayer MX, the AA and AC stacking orders favor FE state while AA and AD prefer AFE state. To verify the little impact of a substrate on the phase transition, which is surprising. Inspired by the intrinsically high magnitude of the electric polarization change and ultrahigh changing rate, we propose a bilayer MX-based energy harvesting NG. The performance predicted using a well-established theoretical model is superior compared with those of the widely studied PENG and TENG devices. This bilayer MX-based device is a promising candidate for future NGs.

**DATA AVAILABILITY**

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Information. Additional data related to this article may be requested from the authors.

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AUTHOR CONTRIBUTIONS

J.D. and J.Z.L. designed the simulations and the framework of this research. B.X. carried out the first-principles calculations. B.X., J.D., and J.Z.L. wrote the paper. J.S. and X.D. performed some data analysis and provide many suggestions.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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