Role of Interfaces in Two-Dimensional Photocatalyst for Water Splitting

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ABSTRACT: Hydrogen generation from the direct splitting of water by photocatalysis is regarded as a promising and renewable solution for the energy crisis. The key to realize this reaction is to find an efficient and robust photocatalyst that ideally makes use of the energy from sunlight. Recently, due to the attractive properties such as appropriate band structure, ultrahigh specific surface area, and more exposed active sites, two-dimensional (2D) photocatalysts have attracted significant attention for photocatalytic water splitting. This Review attempts to summarize recent progress in the fabrication and applications of 2D photocatalysts including graphene-based photocatalysts, 2D oxides, 2D chalcogenides, 2D carbon nitride, and some other emerging 2D materials for water splitting. The construction strategies and characterization techniques for 2D/2D photocatalysts are summarized. Particular attention has been paid to the role of 2D/2D interfaces in these 2D photocatalysts as the interfaces and heterojunctions are critical for facilitating charge separation and improving photocatalysis efficiency. We also critically discuss their stability as photocatalysts for water splitting. Finally, we highlight the ongoing challenges and opportunities for the future development of 2D photocatalysts in this exciting and still emerging area of research.

KEYWORDS: photocatalyst, interface, hydrogen, two-dimensional, water splitting

1. INTRODUCTION

With the development of modern society, environmental pollution and energy shortage have become the focus of world attention. A majority of the global energy supplies are generated from fossil fuel, which gives rise to environmental pollution and climate change.1–3 Therefore, the development of clean and renewable energy is the key way to meet the increasing global energy requirement and to resolve the environmental problems caused by the overuse of large amounts of fossil fuels. Hydrogen possesses the highest energy content per weight among the combustion fuels and produces only water as the product. Hence, hydrogen is regarded as an ultraclean, powerful, environmentally friendly, and promising alternative for meeting future fuel needs.4

Given the natural abundance of water and sunlight, the production of hydrogen from water by using sunlight has been proven to be a regenerative, eco-friendly, and inexhaustible approach to solve both the energy crisis and energy-related environmental pollution. In the photocatalysis process, a stable and efficient photocatalyst is the critical factor to achieve a high yield of hydrogen. Because TiO2 electrodes were used for photocatalytic water splitting by Fujishima and Honda in 1972,5 a wide variety of photocatalysts have been developed for solar energy conversion in the past decades, such as TiO2, CdS, C3N4, and so on.6–10 Up to now, numerous semiconductor photocatalysts were exploited and used for photocatalytic water splitting. According to the composition, the photocatalysts can be generally categorized into three types: metal oxides, metal chalcogenides, and metal-free photocatalysts. Despite the rapid development of these photocatalysts, they still face several significant challenges: (1) Many semiconductors, especially metal oxides, can only absorb the ultraviolet light due to their wide band gap.11 (2) Some semiconductors are not suitable for overall water splitting due to their improper band position and only exhibit either water reduction or oxidation activity.12 (3) During the migration of photogenerated charge carriers to the surface reactive sites, the charge recombination occurs easily in the bulk and on the surface of photocatalysts.13 (4) Most of the reaction active sites in the bulk semiconductor cannot be exposed to the surface and therefore cannot be used for photocatalytic reaction.14

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To address these challenges, development of new and more efficient photocatalysts is needed and has been actively explored in the field. Among the new photactive materials, two-dimensional (2D) materials have recently attracted much attention. 2D materials represent an emerging class of materials that possess sheet-like structures with the thickness of only single or few layers.\(^{13}\) The effort was sparked by the discovery of graphene in 2004, a single-layer carbon material with excellent electrical, thermal, and mechanical properties.\(^{16}\) Since then, various graphene-like 2D photocatalysts have become topical subjects in the photocatalysis field. Photocatalysts show different physical and chemical properties compared with their bulk counterparts. 2D structures with exotic electronic properties and a high specific surface area can be produced from layered materials, which are characterized by strong interplane bonds and a weak van der Waals force between the layers.\(^{17}\) Because of the unusual structural, physical, and chemical properties of 2D materials, the fabrication of a few-layer or single-layer 2D structure has aroused wide interest as promising photocatalysts with several merits: (1) The band gap and the light absorption of 2D semiconductor can be adjusted by tuning the number of layers.\(^{18,19}\) (2) The recombination of electrons and holes in the bulk can be reduced due to the ultrathin nature.\(^{20,21}\) (3) Specific surface area of semiconductors is greatly improved, and most of the active sites can be exposed on the surface and take part in the photocatalytic reaction.\(^{22}\) Among many 2D photocatalysts with just a few layers or single-layer structure, graphene-based photocatalysts, 2D oxides, 2D chalcogenides, 2D graphitic carbon nitride (g-C\(_3\)N\(_4\)), and other 2D semiconductors begin to draw great attention in photocatalysis recently. The band gap energies, band position, and thickness of some 2D photocatalysts related to the redox potentials of water splitting are shown in Figure 1.\(^{23−34}\)

Although 2D photocatalysts are regarded as the promising candidates to convert the solar energy into chemical energy as the form of hydrogen, there are several hurdles that limit their applications, such as the following: (1) The exciton binding energy within 2D photocatalysts was greatly increased due to much smaller electron screening than the bulk material, which is unfavorable for the photocatalytic performance.\(^{35}\) (2) Some 2D semiconductors are not stable in air or aqueous solution, the thin-layer 2D semiconductor can be flocked together or oxidized by photogenerated holes during the reaction, leading to the decrease of the photocatalytic activity.\(^{36}\) (3) Although the recombination of electron–hole pairs is less than that of the bulk semiconductors, it still exists on the 2D photocatalysts.\(^{37}\) (4) The oxidation and reduction potential of some 2D semiconductors are insufficient for the overall water splitting.\(^{37}\)

To overcome these problems, a variety of strategies have been developed to improve the photocatalytic efficiencies of 2D photocatalysts, such as doping with a metal or nonmetal element, inducing defects, and coupling with metal or semiconductors.\(^{23,26−41}\) In fact, the photoactivity of photocatalysts not only depends on their properties, such as crystal structure, band structure, and electron affinity, but also on the interface between the photocatalyst and cocatalyst. Therefore, to achieve efficient conversion of water into hydrogen, the spatial integration of photocatalyst and cocatalyst to form the intimate interface is of great importance. The intimate interface can optimize the light absorption of photocatalysts and promote the separation of charge carriers. Commonly, the larger contact area on the interface can provide sufficient charge transfer and trapping channels for the separation of photo-generated electron–hole pairs.\(^{42}\)

As compared with 0D–1D, 1D–1D, 0D–2D, and 1D–2D interfaces, the 2D–2D coupled interfaces have attracted wide attention in photocatalysis because of their special advantages.\(^{43}\) First, the formation of an intimate interface between two semiconductors is in favor of the exciton dissociation, thus enhancing the photocatalytic quantum efficiency.\(^{12}\) Second, it is facile and efficient to form the intimate interface between 2D semiconductors, even when the 2D semiconductors have high lattice mismatch.\(^{44,45}\) Third, the large lateral size with high surface area leads to large contact area in 2D/2D photocatalysts, which promotes the charge transfer and the separation of electron–hole pairs.\(^{46}\) Fourth, the band potential can be matched for the overall water splitting by integrating a hydrogen evolution photocatalyst and an oxygen evolution photocatalyst. Thus, the oxidation power and reduction power of the semiconductors can be balanced for overall water splitting.\(^{47,48}\) Finally, the formation of 2D/2D heterostructure is beneficial to the improvement of catalyst stability due to the alleviation of photocorrosion and agglomeration.\(^{23,49}\) With these advantages of the 2D/2D interface, plenty of 2D/2D structures were fabricated in recent years to improve the photocatalytic performance of photocatalysts.

Some excellent reviews have been published in the past few years on 2D materials that have focused on the synthesis

Figure 1. Band gap energies, band position, and thickness of several 2D photocatalysts related to the redox potentials of water splitting.
methods, properties, catalytic applications, and routes to tune their electronic states and active sites.\textsuperscript{22,50–65} In addition, some comprehensive reviews with respect to the classification, modification, computational screening, and application of 2D photocatalysts were also reported.\textsuperscript{14,17,36,37,66–77} However, no review has been centered on the role of interfaces in 2D materials for photocatalysis, including the interface types in 2D photocatalysts, construction strategies, characterization techniques of various 2D/2D interfaces, and the function of different components in 2D/2D photocatalyst systems. Therefore, a systematic review focusing on the rational design and construction of 2D/2D interface in 2D photocatalysts is necessary for readers to better understand the latest progress in the field of 2D photocatalysts. This Review will focus on the 2D photocatalysts for photocatalytic water splitting, including the graphene-based photocatalysts, 2D oxides, 2D chalcogenides, 2D graphitic carbon nitride, and a few other 2D semiconductors. The 2D materials we reviewed here refer to low dimensional materials with the thickness ranging from single layer to a few nanometers with the basal plane dominating the total surface area. The photocatalysis principles, synthesis, and stability of these 2D materials will be briefly reviewed. Besides, the construction strategies and characterization techniques of 2D/2D photocatalysts are also summarized. More attention will be paid to the types and the role of interfaces in these 2D photocatalysts for water splitting. Finally, the ongoing challenges and opportunities for the future development of 2D photocatalysts in this exciting yet still emerging area of research will be proposed.

2. BASIC PRINCIPLES OF 2D PHOTOCATALYSTS FOR WATER SPLITTING

2.1. Photocatalysis Principles for Water Splitting on 2D Photocatalysts. Figure 2 shows a schematic illustration of the basic principle of overall water splitting on a semiconductor photocatalyst. Under light irradiation, electrons in the valence band are excited into the conduction band, leaving holes in the valence band. The excited electrons can cause the H\textsuperscript{+} reduction reaction to generate H\textsubscript{2}, while the holes can cause H\textsubscript{2}O oxidation reaction to form O\textsubscript{2}. To realize overall water splitting on the semiconductor, the bottom of the conduction band must be more negative than the reduction potential of H\textsuperscript{+}/H\textsubscript{2} (0 V vs NHE at pH = 0), and the top of the valence band must be more positive than the oxidation potential of H\textsubscript{2}O/O\textsubscript{2} (1.23 V vs NHE at pH = 0). Furthermore, the band gap of the semiconductor must exceed the free energy (1.23 eV) of water splitting. During the photocatalytic water splitting reaction, the recombination of the photogenerated electron–hole pairs can occur in the bulk and on their way to the surface of the bulk photocatalyst.\textsuperscript{78} The recombination of charge carriers will lower the efficiency of the photocatalysts.

To effectively separate the photogenerated electron–hole pairs, the proportion of exposed surface of photocatalyst should be increased and the distance of charge transfer should be shortened to accelerate water splitting. In this respect, 2D photocatalysts can reduce the recombination of charge carriers in the bulk, and the electrons and holes can directly transfer to the surface active sites due to their ultrathin nature. Generally, with the transition from 3D to 2D, the band gap increases because of the quantum confinement effect, which causes a blue-shift of the optical absorption of 2D photocatalysts.\textsuperscript{79} On the other hand, with a larger band gap, the valence band and conduction band will enlarge in an opposite direction. The shift of the valence band and conduction band will enhance the reducing power and oxidizing power of the photocatalysts, respectively. In addition, the Coulomb interactions (exciton binding energy) are greatly enhanced in two-dimensional systems as a result of spatial confinement and reduced Coulomb screening.\textsuperscript{80,81} Consequently, the electron–hole pairs can be bounded by the Coulomb force and go against the photocatalytic reaction. Therefore, strategies need to be developed to enhance the photocatalytic performance of 2D photocatalysts, such as the construction of 2D/2D heterostructures.

2.2. Types of Interfaces in 2D Photocatalysts. Despite the potential merits of 2D structure, the recombination of separated carriers can still exist on 2D photocatalysts. In addition, the excitonic effect, which is caused by the Coulomb interactions between photogenerated electrons and holes, plays an important role in the excitation properties of semiconductors. Because photocatalysis is a typical photoexcitation process, the excitonic effect should be taken into account in the photocatalytic reaction. The bound electron–hole pairs are formed with the generation of excitons, which adversely affect the separation of electrons and holes and thus decrease the photocatalytic activity. Several strategies have been used to promote the separation of the electron–hole pairs in the photocatalysts, such as the construction of metal/2D, doped 2D, 2D/2D structure, and so on, among which 2D/2D structure may be the most promising.\textsuperscript{17} The intimate interfaces in the 2D/2D photocatalysts will accelerate the charge carrier transfer between them, thus suppressing the recombination of electron–hole pairs. Two main ways to construct the 2D/2D semiconductor interface are the intraplane interface and the interplane interface, as shown in Figure 3.

