ARTICLE OPEN Asymmetric MXene/monolayer transition metal dichalcogenide heterostructures for functional applications

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A versatile two-dimensional (2D) molecular bilayer heterostructure of asymmetric MXene/monolayer transition metal dichalcogenide (aMXene/mTMDC) with a high interfacial built-in electric field is here simulated, where aMXene is an aMXene with the top or bottom electronegative atom plane of MXene removed. The asymmetric structural design of aMXene leads to a high dipole moment perpendicular to the 2D molecular plane. Although the unpassivated metal atoms in the aMXene are unstable and electropositive, coupling them to the electronegative chalcogenide atoms in an aMXene/mTMDC bilayer resolves this deficiency. The dipole field tunable by the specific composition of aMXene/mTMDC is leveraged to engineer unusual band structures, band alignments, and charge redistribution/injection in the bilayer. The simulated design of several aMXene/mTMDC bilayers for possible use in spintronics, microelectronics/optoelectronics, and catalysis/photocatalysis are shown.

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INTRODUCTION

A heterostructure merges together two different materials and can thus yield synergetic properties and applications. With the discovery and development of atomic monolayer materials, such as graphene,^{1,2} and molecular monolayer materials,³ such as monolayer transition metal dichalcogenides^{4–11} (referred to as mTMDCs therein), and monolayer boron nitride, the most elegant form of a heterostructure can be realized by synergetically coupling two different stable atomic/molecular monolayers.^{12–25} Indeed, novel hetero-bilayers such as mTMDC/graphene,^{6,13,16} graphene/mTMDC/graphene,²⁵ mTMDC/hBN,¹⁴ mTMDC/hBN/graphene,¹⁴ and monolayer phosphorus/mTMDC¹⁷ have been demonstrated, with versatile industrial relevance to electronics/ optoelectronics,^{12–21} spintronic devices,²¹ energy-storage devices,²² and catalysts.^{23,24} In comparison to the well-known and form its stable atomic form is a stable store.

In comparison to the well-known and functionally versatile mTMDCs, the monolayer family of "MXene"²⁶⁻³² is much younger in development, but it holds a rather unique competitivity against other molecular monolayers. In brief, MXene is a 2D molecular monolayer formed with its central core comprising a stack of "metal-carbon-metal" atom plane. The construction of a stable and free-standing MXene, however, requires the termination of the two electron-rich metal surfaces with electron-accepting groups such as O, F, and OH. These passivating groups are typically referred to as the T groups. Hence, a MXene has a stack of T{M (CM)_i}T, with M in the experimentally known MXenes being Ti, V, Nb, Ta, Ti_{0.5}Nb_{0.5}, and V_{0.5}Cr_{0.5}.^{30,31} Like mTMDCs, MXenes can be semiconducting or metallic; hence, MXenes also share the excellent industrial relevance to energy conversion,³³ energy storage,³⁴ water purification,³⁵ chemical sensors,³⁶ photo- or

electro-catalysis,³⁷ and biomedical^{38,39} applications. Following the rise of MXenes, bilayer heterostructures comprising MXenes emerge quickly. For example, MXene/mTMDC bilayers have already been studied computationally,^{40–43} and those bilayers with the MXene composition of $\{(OH)_xF_{1-x}\}$ TiCTi $\{(OH)_xF_{1-x}\}$ and the mTMDC composition of MOS_2 or WS₂ have been synthesized to form functional nano-field-effect transistors.⁴⁴ In short, the development of bilayer heterostructures comprising MXene or MXene-like monolayers is expected to bear important impacts.

Herein, we disseminate our invention of another new bilayerheterostructure family with a special derivative of MXene as a monolayer constituent. Specifically, this derivative can be created by replacing one of the two T planes of an MXene by an mTMDC. Alternatively, it can also be created by using the mature chemical vapor deposition (CVD) or atomic layer deposition (ALD) approach to deposit one monolayer of metal carbide onto an mTMDC and to subsequently oxidize the top-layer metal atoms. In fact, CVD of large-area, high-quality ultrathin Mo₂C has already been successfully demonstrated.^{45,46} This special derivative of MXene is referred as "asymmetric MXene (aMXene)" to differentiate the obvious asymmetry in $T{M(CM)_i}$ from the structure of $T{M(CM)_i}$. This invention is important because an aMXene has an unusually high dipole perpendicular to the 2D plane to qualify its competitive advantage as outstanding molecular monolayers. The invention is also practical because aMXene/mTMDC is a stable bilayer heterostructure. Indeed, asymmetric 2D monolayer structures such as SMoSe^{47,48} and bilayer heterojunctions such as (Cl₂)-(Bi₁₂O₁₇)-(MoS₂)⁴⁹ have been successfully synthesized. To articulate the chemistry, physics, and engineering applications of aMXenes, we adopt aMXene/mTMDC bilayers as exemplars of all

