Dramatically Enhanced Visible Light Response of Monolayer ZrS₂ via Non-covalent Modification by Double-Ring Tubular B₂₀ Cluster

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Abstract
The ability to strongly absorb light is central to solar energy conversion. We demonstrate here that the hybrid of monolayer ZrS₂ and double-ring tubular B₂₀ cluster exhibits dramatically enhanced light absorption in the entire visible spectrum. The unique near-gap electronic structure and large built-in potential at the interface will lead to the robust separation of photoexcited charge carriers in the hybrid. Interestingly, some Zr and S atoms, which are catalytically inert in isolated monolayer ZrS₂, turn into catalytic active sites. The dramatically enhanced absorption in the entire visible light makes the ZrS₂/B₂₀ hybrid having great applications in photocatalysis or photodetection.

Keywords: Electronic structure, Enhanced visible-light response, ZrS₂/B₂₀ hybrid, First-principles

Background
Atomically thin two-dimensional (2D) transition metal dichalcogenides (TMDs) have intriguing properties that make them highly suitable for many fields including lithium-ion battery, solar cell, and catalysis [1]. Thanks to the dramatic progress in recent experimental advances, many kinds of few-layer or monolayer TMDs have been successfully prepared [2, 3]. However, any one of pure-layered TMDs is not always a perfect material for different applications. To achieve superior performance for some specific cases, various strategies have been developed to engineer the chemical, physical, and electronic properties of 2D TMDs [1, 4, 5]. In particular, coupling 2D TMDs with other materials to create novel functional van der Waals (vdW) heterostructures receives growing significant attention [1].

As one of representative group IVB-TMDs, zirconium disulfide (ZrS₂) has attracted considerable attention and shows great potential in photodetectors [6], solar cells [7], and photocatalysis [8], due to its good thermodynamic stability, environmental friendliness, high sensitivity, and low-cost production. In recent years, monolayer ZrS₂ keeping these advantageous qualities have been successfully fabricated by various methods [9–11]. The band gap of bulk ZrS₂ is around 1.70 eV [12, 13], while it is very interesting that mono-, bi-, and trilayer ZrS₂ have an indirect band gap with 2.01, 1.97, and 1.94 eV [8, 14], respectively, indicating that it undergoes a transition of band gap when the dimensionality decreases from 3D to 2D. Due to its appropriate band gap, monolayer ZrS₂ can utilize the maximum portion of the solar visible light. However, the measured efficiency in solar hydrogen production of monolayer ZrS₂ is quite low compared with the theoretical value owing to its conduction band maximum (CBM) slightly lower than the reduction level of hydrogen [15, 16]. To overcome the drawbacks, many methods have been explored to improve the photocatalytic performance of ZrS₂. Among them, combining with other semiconductors, such as graphene, g-C₃N₄, h-BN, and ZnO, has been demonstrated to be an effective strategy to enhance the stability and photocatalytic activity of ZrS₂ [16, 17].

Boron (1s² 2s² 2p²) can form a wide variety of clusters with fascinating properties, as its neighbor carbon (1s² 2s² 2p²) which is well known showing distinct solid-state allotropes like chains, rings, and fullerenes [18]. The related
study of boron clusters can date back to nearly 30 years ago [19]. A lot of boron fullerenes, such as B_{80} and B_{100} [20, 21], have been studied theoretically. Recently, Zhai et al. have firstly observed the all-boron fullerene B_{40} in experiment [22], triggering renewed interest in these boron clusters [23–25]. Herein, we for the first time study the structural and electronic properties of hybrid monolayer ZrS_{2}/B_{20} vdW heterostructure to explore its potential applications in solar energy conversion by using large-scale density functional theory (DFT) computations. Here, double-ring tubular B_{20} cluster is taken as the typical boron cluster, motivated by its special structure and properties. As a stable non-planar structure formed by 20 boron atoms with high symmetry, double-ring tubular B_{20} is considered to be an important structure due to the 2D-to-3D transition of boron cluster: the boron clusters prefer 2D structures up to 19 atoms and favor 3D structures beginning at 20 atoms in terms of experimental and computational studies [26–29]. More importantly, the band gap of B_{20} ring is about 1.2~1.4 eV [19], suggesting that its spectral response covers the entire visible region, even extending to near-infrared light. It is speculated that the role of B_{20} ring in the hybrid is multiple. The calculated results show that compared to pure monolayer ZrS_{2}, the ZrS_{2}/B_{20} hybrid displays dramatically enhanced visible light response, making it to be great potential in solar energy conversion.

