

Bulk photovoltaic effect in MoSe₂ and Janus MoSSe sliding ferroelectrics

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We present a first-principles study of the nonlinear optical properties of sliding ferroelectric bilayers based on MoSe₂ and Janus MoSSe. Two Janus configurations are considered: (i) one bilayer where the two intralayer polarizations caused by Janus chemical asymmetry cancel each other out, yielding photocurrent spectra comparable to pristine MoSe₂ bilayers; (ii) another bilayer where the intralayer polarizations add up, for which the photoresponses are strongly enhanced. Our results show that photocurrent generation in the polar Janus structures is predominantly governed by vertical chemical asymmetry, with limited dependence on the sliding direction. These findings highlight complementary design strategies: interlayer sliding enables sensitivity to external tuning, while the Janus intralayer polarization enhances photoresponses in the visible range. The interplay between composition and stacking therefore provides a versatile platform for tailoring light-matter interactions in two-dimensional ferroelectric materials.

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I. INTRODUCTION

The efficient conversion of solar energy into electrical power remains a central challenge in the development of next-generation optoelectronic and energy-harvesting technologies. Conventional photovoltaic devices rely on p-n junctions, where built-in electric fields separate the light-induced charge carriers. In contrast, the bulk photovoltaic effect (BPVE) is observed in materials that lack inversion symmetry [1–5]. The main advantage of such systems is that they offer a mechanism for photocurrent generation in the absence of external bias or heterojunctions, which simplifies large-scale device fabrication. Although several studies have reported that the BPVE can produce open-circuit voltages above the material band gap by enabling carrier collection prior to thermalization, which could surpass the Shockley-Queisser limit [6], others have questioned this claim, citing additional factors that may restrict the overall energy conversion efficiency [7,8]. Despite these opposing perspectives, BPVE continues to stimulate significant theoretical [9–14] and experimental [15–23] interest due to its intrinsic relation to band structure and its ability to generate ultrafast, bias-free photocurrents [1,24–29].

BPVE arises from second-order nonlinear optical processes and is composed of two key mechanisms: the shift and the injection current [1,4,30]. The shift current originates from the position shifts of charge centers during interband

transitions [1,5,9,13,31,32], while the injection current arises from asymmetries in the group velocity distribution of excited carriers [1,11,14,33,34]. These mechanisms are strongly influenced by the crystal symmetry and electronic structure of the material. For nonmagnetic materials, the bulk photovoltaic response consists of linear shift current and circular injection current. In contrast, linear injection current requires broken time-reversal symmetry and thus arises only in magnetic systems.

Due to their inherent broken inversion symmetry and spontaneous, switchable polarization, ferroelectric materials have been considered prototype systems for studying the BPVE [9,16,35–43]. The photoresponse typically switches along with the ferroelectric polarization, making the electric field a practical control knob for tuning the direction of the photocurrent [1,44–47]. It was also shown that the BPVE can be significantly enhanced in low-dimensional systems such as strain-engineered MoTe₂ [48], ReS₂ [49], group-IV monochalcogenide monolayers [28,50], and other two-dimensional ferroelectrics [51,52], where the enhancement is often attributed to van Hove singularities in the electronic density of states.

Recently, the discussion of BPVE was extended to a class of materials known as sliding ferroelectrics [53–67]. In these systems, the polarization arises from interlayer charge redistribution in stacking arrangements lacking inversion symmetry. It was shown that even if the monolayers are centrosymmetric, it is possible to build bilayers, which break inversion symmetry and generate out-of-plane polarization [53]. In sliding ferroelectrics, the polarization is fully determined by the interlayer stacking arrangement and can be tuned by diverse external stimuli, offering great potential for advanced information storage and processing applications. Experiments have demonstrated the feasibility of controllable stacking and interlayer sliding in transition metal

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dichalcogenide (TMD) bilayers [57,61,68]. The interlayer sliding mechanism enables reversible polarization switching with potentially lower energy barriers and minimal structural distortion [69]. From a BPVE perspective, such tunability allows dynamic modulation of the nonlinear optical response and may enhance shift and injection currents through engineered stacking configurations, strain control or magnetic order [70–73]. In two-dimensional (2D) sliding ferroelectrics, a nonsynchronous BPVE coupled to the ferroelectric order has been identified [70]: while the in-plane BPVE components, which correspond to photocurrent induced in the xy plane, are invariant under polarization reversal, the out-of-plane components, corresponding to photocurrent induced along the z direction, switch sign [70]. The unswitchable in-plane responses could be advantageous for large-scale photoelectric applications.

In this paper, we perform first-principles calculations based on density functional theory (DFT) to investigate the BPVE in sliding ferroelectric bilayers of MoSe_2 and Janus MoSSe . Janus monolayers inherently lack mirror symmetry due to their vertical compositional asymmetry, which leads to out-of-plane dipole moments and enhanced piezoelectric responses [74–76]. Janus TMD monolayers have been experimentally synthesized, including MoSSe systems [77,78]. Moreover, heterostructures combining Janus MoSeS with other transition metal dichalcogenide monolayers, such as MoS_2 , have been experimentally realized [79], demonstrating the feasibility of integrating Janus layers into stacked two-dimensional architectures. To the best of our knowledge, however, there are currently no experimental reports of bilayers composed of two Janus MoSeS monolayers. Nevertheless, theoretical works have proposed and analyzed these Janus bilayer configurations [76,80–82]. Investigating BPVE in Janus bilayers could help identify possible strategies to enhance nonlinear photovoltaic effects in two-dimensional systems. We study two Janus bilayer configurations: one where the intralayer polarizations induced by Janus asymmetry cancel each other, and another exhibiting a net intralayer polarization. In the latter case, we find that the photocurrents are significantly enhanced compared both to the former and to the MoSe_2 bilayer. While sliding ferroelectricity allows for easy switching of photoreponses, this polar Janus structure is particularly promising for applications, as it generates very large photocurrents exceeding those reported for many other 2D and 3D materials.

The paper is organized as follows: in Sec. II we present the computational details of our *ab initio* simulations; in Sec. III we discuss the crystal structure of the materials in details; Secs. IV–VI include our results, while Sec. VII is devoted to the conclusions.

II. COMPUTATIONAL DETAILS

We performed first-principles calculations using DFT within the projector augmented-wave (PAW) framework, as implemented in the VASP code [83–85]. The exchange-correlation energy was treated using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form [86]. Spin-orbit coupling (SOC) was included in all the simulations, except during structural optimization. A plane-wave kinetic energy cutoff of 400 eV was used through-

out and we employed a $20 \times 20 \times 1$ Monkhorst-Pack k grid centered at the Γ point. To prevent artificial interactions between periodic images, a vacuum spacing of ≈ 35 Å was introduced in our structures. The atomic positions were optimized until the residual forces were smaller than 0.001 eV/Å. To accurately capture interlayer interactions inherent to van der Waals layered systems, dispersion corrections were included via the DFT-D3 scheme of Grimme [87]. The macroscopic electric polarization is evaluated within the modern theory of polarization through the Berry-phase approach [88].

