MnPSe₃ Monolayer: A Promising 2D Visible-Light Photohydrolytic Catalyst with High Carrier Mobility

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Since the experimental realization of graphene,[1] 2D materials have been receiving significant attention due to their unique physical and chemical properties which mainly arise from their topological effects and high surface-bulk ratios. Graphene has predominated as the most widely studied 2D material. Intractably, lack of a band gap limits its practical applications to high speed switching devices, photocatalysts, etc.[2] Nevertheless, the successful preparation of graphene has prompted researchers to investigate more 2D materials such as hexagonal BN,[3] transition metal dichalcogenides (TMDs),[4] silicene,[5] germanane,[5b,6] phosphorene,[7] and MXene.[8] These 2D materials attract intensive interest due to their novel electronic, mechanical or photocatalytic behaviors,[9] making up the shortages of graphene and expanding the applications of 2D materials to field-effect transistors (FETs)[10] and photocatalysts.[11]

Recently, a new kind of 2D materials (exemplified by MnPSe₃) was proposed by Li et al.[12] Then, a series of MPS₃ (M = Fe, Mn, Ni, Cd, Zn) and MPSe₃ (M = Fe, Mn) were explored by Du et al.[13] Particularly, bulk crystals and few-layer samples of MPX₃ (X = S, Se) were obtained and characterized in experiments. The previous reports indicated that the band gaps of these MPX₃ bulks range from 1.3 to 3.5 eV,[13] suggesting the light absorption at a wide wavelength for photocatalysts.

Hydrogen generation by photocatalytic water splitting would present a promising method for solar energy conversion and play a very important role in solving serious environmental problems.[14] However, inability to utilize visible light, low quantum yield, and fast backward reaction limit the practical application of photocatalytic water splitting.[15] 2D materials with an appropriate band gap (i.e., ≈2–3 eV) would exhibit more efficient use of visible light in the photocatalytic process. Moreover, 2D nature means short distance for the generated electrons and holes to migrate, reducing the possibility of electron–hole recombination, and then giving high quantum yields. Enlightened by some 2D materials which are predicted to be photocatalysts for water splitting under visible light,[15b,16] especially some proved good photocatalysts in experiments such as g-C₃N₄,[17] we investigated the band edges and optical properties of MPS₃ (M = Fe, Mn, Ni, Cd, Zn) and MPSe₃ (M = Fe, Mn) monolayers to screen more proper photocatalysts for water splitting. Then the carrier mobility was calculated through deformation potential (DP) theory for MnPSe₃ monolayer which is a direct-band-gap semiconductor and has strong absorption in the visible-light region. The high carrier mobility of MnPSe₃ monolayer (up to 625.9 cm² V⁻¹ s⁻¹) could be comparable to or even higher than those of many other 2D materials, indicating that the transfer of carriers to reactive sites would be easier in the photocatalytic process. Our results disclose that MnPSe₃ monolayer would be a promising photocatalyst for water splitting under visible light.

The structural properties of MPS₃ (M = Fe, Mn, Ni, Cd, Zn) and MPSe₃ (M = Fe, Mn) monolayers were explored first. To determine the ground state of MPS₃ (M = Fe, Mn, Ni, Cd, Zn) and MPSe₃ (M = Fe, Mn), both spin-unpolarized and spin-polarized computations were performed. The results show that spin-polarized total energies are less favorable than spin-unpolarized ones for FePS₃, CdPS₃, ZnPS₃, and FePSe₃ monolayers, indicating that these monolayers have nonmagnetic ground states. However, MnPS₃, NiPS₃, and MnPSe₃ monolayers prefer antiferromagnetic (AFM) coupling, which is more stable than the ferromagnetic (FM) state. The structures of these kinds of monolayers are similar, as shown in Figure 1a.

To check the stability of the monolayers, the phonon spectra along the high-symmetry points in Brillouin zone were computed, and are shown in Figure S1 (Supporting Information). There are no imaginary phonon modes in the phonon spectra of MPS₃ (M = Fe, Mn, Ni, Cd, Zn) and MPSe₃ (M = Fe, Mn) monolayers, which reveals that these monolayers are dynamically stable configurations and could be realized in experiments.