**Methods**

The hybrid is composed of a 5 × 5 ZrS_{2} supercell and a non-planar B_{20} ring cluster, as shown in Fig. 1. A vacuum space is set to be 20 Å in order to avoid artificial interaction. All the DFT calculations are performed using CASTEP module in Materials Studio 8.0 [30]. The core electrons are described with the ultrasoft pseudopotential. The local-density approximation (LDA) with inclusion of the vdW interaction is chosen because the long-range vdW interaction is expected to be significant in such hybrid [31]. However, because the LDA functional underestimates the band gaps of semiconductors [32], all the theoretical calculations are performed using the DFT/LDA + U method. We have performed extensive tests to determine the appropriate Hubbard U parameters (Zr 4d, 3p, and S 2p are 4.0, 3.0, and 3.0 eV, respectively). The cutoff energy for the plane-wave is set to 400 eV. Geometry optimization is carried out before single point energy calculation and the force on the atoms is less than 0.03 eV/Å, the stress on the atoms is less than 0.05 GPa, the atomic displacement is less than 1.0 × 10^{-3} eV/Å, and the energy change per atom is less than 1.0 × 10^{-5} eV. For the Brillouin zone integration, a 3 × 3 × 3 Monkhorst pack k-point mesh is used for geometry optimization and the density-of-states (DOS) plots. The convergence of energy is 1.0 × 10^{-6} eV. To check the reliability of our results, we have also performed a test calculation with higher plane-wave cutoff energy and more k-points. Compared with the results given here, negligible changes are obtained for both structural and electronic structures and difference between the total energies is less than 0.03 %.

**Results and Discussion**

The lattice constant of monolayer ZrS_{2} and diameter of ring B_{20} are calculated to be 3.62 and 5.18 Å, respectively, in good agreement with the previous study [14, 16, 26]. After optimization, the closest distance between a boron atom and top layer of ZrS_{2} is 2.86 Å (Fig. 1), indicating that the interaction between monolayer ZrS_{2} and B_{20} is indeed vdW rather than covalent. In order to examine the stability of the hybrid, the interface adhesion energy have been calculated, which is defined as follows:

![Fig. 1](image-url)
\[ E_{\text{ad}} = E_{\text{comb}} - E_{ZrS_2} - E_{B_{20}}, \]

where \( E_{\text{comb}} \), \( E_{ZrS_2} \), and \( E_{B_{20}} \) represent the total energy of the relaxed \( ZrS_2/B_{20} \) hybrid, monolayer \( ZrS_2 \), \( B_{20} \) ring, respectively. By definition, negative \( E_{\text{ad}} \) suggests that the adsorption is stable [33]. The interface binding energy is calculated to be \(-1.02 \text{ eV}\) for this hybrid, indicating that a rather strong interaction between monolayer \( ZrS_2 \) and \( B_{20} \) ring, and the high thermodynamically stability.

The band structures of monolayer \( ZrS_2 \) and \( ZrS_2/B_{20} \) hybrid are displayed in Fig. 2. It is obvious that monolayer \( ZrS_2 \) has an indirect band gap of 1.97 eV, which is in agreement well with other results obtained from hybrid-DFT method [14, 16]. For the \( ZrS_2/B_{20} \) hybrid, the most striking is the emergence of two almost flat bands located at about \(-1.3 \) and 0 eV, respectively (Fig. 2b). Compared to monolayer \( ZrS_2 \), the band gap of hybrid is reduced to 0.366 eV, thus making it to be a novel material with wide spectral response, from visible light to near-infrared light.

To illuminate the influence of vdW interaction on the electronic properties of \( ZrS_2 \), the total density of states (TDOS) and partial density of states (PDOS) of the monolayer \( ZrS_2 \), double-ring tubular \( B_{20} \) cluster, and \( ZrS_2/B_{20} \) hybrid are calculated and displayed in Fig. 3. The VB top of pure \( ZrS_2 \) (Fig. 3 (a2)) is mainly constituted of S 3p states mixing with small Zr 4d states, while its CB bottom is composed of Zr 4d states, indicating that its near-gap electronic structure is different from that of pure MoS\(_2\) where the CB bottom and VB top are predominately composed of Mo 4d states [34]. Thus, pure monolayer \( ZrS_2 \) is expected to be a better candidate than pure monolayer MoS\(_2\) for light absorption. For isolated ring \( B_{20} \) cluster, its VB top is mainly constituted of B 2p states mixing with small 2s states, and its CB bottom is composed of B 2p states (Fig. 3 (b2)). Obviously, this kind of near-gap electronic structure is not conducive for the electron transition of \( B_{20} \) cluster under illumination. This kind of transition-hostile near-gap electronic structure of pure \( ZrS_2 \) or isolated ring \( B_{20} \) cluster can be changed by combining them through vdW interaction. Figure 3 (c1–c4) shows that the VB top of \( ZrS_2/B_{20} \) hybrid is dominated by B 2p states from ring \( B_{20} \) cluster, coupled by small Zr 4d and S 3p states, whereas its CB bottom is predominately composed of Zr 4d states, which can be more clearly seen from
the electron density distributions of the highest occupied and lowest unoccupied levels (HOL and LUL), respectively, as shown in Figs. 2c, d. This kind of transition-conducive near-gap electronic structure of hybrid ZrS$_2$/B$_{20}$ significantly lowers the effective band gap of the heterostructure and facilitates efficient electron-hole separation, which is the physical mechanism for high light absorption in the visible region. Note that the four nearly straight levels from −1.5 to 0 eV (Fig. 2b) are mainly composed of B 2p or S 3p states, as shown in Fig. 3. Obviously, the electron transition between these levels (i.e., B 2p or S 3p orbitals) will also significantly affect the optical properties of the ZrS$_2$/B$_{20}$ hybrid. However, owing to the electronic transition of angular momentum selection rules ($\Delta l = \pm 1$), the transition between these levels is forbidden; thus, the electrons occupied at B 2p or S 3p states will direct transit to the CB bottom (Zr 4d orbitals), producing well-spatially separated electron-hole pairs.

