Visible Light-Driven Pure Water Splitting by a Nature-Inspired Organic Semiconductor-Based System

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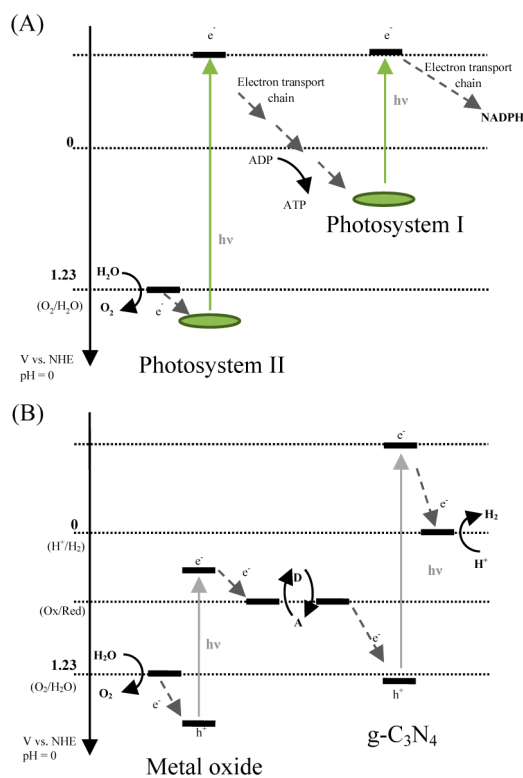
S *Supporting Information*

ABSTRACT: For the first time, it is demonstrated that the robust organic semiconductor g-C_3N_4 can be integrated into a nature-inspired water splitting system, analogous to PSII and PSI in natural photosynthesis. Two parallel systems have been developed for overall water splitting under visible light involving graphitic carbon nitride with two different metal oxides, $BiVO_4$ and WO_3. Consequently, both hydrogen and oxygen can be evolved in an ideal ratio of 2:1, and evolution rates in both systems have been found to be dependent on pH, redox mediator concentration, and mass ratio between the two photocatalysts, leading to a stable and reproducible H_2 and O_2 evolution rate at 36 and 18 μmol h^{-1} g^{-1} from water over 14 h. Our findings demonstrate g-C_3N_4 can serve as a multifunctional robust photocatalyst, which could also be used in other systems such as PEC cells or coupled solar cell systems.

Water splitting using a semiconductor photocatalyst and solar energy is seen to be one the most exciting and environmentally friendly ways of producing renewable fuels from abundant resources. Since the phenomenon's discovery, hundreds of diverse semiconductors have been developed and tested for half reactions of water splitting (either H_2 or O_2 production) in the presence of a sacrificial reagent.[1] More importantly, however, nonsacrificial overall water splitting is the eventual goal of the community. For industrial application, there exists an essential, nondebatable trifecta of being robust, cheap, and efficient. To date, no system has combined all three, with most examples missing at least one of the necessary trio, yet these advances represent important steps toward an eventual "perfect" photocatalytic water splitting system. Developing a photocatalyst that meets these requirements for overall water splitting thus remains a serious challenge within the field.

A single photocatalyst based on a single excitation process for overall water splitting has been explored for several decades but met with little success.[2] Nature splits water into O_2 and the H_2 equivalent species by a double excitation process, in which the two half reactions are spatially separated and take place in PSII and PSI (Scheme 1A).[3] This overcomes the main problems of a singular photocatalytic water splitting system both kinetically and thermodynamically as well described in previous reviews.[4] Inspired by natural photosynthesis, Bard proposed an analogous system composed of two inorganic semiconductor photocatalysts in 1979, and recently there have been some successes

Scheme 1. (A) Natural Photosynthesis and (B) an Artificial Analogy Used in This Study, Composed of an Organic Semiconductor C_3N_4 and a Robust Metal Oxide

in the field based on Rh-doped $SrTiO_3$ or TaON as hydrogen evolving photocatalysts.[5,6]

