g-C$_3$N$_4$/SnS$_2$ Heterostructure: a Promising Water Splitting Photocatalyst

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Graphite-like carbon nitride (g-C$_3$N$_4$) based heterostructures has attracted intensive attention due to their prominent photocatalytic performance. Here, we explore the g-C$_3$N$_4$/SnS$_2$ coupling effect on the electronic structures and optical absorption of the proposed g-C$_3$N$_4$/SnS$_2$ heterostructure through performing extensive hybrid functional calculations. The obtained geometric structure, band structures, band edge positions and optical absorptions clearly reveal that the g-C$_3$N$_4$ monolayer weakly couples to SnS$_2$ sheet, and forms a typical van der Waals heterojunction. The g-C$_3$N$_4$/SnS$_2$ heterostructure can effectively harvest visible light, and its valence band maximum and conduction band minimum locate in energetically favorable positions for both water oxidation and reduction reactions. Remarkably, the charge transfer from the g-C$_3$N$_4$ monolayer to SnS$_2$ sheet leads to the built-in interface polarized electric field, which is desirable for the photogenerated carrier separation. The built-in interface polarized electric field as well as the nice band edge alignment implies that the g-C$_3$N$_4$/SnS$_2$ heterostructure is a promising g-C$_3$N$_4$ based water splitting photocatalyst with good performance.

Key words: First-principles calculation, Coupling effect, Optical absorption, Band edge alignment, Water splitting

I. INTRODUCTION

Hydrogen, produced from water splitting by using renewable solar energy, is an ultimately clean energy and plays a vital role in solving the energy crisis caused by the depletion of fossil fuels and the serious environment problems [1, 2]. Since the pioneering work carried out by Fujishima and Honda that overall water splitting can be achieved via the photocatalyst of TiO$_2$ [3], photocatalytic water splitting has been intensively investigated in the past years [4–8]. Till now, over 130 semiconductor materials, including SrTiO$_3$ [39], Ag$_3$PO$_4$ [10], NaTaO$_3$ [11], and CdS [12], have been widely studied as promising photocatalysts. However, the practical application of photocatalytic water splitting for hydrogen production is limited, since most of photocatalysts are active only under ultraviolet (UV) irradiation (i.e., SrTiO$_3$ and NaTaO$_3$), where others (i.e., Ag$_3$PO$_4$ and CdS) are not stable during the photocatalytic process although they are capable of harvesting visible light. Hence, developing high efficiency and stable photocatalysts for water splitting aspects are theoretically and experimentally needed.

Metal-free photocatalysts have the advantages of nontoxicity and good process ability, and gradually become important catalysts. In 2009, Wang et al. reported that graphite-like carbon nitride (g-C$_3$N$_4$) can produce hydrogen from water under visible light irradiation in the presence of a sacrificial donor [13]. It has attracted intensive attention because of its high chemical and thermal stability, promising electronic properties, and low cost. However, the energy conversion efficiency of the incoming solar energy is low due to the marginal visible light absorption. The g-C$_3$N$_4$ can only absorb the photons with wavelength shorter than 450 nm. Moreover, g-C$_3$N$_4$ suffers from a high recombination rate of photo generated electrons and holes, resulting in low hydrogen production efficiency [14]. Therefore, in order to enhance the photocatalytic activity of this material under visible light, the optical absorption and the separation efficiency of photogenerated electron-hole pairs need to be greatly improved. Many approaches have been proposed to overcome these two limitations, such as doping with heteroatoms and loading surface co-catalysts [15, 16]. A more effective strategy is to construct g-C$_3$N$_4$ based heterostructure, such as g-C$_3$N$_4$/TiO$_2$ [17], g-C$_3$N$_4$/ZnO [18], g-C$_3$N$_4$/rGO
Their reaction conditions.

3 Activity under visible-light irradiation, and their perfor-
hibited enhanced photocatalytic hydrogen evolution ac-

[27] reported that g-C \(_3\) \(_2\) exhibited enhanced photocatalytic hydrogen evolution activity under visible-light irradiation, and their perfor-
mance was comparable to that of Pt/g-C \(_3\) \(_2\) under their reaction conditions.

