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Two-Dimensional SiH/g-C₃N₄ van der Waals Type-II Heterojunction Photocatalyst: A New Effective and Promising Photocatalytic Material

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Abstract: The two-dimensional layered heterostructure have been demonstrated as an effective method for achieving efficient photocatalytic hydrogen production. In this work, we propose, for the first time, the creation of van der Waals heterostructures from monolayers of SiH and $g-C_3N_4$ using first-principle calculations. We also systematically investigated additional properties for the first time, such as the electronic structure and optical behavior of van der Waals heterostructures composed of SiH and $g-C_3N_4$ monolayers. The results of this study show that the SiH/g-C₃N₄ heterostructure is categorized as a type-II heterostructure, which has a bandgap of 2.268 eV. Furthermore, the SiH/g-C $_3N_4$ heterostructure interface was observed to efficiently separate and transfer photogenerated charges, resulting in an enhanced photocatalytic redox performance. Moreover, the calculation of HOMO (Highest occupied molecular orbital) and LUMO (Least unoccupied molecular orbital) and charge density difference can further confirm that the $SiH/g-C_3N_4$ heterojunction is a type-II heterojunction, which has excellent photocatalytic hydrogen production and water decomposition performance. In addition, the $SiH/g-C_3N_4$ heterostructure exhibited excellent HER (Hydrogen evolution reaction) efficiency. This is essential for the process of photocatalytic water splitting. In SiH/g- C_3N_4 heterojunctions, the redox potential required for water splitting is spanned by the band edge potential. Calculating the absorption spectra, it was discovered that the $SiH/g-C_3N_4$ heterostructure possesses outstanding optical properties within the visible-light range, implying its high efficiency in photocatalytic hydrogen production. This research provides a broader research direction for the investigation of novel efficient photocatalysts and offers effective theoretical guidance for future efficient photocatalysts.

Keywords: SiH/g-C₃N₄; first principles; heterostructure; photocatalyst

1. Introduction

The utilization of easily accessible solar energy and water resources to execute the photocatalytic division of water for the production of hydrogen is a praiseworthy and ecologically sound technique. From a solar energy perspective, the photonic energy contained in the sun's rays is used, not the thermal energy. To ensure optimal results in the process of photocatalytic water splitting, it is crucial to optimize the utilization of both ultraviolet and visible solar radiation. In 1972, the decomposition of water into hydrogen using a TiO₂ monocrystalline electrode irradiated by a xenon lamp was reported for the



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). first time by Fujishima and Honda [1], thus initiating the research direction of solar-driven photocatalytic hydrogen production.

The charge transport between the interfaces of photocatalytic materials directly affects the excellent photocatalytic performance, and the interface structure dominates many behaviors of photogenerated charge carriers, which also has a direct impact on photocatalytic efficiency [2]. The heterojunction structure generated based on the interface structure modification also has a direct impact on the photocatalytic efficiency [3,4]. Two-dimensional layered materials have gained prominence in recent years, including heterostructures constructed based on them, opening up a new avenue for designing novel photocatalytic materials [5–9]. Two-dimensional materials have properties that are advantageous for photocatalysis, including a reduced frequency of carrier recombination and an increased ratio of surface area to volume. Therefore, they hold great potential for photocatalytic water splitting [10-13]. Silicane, a 2D material with a hexagonal lattice that is similar to the one found in graphene, has generated notable research interest owing to its remarkable properties. Its objective qualities make it a subject of particular importance [14]. Fully hydrogenated silicane, known as silicane (SiH), shares many of the exceptional electronic characteristics exhibited by graphene. It has been thoroughly researched, both theoretically and empirically [15–20]. Hydrogenation eliminates the conductivity of silicane, stabilizing its structure and allowing for a finite bandgap within the range of visible-light absorption, making it suitable for photocatalysis [21]. In 2014, Mang Niu et al. used computational methods to discover the potential of the SiH/TiO₂ heterostructure as a type-II heterostructure under visible-light, and the results represent a promising avenue for future research into high-performance optoelectronic devices [22]. Subsequently, other systems like GaAs/SiH [23], InSe/SiH [24], AlAs/SiH [25], and SiH/CeO₂. ZENG et al. [26] have since been shown to be type-II heterostructures, and have demonstrated outstanding photocatalytic performance in water splitting under visible-light.

A newly developed two-dimensional layered semiconductor material, $g-C_3N_4$, displays a narrow bandgap (approximately 2.7 eV), outstanding chemical and thermal stability, and is easily modifiable to achieve tunable electronic structures, making it suitable for constructing various composite photocatalysts [27–33].

