# Data-driven discovery of intrinsic direct-gap 2D photocatalysts for overall water splitting

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# ABSTRACT

Intrinsic direct-gap two-dimensional (2D) materials hold great promise as photocatalysts advancing the application of photocatalytic water splitting for hydrogen production. However, the time- and resource-efficient exploration and identification of such 2D materials from a vast compositional and structural chemical space present a significant challenge within the realm of materials science research. To this end, we perform a data-driven study to find new 2D materials with intrinsic direct-gap and desirable photocatalytic properties for overall water splitting. By implementing a three-staged large-scale screening, which incorporates machine learning, high-throughput density functional theory (DFT) and hybrid-DFT calculations, we identify 16 new direct-gap 2D materials as promising photocatalysts. Subsequently, we conduct a comprehensive assessment of material properties that are related with the solar water splitting performance, which includes electronic and optical properties, solar-to-hydrogen conversion efficiencies, and carrier mobilities. Therefore, this study not only presents 16 new 2D photocatalysts but also introduces a rigorous data-driven approach for the future discovery of functional 2D materials from currently unexplored chemical spaces.

## 1 Introduction

Developing clean and renewable energy resources is of utmost imperative in addressing the significant challenges posed by the rising global energy consumption and environmental pollution. Hydrogen, as a clean fuel that neither relies on fossil fuels nor produces carbon dioxide, holds great promise as an energy carrier for the future.<sup>1</sup> Among the various approaches of hydrogen generation, water splitting under solar irradiation stands out as one of the most promising methods<sup>2-4</sup> since the first experimental realization of  $TiO_2$  as a photocatalyst in 1972 by Fujishima and Honda<sup>5</sup>. Despite ongoing research and development, the practical application of photocatalytic water splitting for hydrogen production continues to be hindered by inherent challenges associated with the photocatalysts, such as limited utilization of sunlight and high rates of recombination of photoexcited carriers, thereby restricting its broader implementation.<sup>6,7</sup> To facilitate the efficient splitting of water, photocatalysts need to have specific physical properties.<sup>8–10</sup> First of all, the band gap should be larger than the minimum free energy required to split water into oxygen and hydrogen molecules (1.23 eV at standard pressure and temperature), while also smaller than 3 eV to ensure utilization of the visible part of the solar spectrum. Secondly, the band edge positions of photocatalysts should ideally straddle the reduction and oxidation potentials of water, with the conduction band minimum (CBM) above the reduction potential of  $H^+/H_2$  and the valence band maximum (VBM) below the oxidation potential of  $O_2/H_2O$ , which are -4.44 and -5.67 eV vs (electrostatic) vacuum at pH=0 (standard pressure and temperature), respectively. Thirdly, the photogenerated electron-hole pairs should spatially separate and move to the cathodic and anodic electrode surfaces to participate in water redox reactions.

Two-dimensional (2D) materials, characterized by a large surface-to-volume ratio,<sup>11</sup> are widely regarded as promising photocatalysts for water splitting. In comparison to bulk materials, the inherently larger specific surface area exhibited by 2D materials affords more active sites for photocatalytic reactions.<sup>12, 13</sup> Additionally, the reduced thickness of 2D materials plays a crucial role in minimizing the migration distance of photogenerated carriers to the solid/water interface, thereby reducing the likelihood of electron-hole recombination and potentially enhancing the overall photocatalytic performance.<sup>14</sup> To date, numerous 2D materials, including transition metal dichalcogenides (such as  $MoS_2$ ),<sup>15</sup> g-C<sub>3</sub>N<sub>4</sub>,<sup>16</sup> and phosphorene,<sup>17</sup> have been explored and applied as photocatalysts for water splitting,

Direct-gap materials, where the VBM and the CBM occur at the same **k**-point in the Brillouin Zone (BZ), typically exhibit better solar energy conversion efficiency compared to materials with indirect band gap.<sup>18–21</sup> This is attributed to the fact that direct-gap materials are better optical absorbers, as interband electronic transition in these materials do not require the assistance of phonons.<sup>22, 23</sup> In contrast, indirect-gap materials require thicker films to meet the requirement of larger optical path lengths for efficient light absorption, thereby impacting both the cost of material synthesis and the efficiency of charge carrier transport and extraction.<sup>24–26</sup> While various band gap engineering methods exist to convert indirect-gap materials to direct-gap materials, such as alloying<sup>27</sup> and external strain<sup>28, 29</sup>, intrinsic direct-gap materials possess inherent advantages by exhibiting the desired properties without the necessity for extensive structural modifications. Despite the advantages offered by direct-gap semiconductors, it is crucial to note that they occupy merely a tiny portion of the colossal chemical space of materials. Discovering newly suitable direct-gap materials for specific technological applications, such as solar water splitting, is even more challenging due to the additional criteria mentioned above they must satisfy.

Materials science is witnessing a paradigm shift towards data-driven approaches, facilitated by rapid progress in computing power and the development of theoretical computing tools rooted in first principles, enabling the accelerated discovery and design of novel materials with tailored properties.<sup>30</sup> As of the present, several material databases have been established solely based on calculations of materials' properties.<sup>31–34</sup> These databases contain a wealth of structure-property information, and are being increasingly utilized, for instance through high-throughput (HT) screening to explore the use of materials for various practical applications.<sup>19, 35–38</sup> Within the immense size of the chemical space, existing databases encompass merely a small subset of the feasible materials, yet predictive machine learning (ML) models can leverage their data to extrapolate the properties of unexplored regions in chemical space, <sup>39–42</sup> thus circumventing the necessity for time- and resource-intensive computations that rely on physics-based models. By leveraging ML-predicted properties, materials can undergo a targeted application-oriented rough screening process, followed by detailed computations for further investigation of the selected materials.<sup>43–46</sup> Simultaneously, the calculated data can be fed back into the ML models, enhancing their prediction accuracy and broadening the scope of research. The integration of ML techniques and HT-computational screening provides a potent approach to expedite materials discovery through the exploration of the uncharted zones of chemical space.

In this work, we employ a data-driven approach to effectively screen direct-gap photocatalysts within the structural and compositional variations of 2D materials. Through the implementation of a three-staged screening process (as shown in Figure 1 (a)), which incorporates ML-predicted properties from V2DB<sup>47</sup> and HT-calculated properties from first principles, along with specific screening criteria, we identify a total of 16 direct-gap 2D materials as potential photocatalysts with the capability to efficiently harness visible sunlight and facilitate overall water splitting. Subsequently, a comprehensive evaluation of these 16 photocatalysts is conducted to assess their water-splitting potential, taking into consideration of their electronic structure, optical absorption, solar-to-hydrogen (STH) conversion efficiencies, and charge carrier mobilities. To the best of our knowledge, our study represents the first data-driven discovery of direct-gap 2D materials for photocatalytic applications within a large chemical space. Therefore, this study not only suggests 16 promising 2D direct-gap materials for photocatalysts, but also introduces an effective data-driven approach for the expeditive research on 2D materials.



