Highly-efficient overall water splitting in 2D Janus group-III chalcogenide multilayers: the roles of intrinsic electric filed and vacancy defects

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ABSTRACT

Two-dimensional (2D) van der Waals materials have been widely adopted as photocatalysts for water splitting, but the energy conversion efficiency remains low. On the basis of first-principles calculations, we demonstrate that the 2D Janus group-III chalcogenide multilayers: InGaXY, M2XY and InGaX2 (M = In/Ga; X, Y = S/Se/Te), are promising photocatalysts for highly-efficient overall water splitting. The intrinsic electric field enhances the spatial separations of photogenerated carriers and alters the band alignment, which is more pronounced compared with the Janus monolayers. High solar-to-hydrogen (STH) efficiency with the upper limit of 38.5% was predicted in the Janus multilayers. More excitingly, the Ga vacancy of InGaSSe bilayer effectively lowers the overpotentials of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) to the levels provided solely by the photogenerated carriers. Our theoretical results suggest that the 2D Janus group-III chalcogenide multilayers could be utilized as highly efficient photocatalysts for overall water splitting without the needs of sacrificial reagents.

1. Introduction

As one of the potential strategies to directly convert solar energy into hydrogen fuel, photocatalytic water splitting has attracted growing interest in addressing the imminent energy and environment crisis [1–4]. The lowest solar-to-hydrogen (STH) efficiency that makes photocatalysts be economically viable is about 10% [5,6]. The main challenges in improving the STH efficiency of photocatalysts lie in the following three issues [7–10]: (1) The band gap of the photocatalyst should be larger than 1.23 eV to match the hydrogen reduction potential of $\text{H}^+ / \text{H}_2$ ($\Delta G_0 \approx -4.44 \, \text{eV}$) and water oxidation potential of $\text{H}_2\text{O} / \text{O}_2$ ($\Delta G_0 \approx -5.67 \, \text{eV}$). Hence, the photons with longer wavelength (>1000 nm) cannot be absorbed by the photocatalysts, resulting in a significant loss in the efficiency of infrared light utilization. (2) The photogenerated electrons and holes in these photocatalysts should be capable of fast separation and migration to suppress their recombination, otherwise the STH efficiency will be greatly reduced. Experimental works have showed that the photocatalytic hydrogen evolution could be enhanced roughly ninety times by promoting the separation of carriers [11–13]. (3) The conduction band minimum (CBM) and valence band maximum (VBM) of the photocatalysts should simultaneously satisfy the suitable alignment with respect to the energy levels of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Additionally, overpotential is often required to drive the HER and OER, which further induces efficiency drops. Under ideal conditions, i.e., the efficiencies of light absorbance and carrier separation, as well as the quantum efficiencies are all 100%, the maximal theoretical efficiency can reach ~47% [14]. Taking the additional heat losses and other factors that interact with each other into account, the STH efficiency could not exceed 18% [15,16].

To break through the above limitations, a new mechanism of photocatalytic water splitting in 2D materials emerged [17]. The intrinsic out-of-plane electric field was introduced to alter the alignment of the CBM and VBM of the photocatalysts with respect to the water reduction and oxidation potentials. Not only the bandgap restriction of the conventional photocatalysts (1.23 eV)
is broken, but also stronger redox abilities to drive the HER and OER are preserved. The intrinsic electric field also accelerates the separation and migration of the photogenerated electrons and holes. In one of our previous experimental works, we have achieved this mechanism in WS$_2$ nanosheets and demonstrated near-infrared light activity and high photocatalytic efficiency [18]. A number of 2D materials with intrinsic out-of-plane electric field, such as semihydrogenated BN sheet [19], germanium monochalcogenide [20], III$_2$-VI$_3$ materials [16,21], and Sc$\text{CO}_2$ [22], have been proposed as photocatalysts for water splitting, and high STH efficiencies were predicted in III$_2$-VI$_3$ materials [22], have been proposed as photocatalysts for water splitting, where the intrinsic electric field plays an important role in photocatalytic water splitting.