In 2D materials with similar crystal structures, atomic layer spacing, and thermal stability, when stacked vertically, this "face-to-face" contact results in the formation of an internal electric field. This internal field drives the directional migration of photogenerated electrons and holes between different semiconductors. The two 2D structures in the complex form a "face-to-face" full contact by maintaining the single molecular layer material in the same van der Waals force. Their good size design and large specific surface area, such as interface properties, organically combine the advantages of each 2D material, effectively improving photocatalytic efficiency [34,35]. This is different from surface modification, and the heterojunction is an interface modification starting from the interface structure [36]. Owing to the excellent properties of SiH and the excellent lattice matching of SiH with $g-C_3N_4$, we can reasonably speculate that the SiH/g-C₃N₄ nanocomposite material might be an excellent heterostructure photocatalyst that possesses outstanding properties on its own. In this research work, through first-principles calculations, we comprehensively investigated the photocatalytic performance of a two-dimensional van der Waals heterostructure material composed of SiH and $g-C_3N_4$ for the first time, including its geometric structure, thermodynamic stability band structure, charge density difference, edge potential, Gibbs free energy, and light absorption properties. In conclusion, the computational data show that SiH/g-C₃N₄ provides a conformationally stable and well-performing type-II heterostructure that is favorable for the effective solation of photogenerated photoelectrons and holes, subsequently achieving outstanding photocatalytic outcomes.

In summary, we provided theoretical evidence that the $SiH/g-C_3N_4$ heterostructure in two dimensions is an innovative and effective photocatalyst, providing theoretical guidance for experimentalists for designing highly active catalysts in the field going forward, proving its broad research direction and application prospects. It also provides effective information for experimenters involved in high-quality semiconductor visible-light water-cracking catalysts.

2. Computational Methodology

This study employed density functional theory (DFT) for model structures and performance calculations [37], utilizing the software package Vienna Ab-initio Simulation Package (VASP 5.4.4), which was conceived by the University of Vienna. The software provides a reliable tool for research [38,39]. To ensure precision in representing long-range interactions within the density functional method, we utilized the Perdew–Burke–Ernzerhof (PBE) method of generalized gradient approximation (GGA) [40–43] for modelling the exchange correlation potential. The DFT-D3 approach was utilized to consider the feeble interlayer van der Waals interactions [44,45].

With a cutoff energy of 500 eV for the plane-wave basis, the vacuum layer along the *z*-axis was set to 15 Å. A MonkhorstPack grid with dimensions of $5 \times 5 \times 1$ was used to integrate the Brillouin zone. The total energy and forces were deemed to have converged at 10^{-6} eV and 0.01 eV/Å, respectively. However, for two-dimensional materials, the bandgap values obtained using PBE calculations significantly deviated from the experimental values of the materials themselves. To reduce this discrepancy, the electronic and optical characteristics of the material structure were calculated using a more accurate hybrid function, Hyd-Scuseria-Emzerhof2006 (HSE06) [46,47]. When parameter a is set as the default value, to better satisfy the energy gap in the experiment, the default value 0.25 is set to 0.175, and the calculation results are visualized using VESTA.

3. Results

Before examining the SiH/g-C₃N₄ heterostructure, this study systematically analyzed the geometric structure and corresponding electronic properties of individual monolayers of SiH and g-C₃N₄ molecules. Figure 1a,b shows 2D monolayers of SiH and g-C₃N₄, respectively. The lattice constants for isolated SiH and g-C₃N₄ were calculated to be 3.85 Å and 4.806 Å, respectively. The length of the Si-Si bond was also measured at 2.38 Å, while the Si-H bond was found at 1.5 Å. In addition, the bond lengths for C-N1 and C-N2 were identified as 1.32 Å and 1.42 Å, respectively. This study's observations agree with prior research [23,48–51].



Figure 1. (a) Geometrical structure of a single layer of SiH seen from above and from the side, and (b) geometrical structure of a single layer of $g-C_3N_4$ seen from above and from the side.

The band structures of the SiH and g-C₃N₄ monolayers obtained using the HSE06 functional are illustrated in Figure 1. In this figure, the black dashed line at the y-axis zero position represents the Fermi level. For the single layer of SiH in isolation, the apex of the VBM is positioned at the G point, while the nadir of the CBM is located at the K point, leading to an indirect bandgap of 2.843 eV (as shown by the arrow in Figure 2a). According to the PDOS results on the right panel of Figure 2a, it can be observed that the VBM and CBM of the isolated monolayer of SiH mainly originate from Si atoms. It can be inferred that the isolated monolayer of SiH is a semiconductor with a relatively large bandgap, which is not conducive to efficient carrier transitions. The calculated findings indicate that $g-C_3N_4$ possesses a direct bandgap of 3.5 eV (as shown by the arrow in Figure 2b). Figure 2b illustrates the band structure and PDOS of g-C₃N₄, with both VBM and CBM situated in the same spatial position. During electron transitions, the generated electrons and electron holes absorb energy, categorizing g-C₃N₄ as a direct bandgap semiconductor. From the band structures and PDOS of these two 2D materials, it can be preliminarily inferred that they do not possess the ability for photocatalytic hydrogen production. Therefore, we further investigated the 2D SiH/g- C_3N_4 heterostructure.



