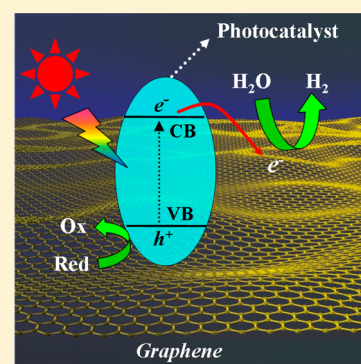


## Graphene-Based Photocatalysts for Hydrogen Generation

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**ABSTRACT:** Graphene-based photocatalysts have gained increasing interest as a viable alternate to increase photocatalytic H<sub>2</sub> production performance in converting solar energy into chemical energy. The use of graphene to enhance the efficiency of photocatalysts has been proved due to its unique two-dimensional conjugated structure and electronic properties. In this Perspective, we have summarized the recent significant advances on the design and applications of graphene-based photocatalytic composites. The rational designs for high-performance photocatalysts using graphene-based materials are described. The applications of the new materials in photocatalytic hydrogen evolution are presented. Finally, the ongoing challenges and opportunities for the future development of graphene-based photocatalysts are also proposed.



The production of chemical fuels by solar energy conversion has been considered as one of the major strategies for solving the global energy problem.<sup>1–5</sup> Photocatalytic water splitting for hydrogen production has become a promising approach for clean, economical, and environmentally friendly production of hydrogen by using solar energy since Fujishima and Honda first reported the photoelectrochemical water splitting on a TiO<sub>2</sub> electrode in 1972.<sup>6</sup> When the semiconductor nanoparticles are exposed to light energy comparable to their band gap, electrons and holes are generated in the conduction and valence bands, respectively. These charge carriers either recombine or migrate to the surface of the photocatalyst to contribute to a series of photocatalytic reactions. For an efficient semiconductor photocatalyst, long-lived charge carriers, fewer charge trapping centers, proper energy level offsets, and stability against light are highly desirable for improving the photocatalytic reactivity.<sup>3</sup> In the past decade, various strategies, including crystal and textural modification, band gap engineering, interfacial heterostructuring, and surface sensitization of semiconductor photocatalysts, have been developed in an attempt to improve the photocatalytic performance of photocatalysts.<sup>3,7,8</sup>

There is an increasing interest in the rational design for high-performance photocatalysts by the introduction of graphene.

In particular, combining graphene with photocatalysts to enhance their photocatalytic performance has attracted considerable attention.<sup>3,9–12</sup> Owing to a unique sp<sup>2</sup> hybrid carbon network, graphene has a very high thermal conductivity

(~5000 W m<sup>-1</sup> K<sup>-1</sup>), presents an excellent mobility of charge carriers at room temperature (200 000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), and shows an extremely high theoretical specific surface area (~2600 m<sup>2</sup>/g).<sup>3</sup> These properties make it become an ideal support of the photocatalyst to enhance the transfer and separation of photogenerated electrons and holes. The potential application of graphene-based photocatalysts to boost the efficiency of solar energy conversion has been explored.<sup>9–12</sup> The mechanism of the enhancement of photocatalytic performance can be briefly summarized into four categories, suppressing the recombination of the photogenerated electron–hole pairs, acting as a support to provide adsorption and catalytic sites, tuning the band gap size of the semiconductor and/or acting as a photosensitizer, and using as a cocatalyst to catalyze the hydrogen evolution. Figure 1 shows the proposed mechanism for graphene-based photocatalysts in enhancing photocatalytic performance. Such beneficial aspects of graphene-based photocatalysts need to be further exploited for designing next-generation photocatalysts for solar energy conversion. The investigation of graphene-enhanced photocatalysis is advancing fast; therefore, the related photochemical and physical chemical aspects on the latest developments greatly need to be summarized.<sup>13,14</sup> The present Perspective is a short overview of recent research activities related to graphene-based H<sub>2</sub> production photocatalysts and discussion of their emerging role in photocatalytic hydrogen evolution.

