The discovery of graphene has stimulated dramatic research interest on other 2D materials including transition metal oxide (TMO) monolayers in order to realize novel functionalization and applications. Due to reduced bonding coordination and strong surface polarization, the structures of most TMOs in the monolayer limit are very different from their bulk counterparts, as well as their physical and chemical properties. In this brief review, the authors summarize recent research progress on atomically thin TMO layers. The focus is on the structural properties of the TMOs and their interaction with the substrates from the computational point of view. The authors also introduce the potential applications of the TMO 2D materials on supercapacitors, photocatalysts, batteries, and sensors.

1. Introduction

The discovery of graphene opened a door of a completely new playground of low dimensional materials.\(^1\)\(^-\)\(^3\) This atomically thin carbon layer with honeycomb lattices, which was realized by exfoliating graphite crystal at the beginning, has attracted tremendous research interest due to its exceptional physical and chemical properties.\(^4\)\(^-\)\(^6\) In order to pursue novel electronic, optical, or energy applications, extensive efforts have been made to explore other 2D materials such as h-BN,\(^7\) transition metal dichalcogenide (TMD) monolayers,\(^8\)\(^-\)\(^9\) silicene,\(^10\) germanene,\(^11\)\(^-\)\(^12\) MXenes,\(^13\) phosphorene,\(^14\)\(^-\)\(^15\) metal oxide monolayers,\(^16\)\(^-\)\(^17\) group IV–VI or I–V monochalcogenides monolayers,\(^18\)\(^-\)\(^19\) as well as recently found borophene.\(^20\)\(^-\)\(^21\) Most of the large variety of 2D materials are derived from their parent van der Waals (vdWs) crystals, thus their atomic structures are identical to the bulk counterparts with some minor lattice constant difference due to the reduced dimensionality and vanished interlayer interaction. Similarly, some 2D monolayers, of which a typical example would be silicene,\(^10\) stem from bulk materials with covalent bonds. Although their bonding may significantly change (silicene: sp\(^2\); bulk silicon: sp\(^3\)) when they go from the bulk material to the 2D monolayer, their atomic structures are analogous. However, a slight atomic relaxation may occur in order to balance the reduced bonding coordination in the 2D forms. Therefore, in these cases, the determination of the 2D atomic structures is quite straightforward.

In contrast, most metal oxides feature strong interlayer ionic bonds. The lack of a strong interlayer interaction in their 2D forms usually introduces dangling bonds, leading to strong surface polarization which induces surface instability of 2D metal oxides. Pronounced lattice relaxation, prominent structural reconstruction and substrate effects have been identified as the main mechanisms for compensating such strong surface polarization in 2D metal oxides, as have been observed for a Pd\(_2\)O\(_4\) overlayer on Pd(111),\(^22\) a strained PdO(101) layer on Pd(100),\(^23\) a Ag\(_{1.83}\)O trilayer on Ag(111),\(^24\) a RhO\(_2\) trilayer on Rh(111),\(^25\) multiple phases of 2D Mn oxides on Pd(100),\(^26\) and TiO\(_2\) on rutile TiO\(_2\)(011).\(^27\) All of these significant changes increase the difficulty of synthesizing 2D metal oxides, as well as pose a challenge to computational structure prediction methods. Notwithstanding, more recently, spectacular progress has been made in prediction, design, preparation, and characterization of oxide monolayers owing to the advancement of growth technologies and novel synthesis routes, as well as the development of computational and theoretical methods.\(^28\)\(^-\)\(^33\) The structural reconstructions in combination with the electron confinement in 2D and the large surface-to-volume ratio endow 2D transition metal oxides (TMOs) with stunning physical/chemical properties. Moreover, the 2D TMOs show...
very diverse properties due to their capability of adopting different binding configurations.\cite{34-37} Perovskite oxide thin film based heterostructures form another interesting class of oxide materials, which exhibit electronic and magnetic properties that are very different from their parent bulk materials, and thus have attracted remarkable attention recently.\cite{38-40} As an example, an unexpected insulator-metal transition has been observed in LaAlO$_3$/SrTiO$_3$ when the thickness of the deposited LaAlO$_3$ layer is larger than 4 unit cells. All these spurious wide interest to investigate fundamental properties of 2D metal oxides and explore their potential applications in supercapacitors,\cite{41} rechargeable batteries,\cite{42,43} photocatalysis,\cite{44,45} electronics,\cite{16,46,47} piezoelectrics,\cite{48-50} superconductivity,\cite{51} etc. We note that there are some excellent reviews published in the past ten years.\cite{46,52-57} However, significant advances in this field have been spotted recently as signified by the successful synthesis of various oxide monolayers using the novel liquid metal–based reaction route in 2017.\cite{31} Herein, we review recent research progress of oxide monolayers, especially on their structural reconstruction, their interaction with substrates, and their potential applications.

2. Synthesis of 2D TMOs

2.1. Layered TMOs

In nature, many layered transition metal oxides are composed of negatively charged slabs with alkaline cations (e.g., K$^+$, Rb$^+$, Cs$^+$, etc.) filling the interlayer spacing. As illustrated in Figure 1, these slabs are commonly made up of corner- or edge-shared octahedral units of MO$_6$ (M = Ti, Nb, Mn, W, Ta, Ru, Mo, etc.).\cite{16,52,58-63} which form ionic bonds with the surrounding alkaline cations. The cation exchange–assisted liquid exfoliation has been developed to reduce these materials into 2D nanosheets (Figure 1g). By treatment with an acid solution, the interlayer alkaline cations can be exchanged with H$^+$ cations to form hydrated protonic compounds. The interlayer protons can be further replaced with organoammonium ions in an aqueous base solution, tetrabutylammonium hydroxide (TBA$^+$OH$^-$; (C$_4$H$_9$)$_4$N$^+$OH$^-$) due to their Brønsted solid acidity. Such a reaction often introduces a massive volume of water, which leads to a drastic decrease in the interlayer electrostatic interaction and the interlayer expansion. Subsequent mechanical shaking or sonication treatments can easily exfoliate the expanded compounds into metal oxide nanosheets, i.e., Ti$_{52}$O$_{136}$–\cite{58} MnO$_2$\textsuperscript{4−}–\cite{59} Nb$_2$O$_7$\textsuperscript{4−}–\cite{60} TaO$_2$\textsuperscript{4−}, or Ca$_2$Nb$_2$O$_9$\textsuperscript{4+}.\cite{62,64}

Some layered transition metal oxides are also found to be bonded by the weak van der Waals force, such as α-MoO$_3$\cite{17} and V$_2$O$_3$.\cite{63} Each layer of MoO$_3$ is similarly composed of edge-shared distorted MoO$_6$ octahedra (see Figure 1e), while for V$_2$O$_3$, the layered anisotropic structure is formed by linking distorted trigonal bipyramidal polyhedral O atoms enclosing V atoms (Figure 1f). Micromechanical cleavage or liquid exfoliation techniques can be applied to produce the 2D monolayers in these oxides.\cite{17,65,66}

In addition to top-down synthesis routes, bottom-up synthesis methods have also been explored to pursue a high yield, high production rate and precise control of layer numbers. Zhao et al. synthesized MnO$_2$ nanosheets with a large surface area via in situ replacement of carbon atoms on the graphene oxide framework.\cite{67} By deploying a wet-chemical one-pot synthesis method, Tae et al. could produce lepidocrocite-type titanate nanosheets, Ti$_{16}$O$_{26}$–\textsuperscript{(e.g., Ti$_{16}$O$_{26}$–)} on a large scale.\cite{68} As another example, Xu et al. recently utilized the atomic layer deposition technique to grow WO$_3$ films in a large area with a controllable thickness,\cite{69} whereas Chen et al. fabricated single-crystal WO$_3$ nanosheets with a thickness of 4–5 nm and lateral size up to micrometer via laterally oriented attachment of tiny WO$_3$ nanocrystals.\cite{70} Table 1 tabulates the layered 2D TMOs and associated synthesis methods.