Notably, the intrinsic electric filed also exists in Janus materials without the out-of-plane mirror symmetry [23–25], enabling them to be promising candidates for high efficiency photocatalysts. The Janus group-III chalcogenide monolayers were firstly proposed from first-principles calculations as enhanced piezoelectric materials [25]. Almost at the same time, experimental realization of MoS$\text{Se}_2$ Janus structure was reported [23,24]. Motivated by these pioneering progresses, a series of Janus structures with intrinsic dipole have been intensively investigated [26–32]. However, the relatively large band gap of the Janus photocatalysts is disadvantagous for high STH efficiencies. Additionally, the role of the intrinsic electric filed in overall water splitting and the redox processes of these Janus photocatalysts have not been clearly addressed. Moreover, if the HER and OER can proceed in the Janus photocatalysts under the electric potential provided solely by the photogenerated carriers without the needs of sacrificial reagents has never been investigated.

In this work, we systematically studied three groups of 2D Janus photocatalysts namely InGaXY, M$_2$XY and InGaX$_2$ ($M = \text{In}/\text{Ga}; X, Y = \text{S}/\text{Se}/\text{Te}$) by using first-principles calculations. The lattice structures of these Janus group-III chalcogenides are very similar to those reported in previous literatures [25,33]. We found that the intrinsic electric field which is more pronounced in Janus multilayers, alters the band alignment and broadens the energy range of light adsorption, leading to high STH efficiency with upper limit of about 38.5%. More excitingly, the Ga vacancy of Janus InGaSe$\text{Se}_2$ bilayer effectively lowers the overpotentials of HER and OER, making these reactions proceed under the potential provided solely by the photo-generated electrons and holes. These results imply the potentials of the 2D Janus group-III chalcogenide multilayers as highly-efficient photocatalysts for overall water splitting without the needs of sacrificial reagents.

2. Methods and computational details

All first-principles calculations were performed using the VASP [33,34] code. Projector-augmented wave (PAW) [35] formalism in conjunction with a generalized gradient approximation (GGA) in the form of Perdew, Burke, and Ernzerhof (PBE) [36] for the exchange-correlation functional. The vdW correction of Grimme’s DFT-D3 (BJ) [37,38] model with Becke-Johnson damping within the PBE functional was involved to describe the interlayer interaction. The dipole correction [39] was also engaged to describe the possible charge redistribution in these heterostructures. All electronic structures were calculated using the screened hybrid HSE06 functional [40] with 25% Hartree-Fock exchange energy which has been demonstrated to reproduce well the experimentally bandwidths of semiconductors. The energy cutoffs used for plane-wave expansion of electron wave functions were set to be 500 eV, ensuring the total energy in $10^{-5}$ eV precision. The $21 \times 21 \times 1$ and $35 \times 35 \times 1$ k-point mesh on the Brillouin zone (BZ) were employed for structure relaxation and static calculations based on PBE functional and an $11 \times 11 \times 1$ k points mesh for static calculations using HSE06 functional. A vacuum space of about 15 Å is applied to separate the neighboring layers interactions. The atomic positions and lattice vectors were fully optimized using the conjugate gradient (CG) scheme without any symmetric restrictions until the maximum force on each atom was less than 0.01 eV/Å. The vibrational properties are obtained with the PHONOPY code, which use the force constants calculated with the finite-displacement method.

3. Results and discussion

3.1. Geometric structures

We started from the Janus monolayers constructed by covalently bonding two group-III chalcogenide monolayers with very close lattice constants, as displayed in Fig. 1a–c. Ten Janus structures are categorized into three groups: InGaXY, M$_2$XY and InGaX$_2$ ($M = \text{In}/\text{Ga}; X, Y = \text{S}/\text{Se}/\text{Te}$). Compared with their binary analogs [25,41–43] (Fig. S1 online), the mirror symmetry in the vertical (out-of-plane) direction is broken, leading to intrinsic vertical electric dipoles. The optimized lattice parameters and layer thickness of these Janus monolayers lie in between the values of their binary analogs, as listed in Tables S2 and S3 (online). We calculated the formation energies ($E_{\text{form}}$) of these Janus monolayers evaluated by the expression $E_{\text{form}} = \left( E_{\text{total}} - \sum_i n_i \mu_i \right) / \sum_i n_i$, where $E_{\text{total}}$ and $n_i$ represent total energy and the number of i-th atom of the Janus structure in one unit cell, $\mu_i$ is the chemical potential of i-th atom in its bulk crystal. The negative formation energies that vary from −0.57 to −1.07 eV/atom (Table S2 online) implies the energetic stability of these Janus structures. These values are comparable to those of the binary analogs (Table S3 online), parts of which have been synthesized in experiments [44–47]. The dynamics stability of the Janus monolayers was confirmed by the phonon spectra which are free from the imagery-frequency modes, as shown in Fig. S2 (online).

