Reduced Graphene Oxide as a Solid-State Electron Mediator in Z-Scheme Photocatalytic Water Splitting under Visible Light

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Supporting Information

ABSTRACT: The effectiveness of reduced graphene oxide as a solid electron mediator for water splitting in the Z-scheme photocatalysis system is demonstrated. We show that a tailor-made, photo-reduced graphene oxide can shuttle photogenerated electrons from an O2-evolving photocatalyst (BiVO4) to a H2-evolving photocatalyst (Ru/SrTiO3:Rh), tripling the consumption of electron–hole pairs in the water splitting reaction under visible-light irradiation.

Production of clean hydrogen fuel from water using sunlight is one of the promising solutions to address the increasing demand for energy and associated environmental concerns. Two methods currently dominate research on splitting of water into H2 and O2 by photocatalysis: photoelectrochemical1–6 and powdered photocatalytic7–10 water splitting. Generally, a photoelectrochemical system involves a rather complicated cell setup that requires the application of an applied bias and an expensive platinum counter electrode; scale-up attempts are always limited by the exposed area of the photoelectrodes. A powdered-type photocatalytic method that requires only a water pool containing photocatalyst powders offers an interesting opportunity to generate H2 in a more energy-efficient manner. For the powdered photocatalytic water splitting reaction, two approaches have been reported. The first approach is the development of a single photocatalyst with sufficient potential to achieve overall water splitting.5,7–12 Although a number of photocatalysts have been found to be active in splitting water, most of them are responsive only to UV illumination.5,7–10 Oxy-nitride solid-solution photocatalysts, such as (Ga1−xZnx)(N1−xOx) and (Zn1−xGe)x(OxN2x), are currently the most established single photocatalysts that work under visible-light irradiation.11,12 The second approach is the construction of a two-step photoexcitation system, often called a Z-scheme photocatalysis system, that mimics natural photosynthesis.13–22 A Z-scheme system employs two photocatalysts, one producing H2 (the H2 photocatalyst) and the other O2 (the O2 photocatalyst), usually with the aid of an electron shuttle.5,9

The Z-scheme photocatalytic system has greater potential to work under sunlight, as an increasing number of visible-light-active H2 and O2 photocatalysts have been developed separately with the proper sacrificial electron donors or acceptors. Neither a H2 photocatalyst nor an O2 photocatalyst can function independently to split water into H2 and O2. When the two are combined, however, electrons generated in the O2 photocatalyst can be transferred to holes in the excited H2 photocatalyst, allowing the oxidation and reduction of water to take place on the O2 and H2 photocatalysts, respectively. Recent development of the Z-scheme system has suggested that electron transfer between the two photocatalysts is the rate-determining step.23,24 Therefore, the presence of an electron transporter is critical to boost effective electron relay. The Fe3+/Fe2+13,16,18 and IO3−/I−15,17,19,20,22 redox couples are the most commonly employed electron mediators for shuttling electrons from the O2 to the H2 photocatalyst. Although these ionic redox couples perform efficiently in relaying electrons, a solid electron mediator is more favorable in terms of recovery of the photocatalyst and reclamation of clean water. The challenge in developing a solid-state electron mediator lies in achieving a dynamic equilibrium between the electron-accepting and -donating abilities of the mediator, allowing it to remain relatively unchanged during reaction. The photocatalyst–mediator–photocatalyst contact interface is another crucial factor in ensuring a continuous flow of electrons between the source and target photocatalysts.

We recently demonstrated that photo-reduced graphene oxide (PRGO) improves the photoelectrochemical performance of BiVO4 and TiO2 photoanodes by providing low-resistance electron pathways to the external circuit under an applied bias.23,24 Also, Kamat and co-workers demonstrated that PRGO carries electrons photogenerated in a TiO2 photocatalyst to reduce Ag+ ions.25 Because of its large two-dimensional matlike structure with a size of several micrometers, the possibility of using PRGO as the conductive medium to interface the H2 and O2 photocatalysts prompted us to investigate its function as an interparticle electron mediator. We report herein that fine-tuning of the PRGO/semiconductor composite allows PRGO to be used as a solid electron mediator for Z-scheme photocatalytic water splitting using BiVO4 and Ru/SrTiO3:Rh as the O2 and H2 photocatalysts, respectively.