Hybrid photocatalysts, consisting of at least two 2D materials, are considered as a promising system to promote the separation of photogenerated electrons and holes, and to extend the light absorption toward visible-light region. These 2D/2D photocatalytic systems can be classified as the Z-structure.
scheme system (such as α-Fe2O3/g-C3N4), the Schottky junction system (such as GeH/graphene), the Type I (such as g-C3N4/ZnIn2S4) and Type II (such as g-C3N4/N−La2Ti2O7) heterostructure system, as shown in Figures 4 and 5.

Figure 4. Schematic diagram of charge transfer for Z-scheme and Schottky junction system.

Figure 5. Schematic diagram of charge transfer for Type I, II heterostructure system.

The Z-scheme system, inspired by natural photosynthesis in green plants, is an effective approach for photoinduced charge separation and water splitting.85 This system uses two semiconductors to achieve band alignment. In this way, the photocatalyst that has either water reduction or oxidation activity can be applied to one side of the Z-scheme system to achieve the separation of photoinduced electron–hole pairs and overall water splitting.41,82,85 For example, by combining the La- and Rh-codoped SrTiO3 (possess reduction activity) with the Mo-doped BiVO4 (possess oxidation activity), photocatalytic water splitting simultaneously into H2 and O2 was realized.86 For the Z-scheme system, as shown in Figure 4, the electrons in the CB of A semiconductor can transfer to the VB of B semiconductor to combine with holes, while the electrons in the CB of B semiconductor are used to reduce H2O into H2, and the holes in the CB of A semiconductor are used to oxidize H2O into O2.

Construction of Schottky junction by fabricating the 2D/2D interface is another effective way to suppress the recombination of photogenerated electron–hole pairs.87,88 For this system, electrons can flow from the photocatalyst to the cocatalyst through the interface (from the higher to the lower Fermi level) to align the Fermi energy levels.89 Thus, the cocatalyst has excess negative charges, while the semiconductor possesses positive charges near the interface. Consequently, a space charge layer is formed at the interface, and the CB and VB of the semiconductor are bent “upward”. This space charge layer leads to the formation of a Schottky junction between the semiconductor and cocatalyst.87 As a result, the Schottky junction can serve as an electron trap to efficiently capture the photoinduced electrons and the photocatalytic activity can be enhanced.87,89,90

2D/2D heterostructured photocatalysts have been widely applied to the photocatalytic water splitting reaction. Herein, we discuss these two main types of the heterostructure system (i.e., Type I and Type II; Figure 5). In Type I, the holes and electrons will accumulate on the B semiconductor because the CB (VB) of the B semiconductor is more positive (negative) than that of the A semiconductor.91 Type II has similar band alignment as the Z-scheme system, but with different electron transfer directions. For the Type II system, the CB electrons of B semiconductor transfer to the CB of A and the VB holes of A transfer to the VB of B; while the CB electrons of the A semiconductor transfer to the VB of B in the Z-scheme system. The p–n junction is a typical Type II system, which is composed of alternate p- and n-type photocatalysts.92,93 Different electronic structures between p- and n-type material result in the accumulation of photoexcited electrons at the coupling interface of the n-type side and holes in the p-type component. Thus, concentration gradients of electrons and holes are formed at the interface, which promotes the transportation of charge carriers and suppresses the recombination of photogenerated electrons and holes, and thus favors an efficient solar-energy conversion.

So far, many types of 2D junctions were developed to modify the optical property, electronic property, and the stability of 2D photocatalysts, such as the metal–2D, doped-2D, 1D–2D, 2D–2D, and so on. In this Review, we will focus on the Z-scheme, Schottky junction, Type I and Type II heterostructure systems with the 2D/2D interfaces.

2.3. Construction of 2D/2D Photocatalysts. The strategy for constructing the 2D/2D interfaces plays an important role on the photocatalytic performance of the 2D photocatalysts, because the quality of interface is determined by construction method. To date, many effective strategies have been explored to fabricate the 2D/2D intimate interface in the 2D photocatalysts, such as the ultrasonic absorption,95 the hydrothermal method,96 the electrostatic self-assembly,97 and the chemical vapor deposition.98

One of the simplest ways to construct the 2D/2D photocatalyst is to disperse two different 2D components in the solution under stirring or sonication to form a mixture. The mixture was dried in an oven to evaporate the solvents, and then the 2D/2D photocatalyst was obtained. For example, 2D/2D CdS/MoS2 and g-C3N4/N-doped La2Ti2O7 2D layered composites were fabricated by ultrasonic dispersion and drying.84,95,99 However, these 2D/2D interfaces were formed by the weak interaction between two 2D components by using this method, the 2D components can be separated easily during the photocatalysis process. For instance, after four recycles, almost 35% of H2-production activity loss was observed on 2D/2D CdS/MoS2 (construction by ultrasonic absorption), which might be ascribed to the slow fall of MoS2 from CdS.76

The hydrothermal method is a practical way to construct a 2D/2D intimate interface between the 2D components. In brief, one 2D component was mixed with the precursor of the other 2D component first, then the solution was transferred to an autoclave for the hydrothermal reaction. Thereafter, the 2D/2D photocatalysts were collected after drying. For example, the 2D/2D p-MoS2/n-rGO photocatalyst was synthesized by the hydrothermal method, and many intimate interfaces were
formed between the p-MoS2 and the n-rGO. The intimate p-MoS2/n-rGO junctions greatly improve the generation of electron-hole pairs and suppress their recombination.96 g-C3N4/ZnIn2S4,49 g-C3N4/CaIn2S4,91 TiO2-g-C3N4,25 et al. were also successfully prepared by the hydrothermal method. Hydrothermal is an energy-saving and environmentally friendly method, because the reaction takes place in closed-system conditions. Additionally, the hydrothermal process is kinetically slow at any given temperature and thus easy to be controlled. A microwave-hydrothermal process was developed to increase the kinetics of crystallization.100 2D/2D TiO2/graphene was synthesized by a simple microwave-hydrothermal process and showed an enhanced photocatalytic H2-production activity compared with TiO2.101

Electrostatic self-assembly is also a viable strategy to fabricate the intimate 2D/2D interfaces in 2D photocatalysts.97,102 For this method, surface charge modification plays a significant role in engineering the 2D/2D photocatalysts with intimate interfacial contact. To attain the electrostatic self-assembly, the surface charges on different 2D photocatalysts need to be tuned by charge modification to obtain the opposite charges (i.e., positive and negative charges). Notably, the zeta potential value can be used to determine the charge of the photocatalyst. For example, to form the 2D/2D g-C3N4/rGO by electrostatic self-assembly, the g-C3N4 was protonated by concentrated H2SO4 and HNO3 under mild ultrasonication to obtain the positively charged surface, the zeta potential value was measured to be +37.2 mV. Then the protonated g-C3N4 was mixed with negatively charged rGO (−32.4 mV), with the assistance of ultrasonication and agitation, the g-C3N4/rGO with the intimate interface was obtained. Moreover, the π-stacking interactions between the sp2 lattices of g-C3N4 and the sp2 graphene lattices as well as the hydrogen-bonding interactions between the nitrogen-contained groups in g-C3N4 are also beneficial for the electrostatic self-assembly. The hydrogen production rate of the g-C3N4/rGO (557 μmol g−1 h−1) was much higher than that of g-C3N4 (158 μmol g−1 h−1) due to the intimate interface and the introduced rGO.97 In addition, the construction of the 2D/2D g-C3N4/rGO by electrostatic self-assembly also facilitates the photocatalytic reduction of carbon dioxide to methane (13.93 μmol g−1), higher activity when compared with that of rGO/pure g-C3N4 (8.29 μmol g−1) without the modification of surface charge on g-C3N4.102

Chemical vapor deposition (CVD) is an effective technique to construct the 2D/2D heterostructures with intimate interfaces, including the intraplane and interplane interfaces,98,103 Generally, mixed gas molecules are injected into a reaction chamber which is set at a certain temperature. When the mixed gases come into contact with the substrate within the reaction chamber, a reaction occurs that creates a material film on the substrate surface. The temperature of the substrate is a key factor for the quality of the obtained 2D material. For example, the intraplane 2D/2D WS2/MoS298 MoS2/MoSe2104 and interplane MoS2/WS2105 MoS2/WSe2105 were fabricated by CVD method and showed good optoelectronic and photovoltaic performance. Although CVD is a powerful technique for the construction of 2D/2D materials, the gaseous byproducts of the process are usually very toxic. Besides, the 2D materials have to stay on the substrate for further use, which is not efficient in the photocatalytic reaction. Moreover, it is still a great challenge to synthesize the 2D materials on a large scale by using the CVD method.

**2.4. Characterization of Interfaces in 2D/2D Photocatalysts.** The quality of the interface in 2D/2D photocatalysts directly determines the activity and stability of the 2D/2D photocatalysts. Therefore, it is very important to investigate the quality and interaction between the 2D components. Powerful characterization techniques have been developed to characterize the interface in 2D materials, such as the transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), conductive atomic force microscopy (CAFM), and Kelvin probe force microscopy (KPFM).

TEM is a useful technique to examine the size, exposed facets, crystallinity, phase, crystal orientation, and exposed crystal facets of materials. Low-magnification TEM images can be used to explore the lateral size and roughly measure the thickness of the nanosheet. Furthermore, the high-resolution TEM (HRTEM) image is a practical way to confirm the crystal orientation and the exposed crystal facets of crystalline nanosheet by measuring the lattice distance. Generally, different crystalline materials have different crystal orientations and lattice distances, and no lattice fringes can be observed from amorphous nanosheet. On the basis of this distinction, HRTEM can be used to explore the interfaces between the 2D/2D materials. Take the BiOI/La2Ti2O7 heterojunction as an example, the low-magnification TEM images show that BiOI nanosheets with a smaller size are randomly dispersed on the surface of the larger La2Ti2O7 nanosheet (Figure 6a). The lattice fringes of La2Ti2O7 and BiOI can be clearly observed in the HRTEM image (Figure 6b), and the measured lattice distances of 0.276 and 0.302 nm correspond to the (002) plane of La2Ti2O7 and (012) plane of BiOI, respectively.

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*Figure 6. TEM and HRTEM images of BiOI/La2Ti2O7. Reproduced with permission from ref 106. Copyright 2016 Royal Society of Chemistry.*
Table 1. Summary of 2D Photocatalysts for Photocatalytic Hydrogen Evolution

