

# Data-Driven Discovery of Transition Metal Dichalcogenide-Based Z-Scheme Photocatalytic Heterostructures

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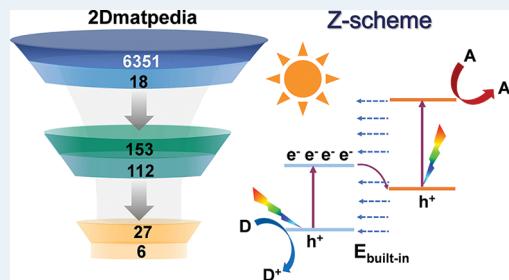
**ABSTRACT:** The Z-scheme heterostructure is a highly promising photocatalyst for its unique electronic structure. However, a thorough examination of the heterostructure design space through experimental or computational means is prohibitively expensive. Here, we propose a highly efficient data-driven approach for fast discovering van der Waals (vdW) Z-scheme heterostructures, bypassing the need for costly calculations and experimentation. By conducting high-throughput calculations with the Heyd–Scuseria–Ernzerhof hybrid density functional (HSE06), we first generate a variety of data of electronic structures for 18 experimentally synthesized 2D transition metal dichalcogenides (TMDs) and 20 of 153 heterostructures (constructed with the 18 TMDs). Using these data, we develop an innovative and robust descriptor: Allen “material” electronegativity. Leveraging this descriptor, we identify 27 2D vdW Z-scheme heterostructures from the pool of 153 heterostructures without expensive HSE calculations. We finally refine our findings by selecting six Z-scheme heterostructures with minimal lattice mismatch, further validating them using high-fidelity *ab initio* calculations and studying their optical absorption. Our research not only paves the way for discovering high-performance Z-scheme photocatalysts using data-driven methods but also contributes a universal charge transfer mechanism for vdW device applications.

**KEYWORDS:** *transition metal dichalcogenides, Z-scheme heterostructure, photocatalyst, material descriptor, high-throughput calculations*

## INTRODUCTION

Photocatalytic technology has emerged as a promising sustainable strategy for addressing the pressing concerns of environmental pollution and global fossil fuel depletion.<sup>1,2</sup> Z-Scheme heterostructures have attracted considerable attention in the field of photocatalytic technology due to their broad solar absorption spectrum and preserve photogenerated reaction carriers with strong redox capability.<sup>3–9</sup> The mechanism and key criteria of Z-scheme heterostructures share similarities with conventional type-II heterostructures in terms of band alignment but exhibit distinctly different photogenerated carrier transfer pathways (see in Scheme 1). To enable such a charge transfer mechanism, the Z-scheme heterostructure must have a small band alignment ( $\delta$ ) and a large directional built-in electric field ( $E_{\text{built-in}}$ ). Consequently, photogenerated electrons and holes with a large redox potential are well-preserved and spatially separated within the Z-scheme heterostructure (Scheme 1).<sup>10–12</sup> Combining two narrow bandgap semiconductors into a Z-scheme heterostructure may resolve the dilemma of single-material or type-II photocatalysts, where strong redox capability and a broad light absorption range cannot be achieved simultaneously.<sup>13–16</sup> Therefore, the discovery and design of Z-scheme heterostructures for photocatalysis is of critical importance.

Instead of relying on the resource-intensive trial-and-error approach of stacking various 2D materials to identify van der Waals (vdW) Z-scheme heterostructures, the data-driven



approach can significantly streamline the design process. The availability of well-developed 2D materials databases, such as 2DMatPedia, C2DB, and JARVIS, allows researchers to access various properties of over 6000 2D materials, such as the exfoliation energy, decomposition energy, band structure, and work function.<sup>17–24</sup> By leveraging these available properties, one may derive effective and practical descriptors for evaluating interfacial electric fields and band alignments of vdW 2D heterostructures, enabling the quick identification of Z-scheme photocatalysts before contact (as illustrated in Scheme 1), without resorting to computationally expensive high-fidelity density functional theory (DFT) calculations, such as GW and Heyd–Scuseria–Ernzerhof hybrid functionals (HSE). The primary challenge lies in predicting the built-in electric field of a vdW 2D heterostructure before contact, including the magnitude and direction of charge transfer. Recent efforts have sought descriptors for charge transfer in vdW 2D heterostructures, including differences in work functions ( $\Delta W$ ), covalent radii ( $\Delta R$ ), and Pauling atomic electronegativities ( $\Delta \chi$ ) between two 2D materials.<sup>25–28</sup>

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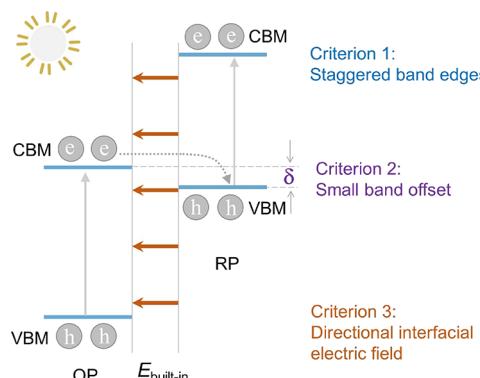
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**Scheme 1. Schematic Z-Scheme Heterostructure and Its Three Key Criteria<sup>a</sup>**



<sup>a</sup>OP and RP represent the oxidation and reduction photocatalyst, respectively.  $E_{\text{built-in}}$  denotes the interfacial built-in electric field, which is induced by the intrinsic charge transfer between the two photocatalysts after contact. The high separation efficiency of electron–hole pairs in the Z-scheme heterostructure is attributed to its small band offset and large directional interfacial electric field. A critical question raised is whether it is possible to obtain these parameters, especially criterion 3 (the interfacial electric field), before forming a heterostructure, thereby avoiding the need for costly heterostructure-based calculations.

However, these descriptors are either inapplicable or imprecise for distinguishing Z-scheme heterostructures from other categories, particularly from their type-II heterostructure parents as they share the same  $\Delta W$ ,  $\Delta R$ , and  $\Delta \chi$ .

