

## Roles of Cocatalysts in Photocatalysis and Photoelectrocatalysis

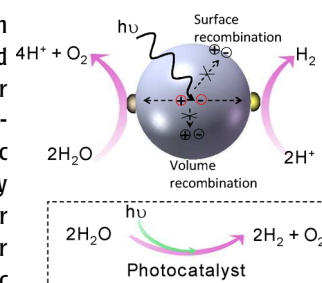
JINHUI YANG, DONGE WANG, HONGXIAN HAN, AND CAN LI\*  
*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics,  
Chinese Academy of Sciences and Dalian National Laboratory for Clean Energy,  
457 Zhongshan Road, Dalian 116023, China*

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### CONSPECTUS

Since the 1970s, splitting water using solar energy has been a focus of great attention as a possible means for converting solar energy to chemical energy in the form of clean and renewable hydrogen fuel. Approaches to solar water splitting include photocatalytic water splitting with homogeneous or heterogeneous photocatalysts, photoelectrochemical or photoelectrocatalytic (PEC) water splitting with a PEC cell, and electrolysis of water with photovoltaic cells coupled to electrocatalysts. Though many materials are capable of photocatalytically producing hydrogen and/or oxygen, the overall energy conversion efficiency is still low and far from practical application. This is mainly due to the fact that the three crucial steps for the water splitting reaction: solar light harvesting, charge separation and transportation, and the catalytic reduction and oxidation reactions, are not efficient enough or simultaneously. Water splitting is a thermodynamically uphill reaction, requiring transfer of multiple electrons, making it one of the most challenging reactions in chemistry.

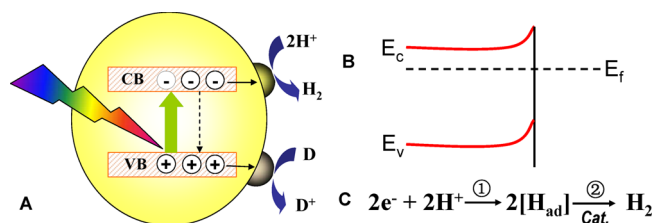
This Account describes the important roles of cocatalysts in photocatalytic and PEC water splitting reactions. For semiconductor-based photocatalytic and PEC systems, we show that loading proper cocatalysts, especially dual cocatalysts for reduction and oxidation, on semiconductors (as light harvesters) can significantly enhance the activities of photocatalytic and PEC water splitting reactions. Loading oxidation and/or reduction cocatalysts on semiconductors can facilitate oxidation and reduction reactions by providing the active sites/reaction sites while suppressing the charge recombination and reverse reactions. In a PEC water splitting system, the water oxidation and reduction reactions occur at opposite electrodes, so cocatalysts loaded on the electrode materials mainly act as active sites/reaction sites spatially separated as natural photosynthesis does. In both cases, the nature of the loaded cocatalysts and their interaction with the semiconductor through the interface/junction are important. The cocatalyst can provide trapping sites for the photogenerated charges and promote the charge separation, thus enhancing the quantum efficiency; the cocatalysts could improve the photostability of the catalysts by timely consuming of the photogenerated charges, particularly the holes; most importantly, the cocatalysts catalyze the reactions by lowering the activation energy. Our research shows that loading suitable dual cocatalysts on semiconductors can significantly increase the photocatalytic activities of hydrogen and oxygen evolution reactions, and even make the overall water splitting reaction possible. All of these findings suggest that dual cocatalysts are necessary for developing highly efficient photocatalysts for water splitting reactions.



### Introduction

Photocatalytic and photoelectrochemical or/and photoelectrocatalytic (PEC) water splitting to obtain solar fuels are attractive strategies to address the environmental crises and energy shortage issues.<sup>1–4</sup> Since the work by Fujishima and Honda<sup>5</sup> in 1972 using rutile TiO<sub>2</sub> anode coupled with a platinum dark cathode for PEC water splitting, extensive efforts have been made to construct efficient heterogeneous photocatalytic and PEC water-splitting systems. In these approaches, semiconductor-based photocatalysts/photoelectrodes are usually combined

with proper cocatalysts. Semiconductor-based photocatalytic system could be regarded as a microintegrated PEC cell without using external bias. The overall photocatalytic/PEC water splitting reaction involves three major steps: (i) absorption of light by semiconductor to generate electron–hole pairs, (ii) charge separation and migration to the surface of semiconductor, and (iii) surface reactions for water reduction or oxidation (Figure 1A). Photocatalytic reactions could be realized when the above three sequential steps are completed. Subject to these major processes, different methodologies have been applied for the improvement

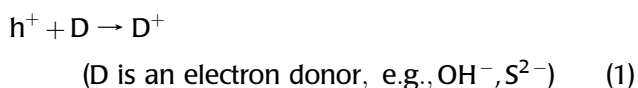


**FIGURE 1.** Schematic descriptions for photocatalytic H<sub>2</sub> production. (A) Overall courses over semiconductor loaded with dual cocatalysts. (B) Fermi level equilibration between semiconductor (n-type) and noble metal by formation of Schottky junction. (C) Two general steps for proton reduction reaction.

of photocatalytic steps. For example, development of narrow band gap semiconductor materials (band gap engineering) for absorbing broader spectrum of solar energy (step i), materials engineering to tune the physical properties (crystal structure, crystallinity and particle size, etc.) for gaining efficient charge separation and migration (step ii), and band level engineering to match the redox potentials of water reduction and oxidation (step iii). However, even if the photogenerated electrons and holes possess thermodynamically sufficient potentials for water splitting reaction, they may recombine if there are no suitable active/reaction sites available on the surface of the light harvesting semiconductor. Therefore, it is absolutely required to facilitate the reactions on the surface through catalytic processes.

The overall water splitting reaction is a thermodynamically uphill reaction ( $\Delta G^\ominus = 237 \text{ kJ/mol}$  equal to 1.23 eV) involving multiple electron transfer processes. In order to screen out the best photocatalyst for the assembly of efficient overall photocatalytic/PEC water splitting system, it is often necessary to investigate hydrogen evolution and oxygen evolution half reactions in the presence of sacrificial electron donors and acceptors, respectively. The study on half reactions is also a meaningful way to provide insight into the mechanism of water splitting.