Another important issue to confirm the stability of 2D materials is whether it can form a freestanding monolayer. Therefore, the in-plane stiffness should be high enough to withstand its own weight or even external load without substrates. To check this, the in-plane stiffness was calculated by $C_{D} = (\delta E_{\text{total}}/\delta \epsilon')/S_0$, where $E_{\text{total}}$, $\epsilon'$, and $S_0$ represent the total energy per unit cell, uniaxial strain, and the area of the optimized unit cell, respectively. The calculated in-plane stiffness is shown in Figure S2 and Table S1 of the Supporting Information. The in-plane stiffness of sulfides is higher than that of the corresponding selenides, which might result from the greater electronegativity of sulfur. Through the elasticity theory, an estimate for the typical out-of-plane deformation $h/l \approx (pg/C_{D})^{1/3}$,[18] where $l$ is the length of the monolayer.
cleavage strength $\sigma$ could be obtained by computing the maximum derivative of $E_{cl}$ as shown in Figure 1b. The cleavage strength of MPS$_3$ (M = Fe, Mn, Ni, Cd, Zn) and MPSe$_3$ (M = Fe, Mn) monolayers computed with Heyd–Scuseria–Ernzerhof (HSE06) functional are shown in Figure 1c and Figure 2.

As shown in Table S3 of the Supporting Information, MnP$_3$ and MnPSe$_3$ monolayers are direct-band-gap semiconductors with the band gap of 3.14 and 2.32 eV, respectively, consistent with the previous report.[12] The valence band maximum (VBM) and the conduction band minimum (CBM) are both located at the K point. Other monolayers are indirect-band-gap semiconductors. More details are provided in the Supporting Information.

To further understand the compositions of VBM and CBM for MPS$_3$ and MPSe$_3$ monolayers, the partial density of states (PDOS) are computed. As shown in Figure 1d and Figure S3 of the Supporting Information, the CBM and VBM of all the monolayers mainly originate from the $p$ states of S/Se and the $d$ states of metal atoms, respectively.

The band structures and PDOS indicate that the band gaps of MPS$_3$ (M = Fe, Mn, Ni, Cd, Zn) and MPSe$_3$ (M = Fe, Mn) monolayers range from 1.90 to 3.44 eV, which exceed the free energy of water splitting of 1.23 eV. In addition to the magnitude of the band gap, the band edges must straddle the redox potentials of water. To check this, the work functions of these monolayers were calculated and are shown in Table S4 of the Supporting Information.

For the water splitting reaction, the redox potential depends on the pH value.[16b,21] The standard reduction potential for $\text{H}_2^+/\text{H}_2$ was calculated by $E_{\text{red}}^\text{st} = -4.44 \text{ eV} + pH \times 0.059 \text{ eV}$ and the oxidation potential for $\text{O}_2^+/\text{H}_2\text{O}$ was calculated by $E_{\text{ox}}^\text{st} = -5.67 \text{ eV} + pH \times 0.059 \text{ eV}$. Considering that sulfides and selenides might be unstable in an acidic environment, the redox potential for water splitting reaction at neutral environment ($pH = 7$) was also calculated. The schematic diagram is shown in Figure 3 for the positions of band edges of MPS$_3$ (M = Fe, Mn, Ni, Cd, Zn) and MPSe$_3$ (M = Fe, Mn) monolayers for photocatalytic water splitting. Except FePSe$_3$, whose CBM is lower than the reduction potential of $\text{H}_2^+/\text{H}_2$ at pH = 7, the band edges of the rest compounds straddle the redox potentials of water at pH = 0 and 7. The results indicate that these materials are candidates for water-splitting photocatalysts without an external bias voltage. More fascinatingly, besides the advantages
of suitable positions of band edges at both acidic and neutral environment, MnPS$_3$ and MnPSe$_3$ are direct-band-gap semiconductors.

Another very important condition for photocatalytic water splitting is that the materials should capture a significant fraction of visible spectrum because it counts for more than 40% of the solar spectrum.

To investigate the performance under light, the optical absorption coefficient was calculated and is shown in Figure 4. The corresponding imaginary parts of the dielectric function is shown in Figure S4 of the Supporting Information. The absorption coefficient is defined as the decay of light intensity spreading in a unit length of medium. FePSe$_3$, MnPSe$_3$, FePS$_3$, and NiPS$_3$ monolayers exhibit obvious optical absorption in visible spectrum and among them, the absorption of FePSe$_3$ and MnPSe$_3$ is stronger. However, FePSe$_3$ might have no photocatalytic activity for water splitting at neutral environment. For MnPSe$_3$, there are two absorption peaks in visible spectrum, indicating the strong optical absorption. Besides, the direct gap would make MnPSe$_3$ more advantageous over other materials. The results indicate that MnPSe$_3$ monolayer would exhibit better performance for photocatalytic water splitting. To investigate the effects of the layer number on the electronic properties and optical absorption of MnPSe$_3$, MnPSe$_3$ bilayer was considered. More details are shown in Figures S5–S7 of the Supporting Information. The results indicate that MnPSe$_3$ bilayer could also exhibit catalytic activity for photocatalytic water splitting under visible light.

