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Impact of edge structures on interfacial interactions and efficient visible-light photocatalytic activity of metal–semiconductor hybrid 2D materials†

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The present work systematically investigates the structural, electronic, and optical properties of a MoS₂/Si₂BN heterostructure based on first-principles calculations. Firstly, the charge transport and optoelectronic properties of MoS₂ and Si₂BN heterostructures are computed in detail. We observed that the positions of the valence and conduction band edges of MoS₂ and Si₂BN change with the Fermi level and form a Schottky contact heterostructure with superior optical absorption spectra. Furthermore, the charge density difference profile and Bader charge analysis indicated that the internal electric field would facilitate the separation of electron–hole (e⁻/h⁺) pairs at the MoS₂/Si₂BN interface and restrain the carrier recombination. This work provides an insightful understanding about the physical mechanism for the better photocatalytic performance of this new material system and offers adequate instructions for fabricating superior Si₂BN-based heterostructure photocatalysts.

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Introduction

In the contemporary era, massive challenges have been imposed on the research community to tackle environmental problems and look for renewable energy sources *i.e.* utilization of solar energy to obtain hydrogen and oxygen by water splitting. Hydrogen is a renewable and clean energy source and the mechanism to generate hydrogen and oxygen through photocatalytic water splitting bears significant challenges that include light harvesting, separation, migration of photogenerated electrons and holes, and the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) on the surface of photocatalysts. To achieve that, the redox potential of water must lie in between the conduction band minima (CBM) and valence band maxima (VBM), where the CBM should be higher than the reduction potential of H⁺/H₂, and the VBM should be lower than the oxidation potential of

H₂O/O₂. Moreover, the surface reactivities for the photocatalysts from the recombination of the irradiation-excited electrons and holes due to the adsorption of sunlight, finding narrow bandgap to dimensional (2D) materials for photocatalysis would be a significant challenge.¹

2D semiconducting materials such as transition metal dichalcogenides (TMDs), metal chalcogenides (*e.g.*, MoS₂, WS₂), hexagonal boron nitrides (h-BNs), and metal oxides have garnered massive interest in experimental studies as well as theoretical studies due to their unique physical and chemical properties.^{2–8} The challenges mentioned above can be easily handled with the band engineering of these semiconductors to develop catalysts with high photocatalysis performance.⁹ The possibilities to explore the recent advances in van der Waals (vdW) solids of atomic layers that form vertical quantum heterojunctions with interfaces between different 2D materials. The in-plane stability of 2D materials induces strong covalent bonding. In contrast, the vdW interactions induce the stacking of different materials with diverse physical and chemical properties appearing to be appropriate for photocatalytic activity. Formation of heterostructures with dissimilar materials can have drastic effects on the photocatalytic activity due to the impact of the built-in electric field formed among the different layers, as reported earlier.¹⁰ The proposed theoretical calculations represent the molecular mechanism for these stacking layers that may matter in deciding the net catalytic performance of

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materials such as graphene and related 2D materials such as MoS₂, functionalized silicene and germanene, various MXenes (like Zr₂CO₂ and Hf₂CO₂), single layer group-III monochalcogenides and group-IVB nitride halides, SnS₂ with a tuned photocatalyst under acidic pH conditions, black phosphorene (Pn) with pseudo Jahn–Teller (PJT) effects buckled in a stapler-clip symmetry, black Pn under strain and heterostructures of h-BN/graphene.^{11–22} The crystal structure of molybdenum disulfide (MoS₂) takes the form of a hexagonal plane of S atoms on either side of a hexagonal plane of Mo atoms. These triple planes stack on top of each other, with strong covalent bonds between the Mo and S atoms, but weak van der Waals forces holding the layers together. This allows them to be mechanically separated to form 2-dimensional sheets of MoS₂.^{23,24} In the case of Si₂BN, it has a graphene-like structure by combining boron and nitrogen that leads to an sp²-bonded single-layer hexagonal boron nitride (BN) structure, which is a wide-band-gap semiconductor with a bandgap of 5.8 eV.²⁵

Van der Waals heterostructures are composite quantum materials consisting of arrays of two-dimensional (2D) layers, which are atomically thin as the electrons are exposed to layer-to-layer coupling in the atomically thin 2D layers.²⁶ The characteristics of van der Waals heterostructures are represented not only by the constituent monolayers but also by the interactions among the layers. Recently, various types of van der Waals heterostructures based on MoS₂ have exhibited several interesting electrical, optical, and magnetic properties,^{27–39} but none has reported the mechanism of interface interactions (vdW heterostructures) between MoS₂ and Si₂BN. We have chosen a 2D Si₂BN (ref. 25) monolayer as a promising candidate as it possesses several characteristic features similar to those of graphene, *e.g.*, physical and mechanical robustness, a good degree of stability at high temperatures around 1000 K, high formation energy, ultra-high ideal strength, and unique electronic properties, making it suitable for optoelectronic, sensor, catalysis and nanoelectronic applications.⁴⁰ As the electrons in atomically thin layers (monolayers) are involved in stacking, forming a heterostructure, different quantum states found in the individual layers can interact and couple to one another. Heterostructures of 2D materials not only offer a way to research structural and electronic anomalies but also create unparalleled possibilities to incorporate them for technical use. Stacked monolayers are very different from traditional heterostructures of 3D semiconductors, since each layer functions concurrently as the bulk material and the interface, reducing the displacement charges within each sheet. Even charge transfers between layers can be very large, producing large electrical fields and providing fascinating band-structure engineering possibilities.⁴¹ Surface reconstruction, charge transfer, and proximity effects (when one material can borrow the properties of another by contact *via* quantum tunneling or by Coulomb interactions) are some of the unique features that one can unravel by studying vdW heterostructures using various 2D materials.