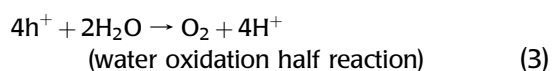
Oxidation half reaction:



Reduction half reaction:



Overall water splitting reaction:



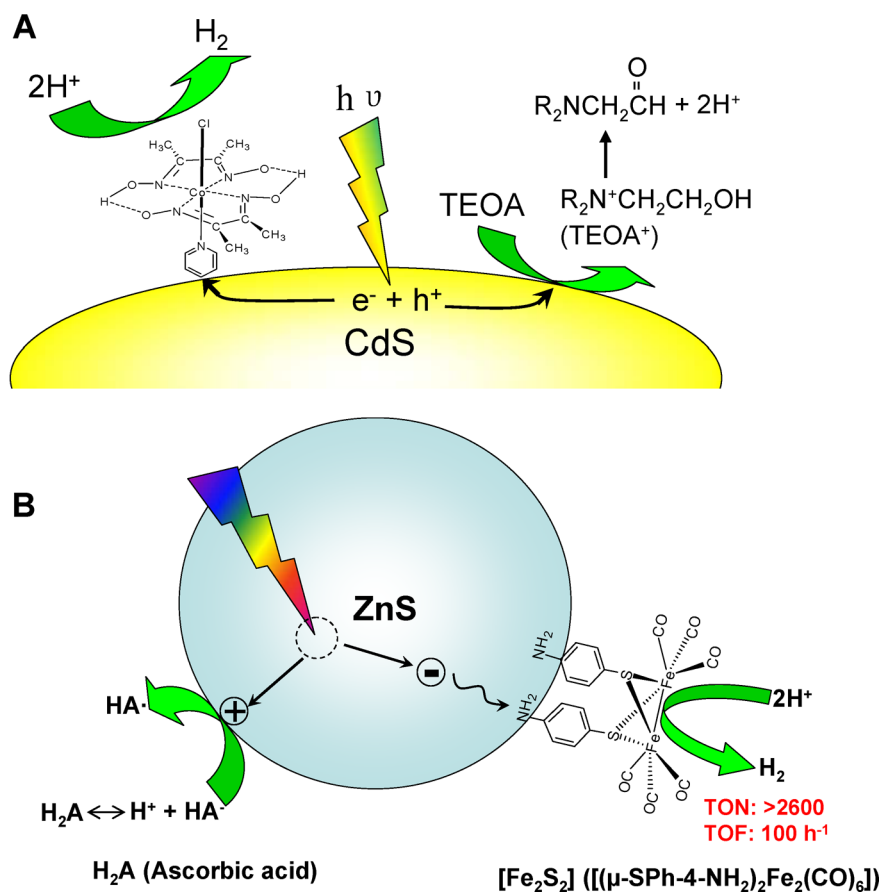
Proper cocatalysts loaded on the light harvesting semiconductor could promote or accelerate the photocatalytic courses. Cocatalyst can serve as the reaction sites and catalyze the reactions, promote the charge separation and transport driven by junctions/interfaces formed between the cocatalyst and the light harvesting semiconductor.

In the following sections, we will focus on the role of cocatalysts in the semiconductor-based photocatalysts and demonstrate (1) noble metal, metal sulfide, and biomimetic hydrogenase acting as efficient proton reduction cocatalysts, (2) synergetic effect of the dual cocatalysts loading for reduction and oxidation reaction, (3) the effect of oxidation cocatalysts (IrO<sub>x</sub>, CoO<sub>x</sub>, and Co<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) loading on the water oxidation reaction, and (4) improvement of the overall water splitting performance by co-loading reduction and oxidation cocatalysts, as well as the fundamental understanding of photocatalytic courses.

## Cocatalysts for Water Reduction Half Reaction

**Proton Reduction for H<sub>2</sub> Evolution on Noble Metal Cocatalysts.** Most semiconductors cannot give high H<sub>2</sub> evolution activities without a cocatalyst even in the presence of sacrificial electron donor. A reason might be due to the facile recombination of electron–hole pairs before migrating to the surface for reactions. Another major reason is that the surface reaction is too slow to efficiently consume the charges. Traditionally, in order to “take” the electrons out to the surface, metals, especially noble metals such as Pt, are used as the cocatalysts. Noble metals not only serve as electron sinks, but also provides effective proton reduction sites, hence dramatically facilitates proton reduction reaction.

As depicted in Figure 1A, photocatalytic H<sub>2</sub> production involves two basic surface reactions followed by band gap excitation of semiconductors and charge migration to the surface: proton reduction with e<sup>-</sup> and oxidation of electron donors with h<sup>+</sup>. The proton reduction course is obviously determined by the readiness of the cocatalyst trapping electrons from the light harvesting semiconductor, the catalytic activity for H<sup>+</sup> reduction and the combination of surface hydrogen atoms into molecular H<sub>2</sub> (catalytic ability). The trapping ability is largely determined by the work functions of the noble metals, which are greater than those



**FIGURE 2.** Photocatalytic systems (A) using a semiconductor (CdS) as the light absorbing semiconductor, a biomimetic hydrogenase (Co(III)(dmgH)<sub>2</sub>pyCl) as the H<sub>2</sub> evolution cocatalyst, and a triethanolamine (TEOA) as the sacrificial electron donor. Reprinted with permission from ref 11. Copyright 2011 Elsevier. (B) Using ZnS as the photoharvester, [Fe<sub>2</sub>S<sub>2</sub>] hydrogenase mimic ((μ-SPh-4-NH<sub>2</sub>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>) as the cocatalyst for H<sub>2</sub> evolution and an ascorbic acid as the sacrificial electron donor. Reprinted with permission from ref 12. Copyright 2012 Wiley.