**Figure 1.** (a) The schematic workflow for the discovery of direct-gap 2D photocatalysts for water splitting. The workflow consists of three screening stages, which utilize ML-predicted data from V2DB and computed properties at the PBE and HSE06 levels, respectively. (b) The distribution of ML-predicted band edges in V2DB. The grey dots represent all 316,505 2D materials from V2DB, while the colored dots within the rectangle represent the 294 selected structures obtained in the first stage of screening based on ML-predicted properties. The color bar corresponds to their ML-predicted band gap center (BGC) energy ( $E_{BGC}^{ML}$ ). The two diagonal dark lines indicate band gaps of 1.23 and 3 eV, while the two dashed dark lines represent  $E_{BGC}^{ML}$  values of -4.44 and -5.67 eV.

## 2 Results and Discussion

#### 2.1 Data-driven screening

#### Pre-screening (ML)

The V2DB database consists of 316,505 potentially stable 2D materials generated by enumerating 22 typical 2D crystal prototypes and incorporating 52 chemical elements from the periodic table.<sup>47</sup> Through extensive ML model training utilizing a large dataset of DFT calculations at the PBE level, key properties such as band gap character (direct or indirect), band gap value, band edges with respect to vacuum level, and magnetic states were predicted and collected in V2DB. Here, we initiate our screening process of direct-gap 2D photocatalysts on the basis of the ML-predicted properties. Figure 1 (b) illustrates the distribution of ML-predicted band edges for all the 2D materials in V2DB, where each gray dot represent a 2D material. Additionally, Figure S1 (a) in Supporting Information provides a comparison between direct- and indirect-gap 2D materials, demonstrating that structures with direct-gap constitute only a small fraction of the entire database. The screening criteria for the ML-predicted band gap  $(1.23 \le E_g^{ML} \le 3 \text{ eV})$  are used, as visually indicated by the two diagonal black solid lines in Figure 1(b).

Concomitantly, to be electrochemically active in water splitting, the band edge positions of the 2D materials must straddle the water redox potentials. Considering that the use of stringent band edge position criteria, based on ML-predicted values, can introduce uncertainties that may cause us to overlook potentially promising photocatalysts. Therefore, to avoid this, we employ the band gap center (BGC) energy  $(E_{BGC} = (E_{VBM} + E_{CBM})/2)^{36,48}$  as a more flexible screening criterion. Materials with  $E_{BGC}$  between the redox potentials of water  $(-5.67 \le E_{BGC}^{ML} \le -4.44 \text{ eV})$ , are likely to meet the photocatalysts requirements when subjected to higher-precision calculations. In Figure 1 (b), these ML-predicted BGC screening criteria are shown as two diagonal black dashed lines.

2D materials positioned within the rectangular area defined by the solid and dashed cutoff lines are considered as prime candidates, as they not only have a direct band gap but also satisfy both the band gap value and the BGC screening criteria. After excluding magnetic structures, primarily due to their complex physics, which poses challenges for HT-calculations, we



**Figure 2.** The ML (dark gray) and PBE (dark cyan) band edges positions with respect to the vacuum level of 294 2D structures obtained after screening based on ML-predicted properties. Each structure is represented by a dot, upward and downward triangle symbols, which denote the BGC, CBM, and VBM, respectively. Based on the PBE results, structures with a direct-gap are highlighted with light cyan color. Two horizontal dashed lines shown in green (at -4.44 eV) and red (at -5.67 eV) correspond to the reduction potential of H<sup>+</sup>/H<sub>2</sub> and the oxidation potential of O<sub>2</sub>/H<sub>2</sub>O at pH=0, respectively.

end up with 294 potential 2D direct-gap photocatalysts based on their ML-predicted properties from V2DB. These materials are given by colored dots in Figure 1 (b), while the color bar represents the  $E_{BGC}^{ML}$  values.

#### **Computational screening (PBE)**

After pre-screening using ML-predicted properties from V2DB, we adopt an HT-computational screening method to identify direct-gap photocatalysts among the 294 candidates selected so far. Employing the basic structure information, including the prototype and atomic composition, we generate the 2D structures for these candidates. Subsequently, a structural optimization process is carried out for each compound to determine the equilibrium structure with the lowest energy. Using their equilibrium structures, we calculate the electronic density of states (DOS) at the DFT (PBE) level, and the results are compiled in Figure S2. Figure 2 shows a concise overview of band edges and BGC positions relative the vacuum level of these 294 candidates, with 47 structures featuring direct band gaps shaded in light cyan color. As PBE underestimates the band gap, a more soft band gap screening criterion is adopt at this step, namely,  $0 \le E_g^{PBE} \le 3$  eV. Consequently, based on PBE-level calculations, we identify 37 non-magnetic semiconductor structures with a direct band gap within this range while simultaneously satisfying the BGC requirements ( $-5.67 \le E_{BGC}^{PBE} \le -4.44$  eV).

These 37 2D structures are examined in more details with regards to their dynamic, thermal, and mechanical stabilities. The dynamic stability is investigated by calculating the phonon dispersion curves, where a structure is considered dynamically stable if it lacks any imaginary phonon frequencies across the entire BZ. In view of the common problem of small imaginary frequencies near the  $\Gamma$  point in first-principles phonon calculations of 2D materials,<sup>49,50</sup> here we only exclude structures that exhibit large imaginary frequencies in the middle of the BZ. The results of phonon calculations are presented in Figure S3, where phonon stable candidates are highlighted with red frames. 14 structures displaying dynamic instability are subsequently dismissed from further consideration.

Next, we evaluate the thermal stability of the remaining 23 2D structures through *ab initio* molecular dynamics (AIMD) simulations at temperatures of 300, 600, and 900 K. Figure S4 summarizes total energy changes during these AIMD runs, as well as snapshots of the structures at the end of each run. A thermally stable structure should maintain a constant average total energy throughout the simulation, and display minimal structural distortion or bond breaking in the end state. To judge thermal stability, the AIMD results at room temperature (300 K) are used. Two structures are identified that exhibit significant distortion at 300 K, leading to their removal from the candidate list. Some of the remaining 21 structures also show a good thermal stability at higher temperatures, see Figure S4, suggesting their potential applications at such temperatures. In this work, we will stick to potential room temperature applications, however.

As an additional check, we evaluate the mechanical stability of the 21 structures that show good dynamic and thermal stabilities, by calculating their elastic constants using the stain-stress method. For a mechanically stable 2D material, the elastic constants must adhere to the Born-Huang criteria<sup>51,52</sup>, which can be determined according to the symmetry of crystal.<sup>53,54</sup> The calculated elastic constants and their corresponding mechanical stability criteria are compiled in Table S1. We find that all the candidate structures satisfy their corresponding criteria, indicating that they are mechanically stable. Utilizing the elastic constants, we also calculate the key mechanical parameters of them, including the orientation-dependent Young's modulus (*Y*), Poisson's ratio (*v*) and shear modulus (*G*) as a function of the in-plane angle ( $\theta$ ). The results of these mechanical parameters are presented in Figure S5.

To sum up, the aforementioned calculations and analysis reveal that 21 direct-gap 2D semiconductors qualify as candidate photocatalysts with favorable dynamic, thermal, and mechanical properties.