In the present work, we mainly focused on the basic mechanism of interface interactions and charge movement and separation in and optical properties of a Si₂BN/MoS₂ heterostructure utilizing density functional theory (DFT) calculations. Our calculations demonstrate that after superimposing MoS₂ with a Si₂BN monolayer, the positions of the band edge of MoS₂ altered correspondingly, forming a semiconductor–metal heterostructure. The charge density differences, work function, and Bader charge analysis showed that the internal electric field between interfaces could further inhibit the recombination of e[−]/h⁺ pairs. Besides, we found that the optical absorption coefficient of the Si₂BN/MoS₂ heterostructure is more prominent than those of individual MoS₂ and Si₂BN under visible-light irradiation. We propose a productive methodology for the understanding of interfacial properties of Si₂BN/MoS₂ heterostructure with two different configurations: (i) monolayer of Si₂BN and MoS₂ system periodic in XY directions used as simple abbreviations rMoS₂/Si₂BN and (ii) nanoribbon of MoS₂ system periodic in x-direction deposited on the monolayer of Si₂BN used as simple abbreviations rMoS₂/Si₂BN. Our investigation suggests the physicochemical system shows the photocatalytic activity of Si₂BN/MoS₂ hybrid heterostructure and envisages to design new hybrid heterostructures for photocatalytic responses.

Methodology

The electronic structure calculations are based on density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) software.^{42–46} The projector augmented wave (PAW) method with generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional is a technique used in *ab initio* electronic structure calculations.^{47–49} The effect of van der Waals interaction has been described by using the empirical correction in the Grimme method *i.e.*, zero damping DFT-D3 during the calculations.⁵⁰ The electron wave functions are described by a plane-wave basis set with a kinetic energy cutoff of 500 eV, and the convergence tolerance throughout the structure relaxation has been set to 10^{−6} eV for energy and 10^{−3} eV Å^{−1} for force, respectively. A vacuum space of 20 Å in the z-direction has been used to prevent the physical interaction between two periodic images. The Brillouin zone (BZ) is sampled using a Monkhorst–Pack *K*-mesh grid of 6 × 6 × 1 for the supercell in the reciprocal space during the structural optimization.⁵¹ The charge distribution and transfer are computed by using Bader charge analysis.⁵² Additionally, *ab initio* molecular dynamics (MD) simulations were performed in the canonical ensemble *i.e.*, fixed particle number, volume, and temperature (NVT) up to 10 ps with a time step of 2 fs. To accelerate the dynamic process, we have used a temperature amounting to 300 K. The AIMD simulations have helped us to determine and examine the thermal stability of the MoS₂/Si₂BN vdW heterostructure. The optical absorption spectra have been extracted from the imaginary part of the



complex dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$ is the real part and $\varepsilon_2(\omega)$ is the imaginary part of the complex dielectric function.⁵³ The optical absorption coefficient is given as:

$$\alpha = \sqrt{2\omega} [|\varepsilon(\omega)| - \varepsilon_1(\omega)]^{\frac{1}{2}}, \quad (1)$$

where,

$$|\varepsilon(\omega)| = \sqrt{\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)}$$

Results and discussion

The structures of the Si₂BN and MoS₂ monolayers are fully optimized and the corresponding lattice parameters $a = b = 3.18$ Å (bond lengths between the atoms of Mo–S = 2.41 Å and S–S = 3.13 Å) and $a = 6.35$ Å and $b = 6.45$ Å (bond lengths between the atoms of Si–Si = 2.25 Å, Si–B = 1.95 Å, Si–N = 1.76 Å, B–N = 1.47 Å) are well consistent with those from previously reported studies.^{40,54–58} Here, we have fabricated the Si₂BN/MoS₂ heterostructure by combining a (2 × 2 × 1) supercell of the Si₂BN monolayer (which contains 16 Si, 8 N and 8 B atoms) and a (4 × 4 × 1) supercell of the MoS₂ monolayer (with 16 Mo and 32 S atoms). In case of mMoS₂/Si₂BN heterostructure, the bottom of S atoms in MoS₂ monolayer has directly situated the top of Si₂BN monolayer as presented in Fig. 1(a). The interlayer van der Waals (vdW) interactions between the Si₂BN and MoS₂ monolayers will directly influence the structural stability and electronic properties of the heterostructure interface. In this case, we have considered the possible minimum energy configuration

structure. Initially, we have fabricated a 3.54 Å vertical distance between the Si₂BN and MoS₂ monolayers for the interfacial vdW interactions and the corresponding relative energy profile is presented in Fig. S1 (see the ESI†). Due to the strong vdW interactions in the heterostructure, the vertical distance is reduced from 3.54 Å to 2.99 Å. For the structural lattice mismatch, we have increased the size of the unit cell of both Si₂BN (1 × 1 × 1 to a 2 × 2 × 1 supercell) and MoS₂ (1 × 1 × 1 to a 4 × 4 × 1 supercell) monolayers and it is defined by $\Delta a = \left(\frac{a_{\text{Si}_2\text{BN}} - a_{\text{MoS}_2}}{a_{\text{Si}_2\text{BN}}} \right) \times 100$, where $a_{\text{Si}_2\text{BN}}$ is the lattice parameter of the Si₂BN monolayer and a_{MoS_2} is the lattice parameter of the MoS₂ monolayer. The calculated values of lattice mismatch Δa in the direction of a and b are 0.1% and 1.4%, which is in the a direction negligible and in the b direction acceptable, respectively.