To compute the bulk photovoltaic response, including both shift and injection current contributions, we followed the method developed by Ibañez-Azpiroz *et al.* [13] and by Puente-Uriona *et al.* [14], which rely on WANNIER interpolation of the DFT electronic structure. The maximally localized WANNIER functions (MLWFs) [89,90] were generated using the WANNIER90 package [91]. The DFT total band structure was projected on the Mo- d and chalcogen (S,Se)- p orbitals to accurately capture low-energy physics. A very dense k -point grid up to $500 \times 500 \times 1$ was employed for the optical calculations to ensure convergence of the computed photoconductivities. A fixed broadening of 0.02 eV was applied to effectively handle van Hove singularities, following the prescription of Ref. [13]. Following previous Refs. [13,28,40,50,70], the renormalized 3D-like responses were obtained by assuming a single active layer with $\sigma_{3D} = \frac{c}{L_{\text{active}}} \sigma_{\text{slab}}$, where c is the lattice parameter, L_{active} is the thickness of the bilayer and σ_{slab} is the calculated BPVE coefficient.

III. CRYSTAL STRUCTURE

The monolayers used to construct the MoSe_2 bilayers belong to the 3R polytype. They exhibit trigonal prismatic coordination around the transition metal atoms and are non-centrosymmetric, nonpolar, and possess horizontal mirror symmetry [70].

To construct the sliding ferroelectric bilayer, two noncentrosymmetric MoSe_2 monolayers are vertically stacked in an AA-type configuration, where each layer is identical and A denotes the monolayer structure, as shown in Figs. 1(a), with the top and bottom layers laterally slid relative to each other. The bilayer belongs to the space group P3m1 (No. 156) and this system exhibits a net out-of-plane polarization, signaling the emergence of ferroelectricity induced by interlayer sliding along the in-plane direction. The out-of-plane ferroelectric polarization can be reversed through in-plane interlayer displacement and the two ferroelectric states with opposite polarization have a low switching barrier, and are related by mirror symmetry [70].

Next, we construct Janus bilayers by replacing the chalcogen atoms in one Se sublayer of each monolayer with S. Two distinct bilayer configurations are examined, which we refer to as Janus I and Janus II, shown in Figs. 1(b) and 1(c), respectively. In the Janus I arrangement, both the bottom of the top monolayer and the top of the bottom monolayer are terminated with Se atoms, forming a S-Mo-Se-Se-Mo-S stacking. In this configuration, the intralayer polarizations induced by the Janus asymmetry are oriented in opposite directions and effectively cancel each other out within the

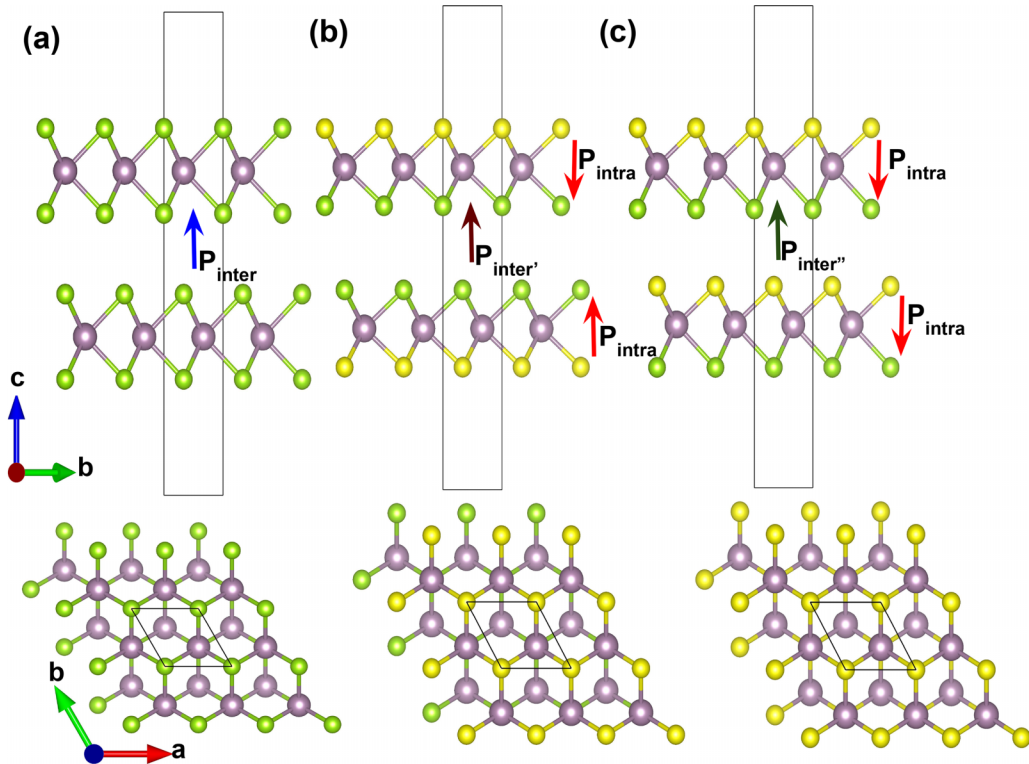


FIG. 1. The side and top views of the bilayer crystal structures of (a) MoSe₂, (b) Janus I, and (c) Janus II, respectively. The Mo, Se, and S atoms are represented by violet, green, and yellow spheres respectively. The blue, maroon, and green arrows represent the direction of the interlayer polarization ($P_{\text{inter}}/P_{\text{inter}'}/P_{\text{inter}''}$) for MoSe₂, Janus I, and Janus II respectively. The red arrows represent the direction of intralayer polarization (P_{intra}) existing within the Janus I and Janus II monolayers.

bilayer. In contrast, the Janus II structure introduces structural asymmetry with a Se-Mo-S-Se-Mo-S stacking, leading to an intrinsic intralayer out-of-plane polarization even in the absence of interlayer sliding. Substituting S for Se also induces local structural distortions arising from differences in atomic radius and electronegativity: the Mo-Se bond length in pristine MoSe₂ bilayers (2.51 Å) changes to 2.40 Å for Mo-S and 2.52 Å for Mo-Se in Janus I. The distortion is more pronounced in Janus II, where the Mo-S bonds measure 2.61 Å and 2.40 Å for the top and bottom monolayers, respectively, further modifying the internal electric field across the sliding bilayers.

We calculated the polarization values for MoSe₂, Janus I, and Janus II, obtaining results that are in good agreement with previously reported data in Ref. [76]. Specifically, for MoSe₂ and Janus I we find polarization values of approximately 0.7 pC/m and 0.5 pC/m, respectively, in good agreement with those reported in Ref. [76]. The polarization of Janus II is nearly two orders of magnitude larger, reaching ≈ 25.0 pC/m. This value is consistent with the polarization of ≈ 20.0 pC/m reported in Ref. [76] for a Janus MoSeS polar structure. The polarization in Janus II is dominated by the intralayer contribution, with the interlayer one being ≈ 0.4 pC/m. The strong enhancement of the polarization in Janus II arises from the vertical chemical asymmetry introduced by the inequivalent dichalcogen layers, which generates an intrinsic out-of-plane electric field, leading to a dominant intralayer dipole. By contrast, the polarization induced by interlayer sliding is two orders of magnitude smaller, as it arises solely from stacking-dependent charge redistribution between the layers.