2.2. Nonlayered TMOs

For nonlayered transition metal oxides, top-down synthesis methods are not applicable due to the presence of strong
interlayer chemical bonds. Nevertheless, some bottom-up strategies have been proposed and successfully applied to the synthesis of either supported or free-standing nonlayered 2D TMOs as summarized in Table 2.

Nonlayered 2D TMOs are often obtained by surface oxidation. For most metals, thin oxide layers can be naturally formed at the metal-air interface. Zhou et al. observed oxide growth during the oxidation of Cu surfaces. They found that oxidation occurs via direct growth of Cu$_2$O on flat terraces, where Cu adatoms detach from steps and diffuse across the terraces. Subsequently, they reported that the presence of surface steps inhibits oxide film growth and leads to oxide decomposition, thereby resulting in an oscillatory oxide film growth (Figure 2a,b). Tao et al. observed a 2D phase of TiO$_2$ on the rutile TiO$_2$ (011) surface when the surface is slightly vacuum-reduced and subsequently annealed in a low-pressure O$_2$ atmosphere. This is ascribed to the re-oxidation of titanium interstitials. For those 2D TMOs formed on surfaces, further isolation from substrates is needed for practical applications, which is usually very challenging.

Physical vapor deposition (PVD) has been widely utilized to deposit 2D nonlayered TMOs layers on metal single crystal surfaces. Up to date, various 2D binary oxides of transition metals (e.g., Fe, W, Co, V, Ni, Mn, Ti, etc.) have been deposited on single crystal metal substrates (e.g., Pt, Pd, Rh, Ag, etc.) and intensively investigated. For instance, iron oxide has been deposited on Pt(111) and identified as a bilayer FeO(111) with the outmost oxygen layer in a close packed structure.
Table 2. Summary of synthesis methods for nonlayered 2D TMOs.

| Synthesis techniques | Nonlayered 2D TMOs | Substrate/template | References |
|----------------------|--------------------|--------------------|------------|
| Surface oxidation    | Cu$_2$O            | Cu(110)            | [72,73]    |
|                      | Pd$_2$O$_4$        | Pd(111)            | [22]       |
|                      | Strained PdO(101)  | Pd(100)            | [23]       |
|                      | RuO$_2$(110)       | Ru$_2$(0001)       | [228]      |
|                      | RhO$_2$(111)       | Rh(111)            | [25]       |
|                      | Ag$_2$O            | Ag(111)            | [229]      |
|                      | Ag$_{1.83}$O       | Ag(111)            | [24]       |
|                      | TiO$_2$            | Ru$_2$(111)        | [27]       |
|                      | PVD                |                    |            |
|                      | Hexagonal O-Fe-O trilayer-like FeO$_2$, c(8 × 2)-FeO(111), hexagonal bilayer-like FeO$_{1.125}$ | Pd(100) | [77] |
|                      |                    |                    |            |
|                      | Bilayer FeO        | Pd(111)            | [78,79]    |
|                      |                    | Pt(111)            | [87]       |
|                      | MnO(2 × 1)         | Ag(100)            | [80]       |
|                      | Ni$_2$O$_3$(6 × 1), Ni$_2$O$_{13}$ (2×3×2) | Rh(111) | [81,82] |
|                      | NiO(100)(1 × 1)    | Ag(100)            | [83,147]   |
|                      | NiO(001)(1 × 1)    | Ag(100)            | [93]       |
|                      | V$_{3}$O$_{9}$ (5 × 3), V$_{3}$O$_{9}$ (5 × 3×3), V$_{3}$O$_{4}$ (9 × 9), Wagon-wheel V$_{3}$O$_{17}$ | Rh(111) | [85,89] |
|                      | Co$_2$O$_3$ (4 × 2), Co$_2$O$_3$(9 × 2) | Pd(100) | [84,230] |
|                      | CeO$_2$            | Cu(110)            | [231]      |
|                      | Ti$_2$O$_3$ kagomé phase | Pt(111) | [86] |
|                      | WO$_3$ (based on (WO$_3$)$_3$) | Pd(100) | [148] |
|                      | (WO$_3$)$_3$       | Pt(111)            | [232]      |
|                      | Boron nitride–like ZnO(0001) | ZnO(0001) | [121,215] |
|                      |                    |                    |            |
|                      | Eu$_2$O$_3$        |                    |            |
|                      | TiO$_2$, ZnO, Co$_2$O$_4$, Fe$_2$O$_3$, MnO$_2$ | CuO | [96] |
|                      |                    |                    |            |
|                      | B$_2$O$_3$         |                    |            |
|                      | Template-assisted synthesis |                    |            |
|                      | Half-unit-cell α-Fe$_2$O$_3$ | CuO | [96] |
|                      | Hexagonal-MoO$_3$, MoO$_2$, MnO, hexagonal-WO$_3$ | Salt | [97] |
|                      | Holey Fe$_2$O$_3$, Co$_2$O$_3$, Mn$_2$O$_3$, Zn$_2$Mn$_2$O$_4$, ZnCo$_2$O$_4$, NiCo$_2$O$_4$, CuFe$_2$O$_4$ | Reduced graphene oxide | [189] |
|                      | Hydrothermal method | CeO$_2$ with surface pits | Eutectic gallium-based alloys | [31] |
|                      |                    | Porous Ir$_2$O$_3$ with rich oxygen vacancies | [101] |
|                      | Solvothermal method | SnO$_2$ | [234] |
|                      |                    | ZnO | [208] |
|                      | Microwave-assisted liquid phase growth | NiO, Co$_2$O$_4$, ZnCo$_2$O$_4$, NiCo$_2$O$_4$, CuCo$_2$O$_4$ | [103,235] |
|                      | Pyrolysis OR fast heating | Co$_2$O$_4$ | [104,105] |
|                      | Electron beam irradiation-driven in situ formation | CuO | [36] |
|                      | CVD                | Y$_2$O$_3$          | Graphene | [106] |
|                      |                    |                    | supported on a Pt(111) surface |
later found that at elevated O₂ pressures, the bilayer FeO(111) on Pt(111) could be further oxidized toward an O-Fe-O structured FeO₂ trilayer. Subsequent investigations suggest that two oxygen-rich phases among them can be described in terms of MnO(111)-like O-Mn-O trilayers, whereas the other two with lower oxygen content are based on a MnO(111)-like monolayer structure. These observed multiple MnO phases might be ascribed to kinetic effects which lead to stabilized metastable metal oxide structures, and the flexibility of transition metals for adopting different binding configurations. Besides, some complex 2D TMOs can also be obtained by using PVD, such as NiO(6 × 1) structure on Rh(111), Ti₂O₃ kagome phase on Pt(111) and (√7×√7)R 19.1° V₂O₅ phase on Rh(111). Beyond 2D binary TMOs, 2D ternary TMOs have recently been epitaxially fabricated via the on-surface solid-state chemical reaction between two 2D binary metal oxides. Martin et al. reported the synthesis of a 2D copper tungstate (CuWO₄) which is composed of three sublayers with stacking O-W/O/Cu from the interface. The single crystalline Cu(110) surface oxide is first covered with a monolayer of (WO₃)₄ and the surface chemical reaction is subsequently initiated by increasing the surface temperature, giving rise to the formation of 2D CuWO₄. Analogously, Pomp et al. observed 2D iron tungstate (Fe₂WO₆) with honeycomb geometry on a Pt(111) surface. In addition to the choice of metal substrate and the tuning of oxygen partial pressure during the growth, the use of an atomic oxygen source might promote the formation of the crystalline oxide monolayer, as evidenced by the formation of a NiO(001) monolayer on the Ag(001) substrate. Similar to those obtained by surface oxidation, these PVD grown 2D TMOs usually strongly bind to the metal substrates. Therefore, it may be very challenging to peel off and transfer the epitaxial 2D TMOs. Nevertheless, it provides us with an ideal platform to investigate the strongly interacting oxide-metal interfaces, and explore their potential applications.