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possible aMXene-based bilayers and draw a set of design rules for the application-oriented development of aMXene/mTMDC bilayers.

The essence of our invention is drawn with the first-principles computational approach with which we survey a vast variety of aMXene/mTMDC combinations and distill from the database of electronic structures and properties those combinations satisfying the currently market-driven application-oriented requirements. Particularly, from such a computational study (as specified in computational methods), we draw design rules covering the choice of the chemical constituents and the synthetic route in making stable aMXene/mTMDC for: (a) spintronics, applications that require proper manipulation of spin polarization; (b) efficient optoelectronics and fast electronics, applications that require proper band structures, proper charge redistribution, and quantum confinement; (c) catalysis, applications that require proper band structures and proper alignment of band structures with the chemical potentials of the relevant catalytic reaction. Obviously, these design rules are also drawn with the objectives of demonstrating the important engineering functions derived from the asymmetry and dipole nature of aMXenes.

RESULTS AND DISCUSSION

An aMXene monolayer is not stable by itself and is best stabilized by a stable monolayer partner having surface termination with electronegative atoms to form a stable functional bilayer heterostructure. While MXenes are known to be thermodynamically and chemically stable, our proposed aMXenes are unstable due to the disruption of the proper surface passivation in MXenes. As such, the first and most important design rule for the development of practical aMXenes is drawn to address this instability. An aMXene is best deposited on a stable monolayer partner having surface termination with electronegative atoms to pair with the "bare" electropositive metal atoms on the unpassivated surface of an aMXene.

Particularly, mTMDC is chosen as the exemplary monolayer partner because mTMDC bears important scientific and technological impacts by itself, and because the chalcogenide surface termination of mTMDC perfectly satisfies the present design rule of adopting an electronegative partner to stabilize aMXene. The origins of such interfacial stabilization are clearly shown by the following bonding parameters that are deduced from the geometry-optimized configurations of the representative aMXene/mTMDC examined in the present work (details of all such configurational data are included in Part A of Supplementary information):

(a) The Heyd–Scuseria–Ernzerhof (HSE) calculated exothermic binding energies of the aMXene/mTMDC bilayer complexes range 0.2-0.95 eV per unit cell, as shown in Table S2. For comparison, the Perdew-Burke-Ernzerhof (PBE) calculated binding energies are in the even higher range of 0.49-1.36 eV (Table S3). As such, aMXene/mTMDC complexes are stable. In comparison, the binding energy for chemically stable complexes formed by hydrogen bonding typically ranges from 0.2 to 0.4 eV, and common van der Waals bonds with the binding energy in the range of 0.1-0.3 eV⁵⁰ are weaker than hydrogen bonds, but are still strong enough to yield stable 2D van der Waals heterostructures with TMDCs. As shown in Table S2, MoS2 and MoSe₂ in the Sc₂CO/MoS₂ and Sc₂CO/MoSe₂ heterostructures are enlarged by 5.26 and 2.24%, while they are compressed by <4.94% in the other aMXene/mTMDC heterostructures. The aMXene monolayers also bear some strains to construct heterostructures, where the largest strain of 5.58% occurs to the V₂CO monolayer in V₂CO/MoSe₂.