of many semiconductors. Taking TiO<sub>2</sub> for an example,<sup>6</sup> a Schottky barrier can be formed at the metal/TiO<sub>2</sub> interface. Schottky barrier is a kind of junction which can facilitate charge separation (Figure 1B). Noble metals with larger work function, that is, lower Fermi level, should more readily trap electrons. Thus, Pt, among many noble metals, with the largest work function, is the best candidate cocatalyst for trapping electrons. Proton reduction course on cocatalysts goes through at least two steps: a discharge step and catalytic step (Figure 1C). Trasatti<sup>7</sup> found a volcano relationship between the exchange current for H<sub>2</sub> evolution and the M–H bond strength (M is a transitional metal). Pt was on the peak of the volcano, showing the lowest activation energy for H<sub>2</sub> evolution. Therefore, from the viewpoint of both electronic and catalytic properties, Pt is usually considered as the most suitable H<sub>2</sub> evolution cocatalyst. Considerably high quantum efficiencies have been reported when Pt was loaded as cocatalyst on CdS semiconductors.<sup>8,9</sup> In the presence of Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> as the sacrificial electron

donor, visible light (420 nm) quantum efficiency (QE) as high as 50% for H<sub>2</sub> evolution was obtained for a Pt/CdS photocatalyst with less than 1 wt % of Pt loading.<sup>10</sup> CdS loaded with other noble metals with lower work function and catalytic ability for proton reduction, showed relatively lower hydrogen evolution activity than Pt loaded CdS.

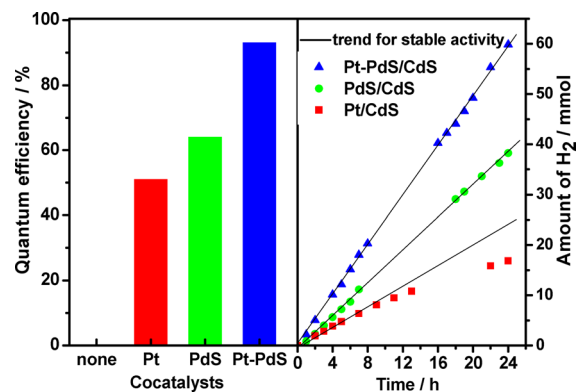
**Proton Reduction for H<sub>2</sub> Evolution on Molecular Cocatalysts.** In recent years, molecular photocatalytic systems based on biomimetic hydrogenase have been extensively studied for proton reduction to H<sub>2</sub>. It has been found that hydrogenase can also be used as the H<sub>2</sub> evolution cocatalyst to semiconductors. We employed cobaloximes (Co(III) complexes) as H<sub>2</sub> evolution cocatalyst on CdS photoharvester in the presence of triethanolamine (TEOA) as sacrificial electron donor (Figure 2A).<sup>11</sup> This photocatalytic system shows high hydrogen evolution activity (turnover number up to 171 based on Co(III)(dmgH)<sub>2</sub>pyCl) under visible light irradiation.) The apparent QE for the hybrid photocatalytic system in acetonitrile solution is calculated to be 9.1% at

420 nm. The interfacial electron transfer from photoexcited CdS to Co(III) complexes is found to be very efficient, which was confirmed by fluorescence spectra. The broad range of light absorption character of CdS semiconductor, the efficient electron transfer from CdS to the Co(III) complex, together with the excellent proton reduction ability of Co(III) complexes, account for the high photocatalytic H<sub>2</sub> evolution activity of this hybrid photocatalytic system. Unlike in molecular system, the molecular hydrogenase fabricated in the inorganic semiconductor system is fairly stable. This demonstrates the feasibility of coupling biomimetic H<sub>2</sub> evolution molecular hydrogenase catalyst with inorganic semiconductor for photocatalytic H<sub>2</sub> evolution.

Inspired by the above primary work, we further examined hydrogenase mimic [( $\mu$ -SPh-4-NH<sub>2</sub>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>6</sub>] (denoted as [Fe<sub>2</sub>S<sub>2</sub>]) as the cocatalyst for H<sub>2</sub> evolution using semiconductor (ZnS) as the photoharvester and ascorbic acid (H<sub>2</sub>A) as the electron donor (Figure 2B).<sup>12</sup> Remarkably, photocatalytic H<sub>2</sub> production with more than 2600 turnover numbers (based on [Fe<sub>2</sub>S<sub>2</sub>]) and an initial TOF of 100 h<sup>-1</sup> were achieved. Photoluminescence spectra showed that the addition of [Fe<sub>2</sub>S<sub>2</sub>] catalyst dramatically quenches both the band-edge emission and the surface trap-state emission of ZnS, while the fluorescence intensity becomes weaker when the amount of [Fe<sub>2</sub>S<sub>2</sub>] added was increased. This verifies that the increase in photocatalytic activity for the hybrid system is mainly due to efficient electron transfer from ZnS to [Fe<sub>2</sub>S<sub>2</sub>] complex, on which the protons are reduced to H<sub>2</sub>. The combination of CdS with [Fe<sub>2</sub>S<sub>2</sub>] complex does not show photocatalytic H<sub>2</sub> production activity, since the conduction band potential of CdS (-0.9 vs NHE, pH7) is not negative enough for the first redox potential of [Fe<sub>2</sub>S<sub>2</sub>] complex (-1.05 V vs NHE, pH7), demonstrating that the energy band matching is indispensable for the efficient charge transfer from the semiconductor to the molecular cocatalyst for H<sub>2</sub> evolution.

Further study shows that the photocatalytic activity of [Fe<sub>2</sub>S<sub>2</sub>]/ZnS hybrid system varies also with the electron donors, in the order of triethylamine (TEA) < triethanolamine < acetic acid < lactic acid < ascorbic acid, indicating that the H<sub>2</sub> production activity can also be dependent on the oxidation half reaction.

**Dual Cocatalysts for Reduction and Oxidation.** PdS was recently developed as an effective oxidation cocatalyst for the oxidation of sulfide and sulfite (Figure 3).<sup>10</sup> The loading of PdS on CdS can dramatically improve the photocatalytic H<sub>2</sub> production activity. The oxidation function of PdS was verified by photoelectrochemical measurement, which shows an obvious enhancement of anodic photocurrent.



