The high-speed channel made of metal for interfacial charge transfer in Z-scheme g–C₃N₄/MoS₂ water-splitting photocatalyst

Lin Ju¹ ² ⁴, Chen Liu¹, Liran Shi³ and Li Sun¹ ³ ⁴

¹ School of Physics and Electric Engineering, Anyang Normal University, Anyang, 455000, People’s Republic of China
² School of Chemistry, Physics and Mechanical Engineering Faculty, Queensland University of Technology, Gardens Point Campus, QLD 4001, Brisbane, Australia
³ Key Lab of Advanced Transducers and Intelligent Control System, Ministry of Education, Taiyuan University of Technology, Taiyuan 030024, People’s Republic of China
⁴ Authors to whom any correspondence should be addressed.

E-mail: sdu_JL@163.com

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Abstract

Z-scheme heterostructures have attracted much attention for their prominent photocatalytic performance. However, the charge transfer mechanism is still ambiguous, and how to design the high-speed channel for interfacial charge transfer is still a big challenge. In the present work, the energy band structure and charge transfer of the MoS₂/g–C₃N₄ heterojunction are studied systematically. MoS₂/g–C₃N₄ heterojunction could be demonstrated to form a direct Z-scheme system via the analysis of the interfacial band bending. Regrettably, this heterojunction has a low tunneling possibility at the surface, seriously limiting the photocatalytic efficiency. To solve this problem, we try to build high-speed channel between the layers with suitable metal. We make a thorough inquiry of the interface of M–C₃N₄ and M–MoS₂ heterojunctions (M = Ag, Al, Au, and Pt). Our results reveals that Ag could improve the recombination efficiency of the majority carriers at the interface, which could pretty explain the enhanced photoactivity for g–C₃N₄/Ag/MoS₂ system found in experiments. More notably, both Schottky and tunneling barriers vanish at the Al–C₃N₄ interface, forming an ohmic contact, which predicts a higher performance for electron transport. So that aluminum with the more excellent performance and higher abundance is a promising candidate for silver in the Z-scheme system.

1. Introduction

Due to the continuous growth of energy crises and environmental pollutions, photocatalysis has attracted significant interest in recent years, which is considered to be a promising technology to solve those problems. Photocatalytic H₂ production with particulate semiconductors is a ‘green’ route to convert solar energy into chemical energy. Since the pioneering work of Fujishima and Honda [1], a lot of efforts are devoted to explore single-component photocatalysts for water splitting [2–5]. Unfortunately, it is found that these single-component photocatalysts hardly possess high charge-separation efficiency, which is the vital feature for ideal H₂ evolution photocatalyst. Composited photocatalytic systems, with type-II band alignment, are usually used to improve the charge separation [6–11]. As shown in figure 1, these composited photocatalytic systems could be majorly categorized as O-scheme and Z-scheme on the basis of the photogenerated charge transfer pathway. For the O-scheme heterojunction photocatalyst (shown in figure 1 (left)), the photogenerated electrons will transfer to semiconductor A₀ from semiconductor B₀, while the photo-excited holes migrate in the opposite direction under light irradiation, resulting in a spatial separation of electron–hole pairs. However, the redox ability of the O-scheme heterojunction photocatalyst is weakened, which is unfavorable for H₂ evolution. Moreover, the O-scheme system demands both the component materials could split water in O₂ and H₂ themselves, which greatly limits the scope of photocatalysts suitable for it. As to the Z-scheme composite (displayed in figure
(right)), there are three components, i.e. photocatalysts for oxidation ($A_o$) and reduction ($B_o$), and a redox mediator for carrier migration. The photo-excited electrons in the CB of $B_o$ take part in the reduction reaction, while the photo-generated holes in the VB of $A_o$ participate in the oxidation reaction, respectively. Then these residual photo-generated carriers migrate to the redox mediator, and recombine there. Therefore, the Z-scheme composite could spatially separate the photogenerated charges and optimize the redox potential. The photocatalysts for the reduction and oxidation, which do not have to be suitable for overall water splitting themselves, are elaborately combined to split water into hydrogen and oxygen. Hence, constructing Z-scheme systems makes more photocatalysts available for overall water splitting and so far, massive efforts have been devoted to this filed [12–17].