<table>
<thead>
<tr>
<th>photocatalyst (thickness)</th>
<th>synthesis method</th>
<th>cocatalyst, sacrificial agent</th>
<th>light source</th>
<th>H₂ production rate</th>
<th>quantum efficiency</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>black TiO₂ (2 nm)</td>
<td>solvothermal treatment</td>
<td>2 mL, 10⁻³ mol L⁻¹ H₂PtCl₆, 10 vol % methanol</td>
<td>300 W Xe-lamp</td>
<td>400 µmol h⁻¹</td>
<td>-</td>
<td>118</td>
</tr>
<tr>
<td>single-atom Rh/TiO₂ (0.7 nm)</td>
<td>thermal annealing</td>
<td>10 vol % methanol</td>
<td>500 W Xe-lamp</td>
<td>51 µmol h⁻¹</td>
<td>-</td>
<td>119</td>
</tr>
<tr>
<td>2H MoS₂ (1.4 nm)</td>
<td>exfoliation/thermal annealing</td>
<td>0.01 M lactic acid</td>
<td>200 W Hg-lamp (&gt;400 nm)</td>
<td>0.3 mmol g⁻¹ h⁻¹</td>
<td>2.57% at 400 nm</td>
<td>87</td>
</tr>
<tr>
<td>CdS (~4 nm)</td>
<td>sonication</td>
<td>0.5 M Na₂S₆O₃</td>
<td>300 W Xe-lamp (&gt;420 nm)</td>
<td>41.1 mmol g⁻¹ h⁻¹</td>
<td>1.38% at 420 nm</td>
<td>120</td>
</tr>
<tr>
<td>C₃N₄ (0.5 nm)</td>
<td>solvothermal exfoliation</td>
<td>3 wt % Pt, 10 vol % triethanolamine</td>
<td>300 W Xe-lamp (&gt;420 nm)</td>
<td>8510 µmol g⁻¹ h⁻¹</td>
<td>5.1% at 420 nm</td>
<td>27</td>
</tr>
<tr>
<td>g-C₃N₄ (~0.64 nm)</td>
<td>thermal oxidation etching</td>
<td>3 wt % Pt, 10 vol % triethanolamine</td>
<td>300 W Xe-lamp (&gt;400 nm)</td>
<td>8874 µmol g⁻¹ h⁻¹</td>
<td>13.7% at 420 nm</td>
<td>28</td>
</tr>
<tr>
<td>carbon nitride (~3.6 nm)</td>
<td>sonication</td>
<td>3 wt % Pt, 10 vol % methanol</td>
<td>(&gt;240 nm)</td>
<td>93 µmol h⁻¹</td>
<td>3.75% at 420 nm</td>
<td>121</td>
</tr>
<tr>
<td>black BiOCl (3 nm)</td>
<td>hydrothermal</td>
<td>10 vol % triethanolamine</td>
<td>300 W Xe-lamp (&gt;420 nm)</td>
<td>2.51 µmol h⁻¹</td>
<td>-</td>
<td>123</td>
</tr>
<tr>
<td>Fe-BiOCl (3.7 nm)</td>
<td>hydrothermal</td>
<td>1 wt % Pt, 10 vol % triethanolamine</td>
<td>300 W Xe-lamp (&gt;420 nm)</td>
<td>3.54 µmol h⁻¹</td>
<td>-</td>
<td>30</td>
</tr>
<tr>
<td>C-BN (3–4 nm)</td>
<td>thermal annealing</td>
<td>0.5 M Na₂SO₄</td>
<td>300 W Xe-lamp</td>
<td>5.6 µmol h⁻¹</td>
<td>0.54% at 405 nm</td>
<td>31</td>
</tr>
<tr>
<td>CoOOH (1.5 nm)</td>
<td>sonication</td>
<td>3 wt % Pt, 10 vol % methanol</td>
<td>(&gt;240 nm)</td>
<td>1200 µmol g⁻¹ h⁻¹</td>
<td>6.9% at 420 nm</td>
<td>124</td>
</tr>
<tr>
<td>O-doped ZnIn₂S₄ (6 nm)</td>
<td>hydrothermal</td>
<td>0.25 M Na₂SO₄ / 0.35 M Na₃S</td>
<td>300 W Xe-lamp (&gt;420 nm)</td>
<td>2120 µmol g⁻¹ h⁻¹</td>
<td>-</td>
<td>125</td>
</tr>
<tr>
<td>SnH₂O₆ (3.0 nm)</td>
<td>hydrothermal</td>
<td>0.3 wt % Pt, 10 vol % lactic acid</td>
<td>300 W Xe-lamp (&gt;400 nm)</td>
<td>13.2 µmol h⁻¹</td>
<td>0.43% at 420 nm</td>
<td>32</td>
</tr>
<tr>
<td>HNfO₃ (1.3 nm)</td>
<td>proton-exchange/ exfoliation</td>
<td>10 vol % triethanolamine</td>
<td>125 W Hg-lamp</td>
<td>~95 µmol h⁻¹</td>
<td>-</td>
<td>126</td>
</tr>
<tr>
<td>HNbWO₆ (1.8–2.0 nm)</td>
<td>intercalation assisted exfoliation</td>
<td>1 wt % Pt, 10 vol % triethanolamine</td>
<td>300 W Xe-lamp (300–700 nm)</td>
<td>158.9 µmol h⁻¹</td>
<td>-</td>
<td>33</td>
</tr>
<tr>
<td>Rh/calcium niobate (~2.8–3.0 nm)</td>
<td>thermal annealing</td>
<td>10 vol % methanol</td>
<td>500 W Xe lamp</td>
<td>384.8 µmol h⁻¹</td>
<td>65% at 300 nm</td>
<td>127</td>
</tr>
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</table>

obvious interface was observed between the La₃Ti₂O₇ and BiO. The lateral interface between MoS₂ and ZnIn₂S₄ can be observed in the 2D/2D MoS₂/Cu-ZnIn₂S₄ photocatalyst. Besides, the interface is easily detected in the 2D/2D g-C₃N₄/MoS₂ and g-C₃N₄/ZnIn₂S₄ because obvious lattice fringes can be observed on MoS₂ or ZnIn₂S₄ but not on g-C₃N₄. It is worth noting that the electron irradiation of TEM from high voltage might decompose or change the structure of ultrathin 2D nanomaterials. Moreover, the normal HRTFM is unable to directly probe and localize different atoms in 2D nanomaterials to find a clearer interface. Scanning transmission electron microscopy (STEM) should be a good choice to separate atoms in 2D materials especially after the introduction of aberration-corrected optics. Especially, annular dark-field scanning transmission electron microscope (ADF-STEM) is able to obtain the atomic resolution images, because the contrast of the atoms is proportional to the atomic number of the atoms. For example, the ADF-STEM was used to identify the different phases of MoS₂ in the single-layer MoS₂, the atomically sharp phase interface between the 2H phase and 1T phase can be clearly observed in the ADF-STEM image.

XPS is a surface-sensitive and spectroscopic technique to identify the elemental composition of a material, as each element has its own characteristic binding energy peaks. In addition, the peak shape for each element is relevant to the electron configuration within the atoms. Therefore, the chemical composition, and electronic state of a material can be determined by analyzing the position and shape of XPS peaks for each element. Intriguingly, XPS can also be used to identify the different phases and quantitatively calculate the concentration of each phase in ultrathin 2D materials. As a typical example, the concentration of 2H and 1T phases in the exfoliated MoS₂ nanosheet can be determined by XPS on the basis of the intensity and location of the element peaks. In most cases, the formation of the interface in the 2D/2D materials will cause a change in the electron configuration because of the interaction between the 2D materials. Consequently, the interaction intensity between the 2D materials can be examined by XPS. For example, the binding energy of Mo in 2D/2D MoS₂/g-C₃N₄ is lower than pure Mo in pure MoS₂ due to the strong chemical interaction (electron coupling) between the MoS₂ layers and the conjugated g-C₃N₄ layers.

X-ray absorption spectroscopy (XAS) is an effective and nondestructive spectroscopic technique to explore the structural characteristics of materials at the atomic scale. The X-ray absorption spectrum includes two regimes: X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS). XANES can be used to characterize the coordination chemistry and oxidation state of an atom, while EXAFS is used to determine the distances, coordination number, and neighboring species of an atom. XAS is also a feasible way to study the interactions between different components in 2D hybrid materials. As a typical example, Qiao et al. used the highly sensitive synchrotron-based XANES to disclose the interactions between the few-layer phosphorene nanosheet (FPS) and Cds. When the FPS was combined with the CdS (1P-CS), an
apparent shift of the P K edge toward low photon energy was observed compared with that of pure FPS. In addition, the S L edge for 1P-CS shifted toward high photon energy compared with that of CdS. Therefore, the strong electronic coupling facilitates the charge separation and is favorable for the hydrogen evolution from water splitting. Of note, the CAFM method requires the use of a conductive sample.

The surface potential of a catalyst can be altered by the interfacial interaction between the 2D materials and is not affected by the thickness of the materials but by the interface structure. Therefore, the detection and control of the potential gradient on the catalyst surface are imperative to expose the interface structure and enhance the photocatalytic performance of the photocatalyst. Kelvin probe force microscopy (KPFM) is a powerful technology to study the surface potential and reveal the interfacial interaction between the 2D materials and is not covered by low energy ion scattering spectroscopy (LEIS).
3. ROLE OF INTERFACES IN 2D PHOTOCATALYSTS FOR WATER SPLITTING

Up to now, many 2D photocatalysts have been successfully prepared and used for the photocatalytic hydrogen evolution from water where the construction of 2D/2D interface plays an important role on the photocatalytic performance of 2D photocatalysts. Table 1 and Table 2 summarize the recent progress of 2D and 2D/2D photocatalysts for photocatalytic hydrogen evolution, respectively. The role of interface in 2D photocatalysts for water splitting will be discussed in detail in the following section.

3.1. Graphene-Based Photocatalysts. 3.1.1. Overview of Graphene-Based Photocatalysts for Photocatalytic Water Splitting. Graphene, single-layer carbon with 2D hexagonal packed lattice structure, has drawn great attention in scientific and engineering fields since its discovery in 2004. Because of many advantages of graphene, such as large specific surface area, excellent electrical conductivity, and high flexibility, graphene has been widely used as a cocatalyst for photocatalysts. For example, graphene can be used as electron acceptor, photosensitizer, or electron transport bridge in photocatalysts. Besides, the conduction-band potential of the semiconductor can be shifted by combining with the graphene. Moreover, the graphene with functional groups can also be used as photocatalysts for water splitting. However, the H2 evolution rate and the stability of the graphene as photocatalysts still need to be developed. The coupling of the photocatalysts with graphene is a promising strategy to promote the photocatalytic water splitting. The contact area and the interfacial interaction between graphene and photocatalysts play an important role in enhancing the efficiency of photocatalytic H2 evolution. Therefore, the construction of the 2D/2D interface between the graphene and photocatalysts has been widely studied.

3.1.2. Synthesis of Graphene-Based Photocatalysts. Since the discovery of graphene, many methods have been explored for the synthesis of graphene. Such as mechanical exfoliation, chemical exfoliation, chemical and thermal reduction, and chemical vapor deposition. Many excellent reviews have summarized the synthesis of graphene systematically. For the graphene-based photocatalysts, graphene was usually used as a cocatalyst for the photocatalysts, in order to combine the graphene with the 2D photocatalysts for the formation of 2D/2D photocatalysts, some effective approaches have been developed, such as thermal annealing, hydrothermal method, and electrostatic self-assembly.

3.1.3. Role of Interface in Graphene-Based Photocatalysts. Graphene has been widely used as an electron acceptor and electron storage center to promote the separation of electron–hole pairs for the photocatalysts because of its high electron storage capacity and excellent electron conductivity. Besides, the Fermi level of graphene is lower than the conduction band of most photocatalysts, and thus, the electrons in the CB of the photocatalysts can be easily transferred from the photocatalysts to the graphene, which enhances the separation of the electrons and holes. For example, in the 2D/2D g-C3N4/rGO, the electrons can be effectively transferred from g-C3N4 to rGO, due to the lower Fermi level of rGO (−0.08 eV vs NHE) relative to the CB of g-C3N4 (−0.842 eV vs NHE), thus restrained the charge recombination. Furthermore, the interfacial interaction on the intimate 2D/2D interface between the rGO and g-C3N4 can effectively promote the charge transfer and separation. Consequently, the enriched electron density on the rGO favors the photocatalytic hydrogen evolution from water. The H2 production rate (557 μmol g−1 h−1) from 2D/2D g-C3N4/rGO is much higher than that of g-C3N4 (158 μmol g−1 h−1).

Graphene can act not only as the electron acceptor and electron storage but also as the electron transport bridge between the photocatalyst and the cocatalyst. As a typical example, for the 2D ternary MoS2-graphene-ZnIn2S4, both the MoS2 and the ZnIn2S4 are connected to the graphene, and the ZnIn2S4 graphene, and MoS2 act as the light-harvesting semiconductor, electron transport bridge, and hydrogen evolution reaction catalyst, respectively. In this ternary photocatalyst, the CB of ZnIn2S4 is more negative than the graphene/graphene— (G/G−) redox potential; thus, the electrons generated from the CB of ZnIn2S4 can be transferred effectively to graphene due to the thermodynamic driving force. Moreover, the G/G− redox potential is more negative than the CB of MoS2 nanosheets, which is beneficial for the electron transfer from the electron-rich graphene— to the CB of MoS2. In addition, the 2D/2D intimate interface also contributed to the improvement of the interfacial charge transfer, and therefore, the charge carrier recombination can be suppressed. With the effective electron transport bridge and the large number of active sites on the 2D MoS2, the H2 evolution rate from MoS2-graphene-ZnIn2S4 was 22.8 times higher than that of pure ZnIn2S4 under visible light. Very recently, using graphene as the electron transport bridge has also been explored in the [ZnTMPyP]4+-MoS2/RGO-TEOA photocatalytic system and the Au-nanoprism/reduced graphene oxide/Pt-nanoframe system.