#### **Computational screening (HSE)**

To improve upon the description of the selected 2D materials that remained after the computational screening at the PBE level described above, we apply the hybrid-DFT functional (HSE06) to calculate their electronic properties. Figure S6 shows the HSE06 band structures of the 21 materials relative to vacuum level, while the values of key parameters, in particular band gaps, BGCs, and positions of band edges, are assembled in Table S2. All candidate materials, which had a direct band gap at



**Figure 3.** The band edges positions with respect to the vacuum level of 21 stable semiconductors with direct-gap, as based on PBE-calculated data. For each structure a dot symbol indicates the BGC, while upward and downward triangle symbols denote the CBM and VBM, respectively. The dark gray, dark cyan, and orange colors represent the ML-predicted, PBE, and HSE values, respectively. Two horizontal dashed lines shown in green (at -4.44 eV) and red (at -5.67 eV) correspond to the reduction potential of H<sup>+</sup>/H<sub>2</sub> and the oxidation potential of O<sub>2</sub>/H<sub>2</sub>O at pH=0, respectively. The black crosses indicate that these structures are excluded at the HSE screening stage, as their band gap values are larger than 3 eV.

the PBE level, maintain this direct-gap characteristic at the HSE06 level. In the majority of cases, the gap is located at  $\Gamma$ , while only two structures feature the gap at the *Y* point. Figure 3 shows an overview of the BGCs and band edge positions relative to the vacuum level for the 21 direct-gap 2D materials at all three levels of screening, *i.e.*, ML (dark gray), PBE (cyan), and HSE06 (orange). The reduction potential of H<sup>+</sup>/H<sub>2</sub> and the oxidation potential of O<sub>2</sub>/H<sub>2</sub>O (at pH = 0) are represented by green and red dashed lines, respectively.

Notably, the BGC values obtained from all three methods, are all situated between the two water redox potential lines. Unsurprisingly, the HSE06 method results in an increase of the band gap for each structure, as compared to the PBE results. While, according to the ML-predictions or PBE calculations, some structures do not have band edge positions that straddle the water redox potentials, the more accurate HSE06 calculations affirm that all of these structures possess the capability for overall water splitting. The fact that none of the remaining materials are rejected by these HSE06 results confirms the validity of using the BGC as a screening criterion in the previous ML and PBE screening stage. Among the remaining structures, there are five with HSE06 band gap values larger than 3 eV, which are labeled by black crosses in Figure 3. As this band gap is larger than the maximum energy of visible light photons, these structures are consequently excluded. As a result, we have 16 structures that remain as potential 2D direct-gap photocatalysts for further investigation.

Based on their structure, these 16 candidates can be grouped into two categories, namely, hexagonal type (*H*-I and *H*-II) and rectangular type (*R*-I and *R*-II). Table 1 provides information about this classification and the HSE06-calculated properties of these materials. A more comprehensive analysis of each material, including their structural views and lattice constants, is supplied in Figures S7–S22 (a). To illustrate the geometric configurations of different structure types, Figure 4 shows the structural views of the compounds with the smallest band gap within each structure type, namely Cd<sub>2</sub>SSe (*H*-I), SrAgSeI (*H*-II), Al<sub>2</sub>Se<sub>2</sub>I<sub>2</sub> (*R*-I), and Al<sub>2</sub>FS<sub>2</sub>Br (*R*-II). Additionally, the phonon spectra and AIMD simulation results are also included in Figure 4.

In Figure 4 (a), one can observe that  $Cd_2SSe$  (*H*-I) has a double-layer honeycomb structure,<sup>55</sup> where each atom forms four bonds with adjacent atoms, and one of the bonds is oriented perpendicular to the plane of the 2D layer. The *H*-II materials, *e.g.*, SrAgSeI as shown in Figure 4 (d), possess a *T*-phase structure consisting of four atomic layers. Intriguingly, all of the three *H*-II structures have silver atoms at the bottom atomic layer. The *R*-I materials, exemplified by  $Al_2Se_2I_2$  as depicted in



**Figure 4.** The top and side structural views of (a)  $Cd_2SSe$ , (d) SrAgSeI, (g)  $Al_2Se_2I_2$ , and (j)  $Al_2FS_2Br$ . The calculated phonon spectrum of (b)  $Cd_2SSe$ , (e) SrAgSeI, (h)  $Al_2Se_2I_2$ , and (k)  $Al_2FS_2Br$ . The variation in total energy during the *ab initio* molecular dynamics (AIMD) simulation at 300 K over 10 ps with a time step of 1 fs for (c)  $Cd_2SSe$ , (f) SrAgSeI, (i)  $Al_2Se_2I_2$ , and (l)  $Al_2FS_2Br$ . The insets show the top and side structural views of the final equilibrium states.

**Table 1.** The HSE06 computational results of 16 2D direct-gap photocatalyst candidates, including material formula, structure type, electronic properties, and solar-to-hydrogen (STH) conversion efficiencies. The electronic properties (in units of eV) include band gaps ( $E_g^{\text{HSE}}$ ), band edge positions ( $E_{\text{VBM}}^{\text{HSE}}$  and  $E_{\text{CBM}}^{\text{HSE}}$ ), and band gap centers ( $E_{\text{BGC}}^{\text{HSE}}$ ) with respect to the vacuum level. The solar-to-hydrogen (STH) conversion efficiency calculation results include optical absorption efficiency ( $\eta_{\text{abs}}$ ), carrier utilization efficiency ( $\eta_{\text{cu}}$ ), and STH conversion efficiency ( $\eta_{\text{STH}}$ ), which are all defined in the Methods section.

Material	Туре	$E_{\rm g}^{\rm HSE}$	$E_{\rm VBM}^{\rm HSE}$	$E_{\rm CBM}^{\rm HSE}$	$E_{\rm BGC}^{\rm HSE}$	$\eta_{ m abs}(\%)$	$\eta_{ m cu}(\%)$	$\eta_{ m STH}(\%)$
Zn <sub>2</sub> SSe	H-I	2.72	-6.43	-3.71	-5.07	11.55	39.97	4.62
ZnCdSSe	$H ext{-I}$	2.73	-6.69	-3.96	-5.33	11.25	39.84	4.48
Ag <sub>2</sub> BrI	$H ext{-I}$	2.66	-6.54	-3.88	-5.21	13.11	40.65	5.33
$Ag_2I_2$	$H ext{-I}$	2.89	-6.19	-3.30	-4.75	7.94	30.50	2.42
$Cd_2S_2$	$H ext{-I}$	2.72	-6.68	-3.96	-5.32	11.55	39.97	4.62
Cd <sub>2</sub> SSe	$H ext{-I}$	2.20	-6.49	-4.29	-5.39	28.18	42.29	11.92
CaAgSBr	$H ext{-II}$	2.57	-6.23	-3.66	-4.95	15.63	38.27	5.98
SrAgSBr	$H ext{-II}$	2.49	-6.33	-3.84	-5.09	18.09	42.60	7.71
SrAgSeI	$H ext{-II}$	2.07	-6.16	-4.09	-5.13	33.36	40.26	13.43
Al <sub>2</sub> S <sub>2</sub> ClI	<i>R</i> -I	2.56	-6.45	-3.89	-5.17	15.95	41.78	6.66
$Al_2S_2BrI$	<i>R</i> -I	2.59	-6.57	-3.98	-5.28	15.14	41.47	6.28
Al <sub>2</sub> SSeBr <sub>2</sub>	<i>R</i> -I	2.75	-6.42	-3.67	-5.05	10.78	39.63	4.27
Al <sub>2</sub> SSeBrI	<i>R</i> -I	2.65	-6.63	-3.98	-5.31	13.42	40.78	5.47
$Al_2Se_2I_2$	R-I	2.27	-6.21	-3.95	-5.08	25.43	40.71	10.35
$AlScS_2I_2$	<i>R</i> -I	2.40	-6.57	-4.17	-5.37	21.03	43.66	9.18
$Al_2FS_2Br$	<i>R</i> -II	2.94	-6.94	-4.00	-5.47	7.08	37.72	2.67

Figure 4 (g), have a typical metal-oxyhalide structure,<sup>56</sup> characterized by an orthorhombic crystal lattice with a 2D network of rectangular sublattices. Within this structure, the metal atoms coordinate to four in-plane chalcogen atoms (mostly S and Se in these materials) and two protruding halogen atoms, resulting in a highly distorted octahedral geometry. The structure of  $Al_2FS_2Br$  (*R*-II), as illustrated in Figure 4 (j), can be regarded as a deformation of the *R*-I type structure. This deformation occurs due to the replacement of internal chalcogen atoms with halogen atoms (F). Consequently, the overall thickness of structure increases, while the in-plane lattice size decreases. Furthermore, the halogen atoms at the bottom layer are replaced with S atoms.

