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## 2D transition metal-based phospho-chalcogenides and their applications in photocatalytic and electrocatalytic hydrogen evolution reactions

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The utilization of hydrogen (H<sub>2</sub>) as a renewable substitute for fossil fuel can mitigate issues related to energy shortage and associated global warming. The generation of H<sub>2</sub> *via* water splitting by photo and electrocatalytic means is of significant importance. The employment of a semiconductor catalyst reduces the high energy barrier (237 kJ mol<sup>-1</sup>) associated with a water-splitting reaction to yield H<sub>2</sub> and O<sub>2</sub>. Sustainable H<sub>2</sub> production demands the utilization of noble-metal-free, efficient, and stable catalysts over a wide pH range. In recent times, layered transition metal thio(seleno) phosphates (MPX<sub>3</sub>, X = S, Se) are reported to be highly efficient for H<sub>2</sub> evolution reaction owing to their earth-abundance, rich active sites, wide spanned band gap of 1.2 to 3.5 eV, and high chemical stability. In this perspective, advances in 2D monometallic and bimetallic MPX<sub>3</sub> compounds are reviewed comprehensively from the viewpoint of water splitting, especially the hydrogen evolution reaction (HER). This study includes the composition, structural engineering, heterostructure, and hierarchically structural design in enhancing the HER activity of MPX<sub>3</sub>. Computational results providing insights into the intrinsic photo and electrocatalytic HER activity of 2D MPX<sub>3</sub> are presented. Finally, the challenges and opportunities in further improving MPX<sub>3</sub> activity towards HER and associated catalysis reactions are discussed.

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### 1. Introduction

The massive utilization of non-renewable fossil fuels to meet ever-increasing global energy requirements is leading to fuel scarcity and CO<sub>2</sub> emission at an alarming rate gives rise to global warming.<sup>1–8</sup> Therefore, establishing global-scale, renewable, efficient, and carbon-free emission combined fuel-combustion technology is of significant importance.<sup>1–4</sup> Fuel cell technology is an environmentally-safe route of generating energy than the other existing methods.<sup>5–7</sup> The fuel cell utilizing hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) as fuels at the anode and cathode, respectively, will be the suitable one amongst the numerous types of fuel cells because it gives only water (H<sub>2</sub>O) as the product.<sup>8–10</sup> The main goal is to generate H<sub>2</sub> from renewable sources, ideally H<sub>2</sub>O. Water can be decomposed into H<sub>2</sub> and O<sub>2</sub> through photochemical, electrochemical, and photo-electrochemical strategies by utilizing solar, electrical energy, and a combination of solar-electricity energy, respectively.<sup>11–14,19</sup> The main challenge is to generate H<sub>2</sub> from renewable sources, preferably H<sub>2</sub>O. But, water splitting  $\left(2\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2\right)$  is

thermodynamically an uphill reaction that involves a large Gibbs free energy change of 237 kJ mol<sup>-1</sup>.<sup>15–18</sup> With the help of an appropriate catalyst one can decrease the energy barrier for water splitting and increase the H<sub>2</sub> evolution rate. Platinum or platinum group materials (PGMs) are regarded as the best catalysts for electrochemical H<sub>2</sub> evolution reaction (HER).<sup>20–22</sup> However, high-cost, stability issues under various electrochemical conditions and intolerance to catalytic poisoning severely limit their applicability as HER catalysts. In the last decade, there is a major thrust into exploiting low-cost, earth-abundant, and stable catalysts, particularly the non-precious metal catalysts.<sup>23–26</sup> Therefore, non-noble 2D metal catalysts, such as transition metal chalcogenides (TMDCs),<sup>27–30</sup> carbides,<sup>31</sup> nitrides,<sup>32</sup> and phosphides,<sup>33</sup> have been investigated for the potential replacement of the noble metal catalysts for water splitting owing to their fascinating optical and electrical properties. It has been reported that the bulk MoS<sub>2</sub> is inactive for the hydrogen evolution reaction (HER), whereas, mono or few-layer MoS<sub>2</sub> shows excellent HER performance.<sup>34,35</sup> The incorporation of Co and Ni into the MoS<sub>2</sub> matrix was reported to enhance the electrocatalytic activity significantly.<sup>36–38</sup> While alloy phases, MoS<sub>x</sub>Se<sub>1-x</sub>, wherein Se in combination with S, permit tuning of HER activity.<sup>39,40</sup>

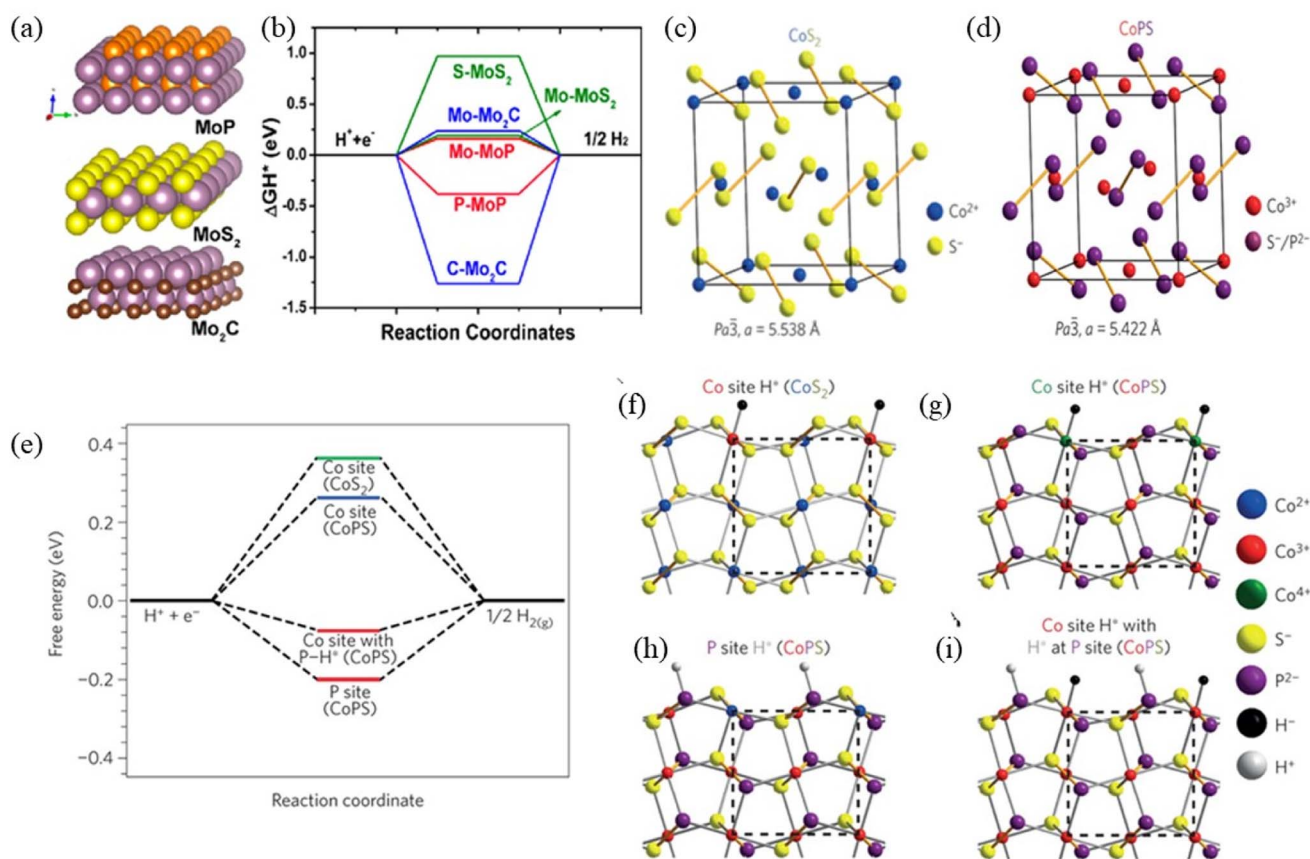
Akin to TMDCs, 2D transition metal phosphides (TMPs) are reported to show bifunctional properties as HER and oxygen evolution reaction (OER) catalysts and also display long-term stability in a wide pH range.<sup>41–44</sup> Theoretically, it is predicted

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that the phosphorous atom of TMPs acts as an active site for intermediate hydrogen adsorption and desorption during water splitting. Jia *et al.*<sup>45</sup> compared the Gibbs free energy change ( $\Delta G_{H^*}$ ) of hydrogen adsorbed, which is a main intermediate state in HER, on to the different active sites MoP, MoS<sub>2</sub>, and Mo<sub>2</sub>C catalysts by density functional theory (DFT) calculations (Fig. 1a and b). According to the Sabatier principle, too strong or too weak adsorption is not favorable for the water reduction reaction. The  $\Delta G_{H^*}$  values for Mo-terminated MoP, MoS<sub>2</sub>, and Mo<sub>2</sub>C were calculated as 0.16, 0.19, and 0.24 eV, respectively. These results indicate that the P atom in MoP plays the equivalent role as S of MoS<sub>2</sub> and C in Mo<sub>2</sub>C. Further, a subtle smaller  $\Delta G_{H^*}$  value for MoP as compared to MoS<sub>2</sub> and Mo<sub>2</sub>C, indicates that MoP possesses higher catalytic activity. In another study, Miguel *et al.*<sup>46</sup> using DFT calculations demonstrated that the ternary pyrite-type cobalt phosphosulfide can be an efficient catalyst for both photocatalytic and electrocatalytic HER since the cobalt octahedra contain more-electron donating P<sup>2-</sup> sites compared to S<sup>2-</sup>, owing to thermoneutral H<sup>+</sup> adsorption at the active sites. The cubic crystal structure of CoPS can be envisaged as Co<sup>3+</sup> octahedra surrounded by dumbbells with a uniform arrangement of P<sup>2-</sup> and S<sup>2-</sup> ligands (Fig. 1c and d). Further,

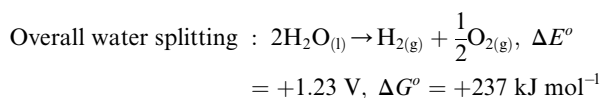
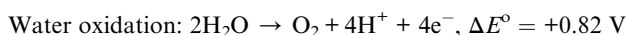
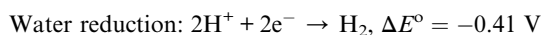
DFT calculations revealed that  $\Delta G_{H^*}$  on the (100) surface of CoPS at the Co site is more favorable compared to the CoS<sub>2</sub> constituent. As shown in Fig. 1f–i, after spontaneous adsorption of H<sup>+</sup> at open P sites, adjacent Co<sup>3+</sup> atoms are reduced to Co<sup>2+</sup>, which brings  $\Delta G_{H^*}$  value for cobalt near the thermoneutral value. Subsequent H<sup>+</sup> adsorption at Co<sup>2+</sup> sites induces the oxidation of Co<sup>2+</sup> to Co<sup>3+</sup> as shown in Fig. 1f–i. Such synergistic interaction is not realized in the case of CoS<sub>2</sub> since Co<sup>3+</sup> sites are energetically more favorable for H<sup>+</sup> adsorption than open S<sup>2-</sup> ligands. In addition, Miguel *et al.*<sup>46</sup> showed that CoPS nanostructures display electrocatalytic HER activity comparable to the Pt/C catalyst with a current density of 10 mA cm<sup>-2</sup> at an overpotential as low as 48 mV and also shows exceptional stability. The Pt/C-like HER activity of CoPS inspired other researchers to study MPX<sub>3</sub> systems containing Mn, Fe, Ni, Cd, *etc.* metals. But, some of the 2D family MPX<sub>3</sub> systems such as MnPS<sub>3</sub>, FePS<sub>3</sub>, and NiPS<sub>3</sub> showed marginal electrocatalytic H<sub>2</sub> evolution activity due to low intrinsic electronic conductivity.<sup>47</sup> Coupling of MPX<sub>3</sub> with conducting graphene<sup>47</sup> and doping of Co into MnPS<sub>3</sub> and NiPS<sub>3</sub> structures was reported to improve HER activity.<sup>48,49</sup> Doping modifies the valence band and conduction edges and improves the electron transport rate. Further, MoS<sub>2</sub>



**Fig. 1** (a) Schematic depiction of the layered structure of 2D molybdenum phosphide (MoP), molybdenum disulfide (MoS<sub>2</sub>), and molybdenum carbide (Mo<sub>2</sub>C). (b) Gibbs free energy diagram of the H<sub>2</sub> evolution for MoP, MoS<sub>2</sub>, and Mo<sub>2</sub>C at different sites. Reprinted with permission.<sup>45</sup> Copyright 2017, American Chemical Society. (c and d) Crystal structures of CoS<sub>2</sub> and CoPS systems. (e) Free energy diagrams of the H<sub>2</sub> evolution for CoS<sub>2</sub> and CoPS at different sites. Structural demonstration of hydrogen adsorption (H\*) at the Co site on (100) plane of CoS<sub>2</sub> (f), at the Co site (g), P site (h), and at the P site after H\* at the Co site (i) on (100) plane of CoPS. Reprinted with permission. Copyright 2015, Springer nature.<sup>46</sup>

in combination with  $\text{MPX}_3$  facilitates hydrogen spillover during HER from  $\text{MoS}_2$  edge sites to TMPCs.<sup>50,51</sup>

As discussed in prior sections, water splitting is thermodynamically energy-intensive as it demands a relatively large free energy of  $237 \text{ kJ mol}^{-1}$  to produce one mole of  $\text{H}_2$  and  $\text{O}_2$  each.<sup>15,19</sup> To overcome this large energy barrier, researchers are utilizing semiconductor photocatalysts for water splitting, which can mimic the natural photosynthesis process involving the following two half-reactions.<sup>52,53</sup>



The high Gibbs free energy barrier for water redox reactions can be reduced by employing semiconductors as photocatalysts and, therefore, the  $\text{H}_2$  evolution rate can be improved. The standard reduction potentials for  $\text{H}^+/\text{H}_2$  reduction and oxidation potential for  $\text{H}_2\text{O}/\text{O}_2$  are estimated to be  $-0.41$  and  $+0.82 \text{ V}$  (vs. NHE), respectively. To achieve overall water splitting by utilizing a semiconductor, the conduction band minimum (CBM) energy of the semiconductor should be higher than the  $\text{H}^+/\text{H}_2$  reduction potential and its valence band maximum (VBM) energy must be lower than the  $\text{H}_2\text{O}/\text{O}_2$  oxidation potential.<sup>54–56</sup> The water splitting utilizing semiconductor photocatalyst comprises three essential steps: (1) absorption of solar energy by the semiconductor; (2) generation and mobilization of electron-hole pair from bulk to the active sites of the semiconductor; (3) water reduction ( $\text{H}^+/\text{H}_2$ ) and oxidation ( $\text{H}_2\text{O}/\text{O}_2$ ) reactions by photogenerated electron and hole pair at the conduction band (CB) and valence band (VB) of the semiconductor, respectively (Fig. 2). As shown in Fig. 2a and b, water splitting using semiconductors could be a one-step or two-step approach based on whether a single component is utilized or a combination of two or more semiconductor systems. The one-step route involves the photoexcitation of the semiconductor and water reduction and oxidation reaction by the electron and holes at the CB and VB of the semiconductor. While the two-step method includes concomitant photoexcitation of two semiconductors, hydrogen ( $\text{H}^+/\text{H}_2$ ) and oxygen ( $\text{H}_2\text{O}/\text{O}_2$ ) evolution occurs individually at different semiconductors similar to the usual Z-scheme photosynthesis.

In 1972, Fujishima *et al.*<sup>57</sup> primarily described the use of  $\text{TiO}_2$  electrodes as photocatalysts for water-splitting reactions, since then, numerous semiconductors such as  $\text{ZnO}$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{WO}_3$ , and  $\text{TiO}_2$  have been utilized as photocatalysts.<sup>58,59</sup> However, the utilization of semiconductor photocatalyst requires the use of noble-metal cocatalysts in combination to realize higher water splitting efficiency.<sup>60,61</sup> Hence, researchers are relentlessly exploring non-noble metal catalysts for water splitting to make the process cost-effective. In this regard, 2D materials such as

metal nitrides, carbides, and phosphides have been explored as proficient catalysts for water reduction reactions. As discussed earlier, photon absorption, electron-hole pair separation and water redox reactions at the catalyst active sites are three crucial stages in photocatalytic water splitting. 2D material band gap can be modified by varying the number of stacked sheets, which fulfills the first condition. Secondly, due to the atomic thickness of 2D material, photogenerated charge-carriers have to cover lesser distances to reach the surface energetic sites. Further, the high specific surface area of 2D materials provides abundant active sites and higher accessibility for  $\text{H}^+$  adsorption. Lately, Ida *et al.*<sup>62</sup> demonstrated how solar flux density and charge carrier lifetime in 0D nanocrystals and 2D crystal affects the water-splitting process (Fig. 3). A nanocrystal requires four excited electrons to ensure complete water splitting. But, photogenerated charge carriers possess a very short average lifetime of  $1 \mu\text{s}$  before recombination. Therefore, to harvest four electrons, the nanocrystal should absorb four photons within a shorter period of  $1 \mu\text{s}$  time. The solar flux density in the Earth's atmosphere is estimated to be  $2000 \mu\text{mol s}^{-1} \text{ m}^{-2}$ . Thus,  $4 \text{ ms}$  is essential for photons to get adsorbed by the 0D nanocrystal and it is tough to afford such high solar flux to achieve water splitting using 0D nanocrystal. 2D materials, on the other hand, could minimize recombination rate by providing shorter pathways for charge-carriers to reach the active sites, thereby low solar energy flux is paramount in the case of 2D materials to achieve water splitting.

2D transition metal thio(seleno) phosphates ( $\text{MPX}_3$ ,  $\text{X} = \text{S}, \text{Se}$ ) nanosheets containing Mn, Fe, Co, Ni, Cu, *etc.* metals have been investigated for photocatalytic HER due to their tunable composition, electronic structure, and wide band gap ranging from  $1.3$  to  $3.5 \text{ eV}$ .<sup>63–65</sup> The electronic structure and properties of the  $\text{MPX}_3$  systems are investigated by optical absorption, photoluminescence, and DFT simulations. Zhang *et al.*<sup>66</sup> calculated the band structure of  $\text{MPS}_3$  ( $\text{M} = \text{Fe}, \text{Mn}, \text{Ni}, \text{Cd}, \text{Zn}$ ) and  $\text{MPSe}_3$  ( $\text{M} = \text{Fe}, \text{Mn}$ ) systems using the Heyd-Scuseria-Ernzerhof (HSE06) functional, which is presented in Fig. 4a–f. This study specifies that the band gap of single-layer  $\text{MPX}_3$  varies from  $1.90$  to  $3.44 \text{ eV}$ , which surpasses the thermodynamic potential of  $1.23 \text{ eV}$  essential for water splitting. In addition, Yang *et al.*<sup>67</sup> calculated the dynamic stability of  $\text{MnPX}_3$  ( $\text{X} = \text{S}$  or  $\text{Se}$ ) nanosheets with the finite displacement method, and the corresponding phonon dispersion curve is shown in Fig. 4h and g. Interestingly, no imaginary phonon modes are observed in the phonon spectra, confirming the dynamic stability and they can be isolated as free-standing nanosheets. As displayed in the right panel of Fig. 4h and g, phonon bands below  $8 \text{ THz}$  are assigned to Mn–S/Se interactions, while the high frequency region above  $8 \text{ THz}$  corresponds to  $\text{P}_2\text{X}_6$  moiety vibrations. Secondly, the radius of Se is greater than that of S, hence, the bond length of Mn–Se is larger than that of Mn–S and phonon bands of  $\text{MnSe}_3$  are shifted towards low frequencies as compared to the  $\text{MnPS}_3$  system.

Apart from the band gap, the valence band and conduction band edges must straddle with  $\text{H}^+/\text{H}_2$  reduction and  $\text{H}_2\text{O}/\text{O}_2$  oxidation potentials. Liu *et al.*<sup>68,69</sup> using HSE06 functional and partial density of states, calculated the orientation of CBM and

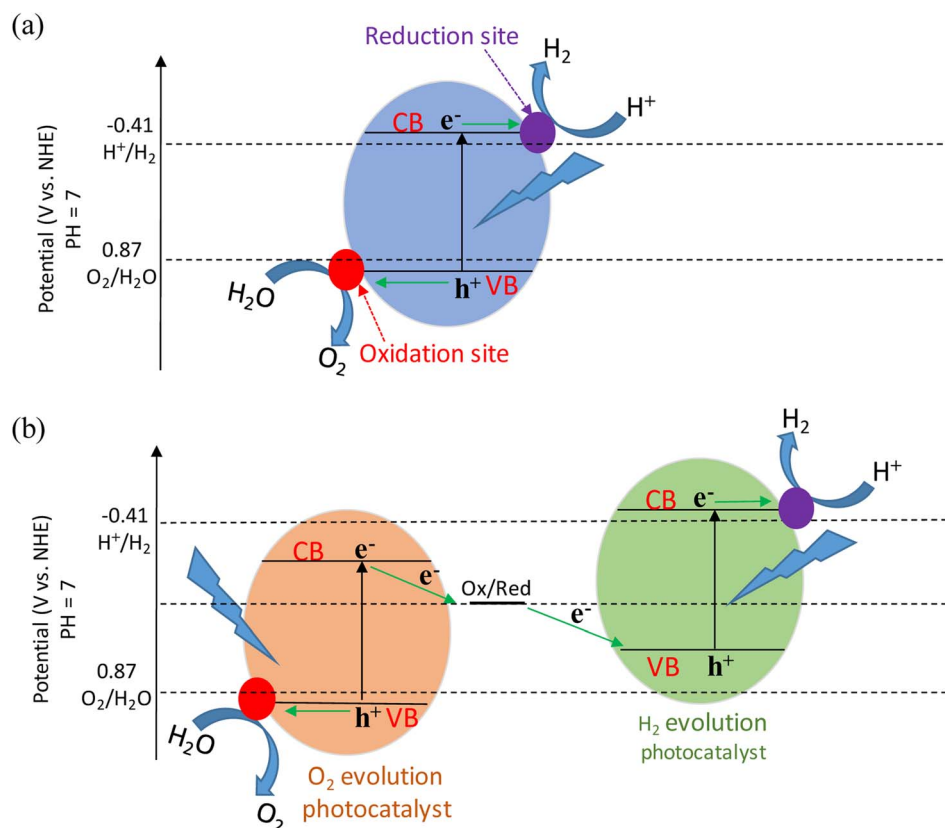
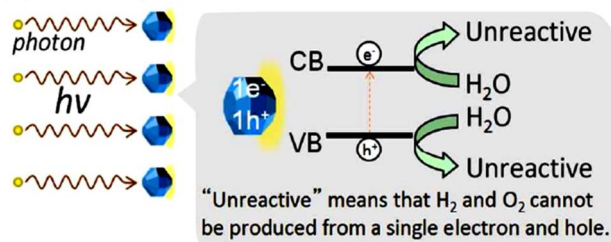


Fig. 2 Schematic of the function and essential role of semiconductor photocatalyst in decreasing the Gibbs free energy for water splitting reaction. (a and b) photocatalytic water splitting using a single-component or combination of two semiconductor systems.