Recently, Sun et al. [28] synthesized free-standing SnS \(_2\) single-layer with three atom thickness through a convenient and scalable liquid exfoliation strategy. And it reached a visible light conversion efficiency of 38.7%, which is expected to offer an excellent platform to achieve efficient visible light water splitting. However, it is not suitable for the H\(_2\) production since its conduction band edge position does not match the reduction potential of water. Motivated by this experimental investigation, we try to examine the possibility of the SnS \(_2\) sheet hybridizing with g-C \(_3\) \(_2\). And it is also interesting to explore the interfacial effect on the structural, electronic and optical properties of the g-C \(_3\) \(_2\)/SnS \(_2\) heterostructure, which are vitally important to characterize its photocatalytic activity. Here, by performing extensive density functional theory (DFT) calculations, we try to explore the interfacial interaction between monolayer g-C \(_3\) \(_2\) and SnS \(_2\) sheet and align the valence and conduction band edge positions of g-C \(_3\) \(_2\) and SnS \(_2\). Theoretical results clearly reveal that a nice type-II band alignment, which is desirable for visible light water splitting, appears in this proposed heterostructure. Moreover, the built-in interfacial electric field due to the charge transfer between g-C \(_3\) \(_2\) and SnS \(_2\) sheet can further enhance the photogenerated electron-hole separation. That is to say, SnS \(_2\) sheet is a promising candidate as a non-noble metal co-catalyst to improve the photocatalytic performance of g-C \(_3\) \(_2\) photocatalyst.

II. COMPUTATIONAL DETAILS

Our calculations are performed using the Vienna \(ab\) initio simulation package (VASP) [29, 30]. We use the frozen-core projector augmented wave approach to describe the interaction between the core and valence electrons [31]. To optimize the geometrical structures, the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) [32] form with van der Waals (vdW) correction proposed by Grimme [33] is chosen due to its good description of long-range vDW interactions. The energy cutoff is set to be 520 eV. A Monkhorst-Pack mesh of \(10 \times 10 \times 1\) and \(2 \times 2 \times 1\) \(k\)-points [34] is used to sample the two-dimensional Brillouin zone for the geometry optimizations and electronic structure calculations, respectively. The vacuum space is set to be at least 20 Å to separate the neighboring slab interactions. All geometry structures are fully relaxed until the convergence criteria of energy and force are less than \(10^{-5}\) eV and 0.01 eV/Å, respectively. The Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [35, 36] is used to obtain the correct electronic structures of g-C \(_3\) \(_2\), SnS \(_2\) sheet, and g-C \(_3\) \(_2\)/SnS \(_2\) heterostructure. The Hartree-Fock exchange mixing parameter (\(\alpha\)) in the default HSE06 functional is set to be 0.25, and the band gaps of monolayer g-C \(_3\) \(_2\) and SnS \(_2\) sheet are predicted to be 3.19 and 2.52 eV, respectively, which are seriously overestimated [13, 28, 37]. In order to reproduce the experimental band gaps of free g-C \(_3\) \(_2\) and SnS \(_2\) sheets, the value of mixing parameter is reduced from 0.25 to 0.175 in this work.

To explore the optical properties of g-C \(_3\) \(_2\)/SnS \(_2\) heterostructure, the optical absorption spectra are simulated by converting the complex dielectric function to the absorption coefficient \(\alpha_{abs}\) according to the following relation [38],

\[
\alpha_{abs} = \frac{4\pi E}{hc} \left( \sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1 \right)^{1/2}
\]

Here, the \(\varepsilon_1\) and \(\varepsilon_2\) are the real and imaginary absorption factors, respectively.