Mixtures of PRGO with BiVO4 (PRGO/BiVO4) and Ru/SrTiO3:Rh (PRGO/Ru/SrTiO3:Rh) were prepared by photocatalytic reduction of GO on BiVO4 and Ru/SrTiO3:Rh, respectively, under visible-light illumination in the presence of methanol as a hole scavenger. To assess the effectiveness of this photocatalytic reduction of GO, a chemical reduction method

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using hydrazine was also performed. Figure 1 shows C 1s X-ray photoelectron spectroscopy (XPS) data for the original GO, hydrazine-reduced GO (N2H4-RGO), PRGO/BiVO4 and PRGO/Ru/SrTiO3:Rh. All of the samples exhibited three peaks due to carbon species with different surroundings: C−C, C−O, and C=O.24 The degree of GO reduction was monitored by the oxygen-bound carbon content, which was calculated using eq 1:

\[
\% \text{ O-bound } C = \frac{A_{C-O} + A_{C=O}}{A_{C-C} + A_{C-O} + A_{C=O}} \times 100\%
\]

where \(A_{C-C}\), \(A_{C-O}\), and \(A_{C=O}\) are the peak areas for graphitic (C−C) and O-bound (C−O and C=O) carbon, respectively.

GO as the precursor contained 43% O-bound carbon, revealing fairly effective oxidation of the commercial graphite. Reaction of GO with hydrazine and the O2 and H2 photocatalysts resulted in different degrees of reduction, as indicated by their O-bound C contents (Figure 1 inset). The O-bound C content of N2H4-RGO decreased drastically relative to GO (9 vs 43%) as expected, while Ru/SrTiO3:Rh and BiVO4 also clearly demonstrated their capabilities in reducing or partially reducing GO to PRGO (O-bound C content = 10% for Ru/SrTiO3:Rh and 28% for BiVO4). The higher degree of GO reduction using Ru/SrTiO3:Rh in comparison with BiVO4 is due to the higher conduction-band energy of Ru/SrTiO3:Rh and the presence of the Ru cocatalyst as highly reductive sites.

Table 1 shows the activity of the Z-scheme systems constructed using various combinations of Ru/SrTiO3:Rh, BiVO4, and reduced GO under visible-light illumination. No water splitting was observed when the activity of Ru/SrTiO3:Rh or BiVO4 alone was measured in the nonsacrificial condition, either with or without PRGO (entries 1−4). When the two were combined (entry 5), H2 and O2 evolved at a steady rate through interparticulate charge transfer. Interacting PRGO/BiVO4 with Ru/SrTiO3:Rh led to a 3-fold enhancement in the gas evolution (entry 8). This improvement is attributable to the presence of PRGO to receive excited electrons from BiVO4 (the O2 photocatalyst) and release them to Ru/SrTiO3:Rh (the H2 photocatalyst). This mechanism of electron flow increased the charge separation efficiency in each photocatalyst, leaving holes in BiVO4 and electrons in Ru/SrTiO3:Rh to split the water. Although the exact mechanism has not yet been clarified, the electrons mainly flow from BiVO4 to Ru/SrTiO3:Rh.

We also measured the apparent quantum yield efficiencies obtained with monochromatic light at 420 nm.25 The efficiencies of the Z-scheme systems consisting of Ru/SrTiO3:Rh and BiVO4 in the presence and absence of PRGO prepared by BiVO4 were 1.03 and 0.97% at 420 nm, respectively. Although the gas evolution was greatly enhanced in the presence of PRGO under full-range visible-light illumination from the Xe lamp (Table 1, entries 5 and 8), the apparent quantum yield efficiencies showed only a modest decrease. When the apparent quantum yield efficiency is measured using low-intensity monochromatic light, which generates only a limited number of electron–hole pairs, interparticulate charge transfer between Ru/SrTiO3:Rh and BiVO4 is not the rate-controlling step. Therefore, only a small enhancement was observed in the apparent quantum yield efficiency when PRGO was incorporated. In contrast, as a more practical full-range visible-light irradiation with higher intensity produces a large number of electron–hole pairs, interparticulate electron transfer from BiVO4 to Ru/SrTiO3:Rh determines the overall rate of water splitting activity. The presence of PRGO overcomes the limitation of interparticulate transfer of populated electrons and holes, thus resulting in a great improvement in the photocatalytic activity. This argument is well-supported by the fact that the enhancement by PRGO disappeared when we reduced the light intensity to 20% using a neutral density filter.

Figure 2 shows the time courses of H2 and O2 evolution from a mixture of PRGO/BiVO4 and Ru/SrTiO3:Rh in acidic water (pH 3.5) under visible-light illumination. The reactions were conducted for 24 h with two intermediate evacuations after every 8 h of irradiation. The activity during the second cycle was slightly decreased, as is normally observed for most systems, and the activity at third cycle was almost the same as that of the second cycle, implying a stable system after the second cycle. The minimum turnover number (TON), calculated as the number of moles of reactive electrons per mole of PRGO (assumed to contain pristine graphitic carbon26) was found to be 3.2 over 24 h. This value is comparable to that for the system employing Fe3+/Fe2+ (TON of 2 over 22 h),27 evidently proving the suitability of