After the optimization of the crystal structure, no structural distortion is found which is very similar to a previously studied graphene/MoS₂ interface.⁵⁹ The vertical distance between the Si₂BN and MoS₂ monolayers are 2.99 Å and 2.20 Å for mMoS₂/Si₂BN and rMoS₂/Si₂BN, respectively and it shows the vdW equilibrium spacing. The S atoms of MoS₂ monolayer shows only physisorption interactions. For the thermodynamic stability of the physical interaction between the Si₂BN and MoS₂ monolayers, we have calculated the adhesion energy as follows:

$$E_{\text{ad}} = E_{\text{Si}_2\text{BN}/\text{MoS}_2} - E_{\text{Si}_2\text{BN}} - E_{\text{MoS}_2} \quad (2)$$

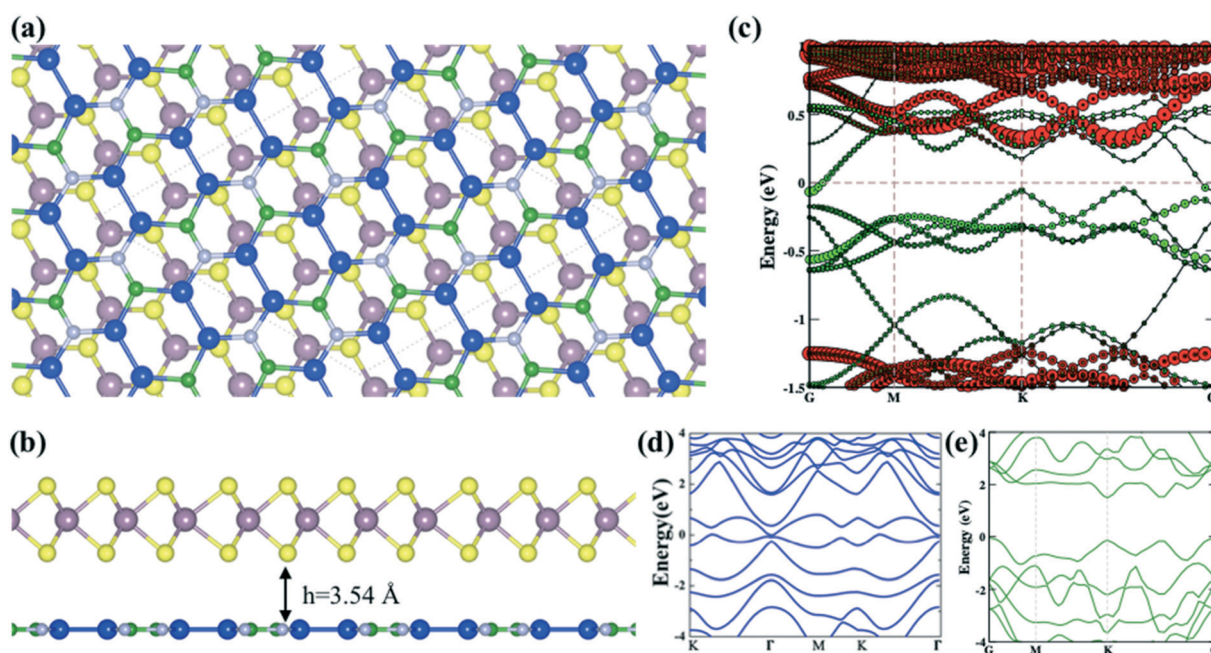


Fig. 1 The optimized mMoS₂/Si₂BN heterostructure viewed from the (a) top and (b) side and the (c) corresponding band structure (green and red colors represent the electronic band lines of Si₂BN and MoS₂, respectively). The electronic band structures of pristine (d) Si₂BN and (e) MoS₂ monolayers.



where $E_{\text{Si}_2\text{BN}/\text{MoS}_2}$, $E_{\text{Si}_2\text{BN}}$, and E_{MoS_2} represent the total energy of the heterostructure, pristine Si_2BN monolayer, and pristine MoS_2 monolayer, respectively. With vdW interactions between the Si_2BN and MoS_2 monolayers, we found an adhesion energy E_{ad} of -5.23 eV (≈ -36 meV \AA^{-2}) and -10.24 eV (≈ -71 meV \AA^{-2}) for $\text{mMoS}_2/\text{Si}_2\text{BN}$ and $\text{rMoS}_2/\text{Si}_2\text{BN}$, respectively, which are lower than that of the previously reported graphene/ MoS_2 heterostructure,⁶⁰ which is the energetically most favorable vdW heterostructure. The interfacial contact between the Si_2BN and MoS_2 monolayers may be a unique feature for its future applications as photocatalytic activity.

To understand the electronic properties of the $\text{mMoS}_2/\text{Si}_2\text{BN}$ heterostructure, we have calculated the atom-decomposed electronic band structure as presented in Fig. 1(c). For the comparison of the electronic band structure of $\text{mMoS}_2/\text{Si}_2\text{BN}$, we have also computed the individual band structures of the Si_2BN and MoS_2 monolayers as shown in Fig. 1(d) and (e), respectively. From the electronic band structure of heterostructure, we can see that the electronic band lines slightly changes at high symmetry points and opens the direct bandgap at Γ and K points as presented in Fig. 1(c). The computed electronic band structure shows the metallic behavior of the Si_2BN monolayer as presented in Fig. 1(d). Additionally, the calculated band structure of the MoS_2 monolayer shows a direct bandgap of 1.64 eV from the valence band maximum, and the conduction band minimum is located at the K-point as shown in Fig. 1(e). The value of the theoretical bandgap 1.64 eV is underestimated compared with the experimental bandgap 1.8 eV.⁶¹ During the contact of Si_2BN with MoS_2 monolayer reduced the bandgap 1.43 eV from 1.64 eV and the Fermi level-shifted towards the conduction band minimum side; due to this, it shows n-type behavior. Also, one band line crosses the Fermi level at the Γ point of the Si_2BN monolayer and the electronic band lines are separated as compared to the pristine case at the Γ point as shown in Fig. 1(c). Predominantly, the metallic conductivity in the complex system is mediated by the Si_2BN surface.

