The rise of 2D dielectrics/ferroelectrics

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ABSTRACT

Ultrathin films with high-k dielectric/ferroelectric properties form the basis of modern electronics. With further miniaturization of electronic devices, conventional materials are expected to experience a challenge because of their critical thickness, where the dielectric/ferroelectric responses are unstable or even disappeared if the film thickness is reduced to the nanometer scale or below a two-dimensional (2D) limit. Owing to the benefit of preparing stable atomically thin film, 2D materials present tantalizing prospects for scaling high-k dielectric/ferroelectric technologies down to the actual atomic scale. Here, we review recent progress in 2D dielectrics/ferroelectrics and related device applications.

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I. INTRODUCTION

Ultrathin films with high-k dielectric/ferroelectric properties form the basis of modern electronics such as memories, field-effect transistors (FETs), capacitors, and sensors. For further miniaturization of electronic devices, the exploration of high-k dielectric/ferroelectric thin films with nanometer thicknesses are strongly needed. However, the so-called size effects present a formidable challenge (Fig. 1). Previous studies on high-k dielectric thin films have consistently observed that the dielectric constant ($\varepsilon_r$) is significantly reduced as the film thickness decreases to 50 nm. For example, perovskite thin films (such as BaTiO$_3$ and PbTiO$_3$) often yield reduced $\varepsilon_r$ values that are 2–3 orders of magnitude smaller than the bulk values. This problem is even more pronounced in ferroelectric thin films. In conventional ferroelectrics (such as BaTiO$_3$, PbTiO$_3$, SrBi$_2$Ta$_2$O$_9$, and Bi$_4$Ti$_3$O$_12$), the electric polarization reduces or even disappears when the film thickness reaches the deep nanoscale regime or a critical thickness. This size effect is often discussed in terms of intrinsic size or depolarizing field effects arising in ultrathin dielectrics/ferroelectrics. Despite intensive studies, the underlying physics behind the critical thickness and size effects is still debatable because competing effects such as the imperfect charge screening and dead-layer effects (the local chemical environment, defects/strains at the interface, and electrical boundary conditions) cause complicated behaviors in measured properties.

With recent advances in thin-film technologies and nanoscale characterization methods, the understanding of nanoscale ferroelectricity has continued to evolve from early studies indicating the complete suppression of ferroelectricity to recent reports demonstrating the enhancement in local ferroelectricity by strain engineering or even the possible absence of a critical thickness. Current nanoscale characterization techniques, including scanning probe microscopy (SPM) and transmission electron microscopy (TEM), have allowed the detection of ferroelectricity in perovskite films down to a thickness of a few unit cells; ferroelectricity could be retained down to 1.2–4 nm (PbTiO$_3$), 1.6–3 nm (BaTiO$_3$), and ~3 nm (BaFeO$_3$). State-of-the-art characterization using high-resolution TEM indicated a possible absence of a critical thickness in ultrathin ferroelectric films; in the PbZr$_{0.2}$Ta$_{0.8}$O$_3$ case, the residual polarization was observed even at 0.8 nm. The integration of high-k dielectrics/ferroelectrics into electronics, this size-effect issue becomes increasingly important since intrinsic size effects may limit the device performance.

Owing to their atomic-scale thickness, 2D nanosheets present a tantalizing prospect for scaling high-k dielectric/ferroelectric technologies down to the actual atomic scale. Since the breakthrough development of graphene, the variety of 2D nanosheets...
has been greatly expanded to inorganic materials including chalcogenides,43,44 oxides,34–37 MXenes,38,39 and black phosphorus.40–42 These inorganic nanosheets are very rich in structural diversity and electronic properties such as superconductivity,42 valley polarization,43 and quantum magnetism.44 Thus, 2D inorganic nanosheets offer a novel platform for exploring emerging phenomena that cannot be realized in graphene. Despite significant advances in graphenelike 2D nanosheets, it remains a challenge to explore their high-k dielectric/ferroelectric counterparts, which have great potential in new 2D electronics.6 Most 2D nanosheets synthesized so far are conducting or semiconducting with a rather small bandgap28 (Fig. 2), precluding their use in high-k dielectrics/ferroelectrics.

