Two dimensional ferroelectrics: Candidate for controllable physical and chemical applications

Jing Shang | Xiao Tang | Liangzhi Kou

School of Mechanical, Medical and Process Engineering, Queensland University of Technology, Brisbane, Australia

Correspondence
Liangzhi Kou School of Mechanical, Medical and Process Engineering, Queensland University of Technology, Brisbane, Qld 4001, Australia.
Email: liangzhi.kou@qut.edu.au

Abstract
The recent emerged two-dimensional (2D) ferroelectrics have attracted tremendous research interests due to their promising application in nonvolatile electronics devices. The reversible electric polarization of ferroelectrics from the off-centered positive and negative surfaces can effectively lift the band states near Fermi level and modulate the charge distribution, which therefore play important roles for the controllable electronic/magnetic properties and chemical reactions. Here, based on the latest revealed 2D ferroelectrics, we reviewed the research progress of ferroelectric controlled physical properties and chemical reactions, including the effects of reversible polarization on magnetic and electronic behaviors, polarization dependent photocatalytic water splitting and gas adsorptions. The associated applications in electronics, sensors and energy conversion are also discussed. At last, the possible research directions of 2D ferroelectrics have also been proposed. The review is expected to inspire the research interests of 2D ferroelectrics in the practical applications.

This article is categorized under:
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KEYWORDS
ferroelectric controlled physical and chemical behaviors, first-principles calculations, intrinsic and reversible polarization, two dimensional layered ferroelectrics

INTRODUCTION

Ferroelectrics (FE) refer to a class of polar materials with stable and switchable electric polarization resulting from the off-centered positive and negative charges. The abundant physics, such as the piezoelectric/dielectric properties, photovoltaic effect, photorefractive and nonlinear optical effect, makes it as a promising candidate for next generation devices. Analogous to ferromagnetism, the direction of spontaneous electric dipoles can be reversed by an external electric field (see Figure 1a), leading to the bistable and switchable polarized states. The characteristic has been proposed to represent logic 0 and 1, therefore could be used in nonvolatile electronics. For example, the appealing applications for next-generation logic data memory storage, waveguide, pressure actuators sensors, capacitors have been widely proposed based on ferroelectrics. As the foundation of the application, stable ferroelectric materials with high Curie temperature have to be secured while the accurate manipulation of the ferroelectric states and the interactions with surroundings need to be clarified.
Over the past several decades, a large number of threedimensional (3D) ferroelectrics were discovered. The representative example is the ABO$_3$ perovskite oxide such as BaTiO$_3$, and PbTiO$_3$ which always possess strong ferroelectric polarization and fast response to external field. The lattice distortion induced by the off-centered displacement of B cation in the paraelectrical structure is responsible for the reversible spontaneous ferroelectric polarization and order–disorder phase transitions. The ferroelectric films, which were exfoliated from bulk counterparts, were used for the fabrication of nonvolatile memories for microelectronics. Even so, the practical application in microelectronic devices is still hampered due to some intrinsic issues such as depolarization and dangling bonds. For example, for the ferroelectric thin films like BaTiO$_3$, PbTiO$_3$, and BiFeO$_3$, when the film thickness is below a critical value like 12, 14, and 30 Å respectively, the Curie temperature would decrease, and ferroelectric polarization may be destroyed and completely disappear as caused by the depolarization field, surface force and electrical boundary conditions. Besides, the surface dangling bonds would make the films chemical and structural unstable, which is still a major challenge for the development of ferroelectric devices based on ABO$_3$. The next generation nanoelectronics is calling for the new ferroelectrics with atomic thickness, fast response, high storage density and low energy consumption.

The emergence of 2D materials provides excellent opportunities to explore the existence of 2D ferroelectrics. Back to 1944, Onsager predicted the existence of 2D ferroelectricity by using the ideal Ising model, which laid the foundation for the following investigations. Indeed, 2D layered ferroelectrics with clean surfaces can overcome the challenges of ferroelectric films as exfoliated from ABO$_3$ structures and realize nanosized ferroelectric devices by utilizing the permanent intrinsic polarization. Theoretical simulations have predicted the existence of ferroelectricity in stable 2D layered materials, including intrinsic in-plane FE such as group IV monochalcogenides with the formula MX (M = Ge, Sn; X = S, Se), 2H and 1T-VSe$_2$, charge doped CrI$_3$ monolayer and atomically thick SnTe film. The 2D materials with out-of-plane FE include but not limit to the distorted 1T-MoTe$_2$, MoS$_2$, monolayers, chemical functionalized phosphorene, graphene analogues (silicene, germanene, and stanene), carbon nitrides, 2D In$_2$Se$_3$, monolayer AgBiP$_2$Se$_6$ and CuInP$_2$S(Se)$_6$ (CIPS), and so on. Especially, the successful synthesis and experimental demonstrations of monolayer SnTe, In$_2$Se$_3$, and CIPS have paved the solid foundations for the exploration of unique physical and chemical properties in 2D ferroelectrics.