Previous investigations suggested that the stability of the MoS_2 nanoribbon is strongly dependent on edge structures in which the sulphur terminated edges (zigzag direction) had the lowest energy configuration.^{60,62,63} In the present work, we have mounted the MoS_2 nanoribbon on the monolayer surface of Si_2BN in which the MoS_2 nanoribbon has S atoms on one terminal edge and Mo atoms on the other edge as presented in Fig. 2(a). In the case of $\text{rMoS}_2/\text{Si}_2\text{BN}$, the lateral separation distance between nanoribbon MoS_2 and its periodic images is 15 \AA to prevent physical interactions. The fully optimized structural configuration has slight distortion at the nanoribbon edges which is consistent with the previous literature.^{60,62,63}

Furthermore, we have calculated the projected density of states (PDOS) of the pristine Si_2BN and MoS_2 monolayers as well as the $\text{mMoS}_2/\text{Si}_2\text{BN}$ and $\text{rMoS}_2/\text{Si}_2\text{BN}$ heterostructures as shown in Fig. S3.† From the electronic density of states of pristine Si_2BN , the monolayer has more contribution from the Si-p orbital and a small contribution comes from the p-orbitals of the B and N atoms at the Fermi level as shown in Fig. S3(a).† Due to the presence of some electronic states at the Fermi level, pristine Si_2BN shows metallic behavior. But in the case of the pristine MoS_2 monolayer, the electronic states are dominated by the d-orbital of Mo atoms and a very small contribution comes from the S p-orbital near the Fermi level in both the VBM and CBM as presented in Fig. S3(b).† We can see that the pristine MoS_2 monolayer shows p-type semiconducting behavior (see Fig. 1e and S3b†). Furthermore, with the interfacial contact between Si_2BN and MoS_2 , the heterostructure ($\text{mMoS}_2/\text{Si}_2\text{BN}$) shows metallic behavior in which the p-orbital of Si atoms is responsible for band crossing at the Fermi level. Also, the electronic states of MoS_2 shifted towards the CBM side due to the significant vdW interactions between the Si_2BN and MoS_2 monolayers. According to this, the Si_2BN and MoS_2 monolayers behave like n-type semiconductors with the contact of the Si_2BN surface. There are no significant changes in the electronic states of the Si_2BN monolayer because it shows metallic

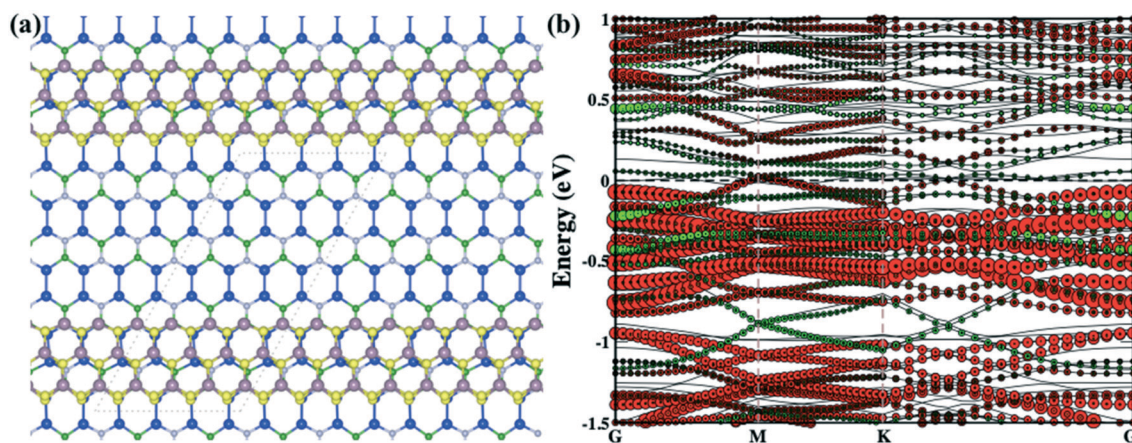


Fig. 2 The optimized $\text{rMoS}_2/\text{Si}_2\text{BN}$ heterostructure (a) and the corresponding band structure (b) (green and red colors represent the electronic band lines of Si_2BN and MoS_2 , respectively).



behavior before and after the contact with the MoS₂ monolayer. Moreover, during the interfacial contact between a monolayer of Si₂BN and MoS₂ shows metallic nature for both vdW heterostructure mMoS₂/Si₂BN and rMoS₂/Si₂BN. But in this case, the p-orbital of the Si atoms is strongly hybridized with the d-orbital of the Mo atoms, which appears near and at the Fermi level, as shown in Fig. 2(b) and S3(d).† The terminal edge S and Mo atoms of the MoS₂ nanoribbon may be a more reactive surface with the Si₂BN monolayer and this is why lots of electronic band lines cross the Fermi level in the electronic band structures.

Charge distribution and work function studies

The entirely distinct electronic properties of both mMoS₂/Si₂BN and rMoS₂/Si₂BN heterostructures are induced by the different termination of the MoS₂ surface, mainly the existence of edge atoms of the MoS₂ nanoribbon. The effect of the MoS₂ edges is determined by the charge density difference plot. The charge density difference plot is calculated by:

$$\Delta\rho = \rho_{\text{Si}_2\text{BN}/\text{MoS}_2} - \rho_{\text{Si}_2\text{BN}} - \rho_{\text{MoS}_2}, \quad (3)$$

where $\rho_{\text{Si}_2\text{BN}}$ and ρ_{MoS_2} are the electron density of isolated Si₂BN and MoS₂ systems, respectively, and $\rho_{\text{Si}_2\text{BN}/\text{MoS}_2}$ is the electron density of a mMoS₂/Si₂BN or rMoS₂/Si₂BN complex system. The electron charge density difference plots are depicted in Fig. 3. In the case of the mMoS₂/Si₂BN heterostructure, electron transfer is detected because we can