Interestingly, the CB potential of a semiconductor can be shifted to be more negative position when coupled with the graphene. For example, in the graphene/Bi2WO6 system, the chemical interaction between graphene and Bi2WO6 led to a shift of the Fermi level and the CB potential of Bi2WO6 decreased from +0.09 to −0.3 V, thus the graphene/Bi2WO6 composite had a more negative CB potential than the potential of H+/H2. Moreover, the chemical bonding between graphene and Bi2WO6 facilitated the electron transportation and suppressed the recombination of photogenerated charge carriers, thus further enhancing the H2 production rate. A similar result was reported by Gao et. al, in the graphene...
B1,W, composite, the CB potential was shifted to a lower position to enhance the degradation rate of rhodamine B.\textsuperscript{145} Besides, the graphene can also be used as the photosensitizer to extend the spectral responsive range of wide band gap semiconductors to visible light, thus further increasing the photon capture.\textsuperscript{71,136}

Reduced graphene oxide nanosheet (rGO) can be changed to be a n-type semiconductor by doping with heteroatoms, such as nitrogen.\textsuperscript{96} The n-type nitrogen-doped rGO can be incorporated with a p-type semiconductor to form the p−n junctions for enhancing the separation of the electron–hole pairs. As a typical example, p-type MoS\textsubscript{2} nanoplatelets were coupled with the n-type nitrogen-doped rGO (n-rGO) nanosheets to form the nanoscale p−n junctions. In this MoS\textsubscript{2}/n-rGO system, the rGO was able to suppress the aggregation of the MoS\textsubscript{2} nanoplatelets effectively, and a large percentage of edge sites could be created on the thin MoS\textsubscript{2}. Furthermore, the contact area was increased in the 2D/2D MoS\textsubscript{2}/n-rGO compared to the 0D/2D MoS\textsubscript{2}/n-rGO. In the 2D/2D MoS\textsubscript{2}/n-rGO, the rGO increases the energy conversion efficiency as a passive charge extraction layer. Besides, with the formation of the nanoscale p−n junction, the space charge layer created a built-in electric field and suppressed recombination of the electrons and holes. The p−n junction changed the role of rGO from passive to active, further enhancing the charge separation. Consequently, the MoS\textsubscript{2}/n-rGO with the p−n junction exhibited much better photocatalytic performance than the p-MoS\textsubscript{2}/undoped-rGO.\textsuperscript{90}

Ideal graphene is a carbon material with no obvious electronic band gap; thus, it is unable to absorb the light energy and used directly as a photocatalyst.\textsuperscript{146} To develop graphene as an efficient photocatalyst, it is imperative to engineer the band gap of graphene with semiconductive properties. Doping with heteroatoms, such as B and N, is a feasible way to open band gap in the graphene.\textsuperscript{147,148} Especially, in-plane doping with h-BN domains in graphene can produce unique planar heterostructures and tunable electronic properties.\textsuperscript{49} Very recently, atomic-level in-plane decoration of h-BN domains in graphene (BN-G) was successfully fabricated by controlling the doping sequence of heteroatoms and the oxygen content of the graphene precursor.\textsuperscript{128} The surface structure and catalytic activity of graphene were greatly affected by the in-plane decoration of h-BN domains. The band gap of BN-G was calculated to be 2.8 eV based on the band structure and DOS around the Fermi level of BN-G. However, the band gaps of graphene (G), B doped-graphene (B-G), N doped-graphene (N-G), and B, N codoped-graphene (B, N-G) were quite narrow (0–1.4 eV), whereas the band gap of bulk h-BN (4.8 eV) was too large (Figure 8). As a result, the BN-G showed a 10-fold increase in H\textsubscript{2} evolution rate compared with those of N-G, B-G, and B,N-N.\textsuperscript{128}

### 3.2. 2D Oxide Photocatalysts

#### 3.2.1. Overview of 2D Oxide for Photocatalytic Water Splitting

Oxide semiconductors are the most widely studied photocatalysts in the field of the water splitting. For example, because of low cost, high chemical stability, and nontoxicity, TiO\textsubscript{2} has been extensively used as photocatalyst in the past decades. However, the application of oxide photocatalysts is limited by the recombination of electrons and holes in the long travel distance to the surface of photocatalysts.\textsuperscript{150,151} Therefore, strategies are needed to solve these problems. In the ultrathin 2D photocatalysts, the migration distance of electrons and holes is shortened to reduce the recombination. Besides, more exposed surface atoms result in the generation of more dangling bonds on the surface atoms, which arouses more reaction active sites to direct contact with the reactants.\textsuperscript{152,153} However, the band gap of 2D oxides was widened due to the quantum confinement effect.\textsuperscript{23} It is noteworthy that a new two-dimensional phase of TiO\textsubscript{2} formed on the surface of rutile TiO\textsubscript{2} (011) shows a reduced band gap from 3 eV (bulk TiO\textsubscript{2}) to 2.1 eV (new surface 2D phase), which endows the TiO\textsubscript{2} to absorb visible light.\textsuperscript{154} However, the new 2D phase of TiO\textsubscript{2} normally covers only 10–60% of the surface, photoexcited electrons in this surface of 2D TiO\textsubscript{2} may diffuse into the bulk and can be scavenged at other surfaces not covered by the new TiO\textsubscript{2} surface.

2D oxides other than TiO\textsubscript{2} have also been explored as photocatalysts including ZnO,\textsuperscript{155} In\textsubscript{2}O\textsubscript{3},\textsuperscript{156} Cu\textsubscript{2}O,\textsuperscript{157} WO\textsubscript{3},\textsuperscript{158} etc. Element doping in ultrathin 2D nanomaterials is more efficient in the improvement of the photocatalytic activity than doping in the bulk materials.\textsuperscript{14} This occurs because most of the dopants in ultrathin 2D nanosheets are located very close to the surface and can directly participate in the surface photocatalytic reaction. For example, in the Rh-doped K\textsubscript{2}Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}, almost all the dopants are present within the bulk of the photocatalyst and have an indirect effect on the surface reaction. In contrast, when the thickness of the Rh-doped Ca–Nb–O nanosheet (exfoliation from Rh-doped K\textsubscript{2}Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10}) is reduced to 1 nm, most of the dopants in the nanosheet present on the surface. Thus, most of the dopants can be expected to directly participate in the catalytic reaction and cause a significant improvement in photocatalytic activity. As a result, the H\textsubscript{2} production rate of the Rh-doped Ca–Nb–O nanosheet (384.8 \textmu mol·h\textsuperscript{−1} was 165 times as high as that of the parent Rh-doped K\textsubscript{2}Ca\textsubscript{2}Nb\textsubscript{3}O\textsubscript{10} (2.3 \textmu mol·h\textsuperscript{−1}), the quantum efficiency of Ca–Nb–O nanosheet was 65% at 300 nm.\textsuperscript{127}

Despite the advantages of 2D oxides, the rapid recombination of electrons and holes still exists in the 2D oxides, and the widened band gap decreases the light absorption of the 2D oxides. In addition, the aggregation can occur in the process of the photocatalytic reaction. Construction of the 2D/2D heterostructure between the 2D oxides and other cocatalyst is a viable way to relieve the aggregation and increase the optical absorption of 2D oxides.\textsuperscript{25} Furthermore, with the intimate 2D/
3.2.2. Synthesis of 2D Oxide Photocatalysts. 2D oxide nanosheets can be prepared by a hydrothermal method, which is simple and easy to operate. In addition, the crystal structure and the morphology of photocatalyst can be controlled by adjusting the types of the precursor, temperature, and reaction time. For instance, 2D TiO$_2$ nanosheet with exposed (001) facets was synthesized by the hydrothermal method, and the exposed (001) facets could be tailored by adding hydrofluoric acid. However, it should be noted that the hydrofluoric acid is a contact poison and extremely corrosive, and thus, it must be handled with extreme care. In addition to TiO$_2$, 2D La$_2$Ti$_2$O$_7$ nanosheets were also successfully synthesized by the hydrothermal method.

Exfoliation of a layered metal oxide composed of single crystal layers is also a feasible way to obtain 2D oxide. Generally, the layered precursors of 2D oxides are first fabricated by a conventional solid-state calcination method at high temperature and then is converted into the protonated form by acid-exchange processing in an acid solution (e.g., HCl). The protons are substituted with sufficient organic ion (e.g., tetrabutylammonium ion) to expand the interlayer spacing. Finally, the 2D oxide nanosheets can be obtained due to the decrease of the electrostatic interaction between the host layers. For example, Ti$_{1.82}$O$_4$, Ca$_2$Nb$_3$O$_{10}$, and TaO$_3$ nanosheets were fabricated successfully by exfoliation. However, the acid-exchange processing and organic ion exchange processing take a long time with the entire preparation process for around 2 weeks. In addition, only a few metal oxides have suitable layered precursor that can be exfoliated to 2D oxide. Moreover, the synthesis of 2D oxide nanosheets on a large scale by exfoliation is also a great challenge.

Another effective way to prepare the 2D oxides is the self-assembly wet chemistry method. The key of this method is the formation of lamellar structures by the molecular self-assembly between the oligomers and surfactant in solution, with hydrated inorganic oligomers confining between the bilayer reverse micelles. In this way, well-crystallized ultrathin TiO$_2$ nanosheets can be obtained after hydrothermal treatment of the solution and the removal of the organic templates. The ultrathin 2D TiO$_2$ nanosheets possess a dominant anatase phase and a trace of rutile phase, high specific surface area and a thickness around 3 nm. However, the band gap of the TiO$_2$ nanosheets was shifted to 3.65 eV, larger than that of the P25 TiO$_2$, which could be attributed to the confined atomic-scale thickness. Except for 2D TiO$_2$ nanosheet, 2D ZnO, Co$_3$O$_4$, WO$_3$, Fe$_3$O$_4$, and MnO$_2$ can also be synthesized by this wet chemistry method. The advantage of this approach is that the synthesis of 2D metal oxide nanosheets is not restricted by the limited numbers of layered materials, and it is possible to synthesize homogeneous nanomaterials in large quantities. However, it is difficult to obtain single monolayer oxide by the wet chemistry method, because this approach still needs to reach thermodynamic equilibrium even if the growth along the thickness dimension is confined by micelles.

3.2.3. Role of Interface in 2D Oxide Photocatalysts. Cocatalysts have been widely used to accelerate the rate of hydrogen evolution over 2D oxide photocatalysts. The interface state between photocatalyst and cocatalyst is of great importance for the separation efficiency of the photoinduced electron–hole pairs and the photocatalytic activity of the photocatalyst. Therefore, construction of 2D nanojunctions between 2D oxide photocatalysts and 2D cocatalysts is a feasible strategy to enhance the photocatalytic hydrogen generation rate of 2D oxide photocatalysts. For example, the 2D/2D MoS$_2$/TiO$_2$ photocatalysts show high photocatalytic H$_2$ evolution activity, which is about 36.4 times higher than that of pure TiO$_2$ nanosheets. Furthermore, the 2D/2D MoS$_2$/TiO$_2$ exhibits H$_2$ evolution rate much higher than noble metal loaded TiO$_2$ photocatalysts (such as Pt, Rh, Ru, Pd, and Au-loaded TiO$_2$). These results can be attributed to intimate and larger contact area between the TiO$_2$ and MoS$_2$ (2D/2D contact interface) than that of the noble metal loaded TiO$_2$ (point contact interface). Moreover, the effective charge transfer from excited TiO$_2$ to MoS$_2$ due to the suitable band alignment is also a key factor for the enhancement of photocatalytic activity of TiO$_2$ (Figure 9). Similarly, the 2D/2D TiO$_2$/MoS$_2$ was also prepared for the photocatalytic reduction of CO$_2$ into CH$_3$OH, and the fast electron transferred from TiO$_2$ to MoS$_2$ could minimize charge recombination and thus improved the photocatalytic activity. Because of the high specific surface area and superior electron conductivity of graphene, it is considered as an efficient cocatalyst for hydrogen production. When graphene was used as the cocatalyst for TiO$_2$ nanosheets, it could act as an electron acceptor to efficiently suppress the recombination of electrons and holes. In the 2D/2D TiO$_2$/graphene system, the 2D π-conjugation structure of graphene promotes the transfer of photogenerated electrons. Additionally, the potential (−0.08 V vs SHE, pH = 0) of graphene/graphene$^{* *}$ is lower than the CB level (−0.24 V) of anatase TiO$_2$, and the photoexcited electrons in the conduction band of TiO$_2$ can be transferred to graphene. Because the potential of graphene (−0.08 V) is higher than the reduction potential of H$^+$/H$_2$(0 V), the protons can be efficiently reduced on the graphene (Figure 10). Moreover, the intimate interaction between TiO$_2$ nanosheets and graphene sheets with the interplane junction will further facilitate the separation of electron–hole pairs. Therefore, the photocatalytic activity of the TiO$_2$ can be greatly improved. With optimal graphene content of 1.0 wt %, the hydrogen production rate was 736 μmol h$^{-1}$ g$^{-1}$ with a quantum efficiency of 3.1%, 41 times higher than that of TiO$_2$ nanosheets. The 2D/2D TiO$_2$/graphene system was also effective for the photocatalytic degradation of organic pollutant and CO$_2$ conversion.