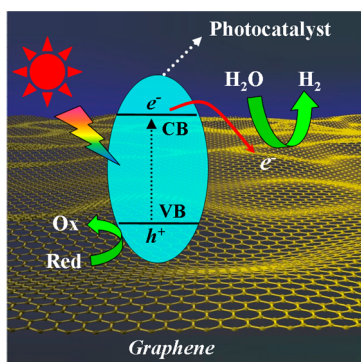
*Designing Graphene-Based Photocatalysts.* There have been several reports highlighting the rational design of graphene-based photocatalysts with high photocatalytic activity.<sup>3</sup>

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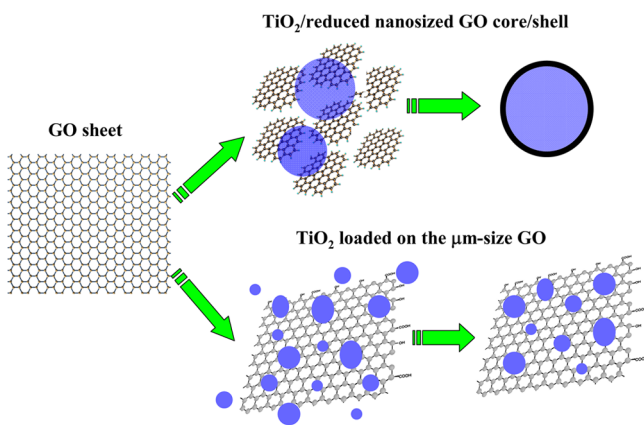
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**Figure 1.** The proposed mechanism for graphene-based photocatalysts in enhancing photocatalytic performance.

Graphenes are known to provide a high-quality two-dimensional (2D) support to increase the specific surface area of the photocatalyst and a 2D circuit board with an attractive potential to efficiently harness their perfect electrical and redox properties.<sup>3,15</sup> In general, when photocatalyst nanoparticles are loaded on graphene sheets, only a small fraction of the nanoparticle's surface is in a direct contact with the graphene sheets. Such a small contact interface between photocatalysts and graphene cannot enable their strong interaction and delays the highly efficient electron transfer for photocatalytic reaction. Therefore, rational design of graphene-based photocatalysts with a large contact interface and strong interaction between the composites is highly desirable. Recently, Kim et al. have developed a new type of reduced nanosized graphene oxide (GO)-TiO<sub>2</sub> nanoparticles (GO/TiO<sub>2</sub>), which have a self-assembled core-shell structure with high photocatalytic and photoelectrochemical activity.<sup>16</sup> The enhanced H<sub>2</sub> production rate and photocurrent generation of GO/TiO<sub>2</sub> as compared to those of TiO<sub>2</sub> loading on the larger graphene oxide (TiO<sub>2</sub>/GO) highlights the beneficial role of a unique core-shell nanoarchitecture in enhancing photocatalytic activity. The intriguing structural design provides a three-dimensional (3D) intimate contact and maximizes the interaction between two composites, which facilitates the charge separation and the subsequent production of hydrogen (see Figure 2). This study on the core-shell nanoarchitecture of nanosized GO/TiO<sub>2</sub> provides new physicochemical insight into the complicated design of