**FIGURE 3.** Quantum efficiencies and time-courses for photocatalytic H<sub>2</sub> production over CdS loaded with Pt, PdS, and Pt-PdS dual-cocatalyst. Adapted with permission from ref 10. Copyright 2009 Elsevier.

Band potential analysis<sup>10</sup> also indicate that the hole transfer from CdS to PdS is favorable. XPS analyses show that the major part of Pd in PdS is in oxidized state, Pd(II), except for a small portion in metallic form, Pd<sup>0</sup>, during the reaction. Therefore, the simultaneous existence of PdS as an oxidation cocatalyst and Pd as a reduction cocatalyst is supposed to be beneficial for the efficient charge separation and surface reactions, which accounts for the higher QE of PdS/CdS (64%) than that of Pt/CdS (50%).

The overall reaction rate is relevant to both oxidation and reduction reactions, so dealing well with both oxidation and reduction half reaction is equally important, but the slower one will be the rate determining step for the overall reaction. While the oxidation half reaction is improved by loading PdS cocatalyst on CdS, the overall H<sub>2</sub> evolution activity can be further enhanced by loading reduction cocatalyst to improve the proton reduction activity. When a Pt is coloaded with PdS on CdS, the three component system, Pt-PdS/CdS, shows a further improvement of the photocatalytic H<sub>2</sub> evolution activity, achieving 93% QE for H<sub>2</sub> production at 420 nm.<sup>10</sup> This illustrated result shows the tremendous effect of coloaded oxidation and reduction cocatalysts on the exceptionally high QE.

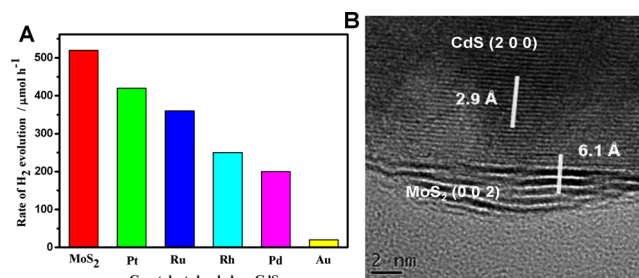
Better understanding such high QE reaction would give further hints for the design and assembly of more efficient photocatalytic systems. By *in situ* photoluminescence characterizations, we found that the fluorescence quenching efficiency of PdS/CdS is greater than that of Pt/CdS, implying that it is the oxidation reaction rather than the reduction reaction that acts as the rate-determining step for prohibiting the recombination of photogenerated charge carriers. Interestingly, over 94% of the fluorescence of CdS can be quenched by coloaded Pt and PdS cocatalysts on CdS, which is in good



agreement with the QE of 93% for H<sub>2</sub> production in Pt–PdS/CdS photocatalyst system.<sup>13</sup>

**Photostability of Photocatalyst Improved by Loading Oxidation Cocatalyst.** The main shortcoming of CdS (and also other sulfide, oxysulfide, oxynitride and nitride semiconductors) is its photoinstability, which is usually due to photocorrosion (e.g.,  $\text{CdS} + 2\text{h}^+ \rightarrow \text{Cd}^{2+} + \text{S}$ ). When PdS is loaded on CdS, the H<sub>2</sub> evolution activities display a very stable trend for over 25 h (Figure 3), and even longer than 100 h for a scale up test. Moreover, the bulk and surface features of PdS loaded CdS keep nearly unchanged after reaction for 25 h. In contrast, the activity of H<sub>2</sub> production on Pt/CdS gradually decreases after only several hours (Figure 3), as was usually seen.<sup>8</sup> Therefore, it is expected that loading of PdS oxidation cocatalyst protects CdS from photocorrosion (here mainly photooxidation), and makes the PdS/CdS and Pt–PdS/CdS very stable under the photocatalytic reaction conditions. This might be general for most photocatalysts, where the semiconductors tend to be oxidized by the photogenerated holes. Since the photogenerated holes can be efficiently removed from the semiconductor by the oxidation cocatalysts, the semiconductors are protected from photo-oxidation. More examples also support this conclusion. For example, the loading of RuO<sub>2</sub> on GaN:ZnO photocatalyst and CoO<sub>x</sub> on TaON photoanode was found to be an effective way for improving the stability in photocatalytic water splitting.<sup>14,15</sup>

**Interfacial Charge Transport between Semiconductor and Cocatalyst.** Morphology study by high resolution transmission electron microscopy (HRTEM) images shows that the PdS cocatalyst was highly dispersed and intimately covered on the CdS surface.<sup>13</sup> A high dispersion of cocatalyst on CdS semiconductor could result in efficient collection of photo-induced charges. Formation of atomically well-defined junctions between CdS and PdS was also observed, which might facilitate charge transfer between CdS and PdS. This reveals that tailor design and fabrication of the interface/junctions between the light harvesting semiconductor and cocatalyst should be very important for improving the activity. A study<sup>16</sup> on MoS<sub>2</sub>/CdS further confirmed this conclusion, where we found that MoS<sub>2</sub>/CdS with intimate junctions between CdS and MoS<sub>2</sub>, which acts as the cocatalyst, shows much higher photocatalytic H<sub>2</sub> evolution activity than Pt/CdS in the presence of lactic acid as the sacrificial electron donor (Figure 4),<sup>16</sup> even though Pt possesses superior performance than MoS<sub>2</sub> for the activation of H<sub>2</sub> in electrochemical systems.<sup>17</sup> Chemically deposited MoS<sub>2</sub>/CdS exhibits much higher activity than the mixture of CdS and MoS<sub>2</sub>,