- (b) The extent of charge redistribution at the interface is adequately high and compositionally tunable (0.16-0.6 electron per metal-chalcogenide pair), as calculated by the standard Bader method, 51-53 and shown in Table S4. The Ti₂CO/MoS₂ bilayer is the highest and Cr₂CO/MoSe₂ is the lowest in charge transfer among all aMXene/mTMDC complexes analyzed in this work. These data and additional pictorial presentations of charge distribution and transfer (Figs. S2 and S3, illustrated in Part B of Supplementary information) further articulate the relevant chemical interactions and bond formation. More importantly, charge distributions also link bonding chemistry to device engineering and catalyst development because adequate charge injection to the conduction/valence band of an optoelectronic/electronic device is the key in device engineering and charge injection to a critical reaction transition state is also fundamental to catalysis.
- (c) The aMXene/mTMDC bilayers have relatively small interfacial separations of 0.18–0.25 nm. These values are significantly shorter than the relevant interfacial separations including 0.31 nm for MoSe₂/MoS₂,⁵⁴ 0.28 nm for Zr₂CO₂/ MoS₂⁴⁰ and other MXene/mTMDC bilayers,⁴² and 0.33 nm for Sc₂CF₂/MS₂ and Sc₂CF₂/MSe₂ (M = Mo, W).⁴¹ Among all these bilayers, Ti₂CO/MoS₂ has the shortest interlayer separation (0.18 nm) and thus has the strongest interfacial interactions with the binding energy of 1.36 eV per unit cell. In these bilayers, Cr₂CO/MoS₂ is the weakest in bilayer interaction with the longest interlayer separation of 0.23 nm and a binding energy of 0.70 eV per unit cell. The interlayer separations for Sc and V are both 0.20 nm.

With the evidence of the stability of aMXene/mTMDC bilayers, we stress that aMXene/mTMDC can be readily synthesized with the prevalent method of forming molecular-layer materials by ALD. This synthetic route is viable because monolayer mTMDCs can now be routinely synthesized by direct vapor deposition and solvothermal precipitation of monolayer mTMDCs, and by chemical exfoliation of bulk mTMDCs. With a monolayer mTMDC as a substrate, one can adopt the known techniques of metalcarbide ALD⁵⁵⁻⁶¹ to deposit a stack of M(CM)_i and yield aMXene/ mTMDC by oxidizing the top surface of the M(CM), stack of metal carbide, or by other similar surface passivation reactions. We note that recently single-layer titanium carbide has been successfully grown on the MXene of Ti_3C_2 .⁶² Conceivably, the same single-layer titanium carbide can also be grown on mTMDC, and the subsequent oxidation of the top metal atom layer can yield aMXene/mTMDC heterostructures.

After establishing the viability of making aMXene/mTMDC, we would like to articulate the rich chemistry in the exemplary family of aMXene/mTMDC bilayer complexes, with the best known mTMDC (MOS_2) and with the best obvious choices of aMXenes (those with Sc, Ti, V, and Cr as the metal constituents) to construct aMXene/mTMDC. To clarify the bonding details, we adopt the scheme of $OM_{-O}CM_{-S}/S_{-M}OS_{-Mo}$ (with the small font labels describing the local chemical bonding condition) to describe the stack of atomic planes in these aMXene/MOS₂ bilayers.

To comprehensively complete the analysis of chemical nature and its implications for these aMXene/MoS₂ bilayers, we adopt the spin-polarized HSE calculation methods to track the atomic origins of unpaired spins and magnetic moments, and to draw later a design rule from such fundamental information for spintronics, optoelectronics, and catalysis. Briefly, while those bilayers with aMXene comprising Sc and Ti have near-zero magnetic moments, as shown in Table S4, those comprising V and Cr have rather high magnetic moments. Based on a 2×2 supercell, we consider four types of magnetic orderings including ferromagnetism (FM) and A-, C-, and G-type anti-FM (AFM) for the V and Cr atoms in the V₂CO/MoS₂ and Cr₂CO/MoS₂ bilayers, as shown in Fig. S4. Our full-optimization computation shows that the A-type ferrimagnetic ordering is the energetically favorable configuration with 0.35 and 0.52 eV per unit cell lower than the energies of the C-type ferrimagnetism for the V2CO/MoS2 and Cr2CO/MoS2 bilayers, respectively. In addition, the initially assigned FM and G-type AFM configurations are optimized to be A-type and C-type ferrimagnetism, respectively. In the A-type ferrimagnetic ordering, the magnetic moments are aligned parallelly and equally within each layer, but alternate in sign and values between layers, as displayed in Fig. S5. In addition, Table S4 shows that the respective atomspecific magnetic moments are 1.57 and $-1.23\mu_B$ for the V_{-O} and V_{-s} atoms in the OVCV/SMoS bilayer stack, and 2.80 and $-2.92\mu_B$ for the Cr-O and Cr-S atoms in the OCr-OCCr-S/SMoS stack. These results clearly show that the V₂CO/MoS₂ and Cr₂CO/MoS₂ bilayers comprise strong magnetic moments and are adequate for spintronic applications.