It is well known that, layer materials with two dimensional (2D) structure usually have larger surface area, more activity sites, and shorter carrier migration distance, consequently possessing higher photocatalytic performance than bulk materials. Both $g$–C$_3$N$_4$ [18–20] and MoS$_2$ [21–23] are typical 2D materials, widely used as catalytic materials. Moreover, through MoS$_2$ nanoparticles loading on $g$–C$_3$N$_4$ nanosheets and bulk $g$–C$_3$N$_4$ coupling with bulk MoS$_2$, some MoS$_2$/g–C$_3$N$_4$ composito photo-catalysts have been prepared [24–26]. Nevertheless, synthesis of 2D MoS$_2$/g–C$_3$N$_4$ heterojunction composed of $g$–C$_3$N$_4$ and MoS$_2$ nanosheets has seldom been reported. Recently, Fang et al successfully synthesized 2D MoS$_2$/g–C$_3$N$_4$ heterojunction (using g–C$_3$N$_4$ sheets, and MoS$_2$ microspheres assembled from tiny nanosheets), which has been found to possess significantly higher activity in photocatalytic H$_2$ generation than pure g–C$_3$N$_4$ and MoS$_2$ [27]. Due to the poor ability of MoS$_2$ in reducing H$^+$ into H$_2$, the previous heterojunction-transfer mechanism (O-scheme) cannot effectively explain the enhanced catalytic activity of g–C$_3$N$_4$/MoS$_2$ in hydrogen evolution [28]. In this article, we will account for it follow the Z-scheme transfer mechanism.

In addition, numerous researches show that noble metal could enhance the photocatalytic efficiency of the Z-scheme [14, 27]. Besides the localized surface plasmon resonance (LSPR) effect, which improve the light absorption property, the noble metal also acts as a unique carrier-transfer-channel. However, the mechanism for forming the unique carrier-transfer-channel is still unclear. Moreover, in order to realize the Z-scheme compounds producing in a large-scale, the product cost should lower. Therefore, finding some cheaper metal to replace the noble metal is pretty necessary. In the present work, we will explore the origin of the improved photocatalytic activity of g–C$_3$N$_4$/Ag/MoS$_2$. We also use other metal (gold, platinum and aluminum) to substitute sliver. Interestingly, we find aluminum is more suitable than sliver to construct the interfacial charge transfer channel.

2. Computational details

In this work, the lattice constants of freestanding monolayer MoS$_2$ and g–C$_3$N$_4$ are predicted to be 3.19 and 4.78 Å, respectively, which are in accord with previous experimental measurements and theoretical results.
[28–30]. A 2 × 2 supercell of C3N4 (12 carbon and 16 nitrogen atoms) and a 3 × 3 supercell of MoS2 (18 sulfur and 9 molybdenum atoms) are selected to construct the hybrid C3N4/MoS2 van der Waals (vdW) heterojunction. As listed in table S1 available online at stacks.iop.org/MRX/6/115545/mmedia, the lattice mismatches for both C3N4 and MoS2 monolayer in the C3N4/MoS2 vdW heterojunction are less than 0.01%. Vienna ab initio simulation package (VASP) is selected to perform our density functional theory (DFT) calculations [31, 32]. The frozen-core projector augmented wave (PAW) and the generalized gradient approximation (GGA) approximation are chosen to describe the interaction between the valence and core electrons [33–35]. The electronic structures are assessed using the Heyd–Scuseria–Ernzerhof (HSE06) [36] hybrid functional to avoid the underestimate of the band gap calculated within Perdew–Burke–Ernzerhof (PBE) functional. Normal to the sheets, a 20 Å vacuum space is applied to the layers. The long-range vdW interactions between layers are described within the PBE + D2 (D stands for dispersion) method with the Grimme vdW correction [37]. For the asymmetric layer arrangement, the dipole correction is considered. The cutoff energy is 500 eV. For the 2D Brillouin zone sampling, 3 × 3 × 1 Monkhorst–Pack k mesh is chosen. The geometrical structure relaxations are carried out until the residual force and energy difference are, respectively, less than 0.02 eV Å⁻¹ and 10⁻⁵ eV.