![Figure 1. C 1s XPS spectra for (a) graphene oxide (GO), (b) hydrazine-reduced GO, (c) GO photoreduced by BiVO4, (d) GO photoreduced by Ru/SrTiO3:Rh, and (e) (Ru/SrTiO3:Rh)−(PRGO/BiVO4) after reaction. Inset: O-bound C contents calculated using eq 1.](image-url)

![Table 1. Overall Water Splitting under Visible-Light Irradiation by the (Ru/SrTiO3:Rh)−(BiVO4) System in the Presence and Absence of Photoreduced Graphene Oxide](table-url)
**Figure 2.** Overall water splitting under visible-light irradiation by the (Ru/SrTiO$_3$:Rh)–(PRGO/BiVO$_4$) system. Conditions: catalysts (0.03 g each) in H$_2$SO$_4$ (aq) (pH 3.5, 120 mL); light source, 300 W Xe lamp with a 420 nm cutoff filter; top-irradiation cell with a Pyrex glass window.

**Figure 3.** Optical microscopy images of Ru/SrTiO$_3$:Rh and PRGO/BiVO$_4$ suspended in water at (a, c) pH 3.5 adjusted by H$_2$SO$_4$ and (b, d) pH 7.0.

**Figure 4.** (a) Schematic image of a suspension of Ru/SrTiO$_3$:Rh and PRGO/BiVO$_4$ in water at pH 3.5. (b) Mechanism of water splitting in a Z-scheme photocatalysis system consisting of Ru/SrTiO$_3$:Rh and PRGO/BiVO$_4$ under visible-light irradiation.

PRGO as a solid electron mediator. This TON value larger than unity and the H$_2$ and O$_2$ evolution in a stoichiometric ratio indicate that this Z-scheme system split water photocatalytically and suggest that PRGO is stable as an electron mediator over a period of 24 h. The stability of PRGO is supported by the XPS results shown in Figure 1e, which indicated that the PRGO did not undergo oxidation/decomposition by the photogenerated holes from the two photocatalysts.

Interestingly, while PRGO prepared by BiVO$_4$ tripled the water splitting, the activity was retarded to a level below the non-PRGO system when PRGO prepared by Ru/SrTiO$_3$:Rh was used (entry 7). On the basis of the XPS results, unlike the partially reduced PRGO prepared by BiVO$_4$ (28% O-bound carbon), PRGO/Ru/SrTiO$_3$:Rh restored most of its graphitic carbon (only 10% O-bound carbon remained). This efficient photoreduction of GO, although in most cases desirable, imparted high hydrophobicity to the PRGO/Ru/SrTiO$_3$:Rh particles, making them immiscible in water. This was visualized in the experiment: PRGO/Ru/SrTiO$_3$:Rh particles were seen floating on the water surface, while BiVO$_4$ particles were suspended in the water during reaction [Figure S2 in the Supporting Information (SI)]. This lack of interparticulate contact between H$_2$ and O$_2$ photocatalysts led to limited gas generation. To provide further evidence for the hydrophobicity effect of RGO in this Z-scheme photocatalytic system, hydrophobic N$_2$H$_4$-RGO was employed as the mediator (entry 10). Activity similar to that of the non-RGO system, together with the observation of poor dispersion in the experiment: PRGO/Ru/SrTiO$_3$:Rh particles were seen integrated with PRGO. Although this image may not represent the exact agglomeration of these particles in the reaction suspension, on the basis of the activity improvement and optical images of the suspension, we believe it reflects a reasonable approximation of the aggregation state.

Since intimate physical interaction between the H$_2$ and O$_2$ photocatalysts must occur to allow the charge transfer, the surface charges of Ru/SrTiO$_3$:Rh and PRGO/BiVO$_4$ were adjusted by pH to induce aggregation within the photocatalysts. Similar to the previous findings for bare BiVO$_4$ and Ru/SrTiO$_3$:Rh, PRGO/BiVO$_4$ and Ru/SrTiO$_3$:Rh photocatalysts were aggregated at pH 3.5 but remained dispersed at pH 7. Reflectance mode images obtained from the optical microscope indicated the location of PRGO/BiVO$_4$ and Ru/SrTiO$_3$:Rh. From the $\zeta$ potential (Figure S3), this aggregation was caused by the electrostatic interaction between the surface charges of Ru/SrTiO$_3$:Rh and PRGO/BiVO$_4$ at different pH (i.e., attractive at pH 3.5 but repulsive at pH 7). As a result of this close assembly of PRGO and the O$_2$ and H$_2$ photocatalysts, the water splitting activity was tripled at pH 3.5 (entries 5 and 8). However, distantly dispersed PRGO/BiVO$_4$ and Ru/SrTiO$_3$:Rh at pH 7 showed negligible variance between the systems with and without PRGO (entries 6 and 9). Scanning electron microscopy (SEM) was also employed to observe that PRGO/BiVO$_4$ and Ru/SrTiO$_3$:Rh do not exist as a composite on the PRGO. Figure S4d shows the SEM image of Ru/SrTiO$_3$:Rh and PRGO/BiVO$_4$ obtained from the pH 3.5 suspension. Both Ru/SrTiO$_3$:Rh and BiVO$_4$ particles were seen to be integrated with PRGO. Although this image may not represent the exact agglomeration of these particles in the reaction suspension, on the basis of the activity improvement and optical images of the suspension, we believe it reflects a reasonable approximation of the aggregation state.