An aMXene monolayer can offer a large dipole moment and thus a high built-in electric field. The simplest aMXene comprises a stack of OMCM atom planes and is referred to as M₂CO therein. Electrons are depleted at the M-terminated side and accumulated at the oxide face of such a simple stack. This polarization induces an internal electric field $\overline{E_1}$ with the direction pointing from the M termination to the O termination. Due to the presence of such an electric field, the emission of electrons is much more difficult on the O-terminated face than on the M-terminated face. In other words, the work function of M₂CO is highly face-dependent, with the work function of the Oterminated face much higher than that of the M-terminated face, as shown in Fig. 1a. Our results on the work functions, spatial electrostatic potential distributions, built-in electric fields, and band alignments of several aMXene/mTMDC examples are summarized in Fig. 1b, with the results on dipole moments included in Fig. 2. Clearly, aMXene/mTMDC bilayers can be designed to compete with other bilayers by taking advantage of the asymmetric and uniquely strong dipolar nature of aMXenes.

Here, we take Sc₂CO/MoS₂ as an example to articulate the dipolar nature of aMXene/mTMDC bilayers, with the labeling protocol of OSc_OCSc_S/S_Sc MoS_Mo to clarify atom locations in the OScCSc/SMoS stack. The aMXene of Sc₂CO has a very strong dipole moment of 0.21 e.Å by itself. Upon the bilayer stack formation, each electropositive Sc.s atom loses 0.24 electrons and each electronegative S_{-Sc} atom gains 0.32 electrons, as shown in Table S4, with additional charge transfer participants to balance the loss/gain of charge. Such a complex process of interfacial charge transfer further increases the original internal electric field $\vec{E_1}$ in Sc₂CO but, at the same time, induces another electric field $\vec{E_2}$ in the opposite direction pointing from Sc_{-S} to S_{-Mo}. This field $\overline{E_2}$ automatically limits the drainage of electrons from Sc_2CO to MoS_2 , and its presence makes the dipole moment of the bilayer of Sc₂CO/MoS₂ smaller than that of the free-standing Sc₂CO monolayer, as shown in Fig. 2. In comparison to the case of Sc_2CO/MoS_2 , the dipole reduction during the formation of $Cr_2CO/$ MoS₂ is smaller because the interfacial interaction of Cr₂CO/MoS₂ is weaker than that of Sc₂CO/MoS₂. As such, the interfacial charge transfer, the strength of $\vec{E_2}$, and the dipole reduction induced by bilayer formation are all compromised accordingly. From the MoS₂ side of Sc_2CO/MoS_{2r} one sees that the electrons donated from Sc_2CO are mainly kept around the S_{-Sc} atoms, as shown in Table S4 and Fig. S2. Hence, the field $\vec{E_2}$ is not evenly distributed but highly spatially localized near the bilayer interface, as shown in Fig. 1b.

Some additional results on several other examples of aMXene/ mTMDC bilayers are included in Fig. S6 in part C of Supplementary information. Consistently in all these aMXene/mTMDC bilayers, the electrons injected from aMXene to mTMDC are highly localized at



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Fig. 1 a The comparison of work functions of the isolated aMXene M_2CO (M = Sc, Ti, V, Cr) and MoX_2 (X = S, Se), evaluated by the difference between vacuum level (VL) and Fermi levels (E_f). The vacuum levels of metal side in M_2CO and MoX_2 are shifted to 0 eV. **b** The plane-averaged electrostatic potential difference of M_2CO and MoS_2 after the formation of M_2CO/MoS_2 heterostructures. The balls and arrows stand for the atom positions and the direction of the internal electric field, respectively

the aMXene/mTMDC interface. If the mTMDC constituent is an intrinsic semiconductor (like MoS₂ and MoSe₂), the internal electric field turns it to n-type, and the electrons injected from aMXene are accumulated in the conduction band edge of the mTMDC and spatially localized at the aMXene/mTMDC interface. Such details and the relevant applications are illustrated and explained later.