Hybridizing 2D oxide photocatalysts with 2D organic semiconductors (such as g-C$_3$N$_4$) to form the Type II heterojunction greatly enhances the photocatalytic H$_2$ production.
production owing to the increasing interface area and interfacial charge transfer rate. A Type II 2D/2D interface can be formed between the anatase TiO$_2$ nanosheets (TiO$_2$-A, 5-6 monolayers) and g-C$_3$N$_4$ nanosheets (∼3 monolayers). With the surface-to-surface heterojunction, the transfer rate of the charge carriers, donor density, light adsorption, and the life of charge carriers was enhanced. Besides, a compromised band gap could be achieved between the TiO$_2$-A (3.3 eV) and g-C$_3$N$_4$ (2.8 eV), leading to a reduced band gap of TiO$_2$-A to 2.91 eV, and a Type II 2D/2D intimate interface was formed between the TiO$_2$-A and g-C$_3$N$_4$, as shown in Figure 11. The quantum efficiency of 2D/2D TiO$_2$-A/g-C$_3$N$_4$ (5.3%) at 380 nm was much higher than that of TiO$_2$-A(1.28%) and g-C$_3$N$_4$(1.07%). Type II band alignment can also be obtained in the 2D/2D g-C$_3$N$_4$/NLTO composite photocatalyst (approximately 2 nm thick g-C$_3$N$_4$ and 7 nm thick N doped La$_2$Ti$_2$O$_7$ nanosheets, NLTO). The g-C$_3$N$_4$/NLTO exhibited a high apparent quantum efficiency of 2.1% for photocalytic H$_2$ evolution at 400 nm, which was 4 times as high as that of NLTO photocatalyst (0.5%).

Another typical Type II heterojunction is the p-n junction structure. When a 2D p-type semiconductor is combined with a 2D n-type oxide semiconductor, the surface potential of the semiconductor will be changed due to the diffusion of free carriers at the 2D/2D interface to balance the Fermi levels of both materials, which will affect the photocatalytic performance of the photocatalyst. Taking 2D/2D n-type calcium niobate/p-type nickel oxide (CNO/NiO) as an example, the surface potential of the 2D CNO/NiO junction part is higher than that of the NiO and lower than that of the CNO. Separated reaction sites can be obtained due to the potential gradient in the CNO/NiO photocatalyst. For example, the CNO/NiO junction parts are photo-oxidation sites, while the nonjunction parts and/or their edges are photoreduction sites. In addition, photocatalytic H$_2$ production rate can be affected by the exposed surfaces of the 2D p-n junction photocatalysts. For instance, the photocatalytic H$_2$ production rate for the CNO/NiO junction (surface: CNO) was higher than that of NiO/CNO junction (surface: NiO), which was attributed to the lower photocatalytic activity of the surface of NiO than that of CNO surface.

3.2.4. Stability of the 2D Oxide Photocatalysts. Some 2D oxides are stable under ambient conditions at room temperature, such as TiO$_2$. However, some 2D oxides are unstable, such as Cu$_2$O. The oxidation of Cu$_2$O itself to CuO is thermodynamically more favorable than water oxidation, and the Cu$_2$O can also be reduced to metallic Cu in the photochemical reaction. Besides, the stability of 2D oxides is different due to their diverse structure. For example, single-layer MoO$_2$ and WO$_2$ are stable in the structure of honeycomb (H), and unstable in the structure of centered honeycomb (T). Single-layer TiO$_2$, CoO$_2$, and NbO$_2$ are unstable in both the H and T structures. In addition, the 2D oxides can still be stacked together through the van der Waals force to form the bulk counterparts. Formation of the 2D oxide/2D cocatalyst heterostructure is an effective way to relieve the aggregation of the 2D oxides. In addition, the stability of oxides can be improved by reducing the surface energies.

3.3. 2D Chalcogenide Photocatalysts. 3.3.1. Overview of 2D Chalcogenides for Photocatalytic Water Splitting. 2D chalcogenides have recently emerged as a fascinating new class of material for photocatalysis. The reduction of the dimension of chalcogenides from 3D to 2D result in novel electronic and mechanical properties. For 2D chalcogenides, most of the catalytically active sites are exposed for catalytic reaction and the ultralarge fraction of low-coordinated atoms is also beneficial to solar light harvesting. Besides, the band gap of the chalcogenides can be adjusted according to the number of layers. For example, the band gap of MoS$_2$ could be enlarged from 1.29 to 1.90 eV when bulk MoS$_2$ exfoliates to monolayer MoS$_2$. The relative position of the CB and VB is di↵erent due to their diverse structure. For example, single-layer MoO$_2$ and WO$_2$ are stable in the structure of honeycomb (H), and unstable in the structure of centered honeycomb (T). Single-layer TiO$_2$, CoO$_2$, and NbO$_2$ are unstable in both the H and T structures. In addition, the 2D oxides can still be stacked together through the van der Waals force to form the bulk counterparts. Formation of the 2D oxide/2D cocatalyst heterostructure is an effective way to relieve the aggregation of the 2D oxides. Furthermore, with the transformation from bulk to monolayer, the band gap of chalcogenides can be changed from indirect to direct band gap, or vice versa. Many 2D chalcogenides have been experimentally demonstrated as photocatalysts for water splitting, such as MoSe$_2$, MoS$_2$, WSe$_2$, MoS$_2$, SnSe$_2$, ReS$_2$, HfS$_2$, TaS$_2$, NbS$_2$, etc. Besides, some 2D chalcogenides, such as HfS$_2$, TaS$_2$, etc. were also predicted as promising photocatalysts for water splitting. Interestingly, some monochalcogenides show high photocatalytic water splitting in the form of both 3D phase and 2D phase. In contrast, the 2D layered transition-metal dichalcogenides (TMDs) such as 2D MoS$_2$ shows high activity for photocatalytic water splitting under visible light irradiation, while the bulk MoS$_2$ has no photocatalytic activity due to the narrow band gap. Therefore, the construction of the 2D structure is of significance for the application of TMDs in the photocatalytic water splitting.

Despite the potential advantages of 2D chalcogenides for photocatalysis, the hydrogen yield from water splitting is still low due to the ultrafast recombination of the photogenerated...
holes and electrons. Moreover, the photocorrosion driven by photoexcited holes can occur on some 2D chalcogenides. Besides, 2D chalcogenides tends to restack during the course of reaction and blocks the surface sites, making them inaccessible for the water splitting and leading to the reduction in activity. 190 To overcome these problems, strategies such as doping with metal and nonmetal, combining with cocatalyst, the formation of 2D/2D junction have been employed to modify their electronic property and improve their stability. Among them, the 2D/2D junction is the most promising way to enhance their photocatalytic activity by reducing the photocorrosion, regulating electron property and enhancing the photochemical stability.

3.3.2. Synthesis of 2D Chalcogenide Photocatalysts. Many 2D chalcogenide nanosheets have been successfully synthesized. For monochalcogenides, sonication 112 and hydrothermal method are able to achieve the ultrathin 2D structures. For example, inorganic–organic hybrid CdS-amine nanosheets synthesized via hydrothermal method were used as the starting material to obtain the CdS nanosheets. 112 The H2-production rate was remarkably enhanced with the CdS nanosheet as the photocatalyst in comparison to the nanoparticle counterpart. However, l-cysteine must be added to the solution as a stabilizing agent to avoid the quick aggregation of the as-prepared sheets, and the stability of the CdS nanosheet dispersion was affected by the pH value. 120,191

Quite different from monochalcogenides, TMDs consist of two close-packed chalcogenide planes sandwiching a transition-metal layer but have a similar layered structure to that of graphite and therefore can also exfoliate into monolayer by chemical and physical methods. Up to now, many strategies have been developed to fabricate the monolayer TMDs including mechanical exfoliation, 192 liquid-phase exfoliation, 193 chemical intercalation exfoliation, 187,194,195 lithium molten salt method, 196 and chemical vapor deposition 197 etc. Mechanical exfoliation, the so-called “Scotch Tape Method”, the Scotch tape-based mechanical exfoliation is the easiest and fastest way to obtain the pristine, highly crystalline, atomically thin layers of 2D TMDs. 192 However, the adhesive tape procedure is clearly not a scalable process. The liquid-phase exfoliation can be used for the large-scale production of monolayer chalcogenide, however, rigorous solvent inhibits its applicability. Furthermore, the liquid-phase exfoliation method is an aqueous solution processing and therefore has significant economic and environmental disadvantages over the use of organic solvents or ionic liquids.

For the chemical intercalation exfoliation, intercalation of external ions or molecules is a critical step in the production of 2D chalcogenides in the solution exfoliation of their layered bulk counterparts. The neighboring layers can be weakened by the interlayer expansion. Lithium intercalation exfoliation is an effective route to obtain the monolayer chalcogenide with high crystallinity. However, a long time (for example, 3 days at 100 °C) is typically needed for the lihtiation process. 87 Besides, assisted sonication is usually required for solution exfoliation. Therefore, it is hard to obtain large sizes and high quality 2D chalcogenides by solution-phase routes due to the high-energy processing and therefore has significant economic and environmental disadvantages over the use of organic solvents or ionic liquids.

High-quality monolayers with very large size 2D TMD were successfully synthesized by a total single-crystal exfoliation method. 194 In this method, homogeneous monolayers TMD with submillimeter scale sizes and high crystallinity can be obtained by only simple manual shaking within several seconds. However, the complex procedure and high risk of using metallic lithium as a reagent are still a big disadvantage for chemical intercalation exfoliation.

Lithium molten salt method can be used to obtain the 2D TMD without using the rigorous solvent and metallic lithium. In this method, lithium molten salt plays as the fluxing medium and controls the TMD phases. For instance, (NH4)2MoS4 and LiOH were employed as the starting materials, and different phases of MoS2 precursors can be obtained by controlling the calcination temperature. The 2H-phase MoS2 precursors were obtained at 400 °C while 1T-phase MoS2 precursors were gained at 1000 °C, and these precursors can exfoliate into 2H- and 1T-phase MoS2 monolayers. 196 Supercritical carbon dioxide (sc-CO2) has also been used to assist the exfoliation of layered materials, owing to its excellent performance, for example, high diffusion coefficients, outstanding wetting of surfaces, and low interfacial tension. 199

With the advantages of high crystallinity, simple operation and low cost, chemical vapor deposition (CVD) is regarded as a promising technique to grow various 2D TMD directly on dielectric substrates. 200 Many 2D TMDs, such as MoS2 201,202 WS2,203 MoSe2,204 ZrS2,205 etc. have been successfully synthesized. More importantly, CVD is a practical method to construct the 2D lateral and vertical TMD heterostructures. 104,206,207 Despite the advantages, the CVD method still has some drawbacks. Ultrathin 2D TMD obtained by the CVD method are always grow on the substrates, and it is needed to be transferred to other substrates for further application. For photocatalytic water splitting reaction, freestanding 2D nanosheets are more efficient compared to the 2D nanosheets deposited on the substrate. Therefore, the wet chemical route is more appealing for making 2D TMD photocatalysts compared to the CVD method.

3.3.3. Role of Interface in 2D Chalcogenide Photocatalysts. Combining the 2D chalcogenide nanosheets with other 2D semiconductors is an effective strategy to enhance the photocatalytic activity of the photocatalyst for water splitting. For example, when CdS nanosheets were coupled with the ultrathin MoS2 nanosheets, the photogenerated electrons in the CB of CdS can rapidly transfer to MoS2 edge defect sites due to the matched band alignments and intimate 2D/2D coupling interfaces, as shown in Figure 12. Furthermore, the surface 2D MoS2 on 2D CdS as cocatalysts can also greatly accelerate their H2-evolution kinetics. 35 However, this 2D/2D CdS/MoS2 photocatalyst is unstable, with almost 35% H2 production.
activity loss after four recycles, which might be attributed to the slow falloff of MoS2 nanosheets from Cds. Similarly, a few-layered MoS2/Cds van der Waals 2D/2D heterostructure was fabricated by bubble exfoliation of MoS2 nanosheets into few-layered flakes and further in situ stacking with the ultrathin Cds. By using the few-layered MoS2/Cds photocatalyst, the H2 evolution rate was 140 mmol g−1 h−1 with an apparent quantum yield of 66% at 420 nm. The nonlayered Cds epitaxially grown on the 2D layered MoS2 substrate to form a new quasi vertical heterostructure with the clean interface was also successfully prepared. In the 2D/2D MoS2/Cds photocatalyst system, 2D CdS act as a photosensitizer to absorb light and subsequently generate electron–hole pairs, while MoS2 is the cocatalyst offering active sites for H2 evolution with low activation potential.

Different phases of the TMDs show different physical and chemical properties and thus can be utilized to build intraplane heterojunctions for improving the photocatalysis. For example, metastable metallic 1T and quasi-metallic 1T’ phases MoS2 possess higher electric conductivity, while 2H phase MoS2 is a semiconductor with narrow direct band gap (~2 eV). Although the 2H phase MoS2 could be considered as a visible light photocatalyst, the electron transfer in the MoS2 plane is slow, which led to the rapid recombination of photogenerated electrons and holes. It is possible that if the 2H phase MoS2 and the 1T/1T’ phases MoS2 can be formed in the same plane, the recombination of photogenerated electrons and holes will be restrained due to fast electron transfer from the 2H phase MoS2 to 1T/1T’ phases MoS2. On the basis of this assumption, multiphasic single-layer MoS2 was constructed and acts as an efficient photocatalyst for hydrogen evolution from water reduction. The 2H phase MoS2 was assumed to be responsible for the absorption of visible light and charge carrier generation, and photogenerated carriers were separated through the heterojunctions between 1T’ MoS2 and 2H MoS2. The H2 evolution occurs over both basal and edge sites of 1T’ MoS2 as well as edge sites of 2H MoS2, resulting in 4 times higher HER rate than that of pure 2H MoS2. The formation of heterojunctions at the 2H and 1T’ phases MoS2 interfaces is illustrated on Figure 13. Du et al. also reported that electrons were preferably transferred from the 2H to 1T’ phases MoS2 but the 1T’ MoS2 structure showed comparable hydrogen evolution reaction activity to the 2H MoS2 structure under electrochemical condition.