As an alternative, self-assembly has been proven to be a promising technique for the synthesis of free-standing nonlayered 2D TMOs. Using 0D and 1D nanocrystals as building blocks, Liu et al. self-assembled CuO monocrystalline materials with controlled dimensionality. The 2D CuO nanosheets were formed by tuning the pH value to 8.5. Analogously, Yao and co-workers reported the synthesis of Eu₂O₃ nanosheets from the assembly of Eu₂O₃ nanowires. In addition, Sun et al. generalized the self-assembly method for the synthesis of 2D transition metal oxide nanosheets by strategic and collaborative self-assembly of metal oxide precursor oligomers into lamellar structures with polymer surfactant molecules, before they are condensed, polymerized and crystallized into 2D metal oxide nanosheets with atomic thickness. Reproduced with permission. Copyright 2014, Springer Nature. 

Figure 2. a–b) Sequence of high-resolution TEM images of surface-step-induced oscillatory growth of a single Cu₂O layer on a stepped Cu(110) surface; insets show schematically the different growth stages of the oxide film with respect to the propagation of the surface step of the Cu substrate. Reproduced with permission. Copyright 2014, American Physical Society. c) Schematic drawing of self-assembly of 2D metal oxide nanosheets, where metal oxide precursor oligomers are strategically and collaboratively self-assembled into lamellar structures with polymer surfactant molecules, before they are condensed, polymerized and crystallized into 2D metal oxide nanosheets with atomic thickness. Reproduced with permission. Copyright 2014, Nature Publishing Group. d) Schematic representation of the salt-templated synthesis of 2D transition metal oxides. Reproduced with permission. Copyright 2016, American Physical Society. e,f) Liquid metal-based reaction route to create 2D TMOs at room temperature according to Gibbs free energy of formation. f) Oxides to the right of the red dashed line are expected to dominate the interface. g) A cross-sectional diagram of a liquid metal droplet, with possible crystal structures of thin layers of HfO₂, Al₂O₃ and Gd₂O₃. Reproduced with permission.
template, Cheng et al. synthesized 2D ferromagnetic \( \alpha \)-Fe\(_2\)O\(_3\) semiconductor nanosheets with only half-unit cell thickness.[96] Recently, this synthetic strategy (Figure 2d) was further confirmed by Gogotsi and co-workers.[97] They reported the growth of 2D hexagonal-MoO\(_3\), MoO\(_2\), MnO and hexagonal-WO\(_3\) with the aid of water-soluble salt crystals as growth templates. They proposed that both the salt crystal geometry and lattice matching could guide and promote the lateral growth of 2D oxides, while the thickness could be restrained by the raw material supply.

More recently, Zavabeti et al. proposed a liquid metal-based reaction route to create 2D TMOs at room temperature.[31] They showed that a self-limiting interfacial oxide could be formed thermodynamically, when nontoxic eutectic gallium-based alloys are used as solvent and desired metals are co-alloyed into the melt, as shown in Figure 2e,f. Taking room-temperature liquid gallium alloys as the solvent, this route potentially enables access to the 2D nanostructures of all lanthanide oxides and a sizable portion of the transition metal and post-transition metal oxides. Moreover, the accessibility to 2D metal oxides can be further extended when eutectic bismuth-tin alloy (melting point: 138 °C) is used as the reaction medium at an elevated temperature. This strategy was confirmed by successful synthesis of 2D HfO\(_2\), Al\(_2\)O\(_3\) and Gd\(_2\)O\(_3\).

Recently, epitaxial growth of perovskite oxide ultrathin films has been realized by using the pulsed laser deposition (PLD) technique, molecular beam epitaxy (MBE), or metal-organic chemical vapor deposition (MOCVD), in which PLD is the most commonly used method to grow perovskite ABO\(_3\) thin films.[18–40,98–100] The model example is the growth of LaAlO\(_3\)(001) on SrTiO\(_3\)(001) substrates, where the layer-by-layer epitaxial growth can be achieved by tuning the deposition parameters and the substrate temperature as in situ monitored by the related reflection high-energy electron diffraction pattern. Based on this PLD growth process, a large variety of binary or ternary complex oxide films have been grown epitaxially with various different crystal structures such as rocksalt, wurtzite, or fluorite structures for binary oxides, and ilmenite, spinel, or perovskite structures for ternary complex oxides.[100]

Some other synthetic methods have also been developed for the synthesis of nonlayered 2D TMOs. For example, atomically thin CeO\(_2\) sheets and ultrathin In\(_2\)O\(_3\) porous sheets have been successfully grown via the hydrothermal method.[101,102] Zhu et al. demonstrated the synthesis of binary and ternary TMO nanosheets (NiO, Co\(_x\)O\(_y\), Zn\(_x\)Co\(_{1-x}\)O\(_y\), NiCo\(_2\)O\(_4\), and CuCo\(_2\)O\(_4\)) via microwave-assisted liquid phase growth.[103] For 2D CoO\(_2\), other synthetic methods are also reported, i.e., single pyrolysis of Co\(_x\)O\(_y\) at 700 °C or fast heating of presynthesized CoO nanosheets.[105] In addition, Addou et al. reported the formation of 2D Y\(_2\)O\(_3\) by evaporating yttrium in the low pressure of oxygen environment.[100]

3. Theoretical Aspects of 2D-TMOs

First-principles calculations based on density functional theory (DFT) emerge as another attractive and effective technique to investigate 2D TMOs.[107] It can be utilized not only to elucidate experimental observations, but also to theoretically predict new 2D TMOs and study the associated physical or chemical properties. The two aspects are further boosted by the recent development of advanced algorithms for structure prediction, such as CALYPSO[13] and USPEX.[13] CALYPSO is based on the particle swarm optimization algorithm, whereas USPEX implements the evolutionary algorithm.

3.1. Prediction of new 2D TMOs

Theoretical calculations can allow us to explore new 2D TMOs without having to synthesize them first. In particular, the availability of unprecedented computational resources nowadays enables high-throughput calculations to be carried out to explore material space and to screen materials for specialized applications on a large scale, which is more cost-effective than the traditional trial-and-error method in experiments.[108–110]

Recently, Mounet et al. computationally analyzed and screened experimental structures from the Inorganic Crystal Structure Database[111] (ICSD) and the Crystallographic Open Database[112] (COD) to search for potential 2D materials.[113] Among the identified exfoliable 2D materials, there are various potential 2D TMOs, such as FeO\(_2\), CoO\(_2\), PbO, and PtO\(_2\). More interestingly, the theoretical calculations show that 2D CoO\(_2\) is a ferromagnetic metal and 2D FeO\(_2\) an antiferromagnetic metal. Likewise, Zhang et al. investigated more than 60 000 inorganic compounds in the Materials Project[114,115] (MP) Database to search for potential insertion-type electrode materials for sodium-ion batteries (SIBs).[116] Based on massive calculations, they identified layered Na(CuO\(_2\))\(_2\) and Na\(_3\)Co\(_2\)SbO\(_6\) as promising cathode materials for SIBs.

In contrast to the above-mentioned top-down approach, the computational bottom-up methods have also been employed to explore 2D TMOs. By means of elemental substitution, Lu et al. proposed a metastable phase of 2D TiO\(_2\) which bears the same lattice as MoS\(_2\).[117] Compared to rutile and anatase phases of TiO\(_2\), the proposed TiO\(_2\) monolayer has a relatively small bandgap (2.1 eV), which makes it a good photocatalyst candidate. Similarly, Ataca et al. applied the elemental substitution strategy to systematically investigate single-layer honeycomb-structured transition metal oxides in both 2H- and 1T-phases.[118] They focused on structural, mechanical, electronic as well as magnetic properties of these 2H- and 1T-TMOs. Rasmussen and Thygesen later expanded the scope of investigation to 2H and 1T-phases of 2D TMOs by taking into account more transition metals.[119] Wherein, electronic structures and optical properties of these honeycomb-structured 2D TMOs are comprehensively studied. They found that bandgaps of honeycomb-structured 2D TMOs vary in a wide range (1.64–7.98 eV at the G\(_0\)W\(_0\) level of theory). Among them, 2D TMOs with wide bandgaps like 1T-HfO\(_2\) (7.98 eV) and 1T-GeO\(_2\) (7.07 eV) might be promising high-k materials, while those with small bandgaps like 2H-MoO\(_3\) (2.20 eV) and 1T-NiO\(_2\) (2.15 eV) might be potential photocatalysts.