In this work, we first calculate the HSE electronic structure of 18 experimentally synthesized H-phase transition metal dichalcogenides (TMD), namely, HfTe<sub>2</sub>, MoS<sub>2</sub>, TiSe<sub>2</sub>, WSe<sub>2</sub>, ZrSe<sub>2</sub>, CrSe<sub>2</sub>, HfSe<sub>2</sub>, TiTe<sub>2</sub>, WTe<sub>2</sub>, ZrS<sub>2</sub>, CrTe<sub>2</sub>, HfS<sub>2</sub>, TiS<sub>2</sub>, WS<sub>2</sub>, CrS<sub>2</sub>, MoSe<sub>2</sub>, MoTe<sub>2</sub>, and ZrTe<sub>2</sub> (see details in Table 1).<sup>29,30</sup> Using their HSE electronic structures and Anderson's

rule, we screen 112 of the 153 heterostructures (formed by the 18 TMDs) with type-II band alignment. Next, we select 20 of the 112 type-II heterostructures and systematically calculate their HSE electronic structures, amount of charge transfer, and built-in interfacial electric field (see details in Table 2). Leveraging the high-fidelity data from the 18 TMDs and 20 vdW heterostructures, we develop a novel descriptor known as Allen “material” electronegativity ( $\Delta \chi_m$ ). It is important to note that this differs from the traditional concept of Pauling electronegativity, which applies to atoms. The material electronegativity enables us to further identify a total of 27 Z-scheme candidates from 112 type-II heterostructures bypassing the need for expensive HSE calculations on large supercells of heterostructures. Among them, three have been previously reported in the literature, while the remaining 24 have never been reported hitherto. We finally refine the 27 candidates by selecting six Z-scheme heterostructures (TiS<sub>2</sub>/CrSe<sub>2</sub>, TiS<sub>2</sub>/MoS<sub>2</sub>, TiS<sub>2</sub>/MoSe<sub>2</sub>, TiSe<sub>2</sub>/MoSe<sub>2</sub>, TiS<sub>2</sub>/WS<sub>2</sub>, and TiSe<sub>2</sub>/WSe<sub>2</sub>) with minimal lattice mismatch and verify them by DFT calculations. Our optical calculations show that TiS<sub>2</sub>/CrSe<sub>2</sub> has near-infrared light absorption and large reaction driving force, showing enormous potential for photocatalytic applications. The data-driven discovery of effective descriptors not only provides new high-potential Z-scheme heterostructure candidates but also offers a simple yet effective means of accelerating future development of solar-to-hydrogen, CO<sub>2</sub>, and other essential photocatalysis reactions.

## COMPUTATIONAL DETAILS

DFT calculations were executed using the Vienna *ab initio* simulation package (VASP).<sup>31</sup> The core-electron interactions were described by the frozen-core projector augmented wave (PAW) method.<sup>32</sup> The electronic exchange-correlation energy was treated using the generalized gradient approximation in the form of Perdew–Burke–Ernzerhof (GGA-PBE) formalism.<sup>33</sup> The Heyd–Scuseria–Ernzerhof hybrid density functional

**Table 1. The Calculated Lattice (Å), Band Gap (eV), Gap Type, Band Alignment of the VBM and CBM with Respect to the Vacuum Level, and Magnetism of 18 Experimentally Synthesized 2H-Phase TMD Semiconductors Used in This Work as Building Blocks for Constructing vdW Heterostructures<sup>a</sup>**

2H-TMD	lattice	HSE band gap	gap type	VBM	CBM	magnetism	experiment
HfTe <sub>2</sub>	$a = b = 3.91$	1.19	indirect	-6.40	-5.20	NM	ref 29
MoS <sub>2</sub>	$a = b = 3.18$	2.10	direct	-6.70	-4.59	NM	ref 29
TiSe <sub>2</sub>	$a = b = 3.50$	1.60	indirect	-7.10	-5.51	NM	ref 29
WSe <sub>2</sub>	$a = b = 3.32$	1.96	direct	-5.82	-3.86	NM	ref 29
ZrSe <sub>2</sub>	$a = b = 3.70$	1.67	indirect	-7.28	-5.62	NM	ref 29
CrSe <sub>2</sub>	$a = b = 3.21$	1.04	direct	-6.02	-4.98	NM	ref 29
HfSe <sub>2</sub>	$a = b = 3.68$	1.74	indirect	-7.31	-5.57	NM	ref 29
TiTe <sub>2</sub>	$a = b = 3.74$	1.30	indirect	-6.31	-5.01	NM	ref 29
WTe <sub>2</sub>	$a = b = 3.55$	1.41	direct	-5.26	-3.85	NM	ref 29
ZrS <sub>2</sub>	$a = b = 3.57$	1.96	indirect	-7.90	-5.94	NM	ref 29
CrTe <sub>2</sub>	$a = b = 3.47$	0.89	direct	-5.44	-4.55	NM	ref 30
HfS <sub>2</sub>	$a = b = 4.31$	2.05	indirect	-7.94	-5.90	NM	ref 29
TiS <sub>2</sub>	$a = b = 3.35$	1.78	indirect	-7.76	-5.99	NM	ref 29
WS <sub>2</sub>	$a = b = 3.19$	2.28	direct	-6.45	-4.17	NM	ref 29
CrS <sub>2</sub>	$a = b = 3.05$	1.24	direct	-6.64	-5.40	NM	ref 30
MoSe <sub>2</sub>	$a = b = 3.32$	1.83	direct	-6.06	-4.23	NM	ref 29
MoTe <sub>2</sub>	$a = b = 3.55$	1.43	direct	-5.48	-4.05	NM	ref 29
ZrTe <sub>2</sub>	$a = b = 3.92$	1.25	indirect	-6.49	-5.24	NM	ref 29

<sup>a</sup>The HSE hybrid functional is used in this work for getting more accurate electronic structures of these 2D semiconductors. NM means nonmagnetism.

**Table 2. Structural Details and HSE Calculation Results of 20 Samples of Heterostructure Supercells, Including the Acceptor and Donor in a Heterostructure, the Size of the Supercell, the Total Number of Atoms in the Supercell, the Lattice Mismatch between Two Materials, the Distance between Two Materials ( $\Delta d$  in Å), and the Binding Energy  $E_b$  of Two Materials in meV<sup>a</sup>**