IV. ELECTRONIC PROPERTIES

The electronic band structures of the sliding ferroelectric bilayers MoSe₂, Janus I, and Janus II along the high-symmetry path $\Gamma-M-K-\Gamma$, are presented in Figs. 2(a)–2(c). All three systems exhibit an indirect bandgap, with variations in the positions of the valence band maximum (VBM) and conduction band minimum (CBM). From the orbital projected band structure, we obtain that the VBM and CBM are predominantly composed of Mo-*d* orbitals. In all three systems in Fig. 2, the VBM is located near the K point, while the CBM appears along the $K-\Gamma$ direction. The band gaps are of the order of 1.0 eV, 1.2 eV, and 0.9 eV for MoSe₂, Janus I and Janus II, respectively. In all three cases the values of the band gap are within the visible range, making these systems promising candidates for bulk photovoltaic applications. Although it is well known that GGA calculations tend to underestimate band gaps, additional calculations performed using the hybrid functional confirm that the band gaps remain within the visible range, as shown in the Supplemental Material [92]. The Janus II configuration, in which the structural and chemical asymmetries are maximized, exhibits pronounced splitting of the bands, as shown in Fig. 2(c).

V. BPVE IN SLIDING BILAYER

To investigate the nonlinear optical response of the sliding ferroelectric MoSe₂ bilayer, we compute the second-order photoconductivity tensor elements that govern the BPVE,

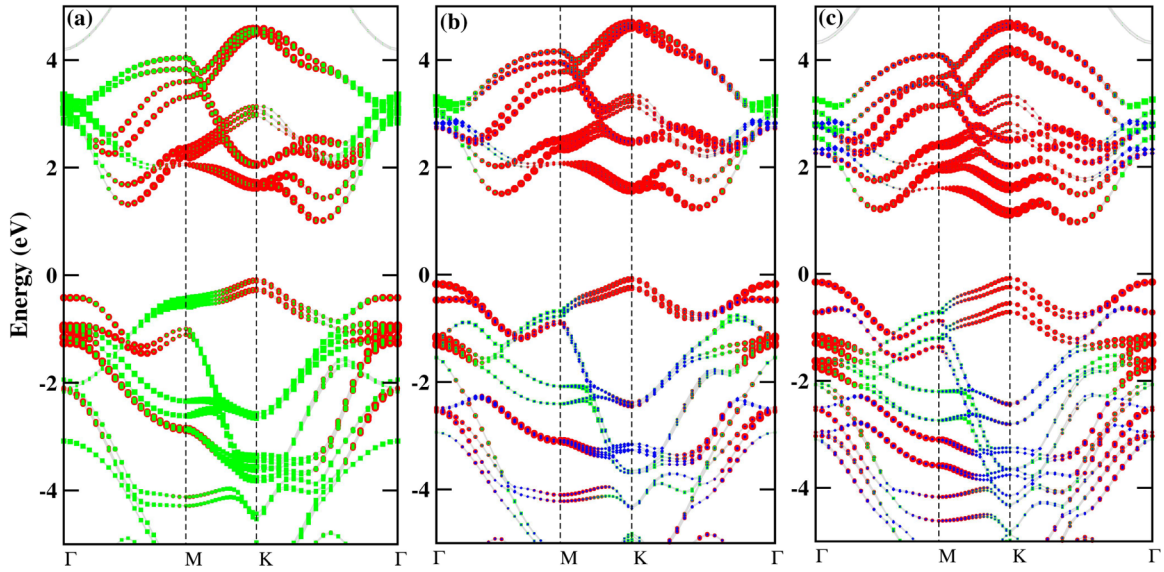


FIG. 2. The orbital projected band structure along the high symmetry k points for the bilayers of (a) MoSe₂, (b) Janus I, (c) Janus II. The size of the red circle, green square and blue diamonds represents the relative contributions from Mo- d , Se- p and S- p orbitals, respectively. The Fermi energy is set to zero in the energy scale.

including both shift and injection current contributions. Regarding the shift current response σ^{abc} , the symmetry-allowed, nonzero components for the space group P3m1 can be categorized into in-plane and out-of-plane contributions. Here, the in-plane components correspond to photocurrents induced in the xy plane, while the out-of-plane components correspond to photocurrents induced along the z direction. For the in-plane response, symmetry analysis yields the relation $\sigma^{xy} = \sigma^{yx} = -\sigma^{yy}$, whereas for the dominant out-of-plane one we have $\sigma^{zx} = \sigma^{zy}$. Other symmetry-allowed components, namely $\sigma^{xz} = \sigma^{yz}$ and σ^{zz} , are not shown because their contributions are negligible compared with the dominant ones. The σ^{xy} contribution is shown in Fig. 3(a), it exhibits prominent peaks at approximately 2.5 and 3 eV, with a maximum intensity of around 70 $\mu\text{A}/\text{V}^2$. The out-of-plane shift current component σ^{zx} , also shown in Fig. 3(a), remains large, even if smaller compared to the in-plane components,

and features prominent peaks at around 1.9 eV and 2.5 eV, with largest intensity of about 15 $\mu\text{A}/\text{V}^2$. The values of both σ^{xy} and σ^{zx} in the visible range are comparable or larger than those of other ferroelectric materials [9,38], although smaller than the responses observed in various low-dimensional systems [28,40]. For the circular injection current response η^{abc} , the allowed elements are $\eta^{xx} = -\eta^{yy}$, with just one independent component. In Fig. 3(b), we show the circular injection current component η^{xx} . The spectral response shows intense peaks of about $3 \times 10^8 \text{ A}/(\text{V}^2\text{s})$ and $7 \times 10^8 \text{ A}/(\text{V}^2\text{s})$ in the visible region, as well as pronounced peaks at larger energies. These values are larger than those reported for the Weyl semimetal TaIrTe₄ [14], which exhibits a giant BPVE. Further, the in-plane components of the BPVE tensor exhibit identical spectra for the $+P$ and $-P$ states, whereas the out-of-plane components reverse their sign upon polarization switching (see Supplemental Material [92]). This behavior originates

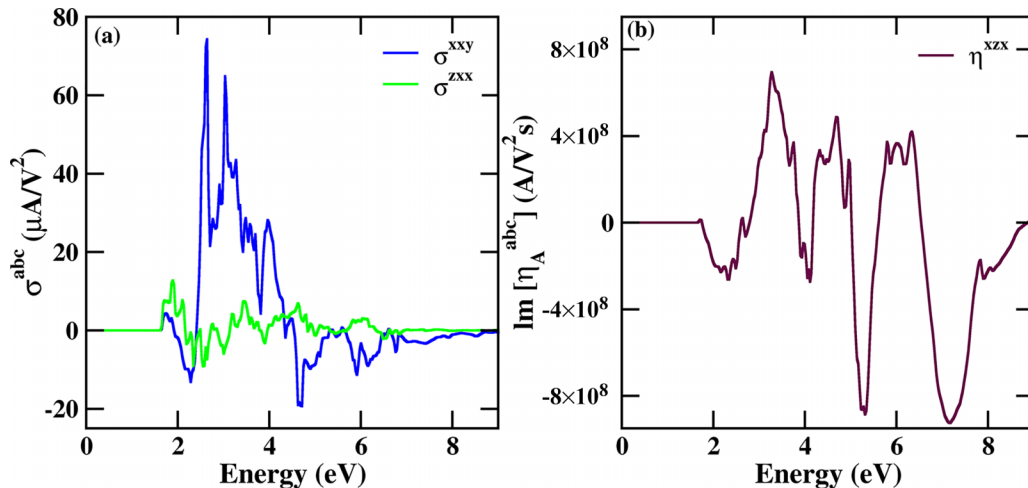


FIG. 3. The nonzero, independent components of the photoconductivity tensor for MoSe₂. (a) Shift current components. (b) Circular injection current components.