see that a significant electron cloud is present at the interface. Both cases have significant electron clouds at the interface of the heterostructure. But in the case of mMoS₂/Si₂BN heterostructure, the charge transfer between MoS₂ and Si₂BN is relatively less as compared to rMoS₂/Si₂BN heterostructure, as shown in Fig. 3(a and b). The charge transfer is consistent with adhesion energy that is a physical interaction between monolayer MoS₂ on Si₂BN is relatively half as compared to nanoribbon MoS₂ on the Si₂BN system. It is observed that excess electrons accumulate at the S-edge of the MoS₂ monolayer and MoS₂ ribbon. Due to the edge-effect of nanoribbon MoS₂, it has more electron clouds at the S-edge. This phenomenon is also observed in rMoS₂/Si₂BN, as demonstrated in Fig. 3b, as the clouds that represent electron accumulation spread systematically over the MoS₂ nanoribbon. The accumulation of electrons at the MoS₂ surface would be important for the edge atoms to act as active sites in catalysis. It was experimentally reported that the presence of edge atoms in the MoS₂ system in the case of the MoS₂/graphene heterostructure causes it to have high activities for catalysis and potential applications for sensing and energy storage devices.^{59,60,64–67} Our findings also suggest that the edge states are responsible for enhancing the charge-transport properties.

Additionally, we have calculated the planar averaged charge density difference along the z-direction, as shown in Fig. 4(a and b). The positive value on the y-axis indicates electron accumulation and the negative value on the y-axis indicates electron depletion. It is noticed that the electron transfer occurs from the Si₂BN monolayer to the MoS₂ surface in the heterostructure appearing at the interface

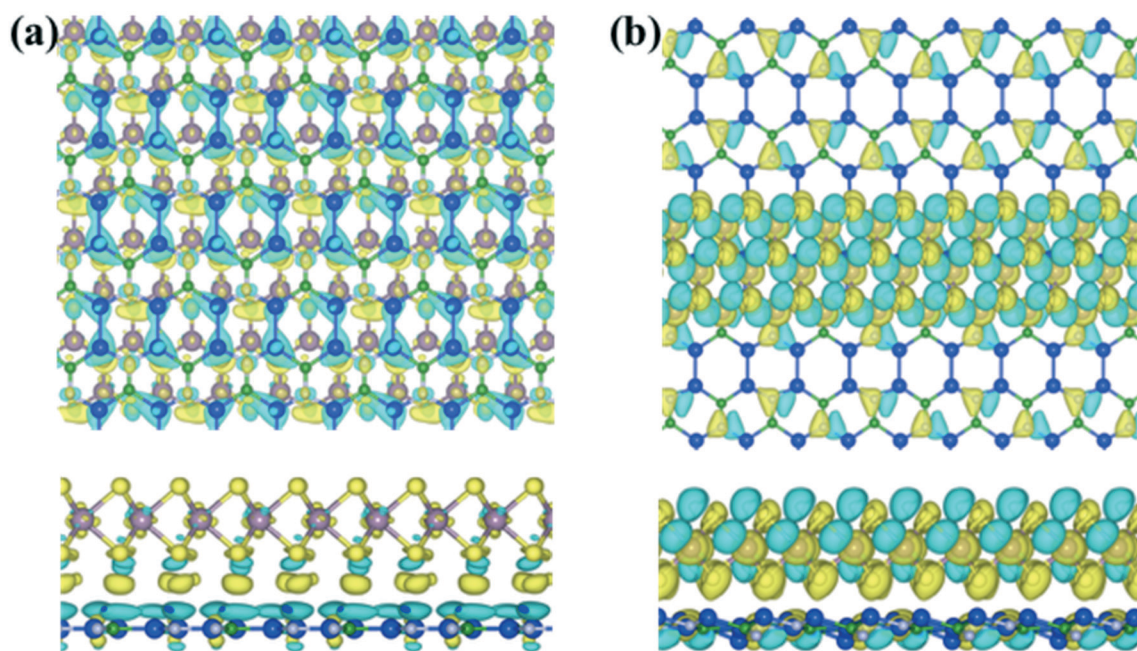


Fig. 3 Top view (upper panel) and side view (lower panel) of the electron density difference plots for the (a) mMoS₂/Si₂BN and (b) rMoS₂/Si₂BN heterostructures. The iso-value is set as $10^{-3} \text{ e } \text{\AA}^{-3}$. The cyan and yellow colors represent the charge depletion and accumulation in space, respectively.



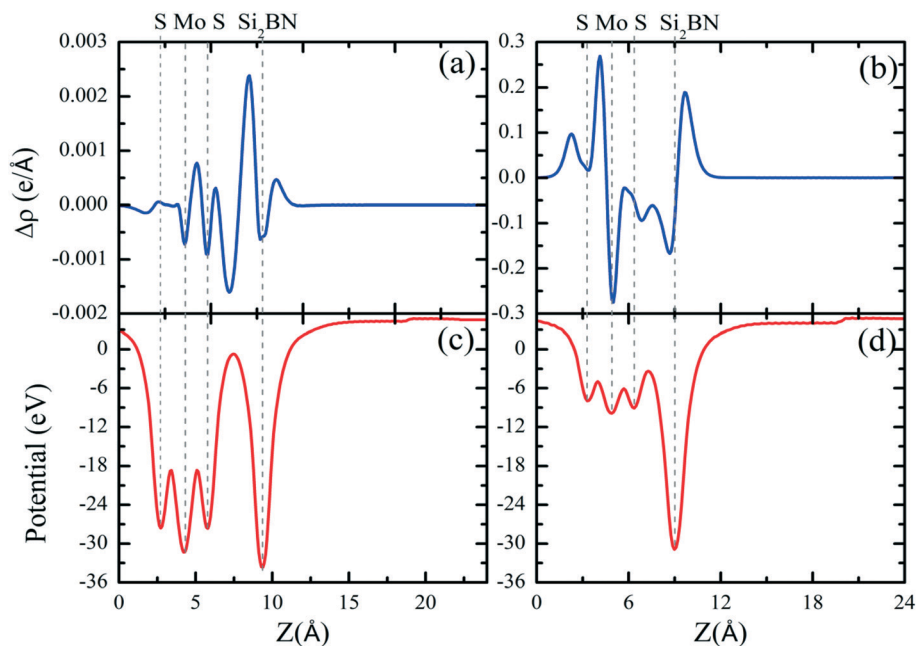


Fig. 4 Planar-averaged electron density differences $\Delta\rho(z)$ for the (a) mMoS₂/Si₂BN and (b) rMoS₂/Si₂BN heterostructures. The electrostatic potentials for the (c) mMoS₂/Si₂BN and (d) rMoS₂/Si₂BN heterostructures.