The ideal artificial double excitation process is illustrated in Scheme 1B. Briefly, each photocatalyst is responsible for one half-reaction, and a soluble redox mediator helps electron transfer between the two photocatalysts so that an ideal cycle can be completed. The mediator is very important because it dramatically inhibits the fast unfavorable recombination of charge, analogous to the electron transport chain between PSII and PSI. Given such advantages of a double excitation process, there are many researchers working on either two photocatalysts each of which favors either H_2 or O_2 production or a new mediator to efficiently transfer the charges between two

photocatalysts. WO_3 and $BiVO_4$ have been developed over the last two decades as cheap and robust photocatalysts for oxygen production from water, however, a counterpart for efficient and cheap hydrogen evolution remains a crucial challenge for a nature-inspired double excitation system. In this study, for the first time, we explore the feasibility of a robust organic semiconductor-based double excitation system for overall water splitting. Graphitic carbon nitride ($g-C_3N_4$) has recently attracted much attention due to its robust nature (stable in both alkaline and acidic conditions),[7] and we found it can be extremely efficient for H_2 evolution from water by manipulating the degree of polymerization and protonation.[8] Here, we demonstrate that when $g-C_3N_4$ is paired with WO_3 or $BiVO_4$, water can be split into H_2 and O_2 in an ideal ratio of 2:1 with excellent stability, opening up a window for a new, low cost, robust system for H_2 fuel synthesis from the abundant resource water.

In a typical run, efficient $g-C_3N_4$ was fabricated by thermal decomposition of urea using specific synthetic parameters.[8] $BiVO_4$ was synthesized as per the methodology used by Kudo et al.[9] WO_3 was purchased directly from Sigma-Aldrich. The Supporting Information (SI) contains all other parameters regarding synthesis, characterization, and photocatalytic reactions. Figure 1A shows the XRD data of synthesized $g-C_3N_4$,
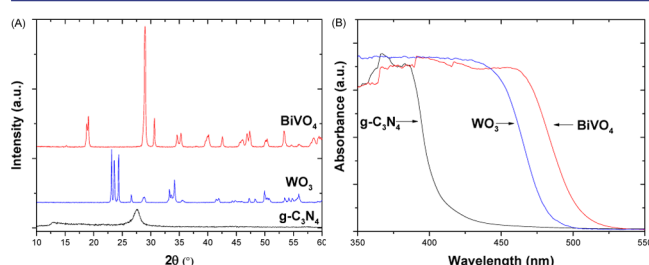

Figure 1. (A) Powder XRD pattern and (B) UV−vis absorbance spectra of $g-C_3N_4$, WO_3, and $BiVO_4$ compounds prior to water splitting reactions.

$BiVO_4$, and WO_3. Urea derived $g-C_3N_4$ exhibits the usual weak diffraction peaks at 13.0° ($d = 0.681$ nm) and 27.4° ($d = 0.326$ nm), corresponding to the approximate dimension of the heptazine unit and the distance between graphitic layers, respectively.[10] The phase and purity of the synthesized $BiVO_4$ were consistent with the parent literature; pure phase monoclinic point group, space group $I2/a$.[9] Commercial WO_3 phase identical to photocatalytically active compounds reported in the literature; pure phase monoclinic point group, space group $P21/n$.[11,12] Figure S1 shows the SEM and TEM micrographs of these semiconductors. WO_3 particles are large agglomerates (~10 μm), consisting of smaller particles about 0.5−1 μm

(Figure S1A,B). $BiVO_4$ particles range from 100 nm upward to 0.5 μm, in dendritic agglomerates (Figure S1C). Graphitic carbon nitride is sheet-like and has no fixed particle size (Figure S1D,E). UV−vis spectra in Figure 1B shows all materials have visible light absorption, increasing in the order: $g-C_3N_4$, WO_3, and $BiVO_4$; in agreement with the previous reports and signifying the different systems have the necessary band gaps for visible light water splitting.[13,14]

Initially, $Pt-g-C_3N_4$ was tested for water splitting in the absence of redox mediators as shown in Table 1 (run 1), to which there was no water splitting activity. Pt-loaded $g-C_3N_4$ (via photodeposition) is shown to be active for both oxidation of NaI (I^-, run 2) and $FeCl_2$ (Fe^{2+}, run 3), and also hydrogen is produced more readily. However, no oxygen evolution is observed. Then, $Pt-g-C_3N_4$ was tested for water splitting using only efficient redox mediators which can trap holes from $g-C_3N_4$. When coupled with an appropriate redox mediator and in combination with either Pt-loaded WO_3 or $BiVO_4$, pure water splitting is successfully observed.

