

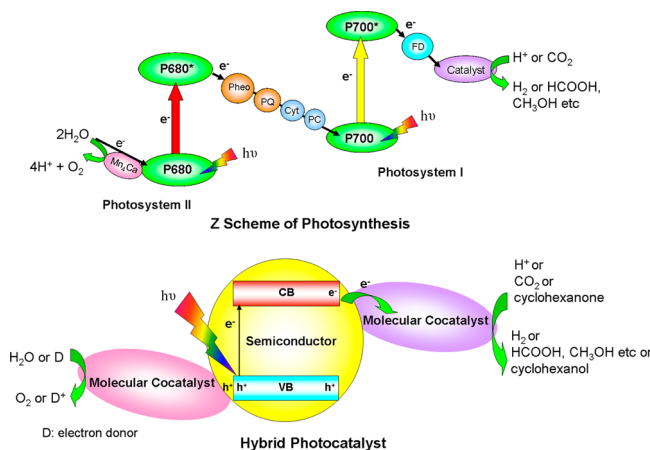
Hybrid Artificial Photosynthetic Systems Comprising Semiconductors as Light Harvesters and Biomimetic Complexes as Molecular Cocatalysts

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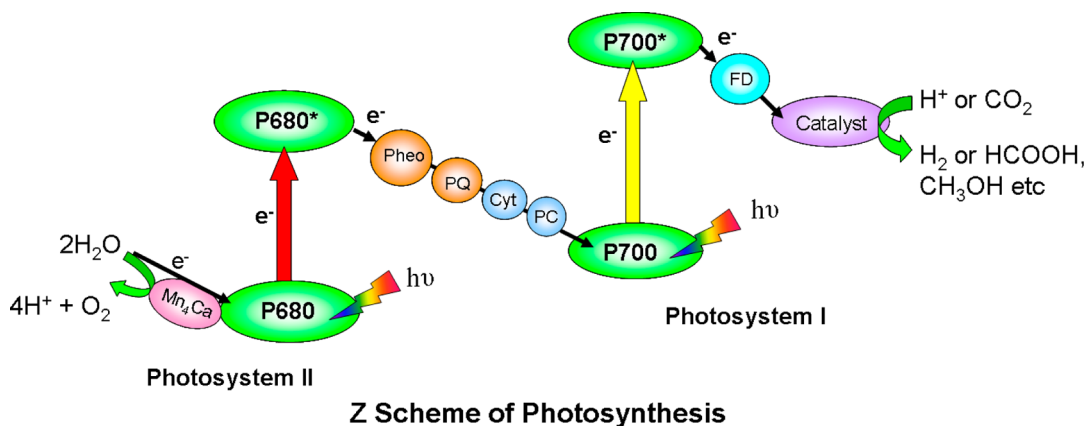
Solar fuel production through artificial photosynthesis may be a key to generating abundant and clean energy, thus addressing the high energy needs of the world's expanding population. As the crucial components of photosynthesis, the artificial photosynthetic system should be composed of a light harvester (e.g., semiconductor or molecular dye), a reduction cocatalyst (e.g., hydrogenase mimic, noble metal), and an oxidation cocatalyst (e.g., photosystem II mimic for oxygen evolution from water oxidation). Solar fuel production catalyzed by an artificial photosynthetic system starts from the absorption of sunlight by the light harvester, where charge separation takes place, followed by a charge transfer to the reduction and oxidation cocatalysts, where redox reaction processes occur. One of the most challenging problems is to develop an artificial photosynthetic solar fuel production system that is both highly efficient and stable. The assembly of cocatalysts on the semiconductor (light harvester) not only can facilitate the charge separation, but also can lower the activation energy or overpotential for the reactions. An efficient light harvester loaded with suitable reduction and oxidation cocatalysts is the key for high efficiency of artificial photosynthetic systems.

In this Account, we describe our strategy of hybrid photocatalysts using semiconductors as light harvesters with biomimetic complexes as molecular cocatalysts to construct efficient and stable artificial photosynthetic systems. We chose semiconductor nanoparticles as light harvesters because of their broad spectral absorption and relatively robust properties compared with a natural photosynthesis system. Using biomimetic complexes as cocatalysts can significantly facilitate charge separation via fast charge transfer from the semiconductor to the molecular cocatalysts and also catalyze the chemical reactions of solar fuel production. The hybrid photocatalysts supply us with a platform to study the photocatalytic mechanisms of H₂/O₂ evolution and CO₂ reduction at the molecular level and to bridge natural and artificial photosynthesis. We demonstrate the feasibility of the hybrid photocatalyst, biomimetic molecular cocatalysts, and semiconductor light harvester for artificial photosynthesis and therefore provide a promising approach for rational design and construction of highly efficient and stable artificial photosynthetic systems.