acceptor–donor	supercell	lattice (Å)	atoms	mismatch	$\Delta d$	$E_b$	$E_g$ (eV)	$\Delta\chi_m$	$\Delta Q$ (e)
MoS <sub>2</sub> /TiSe <sub>2</sub>	$3 \times 3 \times 1/\sqrt{7} \times \sqrt{7} \times 1$	9.48	48	3.19%	3.40	-31.14	1.11	0.061	0.084
MoS <sub>2</sub> /ZrSe <sub>2</sub>	$2 \times 2 \times 1/\sqrt{3} \times \sqrt{3} \times 1$	6.41	21	-0.89%	3.43	-32.00	1.09	0.052	0.033
MoS <sub>2</sub> /HfSe <sub>2</sub>	$2 \times 2 \times 1/\sqrt{3} \times \sqrt{3} \times 1$	6.39	21	0.04%	3.44	-31.44	1.14	0.059	0.049
TiS <sub>2</sub> /MoS <sub>2</sub>	$1 \times 1 \times 1/1 \times 1 \times 1$	3.27	6	-4.97%	3.60	-27.23	0.72	0.079	0.001
MoS <sub>2</sub> /WSe <sub>2</sub>	$1 \times 1 \times 1/1 \times 1 \times 1$	3.27	6	-4.18%	3.79	-25.74	0.76	0.124	0.004
MoS <sub>2</sub> /WTe <sub>2</sub>	$2 \times 2 \times 1/\sqrt{3} \times \sqrt{3} \times 1$	6.32	21	3.12%	3.71	-30.98	1.01	0.314	0.101
WS <sub>2</sub> /MoS <sub>2</sub>	$1 \times 1 \times 1/1 \times 1 \times 1$	3.20	6	-0.06%	3.74	-25.18	0.99	0.121	0.013
MoS <sub>2</sub> /MoSe <sub>2</sub>	$1 \times 1 \times 1/1 \times 1 \times 1$	3.26	6	-4.20%	3.80	-25.67	1.22	0.308	0.102
MoS <sub>2</sub> /MoTe <sub>2</sub>	$2 \times 2 \times 1/\sqrt{3} \times \sqrt{3} \times 1$	6.32	21	3.13%	3.69	-30.92	1.13	0.123	0.020
CrS <sub>2</sub> /TiSe <sub>2</sub>	$2 \times 2 \times 1/\sqrt{3} \times \sqrt{3} \times 1$	6.11	21	-0.68%	3.51	-30.32	0.69	0.016	0.115
TiS <sub>2</sub> /CrS <sub>2</sub>	$\sqrt{7} \times \sqrt{7} \times 1/3 \times 3 \times 1$	9.06	48	-3.37%	3.27	-30.04	0.76	0.060	0.003
TiSe <sub>2</sub> /MoSe <sub>2</sub>	$1 \times 1 \times 1/1 \times 1 \times 1$	3.42	6	5.26%	3.80	-28.30	0.53	0.063	0.028
TiSe <sub>2</sub> /WSe <sub>2</sub>	$1 \times 1 \times 1/1 \times 1 \times 1$	3.41	6	5.28%	3.80	-28.15	0.62	0.093	0.020
ZrS <sub>2</sub> /WS <sub>2</sub>	$\sqrt{3} \times \sqrt{3} \times 1/2 \times 2 \times 1$	6.33	21	2.86%	3.39	-31.00	0.81	0.088	0.003
HfS <sub>2</sub> /MoS <sub>2</sub>	$\sqrt{3} \times \sqrt{3} \times 1/2 \times 2 \times 1$	6.29	21	4.01%	3.40	-30.56	0.90	0.026	0.006
HfS <sub>2</sub> /CrS <sub>2</sub>	$\sqrt{3} \times \sqrt{3} \times 1/2 \times 2 \times 1$	6.13	21	0.18%	3.41	-29.96	0.79	0.031	0.015
ZrS <sub>2</sub> /CrS <sub>2</sub>	$2 \times 2 \times 1/\sqrt{3} \times \sqrt{3} \times 1$	6.16	21	1.45%	3.37	-30.47	1.79	-0.001	0.001
TiS <sub>2</sub> /CrSe <sub>2</sub>	$1 \times 1 \times 1/1 \times 1 \times 1$	3.23	6	-3.83%	3.68	-28.21	0.76	0.134	0.046
TiS <sub>2</sub> /WS <sub>2</sub>	$1 \times 1 \times 1/1 \times 1 \times 1$	3.36	6	0.56%	3.63	-27.12	0.23	0.079	0.010
TiS <sub>2</sub> /MoSe <sub>2</sub>	$1 \times 1 \times 1/1 \times 1 \times 1$	3.36	6	4.68%	3.70	-28.17	0.32	0.200	0.034

<sup>a</sup>Furthermore, the calculated HSE06 band gap, the Allen material electronegativity difference  $\Delta\chi_m$  between two materials, and the calculated amount of Bader charge transfer  $\Delta Q$  between the donor and acceptor are also given in the table below.

(HSE06) was used to obtain the accurate band gap and band edges.<sup>34,35</sup> The optPBE exchange-correlation energy was employed, incorporating vdW interaction corrections.<sup>36</sup> The plane-wave cutoff energy was set to 500 eV, and the Brillouin zone was integrated using Gamma-centered grids with consistent spacing density for all cell sizes (KSPACING = 0.25 Å<sup>-1</sup> for geometric optimization). A vacuum layer of 15 Å in the Z-direction was introduced to prevent spurious interactions between adjacent slabs. For geometry optimization, convergence criteria of energy and forces acting on each atom were set at 10<sup>-4</sup> eV and 0.01 eV Å<sup>-1</sup>. Atomic positions and charge density illustrations were obtained using VESTA.<sup>37</sup> Further analysis was conducted using the postprocessing program VASPKIT.<sup>38</sup> Partial atomic charges were obtained using Bader charge analysis as implemented by Henkelman and coworkers.<sup>39–41</sup>

## RESULTS AND DISCUSSION

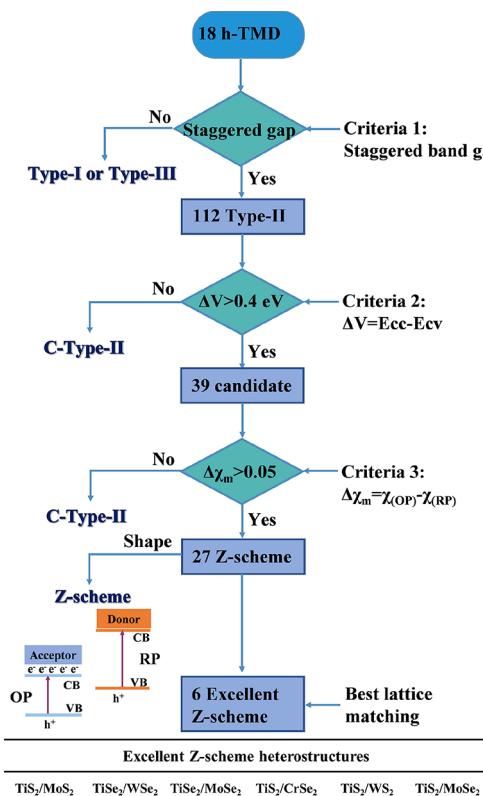
Based on the Z-scheme photocatalytic mechanism (Scheme 1), three key characteristics are deemed necessary. Criterion 1 is the prerequisite that a staggered band alignment is the main feature for a type-II heterostructure. Criterion 2 involves a small band offset for a low energy barrier. The directional interfacial electronic field is the most crucial criterion 3 for identifying the Z-scheme heterostructure. A larger charge transfer from RP to OP results in a stronger built-in electric field, which is critical for facilitating the combination of “useless” photogenerated electrons at OP and holes at RP.<sup>42</sup> This study aims to develop effective descriptors for accelerating the screening process for identifying TMD-based Z-scheme heterostructures.