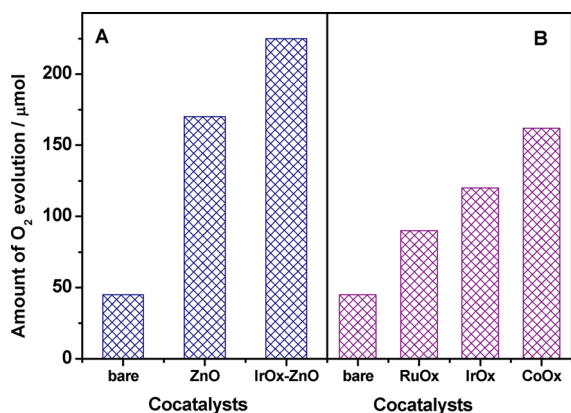
**FIGURE 4.** (A) Photocatalytic H<sub>2</sub> production activities over CdS loaded with MoS<sub>2</sub> and common noble metals. (B) HRTEM images of MoS<sub>2</sub>/CdS showing the intimate junctions formed between MoS<sub>2</sub> and CdS. Panels A and B adapted with permission from ref 16. Copyright 2008 American Chemical Society.

indicating that the intimate contact between CdS and MoS<sub>2</sub> is crucial for the charge transport from semiconductor (CdS) to the cocatalyst (MoS<sub>2</sub>). Because both components have the common S<sup>2-</sup> anions, the junctions between MoS<sub>2</sub> and CdS can be readily formed. Similar results were found for WS<sub>2</sub>/CdS, which also shows high H<sub>2</sub> production activity, where WS<sub>2</sub> acts as the cocatalyst.<sup>18</sup> Frame and Osterloh reported that MoS<sub>2</sub> is a more effective H<sub>2</sub> evolution cocatalyst on CdSe-nanoribbon semiconductor than Pt.<sup>19</sup> These results all highlight the importance of the interfacial charge transport between light harvesting semiconductor and cocatalysts for the improvement of photocatalytic activity.

## Cocatalysts for Water Oxidation in Photocatalysis and Photoelectrocatalysis

**Cocatalysts for O<sub>2</sub> Evolution from Water Oxidation.** As mentioned above, cocatalyst, especially the oxidation cocatalyst is crucial for photocatalytic systems. The functions of oxidation cocatalyst are applied to O<sub>2</sub> evolution from the photocatalytic water oxidation. Representative water oxidation inorganic cocatalysts include ruthenium oxide, cobalt oxide and iridium oxide, etc.

Figure 5A shows the photocatalytic activity of O<sub>2</sub> evolution on Zn<sub>2-x</sub>GeO<sub>4-x-3y</sub>N<sub>2y</sub> semiconductor (Denoted as ZGON) loaded with various cocatalysts. ZGON coupled with ZnO shows higher O<sub>2</sub> evolution activity due to the formation of solid solution phase junction.<sup>20</sup> The presence of IrO<sub>x</sub> as the cocatalyst can further enhance the activity (Figure 5A). Deposition of IrO<sub>x</sub>, CoO<sub>x</sub> and RuO<sub>x</sub> cocatalysts on ZGON can all enhance the activity for O<sub>2</sub> evolution as shown in Figure 5B, and CoO<sub>x</sub> was found to be the best one. In other systems, loading these cocatalysts are also effective for enhancing the O<sub>2</sub> evolution activity.<sup>21–23</sup> And very recently, metal-free boron oxynitride cluster was found to be an

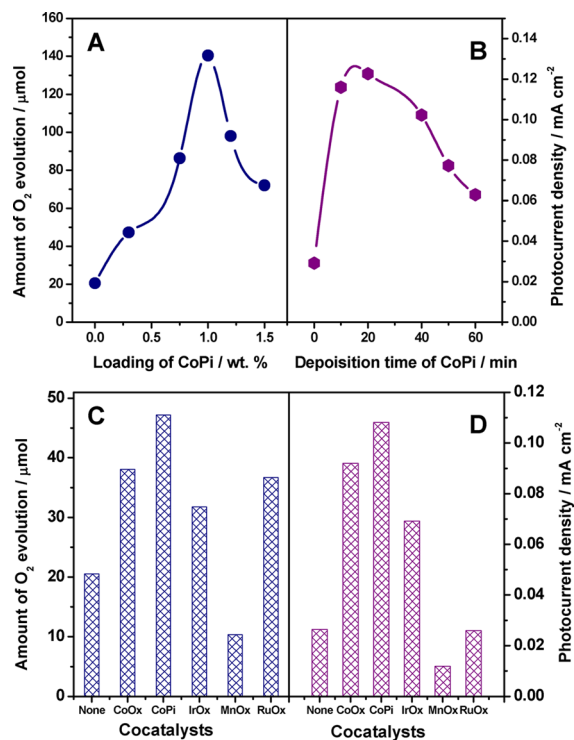


**FIGURE 5.** Photocatalytic activities of O<sub>2</sub> evolution on Zn<sub>2-x</sub>GeO<sub>4-x-3y</sub>N<sub>2y</sub> loaded with various cocatalysts: (A) coupling with ZnO and loading with IrO<sub>x</sub> and (B) deposition of IrO<sub>x</sub>, CoO<sub>x</sub>, and RuO<sub>x</sub> cocatalysts.<sup>20</sup>

oxidation cocatalyst to improve the photocatalytic oxygen evolution activity when it is loaded on WO<sub>3</sub>.<sup>24</sup> These results indicate that water oxidation cocatalyst is also indispensable, in order to achieve high water splitting efficiency.