2D nanosheets with high polarizability or noncentrosymmetric structures have great potentials for high-k dielectrics/ferroelectrics. In particular, 2D oxides possess a wide bandgap (3–4 eV),45 which is favorable for realizing high-k dielectrics with a highly insulating nature (Fig. 2). In fact, $\delta^d$ transition metal oxides (with Ti$^{4+}$, Nb$^{5+}$, Ta$^{5+}$, and W$^{6+}$) can be tailored to yield high-k values ($\varepsilon_r > 100$).29 To date, two kinds of high-k nanosheets have been developed with dielectric constant values above 100. One kind comprises simple oxides46,47 with a modest permittivity ($\varepsilon_r \approx 100$), e.g., $\text{Ti}_1\delta\text{O}_2$ and $\text{Nb}_3\text{O}_8$; the other comprises perovskites48,49 with higher permittivity ($\varepsilon_r > 200$). Noncentrosymmetric materials are an important target for 2D ferroelectrics because of spontaneous symmetry breaking and its associated ferroelectric polarization. Recently, a range of 2D nanosheets and/or van der Waals (vdW) materials have been theoretically predicted or experimentally confirmed as ferroelectrics,50–52 including transition metal dichalcogenides (e.g., MoS$_2$, MoTe$_2$, and WTe$_2$), group IV monochalcogenides (e.g., SnS, SnSe, GeS, and GeSe), group III–V compounds (e.g., AlSb, GaP, GaAs, and InSb), MXenes ($\text{Sc}_2\text{C}_2\text{O}_2$), CuInP$_2$S$_6$, and perovskite oxides ($\text{Ca}_3\text{Na}_2\text{Nb}_5\text{O}_{16}$).

From this perspective, we review recent progress in 2D dielectrics/ferroelectrics. We begin with the introduction of 2D dielectrics/ferroelectrics. We also present a perspective on
the advantages offered by this class of materials for future electronics.

II. 2D DIELECTRICS

2D oxide nanosheets may be the perfect solution as a new era unfolds in 2D dielectrics. A variety of oxide nanosheets have been synthesized by delaminating layered oxides into their single sheets.\cite{32,46} Most oxide nanosheets synthesized so far are transition metal oxides comprising \(d^x\) cations (Ti\(^{4+}\), Nb\(^{5+}\), Ta\(^{5+}\), and W\(^{6+}\)). Such \(d^x\) oxide nanosheets are wide bandgap semiconductors and can thus be utilized as high-\(k\) dielectrics.

We investigated such possibilities in \(d^x\) oxide nanosheets. Table I summarizes the experimentally confirmed 2D dielectrics. The optimal property was observed in Ti\(\text{O}_2\) [Fig. 3(b)]. The optimal property was realized in simple oxide dielectrics in the ultrathin region (<30 nm).

Another family of 2D dielectrics is the perovskite nanosheets.\cite{55} Parent layered perovskites form the basis of interesting classes of high-\(k\) dielectric/ferroelectric materials including Dion-Jacobson \(A'\) [\(A_{m-1}B_mO_{3m+1}\)], Ruddlesden-Popper \(A'\) [\(A_{m-1}B_mO_{3m+1}\)], and Aurivillius [\(Bi_2O_2][A_{m-1}B_mO_{3m+1}\] \(A' = \) proton, alkali metals, and alkali earth metals, for example; \(A = \) lanthanides and Bi; \(B = \) Ti, Nb, and Ta; and \(m = \) thickness of perovskite slabs)]. These layered perovskites have very diverse structures and physical properties depending on the \(A\) and \(B\) cations as well as the number of ABO\(_3\) type perovskite layers \((m)\). They consist of perovskitelike layers incorporated with cations or Bi\(_2\)O\(_3\) layers in the interlayer space. Due to their rich chemical reactivity in the interlayer spaces, these compounds have been investigated as important targets for ion-exchange reactions and exfoliated nanosheets. The exfoliation of layered perovskites has been reported for Dion-Jacobson phases \cite{48,71} [\(LaNb_2O_7\), \(Ca_3Sr_2(Ti,Ta)_3Ta_2O_{11}\), \(Ba_2Ta_2O_7\), \(Ca_2Ta_2O_{11+x}\), \(Ca_2Ta_2O_{11−x}\), \(Ca_2Nb_{3m−3}O_{3m+1}\) \(m = 4−6\), \(CaLaNb_2TiO_{10}\), and \(La_3Ti_2NbO_{10}\)] and for others with Ruddlesden-Popper phases \cite{56,65} \([Eu_{0.56}Ta_2O_7\), \(SrLaTi_2Ta_2O_{10}\), and \(Ca_2Ta_2TiO_{15}\)] and Aurivillius \([Bi_2WO_6, SrBi_2Ta_2O_9, Bi_3(TaTaO_3)\)] phases.\cite{68} These nanosheets consist of only a few octahedral units (TiO\(_6\), NbO\(_6\), or TaO\(_6\)), a key building block for high-\(k\) dielectrics/ferroelectrics in perovskites. Perovskite nanosheets can thus be viewed as an ideal basis for high-\(k\) dielectric/ferroelectric materials with a critical thickness.