#### 2.2 Property analysis

#### **Electronic properties**

Valuable insight into the solar water splitting potential of the candidate 2D materials can be gained through the analysis of electronic properties. We calculate the element and orbital projected HSE06 fat band structures of all 16 candidate structures, and the results are given in Figure S7–S22 (b) and (c), respectively. For the four representative compounds, the element projected band structures are shown in Figure 5. Starting with Cd<sub>2</sub>SSe, one can observe that the states of the upper valence bands are dominated by contributions from the S and Se atoms, as illustrated in Figure 5 (a), particularly their *p* orbitals (see Figure S12 (c)). The lower conduction bands have a more mixed character, with a significant contribution from the Cd atoms, especially their *s* orbitals. The fact that VBM and CBM have different characters, *i.e.*, anion and cation, respectively, may lead to small non-radiative coupling and longer recombination time of photogenerated carriers. To visualize this, we further plot the local charge density distribution of band edges in real-space. As shown Figure 5 (b), the spatial separation of hole and electron states is evident in Cd<sub>2</sub>SSe, as the former are mainly located on the S atoms on one side of the 2D layer, whereas the latter have their main amplitude on the Cd atoms on the other side. For SrAgSeI, the characters of both the upper valence and the lower conduction bands are dominated by the AgSe layer on one side of the 2D slab, as evident in Figures 5 (d, e) and Figure S16.



**Figure 5.** The HSE06 fat band structure with element projection, the spatial distribution of the CBM and VBM, and the optical absorbance of (a, b, c) Cd<sub>2</sub>SSe, (d, e, f) SrAgSeI, (g, h, i) Al<sub>2</sub>Se<sub>2</sub>I<sub>2</sub>, and (j, k, l) Al<sub>2</sub>FS<sub>2</sub>Br, respectively. The band structure figures visualize the contribution of different elements using color and size distinctions, with the corresponding colors marked at the bottom. The local charge density distribution of the VBM and CBM are denoted with red and blue colors, respectively, where the isosurface value is set to  $5 \times 10^{-5}$  eV Å<sup>-3</sup>. The visible light region (1.6–3.1 eV) is represented by an iridescent color scale. The figures also include the standard AM1.5G solar spectrum<sup>57</sup>, represented by a light gray line along the photon energy, with its intensity indicated on the right scale.

Again, the VBM has anion (Se) character, and the CBM has cation (Ag) character, but their dominance is less pronounced.

Moving to  $Al_2Se_2I_2$ , Figures 5 (g) and S21 show that, in this case as well, the upper valence and lower conduction bands exhibit anion (Se, I) and cation (Al) character, respectively. Remarkably, the states at the VBM are dominated by one anion type only (Se), as seen in Figure 5 (h). As the CBM has dominant cation (Al) character, this implies that the lowest energy excitations are localized on the AlSe layers in the middle of the 2D slab. Finally, for  $Al_2FS_2Br$ , the upper valence bands and the lower conduction bands have dominant S and Al character, respectively. It is noticeable that the VBM states are dominated by the S atoms on one side of the 2D layer, whereas the CBM states obtain their character from the Al atoms on the other side, see Figures 5 (j, k) and S23.

#### **Optical absorption**

The selected 16 materials have band gaps and band edge positions that would in principle make them suitable as photocatalysts for water splitting, but obviously they should also have a sufficiently strong optical absorption in the visible region, as well as in the near ultraviolet.<sup>6,8</sup> When computing optical properties for 2D materials, it is necessary to account for exciton effects due to the reduced Coulomb screening in the vacuum direction.<sup>10</sup> However, employing computationally expensive techniques like GW/BSE is impractical for this study due to the large number of compounds involved. Nevertheless, calculations on the basis of single-particle excitations should already provide a basis for qualitative assessment of the absorption strength for these present materials. Here, we calculate the absorbance of these 2D layers on the basis of the HSE06 band structure and single-particle states. The results are shown in Figure 5 and Figures S7–S22 (d).

Of the four representative materials shown in Figure 5, it can be observed that three of them (Cd<sub>2</sub>SSe, SrAgSeI, and Al<sub>2</sub>FS<sub>2</sub>Br) exhibit prominent absorption peaks in the visible light region, while Al<sub>2</sub>Se<sub>2</sub>I<sub>2</sub> shows an absorption peak in the near-ultraviolet region. In an absolute sense, three of the materials have an absorbance lager than 1% in these peaks (Cd<sub>2</sub>SSe, SrAgSeI, and Al<sub>2</sub>Se<sub>2</sub>I<sub>2</sub>). Of the 16 materials shown in Figures S7–S22 (d), 11 have prominent absorbance peaks in the visible region, whereas the other 5 have their first absorbance peak in the near ultraviolet, and 10 have an absorbance value > 1% in these peaks.

When comparing the absorbance for light polarized in the two perpendicular in-plane directions, it is evident that there are no significant differences between x and y for the H-I and H-II structures, which is consistent with the inherent isotropy of their structures. In contrast, the anisotropic R-I and R-II structures exhibit notable differences between x and y polarizations, as illustrated in Figures 5 (i and 1). Additionally, in the R-I structure, the first absorption peak in the y-direction occurs at lower photon energies compared to the x-direction, whereas in the R-II structure, it is the opposite.

#### STH conversion efficiency

An indication of the energy conversion efficiency of sunlight-induced photocatalytic water splitting can be obtained by calculating the solar-to-hydrogen (STH) conversion efficiency ( $\eta_{STH}$ ), as defined in the Methods section. This parameter quantifies the photons with sufficient energy to be absorbed by the material and incite a water splitting reaction, accounting for the necessary overpotentials, and relates the energy that goes into making the products of the water splitting reaction to the total energy of the incoming sunlight.  $\eta_{STH}$  can be expressed as the product of two components: the light absorption efficiency ( $\eta_{abs}$ ) and the carrier utilization efficiency ( $\eta_{cu}$ ). Here  $\eta_{abs}$  measures the part of the sunlight power where the photons have sufficient energy to be absorbed by the material, while  $\eta_{cu}$  measures the conversion efficiency of that energy to the products of the water splitting reaction. Per definition, materials possessing a band gap exceeds the minimum energy required for water splitting, along with band edges that straddle the reduction and oxidation potentials of water (incorporating the overpotentials), will have the largest  $\eta_{STH}$  value, indicating the best potential for STH conversion efficiency.