### (a) Nanocrystal, diameter:1nm



### (b) 2D-crystal, thickness:1nm

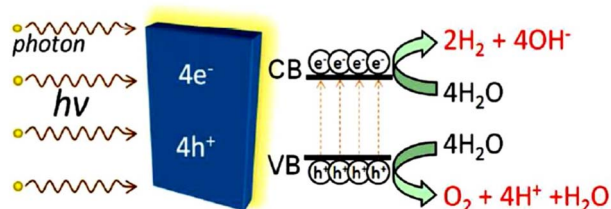


Fig. 3 Schematic illustration of the photocatalytic water redox reaction under solar light illumination for (a) 0D crystal and (b) 2D system. Replicated with the agreement.<sup>62</sup> Copyright 2014, American Chemical Society.

VBM edges relative to water redox potential (Fig. 5a). Further, Zhang *et al.*<sup>66</sup> by taking into consideration of stability of monolayered MPX<sub>3</sub> systems and variation in their redox potentials

with changes in pH, calculated the band edges based on HSE06 functional studies (Fig. 5b). Among the studied materials, FePSe<sub>3</sub> displayed the narrowest band gap, which was further confirmed by optical absorption spectra as well. However, at pH = 7, FePSe<sub>3</sub> displayed a CBM edge lower than water reduction potential and hence it is not suitable for H<sup>+</sup>/H<sub>2</sub> reduction. Therefore, a particular MPX<sub>3</sub> system can be chosen for either HER or OER based on the alignment of VBM and CBM edges relative to water redox potential. In addition, MnPS<sub>3</sub>, FePS<sub>3</sub>, and NiPS<sub>3</sub> displayed strong optical absorption in the visible range, which indicates their high capability to harvest visible light (Fig. 5c). These simulations have been experimentally verified by Du *et al.*<sup>70</sup> as well.

Strong visible light absorption characteristics and high carrier mobility (625.9 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for MnPSe<sub>3</sub>) specify the MPX<sub>3</sub> system's potential capability for H<sub>2</sub> generation under solar light.<sup>65,66,70</sup> In addition, members of the MPX<sub>3</sub> family possess the aforementioned properties along with abundant phosphorous active sites for HER in mono or few-layer form; thus, it is realistic to assume that they can be good candidates for many catalysis reactions as non-precious metal catalysts. 2D CdPS<sub>3</sub> showed high HER performance of 10 880 μmol h<sup>-1</sup> g<sup>-1</sup> while MnPS<sub>3</sub> and FePS<sub>3</sub> displayed 21.2 and 141.9 μmol h<sup>-1</sup> g<sup>-1</sup>, respectively, under solar light.<sup>65,71,72</sup> One drawback of 2D TMPCs is their weak oxidizing ability of the photogenerated holes because of the misaligned valence band maximum (VBM) edge for H<sub>2</sub>O/O<sub>2</sub> oxidation potential and hence shows low stability

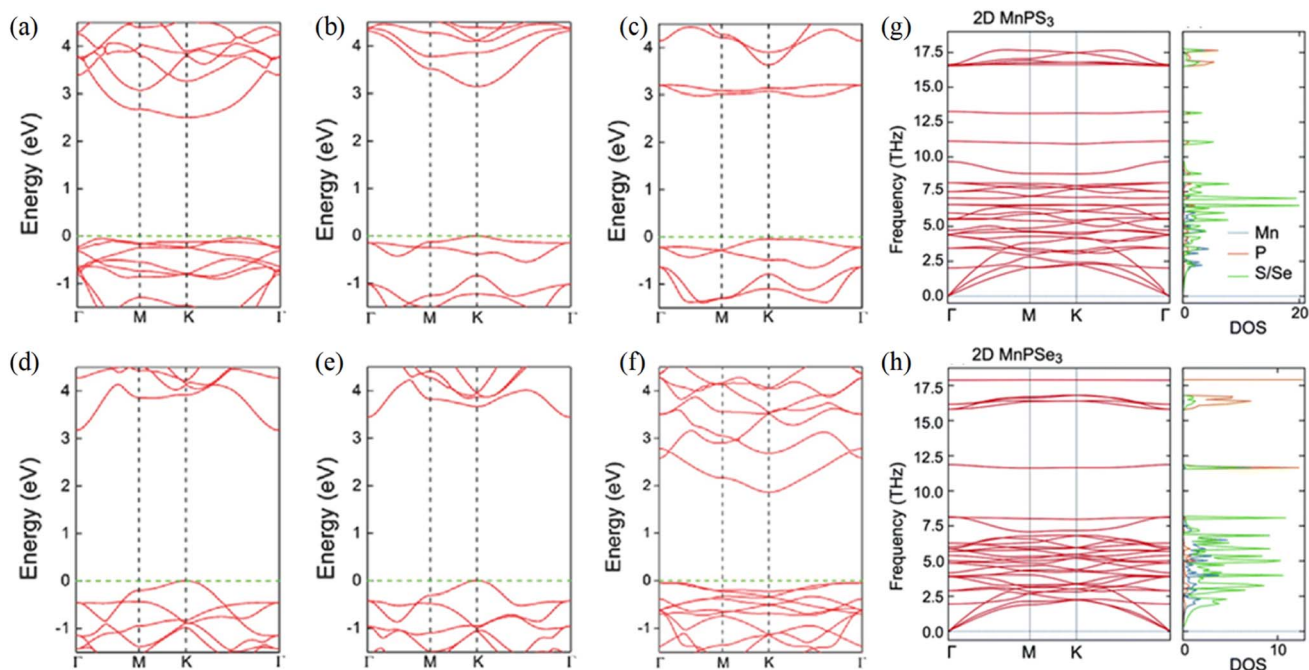


Fig. 4 Band structure near the Fermi level for (a) FePS<sub>3</sub>, (b) MnPS<sub>3</sub>, (c) NiPS<sub>3</sub>, (d) CdPS<sub>3</sub>, (e) ZnPS<sub>3</sub>, and (f) FePSe<sub>3</sub> single-layers. Reprinted with permission.<sup>66</sup> Copyright 2018, Wiley publication. Phonon dispersion and the corresponding density of states for (g) MnPS<sub>3</sub> and (h) MnPSe<sub>3</sub> nanosheets. Reprinted with permission.<sup>67</sup> Copyright 2020, The Royal Society of Chemistry.

because of photocorrosion.<sup>64,73</sup> Combination of 2D MPX<sub>3</sub> with other Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub>, CdS, TiO<sub>2</sub>, and g-C<sub>3</sub>N<sub>4</sub> nanostructures is reported to be beneficial for water splitting as latter systems possess strong hole oxidizing ability.

In this perspective, we provide an overview of various 2D TMPCs utilized for photocatalytic and electrocatalytic HER applications. The chemical vapor transport (CVT) method for bulk MPX<sub>3</sub> preparation is mentioned briefly and

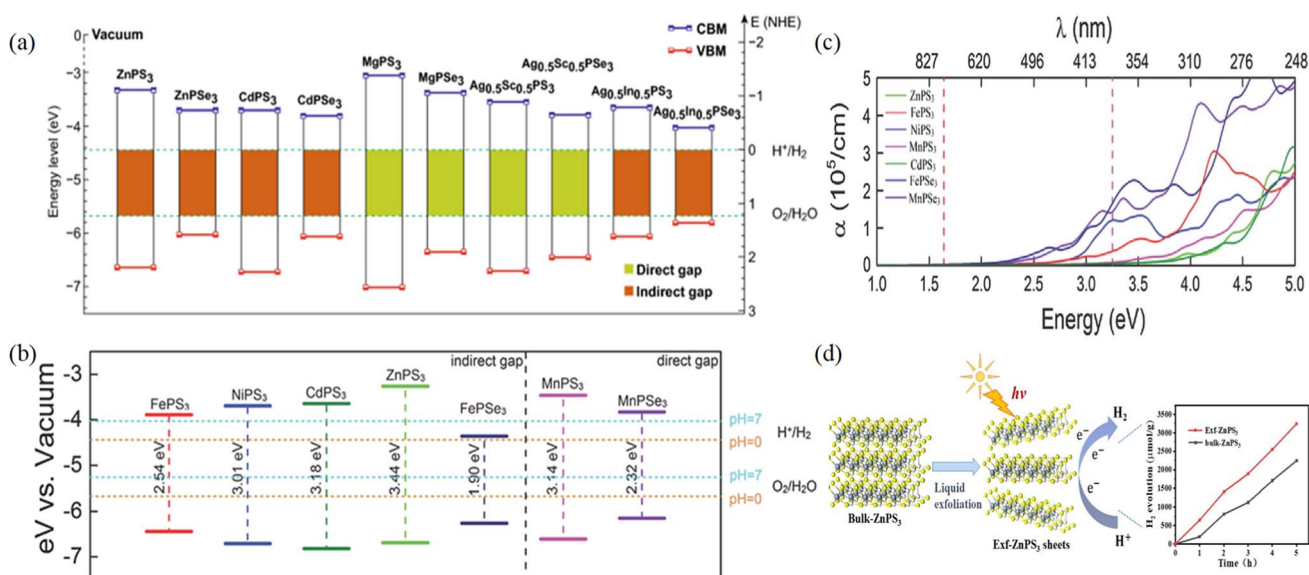


Fig. 5 (a) Band edge potential of mono-layered MPX<sub>3</sub> compounds. The energy scale is represented with respect to the normal hydrogen electrode (right y-axis) and vacuum level (left y-axis) in eV for reference. The redox potential of water is incorporated for assessment. Reproduced with permission.<sup>68</sup> Copyright 2001, Macmillan Publishers Ltd. (b) Location of VBM and CBM edge potentials of monolayer MPS<sub>3</sub> and MPSe<sub>3</sub> calculated using HSE06 functional. The redox potential of water at pH = 0 and pH = 7 is incorporated for comparison. (c) The optical absorption coefficient for MPS<sub>3</sub> compounds. The region between the red and purple lines indicates the visible range. Reprinted with permission.<sup>66</sup> Copyright 2018, Wiley publication. (d) Schematic shows that the exfoliated ZnPS<sub>3</sub> shows higher photocatalytic HER activity as compared to the bulk due to more exposed edge sites.<sup>112</sup>

micromechanical exfoliation and liquid-phase exfoliation approaches to prepare 2D  $\text{MPX}_3$  from bulk crystal are discussed. The DFT approach demonstrating the significance of proper alignment of VBM and conduction band minimum (CBM) edges of 2D  $\text{MPX}_3$  concerning water redox potential towards HER is discussed at length. To improve the catalytic activity of  $\text{MPX}_3$ , phase engineering, band structure engineering, and electronic state modulation by doping strategies have been employed (Fig. 6). Generation of the heterojunction between 2D  $\text{MPX}_3$  with other  $\text{Cs}_4\text{W}_{11}\text{O}_{35}$ ,  $\text{CdS}$ ,  $\text{TiO}_2$ , and  $\text{g-C}_3\text{N}_4$  nanostructures is reported to improve hole oxidizing ability. Further, photogenerated electrons are readily available for water reduction due to an in-built electric field gradient and therefore heterostructures are likely to display a higher HER rate and good stability. Besides, ferroelectric  $\text{CuInP}_2\text{S}_6$  displays good HER characteristics and its activity can be further enhanced by coupling with other photocatalytically HER-active materials such as  $\text{g-C}_3\text{N}_4$  and  $\text{ZnIn}_2\text{S}_4$ . The permanent polarization electric field and large exciton binding energy characteristics of ferroelectric  $\text{CuInP}_2\text{S}_6$  induce spatial separation of the

photogenerated carriers and reduction potential of electrons, respectively, thereby showing good  $\text{H}_2$  evolution. Notably, the  $\text{CuInP}_2\text{S}_6/\text{g-C}_3\text{N}_4$  heterostructure shows extraordinary stability under harsh photochemical conditions, suggesting its practical applicability.

## 2. Structure and composition

All the members in the  $\text{MPX}_3$  family show a typical characteristic that  $(\text{P}_2\text{S}_6)^{4-}$  or  $(\text{P}_2\text{Se}_6)^{4-}$  anion sublattice is present within each layered crystal. While the metal ions are dispersed around the  $(\text{P}_2\text{X}_6)^{4-}$  bipyramids in a honeycomb arrangement.<sup>74</sup> In Fig. 7b–d, we have shown the comparison of the crystal structure of the typical layered  $\text{MoS}_2$  and  $\text{MPX}_3$  systems. The van der Waals gap (the smallest gap between the S layers) in the  $\text{MPX}_3$  system containing first-row transition metals is in the range of 3.22–3.24 Å, which is relatively higher than that of metal dichalcogenide ( $\text{MS}_2$ ) systems.<sup>74</sup> Various metal cations can be accommodated in the  $\text{MPX}_3$  system with a change in the size of the slab. As for the  $(\text{P}_2\text{X}_6)^{4-}$  bipyramid structure modification,

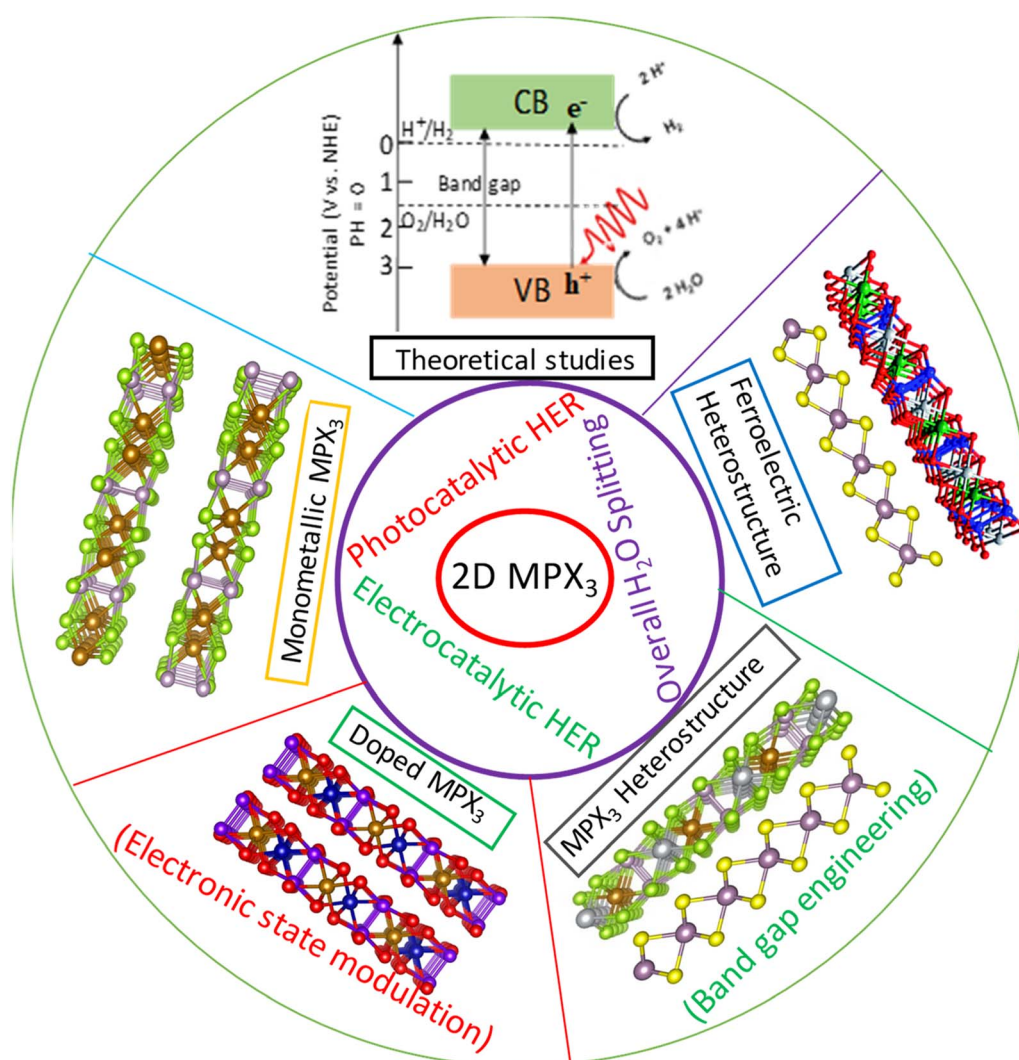


Fig. 6 Schematic highlights of 2D  $\text{MPX}_3$  compounds and their nanocomposites for photocatalytic and electrocatalytic HER applications.

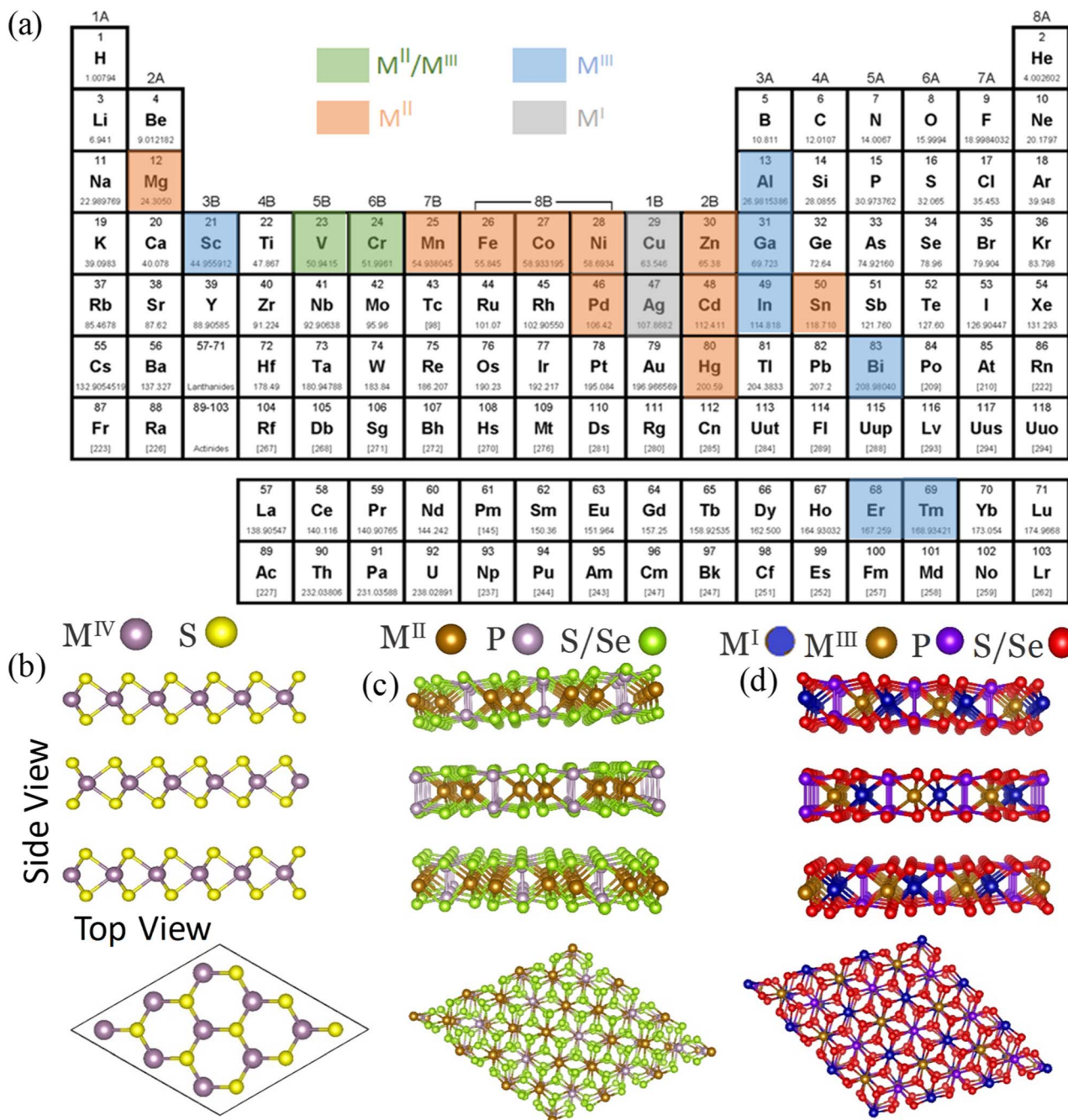


Fig. 7 Composition and crystal structure of  $MPX_3$  compounds. (a) Periodic table highlighting the transition elements and their valence states constituting the  $MPX_3$  system. Crystal structure of (b)  $MoS_2$ , (c)  $M^{II}PQ_3$  ( $M^{II} = Zn, Cd, Mg$ ;  $Q = S, Se$ ) and (d)  $Ag_{0.5}M^{III}_{0.5}PQ_3$  ( $M^{III} = Sc, In$ ;  $Q = S, Se$ ).

$S^{2-}$  remains intact while the P–P bond distance is altered to accommodate metal ions of different sizes. An increase in P–P bond distance of 2.148 to 2.222 Å is reported on substituting  $Cd^{2+}$  with  $Ni^{2+}$  in the  $MPS_3$  system.<sup>75</sup> Besides, the layer thickness of the  $MPX_3$  system is positively enhanced with an increase in P–P bond distance. On the cation side, the  $MPX_3$  system can accommodate either divalent metal ions or a combination of monovalent and trivalent metal ions. In literature, bimetallic  $Ni_2P_2S_6-xSe_x$ ,<sup>76</sup>  $CuInP_2S_6-xSe_x$ ,<sup>77</sup> and  $Sn_2P_2S_6-xSe_x$ <sup>78</sup> systems, with alloying of  $(P_2S_6)^{4-}$  and  $(P_2Se_6)^{4-}$  anion units are also

reported. To date,  $MPX_3$  systems containing Fe, Co, and Ni metal ions have been widely explored due to magnetic ordering and their catalytic properties towards photocatalytic and electrocatalytic water splitting.

### 2.1 Monometallic $MPX_3$

If there is only one type of metal occupying the cationic site of  $MPX_3$ , as shown in Fig. 7c, these systems are termed monometallic. It is convenient to study the  $M^{II}PX_3$  system by comparing it with  $M^{IV}S_2$  (example:  $MoS_2$ ) crystal structure.