Introduction

Artificial photosynthetic solar fuel production, which converts solar energy into storable chemical energy has

attracted much attention.^{1–3} The artificial photosynthetic system can be a simplified model wherein the key structural elements and key functions of natural photosynthesis are



Z Scheme of Photosynthesis

FIGURE 1. Z-Scheme of natural photosynthesis.

mimicked. The key elements and processes of natural photosynthesis can be divided into three steps (Figure 1): (1) initial light-harvesting processes and charge separations in photosystem II (PS II) and photosystem I (PS I); (2) spatial charge separation through electron transfer between redox cofactors, and (3) fuel and oxygen formation at active sites. High efficiency in all three of these processes is the key for constructing efficient artificial photosynthetic systems.

To achieve high efficiency in light harvesting, light harvesters in artificial photosynthetic systems must absorb the majority of sunlight. Both molecular dyes and semiconductors can be used as light harvesters; however, semiconductors seem to be more promising for their broad spectral absorption and relatively higher stability. It is well-known that the probability of light absorption is related to the characteristics of the states involved. Only the light with an energy that matches a possible electronic transition of the molecule could be absorbed to excite the molecule to a highly excited state (e.g., $Ru(bpy)_3^{2+}$, as shown in Figure 2). In natural photosynthesis, the light harvesters are chlorophyll molecules along with some accessory pigments such as xanthophylls and carotenoids (Figure 2). As in the case of $Ru(bpy)_3^{2+}$, the spectral absorption of these molecular pigments is discontinuous and is mainly centered in the blue and red spectral regions. In the case of a semiconductor, the absorption band is broad and continuous (Figure 2). Using semiconductors as light harvesters could overcome the drawbacks of narrow spectral absorption and poor stability of molecular dyes.⁴

To achieve high efficiency in spatial charge separation, loading and assembling of cocatalyst is necessary. Cocatalysts are the active sites where reduction and oxidation reactions take place. The loading of cocatalyst not only can facilitate the charge separation but also can lower the

activation energy or overpotential for the reactions. Basically, cocatalysts can be divided into two categories by the role they play, namely, reduction cocatalyst and oxidation cocatalyst. By spatial separation of the reduction active center and the oxidation active center, nearly 100% of initial quantum efficiency for photosynthesis was achieved.⁵ Taking advantage of natural photosynthesis, the coloaded and spatial separation of reduction and oxidation cocatalysts are necessary for artificial photosynthetic systems to achieve high efficiency in charge separation. A proper light harvester coloaded with suitable reduction and oxidation cocatalysts is the key for constructing highly efficient artificial photosynthetic systems.^{6–10}

Highly active cocatalysts are essentially also excellent electrocatalysts for redox reactions. For H_2 evolution, the volcano plot of the exchange current density as a function of the free energy of adsorbed H on catalysts is an important reference for judging good electrocatalysts.¹¹ Electrocatalysts on the top region of the volcano plot such as Pt, Pd, Rh, Ir, and MoS_2 usually show high electrocatalytic H_2 evolution activities. When loaded on semiconductor light harvesters, they are also excellent cocatalysts for photocatalytic H_2 evolution.^{12–14} The free energy of adsorbed H on hydrogenases is calculated to be close to that for Pt,¹⁵ showing the potential of hydrogenase as an excellent cocatalyst for H_2 evolution. When hydrogenases,^{16,17} which consist of abundant elements such as Fe or Ni, were loaded on semiconductors, photocatalytic H_2 evolution could be successfully achieved.^{18–22} The hybrid systems comprising CO_2 fixation enzymes²³ and semiconductors show high photocatalytic CO_2 reduction activity and excellent selectivity.^{24–26} However, the high O_2 sensitivity and the high cost for separation and cultivation of the enzymes limit its large scale application. Relatively speaking, biomimetic molecular complexes