For the configuration stability of heterojunction to be evaluated, the binding energy was calculated by the following formula,

\[ E_b = \frac{(E_{A/B} - E_A - E_B)}{N} \]

where \( E_{A/B}, E_A, \) and \( E_B \) are the total energies of the stacked A/B heterostructure, the component A and B, respectively; \( N \) is the number of atoms at the interface of the heterostructure.

The plane-integrated charge density difference was performed according to the following equation:

\[ \Delta \rho = \rho_{A/B} - \rho_A - \rho_B \]

where \( \rho_{A/B}, \rho_A, \) and \( \rho_B \) are the plane-averaged electron densities of the composite A/B, the component A and B, respectively. By charge difference analysis, the charge redistribution along the Z direction perpendicular to the interface was derived.

Here, we use a square potential barrier to replace the real potential barrier and evaluate the tunneling probability (\( T_B \)) by using the WKB formula

\[ T_B = \exp \left( -2 \frac{\sqrt{2mV}}{\hbar} \times w_B \right) \]

Where \( m \) and \( \hbar \) are the mass of free electrons and reduced Planck’s constant, \( V \) and \( w_B \) are respectively the height and width of the assumed square potential barrier.

3. Results and discussion

3.1. Isolated MoS2 and g–C3N4 monolayer

As a preliminary, we checked the structural and electronic properties of isolated MoS2 and g–C3N4 monolayers, respectively. As shown in figures S1(a) and (b), the optimized MoS2 sheet has a honeycomb structure. The length of Mo–S bond is 2.41 Å, while the vertical S–S distance is 3.12 Å. Clearly, the MoS2 monolayer has a direct band gap of 1.98 eV and both the valence band maximum (VBM) and the conduction band minimum (CBM) locate at the K point (As illustrated in figure S4 (left)). According to the partial density of states (PDOS) of MoS2 monolayer (shown in figure S4 (right)), both the VBM and CBM are mainly contributed by the hybrid orbitals of Mo 4d and S 3p. As to the planar g–C3N4 monolayer, there are two kinds of N atoms (N1 and N2) in terms of chemical environments. As shown in figure S1(c), N1 atoms only connect two C atoms, leaving a non-bonding character, whereas N2 atoms are fully saturated by the surrounding C atoms. Each C atom is surrounded by three nearest neighbor N atoms. The lengths of C–N1 and C–N2 bonds are 1.33 and 1.46 Å, respectively. As plotted in figure S1 (left), the g–C3N4 monolayer is a semiconductor with a direct energy gap of 2.81 eV, meanwhile the VBM and CBM both locate at the Γ point. Based on the PDOS of g–C3N4 monolayer shown in figure S2 (right) and figures S4(a)–(c), we find the VBM is dominated by the N1 2p orbital and the CBM is largely contributed by the hybridization of N1 2p and C 2p orbitals. Besides, PDOS obviously reflects the difference of chemical bonding environments for N atoms. All these observations of isolated MoS2 and g–C3N4 monolayer are in accordance with the previous results [29, 38].

In order to evaluate the activity of photocatalytic water splitting for isolated g–C3N4 and MoS2 monolayers, we calculated their band diagrams with reference to the vacuum level, which are presented in figure 4 (c) (left). The CBM of the isolated g–C3N4 and MoS2 monolayers −3.25 and −4.29 eV versus the vacuum level, while the VBM are −6.07 and −6.27 eV, respectively. They surpass the standard reduction potential of H⁺/H₂ (−0.44 eV versus the vacuum level) and the standard oxidation potential of O₂/H₂O (−5.67 eV versus the vacuum level),
which identified the suitability of g–C₃N₄ and MoS₂ monolayers for applications in water splitting, consistent with the previous theoretical results [22, 39].

3.2. MoS₂/g–C₃N₄ vdW heterojunction

3.2.1. Geometric and electronic structures

We construct the MoS₂/g–C₃N₄ heterojunction with stacking MoS₂ and g–C₃N₄ monolayers sequentially. For the optimized MoS₂/g–C₃N₄ heterojunction, the calculated details are listed in Table 1. As illustrated in Figure 2(b), there is an obvious geometric distortion in g–C₃N₄ sheet and the corresponding buckling distance ($d_2$) is about 0.89 Å. The vertical separation ($d_1$) is about 3.05 Å and the binding energy is 31.96 meV per atom, which is larger than the one of bilayer graphene (27.08 meV per atom) [40]. Since the bilayer graphene has been tested to be stable in water at room temperature by the molecular dynamics simulation [41], the MoS₂/g–C₃N₄ heterojunction is believed to be stable in water at room temperature as well. All these results are in accordance with the previous results [28].