Considering multilayers are generally more accessible than monolayers in experiments, we further constructed Janus bilayers by stacking Janus monolayers via the interlayer van der Waals (vdW) interaction. Five highly-symmetric stacking patterns were considered, as shown in Figs. 1d and S3 (online), where the two monolayers have the parallel electric polarization directions. We calculated the geometric and electronic properties of three representative Janus bilayers, InGaSe$\text{Se}_2$, Ga$_2$Se$\text{Te}$ and InGaSe$_2$, with different stacking patterns, as summarized in Table S4 (online). The negative formation energies of these Janus bilayers indicate their energetic stability. Among the five patterns, type-II stacking pattern (Fig. 1d) is energetically most favorable, except Ga$_2$Se$\text{Te}$, where type-I and type-II patterns are nearly degenerate in energy. In addition, the electronic properties show weak dependence on the stacking patterns. We therefore only focus on the type-II stacking pattern for all the Janus bilayers. As shown in Table S5 (online), the formation energies with respect to the isolated monolayers vary from −17.71 to −19.48 meV/Å$^2$. These values are in the range of typical vdW materials (−13−20 meV/Å$^2$), confirming the thermodynamic stability. More details of the geometric structures can be found in the Supplementary materials (online).

3.2. Electronic structures and photocatalytic mechanism

The electronic band structures of the Janus materials were calculated by using the density-functional theory (DFT) within the HSE06 hybrid functional, as shown in Figs. 2, S4 and S5 (online). Obviously, all the Janus monolayers and bilayers are semiconductors. For the Janus monolayers, the band gaps vary from 1.85 to...
3.19 eV, which are slightly smaller than those of the binary analogs (Fig. S6 online). The band gaps of the Janus monolayers obtained from the HSE06 functional in this work are larger than those given by using the PBE functional [25]. Notably, InGaSTe, Ga2SeTe, In2SeTe and InGaTe2 monolayers have direct gaps at the Γ points, in contrast to their binary analogs. Different from the monolayers, all the Janus bilayers are indirect band gap semiconductors, as shown in Figs. 2b and S5 (online). The VBM locates between the Γ and M points, while the CBM resides at Γ points. Unsurprisingly, all the Janus bilayers possess smaller band gaps (1.32–2.55 eV) compared to the monolayers (1.85–3.19 eV). The absence of vertical mirror symmetry leads to the charge transfers between the top and bottom surfaces of the Janus structures, inducing intrinsic electric dipoles. The dipoles moments for all the Janus bilayers (0.11–0.52 Debye) are about twice as large as those of monolayers (0.05–0.27 Debye), enhancing the vertical built-in electric field effects (Tables 1 and S2 online). These values are comparable to other polar materials, such as Janus transition metal dichalcogenides (0.19–0.77 Debye) [27], germanium monochalcogenides (0.16–0.46 Debye) [20], and III2-VI3 materials (0.45–0.61 Debye) [21]. The vertical built-in electric fields arising from the electric dipoles have the following effects. (1) The energies of the vacuum levels are no longer equal (characterized by nonzero ΔV) on the two sides of the Janus structures, as shown in Figs. S7 and S8 (online). This alters the alignment of the water reduction and oxidation potentials with respect to the band edges of the Janus structures which breaks through the bandgap restriction of the conventional photocatalysts. (2) The built-in electric field facilitates the separation of the photogenerated electrons and holes and suppresses their recombination, which is beneficial for improving the STH efficiencies of the Janus photocatalysts. The photoexcited electrons transfer to the top surface (layer) whereas the photoinduced holes migrate to the bottom surface (layer) for the Janus monolayers (bilayers) driven by the intrinsic electric field.