$M^{II}PX_3$  compounds can be visualized as a layered  $MS_2$  system with  $1/3$  of the M site occupied by P–P ( $P_2$ ) pairs, *i.e.*,  $M^{II}_{2/3}(P)_{1/3}S_2$ . The sulfur atom comprises surfaces within the individual lamella. The octahedrally coordinated  $M^{II}PX_3$  system can be envisaged as  $M^{II}$  ions occupying the  $2/3$  site and the rest  $1/3$  site is filled by P–P pairs. Further, the P–P pair bonded to six sulfur atoms to form an ethane-like  $(P_2S_6)^{2-}$  sublattice, within individual phosphor atoms tetrahedrally coordinated to three sulfur atoms. Meanwhile, the sulfur atom coordinated with two  $M^{II}$  ions and covalently attached to one phosphorous atom. Commonly,  $M^{II}PS_3$  systems exhibit the  $C2/m$  symmetry with a monoclinic crystal structure and show a layer stacking sequence of “AAA”.<sup>79</sup> The monoclinic lattice parameter  $\beta$  value calculated for  $CoPS_3$  and  $FePS_3$  is  $107.16^\circ$ , indicating that these systems possess an undistorted monoclinic crystal structure. On the other hand,  $M^{II}PSe_3$  possess  $R3(-)H$  symmetry because of the higher P–Se bond distance and P–Se–P bond angle, whereas  $NiPSe_3$  shows  $C2/m$  symmetry similar to  $NiPS_3$ .<sup>80,81</sup>

## 2.2 Bimetallic $MPX_3$

The “M” atom of  $MPX_3$  can be exchanged with other metal atoms, containing homo and hetero-charge substitutions. For instance, in systems such as  $Zn_{1-x}Fe_xPS_3$ ,  $Zn_{1-x}Ni_xPS_3$  (ref. 75) ( $0 \leq x \leq 1$ ), and  $Cd_xFe_{1-x}P_2S_6$  ( $0 \leq x \leq 1$ )<sup>82</sup> homo-charge distribution can be easily realized due to similar sizes of  $M_1^{II}$  and  $M_2^{II}$  ions. Most of the homo-charge mixed sulfides are monoclinic while selenides display trigonal symmetry. Hetero-charge  $MPX_3$  containing  $\frac{1}{2}M_1^I$  (Ag or Cu) and  $\frac{1}{2}M_2^{III}$  trivalent metal ion (Cr, V, Al or In) where “x” being S or Se atom are also reported. These mixed-cationic sulphides broadly show two stoichiometric ratios;  $M^{1+}M^{3+}[P_2S_6]^{4-}$  (*e.g.*,  $AgInP_2S_6$ ,<sup>83</sup>  $AgScP_2S_6$  and  $CuVP_2S_6$  (ref. 84)) and  $M_2^{1+}M^{2+}[P_2S_6]^{4-}$  (*e.g.*,  $Ag_2MgP_2S_6$  and  $Ag_2MnP_2S_6$ ).<sup>79</sup> Among these sulfides,  $AgInP_2S_6$ , and  $AgScP_2S_6$  are trigonal and centrosymmetric, while  $CuVP_2S_6$  is non-centrosymmetric. Mixed selenides exist in two stoichiometry:  $M^{1+}M^{3+}[P_2Se_6]^{4-}$  (*e.g.*,  $CuAlP_2Se_6$  (ref. 85) with random  $Cu^{1+}$  and  $Al^{3+}$  arrangement) and  $M_{4/3}^{1+}Y_{2/3}[P_2Se_6]^{4-}$ , where Y signifies an unfilled site (*e.g.*,  $In_{4/3}P_2Se_6$ ).<sup>86</sup>

## 3. Synthetic methods

Production of single-layer graphene from graphite by the scotch-tape method has opened a plethora of opportunities for researchers to realize other atomically-thin 2D materials such as  $MoS_2$ , phosphorene, and bismuthene.<sup>87,88</sup> Lee *et al.* successfully adapted micromechanical exfoliation of bulk  $MnPS_3$  to prepare a few-layer  $MnPS_3$  of high-quality and large lateral size.<sup>89</sup> Fig. 8a–c shows the optical microscopy and atomic force microscopy (AFM) images of the few-layer  $MnPS_3$ . Using the AFM height profile graph one can easily find out the number of stacked layers and lateral dimension of the nanosheet. For large-scale exfoliation, physical routes such as ball milling and liquid-phase exfoliation<sup>90,91</sup> in solvents such as N, *N*-dimethylformamide, and *N*-methyl-2-pyrrolidone have been reported. In addition, the chemical vapor deposition (CVD) strategy is also used to prepare monolayers of  $MnPS_3$ .<sup>65</sup> The CVD

strategy involves simultaneous phosphorization and sulfurization of the  $MnO_2$  template using sulfur and phosphor precursors, respectively in the two-zone furnace.  $MnPSe_3$  has also been synthesized by the CVD method by utilizing a Se source instead of S powder. Recently, Li *et al.*<sup>92</sup> exfoliated bulk  $Ni_2PS_3$  in an electrolyte containing tetra-*n*-butylammonium tetrafluoroborate as cationic intercalation salt by applying bias voltage ( $-3$  V) to the bulk electrode and obtained exfoliated sheets in higher yields. The mechanism involves the intercalation of tetra-*n*-butylammonium salts, which considerably declines the van der Waals attractions between the stacked layers. Then, after applying voltage for a longer time, the intercalated tetra-*n*-butylammonium decomposes into the gaseous species which assists in delamination of the sheets from stratified bulk  $NiPS_3$  crystals.

Rao and coworkers<sup>93</sup> extended the chemical vapor transport (CVT) method to prepare monometallic ( $MnPS_3$ ,  $FePS_3$ ,  $NiPS_3$ ,  $ZnPS_3$ ,  $CdPS_3$ ,  $FePSe_3$ , and  $CdPSe_3$ ) and bimetallic  $Ag_{0.5}In_{0.5}PS_3$  and  $Ag_{0.5}In_{0.5}PSe_3$   $MPX_3$  systems (Fig. 8d and e). The synthesis involved heating the stoichiometric ratios of the constituent elements sealed in a quartz ampoule to  $\sim 700$  °C under an inert atmosphere. The pure bulk  $MPX_3$  compounds were formed at the other end of the quartz ampoule. The presence of sulfur and phosphor elements enhanced the vapor transport rate during material growth and well-developed crystals are obtained. The obtained bulk crystals were exfoliated in a water and ethanol mixture under sonication conditions. Fig. 8f and g shows the TEM images of the exfoliated  $Ag_{0.5}In_{0.5}PS_3$  and  $Ag_{0.5}In_{0.5}PSe_3$  systems, which revealed a few-layer nature. In literature, the majority of  $MPX_3$  at large-scale are prepared using the CVT method and this strategy is even applicable for doping other transition (Ni, Fe or Co) elements into  $MnPS_3$  (ref. 94) as well as for the synthesis of ferroelectric  $CuInP_2S_6$  (ref. 95) and  $CuBiP_2S_6$  materials.

## 4. Electrocatalysis

Electronic structure analysis can predict probable reasons behind the catalytic activity of various materials. Orbitals of both metal and non-metal impact the catalytic activity depending on the redox reaction and related interactions. Transition metals require  $d_{z^2}$  orbitals for hydrogen adsorption, while oxygen evolution reactions require  $d_{xz}$  and  $d_{yz}$  orbital  $O^{2-}$ ,  $OH^-$ , and  $OOH^-$  adsorption. The catalytic system involving all three orbitals ( $d_{xz}$ ,  $d_{yz}$ , and  $d_{z^2}$ ) is considered to be superior for overall water splitting. In the case of a non-metallic system, P and S atoms are reported to be active sites for electrochemical reactions. The hydrogen adsorption free energy ( $\Delta_{GH}$ ) of a catalyst is broadly recognized as a good descriptor in evaluating the  $H_2$  evolution activity of a particular material.<sup>47</sup> The ideal catalyst should possess a thermoneutral  $H^+$  adsorption value. Song *et al.*<sup>96</sup> calculated the  $\Delta_{GH}$  value on the basal plane and edges of  $NiPS_3$ ,  $FePS_3$ , and  $NiFePS_3$  compounds using DFT calculations (Fig. 9a). These calculations suggested that the  $\Delta_{GH}$  value on the basal plane of  $NiPS_3$ ,  $FePS_3$ , and  $NiFePS_3$  is very high ( $\sim 0.5$  eV). Interestingly, 10% Fe-doped  $NiPS_3$  formed  $Ni_{0.9}Fe_{0.1}PS_3$ ; the  $\Delta_{GH}$  value on P and S edge sites was reduced to the



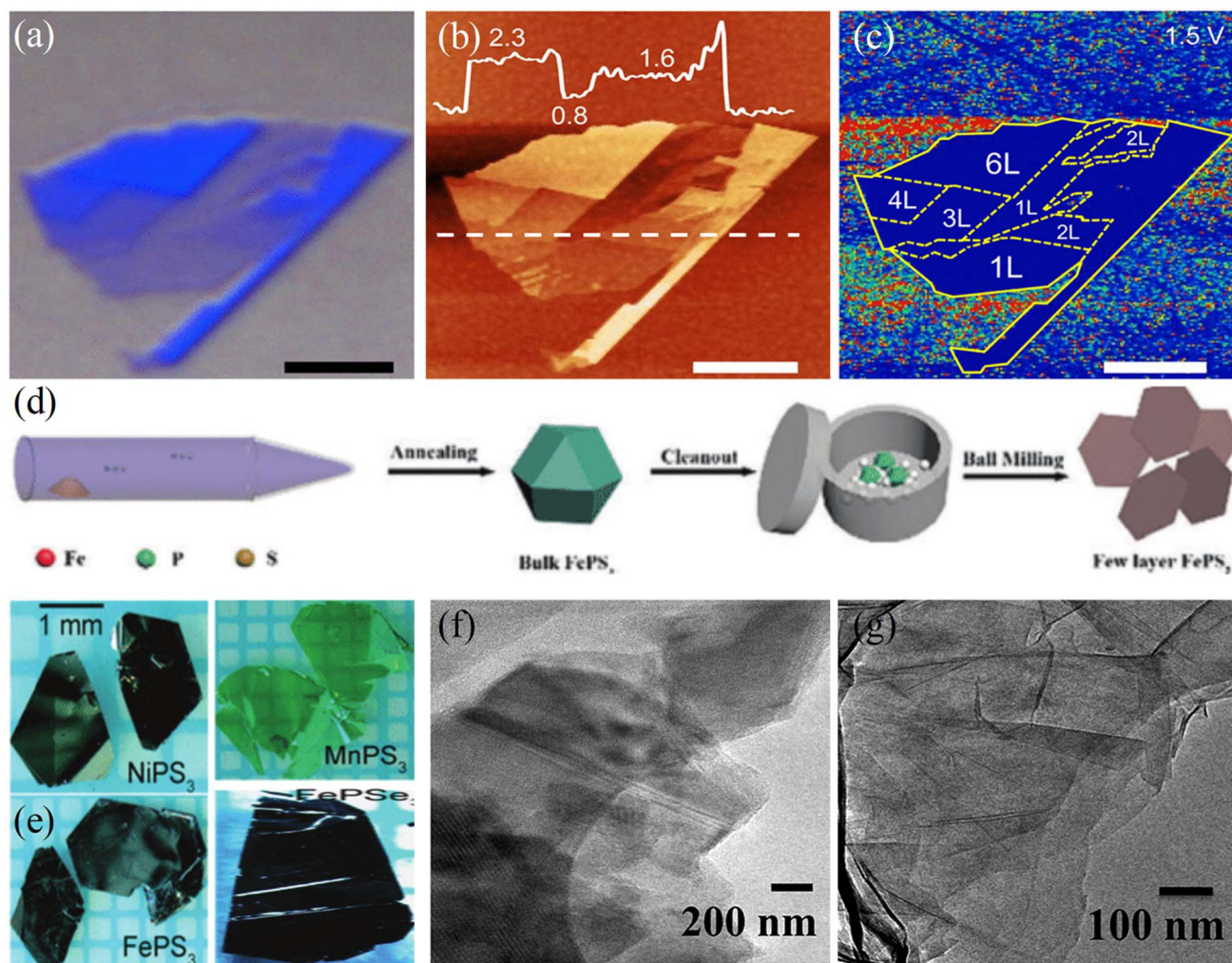


Fig. 8 (a) Optical microscopy, (b) AFM, and (c) conductive AFM image of few-layer  $\text{MnPS}_3$  obtained by the scotch-tape exfoliation method. Adapted with permission.<sup>89</sup> Copyright 2016, AIP Publishing. (d) Schematic representation of the CVT method adapted for the preparation of  $\text{MPX}_3$  crystals and (e) photographs of the bulk  $\text{NiPS}_3$ ,  $\text{FePS}_3$ ,  $\text{MnPS}_3$ , and  $\text{FePSe}_3$  prepared by the CVT method. TEM images of the exfoliated (f)  $\text{Ag}_{0.5}\text{In}_{0.5}\text{PS}_3$  and (g)  $\text{Ag}_{0.5}\text{In}_{0.5}\text{PSe}_3$  nanosheets.<sup>93</sup>

thermoneutral value, indicating that the bimetallic  $\text{MPX}_3$  systems can be an ideal catalyst for HER. In another study, Sun *et al.*<sup>97</sup> anchored different transition metals (*e.g.*, Sc, Ti, V, Cr, Mn, Fe, Co, and Ni) on monolayer  $\text{CuPS}_3$  and examined the catalytic performance towards HER. As shown in Fig. 9b, V, Fe, and Ni decorated  $\text{CuPS}_3$  were situated at the peak of the volcano curve, suggesting that these systems are potentially good for water splitting. Further, the authors also calculated the influence of hydrogen cover rate and found that V anchored  $\text{CuPS}_3$  was catalytically active for HER over a wide hydrogen coverage. Apart from the  $\Delta G_{\text{H}}$  value, the electron transport ability at active sites of the catalyst plays a crucial role in determining the overall HER activity. In view of this, Mayorga *et al.*<sup>98</sup> calculated the heterogeneous electron-transfer (HET) rates for  $\text{CrPS}_4$ ,  $\text{MnPS}_3$ ,  $\text{FePS}_3$ ,  $\text{CoPS}_3$ ,  $\text{NiPS}_3$ ,  $\text{ZnPS}_3$ ,  $\text{CdPS}_3$ ,  $\text{GaPS}_4$ ,  $\text{SnPS}_3$ , and  $\text{BiPS}_4$  using cyclic voltammograms recorded in  $[\text{Fe}(\text{CN})_6]^{3/4}$  redox couple by the Nicholson's method (Fig. 9c). The HET performance of  $\text{BiPS}_4$  ( $k_{\text{obs}}^0 \sim 0.024 \text{ cm s}^{-1}$ ) was comparable with

a glassy carbon substrate, which then decreased in the following order  $\text{CdPS}_3 > \text{CrPS}_4 > \text{SnPS}_3 > \text{CoPS}_3$ . The HET rate is generally related to the inherent orbital orientation of the particular material and higher HET in the case of  $\text{BiPS}_4$  suggests that this catalyst is electrochemically more active than the other studied  $\text{MPX}_3$  systems. Further, the charge-transfer resistance ( $R_{\text{ct}}$ ) calculated for  $\text{MPX}_3$  using electron impedance spectroscopy is in the range of 0.5 to 6.5  $\text{k}\Omega$  with  $\text{CdPS}_3$  and  $\text{BiPS}_4$  showing lower  $R_{\text{ct}}$  value, indicating that these  $\text{MPX}_3$  systems are semi-conducting in nature (Fig. 9d). Incorporation of conducting matrix such as graphene and carbon nanotubes is reported to enhance charge-transfer characteristics and HER yield of some  $\text{MPX}_3$  systems.<sup>47</sup>

During electrolytic water splitting, the catalyst material is coated on the substrate (glassy carbon and indium tin oxide) and utilized as the anode. As depicted in Fig. 10a, the water-splitting electrolyzer consists of three main constituents, the anode, cathode, and electrolyte. Irrespective of the electrolytic

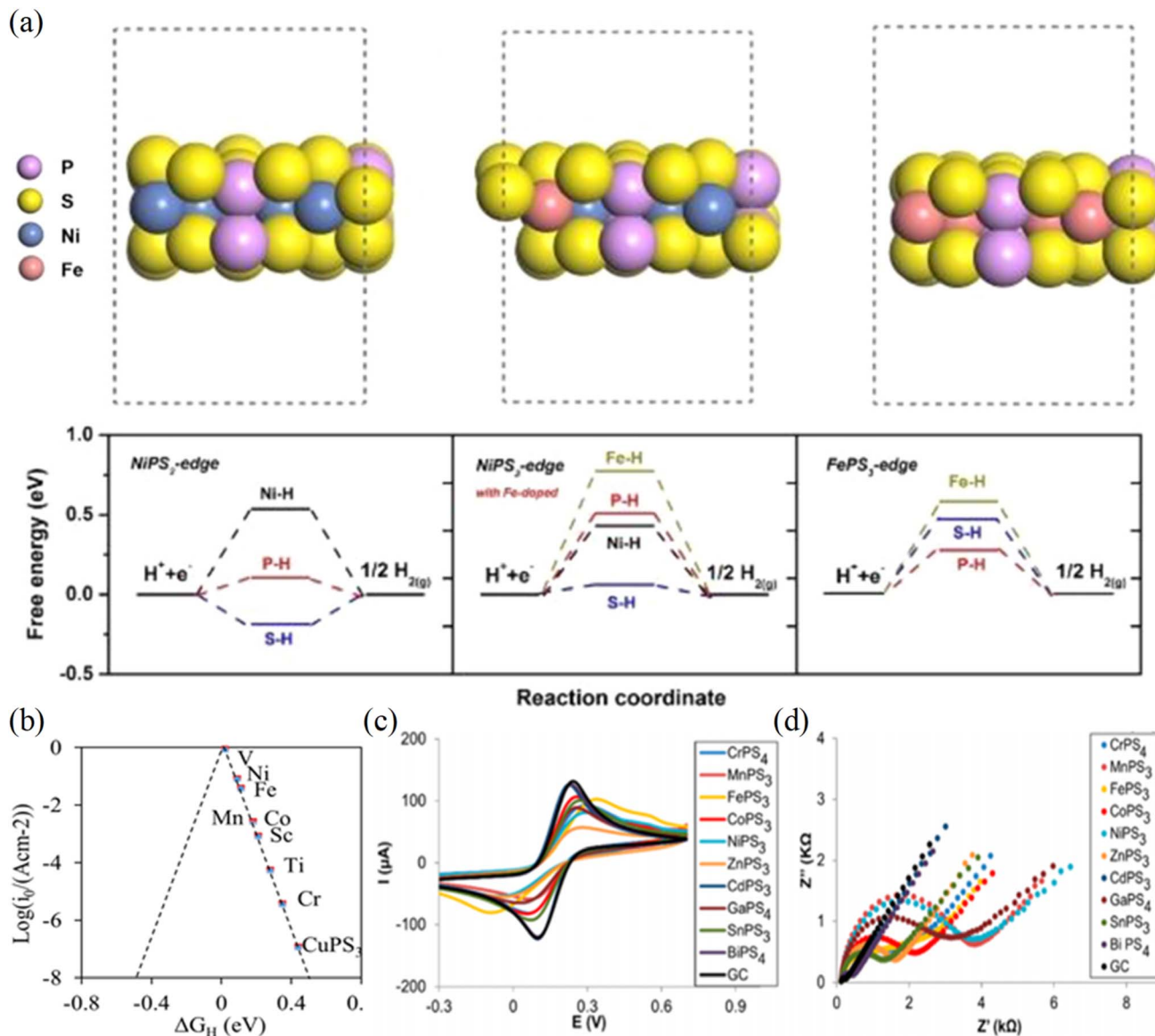
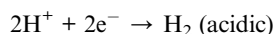


Fig. 9 (a) Structure and the corresponding free energy diagram of hydrogen evolution at equilibrium for NiPS<sub>3</sub>, Ni<sub>0.9</sub>Fe<sub>0.1</sub>PS<sub>3</sub>, and FePS<sub>3</sub>. Reprinted with permission.<sup>96</sup> Copyright 2019, American Chemical Society. (b) The Volcano curve of exchange current density for various transition metal anchored CuPS<sub>3</sub>. Reprinted with permission.<sup>97</sup> Copyright 2022, Springer. (c and d) Cyclic voltammograms recorded in the ferri/ferrocyanide redox probe and the Nyquist plots of various 2D TMPCs. Reprinted with permission.<sup>98</sup> Copyright 2017, American Chemical Society.

media (acidic or basic), the water splitting reaction involves a change in free energy of 237 kJ mol<sup>-1</sup> at 1 atm and 25 °C, corresponding to a theoretical cell voltage of 1.23 V to initiate water splitting.<sup>99</sup> However, experimentally a voltage higher than 1.23 V is required due to mass, electrolyte, and transport resistances and also because of the sluggish kinetics of HER and OER reactions.<sup>100</sup> The overpotential can be reduced by coating the catalyst at the anode and cathode surfaces, which decreases the energy barrier. Water splitting *via* HER involves the reduction of a H<sup>+</sup> ion or H<sub>2</sub>O, based on the pH of the electrolytic medium.<sup>100,101</sup>



Under acidic conditions, HER follows three possible reaction pathways, namely Volmer, Tafel, or Heyrovsky pathways. The Volmer step involves the reaction of electrons with H<sub>3</sub>O<sup>+</sup> to yield catalytically adsorbed H<sup>+</sup> ion (H<sub>ad</sub>) (2H<sup>+</sup> + e<sup>-</sup> → H<sub>ads</sub>). Subsequently, H<sub>2</sub> evolution occurs either by following the Tafel (2H<sub>ads</sub> → H<sub>2</sub>) or Heyrovsky (H<sub>ads</sub> + H<sup>+</sup>+e<sup>-</sup> → H<sub>2</sub>) pathway or both (Fig. 10b).<sup>41–43</sup> Irrespective of the paths by which H<sub>2</sub> evolution happens, H<sub>ad</sub> is always associated with the water reduction reaction. The Tafel plots could help in obtaining the reaction kinetics and mechanistic pathways for any catalyst, which shows water splitting *via* HER. The slope corresponds to the log(current density) *versus* overpotential, in the cathodic