Based on the three criteria discussed in Scheme 1, we design an overall three-step workflow (Scheme 2) to identify Z-scheme heterostructures from 153 vdW heterostructures composed by 18 2D materials. To meet criterion 1, we apply

Anderson’s rule and predict that 112 over 153 heterostructures exhibit type-II band alignment. In the second step for meeting criterion 2, we use  $\Delta V > 0.4$  eV to filter out 39 potential candidates with a low transfer barrier for the Z-scheme pathway. Lastly, by comparing  $\Delta\chi_m > 0.05$  and determining the electron transfer direction (to satisfy criterion 3), we identify 27 Z-scheme heterostructures (Supporting Information, refer to Table S1). It is worth noting that three of them, CrS<sub>2</sub>/MoSe<sub>2</sub>, CrS<sub>2</sub>/MoTe<sub>2</sub>, and ZrS<sub>2</sub>/WS<sub>2</sub>, have already been reported as Z-scheme heterostructures in the literature,<sup>43,44</sup> validating our descriptors, while 24 Z-scheme heterostructures have heterostructures with lattice mismatch below 5%. Ultimately, we recognize six exceptional Z-scheme heterostructures, MoS<sub>2</sub>/TiS<sub>2</sub>, TiSe<sub>2</sub>/WSe<sub>2</sub>, TiSe<sub>2</sub>/MoSe<sub>2</sub>, CrSe<sub>2</sub>/TiS<sub>2</sub>, TiS<sub>2</sub>/WS<sub>2</sub>, and TiS<sub>2</sub>/MoSe<sub>2</sub>. In the following, we will show the detailed method to find descriptors for discovering Z-scheme heterostructures and discuss the two descriptors  $\Delta V$  and  $\Delta\chi_m$  in detail.

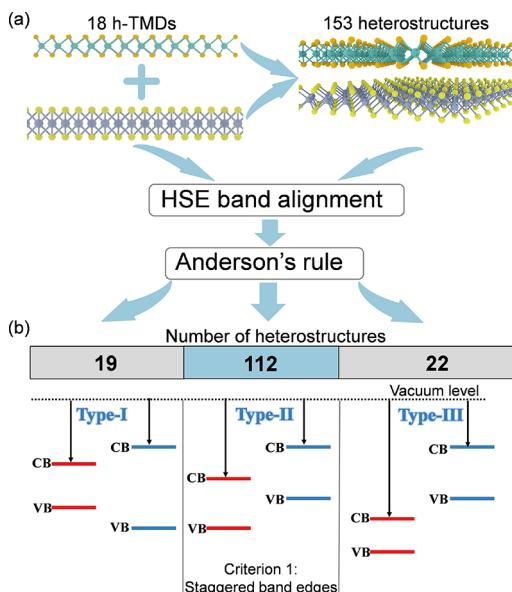
We start from 18 MoS<sub>2</sub>-like nonmagnetic H-phase TMD semiconductors because they have been synthesized experimentally.<sup>29,30</sup> We systematically calculate their geometric structure, electronic structure, and magnetic properties using the DFT+HSE hybrid functional. Table 1 lists the 18 materials and their calculated properties, including lattice parameters, HSE band gap, gap type, conduction band minimum (CBM), and valence band maximum (VBM) positions relative to the vacuum level, as well as magnetic ordering. The h-TMD material is the H-phased MX<sub>2</sub> (such as 2H-MoS<sub>2</sub>), in which an M-layer is covalently bonded to an X-layer, resulting in Bernal (ABA) stacking and belonging to the P<sub>6</sub>m2 space group. The lattice parameters and HSE06 band gaps of these structures range between 3.05 and 4.88 Å and 0.89 and 2.28 eV, respectively. The VBM and CBM values span from -5.26 to -7.94 eV and -3.85 to -5.99 eV, respectively, making these materials suitable for heterostructure photocatalysts. Note that

**Scheme 2. Overall Workflow for Identifying Z-Scheme Heterostructures in This Work<sup>a</sup>**



all 18 h-TMD materials and some of their heterostructures have already been synthesized experimentally using the universal chemical vapor deposition method.<sup>29,30</sup>

**Figure 1a** exhibits the formation of 153 vdW 2D heterostructures, which result from pairing 18 H-phase TMDs. Previous research works have indicated that stacking configurations have a minimal influence on the electronic structure of h-TMD vdW heterostructures.<sup>45–47</sup> For example, the band structure of a heterostructure is a simple superposition of 2D material layers due to the weak vdW interaction.<sup>47,48</sup> In order to discover Z-scheme heterostructures from the 153 heterostructures, it is essential to first identify their parent structures: type-II heterostructures. Thus, we classify the 153 vdW heterostructures into type-I, type-II, and type-III (Figure 1b) based on the HSE band edge of each 2D material and Anderson's rule.<sup>49</sup> Anderson's rule serves as a distinctive physical model in the data-driven discovery of 2D functional heterostructures, which are connected by weak vdW interactions, preserving their intrinsic electronic structure and weak interfacial charge transfer.<sup>50–52</sup> Figure 1b illustrates 19 type-I (straddling alignment), 112 type-II (staggered alignment), and 22 type-III (broken alignment) heterostructures from total 153 heterostructures. It is worth noting that type-I and type-III heterostructures are unsuitable for photocatalysis applications because of their charge transfer pathways, which