To verify the photocatalytic abilities, we first aligned the band edges of these Janus structures to the vacuum levels determined from the plane-averaged electrostatic potential [42]. As shown in Fig. 2c, d, except for the InGaTe2 bilayer, all the Janus monolayers and bilayers satisfy the band edges requirements for overall water splitting at pH 0. For the InGaTe2 bilayer, by increasing the pH value of the solution to 7, redox potentials will shift upward making the band energy alignment suitable for overall water splitting (Fig. S9 online). The overpotentials that the photogenerated carriers can provide to drive the OER and HER processes for water splitting can be evaluated respectively from the energy differences (ΔE1 and ΔE2) between the water oxidation potential (H2O/O2) and the VBM and between the CBM and the hydrogen reduction potential (H+/H2), as shown in Fig. 3. From in Tables 1 and S2 (online), we can see that the ΔE1 and ΔE2 of the Janus bilayers are very close to the corresponding values of monolayers. Meanwhile, except for the ΔE1 of InGaTe2, Ga2SeTe and In2SeTe and the ΔE2 of In2SeTe, InGaSe2 and InGaTe2, all the ΔE1 and ΔE2 are larger than 0.4 eV, manifesting strong redox abilities of the Janus monolayers and bilayers for HER and OER. Notably, the overpotentials of the photogenerated carriers in InGaXY structures are significantly larger than those in the M2XY and InGaX2 systems, due to the stronger intrinsic electric dipole effects, providing enough driving force to trigger both HER and OER processes.

The separation of photogenerated electrons and holes, which facilitate the high STH efficiencies of photocatalysts, is closely related to the spatial distribution of partial charge densities for VBM and CBM. In an ideal case, the charge density distributes of VBM and CBM are consistent with the distribution of photoexcited carriers induced by the build-in electric field. For the Janus monolayers considered in this work, however, only the Janus InGaTe2 monolayer fulfills this requirement, i.e., the CBM originates from the top surface of GaTe and the VBM is contributed by the down surface of InTe (Fig. S10 online). The photogenerated electron-hole pairs cannot be separated effectively for other nine Janus monolayers, which will significantly decrease the STH efficiencies. Fortunately, the enhanced intrinsic electric filed in the Janus bilayers enable them perfectly meet this requirement, as shown in Figs. 2b and S11 (online). The electron wavefunctions of VBM reside mainly on the bottom layer, while those of the CBM are originated from the top layer. Therefore, the photoexcited holes incline to distribute on the bottom layer, while the electrons prefer the top layers. This behavior will effectively reduce the rates of recombination for carriers and ensure the OER and HER occurring in different layers, which are beneficial for achieving high photocatalytic efficiency. We therefore focus on the Janus bilayers in the following parts and present the results of monolayers in the Supplementary materials (online).

It is noteworthy that the intrinsic vertical electric field in the Janus bilayers not only enhances the spatial separations of
photogenerated carriers, but also breaks the rules of band gap requirements for the conventional photocatalysts and increases the overpotentials of the photogenerated carriers. Taking the InGaSTe bilayer as an example, the schematic diagram of this mechanism is illustrated in Fig. 3. Under solar light irradiation, electrons and holes are generated in the conduction and valence bands, respectively. Subsequently, driven by the intrinsic electric field, these photogenerated electrons and holes transfer respectively to the top and bottom surfaces and contribute to the HER and OER. Due to the different vacuum levels of the two sides of the Janus materials, the redox potentials of \( \text{H}^+/\text{H}_2 \) and \( \text{H}_2\text{O}/\text{O}_2 \) determined with respect to the vacuum levels are also altered, enlarging the overpotentials (\( \Delta E_1 \) and \( \Delta E_2 \)) of the photogenerated carriers. More interestingly, the \( \Delta V \) of the InGaSTe Janus bilayer is larger than 1.23 eV, lifting the conventional limit of band gap for overall water splitting.

To further verify the effect of the intrinsic electric field on the water splitting processes, we calculated electron density of states (DOS) of the water molecules adsorbed on the top and bottom layers of the Janus InGaSTe bilayer, as shown in Fig. S12 (online). Clearly, there is an energy shift of about 1.09 eV between the DOSs of the top and bottom water molecules, suggesting the different electrostatic potential environment of the water molecules on the two surfaces of the Janus material, in consistent with the shift of the vacuum levels due to the intrinsic electric field. Therefore, the water molecules on the two surfaces of the Janus material have different water oxidation potential (\( \text{H}_2\text{O}/\text{O}_2 \)) and hydrogen reduction potential of (\( \text{H}^+/\text{H}_2 \)) where the intrinsic electric filed effect (\( \Delta V \)) is involved.