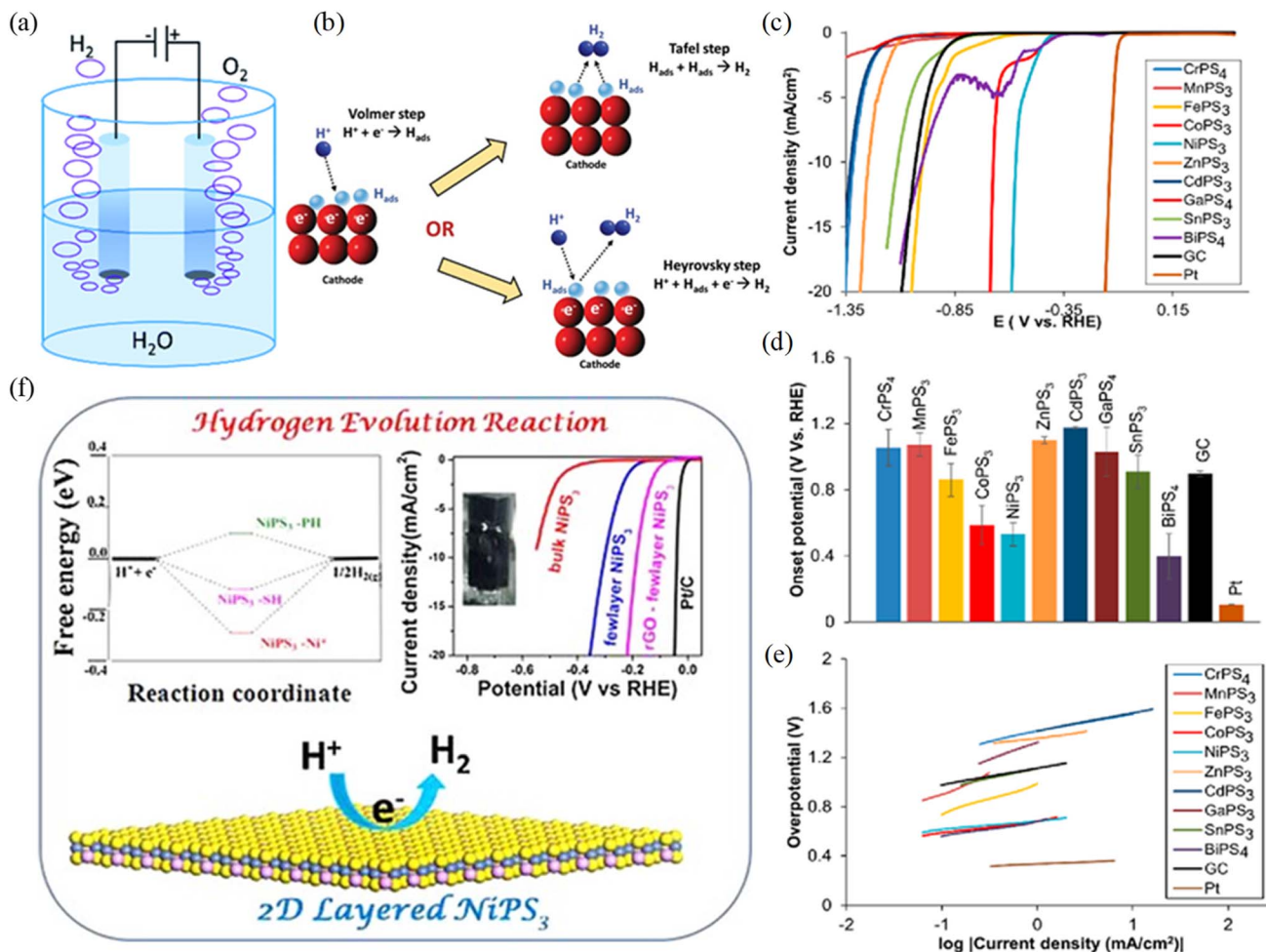


Fig. 10 Schematic of the (a) water-splitting electrolyzer and (b) possible reaction routes for electrocatalytic HER in the acidic medium. Reproduced with permission.<sup>122</sup> Copyright 2019, Elsevier. (c and d) Linear sweep voltammogram (LSV) curves obtained in 0.5 M H<sub>2</sub>SO<sub>4</sub> and (e) Tafel plots for various bulk MPX<sub>3</sub>. Reproduced with permission.<sup>123</sup> Copyright 2017, American Chemical Society. (f) Free energy diagram of the H<sub>2</sub> evolution for NiPS<sub>3</sub> and LSV curves of bulk NiPS<sub>3</sub>, exfoliated NiPS<sub>3</sub>, and NiPS<sub>3</sub>/RGO composites. Reproduced with permission.<sup>106</sup> Copyright 2016, Wiley publication.

potential ( $\eta$ ) range, which gives the Tafel slope value. The Tafel slope value signifies the amount of additional potential essential to increase a current density by 10 mA cm<sup>-2</sup>. For an ideal catalyst Pt, the Tafel slope values of 30, 40, and 120 mV dec<sup>-1</sup> indicate that the Volmer, Heyrovsky, and Tafel steps are the rate-determining steps.<sup>102,103</sup> The charge carrier mobility and the number of active sites also play an important role in describing the intrinsic HER activity for MPX<sub>3</sub>. For instance, MnPSe<sub>3</sub> shows high charge carrier mobility (electron and hole mobilities of 625.9 and 34.7 cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup>, respectively), and the massive divergence in the carrier mobility values suggests that efficient charge-separation for H<sub>2</sub> and O<sub>2</sub> evolution reactions.<sup>66</sup> Further, exfoliated layers show high water redox activity compared to the bulk due to increasing in-plane conductivity and more exposed edge sites.

2D MPX<sub>3</sub>-based electrocatalysts display H<sub>2</sub> evolution activity starting from very low to high, some of them even showing activity comparable to benchmark Pt/C catalysts. Experimentally, the electrocatalytic HER performance is accessed by the

onset potential with respect to a standard hydrogen electrode, Tafel slope, and charge-transfer resistance concerning the benchmark Pt/C catalyst. The lower the value of these factors, the superior the catalytic activity. We have compared these parameters of 2D MPX<sub>3</sub>-based catalysts in Table 1, which suggest that the MPX<sub>3</sub> containing Ni, Co, and Fe atoms, bimetallic TMPCs and their composite with other 2D systems display superior activity. Generally, it has been described that bimetallic phosphochalcogenides show better activity than monometallic systems due to synergistic interactions. Some of the widely examined 2D MPX<sub>3</sub> and their heterostructures are discussed in the following section.

In recent work, Martinez *et al.*<sup>98</sup> studied the electrocatalytic HER performance of a series of bulk MPX<sub>3</sub> (M = Mn, Fe, Co, Ni, Zn, Cd, Ga, and Sn) in acid electrolytes. Fig. 10c and d show the HER polarization curves for these MPS<sub>3</sub> compounds and the resulting onset potential values at 10 mA cm<sup>-2</sup>. Among these MPX<sub>3</sub> compounds, only NiPS<sub>3</sub> and CoPS<sub>3</sub> showed lower overpotential, -590 and -530 mV (vs. RHE), respectively, than bare

Table 1 Comparison of electrocatalytic HER activity of 2D TMPs and their nanocomposites reported in the literature

Catalysts	Electrode substrate	Overpotential at 10 mA cm <sup>-2</sup> vs. RHE (mV)	Tafel slope (mV dec <sup>-1</sup> )	Electrolyte	Reference
<b>Exfoliated MPX<sub>3</sub> nanosheets</b>					
MnPS <sub>3</sub>	GCE <sup>a</sup>	835 ± 68	—	0.5 M H <sub>2</sub> SO <sub>4</sub>	124
MnPS <sub>3</sub>	GCE	632	272	0.5 M H <sub>2</sub> SO <sub>4</sub>	94
MnPS <sub>3</sub>	GCE	1090 ± 71	—	0.1 M KOH	124
MnPS <sub>3</sub>	GCE	640 ± 87	—	0.5 M H <sub>2</sub> SO <sub>4</sub>	124
MnPS <sub>3</sub>	GCE	992 ± 56	—	0.1 M KOH	124
FePS <sub>3</sub>	GCE	211 ± 3	42	0.5 M H <sub>2</sub> SO <sub>4</sub>	47
FePS <sub>3</sub>	GCE	337 ± 4	—	1M KOH	47
FePS <sub>3</sub>	GCE	673 ± 4	—	3.5 wt% NaCl	47
FePS <sub>3</sub>	GCE	530	56	0.5 M H <sub>2</sub> SO <sub>4</sub>	98
CoPS <sub>3</sub>	Graphite	222 ± 2	71 ± 5	0.5 M H <sub>2</sub> SO <sub>4</sub>	125
CoPS <sub>3</sub>	GCE	590	84	0.5 M H <sub>2</sub> SO <sub>4</sub>	98
NiPS <sub>3</sub>	GCE	297	69	0.5 M H <sub>2</sub> SO <sub>4</sub>	106
NiPS <sub>3</sub>	GCE	398	159	1M KOH	106
NiPS <sub>3</sub>	GCE	816	54	3.5 wt% NaCl	106
NiPS <sub>3</sub>	GCE	205	74	0.5 M H <sub>2</sub> SO <sub>4</sub>	126
<b>MPX<sub>3</sub> nanosheet composite with reduced graphene oxide (RGO)</b>					
FePS <sub>3</sub> /RGO	GCE	108 ± 2	54	0.5 M H <sub>2</sub> SO <sub>4</sub>	47
FePS <sub>3</sub> /RGO	GCE	467 ± 3	—	1M KOH	47
FePS <sub>3</sub> /RGO	GCE	192 ± 2	—	3.5 wt% NaCl	47
NiPS <sub>3</sub> /RGO	GCE	178	55	0.5 M H <sub>2</sub> SO <sub>4</sub>	106
NiPS <sub>3</sub> /RGO	GCE	281	48	1M KOH	106
NiPS <sub>3</sub> /RGO	GCE	543	94	3.5 wt% NaCl	106
<b>Transition element doped MPX<sub>3</sub> nanosheets</b>					
Ni <sub>0.95</sub> Fe <sub>0.05</sub> PS <sub>3</sub>	GCE	130	114	1M KOH	96
Ni <sub>0.9</sub> Fe <sub>0.1</sub> PS <sub>3</sub>	GCE	72	73	1M KOH	96
Ni <sub>0.85</sub> Fe <sub>0.15</sub> PS <sub>3</sub>	GCE	152	187	1M KOH	96
Ni <sub>0.95</sub> Mn <sub>0.05</sub> PS <sub>3</sub>	GCE	—	135	1M KOH	94
Ni <sub>0.90</sub> Mn <sub>0.10</sub> PS <sub>3</sub>	GCE	—	142	1M KOH	94
Ni <sub>0.85</sub> Mn <sub>0.15</sub> PS <sub>3</sub>	GCE	—	143	1M KOH	94
Ni <sub>0.97</sub> Co <sub>0.03</sub> PS <sub>3</sub>	GCE	112	103	1M KOH	49
Ni <sub>0.95</sub> Co <sub>0.05</sub> PS <sub>3</sub>	GCE	71	77	1M KOH	49
Ni <sub>0.93</sub> Co <sub>0.07</sub> PS <sub>3</sub>	GCE	105	110	1M KOH	49
Ni <sub>0.91</sub> Co <sub>0.09</sub> PS <sub>3</sub>	GCE	145	113	1M KOH	49
Co <sub>0.6</sub> (VMnNiZn) <sub>0.4</sub> PS <sub>3</sub>	GCE	66	65	1M KOH	107
MnFePS <sub>3</sub>	Carbon paper	102	49	1M KOH	127
NiCoFePS <sub>3</sub>	Ni foam	231	86	1M KOH	128
<b>Single-atom anchored MPX<sub>3</sub> nanosheets</b>					
NiFePS <sub>3</sub>	GCE	356	170	1M KOH	109
CoFePS <sub>3</sub>	GCE	490	132	1M KOH	109
PdFePS <sub>3</sub>	GCE	471	128	1M KOH	109
<b>2D MPX<sub>3</sub>-based heterostructures</b>					
FePS <sub>3</sub> /MoS <sub>2</sub>	Ni foam	175	127	0.5 M H <sub>2</sub> SO <sub>4</sub>	50
FePS <sub>3</sub> /MoS <sub>2</sub>	Ni foam	168	107	1 M KOH	50
NiPS <sub>3</sub> /MoS <sub>2</sub>	GCE	112	64	1 M KOH	51
NiPS <sub>3</sub> /Ni <sub>2</sub> P	GCE	85	82	1 M KOH	110
NiPS <sub>3</sub> /Ni foam	Ni foam	74	86	1 M KOH	129
CoNiPS <sub>3</sub> /N-doped carbon	GCE	140	60	1 M KOH	130

<sup>a</sup> GCE – glassy carbon electrode.

GCE (−890 mV vs. RHE), indicating that these systems can be beneficial for electrocatalysis.<sup>69,98</sup> The high H<sub>2</sub> evolution activity of NiPS<sub>3</sub> and CoPS<sub>3</sub> is ascribed to preferential orientation of these systems in the (001) crystal plane, as these planes are reported to be highly HER active in the case of Ni<sub>2</sub>P catalyst.<sup>33,104</sup> Further, the MPS<sub>3</sub> system containing Ni and Co metals is

estimated to display ΔG<sub>H\*</sub> value near to thermoneutral potential, thereby display superior HER activity.<sup>49,92,105</sup> In another study, Sampath and coworkers<sup>106</sup> have shown that HER activity of bulk NiPS<sub>3</sub> can be further improved by exfoliating bulk crystals into few-layers by liquid phase exfoliation. These few-layer NiPS<sub>3</sub> showed stable H<sub>2</sub> evolution over a long period in

a wide pH range of 1 to 14, including in 3.5 wt% NaCl solution, which is close to seawater composition. Fig. 10f shows the *iR*-corrected LSV polarization curves for bulk and exfoliated NiPS<sub>3</sub>, which show the onset potential of -450 and -159 mV, respectively, in 0.5 M H<sub>2</sub>SO<sub>4</sub>, indicating a higher activity in the case of the latter. Further, bulk NiPS<sub>3</sub> exhibited a Tafel slope value of -119 mV dec<sup>-1</sup>, while a few-layer sample revealed a value of -69 mV dec<sup>-1</sup>. Further, exfoliated NiPS<sub>3</sub> showed an overpotential of 297, 398 and -816 mV in acidic (pH = 1), basic (pH = 14) and in neutral 3.5 wt% NaCl electrolyte, respectively, at 10 mA cm<sup>-2</sup>. These studies indicate that the kinetics of HER is more facile in the case of exfoliated samples due to an enhanced charge-transfer rate. The authors also showed by DFT calculation that the P atom is the most favorable site for hydrogen adsorption by evaluating the  $\Delta G_{H^*}$  value (Fig. 10f).

Sampath and coworkers<sup>47</sup> reported HER activity of the exfoliated FePS<sub>3</sub> system as well. The reported overpotentials at 10 mA cm<sup>-2</sup> for exfoliated FePS<sub>3</sub> in pH = 1, 14, and in neutral 3.5 wt% NaCl were -211, -337, and -637 mV respectively. According to Sampath and coworkers, exfoliated NiPS<sub>3</sub> showed higher overpotential at 10 mA cm<sup>-2</sup> and hence lower activity than FePS<sub>3</sub>. On the contrary, Martinez *et al.*<sup>98</sup> reported that bulk NiPS<sub>3</sub> showed lower overpotential at 10 mA m<sup>-2</sup> as compared to FePS<sub>3</sub>. Therefore, the physicochemical properties of these materials need to be investigated in detail to provide further insights into the activity and mechanism of H<sub>2</sub> evolution. In addition, coupling of exfoliated NiPS<sub>3</sub>/FePS<sub>3</sub> with conductive reduced graphene oxide (RGO) substrate further improved HER activity as reported by Sampath and coworkers.<sup>47,106</sup> The onset potential values obtained for exfoliated NiPS<sub>3</sub> and FePS<sub>3</sub> were -159 mV and -95 mV, while NiPS<sub>3</sub>/RGO and FePS<sub>3</sub>/RGO show -62 and -50 mV, respectively. The charge-transfer resistance ( $R_{ct}$ ) value obtained from AC impedance measurements indicates that the  $R_{ct}$  value for NiPS<sub>3</sub> and FePS<sub>3</sub> was lowered on coupling with graphene. This implied that the conductive RGO support improved the HER activity of the MPX<sub>3</sub> system due to enhanced charge-transfer characteristics. Also, NiPS<sub>3</sub>/RGO and FePS<sub>3</sub>/RGO nanocomposites showed long-term stability, suggesting these materials can be highly efficient electrocatalysts for HER in a wide pH range.

As indicated earlier, 2D MPS<sub>3</sub> showed marginal electrocatalytic performance due to poor electronic conductivity; thus conductive graphene is coupled to improve the HER performance. Even though, NiPS<sub>3</sub>/RGO and FePS<sub>3</sub>/RGO composite required overpotentials of -178 and -192 mV, respectively, to reach 10 mA cm<sup>-2</sup> in a basic electrolyte. In general, the catalyst electrocatalytic activity can be improved either by increasing the active site through catalyst loading or exposing the edge site *via* nanostructuring, or enhancing the intrinsic activity of the individual site. With this in mind, Li *et al.*<sup>49</sup> doped Co into NiPS<sub>3</sub> and with Ni<sub>0.95</sub>Co<sub>0.05</sub>PS<sub>3</sub> nanosheets achieved a current density of 10 mA cm<sup>-2</sup> at an overpotential of as low as -48 mV (*vs.* RHE) with a Tafel slope of 77 mV dec<sup>-1</sup> in 1.0 M KOH electrolyte (Fig. 11a). The synthetic procedure involved initially obtaining the bulk NiCoPS<sub>3</sub> by heating the stoichiometric ratio of individual elements in a sealed quartz ampoule. Later, the bulk sample was ultrasonicated in *N,N*-dimethyl formamide solvent

to obtain 2D nanosheets. The authors also prepared Ni<sub>1-x</sub>Co<sub>x</sub>-PS<sub>3</sub> containing various cobalt amounts ( $x = 0.03, 0.05, \text{ and } 0.07$ ) to know the effect of Co doping content on HER activity. The  $R_{ct}$  values of 18.6, 12.1, 23.4, and 41.7  $\Omega$  were obtained for Ni<sub>1-x</sub>Co<sub>x</sub>PS<sub>3</sub> with cobalt doping amounts of  $x = 0.03, 0.05, 0.07$ , respectively, while bare NiPS<sub>3</sub> showed 82.3  $\Omega$  (Fig. 11b). The reduced  $R_{ct}$  value in the case of Ni<sub>1-x</sub>Co<sub>x</sub>PS<sub>3</sub> implied that Co doping improved intrinsic HER kinetics of NiPS<sub>3</sub> through a higher charge-transfer rate. However, an increase or decrease of Co amount other than  $x = 0.05$ , more or fewer declines HER performance. Later, theoretical studies have shown that H affinity at the P site can be improved by Co doping along with electrical conductivity.<sup>48</sup> In another study, Rakov *et al.*<sup>94</sup> showed that Ni-doped (lower oxophilicity) MnPS<sub>3</sub> displayed higher HER activity than the bare sample. With Ni doping, the ability of binding of the surface intermediate into the catalyst surface decreased, which in turn assisted the desorption steps such as the Tafel or Heyrovsky steps. In addition, doping of multi-metal atoms such as V, Mn, Ni, and Zn into CoPS<sub>3</sub> increased the density of active sites due to the formation of high entropy alloys.<sup>107</sup> The generated S edge sites and basal plane P sites improved H<sup>+</sup> ion adsorption, whereas Mn ion boosted water dissociation during the Heyrovsky step. Recently, Megha *et al.*<sup>108</sup> using DFT calculations showed that Sc, Y, and Mo elemental doping into the MnPSe<sub>3</sub> lattice reduced the  $\Delta_{GH}$  value of pristine MnPSe<sub>3</sub> to 1.41 eV, to 0.24, 0.18, and 0.23 eV, respectively. Further, the density of state (DOS) plots suggested that DOS at the Fermi energy was infinite for 25, 12.5, and 6.25% Sc elemental doping concentrations in MnPSe<sub>3</sub>, indicating activation of the inert basal plane of MnPSe<sub>3</sub> towards HER (Fig. 11c and d). Apart from metal atom doping, non-metal carbon doping can transform semiconducting FePS<sub>3</sub> into metallic form and show enhanced HER activity. The dopant with fewer electrons than the substitutional atom can improve electronic conductivity and also greatly activate surface sites for hydrogen adsorption. Further, C, N-codoping in FePS<sub>3</sub> pushed  $\Delta G_{H^*}$  (-0.188 eV) value closer to zero and showed HER activity comparable to that of Pt/C with a small overpotential of 53.2 mV to achieve a current density of 10 mA cm<sup>-2</sup>.<sup>105</sup> However, studies on non-metal doping in 2D MPX<sub>3</sub> are very limited and these systems need to be investigated in detail both by computational and experimental studies.