from the fact that the $+P$ and $-P$ states are related by the mirror symmetry operator M_{xy} . Under this mirror operation, in-plane vectors remain invariant, while out-of-plane vectors reverse their direction. Since the BPVE tensor transforms under a symmetry operation according to

$$\sigma^{ijk} = \sum_{abc} R_{ia} R_{jb} R_{kc} \sigma^{abc}, \quad (1)$$

where R_{ia} denotes the matrix representation of the symmetry operator R , and in the present case $R = M_{xy} = \text{diag}(1, 1, -1)$, clear symmetry constraints on the tensor components emerge. In particular, BPVE tensor elements containing an even number of z indices remain invariant under polarization reversal, whereas those with an odd number of z indices change sign. Therefore, mirror-related ferroelectric states lead to a nonsynchronous BPVE by preserving specific tensor components, as already demonstrated in Ref. [70].

Further, to assess the robustness of our results with respect to the choice of exchange-correlation functional, we have additionally displayed the dominant shift and injection current components using the HSE hybrid functional in the Supplemental Material [92], which show good qualitative agreement in comparison with PBE results in Fig. 3.

VI. BPVE IN SLIDING JANUS BILAYERS

To elucidate the impact of chemical asymmetry on the BPVE of bilayers, we compare the shift current and the circular injection current components for MoSe₂, Janus I, and Janus II structures, as shown in Fig. 4. All the three structures belong to the space group P3m1 (No. 156), therefore we compare the same allowed components of the photocurrents.

Among the three, Janus II displays remarkable enhancement in all the components of the photocurrent. The σ^{xy} response of Janus II shows a sharp, well-defined peak at around 3 eV of about 90 $\mu\text{A}/\text{V}^2$, and maintains elevated values over a broad photon energy range, as shown in Fig. 4(a). In contrast, Janus I and MoSe₂ exhibit less intense largest peaks of around 80 $\mu\text{A}/\text{V}^2$ and 70 $\mu\text{A}/\text{V}^2$, respectively.

The shift current component σ^{zx} and the circular injection current component η^{zx} show even more pronounced enhancements in the Janus II system. As we can see from Fig. 4(b), σ^{zx} of Janus II configuration reaches peaks of around 40 $\mu\text{A}/\text{V}^2$ in the visible region, while the peaks of Janus I and MoSe₂ bilayers are much smaller, being around 10–20 $\mu\text{A}/\text{V}^2$ in the visible range. Regarding the circular injection current, Janus II attains peak values nearly an order of magnitude greater than both MoSe₂ and Janus I, as shown in Fig. 4(c). The largest peaks are of around $4 \times 10^9 \text{ A}/(\text{V}^2\text{s})$, with a very intense spectrum in both the visible and the ultraviolet regions. These values are of the same order of magnitude of the circular responses reported for EuO [34], which was previously regarded as exhibiting a colossal BPVE in both its linear and circular components. Moreover, they exceed the values reported for several materials, both 3D and 2D [50], although they remain lower than those found in certain group-IV monochalcogenide monolayers [50]. This suggests highly efficient photoresponses in the polar Janus II structure, making it a potentially interesting candidate for applications. The enhanced BPVE in Janus II can be quali-

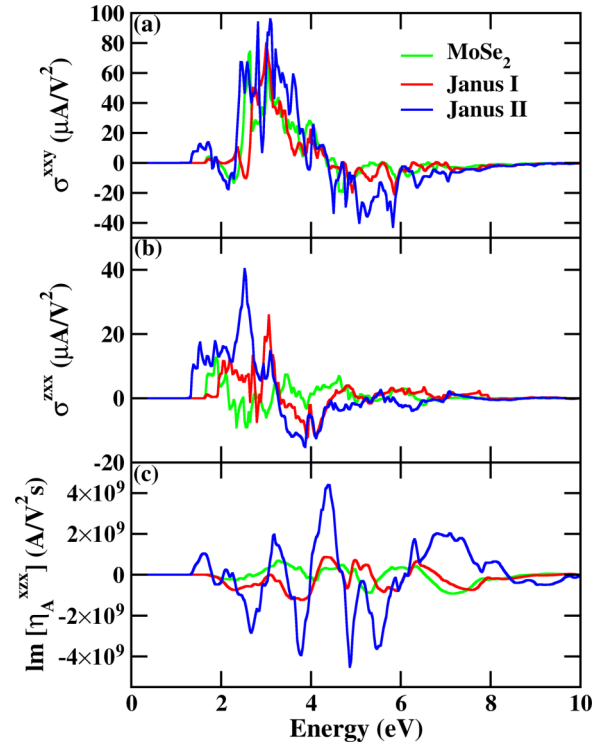


FIG. 4. Comparison of BPVE response for MoSe₂, Janus I, and Janus II bilayers for (a) in-plane shift current component σ^{xy} , (b) out-of-plane shift current component σ^{zx} , and (c) circular injection current component η^{zx} .

tatively understood in terms of intrinsic factors identified in previous studies [1]. In particular, the shift current is sensitive to the asymmetry of the bonding character, which reflects the asymmetric local chemical environment around the atoms in the structure. Greater asymmetry in this environment leads to larger photocurrents. Additionally, the macroscopic electric polarization has been identified as one of the factors influencing the BPVE, although the relationship between the shift current and the ground-state polarization is generally nontrivial. In Janus structures, these factors are naturally enhanced compared to the parent MoSe₂ bilayer, due to the intrinsic chemical asymmetry introduced by replacing one of the two chalcogen planes with a plane of a different element. In the Janus II configuration, this asymmetry is effective, leading to strongly enhanced photocurrents, whereas in Janus I the intralayer polarizations cancel, resulting in similar band structure features and photocurrent intensities comparable to those of the sliding MoSe₂ bilayer. These observations are consistent with previous reports of strongly enhanced out-of-plane nonlinear responses in Janus monolayers [93,94].