Based on HSE06 band gaps and edges, we calculated the  $\eta_{abs}$ ,  $\eta_{cu}$ , and  $\eta_{STH}$  for the 16 selected compounds, as presented in Table 1. It can be observed  $\eta_{abs}$  monotonically decreases with increasing band gap. The maximal  $\eta_{abs}$  (33.36%) in our list is observed for the material with the smallest band gap (SrAgSeI; 2.07 eV), whereas the minimal value (7.08%) correspond to the one with the largest band gap (Al<sub>2</sub>FS<sub>2</sub>Br; 2.94 eV). In contrast,  $\eta_{cu}$  varies much less among the 16 compounds, with values



**Figure 6.** (a) The calculated STH conversion efficiencies as a function of the band edge positions of 16 direct-gap 2D photocatalysts. The  $\eta_{\text{STH}}$  values are represented by weighted colors. The horizontal green line at -4.44 eV and the vertical red line at -5.67 eV correspond to the reduction potential of H<sup>+</sup>/H<sub>2</sub> and the oxidation potential of O<sub>2</sub>/H<sub>2</sub>O at pH=0, respectively. The two diagonal dark lines indicate band gaps of 1.23 and 3 eV. Structures marked with circles are the three candidates with  $\eta_{\text{STH}} > 10\%$ , while the structures indicated by gray arrows are the reference materials. (b) The calculated carrier mobility data of the compounds as presented in a bar graph, which also shows carrier type and transport direction.

~ 40 ± 2%, the only exception being Ag<sub>2</sub>I<sub>2</sub>, which has a somewhat lower  $\eta_{cu}$  of 30.5%. Numerically,  $\eta_{STH}$  ranges from 2.42% to 13.43%, and most compounds having  $\eta_{STH} > 4$  %, except for the large band gap materials such as Ag<sub>2</sub>I<sub>2</sub> and Al<sub>2</sub>FS<sub>2</sub>Br.

The calculated STH conversion efficiencies are visualized in Figure 6 (a) as a function of the band edge positions. All 16 materials fall within the right triangular region defined by the water redox potential and the band gap range of 1.23–3 eV. Among them, SrAgSeI is located closest to the bottom-right angle, corresponding to its highest  $\eta_{STH}$  value (13.43%). In the same figure, we have also included three well-known photocatalysts, namely the benchmark anatase-TiO<sub>2</sub><sup>58</sup>, and the 2D materials g-C<sub>3</sub>N<sub>4</sub><sup>59</sup> and H-MoS<sub>2</sub><sup>33</sup>, by calculating their  $\eta_{STH}$  values based on the collected data of band gaps and band edges from the literature. Anatase-TiO<sub>2</sub> falls outside the triangular region due to its well-known large band gap (> 3 eV), which results in a very low  $\eta_{STH}$  (~ 0.8%). Similarly, H-MoS<sub>2</sub> has a larger value of ~ 9.5% than g-C<sub>3</sub>N<sub>4</sub> (~ 2.2%), which is mostly due to its smaller band gap. Notably, although SrAgSeI has band gap similar to H-MoS<sub>2</sub>, its  $\eta_{STH}$  is significantly larger due to more favorable band edge positions, underscoring the importance of band edge positions in photocatalysts. All the identified photocatalyst candidates in this study demonstrate a larger  $\eta_{STH}$  than anatase-TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>, with three of them surpassing H-MoS<sub>2</sub>, indicating their potential for superior energy conversion performance.

It is posed that photocatalytic materials with  $\eta_{\text{STH}}$  values that are around 10% could be economically viable.<sup>6,60–62</sup> Accordingly, we have three candidates with  $\eta_{\text{STH}} > 10\%$ , namely Al<sub>2</sub>Se<sub>2</sub>I<sub>2</sub> (10.35%), Cd<sub>2</sub>SSe (11.92%), and SrAgSeI (13.43%).

#### **Carrier mobility**

A fast migration of photoexcited free carriers to the chemically active sites is crucial for the water splitting performance of photocatalysts, which can be evaluated by the carrier mobility ( $\mu$ ). Mobilities are influenced by both external factors, like the type and quantity of defects in the material, as well as internal factors, such as electron-phonon scattering. Without experimental input, external factors are beyond the reach of computations, and a full calculation of all electron-phonon scattering channels is beyond the scope of present work. In the field of 2D materials, it is custom to compare charge carrier mobilities calculated using a simplified model, based upon deformation potential (DP) theory, which assumes longitudinal-acoustic phonon scattering to be dominant.<sup>63–65</sup> Eq. 5 shows that within DP theory, the carrier mobility is determined by three factors: the effective mass of

**Table 2.** The material formula, structure type, transport direction (D), effective mass of electrons  $(m_e^*)$  and holes  $(m_h^*)$ , in-plane stiffness  $(C_{2D})$ , in units of N m<sup>-1</sup>), deformation potential constants of electrons  $(E_{dp_e})$  and holes  $(E_{dp_e})$  (in units of eV), carrier mobilities at room temperature of electrons  $(\mu_e)$  and holes  $(\mu_h)$  (in units of  $\times 10^3$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>).  $R_{ani_e}$  and  $R_{ani_h}$  denote the anistropic mobility ratio of electrons and holes, respectively.  $R_{carri}$  represents the mobility ratio of different carrier types along a specific direction.