Recently, Tang *et al.*<sup>109</sup> showed that anchoring of single-atom (SA) catalysts such as Ni, Co, and Pd over 2D FePS<sub>3</sub> can tune the surface electronic structure and reinforces water adsorption and dissociation capacity for both OER and HER. DFT calculations showed that Ni SA anchored FePS<sub>3</sub> facilitated electron aggregation from Fe to Ni-S and enhanced electron-transfer rate at Ni and S sites (Fig. 11e and f). In addition, the electron-rich Ni site acted as an active site to diminish hybridization between O and Ni in Ni-FePS<sub>3</sub>, thereby, facilitating conversion from O\* to OOH\* group and reducing the barrier for OER. Ni-FePS<sub>3</sub> delivered an outstanding performance as a bifunctional catalyst for water splitting with an overpotential of 356 and 287 mV at a current density of 10 mA cm<sup>-2</sup> for HER and OER, respectively (Fig. 11g-i). This study indicates that engineering surface active sites at the atomic scale are an

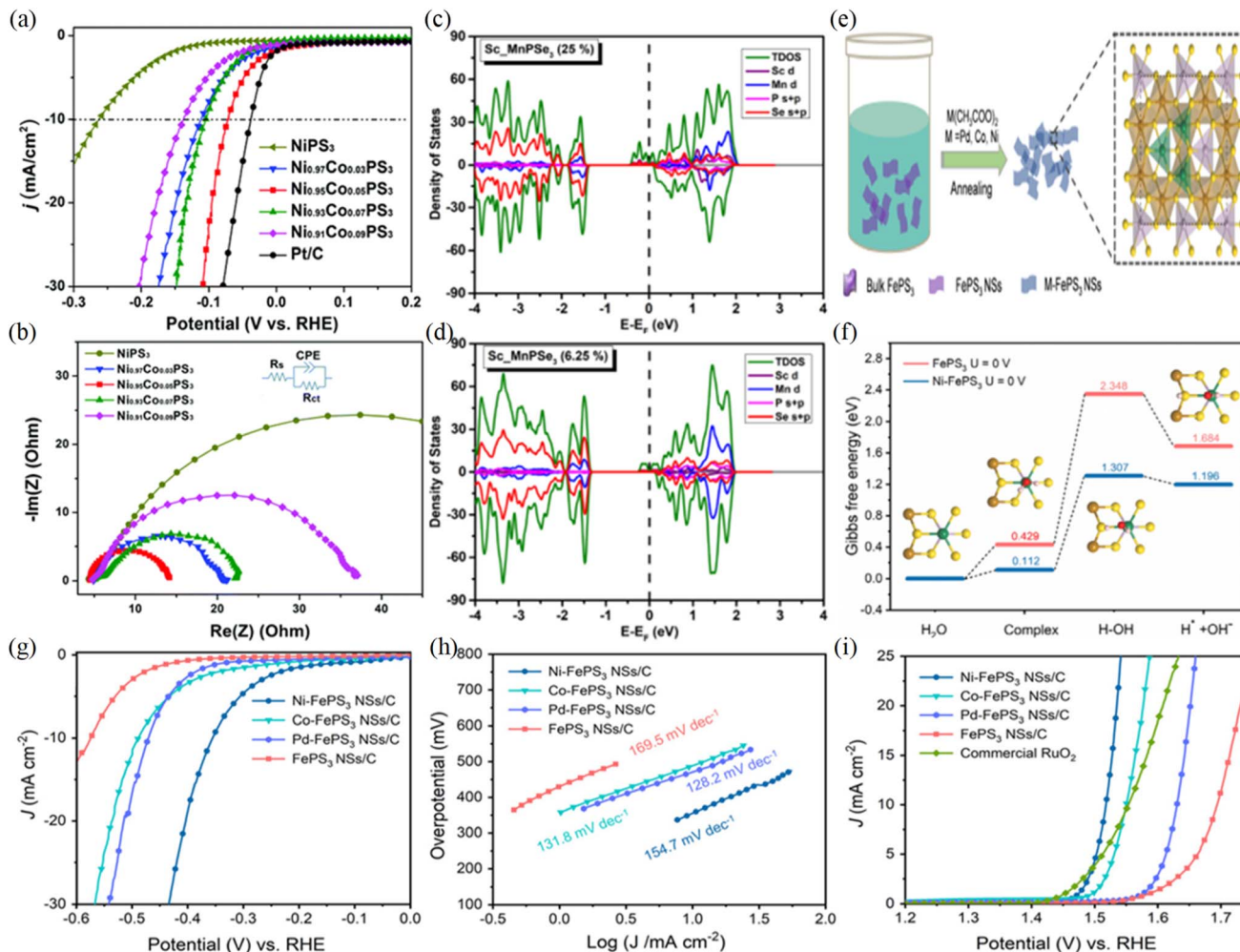


Fig. 11 (a) LSV polarization curves and (b) Nyquist plots for  $\text{Ni}_{1-x}\text{Co}_x\text{PS}_3$  containing various cobalt amounts ( $x = 0.03, 0.05, 0.07$ ).<sup>49</sup> (c and d) Density of states plots for 25 and 6.25% Sc element doped  $\text{MnPS}_3$ . Reproduced with permission.<sup>108</sup> Copyright 2023, Elsevier. (e) Schematic illustration of anchoring single-atom catalysts (Pt, Co, and Ni) over 2D  $\text{FePS}_3$ . (f) Gibbs free energy profile of  $\text{FePS}_3$  and  $\text{Ni-FePS}_3$ . (g and h) LSV polarization curves for HER and the corresponding Tafel plots. (i) polarization curves for OER for  $\text{FePS}_3$ ,  $\text{Ni-FePS}_3$ ,  $\text{Co-FePS}_3$ , and  $\text{Pd-FePS}_3$  catalysts. Reproduced with permission.<sup>109</sup> Copyright 2022, Wiley publication.

effective way to modulate the catalytic activity of 2D  $\text{MPX}_3$  systems.

$\text{MPX}_3$  nanostructures with a large number of active phosphorus edges are considered to be efficient water-splitting catalysts by both theoretical and experimental studies. The generation of heterojunctions by coupling two or more different materials can incorporate the advantages of distinct materials into one hybrid. Huang *et al.*<sup>50</sup> reported the 2D/2D  $\text{FePS}_3/\text{MoS}_2$  heterojunction, in which interfacial coupling between  $\text{FePS}_3$  and  $\text{MoS}_2$  causes significant enhancement in  $\text{H}_2$  evolution performance.  $\text{FePS}_3/\text{MoS}_2$  requires low overpotentials of only 175 and 168 mV to reach  $10 \text{ mA cm}^{-2}$  current density under acidic and basic conditions, respectively (Fig. 12a and b). Further,  $\text{FePS}_3/\text{MoS}_2$  showed lower Tafel slope values of 107 and  $125 \text{ mV dec}^{-1}$  at pH = 1 and pH = 14, respectively, with little decay in potential even after 1000 cycles (Fig. 12c). The *in situ* grown  $\text{MoS}_2$  can provide more exposed active sites, which facilitate diffusion of active species and release of the formed  $\text{H}_2$

bubble. Secondly, the intercalated  $\text{MoS}_2$  layers can stop restacking of  $\text{FePS}_3$  layers, enhancing conductivity and exposing active sites of  $\text{FePS}_3$ . Since the electron transfer resistance is higher in adjacent layers than along the  $\text{MPX}_3$  layer, reduction in the stacking of the number of  $\text{FePS}_3$  layers improves electronic conductivity and carrier flow to  $\text{MoS}_2$ .<sup>50</sup> In another study, Liu *et al.*<sup>51</sup> synthesized  $\text{NiPS}_3/\text{MoS}_2$  composite and demonstrated that internal polarization field (IPF) facilitates hydrogen spillover (HSO) during HER from the  $\text{MoS}_2$  edge site to  $\text{NiPS}_3$ . Secondly, IPF boosts the hydroxyl ion diffusion pathway, thereby enhancing the rate of oxygen evolution reaction (Fig. 12d). The  $\text{NiPS}_3/\text{MoS}_2$  composite requires a low overpotential of 112 and 296 mV to reach  $10 \text{ mA cm}^{-2}$  current density for  $\text{H}_2$  and  $\text{O}_2$  evolution reactions, respectively. Further, the  $\text{NiPS}_3/\text{MoS}_2$  composite delivered overall water splitting with a cell voltage of 1.64 V at  $10 \text{ mA cm}^{-2}$  and exhibited long-term stability up to 100 h (Fig. 12e). The chronopotentiometry study conducted for 50 h indicates that  $\text{NiPS}_3/\text{MoS}_2$  does not lose any

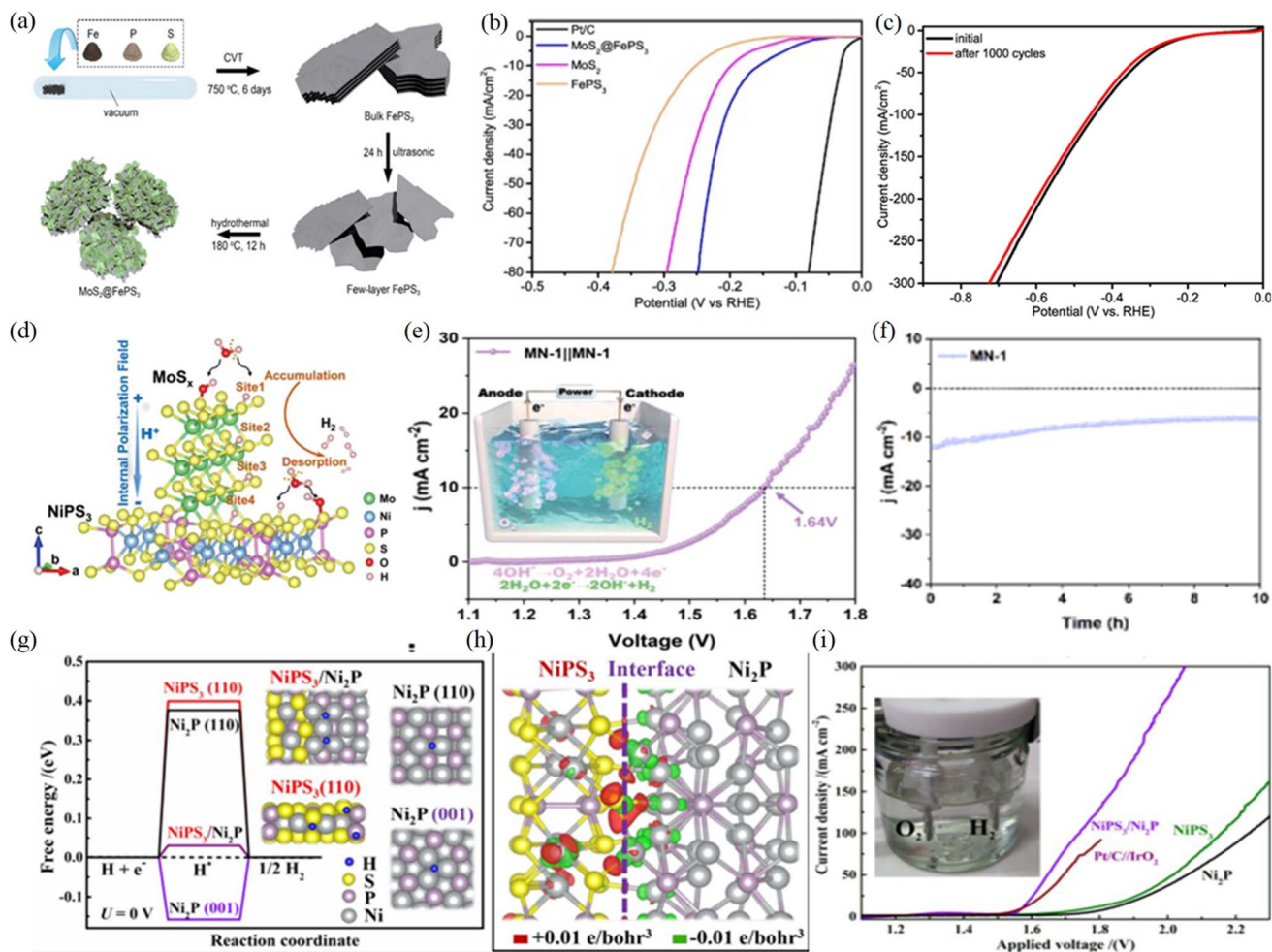


Fig. 12 (a) Schematic of the *in situ* CVT method adapted for the growth of FePS<sub>3</sub>/MoS<sub>2</sub> heterostructure. (b) Polarization curves for FePS<sub>3</sub>/MoS<sub>2</sub> heterostructure. (c) Electrochemical durability of FePS<sub>3</sub>/MoS<sub>2</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Reproduced with permission.<sup>50</sup> Copyright 2020, Elsevier. (d and e) Polarization curve of NiPS<sub>3</sub>/MoS<sub>2</sub> as both anode and cathode catalyst for overall water splitting driven by a solar cell (~1.65 V). (f) Chronopotentiometry study for NiPS<sub>3</sub>/MoS<sub>2</sub> carried for 50 h. Reproduced with permission.<sup>51</sup> Copyright 2012, Wiley publication. (g) Gibbs free energy of hydrogen adsorption estimated for NiPS<sub>3</sub>/Ni<sub>2</sub>P composite, NiPS<sub>3</sub> (110), Ni<sub>2</sub>P (110) and Ni<sub>2</sub>P (001) planes. (h) Charge density distribution at the junction of NiPS<sub>3</sub>/Ni<sub>2</sub>P composite. (i) Polarization curve of the NiPS<sub>3</sub>/Ni<sub>2</sub>P heterocatalyst for overall water splitting compared with the benchmark Pt/C//IrO<sub>2</sub> electrocatalyst. Reproduced with permission.<sup>110</sup> Copyright 2019, American Chemical Society.

catalytic activity, implying the practical advantages of the catalyst in terms of stability (Fig. 12f). Besides, Liang *et al.*<sup>110</sup> grew nickel phosphide nanostructures on NiPS<sub>3</sub>, which showed a lower bias voltage of 1.65 V for overall water splitting, even surpassing that of the commercial Pt/C//IrO<sub>2</sub> electrocatalyst (Fig. 12g–i). Generation of the MPX<sub>3</sub> heterostructure with MoS<sub>2</sub> would be beneficial as a bifunctional catalyst since these systems decrease the energy barrier for hydrogen adsorption and also improve sluggish OER kinetics due to built-in electric field gradient.<sup>115</sup>

## 5. Photocatalytic water splitting

2D MPX<sub>3</sub> compounds band gap ranges from 1.3 to 3.5 eV, which appears to be advantageous for optoelectronic and catalysis applications. Secondly, abundant active sites such as P and S edges of 2D MPX<sub>3</sub> facilitate hydrogen adsorption and

desorption, these characteristics extend their application as photocatalysts for water-splitting applications. In this context, Shifa *et al.*<sup>65</sup> prepared MnPS<sub>3</sub> and MnPSe<sub>3</sub> nanosheets by the CVD method and examined their photocatalytic HER performance under solar light (AM 1.5G) without any sacrificial agent. Atomic force microscopy images revealed that MnPS<sub>3</sub> and MnPSe<sub>3</sub> show layer thicknesses of ~6 and 28 nm with lateral dimensions of ~1.5 and 0.45 μm, respectively (Fig. 13a and b). Tauc plots derived from UV-vis diffuse reflectance spectroscopy show a red shift in absorption edge for the MnPSe<sub>3</sub> as compared to MnPS<sub>3</sub>, indicating the better light harvesting capability of the former system (Fig. 13c). As depicted in Fig. 13d, both MnPS<sub>3</sub> and MnPSe<sub>3</sub> showed good HER activity with H<sub>2</sub> evolution rates of 3.1 and 6.5 μmol h<sup>-1</sup> g<sup>-1</sup>, respectively. The high H<sub>2</sub> evolution rate of MnPSe<sub>3</sub> as compared to MnPS<sub>3</sub> can be ascribed to the superior light-harvesting ability and high charge carrier mobility in the former system. Secondly, the higher

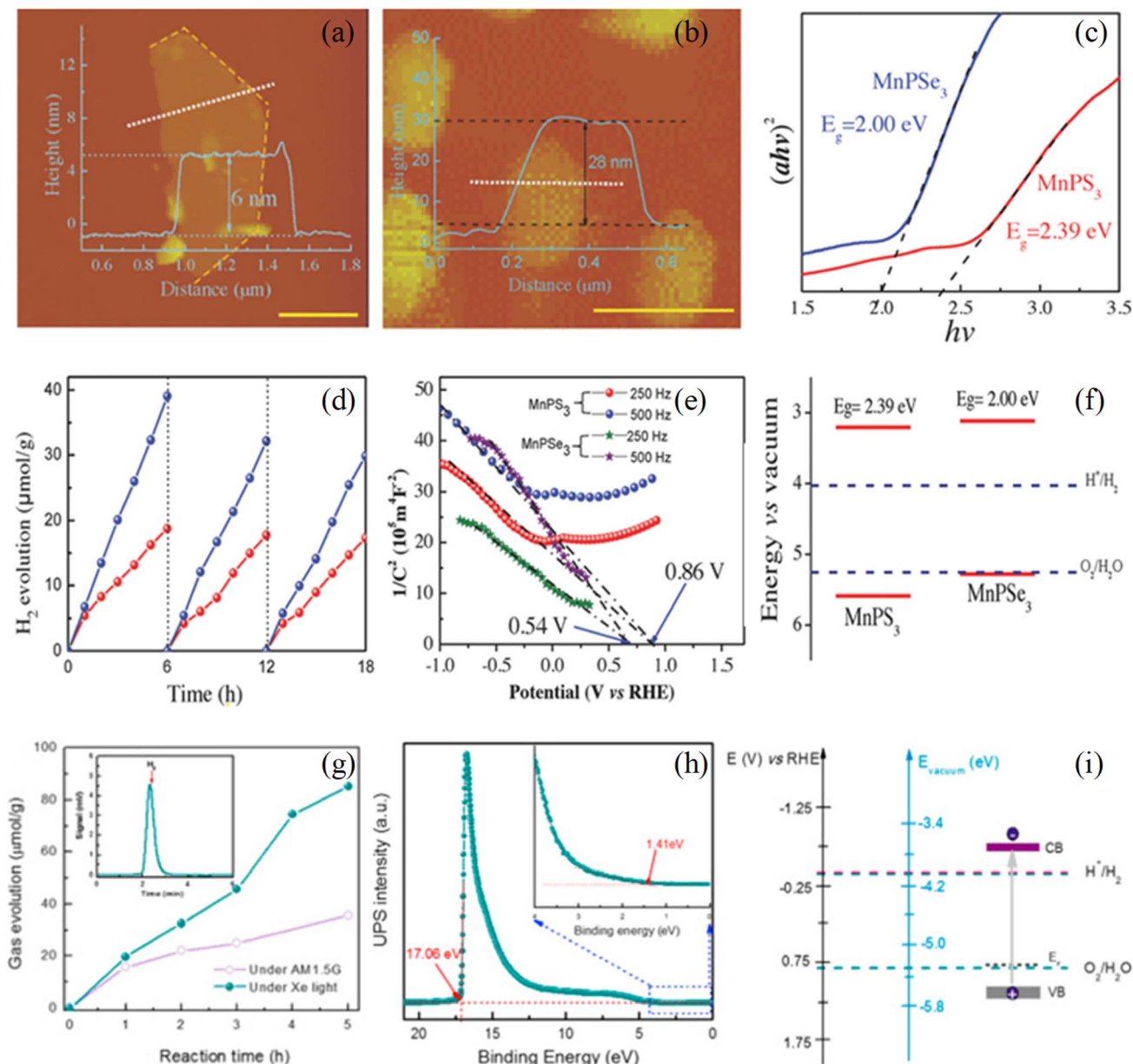


Fig. 13 AFM images of  $\text{MnPS}_3$  (a),  $\text{MnPSe}_3$  (b), Tauc plot (c), HER data (d), Mott–Schottky plots (e), and schematic illustration of alignment of VBM and CBM edge potentials with respect to water reduction potential derived from Mott–Schottky plots (f) for  $\text{MnPS}_3$  and  $\text{MnPSe}_3$ . Reprinted with permission.<sup>65</sup> Copyright 2018, Wiley publication. Two-dimensional  $\text{NiPS}_3$  HER data under a xenon lamp and in solar simulated light (g), ultraviolet photoelectron spectroscopy data (h), and schematic illustration of alignment of VBM and CBM edge potentials of  $\text{NiPS}_3$  with respect to water reduction potential derived from Mott–Schottky plots (i). Reproduced with permission. Copyright 2017, Elsevier.<sup>113</sup>

electronegativity of Se compared to S of  $\text{P}_2\text{X}_6^{4-}$  cluster orbitals could result in better  $\text{H}^+$  adsorption and  $\text{H}_2$  desorption. Further, the addition of  $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$  as a sacrificial electron donor enhanced the  $\text{H}_2$  evolution rate of the  $\text{MnPS}_3$  and  $\text{MnPSe}_3$  photocatalysts to 21.2 and 43.5  $\mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively. The energy level of  $\text{MnPSe}_3$  as derived from the Mott–Schottky plots indicated that VB was just fractionally below the water oxidation potential, which defied the oxygen evolution characteristics (Fig. 13e and f). Even though  $\text{MnPSe}_3$  showed promising HER performance, most of the research on the  $\text{MnPSe}_3$  system still focused on studying fundamental physical characteristics.

Layered metal thiophosphates containing Fe, Ni, Sn, and Zn have also been reported as efficient catalysts for photocatalytic hydrogen evolution reactions. For instance, Sendeku *et al.*<sup>111</sup> synthesized  $\text{Sn}_2\text{P}_2\text{S}_6$  nanosheets with Pc monoclinic phase by chemical vapor conversion process employing  $\text{SnS}_2$ , P, and S precursors (Fig. 14a and b) and further utilized for  $\text{H}_2$  generation from pure water under solar light irradiation. To reveal the light-harvesting ability of  $\text{Sn}_2\text{P}_2\text{S}_6$ , the UV-vis diffuse reflectance spectrum was recorded, as shown in Fig. 14c. The absorption edge of  $\text{Sn}_2\text{P}_2\text{S}_6$  was up to 520 nm with a weak absorption in the 520–600 nm region. Meanwhile, the corresponding Tauc plot



shown in the inset of Fig. 14c shows the estimated band gap ( $E_g$ ) value of 2.25 eV. Further, Mott–Schottky plots gave a positive slope revealing the n-type feature along with a flat band potential of  $-0.48$  V (Fig. 14d). Secondly, ultraviolet photoelectron spectroscopy (UPS) studies were also carried out to obtain the band alignment of  $\text{Sn}_2\text{P}_2\text{S}_6$  nanosheets. From the UPS spectrum, the VB edge of  $\text{Sn}_2\text{P}_2\text{S}_6$  was calculated to be at  $-5.68$  versus the vacuum level, as shown in Fig. 14e. The CB level was calculated from the equation  $E_{\text{CB}} = E_{\text{VB}} - E_g$ , which was estimated to be at  $-3.43$  eV versus the vacuum level. On the basis of the previous results, a schematic band diagram of  $\text{Sn}_2\text{P}_2\text{S}_6$  is described in Fig. 14e, which implied that the VB and

CB edges were suitably oriented to employ a water redox reaction. Fig. 14f shows the time course hydrogen evolution curve of  $\text{Sn}_2\text{P}_2\text{S}_6$  under simulated solar light (AM 1.5G) without any sacrificial agent. The  $\text{H}_2$  evolution rate increases linearly over time with a rate of  $202.06 \mu\text{mol h}^{-1} \text{g}^{-1}$ , which is  $\sim 10$  times higher than previously discussed  $\text{MnPS}_3$  nanosheets. In another study, Zhao *et al.*<sup>112</sup> prepared exfoliated  $\text{ZnPS}_3$  by a liquid-phase exfoliation from its bulk crystal and realized a high HER activity of  $640 \mu\text{mol h}^{-1} \text{g}^{-1}$  under a xenon lamp using  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$  as sacrificial agents (Fig. 14g–i). While bulk  $\text{ZnPS}_3$  showed relatively low activity of  $640 \mu\text{mol h}^{-1} \text{g}^{-1}$  under similar conditions. The enhanced activity in the case of exfoliated