The variation of the DOSs implies that the interaction between ZrS$_2$ and ring B$_{20}$ cluster leads to charge transfer between the involved constituents. This can be visualized (as shown in Fig. 4b) by the three-dimensional...
charge density difference $\Delta \rho = \rho_{\text{ZrS}_2/B_{20}} - \rho_{\text{ZrS}_2} - \rho_{B_{20}}$, where $\rho_{\text{ZrS}_2/B_{20}}$, $\rho_{\text{ZrS}_2}$, and $\rho_{B_{20}}$ are the charge densities of the hybrid, monolayer ZrS$_2$, and ring B$_{20}$ cluster in the same configuration, respectively. Owing to the non-covalent interaction, a very interesting charge redistribution at the hybrid ZrS$_2$/B$_{20}$ can be clearly seen, which is different from those of the MoS$_2$/SnO$_2$ and Ag$_3$PO$_4$/GR heterostructures [33, 35]. A strong charge accumulation (blue part in Fig. 4b), mainly from the B atoms at lower layer of ring B$_{20}$ cluster and from the S atoms below the B$_{20}$ cluster, is found just above the top S atoms. Whereas the charge depletion occurs at both sides of the S atoms below the ring B$_{20}$ cluster and the B atoms at the cluster. Moreover, the B atoms at the lower layer (i.e., adjacent to ZrS$_2$) lose more electron than those at the top layer.

To offer quantitative results of charge redistribution, Fig. 4c plots the planar averaged charge density difference along the direction perpendicular to the monolayer ZrS$_2$, where the positive value indicates the charge accumulation, and negative value represents the charge depletion. It is obvious that the largest efficient electron accumulation appears between the S atom and the B atom and is about $4.3 \times 10^{-4}$ e/Å$^3$ and the largest efficient electron depletion occurs both at lower side of B$_{20}$ and Zr atom are about $-1.9 \times 10^{-4}$ e/Å$^3$. In order to quantitatively analyze the effective net charge variation between the two constituents, we further analyze the charge transfer by Bader method, which demonstrates that 0.302 electron transfers from B$_{20}$ to ZrS$_2$, similar to the case of the MoS$_2$/C$_{20}$ hybrid [34]. To unveil the mechanism of such an interface electron transfer in the hybrid, work functions for the ring B$_{20}$ cluster and monolayer ZrS$_2$ are calculated by aligning the Fermi level relative to the vacuum energy level. They are calculated to be 4.71 and 5.99 eV for B$_{20}$ and monolayer ZrS$_2$, respectively. The spontaneous interfacial charge transfer in the hybrid ZrS$_2$/B$_{20}$ can be simply rationalized in terms of the difference of these work functions. Most importantly, Bader analysis also shows that some Zr atoms obtains charge up to 1.768 e, while some S atoms lose charge up to 0.89 e in the ZrS$_2$ layer, indicating that the vdW interaction results into some positively charged Zr atoms and negatively charged S atoms in the ZrS$_2$ layer. This finding suggests that some Zr and S atoms at basal planes, initially catalytically inert, would turn out to be active sites, which would be one of the key factors to enhance the photocatalytic performance of the monolayer ZrS$_2$/B$_{20}$ hybrid.