Material	Туре	D	$m_{\rm e}^*/m_0$	$m_{ m h}^*/m_0$	$C_{2\mathrm{D}}$	$E_{dp_e}$	$E_{dp_h}$	$\mu_{ m e}$	$\mu_{ m h}$	$R_{\text{ani}\_e}$	$R_{\text{ani}_h}$	R <sub>carri</sub>
Zn <sub>2</sub> SSe	H-I	x	0.20	0.31	58.63	5.22	3.58	0.76	0.68	1.13	1.13	1.12
		у	0.20	0.32	56.61	4.84	3.62	0.86	0.60			1.43
ZnCdSSe	иī	x	0.16	0.38	47.11	4.48	1.98	1.30	1.18	1.48	1.87	1.10
	<i>п</i> -1	у	0.16	0.41	65.29	4.34	1.58	1.92	2.21			1.15
Ag <sub>2</sub> BrI	ыı	x	0.44	0.51	18.81	0.24	2.36	23.92	0.18	2.56	1.50	132.89
	11-1	у	0.43	0.50	21.50	0.42	2.12	9.35	0.27			34.63
$Ag_2I_2$	H-I	x	0.37	0.51	19.55	0.30	1.82	22.50	0.32	1.56	1.09	70.31
		У	0.37	0.51	19.48	0.24	1.74	35.03	0.35			100.09
$Cd_2S_2$	H-I	x	0.20	0.89	49.61	2.52	0.62	2.77	2.31	1.33	3.53	1.20
		У	0.20	0.95	46.74	2.12	0.30	3.69	8.16			2.21
Cd <sub>2</sub> SSe	<i>11</i> T	x	0.23	0.33	42.12	1.44	1.54	5.44	2.31	1.39	1.13	2.35
	<i>I</i> I-1	У	0.23	0.32	44.68	1.26	1.54	7.54	2.61			2.89
CaAgSBr	ип	x	0.28	0.53	49.22	3.74	1.62	0.64	0.95	1.60	2.99	1.48
	11-11	У	0.29	0.49	50.22	2.94	1.02	0.98	2.85			2.91
SrAgSBr	H-II	x	0.24	0.49	49.29	2.90	1.60	1.44	1.14	1.36	1.48	1.26
		у	0.25	0.47	49.15	3.24	2.02	1.06	0.77			1.38
SrAgSeI	H-II	x	0.16	0.39	40.93	3.60	2.04	1.75	0.92	1.03	1.92	1.90
		у	0.16	0.38	36.83	3.36	2.74	1.81	0.48			3.77
Al <sub>2</sub> S <sub>2</sub> ClI	<i>R</i> -I	x	0.81	3.22	61.77	0.36	1.08	10.30	0.07	49.05	3.00	147.14
		у	0.20	0.21	107.71	13.40	12.90	0.21	0.21			1.00
$Al_2S_2BrI$	R-I	x	0.76	3.10	61.97	0.92	0.58	1.80	0.27	7.83	1.13	6.67
		у	0.20	0.22	101.52	12.50	11.14	0.23	0.24			1.04
Al <sub>2</sub> SSeBr <sub>2</sub>	R-I	x	1.03	0.81	65.40	1.24	4.14	0.57	0.08	2.28	3.13	7.13
		у	0.20	0.24	99.32	11.90	9.96	0.25	0.25			1.00
Al <sub>2</sub> SSeBrI	R-I	x	0.83	0.78	47.11	1.30	5.82	0.57	0.03	2.19	7.00	19.00
		у	0.19	0.28	95.21	11.98	9.14	0.26	0.21			1.24
$Al_2Se_2I_2$	R-I	x	0.83	0.64	57.41	1.62	4.76	0.45	0.09	1.50	4.56	5.00
		У	0.17	0.22	82.10	11.60	7.70	0.30	0.41			1.37
AlScS <sub>2</sub> I <sub>2</sub>	R-I	x	0.96	1.35	61.96	0.54	1.58	3.27	0.19	11.28	1.74	17.21
		У	0.32	0.22	79.26	6.14	8.36	0.29	0.33			1.14
Al <sub>2</sub> FS <sub>2</sub> Br	<i>R</i> -II	x	0.87	0.48	115.42	0.64	5.64	5.28	0.22	18.86	2.59	24.00
		У	1.56	2.06	121.14	1.60	0.84	0.28	0.57			2.04

charge carriers ( $m^*$ ), the in-plane elastic stiffness of 2D material ( $C_{2D}$ ), and the deformation potential constant ( $E_{dp}$ ). These three factors, and the resulting carrier mobilities, are calculated and tabulated in Table 2 for the 16 candidate 2D materials. More detailed results for the in-plane stiffness and the deformation potential constants can be found in Figures S7–S22 (e).

According to DP theory, carrier mobility is inversely proportional to the square of the effective mass. Therefore, smaller  $m^*$  values are much more favorable for higher mobilities. As shown in Table 2, the electron effective masses  $(m_e^*)$  range from 0.16 to 1.56  $m_0$  (the rest mass of an electron in vacuum), while hole effective masses  $(m_h^*)$  vary from 0.21 to 3.22  $m_0$ . These are in the ballpark of common semiconductors, indicating that all our structures have bands with a sizeable dispersion. In most

structures, the  $m_e^*$  is smaller than its corresponding  $m_h^*$  along the same direction, reflecting a more dispersing lower conduction band, as compared to the upper valence band. This is likely the result of the (empty) cation states being more extended than the (filled) outer anion states, where these states determine the lower conduction band and the upper valence band, respectively. When comparing the effective masses calculated along different directions, materials with a hexagonal structure show very little variation due to structural symmetry. In contrast, materials with a rectangular structure have significantly different effective masses in *x*- and *y*-directions. For example, in (hexagonal) Cd<sub>2</sub>SSe (*H*-I), the  $m_e^*$  and  $m_h^*$  along the *x*-/*y*-direction are 0.23/0.23  $m_0$  and 0.33/0.32  $m_0$ , respectively. As a comparison, for (rectangular) Al<sub>2</sub>Se<sub>2</sub>I<sub>2</sub> (*R*-I), the  $m_e^*$  and  $m_h^*$  along the *x*-/*y*-direction are 0.83/0.17  $m_0$  and 0.64/0.22  $m_0$ , respectively.

The second factor influencing carrier mobility is the 2D in-plane stiffness ( $C_{2D}$ ), to which mobility are directly proportional. The calculated  $C_{2D}$  values listed in Table 2 demonstrate that the selected candidate photocatalytic materials exhibit elastic moduli ranging from ~ 20 N m<sup>-1</sup> (Ag<sub>2</sub>BrI and Ag<sub>2</sub>I<sub>2</sub>) to ~ 120 N m<sup>-1</sup> (Al<sub>2</sub>FS<sub>2</sub>Br). The larger  $C_{2D}$  values are prominently shown in the *R*-I and -II structures, where in particular the Al-S bonds seem to lead to a relatively stiff bonding network. On the other end of the scale, the smaller  $C_{2D}$  results are found among the *H*-I structures, where the Ag-I and Ag-Br bonds lead to a relatively soft bonding network. Furthermore, anisotropic materials possess disparities in  $C_{2D}$  along the *x*- and *y*-directions.

Another factor that determines the carrier mobility is the deformation potential constant ( $E_{dp}$ ), where the mobility is inversely proportional to the square of it. The magnitude of  $E_{dp}$  describes the change in energy of the band edges due to elastic deformation, reflecting the extent of interaction between charge carriers and phonons. A lower value of  $E_{dp}$  indicates a weaker electron-phonon coupling in the conduction (valence) band, contributing to an increase in the mobility of electrons (holes).<sup>63,66</sup> The calculated  $E_{dp}$  values given in Table 2 show dependence on the type of carriers, as well as on the transport directions. Among the 16 compounds, electron deformation constants ( $E_{dp.e}$ ) vary from a minimum of 0.24 eV (x-direction of Ag<sub>2</sub>BrI and y-direction Ag<sub>2</sub>I<sub>2</sub>) to a maximum of 13.40 eV (y-direction of Al<sub>2</sub>S<sub>2</sub>CII), representing a 56-fold difference. The deformation potential constants of holes ( $E_{dp.h}$ ) also exhibit similar variations. The larger deformation potential constants seem to be dominantly found in compounds with the *R*-I structure, where the relatively stiff Al-S bonding network apparently also gives a stronger electron-phonon coupling. Conversely, the *H*-I structures feature smaller deformation constants, attributed to the softer bonding network of Ag-I and Ag-Br bonds, leading to a weaker electron-phonon coupling. Additionally, anisotropic materials, such as Al<sub>2</sub>S<sub>2</sub>CII, show significantly different values of  $E_{dp.e}$  ( $E_{dp.h}$ ) in different transport directions, with maximum x/y or y/x ratios of ~ 37 (~ 12).