Spintronics can be designed with aMXene/mTMDC having adequate constituents to engineer appropriate spin-polarization and spin-specific properties. The combination of both semiconducting and spin-specific properties in some aMXenes and mTMDCs offers a rather unique opportunity for the development of novel spintronics with our proposed aMXene/mTMDC bilayer heterostructures. Since the spin-specific nature of mTMDCs, particularly those of VS₂ and VSe₂,^{63,64} have already been adequately reported, we focus on the nature of V₂CO/MoS₂ and Cr₂CO/MoS₂ to demonstrate how spintronics can be developed by coupling spin-specific aMXenes to mTMDCs having no spin polarization.



Fig. 2 The HSE calculated dipole moments of the most stable a MXene M_2CO and $M_2CO/MoX_2~(M=Sc,\ Ti,\ V,\ Cr;\ X=S,\ Se)$ heterostructures

The band structures shown in Fig. 3a, b, as well as Fig. S8a, b highlight such opportunities in developing spintronics with $V_2CO/$ MoS₂ and Cr₂CO/MoS₂, as well as V₂CO/MoSe₂ and Cr₂CO/MoSe₂. First, the semiconducting nature of MoS₂, and then the halfmetallic properties of V₂CO and Cr₂CO (Fig. S7a, b) are largely preserved in their complexes, likely due to the relatively weak interfacial interactions in V₂CO/MoS₂ and Cr₂CO/MoS₂ in reference to all aMXene/mTMDC complexes analyzed in this work. More specifically, the partial band structure assignable to MoS₂ shows a bandgap of about 2.0 eV, good for electronic applications requiring a wide operational range in temperature. For the case of V_2CO/MoS_2 (Fig. 3a), the partial band structure of V_2CO shows a very narrow bandgap (about 0.1 eV) in the spin-up channel. In this channel, the Fermi level of the bilayer crosses the edge of the conduction band, with the CBM locating between the K and G points and valence band maximum (VBM) staying at the K-point. More importantly, the CBM mainly comprises the hybridized Mo-4d, S_{-V} -3p, and S_{-Mo} -3p orbitals belonging to the MoS₂ constituent and VBM mainly comprises the V_{-S} -3d states belonging to the aMXene constituent, and this facilitates desirable spatial charge separation when e-h pairs are produced in V₂CO/MoS₂. Overall, our results show an approximate device model of V₂CO/MoS₂ in which V₂CO forms an ohmic contact on n-type MoS₂.

In the spin-down channel, V₂CO/MoS₂ shows a rather dispersed band structure around the Fermi level. Although the MoS₂ bands hybridize with V₂CO to some extent, the characteristics of MoS₂ can still be identified at the vicinity of the Fermi level, as marked by the blue circles in Fig. 3a. Most importantly, the Fermi level lying in the band gap of MoS₂ and the partial bands of V₂CO show the presence of an n-type Schottky barrier with the height of 0.49 eV. As such, electrons are transferred from V₂CO to MoS₂ via the spin-up channel while the transfer is hindered in the spindown channel, due to the presence of a very small band gap in the spin-up channel and of a large Schottky-barrier height in the spin-down channel. Therefore, the spintronic function of spin filtering can be realized in the V₂CO/MoS₂ bilayer.

In the case of Cr₂CO/MoS₂, the presence of a striking halfmetallic magnetism is evident, as shown in the band-structure results in Fig. 3b. Specifically, an intrinsic semiconductor feature is found in the spin-up channel and a metallic-like character appears in the spin-down channel. The half-metal gap ($E_{hg} = E_f - E_{VBM}$) is calculated to be 0.88 eV, suggesting that electrons transported near the Fermi level are virtually 100% spin polarized even when the heterostructure is under a relative large external voltage bias. In contrary to the case of V₂CO/MoS₂, electron transport is impeded in the spin-up channel, but facilitated in the metallic-like spin-down channel. It is important to note that the partially occupied bands crossing E_f along the high-symmetry zone axes of G–M and K–G in the spin-down channel, as shown in Fig. 3b, are mainly hybrids of Cr_{-S} -3d and Mo-4d states. This critically shows the spintronic function of spin injection from Cr_2CO into MoS_2 in Cr_2CO/MoS_2 can be readily realized. In this context, V_2CO/MoS_2 is inferior to Cr_2CO/MoS_2 .