BiVO<sub>4</sub>, an inexpensive and robust semiconductor, has been studied extensively. To understand the cocatalyst effect on photocatalytic water oxidation, modification of BiVO<sub>4</sub> with cobalt-phosphate ("CoPi") was investigated.<sup>25</sup> Figure 6A shows the photocatalytic activities of O<sub>2</sub> evolution on BiVO<sub>4</sub> loaded with different amount of CoPi cocatalyst. As the loading amounts of CoPi on BiVO<sub>4</sub> were increased, the photocatalytic activity of O<sub>2</sub> evolution on CoPi/BiVO<sub>4</sub> is greatly enhanced, reaching the maximum when the loading amount of CoPi is about 1.0 wt %. The activity of O<sub>2</sub> evolution is increased by up to 6.8 times in comparison with that of bare BiVO<sub>4</sub>. It indicates that the loaded CoPi acts as an efficient cocatalyst for photocatalytic O<sub>2</sub> evolution from water oxidation. Figure 6B shows the photocurrent density measured at a constant bias voltage of 0.3 V (vs SCE) for BiVO<sub>4</sub> electrode upon different loadings of CoPi. For the bare BiVO<sub>4</sub> electrode, the photocurrent density is quite low. The photocurrent density increases approximately linearly with the increase of the amount of CoPi deposited on BiVO<sub>4</sub>. Therefore, both photocatalytic O<sub>2</sub> evolution activity and photocurrent density are greatly enhanced when CoPi cocatalyst was loaded on BiVO<sub>4</sub>.

A similar trend was found for MO<sub>x</sub>/BiVO<sub>4</sub> upon loading a series of other cocatalysts (MO<sub>x</sub>: CoO<sub>x</sub>, IrO<sub>x</sub>, MnO<sub>x</sub>, RuO<sub>x</sub>) (Figure 6C, D). Among the cocatalysts loaded on BiVO<sub>4</sub>, the rate of O<sub>2</sub> evolution on CoO<sub>x</sub>/BiVO<sub>4</sub> is only slightly lower than that for CoPi/BiVO<sub>4</sub>, indicating that CoO<sub>x</sub> is also an excellent water oxidation cocatalyst (Figure 6C). And the IrO<sub>x</sub>



**FIGURE 6.** Photocatalytic activity of O<sub>2</sub> evolution (A, C) and photocurrent density (B, D) on BiVO<sub>4</sub> with different loadings of CoPi or with different cocatalysts. Panels A and B adapted with permission from ref 25. Copyright 2012 American Chemical Society.

and RuO<sub>x</sub> loaded BiVO<sub>4</sub> catalysts exhibit relatively lower oxygen evolution activity compared to CoO<sub>x</sub>/BiVO<sub>4</sub>. Figure 6D shows the photocurrent densities measured at a constant bias voltage of 0.5 V (Vs. SCE) for CoPi/BiVO<sub>4</sub> and MO<sub>x</sub>/BiVO<sub>4</sub> electrodes. The change of photocurrent density shows a similar trend with that of the photocatalytic activity of O<sub>2</sub> evolution.<sup>25</sup> In addition, all the cocatalysts result in a cathodic shift of onset potential, and CoPi shows the most remarkable effect.<sup>26</sup> When CoPi was loaded on other photoanodes, for example, W:BiVO<sub>4</sub>,<sup>26,27</sup> α-Fe<sub>2</sub>O<sub>3</sub>,<sup>28</sup> ZnO,<sup>29</sup> WO<sub>3</sub>,<sup>30</sup> and Si/Co,<sup>31</sup> the PEC water oxidation performances were also markedly improved, accompanied by large cathodic shifts of the onset potentials. Similar results were obtained after loading IrO<sub>2</sub> cocatalyst on TaON and SrNbO<sub>2</sub>N photoanode.<sup>32,33</sup> These results demonstrate that the oxidation cocatalysts play the key role in water oxidation for both photocatalytic and PEC water splitting.

**Activation Energy of Photocatalysis and Overpotential of PEC.** Photocatalyst particles could be considered as an integrated micro-PEC cell, in which the reduction reaction sites (e.g., H<sub>2</sub> evolution sites) are the cathodes, while oxidation reaction sites (e.g., O<sub>2</sub> evolution sites) are on the anode. Figure 7 schematically describes the role of cocatalysts

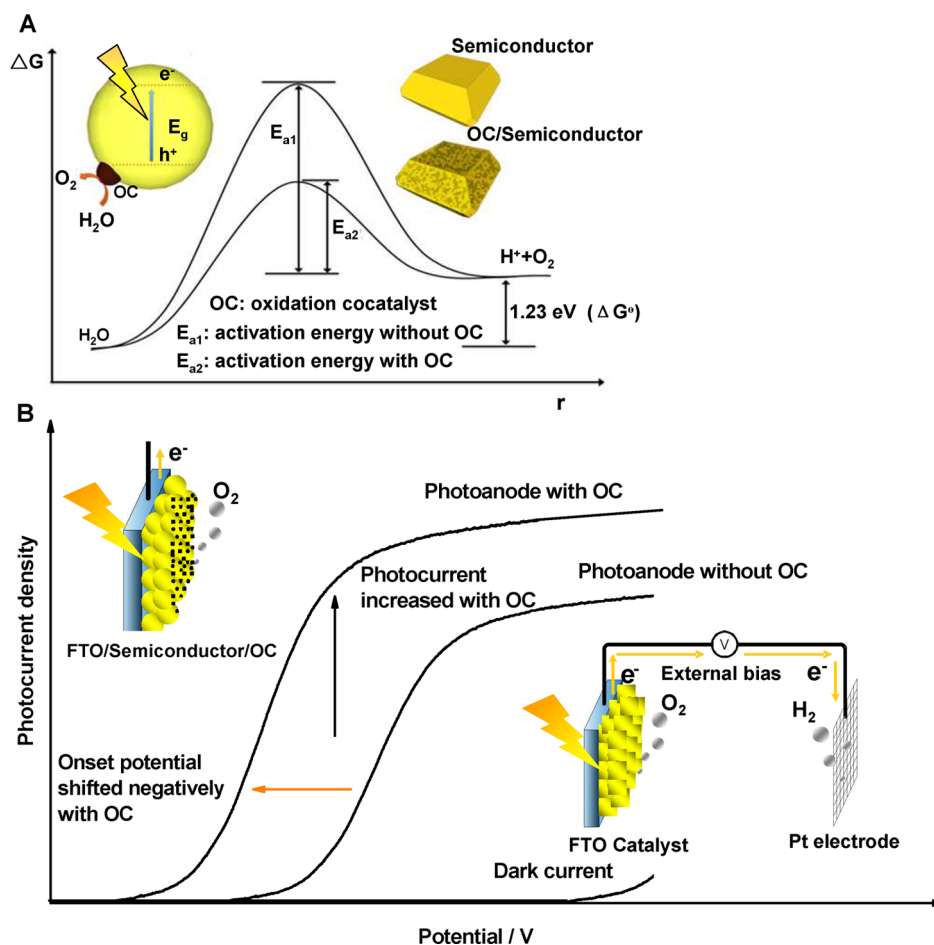


FIGURE 7. Schematic description of the role of oxidation cocatalyst in (A) photocatalytic water oxidation and (B) PEC water oxidation.