**Figure 2.** Scheme illustration of the preparation procedure of GO/TiO<sub>2</sub> and TiO<sub>2</sub>/GO.

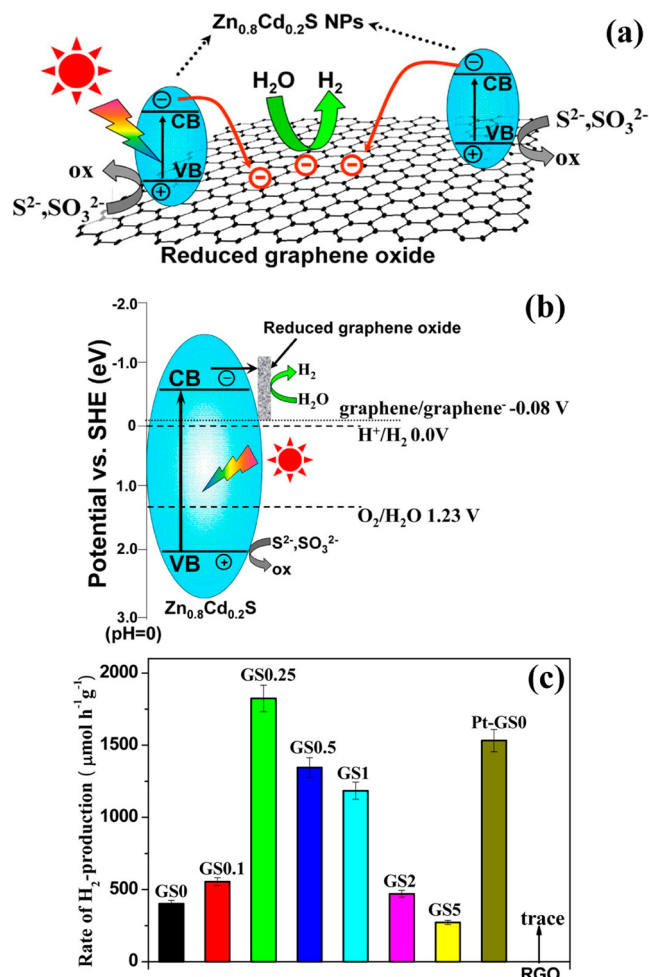
novel 3D nanostructure graphene-based photocatalysts for solar conversion application.

Recently, much interest has been dedicated to the visible-light photocatalytic applications of graphene-based photocatalysts by reducing the band gap of the photocatalyst and/or by using graphene as a photosensitizer to extend the light-response range.<sup>17,18</sup> Much effort has been made in constructing a visible-light-driven TiO<sub>2</sub> photocatalyst because TiO<sub>2</sub> has good biological and chemical inertness, nontoxicity, low cost, and long-term stability against photo and chemical corrosion, but it has a large band gap.<sup>3</sup> Modifying the surface of TiO<sub>2</sub> with graphene can induce visible-light-responsive photocatalytic activity. The carbonate structural fragments of graphene oxide with unpaired  $\pi$  electrons are bonded with titanium atoms on the surface of TiO<sub>2</sub>. Such an interaction between unpaired  $\pi$  electrons and Ti atoms can result in the shift of the band edge and the significant reduction of the band gap of graphene-TiO<sub>2</sub>. Therefore, it can be inferred that graphene with unpaired  $\pi$  electrons could be used to modify the TiO<sub>2</sub> surface to contrive a visible-light-responsive photocatalyst. Lee et al. have demonstrated the band gap narrowing of a graphene-wrapped anatase TiO<sub>2</sub> composite.<sup>17</sup> The enhanced photocatalytic activity of graphene-TiO<sub>2</sub> under visible light illumination is attributed to a red shift of the band edge and a significant reduction of the band gap of the graphene-TiO<sub>2</sub> composite, which consequently allows the enhanced absorption of visible light and efficient transfer of photogenerated electrons through graphene nanosheets.