The spintronic operation in Cr_2CO/MOS_2 is expected to facilitate fast electron transport with several good reasons. First, the bands crossing the Fermi level are largely dispersed, as shown in the right panel of Fig. 3b. This suggests high electron mobility. Second, electron injection from Cr_2CO/MOS_2 is facilitated by the special asymmetric and dipolar nature of aMXene, not by the reliance of dopants and defects. As such, detrimental deficiencies in ordinary approaches of designing and fabricating MOS_2 electronics, such as Coulombic impurity scattering,⁶⁵ deficiencies which bar high carrier mobility, are circumvented in aMXene/ mTMDC bilayers, with Cr_2CO/MOS_2 as an exemplar. Third, only spin-down electrons participate in the spintronic operation of Cr_2CO/MOS_2 ; this also further supports fast transport.

With the promising results on Cr_2CO/MoS_2 , we extend the investigation to $Cr_2CO/MoSe_2$, Cr_2CO/WS_2 , and Cr_2CO/WSe_2 ; unsurprisingly, all these bilayers possess similar half-metallic properties (see Fig. S8(b) and S9 in Part E of Supplementary information). The origin of the magnetism is further explained by Fig. S10 in Part F of Supplementary information.

Efficient optoelectronics and fast electronics can be designed with aMXene/mTMDC having adequate semiconducting constituents to facilitate optoelectronic and fast-electronic operations. Since many known MXenes are semiconductors with very high carrier mobility and many mTMDCs have bandgaps around 1-2 eV with reasonably high carrier mobility, aMXene/mTMDC bilayers can potentially function as high-efficiency optoelectronics and fast electronics. Further, the bilayer formation does not simply juxtapose the two sets of virgin band structures of the two monolayer constituents but promises additional merits. For example, prior to forming a bilayer, Sc₂CO and MoS₂ are calculated to be two semiconductors with respective bandgaps of 0.55 (Fig. S7(c), as well as Fig. S11 in part G of Supplementary information) and 2.21 eV, and with a rather large band offset. In addition, the electron affinity of Sc₂CO is much smaller than that of MoS₂ and $MoSe_2$, as shown in Fig. 4. In the Sc_2CO/MoS_2 bilayer, the positively charged Sc.s atom of Sc2CO, with the loss of 0.24 electrons during the bilayer formation (Table S4), sets a strong field to push the conduction band of the underlying MoS₂ constituent all the way down until it crosses the Fermi level of the bilayer. As such, the MoS₂ constituent is an n-type 2Dsemiconducting molecular layer. At the same time, the negatively charged S-Sc atom, with the gain of 0.36 electrons during the bilayer formation (Table S4), also sets an opposite field to pull the valence band of the overlaying Sc₂CO constituent all the way up until it touches the Fermi level of the bilayer. As such, the Sc₂CO constituent is a p-type 2D-semiconducting molecular layer. Therefore, a peculiar heterostructure having a p-type 2Dsemiconducting molecular layer on an n-type 2D-semiconducting molecular layer is constructed. Across the 2D plane, the bilayer is metallic-like with electron transport responsible for electrical conductivity along the MoS₂ layer, and with hole transport responsible for electrical conductivity along the Sc₂CO layer. As discussed earlier, these carrier transports are expected to be highly mobile because the carrier generation is induced by an adequate electric field and not by doping. As such, mobility reduction by scattering is prevented. While fast carrier transport along the bilayer plane is facilitated with no directional restriction, any current flow crossing the plane is dictated and directionally controlled by the rectifying diode property of the p-n junction.

Importantly, a thorough examination of the band structure evolution during the Sc_2CO/MoS_2 bilayer formation shows that the



Fig. 3 The HSE calculated spin-polarized band structures of V₂CO/MoS₂ **a**, Cr₂CO/MoS₂ **b**, Sc₂CO/MoS₂ **c**, and Ti₂CO/MoS₂ **d** heterostructures. The components and weight of the orbitals are represented by the bubbles in different color and size, respectively. The Fermi level is shifted to 0 eV