Figure 2. (a) Band structure (**left panel**) and Density of States (PDOS, **right panel**) of the monolayer of SiH, and (b) Band structure (**left panel**) and Density of States (PDOS, **right panel**) of the monolayer of $g-C_3N_4$.

Considering various factors, we chose to form a heterostructure with a two-dimensional monolayer of SiH and g-C₃N₄, aiming to compensate for the deficiencies caused by the individual materials in photocatalytic hydrogen production and water splitting. As shown in Figure 3, to construct a matched periodic interface in the SiH/g-C₃N₄ heterostructure, SiH (2 × 2) was stacked with g-C₃N₄ ($\sqrt{3} \times \sqrt{3}$). After structural optimization, the SiH/g-C₃N₄ heterostructure's lattice constant is 7.89 Å, with a lattice mismatch of less than 0.5%, all within a controllable range. To improve the durability assessment of the SiH/g-C₃N₄ heterostructure model, we calculated the interface binding energy Δ E:

$$\Delta E = E_{\text{whole}} - E_{\text{SiH}} - E_{\text{g-}C_3N_4} \tag{1}$$

In this context, the energies of the SiH/g-C₃N₄ heterostructure, SiH, and g-C₃N₄ monolayers are represented by E_{whole} , E_{SiH} , and E_{g-C3N4} , respectively. In the SiH/g-C₃N₄ heterojunction model, the binding energy of the supercell is -0.39 eV, and the binding energy of the cellular is -0.0975 eV. Typically, a lower binding energy indicates greater stability of the model's structure [52]. Thus, the binding energy of -0.39 eV suggests that the SiH/g-C₃N₄ heterostructure model has a certain energy advantage and is structurally stable.

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Figure 3. The SiH/g-C₃N₄ heterostructure is shown in both the top and side views.

To confirm the theoretical and practical research value of the SiH/g-C₃N₄ heterostructure under study, we conducted a deeper validation of its structural stability using thermodynamic (AIMD) and dynamic (PHONOPY) approaches. As shown in Figure 4a, we expanded the supercell to 2×2 in our study. In Figure 4b, it can be observed that after continuous heating for 3.0 ps at room temperature, the structural integrity of the SiH/g-C₃N₄ heterostructure model remains intact, and there are no occurrences of bond breakage. Furthermore, the results of calculating the dynamic stability, as shown in Figure 4c, show that the majority of the phonon branch frequencies in the Brillouin zone are positive, with some negligible imaginary frequencies [53,54]. This further verified the stability of the SiH/g-C₃N₄ heterostructure for research purposes.



Figure 4. (a) View from the top of the 2×2 supercell heterostructure of SiH/g-C₃N₄. (b) Variation curve of total potential energy during molecular dynamics simulation, where the temperature was set at 300 K. (c) Calculated phonon dispersion spectrum.

We acquired the SiH/g-C₃N₄ heterostructure's projected band structure, PDOS, HOMO, and LUMO outcomes via HSE06 calculations, as demonstrated in Figure 5. In the projected band structure, there is a band overlap visible on the left-hand side of Figure 5. Analyzing the PDOS plot in the middle panel of Figure 5, we find that SiH contributes signif-

icantly to the VBM, whereas $g-C_3N_4$ plays an important role in the CBM. This suggests that the VBM and CBM of the SiH/g-C₃N₄ heterostructure arise in separate components, thus confirming its classification as a typical type-II heterostructure. Furthermore, the band gap of the SiH/g-C₃N₄ heterostructure was computed to be 2.268 eV (as shown by the arrow in the left panel of Figure 5), indicating a lower value than that of the separate SiH and g-C₃N₄ monolayers. This enhanced the chemical activity of the SiH/g-C₃N₄ heterostructure by facilitating electronic transitions between its valence and conduction bands.



Figure 5. Presents the electronic structure of the SiH/g-C₃N₄ heterostructure. The band structure (**left panel**), PDOS (**middle panel**), LUMO, and HOMO (**right panel**) are displayed.

Additionally, we computed the charge densities of the LUMO and HOMO of the SiH/g-C₃N₄ heterostructures. The right-hand section of Figure 5 clearly illustrates the results. The SiH monolayer contributes to the HOMO, whereas g-C₃N₄ primarily produces the LUMO. This aligns with the information obtained from the band structure and PDOS calculations, confirming that in the SiH/g-C₃N₄ heterostructure, the VBM is composed of a SiH monolayer, and the CBM is contributed by the g-C₃N₄ monolayer.

In conclusion, in the SiH/g-C₃N₄ heterostructure, the charge carriers created by light move from the valence band maximum originating from the SiH layer to the conduction band minimum associated with the g-C₃N₄ layer. This creates a spatial potential gradient that stimulates the splitting of electron-hole pairs created through light absorption at a particular location. Hence, this type-II SiH/g-C₃N₄ heterostructure effectively broadens light absorption, facilitates photogenerated charge separation and transport, and enhances photocatalytic redox capabilities, ultimately achieving efficient photocatalytic hydrogen production.