The fat band structures of the MoS₂/g–C₃N₄ heterojunction based on the hybrid functional is plotted in Figure 3. Obviously, this heterojunction has a direct band gap of 1.70 eV. From the plots we can see that, there is a typical type-II band alignment structure in the MoS₂/g–C₃N₄ heterojunction. Both the CBM and VBM for the two kinds of monolayers are found at the Γ point. The calculated band gap of g–C₃N₄ and MoS₂ monolayers is 2.71 and 1.96 eV, respectively, which means that both of them may be response to visible light. In the MoS₂/g–C₃N₄ heterojunction, the band gap of g–C₃N₄ monolayer (2.71 eV) is slightly smaller than the one of the isolated g–C₃N₄ (2.81 eV) monolayer because of the distortions introduced by the interface effect. Moreover, the partial density of states (PDOS) as well as the total density of states (TDOS) of the MoS₂/g–C₃N₄ heterojunction is calculated, which is shown in Figure 3 (right). The content of the calculated DOS projected on two different layers in the MoS₂/g–C₃N₄ heterojunction is similar to that of the TDOS of isolated ones, respectively.

3.2.2. Activity of photocatalytic water splitting for MoS₂/g–C₃N₄ heterojunction

In an overall water splitting photocatalyst, the potential of the CBM should be higher than the reduction level of hydrogen ($-4.44$ eV at pH = 0), and the potential of the VBM should be lower than the oxidation level of oxygen ($-5.67$ eV at pH = 0). As shown in Figure 4(c) (right), for both MoS₂ and g–C₃N₄ monolayer in this heterostructure, the CBM and VBM still surpass and the standard oxidation potential of H₂O/O₂ and the

![Image](https://via.placeholder.com/150)

**Figure 2.** Top (a) and side (b) views of the optimized MoS₂/g–C₃N₄ heterojunction geometric structure. The Brillouin zone (c).

**Table 1.** Calculated properties of the g–C₃N₄/MoS₂ vdW heterostructure: Equilibrium interface distance ($d_1$ in Å), Buckling distance ($d_2$ in Å), Binding energy ($E_b$ in meV/atom), Transfer electron ($Q_T$ in e), Tunneling width ($w_B$ in Å), Tunneling height ($V$ in eV) and Tunneling probability ($T_B$)．

| Material     | d₁   | d₂   | E_b  | Q_T  | w_B  | V    | T_B (%) |
|--------------|------|------|------|------|------|------|---------|
| C₃N₄/MoS₂    | 0.89 | 3.05 | -31.96 | 0.19 | 1.75 | 3.41 | 3.67    |

![Table 1](https://via.placeholder.com/150)
from the VB of MoS2 to the VB of g
Meanwhile, it also could effectively prevent the adverse photoexcited carrier migration, such as the hole transfer substantialy accelerate photogenerated electron from g
heterojunction, the process of charge transfer between layers could induce internal electric monolayer, and the holes accumulate in the region next to the g
standard reduction potential of H\textsuperscript{+}/H\textsubscript{2}, indicating their sufficient activity for both the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), respectively. Compared with the band edge position of pristine MoS\textsubscript{2} illustrated in figure 4(c) (left), we find that, in the MoS\textsubscript{2}/g–C\textsubscript{3}N\textsubscript{4} heterojunction, the potential of the VBM of MoS\textsubscript{2} reduces by 50 meV, which implies that the design of heterojunction can slightly enhance the oxidation capacity of MoS\textsubscript{2}. In addition, in the MoS\textsubscript{2}/g–C\textsubscript{3}N\textsubscript{4} heterojunction, the VBM of g–C\textsubscript{3}N\textsubscript{4} is 1.82 eV lower than the CBM of MoS\textsubscript{2}, which indicates the possibility of the carriers migrating between the valence band (VB) of g–C\textsubscript{3}N\textsubscript{4} and the conduction band (CB) of MoS\textsubscript{2}.