A similar strategy can be further extended by using graphene as a photosensitizer of a wide-band-gap semiconductor to design visible-light-responsive photocatalytic materials. Early studies have demonstrated that C<sub>60</sub> in the C<sub>60</sub>-TiO<sub>2</sub> composite photocatalyst can act a photosensitizer of TiO<sub>2</sub>.<sup>19</sup> Under visible laser beam irradiation, the photoinduced electrons from C<sub>60</sub> could transfer to the conductor band of TiO<sub>2</sub>. Very recently, Zhang et al. reported the visible-light-driven photocatalytic activity of ZnS-graphene oxide nanocomposites by using graphene as a macromolecular photosensitizer.<sup>20</sup> In the aforementioned study, wide-band-gap ZnS cannot produce excited states under visible light irradiation. Conversely, graphene is photoexcited from the ground state to the excited state and acts as an organic dye-like macromolecular photosensitizer and as an electron carrier in the composite, leading to the visible-light-responsive photocatalytic activity. Such a photocatalytic process for ZnS-graphene under visible light irradiation seems to be very similar to the well-known strategy of dye-sensitized semiconductors and/or dye-sensitized solar cells. It should be noted that the role of graphene in this case is different from that in the previous many works on graphene acting as a support for photocatalysts. In the previous works, graphene is used as a support for photocatalysts and/or photoabsorbers to increase the specific surface area of the photocatalysts and to capture/shuttle the photogenerated electrons from the photocatalysts.<sup>3</sup> On the contrary, in this work, graphene is photoexcited and acts as photoabsorber itself to extend the absorption wavelength of light. As a proof-of-concept, although the visible-light-driven photocatalytic activity of ZnS-graphene has been achieved, the proposed photocatalytic reaction mechanisms are at the primary stage, and further developments are required. For example, the utilization of monochromatic light with the wavelength in the range of 420–1000 nm may provide research opportunities to further explore the proposed photocatalytic mechanisms.

**Photocatalytic Hydrogen Generation.** Hydrogen is regarded as one of the ultimate clean fuels. Photocatalytic hydrogen evolution using a proper photocatalyst and solar energy has been considered as a promising and attractive approach to produce hydrogen energy.<sup>21,22</sup> In the last decades, a variety of semiconductor photocatalysts have been reported to catalyze the evolution of hydrogen from water.<sup>23,24</sup> Efforts are also being made to utilize graphene-based composites for photocatalytic hydrogen generation. An important approach is to develop graphene as a substitute for noble metals (such as Pt) in the photocatalytic H<sub>2</sub> production and enhance the photoactivity of graphene-based photocatalysts. Although the previous work showed that the formation of hydrogen pairs on a single graphite sheet (graphene) was limited due to barrierless adsorption of hydrogen atoms,<sup>25</sup> it would be possible for graphene-based photocatalysts to generate hydrogen on the surface of graphene. This is because the photogenerated electrons of the photocatalysts accumulate on graphene; the Fermi level of graphene would shift upward and closer to the conduction band of the photocatalyst due to the metallic behavior of graphene. Therefore, the carbon atoms on the graphene sheets can catalyze the reduction of H<sup>+</sup> and production of hydrogen molecules on the surface of graphene by accepting photogenerated electrons. For example, our group has reported the high solar photocatalytic H<sub>2</sub> production activity over the noble-metal-free reduced graphene oxide (RGO)–Zn<sub>0.8</sub>Cd<sub>0.2</sub>S nanocomposite.<sup>26</sup> The above study highlights the beneficial role of RGO in enhancing H<sub>2</sub> production photoactivity of Zn<sub>0.8</sub>Cd<sub>0.2</sub>S nanoparticles and using RGO as a promising substitute for noble metals in photocatalytic H<sub>2</sub> production. As shown in Figure 3a and b, the beneficial effects of RGO are because it acts as an excellent supporting material for Zn<sub>0.8</sub>Cd<sub>0.2</sub>S nanoparticles as well as a good electron collector and transporter to separate photogenerated electron–hole pairs. When we compared with the pristine Zn<sub>0.8</sub>Cd<sub>0.2</sub>S, the RGO–Zn<sub>0.8</sub>Cd<sub>0.2</sub>S composite photocatalyst showed a significantly enhanced H<sub>2</sub> production performance by a factor of 4.5 and even higher than that of the optimized Pt–Zn<sub>0.8</sub>Cd<sub>0.2</sub>S sample under the same reaction conditions (see Figure 3c), showing that the RGO–Zn<sub>0.8</sub>Cd<sub>0.2</sub>S composite represents one of the most highly active metal sulfide photocatalysts in the absence of noble metal cocatalysts. The above results strongly suggest that RGO can act as a cost-effective and efficient cocatalyst catalyzing the reduction of H<sup>+</sup> and production of hydrogen molecules on the surface of RGO. In fact, the reduction method and the degree of reduction of graphene oxide strongly influence its photocatalytic H<sub>2</sub> production activity. For example, Fan et al. demonstrated that the composites of TiO<sub>2</sub> and RGO prepared by the hydrothermal method showed better photocatalytic performances for H<sub>2</sub> evolution than for the sample prepared by UV-assisted photocatalytic reduction and chemical reduction using the hydrazine method.<sup>27</sup> The above studies have opened a new doorway for the utilization of low-cost graphene sheets as a substitute for noble metals in photocatalytic hydrogen production.