Structure prediction software also plays an important role in exploring new 2D TMOs. Recently, Song et al. employed CALYPSO to predict a planar Al\(_2\)O\(_3\) monolayer.[120] It is found that this Al\(_2\)O\(_3\) monolayer is energetically and thermodynamically stable up to 1100 K. It has a direct wide bandgap of 5.99 eV
and the calculated static dielectric constant is comparable to that of SiO2 bulk although smaller than that of $\alpha$-Al2O3 bulk. In addition, they investigated the interface between graphene and Al2O3 monolayer, as shown in Figure 4d. It is found that van der Waals and red colors represent Ti and O atoms, respectively. The simulated STM image of Ti4O4-$2 \times 1$. e–g) Reproduced with permission[125] Copyright 2016, American Chemical Society. f) The anatase (101)-like reconstructed surface structure in the side view (the top panel) and the top view (the bottom left panel) and the simulated STM image (the bottom right panel). The Ti and O atoms in the surface and subsurface oxide layer are shown in the ball and frame modes, respectively. Atoms in the gray color represent Ti atoms. Atoms in red, yellow, and green colors represent O atoms in the topmost, middle, and downmost positions of the surface oxide layer, respectively. g) Structures of water on the anatase (101)-like surface. The left and right panels are the structures before and after dissociation, respectively. The anatase (101)-like structure and adsorbed water are shown in the frame and ball modes, respectively. Atoms in light gray and red colors represent the H and O atoms of water, respectively. g) Reproduced with permission[123] Copyright 2017, American Chemical Society.

3.2. Understanding Experimental Observations

Due to inherent limitations of experimental techniques, some information about the materials of interest, e.g., detailed atomistic structures, might not always be obtained at ease. Theoretical investigations as a complement to the experiment may facilitate understanding experimental observations.[36,121–124] Since Tao et al. reported the synthesis of 2D phase of TiO2 with a reduced bandgap,[27] a large amount of attention has been paid to resolve its atomistic structure, owing to its potential application as a photocatalyst in the visible light range (Figure 3a–c). Zhou et al. used the USPEX package to predict a Ti4O4-$2 \times 1$ surface model.[125] They claimed that both the simulated STM images and electronic structures are in agreement with those of experimental observations, as shown in Figure 3d,e. Meanwhile, by means of CALYPSO, Xu et al. proposed an anatase (101)-like structural model (Figure 3f).[123] It is found that this anatase (101)-like structure could explain not only the observed STM images and the electronic bandgap, but also the measured oxidation state of Ti4$^+$. Furthermore, they demonstrated that water and formic acid molecules could spontaneously dissociate on the anatase (101)-like structure, indicating its high photocatalytic activity (Figure 3g). But so far, it is still under debate on the exact atomistic structure of the novel 2D TiO2 phase, and further attempts should be carried out to understand its structural and electronic properties.

In 2012, Addou et al. successfully deposited monolayer yttria (Y2O3) on platinum-supported graphene.[106] The scanning tunneling microscopy reveals that Y2O3 monolayer features a hexagonal lattice and the XPS measurements show that graphene is changed from p-type doping on pure platinum to n-type doping after the deposition of yttria ultrathin films on it (Figure 4a). Via first-principles calculations, Song et al. predicted a stable Y2O3 (111) monolayer with a hexagonal lattice.[124] They found that due to the suppression of surface polarization, Y and O atoms of the free-standing Y2O3 layer prefer to lie in the same plane. However, when the Y2O3 (111)
monolayer is supported on graphene, the interfacial interaction between them would pull Y atoms out of the plane toward graphene, forming a slightly buckled structure (Figure 4b). As a result, the planar Y$_2$O$_3$ (111) monolayer is further stabilized. On the other hand, the presence of the slightly buckled Y$_2$O$_3$ (111) monolayer in turn opens the bandgap of graphene (about 0.21 eV), where the interfacial electrostatic potential interaction only contributes a small fraction and the inter-layer orbital hybridization plays the key role. It is also found that the slightly buckled Y$_2$O$_3$ (111) monolayer makes the graphene slightly n-doped. The doping concentration is enhanced as the buckling of the Y$_2$O$_3$ (111) monolayer becomes more pronounced (see Figure 4c), in agreement with the experimental observations.

Figure 4. a) The High-resolution STM image (22×23 nm) of the atomic honeycomb lattice of the yttria film (top left panel) and a possible model for the yttria unit-cell structure with a Y$_2$O$_3$ composition and hexagonal symmetry (top right panel). The bottom panel of (a) shows C 1s XPS spectra before and after yttria growth. The yttria growth shifts the peak position by ≈0.6 eV to higher binding energy. Reproduced with permission.[106] Copyright 2013, Springer Nature. b) Top and side views of the planar Y$_2$O$_3$ (111) monolayer on the (3×3×1) graphene (top and middle panels), and the orbital projected band structure (bottom panel). The charge density difference ($\Delta \rho$), which is defined by $\Delta \rho = \rho(G+Y_2O_3) - \rho_G - \rho_{Y_2O_3}$, is visualized in the side view. c) Top and side views of the atomic structure for buckled Y$_2$O$_3$ (111) monolayer on (2×2×1) graphene (top and middle panels) and the corresponding band structure (bottom panel). Reproduced with permission.[124] Copyright 2015, Royal Society of Chemistry. d) Top view of the Al$_2$O$_3$ monolayer on graphene with contour plot charge density difference projected on the graphene plane and the associated band structure. The blue/red color denotes the excess/depleted charge in the top panel. Reproduced with permission.[120] Copyright 2016, Springer Nature. e) Side view of MoS$_2$ monolayer on the Hf-terminated HfO$_2$ (111) surface with imposed differential charge density (the isosurface value: 2.0×1.0×1.0×10$^{-3}$ eÅ$^{-3}$) (left panel) and the total and projected DOS (right panel). The Fermi energy is shifted to 0 eV. f) The total DOS and partial DOS for the O-terminated HfO$_2$ (111)/MoS2 monolayer hybrid structure with the Fermi level shifted to 0 eV. g) Contour plot for charge density difference of MoS$_2$ monolayer on the O-terminated HfO$_2$ (111) surface without and with a surface oxygen vacancy, and the total and projected DOS of the hybrid structure with a surface oxygen vacancy. The contour plot is visualized through the Mo plane with an iso-value of 0.002 eÅ$^{-2}$, where the red/blue color denotes increased/depleted charge density. Reproduced with permission.[132] Copyright 2016, American Chemical Society.
4. Interactions between 2D TMOs and Substrates/2D Materials

For fundamental science and practical applications, a substrate is indispensable for supporting the 2D TMOs, because the interaction between 2D TMOs and substrates might influence structural, electronic, and chemical properties of 2D TMOs due to their atomically thin thickness. On the one hand, the interfacial interactions may bring in intriguing phenomena, such as superconductivity\(^{126}\) and quantum Hall effects\(^{127}\). On the other hand, the hybridization of 2D TMOs with substrates or 2D materials may tailor 2D TMOs or compensate shortcomings of both parent materials for real applications.\(^{50,128,129}\)

Herein, we focus on the interfacial interactions of 2D TMOs with channel materials, co-catalysts, metals and TMOs as well.