region. To quantify the amount of charge transferred, we have used Bader charge analysis for such an interfacial interaction surface. We found that the monolayer Si₂BN transfers 0.122 e⁻ and 0.553 e⁻ to the monolayer and nanoribbon MoS₂, respectively. This phenomenon can be easily understood by analyzing the electrostatic potential and corresponding simulated work function of the pristine MoS₂ and Si₂BN monolayers, as presented in Fig. 4(c and d) and 5. The work functions of the pristine MoS₂ and Si₂BN monolayers are 5.82 eV and 4.32 eV, respectively. However, the mMoS₂/Si₂BN and rMoS₂/Si₂BN heterostructures have work functions situated between those of the pristine MoS₂ and Si₂BN layers. This means that the significant changes in the electrostatic potential regulate the charge redistribution in the heterostructure system. According to that, spontaneous interfacial electron transfer occurs from the Si₂BN layer to

the MoS₂ layer, which is easily justified in terms of the large difference in work functions. It is also known that the electrons transfer from a lower potential region to a higher potential region.⁶⁸ Due to the significant charge transfer at the interfacial region, an internal electric field is generated which can effectively enhance the photogenerated electron-hole (e⁻/h⁺) pair separation between the MoS₂ and Si₂BN layers. In previous investigations, it was found that a similar charge redistribution occurred in hybrid MoS₂/graphene⁶⁰ and black phosphorus/BiVO₄.⁶⁸

Mechanism of photocatalytic activity

For the purpose of exploring in detail the regioselectivity of hydrogen atoms, the binding characteristics on different sides of both MoS₂/Si₂BN heterostructures (monolayer and ribbon) were explored in our calculations. Fig. 6(a–d) shows the top and side views of mMoS₂/Si₂BN and rMoS₂/Si₂BN with a H-atom adsorbed on either the MoS₂-side or Si₂BN-side. To get a better understanding of the favorable binding sites on both sides of mMoS₂/Si₂BN and rMoS₂/Si₂BN, distinct binding sites were examined. In the case of the Si₂BN-side, the sites were located above the B, N, and Si atoms and Si-Si, B-N, N-Si, and Si-Si bridges, and hollow sites. In the case of the MoS₂-side, four kinds of binding sites were considered, in which the first one is located above the Mo-atoms, the second is above the S-atoms, the third is between the Mo-S bonds and the last one is at the hollow site of the hexagons that contain 3Mo- and 3S-atoms. The summarized adsorption energies at the most stable binding sites for an H-atom adsorbed on both sides are described in Table 1. It is obvious from this table that the adsorption process of a H-atom on

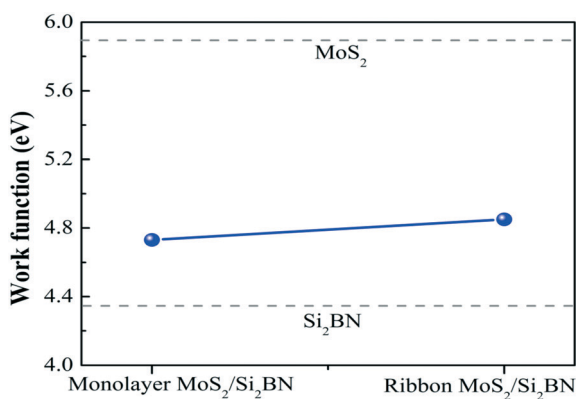


Fig. 5 Work functions of mMoS₂/Si₂BN and rMoS₂/Si₂BN. The dotted lines for pristine MoS₂ and Si₂BN are also shown for comparison.