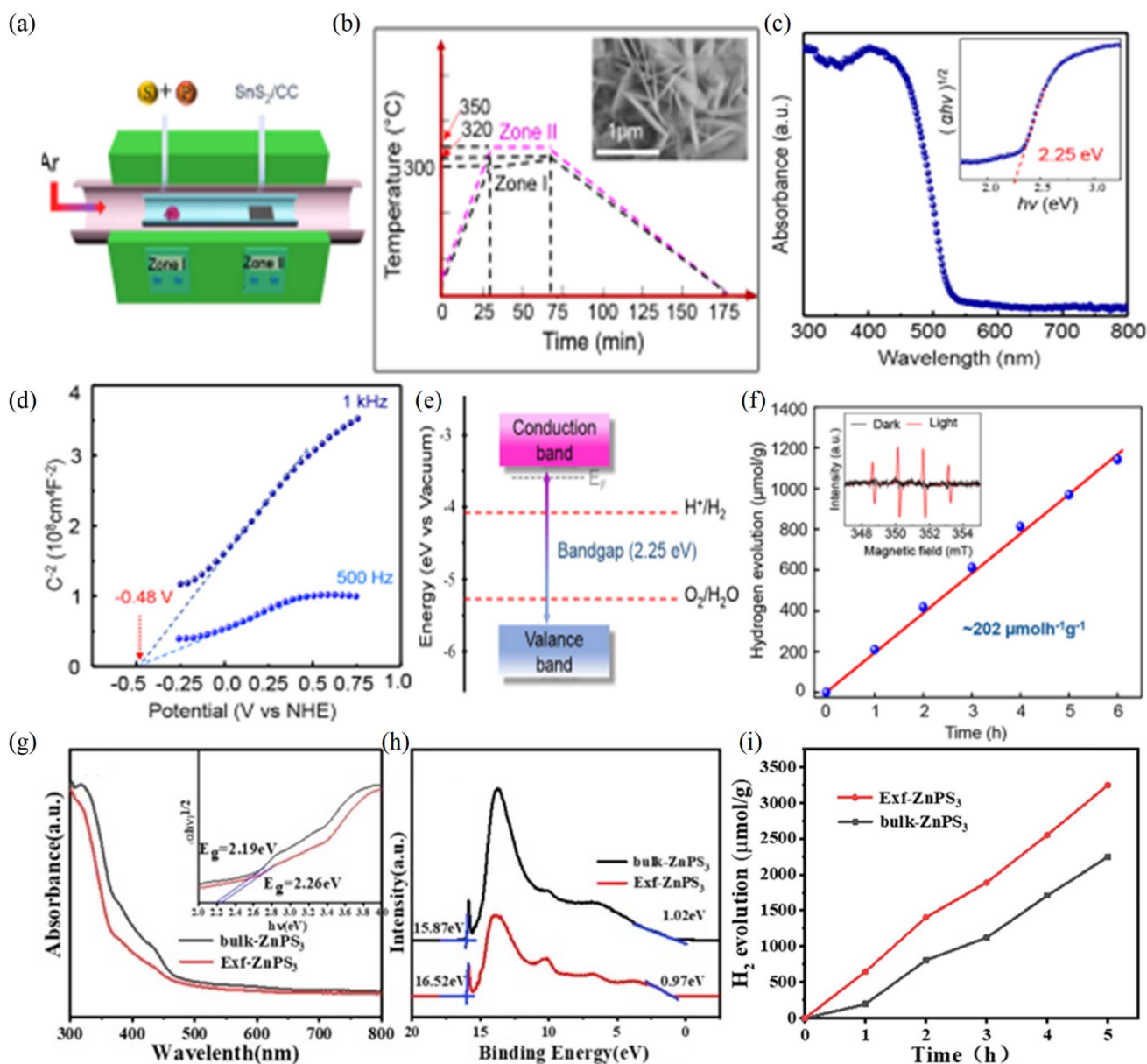


Fig. 14 (a and b) Schematic of the synthesis of  $\text{Sn}_2\text{P}_2\text{S}_6$  nanosheets using a tubular furnace. UV-vis diffuse reflectance spectrum (c), Mott–Schottky plots (d), energy band diagram (e), and HER data (f) for  $\text{Sn}_2\text{P}_2\text{S}_6$  nanosheets. Reprinted with permission.<sup>111</sup> Copyright 2021, The American Chemical Society. UV-vis extinction spectra (g), UPS spectra (h), and time course HER curves (i) for bulk and exfoliated  $\text{ZnPS}_3$  catalyst. Reprinted with permission.<sup>112</sup> Copyright 2022, Elsevier.

ZnPS<sub>3</sub> is attributed to a high specific area and more exposed edge sites.

In 2017, Wang *et al.*<sup>113</sup> prepared NiPS<sub>3</sub> nanosheets by a modified CVD method and studied their HER activity under xenon light without any cocatalyst or sacrificial agent. As shown in Fig. 7g, NiPS<sub>3</sub> showed the HER activity of 26.42  $\mu\text{mol h}^{-1} \text{g}^{-1}$  in neutral or pure water until the light irradiation was turned off. Further, the addition of the hole scavenger Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> to the photosystem enhanced the H<sub>2</sub> yield to 74.67  $\mu\text{mol h}^{-1} \text{g}^{-1}$ . While the NiPS<sub>3</sub> catalyst under simulated solar light showed a lower HER activity of 6.46  $\mu\text{mol h}^{-1} \text{g}^{-1}$  in the sacrificial agent-free water. The band structure of NiPS<sub>3</sub> was studied by using ultraviolet photoelectron spectroscopy and electrochemical impedance measurements indicated that the VB of NiPS<sub>3</sub> was not straddling with water oxidation potential and hence was not energetically favorable to offer holes for oxygen evolution (Fig. 7h and i). Therefore, some of the single-component MPX<sub>3</sub> systems utilized for photochemical HER without the cocatalyst or sacrificial agent did not evolve oxygen due to misalignment of the VB relative to the water oxidation potential. Thus, the MPX<sub>3</sub> catalyst also possesses the common disadvantage of the single-catalyst photosystem, wherein photoactivity decreases with time due to photocorrosion. The photogenerated electrons at CB are consumed by H<sup>+</sup> to generate H<sub>2</sub> while holes accumulate at the VB due to misalignment. These highly reactive holes further react with the semiconductor itself, which results in decomposition and reduced activity of the catalyst. Even with the presence of a sacrificial agent, the activity of ZnPS<sub>3</sub> and NiPS<sub>3</sub> nanosheets was reduced by more than half of the initial value only after 24 h of the hydrogen evolution test, which suggests deprivation in structural stability under photochemical conditions. Therefore, the activity and stability obtained with a single-component MPX<sub>3</sub> system are still far from reality, and photocorrosion of these materials under photocatalytic conditions impedes their applicability as photocatalysts.

In an effort to increase the H<sub>2</sub> evolution yield, Barua *et al.*<sup>93</sup> examined the photocatalytic HER activity of a range of MPX<sub>3</sub> systems (MnPS<sub>3</sub>, FePS<sub>3</sub>, NiPS<sub>3</sub>, ZnPS<sub>3</sub>, CdPS<sub>3</sub>, FePSe<sub>3</sub>, CdPSe<sub>3</sub>, Ag<sub>0.5</sub>In<sub>0.5</sub>PS<sub>3</sub>, and Ag<sub>0.5</sub>In<sub>0.5</sub>PSe<sub>3</sub>) using eosin Y as a photosensitizer and triethanolamine (TEOA) as a sacrificial agent. This study indicated that the combination of photosensitizer and sacrificial agent somewhat assisted in extending the structural stability and long-term H<sub>2</sub> evolution activity. Experimentally, band gaps of all synthesized MPX<sub>3</sub> systems were obtained using absorption spectra and the corresponding Taucs plots revealed band gaps varied in the range of 1.29–3.3 eV, suggesting that the band gap and band edges of MPX<sub>3</sub> were thermodynamically suitable for the water reduction reaction. Fig. 15a shows the schematic of the probable mechanism of HER by MPX<sub>3</sub> compounds in the presence of Eosin Y and TEOA. Initially, the dye molecule absorbs light to yield a photoexcited dye (EY\*), which then transforms to a triplet excited state (EY<sup>3\*</sup>) *via* an intersystem crossing. The intermediate EY<sup>3\*</sup> then takes an electron from TEOA *via* reductive quenching forming EY<sup>-</sup> species. The electrons from EY<sup>-</sup> are then transported to the CBM of the MPX<sub>3</sub> where H<sup>+</sup>/H<sub>2</sub> reduction takes place.<sup>97</sup> The HER activity of monometallic TMPCs varies in the order NiPS<sub>3</sub> >

FePS<sub>3</sub> > CdPS<sub>3</sub> ~ MnPS<sub>3</sub> ~ ZnPS<sub>3</sub> where NiPS<sub>3</sub> displays the highest HER rate of 2600  $\mu\text{mol h}^{-1} \text{g}^{-1}$  (Fig. 15b and c). Fig. 15d presents the variation in the H<sub>2</sub> evolution rate of the monometallic MPX<sub>3</sub> with a change in P–P bond distance. The enhancement in the P–P bond distance leads to a reduction in the population of electrons at the P center, which is the active site, and therefore overall H<sub>2</sub> evolution rate decreases. Under similar conditions, bimetallic Ag<sub>0.5</sub>In<sub>0.5</sub>PS<sub>3</sub> and Ag<sub>0.5</sub>In<sub>0.5</sub>PSe<sub>3</sub> showed appreciable hydrogen yields of 1900 and 500  $\mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively (Fig. 15c). The catalytic stability is the additional significant factor for an HER catalyst. Under photochemical conditions, the NiPS<sub>3</sub> system showed steady H<sub>2</sub> evolution up to 5 cycles (25 h) without any decrement in H<sub>2</sub> evolution, suggesting long-term stability of the photocatalyst (Fig. 15e).

2D MPX<sub>3</sub> compounds are coupled with other semiconductors possessing good oxidation capability of holes to enhance H<sub>2</sub> evolution yield and avoid photocorrosion. Theoretically, Mi and coworkers<sup>114</sup> investigated the electronic structure of the MnPSe<sub>3</sub> heterostructure with MoS<sub>2</sub> using DFT calculations, where different stacking patterns of mono-layer MnPSe<sub>3</sub> with MoS<sub>2</sub> were investigated, as shown in Fig. 16a and b. In some stacking patterns, spin splitting at VBM of MnPSe<sub>3</sub> is evident due to the hybridization of the d orbital of Mn, which enhances electron mobility. Secondly, MnPSe<sub>3</sub>/MoS<sub>2</sub> forms a type II heterostructure where the top of the VB is majorly contributed by MnPSe<sub>3</sub> while the bottom of CB is from MoS<sub>2</sub>. Normally, the type I heterojunction possesses a symmetrical offset of potential barriers, where direct exciton transition occurs at the heterointerface. While in the case of type II heterojunction holes and electrons are accumulated on different sides of the heterointerface, leading to indirect exciton transition. In type II heterojunction, the spatial separation of photoexcited electrons and holes as they are localized in different sides of heterojunction, reduces the recombination rate and enhances the photocatalytic efficiency. In the case of MnPSe<sub>3</sub>/CrSiTe<sub>3</sub> heterojunction type I heterostructure is formed due to a similar crystal structure and low lattice mismatch. However, under tensile strain the band alignment changes from type I to type II due to the transition from an indirect bandgap to a direct bandgap. The above studies demonstrated the possibility of the modulation of the electronic structure of MPX<sub>3</sub> by forming heterojunctions, implying the potential applicability of heterojunctions for photocatalysis applications.

Experimentally, Chen *et al.*<sup>73</sup> anchored 0D Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> nanoparticles onto 2D MnPS<sub>3</sub> and reported higher HER yield in the case of MnPS<sub>3</sub>–Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> as compared to bare MnPS<sub>3</sub>. 2D MnPS<sub>3</sub> is reported to be a non-toxic direct band gap semiconductor with appropriate VBM and CBM band edge potentials for photocatalytic water redox reaction. However, higher electron–hole recombination rates and their inability to oxidize water to generate oxygen limit their photo applicability. Bare MnPS<sub>3</sub> was reported to show a low H<sub>2</sub> production yield of 21.2  $\mu\text{mol h}^{-1} \text{g}^{-1}$  under solar light illumination. To prepare MnPS<sub>3</sub>–Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> composites, initially, MnPS<sub>3</sub> sheets are exfoliated in NMP solvent and then tetrabutylammonium hydroxide-modified Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> nanoparticles are anchored onto the

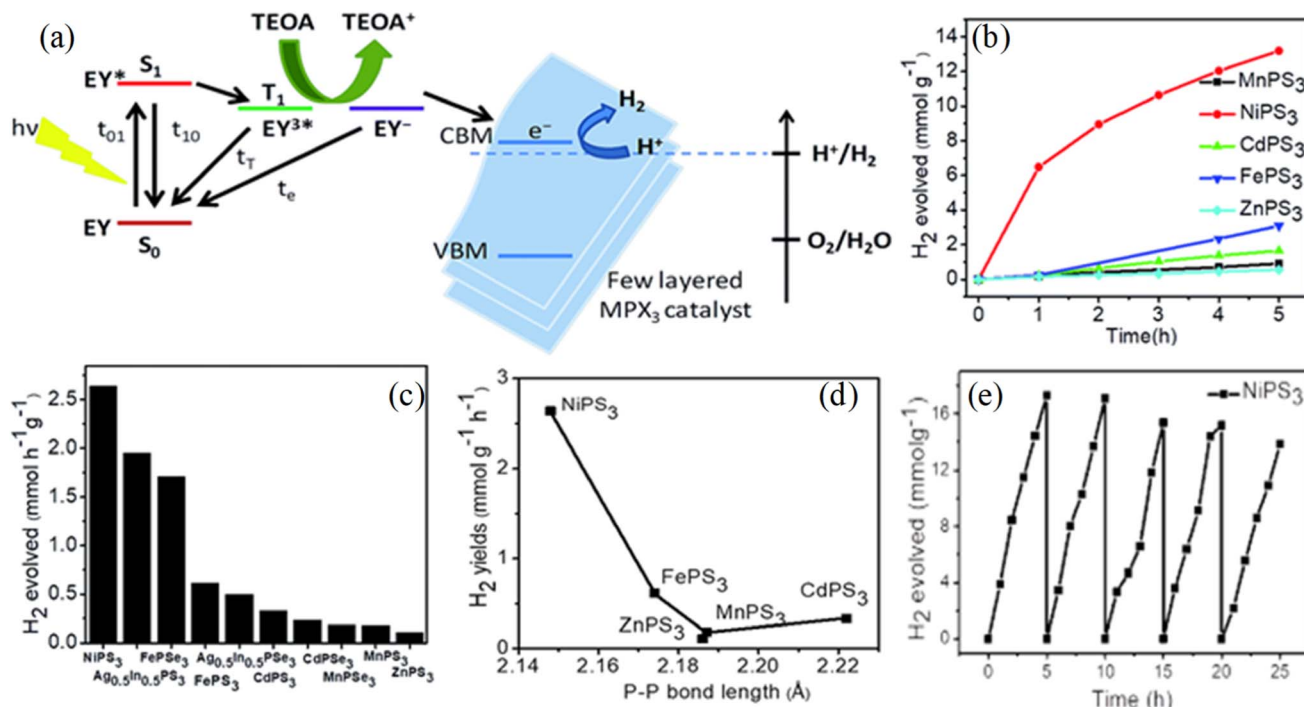


Fig. 15 (a) Schematic illustration of the mechanism of HER by exfoliated TMPCs nanosheets under a xenon lamp using eosin Y photosensitizer and TEOA sacrificial agent. (b) The yield of hydrogen evolved using monometallic ( $MnPS_3$ ,  $FePS_3$ ,  $NiPS_3$ ,  $ZnPS_3$ ,  $CdPS_3$ ) phosphosulfides. (c) Comparison of HER activity of monometallic ( $MnPS_3$ ,  $FePS_3$ ,  $NiPS_3$ ,  $ZnPS_3$ ,  $CdPS_3$  and bimetallic ( $Ag_{0.5}In_{0.5}PS_3$ ,  $Ag_{0.5}In_{0.5}PSe_3$ ) phosphosulfides. (d) Variation of  $H_2$  evolution rate of monometallic phosphosulfides with p-p bond distance. (e) Cyclic stability curves for  $NiPS_3$  studied up to 5 cycles for 25 h.<sup>93</sup>

$MnPS_3$  sheets by electrostatic interaction. The homogeneous distribution of  $Cs_4W_{11}O_{35}$  nanoparticles on the  $MnPS_3$  sheets *via* strong interfacial interaction of the S-W-O bond is evident in TEM images (Fig. 17a). The photocatalytic HER performance of the  $MnPS_3$ - $Cs_4W_{11}O_{35}$  hybrid was examined under solar light

with the sacrificial  $Na_2S/Na_2SO_3$  solution. Fig. 17b depicts the photocatalytic  $H_2$  evolution rate of bare  $MnPS_3$ ,  $MnPS_3$ - $Cs_4W_{11}O_{35}$  hybrid composites with  $Cs_4W_{11}O_{35}$  mass percentages of 5.4, 10.9, and 16.5%. The  $H_2$  evolution rates for  $MnPS_3$ - $Cs_4W_{11}O_{35}$  with 5.4, 10.9 and 16.5% of  $Cs_4W_{11}O_{35}$  were 38, 99,

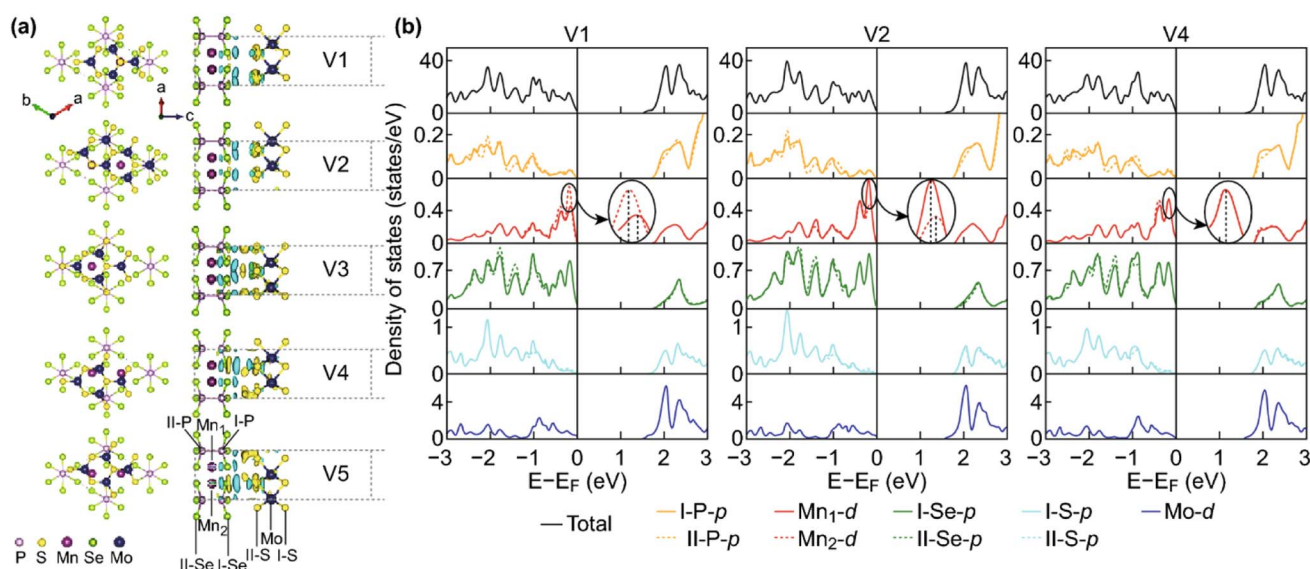


Fig. 16 (a) Structure and side view of the charge density difference of the  $MnPSe_3/MoSe_2$  nanocomposite with various stacking orders V1-V5. (b) Total and partial DOS of V1, V2, and V4 arrangements. The Fermi level is represented by the vertical shadow line and set to zero. Reprinted with permission.<sup>114</sup> Copyright 2017, Springer Nature.

and  $58 \mu\text{mol h}^{-1} \text{g}^{-1}$ , respectively, while bare  $\text{MnPS}_3$  showed HER activity of  $21.2 \mu\text{mol h}^{-1} \text{g}^{-1}$  only. With the addition of  $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  nanoparticles, the photocatalytic HER activity increased first and then decreased. The maximum  $\text{H}_2$  evolution rate of  $99.6 \mu\text{mol h}^{-1} \text{g}^{-1}$  was achieved with the  $\text{MnPS}_3$ -

$\text{Cs}_4\text{W}_{11}\text{O}_{35}$  composite with a  $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  mass percentage of 10.9%. In order to investigate the long-term stability of the  $\text{MnPS}_3$ - $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  composite, photocatalytic HER experiments were performed for four cycles, and during each cycle, the quartz reactor is evacuated prior to the start of the new

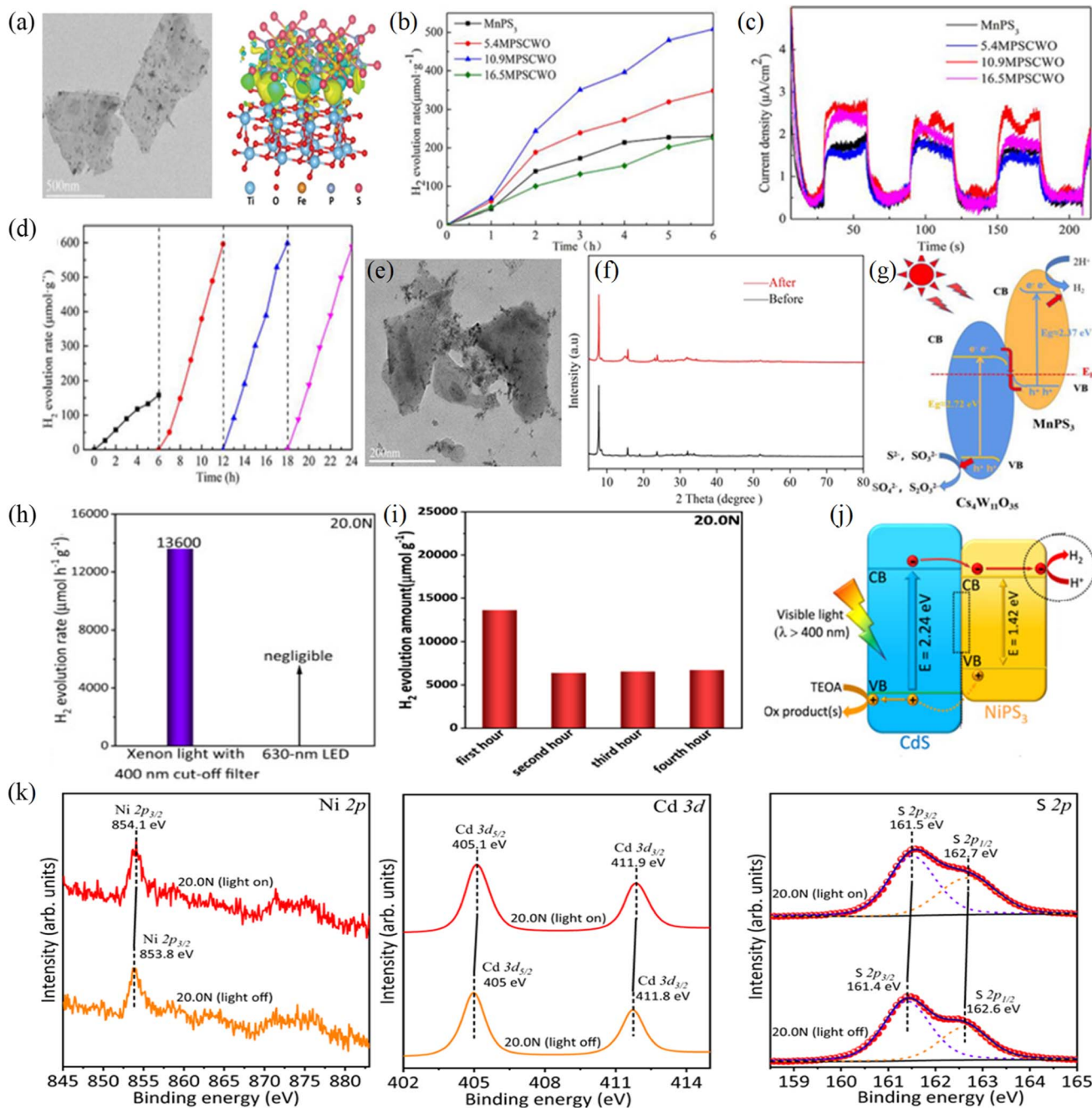


Fig. 17 (a) TEM image of the  $\text{MnPS}_3$ - $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  heterojunction. (b and c) Time course hydrogen production data and photocurrent responses for  $\text{MnPS}_3$ - $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  catalyst with 0, 5.4, 10.9, and 16.5% of  $\text{Cs}_4\text{W}_{11}\text{O}_{35}$ , and these composites designated as  $\text{MnPS}_3$ , 5.4MPSCWO, 10.9MPSCWO, and 16.5MPSCWO, respectively. (d) Cyclic stability curves for HER of  $\text{MnPS}_3$ - $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  catalyst recorded for 4 cycles and 24 h. (e) TEM image of  $\text{MnPS}_3$ - $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  after photocatalytic HER studies. (f) Raman spectra of  $\text{MnPS}_3$ - $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  before and after photocatalytic HER studies and (g) schematic of the reaction mechanism of photocatalytic HER on Z-scheme  $\text{MnPS}_3$ - $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  heterojunction. Adapted with permission.<sup>73</sup> Copyright 2021, Elsevier. (h) Time course HER curves for  $\text{NiPS}_3/\text{CdS}$  composite. (i) Cyclic stability curves for HER of  $\text{MnPS}_3$ - $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  catalyst recorded for 4 h and (j) Schematic representation of generated type-I (straddling type) heterostructure between  $\text{NiPS}_3$  and  $\text{CdS}$  components. (k) XPS spectra of  $\text{NiPS}_3/\text{CdS}$  composite with light on and off respectively. Adapted with permission.<sup>115</sup> Copyright 2022, Springer Nature.