III. RESULTS AND DISCUSSION

To examine the reliability of the computational parameters, we perform benchmark calculations for the isolated single-layer g-C \(_3\) \(_2\) and SnS \(_2\) sheets. Figure 1(a) shows the optimized g-C \(_3\) \(_2\) monolayer, the lattice parameters \(a=b=4.79\) Å. All C atoms have three nearest N atoms, which are divided into two kinds (labeled as N1 and N2, the N1 atoms are coordinated with two C atoms, leaving a non-bonding character, while the N2 atoms are fully connected with three C atoms). The C–N1 and C–N2 bonding lengths are about 1.33 and 1.47 Å, respectively. The calculated band structure, as shown in Fig.1(c), shows that the g-C \(_3\) \(_2\) monolayer is a semiconductor with a direct energy gap of 2.71 eV. Figure 1(e) shows the calculated density of states (DOS) displays that the valence band maximum (VBM) is mainly dominated by the p orbitals of N1 atoms, and the conduction band minimum (CBM) is composed of p orbitals of N2 and C, which well reflects the different chemical bonding environments of monolayer g-C \(_3\) \(_2\). These results agree well with previous experimental measurements and theoretical results [13, 28, 37, 39]. As for SnS \(_2\) sheet, the top and side views of an optimized SnS \(_2\) sheet are illustrated in Fig.1(b). Clearly, it has a CdI\(_2\)-type hexagonal structure consisting of a S-Sn-S triple layer. The vertical S–S distance is...
2.99 Å and the Sn–S bond length is 2.58 Å. The band-structures and DOS results are shown in Fig.1 (e) and (f), respectively. It is clear that SnS$_2$ sheet displays an indirect band gap energy with a suitable size of 2.12 eV from the HSE06 functional, which is consistent with the experimental data [28]. In the energy range of $-1.0$ eV to $0.0$ eV, the valence bands mainly originate from S3p orbitals. As for the CBM, it is contributed by the hybridized states between S3p and Sn5s orbitals. This is a little different from TMD. For example, the conduction bands of single-layer MoS$_2$ come from the hybridization between S3p and Mo3d orbitals [40]. These calculations imply that the adopted computational method and parameters are appropriate.

To improve the optical absorption and the separation efficiency of photogenerated carriers of g-C$_3$N$_4$, a single-layer SnS$_2$ can be loaded on it and act as a non-noble metal co-catalyst. The top and side views of this proposed heterostructure are illustrated in Fig.2 (a) and (b), respectively. Here, a 4×4 supercell of SnS$_2$ (including 16 Sn and 32 S atoms) is covered on a 3×3 supercell of g-C$_3$N$_4$ (27 C and 36 N atoms) with the small lattice mismatch of less than 3.0%. Clearly, the g-C$_3$N$_4$ monolayer displays an obvious geometric distortion due to the presence of SnS$_2$ sheet, and the corresponding buckling distance ($h_1$) is about 0.98 Å. The vertical distance ($h_2$) between monolayer g-C$_3$N$_4$ and SnS$_2$ sheet is predicted to be 3.09 Å. This is a typical vDW equilibrium space, which is consistent with other g-C$_3$N$_4$-based semiconductor heterostructures [19, 20, 23, 37, 41, 42].

To describe the thermodynamic stability of this proposed g-C$_3$N$_4$/SnS$_2$ heterostructure, we calculate the interface formation energy ($E_f$), which is defined as

$$E_f = E_{g-C_3N_4/\text{SnS}_2} - E_{\text{SnS}_2} - E_{g-C_3N_4}$$

FIG. 1 (a) g-C$_3$N$_4$ monolayer. Green and blue spheres represent the C and N atoms, respectively. The black circles stand for the unit cell in our calculation. The different N atoms (labeled as N1 and N2) are shown in the red squares. (b) Top and side views of the SnS$_2$ sheet. Here, the gray and yellow atoms represent the Sn and S atoms, respectively. (c) The corresponding calculated band structure and (d) calculated PDOS of monolayer g-C$_3$N$_4$. The green vertical dashed line stands for the Fermi energy. The corresponding calculated band structure (e) and PDOS (f) of single layer SnS$_2$ are also shown.
The red shift of the optical absorption edge. The VBM of g-C\textsubscript{3}N\textsubscript{4} excited to the CB, consequently, it will result in the charge transfer from the g-C\textsubscript{3}N\textsubscript{4} sheet. Due to the relative large separation and the weak interaction between the g-C\textsubscript{3}N\textsubscript{4} and SnS\textsubscript{2}, the main features of the calculated partial DOS of Sn, S, N, and C atoms in the g-C\textsubscript{3}N\textsubscript{4}/SnS\textsubscript{2} heterostructure, as shown in Fig.3, are similar to the results for the isolated g-C\textsubscript{3}N\textsubscript{4} monolayer and the SnS\textsubscript{2} sheet, as shown in Fig.1(c) and (f), respectively. While the CBM mainly comes from the states of SnS\textsubscript{2} sheet. Moreover, the VBM of g-C\textsubscript{3}N\textsubscript{4} is 0.22 eV higher than that of g-C\textsubscript{3}N\textsubscript{4}, whereas the CBM of g-C\textsubscript{3}N\textsubscript{4} is 1.01 eV lower than that of SnS\textsubscript{2}. That is to say, the proposed g-C\textsubscript{3}N\textsubscript{4}/SnS\textsubscript{2} heterostructure is a typical type-II band alignment structure, in which the valence band offset (VBO) between g-C\textsubscript{3}N\textsubscript{4} and SnS\textsubscript{2} is about 0.22 eV, and the conduction band offset (CBO) is about 1.01 eV.