\(Ca_2Nb_{3m−3}O_{3m+1}\) nanosheets have been extensively investigated as high-\(k\) dielectrics.\cite{68,69} Layer-by-layer assembly of \(Ca_2Nb_{3m−3}O_{3m+1}\) nanosheets enables engineering of dielectric responses and breakdown voltages to obtain miniaturized capacitors with improved performance. Multilayer stacked nanosheet films exhibited a stable dielectric response (\(\varepsilon_r ≈ 210\) up to 10 GHz. Moreover, the nanosheet films realized a high capacitance density (~20 \(\mu F/cm^2\)),

### Table I. Summary of the experimentally confirmed 2D dielectrics.

| 2D materials | \(\varepsilon_r\) | \(\tau\) (ppm/K) | \(J\) (A/cm\(^2\)) at +1 V | Breakdown (MV/cm) | References |
|--------------|------------------|----------------|------------------|------------------|-----------|
| Ti\(\text{O}_2\) | 125 | +106 | \(3 \times 10^{-8}\) | 3.8 | 46 and 47 |
| Ti\(\text{O}_2\) | 90 | -12 | \(9 \times 10^{-9}\) | 3.4 | 47 |
| Ti\(\text{O}_2\) | 155 | -12 | \(9 \times 10^{-9}\) | 3.4 | 47 |
| Ti\(\text{O}_2\) | 320 | -324 | \(2 \times 10^{-8}\) | 3.4 | 47 |
| Ti\(\text{O}_2\) | 300 | +5 | \(10^{-7}\) | 3.4 | 47 |
| Nb\(\text{O}_2\) | 80 | -876 | \(2 \times 10^{-6}\) | 3.0 | 47 |
| La\(0.56\)Ta\(0.44\)O\(_2\) | 45 | \(-10^{-6}\) | 3.1 | 68 |
| La\(0.80\)Na\(0.20\)Ta\(0.44\)O\(_2\) | 68 | \(-10^{-6}\) | 3.6 | 68 |
| La\(0.56\)Ta\(0.44\)O\(_2\) | 12 | \(-10^{-7}\) | 3.8 | 68 |
| Ca\(_2\)Nb\(_3\)O\(_{10}\) | 210 | -50 | \(3 \times 10^{-8}\) | 3.4–6.0 | 48 and 49 |
| Ca\(_2\)Na\(_2\)Nb\(_3\)O\(_{13}\) | 320 | \(-10^{-9}\) | 3.3 | 49 |
| Ca\(_2\)Na\(_2\)Nb\(_3\)O\(_{16}\) | 390 | \(-10^{-8}\) | 3.2 | 49 |
| Ca\(_2\)Na\(_2\)Nb\(_3\)O\(_{19}\) | 470 | \(-10^{-7}\) | 3.0 | 49 |
| Sr\(_2\)Nb\(_3\)O\(_{10}\) | 240 | \(+60\) | \(3 \times 10^{-8}\) | 3.2 | 68 |
| Ca\(_2\)Ta\(_3\)O\(_{10}\) | 145 | \(-150\) | \(6 \times 10^{-9}\) | 3.6 | 68 |
| Sr\(_2\)Ta\(_3\)O\(_{10}\) | 175 | \(+80\) | \(7 \times 10^{-9}\) | 3.5 | 68 |
insulating properties (<10⁻⁷ A/cm²), a strong breakdown field (~6 MV/cm), and a robust thermal stability up to 250 °C. These excellent dielectric properties of Ca₂Nb₃O₁₀ nanosheets offer a new solution for capacitor dielectrics.