Water splitting over $Pt-g-C_3N_4/BiVO_4$ in an aqueous $Fe^{2+/3+}$ solution was tested with different starting oxidation states of the redox precursors; $FeCl_2$ (run 4) and $FeCl_3$ (run 5). Starting with Fe^{2+} species, pure water splitting under full arc commences instantly and after an initial 1 h of equilibration continues steadily. However, if the starting species is Fe^{3+}, only O_2 evolution occurs, and water splitting does not occur instantaneously. After 15 h and repurging for 2 h, water splitting occurs due to sufficient Fe^{2+} existing in the system produced by the previous 15 h photoreduction process, indicating this side of the reaction proceeds much slower (reduction of Fe^{3+} by CB electrons by $BiVO_4$). We further measured the concentration of Fe species after 15 h photoreduction using UV−vis spectroscopy (Figure S2). The resultant concentration of Fe^{3+} was found to be 0.4 mM (±0.1 mM) and that of Fe^{2+} to be 1.6 mM (±0.1 mM). This confirms that reduction of the mediator by photogenerated electrons occurs in the present system. As shown in Figure S3, certain optimization procedures were performed, which involved altering pH, photocatalyst mass, and $FeCl_2$ concentration. Since $Fe^{2+/3+}$ systems have previously reported to be sensitive to pH, we varied the acidity of the system using H_2SO_4 and observed an optimum water splitting rate at pH 2.4−3.[13] Despite this, post water splitting XRD data (Figure S4) indicate that BiOCl is formed as a subphase during the reaction at pH 2.4, while at pH 3, $BiVO_4$ did not suffer any degradation. Therefore, further testing of the $g-C_3N_4$ (3 wt % Pt)−$BiVO_4$ system was conducted at pH 3, as shown in Figure 2, for a reasonable comparison. Under full arc, both H_2 and O_2 evolve. With first hour equilibration, gaseous products evolve linearly for the next 7 h with a ratio of ca. 2:1 (H_2 and O_2: 15 and 8 μmol h^{-1} g^{-1}). Under visible irradiation (a

Table 1. Overall Water Splitting under Full Arc Irradiation (300 W Xe lamp) Using Different Redox-Mediated Systems

run	H$_2$ photocatalyst	O$_2$ photocatalyst	weight ratio (g:g)	pH	redox mediator	initial gas evolution rate (μmol h^{-1} g^{-1})	
						H$_2$	O$_2$
1	g-C$_3$N$_4$ (3 wt % Pt)	—	—	7	—	0	—
2	g-C$_3$N$_4$ (3 wt % Pt)	—	—	8.3	NaI (5 mM)	5	—
3	g-C$_3$N$_4$ (3 wt % Pt)	—	—	3	FeCl$_2$ (2 mM)	4	—
4	g-C$_3$N$_4$ (3 wt % Pt)	BiVO$_4$	1:1	3	FeCl$_2$ (2 mM)	15	8
5	g-C$_3$N$_4$ (3 wt % Pt)	BiVO$_4$	1:1	3	FeCl$_3$ (2 mM)[a]	—	3
6	g-C$_3$N$_4$ (3 wt % Pt)	WO$_3$ (0.5 wt % Pt)	1:1	8.3	NaI (5 mM)	74	37