The hydrogen atom adsorption activity during the hydrogen evolution reaction (HER) process for photocatalytic water splitting, resulting in hydrogen production, was investigated to enhance the credibility of the photocatalytic function of the SiH/g-C₃N₄ heterostructure. The reaction process for HER can be represented as follows:

$$\mathrm{H}^{+} + \mathrm{e}^{-} + \ast \to \mathrm{H} \tag{2}$$

$$H \to 1/2H_2 \tag{3}$$

Here, * denotes the SiH/g-C₃N₄ heterostructure, and its surface sites are available for free adsorption in this study, while H* represents the material with adsorbed H ions at the top. The Gibbs free energy (Δ G) of the intermediate state may be expressed as shown [55]:

$$\Delta G = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S \tag{4}$$

Here, the adsorption energy of hydrogen for each of the intermediate reactions is given by ΔE_{ads} , ΔE_{ZPE} , and ΔS , the zero-point energy (ZPE) for hydrogen adsorption on H₂, and the entropy (ΔS), respectively. The overall temperature (T) in this study was set to 298.15 K. If ΔG is close to zero, then the catalyst can achieve a faster hydrogen evolution efficiency [56,57]. In this study, hydrogen evolution reactions were performed on the carbon and nitrogen atoms of the SiH/g-C₃N₄ heterostructure. The ΔG values obtained from the reaction results are shown in Figure 6. The value of ΔG was calculated to be 1.578 eV for the hydrogen evolution reaction on the carbon atom, whereas, for the reaction on the N atom, ΔG is calculated to be 0.734 eV.



Reaction corrdinate

Figure 6. Presents the hydrogen evolution Gibbs free energy diagrams of the C and N atoms of the SiH/g-C₃N₄ heterostructure (T = 298.15 K).

These findings suggest that the nitrogen atom serves as a more suitable adsorption site for the hydrogen evolution reaction on the SiH/g-C₃N₄ heterostructure when compared to the carbon atom. For the nitrogen atom to react, the Gibbs free energy, which is the adsorption point on the SiH/g-C₃N₄ heterostructure, was calculated, and it was the smallest and closest to zero. Therefore, the SiH/g-C₃N₄ heterostructure possesses the capability for photocatalytic water splitting and holds promising prospects for practical hydrogen production, especially when the hydrogen evolution reaction takes place on the nitrogen atom.

The band-edge potentials of the SiH monolayer, g-C₃N₄ monolayer, and SiH/g-C₃N₄ heterostructure were calculated and compared with the standard hydrogen electrolyte using Figure 7a. Their VBM (CBM) potentials relative to the normal hydrogen electrode are 1.29 (-1.62) eV, 2.1 (-1.38) eV, and 1.26 (-1.38) eV, respectively. From the graph, it is evident that the bandgaps of these materials span the redox potentials for water decomposition, with the oxidation potential of water (E_{o_2/H_2O}) being 1.23 eV and the reduction potential of water (E_{H^+/H_2}) being 0 eV. This indicates that photocatalytic water splitting redox reactions can be effectively carried out on the SiH/g-C₃N₄ heterostructure.



Figure 7. (a) Shows the band edge potentials of the SiH monolayer, $g-C_3N_4$ monolayer, and SiH/g-C₃N₄ heterostructure relative to the normal hydrogen electrode. (b) Interface charge transfer diagram of the SiH/g-C₃N₄ heterojunction.

In addition, we sketch the charge transfer between the SiH/g-C₃N₄ heterojunction interfaces and the principle of photocatalysis in Figure 7b. First, the electrons in the VBM layer in SiH and g-C₃N₄ were photoexcited and transitioned to the CBM layer, and the holes remained in the VBM. Then, under the driving force of the valence band shift (VBO) and conduction band shift (CBO), photogenerated electrons and holes are collected on the CBM of g-C₃N₄ and VBM of SiH, respectively, and the effective separation of electrons and holes is realized. In addition, the recombination of photogenerated carriers can be alleviated within a certain range. In turn, the electrons and holes generated by photoexcitation can be applied to a great extent in the REDOX reaction, which also allows the hydrogen evolution and oxygen evolution reactions to be effectively carried out independently on different components, thus greatly improving the efficiency of photocatalysis.