4.1. Interactions between 2D TMOs and Channel Materials

Integrating high-k dielectrics into microelectronic devices is very challenging but highly desirable because high-k dielectrics can significantly increase the gate capacitance of transistors and also effectively suppress electron scattering from interfacial charged impurities.\(^{130}\) 2D TMOs with wide bandgaps might be potential high-k dielectrics to replace conventional gate dielectric SiO\(_2\). In this regard, theoretical calculations might shed light on the integration of potential high-k TMOs into 2D materials based electronic devices.

As discussed above, we predicted stable 2D high-k dielectric Y\(_2\)O\(_3\) and Al\(_2\)O\(_3\) monolayers and investigated their interaction with graphene.\(^{120,124}\) We found that both Y\(_2\)O\(_3\) and Al\(_2\)O\(_3\) weakly bind to graphene via van der Waals forces (see Figure 4b–d). The presence of graphene further stabilizes Y\(_2\)O\(_3\) and Al\(_2\)O\(_3\). The weak interaction indicates that graphene is an excellent substrate to grow high-k dielectric Y\(_2\)O\(_3\) and Al\(_2\)O\(_3\). It is worth noting that the growth of Y\(_2\)O\(_3\) monolayer on graphene has been demonstrated.\(^{106}\)

Interestingly, for the interfacial interaction between Y\(_2\)O\(_3\) monolayer and graphene, although the calculated adsorption energy is weak, in the typical vdW interaction range, noticeable structural distortion is found in the Y\(_2\)O\(_3\) monolayer with the presence of the graphene. Meanwhile, the electronic structures of graphene are altered significantly. As Figure 4b shows, the graphene monolayer becomes n-doping with a bandgap about 0.2 eV. Detailed DFT calculations further reveal that this sizable bandgap in graphene is mainly due to the interfacial hybridization between O\(_{p}\) and C\(_{p}\) orbitals. Besides, electrostatic potential interaction between graphene and Y\(_2\)O\(_3\) monolayer also contributes to the bandgap because the electrostatic potential difference is large in graphene AB lattices. This is similar to that of graphene on Ni\(_{1,11}\) where the adsorption is a typical vdW interaction, but the electronic properties are determined by the interfacial orbital hybridization. In contrast, the electronic structure of graphene is nearly intact with the presence of Al\(_2\)O\(_3\) monolayer as the orbital hybridization near the Fermi level is weak.

Meanwhile, we comprehensively evaluated the growth kinetics of high-k dielectric HfO\(_2\) on MoS\(_2\) using first-principles calculations.\(^{132}\) For the interface between Hf-terminated HfO\(_2\)(111) and MoS\(_2\) monolayer, a strong interfacial interaction is found because of the formation of Hf–S bonds and pronounced charge transfer, giving rise to inferior electronic properties (Figure 4e). In contrast, the weak van der Waals force is dominant between oxygen-terminated HfO\(_2\)(111) and the MoS\(_2\) monolayer. The weak interfacial interaction leads to symmetric band offsets of more than 1 eV (Figure 4f). However, the interlayer interaction will be significantly strengthened upon the formation of oxygen vacancies in HfO\(_2\), which incurs unfavorable electron–hole puddles, larger effective masses and localized midgap states in MoS\(_2\) (Figure 4g). In addition, it is found that with the increase in thickness of MoS\(_2\), the formation of an oxygen-terminated HfO\(_2\) thin film on MoS\(_2\) becomes endothermic and the band offsets increase asymmetrically.

4.2. Interactions between 2D TMOs and Cocatalysts

Since the discovery of water splitting on TiO\(_2\),\(^{133}\) metal oxides have been intensively studied for photocatalytic applications. Among them, 2D semiconducting TMOs appear to be promising photocatalysts. However, the photocatalytic performance of 2D TMOs is usually hindered by many factors, such as wide bandgaps, fast electron–hole recombination and aggregations. Hybridization with co-catalysts can enhance photocatalytic activities of 2D TMOs in several ways.\(^ {45,134–139}\) Here, we mainly focus on the interfacial interactions. Taking g-C\(_3\)N\(_4\)–TiO\(_2\) as an example, Ma et al. compared the photocatalytic oxidation capability of two kinds of g-C\(_3\)N\(_4\)–TiO\(_2\) nanocomposites which were obtained by a calcination routine and a simple mechanical mixing, respectively.\(^ {140}\) The former was found to have a superior oxidation capability over the latter. This superior performance is partially ascribed to the interfacial interaction, where the type-II band alignment between g-C\(_3\)N\(_4\) and TiO\(_2\) is achieved and recombination of photogenerated electrons and holes is efficiently suppressed. When both g-C\(_3\)N\(_4\) and TiO\(_2\) are reduced to nanosheets, the intimate and larger contact area between them further improves the rate of electron–hole separation. Moreover, as Figure 5a shows, the interfacial interaction also reduces the bandgap of TiO\(_2\) in the surface-to-surface heterojunction from 3.3 to 2.91 eV, extending the light absorption range of TiO\(_2\) nanosheets.\(^ {141}\)

Noting that p–n junctions can potentially act to suppress the electron–hole recombination, Ida et al. demonstrated that the induced potential gradient in p–n junctions could affect the photocatalytic activity (Figure 5b).\(^ {142}\) They prepared a p–n junction made up of 2D p-type NiO and 2D n-type calcium niobate (CNO). It was found that the CNO surface potential of the CNO/NiO junction was lower than that of the CNO crystals in the same crystal face. The induced potential gradient separates reaction sites, i.e., the CNO/NiO junction parts for photo-oxidation and the nonjunction parts or their edges for photoreduction. As a consequence, the recombination reaction was effectively suppressed and an enhanced photocatalytic performance was obtained.

To alleviate the impact of poor conductivity of most 2D TMOs, graphene has been considered as an ideal cocatalyst for 2D TMOs due to its high specific surface area and excellent electrical conductivity. Xiang et al. reported an enhanced...
photocatalytic H2-production activity of TiO2 nanosheets when graphene is used as cocatalysts.[136] It is reported that the confluence of the good conductivity of graphene and the appropriate potential of graphene/graphene− (−0.08 V vs SHE, pH = 0), which is lower than the conduction band of TiO2 (−0.24 V) but higher than the reduction potential of H+/H2 (0 V), not only promotes the transfer of photogenerated electrons, but also makes the reduction of protons more efficient (Figure 5c).

Moreover, Yuan et al. found that the hybridization of SnNb2O6 nanosheets with graphene exhibits improved photocatalytic activity toward degradation of organic dye in water in the visible light range, where the presence of graphene facilitates the transfer and separation of photogenerated charge carriers.[134] It is worth noting that hybridization of 2D TMOs with conducting materials also benefits 2D TMOs in other fields, such as supercapacitor applications (see detailed description in Section 5.1).

4.3. Interactions between 2D TMOs and Metals

4.3.1. Metal Substrate Effects on Properties of 2D TMOs

When exposed to an oxidizing environment, nearly all metals will develop an ultrathin surface oxide layer. This oxidation process is spontaneous even under an ultrahigh vacuum.[143,144] In turn, the spontaneously formed ultrathin oxide layers might protect metals from undergoing further environmental degradations or change mechanical properties of nanostructures.

Fatih et al. showed that the formation of oxide layer could enhance the aluminum nanowire ductility by means of reaction molecular dynamics simulations (Figure 6a,b).[145] The oxide layer exhibits a superplastic behavior, which is due to viscous flow as a result of healing of the broken aluminum-oxygen bonds by oxygen diffusion. This theoretical result is elaborated by the recent experimental observations of Yang et al.[146] Using the environmental transmission electron microscopy (ETEM) technique, they discovered that aluminum oxide formed on Al indeed deforms like liquid and can match the deformation of Al without any cracks/spallation at moderate strain rate (see Figure 6c). On the other hand, when the strain rate is so high that fresh metal surface is exposed, they observed the self-healing process of aluminum oxide and subsequent seamless coalescence between new oxide islands and new/old oxide nearby without forming any surface grooves (Figure 6d). These discoveries indicate the greatly accelerated glass kinetics of oxide layers on metal surfaces. The triggered self-healing function also suggests that a bilayer coating containing both aluminum and aluminum oxide may have better mechanical performance in an oxidative environment than a standalone layer of aluminum oxide.