Recent research on perovskite nanosheets is directed toward material design by tailoring the composition and structure and improving their high-κ performance. In bulk perovskites, a variety of strategies have been utilized for designing new high-κ dielectrics, either by doping more polarizable ions into the lattice or tuning the structural distortion. Such a material design has been achieved in perovskite nanosheets. In (Ca₁₋ₓSrₓ)₂(Nb₁₋ₓTaₓ)₃O₁₀ nanosheets, for example, A-site modification with Sr²⁺ ions increased the εᵣ value, whereas B-site modification with Ta⁵⁺ ions improved the insulating characteristics with enlarged bandgap and breakdown voltage.⁶⁸ Even elegant engineering was found in 2D homologous perovskite nanosheets (Ca₂Naₘ₋₃NbₘO₃ₘ₊₁; m = 3–6) (Fig. 4).⁴⁹

![FIG. 3](image)

**FIG. 3.** (a) Structure of Ti-based high-κ dielectric nanosheets (Ti₀.₈₇O₂, Ti₂NbO₇, TiNbO₅). (b) Composition dependence of εᵣ in multilayer films of Ti₀.₈₇O₂, Ti₂NbO₇, Ti₂NbO₇, TiNbO₅, and Nb₃O₈. Reproduced with permission from Osada et al., Adv. Funct. Mater. 21, 3482 (2011). Copyright 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

![FIG. 4](image)

**FIG. 4.** Structures and AFM images of Ca₂Naₘ₋₃NbₘO₃ₘ₊₁ nanosheets. The thicknesses were approximately 1.9, 2.3, 2.7, and 3.2 nm for m = 3, 4, 5, and 6, respectively. The increment of ~0.4 nm corresponds to the thickness of one NbO₆ octahedron, which is consistent with the homologous structural aspect of layered perovskites. Reproduced with permission from Li et al., J. Am. Chem. Soc. 139, 10868 (2017). Copyright 2017 American Chemical Society.
In Ca$_2$Na$_{m-3}$Nb$_m$O$_{3m+1}$, the thickness of perovskite layers can be incrementally controlled by changing $m$, and such a unit-cell level engineering enhanced the high-$k$ dielectric response. The $m = 6$ member (Ca$_2$Na$_4$Nb$_6$O$_{19}$) attained a high dielectric constant of $\sim 470$, which is the highest among all known perovskite dielectrics in the ultrathin region ($<10$ nm) (Fig. 5). Importantly, the high $\varepsilon_r$ values of perovskite nanosheets persist even in the $<10$ nm region, which is in contrast to the size-induced degradation observed in typical perovskite dielectrics. The unique features of 2D nanosheets make them important and fascinating research targets for ultrascaled high-density capacitors and new energy storage devices.

### III. 2D FERROELECTRICS

The existence of 2D ferroelectricity was theoretically predicted long ago. However, there have been a limited number of reports on 2D ferroelectricity until recently since realistic materials suffer from the fundamental constraint of size effects. In addition, the dead-layer effects due to interfacial strain and local chemical environment can deteriorate ferroelectricity in ultrathin films. In contrast, 2D layered or vdW materials have strong in-plane bonds but weak coupling between the layers, and thus exfoliated 2D nanosheets could provide a pathway to realize 2D ferroelectricity while eliminating the so-called “dead-layer” issues. In recent years, several 2D ferroelectric candidates have been theoretically predicted and experimentally verified (Fig. 6).

Early studies were devoted to theoretical investigations. In principle, 2D nanosheets allow the exploration of ferroelectricity in both the in-plane and out-of-plane directions. In 2014, intrinsic 2D ferroelectricity with out-of-plane (vertical) polarizations was theoretically predicted in 1T MoS$_2$ monolayers. Using the Landau theoretical analysis with first-principles calculations, Shirodkar and Waghmare demonstrated spontaneous symmetry breaking even in 1T MoS$_2$ monolayers. Even in the metallic state, 1T MoS$_2$ induced both bandgap opening and robust ferroelectricity with ordering of electric dipoles perpendicular to its plane. In 2015, Di Sante et al. also predicted out-of-plane ferroelectricity in 2D AB binary monolayers (e.g., GeSe and AlSb) with trigonal symmetry, where the A and B atoms belonged to groups IV–V. In these compounds, the dipoles arise from the buckled structure, where the A and B ions are located on the sites of a bipartite corrugated honeycomb lattice. Similar out-of-plane ferroelectricity existed in many other 2D materials such as In$_2$Se$_3$, III–V compounds, phosphorene oxides, CrN, CrB$_2$, and MXenes (Sc$_2$CO$_3$). A branch of 2D families based on In$_2$Se$_3$ and other III–V1 vdW materials has exhibited room-temperature ferroelectricity with reversible spontaneous electric polarization in both out-of-plane and in-plane orientations. Interestingly, multiferroic properties were also found in 2D CrN and CrB$_2$. 2D CrN is found to be a 2D hyperferroelectric metal and ferromagnetic-ferroelectric multiferroic with a high critical temperature ($T_c$), while CrB$_2$ is a 2D asymmetric multiferroic suitable for realizing electric field control of magnetism. Recent first-principles calculations also predicted the possible existence of ferroelectricity in the AB stacking graphitic bilayers of BN, AlN, ZnO, etc.