Another approach is to use graphene as a solid-state electron mediator for water splitting in an ingenious Z-scheme photocatalysis system. Generally, the electron transfer between two distinct photocatalysts in the Z-scheme photocatalysis system is the determining process for producing H<sub>2</sub> and O<sub>2</sub> from water splitting.<sup>28</sup> The presence of an electron mediator is critical to boost the efficient transfer of electrons. The unique

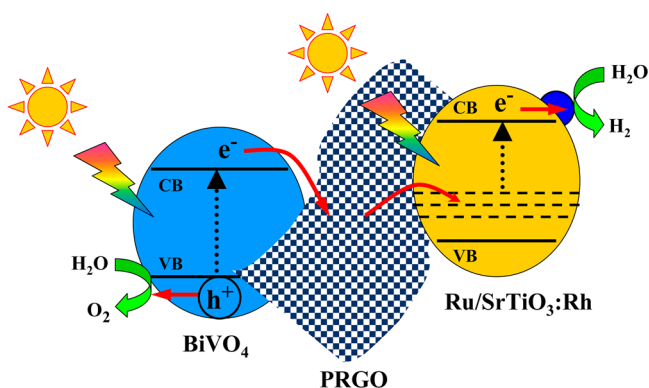


**Figure 3.** (a) Schematic diagram of charge carrier transfer in the RGO–Zn<sub>0.8</sub>Cd<sub>0.2</sub>S composites under simulated solar irradiation. (b) Proposed mechanism for the enhanced electron transfer over the RGO–Zn<sub>0.8</sub>Cd<sub>0.2</sub>S system for the hydrogen production under simulated solar irradiation. (c) Hydrogen evolution rates of RGO–Zn<sub>0.8</sub>Cd<sub>0.2</sub>S composites with different content of RGO under simulated solar irradiation; Pt–GS0: GS0 loaded with the optimized 1 wt % of Pt cocatalyst. (Reprinted from ref 26. Copyright, The American Chemical Society.)

features of graphene enable it to become an interparticulate electron mediator for water splitting in the Z-scheme photocatalysis system. For instance, Amal and co-workers demonstrated the effectiveness of photoreduced graphene oxide (PRGO) as a solid electron mediator for the Z-scheme photocatalytic water splitting using BiVO<sub>4</sub> and Ru/SrTiO<sub>3</sub>:Rh as the O<sub>2</sub> and H<sub>2</sub> photocatalysts, respectively.<sup>29</sup> They found that the photocatalytic H<sub>2</sub> production rate of the (Ru/SrTiO<sub>3</sub>:Rh)–(PRGO/BiVO<sub>4</sub>) system was higher than that of the (Ru/SrTiO<sub>3</sub>:Rh)–BiVO<sub>4</sub> system without graphene. Under visible light illumination, photogenerated electrons from the conduction band of BiVO<sub>4</sub> transfer to Ru–SrTiO<sub>3</sub>:Rh via graphene as an electron conductor (Figure 4). The electrons in Ru/SrTiO<sub>3</sub>:Rh reduce water to H<sub>2</sub> on the Ru cocatalyst, while the holes in BiVO<sub>4</sub> oxidize water to O<sub>2</sub>, accomplishing a complete water splitting cycle. This work provides a new way of using the attractive graphene in the rational design of new and efficient systems for photocatalytic overall water splitting.