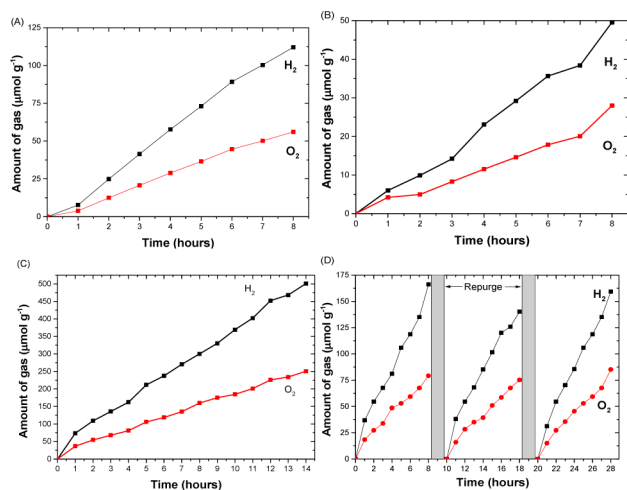[a]No water splitting observed until 15 h irradiation due to the generation of Fe^{2+}/Fe^{3+} couple.

Figure 2. Stoichiometric water splitting (300 W Xe lamp source): (A) g-C_3N_4 (3 wt % Pt)−$FeCl_2$−$BiVO_4$ under full arc irradiation, pH 3, 1:1 photocatalyst weight ratio, 2 mM $FeCl_2$. (B) g-C_3N_4 (3 wt % Pt)−$FeCl_2$−$BiVO_4$ under visible light irradiation (λ > 395 nm), pH 3, 1:1 photocatalyst weight ratio, 2 mM $FeCl_2$. (C) g-C_3N_4 (3 wt % Pt)−NaI−WO_3 (0.5 wt % Pt) under full arc irradiation, pH 8.3, 1:1 photocatalyst weight ratio, 5 mM NaI. (D) g-C_3N_4 (3 wt % Pt)−NaI−WO_3 (0.5 wt % Pt) under visible light irradiation (λ > 395 nm), pH 8.3, 1:1 photocatalyst weight ratio, 5 mM NaI.

cutoff filter of 395 nm was used), an average 6 and 3 μmol h^{-1} g^{-1} of H_2 and O_2 was observed.

Pt-loaded g-C_3N_4 was further tested for water splitting using NaI as a redox mediator. Pt-WO_3 was used as a relatively robust photocatalyst for the reduction of IO_3^- species produced as a result of I$^-$ oxidation by Pt-g-C_3N_4. In the Pt-WO_3 sample, platinum acts as an electron trap for photogenerated electrons in WO_3 so that they may easily migrate to the mediator. Again, the weight ratio of photocatalysts, pH, and mediator concentration was carefully tailored to increase gas evolution rates from water splitting (Figure S5). While Fe$^{2+/3+}$ redox systems are required to operate in acidic conditions, NaI/IO_3^- redox systems have been reported to be stable in a pH range of 7−10, with pH 9 being optimal;[14] iodide-based systems are very inefficient in acidic environments, as the ion I_3^- is produced, which is a poor electron scavenger, and cannot be reduced by electrons in Pt-WO_3. In line with similar reports, WO_3 is unstable in alkaline media; it is therefore not surprising that the Pt-g-C_3N_4 - Pt-WO_3 system is most efficient at pH 8.3 when using NaI/IO_3^- redox (Table 1, run 6).[15] In acidic conditions, production of the undesirable and ineffective I_3^- anion are known to be detrimental to I$^-$/IO_3^--based Z-scheme systems, as I_3^- does not act as an effective electron scavenger.[14] Furthermore, we also varied the weight ratio of the two photocatalysts and found that similar to the above g-C_3N_4−$BiVO_4$ system, this ratio influences the ratio of H_2 to O_2 even. The optimum weight ratio is 1:1. If the ratio is raised beyond this, water splitting rates decrease, presumably because of an imbalance in light absorption between respective photocatalysts.