To further evaluate the performance of MnPSe$_3$ monolayer as photocatalysts, the carrier effective mass and carrier mobility were investigated for quantitative evaluation on the ability to transfer electron/hole along the specific direction. The effective masses of electrons ($m^*_{e}$) and holes ($m^*_{h}$) are calculated by fitting parabolic functions to CBM and VBM, respectively. As shown in Table 1, $m^*_{e}$ and $m^*_{h}$ along the direction of $a$ (Figure 1a) were calculated, which are in

![Figure 2. Band structures near Fermi level for a) FePS$_3$, b) MnPS$_3$, c) NiPS$_3$, d) CdPS$_3$, e) ZnPS$_3$, and f) FePSe$_3$ monolayers.](image1)

![Figure 3. The location of VBM and CBM calculated with HSE06 functional of MPS$_3$ and MPSe$_3$ monolayers. The redox potentials of water splitting at pH = 0 (orange dashed lines) and pH = 7 (cyan dashed lines) are shown for comparison.](image2)
First-principles computations, which indicate that these 2D monolayers could be obtained in experiments by exfoliating the corresponding bulk. The calculated band gaps and band edge positions from accurate HSE06 functional predict that MPS$_3$ (M = Fe, Mn, Ni, Cd, Zn) and MPSe$_3$ (M = Fe, Mn) monolayers are promising candidates as photocatalysts for water splitting. Particularly, MnPSe$_3$ monolayer is a direct-band-gap semiconductor which exhibits obvious absorption in visible-light spectrum. Moreover, our calculations of effective mass and carrier mobility for MnPSe$_3$ monolayer illustrate the transfer of carriers to the reactive sites would be easier and the probability of recombination would be lower for photogenerated carriers in the photocatalytic process. These results reflect that 2D MnPSe$_3$ monolayer could be a promising photocatalyst for water splitting.

**Experimental Section**

Our first-principles computations based on density functional theory (DFT) were performed with a plan-wave basis set as implemented in the Vienna ab initio simulation package (VASP). The projector augmented wave (PAW) was used to describe the ion–electron interaction. The generalized gradient approximation (GGA) expressed by the functional of Perdew, Burke, and Ernzerhof (PBE) was adopted to accurately account for the van der Waals force for weak interactions. A Monkhorst–Pack k-point mesh of $7 \times 7 \times 1$ was used for 2D sheet, $7 \times 7 \times 2$ for selenide bulk and $6 \times 3 \times 5$ for sulfide bulk. To study 2D systems under periodic boundary conditions (PBC), a vacuum space with at least 15 Å was inserted between the MPX$_3$ sheets and the periodically repeated images. Moreover, considering that GGA functional systematically underestimates the band gaps, we computed the band structures with the HSE06 hybrid functional. The computation of the phonon dispersion spectrums was calculated through CASTEP code with finite displacement method as implemented in Materials Studio.

To investigate the optical absorption, the imaginary part of dielectric function $\varepsilon_2$ was calculated. The expression for $\varepsilon_2$ was given as

$$\varepsilon_2(\omega) = \frac{4\pi^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{k,k'} \frac{\delta}{\varepsilon_{c,k} - \varepsilon_{v,k} - \omega} \left( u_{c,k} \times u_{v,k} \right)$$

(1)

where the indices $c$ and $v$ refer to the conduction and valence band states, respectively, which were determined by the HSE06 functional here, and $u_{c,v}^\text{cell}$ is the cell periodic part of the orbital at the k-point $k'$. The absorption coefficient $\alpha(\omega)$ was calculated by

$$\alpha(\omega) = \sqrt{2} \omega \left( \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right)^{1/2}$$

(2)

where $\varepsilon_1$ is the real part of dielectric function, which could be obtained from $\varepsilon_2$ by Kramer–Kronig relationship. For inorganic semiconductors, the electron coherence length is close to the acoustic phonon wavelength, which is much longer than the bonds. As a result, phonon scattering dominates the intrinsic mobility which can be described by the deformation potential theory. For 2D materials, the carrier mobility is given by

| $m^*$ | $C_{2D}$ | $|E_i|$ | $\mu$ |
|-------|----------|----------|-------|
| Electrons (K$\to$Γ) | 0.55 | 60.8 | 2.12 | 625.9 |
| Holes (K$\to$Γ) | 1.22 | 60.8 | 4.08 | 34.7 |
where $T$ is the temperature, 300 K was adopted in this study, $e$ is the electron charge, and $\hbar$ is the reduced Planck constant. $m^*$ is the effect mass defined as $m^* = \frac{\hbar^2}{E(k)\partial^2E(k)/\partial k^2}$, where $k$ is the wave vector, and $E(k)$ is the energy corresponding to the wave vector $k$. $E_1$ is the DP constant denoting the shift of band edges induced by uniaxial strain, $E_2 = \partial E_{edge}/\partial k$. $C_{2D}$ is the in-plane stiffness as shown in Table S1 of the Supporting Information.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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