In the previous research of graphene-based photocatalysts, photocatalyst nanoparticles were usually loaded on graphene

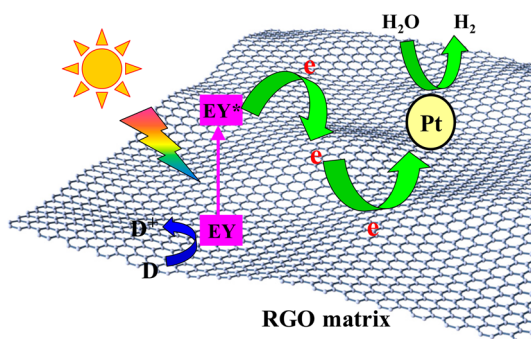




**Figure 4.** The proposed mechanism for PRGO to serve as a solid-state electron mediator in a Z-scheme (Ru/SrTiO<sub>3</sub>:Rh)–(PRGO/BiVO<sub>4</sub>) photocatalytic water splitting system under visible light irradiation.

Graphene-based photocatalysts provide us with new insight to improve the efficiency of photocatalytic hydrogen generation.

sheets to increase the active surface area and stability of electrons for the photocatalytic reaction. Recently, a novel dye-sensitized RGO photocatalytic hydrogen evolution system has been developed.<sup>30</sup> In this system, the dye Eosin Y (EY) molecules as a photosensitizer were adsorbed on the surface of RGO sheets with dispersed Pt cocatalyst. As shown in Figure 5,



**Figure 5.** The proposed mechanism for the electron transfer over the EY–RGO/Pt photocatalyst for the hydrogen production under visible light irradiation.

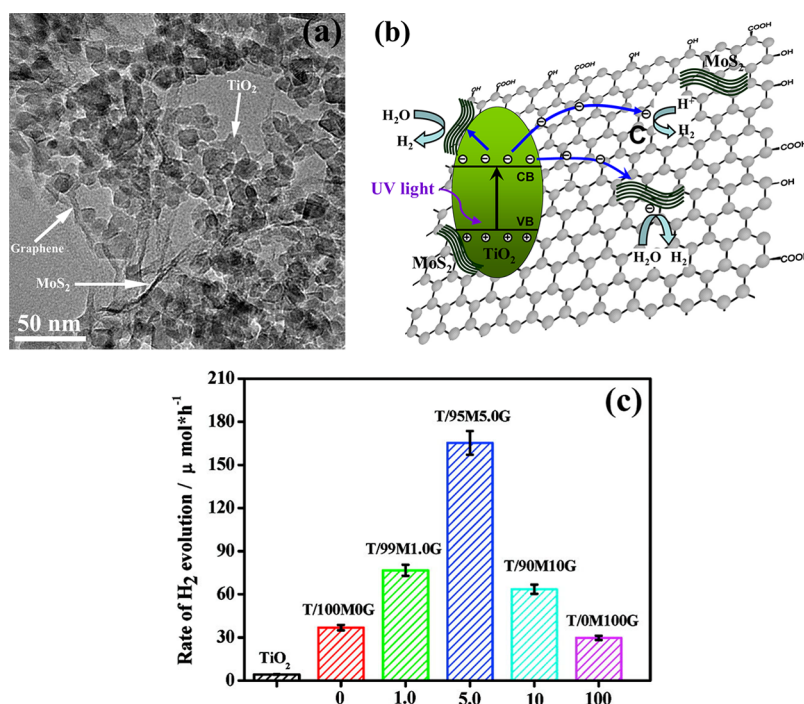
the excellent electron-accepting and electron-transporting properties of RGO can facilitate the electron transfer from excited dye molecules to the Pt cocatalyst, which promotes the photocatalytic activity for hydrogen evolution. Similarly, an efficient and stable photocatalytic H<sub>2</sub> evolution system was also constructed on Pt-deposited graphene sheets cosensitized by EY and Rose Bengal.<sup>31</sup> Further efforts are likely to involve the development of organic dye-sensitized graphene systems for highly solar photocatalytic H<sub>2</sub> production performance.