The calculated ionization energy of g–C\textsubscript{3}N\textsubscript{4} (5.09 eV) is smaller than the one of MoS\textsubscript{2} (6.05 eV). When g–C\textsubscript{3}N\textsubscript{4} contacts with MoS\textsubscript{2}, electrons would be inclined to transfer from g–C\textsubscript{3}N\textsubscript{4} to MoS\textsubscript{2}. As reflected in the average effective potential shown in figure 4(a), the difference of microscopy average electrostatic potential between g–C\textsubscript{3}N\textsubscript{4} and MoS\textsubscript{2} sides is about 0.92 eV at the interface, which leads to an upward band bending of g–C\textsubscript{3}N\textsubscript{4} and a downward band bending of MoS\textsubscript{2} (displayed in figure 4(c) (right)). As shown in figure 4(b), the Bader charge analysis shows a substantial charge distribution in the form of electron accumulation at the interface and a significant electron transfer of 0.14 e. The electrons assemble in the region near the MoS\textsubscript{2} monolayer, and the holes accumulate in the region next to the g–C\textsubscript{3}N\textsubscript{4} monolayer. In the MoS\textsubscript{2}/g–C\textsubscript{3}N\textsubscript{4} heterojunction, the process of charge transfer between layers could induce internal electric field, which points from g–C\textsubscript{3}N\textsubscript{4} to MoS\textsubscript{2}. As illustrated in figure 4(c) (right), upon light irradiation, electrons in the VB of both MoS\textsubscript{2} and g–C\textsubscript{3}N\textsubscript{4} monolayers are excited to their respective CB, leaving holes in the VB. The photogenerated holes in the VB of MoS\textsubscript{2} take part in OER, while the photoexcited electrons in the CB of g–C\textsubscript{3}N\textsubscript{4} participate HER. The photoexcited holes and electrons left will assemble in the VB of g–C\textsubscript{3}N\textsubscript{4} and the CB of MoS\textsubscript{2}, respectively. In the heterointerface region, the presence of the band bending provides driving force and pushes photoexcited charges to move along the ‘Z’ pathway. The g–C\textsubscript{3}N\textsubscript{4} monolayer with high energy band level has an upward band bending and the MoS\textsubscript{2} monolayer has a downward band bending. Hence the charge transfer channel for the photogenerated electrons of g–C\textsubscript{3}N\textsubscript{4} moving to MoS\textsubscript{2} and the holes of MoS\textsubscript{2} transferring to g–C\textsubscript{3}N\textsubscript{4} is disrupted at the interface. The photoexcited electrons of MoS\textsubscript{2} and holes of g–C\textsubscript{3}N\textsubscript{4} will migrate to the interface but cannot flow into the energy bands of the other semiconductor, so they have to recombine with each other at the interface. Then the photo–induced electrons of g–C\textsubscript{3}N\textsubscript{4} and holes of MoS\textsubscript{2} are remained for photocatalysis. The electrons flow along the potential rise and holes move in the opposite direction. The internal electric field could substantially accelerate photogenerated electron–hole migration following the Z-scheme mechanism. Meanwhile, it also could effectively prevent the adverse photoexcited carrier migration, such as the hole transfer from the VB of MoS\textsubscript{2} to the VB of g–C\textsubscript{3}N\textsubscript{4}. Consequently, the MoS\textsubscript{2}/g–C\textsubscript{3}N\textsubscript{4} heterojunction could be a Z-scheme photocatalyst with visible-light activity. The direct Z-scheme g–C\textsubscript{3}N\textsubscript{4}/TiO\textsubscript{2} photocatalysts also follow this mechanism [42]. In addition, g–C\textsubscript{3}N\textsubscript{4} samples synthesized in experiments, usually includes a few atomic layers and the electronic structure is sensitive to the structure. However, it has been found that the band alignment of bilayer g–C\textsubscript{3}N\textsubscript{4}/MoS\textsubscript{2} nanocomposite is similar to the one in monolayer g–C\textsubscript{3}N\textsubscript{4}/MoS\textsubscript{2} [28], so the effect of the number of layers will not be discussed here anymore.