In this perspective, we briefly review the theoretically and experimentally revealed 2D layered FE materials, and then focus on the recent research progresses of the ferroelectric mediated physical and chemical applications by utilizing the intrinsic and reversible polarization of 2D layered ferroelectrics. Four representative examples including ferroelectric controlled magnetism, electronic modulation by ferroelectric switch, polarization dependent chemical reaction and gas sensing, are exhibited and discussed, as summarized in Figure 1. At the end of this review, we provide an outlook for future research directions based on 2D ferroelectrics.
2D FERROELECTRICS FAMILY AND MECHANISM OF FERROELECTRICITY CONTROLLED CHEMICAL/PHYSICAL APPLICATIONS

2.1 Discovered 2D ferroelectrics family

Although the ferroelectricity was reported in ABO₃ films early at 1999, they were excluded as the true 2D ferroelectric materials due to the structure instability and depolarization in the ultra-thin thickness as discussed above. The structural and thermal stabilities, atomic thickness and reversible polarization are the prerequisites as the 2D ferroelectrics. In this sense, numerous 2D layered materials were theoretically proposed to be ferroelectrics in recent years based on the simulations, the examples include but not limit to hydroxylized graphene, chemical functionalized 2D Group IV, graphite analogues (silicene, germanene, and stanene) and Li doped CrI₃ monolayers, and more as summarized in Tang’s recent review. However, most of them are barely verified by the measurements or even not experimental synthesized yet. The first confirmed 2D ferroelectrics is mono- and few-layer of SnTe, which was experimentally synthesized at 2016. The off-centered positive charged Sn and negative charged Te atoms create an in-plane polarization, which is reversible under external stimuli. The stable in-plane spontaneous polarization in atomic-thick SnTe down to a one-unit cell was observed experimentally. The applications like nonvolatile ferroelectric random-access memory device, valleytronics, and photovoltaics were thus proposed by taking advantage of the ferroelectricity. The successful synthesis and direct demonstration of ferroelectricity in the atomic thick SnTe revived the research enthusiasm of real 2D ferroelectrics. Subsequently, the similar in-plane ferroelectricity was reported in the family IV monochalcogenides MX (M = Ge, Sn; X = S, Se) monolayers and similar structures like γ-SbX (X = As, P) and β-GeS₄ monolayers due to the broken structural symmetry along xy-plane, where the spontaneous polarization is predicted to be 3.8 × 10⁻¹⁰ C/m and 2 × 10⁻¹⁰ C/m, respectively. As seen from Figure 2a–c, these in-plane ferroelectric materials share the similar structure characteristic, the relative displacements between negative and positive charged atoms are the underlying mechanism of ferroelectric switch, they are therefore generally robust and possess high Curie temperatures. However, the in-plane polarization is not easy to manipulate, the application potential is therefore limited.

In contrast, 2D out-of-plane ferroelectrics with dipole surfaces is relatively easy to be tuned and controlled by external stimuli, which is thus more promising for practical applications. Early at 2014, out-of-plane spontaneous ferroelectricity (∼0.28 μC/cm²) was theoretically discovered in 1T-MoS₂ monolayer based on first-principle calculations and Landau theoretical analysis. Similar phenomena was also found in other 1T-MX₂ (M = Mo, W and X = S, Se) structures. Due to the coexistence of structural symmetry breaking and spin-orbit coupling, the obvious band splitting and Rashba effect were observed. However, for most MX₂ monolayers, 2H phases are more energetically preferred; the ferroelectric 1T-phase is thermally unstable, rendering them unsuitable for the extended investigations. Except MX₂ layers, the out-of-plane ferroelectricity was also proposed in freestanding buckled AB binary monolayer (A and B refer to the atoms in group IV or III–V, respectively) and phosphorus oxides, however the large energy barrier for polarization reversal will be a challenge to verify the ferroelectricity in experiments. Hyperferroelectric metal is another unique family of 2D ferroelectric material as recently predicted from first-principle calculations, where CrN and CrB₂ monolayers possess in-plane ferroelectricity and LiOsO₃ ultrathin films have the out-of-plane electric dipole moment, the combinations of metallicity and noncentrosymmetric structures extend 2D FE materials from insulators (semiconductors) to metals. Although these theoretical predictions expand the family of 2D ferroelectrics; the absence of experimental demonstrations renders the investigations unconvincing. Even so, the recent synthesis of atomically layered ferroelectric materials with out-of-plane polarization, such as CuInP₂S₆ and In₂Se₃, opens the new era of 2D ferroelectrics. Subsequent investigations indicate that ferroelectricity also exists in similar structures including AgBiP₂Se₆, CuInP₂Se₆, CuMP₂X₆ (M = Cr; V; X = S, Se) monolayer, and other III-VI₃ (III = Al, Ga, In; VI = S, Se, Te) van der Waals materials as shown in Figure 2d–f. More interesting, both in-plane and out-of-plane FE polarizations can coexist in ultrathin layered In₂Se₃ and also can be reversed simultaneously due to the dipole locking, as experimentally demonstrated. In CIPS family, the out-of-plane polarization is intrinsic and strong as the ferroelectricity origins from the off-centring antiparallel displacements of cation such as Ag⁺ and Bi³⁺ ions in AgBiP₂Se₆ monolayer. Theoretical simulations even predicted the type II 2D multiferroics, MXenes (Hf₂VC₃F₁₄) monolayer, the switchable FE polarization is originated from the space break of the magnetism, which is however waiting for the experimental demonstration. This intrinsic and reversible vertical polarization in these ferroelectric materials provides a good platform to explore rich physical and chemical applications by utilizing the different dipole surfaces.
2.2 Mechanism of ferroelectricity-controlled physics and chemical reaction