4.3.2. Metal Substrate Effects on the Stabilization and Growth of 2D TMOs

As discussed in Section 2.2, a number of 2D nonlayered TMOs have been deposited on metal single crystal substrates via PVD. The strong interfacial interaction between 2D TMOs and metal substrates plays a significant role in growing and stabilizing 2D TMOs, which can be attributed to multiple aspects, such as...
polarity compensation, strain release, interlayer charge transfer, and interlayer bond formation.\cite{80,83,147}

For the epitaxial FeO(111) bilayer on Pt(111), the Fe−O interlayer distance is observed to be dramatically compressed by about 50% compared to bulk FeO, which reduces the large surface dipole and therefore stabilizes the FeO(111) bilayer.\cite{78–80,83,147}

Meanwhile, this polar surface is further stabilized by an image dipole in the platinum substrate. Another example is the growth of a NiO(100)(1×1) island on a Ag(100) substrate.\cite{83,147} Interestingly, it turns out that at sub-monolayer coverages, the as-grown NiO(100)(1×1) islands are likely embedded in Ag(100) with many second NiO layer patches incorporated as shown
4.4. Interaction between Metal Oxides

Various degrees of coupling among charge, spin, and lattice in oxide materials give rise to a rich playground for novel physics and exotic physical and chemical properties. The combination of these complex oxides leads to very different electronic and magnetic properties in the heterostructures compared with their parent bulks, which gives us another degree of freedom to tailor the properties. Taking the heterostructures of LaAlO$_3$ and SrTiO$_3$ as an example, both LaAlO$_3$ and SrTiO$_3$ bulks are insulators. When a polar LaAlO$_3$ thin film is deposited on the nonpolar SrTiO$_3$(001) substrate with a TiO$_2$ terminated surface, an insulator-metal transition is found when the thickness of the deposited LaAlO$_3$ layers is larger than 4 unit cells. It has been suggested that the transition is due to charge transfer from the LaAlO$_3$ surface to the LaAlO$_3$/SrTiO$_3$ interface in order to compensate the divergent polarization potential in LaAlO$_3$ films when the grown LaAlO$_3$ film approaches the critical thickness. Along with the interfacial electronic reconstruction, magnetic ordering reconstruction is also found at the interface, although the LaAlO$_3$ and SrTiO$_3$ bulks themselves are nonmagnetic.

Further studies suggest that the interplay between charge transfer, lattice distortion, and the formation of defects might be responsible for the interfacial electronic and magnetic reconstruction in LaAlO$_3$/SrTiO$_3$ heterostructures. Zhou et al. reported that below the critical thickness, it is the lattice distortion in LaAlO$_3$ layers that partially compensates the polar divergence. While above the critical thickness, the formation of surface oxygen vacancies in LaAlO$_3$ becomes energetically favorable and triggers the charge transfer from the surface into the interfacial TiO$_2$ sublayers. This charge transfer fully compensates the polarization potential, resulting in a quasi-2D electron gas at the interface as well. Similarly, Yu and Zunger also proposed that the formation of surface oxygen vacancies leads to a conducting interface, and the formation of Ti-on-Al antisite defects might be responsible for the interfacial magnetic ordering. More recently, Yang et al. further elaborated the relation between interfacial defects and interfacial conductivity with the interfacial magnetic ordering, in which they suggested that the strong ferromagnetism in the LaAlO$_3$/SrTiO$_3$ heterostructures prepared at high oxygen partial pressure is due to the coexistence of surface oxygen vacancies and interfacial antisite defects. In contrast, the weak magnetism found in more conductive LaAlO$_3$/SrTiO$_3$ heterostructures prepared at low oxygen partial pressure is due to the formation of surface oxygen vacancies alone. Apart from the above efforts made to understand the electronic and magnetic reconstruction in the LaAlO$_3$/SrTiO$_3$ heterostructures, an extensive number of attempts have been made to tune the multidegree coupling at the interface, which includes interfacial strain, doping, ferroelectric substrates, or gate voltage. All these not only enrich our understanding of the complex oxide interfaces, but also shed light on further functionalization and potential applications of these strategic oxide heterostructures.

5. Potential Applications of 2D-TMOs

5.1. Supercapacitors

Supercapacitors are among the candidates for future major energy storage devices with the typical characteristics of a high power density and reliability. As electrode materials for supercapacitors up to now metal oxides/hydroxides, carbon materials and conducting polymers have been employed. Among those, transition metal oxides have the highest theoretical specific capacitance. Compared to their bulk counterparts, 2D TMOs in addition benefit from large surface areas for redox reactions. Therefore, nowadays various 2D TMOs have been studied as supercapacitor electrode materials, including binary (e.g., RuO$_2$, MnO$_2$, Co$_3$O$_4$, MoO$_3$, V$_2$O$_5$, etc.) and ternary (e.g., NiCo$_2$O$_4$, LiCoO$_2$, MnFe$_2$O$_4$, Ni$_2$V$_2$O$_8$, Co$_3$V$_2$O$_8$, etc.) 2D TMOs, which will be detailed in the following.

RuO$_2$ is a typical material with a high theoretical capacitance (2000 F g$^{-1}$). Its hydroxide counterpart has a higher electronic conductivity than most other oxides. With 2D RuO$_2$ as the supercapacitor electrode material, a high specific capacitance of 658 F g$^{-1}$ at 2 mV s$^{-1}$ has been experimentally measured by Sugimoto et al. It is about ten times larger than that of its bulk counterpart. However, the cost and need for using acidic electrolytes limit the applicability of 2D RuO$_2$. In contrast to RuO$_2$, MnO$_2$ and Co$_3$O$_4$ are inexpensive while still featuring a relatively high theoretical capacitance (1370 F g$^{-1}$ for MnO$_2$; 3560 F g$^{-1}$ for Co$_3$O$_4$). Zhao et al. used graphene oxide as a template to synthesize δ-type MnO$_2$ nanosheets and observed a prominent capacitance (=1017 F g$^{-1}$ at 3 mV s$^{-1}$). For Co$_3$O$_4$ nanosheets, Jiang et al. reported a remarkable specific capacitance of 1500 F g$^{-1}$ at 1 A g$^{-1}$ and a high energy density of 15.4 Wh kg$^{-1}$ in the asymmetric supercapacitor cell device configuration (Figure 7a).
Poor electronic conductivity is a main shortcoming of most TMOs due to their insulating or semiconducting nature. Hybridization with electrically conducting nanosheets or other nano-materials has been attempted to surmount this shortcoming. Peng et al. developed a planar supercapacitor by hybridizing MnO₂ and graphene, which showed high specific capacitances of 208 F g⁻¹ at 10 A g⁻¹ as well as excellent cycling stability. [128] Nagaraju et al. demonstrated that the 2D heterostructure of V₂O₅ and reduced graphene oxide exhibits a specific capacitance of 635 F g⁻¹ at 1 A g⁻¹, which is about 2.5 times higher than that of the 2D V₂O₅ nanosheets alone.[129] Besides, Liu et al. reported the performance enhancement via hybridization of 2D TMOs with 0D materials.[182] They grew Co₃V₂O₈ nanoparticles on the surface of Ni₃V₂O₈ nanoflakes. It was found that this nano-composite inherits advantages of both Ni₃V₂O₈ and Co₃V₂O₈, showing higher specific capacitance than Co₃V₂O₈ and superior rate capability and better cycling stability to Ni₃V₂O₈.