In addition to the formation of intraplane heterostructure in the same TMD material, the intraplane heterojunctions constructed by different TMD layers are also possible. Due to the same honeycomb lattice structure and matched lattice constant MX2 (M = Mo, W; X = S, Se), the intraplane heterojunctions can be constructed by seamless stitching of different MX2. For example, intraplane WS2/MoS2 heterostructures with high crystallinity and subnanometer interfaces can be constructed by ambient pressure chemical vapor deposition. In these WS2/MoS2 heterostructures, MoS2 nanosheets were laterally joint to the WS2 peripheral edges to predominantly exhibit triangular geometry and possessed the single-layer nature with a height of 0.8 nm. Due to the higher Fermi level of WS2 than that of MoS2, when the intraplane heterostructure was formed between WS2 and MoS2, the electrons will diffuse from WS2 to MoS2, which makes the potential of WS2 region higher than that of MoS2 region. Therefore, the WS2/MoS2 in-plane heterostructures can serve as quasi p–n junctions, where WS2 is quasi n-side and MoS2 is quasi p-side. The built-in potential or the built-in electrical field within this heterojunction structure will cause charge redistribution and separate electrons and holes in two different regions. Then photovoltaic responses and light emission efficiency in WS2/MoS2 heterostructures would be dominated. However, the photocatalytic water splitting activity of these WS2/MoS2 heterostructures has not been studied yet.

### 3.3.4. Stability of 2D Chalcogenide Photocatalysts

Due to the higher thermal dynamic stability of oxide over sulfide, some 2D chalcogenides can be oxidized by photoexcited holes even in the presence of sacrificial agent (such as lactic acid), which will reduce the photocatalytic activity of the photocatalyst, such as Cds. 2D chalcogenides are more stable in the Na2S–Na2SO3 solution, since the generated S2− ions in Na2S–Na2SO3 can protect the 2D chalcogenide from photocorrosion by the abundance of holes left behind. Besides, the restack of 2D chalcogenides occurred during the reaction is also a big problem for the stability of photocatalysts. For example, the GaS sheets appear to restack during the course of reaction and block the surface reaction active sites of the photocatalyst, leading to a decrease of the active sites for the photocatalytic hydrogen evolution and consequently a decrease of the activity from 887 μmol h−1 g−1 (the first cycle) to 566 μmol h−1 g−1 (the third cycle). Notably, no photocorrosion was observed on GaS. Doping the 2D chalcogenide lattice with a donor atom is a good way to increase their stability. Chemical modification via functional groups is also identified as a feasible way for stabilization of the 2D chalcogenides. For instance, the metastable 1T-MoS2 can be transformed into the stable phase after a crossover coverage of functionalization. However, the covering of the surface sites with these functional groups might decrease the number of active sites for HER and thus the applicability of this method to photocatalysis is yet to be determined.

### 3.4. 2D Graphitic Carbon Nitride Photocatalysts

#### 3.4.1. Overview of 2D Graphitic Carbon Nitride for Photocatalytic Water Splitting

Graphitic carbon nitride (g-C3N4) has attracted dramatic interest in the field of visible-light-induced photocatalytic hydrogen production since it was first used as photocatalyst for water splitting by Wang et al. in 2009. The structure of g-C3N4 is two-dimensional frameworks consisting of tri-s-triazine connected via tertiary amines (Figure 14). g-C3N4 possesses a band gap of ~2.7 eV, corresponding to a wavelength of ~460 nm, which allows it to be a visible-light-response photocatalyst. Furthermore, the bottom of CB of the g-C3N4 is more negative than the reduction potential of H2O to H2, and the top of the VB is more positive than the oxidation potential of H2O to O2.

![Figure 13. Schematic of the formation of heterojunctions at the 2H and 1T’ phases MoS2 interfaces. Reproduced with permission from ref 87. Copyright 2016 American Chemical Society.](image-url)
Therefore, g-C₃N₄ can be used as the photocatalyst for the overall water splitting under visible light. Note that, the band gap of the g-C₃N₄ will increase when the bulk g-C₃N₄ exfoliates to monolayer due to the quantum confinement effect, as shown in Figure 14.²⁷,²¹⁸

Although g-C₃N₄ has the appropriate band gap and band structure for both water reduction and oxidation, the photocatalytic activity of g-C₃N₄ is usually restricted by poor efficiency due to the rapid recombination of photogenerated electron–hole pairs. For bare g-C₃N₄, the H₂ production rate was only a few micromoles per hour per gram, and the thermodynamic driving force of g-C₃N₄ for O₂ evolution was much smaller than that for H₂ evolution.¹⁷² In the g-C₃N₄, nitrogen atoms would be the preferred oxidation sites for H₂O to form O₂ but whereas the carbon atoms provided the reduction sites for H⁺ to H₂.¹⁷³ Therefore, one approach to enhance the photocatalytic activity is to maximize the exposed surface C and N atoms by fabricating the 2D g-C₃N₄. However, the problem of fast recombination of electron–hole pairs and excitonic effects still inhibit the photocatalytic activity of the g-C₃N₄.²¹⁹ Therefore, many strategies are applied to improve the photocatalytic activity of g-C₃N₄ such as structural modification,²²⁰ metal and nonmetal doping,²²¹–²²³ copolymerization,²²⁴ and coupling with other semiconductors or cocatalysts.²²⁵ Among these strategies, combining 2D g-C₃N₄ with other 2D materials is an effective way to enhance the photocatalytic performance due to the 2D framework of g-C₃N₄. The 2D/2D structure with the largest and intimate contact interface in two 2D materials promotes the electron transfer between them. Furthermore, electronic properties of g-C₃N₄ can be tuned and thus changes the excitation dissociation in the g-C₃N₄.²²⁶ Hence the photogenerated electrons and holes can be separated more efficiently and then increase the photocatalytic activity of the 2D g-C₃N₄.

3.4.2. Synthesis of 2D Graphitic Carbon Nitride Photocatalysts. In general, g-C₃N₄ can be synthesized by the thermal polymerization of nitrogen-rich precursors such as urea, cyanamide, dicyandiamide, melamine, semicarbazide hydrochloride, and so forth. In order to enhance the photocatalytic activity, several synthetic methods of g-C₃N₄ are modified to alter the optical and electronic properties of g-C₃N₄. For example, the optical absorption of g-C₃N₄ semiconductor can be extended to visible light region up to 750 nm by copolymerization of dicyandiamide with barbituric acid, and the band gap of the g-C₃N₄ decreases with the increasing of the barbituric acid content.³¹ In addition, the absorption edge of g-C₃N₄ can red shift toward to visible light by the introduction of nitrogen defects. Nitrogen-deficient g-C₃N₄ can be synthesized by thermal polymerization at high temperature,³² hydrogen reduction,³³ hydrothermal process,³⁴ and the thermal polymerization with the assistance of the alkali (such as KOH, NaOH, Ba(OH)₂).³⁵ The nitrogen-deficient structures of g-C₃N₄ not only broadened the visible-light absorption of g-C₃N₄ but also promoted the separation of electron–hole pairs. Furthermore, the band gap of g-C₃N₄ is dependent on the number of nitrogen defects, which can be easily tuned by the alkali/precursor ratio.²³⁵ To obtain the 2D g-C₃N₄ nanosheets, several exfoliation methods have been used to delaminate the bulk g-C₃N₄ such as thermal oxidation exfoliation,²⁰ ultrasonic exfoliation,²⁶ liquid-phase exfoliation,²⁹ and so on. For the thermal oxidation exfoliation, g-C₃N₄ nanosheets can be synthesized by calcinating bulk g-C₃N₄ in the air atmosphere at 500–550 °C due to the thermal oxidation etching effect.²³⁶ This is an effective way to obtain the g-C₃N₄ nanosheets with high specific surface area. However, the polymeric melon chain is not stable enough against the oxidation of O₂ at high temperature, which leads to the low yield of g-C₃N₄ nanosheets.¹⁹ Ultrasonic exfoliation has been widely used for liquid exfoliation of layered materials, and it has been demonstrated to be a simple and scalable method to delaminate the bulk g-C₃N₄.²³⁹ The exfoliation efficiency of g-C₃N₄ using ultrasonic depends on the ultrasonic power and solvent. Nonetheless, the 2D g-C₃N₄ disintegrates into submicron-sized nanosheets due to the high-energy driving input, and the exfoliation efficiency was still not high enough. Liquid-phase exfoliation through redox reactions and intercalation is a high-efficiency approach for the exfoliation of g-C₃N₄.³⁴ For example, g-C₃N₄ nanosheets with a thickness of 1.4–2.3 nm can be achieved by H₂SO₄ liquid-phase exfoliation.³⁴⁰ Single-layer g-C₃N₄ was obtained by using the HNO₃ (98%).³⁴¹ In addition, HCl³⁴² and H₃PO₄³⁴⁳ can also be applied to delaminate the g-C₃N₄.

3.4.3. Role of Interfaces in 2D Graphitic Carbon Nitride for Water Splitting. An effective strategy for improving the photocatalytic activity of the g-C₃N₄ is coupling with a 2D material that possesses excellent electronic conductivity and reaction active sites, such as graphene. 2D/2D graphene/g-C₃N₄ composites were synthesized by a combined impregnation chemical reduction strategy.³¹² Because of the high specific surface area (2600 m²·g⁻¹) and excellent mobility of charge carriers (200 000 cm²·V⁻¹·s⁻¹), the graphene part can act as electronic conductive channels to efficiently separate the photogenerated charge carriers, thus enhancing the visible-light photocatalytic H₂-production activity of g-C₃N₄. With the optimal graphene content of 1.0 wt %, the H₂-production rate of the graphene/g-C₃N₄ is about 3 times as high as that of pure g-C₃N₄ and the apparent quantum efficiency reached 2.6%.

To gain more insights into the interface between the electronically active graphene and optically active g-C₃N₄, theoretical calculation based on the hybrid density functional theory was carried out by Du et al.⁴⁴ The results show that the graphene/g-C₃N₄ interface displays strong interlayer electron coupling. A gap (70 meV) was opened for a g-C₃N₄ supported graphene layer, and the visible light response of g-C₃N₄ was enhanced in the presence of graphene. Moreover, the charge density is redistributed by forming triangular-shaped electron-rich and hole-rich regions (the interlayer charge transfer from graphene to g-C₃N₄) within the graphene layer (Figure 15). With the open gap in graphene, electrons can be directly excited from the VB of graphene to the CB of g-C₃N₄. The charge transfer at the graphene/g-C₃N₄ interface was predicted to significantly enhance the electron conductivity in a g-C₃N₄ layer, which was beneficial to the photocatalysis.

RGO is also a good cocatalyst for g-C₃N₄ in photocatalysis. Zhang et al. found that the band structure of g-C₃N₄ could be well modulated by coupling with RGO.⁴⁴ The mechanism for
the enhanced photocatalysis of the g-C3N4/RGO composites with various concentrations of O atom was investigated by density functional theory calculations. The interaction between g-C3N4 and RGO varies with the concentration of O atom, and the band gap of g-C3N4/RGO is decreased and dependent on the concentration of O atom. It is worth noting that the g-C3N4/RGO composites with appropriate concentration of O atom are good visible light harvesting semiconductors. Most importantly, with a higher O concentration in g-C3N4/RGO, a type-II staggered band alignment can be obtained in the g-C3N4/RGO interface, leading to the high hydrogen-evolution activity at the negatively charged O atoms (active sites) in the RGO.