Essentially speaking, the polarization in ferroelectrics should be equivalent to the external electric field; the polarized surfaces can be regarded as the negative/positive charged sides of the capacitor. Due to the atomic thickness of 2D materials, the induced effective electric field will be very large, which is enough to produce significant effects on the contacted materials or reactants. For example, it will significantly lift the band states and spin polarization near the Fermi level and therefore remarkably modulate the electronic/magnetic properties due to the Stark effects when an additional material is placed on top of ferroelectrics; Meanwhile, the polarization field can also enhance or weaken the interlayer electron transfer, which will control the chemical activity of the reactants, as shown in Figure 1b. More interestingly, as the distinguishable characteristic, the polarization direction of ferroelectrics is reversible, which can act as a switchable electric field, therefore providing a feasible approach to modulate the physical properties and chemical reaction. Compared with the external applied electric field, to utilize the intrinsic polarization (effective electric field) of FE material for physical/chemical modulations and controllable applications possesses a couple of advantages. First of all, 2D FE materials processes the potential to achieve nonvolatile applications due to the presence of the reversible and bistable polarization states, which can avoid energy consumption caused by sustained electric field. Although the intriguing physical properties of 2D layered materials can also be effectively modulated by external electric field90 or...
electrostatic doping, this is however an volatile process; the electronic or magnetic states will recover once the applied electric field is removed. The sustained field is essential to maintain the desired state, leading to huge energy consumption. Second, the positive/negative charged surfaces of 2D FE materials will exhibit the different chemical activity, the ferroelectric switch provides excellent opportunity to control catalytic activity and reaction pathway. These two working mechanisms and the synergic effects laid the theoretical foundations for observed physical and chemical phenomena. In the following, we will review the physical and chemical applications from aspects of tuneable magnetic/electric behaviors, water splitting and reversible gas sensing by the FE polarization in 2D layered ferroelectrics, and make the corresponding discussions based on the underlying mechanisms.

3 | FERROELECTRIC CONTROLLABLE APPLICATIONS IN PHYSICS AND CHEMICAL REACTIONS

3.1 | Magnetism tuned by ferroelectricity

The manipulation of magnetism in 2D layered magnets by electric field or electrostatic doping through magnetoelectric effect is one of the promising avenues to achieve high-density energy-efficient magnetic data storage. Although some success examples were reported, numerous issues are to be solved yet. For instance, for some cases of electric-field-controlled magnetism, the easy axes rather than the magnetic orders or moments are rotated by electric field or domain structures, it is easy to be flip back by the environmental thermal fluctuations. Besides, the process of electric-field-controlled magnetism is volatile; the magnetic states would be recovered once the external electric field is removed. The pursuit of lower energy cost and higher data density in information storage has prompted researchers to explore better solutions, rather than using external electric fields to manipulate magnetization in spintronic devices. FE materials provide promising chances to achieve the goal, since it can be regarded as a source of switchable electric fields when interfaced with a ferromagnet. The polarization will significantly control spin texture, spin polarization and Fermi level, leading to the ferroelectric manipulation of magnetic behaviors. Over last few years, although there were some reports about ferroelectric tuned magnetism, the FE dipole was mainly from ABO₃ FE films or bulk ferroelectrics, the issues such as the instability of FE structure or depolarization limit their practical applications in spintronics.