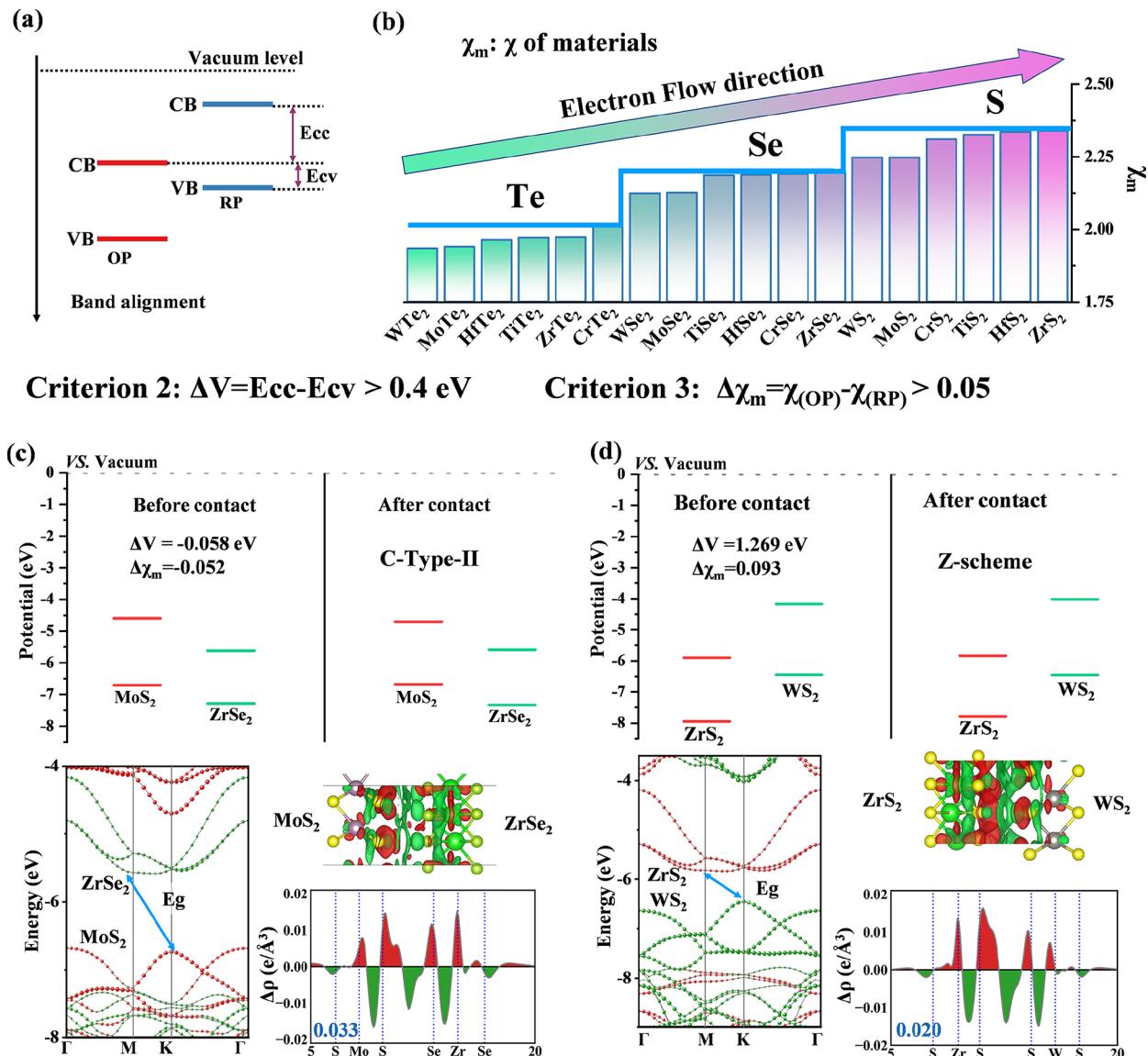


**Figure 1.** (a) Detailed diagram depicting the 153 vdW heterostructures formed by 18 individual monolayer TMDs. (b) Classification of heterostructures into three types based on Anderson's rule. Type-II heterostructures (112) are screened out in a pool for further identifying Z-scheme heterostructures.

cannot spatially separate photogenerated electrons and holes, thus not impeding their recombination. Therefore, our following study focuses exclusively on the 112 type-II band alignment heterostructures.

To accurately predict band alignment in heterostructures and identify appropriate Z-scheme candidates, we suggest the use of  $\Delta V$ , as depicted in Figure 2a, rather than utilizing  $\delta$  (or  $E_{CV}$ ) as stated in Scheme 1. This is because carriers will follow the type-II pathway if  $E_{CC}$  is smaller than  $E_{CV}$ , even in cases where  $\delta$  or  $E_{CV}$  is small. A larger value of  $\Delta V$  indicates a closer conduction band (CB) of OP to the valence band (VB) of RP and a greater distance from the CB of RP. This suggests facilitated electron transfer from the CB of OP to the VB of RP while hindering electron transfer from the CB of RP to the CB of OP. Consequently, the heterostructure is of the Z-scheme type. The value of  $\Delta V$  is critical in screening potential Z-scheme candidates. A high  $\Delta V$  may exclude relevant candidates, while an excessively low value may include non-Z-scheme candidates. As shown in Table S2, gradually increasing  $\Delta V$  ( $\Delta\chi_m$ ) from 0 (0 eV) to 1.0 eV (0.10 eV) reduces the screened Z-scheme heterostructures from 43 to 5. Upon such analysis, our results confirm that setting  $\Delta V$  above 0.6 eV may exclude many Z-scheme heterostructures, such as  $HfS_2/MoS_2$  ( $\Delta V = 0.497$  eV) and  $CrS_2/MoSe_2$ .<sup>43</sup> Conversely, setting  $\Delta V$  below 0.2 eV may include non-Z-scheme heterostructures, such as  $MoS_2/WTe_2$  ( $\Delta V = 0.08$  eV). Therefore, we rationally select  $\Delta V = 0.4$  eV as the optimized value for screening Z-scheme heterostructures (Scheme 2).

Most importantly, to predict the charge transfer direction in the heterostructure for determining the Z-scheme type, we propose a novel descriptor: Allen material electronegativity ( $\chi_m$ ), derived from Allen element electronegativity ( $\chi_e$ ).<sup>53–55</sup> Allen element electronegativity primarily relies on the average energy of the valence electrons in free atoms. The rationale for employing Allen electronegativity is the principle of energy transfer from high to low levels, including valence electron



**Figure 2.** (a) Criteria of band alignment. (b) Allen material electronegativity of 18 h-TMD materials. Calculated electronic structures of (c) MoS<sub>2</sub>/ZrSe<sub>2</sub> and (d) MoSe<sub>2</sub>/TiSe<sub>2</sub>, including HSE band structures, charge transfer difference, plane-integrated electron density difference along the vertical direction, and band alignment. The red and green regions represent electron accumulation and depletion, respectively. The isosurface value is  $\pm 0.0001 \text{ e Å}^{-3}$ . The number labeled in blue is the amount of the interlayer charge transfer calculated by the Bader charge analysis.

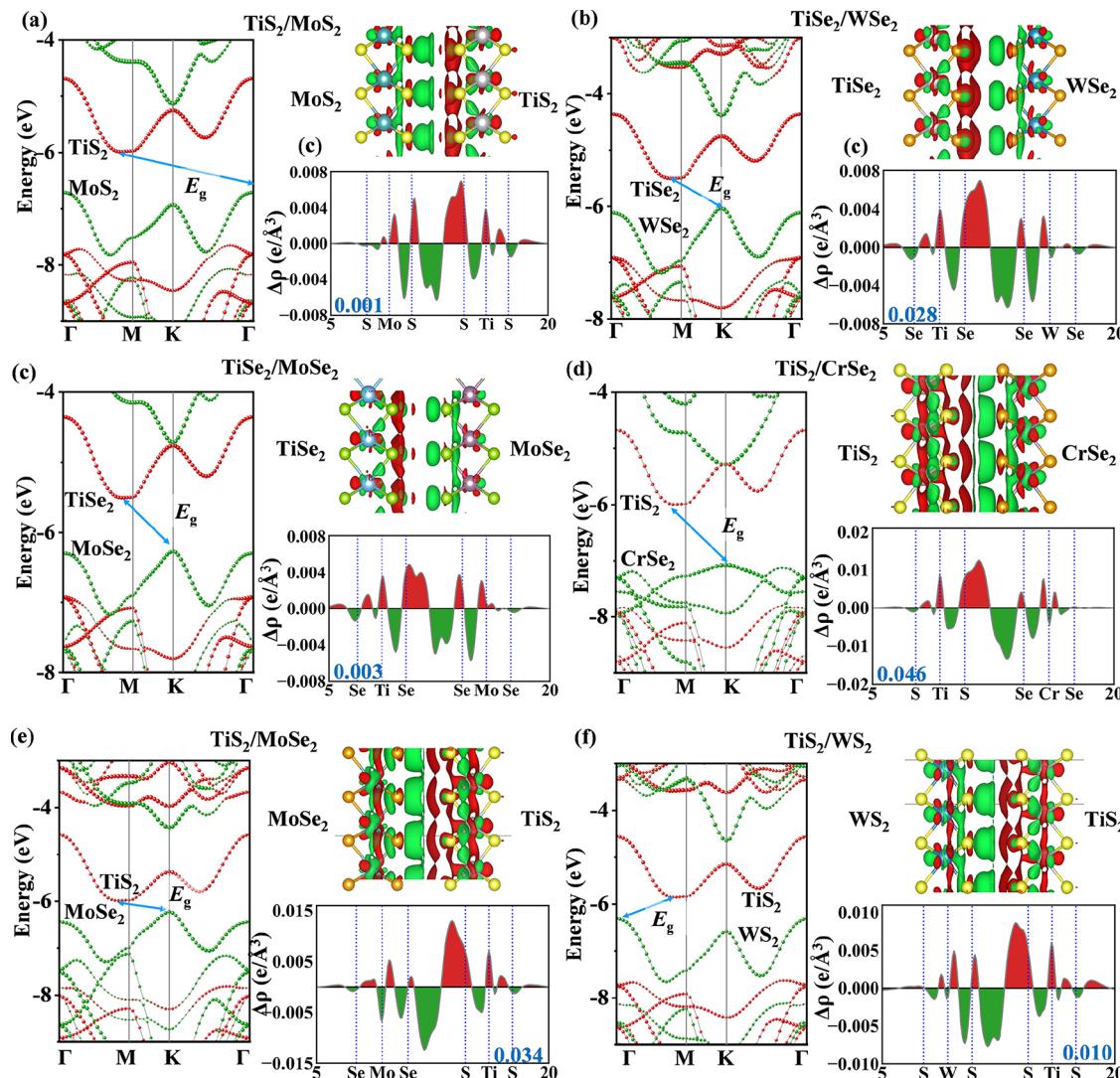
energy. The  $\chi_m$  for the 18 MX<sub>2</sub>-type h-TMD materials is calculated using the formula, as expressed,