Combining g-C3N4 with a non-noble-metal cocatalyst that possesses plenty of active sites for hydrogen evolution such as TMDs is attested to be an effective way for photocatalytic water splitting. For example, taking advantage of the analogous 2D layered structures of the g-C3N4 and MoS2, g-C3N4/MoS2 with layered nanojunction was synthesized by gas-phase sulfidation technique. The mesoporous structure of g-C3N4 facilitates and stabilizes the high dispersion of MoS2 over the g-C3N4 surface and the formation of the thin MoS2/g-C3N4 intimate junction. The organic–inorganic hybrid with graphene-like thin-layered g-C3N4/MoS2 heterojunctions increase the accessible area between the planar interface of the MoS2 and the g-C3N4 layers. Furthermore, the barrier for electron transport from the g-C3N4 to the MoS2 was diminished, thus facilitating fast electron transfer across the interface by the electron tunneling effect. In addition, the thin layers of the cocatalyst can lessen the light blocking effect and improve the light utilization by g-C3N4. Moreover, the band alignment of g-C3N4 and MoS2 in favor of the directional migration of photogenerated electrons from g-C3N4 to MoS2, while keeping adequate chemical potential to reduce H^+ to H2 at the active sites of MoS2 (Figure 16). With the presence of the layered g-C3N4/MoS2 interface, the hydrogen-evolution rate over 0.5 wt % MoS2/g-C3N4 reaches 20.6 μmol h^{-1}, even about 4 times higher than that of 0.5 wt % Pt/g-C3N4 (4.8 μmol h^{-1}).

Integration of 2D g-C3N4 with different 2D semiconductors to form the Type I system is another effective approach to increase the utilization of g-C3N4 for visible light photocatalytic hydrogen generation. For example, combining the 2D g-C3N4 with 2D ternary metal sulfide (such as g-C3N4/ZnInS4, g-C3N4/CaIn2S4) has been demonstrated as a successful way to improve the photocatalytic activity for water splitting by enhancing the light absorption and charge separation. For the g-C3N4/ZnInS4, the 2D/2D interface between 2D g-C3N4 and 2D ZnInS4 provides larger contact areas and much faster charge transfer rate than the 2D/0D structure of g-C3N4 nanosheet@ZnInS4 microsphere, as shown in Figure 17.

Moreover, abundant intimate and high-speed charge transfer nanochannels are formed in the 2D/2D interfacial junctions, thus enhancing the separation and migration efficiency of the photogenerated electrons and holes. The H2 evolution rate of 2D/2D g-C3N4/ZnInS4 is 69.5, 15.4, 8.2, and 1.9 times higher than that of pure g-C3N4 nanosheet, pure ZnInS4 microsphere, 2D/0D g-C3N4 nanosheet@ZnInS4 microsphere and pure ZnInS4 nanoleaf, respectively. In this Type I system, the photogenerated electrons and holes were excited from the g-C3N4 and then transferred to the CB and VB of ZnInS4, respectively, and the photocatalytic H2 generation mainly occurred on the surface of ZnInS4. Similar results were reported on the 2D/2D CaIn2S4/g-C3N4 heterostructures.

Formation of the solid-state Z-scheme structure is a promising protocol to separate the photogenerated electron–hole pairs and enhance the photocatalytic H2 production. Very recently, the 2D/2D α-Fe2O3/g-C3N4 Z-scheme system was fabricated and used for hydrogen evolution. This 2D/2D α-
Fe$_2$O$_3$/g-C$_3$N$_4$ system exhibits a significantly enhanced quantum efficiency up to 44.35% at 420 nm. The tight interface and band alignment between 2D α-Fe$_2$O$_3$ and 2D g-C$_3$N$_4$ lead to the formation of Z-scheme structure, and play a pivotal role in enhancing the photocatalytic activity of α-Fe$_2$O$_3$/g-C$_3$N$_4$ toward H$_2$ evolution. For this 2D/2D α-Fe$_2$O$_3$/g-C$_3$N$_4$ Z-scheme system, the photogenerated electrons at the CB of α-Fe$_2$O$_3$ can directly move to recombine with photoinduced holes at the VB of 2D g-C$_3$N$_4$. Electrons generated at the CB of 2D g-C$_3$N$_4$ can promptly transfer to the surface to reduce the H$^+$ into H$_2$, while holes generated in the valence band of 2D α-Fe$_2$O$_3$ can be used in the oxidation of TEOA or oxygen evolution reaction, thus significantly improves the photocatalytic water splitting performance. Moreover, the 2D α-Fe$_2$O$_3$/g-C$_3$N$_4$ shows potential for overall water splitting.

The construction of order–disorder interfaces is an effective strategy to accelerate exciton dissociation in the bulk g-C$_3$N$_4$. On the order–disorder interfaces of g-C$_3$N$_4$, the electrons were injected into the ordered chains and holes were blocked in the disordered chains, resulting in the exciton dissociation and the separation of electrons and holes. Besides, the recombination of photoinduced electron–hole pairs can also be suppressed by constructing heterojunctions between two different g-C$_3$N$_4$ (1-g-C$_3$N$_4$/2-g-C$_3$N$_4$) synthesized from different precursors. However, the construction of order–disorder and 1-g-C$_3$N$_4$/2-g-C$_3$N$_4$ interfaces in the 2D g-C$_3$N$_4$ has not been reported. According to the merits of 2D materials, the separation efficiency of electrons and holes might be greatly improved if these two kinds of heterostructures can be constructed as the form 2D/2D interface in g-C$_3$N$_4$.

### 3.4.4. Stability of 2D Graphitic Carbon Nitride Photocatalysts

The stability of g-C$_3$N$_4$ is identified as the most stable allotrope compared with various carbon nitrides under ambient conditions. With the structure of tri-s-triazine, it possesses high thermal stability and chemical stability. g-C$_3$N$_4$ is stable up to 600 °C in the air and insoluble in acid, base, and organic solvents. g-C$_3$N$_4$ is stable under light irradiation in solution (pH = 0–14) due to the strong covalent bonds between carbon and nitride atoms. Therefore, g-C$_3$N$_4$ is a stable and promising photocatalyst in the reaction of the water splitting.

### 3.5. Other 2D Photocatalysts and 2D/2D Composite Photocatalysts

#### 3.5.1. 2D Photocatalysts for Overall Water Splitting

Photocatalytic overall water splitting to produce H$_2$ and O$_2$ is a promising technology to convert solar energy into chemical energy. To make overall water splitting feasible, the band gap of the semiconductor has to straddle the energy level of H$^+$/H$_2$ and the oxidation potential of H$_2$O/O$_2$, as shown in Figure 2. Many semiconductors possess suitable band gap for overall water splitting, such as TiO$_2$, C$_9$N$_6$O$_2$, and Zn$_2$GeO$_4$. However, owing to the fast recombination of photogenerated electron–hole pairs and a lack of surface redox active sites, it is difficult to achieve water splitting with high-efficiency on a single bulk semiconductor.

With more exposed active sites, 2D semiconductor should be more efficient than their bulk counterparts for the photocatalytic overall water splitting. Furthermore, some 2D semiconductors show photocatalytic overall water splitting activity while their bulk counterparts were inactive. For example, the monolayer γ-Ga$_2$O$_3$ can photocatalyze overall water splitting into hydrogen and oxygen while bulk γ-Ga$_2$O$_3$ samples were inactive for oxygen evolution. This monolayer-γ-Ga$_2$O$_3$ is a wide-bandgap photocatalyst, which can only absorb ultraviolet light. Thus, ultrathin 2D visible-response photocatalysts are worthy of exploitation.

Modification of photocatalyst with redox cocatalysts is an effective way to enhance the overall water splitting activity.

For example, Mn$_3$O$_4$–GaN:ZnO–Rh/Cr$_2$O$_3$, SrTiO$_3$–NiO$_2$, and TiO$_2$–Pt$^6$ have been successfully prepared and used for photocatalytic overall water splitting. However, because of the fast recombination of the electrons and holes in the bulk semiconductor, the photocatalytic efficiency is still low. Recently, 2D semiconductor modified with cocatalyst for overall water splitting was reported. For instance, 2D Pt/g-C$_3$N$_4$ synthesized by in situ deposition method is able to photocatalytic pure water into H$_2$ and O$_2$ with an apparent quantum efficiency of 0.3% at 405 nm. In this system, both Pt$^6$ and PtO$_2$ was formed on the g-C$_3$N$_4$, and the Pt$^6$ was effective for H$_2$ evolution while PtO$_2$ was able to accelerate O$_2$ evolution. Notably, pure 2D g-C$_3$N$_4$ showed no activity, and the Pt$^6$ and PtO$_2$ are indispensable for the overall water splitting. Pt and Co co-deposited carbon nitride with a crystalline poly(triazine imide) framework was also reported for the overall water splitting, and the apparent quantum yield reached 2.1% at 380 nm. The efficiency of overall water splitting can also be improved by altering the reaction pathway. Compared to the typical four-electron pathway for water splitting, a high-efficiency two-electron pathway was studied by Kang and his co-worker. Carbon nanodot-carbon nitride (CDots-C$_3$N$_4$) nanocomposite was used as the photocatalyst in this two-electron pathway. With the optimum CDots/C$_3$N$_4$ ratio, the quantum efficiency reached 16% at 420 ± 20 nm, and showed an overall solar energy conversion efficiency of 2.0%. Nevertheless, the solar-to-hydrogen efficiency still needs to be improved for large-scale production.

Construction of heterostructure in photocatalysts is another efficient strategy to enhance the photocatalytic performance for overall water splitting. Fabrication of phase junction, Type II heterostructure, and Z-scheme system have been reported for overall water splitting. Among them, Z-scheme photocatalytic system, with the H$_2$ production photocatalyst and the O$_2$ production photocatalyst, is the most promising approach for overall water splitting. With a staggered alignment of band structures in the Z-scheme system (Figure 4), the recombination of the electron–hole pairs can be greatly reduced, thus allowing the reduction and oxidation of water to take place on the H$_2$ production photocatalyst and O$_2$ production photocatalyst, respectively. Many Z-scheme photocatalytic system, such as Au–TiO$_2$/SrTiO$_3$–Rh, BiVO$_4$/CaFe$_2$O$_4$, and SrTiO$_3$–La/Rh/Au/BiVO$_4$–Mo, have been developed for overall water splitting. However, the overall water splitting efficiency is still in need of improvement. Given the advantages of the 2D/2D interface as described in the previous sections, construction of the 2D/2D Z-scheme system should be an advisable approach for charge separation and the enhancement of overall water splitting. Theoretical calculation based on density functional theory (DFT) has been studied on 2D Z-scheme heterostructure to confirm its feasibility for the overall water splitting. For example, MoSe$_2$/graphene/HfS$_2$ and MoSe$_2$/N-doped graphene/HfS$_2$ with graphene (N-doped graphene) as the redox mediator were predicted to be a feasible 2D Z-scheme photocatalyst for the overall water splitting. Furthermore, a 2D/2D MoSe$_2$/HfS$_2$ and GeS/WS$_2$ without redox mediators is also verified by DFT calculations as a direct Z-scheme system for photocatalytic overall water splitting. The internal electric field induced by the...
electron transfer at the 2D/2D Z-scheme interface can suppress the recombination of photogenerated electrons and holes; thus, the hydrogen evolution and oxygen evolution reaction can take place at the different part of the Z-scheme system.

To date, there are few experimental reports on the 2D/2D Z-scheme for overall water splitting, which might be due to the difficulty in the synthesis of the 2D H₂ (or O₂) production photocatalyst and the construction of 2D/2D Z-scheme heterostructure. Very recently, 2D/2D Black Phosphorus/Bismuth Vanadate (BP/BiVO₄) Z-scheme heterostructure was fabricated and tested for overall water splitting.²⁶³ The BP and BiVO₄ nanosheets were easily combined by electrostatic interactions owing to the 2D structures, and the interfacial interaction promoted the separation of the charge carriers. In this system, under visible light irradiation, the photogenerated electrons in the CB of BiVO₄ rapidly combine with the photogenerated holes in the VB of BP owing to their close band positions. Consequently, the photogenerated electrons in the CB of BP can be used for the reduction reaction, while the photogenerated holes in the VB of BiVO₄ be used for the oxidation reaction (Figure 18). The optimum H₂ and O₂ production rates on BP/BiVO₄ were 160 and 102 μmol g⁻¹ h⁻¹, respectively, under irradiation of light (>420 nm) with an apparent quantum efficiency of 0.89% (420 nm). Apparently, more efficient construction technology for 2D and 2D/2D photocatalysts should be exploited to enhance the efficiency of the photocatalytic overall water splitting.

3.5.2. Recent Emerging 2D Photocatalysts. Since the discovery of 2D graphene, numerous new-types of 2D materials have been synthesized. Except for the aforementioned mentioned ones, a few 2D materials were recently reported and showed potential as photocatalysts such as GeH,²⁶⁶ graphene oxide,²⁶⁷ HNb₃O₈,¹²⁶ HNbWO₆,³³ SnNb₂O₆,³² ZnIn₂S₄,⁴² Cu₂ZnSnS₄,¹⁶⁸ SiC,¹³³ CoOOH,¹²⁴ etc. They have been synthesized. Except for the aforementioned mentioned ones, a few 2D materials were recently reported and showed potential as photocatalysts such as GeH, graphene oxide, HNb₃O₈, HNbWO₆, SnNb₂O₆, ZnIn₂S₄, Cu₂ZnSnS₄, SiC, CoOOH, etc. They have been promising prospects to convert the solar energy into chemical energy by photocatalytic water splitting.