These findings underscore the strong tunability of the BPVE through chemical engineering. Janus II combines both intralayer polarization from chalcogen asymmetry and interlayer sliding ferroelectricity, leading to strongly enhanced bulk photovoltaic responses. To disentangle the relative importance of these two contributions, we analyze the evolution of photocurrents under controlled structural modifications, as illustrated in Fig. 5. First, we laterally slide the two monolayers relative to each other, thereby reversing the interlayer

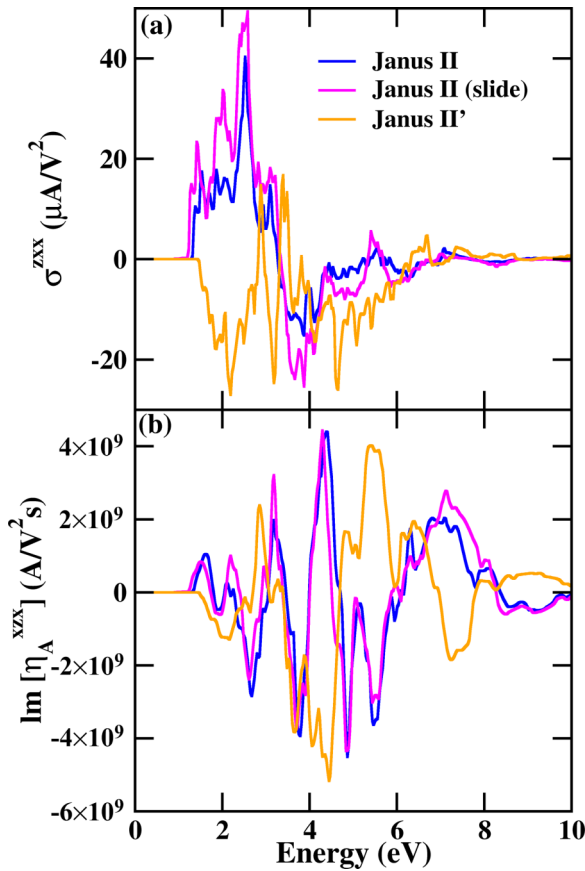


FIG. 5. Evolution of the (a) out-of-plane shift current σ_{zxx} and (b) circular injection current η_{zxx} components for Janus II, Janus II (slide), and Janus II'.

sliding polarization; we refer to this configuration as Janus II (slide). Second, we reverse the intralayer polarization by interchanging the S and Se atoms within each monolayer, creating a modified structure denoted as Janus II'. The structural details of Janus II (slide) and Janus II' can be found in the Supplemental Material [92]. Our results show that the photocurrent response is overwhelmingly dictated by the vertical chemical asymmetry of the Janus structure. Switching the intralayer polarization (Janus II') reverses both the shift and injection current components, underscoring the dominant role of the chemically driven dipole. In contrast, when only the sliding direction is modified, the photocurrent spectra exhibit only modest variations in intensity while retaining their original sign.

The comparatively weak contribution of the sliding-induced interlayer polarization to the BPVE can be understood by comparing the magnitude of the photoresponses associated with sliding ferroelectricity to those induced by the Janus chemical asymmetry, introduced in the Janus II system. Due to the large difference in magnitude between the two contributions, the overall BPVE in Janus II is primarily governed by the intralayer Janus dipole. It has already been shown that in Janus XMY-XMY structures the intralayer polarization dominates over the interlayer contribution by nearly

two orders of magnitude [76]. As a result, when the interlayer polarization is reversed, the total polarization preserves its sign, since it remains dominated by the intralayer component [76]. The same behavior is reflected in the BPVE, which follows the polarization direction.

VII. CONCLUSIONS

We investigated the BPVE in sliding ferroelectric MoSe₂ and Janus MoSSe bilayers. For the Janus structures, we considered two configurations: one where the intralayer polarizations induced by Janus asymmetry cancel each other, and another exhibiting a net intralayer polarization. In the first case, photocurrent intensities are comparable to those of the MoSe₂ bilayer. In contrast, the Janus II shows significantly enhanced photoresponse, particularly in the circular injection current, which reaches values an order of magnitude higher than in the other cases. It exhibits pronounced photoresponses across the whole visible spectrum, making it a promising candidate for optoelectronic applications. Our analysis indicates that the BPVE in the polar Janus structure is predominantly driven by chemical asymmetry, with interlayer sliding polarization playing a smaller role. As a result, in polar Janus structures, where intralayer mechanisms dominate, photocurrents cannot be simply inverted by reversing the sliding direction. While interlayer sliding ferroelectricity allows for easier switching of photocurrents, intralayer and chemically induced polarizations enhance the photoresponses but they cannot be reversed. These two mechanisms thus offer complementary functionalities: one enables tunable and reversible control, while the other provides strong enhancement of the response. Overall, chemical and structural engineering, particularly combining Janus-type asymmetry with ferroelectric stacking, provides a versatile strategy to design two-dimensional materials with highly responsive and tunable nonlinear optical properties.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