Figure 4 shows a proposed mechanism for the activity of PRGO as a solid-state electron mediator in a Z-scheme photocatalytic water splitting system. The PRGO/BiVO$_4$ (O$_2$ photocatalyst) and Ru/SrTiO$_3$:Rh (H$_2$ photocatalyst) are attracted to each other by surface charge modulation under acidic conditions (pH 3.5), as depicted in Figure 4a. Upon excitation with visible light, electrons are photoexcited from the valence band (BiVO$_4$) or an impurity level formed by Rh (Ru/SrTiO$_3$:Rh) to the
conduction band. On the basis of the UV–vis spectrum of PRGO/BiVO₄ (Figure S1), the absence of an absorption edge for PRGO indicates that the PRGO in the current system does not have an energy gap. Moreover, the PRGO powder showed a sheet resistance of 6.14 kΩ/□, which is comparable with the value of 6.85 kΩ/□ for graphite (see the SI); a conductor usually does not have an energy gap. These indicate that the PRGO does not contribute to the generation of electrons and holes by absorption of visible light. In other words, the RGO in this work behaves as an electron conductor. PRGO transfers the electrons from the conduction band of BiVO₄ to the vacancies in the impurity levels of Ru/SrTiO₃:Rh. Simultaneously, the electrons in Ru/SrTiO₃:Rh reduce water to H₂ on the Ru cocatalyst, while the holes in BiVO₄ oxidize water to O₂, accomplishing a complete water splitting cycle. This electron flow direction is supported by our previous study on the BiVO₄–PRGO photoelectrode system: the PRGO provides pathways for electrons photogenerated in the BiVO₄ photocatalyst to reach the electrode substrate, which subsequently reduces water to H₂ on the counter electrode while the holes oxidize water to O₂ on the BiVO₄ surface. Unlike the photoelectrode system, where electron flow is driven by an external bias, it is electrodynamically possible to flow electrons through the PRGO in the opposite direction (from Ru/SrTiO₃:Rh to BiVO₄) in the current system. However, the driving force for this opposite electron flow is suppressed by two factors. The first involves electrons in the conduction band of Ru/SrTiO₃:Rh and holes in the valence band of BiVO₄. Each of these can migrate in two ways: reduction of water and transfer to PRGO for electrons and oxidation of water and transfer to PRGO for holes. Since the majority of the photocatalysts’ surfaces are surrounded by water (reactant) and only relatively small portions are in contact with PRGO, most of the electrons in Ru/SrTiO₃:Rh and holes in BiVO₄ are consumed for water splitting. The second factor involves electrons in the conduction band of BiVO₄ and holes in the electron-donor level of Ru/SrTiO₃:Rh. To undergo recombination, electrons in BiVO₄ must migrate to holes in Ru/SrTiO₃:Rh through PRGO because electrons in BiVO₄ and holes in Ru/SrTiO₃:Rh cannot reduce and oxidize water, respectively.

In conclusion, we have demonstrated that photoreduced graphene oxide prepared using BiVO₄ can be used as a solid-state electron mediator for a Z-scheme photocatalytic water splitting system. Unlike hydrazine-reduced GO and GO photocatalytically reduced by Ru/SrTiO₃:Rh, which exhibit significant hydrophobicity, GO photoreduced by BiVO₄ is miscible in water and provides a great improvement in the activity for water splitting by efficiently transferring photoexcited electrons from the O₂ photocatalyst to the H₂ photocatalyst. The key factor that enables efficient electron transfer in a Z-scheme system lies in achieving a balance between the degree of GO reduction (for conductivity restoration) and the level of hydrophobicity. The PRGO prepared by BiVO₄ demonstrated in this work possesses a high electron conductivity and a low degree of hydrophobicity. The present study has paved a new way of using the attractive graphitic carbon material graphene in the design of new and efficient systems for water splitting.

**ASSOCIATED CONTENT**

Supporting Information. Additional figures and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**


(26) Apparent quantum yield = 100% × ([no. of evolved H₂ molecules] × 4)/(no. of incident photons).

(27) Assuming that the PRGO contains partially oxidized carbon (greater molecular weight) would give a TON > 3.2 because the TON is determined by the number of moles of reactive electrons per mole of PRGO. Assuming that the PRGO contains pristine graphitic carbon ensures that our calculated TON of 3.2 is not overestimated.