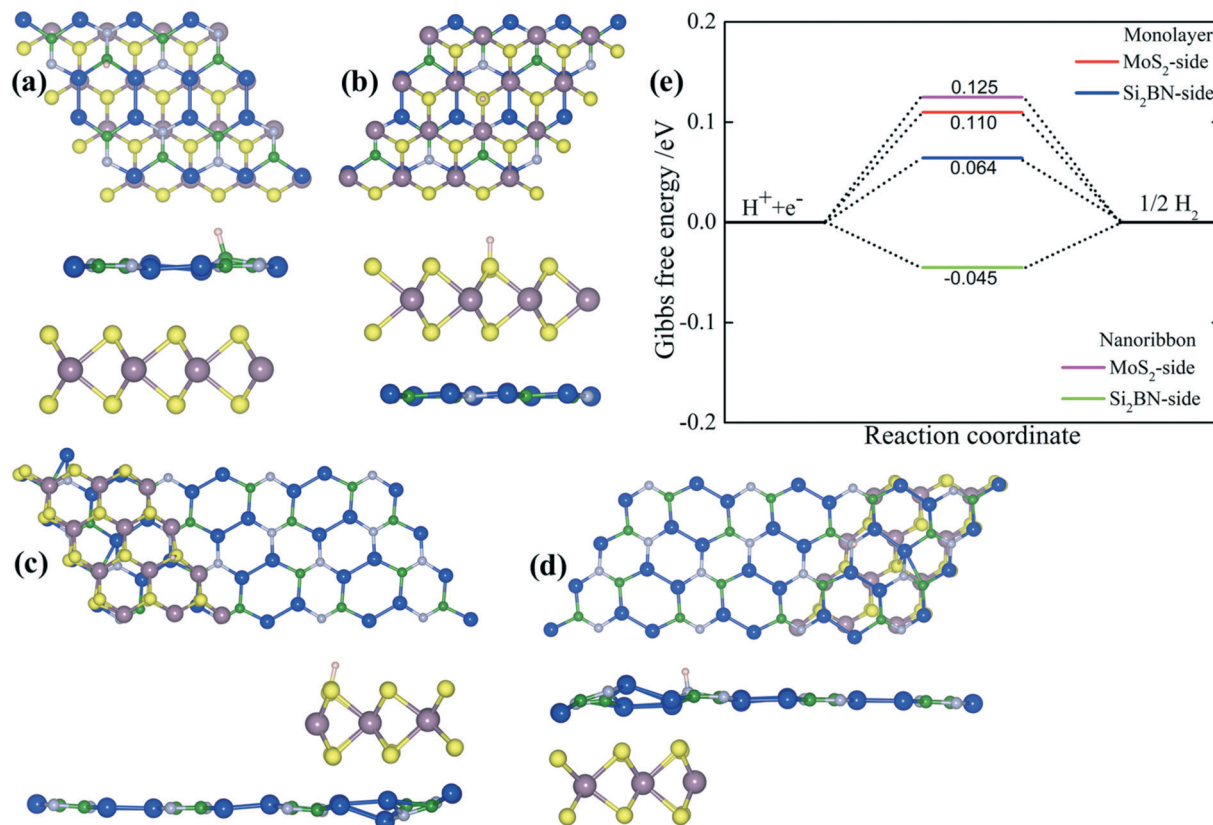


Fig. 6 (a–d) Top and side views of monolayer and ribbon MoS₂/Si₂BN with a hydrogen atom adsorbed at the most favorable site on both sides. (e) Calculated Gibbs free energy profile for the hydrogen evolution reaction (HER) on both sides of monolayer MoS₂/Si₂BN and ribbon MoS₂/Si₂BN.

Table 1 The adsorption energies of a H-atom E_{ad} (eV) adsorbed on the most stable binding site and the adsorption free energies (ΔG_{H^*}) on both sides of mMoS₂/Si₂BN and rMoS₂/Si₂BN (see Fig. 6a–d). Bader charge analysis of a hydrogen atom on the MoS₂- and Si₂BN-sides of both heterostructures, monolayer MoS₂/Si₂BN and ribbon MoS₂/Si₂BN

Systems	E_a (eV)		ΔG_{H^*} (eV)		Bader analysis	
	MoS ₂ -Side	Si ₂ BN-Side	MoS ₂ -Side	Si ₂ BN-Side	MoS ₂ -Side	Si ₂ BN-Side
Monolayer MoS ₂	-0.13	-0.115	0.11	0.125	0.056	0.14
Ribbon MoS ₂	-0.176	-0.285	0.064	-0.045	0.062	0.99

rMoS₂/Si₂BN is better than that on mMoS₂/Si₂BN, with the adsorption energy being -0.176 eV in the case of the MoS₂-side and -0.285 eV in the case of the Si₂BN-side. The thermodynamic stability of the MoS₂/Si₂BN vdW heterostructure at 300 K was investigated by *ab initio* molecular dynamics (MD) simulations based on the Nose thermostat algorithm. The evolution of the total potential energy with simulation time and the final snapshot after 10 ps are shown in Fig. S4.† The total energies at 300 K remain almost invariant during the simulation. One can see in Fig. S4† that the final energy fluctuations tend to smoothen in the energy range up to 3 eV for mMoS₂/Si₂BN and 5 eV for rMoS₂/Si₂BN. Our results indicate that the honeycomb network of the MoS₂ and Si₂BN regions remain unchanged which led to a stable structure with no breaking of bonds, basically, under 300 K. MD simulations suggest that the MoS₂/Si₂BN vdW heterostructure is thermally stable at 300 K.

To gain insight into the adsorption mechanisms, the adsorption free energy (ΔG_{H^*}) in the different sides of both heterostructures was also calculated, as illustrated in Table 1 and Fig. 6e. Generally, a potential catalyst with a better and efficient HER activity should be characterized by zero adsorption free energy ($\Delta G_{H^*} \rightarrow 0$). It is noted that the adsorption free energies are near zero in the case of rMoS₂/Si₂BN with about -0.045 eV and -0.062 eV when hydrogen is adsorbed on the MoS₂-side and Si₂BN-side, respectively, which is better compared to mMoS₂/Si₂BN with ΔG_{H^*} of about 0.11 eV and 0.125 eV for the MoS₂-side and Si₂BN-side, respectively. Consequently, the hydrogen evolution reaction activity in the case of ribbon MoS₂/Si₂BN is ideal compared to that of the monolayer MoS₂/Si₂BN. As previously reported, the Gibbs free energy on the pristine MoS₂ and Si₂BN monolayers were found to be 1.29–1.80 eV (ref. 60) and 0.122 eV (ref. 54), respectively.



To further quantify this detail, the charge transfer mechanism was evaluated by Bader charge analysis to consider the distribution of charge when an H-atom is adsorbed on the different sides of the MoS₂/Si₂BN heterostructures. In the case of a hydrogen atom adsorbed either on the MoS₂-side or Si₂BN-side of mMoS₂/Si₂BN, the hydrogen gains a net amount of charge of 0.056 |e| and 0.014 |e|, respectively, and when a hydrogen atom is adsorbed either on the MoS₂-side and Si₂BN-side of rMoS₂/Si₂BN, the hydrogen atom gains a charge of 0.062 |e| and 0.99 |e|, respectively, indicating that the charge transfer mechanism arises through the MoS₂- and Si₂BN-sides of the heterostructures to the H-atom.