- [1] Z. Dai and A. M. Rappe, Recent progress in the theory of bulk photovoltaic effect, *Chem. Phys. Rev.* **4**, 011303 (2023).
- [2] V. M. Fridkin, Bulk photovoltaic effect in noncentrosymmetric crystals, *Crystalllogr. Rep.* **46**, 654 (2001).
- [3] A. M. Glass, D. von der Linde, and T. J. Negran, High-voltage bulk photovoltaic effect and the photorefractive process in LiNbO₃, *Appl. Phys. Lett.* **25**, 233 (1974).
- [4] J. E. Sipe and A. I. Shkrebtii, Second-order optical response in semiconductors, *Phys. Rev. B* **61**, 5337 (2000).
- [5] R. von Baltz and W. Kraut, Theory of the bulk photovoltaic effect in pure crystals, *Phys. Rev. B* **23**, 5590 (1981).
- [6] J. E. Spanier, V. M. Fridkin, A. M. Rappe, A. R. Akbashev, A. Polemi, Y. Qi, Z. Gu, S. M. Young, C. J. Hawley, D. Imbrenda, G. Xiao, A. L. Bennett-Jackson, and C. L. Johnson, Power conversion efficiency exceeding the Shockley-Queisser limit in a ferroelectric insulator, *Nat. Photon.* **10**, 611 (2016).
- [7] A. P. Kirk and D. W. Cardwell, Reconsidering the Shockley-Queisser limit of a ferroelectric insulator device, *Nat. Photon.* **11**, 329 (2017).
- [8] A. Pusch, U. Römer, D. Culcer, and N. J. Ekins-Daukes, Energy conversion efficiency of the bulk photovoltaic effect, *PRX Energy* **2**, 013006 (2023).
- [9] S. M. Young and A. M. Rappe, First principles calculation of the shift current photovoltaic effect in ferroelectrics, *Phys. Rev. Lett.* **109**, 116601 (2012).
- [10] A. M. Cook, B. M. Fregoso, F. de Juan, S. Coh, and J. E. Moore, Design principles for shift current photovoltaics, *Nat. Commun.* **8**, 14176 (2017).
- [11] Y. Zhang, T. Holder, H. Ishizuka, F. de Juan, N. Nagaosa, C. Felser, and B. Yan, Switchable magnetic bulk photovoltaic effect in the two-dimensional magnet CrI₃, *Nat. Commun.* **10**, 3783 (2019).
- [12] Y. Zhang, H. Ishizuka, J. van den Brink, C. Felser, B. Yan, and N. Nagaosa, Photogalvanic effect in Weyl semimetals from first principles, *Phys. Rev. B* **97**, 241118(R) (2018).
- [13] J. Ibañez-Azpiroz, S. S. Tsirkin, and I. Souza, *Ab initio* calculation of the shift photocurrent by WANNIER interpolation, *Phys. Rev. B* **97**, 245143 (2018).
- [14] A. R. Puente-Uribe, S. S. Tsirkin, I. Souza, and J. Ibañez-Azpiroz, *Ab initio* study of the nonlinear optical properties and dc photocurrent of the Weyl semimetal TaIrTe₄, *Phys. Rev. B* **107**, 205204 (2023).
- [15] D. Côté, N. Laman, and H. M. van Driel, Rectification and shift currents in GaAs, *Appl. Phys. Lett.* **80**, 905 (2002).
- [16] M. Nakamura, S. Horiuchi, F. Kagawa, N. Ogawa, T. Kurumaji, Y. Tokura, and M. Kawasaki, Shift current photovoltaic effect in a ferroelectric charge-transfer complex, *Nat. Commun.* **8**, 281 (2017).
- [17] D. Rees, K. Manna, B. Lu, T. Morimoto, H. Borrmann, C. Felser, J. E. Moore, D. H. Torchinsky, and J. Orenstein, Helicity-dependent photocurrents in the chiral Weyl semimetal RhSi, *Sci. Adv.* **6**, eaba0509 (2020).
- [18] J. W. McIver, D. Hsieh, H. Steinberg, P. Jarillo-Herrero, and N. Gedik, Control over topological insulator photocurrents with light polarization, *Nat. Nanotechnol.* **7**, 96 (2012).
- [19] H. Yuan, X. Wang, B. Lian, H. Zhang, X. Fang, B. Shen, G. Xu, Y. Xu, S.-C. Zhang, H. Y. Hwang, and Y. Cui, Generation and electric control of spin-valley-coupled circular photogalvanic current in WSe₂, *Nat. Nanotechnol.* **9**, 851 (2014).
- [20] C. Niu, S. Huang, N. Ghosh, P. Tan, M. Wang, W. Wu, X. Xu, and P. D. Ye, Tunable circular photogalvanic and photovoltaic effect in 2D tellurium with different chirality, *Nano Lett.* **23**, 3599 (2023).
- [21] J. Lin, H. Wang, Y. Zheng, Y. Kan, R. Chen, M. Long, Y. Chen, Z. Zhou, R. Qi, F. Yue, C.-G. Duan, J. Chu, and L. Sun, Enhanced bulk photovoltaic effect of single-domain freestanding BiFeO₃ membranes, *Adv. Mater.* **37**, 2414113 (2025).
- [22] N. Urakami, S. Ozaki, and Y. Hashimoto, Bulk photovoltaic effect of an alpha-phase indium selenide (α -In₂Se₃) crystal along the out-of-plane direction, *Appl. Phys. Lett.* **125**, 073102 (2024).
- [23] Q. Song, S. Stavrić, P. Barone, A. Droghetti, D. S. Antonenko, J. W. F. Venderbos, C. A. Occhialini, B. Ilyas, E. Ergeçen, N. Gedik, S.-W. Cheong, R. M. Fernandes, S. Picozzi, and R. Comin, Electrical switching of a p-wave magnet, *Nature (London)* **642**, 64 (2025).
- [24] J. Ahn, G.-Y. Guo, and N. Nagaosa, Low-frequency divergence and quantum geometry of the bulk photovoltaic effect in topological semimetals, *Phys. Rev. X* **10**, 041041 (2020).
- [25] T. Morimoto and N. Nagaosa, Topological nature of nonlinear optical effects in solids, *Sci. Adv.* **2**, e1501524 (2016).
- [26] D. E. Parker, T. Morimoto, J. Orenstein, and J. E. Moore, Diagrammatic approach to nonlinear optical response with application to Weyl semimetals, *Phys. Rev. B* **99**, 045121 (2019).
- [27] F. He, D. Chen, X. Ren, S. Meng, and L. He, Ultrafast shift current dynamics in WS₂ monolayer, *Phys. Rev. Res.* **6**, 013123 (2024).
- [28] T. Rangel, B. M. Fregoso, B. S. Mendoza, T. Morimoto, J. E. Moore, and J. B. Neaton, Large bulk photovoltaic effect and spontaneous polarization of single-layer monochalcogenides, *Phys. Rev. Lett.* **119**, 067402 (2017).
- [29] Q. Ma, R. Krishna Kumar, S.-Y. Xu, F. H. L. Koppens, and J. C. W. Song, Photocurrent as a multiphysics diagnostic of quantum materials, *Nat. Rev. Phys.* **5**, 170 (2023).
- [30] B. I. Sturman, Ballistic and shift currents in the bulk photovoltaic effect theory, *Phys. Usp.* **63**, 407 (2020).
- [31] F. Nastos and J. E. Sipe, Optical rectification and shift currents in GaAs and GaP response: Below and above the band gap, *Phys. Rev. B* **74**, 035201 (2006).
- [32] R. Resta, Geometrical theory of the shift current in presence of disorder and interaction, *Phys. Rev. Lett.* **133**, 206903 (2024).
- [33] Z. Dai, A. M. Schankler, L. Gao, L. Z. Tan, and A. M. Rappe, Phonon-assisted ballistic current from first-principles calculations, *Phys. Rev. Lett.* **126**, 177403 (2021).
- [34] S. Stavrić, G. Cuono, B. Yang, Á. R. Puente-Uribe, J. Ibañez-Azpiroz, P. Barone, A. Droghetti, and S. Picozzi, Giant nonreciprocal band structure effect in a multiferroic material, *Phys. Rev. Lett.* **135**, 206401 (2025).
- [35] S. M. Young, F. Zheng, and A. M. Rappe, First-principles calculation of the bulk photovoltaic effect in bismuth ferrite, *Phys. Rev. Lett.* **109**, 236601 (2012).
- [36] K. T. Butler, J. M. Frost, and A. Walsh, Ferroelectric materials for solar energy conversion: photoferroics revisited, *Energy Environ. Sci.* **8**, 838 (2015).
- [37] L. Z. Tan, F. Zheng, S. M. Young, F. Wang, S. Liu, and A. M. Rappe, Shift current bulk photovoltaic effect in polar materials-hybrid and oxide perovskites and beyond, *npj Comput. Mater.* **2**, 16026 (2016).