$$\chi_m = \frac{(n_{sm}\epsilon_{sm} + n_{dm}\epsilon_{dm}) + 2(n_{sx}\epsilon_{sx} + n_{px}\epsilon_{px})}{(n_{sm} + n_{dm}) + 2(n_{sx} + n_{px})}$$

where  $\epsilon_{sm,dm,sx,px}$  are the one-electron energy of s and d electrons in the M atom and s and p electrons in the X atom, respectively.  $n_{sm,dm,sx,px}$  are the number of s and d electrons in the valence shell of M and s and p electrons in the valence shell of X, respectively. The one-electron energy can be determined directly from spectroscopic data, which are available for most elements. The number of s, p, and d electrons can be obtained through the Bader charge analysis (see in Table S3 for more details). Overall, we develop a novel method to estimate the material electronegativity.

The trend of  $\chi_m$  is that higher  $\chi_m$  corresponds to a greater tendency to attract electrons. Additionally, a larger difference in  $\chi_m$  between the two materials comprising the hetero-

structure leads to more charge transfer and a large interfacial electric field. Figure 2b presents a summary of  $\chi_m$  for 18 h-TMD materials, arranged in ascending order, and highlights the direction of electron flow in the resulting heterostructure upon contact. Note that the  $\chi_m$  trend follows the order MT<sub>2</sub> < MS<sub>2</sub> < MS<sub>2</sub>, (M = Ti, Zr, Hf, Cr, Mo, and W) due to the increased Allen element electronegativity from Te (2.158) to Se (2.424) and S (2.589), indicating that the anion has a more substantial impact on  $\chi_m$ . Therefore, the charge transfer direction can be predicted simply based on the electronegativity of surface atoms when two materials with different surface atomic elements form a heterostructure. This prediction has been validated by numerous vdW heterostructure reports, including MoSe<sub>2</sub>/SnS<sub>2</sub>, MoSe<sub>2</sub>/CrS<sub>2</sub>, MoTe<sub>2</sub>/SnS<sub>2</sub>, MoTe<sub>2</sub>/SnSe<sub>2</sub>, MoTe<sub>2</sub>/CrS<sub>2</sub>, PtSe<sub>2</sub>/WS<sub>2</sub>, MoTe<sub>2</sub>/ZrS<sub>2</sub>, MoTe<sub>2</sub>/NbSe<sub>2</sub>, and MoS<sub>2</sub>/In<sub>2</sub>Se<sub>3</sub>.<sup>43,44,56,57</sup> However, for two materials with the same surface atom, such as MoTe<sub>2</sub> and WTe<sub>2</sub>, the Allen element electronegativity is not



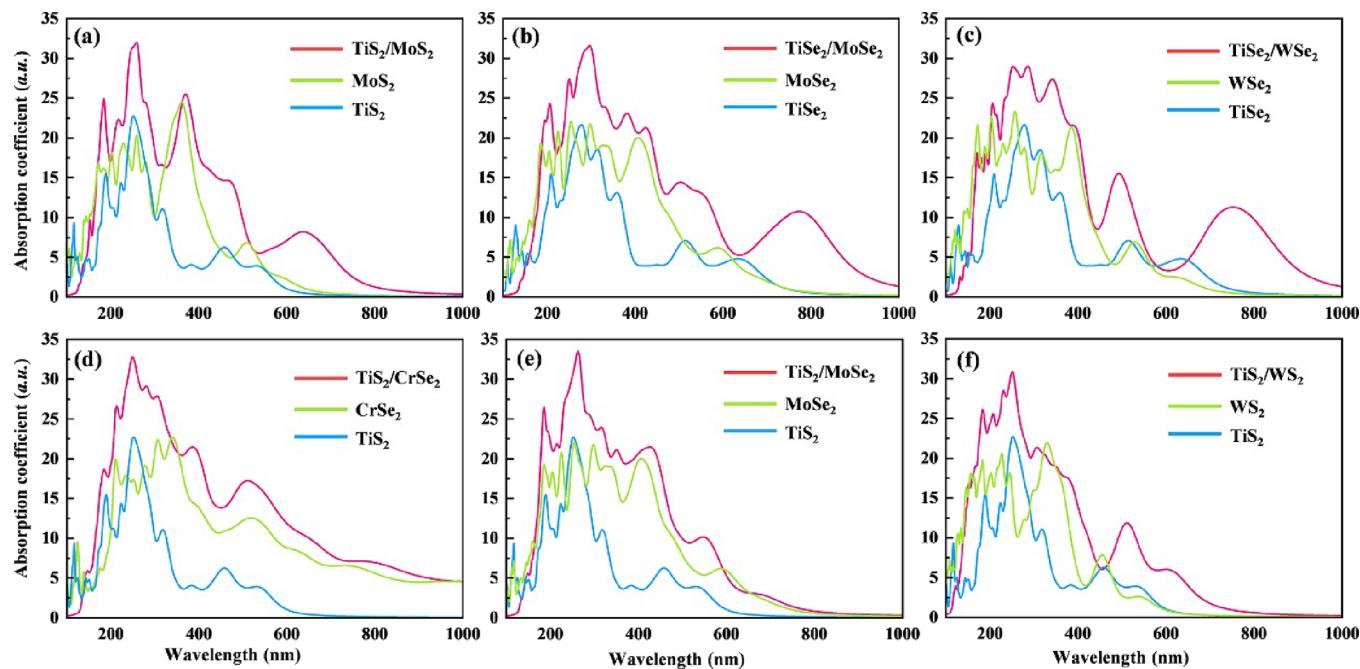
**Figure 3.** Calculated electronic structures of six identified candidates (a)  $\text{TiS}_2/\text{MoS}_2$ , (b)  $\text{TiSe}_2/\text{WSe}_2$ , (c)  $\text{TiSe}_2/\text{MoSe}_2$ , (d)  $\text{TiS}_2/\text{CrSe}_2$ , (e)  $\text{TiS}_2/\text{MoSe}_2$ , and (f)  $\text{TiS}_2/\text{WS}_2$ , including HSE band structures, charge transfer difference, and plane-integrated electron density difference along the out-of-plane direction. The red and green regions represent electron accumulation and depletion, respectively. The isosurface value is  $\pm 0.0001 e \text{\AA}^{-3}$ . The amount of the interlayer charge transfer calculated by the Bader charge analysis is highlighted in blue.