In contrast, the stable ferroelectricity in 2D layered materials can be fully utilized to control magnetic behaviors. For example, the rotation direction (clockwise or anticlockwise) of spin texture can be controlled by ferroelectric switch of GeTe layer as shown in Figure 3a. Although the in-plane FE polarization in GeTe is not easy to be reversed by external field in practical situation, this tunable spin texture by ferroelectric switch still opened new era of magnetic manipulations. Placing magnetic layered materials on top of ferroelectrics to build vdW heterostructures is another feasible and effective approach to modulate the magnetic behaviors via magnetoelectric effects, although they generally belong to type-I multiferroics with weak magnetoelectric coupling. The interlayer electron transfer and energy level shift of half-filled d orbital are the main ingredients of the physical phenomena. For example, Gong et al. theoretically demonstrated that the magnetic easy axis of Cr₂Ge₂Te₆ layer can be switched from in-plane to out-plane when ferroelectric In₂Se₃ reverses its polarization in atomically layered Cr₂Ge₂Te₆/In₂Se₃ heterostructures. Meanwhile, Sun et al. also achieved the robust magnetic control in 2D FeI₂/In₂Se₃ van der Waals heterostructure via strong interlayer magnetoelectric coupling as revealed from first-principle calculations, where FeI₂ monolayer undergoes a magnetic ground state transition from ferromagnetic (FM) to antiferromagnetic (AFM) due to the Fe-d orbital splitting when the FE polarization direction in In₂Se₃ layer is reversed, as shown in Figure 3b. Except the easy axis and ground magnetic states, the interlayer magnetic coupling can be also significantly controlled by the polarization of ferroelectric materials. Y. Lu et al. proposed an artificial 2D multiferroics with bilayer chromium triiodide (CrI₃) and FE monolayer Sc₂CO₂, where the magnetic ground state of bilayer CrI₃ can be converted from FM to AFM with the FE polarization in Sc₂CO₂ monolayer being switched from upwards to downwards, as shown in Figure 3c. Associated with the magnetic behavior manipulation, the band states near the Fermi level will be shifted upwards or downwards, which not only induce the electronic variation, but also the transition between different magnetic states. One example is MnCl₃/CuInP₂S₆ heterostructure, it was showed that, the Dirac cones of MnCl₃ is destroyed by the upwards polarization of CuInP₂S₆ although the half-mental characteristic is preserved. In contrast, 2D MnCl₃ changes to a magnetic semiconductor when FE dipole in CuInP₂S₆ is pointing downwards. Based on this finding, atom-thick multiferroic memory whose data writing and reading are dependent on the FE polar directions of CuInP₂S₆ can be proposed, as shown in Figure 3d. For
the observed phenomena, the charge transfer plays an indispensable role between MnCl₃ and FE CuInP₂S₆ layers, as shown in Figure 3e. Besides, the magnetism reversed by ferroelectricity can be also discovered in multiferroics where robust magnetism and ferroelectricity coexist in one material. For example, in multiferroic MXene, VS₂, MoN₂ bilayers⁷⁶ and ultrathin CuCrS₂ or CuCrSe₂,⁷⁷ it was found that the magnetizations can be reversed by the FE switching owing to strong magnetoelectric coupling. Furthermore, when metal porphyrin (MP) molecule is intercalated in 2D materials like bilayer MoS₂ or FM CrI₃, the magnetization, spin distribution or direction of single MP molecules can be switched upon FE reversal.⁴⁶

Compared with the electric field controlled magnetism in nanomaterials, the advantage of magnetic behavior manipulation via ferroelectric polarization switch is obvious. The magnetism transition process does not depend on external stimuli but only the intrinsic ferroelectricity due to the inner broken spatial inversion symmetry. Although the polarized states of 2D FE layer need to be switched by external electric field, the reversed states can be reserved when the external load is removed. These results indicate that the nonvolatile modulation of magnetism by FE switch in 2D ferroelectrics is a promising and low-energy costing strategy, which can act as a promising platform to achieve nonvolatile magnetic on/off control by switching FE polarization in 2D heterostructures.

3.2 | Electronic properties tuned by ferroelectricity

The magnetic control is closely related with the lifts of spin polarized band state induced by reversible FE polarization of 2D ferroelectrics, which can offer new ideas for the unique physical phenomena. Analogue to magnetic behaviors, electronic properties of layered materials can be also remarkably modulated when they are placed on top of ferroelectrics due to the similar working mechanism, namely the interlayer charge transfer and polarization shifted band states.
Taking In$_2$Se$_3$ as the typical example, in Ding's work,\textsuperscript{36} it was demonstrated that the Schottky barrier across the graphene/In$_2$Se$_3$ interface can be altered through switching the dipole orientation of In$_2$Se$_3$, where the Dirac Cone of graphene can be shifted to the conduction band or valence band areas due to the charge transfer and doping effects, as shown in Figure 4a. The conclusion was further demonstrated by Ayadi et al.\textsuperscript{81} that the position of Dirac point is dependent on the polarization direction of In$_2$Se$_3$. It was confirmed that the Dirac point shifts to higher energy level when the intrinsic dipole of In$_2$Se$_3$ points away from graphene due to the larger transferred charge from graphene to In$_2$Se$_3$. The differences of electron redistribution can be clearly seen in the sandwiched In$_2$Se$_3$–graphene–graphene–In$_2$Se$_3$ system that the interlayer charge transfers on the two polarized surfaces are distinct depending on the ferroelectric