Fig. 4 The band alignment of Sc_2CO and MoS_2 a, as well as Sc_2CO and $MoSe_2$ b

interlayer charge re-distributions also wipe out nearly all density of states (DOS) of Sc₂CO from its VMB to 3.0 and 3.5 eV above the VBM, and nearly all DOS of MoS₂ from its CBM to 2.01 and 1.68 eV below this CBM in the spin-up and spin-down channels, respectively. In addition, the respective effective masses of hole $(m_{\rm h}^*)$ and electron $(m_{\rm e}^*)$ of MoS₂ part in Sc₂CO/MoS₂ at the Kpoint are 0.12 and $0.08m_{\rm e}$ and are much smaller than the values of the pristine single-layer MoS_2 .^{66–68} As such, the carrier mobility in MoS₂ of Sc₂CO/MoS₂ can be significantly improved. This set of data, which are included in Fig. S12 in part G of Supplementary information, and the band-structure data in Fig. 3c thus show the presence of a p-n junction with an extremely large built-in voltage and with high carrier mobility. We expect that with a small external bias, the diode is conductive via electron tunneling across the junction. With a moderate forward bias, the diode returns to its normal-off state and supports no current flow. After reaching an appropriate forward biasing, the diode allows a current flow with the typical operation of a forward-biased diode.

In addition, the peculiar band structures of the Sc_2CO/MoS_2 bilayer also imply that the bilayer can absorb photon irradiation in the solar spectrum for the generation of electron-hole pairs, mainly with electrons from the filled DOS derived from the Sc_{-S} and C atoms of Sc_2CO to the empty DOS derived from the Mo atoms of MoS_2 . As such, photo-induced electron-hole pairs are very well spatially separated. Undesirable electron-hole recombination is thus prevented, and high-performance optoelectronics can thus be designed.

Similar to Sc₂CO/MoS₂, partially occupied bands crossing the Fermi level are also present in the band structure of Ti₂CO/MoS₂. Thus, Ti₂CO effectively serves as an ohmic contact and an agent to maintain MoS₂ as an n-type semiconductor (Fig. 3d). The strong interfacial interaction in Ti₂CO/MoS₂ alters the partial band structures of Ti₂CO and MoS₂ significantly from the free-standing monolayer counterparts. The spin-polarizing property of the pristine Ti₂CO (Fig. S7(d)) induced by the unpaired electrons almost vanishes in the Ti₂CO/MoS₂ complex. The partial band structure of MoS₂ shows a bandgap of around 1.2 eV, significantly smaller than that of the free-standing monolayer MoS₂. Nevertheless, this bandgap is large enough for electronic operation in a wide temperature range.

Catalysts and photocatalysts can be designed with aMXene/ mTMDC having adequate constituents to supply electrons/holes at an appropriate chemical potential for the facilitation of catalytic reactions. Since the controllable internal electric field of an aMXene/mTMDC can be tuned by its bilayer composition, this tunability is a powerful means to adjust the electronic states of the constituents of the aMXene/mTMDC to match the chemical potential requirement of a specific chemical reaction for enhancing the reaction rate. For example, MoS₂ and other mTMDCs are known to catalyze the hydrogen evolution reaction (HER: $2H^+ + 2e \rightarrow H_2\uparrow$), as long as the location of the reduction potential in reference to the standard hydrogen electrode is below the

conduction band minimum of the mTMDC catalyst. In principle, this "state-alignment" condition is satisfied in the case of MoS₂ because the reduction potential for HER is indeed below the conduction band of MoS₂. As such, an n-type MoS₂ with an ohmic contact to supply a flow of electrons can adequately facilitate HER. In another scenario, an intrinsic semiconducting MoS₂ can also facilitate HER under the irradiation of photons having high enough energy to excite electrons from the valence band to the conduction band. In practice, an applied voltage bias of the MoS₂ electrode in the reaction bath is required to push forwards the HER, and such an additional reaction requirement is often referred to as a means to overcome the overpotential of the electrode. This overpotential problem typically is caused by the presence of surface states and thereby a surface band bending on the electrode surface. The presence of the strong internal electric field and dipole moment in aMXene/mTMDC can be engineered to circumvent this overpotential problem.

In compliance to the present Design Rule, the band structures of Sc₂CO/MoS₂ and Ti₂CO/MoS₂ shown in Fig. 3c, d indicate that both are good catalysts for HER because Sc₂CO and Ti₂CO in these M₂CO/MoS₂ bilayers are both narrow bandgap materials and readily serve as an ohmic contact to supply a flow of electrons to MoS₂. Further, the presence of Sc₂CO or Ti₂CO exerts an appropriate electric field to maintain MoS₂ as an n-type semiconductor with Fermi level well above the reduction potential for HER. The schematic energy diagrams in Fig. 1b pictorially show that these M₂CO/MoS₂ bilayers analyzed in this present work can outperform MoS₂ in HER catalysis. Indeed, the expectation is verified by the HER calculations. The Gibbs free energy changes $\Delta G_{\rm H}$ are -0.3 and 4.4 meV for one H adsorption at the S-vacancy site on the 3×3 MoS₂ supercell basal plane of the Sc₂CO/MoS₂ and Ti₂CO/MoS₂ bilayers, respectively. In comparison, the value of $\Delta G_{\rm H}$ is calculated to 68.2 meV for the free-standing MoS₂ with the same S-vacancy concentration, and the result is consistent with other theoretical results.6