5.2. Batteries

2D TMOs have also been extensively investigated as potential electrode materials for rechargeable lithium and sodium batteries owing to their ample active sites and shortened ion-diffusion lengths.[42,43,54,103,188] As mentioned, one of the major drawbacks of 2D TMOs, especially for binary compounds, is the relatively low conductivity. As a consequence, they suffer from a drastic volume change during repeated charging/discharging processes. Recently, Peng et al. reported a two-step strategy for controlled synthesis of holey 2D TMOs nanosheets with tunable pore sizes (e.g., Fe₂O₃, Co₃O₄, Mn₂O₃, ZnMn₂O₄, ZnCo₂O₄, etc.) (Figure 7b). [189] They found that these holey 2D TMOs exhibit strong mechanical stability and display minimal structural changes during charging/discharging processes, and hence might be potential anode materials for both lithium and sodium ion storage. With regard to cathode materials, layered TMOs, such as MnO₂ and V₂O₅, have been reported as promising candidates.[65,190,191] For example, the exfoliated V₂O₅ nanosheets showed stable cycling stability (117 mAh g⁻¹ after 200 cycles at 50 °C) and large reversible capacity with the first discharge capacity of 292 mAh g⁻¹ at 59 mA g⁻¹.[65] The 2D structure wherein enables surface lithium storage with extremely short lithium insertion paths during Li insertion.

Among various rechargeable batteries, Li-O₂ batteries attract intensive attention because of their high theoretical energy density.[192] 2D TMOs have been reported to act as cathode...
materials as well.\textsuperscript{[63,193–195]} RuO\textsubscript{2}, which is metallic and a bi-catalyst for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), is a promising candidate. Liao et al. discovered that with the RuO\textsubscript{2} nanosheet, the Li\textsubscript{2}O battery is operable under full discharge-charge condition with a high specific capacity (\textasciitilde900 mAh g\textsuperscript{-1}) and stable discharge-charge over-potentials (0.15/0.59 V) over 50 cycles (Figure 7c).\textsuperscript{[63]} Recently, Zhang et al. investigated MoO\textsubscript{3} nanosheets for Li\textsubscript{2}O2 batteries.\textsuperscript{[196]}

It is found that the MoO\textsubscript{3} nanosheets with high density of oxygen vacancies can significantly lower the overpotential to \textasciitilde0.5 V while still maintaining a high cycling stability (over 60 cycles).

### 5.3. Photocatalysis

TMOs have been extensively studied as photocatalyst candidates in the past several decades due to their high chemical stability, low cost and nontoxicity. In particular, the large surface-to-volume ratio and the ability to obtain sufficient photon flux density for multiple-electron reactions (e.g., water splitting: 2H\textsubscript{2}O + 4 e\textsuperscript{-} \rightarrow 2H\textsubscript{2} + O\textsubscript{2}) make 2D TMOs superior to 0D, 1D, and 3D TMOs.\textsuperscript{[44]} A typical example of TMO photocatalysts is the TiO\textsubscript{2} nanosheet. Han et al. reported that (001)-terminated TiO\textsubscript{2} nanosheet exhibits an excellent photocatalytic activity, which is even better than commercial Degussa P25 TiO\textsubscript{2}.\textsuperscript{[195]} It is noteworthy that apart from widely investigated photocatalytic water splitting, 2D TMOs are emerging as promising photocatalysts for other value-added chemical reactions in recent years.\textsuperscript{[70,198]}

For instance, Chen et al. synthesized ultrathin, single-crystal WO\textsubscript{3} nanosheets by 2D oriented attachment.\textsuperscript{[70]} They found that the dimensionality reduction alters the bandgap of WO\textsubscript{3} such that the WO\textsubscript{3} nanosheet becomes active in the photocatalytic reduction of CO\textsubscript{2} into CH\textsubscript{4} in the presence of water. More recently, Li et al. discovered that on anatase (101)-terminated TiO\textsubscript{2}, CO can be produced via photocatalytic oxidation of CH\textsubscript{4} with a remarkably high yield of 81.9%.\textsuperscript{[198]}

They proposed that such high selectivity for CO formation stems from the existence of surface Ti\textsuperscript{3+} sites.

Despite of all the remarkable performance that have been experimentally observed, the photocatalytic application of 2D TMOs is still hindered by several shortcomings, i.e., wide optical bandgaps, poor electronic conductivity (namely high electron–hole recombination rate), or improper band edge positions for either reduction or oxidation reactions. To date, many strategies have been proposed to overcome these shortcomings.\textsuperscript{[57]}

Metal doping, nonmetal doping and introducing oxygen vacancies are reported for narrowing the wide bandgaps of 2D TMOs toward visible light harvesting by inducing gap states.\textsuperscript{[44,45,102,199–201]} As discussed before, hybridizing 2D TMOs with other materials could alleviate the impact of the poor electronic conductivity and meet the harsh requirement on the band edge positions by forming type II band alignment. Additionally, Zhou et al. recently proposed a bottom-up route to prepare the monolayer materials with ultrafast charge separation and highly active surface.\textsuperscript{[95]}

They fabricated Bi\textsubscript{1-x}WO\textsubscript{x} nanosheets with monolayer thickness and sandwich substructure of [BiO]\textsuperscript{2-}·[WO\textsubscript{3}]\textsuperscript{2-}·[BiO]\textsuperscript{2-}, where the sublayers are held together by strong chemical bonds rather than weak van der Waals interactions (Figure 7d). The presence of unsaturated Bi atoms leads to a highly active surface and a reduced bandgap is observed compared to Bi\textsubscript{1-x}WO\textsubscript{x} nanocrystals. Upon irradiation, they found ultrafast charge transfer and separation in this heterostructure-like Bi\textsubscript{1-x}WO\textsubscript{x} (photogenerated holes on the surface and photogenerated electrons in the middle layer), leading to an improved photocatalytic performance for visible-light-driven degradation of Rhodamine B and hydrogen production.

#### 5.4. Gas Sensing and Biosensing

Metal oxides are well-known gas sensing materials, i.e., WO\textsubscript{3}, TiO\textsubscript{2}, ZnO and SnO\textsubscript{2}.\textsuperscript{[202]} For 2D TMOs, the large surface area provides tremendous reactive adsorption sites for gaseous molecules. Therefore, a high response, a short recovery time and a high selectivity toward a certain target gas could be expected for 2D TMOs.\textsuperscript{[203]}

For example, Shendage et al. fabricated WO\textsubscript{3} nanoplates with a high selectivity toward NO\textsubscript{2} gas and an excellent sensing response (the ratio of the electrical resistance when WO\textsubscript{3} is exposed to NO\textsubscript{2} gas and in ambient air) at low operating temperature (10 for 5 ppm NO\textsubscript{2} and about 131.75 for 100 ppm NO\textsubscript{2} at 100 °C).\textsuperscript{[204]} The fast response-recovery capability of WO\textsubscript{3} toward NO\textsubscript{2} gas was recently reported by Harale et al., i.e., gas response time of 16 s and recovery time of 260 s at 100 ppm (Figure 7e).\textsuperscript{[205]} As another example, Alsaif et al. found that the α-MoO\textsubscript{3} nanoflakes with a thickness of \textasciitilde1.4 nm show large responses to H\textsubscript{2} gas.\textsuperscript{[206]} The response and recovery time toward 1% of H\textsubscript{2} gas are 7 and 24 s at 200 °C, respectively.

Similarly, further improvement of sensing response could be made by hybridizing 2D TMOs with other materials. Fu et al. designed a porous 2D net-like SnO\textsubscript{2}/ZnO heterostructures.\textsuperscript{[207]} It was found that the SnO\textsubscript{2}/ZnO could detect 10 ppb H\textsubscript{2}S gas at 100 °C, which is more sensitive than net-like SnO\textsubscript{2} and ZnO homostructures. Besides, Liu et al. investigated the sensing properties of ultrathin ZnO nanosheets toward ethanol.\textsuperscript{[208]}

Although the pristine ZnO nanosheets already show a high ethanol sensing response, decorating the nanosheets with CuO nanoparticles leads to further up to twofold enhanced response to ethanol vapor.