**FIGURE 4** The effect of FE polarization in 2D ferroelectrics on the bandstructures of nonpolar 2D materials. (a) The graphene/In$_2$Se$_3$ heterostructures with polarization up ($P^+$) and down ($P^-$); the bands derived from the In$_2$Se$_3$ layer and the graphene layer are highlighted in red and yellow, respectively. The green circles indicate the Dirac points of the graphene layer; (b) charge density difference; charge accumulation and depletion indicated by yellow and cyan with isosurfaces value 0.00015e/A$^3$ of sandwiched In$_2$Se$_3$–graphene–In$_2$Se$_3$. (c) Band alignments of monolayer InTe, monolayer In$_2$Se$_3$ and InTe/In$_2$Se$_3$ heterostructures. The horizontal dark dashed lines are the Fermi level. The vacuum level is taken as reference. The insets are side view of the InTe/In$_2$Se$_3$ heterostructures with the direction of ferroelectric up and down. (d) Schematic diagram of the proposed p-n junction based on graphene/In$_2$Se$_3$–graphene. The Electronic band structures of MnCl$_3$/P$^+$–CuInP$_2$S$_6$ (e) and MnCl$_3$/P$^-$–CuInP$_2$S$_6$ (f) heterostructures with respect to Fermi level. Red and green lines represent the contributions from spin-up ($S^+$) and spin-down ($S^-$) channels of MnCl$_3$, while blue lines denote the contributions from CuInP$_2$S$_6$. The insets are MnCl$_3$/P–CuInP$_2$S$_6$ heterostructures with FE polarization up and down in CuInP$_2$S$_6$. ((a) Reprinted with permission from Ref. [36]. Copyright 2017 Nature Publishing Group; (b) Ref. [78]. Copyright 2020 Elsevier; (c) Ref. [79]. Copyright 2019 IOP Publishing Ltd.; (d) Ref. [80]. Copyright 2020 The Royal Society of Chemistry; (e,f) Ref. [74]. Copyright 2020 The Royal Society of Chemistry)
polarization, see Figure 4b. These findings not only explicitly reveal the physical mechanism of electronic modulation by ferroelectric switch, but also provide a feasible method to control the Schottky barrier. Besides metallic graphene, the electronic structures of semiconducting WSe₂ can be also modulated by FE In₅Se₃ layer; the induced band shift leads to a significant band gap reduction and staggered band alignment when electric dipole orientation is reversed. For example, in the CrI₃/Sc₂CO₃ heterostructures, 2H-MoS₂/In₅Se₃ and InTe/In₅Se₃ heterostructure, the band alignment is closely dependent on the polarization of 2D ferroelectrics, due to the different responses to the two contacted polar surfaces, see Figure 4c. As a result, the electron transfer and associated electronic properties of the heterostructures will be modulated by the ferroelectric switch. The ferroelectric controlled electronic properties and semiconductor/ferroelectrics have been used for the design of electronics device. Based on atomic heterostructure composed by semiconducting MoS₂ and isolating ferroelectric CuInP₂S₆, Si et al. fabricated a ferroelectric field-effect transistor as a stable nonvolatile memory by taking the advantage of semiconductor/insulator interface effect. As indicated above, interlayer electron transfer between different layers in heterostructures plays an important role to determine the electronic properties of the system, it is interesting to note that self-doping in the homogeneous junction can also modulate the interlayer charge distribution and electronic properties. For instance, Peng et al. revealed the self-doping effects in triple-layer InₓX₃ (X = S, Se) because of the naturally intrinsic dipole induced by their asymmetric structures, and therefore intriguing atomically thin p-n junctions was proposed. With sandwiched graphene as the electrodes, the prototype self-doped p-n junctions can be built and tested as shown in Figure 4d. For the ferroelectrics, the external electric field has to be applied to switch FE polarization and then modulate the electronic properties. Alternatively, Wu et al. proposed another feasible approach to achieve the similar goal in phosphorene analogues and atomically thin bismuth oxychalcogenides, the corresponding electronic properties can be tuned via the mechanical methods due to the coexistence of ferroelectricity and ferroelasticity, the ferroelastic switch will lead to the FE reversal.