The distribution of electric potential in the ZrS$_2$/B$_{20}$ hybrid will be altered due to the interfacial charge transfer. To display the quantitative analysis, the profile of the planar averaged self-consistent electrostatic potential for the ZrS$_2$/B$_{20}$ hybrid as a function of position in the z-direction is displayed in Fig. 4a. One can see that the electrostatic potential at two B atomic planes is lower than that at their middle region in ring B$_{20}$ cluster, and obvious potential difference between the Zr atomic plane and two S atomic planes can be observed, rendering a typical S-Zr-S sandwich distribution. Note that the potential at the upper S atomic plane is slightly higher than that at the lower S atomic plane (upper $-25.05$ eV, lower $-25.26$ eV), verifying that the S atoms at the upper layer lose some electrons due to the ring B$_{20}$ cluster modification (as displayed in Fig. 4b).

The potential at the monolayer ZrS$_2$ plane is much lower than that at ring B$_{20}$ cluster, resulting into a large potential difference between the two constituents. The built-in potential at the interface promotes the separation of electron-hole pairs. Moreover, under light irradiation, the separation and migration of photogenerated carriers at the interface will be more effective due to the appearance of this built-in potential, i.e., the existence of a potential well can effectively hinder the recombination of photogenerated charge carriers in the ZrS$_2$/B$_{20}$ hybrid. The results suggest that the ZrS$_2$/B$_{20}$ hybrid would be a potential photocatalyst with high quantum efficiency.

The high light harvesting is vital for a high-efficiency photocatalyst or photodetector except for a low recombination rate of photogenerated carriers. It has been demonstrated that non-covalent modification by graphene or monolayer MoS$_2$ can extend the absorption edge of semiconductors (like TiO$_2$, Ag$_3$PO$_4$ and SnO$_2$) to the vis-light region [33, 35, 36]. Similarly, coupling fullerene with photocatalysts is also an effective strategy to enhance the light absorption [34]. To explore the influence of ring B$_{20}$ cluster on the light absorption of ZrS$_2$, the UV-vis absorption spectra of the ZrS$_2$/B$_{20}$ hybrid, and its constituents are calculated, as shown in Fig. 5. For monolayer ZrS$_2$, the optical absorption edge occurs at about 620 nm, which is attributed to the intrinsic transition from the S 3d to Zr 4d orbital, in agreement with other theoretical results [16]. This adsorption edge. Owing to its small band gap (as shown in Fig. 3b), the isolated ring B$_{20}$ cluster can absorb some near-infrared light (800~1200 nm), but the absorb intensity is very weak, as shown in Fig. 5. Part of visible light (<520 nm) can also be absorbed by the isolated ring B$_{20}$ cluster. The most striking feature in Fig. 5 is that visible light response of the ZrS$_2$/B$_{20}$ hybrid has been dramatically enhanced in the region from 450 to 700 nm compared to that of the monolayer ZrS$_2$. That is to say, the ZrS$_2$/B$_{20}$ hybrid very efficiently absorb most of the visible light. The significant increase of optical absorption of the ZrS$_2$/B$_{20}$ hybrid is close related to the unique near band-gap electronic structure (Fig. 3). Considering that the separation and migration of photogenerated carriers in
the hybrid will be facilitated due to the existence of the built-in potential at the interface, one can conclude that the ZrS$_2$/B$_{20}$ hybrid would be an active photocatalyst or photodetector in the main part of the solar spectrum, and ever poor illumination of interior lighting.

Conclusions
In summary, we have studied the electronic structure, charge transfer, and optical properties of the ZrS$_2$/B$_{20}$ hybrid by using DFT calculation. It is found that the band gap and near-gap electronic structure of the monolayer ZrS$_2$ can be tuned by the non-covalent modification of double-ring tubular B$_{20}$ cluster. The interfacial charge transfer results into some positively charged Zr atoms and negatively charged S atoms in the hybrid, thus to be active sites, which are initially catalytically inert in the isolated monolayer ZrS$_2$. The ZrS$_2$/B$_{20}$ hybrid exhibits dramatically enhanced absorption in the entire visible light due to its small band gap and unique near-gap electronic structure caused by interfacial interaction. These results suggest that not only the ZrS$_2$/B$_{20}$ hybrid would be an active photocatalyst or photodetector in the main part of the solar spectrum, and ever poor illumination of interior lighting, but also ring B$_{20}$ cluster modification would be an effective strategy to tune the performance of monolayer TMDs.

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Authors’ Contributions
WQH and GJF proposed the work and revised the paper. YS calculated the first principles results and wrote the manuscript. HYW, HMY, KY, and PP have devoted valuable discussion. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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Fig. 5 Calculated absorption spectra of the monolayer ZrS$_2$ (green dashed line), ring B$_{20}$ cluster (red dashed line), and the ZrS$_2$/B$_{20}$ hybrid (blue solid line) for the polarization vector perpendicular to the surface. Inset: the absorption spectra from 700 to 1300 nm.
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