In addition to the mentioned characteristics, further research and analysis are needed for the properties of the heterojunction interface. The charge density distribution can reflect the distribution of electrons in the entire lattice space in an equilibrium system and intuitively represent information such as the direction of electron transfer and bonding between different atoms. Therefore, we plotted Figure 8 based on the calculation results. In (a), a 3D plot is shown to illustrate the variation in the charge density. The corresponding function curve of the average difference in the charge density at different positions along the *z*-axis is also shown. The method for calculating the 3D charge density is as follows:

$$\Delta \rho = \rho_{\text{SiH}/\text{g-C}_3\text{N}_4} - \rho_{\text{SiH}} - \rho_{\text{g-C}_3\text{N}_4} \tag{5}$$

Here, $\rho_{SiH/g-C_3N_4}$, ρ_{SiH} , and $\rho_{g-C_3N_4}$ represent the charge densities of the SiH/g-C₃N₄ heterostructure, SiH monolayer, and g-C₃N₄ monolayer, respectively. This is shown in Figure 8a,b from the planar and 3D differences in charge density. At the interface of the SiH/g-C₃N₄ heterostructure, especially in the positive x-direction from SiH, charge transfer is significantly active. This illustrates the SiH/g-C₃N₄ heterostructure's excellent chemical activity. The separation and transfer of photogenerated charges can effectively operate in the SiH/g-C₃N₄ heterostructure. From Bader's calculations in Table 1, it is clear that 0.013 electrons were transferred from the SiH layer to the g-C₃N₄ layer. Furthermore, the nitrogen atoms located within the g-C₃N₄ layer have the capability to hold an average of 1.1637 electrons, indicating the existence of a SiH/g-C₃N₄ heterojunction. The N atom symbolizes the active centre site in the g-C₃N₄ layer.



Figure 8. (a) Displays the outcomes of the planar average charge density difference and 3D charge density difference for the $SiH/g-C_3N_4$ heterojunction. The regions in yellow and blue–green depict electron accumulation and depletion, respectively. (b) the diagram shows the average electrostatic potential across the surface of the $SiH/g-C_3N_4$ heterostructure.

Table 1. The Bader charge analysis of SiH, g-C₃N₄ monolayer, and SiH/g-C₃N₄ vdW heterojunctions.

Structure	SiH		g-C ₃ N ₄		SiH/g-C ₃ N ₄	
Bader	Si	-0.5782	С	-1.5502	SiH	-0.013
charge (e)	Н	0.5766	Ν	1.1637	$g-C_3N_4$	0.013

Optical properties are essential for the photocatalysts to perform well, besides the electronic and interfacial properties stated earlier. The electronic structure of photocatalytic materials determines properties such as the generation, recombination, and transport of photoinduced carriers, whereas the optical properties directly determine the material's absorption of incident light, which is the first crucial step in photocatalytic reactions. Most of the capacity of the solar spectrum is concentrated in the visible-light and infrared light regions, so the calculation and confirmation of the utilization of sunlight by the optical absorption spectrum plays a very important role in the photocatalytic decomposition of water. Figure 9 illustrates the optical absorption spectra of the SiH monolayer, $g-C_3N_4$ monolayer, and SiH/g-C₃N₄ heterostructure calculated using the HSE06 method. As can be seen in Figure 9, the g- C_3N_4 monolayer shows the highest absorption peak in the ultraviolet region, while it absorbs very little of the visible-light. The SiH monolayer, on the other hand, shows commendable light absorption capabilities in the visible range. The SiH/g-C₃N₄ heterostructure shows superior light absorption in the visible region over the SiH and g-C3N4 monolayers after heterostructure construction. Thus, it is evident that the ability of g-C₃N₄ to capture visible-light is enhanced by the modification and support of the SiH. Hence, the $SiH/g-C_3N_4$ heterostructure shows considerable potential as a photocatalyst for utilizing visible-light during the process of water splitting. Its vast potential positions it as a suitable research candidate for further investigation in this field.



Figure 9. Displays the optical absorption spectra of SiH, $g-C_3N_4$, and the SiH/ $g-C_3N_4$ heterostructure. The colored band region represents the absorption range of visible-light.

4. Conclusions

In summary, a photocatalyst composed of a monolayer of SiH and g-C₃N₄ in a van der Waals heterostructure was examined through first-principles calculations for the first time. Analysis of the band structure and electronic properties reveals that the SiH/g-C₃N₄ heterostructure is a conventional type-II heterostructure. The material possesses a direct bandgap of 2.268 eV, allowing for the spatial separation of photoinduced electrons and holes. Furthermore, molecular dynamics simulations and phonon dispersion calculations demonstrated the stability of the SiH/g-C₃N₄ heterostructure studied in this research. Moreover, the calculated ΔG values for the adsorption points on N atoms in the SiH/g-C₃N₄ heterostructure were lower and closer to zero, indicating excellent catalytic ability for hydrogen production and water reduction. Additionally, the interfacial properties of the SiH/g-C₃N₄ heterostructure were calculated. These results indicate that there is a spatial potential difference on each side of the interface that drives a significant amount of electrons from g- C_3N_4 to SiH. This study highlights the exceptional potential of the $SiH/g-C_3N_4$ heterostructure as a photocatalyst for the efficient separation and transfer of photoinduced charges, and it also exhibits efficient photocatalytic capabilities for producing hydrogen by splitting water. These research findings provide feasible directions for future experimental researchers to design efficient and high-quality semiconductor photocatalysts. It also provides a feasible direction for the development of green energy in the future.