In addition to the detection of target gases, some reports suggest that 2D TMOs could be potential biosensing materials, especially 2D α-MoO\textsubscript{3} and MnO\textsubscript{2}. Balandhran et al. fabricated a field effect transistor based biosensing platform with 2D α-MoO\textsubscript{3} nanoflakes as the conduction channel.\textsuperscript{[209]} They found that this biosensor can respond to bovine serum albumin within 10 s and the detection limit is as small as 250 μg mL\textsuperscript{-1}, where the excellent response properties are ascribed to the high permittivity of 2D α-MoO\textsubscript{3}. It is noteworthy that the detection limit of α-MoO\textsubscript{3} toward bovine serum albumin recently has been pushed to 1 pg mL\textsuperscript{-1}, where heavy n-doping makes α-MoO\textsubscript{3} a plasmonic biosensing platform.\textsuperscript{[210]}

For 2D MnO\textsubscript{2}, Yuan et al. used MnO\textsubscript{2} nanosheets to construct two biosensors with respective favorable performance for ochratoxin A and cathcacin D, indicating that MnO\textsubscript{2} nanosheets could act as label-free nanoplatform for homogeneous biosensing.\textsuperscript{[211]} On the other hand, Zhai et al. investigated the mechanism for single-layer MnO\textsubscript{2} nanosheets suppressing 7-hydroxycoumarin.\textsuperscript{[212]} Based on it, they developed a new method with MnO\textsubscript{2} nanosheets for sensing ascorbic acid in vivo with improved efficiency.
5.5. Other Potential Applications

Besides the potential applications as discussed above, there are still other fields, where employing 2D TMOs would be beneficial. For example, without any guarantee for completeness, layered MoO₃ has also been extensively studied for electrochromic based systems (e.g., smart windows and optical displays).[213] Metal oxide thin films could protect metals from corrosion.[53,145,146] 2D MnO₂ nanosheets can promote pH-triggered theranostics of cancer.[214] Apart from photocatalysts, CeO₂ nanosheets with 20% pit occupancy exhibit 50% CO conversion at 131 °C, whereas porous Co₃O₄ nanosheets are found as a promising electrocatalyst toward oxygen evolution reaction.[101,105] Besides, 2D ZnO nanosheets and their derivatives are reported for efficient direct current power generation.[48–50]

6. Conclusions and Future Perspectives

In this paper, we have summarized recent advances on the state-of-the-art synthetic and theoretical aspects of 2D TMOs, the interfacial interactions between 2D TMOs and substrates/2D materials, and potential applications. In the past decades, the emergence of multiple synthetic methods (e.g., PVD, self-assembly, template-assisted synthesis, and liquid metal-based reaction route) have made more and more 2D TMOs achievable experimentally, especially those 2D TMOs whose bulk counterparts are not naturally layered. Besides, the use of atomic oxygen source might be beneficial for the formation of crystalline oxide layers. We may expect that the family of 2D TMOs will be further expanded with the development of novel cost-effective and scalable synthetic approaches. Following synthetic improvement, 2D TMOs have been studied and demonstrated as candidate materials for a wide range of applications, such as energy storage devices and photocatalysis. Although great progress on 2D TMOs has been made, there are still some remaining challenges.

For layered metal oxides, most share similar structures: negatively charged slabs with intercalated alkaline cations. Therefore, cation exchange-assisted liquid exfoliation is applicable to produce most layered 2D metal oxides. However, when thinned to atomic thickness, nonlayered 2D metal oxides likely undergo pronounced structural reconstruction due to polarity compensation and other substrate-induced effects. PVD turns out to be a powerful technique for depositing varying amounts of nonlayered 2D oxides, in particular on metal substrates. But the strong oxide-metal interaction makes it challenging to peel off and transfer the as-grown nonlayered 2D oxides. Therefore, various alternative methods have been proposed to directly fabricate freestanding nonlayered 2D oxides. In consequence, unlike the synthesis of layered 2D metal oxides, the growth of nonlayered 2D oxides so far relies on a rather large number of methods. Attention should be paid to the development of cost-effective and scalable synthetic techniques for 2D metal oxides, especially the nonlayered ones.

Identification of atomistic structures is more challenging for 2D TMOs that are not naturally layered. Many studies have indicated prominent structural reconstructions of 2D TMOs in comparison to corresponding bulk materials.[22–26,106,215] For instance, Lundgren et al. reported that the 2D Pd₃O₄ overlayer grown on Pd (111) exhibits no resemblance to bulk oxides of Pd.[22] Tusche et al. observed that when the thickness of ZnO is less than three or four layers, the as-synthesized ZnO exhibits a graphene-like structure in contrast to the bulk wurtzite structure.[215] A decrease in the number of dangling bonds and the suppression of surface polarization are responsible for the distinct difference between 2D TMOs and their bulk materials.[124] Such difference might make it very difficult to figure out the atomistic structures of 2D TMOs. Applications of 2D TMOs will be definitely impeded without the detailed atomistic structures. Therefore, in addition to synthesis of new 2D TMOs, more efforts should be made to identify atomistic structures of 2D TMOs both experimentally and theoretically.

We note that recent studies have shown improved efficiency and accuracy on the structural prediction and identification of bulk materials by employing machine learning or optimizing theoretical and experimental data simultaneously.[216–218] Similarly, we can expect that those methods will be extended for 2D materials in the near future, and their combination with the high-throughput calculations might further result in more effective and efficient structural prediction and identification of 2D TMOs.

It will be also interesting to study the exotic physical and chemical properties of the oxide layers in the 2D limit. The dimensionality reduction and strong structural reconstruction might lead to very different properties compared with their parent bulks. For example, the Coulomb screening is much reduced due to the lower dimension in the 2D TMOs, which might give us more strongly bound excitons.[119] Moreover, lattice vibrations or electron–phonon interactions in 2D TMOs may also be different from that of the bulk oxides. So ferroelectricity, polaronic effect, or superconductivity might also emerge in the 2D TMOs, as inferred by recent investigations in other 2D materials, i.e., MoS₂ and CrBr₃ monolayers.[219–221]

With respect to applications, the nature of layered structures makes layered metal oxides promising electrode materials for supercapacitors or batteries. For nonlayered metal oxides, the dimensionality reduction leads to a large number of dangling bonds and chemically active sites, based on which we may expect that nonlayered 2D metal oxides probably have excellent catalytic or sensing applications. However, the potential applications of layered and nonlayered 2D metal oxides definitely go beyond those based on such intuitive structural analysis. For example, Peng et al. reported that holey nonlayered metal oxides (e.g., Fe₂O₃, Co₃O₄, Mn₃O₄, etc.) are promising anode materials for batteries,[189] whereas α-MoO₃ has been identified to be a potential gas- or bio-sensing material.[206,209] In particular for nonlayered 2D metal oxides, their potential applications might be dramatically extended by considering their diverse metastable phases. It is worth investigating properties and potential applications of these metastable phases of 2D metal oxides.

As discussed, the interfacial interaction of 2D functional materials with substrates or 2D materials is of importance for applications.[44,106,122,141,174,176,207,208,222,223] Zavabeti et al. synthesized 2D HFO₂ sheets with a minimum thickness of ≈0.5 nm and found that the HFO₂ nanosheets have a large dielectric constant of ≈39 and a wide bandgap of ≈6 eV.[31] To integrate
the high-k HfO₂ nanosheet into field-effect transistors, the interfacial interaction between 2D HfO₂ and channel materials must be taken into account. Additionally, hybridization of 2D TMOs with other materials has been proven to effectively overcome shortcomings and enhance performance of 2D TMOs for a variety of other applications, such as extension of the light absorption range and improvement of charge transport for photocatalysis and enhancement of sensing response for gas sensors. [44,207,223] Despite the fact that theoretical calculations are a more cost-effective approach to understand the high-interfacial interaction between 2D TMOs and substrates/2D materials, theoretical studies are severely lacking in this regard. Intensive collaboration between experimental and theoretical researchers should be made and might speed up the realization of practical applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, interfacial interaction, structural re-construction, ultrathin transition metal oxide

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