experimental cycle. Cyclic stability curves shown in Fig. 17d indicate that HER activity for the second cycle is significantly higher than the first one and there is stable H<sub>2</sub> evolution after the second cycle. The stable H<sub>2</sub> evolution rate after the second cycle to the fourth cycle signifies the long-term photostability of the MnPS<sub>3</sub>-Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> composite. Further, TEM images of the MnPS<sub>3</sub>-Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> composite after photocatalytic HER studies, shown in Fig. 17e, reveal that Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> nanoparticles are coupled with MnPS<sub>3</sub> sheets even after 24 h reaction. The PXRD pattern of MnPS<sub>3</sub>-Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> recorded after HER studies also showed that the catalyst was stable (Fig. 17f). Based on UV-vis, photoluminescence, valence band XPS spectra, and electrochemical impedance spectra studies, Chen *et al.*<sup>60,73</sup> proposed the formation of the Z-scheme heterojunction, which effectively suppresses the charge-hole recombination rate, charge-transfer ability, and hole oxidation ability (Fig. 17g). The internal polarization field generated due to the heterojunction formation generates more positive charges on MnPS<sub>3</sub> and more negative charges on Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub>. Upon light irradiation, electrons and holes are produced in VB and CB of both MnPS<sub>3</sub> and Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> components of the composite. Further, the internal electric field suppresses the electron transfer from CB of Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> to CB MnPS<sub>3</sub> and facilitates the electron migration from CB of Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> to VB of MnPS<sub>3</sub>, which results in the formation of the Z-scheme heterojunction. Hence, photogenerated electrons left in the CB of MnPS<sub>3</sub> are utilized for water reduction whereas holes in the VB of Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> are utilized for the oxidation of Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub>.

As indicated earlier, in the case of 2D NiPS<sub>3</sub>, due to rapid charge recombination rate and photo-corrosion issues because of misalignment of the VBM concerning water oxidation potential, their reported HER activity is marginal. To overcome the weak oxidizing ability of NiPS<sub>3</sub>, Ran *et al.*<sup>115</sup> coupled 2D NiPS<sub>3</sub> with 0D CdS photocatalyst, which can supply oxidative photogenerated holes rather than being utilized. Cadmium sulfide (CdS) was reported to show a narrow band gap of 2.4 eV at room temperature, which accounted for its proficient visible light absorption characteristics. Secondly, CdS possess suitable VB and CB positions for water redox reactions, which make it an excellent photocatalyst for water redox reactions. Ran *et al.* examined the photocatalytic water splitting performance of NiPS<sub>3</sub>/CdS under visible-light illumination ( $\lambda > 400$  nm) using TEOA as a sacrificial agent. Under light illumination, NiPS<sub>3</sub>/CdS showed an extremely high H<sub>2</sub> evolution rate of 13 600  $\mu\text{mol h}^{-1} \text{g}^{-1}$  while bare NiPS<sub>3</sub> showed negligible activity under similar conditions (Fig. 17h). The stability of NiPS<sub>3</sub>/CdS for photocatalytic HER was examined for 9 h, with a cycle every 3 h. As shown in Fig. 17i, the H<sub>2</sub> evolution rate at cycle 3 (6687  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ) accounted for 49.17% of that in the first cycle (13 600  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ). This result implied the appreciable stability of the NiPS<sub>3</sub>/CdS catalyst. In addition, *in situ* XPS measurements were conducted to reveal the dissociation and migration pathways of photogenerated electrons and holes on the surface of the NiPS<sub>3</sub>/CdS catalyst (Fig. 17k). During the *in situ* XPS measurement, a light-emitting diode was utilized as the light source to excite the catalyst. As presented in Fig. 17k, under light irradiation Ni 2p, P 2p and S 2p signals shifted towards higher binding energy

as compared to dark conditions, signifying that more photo-generated holes than electrons migrate to the surface of both NiPS<sub>3</sub> and CdPS<sub>3</sub> components. This study suggests that during photocatalysis, holes migrate to the surface and are captured by the sacrificial agent, TEOA, leaving the electrons for HER. To explain the origin of such high HER activity of the NiPS<sub>3</sub>/CdS catalyst, the authors proposed a formation of type-I (straddling type) heterostructure between NiPS<sub>3</sub> and CdS based on photoluminescence, Mott-Schottky plots, ultrafast transient absorption spectroscopy, steady-state and transient-state surface photovoltage (SPV) spectroscopy studies (Fig. 17j). Upon light irradiation, electrons and holes are photogenerated in both NiPS<sub>3</sub> and CdS systems. Due to strong interfacial electronic coupling between NiPS<sub>3</sub> and CdS, the electrons and holes in CB and VB of CdS migrate to NiPS<sub>3</sub>. However, most of the holes generated in CdS are consumed by sacrificial hole quencher TEOA before migrating to NiPS<sub>3</sub>, resulting in the oxidation of TEOA. While a low fraction of photogenerated holes are transported from VB of CdS to VB of NiPS<sub>3</sub>. On the other hand, much more photogenerated electrons in the CB of NiPS<sub>3</sub> are utilized for the water reduction reaction. The significantly high HER activity of NiPS<sub>3</sub>/CdS can be attributed to the decreased recombination rate of photogenerated electron-hole pairs and abundant active sites on NiPS<sub>3</sub> for hydrogen evolution.

Xia *et al.*<sup>116</sup> reported the formation of S-scheme heterojunction between TiO<sub>2</sub> and 2D FePS<sub>3</sub> by self-assembling TiO<sub>2</sub> nanoparticles on FePS<sub>3</sub> nanosheets. In this study, FePS<sub>3</sub>/TiO<sub>2</sub> nanocomposites are obtained by adding TiO<sub>2</sub> (P25, Degussa AG) nanoparticles to the exfoliated FePS<sub>3</sub> suspension under grinding conditions at room temperature. FePS<sub>3</sub>/TiO<sub>2</sub> showed a higher hydrogen evolution rate of 99.5  $\mu\text{mol h}^{-1} \text{g}^{-1}$  using ethanol solvent as a sacrificial electron donor under UV light illumination (Fig. 18a). While bare 2D FePS<sub>3</sub> showed negligible H<sub>2</sub> evolution under similar conditions. The Mott-Schottky plot for the FePS<sub>3</sub>/TiO<sub>2</sub> composite indicated that both positive and negative slopes were obtained in distinct regions of the composite, implying the successful formation of the p-n heterojunction between 2D FePS<sub>3</sub> and TiO<sub>2</sub> (Fig. 18b). Further, *in situ* atomic force microscopy (AFM) combined with Kelvin probe force microscopy (AFM-KPFM) was utilized to investigate the electron transport pathway of the FePS<sub>3</sub>/TiO<sub>2</sub> composite under light irradiation. As shown in Fig. 18d, aggregation of the TiO<sub>2</sub> nanoparticles on the surface of FePS<sub>3</sub> was evident in the AFM image of the FePS<sub>3</sub>/TiO<sub>2</sub> composite. Fig. 18e and f show the corresponding KPFM images of FePS<sub>3</sub>/TiO<sub>2</sub> in the dark and with 365 nm UV light irradiation, respectively. Accordingly, the surface potential plots of FePS<sub>3</sub>/TiO<sub>2</sub> in dark and UV light irradiation are displayed in Fig. 18g. The surface potential across the line is enhanced under light illumination as compared to dark conditions. Particularly, the surface potential at A1 is elevated by 124 mV. This result indicated that the photo-generated holes accumulate at the surface of FePS<sub>3</sub> and TiO<sub>2</sub> components under light illumination. Upon light excitation, photoexcited electrons and holes are produced in both FePS<sub>3</sub> and TiO<sub>2</sub> components. Then, photogenerated electrons are retained in the CB of the FePS<sub>3</sub> and holes preserved in VB of TiO<sub>2</sub> to carry water reduction and oxidation, respectively,

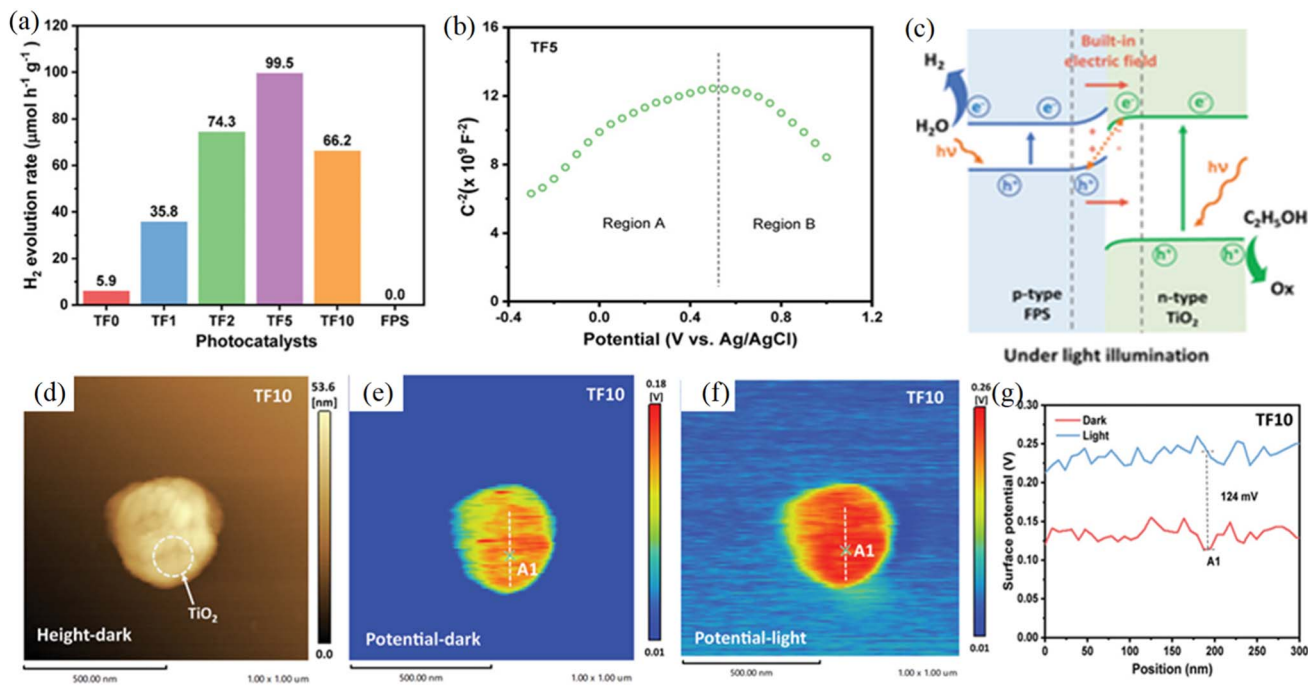
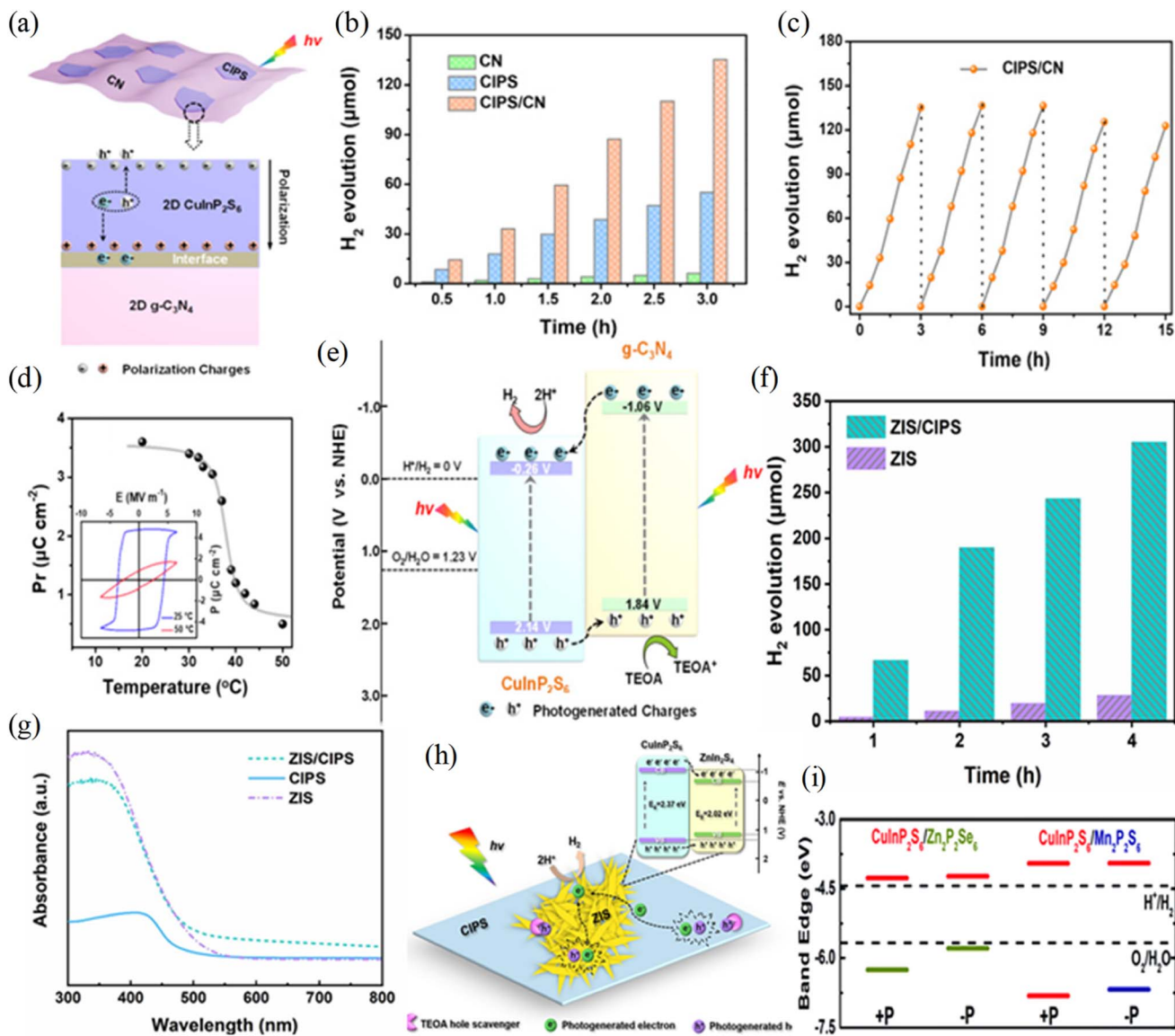


Fig. 18 (a) Photocatalytic HER activity of FePS<sub>3</sub>/TiO<sub>2</sub> with various amounts of FePS<sub>3</sub>. (b) Mott–Schottky plots for FePS<sub>3</sub>/TiO<sub>2</sub> acquired in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at 3000 MHz. (c) Schematic of the reaction mechanism of photocatalytic HER on S-scheme FePS<sub>3</sub>/TiO<sub>2</sub> components. (d and e) Atomic force microscopy (AFM) and Kelvin probe force microscopy (AFM-KPFM) image of FePS<sub>3</sub>/TiO<sub>2</sub> in dark conditions. (f) KPFM image with UV light irradiation. (g) The corresponding surface potential plot of FePS<sub>3</sub>/TiO<sub>2</sub> in dark and UV light irradiation. Reprinted with permission.<sup>116</sup> Copyright 2018, Wiley publication.

attributed to a strong in-built electric field gradient between the individual components. Meanwhile, photogenerated electrons in the VB of TiO<sub>2</sub> recombine with the holes in the CB of FePS<sub>3</sub>. Due to the generation of the S-scheme heterojunction, the reduction ability of photogenerated electrons in FePS<sub>3</sub> and the oxidation ability of holes in TiO<sub>2</sub> are preserved (Fig. 18c). Secondly, a reduced recombination rate between the photogenerated electrons and holes was also simultaneously achieved. The photogenerated holes in VB of TiO<sub>2</sub> were utilized for the oxidation of ethanol to produce the oxidized products.

In recent years, 2D ferroelectric materials such as CuInP<sub>2</sub>S<sub>6</sub>, CuBiP<sub>2</sub>S<sub>6</sub>, and AgInP<sub>2</sub>Se<sub>6</sub> are receiving increased attention as HER photocatalysts. The permanent polarization electric field in these materials serves as a driving force for the spatial separation of charges, thereby showing good HER activity.<sup>117–119</sup> Secondly, large exciton binding energy suppresses the reduction potential of the photogenerated electrons, prompting electrons readily available for the water reduction reaction. Among these MPX<sub>3</sub> compounds, CuInP<sub>2</sub>S<sub>6</sub> experimentally showed good HER characteristics due to intermediate band gap and room temperature ferroelectricity.<sup>119</sup> Lin *et al.*<sup>120</sup> studied the photocatalytic HER performance of CuInP<sub>2</sub>S<sub>6</sub>, prepared by the solid-state reaction under visible light using a TEOA sacrificial electron donor. Bare CuInP<sub>2</sub>S<sub>6</sub> nanosheets showed moderate HER activity of 18.3 μmol h<sup>-1</sup> g<sup>-1</sup> due to the high charge-transfer ability of the ferroelectric material. Further, the formation of 2D/2D heterojunction between CuInP<sub>2</sub>S<sub>6</sub> and graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) substantially accelerated the charge-transfer

rate, due to which CuInP<sub>2</sub>S<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> displayed 2.5 times higher (45.1 μmol h<sup>-1</sup> g<sup>-1</sup>) activity than that of bare CuInP<sub>2</sub>S<sub>6</sub> (Fig. 19a–d). Transient photocurrent response studies indicated that the composite showed a higher photocurrent density of 2.92 μA cm<sup>-2</sup>, which was 1.62 and 2.25 times higher than that of individual CuInP<sub>2</sub>S<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub>, respectively. This result implies the rapid charge separation and migration in the composite through high-speed microchannels. Further, photoluminescence studies implied a much lower emission intensity for the CuInP<sub>2</sub>S<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> composite compared to g-C<sub>3</sub>N<sub>4</sub>, indicating a much reduced electron–hole recombination rate in the composite. Based on the above results, the generation of type-II heterojunction between CuInP<sub>2</sub>S<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub> components is projected, as depicted in Fig. 19e. Upon light illumination, owing to the intrinsic dipole moment, CuInP<sub>2</sub>S<sub>6</sub> can generate ferroelectric polarization fields with the deposition of negative and positive at opposite directions of the surface, which induces spatial charge separation. These photogenerated electrons at the CuInP<sub>2</sub>S<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> interface are utilized for water reduction to generate hydrogen, while holes are consumed by the sacrificial hole scavenger TEOA. Further, due to the in-built electric field gradient holes in the VB of g-C<sub>3</sub>N<sub>4</sub> are transferred to the VB of CuInP<sub>2</sub>S<sub>6</sub> by nanochannels, which further reduced the electron–hole recombination rate. Further, the cyclic stability curve shown in Fig. 19c implies that CuInP<sub>2</sub>S<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> still keeps high activity even after 5 cycles (15 h), suggesting their promising potential application in solar-energy conversion. In another study, Ren *et al.*<sup>121</sup> synthesized a CuInP<sub>2</sub>S<sub>6</sub>/ZnIn<sub>2</sub>S<sub>4</sub>



**Fig. 19** (a) Schematic of the photogenerated charge carriers in 2D CuInP<sub>2</sub>S<sub>6</sub>. (b) Time course H<sub>2</sub> evolution data for g-C<sub>3</sub>N<sub>4</sub>(CN), CuInP<sub>2</sub>S<sub>6</sub> (CIPS) and CuInP<sub>2</sub>S<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> (CN/CIPS). (c) Cyclic stability curve of HER for the CuInP<sub>2</sub>S<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> (CN/CIPS) heterojunction. (d) Temperature-dependent remnant polarization of CuInP<sub>2</sub>S<sub>6</sub> inset: polarization-electric field (P-E) hysteresis loop obtained using piezoresponse force microscopy and (e) schematic representation of generated type-II heterostructure between CuInP<sub>2</sub>S<sub>6</sub> and g-C<sub>3</sub>N<sub>4</sub> components. Adapted with permission.<sup>120</sup> Copyright 2020, Elsevier. (f) Time course H<sub>2</sub> evolution data for ZnIn<sub>2</sub>S<sub>4</sub> (ZIS) and CuInP<sub>2</sub>S<sub>6</sub>/ZnIn<sub>2</sub>S<sub>4</sub> (CIPS/ZIS). (g) UV-vis diffuse reflectance spectrum of ZnIn<sub>2</sub>S<sub>4</sub> (ZIS), CuInP<sub>2</sub>S<sub>6</sub> (CIPS), and CuInP<sub>2</sub>S<sub>6</sub>/ZnIn<sub>2</sub>S<sub>4</sub> (CIPS/ZIS) and (h) schematic illustration of generated type-I heterostructure at CuInP<sub>2</sub>S<sub>6</sub>/ZnIn<sub>2</sub>S<sub>4</sub> interface. Adapted with permission.<sup>121</sup> Copyright 2023, Elsevier. (i) Band edge potentials of CuInP<sub>2</sub>S<sub>6</sub>/Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and CuInP<sub>2</sub>S<sub>6</sub>/Zn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> ferroelectric heterostructures obtained using DFT+U method. The HER and OER potentials are shown for comparison. +P and -P designate CuInP<sub>2</sub>S<sub>6</sub> in two oppositely polarized states.<sup>119</sup>

heterostructure by a surfactant-assisted hydrothermal method and utilized it for photocatalytic H<sub>2</sub> generation. As shown in Fig. 19f, bare ZnIn<sub>2</sub>S<sub>4</sub> showed a quite inferior H<sub>2</sub> evolution rate of 5.88 μmol h<sup>-1</sup> g<sup>-1</sup>, while CuInP<sub>2</sub>S<sub>6</sub>/ZnIn<sub>2</sub>S<sub>4</sub> displayed an enhanced activity of 76.2 μmol h<sup>-1</sup> g<sup>-1</sup>. The band gap energy values for CuInP<sub>2</sub>S<sub>6</sub> and ZnIn<sub>2</sub>S<sub>4</sub> estimated using a UV-vis diffuse reflectance study were 2.37 and 2.02 eV, respectively (Fig. 19g). Owing to the matched band gap energy value between CuInP<sub>2</sub>S<sub>6</sub> and ZnIn<sub>2</sub>S<sub>4</sub>, a type I heterostructure was effectively generated, which led to the efficient separation of the photogenerated electrons and holes (Fig. 19h). On visible-light

irradiation, photogenerated electrons in the CB of CuInP<sub>2</sub>S<sub>6</sub> migrated to the CB of ZnIn<sub>2</sub>S<sub>4</sub> at the interface and were utilized for H<sup>+</sup> reduction to yield H<sub>2</sub>. While photogenerated holes in the VB of CuInP<sub>2</sub>S<sub>6</sub> migrated to the VB of ZnIn<sub>2</sub>S<sub>4</sub> and were finally captured by the sacrificial agent TEOA. Markedly, due to the generation of the heterostructure, abundant charge-migration pathways were created, which reduced the charge recombination rate and improved the HER yield.