Figure 3. The calculated band structure (left) and the calculated PDOS (right) of the MoS\textsubscript{2}/g–C\textsubscript{3}N\textsubscript{4} heterojunction using HSE06 + D2. The Fermi level is set to zero.

3.2.3. The tunneling barrier for MoS$_2$/g–C$_3$N$_4$ heterojunction

The tunnel barrier at the interface influences the photorecycled carrier transfer efficiency, playing an important role in the Z-scheme photocatalysis system of vdW heterostructure. The tunnel barrier is evaluated by its width ($w_B$) and height ($V$), and forms when electrons cross the vdW gap at the interface, and measured by the electrostatic potential [43, 44]. As shown in figure 4(a), there is an obvious tunneling barrier at the MoS$_2$/g–C$_3$N$_4$ interface with a barrier height of 3.41 eV. As listed in table 1, the calculated tunneling possibility ($T_B$) of the MoS$_2$/g–C$_3$N$_4$ heterostructure is only 3.67%. The low $T_B$ will prevent the majority carriers in the photo-oxidation catalyst (MoS$_2$) and the photo-reduction catalyst (g–C$_3$N$_4$) from getting near the interface, which must be an obstacle for the efficiency of the Z-scheme water splitting. To overcome this negative effect, one way is to introduce electronic states in the gap between the VBM of g–C$_3$N$_4$ and the CBM of MoS$_2$ in the MoS$_2$/g–C$_3$N$_4$ heterojunction [45], e.g. built high-speed channel between the layers with suitable metal, such as CdSe/Ag/TiO$_2$ nanotube [46], and g–C$_3$N$_4$/Ag/WS$_2$ [47]. With the help of high-speed channel, the recombination of the majority carriers at the interfaces can become faster.

3.2.4. High-speed channel made of suitable metal

Fang et al reported that the visible-light-induced photocatalytic activity of g–C$_3$N$_4$/Ag/MoS$_2$ system is 2.08-fold of g–C$_3$N$_4$/MoS$_2$ systems in the production of hydrogen out of water [27]. The enhanced photoactivity in $H_2$ generation is due to Ag nano-particles, which may serve as a charge transport center to form the Z-scheme g–C$_3$N$_4$/Ag/MoS$_2$ system. In order to get deeper insight into the details affecting and find more suitable metal, we analyze the interfacial properties between common metals (e.g. Ag, Au, Al, and Pt) and monolayer g–C$_3$N$_4$.
MoS$_2$, respectively. As shown in figure 5, We choose four layers of metal atoms to simulate the metal surfaces and construct a supercell with monolayer g–C$_3$N$_4$, MoS$_2$ absorbed on one side of the metal surfaces (M–C$_3$N$_4$ and M–MoS$_2$), respectively. (More details about structure parameters are listed in table S2). After a full optimization, the interlayer spacing are in the order of $d_{pt} < d_{Au} < d_{Ag} < d_{Al}$ for M–MoS$_2$ and of $d_{Al} < d_{Ag} < d_{Au} < d_{pt}$ for M–C$_3$N$_4$. Usually, a smaller equilibrium interlayer distance causes a larger binding energy [48], which was met well by our results of M–MoS$_2$. Nevertheless, the case of M–C$_3$N$_4$ defies this general rule. Pt–C$_3$N$_4$ with the largest interlayer distance has the most binding energy. In addition, as illustrated in figure S5, the aluminum and C$_3$N$_4$ monolayer form a chemisorption interface in the Al–C$_3$N$_4$ system. There exists a bonding interaction between the Al atoms at first layer of the Al(1 1 1) surface and the three N1 atoms nearby, resulting in an obvious wrinkle at the Al(1 1 1) surface. The Ag/g–C$_3$N$_4$ nanocomposites has been successfully synthesized by chemical reduction methods [49, 50], Al–C$_3$N$_4$–C$_3$N$_4$ heterostructure with the comparable formation energy is promising to be synthesized experimentally.