The mechanism in Figure 1b represents a universal approach to control the electronic properties of contacted materials with reversible polarization, which was not only verified by the research progress, but also provides a guideline for designing the material system with desired performance. However, it should be noticed that, since both the electronic and magnetic properties in ferromagnets/ferroelectrics heterostructures are related with band states near the Fermi level, they can be modulated simultaneously by ferroelectric switch. For example, in MnCl₃/CuInP₂S₆ heterostructure, not only the magnetic states mentioned above can be changed through FE dipole effect of CuInP₂S₆, but also the electronic structures can be well controlled. MnCl₃ preserves the half-metal characteristic when the polarization in CuInP₂S₆ is upwards, but semiconducting upon contacting with CuInP₂S₆ in the polarization down state, as seen Figure 4e,f.

### 3.3 Photocatalytic water-splitting based on 2D ferroelectrics

As indicated above, the intrinsic polarization of 2D material is originated from the positive and negative charged surfaces, which offer a platform with distinct chemical and reaction activities. As an evidence, it has been shown that the out-of-plane polarization of Janus transition metal dichalcogenides (TMDs) can tune/improve the photocatalytic performance for water splitting due to the asymmetric structure of the two surfaces, the water splitting reaction is different in S or Se side due to the presence of intrinsic polarization. However, from the viewpoint of controllable activities of the chemical reaction, the 2D ferroelectrics with reversible electric dipole possesses better potential owing to the switched FE polarization. In the following, we will demonstrate the point from photocatalytic water splitting of 2D ferroelectrics.

Photocatalysis as a “green” approach can convert solar energy into chemical energy without environmental pollutions. Especially the photocatalytic water splitting process can split H₂O into the value-added chemical fuels, hydrogen and oxygen, which is a promising technology and attracted significant interests. 2D materials emerge to be good candidates that exhibit giant potential due to their large surface-volume ratio, numerous catalytic reactive sites and the proper optical adsorption. Particularly, by taking advantages of the permanent internal polarization in 2D FE materials, the unique photochemical properties can be expected and possess three advantages: (a) the photogenerated electrons and holes can be efficiently separated by the FE dipole, where the valence band maximum (VBM) and conduction band minimum (CBM) tend to distribute on different side. (b) The recombination possibility of photoexcited carriers can be significantly reduced due to the presence of internal dipole, which will obviously increase the efficiency of photocatalytic reaction. (c) The chemical activity can be modulated due to the polarization dependent electron
transfer between reactant and catalysts (see Figure 1b). These unique behaviors have been demonstrated in previous research works and collected in Khan’s review.

The advantages of photocatalytic water-splitting in 2D ferroelectrics have been revealed in recent several works; For example, it was predicted that 2D FE M$_2$X$_3$ (M = Al, Ga, In; X = S, Se, Te) family exhibits excellent optical absorption under visible light spectrum due to the suitable band structures. The charge carriers (electrons and holes) can be well separated by the intrinsic polarization along out-of-plane direction. In addition, the high carrier mobility helps to promote the photocatalytic reaction and increase the catalytic efficiency. Therefore, 2D M$_2$X$_3$ family was revealed as the promising photocatalysts for overall water splitting, due to the visible-light region and the separation of charge carriers. The research findings were further confirmed by another independent work, Zhao et al. also found that ferroelectric M$_2$X$_3$ family has the good optical absorption within visible-light region (In$_2$Te$_3$ to infrared-light) as seen in Figure 5a and the special band characteristics of polarized semiconductors with indirect band gaps in In$_2$X$_3$ (X = S, Se, and Te) monolayers, as shown in Figure 5b. These wide optical adsorption spectrums make them as active photocatalysts in the near-infrared light region. The intrinsic polarization of α-In$_2$X$_3$ not only move electrons and holes to opposite directions, but also lead to the relative weak exciton effects, thus reducing the carrier recombination and promoting the water splitting efficiency. It should be especially noted that in the process of photocatalytic water splitting, the protons and hydroxyl ions will gradually accumulate on the two respective surfaces, resulting to the decline or even vanish of the intrinsic ferroelectricity. Accordingly, the photocatalytic water splitting will not be boosted by the built-in electric field. Fortunately, the intrinsic ferroelectricity and catalytic activities can be fully recovered by applying external electric