### 3.3. Carrier mobilities

High carrier mobility of photocatalysts promotes the migration and separation of the photo-generated electron-hole pairs, ensuring the high photocatalytic efficiency. Theoretically, carriers mobility can be evaluated approximately by using the phonon-limited scattering model [48] (details see the Supplementary materials online). The predicted mobilities of the electrons and holes along \( x \)- and \( y \)-directions are displayed in Table S6 (online). From this table, we can see that these Janus bilayers have high electron mobility ranging from 1307 to 5534 cm\(^2\) V\(^{-1}\) S\(^{-1}\). These values are higher than that of the Janus TMDs and comparable to that of the InSe monolayer demonstrated in experiments [44,49]. The hole...
mobility, however, is much lower than the electron mobility, and can be as low as 11 cm² V⁻¹ S⁻¹ for InGaS₂. The highest hole mobility of 3801 cm² V⁻¹ S⁻¹ was predicted in InGaTe₂. The large difference of mobilities between electrons and holes facilitates their separation. For comparison, we also calculated the carrier mobilities of monolayers and their binary analogs as displaced in Tables S7 and S8 (online). Generally, the carrier mobilities of the Janus bilayers are higher than the monolayers and their binary analogs.

### 3.4. Light adsorption and STH efficiencies

Light adsorption ability is another key factor in determining the STH efficiency of photocatalysts. Here, we calculated the light absorption properties of the Janus bilayers from the complex dielectric function obtained at the DFT-HSE06 level [50] (Supplementary materials online). As shown in Fig. 4, all the Janus bilayers exhibit remarkable absorption in the visible light region. The optical absorption edge has also been extended to infrared light. There are absorption peaks in the infrared region for the Ga₂SeTe, In₂SeTe and InGaTe₂ Janus bilayers. This is consistent with their band gaps smaller than 1.61 eV. Moreover, the energies of the first absorption peaks agree well with their band gaps. Clearly, the out-band gaps smaller than 1.61 eV. The STH efficiency of the photo-catalytic water splitting is corrected as [16]

\[
\eta_{\text{STH}} = \eta_{\text{STH}}^0 \times \frac{\int_0^{\infty} P(\hbar \omega) d(\hbar \omega)}{\int_0^{\infty} P(\hbar \omega) d(\hbar \omega) + \Delta V \int_0^{\infty} \frac{P(\hbar \omega)}{\hbar \omega} d(\hbar \omega)},
\]

where \( E_g \) is the band gap and \( \Delta V \) is the vacuum level difference on the two sides of the Janus photocatalysts. The second term in the denominator represents the contribution of the vertical electric field. It should be mentioned that the STH efficiency given by using the above strategy corresponds to the theoretical upper limit of efficiency in the ideal conditions where the efficiencies of light absorption, carrier separation and quantum efficiencies are all 100%, and cannot be compared directly to the experimental values. However, this theoretical STH efficiency is still meaningful in evaluating the performance of photocatalysts in energy conversion [14,16,51].

The \( \eta_{\text{STH}} \) of these Janus photocatalysts exhibits obvious dependence on the band gap of the Janus bilayers, as listed in Table 1, because the suitable band edge positions guarantee reasonable overpotentials to drive the HER and OER processes. Generally, \( \eta_{\text{STH}}^0 \) decreases with the increase of bandgap. Notably, all the Janus bilayers (except for Ga₂SSe) have the \( \eta_{\text{STH}}^0 \) larger than 10%. What’s more, the conventional theoretical limitation of STH efficiency ~18% is lifted in many Janus bilayers, such as InGaStTe, GaSeTe, In₂SeTe, InSSe, InSeTe, InGaSe₂ and InGaTe₂, thanks to the relatively small band gaps (< 1.83 eV). The \( \eta_{\text{STH}} \) in the Janus InSeTe bilayer even attains 28.9%, owing to the high capability in absorbing infrared light for full water splitting.