In order to investigate the built-in electric fields at the interfaces of M–MoS$_2$ and M–C$_3$N$_4$, the difference charge density and plane averaged charge density are calculated to intuitively see the redistribution of charge. As is indicated in figure 6, charges locate at the interfacial regions, which indicate an orbital overlap. Interestingly, we observed that the direction of charge transfer is different in M–MoS$_2$ and M–C$_3$N$_4$. For the cases of M–C$_3$N$_4$ (M = Ag, Au, and Pt), clearly, the electrons assemble in the region near the metal surface, while the holes assemble in the region next to the g–C$_3$N$_4$ monolayer, inducing an internal electric field at the interface with a direction from g–C$_3$N$_4$ to metal. As listed in table 2, the transfer electron for Ag–g–C$_3$N$_4$, Au–g–C$_3$N$_4$, and Pt–C$_3$N$_4$ is 0.18, 0.12, and 0.09 e. As to the case of Al–C$_3$N$_4$, the electrons assemble in the middle of the Al atoms and N1 atoms, indicating the covalent bonds between them. For the cases of Ag–MoS$_2$ and Al–MoS$_2$, electrons amass in the place next to the Mo$_2$S$_4$ monolayer, while the holes amass in the place near the metal surface, consisting with the previous results of Al–MoS$_2$ [51]. Bader charge analysis indicates 0.15 and 0.36 e transfers from the Ag and Al surface to Mo$_2$S$_4$, respectively. Hence, the direction of built-in electric field is from metal surface to Mo$_2$S$_4$ monolayer. For the cases of Au–MoS$_2$ and Pt–MoS$_2$, most charges accumulate in the middle of the interfaces. Only very few electrons transfer from Au (0.078 e) and Pt (4.66 $\times$ 10$^{-3}$ e) surface to Mo$_2$S$_4$, causing the weak built-in electric field with the same direction as the one in Ag–MoS$_2$ and Al–MoS$_2$. The weak built-in electric field caused by electrons transfer at the interface also been found in many other system [17, 52, 53]. Besides, the photo-exited carriers transfer following the built-in electric field direction, which is predicted by us in this paper, has been experimentally verified in many systems, such as Au/g–C$_3$N$_4$, Ag/g–C$_3$N$_4$, and so forth [47, 54].

Through the above analysis, we could predict that in the g–C$_3$N$_4$/M/MoS$_2$ (M = Ag, Al, Au, and Pt) heterostructure, the internal electric field points from Mo$_2$S$_4$ through M to g–C$_3$N$_4$, which will significantly promote the transfer of photoexcited electron from the CB of Mo$_2$S$_4$ to the VB of g–C$_3$N$_4$. According to the estimated values listed in table S3, we find most of the M–Mo$_2$S$_4$, and M–C$_3$N$_4$, heterostructure have a stronger...
internal electric filed than the one in MoS$_2$/g–C$_3$N$_4$. Especially, the electric field strength at the Al–MoS$_2$ interface could be more than five times stronger than that of MoS$_2$/g–C$_3$N$_4$. The enhancement of internal electric field strength will further promote the recombination of photoexcited electron from the CB of MoS$_2$ and photoexcited holes from the VB of g–C$_3$N$_4$.

Figure 6. The plane-integrated electron density difference along the vertical direction for the M–C$_3$N$_4$ ((a)–(d)) and M–MoS$_2$ ((e)–(h)) heterojunctions (M = Ag, Al, Au, and Pt). The insert represents the 3D isosurface of the electron density difference. The red and green regions represent electron accumulation and depletion, respectively. For Al–C$_3$N$_4$ system, the isosurface value is 0.004 e/Å$^3$, and for other systems, it is 0.0004 e/Å$^3$.

Table 2. Calculated properties of the M–C$_3$N$_4$, and M–MoS$_2$ (M = Ag, Al, Au, and Pt) vdW heterostructure: Equilibrium interface distance (d in Å), Binding energy (E$_b$ in meV/atom), Transfer electron (Q$_T$ in e), Tunneling width ($w_B$ in Å), Tunneling height (V in eV) and Tunneling probability ($T_B$)
With the purpose of completing the analysis of contacts, we further investigate the electrostatic potential at the M–C$_3$N$_4$ and M–MoS$_2$ (M = Ag, Al, Au and Pt) interfaces and show the results in figure 7. As listed in table 2, most M–C$_3$N$_4$ and M–MoS$_2$ in our study has a higher TB comparing with MoS$_2$/$g$–C$_3$N$_4$ heterostructure, which will surely be in favor of speeding up the migration of photon-generated carrier at the interfaces of $g$–C$_3$N$_4$/M/MoS$_2$. Surprisingly, we find that there is an ohmic contact at the Al–C$_3$N$_4$ interface (the tunneling probabilities can reach 100%), which is induced by the strong interfacial hybridization.