**FIGURE 5** The applications of 2D ferroelectric In$_2$Se$_3$ and AgBiP$_2$Se$_6$ monolayers in photocatalytic water-splitting. (a) Imagery parts of dielectric functions and optical absorption (α) of In$_2$X$_3$ monolayers based on G$_0$W$_0$-BSE level. The white dashed vertical lines represent the optical absorption peaks of In$_2$X$_3$ monolayers. (b) Band alignments and partial charge density of VBM and CBM for In$_2$S$_3$, In$_2$Se$_3$, and In$_2$Te$_3$ monoalyers, respectively. (c) Band-edge positions with respect to water redox potential for paraelectric (upper panel) and ferroelectric (lower panel) AgBiP$_2$Se$_6$ monolayers based on the HSE06 functional. The blue and red lines represent the thermodynamic oxidation potential ($\phi^\circ$) and reduction potential ($\phi^\circ$), respectively. Blue and purplish-red bars represent the positions of the CBM (blue) and VBM (red), respectively. The value of the isosurface is set as 0.006 e/Å$^3$. ((a,b) Reprinted with permission from Ref. [94]. Copyright 2018 Elsevier; (c) Ref. [95]. Copyright 2019 American Chemical Society)
field, which reverse FE polarization in M₂X₃ and remove the protons and hydroxyl ions on the surfaces. The distinct feature and advantages in ferroelectrics can distinguish Janus and other 2D structures, making M₂X₃ family unique and potential for the application in photocatalytic water splitting.

Apart from 2D M₂X₃, ABP₂X₆ (A and B can be transition metals or rare earths atoms, and X represents the atoms from the sixth main group) is another 2D ferroelectric candidate for photocatalytic water splitting that has been discovered from simulations and experiments. Xu et al. 38 found that AgBiP₂Se₆ monolayer is an atomically thin ferroelectric semiconductor with out-of-plane polarization, and pointed out that this material is a possible candidate as a photocatalyst for water-splitting due to the visible-light adsorption and suitable band edge alignments. However, the prediction is quite rough since the simple optical calculations and band alignments cannot provide a convinced evidence to judge if it is really suitable for water splitting. Recently, Ju et al. 35 systemically confirmed the potential of AgBiP₂Se₆ in photocatalytic water splitting from the prospects of optical adsorption, band alignment, charge separation, reaction barriers and photoinduced corrosion, and investigated the inner effects of FE and paraelectric (PE) phases on the photocatalytic water splitting, and found that the solar-to-energy solar conversion efficiency can increase from 6.66% at PE phase to 10.04% at FE phase due to higher carrier utilization. For the PE phase, both VBM and CBM distribute uniformly over both up and bottom surfaces, presenting the same reactivities of the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) at both surfaces. In contrast, for the FE phase, the VBM and CBM are separated to mainly distribute at the top and bottom surfaces, respectively (see Figure 5c), which would effectively decrease the carrier recombination and increase the photocatalytic efficiency. By analysis the ability of the photocatalytic water splitting, it was concluded that PE phase has a stronger reducibility, while the FE phase possesses a higher oxidizability. Therefore, the switched FE and PE phases in AgBiP₂Se₆ monolayer provide an available approach to tune the reactivities. Besides, in the heterostructures such as α-Ga₃S₅/Ga₃S₇, 96 it was shown that the band edges can be shifted and thus are suitable for water splitting by switching electric dipoles of α-Ga₃S₅.

These results provide convincing proofs that 2D ferroelectric materials with vertical intrinsic ferroelectricity, suitable band edges and strong visible-light adsorption can be potential candidates for the application in efficient photocatalysts to achieve overall water splitting.