For example, when using 0.3 g of Pt-g-C_3N_4, the hydrogen production rate is initially higher, yet eventually drops off; this is attributed to Pt-WO_3 not receiving the same flux of light as Pt-g-C_3N_4 (Figure S5C). At 1:1 weight ratio, stable water splitting rates are observed. Averaging over 14 h, 36 and 18 μmol h^{-1} g^{-1} of H_2 and O_2 are produced and linearly increase under full arc (Figure 2C). Under visible irradiation (λ > 395 nm), average

rates of 21.2 and 11.0 μmol h^{-1} g^{-1} of H_2 and O_2 are observed, and the activity is very stable as indicated by three cycles in Figure 2D. Figure S6 illustrates the unchanged crystal structure of the system post 24 h water splitting; demonstrating two organic semiconductor-based systems are extremely stable for pure water splitting.

By far the most efficient system in this study was g-C_3N_4−NaI−WO_3. Therefore, there is plenty of room for advancing this system even further, for example, optimizing WO_3 morphology to make particles smaller (currently the size is >5 μm, see Figure S1A,B for evidence of nonoptimal morphology). Alternatively, increasing the BET specific surface area (thus increasing active sites) of either $BiVO_4$ (3.94 m^{2}g^{-1}) or WO_3 (1.2 m^{2}g^{-1}) could increase the water splitting efficiency, as these values are small in comparison to the surface area of g-C_3N_4 (43.8 m^{2}g^{-1}). Theoretically, it might also be possible to use other varieties of g-C_3N_4 which have shown to be active for hydrogen production, for example triazine-based g-C_3N_4 (this study uses heptazine-based g-C_3N_4).[16] Furthermore, to increase the efficiency of our system, a viable strategy would seek to increase the absorbance of g-C_3N_4, providing the enhanced adsorption can provide a larger quantum yield in terms of hydrogen production. However, it is important to note that thiourea and dicyandiamide derived g-C_3N_4 was not active for overall water splitting, despite previous reports showing that it can photocatalytically produce hydrogen from water. As shown by Martin et al., urea-derived carbon nitride possesses a more polymeric structure, which inherently reduces the surface acidity (protonation, from ζ potential measurements) and consequently increases hydrogen production from water.[8] We therefore postulate that this reduction in surface protonation increases the adsorption of I$^-$ or Fe^{2+} ions onto the surface of g-C_3N_4, enabling the oxidation of either species and facilitating an overall water splitting reaction. Consequently iodide ions are not easily oxidized by WO_3 but are instead bound to the more positively charged surface of organic material C_3N_4, which is analogous to the reaction in dye-sensitized solar cells, whereby iodide ions are oxidized by photoholes in the photoexcited dye molecules. On the other hand as demonstrated by Abe et al., iodate ions selectively adsorb on rutile TiO_2 and WO_3, in comparison to anatase TiO_2 which poorly adsorbs iodate ions. In fact, both rutile TiO_2 and WO_3 have the ability to evolve molecular oxygen from water in an overall water spitting reaction, whereas iodate ions are reduced to iodide ions.[14] Abe et al. therefore definitively show that ion adsorption, either due to surface charge/acidity or because of some other factor, influences the selection of either photocatalyst for respective reduction or oxidation reactions.

One other way of overall water splitting using two different photocatalysts is to use a solid-state redox mediator or by direct contact between to appropriate photocatalysts, which have shown in some cases to be more efficient than Z-schemes with soluble redox mediators. Currently, overall water splitting has not been reported using these solid systems, however, extensive efforts have been made, as excellently described by Zhou et al.[17]

To summarize, we have demonstrated for the first time two nature-inspired organic semiconductor-based systems for pure water splitting under both UV and visible light irradiation. The most efficient system is composed of g-C_3N_4 and WO_3 using I$^-$/IO_3^- as a soluble mediator, yielding reproducible H_2 and O_2 evolution (21.2 and 11.0 μmol h^{-1} g^{-1}, respectively) from water under visible light for over 24 h. Furthermore, graphitic carbon nitride was synthesized using a completely facile method from an extremely cheap precursor, urea, which is a vital component for a

cost-efficiency argument for industrial scale up projects. Further optimization and greater understanding is thus required to enhance g-C_3N_4 systems, which is now underway. Yet, this work paves the way for more systems to be created based on urea-derived g-C_3N_4.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods, SEM micrographs, optimization procedures, and post-XRD graphs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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