As shown in figure 8, the band structure of Pt–MoS$_2$ heterojunctions reveals that the Fermi Level of the combined system lies in the band gap region of MoS$_2$, resulting in the formation of a Schottky barrier (0.48 eV) at the interface. The Fermi Levels of the M–C$_3$N$_4$ (M = Ag, Au, and Pt) combined systems pass through the band gap region of $g$–C$_3$N$_4$ and the calculated Schottky barrier heights corresponding to the energy differences between the CBM and the Fermi Levels are 0.11 eV, 0.87 eV, and 1.23 eV for Ag, Au, and Pt, respectively. Strong band hybridization has taken place for M–MoS$_2$ (M = Ag, Al, and Au) and Al–C$_3$N$_4$ interface, leading to the metallization of MoS$_2$ and $g$–C$_3$N$_4$, respectively. The vertical Schottky barrier for the four contacts is absent and the metallization makes electrons transfer between metal to semiconductor freely. According the above calculated results, we have the good fortune of discover that, due to the low Schottky barrier heights (SBH), Al

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**Figure 7.** Average electrostatic potential in the plane normal to the interface of the M–C$_3$N$_4$, M–C$_3$N$_4$ (a)–(d) and M–MoS$_2$, (e)–(h)) heterojunctions (M = Ag, Al, Au, and Pt). The rectangular box with dashed red line indicates the tunneling barrier.

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and Ag are suitable to be used as a contact electrode for both MoS$_2$ and g–C$_3$N$_4$ monolayer. Furthermore, it has been observed that, due to the interlayer coupling, the bilayer MoS$_2$-metal contacts usually have a smaller SBH than the monolayer MoS$_2$-metal contacts [48]. Therefore, in the g–C$_3$N$_4$/M/MoS$_2$ (M = Ag, Au, and Pt) system, we may reduce the SBH and improve the electron injection efficiency by increasing the layers of the semiconductors. Of course, further theoretical and experimental research is necessary next.

4. Conclusion

In summary, we theoretically explored the electronic and chemical properties of MoS$_2$/g–C$_3$N$_4$ heterojunction by DFT calculations. On the basis of the interfacial band bending, the MoS$_2$/g–C$_3$N$_4$ heterojunction is verified to be a direct Z-scheme system instead of O-scheme, which fully interprets the enhanced catalytic activity of hydrogen evolution observed in the experiments. The MoS$_2$ and g–C$_3$N$_4$ monolayers perform as photocatalysts for the OER and HER, respectively. Unfortunately, the low tunneling possibility at the surface of MoS$_2$/g–C$_3$N$_4$ heterojunction limits the efficiency of the Z-scheme water splitting. In order to build high-speed channel between the layers using suitable metal, we make a thorough inquiry in the tunneling possibility, internal electric field, and Schottky barrier of the interface of M–C$_3$N$_4$ and M–MoS$_2$ heterojunctions (M = Ag, Al, Au, and Pt). The results reveals that Ag could obviously improve the recombination efficiency of the majority carriers in the photo-oxidation catalyst (MoS$_2$) and the photo-reduction catalyst (g–C$_3$N$_4$) at the interface, serving as a charge transport center to form the Z-scheme g–C$_3$N$_4$/Ag/MoS$_2$ system. More notably, aluminum with a more excellent performance and lower price is promising candidate for silver in the Z-scheme system. This work is expected to give deep insights into understanding the charge transfer in semiconductor composites and rationally designing highly active Z-scheme photocatalyst for hydrogen evolution.

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ORCID iDs

Lin Ju @ https://orcid.org/0000-0002-7213-3828
Liran Shi @ https://orcid.org/0000-0001-9681-2596
Li Sun @ https://orcid.org/0000-0002-3025-4285
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