To explore the charge transfer between g-C\textsubscript{3}N\textsubscript{4} monolayer and SnS\textsubscript{2} sheet in the proposed heterostructure, we calculate the charge density difference by subtracting the charge density of free-standing g-C\textsubscript{3}N\textsubscript{4} monolayer and SnS\textsubscript{2} sheet, and plot in Fig.4(a). The cyan region indicates the charge accumulation while the purple region represents the charge depletion. Clearly, charge redistribution mainly occurs at the g-C\textsubscript{3}N\textsubscript{4}/SnS\textsubscript{2} interface region, while there is almost no charge change in the SnS\textsubscript{2} sheet. To illustrate the charge transfer more clearly, Fig.4(b) shows the planar-averaged charge density difference along the z-direction, here, the positive values represent electron accumulation, while the negative values indicate the electron depletion. It is clear that the charge transfer from the g-C\textsubscript{3}N\textsubscript{4} to the SnS\textsubscript{2} sheet in the heterostructure occurs at the interface region. Based on the Bader analysis, the average charge transfer from

FIG. 2 (a) The top view and (b) the side view of the proposed SnS\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} heterostructure. (c) The calculated band structure and the total DOS of the SnS\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} heterostructure. Here, the Fermi energy is set to zero for clarity.

FIG. 3 (a) The calculated total DOS of the g-C\textsubscript{3}N\textsubscript{4}/SnS\textsubscript{2} heterostructure. (b) The partial DOS of SnS\textsubscript{2} sheet in the heterostructure. (c) The partial DOS of the g-C\textsubscript{3}N\textsubscript{4} monolayer. Here, the black circle illustrate for the first DOS peak, and the green vertical dashed line is the Fermi energy.
g-C\textsubscript{3}N\textsubscript{4} to SnS\textsubscript{2} sheet is about 0.33 eV. This can be easily understood, since the work functions of the g-C\textsubscript{3}N\textsubscript{4} monolayer and SnS\textsubscript{2} sheet are predicted to be 5.17 and 6.98 eV, respectively. That is to say, the spontaneous interfacial charge transfer from the g-C\textsubscript{3}N\textsubscript{4} monolayer to SnS\textsubscript{2} sheet can be simply rationalized in terms of the large difference between two calculated work functions. Note that this spontaneous interfacial charge transfer result in a built-in electric field at the interface region, which can promote photogenerated electrons from the CB of SnS\textsubscript{2} to the CB of g-C\textsubscript{3}N\textsubscript{4}, and also improve photogenerated holes transfer from the VB of g-C\textsubscript{3}N\textsubscript{4} to the VB of SnS\textsubscript{2}. It means that this built-in interface electric filed can effectively enhance the photogenerated electron-hole separation.