Based on the effective masses, elastic modulus and deformation potential constants, we calculate the carrier mobilities at room temperature of the 16 candidate 2D photocatalysts according to Eq. 5 and list them in Table 2. For a better visualization, the carrier mobility results are also plotted in Figure 6 (b) as a bar graph, separated by carrier type and transport direction. The high mobilities reflects the absence of any scattering by impurities or defects, and the use of DP theory to incorporate phonon scattering. The tabulated mobilities are then likely to be upper bounds, but nevertheless it still makes sense to do relative comparisons among them. The highest electron mobility ( $\mu_e$ ) is observed in Ag<sub>2</sub>I<sub>2</sub>, reaching 35.03 ×10<sup>3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> along the *y*-direction, while Ag<sub>2</sub>BrI has a very close value of 23.92 ×10<sup>3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> along the *x*-direction. The key factor contributing to such large values is the small values of  $E_{dp_e}$ . Similarly, owing to its small  $E_{dp_e}$ , Cd<sub>2</sub>S<sub>2</sub> has the highest hole mobility ( $\mu_h$ ) of 8.16 ×10<sup>3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in the *y*-direction.

One can compare these carrier mobilities with those previously reported 2D materials, yet calculated within the same model and approximations. Benchmark materials would be transition metal dichalcogenides (TMDs) such as  $MoS_2^{67}$ , which has electron and hole mobilities of  $0.20 \times 10^3$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and  $0.15 \times 10^3$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, within the DP model. In more complex TMDs with a Janus structure such as WSSe<sup>68</sup>, the calculated value for  $\mu_e$  is  $0.13 \times 10^3$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, while for  $\mu_h$  is  $0.72 \times 10^3$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. From the results shown in Table 2, it is clear that all 16 candidate materials have mobilities at least comparable to those of TMDs, with some significantly higher. For example, Ag<sub>2</sub>I<sub>2</sub> and Ag<sub>2</sub>BrI exhibit calculated  $\mu_e$ values that are more than two orders of magnitude greater than those of the TMDs, even approaching the high value of few-layer AuSe<sup>69</sup> (39.84 × 10<sup>3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), whereas Cd<sub>2</sub>S<sub>2</sub> has a  $\mu_h$  that is one order of magnitude higher than that of WSSe. In general, materials exhibit directional variations in their carrier mobilities. We characterize their anisotropy by calculating the ratio of  $R_{ani\_e}$  and  $R_{ani\_h}$  in two perpendicular in-plane directions using Eq. 9, and present the results in Table 2. The anisotropy in the hexagonal structures, *H*-I and *H*-II, is relatively small, with  $R_{ani\_e}$  and  $R_{ani\_h}$  both < 3. In contrast, *R*-I and *R*-II structures exhibit significantly greater anisotropy. Among them, Al<sub>2</sub>S<sub>2</sub>ClI has the largest  $R_{ani\_e} = 49.05$ , surpassing even that of monolayer black phosphorus<sup>70</sup>. Additionally, to quantify the difference between electron to hole mobilities per material, we calculate their ratio per direction ( $R_{carri}$ ) using Eq. 10 and include the results in Table 2. Most of the structures have  $R_{carri} < 3$ , indicating that they are very suitable for ambipolar transport, as one might want for a photocatalyst. Materials with notably high values of  $R_{carri}$  are Ag<sub>2</sub>I<sub>2</sub>, Ag<sub>2</sub>BrI, and Al<sub>2</sub>S<sub>2</sub>ClI, which have very large electron mobilities.

## **3** Conclusion

In this study, we present a data-driven systematic exploration to find novel 2D photocatalysts with intrinsic direct-gaps suitable for solar water splitting. Our workflow consists of a three-staged screening process to identify candidate 2D materials, followed by a comprehensive evaluation of their properties that relate to their photocatalytic performance.

The screening process begins with applying the machine-learning (ML) predicted properties from the V2DB database, encompassing band gap character, band gap, and band gap center (BGC) values, enabling the identification of 294 direct-gap candidates from a pool of 316,505 2D materials. Subsequently, we perform high-throughput DFT (PBE level) computations, including structure optimization and electronic properties calculations, to precisely identify direct-gap semiconductors. A thorough stability assessment, involving phonon spectrum calculations, *ab initio* molecular dynamics simulations, and mechanical stability evaluations, further narrow down the candidates to 21 stable 2D materials with a direct-gap. In the third stage, we employ HSE06 band structure calculations to accurately determine the band gap and band edge positions of the 21 candidates, resulting in the identification of 16 direct-gap 2D photocatalysts with the potential for efficient overall water splitting under sunlight irradiation.

Following the screening process, we determine key parameters of the 16 materials that may be important for their performance. This assessment includes calculations of their electronic properties, light absorbances, solar-to-hydrogen (STH) conversion efficiencies, and carrier mobilities. The elemental and orbital projected band structures show that the upper valence bands typically have dominant anion character, whereas the lower conduction bands have considerable cation contribution. Moreover, the local charge density distribution analyses show that in several compounds the states belonging to valence and conduction band edges are spatially separated, facilitating efficient separation of photogenerated carriers across the 2D slab. The majority of the 16 selected materials demonstrate significant light absorption in the visible or near-ultraviolet range, enabling effective utilization of solar irradiation. Comparative analysis of the STH conversion efficiencies with previously reported photocatalysts demonstrates that all 16 candidates are fit for water splitting. Additionally, these materials exhibit high intrinsic carrier mobilities, indicating favorable transport performance of photogenerated carriers.

In summary, this study provides, by integrating ML-predictions with physics-based high-throughput computations and employing carefully designed screening criteria, 16 promising direct-gap 2D photocatalysts. Additionally, the research highlights the effectiveness of this integrated approach for the resource- and time-efficient exploring specific functional 2D materials over a vast chemical space.

## 4 Methods

First-principles calculations on the basis of density functional theory (DFT) are performed using the Vienna *ab initio* simulation package (VASP)<sup>71,72</sup> to investigate the equilibrium structure, stability, mechanical, electronic, optical, and carrier mobility properties. The VASPKIT<sup>73</sup> package is used as a high-throughput interface, to both pre-process the input files and post-process the data obtained from VASP calculations. The equilibrium structures are visualized using the VESTA<sup>74</sup> package.

The Perdew–Burke–Ernzerhof (PBE) scheme of the generalized gradient approximation (GGA) is employed to describe the exchange-correlation functional.<sup>75</sup> The ion-electron interaction are described using the projector-augmented plane wave (PAW)

approach.<sup>76</sup> A vacuum space of 20 Å in the vertical direction is included in the unit cell to avoid the direct interactions between images resulting from the periodic boundary conditions. The plane wave cutoff kinetic energy is set to 500 eV. During geometry optimization, convergence criteria of  $10^{-5}$  eV in energy between the consecutive relaxation steps and 0.01 eV Å<sup>-1</sup> in the forces remaining on atoms, are enforced. Electronic band structure calculations are performed using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid density functional, which incorporates 25% exact Hartree–Fock (HF) exchange.<sup>77</sup> The band edge positions relative to the vacuum level are determined using alignment of the electrostatic potentials (using the vacuum level as zero point). In all electronic property calculations, spin–orbit coupling (SOC) is included.