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References

- 1. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38. [CrossRef]
- Qian, G.; Mao, Y.; Shuai, Y.; Zeng, Z.; Peng, S.; Shuai, C. Enhancing bone scaffold interfacial reinforcement through in situ growth of metal–organic frameworks (MOFs) on strontium carbonate: Achieving high strength and osteoimmunomodulation. *J. Colloid Interface Sci.* 2024, 655, 43–57. [CrossRef]
- 3. Khan, A.; Nilam, B.; Rukhsar, C.; Sayali, G.; Mandlekar, B.; Kadam, A. A review article based on composite graphene @tungsten oxide thin films for various applications. *Tungsten* **2023**, *5*, 391–418. [CrossRef]
- Gao, J.-X.; Tian, W.-J.; Zhang, H.-Y. Progress of Nb-containing catalysts for carbon dioxide reduction: A minireview. *Tungsten* 2022, 4, 284–295. [CrossRef]
- Tao, J.; Xu, L.; Shao, J.; Li, C.; Cao, L.; Xiong, S.; Dong, K.; Wang, L.-L.; Zhang, Y.; Xu, Z. Two-dimensional AlN/TMOs van der Waals heterojunction as promising photocatalyst for water splitting driven by visible light. *Phys. Chem. Chem. Phys.* 2023, 25, 30924–30933. [CrossRef]
- Su, T.; Qin, Z.; Ji, H.; Wu, Z. An overview of photocatalysis facilitated by 2D heterojunctions. *Nanotechnology* 2019, 30, 502002. [CrossRef]
- Wu, Z.; Qi, J.; Wang, W.; Zeng, Z.; He, Q. Emerging elemental two-dimensional materials for energy applications. J. Mater. Chem. A 2021, 9, 18793–18817. [CrossRef]
- Xu, L.; Zeng, Q.; Xiong, S.; Zhang, Y.; Cao, L.; Tao, J.; Li, Z.; Wang, L.-L.; Dong, K. Two-dimensional MoSe₂/PtSe₂ van der Waals type-II heterostructure: Promising visible light photocatalyst for overall water splitting. *Int. J. Hydrogen Energy* 2024, *50*, 352–364. [CrossRef]
- 9. Tang, S.; Xu, L.; Dong, K.; Wang, Q.; Zeng, J.; Huang, X.; Li, H.; Xia, L.; Wang, L. Curvature effect on graphene-based Co/Ni single-atom catalysts. *Appl. Surf. Sci.* 2023, 615, 156357. [CrossRef]
- 10. Novoselov, K.; Mishchenko, A.; Carvalho, A.; Castro Neto, A. 2D materials and van der Waals heterostructures. *Science* **2016**, *353*, aac9439. [CrossRef]
- 11. Su, T.; Shao, Q.; Qin, Z.; Guo, Z.; Wu, Z. Role of interfaces in two-dimensional photocatalyst for water splitting. *ACS Catal.* 2018, *8*, 2253–2276. [CrossRef]
- 12. Mu, X.; Wang, J.; Sun, M. Two-dimensional black phosphorus: Physical properties and applications. *Mater. Today Phys.* **2019**, *8*, 92–111. [CrossRef]
- Xu, L.; Li, C.; Xiong, S.; Tang, S.; Xu, Z.; Cao, L.; Tao, J.; Zhang, Y.; Dong, K.; Wang, L.-L. The bicomponent synergistic Mo_xW₁xS₂/Aluminum nitride vdW heterojunction for enhanced photocatalytic hydrogen evolution: A first principles study. *Phys. Chem. Chem. Phys.* 2024, 26, 2973–2985. [CrossRef] [PubMed]
- 14. Wang, S.; Wang, C.; Pan, W.; Sun, W.; Yang, D. Two-Dimensional Silicon for (Photo) Catalysis. *Sol. RRL* 2021, *5*, 2000392. [CrossRef]