Germanane (GeH), which was synthesized by an ion-exchange approach, exhibits photocatalytic activity for water splitting under visible light.³⁶ GeH possesses a band gap of 1.58 eV, and thus has a strong light absorption in the whole visible region. In addition, the suitable energy potential (CB = −0.313 eV, VB = 1.267 eV vs NHE) endows it to reduce the H⁺ into H₂. Furthermore, after the cycling photocatalytic experiments, the H₂ evolution rate remained constant, and the original structures and morphologies of GeH were retained. These results indicate that the GeH samples are stable for photocatalytic applications. However, it shows relatively low photocatalytic activity due to the fast recombination rate of the photogenerated electrons and holes. To address this problem, a 2D/2D GeH/graphene heterostructure was studied on the basis of hybrid density functional calculations.²⁶⁶ When graphene was intimately combined with the GeH monolayer, a driving force was generated due to the interaction between carbon and hydrogen atoms, which led to the electron transfer from the graphene to GeH monolayer, while holes moved in the opposite way. Thus, a built-in electric field is induced (E_b). With the semimetal nature of graphene and the semiconductor nature of GeH, the space charge region of the GeH/graphene heterointerface leads to the formation of a Schottky barrier. The calculated Schottky barrier for holes to diffuse from graphene to GeH is only 0.83 eV (Figure 19). Consequently, photoexcited holes and electrons can be separated effectively at the GeH/graphene interfaces, which can lead to the improved photocatalytic performance.

Ultrathin HNbO₈ nanosheets with a thickness of about 1.30 nm show a widened band gap (3.68 eV) compared with its bulk counterpart (3.59 eV) because of the quantum size effect. Benefiting from the 2D structure, the separation of the photogenerated carriers was greatly enhanced. Thus, the photocatalytic hydrogen evolution activity of the HNbO₈ nanosheet was improved by 4 times higher than that of bulk HNbO₈. Besides, ultrathin HNbWO₆ nanosheets can be obtained by the exfoliation method based on an acid—base reaction and ion intercalation strategy.³⁵ The as-prepared monolayer HNbWO₆ suspensions are stable and highly dispersed and efficient in photocatalytic hydrogen production. The apparent quantum yield of 1.0 wt % Pt loaded monolayer HNbWO₆ was about 6 times higher than that of Pt loaded restacked-HNbWO₆.

β-CoOOH nanosheets (1.5 nm thickness) exfoliated from bulk β-CoOOH possess a band gap of 2.4 eV and can effectively absorb visible light up to 500 nm.²⁵ β-CoOOH nanosheets can photocatalytically evolve hydrogen from water directly in a rate of 1200 μmol g⁻¹ h⁻¹ and the quantum efficiencies at 380, 420, and 450 nm were 10.7%, 6.9%, and
2.3%, respectively. In the process of photocatalytic hydrogen evolution over ultrathin β-CoOOH nanosheets, the low-coordinated surface Co ion strengthens the hybridization of Co 3d states and S 2p states of the SO_4^{2−}−hole scavenger. Thus, the hole transfer rate between Co ions and SO_4^{2−} and the electron transfer between the surface catalytic sites and H^+ ions can be facilitated by the strong electron state hybridization, leading to the enhancement of photocatalytic hydrogen evolution activity.

### 3.5.3. Theoretically Predicted 2D Photocatalysts

Except for experimental efforts, theoretical modeling has also been devoted to predicting effective 2D photocatalysts. Based on the extensive density functional theory calculations, many new 2D photocatalysts such as phosphorene, BiOCl, C_2N, metal phosphorus trichalcogenides, zinc-blendes, among others, with suitable band gap were predicted to be promising for the photocatalytic water splitting.

In 2014, monolayer black phosphorus was synthesized using sticky-tape technique and was called “phosphorene.” Phosphorene is a direct and narrow band gap semiconductor, possesses an adjustable electronic band gap (0.3 to 2.29 eV), and exhibits visible to infrared photon absorption capabilities. Thus, phosphorene was predicted as an efficient photocatalyst for visible light water splitting. Theoretical calculation results show that the freestanding single- and few-layer BiOCl have a greater number of active sites for surface atoms, reduced electron–hole recombination rate and faster charge carrier mobility than bulk BP. However, at ambient condition, the phosphorene can only trigger the hydrogen evolution from water, but is not suitable for the oxidation of water into O_2 since the VB of phosphorene is not more positive than the redox potential of O_2/H_2O. Notably, the phosphorene shows a favorable band position for overall water splitting in pH = 8.0 solutions. The water splitting process on phosphorene is energetically favorable, and the water oxidation and reduction process will take place separately on different sides of the monolayer phosphorene.

Single- and few-layer bismuth oxyhalides were predicted as promising photocatalysts for solar water splitting. The theoretical calculation results show that the freestanding single-layer BiOCl has a high dynamic stability and possesses a suitable band gap for the overall water splitting. The single-layer and few-layer BiOCl exhibits an indirect band gap, and the band gap of single-layer BiOCl is predicted to be 2.28 eV, and the band gap decreases very slightly with the increase in thickness. Most importantly, the band gap of few-layer BiOCl is almost insensitive to the layer thickness, which is due to the weak interlayer interactions. From single-layer to a few layers (1−5 layers), the BiOCl can harvest the major portion of solar light (400−500 nm), demonstrating its potential as a visible light photocatalyst for water splitting. However, the CB positions are located just slightly above the reduction potential of water to H_2, which might not have enough thermodynamic driving force for the hydrogen reduction reaction. However, this band edge positions can be tuned by applying the compressive strain on single- and few-layer BiOCl. The BiOCl and BiOBr were also predicted to be promising photocatalysts for water splitting. Notably, ultrathin BiOCl nanosheets have been experimentally demonstrated as efficient photocatalysts for photocatalytic H_2 production from water under visible light irradiation.

Monolayer C_2N with a band gap of 2.47 eV is predicted to be a promising photocatalyst for water splitting based on density functional calculations. Moreover, monolayer C_2N has high structural stability due to the high-frequency phonon modes, which is close to that of graphene. In addition, C_2−Si_N and C_2−Ge_N monolayers obtained by isoelectronic substitutions at the C-site of C_2N possess a reduced band gap and an enhanced absorption of visible light. Furthermore, the band edge positions are even more favorable than the pristine C_2N for the separation of electron–hole pairs and the photocatalytic water splitting. On the basis of first-principles calculations, the C_2N combined with the C_2N was demonstrated to be a promising photocatalyst by forming the type II band alignment with relatively big chemical potential differences.

Monolayer metal phosphorus trichalcogenides were demonstrated as promising photocatalysts by first-principles computations. Take MnPSe_3 as an example, with the band gap of 2.32 eV, it shows strong absorption in visible-light spectrum. Furthermore, MnPSe_3 can be used to photocatalytically water splitting into H_2 and O_2 simultaneously due to its suitable band edge location. Besides, the exfoliation of bulk MnPSe_3 is viable in experiments and it can form a freestanding monolayer. The high carrier mobility of monolayer MnPSe_3 (up to 625.9 cm^2 V^{-1} s^{-1}) is in favor of the transfer of charge carriers to reactive sites for the photocatalytic water splitting. With these features, monolayer MnPSe_3 is a promising candidate as photocatalyst for water splitting. Additionally, FePSe_3, NiPSe_3, CdPSe_3, ZnPSe_3, FePSe_3, MnPSe_3 and MnPS_3 were also predicted to be potential photocatalysts for water splitting.

MXenes, a new family of 2D transition-metal carbides and carbonitrides, were first reported in 2011 and have been widely studied for various applications. Recently, MXene was predicted to be a promising photocatalyst for water splitting and CO_2 reduction based on density functional theory. Particularly, 2D ZrC_2O_2 and HfC_2O_2 MXene are potential photocatalysts for water splitting due to their suitable band edges for the redox reaction of water splitting. In addition, they possess a narrow band gap (1.76 eV for ZrC_2O_2 and 1.79 eV for HfC_2O_2) and directionally anisotropic carrier mobility, thus they exhibit good optical absorption performance in visible light and the migration and separation of photogenerated electron–hole pairs can be effectively promoted. Meanwhile, these two MXenes also exhibit good stability in water. Furthermore, the adsorption of H_2O and the formation of H_2 on the MXene are energetically favorable, which is in favor of photocatalytic hydrogen evolution.

MXenes are also verified to be cocatalysts for photocatalysts to promote the separation of the charge carriers. Ti_6C_7T_5O_5 and Nb_2CT_2 were demonstrated as efficient cocatalysts for TiO_2 photocatalyst. By formation of the Schottky barrier at the MXene/TiO_2 interface, the separation of photogenerated charge carriers can be promoted.

### 4. CONCLUSIONS AND PERSPECTIVE

In summary, we have reviewed a few major types of 2D materials-based photocatalysts for water splitting and critically assessed the role of interfaces in the 2D/2D photocatalysts. The 2D/2D interface plays an important role in the photocatalytic water splitting activity of the photocatalysts due to several reasons. First, the combination of 2D semiconductors with other 2D cocatalysts creates a large intimate interface, which is beneficial for the separation of electron–hole pairs. Second, the formation of heterostructure junctions with band alignment can be used to promote the separation and transportation of electron–hole pairs between the 2D semiconductors and 2D cocatalysts. Third, the utilization of sunlight is enhanced due to the broadened...
absorption regime caused by the synergistic effect of the 2D semiconductors and 2D cocatalysts. Last but not least, the formation of intimate interface also enhances the stability of the photocatalysts due to the alleviation of photocorrosion and agglomeration. Numerous examples with different types of 2D/2D heterostructures have shown that forming 2D/2D intimate interface is a promising route to enhance the photocatalytic efficiency of the 2D semiconductors.

Despite the encouraging progress made in the 2D photocatalysts, there are also enormous challenges in the photocatalytic water splitting over these 2D materials. First, the synthetic method of 2D nanosheet from nonlayered or layered precursor should be improved to control the number of layers and obtain large-scale production of 2D photocatalyst. Despite many synthetic routes exist, such as hydrothermal method, ultrasonic exfoliation, ion intercalated exfoliation etc., they are not feasible for large-scale production, especially for the nonlayered semiconductors. Some layered semiconductors are easier to delaminate; however, organic solvents or metallic lithium are usually needed for intercalation exfoliation, which is dangerous and has a harmful effect on the environment. Chemical vapor deposition is an efficient method to synthesize 2D materials, yet a substrate is necessary for this process. Generally, freestanding 2D nanosheets are more efficient for the photocatalytic reaction in an aqueous solution. Therefore, more effective synthetic routes need to be developed to satisfy the high efficiency, the large-scale production, and the stability of 2D photocatalysts.

Second, many 2D photocatalysts are not stable in the water splitting reaction due to the self-oxidation, photocorrosion or agglomeration. Therefore, strategies should be developed to enhance the stability of 2D photocatalysts, such as structural distortion, surface functionalization, and so on. Controlling the structural distortion of the 2D photocatalysts to minimize the surface energy is an effective method to improve their stability. The severe agglomeration of 2D photocatalysts can occur during the water splitting reaction period, which can decrease the number of surface active sites and limit their practical application. Therefore, effective strategies should be exploited to stabilize the 2D photocatalysts, such as the construction of 2D/2D heterojunction by a layer-by-layer assembly or electrostatic self-assembly techniques.

Third, due to the fast recombination of electron−hole pairs, sacrificial reagents (such as CH₃OH, lactic acid, triethanolamine, etc.) are usually needed to obtain the high photoactivity, which goes against with the practical application of 2D photocatalysts. Although the formation of 2D/2D interface by coupling two 2D photocatalysts can help to separate the photogenerated charge carriers to a certain degree, more efficient separation of electron−hole pairs is still highly desirable. Similar to the interface engineering of bulk photocatalysts, multiple interfaces among 2D, 1D, and 0D should be explored beyond the 2D/2D interfaces to significantly improve the charge carrier separation efficiency.

Finally, the mechanism of photocatalytic enhancement by the construction of the 2D/2D interfaces still remains to be explored. Some explanations of the enhanced activity of the 2D/2D photocatalysts have been proposed, but some are still in controversy. Therefore, a fundamental understanding of the charge transport process in the 2D/2D interface is in great need to help improve the fabrication of more efficient interfaces. First-principles calculations and advanced in situ techniques such as pump–probe spectroscopy on model 2D/2D interfaces hold the promise to illuminate functions of each of these 2D parts and the mechanism of charge transport between the 2D/2D interface.

With the fast development of synthesis science and in situ/operando characterizations, there is no doubt that the above-mentioned hurdles will be overcome and more highly efficient and robust 2D-based photocatalysts will emerge in the years to come.

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**Notes**

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