Based on the above-mentioned results of work function, Fig. 7 shows the activity of MoS₂/Si₂BN for photocatalytic water splitting, which is explored by comparing the band positions of MoS₂ and Si₂BN before and after contact to the reduction and oxidation potentials. The Fermi level of MoS₂ before contact is very close to the VB, and that of Si₂BN is located near the CB. Furthermore, the Fermi level equilibration leads to the generation of an internal electric field and hence charge diffusion; this, in turn, shifts the band positions of MoS₂. Thus, the energy levels of MoS₂ shift upward along with the Fermi level, whereas those of Si₂BN shift downward along with the Fermi level until the Fermi level of MoS₂ and Si₂BN reach an equilibrium; this leads to the generation of an internal electric field with a negatively charged portion at the interface of the MoS₂ region and a positively charged portion at the interface of the Si₂BN region. On the other hand, by definition, the CBM must be situated above the H⁺/H₂ reduction potential (0 V vs. NHE), while the VBM must be located below the O₂/H₂O oxidation potential (1.23 V vs. NHE). In the case of before contact, the CBM potential of MoS₂ is -0.33 eV lower than the reduction potential of H⁺/H₂, while the VBM potential is 0.08 eV higher than the oxidation potential of O₂/H₂O, which is sufficient for oxidation and reduction of water considering the overpotential factor. After contact, the relative positions of the CBM and VBM of MoS₂ will change with the Fermi level due to the charge redistribution. The CBM potential (about

-0.84 eV) becomes much lower than the reduction potential of H⁺/H₂, while the VBM potential (0.80 eV) of MoS₂ becomes -0.43 eV lower than the oxidation potential of O₂/H₂O.

The optical absorption spectra is an important factor in describing the performance of the photocatalyst of vdW heterostructures for photocatalytic activities. Thus, the absorption spectra of the fully optimized pristine MoS₂ and Si₂BN monolayers, as well as the heterostructures mMoS₂/Si₂BN and rMoS₂/Si₂BN, were studied by computing the imaginary component of the complex dielectric function as illustrated in Fig. 8. According to the computed absorption coefficients in the visible light range between 1.55 eV and 3.1 eV, the Si₂BN monolayer scarcely absorbs visible light compared to MoS₂, which displays a significant absorption capacity. However, in the case of the MoS₂/Si₂BN heterostructures, the optical absorption of mMoS₂/Si₂BN is significantly greater compared to that of rMoS₂/Si₂BN and the Si₂BN monolayer but is slightly less than that of the MoS₂ monolayer. These indicate the promising application of the mMoS₂/Si₂BN heterostructure as a great light absorber.

Conclusions

In summary, the effects of MoS₂ edge structure on the electronic structures, charge transport, and work functions of MoS₂/Si₂BN heterostructures have been investigated using first-principles calculations. The interfacial interactions between edge-free MoS₂ and a Si₂BN monolayer are weak vdW interactions which do not affect the properties of Si₂BN and the semiconducting behavior of the MoS₂ monolayer; however, the Fermi level is shifted towards the conduction band side (n-type semiconductor conductivity) in the case of the MoS₂ monolayer. When MoS₂ has exposed edges, the MoS₂ ribbon on a Si₂BN monolayer in the current study, the binding strength and electronic coupling at the interface are enhanced, resulting in more electrons transferred from the Si₂BN surface to the MoS₂ nanoribbon surface which can

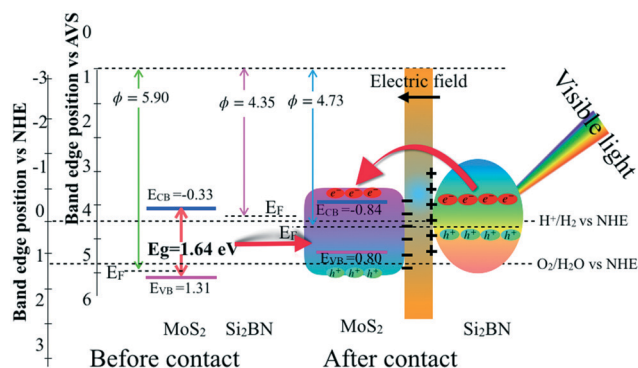


Fig. 7 A schematic diagram of the band configuration and the charge separation at the interface of MoS₂/Si₂BN under visible-light irradiation.

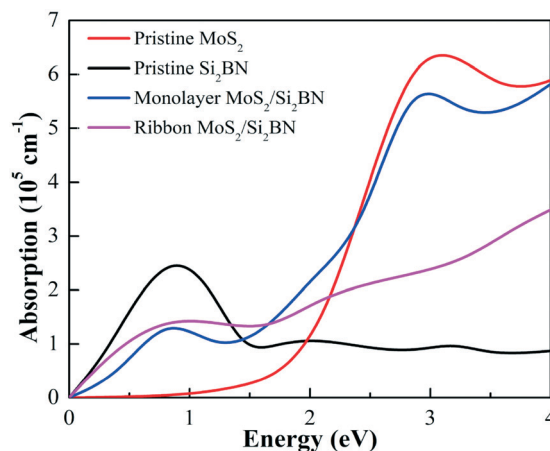


Fig. 8 Optical absorption spectra of the pristine MoS₂ monolayer, Si₂BN monolayer, mMoS₂/Si₂BN, and rMoS₂/Si₂BN, represented by red, black, blue, and magenta lines, respectively.



effectively enhance the photogenerated electron-hole pair separation between the MoS₂ and Si₂BN nanosheets. Additionally, the excess electrons at the MoS₂ surface are chemically more active, which can be used for energy storage and gas sensing applications. The electronic properties of MoS₂/Si₂BN heterostructures is strongly influenced by the MoS₂ dimensions, which could be potential materials for nanoelectronic devices and catalytic materials.

Conflicts of interest

There are no conflicts to declare.

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