applicable, and only the universal Allen “material” electronegativity can be used to predict the trend of the charge transfer and interface electric field between these two materials.

Considering the aforementioned understanding, we propose using the material electronegativity difference of two 2D materials,  $\Delta\chi_m = \chi_{(\text{OP})} - \chi_{(\text{RP})}$ , as a descriptor for predicting the charge transfer direction in the heterostructure (Figure 2b). A larger value of  $\Delta\chi_m$  is expected to correspond to a more definite charge transfer direction from a material with lower  $\chi_m$  to one with higher  $\chi_m$ . However, if  $\Delta\chi_m$  is too small, accurately determining the electron transfer direction may be difficult. Consequently, it is crucial to select an appropriate value for reliable charge transfer direction prediction. To validate this descriptor  $\Delta\chi_m$ , we systematically calculate and analyze HSE electronic structures of 20 heterostructures out of 112 type-II vdW heterostructures (see details in Table 2). It is worth noting that the HSE calculation of supercells for all 112 heterostructures is too computing expensive. The selection criteria for the 20 heterostructures are as follows: (1) including the well-reported materials,  $\text{MoS}_2$  and  $\text{TiS}_2$  (around 25 and 15% in the 112 type-II heterostructures), (2) excluding less

commonly utilized materials, such as  $\text{TiTe}_2$ ,  $\text{ZrTe}_2$ ,  $\text{HfTe}_2$ , and  $\text{CrTe}_2$ , and (3) a uniform distribution of the 20 calculated heterostructures to the 112 heterostructures. Because of the lattice mismatch, we perform various supercell expansion combinations for different pairings to maintain the lattice mismatch within a reasonable range (-4.97 to 5.28%). Table 2 shows the 20 supercells comprising  $(1 \times 1 \times 1)(1 \times 1 \times 1)$ ,  $(2 \times 2 \times 1)(\sqrt{3} \times \sqrt{3} \times 1)$ , and  $(3 \times 3 \times 1)(\sqrt{7} \times \sqrt{7} \times 1)$  configurations, containing 6, 21, and 48 atoms in these heterostructures, respectively. Furthermore, the lattice parameters and interlayer distances of these systems range from 3.27 to 9.48  $\text{\AA}$  and 3.27 to 3.80  $\text{\AA}$ , respectively. The binding energy ( $E_b$ ) varies within a narrow range of -25.18 to -31.44 meV per atom, indicating that these heterostructures are representative vdW heterostructures.

We further conduct an in-depth study on the charge transfer and  $\Delta\chi_m$  relationship in the 20 calculated heterostructures. As shown in Table 2,  $\Delta\chi_m$  and  $\Delta Q$  range from -0.001 to 0.314 and 0.001 to 0.115  $e$ , respectively. It is worth noting that a larger  $\chi_m$  indicates a higher probability of electron transfer to the material. Moreover, the band gaps of these heterostructures



**Figure 4.** Calculated absorption coefficients of the six best Z-scheme heterostructure candidates (a)  $\text{TiS}_2/\text{MoS}_2$ , (b)  $\text{TiSe}_2/\text{MoSe}_2$ , (c)  $\text{TiSe}_2/\text{WSe}_2$ , (d)  $\text{TiS}_2/\text{CrSe}_2$ , (e)  $\text{TiS}_2/\text{MoSe}_2$ , and (f)  $\text{TiS}_2/\text{WS}_2$ .

span from 0.23 to 1.79 eV, suggesting their potential as photocatalysts with suitable energy levels for producing photogenerated carriers. It is important to note that the  $\chi_m$  of  $\text{MoS}_2$  (2.247) is close to that of  $\text{WS}_2$  (2.246), resulting in a  $\Delta\chi_m$  of 0.001. On the one hand, this tiny  $\Delta\chi_m$  makes it challenging to accurately predict the charge transfer direction between  $\text{MoS}_2$  and  $\text{WS}_2$ , consistent with our DFT calculations for this heterostructure (evidenced by a charge transfer of merely 0.001 e as determined by Bader analysis; see Table 2 and Figures S1–S12). On the other hand, a large  $\Delta\chi_m$  ( $>0.1$ ) may cause us to overlook some Z-scheme heterostructure candidates, such as the following confirmed Z-scheme heterostructures:  $\text{TiSe}_2/\text{WSe}_2$  (0.063),  $\text{TiS}_2/\text{MoS}_2$  (0.079),  $\text{TiSe}_2/\text{MoSe}_2$  (0.06),  $\text{ZrS}_2/\text{WS}_2$  (0.093), and  $\text{HfS}_2/\text{MoS}_2$  (0.088). Overall, we establish that  $\Delta\chi_m > 0.05$  is the more appropriate criterion for predicting the charge transfer direction (Scheme 2).

Figure 2c,d shows the DFT electronic structures of two representative heterostructures— $\text{MoS}_2/\text{ZrSe}_2$  as a C-type-II heterostructure and  $\text{ZrS}_2/\text{WS}_2$  as a Z-scheme heterostructure—to validate the proposed  $\Delta V$  and  $\Delta\chi_m$  descriptors. Figure 2c demonstrates that  $\text{MoS}_2/\text{ZrSe}_2$  is a typical C-type-II heterostructure due to its band alignment and charge transfer pathway. The VBM and CBM primarily consist of  $\text{MoS}_2$  and  $\text{ZrSe}_2$ , respectively, leading to a staggered band gap. Charge transfer, plane-integrated electron density difference, and Bader charge analysis all reveal that  $\text{MoS}_2$ , acting as an acceptor, gains electrons and has a VBM positioned higher than that of  $\text{ZrSe}_2$  (donor). In contrast, for  $\text{ZrS}_2/\text{WS}_2$  (Figure 2d), the VBM and CBM are composed of  $\text{WS}_2$  and  $\text{ZrS}_2$ , respectively. This heterostructure displays a staggered band gap, like  $\text{MoS}_2/\text{ZrSe}_2$ . However, electrons accumulate on the  $\text{ZrS}_2$  side (from the  $\text{WS}_2$  donor) with a lower CBM and VBM position than  $\text{WS}_2$ , resulting in charge transfer in the opposite direction of  $\text{MoS}_2/\text{ZrSe}_2$ . This observation indicates that  $\text{ZrS}_2/\text{WS}_2$  is a typically Z-scheme heterostructure.