### 3.4 | Reversible gas capture based on 2D ferroelectrics

Gas sensors and traps with a controlled adsorption manner, which can detect and remove harmful gases in the air, are regarded as advanced technologies to solve global air pollution and greenhouse effects. 97 2D materials are the promising candidates to capture the harmful gas due to the large volume-surface ratio and active surface. 96 However, the controllability and the gas desorption are still the open questions. Previous investigations show that the adsorption and desorption of the gas molecules can be effectively modulated by external electric field since the electron transfer between adsorbs and sensing materials which determine the interaction strength is tunable. The typical examples include, but not limited to enhanced gas sensitivity of NO, NO₂ on MoS₂, 99 hydrogen adsorption (for hydrogen storage between adsorbents and sensing materials which determine the interaction strength is tunable. The typical examples include, but not limited to enhanced gas sensitivity of NO, NO₂ on MoS₂, 99 hydrogen adsorption (for hydrogen storage application) on top of BN by vertically applied electric field. 100 However, to accurately apply an electric field in the nanoscale is quite challenge, it is also an energy costing process. Alternatively, the intrinsic and reversible polarization in 2D FE materials would be promising used to adsorb and desorb the toxic gases. In fact, it has been shown that the polarization of asymmetric materials can enhance or weaken the gas adsorption. For instance, Jin et al. found the distinct adsorption behaviors on the S/Se sides of Janus MoSSe monolayer, 101 where the electron transfer and adsorption energies can be modulated by the polarization. However, the built-in electric field in Janus structure cannot be reversed to achieve the process of recycling capture and release. To overcome the disadvantage, Tang et al. 102 checked the gas adsorption on ferroelectric surfaces, and found the distinct gas adsorption behaviors of NH₃, NO, and NO₂ on FE surfaces of In₂Se₃ monolayer, where the adsorption strength, electron transfer and electronic variation strongly depend on the polarization directions as shown in Figure 6a. The underlying mechanism can be attributed to the different electron transfer originated from the polarization modulated band alignment between adsorbents and ferroelectric surface, as seen in Figure 6b. Taken toxic NH₃ as an example, the adsorption energy on downwards polarized surface is about 0.5 eV (chemical adsorption), but smaller than 0.2 eV (physical adsorption) on opposite surface. Since the polarization direction of In₂Se₃ as a ferroelectrics is reversible after overcoming a reasonable energy barrier, NH₃ can be adsorbed/desorbed, namely the reversible gas capture/release can be controlled by the switched FE orientations in In₂Se₃. The work revealed the potential of ferroelectrics used as the promising candidate for reversible gas sensing or capture.
Overall, based on 2D ferroelectrics, it was found that the reversible polarization which is equivalent to the switchable external field can be used to achieve controllable physics and chemical reactions. Four examples are presented, including ferroelectric controlled magnetism, polarization dependent electronic behaviors, photocatalytic water splitting and gas adsorption/release. These interesting works provide convincing proofs that 2D ferroelectrics are promising candidates to explore intriguing controllable applications with high performance by utilizing the unique FE feature.

We also noticed that the exploration of 2D layered ferroelectrics for possible physical and chemical applications is quite rare, which can be contributed to very limited choice of ferroelectric materials. Until now, the synthesized true 2D ferroelectrics is scare despite of numerous theoretical predicted candidates, mainly including monolayer SnTe, In$_2$Se$_3$ and CIPS family, the extended studies are therefore significantly limited. Even so, based on the fact that electric field and associated electron doping have been widely demonstrated to be effective and universal approaches to modulate the physical properties of nanomaterials and chemical reactions, it is expected that the reversible polarization of 2D ferroelectrics will be generalized and used to achieve the similar goals, but with higher controllability and much lower energy costing as a nonvolatile process. Inspired by findings of nanomaterials under the electric field, except the reviewed progresses as above, lots of possible research directions of ferroelectric tuned physical and chemical properties can be expected. For example, the band gap modulation and controllable topological state via polarization switch. It is known that the horizontal electric field in nanoribbons can induce the semiconducting to metallic transition due to strong Stark effects, like BN and MoS$_2$ ribbons. Similar phenomena can be expected in ferroelectric ribbons. Taken SnTe as an example, the in-plane ferroelectricity can act as a horizontal electric field to reduce the band gaps when it is cut as a nanoribbon, the paraelectric-ferroelectric transition will be the trigger to turn on/off the electric field. On the other hand, topological-trivial transition was found in Sb$_2$Te$_3$ films under electric field. When suitable ferroelectric substrate is chosen, Rashba effect, spin texture and the topological nontrivial-trivial transition are expected to be controlled by the switchable polarization when the topological insulator is placed on the top. At chemical side, similar to the water splitting and reversible gas adsorption, ferroelectricity of 2D materials should be easily applied for reversible hydrogen storage controlled by polarization switch as inspired by electric-field enhanced hydrogen storage on BN, reversible CO$_2$ capture; and controllable catalysis like CO$_2$ reduction reaction and N$_2$ fixation. For all these promising chemical reactions, the interlayer electron transfers that can be controlled by switchable polarization of ferroelectrics as depicted in Figure 1b will play a critical role and directly determine the chemical activity and catalytic performance.

As reviewed above, the researches regarding the physical and chemical applications of 2D ferroelectrics are quite limited until now due to limited choices of experimentally confirmed ferroelectric materials in 2D size, however the academic and application potentials along the directions are huge. The feature of reversible polarization in 2D ferroelectric can be not only used for the electronics and spintronics, but also is promising for energy conversion and storage.
is expected that the present review can inspire more research interests from board academic communities to study the controllable physics and chemical reactions and explore their application in nanodevices, meanwhile attract the experimental demonstrations.

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AUTHOR CONTRIBUTIONS
Jing Shang: Data curation; writing-original draft. Xiao Tang: Writing-original draft. Liangzhi Kou: Conceptualization; supervision; writing-review and editing.

ORCID
Jing Shang https://orcid.org/0000-0003-0195-4415
Xiao Tang https://orcid.org/0000-0003-3618-3817
Liangzhi Kou https://orcid.org/0000-0002-3978-117X

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