The phonon dispersion curves are calculated using density functional perturbation theory (DFPT)<sup>78</sup> as implemented in the PHONOPY<sup>79</sup> code. The *ab initio* molecular dynamics (AIMD) simulations are performed by using the VASP code in the *NVT* ensemble<sup>80</sup> at temperatures of 300, 600 and 900 K. Each run simulates 10 picoseconds (ps), using a time step of 1 femtosecond (fs). For both phonon calculations and AIMD simulations,  $4 \times 4 \times 1$  supercells are constructed to abate the effects of periodic boundary conditions. The elastic constants are calculated by finite distortion method, specifically by taking the first derivative of the fitted stress-strain curve. The orientation-dependent Young's modulus (*Y*), Poisson's ratio (*v*) and shear modulus (*G*) of monolayer along the in-plane angle ( $\theta$ ) are derived using VASPKIT from the elastic constants calculation results.<sup>53</sup>

The linear optical properties can be obtained from the frequency-dependent complex dielectric tensor  $\varepsilon_{\alpha\beta}(\omega)$ . Its imaginary part is calculated on the basis of the DFT wave functions, using the standard (longitudinal) independent particle expression, and the real part is obtained via a Kramers–Kronig transform of the imaginary part.<sup>81</sup> The calculated dielectric function is that of an artificial periodic 3D system, consisting of 2D layers separated by vacuum regions. The dielectric response of a single, isolated 2D layer can be extracted from that function, and from that response the optical properties of the 2D layer, such as its absorbance  $A(\omega)$ .<sup>73,82,83</sup>

By assuming 100% efficiency of the catalytic reaction, the solar-to-hydrogen (STH) conversion efficiency ( $\eta_{STH}$ ) is obtained from<sup>84</sup>

$$\eta_{\text{STH}} = \eta_{\text{abs}} \times \eta_{\text{cu}} \tag{1}$$

where  $\eta_{abs}$  is the optical absorption efficiency and  $\eta_{cu}$  is the carrier utilization efficiency. The efficiency of optical absorption is calculated by using the following expression

$$\eta_{\rm abs} = \frac{\int_{E_{\rm g}}^{\infty} P(h\omega) d(h\omega)}{\int_{0}^{\infty} P(h\omega) d(h\omega)} \times 100\%$$
<sup>(2)</sup>

where  $P(h\omega)$  is the AM1.5G solar energy flux<sup>57</sup> at the photon energy  $h\omega$  and  $E_g$  is the direct-gap<sup>68,84</sup> of the photocatalyst calculated at the HSE-level. The denominator represents the total power density of the reference sunlight spectrum (AM1.5G) and the numerator gives the light power density absorbed by the photocatalyst. The efficiency of carrier utilization is defined as

$$\eta_{\rm cu} = \frac{\Delta G_{\rm H_2O} \int_E^{\infty} \frac{P(h\omega)}{h\omega} d(h\omega)}{\int_{E_g}^{\infty} P(h\omega) d(h\omega)} \times 100\%$$
(3)

where  $\Delta G_{\text{H}_2\text{O}}$  is the free energy of water splitting at standard conditions (1.23 eV) and the rest of numerator represents the effective photo-current density. Here, *E* represents the energy of photons that can be actually utilized in the process of water splitting, which can be defined as

$$E = \begin{cases} E_{g}, & (\chi(H_{2}) \ge 0.2, \quad \chi(O_{2}) \ge 0.6) \\ E_{g} + 0.2 - \chi(H_{2}), & (\chi(H_{2}) < 0.2, \quad \chi(O_{2}) \ge 0.6) \\ E_{g} + 0.6 - \chi(O_{2}), & (\chi(H_{2}) \ge 0.2, \quad \chi(O_{2}) < 0.6) \\ E_{g} + 0.2 + 0.6 - \chi(H_{2}) - \chi(O_{2}), & (\chi(H_{2}) < 0.2, \quad \chi(O_{2}) < 0.6) \end{cases}$$
(4)

where  $\chi(H_2)$  represents the overpotential for hydrogen evolution reaction (HER), calculated by the energy difference between CBM of photocatalyst and the redox potentials of H<sup>+</sup>/H<sub>2</sub>;  $\chi(O_2)$  is the overpotential for oxygen evolution reaction (OER), calculated by the energy difference between VBM of photocatalyst and the redox potentials of O<sub>2</sub>/H<sub>2</sub>O. The required overpotentials for HER and OER are assumed to be 0.2 and 0.6 eV, respectively, according to the previous experiments and theoretical calculation reports.<sup>84–87</sup>

Using the deformation potential (DP) approximation method,<sup>63–65</sup> the acoustic phonon-limited carrier mobility ( $\mu$ ) of 2D materials can be evaluated with the following formula<sup>84</sup>

$$\mu = \frac{2e\hbar^3 C_{2\rm D}}{3K_{\rm B}T |m^*|^2 E_{\rm dp}{}^2} \tag{5}$$

where we use T = 300 K, *i.e.*, room temperature;  $\hbar$ ,  $K_B$ , and *e* represent the reduced Planck constant, Boltzmann constant, and electron charge, respectively. By fitting parabolic functions to the band edge states, the effective masses of electrons ( $m_e^*$ ) and holes ( $m_h^*$ ) are obtained by

$$m^* = \pm \hbar^2 \left(\frac{d^2 E_k}{dk^2}\right)^{-1} \tag{6}$$

where k and  $E_k$  represent the wave vector and corresponding energy of the VBM (for holes) and CBM (for electrons), respectively.  $C_{2D}$  represents the 2D in-plane stiffness, and it is calculated as

$$C_{\rm 2D} = \frac{\partial^2 E_{\rm tot}}{\partial \varepsilon^2} \times \frac{1}{S_0} \tag{7}$$

where  $E_{tot}$  is the total energy,  $\varepsilon$  is an applied external uniaxial strain, and  $S_0$  is the area of a unit cell at equilibrium for a 2D system.  $E_{dp}$  represents the deformation potential, and it is obtained from

$$E_{\rm dp} = \left| \frac{dE_{\rm edge}}{d\varepsilon} \right| \tag{8}$$

where  $\varepsilon$  and  $dE_{edge}$  are uniaxial strain and corresponding band edge energy, respectively. In the calculation, square supercells with perpendicular lattice directions are built for the structures with hexagonal unit cells. The structural representation indicating the *x*- and *y*-directions for each structure are shown in Figures S7–S22 (e). In the current study, uniaxial strains of up to  $\pm 1\%$ , with 0.5% change for each step, are applied to the 2D structures. These calculations are performed using the PBE functional, which had yielded a good estimation of these properties in the previous studies on 2D monolayers.<sup>88,89</sup> The carrier mobility anisotropic ratio ( $R_{ani}$ ) is calculated as

$$R_{\rm ani} = \frac{{\rm Max}(\mu_x, \mu_y)}{{\rm Min}(\mu_x, \mu_y)} \tag{9}$$

where  $\mu_x$  and  $\mu_y$  are the mobility value of the specific carrier type along *x* and *y* transport directions, respectively. The mobility ratio of different type of carriers along one direction ( $R_{carri}$ ) is defined as

$$R_{\text{carri}} = \frac{\text{Max}(\mu_{\text{e}}, \mu_{\text{h}})}{\text{Min}(\mu_{\text{e}}, \mu_{\text{h}})}$$
(10)

where  $\mu_e$  and  $\mu_h$  are the calculated mobility value of electron and hole along the same specific direction, respectively.

## Additional information

The Supporting Information is available for this paper.

## Author contributions statement

Y.W. performed the calculations and formal analysis. Y.W. wrote the original draft of the manuscript. S.E. conceptualized the project. S.E. and G.B. supervised the project. All authors contributed to the investigation and discussion on the results, as well as to the writing, reviewing, and editing of the manuscript.

# **Competing interests**

The authors declare no competing interests.

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