played in the photocatalytic and PEC water oxidation. By loading water oxidation electrocatalysts as the cocatalysts on the semiconductor, the photocatalytic performance can be significantly enhanced, indicating that loading of cocatalyst decreases the activation energy ( $E_a$ ) of water oxidation. In PEC water splitting, overpotentials are usually needed to realize the reaction. The presence of electrocatalysts on photoanode as cocatalysts can enhance the photocurrent density and also result in negative shift of onset potential. The negative shift of onset potential corresponds to lowering the overpotential. Therefore, we have the following relations for photocatalysis and photoelectrocatalysis for water oxidation,

$$\text{photocatalysis: } E \geq \Delta G^\ominus + E_a \quad (6)$$

$$\text{photoelectrocatalysis: } E \geq \Delta G^\ominus + E_{AOP} \quad (7)$$

where  $E$  is the minimum energy required for the water oxidation reaction to take place,  $\Delta G^\ominus$  is standard free

energy for the reaction, 237 kJ/mol for water splitting,  $E_a$  is the activation energy in photocatalysis, and  $E_{AOP}$  is the activation overpotential. In PEC water oxidation, the activation overpotential is essentially related to the activation energy in photocatalysis, namely,  $E_a \sim E_{AOP}$ .

For overall water splitting, the activation energy should include those of the two half reactions, water reduction and oxidation, while the water oxidation half reaction, which is a multistep, four-electron and four-proton process, is considered to be the greatest challenging step in the photocatalytic water splitting. The activation energy of the water oxidation dominates the activation energy of the overall water splitting reaction. In order to split water more efficiently, more efficient water oxidation cocatalysts are needed to be explored.

**The Cocatalysts Involved in the Multielectron Process for Photocatalytic Water Oxidation.** The water oxidation cocatalysts applied for photocatalytic water splitting, such as iridium oxide, ruthenium oxide, cobalt phosphate, cobalt oxide, and so forth, usually possess metals with variable

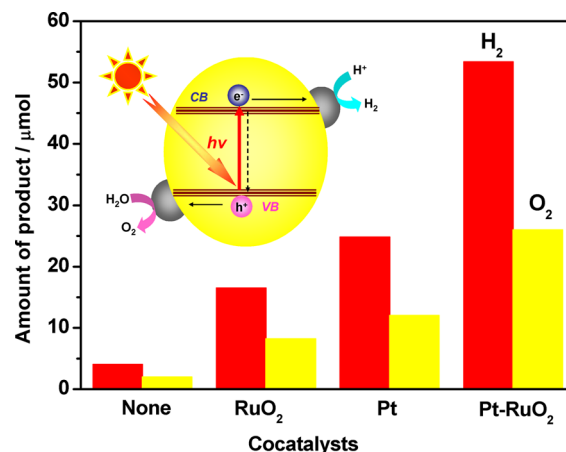
valence states. Taking cobalt oxide as an example, the valence state of Co recycles from +2 to +4 for collecting photogenerated holes and backs to +2 again after oxidizing water liberating O<sub>2</sub>.<sup>27,34</sup> Since evolution of one O<sub>2</sub> molecule requires four-electron-transfer, it is inevitable to go through the oxidized intermediates in water oxidation. A surface hydroperoxide intermediate has been detected upon water oxidation at an Ir oxide cluster by recording the O–O vibrational mode at 830 cm<sup>-1</sup> in rapid-scan FT-IR spectroscopic study, which is identified as an intermediate of water oxidation.<sup>35</sup> The O–O bond is formed by the reaction of an Ir<sup>V</sup> oxo intermediate with water or hydroxide group.

Kinetically, another key requirement for photocatalytic water oxidation is generation of holes with lifetime in the order of at least milliseconds. Transient absorption spectroscopic study reveals that the rate-determining steps for water oxidation are mainly associated with hole transfer from the light harvesting semiconductor to the cocatalyst and then to the surface-bound water species.<sup>36</sup> The loading of cobalt-based cocatalysts on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was found to increase the lifetime of photogenerated holes by more than 3 orders of magnitude. Cobalt oxide overlayers such as CoPi also can increase the lifetime of photogenerated holes in hematite photoanodes, demonstrating that deposition of CoPi on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> kinetically retards e<sup>-</sup>/h<sup>+</sup> recombination.<sup>28</sup>

### Dual Cocatalysts for Overall Water Splitting

Although some photocatalytic reactions could take place on semiconductors without the assistance of cocatalyst, the efficiency is usually quite low. In most cases, cocatalysts are required to achieve higher photocatalytic activity. We have already discussed that coloaded of both reduction and oxidation cocatalysts on the light harvesting semiconductor can improve the photocatalytic activity for H<sub>2</sub> production in the presence of sacrificial reagents. And such strategy can be further extended to the assembly of photocatalytic overall water splitting systems.

Zn<sub>2</sub>GeO<sub>4</sub> coloaded with noble metals (Pt, Pd, Rh, Au) and metal oxides (RuO<sub>2</sub>, IrO<sub>2</sub>) shows considerably synergistic effect on the photocatalytic activity for overall water splitting. We found that the photocatalytic activities of dual cocatalyst loaded Zn<sub>2</sub>GeO<sub>4</sub> samples are much higher than those loaded with only individual cocatalysts, and even higher than the sum of the two individual cocatalysts.<sup>37</sup> Figure 8 shows the photocatalytic activity for overall water splitting on Zn<sub>2</sub>GeO<sub>4</sub> coloaded with noble metals (Pt) and metal oxides (RuO<sub>2</sub>). The photocatalytic activity of Pt-RuO<sub>2</sub>/Zn<sub>2</sub>GeO<sub>4</sub> for overall water splitting is 2.2 times of Pt/



**FIGURE 8.** Photocatalytic activity of overall water splitting on ZnGeO<sub>4</sub> loaded with reduction cocatalyst Pt and/or oxidation cocatalyst RuO<sub>2</sub>. Adapted with permission from ref 37. Copyright 2010 Elsevier.