The first experimental realization for 2D ferroelectricity was in layered CuInP$_2$S$_6$. In 2015, Belianinov et al. reported the observation of room-temperature out-of-plane ferroelectricity in bulk CuInP$_2$S$_6$ for film thicknesses greater than 100 nm. This finding also inspired further exploration of 2D ferroelectrics in the atomically thin form. In 2016, Liu et al. confirmed the out-of-plane polarization in few-layer CuInP$_2$S$_6$. Using piezoresponse force microscopy (PFM) and second-harmonic generation (SHG), they observed the ferroelectric phase transition at 320 K. In 2016, Chang et al. experimentally reported the first 2D ferroelectric with single atomic layer thickness in monolayer SnTe. They studied the monolayer SnTe with a distorted lattice at cryogenic temperature and verified the in-plane ferroelectricity with spontaneous domains and electric polarization. Recently, intrinsic room-temperature 2D ferroelectricity with a thickness down to the 2D limit was also observed in 3 nm $\alpha$-In$_2$Se$_3$ (3 layers), 1.4 nm WTe$_2$ (2 layers), 1.2 nm $\alpha$-In$_2$Se$_3$ (1–2 layers), and 0.6 nm 1T MoTe$_2$ (1 layer). These findings open up a route toward 2D ferroelectricity with a thickness down to the 2D limit.

The existence of 2D ferroelectricity was also confirmed in perovskites. So far, perovskite oxides (such as BaTiO$_3$, PbTiO$_3$, etc.)
SrBi$_2$Ta$_2$O$_9$ and Bi$_4$Ti$_3$O$_{12}$) have been a central target for ferroelectricity in a bulk 3D system. Typically, $d^0$ cations (Ti$^{4+}$, Nb$^{5+}$, and Ta$^{5+}$) in BO$_6$ octahedral units exhibit an asymmetric second-order Jahn-Teller distortion, causing a spontaneous polarization. Recently, we investigated ferroelectric properties in 2D homologous perovskite nanosheets (Ca$_2$Na$_m$-3Nb$_m$O$_{3m+1}$; $m = 3$–6) by using PFM and density functional theory (DFT) calculations (Fig. 7). From Berry-phase calculations and soft-mode spectroscopy, we found that perovskite layer stacking ($m$) promoted local ferroelectric instability and that large distortions were observed in Ca$_2$Na$_2$Nb$_5$O$_{16}$, where off-center displacements of Nb$^{5+}$ ions would be expected due to cooperative NbO$_6$ octahedral tilting with disordering at the A site. From PFM, we confirmed room-temperature out-of-plane ferroelectricity in Ca$_2$Na$_2$Nb$_5$O$_{16}$ with a thickness of 2.7 nm. More recently, Ji et al. demonstrated the realization of monolayer freestanding ferroelectric perovskite oxides. They synthesized freestanding SrTiO$_3$ and BiFeO$_3$ ultrathin films by molecular beam epitaxy and transfer them to various substrates. Freestanding BiFeO$_3$ films exhibited giant tetragonality and polarization even in three-unit-cell thick. Although there were still limited numbers of reports on 2D ferroelectricity in perovskites, these works provide a key for a long-standing conundrum of the size effect in perovskites.

IV. APPLICATIONS OF 2D DIELECTRICS/FERROELECTRICS

The unique features of 2D dielectrics/ferroelectrics make them important and fascinating research targets for device applications (Fig. 8). An important aspect of 2D nanosheets is that various nanoarchitectures can be fabricated using LEGO-like building blocks. By applying layer-by-layer assembly, 2D nanosheets can be organized into highly organized lamellar nanostructures and superlattices. This LEGO-like construction of 2D nanosheets opens up new avenues for creating new artificial materials and fusion devices. Furthermore, owing to the benefit of preparing stable atomically thin films, 2D nanosheets present a tantalizing prospect of scaling all electronic technology down to a truly atomic scale.