As we have seen, graphene-based photocatalytic hydrogen generation is still a hot topic. However, it should be noted that the studies on graphene-based photocatalysts often focus on binary nanocomposites. Anisotropic multicomponent hybrid nanomaterials composed of graphene and different metals and/or semiconductors are highly desirable in the field of photocatalysis because of their ability to tune the charge

separation behavior through the interaction between them by their favorable band alignment. The efficient separation of photoinduced charge carriers in graphene-based multicomponent composites has been found to enhance photocurrent generation and photocatalytic activity by using proper heterostructure constituents.<sup>32,33</sup> For example, Kamat and co-workers constructed organic/inorganic ternary composites of porphyrin, ZnO nanoparticles, and RGO on a semiconducting electrode by a bottom-up strategy.<sup>32</sup> This hierarchical electron-transfer cascade system exhibited remarkably high photocurrent generation due to the occurrence of multistep electron transfer on the electrode. Our recent photocatalytic H<sub>2</sub> production results by using a ternary TiO<sub>2</sub>/MoS<sub>2</sub>/graphene composite highlight the pivotal role of graphene-based multicomponents in transferring interfacial charge and improving the photocatalytic performance of graphene-based photocatalysts (Figure 6).<sup>33</sup> When we compared the photocatalytic H<sub>2</sub> production activity of the binary TiO<sub>2</sub>/MoS<sub>2</sub> and TiO<sub>2</sub>/graphene composite photocatalysts, the H<sub>2</sub> production rate of ternary TiO<sub>2</sub>/MoS<sub>2</sub>/graphene composites exceeded that obtained on binary TiO<sub>2</sub>/MoS<sub>2</sub> and TiO<sub>2</sub>/graphene by more than 4 and 5 times, respectively. The enhanced photocatalytic H<sub>2</sub> production activity is attributed to the positive synergetic effect between MoS<sub>2</sub> and graphene components in this hybrid cocatalyst, which can efficiently suppress charge recombination, improve interfacial charge transfer, and provide a greater number of active adsorption sites and photocatalytic reaction centers. In addition, in order to get the positive synergetic effect between MoS<sub>2</sub> and graphene, it is crucial to control the addition ratios of graphene, which thus leads to an optimum photoactivity. Excessive addition of black color graphene will lead to shielding of the active sites on the catalyst surface and also rapidly decrease the intensity of light through the depth of the reaction solution, thus resulting in the decreased photoactivity.

In fact, the charge carriers in graphene-based multicomponent photocatalysts can be transported away from each other to delay their instant recombination. The charge separation at different levels can be tuned by the proper choice of band gap width of the constituent material in graphene-based multicomponent composites. Such beneficial aspects of the new multicomponent composites need to be further exploited for designing next-generation photocatalysts for highly efficient solar energy conversion. Indeed, one such strategy of coupling graphene with multiple semiconductor compounds for enhanced visible light photocatalytic activity was also demonstrated recently.<sup>34</sup> Therefore, there are opportunities to develop graphene-based multicomponent photocatalysts with improved photocatalytic performance toward specific applications.