- [38] G. Cuono, S. Bandyopadhyay, A. Droghetti, and S. Picozzi, Bulk photovoltaic effect in ferroelectric and antiferroelectric phases of antimony sulphoiodide investigated by means of *ab initio* simulations, *Phys. Rev. Mater.* **9**, 064412 (2025).
- [39] R. Pandey, G. Vats, J. Yun, C. R. Bowen, A. W. Y. Ho-Baillie, J. Seidel, K. T. Butler, and S. I. Seok, Mutual insight on ferroelectrics and hybrid halide perovskites: A platform for future multifunctional energy conversion, *Adv. Mater.* **31**, 1807376 (2019).
- [40] R. P. Tiwari, Enhanced shift current bulk photovoltaic effect in ferroelectric Rashba semiconductor α -GeTe: *ab initio* study from three- to two-dimensional van der Waals layered structures, *J. Phys.: Condens. Matter* **34**, 435404 (2022).
- [41] M. Sotome, M. Nakamura, J. Fujioka, M. Ogino, Y. Kaneko, T. Morimoto, Y. Zhang, M. Kawasaki, N. Nagaosa, Y. Tokura, and N. Ogawa, Spectral dynamics of shift current in ferroelectric semiconductor SbSI, *Proc. Natl. Acad. Sci. USA* **116**, 1929 (2019).
- [42] N. Ogawa, M. Sotome, Y. Kaneko, M. Ogino, and Y. Tokura, Shift current in the ferroelectric semiconductor SbSI, *Phys. Rev. B* **96**, 241203(R) (2017).
- [43] M. Nakamura, H. Hatada, Y. Kaneko, N. Ogawa, Y. Tokura, and M. Kawasaki, Impact of electrodes on the extraction of shift current from a ferroelectric semiconductor SbSI, *Appl. Phys. Lett.* **113**, 232901 (2018).
- [44] J. Kim, K.-W. Kim, D. Shin, S.-H. Lee, J. Sinova, N. Park, and H. Jin, Prediction of ferroelectricity-driven Berry curvature enabling charge- and spin-controllable photocurrent in tin telluride monolayers, *Nat. Commun.* **10**, 3965 (2019).
- [45] T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin, and S.-W. Cheong, Switchable ferroelectric diode and photovoltaic effect in BiFeO₃, *Science* **324**, 63 (2009).
- [46] W. Ji, K. Yao, and Y. C. Liang, Bulk photovoltaic effect at visible wavelength in epitaxial ferroelectric BiFeO₃ Thin Films, *Adv. Mater.* **22**, 1763 (2010).
- [47] I. Grinberg, D. V. West, M. Torres, G. Gou, D. M. Stein, L. Wu, G. Chen, E. M. Gallo, A. R. Akbashev, P. K. Davies, J. E. Spanier, and A. M. Rappe, Perovskite oxides for visible-light-absorbing ferroelectric and photovoltaic materials, *Nature (London)* **503**, 509 (2013).
- [48] S. Aftab, M. A. Shehzad, H. M. S. Ajmal, F. Kabir, M. Z. Iqbal, and A. A. Al-Kahtani, Bulk photovoltaic effect in two-dimensional distorted MoTe₂, *ACS Nano* **17**, 17884 (2023).
- [49] M. Ramos, T. Ahmed, B. Q. Tu, E. Chatzikyriakou, L. Olano-Vegas, B. Martín-García, M. R. Calvo, S. S. Tsirkin, I. Souza, F. Casanova, F. de Juan, M. Gobbi, and L. E. Hueso, Unveiling intrinsic bulk photovoltaic effect in atomically thin ReS₂, *Nano Lett.* **24**, 14728 (2024).
- [50] S. R. Pandey, S. Barraza-Lopez, T. Rangel, and B. M. Fregoso, Injection current in ferroelectric group-IV monochalcogenide monolayers, *Phys. Rev. B* **100**, 195305 (2019).
- [51] Y. Li, J. Fu, X. Mao, C. Chen, H. Liu, M. Gong, and H. Zeng, Enhanced bulk photovoltaic effect in two-dimensional ferroelectric CuInP₂S₆, *Nat. Commun.* **12**, 5896 (2021).
- [52] Z. Qian, J. Zhou, H. Wang, and S. Liu, Shift current response in elemental two-dimensional ferroelectrics, *npj Comput. Mater.* **9**, 67 (2023).
- [53] Q. Zhang, A. Fan, Y. Wang, F. Wu, L. Li, H. Meng, and D. Geng, Emerging frontiers in two-dimensional sliding ferroelectrics, *npj 2D Mater. Appl.* **9**, 76 (2025).
- [54] Z. Fei, W. Zhao, T. A. Palomaki, B. Sun, M. K. Miller, Z. Zhao, J. Yan, X. Xu, and D. H. Cobden, Ferroelectric switching of a two-dimensional metal, *Nature (London)* **560**, 336 (2018).
- [55] S. C. de la Barrera, Q. Cao, Y. Gao, Y. Gao, V. S. Bheemarasetty, J. Yan, D. G. Mandrus, W. Zhu, D. Xiao, and B. M. Hunt, Direct measurement of ferroelectric polarization in a tunable semimetal, *Nat. Commun.* **12**, 5298 (2021).
- [56] K. Yasuda, X. Wang, K. Watanabe, T. Taniguchi, and P. Jarillo-Herrero, Stacking-engineered ferroelectricity in bilayer boron nitride, *Science* **372**, 1458 (2021).
- [57] M. V. Stern, Y. Waschitz, W. Cao, I. Nevo, K. Watanabe, T. Taniguchi, E. Sela, M. Urbakh, O. Hod, and M. Ben Shalom, Interfacial ferroelectricity by van der Waals sliding, *Science* **372**, 1462(2021).
- [58] H. Hu, Y. Sun, M. Chai, D. Xie, J. Ma, and H. Zhu, Room-temperature out-of-plane and in-plane ferroelectricity of two-dimensional β -InSe nanoflakes, *Appl. Phys. Lett.* **114**, 252903 (2019).
- [59] H. Hu, H. Wang, Y. Sun, J. Li, J. Wei, D. Xie, and H. Zhu, Out-of-plane and in-plane ferroelectricity of atom-thick two-dimensional InSe, *Nanotechnology* **32**, 385202 (2021).
- [60] L. Lin, X. Hu, R. Meng, X. Li, Y. Guo, H. Da, Y. Jiang, D. Wang, Y. Yang, and X. Yan, Sliding ferroelectricity and the moiré effect in Janus bilayer MoSSe, *Nanoscale* **16**, 4841 (2024).
- [61] X. Wang, K. Yasuda, Y. Zhang, S. Liu, K. Watanabe, T. Taniguchi, J. Hone, L. Fu, and P. Jarillo-Herrero, Interfacial ferroelectricity in rhombohedral-stacked bilayer transition metal dichalcogenides *Nat. Nanotechnol.* **17**, 367 (2022).
- [62] A. Weston, E. G. Castanon, V. Enaldiev, F. Ferreira, S. Bhattacharjee, S. Xu, H. Corte-León, Z. Wu, N. Clark, A. Summerfield, T. Hashimoto, Y. Gao, W. Wang, M. Hamer, H. Read, L. Fumagalli, A. V. Kretinin, S. J. Haigh, O. Kazakova, A. K. Geim, *et al.*, Interfacial ferroelectricity in marginally twisted 2D semiconductors, *Nat. Nanotechnol.* **17**, 390 (2022).
- [63] P. Meng, Y. Wu, R. Bian, E. Pan, B. Dong, X. Zhao, J. Chen, L. Wu, Y. Sun, Q. Fu, Q. Liu, D. Shi, Q. Zhang, Y.-W. Zhang, Z. Liu, and F. Liu, Sliding induced multiple polarization states in two-dimensional ferroelectrics, *Nat. Commun.* **13**, 7696 (2022).
- [64] F. Sui, M. Jin, Y. Zhang, R. Qi, R. Huang, F. Yue, Junhao Chu, and Y.-N. Wu, Sliding ferroelectricity in van der Waals layered γ -InSe semiconductor, *Nat. Commun.* **14**, 36 (2023).
- [65] Z. Wang, Z. Gui, and L. Huang, Sliding ferroelectricity in bilayer honeycomb structures: A first-principles study, *Phys. Rev. B* **107**, 035426 (2023).
- [66] X. Sun, Q. Xia, T. Cao, and S. Yuan, Sliding ferroelectricity in two-dimensional materials and device applications, *Mater. Sci. Eng.: R: Rep.* **163**, 100927 (2025).
- [67] L. Li and M. Wu, Binary Compound Bilayer and Multilayer with Vertical Polarizations: Two-Dimensional Ferroelectrics, Multiferroics, and Nanogenerators, *ACS Nano* **11**, 6382 (2017).
- [68] M. Wu and J. Li, Sliding ferroelectricity in 2D van der Waals materials: Related physics and future opportunities, *Proc. Natl. Acad. Sci.* **118**, e2115703118 (2021).
- [69] X. Chen, X. Ding, G. Gou, and X. C. Zeng, Strong sliding ferroelectricity and interlayer sliding controllable spintronic effect in two-dimensional HgI₂ layers, *Nano Lett.* **24**, 3089 (2024).