For 2D dielectrics, an important target is the development of dielectric capacitors that are the largest components in current electronic devices [Fig. 8(a)]. For future capacitor devices, there is
a strong need to explore miniaturized dielectrics with increased $\varepsilon_r$, decreased tan$\delta$, and reduced leakage current. It is also crucial that the capacitor components exhibit constant fidelity over wide ranges of operating conditions such as frequency and temperature (preferably up to 150°C). 2D oxide nanosheets can satisfy these demands. Ti- or Nb-based oxide nanosheets realized excellent high-$k$ performance ($\varepsilon_r=100–470$) even at a thickness of only a few nanometers. Because the areal capacitance ($C$) is governed by $C=\varepsilon_0\varepsilon_r/d$, where $\varepsilon_0$ and $d$ are the vacuum permittivity and thickness, respectively, 2D oxide nanosheets provide a large capacitance density based on high $\varepsilon_r$ values and molecular thicknesses. In this context, we developed high-performance all-nanosheet capacitors by sandwiching alternating metallic RuO$_2$ and dielectric Ca$_2$Nb$_3$O$_{10}$ nanosheets ($\varepsilon_r=\sim210$). Manufactured all-nanosheet capacitors exceeded the performance of current multilayer ceramic condensers (MLCCs), opening a route to new capacitor and energy storage devices. This component is the smallest with a total thickness of $\sim$30 nm and exhibited a high capacitance density ($>30 \mu F/cm^2$) and good thermal stability (up to 250°C). This is just a prototype capacitor equivalent to one unit of the metal-insulator-metal structure of MLCCs, and the multilayer implementation is still challenging.

2D oxide nanosheets are a fascinating target for high-temperature applications. The development of high-temperature electronics has been a significant challenge in recent years. For example, the automotive industry requires electronic components that are operable at high temperatures (>$200^\circ$C). Most of 2D oxide nanosheets (TiO$_2$, Ti$_2$Nb$_2$O$_7$, and (Ca,Sr)$_2$Nb$_3$O$_{10}$) are paraelectric, thus yielding a very small temperature coefficient ($\tau$), in contrast to the large variation of ferroelectrics materials. Another important aspect is their thermal stability. In 2D nanosheets, the crystallization and nucleation are severely hindered even at high temperatures (>800°C). For instance, 2D oxide nanosheets (Ti$_{0.87}$O$_2$ and (Ca,Sr)$_2$Nb$_3$O$_{10}$) showed a high thermal stability up to 700°C in a monolayer film with an extremely small thickness of $\sim2$ nm. Simultaneous improvements in the dielectric constant ($\varepsilon_r$) and thermal stability are desirable for future applications, and 2D oxide nanosheets have great potential for the rational design of high-temperature capacitors and energy storage devices.

Owing to their atomically thin and flat nature, high-$k$ nanosheets may also be used as gate dielectrics. In this context, hexagonal boron nitride (h-BN) nanosheets have been highlighted for dielectric applications. Unlike graphene, h-BN nanosheets are an electrical insulator with a band gap of $\sim$5.8 eV. h-BN nanosheets also possess superb chemical and thermal stability, excellent mechanical properties, and high thermal conductivity. Due to these unique features, h-BN is suitable for insulating substrates, gate dielectric layers, and tunnel barrier layers. Now, h-BN is becoming a standard substrate for graphene and 2D vdW devices [Fig. 8(b)]. where an ultraflat nature reduces charge fluctuations and thus enhances electron/hole mobility as compared with those of SiO$_2$, which could improve the device performance.

Ferroelectric materials have been widely used for a range of technological applications, such as nonvolatile memories, FETs, sensors, and energy harvesting devices. Compared with that of conventional ferroelectrics in bulk and thin-film forms, 2D ferroelectrics have various advantages, such as high capacitance density, low voltage operation, flexibility, and bandgap tunability, along with promising applications as memories, FETs, and sensors. For memory devices, 2D nanosheets would enable high capacitance density (higher density data storage) with low voltage operation (low
FIG. 8. Applications of 2D dielectrics/ferroelectrics: (a) high-$k$ nanocapacitor fabricated from perovskite nanosheets, (b) h-BN dielectrics for vdW devices, (c) ferroelectric diode using CuInP$_2$S$_6$, (d) ferroelectric memory using SnTe, (e) nanogenerator based on WSe$_2$, (f) ferroelectric topological transistor, (g) ferroelectric topological insulator based on bismuthene, and (h) artificial multiferroic superlattice composed of ferromagnetic Ti$_{0.8}$Co$_{0.2}$O$_2$ and dielectric Ca$_2$Nb$_3$O$_{10}$ nanosheets. Reproduced with permission from Novoselov et al., Science 353, 9439 (2016). Copyright 2016 AAAS; Liu et al., Nat. Commun. 7, 12357 (2016). Copyright 2016 Springer Nature; Chang et al., Science 353, 7309 (2016). Copyright 2016 American Chemical Society; Hu et al., J. Mater. Chem. C 7, 9406 (2019). Copyright 2019 RSC; and Li et al., J. Am. Chem. Soc. 138, 7621 (2016). Copyright 2016 American Chemical Society.