Theoretically, Huang *et al.*<sup>119</sup> projected that the generation of ferroelectric hetero-interfaces such as CuInP<sub>2</sub>S<sub>6</sub>/Mn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and CuInP<sub>2</sub>S<sub>6</sub>/Zn<sub>2</sub>P<sub>2</sub>Se<sub>6</sub> would be beneficial for photocatalytic water

splitting due to strong visible light absorption and type-II band alignment, which can facilitate rapid charge separation (Fig. 19i). To date, there are very limited experimental studies on ferroelectric hetero-interfaces containing 2D MPX<sub>3</sub> compounds for photocatalysis and these systems need to be investigated in more detail. In Table 2, we have listed the photocatalytic HER activity of various 2D metal thiophosphates and their heterostructures reported in the literature along with the reaction conditions. It should be noted that, while comparing the HER activity between two individual systems, the strength of the light source (simulated solar light or xenon lamp, 300 W or 400 W), photosensitizer added and type of sacrificial agent (TEOA and Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub>) need to be taken into consideration since these factors can affect the activity significantly. Secondly, different synthetic approaches generate MPX<sub>3</sub> layers of various

thicknesses, which further affect the HER activity as accessibility for catalytic edge (active) sites decreases with an increase in the layer thickness.

Among the reported various 2D MPX<sub>3</sub> compounds, CdPS<sub>3</sub> showed a significantly high H<sub>2</sub> evolution rate of 10 880 μmol h<sup>-1</sup> g<sup>-1</sup>, while CuPS<sub>3</sub> and ZnPS<sub>3</sub> displayed 2085 and 640 μmol h<sup>-1</sup> g<sup>-1</sup>, respectively (Table 1). However, in a single-component MPX<sub>3</sub> system, the photogenerated holes are confined to the semiconductor and not available for water oxidation, hence resulting in photocorrosion of the semiconductor. The combination of sacrificial hole scavengers such as Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> or triethanolamine with 2D MPX<sub>3</sub> alleviates photocorrosion, and increases the activity to some extent. Generally, the formation of hetero-interfaces between 2D MPX<sub>3</sub> compounds and material with good oxidation capability for holes such as Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub> and

Table 2 Comparison of photocatalytic HER activity of 2D TNPCs and their nanocomposites with Cs<sub>4</sub>W<sub>11</sub>O<sub>35</sub>, CdS, TiO<sub>2</sub>, and g-C<sub>3</sub>N<sub>4</sub>

Photocatalyst system	Synthesis method, layer thickness	Light source	Sacrificial agent	HER activity (μmol h <sup>-1</sup> g <sup>-1</sup> )	Ref.
MnPS <sub>3</sub>	CVD <sup>a</sup> , 6 nm	AM 1.5G <sup>b</sup>	—	3.1	55
MnPS <sub>3</sub>	CVD, 6 nm	AM 1.5G	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	21.2	55
MnPSe <sub>3</sub>	CVD, 28 nm	AM 1.5G	—	6.5	55
MnPSe <sub>3</sub>	CVD, 28 nm	AM 1.5G	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	43.5	55
FePS <sub>3</sub>	CVD, 20 nm	300 W Xe lamp	FeSO <sub>4</sub>	46.6	131
FePS <sub>3</sub>	CVD, 20 nm	300 W Xe lamp	Triethanolamine	141.9	131
FePS <sub>3</sub>	CVD, 20 nm	300 W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	402.4	131
FePS <sub>3</sub>	SS method <sup>c</sup>	300 W Xe lamp	Triethanolamine	166.2	132
FePS <sub>3</sub>	LPE <sup>d</sup> , 10 nm	300 W Xe lamp	Triethanolamine	290.0	133
Porous FePS <sub>3</sub>	SS 7 nm	300 W Xe lamp	Triethanolamine	305.6	132
NiPS <sub>3</sub>	CVD, 3.5 nm	AM 1.5G	—	26.42	113
NiPS <sub>3</sub>	CVD, 3.5 nm	AM 1.5G	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	74.67	113
CuPS <sub>3</sub>	Hot injection	150W simulator	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	2085	63
ZnPS <sub>3</sub>	LPE	300 W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	640.0	112
CdPS <sub>3</sub>	CVD	AM 1.5G	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	786.6	131
CdPS <sub>3</sub>	LPE, 3 nm	300 W Xe lamp	Ethanol	10 880.0	71
N-doped CdPS <sub>3</sub>	LPE	300 W Xe lamp	DL-lactic acid	6280.0	134
InPS <sub>3</sub>	CVD	AM 1.5G	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	379.1	131
Sn <sub>2</sub> P <sub>2</sub> S <sub>6</sub>	CVD	AM 1.5G	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	202.06	135
ZnIn <sub>2</sub> S <sub>4</sub>	SS method	Visible light (λ ≥ 420 nm)	—	5.88	121
<b>2D MPX<sub>3</sub> HER activity reported with photosensitizer eosin Y (EY)</b>					
EY/MnPS <sub>3</sub>	LPE	400 W Xe lamp	Triethanolamine	200.0	93
EY/FePS <sub>3</sub>	LPE	400 W Xe lamp	Triethanolamine	600.0	93
EY/NiPS <sub>3</sub>	LPE, 4.9 nm	400 W Xe lamp	Triethanolamine	2600.0	93
EY/ZnPS <sub>3</sub>	LPE	400 W Xe lamp	Triethanolamine	100.0	93
EY/CdPS <sub>3</sub>	LPE	400 W Xe lamp	Triethanolamine	300.0	93
EY/MnPSe <sub>3</sub>	LPE	400 W Xe lamp	Triethanolamine	200.0	93
EY/FePSe <sub>3</sub>	LPE, 6.2 nm	400 W Xe lamp	Triethanolamine	1700.0	93
EY/CdPSe <sub>3</sub>	LPE	400 W Xe lamp	Triethanolamine	200.0	93
EY/Ag <sub>0.5</sub> In <sub>0.5</sub> PS <sub>3</sub>	LPE, 2.1 nm	400 W Xe lamp	Triethanolamine	1900.0	93
EY/Ag <sub>0.5</sub> In <sub>0.5</sub> PS <sub>3</sub>	LPE, 3.1 nm	400 W Xe lamp	Triethanolamine	500.0	93
<b>2D MPX<sub>3</sub> heterojunctions</b>					
MnPS <sub>3</sub> /Cs <sub>4</sub> W <sub>11</sub> O <sub>35</sub>	—	300 W Xe lamp	Na <sub>2</sub> S/Na <sub>2</sub> SO <sub>3</sub>	99.0	73
NiPS <sub>3</sub> /CdS	—	300 W Xe lamp	Triethanolamine	13 600.0	64
FePS <sub>3</sub> /TiO <sub>2</sub>	—	350 W Xe lamp	Ethanol	99.5	116
MnPS <sub>3</sub> /carbon dot	—	300 W Xe lamp	—	339.63	136
CuInP <sub>2</sub> S <sub>6</sub>	—	300 W Xe lamp	Triethanolamine	18.3	120
CuInP <sub>2</sub> S <sub>6</sub> /g-C <sub>3</sub> N <sub>4</sub>	—	300 W Xe lamp	Triethanolamine	45.1	120
CuInP <sub>2</sub> S <sub>6</sub> /ZnIn <sub>2</sub> S <sub>4</sub>	SS method	Visible light (λ ≥ 420 nm)	—	76.2	121

<sup>a</sup> CVD – chemical vapor deposition. <sup>b</sup> AM 1.5G – simulated solar light. <sup>c</sup> SS – solid state method. <sup>d</sup> LPE – liquid phase exfoliation.



**Table 3** Comparison of photocatalytic HER activity of mono and bimetallic 2D TMPCs and their nanocomposites with other 2D material nanocomposites reported in the literature

Photocatalyst system	Light source	Sacrificial agent	HER activity ( $\mu\text{mol h}^{-1} \text{g}^{-1}$ )	Cyclic stability		HER activity after cyclic stability as compared with 1 <sup>st</sup> cycle	References
				No. of cycles	Total time of cycle (h)		
$\text{C}_3\text{N}_4$	300 W Xe lamp	TEOA <sup>a</sup>	169.5	4	20	Negligible change	137
$\text{MoS}_2$	300 W Xe lamp	TEOA	339.5	—	—	NR <sup>b</sup>	138
$\text{ZnInS}_4$	300 W Xe lamp	$\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$	3890.0	3	9	Negligible change	139
CdS	300 W Xe lamp	MeOH	370.0	—	—	NR	140
$\text{FeSe}_2$	300 W Xe lamp	$\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$	955.3	—	—	NR	141
Fe-BiOCl	300 W Xe lamp	$\text{Na}_2\text{SO}_4$	3540.0	—	—	NR	142
Phosphorene	300 W Xe lamp	$\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$	512.0	2	20	Negligible change	143
$\text{CuPS}_3^c$	150W simulator	$\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$	2085.0	3	24	Negligible change	63
EY/NiPS <sub>3</sub> <sup>c,d</sup>	400 W Xe lamp	TEOA	2600.0	5	25	Negligible change	93
$\text{CdPS}_3^c$	300 W Xe lamp	Ethanol	10 880.0	—	—	NR	71
<b>2D nanomaterial-based heterostructures</b>							
$\text{MoS}_2/\text{CdS}$	300 W Xe lamp	Lactic acid	4060.0	3	15	Negligible change	144
$\text{MoS}_2/\text{TiO}_2$	300 W Xe lamp	TEOA	10 046.0	3	12	Negligible change	145
$\text{MoS}_2/\text{C}_3\text{N}_4$	300 W Xe lamp	TEOA	1155.0	3	12	1098 $\mu\text{mol h}^{-1} \text{g}^{-1}$	146
$\text{MoS}_2/\text{C}_3\text{N}_4$	AM 1.5G	TEOA	8300.0	6	16	Negligible change	147
$\text{Ti}_3\text{C}_2/\text{CdS}$	530 W Xenon lamp	MeOH	1730.0	3	18	Negligible change	140
$\text{Cu}_3\text{P}/\text{ZnInS}_4$	300 W Xe lamp	TEOA	5461.0	6	18	Negligible change	148
$\text{WS}_2/\text{CdS}$	400 W Xe lamp	Lactic acid	13 132.0	4	12	Negligible change	149
$\text{FeSe}_2/\text{C}_3\text{N}_4$	300 W Xe lamp	$\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$	1655.6	2	12	Negligible change	141
$\text{Ti}_3\text{C}_2/\text{TiO}_2$	300 W Xe lamp	MeOH	4672.0	5	25	Negligible change	150
$\text{C}_3\text{N}_4/\text{phosphorene}$	300 W Xe lamp	TEOA	5850.0	3	12	Negligible change	151
$\text{MnPS}_3/$	300 W Xe lamp	$\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$	99.0	4	24	Negligible change	73
$\text{Cs}_4\text{W}_{11}\text{O}_{35}^c$							
$\text{NiPS}_3/\text{CdS}^c$	300 W Xe lamp	TEOA	13 600.0	4	4	6800 $\mu\text{mol h}^{-1} \text{g}^{-1}$	64

<sup>a</sup> TEOA – triethanolamine. <sup>b</sup> NR – not reported. <sup>c</sup> 2D phosphochalcogenides. <sup>d</sup> EY – eosin Y dye.

CdS enhances the HER yield and photostability of 2D  $\text{MnPS}_3$ . The combination of  $\text{NiPS}_3$  and  $\text{FePS}_3$  with CdS and  $\text{TiO}_2$  appears to be advantageous for photocatalytic HER. Mainly, the  $\text{NiPS}_3/\text{CdS}$  heterostructure displayed a significantly high  $\text{H}_2$  evolution rate of 13 600  $\mu\text{mol h}^{-1} \text{g}^{-1}$ . The generation of heterojunction effectively suppresses the electron–hole recombination rate and improves the charge-transfer and hole oxidation ability due to the internal polarization field. In Table 3, we have compared the photocatalytic HER activity of 2D  $\text{MPX}_3$  nanocomposites with other 2D materials ( $\text{C}_3\text{N}_4$ , metal sulfides, phosphides, and carbides) and their nanocomposites reported in the literature. The HER activity obtained with  $\text{NiPS}_3/\text{CdS}$  surpasses the highest reported for TMDCs-based nanocomposites, indicating that 2D  $\text{MPX}_3$ -based composites could be beneficial for large-scale hydrogen production with exceptional stability.

## 6. Conclusions and future opportunities

The global energy crisis and environmental pollution problems have become increasingly severe and the search for clean and

sustainable energy resources is vital. Water splitting utilizing solar energy, electrical energy, or a combination of solar-electrical energy is demonstrated to be the environment-friendly route for future green hydrogen production. From the practical application viewpoint, designing a high-performance and cost-effective, yet metal-free catalyst, for photocatalytic/electrocatalytic water splitting is technologically essential and urgently needed.

In this perspective, we discussed the recent development of non-noble metal catalysts for water-splitting reactions with a focus on 2D  $\text{MPX}_3$  compounds by emphasizing novel strategies developed for activating  $\text{MPX}_3$  for photocatalytic and electrocatalytic HER. Theoretically, Gibbs free energy of hydrogen adsorption is considered to be a good descriptor in evaluating HER performance, and material with an approximate  $\Delta G_{\text{H}}$  value of zero is considered to be an ideal catalyst. DFT calculations revealed that pyrite type CoPS shows thermoneutral  $\text{H}^+$  adsorption, and also experimentally substantiated that CoPS possess Pt/C-like electrocatalytic  $\text{H}_2$  evolution activity. The exfoliation of bulk  $\text{MPX}_3$  into thin sheets enhances the HER activity due to the increased in-plane conductivity and more exposed edge sites. The electronic conductivity and HER activity

of  $\text{MPS}_3$  sheets can be further improved by coupling a conducting matrix such as graphene. Doping of Co atoms into  $\text{FePS}_3$  and  $\text{NiPS}_3$  systems also enhances HER kinetics due to the electronic state modulation with doping. Coupling of TMPCs with other 2D systems such as  $\text{MoS}_2$  facilitates hydrogen spillover during  $\text{H}_2$  evolution from the  $\text{MoS}_2$  edge site to  $\text{MPX}_3$ . These  $\text{MPX}_3/\text{MoS}_2$  composites also showed good OER characteristics, indicating that these composites can be useful for overall water-splitting applications.

Strong visible light absorption characteristics, high carrier mobility, and thermoneutral  $\text{H}^+$  adsorption of 2D  $\text{MPX}_3$  make them suitable catalysts for photocatalytic water splitting. However, single-component  $\text{MPX}_3$  as a photocatalyst showed marginal HER activity and low stability due to misaligned VBM with respect to water oxidation potential. The development of  $\text{MPX}_3$  for photocatalytic HER is presently concentrating on enhancing the light absorption efficiency, the alleviation of photocorrosion, industrial scale  $\text{H}_2$  production, and improving stability. The addition of sacrificial hole scavengers such as  $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$  or triethanolamine alleviates photocorrosion, and increases the activity and stability to some extent. Nevertheless, band gap engineering is required to enhance light absorption and reduce the photogenerated electron-hole recombination rate.

By coupling  $\text{MnPS}_3$  with a  $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  semiconductor possessing good oxidation capability of holes, the HER activity of individual components can be enhanced. The generation of Z-scheme heterojunction between  $\text{MnPS}_3$  and  $\text{Cs}_4\text{W}_{11}\text{O}_{35}$  effectively suppresses the electron-hole recombination rate and improves charge-transfer and hole oxidation ability due to the internal polarization field. Further, a combination of  $\text{NiPS}_3$  and  $\text{FePS}_3$  with  $\text{CdS}$  and  $\text{TiO}_2$ , respectively appears to be advantageous for photocatalytic HER. Particularly, the  $\text{NiPS}_3/\text{CdS}$  heterojunction showed superior HER activity of  $13\,600\ \mu\text{mol h}^{-1}\ \text{g}^{-1}$ , which is comparable to that of some of the highest reported transition metal-based nanocomposites reported in the literature.

In spite of the overwhelming progress in photocatalysis/electrocatalysis of 2D  $\text{MPX}_3$ , there is still a lot of scope to enhance the performance and stability towards commercialization, some points are listed below.

### 6.1 Synthesis of atomically thin 2D $\text{MPX}_3$ nanosheets

The chemical vapor transport method is the most widely utilized strategy to obtain bulk  $\text{MPX}_3$  and is then converted to a few-layer form by liquid-phase exfoliation. Most of the liquid-phase exfoliation strategies yield few-layer  $\text{MPX}_3$  nanosheets, which are semiconducting in nature. In the case of  $\text{MoS}_2$ , lithium-intercalation of bulk material is exploited to produce atomically-thin metallic 2D sheets on a large scale. However, the lithium-intercalation approach in preparing atomically-thin  $\text{MPX}_3$  is not reported and these exfoliated can show enhanced HER characteristics if they are converted to the metallic form due to the increased in-plane conductivity and exposed edge sites. Further, the crystal structure and HER properties of these exfoliated systems need to be optimized with combined

theoretical and experimental work to maximize their catalytic efficiency.

### 6.2 Surface functionalization

Similar to TMDCs, most of the 2D  $\text{MPX}_3$  systems show poor ambient stability due to reactive sulfur and phosphorous atoms. Covalent functionalization with electron-donating and withdrawing moieties can enhance the ambient stability and dispersibility of 2D  $\text{MPX}_3$ , which is crucial for catalysis applications. Secondly, surface functionalization can improve the hydrogen adsorption/desorption ability of 2D  $\text{MPX}_3$  under various electrolytic conditions. The generation of heterojunction between functionalized 2D  $\text{MPX}_3$  with other 2D materials using covalent cross-linking or electro-restacking strategies could further improve charge-transfer characteristics and expose edge sites for HER.

### 6.3 Doping of non-metal atoms

Doping metal atoms of 2D  $\text{MPX}_3$  with other transition elements to form bimetallic compounds improves the HER characteristics through the electronic state modulation. However, a very limited reports on doping P and S/Se species, and these sites are reported to be active for hydrogen adsorption and desorption during HER. Therefore, controlled doping of non-metal elements, such as N and O can alter the electron donating/withdrawing ability of the active site, thereby improving HER characteristics. Secondly, co-doping of metal and non-metal elements would give rise to synergistic interactions. Theoretical insights of co-doping to modulate the electronic structure will assist experimental studies to tailor the transport properties of the system.

### 6.4 Ternary and mixed dimensional heterostructures

The generation of a ternary heterostructure of graphene, 2D  $\text{MPX}_3$ , and layered double hydroxides (LDHs)/MXenes is worth exploring for overall water splitting as this system possesses optimum HER and OER sites with good electronic conductivity. It is important to note that some of the  $\text{MPX}_3$  systems, which show high HER activity suffer from issues related to stability and *vice versa*. In the case of a ternary superlattice-like structure, the 2D  $\text{MPX}_3$  layer is sandwiched between other 2D components, which can improve the structural and catalytic stability along with the activity. Further, coupling of 2D TMPCs with other 1D carbon nanotubes or with 1D  $\text{MoS}_2$  can generate a 3D porous framework with more accessibility for electrolytes, highly exposed edge sites, and interconnected electron-transfer channels, which will be useful for other HER-related catalysis applications.

After potential developments of proficient  $\text{H}_2$  evolution catalysts, recent research has demonstrated that 2D  $\text{MPX}_3$  catalysts can be highly efficient for photocatalytic and electrocatalytic water splitting. Solar water-splitting reactors need to be established to sustain large-scale  $\text{H}_2$  production at a low cost. In this context, photoelectrochemical cells (PECs) have the benefit of exploiting both solar and electrical energy and concurrently separating evolved  $\text{H}_2$  from  $\text{O}_2$ . Band gap tunability and good

electronic conductivity make 2D MPX<sub>3</sub> a potential candidate for HER with high solar-to-hydrogen conversion efficiency. Also, strategies for safe H<sub>2</sub> storage and transport need to be developed.

## Conflicts of interest

The authors declare no conflicts of interest.

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