- 15. Qiu, J.; Fu, H.; Xu, Y.; Zhou, Q.; Meng, S.; Li, H.; Chen, L.; Wu, K. From silicene to half-silicane by hydrogenation. *ACS Nano* 2015, *9*, 11192–11199. [CrossRef] [PubMed]
- 16. Houssa, M.; Scalise, E.; Sankaran, K.; Pourtois, G.; Afanas'Ev, V.; Stesmans, A. Electronic properties of hydrogenated silicene and germanene. *Appl. Phys. Lett.* 2011, *98*, 223107. [CrossRef]
- 17. Wei, W.; Dai, Y.; Huang, B.; Jacob, T. Many-body effects in silicene, silicane, germanene and germanane. *Phys. Chem. Chem. Phys.* **2013**, *15*, 8789–8794. [CrossRef]
- 18. Vogt, P.; De Padova, P.; Quaresima, C.; Avila, J.; Frantzeskakis, E.; Asensio, M.C.; Resta, A.; Ealet, B.; Le Lay, G. Silicene: Compelling experimental evidence for graphenelike two-dimensional silicon. *Phys. Rev. Lett.* **2012**, *108*, 155501. [CrossRef]
- 19. Fleurence, A.; Friedlein, R.; Ozaki, T.; Kawai, H.; Wang, Y.; Yamada-Takamura, Y. Experimental evidence for epitaxial silicene on diboride thin films. *Phys. Rev. Lett.* **2012**, *108*, 245501. [CrossRef]
- 20. Aizawa, T.; Suehara, S.; Otani, S. Silicene on zirconium carbide (111). J. Phys. Chem. C 2014, 118, 23049–23057. [CrossRef]
- 21. Hu, W.; Li, Z.; Yang, J. Water on silicene: A hydrogen bond-autocatalyzed physisorption–chemisorption–dissociation transition. *Nano Res.* **2017**, *10*, 2223–2233. [CrossRef]
- 22. Niu, M.; Cheng, D.; Cao, D. SiH/TiO₂ and GeH/TiO₂ heterojunctions: Promising TiO₂-based photocatalysts under visible light. *Sci. Rep.* **2014**, *4*, 4810. [CrossRef]
- 23. Han, S.; Li, Y.; Chai, J.; Wang, Z. Study of the GaAs/SiH van der Waals type-II heterostructure: A high efficiency photocatalyst promoted by a built-in electric field. *Phys. Chem. Chem. Phys.* **2020**, *22*, 8565–8571. [CrossRef]
- 24. Sheng, W.; Xu, Y.; Liu, M.; Nie, G.; Wang, J.; Gong, S. The InSe/SiH type-II van der Waals heterostructure as a promising water splitting photocatalyst: A first-principles study. *Phys. Chem. Chem. Phys.* **2020**, *22*, 21436–21444. [CrossRef]
- 25. Han, S.; Li, Y.; Wang, Z. AlAs/SiH van der Waals heterostructures: A promising photocatalyst for water splitting. *Phys. E Low-Dimens. Syst. Nanostruct.* **2021**, 134, 114869. [CrossRef]
- Zeng, J.; Xu, L.; Luo, X.; Peng, B.; Ma, Z.; Wang, L.-L.; Yang, Y.; Shuai, C. A novel design of SiH/CeO₂ (111) van der Waals type-II heterojunction for water splitting. *Phys. Chem. Chem. Phys.* 2021, 23, 2812–2818. [CrossRef]
- 27. Chu, Y.-C.; Lin, T.-J.; Lin, Y.-R.; Chiu, W.-L.; Nguyen, B.-S.; Hu, C. Influence of P, S, O-Doping on g-C₃N₄ for hydrogel formation and photocatalysis: An experimental and theoretical study. *Carbon* **2020**, *169*, 338–348. [CrossRef]
- Ortega, J.; Sankey, O.F. Relative stability of hexagonal and planar structures of hypothetical C₃N₄ solids. *Phys. Rev. B* 1995, 51, 2624. [CrossRef]