A key index to the photocatalyst performance is the optical absorption since it is strongly related to their photocatalytic activities. We calculate the optical absorption curves of the g-C\textsubscript{3}N\textsubscript{4} and the g-C\textsubscript{3}N\textsubscript{4}/SnS\textsubscript{2} heterostructure, and plot them in Fig. 5, respectively. The optical absorption for the free-standing g-C\textsubscript{3}N\textsubscript{4} monolayer occurs at about 3.0 eV, which is attributed to the intrinsic transition from the N1 2p orbitals to the CB. Clearly, the g-C\textsubscript{3}N\textsubscript{4}/SnS\textsubscript{2} heterostructure can effectively harvest the visible light since the absorption edge shifts from UV region to infrared light. Moreover, the predicted absorption spectra depend on the polarization direction. The optical absorption coefficients along the vertical direction are significantly larger than that along the parallel direction.

In general, the oxidation/reduction ability of a photocatalyst for water splitting can be evaluated by the band edge positions of VBM and CBM, compared with the reduction and oxidation potentials of water. We thus determine the band edge positions of the free-standing g-C\textsubscript{3}N\textsubscript{4} monolayer and SnS\textsubscript{2} sheet, according to the method of Toroker et al. [43]. Figure 6 illustrates the band edge alignments versus the normal hydrogen electrode (NHE), where the band edge positions of CBM and VBM of g-C\textsubscript{3}N\textsubscript{4} monolayer are −0.83 and 0.65 eV, while the CBM and VBM of SnS\textsubscript{2} sheet locate at 0.58 and 1.47 eV, respectively. These results agree well with the previous experimental and theoretical investigations [24, 44]. Note that the CBM of SnS\textsubscript{2} sheet is more positive than the reduction potential of H\textsuperscript{+}/H\textsubscript{2}, thus a bias potential of at least 0.58 V is required to drive the hydrogen evolution.

When the g-C\textsubscript{3}N\textsubscript{4} monolayer covers on SnS\textsubscript{2} sheet, the relative positions of the CB and VB of g-C\textsubscript{3}N\textsubscript{4} and
SnS$_2$ will change with the Fermi level due to the charge redistribution [41]. According to the above calculated DOS, as shown in Fig.2, the CBM and VBM positions of the proposed g-C$_3$N$_4$/SnS$_2$ heterostructure are plotted in Fig.6 (right side). As mentioned above, this heterostructure is a type-II heterojunction. When the g-C$_3$N$_4$/SnS$_2$ heterostructure absorbs photon energy under solar light irradiation, electrons in the VB are excited to the CB, and simultaneously, photogenerated holes are generated in the VB. These photogenerated electrons in the CB of SnS$_2$ sheet can be easily moved to the CB of the g-C$_3$N$_4$ due to the observed CBO. Conversely, the existence of VBO induced the photogenerated holes in the VB of g-C$_3$N$_4$ moving to the VB of SnS$_2$. That is to say, the oxidation and redox reactions will take place in g-C$_3$N$_4$ and SnS$_2$ sheets, respectively.

In short, due to the observed band offsets built-in interface polarized electric field, we believe that in the proposed g-C$_3$N$_4$/SnS$_2$ heterostructure the energy-wasteful electron-hole recombination could be effectively reduced, and then, the photocatalytic quantum efficiency can be greatly improved. That is to say, the proposed g-C$_3$N$_4$/SnS$_2$ heterostructure is a promising g-C$_3$N$_4$ based water splitting photocatalyst.

IV. CONCLUSION

In summary, we perform extensive hybrid DFT calculations to examine the geometric, electronic, optical properties as well as the band edge alignment of the proposed g-C$_3$N$_4$/SnS$_2$ heterostructure. Theoretical results clearly reveal that the g-C$_3$N$_4$ monolayer weakly couples to SnS$_2$ sheet, and forms a typical vdW heterojunction. The predicted band gaps, band edge positions and optical absorptions suggest that the g-C$_3$N$_4$/SnS$_2$ heterostructure can effectively harvest visible light, and both VBM and CBM locate in energetically favorable positions for both water oxidation and reduction reactions. Moreover, the built-in interface polarized electric field within the interface region, owing to the charge transfer from the g-C$_3$N$_4$ monolayer to SnS$_2$ sheet, is desirable for the photogenerated carrier separation. The built-in interface polarized electric field and the nice band edge alignment imply that the g-C$_3$N$_4$/SnS$_2$ heterostructure is a promising water splitting photocatalyst with good performance.

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