![Fig. 4.](Image) The calculated absorption coefficients of the Janus bilayers (a) InGaXY, (b) M₂XY and (c) InGaX₂, respectively.

Table 1

<table>
<thead>
<tr>
<th>Janus</th>
<th>Bilayers</th>
<th>( E_g ) (eV)</th>
<th>( \Delta E_1 ) (eV)</th>
<th>( \Delta E_2 ) (eV)</th>
<th>( P ) (debye)</th>
<th>( \Delta V ) (V)</th>
<th>( \eta_{\text{STH}} ) (%)</th>
<th>( \eta_{\text{STH}}^0 ) (%)</th>
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<tr>
<td>InGaXY</td>
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<td>1.99</td>
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<td>0.86</td>
<td>1.01</td>
<td>0.52</td>
<td>28.5</td>
<td>21.4</td>
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<td>InGaTe</td>
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<td>0.45</td>
<td>0.37</td>
<td>0.97</td>
<td>25.1</td>
<td>20.9</td>
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<td>6.90</td>
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<td>InSeTe</td>
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<td>0.78</td>
<td>0.25</td>
<td>20.6</td>
<td>18.5</td>
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<tr>
<td>InGaX₂</td>
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<td>1.83</td>
<td>0.82</td>
<td>0.17</td>
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<td>InGaTe₂</td>
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<td>InGa₄Te²</td>
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<td>0.11</td>
<td>25.6</td>
<td>24.2</td>
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</table>

* The pH value of the solution is set to 7 for InGaTe₂ bilayer.
3.5. Janus multilayers

In order to further enhance the electric field effect, the Janus multilayers containing more monolayers which are built analogously to Janus bilayers. The band gaps of the Janus multilayers can be further decreased by increasing the layer thickness due to the quantum confinement effect [47], as shown in Fig. S13 (online), resulting in higher STH efficiencies. Taking the Janus InGaSe2 multilayers as an example, we demonstrated this tendency from first-principles. As we expected, the band gaps are reduced to 1.37, 1.14 and 0.94 eV for the Janus InGaSe2 multilayers containing three, four and five monolayers, respectively, which means that the full solar spectrum can be utilized for water splitting (Table S9 and Fig. S14 online). The VBM and CBM energy levels not only meet the band alignment requirements for overall water splitting, but also provide suitable overpotentials to drive the OER and HER. The intrinsic electric fields can also tune the spatial distributions of partial charge densities for VBM and CBM, making them consist with the migration paths of photoexcited carriers induced by the intrinsic electric field. This result effectively promotes the spatial separations of the photogenerated electrons and holes, which ensures the OER and HER occurring in the bottom and top layers, respectively. The corrected of STH efficiencies ($\eta_{\text{STH}}$) in the Janus InGaSe multilayers can achieve 32.6% (three monolayers), 35.8% (four monolayers) and 38.5% (five monolayers), respectively. Such high STH efficiencies are close to the theoretical limit of ~47%, and higher than those predicted in other materials by using the same theoretical strategy [16,51].

3.6. Overall water splitting on Janus InGaSSe bilayer

The suitable band edge positions of the Janus materials do not guarantee that the overall water splitting can take place under visible light irradiation. The photoexcited electrons and holes should provide an adequate driving force to trigger both HER and OER processes, otherwise additional treatments, such as adding sacrificial reagents, should be made to ensure the two reactions can proceed. For photocatalytic water splitting processes, the external potential that determines whether the water splitting can proceed is provided by photogenerated carriers. The potential of photogenerated electrons for HER ($U_e$) is defined as the energy difference between the hydrogen reduction potential and the CBM, while the potential

![Fig. 5. (Color online) Proposed photocatalytic pathways of (a) hydrogen reduction and (b) water oxidation half reactions with the most energetically favorable absorbed intermediates (H*, OH*, O*, OOH*) in the Janus InGaSe bilayer with Ga vacancy defect. The white and red balls represent H and O atoms, respectively. Free energy diagrams for (c) the 2e pathways of hydrogen reduction and (d) 4e pathways of water oxidation reactions in the Janus InGaSe bilayer under different conditions. $U = 0.68$ V and $U = 2.37$ V are potentials provided by photogenerated electrons and holes for hydrogen and water oxidation reduction reactions at pH = 0, respectively.](image-url)
of photogenerated holes for OER \((U_H)\) is defined as the energy difference between the VBM and the hydrogen reduction potential \([52–56]\). Both \(U_e\) and \(U_H\) are defined relative to the normal hydrogen electrode (NHE). For the Janus InGaSbSe bilayer, we got \(U_e = 0.68\) V and \(U_H = 2.37\) V at pH 0, respectively.