Judging by the recent development in both practical synthesis and HER applications of nanopolygons of mTMDCs,^{10,70,71} we add here that deposition of proper aMXene on nanopolygon mTMDC instead of large domains of mTMDCs is the best way to engineer the next generation of highly effective HER catalysts.

In closing this section by designing effective catalysts with aMXene/mTMDCs, we add that while engineering HER catalysts with aMXene/mTMDCs of Sc_2CO/MoS_2 and Ti_2CO/MoS_2 is scientifically sound, these Sc_2CO/MoS_2 and Ti_2CO/MoS_2 bilayers both have interfacial interactions that shrink the bandgap of the partial band structure of MoS_2 significantly in reference to the bandgap of the free-standing monolayer MoS_2 . Although HER is facilitated, the half-reaction of oxygen evolution reaction (OER) in water splitting is not supported. Interestingly, the band structures of bilayers with weak interfacial interactions, such as V_2CO/MoS_2 and Cr_2CO/MoS_2 (Fig. 3a, b), seem to fit the design attributes for

catalyzing both HER and OER. In short, aMXene/mTMDCs expand the horizon of catalysis with 2D molecular layers.

In conclusion, a new 2D molecular-layer family, aMXenes, is created by shaving off the surface-passivating atoms/functional groups on one of the two faces of an MXene. Practically, an aMXene is made and stabilized by depositing a metal-carbide stack on a substrate surface terminated with electronegative atoms/functional groups. When the substrate is also a molecular monolayer such as mTMDC, an omnipotent bilayer is yielded. We show that such aMXene/mTMDC bilayers are stable and can be best made by ALD. We also show that the unique strong dipole nature of aMXene can be translated to a large variety of novel electronic structures and innovative applications in aMXene/mTMDC. The same design concepts can be adopted to develop other aMXene/2D-monolayer heterostructures.

METHODS

Spin-polarized first-principles calculations were performed by using the Vienna Ab initio Simulation Package (VASP).⁷² The projector augmented wave (PAW) potentials⁷³ were used for the treatment of core electrons. The exchange correlation interactions were treated within the generalized gradient approximation using the PBE functional.⁷⁴ In addition, we applied the Heyd–Scuseria–Ernzerhof (HSE)^{75–77} method to calculate the electronic structures, in order to overcome the deficiency of standard Density Functional Theory (DFT) in describing the exchange correlation energy. To avoid interactions between the slabs along the vertical direction, a vacuum layer with the total thickness of 3.0 nm was used at the both sides of the heterostructures. The energy cutoff was set to 450 eV and a force tolerance of 0.02 eV/Å on each atom was used for convergence criterion. For HSE calculations, the exact exchange contribution is represented by a combination of 25% HF (exchange with exact) and 75% PBE. The Monkhorst-Pack⁷⁸ K-points sampling of $15 \times 15 \times 1$ and $7 \times 7 \times 1$ were employed in the conventional DFT and HSE calculations, respectively. The interfacial adhesion energy (E_{adh}) is calculated by: $E_{adh} = E_{MXene} + E_{TMD}$ E_{heteror} in which E_{heteror} , E_{TMD} , and E_{MXene} represent the total energies of the heterostructures, MoS_2 (or $MoSe_2$) and MXene, respectively.

DATA AVAILABILITY

All data generated or analyzed during this study are included in this published article (and its supplementary information files).

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AUTHOR CONTRIBUTIONS

B.L. and L.C. designed research; Y.W., H.G., and B.L. performed research; W.Z., Q.Z., L.C., X.F., W.Z, Y.L., and W.-M.-L. analyzed data; and B.L., L.C., and W.-M.L. wrote the paper. All authors discussed and commented on the manuscript.

ADDITIONAL INFORMATION

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