To validate the accuracy of the screening results, we perform high-fidelity DFT calculations on these six heterostructure candidates (Scheme 2), including HSE band structures, band alignment, and charge transfer as shown in Figure 3a–f. In the case of  $\text{TiS}_2/\text{MoS}_2$  (Figure 3a), the VBM and CBM consist of  $\text{MoS}_2$  and  $\text{TiS}_2$ , respectively. The band structure of this heterostructure displays a staggered band gap. The band alignment and formation of a built-in electric field from  $\text{MoS}_2$  to  $\text{TiS}_2$  indicate that the  $\text{TiS}_2/\text{MoS}_2$  heterostructure has typical Z-scheme behavior. The other five heterostructures also display similar band alignments and built-in electric fields, suggesting that they also are Z-scheme heterostructures, validating the accuracy of descriptors.

In a short summary, the aforementioned findings indicate that using  $\Delta V$  and  $\Delta\chi_m$  to forecast band alignment and charge transfer between h-TMD 2D materials (or other 2D materials because of the universality of Allen material negativity) is highly accurate and verifiable, making it a valuable tool for quick identifying suitable combinations before contact that could potentially serve as photocatalysts. The efficacy of the proposed time-saving descriptor approach is validated by both previous reports<sup>43,44</sup> and our DFT calculations.

Optical absorption plays a crucial role in the initial stage of photocatalysis, as it offers insights into the properties of photocatalysts. Thus, we also investigate the optical absorption of the six best Z-scheme heterostructure candidates identified by descriptors. Figure 4 shows the absorption spectra of the six Z-scheme photocatalysts, and the optical absorption properties of these heterostructures have been thoroughly investigated. The optical absorption of  $\text{MoS}_2/\text{TiS}_2$ ,  $\text{TiSe}_2/\text{MoSe}_2$ , and  $\text{TiSe}_2/\text{WSe}_2$  heterostructures is enhanced in the visible-light range (300 to 600 nm) due to the small direct band gaps of  $\text{MoS}_2$  (2.10 eV),  $\text{MoSe}_2$  (1.83 eV), and  $\text{WSe}_2$  (1.96 eV) monolayers. As indirect semiconductors,  $\text{TiS}_2$  and  $\text{TiSe}_2$  monolayers contribute minimally to absorption due to their weak absorption at the absorption edge. Interlayer excitation, or the transfer of electrons from the VB of one material to the

CB of the other, may also contribute to the absorption spectra in the infrared region, as observed in MoS<sub>2</sub>/TiS<sub>2</sub>, TiSe<sub>2</sub>/MoSe<sub>2</sub>, and TiSe<sub>2</sub>/WSe<sub>2</sub> heterostructures (peaks at 641, 772, and 751 nm, respectively). However, it is worth noting that such a type of interlayer excitation is not useful for Z-scheme photocatalysts.

In contrast, the CrSe<sub>2</sub> monolayer exhibits direct semiconductor behavior with a small band gap of 1.04 eV, resulting in near-infrared light absorption (~700–1000 nm) in the CrSe<sub>2</sub>/TiS<sub>2</sub> heterostructure. TiS<sub>2</sub>/MoSe<sub>2</sub> and TiS<sub>2</sub>/WS<sub>2</sub> heterostructures exhibit strong optical absorption in the visible- and ultraviolet-light range (~200 to 700 nm), with the primary absorption dominated by MoSe<sub>2</sub> and WS<sub>2</sub> monolayers. In this context, band positions with edges are considered to evaluate the feasibility of employing these photocatalysts for water catalytic applications (Figure S13). The results indicate that all six heterostructures displayed high potential for the oxygen evolution reaction. Among them, TiSe<sub>2</sub>/WSe<sub>2</sub> and TiS<sub>2</sub>/MoSe<sub>2</sub> demonstrate the capability to concurrently perform the hydrogen evolution reaction. Overall, the optical absorption properties of Z-scheme heterostructures are enhanced in the visible-light range due to the small direct band gaps of the monolayers forming the heterostructure. The CrSe<sub>2</sub>/TiS<sub>2</sub> heterostructure exhibits near-infrared light absorption owing to the direct semiconductor behavior of the CrSe<sub>2</sub> monolayer. Note that further calculations on catalytic properties, such as the carrier mobility, exciton binding energy, and Gibbs free energy, are beyond the scope of this work, which focuses on developing descriptors to accelerate the discovery of Z-scheme vdW heterostructures. Nonetheless, we hope that our research will stimulate increased theoretical and experimental investigations into various photocatalytic applications involving Z-scheme vdW heterostructures.

## CONCLUSIONS AND OUTLOOK

In summary, through a data-driven discovery approach, we develop a descriptor method for identifying Z-scheme vdW heterostructures before contact, bypassing the need of expensive high-fidelity calculations on heterostructure supercells. Using electronic structures of dozens of experimentally synthesized monolayer 2D materials and heterostructures, we propose the Allen “material” electronegativity difference  $\Delta\chi_m$  as an efficient and effective descriptor for identifying Z-scheme heterostructures. Such a data-driven descriptor method allows us to identify 24 Z-scheme candidates, which have never been reported before. We finally screen six exceptional Z-scheme heterostructures—MoS<sub>2</sub>/TiS<sub>2</sub>, TiSe<sub>2</sub>/WSe<sub>2</sub>, TiSe<sub>2</sub>/MoSe<sub>2</sub>, CrSe<sub>2</sub>/TiS<sub>2</sub>, TiS<sub>2</sub>/WS<sub>2</sub>, and TiS<sub>2</sub>/MoSe<sub>2</sub>—all confirmed by DFT+HSE calculations. Among them, the CrSe<sub>2</sub>/TiS<sub>2</sub> heterostructure demonstrates an outstanding photocatalytic activity due to its absorption of near-infrared light. Our findings not only contribute to the accelerated discovery of highly efficient heterostructure photocatalysts but also provide a universal descriptor for exploring charge transfer in 2D material interfaces, providing guidelines for nanodevice design.

In heterostructures composed of nonlayered materials and no interfacial chemical bonding, such as oxide/nitride Z-scheme heterojunctions, the direction of charge transfer can still be discerned through a variant descriptor of Allen material electronegativity of the materials’ surface atoms, termed “Allen surface electronegativity”. This is defined by the average energy of the valence electrons of all surface atoms of the materials. It is encouraged that more computational and experimental

studies adapt Allen material/surface electronegativity to further investigate charge transfer and internal electric fields across a wider range of material interfaces, including but not limited to layered van der Waals interfaces.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.3c02315>.

Detailed calculation methods, Allen material electronegativity of single materials, predicted 27 Z-scheme heterostructures, and electronic structures of heterostructures’ band alignment of the best candidates ([PDF](#))

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### Notes

The authors declare no competing financial interest.

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