We first evaluated the HER on a perfect Janus InGaSbSe bilayer (Fig. S15 online). Hydrogen atom prefers to bind to the Se site. Free energy calculations show that the overpotential of HER on the perfect Janus InGaSbSe bilayer is about 2.16 V. This value exceeds the potential of the photogenerated electrons \(U_e = 0.68\) V, suggesting that HER cannot be solely triggered by the photogenerated electrons in the perfect Janus InGaSbSe bilayer.

To increase the reactivity of the InGaSbSe surface, we introduce vacancy defects into top layer of the Janus bilayer, which has been proved to be an efficient method to enhancing the HER catalytic activity \([32,57–61]\). It is found that when Ga vacancy defects are created in the Janus InGaSbSe bilayer, the overpotential of HER is reduced to only −0.21 V. Under the potential provided by the photogenerated electrons, 0.68 V, the free energy profile of HER becomes downhill, as shown in Fig. 5c, implying that HER can proceed driven solely by the photogenerated electrons. We also studied the HER on the defective Janus InGaSbSe bilayer following the four-electron reaction pathway accompanied by the formation of adsorbed OH*, O* and OOH* intermediates. The free energy diagram of the OER pathway is plotted in Fig. 5. Clearly, under the external potential provided by the photogenerated holes, the free energy profile becomes downhill, suggesting the OER can proceed under this condition. Therefore, the Ga vacancy defects can reduce the HER and OER overpotentials of the Janus InGaSbSe bilayer to the levels that can be provided by the photogenerated carriers, enabling the overall water splitting without the needs of sacrificial reagents.

4. Conclusion

In summary, on the basis of first-principles calculations, we demonstrated that the multilayer structures of the 2D Janus group-III chalcogenides are promising photocatalysts for overall water splitting. The intrinsic electric field and high carrier mobilities facilitate the separation of photogenerated electrons and holes, which is quite crucial for high photocatalytic performance. The intrinsic electric field also alters the band alignment of the Janus photocatalysts, breaking the restriction of band gap (1.23 eV) for overall water splitting. Janus multilayers have enhanced intrinsic electric field and thus more excellent photocatalytic performance than the Janus monolayers. For the Janus bilayers, the reduced electronic band gap extends the light absorption range from the visible-light region to the infrared-light region. The spatial charge separations ensure the redox reactions occurring on different layers. High STH efficiencies will be achieved in the Janus bilayers, especially in the Janus InGaSe2, multilayer containing five monolayers. Additionally, the Ga vacancy in the InGaSbSe bilayer effectively lowers the overpotentials of HER and OER to the level that can be solely by the photo-generated electrons and holes. Our simulation results demonstrate the possibility of the 2D Janus group-III chalcogenides multilayers as efficient photocatalysts for overall water splitting without the needs of sacrificial reagents, as well as a promising strategy for the design of highly-efficient photocatalysts.

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Author contributions

Yingcai Fan and Xikui Ma performed DFT calculations and contributed to data interpretation and writing the manuscript. Junru Wang, Xiaohan Song and Aizhu Wang contributed to the data interpretation. Hong Liu contributed to the data interpretation and writing the manuscript. Mingwen Zhao designed the study and contributed to the data interpretation and writing the manuscript. All authors have given approval to the final version of the manuscript.

Appendix A. Supplementary materials

Supplementary materials to this article can be found online at https://doi.org/10.1016/j.scib.2019.10.018.

References

[12] Faraji M, Yousefi M, Yousefzadeh S, et al. Two-dimensional materials in InGaSbSe bilayer effectively reducing the overpotentials of HER is 2.16 V. This value exceeds the potential of the photogenerated electrons, \(U_e = 0.68\) V, suggesting that HER cannot be solely triggered by the photogenerated electrons in the perfect Janus InGaSbSe bilayer.

Conflict of interest

The authors declare that they have no conflict of interest.