energy consumption) relying on a high $\varepsilon_r$ value and atomic thickness. 2D ferroelectric nanosheets may also realize both efficient charge injection and mobility enhancement by dielectric screening, from which we can explore high-performance FETs. Such possibilities have recently been demonstrated in some vdW materials with a small bandgap, which is desirable for high mobility and high on/off ratio transistors. In bismuth oxychalcogenides (such as Bi$_2$O$_2$S, Bi$_2$O$_2$Se, and Bi$_2$O$_2$Te), for example, conducting properties can be controlled by changing their ferroelectric dipolar structure with a gate voltage, providing the possibility of dipole engineering nanodevices. 2D ferroelectric FETs can induce the metal–insulator transition and other novel electronic phases, which may enable a variety of applications, such as chemical sensors and catalytic structures. In addition to these applications, practical devices based on 2D ferroelectric were also demonstrated, including switchable ferroelectric diodes, ferroelectric semiconductor FETs, and nanogenerators [Figs. 8(c)–8(e)]. Furthermore, ferroelectric switching allows the control of asymmetry-induced properties such as spin-orbit coupling, valley degree of freedom, memristors, and anisotropic transport [Figs. 8(f) and 8(g)].

The LEGO-like construction of 2D nanosheets opens up new approaches for creating new artificial materials and fusion devices by promoting interface engineering and cooperative interactions. An interesting strategy is layering noncentrosymmetric materials in a targeted manner that lifts inversion symmetry. In current studies, the main focus has centered on the state-of-the-art layer-by-layer
V. SUMMARY

We have reviewed recent progress in high-k dielectric/ferroelectric properties in 2D materials. 2D nanosheets with high polarizability or noncentrosymmetric structures have great potential for high-k dielectrics/ferroelectrics. In particular, 2D oxides possess a wide bandgap (3–4 eV), which is favorable for realizing high-k dielectrics with a highly insulating nature. Newly developed high-k nanosheets (TiO$_2$, Ti$_2$NbO$_7$, Ca$_2$Na$_{2x-}$3Nb$_x$O$_{3y+1}$) exhibited the highest permittivity ($\varepsilon_r > 100$) ever realized in all known dielectrics in the ultrathin region (<10 nm).

The existence of 2D ferroelectricity was theoretically predicted for a long time ago. However, there were limited numbers of reports on 2D ferroelectricity until 2014 since practical materials suffer from the fundamental constraint of size effects. In recent years, a range of 2D materials has been theoretically predicted or experimentally confirmed as ferroelectrics, those including transition metal dichalcogenides, group IV or group III–V compounds, MXenes, CuInP$_2$S$_4$, and perovskite oxides. An important aspect is that 2D nanosheets could provide a pathway to realize 2D ferroelectricity while eliminating the so-called size-effect issues. Recently, intrinsic room-temperature 2D ferroelectricity was even observed in a monolayer of SnTe and 1T MoTe$_2$ with atomic-layer thickness.

The recent blossoming of high-k dielectric/ferroelectric nanosheets also provides evidence of their potential technological impact on 2D electronic devices. The addition of dielectric/ferroelectric functions to the 2D family opens up possibilities for numerous novel applications, including capacitors, sensors, actuators, nonvolatile memory devices, and various heterostructures based on 2D dielectrics/ferroelectrics. To promote such applications, we need methods for quantitative characterization of 2D dielectrics/ferroelectrics. Such chemical protocols using 2D nanosheets open new possibilities for designing polar behavior while retaining other electronic, magnetic, or optical functionalities found in the constituent materials, thus enabling new multiferroics or polar materials [Fig. 8(h)].

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