- Zheng, Y.; Jiao, Y.; Chen, J.; Liu, J.; Liang, J.; Du, A.; Zhang, W.; Zhu, Z.; Smith, S.C.; Jaroniec, M. Nanoporous graphitic-C₃N₄@carbon metal-free electrocatalysts for highly efficient oxygen reduction. *J. Am. Chem. Soc.* 2011, 133, 20116–20119. [CrossRef]
- Liao, G.; Gong, Y.; Zhang, L.; Gao, H.; Yang, G.-J.; Fang, B. Semiconductor polymeric graphitic carbon nitride photocatalysts: The "holy grail" for the photocatalytic hydrogen evolution reaction under visible light. *Energy Environ. Sci.* 2019, 12, 2080–2147. [CrossRef]
- Hu, Z.; Zhou, J.; Ai, Y.; Liu, L.; Qi, L.; Jiang, R.; Bao, H.; Wang, J.; Hu, J.; Sun, H.-B. Two dimensional Rh/Fe₃O₄/g-C₃N₄-N enabled hydrazine mediated catalytic transfer hydrogenation of nitroaromatics: A predictable catalyst model with adjoining Rh. *J. Catal.* 2018, 368, 20–30. [CrossRef]
- 32. Guo, Y.; Yang, J.; Zhuang, J.; Sun, H.; Zhang, H.; Yue, Y.; Zhu, H.; Bao, X.; Yuan, P. Selectively catalytic hydrogenation of styrene-butadiene rubber over Pd/g-C₃N₄ catalyst. *Appl. Catal. A Gen.* **2020**, *589*, 117312. [CrossRef]
- Ran, J.; Guo, W.; Wang, H.; Zhu, B.; Yu, J.; Qiao, S.Z. Metal-free 2D/2D phosphorene/g-C₃N₄ Van der Waals heterojunction for highly enhanced visible-light photocatalytic H2 production. *Adv. Mater.* 2018, *30*, 1800128. [CrossRef]
- Low, J.; Yu, J.; Jaroniec, M.; Wageh, S.; Al-Ghamdi, A.A. Heterojunction photocatalysts. *Adv. Mater.* 2017, 29, 1601694. [CrossRef] [PubMed]
- 35. Ren, K.; Sun, M.; Luo, Y.; Wang, S.; Yu, J.; Tang, W. First-principle study of electronic and optical properties of two-dimensional materials-based heterostructures based on transition metal dichalcogenides and boron phosphide. *Appl. Surf. Sci.* **2019**, 476, 70–75. [CrossRef]
- Ralls, A.M.; Kasar, A.K.; Daroonparvar, M.; Siddaiah, A.; Kumar, P.; Kay, C.M.; Misra, M.; Menezes, P.L. Effect of Gas Propellant Temperature on the Microstructure, Friction, and Wear Resistance of High-Pressure Cold Sprayed Zr702 Coatings on Al6061 Alloy. *Coatings* 2022, 12, 263. [CrossRef]
- Yan, Y.-G.; Lu, D.; Wang, K. Overview: Recent studies of machine learning in phase prediction of high entropy alloys. *Tungsten* 2023, 5, 32–49. [CrossRef]
- Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* 1996, 6, 15–50. [CrossRef]
- 39. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 1999, 59, 1758. [CrossRef]
- 40. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865. [CrossRef]
- 41. Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. Phys. Rev. B 1993, 47, 558. [CrossRef]
- 42. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev.* B **1996**, *54*, 11169. [CrossRef] [PubMed]
- 43. Tran, F.; Blaha, P. Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. *Phys. Rev. Lett.* **2009**, *102*, 226401. [CrossRef] [PubMed]
- 44. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104. [CrossRef] [PubMed]
- 45. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799. [CrossRef] [PubMed]
- 46. Heyd, J.; Scuseria, G.E.; Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* 2003, 118, 8207–8215. [CrossRef]
- 47. Feng, J.; Xiao, B. Crystal structures, optical properties, and effective mass tensors of CH₃NH₃PbX₃ (X = I and Br) phases predicted from HSE06. *J. Phys. Chem. Lett.* **2014**, *5*, 1278–1282. [CrossRef]
- Ma, Z.; Xu, L.; Dong, K.; Chen, T.; Xiong, S.; Peng, B.; Zeng, J.; Tang, S.; Li, H.; Huang, X. GaN/Surface-modified graphitic carbon nitride heterojunction: Promising photocatalytic hydrogen evolution materials. *Int. J. Hydrogen Energy* 2022, 47, 7202–7213. [CrossRef]
- 49. Zhu, B.; Zhang, J.; Jiang, C.; Cheng, B.; Yu, J. First principle investigation of halogen-doped monolayer g-C₃N₄ photocatalyst. *Appl. Catal. B Environ.* **2017**, 207, 27–34. [CrossRef]
- 50. Cheng, Y.; Song, Y.; Zhang, Y. A systematic investigation of the catalytic performances of monolayer carbon nitride nanosheets C_{1-x}N_x. *Phys. Chem. Chem. Phys.* **2020**, *22*, 6772–6782. [CrossRef]
- Han, S.; Li, Y.; Wang, Z. PtSe₂/SiH van der Waals type-II heterostructure: A high efficiency photocatalyst for water splitting. *Phys. Chem. Chem. Phys.* 2020, 22, 17145–17151. [CrossRef] [PubMed]
- 52. Xu, L.; Huang, W.-Q.; Wang, L.-L.; Huang, G.-F.; Peng, P. Mechanism of superior visible-light photocatalytic activity and stability of hybrid Ag₃PO₄/graphene nanocomposite. *J. Phys. Chem. C* **2014**, *118*, 12972–12979. [CrossRef]
- Zólyomi, V.; Drummond, N.; Fal'Ko, V. Electrons and phonons in single layers of hexagonal indium chalcogenides from ab initio calculations. *Phys. Rev. B* 2014, *89*, 205416. [CrossRef]
- 54. Wang, Z.; Zhou, G. Lattice-strain control of flexible janus indium chalcogenide monolayers for photocatalytic water splitting. *J. Phys. Chem. C* 2019, 124, 167–174. [CrossRef]
- 55. Wang, X.; Tian, H.; Pi, M.; Zhang, D.; Chen, S. Tuning the electronic structure of NiSe₂ nanosheets by Mn dopant for hydrogen evolution reaction. *Int. J. Hydrogen Energy* **2020**, *45*, 12237–12243. [CrossRef]

- 56. Nørskov, J.K.; Bligaard, T.; Logadottir, A.; Kitchin, J.; Chen, J.G.; Pandelov, S.; Stimming, U. Trends in the exchange current for hydrogen evolution. *J. Electrochem. Soc.* **2005**, *152*, J23. [CrossRef]
- 57. Banu, A.A.; Karazhanov, S.Z.; Kumar, K.V.; Jose, S.P. Platinum doped iron carbide for the hydrogen evolution reaction: The effects of charge transfer and magnetic moment by first-principles approach. *Int. J. Hydrogen Energy* **2020**, *45*, 31825–31840. [CrossRef]

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