Zn<sub>2</sub>GeO<sub>4</sub> and 3.3 times of RuO<sub>2</sub>/Zn<sub>2</sub>GeO<sub>4</sub>. Studies on H<sub>2</sub> and O<sub>2</sub> evolution half reaction in the presence of the sacrificial reagents show that Pt acts as the H<sub>2</sub> evolution cocatalyst and RuO<sub>2</sub> acts as O<sub>2</sub> evolution cocatalyst, which can be considered as the state of the art proof of dual cocatalyst concept for improving photocatalytic water splitting activity. Upon coloaded of CoPi as oxidation cocatalyst and Pt as reduction cocatalyst on Bi<sub>0.5</sub>Y<sub>0.5</sub>VO<sub>4</sub>, the activities of H<sub>2</sub> and O<sub>2</sub> evolution activities can be enhanced to almost 3 times of that of Pt/Bi<sub>0.5</sub>Y<sub>0.5</sub>VO<sub>4</sub>.<sup>25</sup> Domen et al. also reported that the simultaneous loading of Rh/Cr<sub>2</sub>O<sub>3</sub> (core/shell) and Mn<sub>3</sub>O<sub>4</sub> nanoparticles as reduction and oxidation cocatalysts, respectively, on GaN:ZnO can enhance overall water splitting activity.<sup>38</sup> Recently, we also extended dual cocatalyst concept to Pt-RuO<sub>2</sub>/BiVO<sub>4</sub> photocatalyst for photocatalytic oxidation of thiophene using molecular O<sub>2</sub> as the electron acceptor, and 100% conversion efficiency of thiophene oxidation has been achieved.<sup>39</sup> Based on these experimental observations, we believe that dual cocatalyst approach is a general strategy for developing efficient photocatalytic systems.

### Concluding Remarks and Prospects

Suitable cocatalysts are indispensable for achieving high efficiency in photocatalytic and PEC water splitting. Cocatalysts can provide reduction or oxidation active sites, catalyze the surface reactions by lowering the activation energies, trap the charge carriers, and suppress the recombination of photogenerated electrons and holes. Noble metals, biomimetic hydrogenase, transition-metal oxides, and sulfides can serve as either reduction or oxidation cocatalysts for photocatalytic reactions. The photocatalytic performance



largely depends on the nature of the light harvesting semiconductor and the functions of cocatalysts. Generally speaking, a photocatalyst should be composed of components with three necessary functions, that is, light harvesting (i.e., semiconductor), reduction and oxidation reaction (dual cocatalysts). An efficient cocatalyst should be in harmony with the semiconductors in terms of energy levels and electronic structures; that is, the cocatalyst and light harvesting semiconductor should have compatible lattice and electronic structures with suitable Fermi-levels or band levels, so that the charge transport processes are in the right direction between semiconductor and cocatalysts driven by the built-in electric field at the interface. Compared to the H<sub>2</sub> production half reaction, the water oxidation half reaction is more challenging both thermodynamically and kinetically, and is considered as the rate-determining step of overall water splitting for most of the water splitting photocatalysts. Exploration of more efficient cocatalysts for water oxidation is absolutely necessary to achieve highly efficient overall water splitting. It is also demonstrated that the oxidation cocatalysts can effectively protect the light harvesting semiconductor (such as CdS) from photocorrosion, which is a fatal problem particularly for semiconductors with narrow band gap, for example, oxynitride and oxysulfide. Our experimental results, together with recent progress on photocatalytic water splitting made in other research groups, clearly demonstrate that dual cocatalysts are absolutely necessary to achieve high activity for photocatalytic overall water splitting.

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#### BIOGRAPHICAL INFORMATION

**Jinhui Yang** received her B.S. degree in Chemistry from Hunan Normal University, China (2005). She got her Ph.D. degree in Physical Chemistry at the Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences (CAS), under the supervision of Prof. Can Li (2012). Her research interests include semiconductor material based photocatalysis and photoelectrocatalysis.

**Donge Wang** received her B.S. degree in Chemical Engineering from Jilin University, China (2005). She obtained her Ph.D. degree in Physical Chemistry at DICP, under the supervision of Prof. Can Li (2012). Her work is focused on the effects of the morphology of photocatalyst and the oxidation cocatalyst on photocatalytic water oxidation.

**Hongxian Han** received his Ph.D. degree in chemistry from the University of New South Wales, Australia (2003). He was a post-doctoral research associate at the University of Nebraska—Lincoln (2003) and postdoctoral fellow/project research scientist at Lawrence Berkeley National Laboratory (2003–2009). He joined DICP, China in 2009, supported by “Hundred Talents Program” of the Chinese Academy of Sciences. And now he is a professor at DICP. His research interests are the development photocatalytic systems for water splitting, CO<sub>2</sub> reduction, and biomass reforming.

**Can Li** received his Ph.D. degree in 1989 from DICP and was promoted to full professor in 1993 in the same institute. His research interests include (1) UV Raman spectroscopy and ultrafast spectroscopy; (2) environmental catalysis and green catalysis; (3) heterogeneous asymmetric catalysis, and (4) solar energy utilization based on photocatalysis, photoelectrocatalysis, and photovoltaic cells. He is currently the director of the State Key Laboratory of Catalysis and the director of Dalian National Laboratory of Clean Energy, the chairman of the Catalysis Society of China, and the President of the International Association of Catalysis Societies (2008–2012).

#### FOOTNOTES

\*To whom correspondence should be addressed.  
The authors declare no competing financial interest.

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