- [70] R.-C. Xiao, Y. Gao, H. Jiang, W. Gan, C. Zhang, and H. Li, Non-synchronous bulk photovoltaic effect in two-dimensional interlayer-sliding ferroelectrics, *npj Comput. Mater.* **8**, 138 (2022).
- [71] C. Zhang, P. Guo, and J. Zhou, Tailoring bulk photovoltaic effects in magnetic sliding ferroelectric materials, *Nano Lett.* **22**, 9297 (2022).
- [72] Q. Liang, G. Zheng, S. Fan, L. Yang, and S. Zheng, Multidirectional sliding ferroelectricity of rhombohedral-stacked InSe for reconfigurable photovoltaics and imaging applications, *Adv. Mater.* **37**, 2416117 (2025).
- [73] W. Ji, T. Lu, and Y. Liu, Nanostructure engineering for ferroelectric photovoltaics, *Nanoscale* **17**, 6938 (2025).
- [74] M. Yagmurcukardes and F. M. Peeters, Stable single layer of Janus MoSO: Strong out-of-plane piezoelectricity, *Phys. Rev. B* **101**, 155205 (2020).
- [75] T. H. Pham, H. Ullah, A. Shafique, H. J. Kima, and Y.-H. Shin, Enhanced out-of-plane electromechanical response of Janus ZrSeO, *Phys. Chem. Chem. Phys.* **23**, 16289 (2021).
- [76] C. Zhang, Z. Zhang, Z. Wu, X. Li, Y. Wu, and J. Kang, Modulation of polarization in sliding ferroelectrics by introducing intrinsic electric fields, *J. Phys. Chem. Lett.* **15**, 8049 (2024).
- [77] J. Zhang, S. Jia, I. Kholmanov, L. Dong, D. Er, W. Chen, H. Guo, Z. Jin, V. B. Shenoy, L. Shi, and J. Lou, Janus monolayer transition-metal dichalcogenides, *ACS Nano* **11**, 8192 (2017).
- [78] A.-Y. Lu, H. Zhu, J. Xiao, C.-P. Chu, Y. Han, M.-H. Chiu, C.-C. Cheng, C.-W. Yang, K.-H. Wei, Y. Yang, Y. Wang, D. Sokaras, D. Nordlund, P. Yang, D. A. Muller, M.-Y. Chou, X. Zhang, and L.-J. Li, Janus monolayers of transition metal dichalcogenides, *Nat. Nanotechnol.* **12**, 744 (2017).
- [79] K. Zhang, Y. Guo, Q. Ji, A.-Y. Lu, C. Su, H. Wang, A. A. Puretzky, D. B. Geohegan, X. Qian, S. Fang, E. Kaxiras, J. Kong, and S. Huang, Enhancement of van der Waals interlayer coupling through polar Janus MoSSe, *J. Am. Chem. Soc.* **142**, 17499 (2020).
- [80] L. Zhang, Z. Yang, T. Gong, R. Pan, H. Wang, Z. Guo, H. Zhang, and X. Fu, Recent advances in emerging Janus two-dimensional materials: from fundamental physics to device applications, *J. Mater. Chem. A* **8**, 8813 (2020).
- [81] D. Dong, Y. Peng, C. Liu, Y. Xia, S. Liu, P. Zhang, and Z. Wang, Origin of Janus-induced polarization enhancement in sliding ferroelectrics, *Phys. Rev. B* **112**, 205403 (2025).
- [82] A. Mahajan and A. Narayan, Modulation of polarization and metallicity in Janus sliding ferroelectrics, *2D Mater.* **13**, 015031 (2026).
- [83] G. Kresse and J. Hafner, *Ab initio* molecular dynamics for liquid metals, *Phys. Rev. B* **47**, 558(R) (1993).
- [84] G. Kresse and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.* **6**, 15 (1996).
- [85] G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54**, 11169 (1996).
- [86] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [87] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.* **132**, 154104 (2010).
- [88] R. D. King-Smith and D. Vanderbilt, Theory of polarization of crystalline solids, *Phys. Rev. B* **47**, 1651 (1993).
- [89] N. Marzari and D. Vanderbilt, Maximally localized generalized WANNIER functions for composite energy bands, *Phys. Rev. B* **56**, 12847 (1997).
- [90] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, WANNIER90: A tool for obtaining maximally-localised WANNIER functions, *Comput. Phys. Commun.* **178**, 685 (2008).
- [91] G. Pizzi, V. Vitale, R. Arita, S. Blügel, F. Freimuth, G. Géranton, M. Gibertini, D. Gresch, C. Johnson, T. Koretsune, J. Ibañez-Azpiroz, H. Lee, J.-M. Lihm, D. Marchand, A. Marrazzo, Y. Mokrousov, J. I. Mustafa, Y. Nohara, Y. Nomura, L. Paulatto, *et al.*, WANNIER90 as a community code: new features and applications, *J. Phys.: Condens. Matter* **32**, 165902 (2020).
- [92] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/2pvc-zj4c> for additional information on structural properties, effect of polarization and exchange correlation functional on photocurrents, and joint density of states, which includes Refs. [95,96].
- [93] A. Strasser, H. Wang, and X. Qian, Nonlinear optical and photocurrent responses in Janus MoSSe monolayer and MoS₂-MoSSe van der Waals Heterostructure, *Nano Lett.* **22**, 4145 (2022).
- [94] M. Chen, S.-B. Yu, D. Zhang, and J. Li, Nonlinear photocurrent responses in Janus WS₂ monolayer, *Chin. Phys. Lett.* **40**, 087201 (2023).
- [95] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, Influence of the exchange screening parameter on the performance of screened hybrid functionals, *J. Chem. Phys.* **125**, 224106 (2006).
- [96] J. Paier, M. Marsman, K. Hummer, G. Kresse, I. C. Gerber, and J. G. Ángyán, Screened hybrid density functionals applied to solids, *J. Chem. Phys.* **124**, 154709 (2006).