In addition to the above-mentioned graphene-based photocatalysts, graphite oxide with an appropriately oxidized level can also serve as a photocatalyst for hydrogen production from water. Teng and co-workers have reported that graphite oxide photocatalysts with a band gap of 2.4–4.3 eV can steadily produce H<sub>2</sub> from water in an aqueous methanol solution under Mercury lamp irradiation.<sup>35</sup> Efficient H<sub>2</sub> generation on graphite oxide can be attributed to the fact that the electronic structure of graphite oxide is suitable for both reduction and oxidation of water because the carbon atoms on graphite oxide sheets are easily approached by protons, where protons are reduced into hydrogen molecules by accepting photogenerated electrons from the carbon atoms. This preliminary result highlights the interesting application of graphitic materials in developing



**Figure 6.** (a) TEM image of TiO<sub>2</sub> nanocrystals grown on layered MoS<sub>2</sub>/graphene (MG) hybrids (T/95M0.5G). (b) Schematic diagram for charge carrier separation and photocatalytic H<sub>2</sub> production on the ternary TiO<sub>2</sub>/MG composites under UV light irradiation. (c) Comparison of the photocatalytic H<sub>2</sub> production activity under UV irradiation over the photocatalyst TiO<sub>2</sub>/MG composites with different MoS<sub>2</sub> and graphene contents in the MG hybrid as a cocatalyst. (Reprinted from ref 33. Copyright, The American Chemical Society.)

efficient photocatalysts for H<sub>2</sub> generation under solar illumination.

Graphene-based photocatalysts have been widely investigated and proved to be promising photocatalytic materials for future photocatalytic hydrogen production. So far, the most promising RGO–Zn<sub>0.8</sub>Cd<sub>0.2</sub>S composite reached the higher apparent quantum efficiency (QE) of 23.4% at 420 nm, representing one of the most highly active metal sulfide photocatalysts in the absence of noble metal cocatalysts. In this Perspective, we summarized the recent significant advances on the design and efficient utilization of graphene-based photocatalysts in photocatalytic hydrogen generation. The presence of graphene in these composites can enhance the photocatalytic H<sub>2</sub>-production performance of photocatalysts, owing to the extended light absorption range, high adsorption capacity, specific surface area, and superior electron conductivity of graphene.

The presence of graphene in RGO–Zn<sub>0.8</sub>Cd<sub>0.2</sub>S composites can enhance the photocatalytic H<sub>2</sub>-production performance of photocatalysts, owing to the extended light absorption range, high adsorption capacity, specific surface area, and superior electron conductivity of graphene.

Although some significant progress has been achieved, further efforts are still required in this emerging area to obtain highly efficient graphene-based photocatalysts for advanced

energy-related applications. For example, a better understanding on the underlying mechanisms of photocatalytic activity enhancement by graphene is a challenge but crucial for designing novel and highly photoactive graphene-based photocatalysts. To clarify the mechanism of photocatalytic reaction, all aspects in the synthesis–structure–property relationship will need to be better understood. In this regard, the mechanisms can be analyzed through the utilization of single-layer graphene sheets, whose high-quality two-dimensional support for photocatalysts and well-defined electronic properties may provide research opportunities to explore the proposed mechanisms. Further studies are still needed on the development of more complex components, especially some ternary and/or multicomponent graphene-based hybrid composites. Recent results on the efficient photocatalysis achieved by multicomponent graphene-based photocatalysts have demonstrated their effectiveness in photocatalytic reactions.<sup>33</sup> In the multicomponent composites, the tuning of the band gap of the constituent material can facilitate the charge separation efficiently at different levels. Also, through the proper choice of size, shape, and composition of the multicomponent graphene-based photocatalysts, momentous improvements can be attained in the photocatalysis. In addition, the development of more efficient synthesis methods or strategies is highly desirable to improve the interfacial contact between graphene and photocatalyst components in graphene-based photocatalysts in order to improve the overall photocatalytic performance. Recently, Kim and Park reported that the key physicochemical properties of graphene in graphene–CdSe composites play an important role in the photocatalytic H<sub>2</sub> production.<sup>36</sup> Their studies demonstrated that the electrical conductivity in the interfacial contact between graphene and photocatalyst components is a primary factor in determining the overall photocatalytic H<sub>2</sub> production, rather than other factors of graphene, such as the

surface area and degrees of disordered carbon. Thus, more efficient synthetic strategies for graphene-based photocatalysts would need to be developed to address this issue.

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