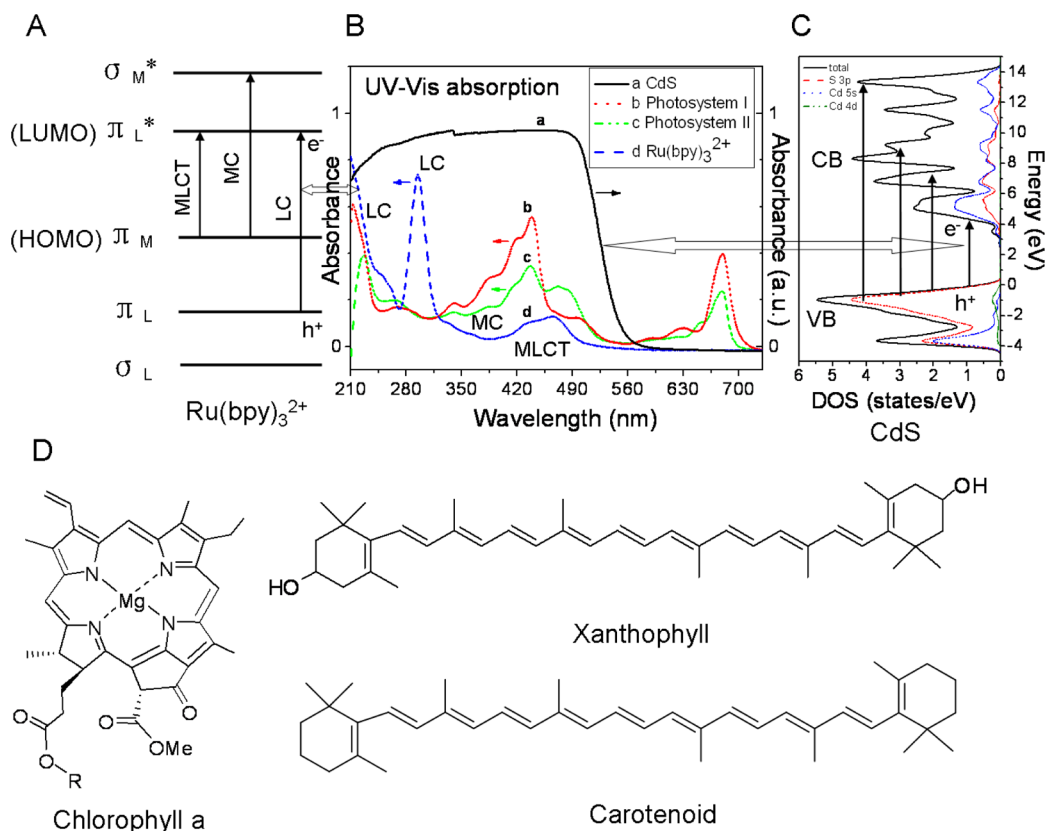


FIGURE 2. (A) Molecular orbital diagrams of Ru(bpy)₃²⁺ photosensitizer, (B) UV-vis absorption spectra of Ru(bpy)₃²⁺ (0.01 mM), photosystem II in spinach, photosystem I in spinach, and semiconductor CdS, (C) density of states (DOS) of CdS, and (D) molecular structures of chlorophyll a, xanthophyll, and carotenoid.

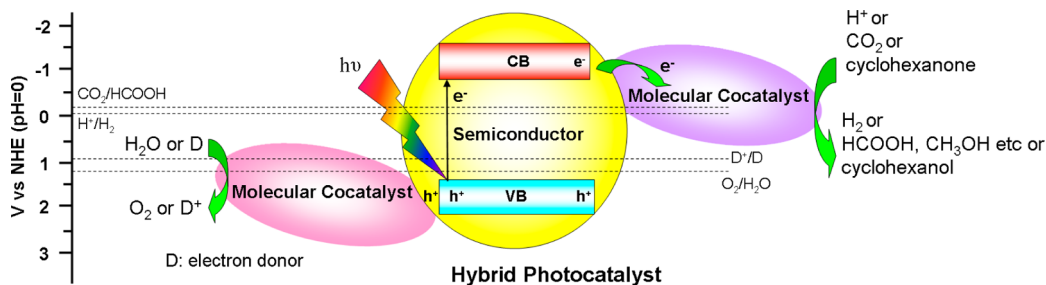


FIGURE 3. Solar fuel production and light-driven transfer hydrogenation in hybrid artificial photosynthetic system.

that possess the same function as natural enzymes seem to be more promising, because they are more tolerant to O₂ and the structures are tunable. Using a biomimetic complex as cocatalyst not only can facilitate charge separation but also, more importantly, can provide us the mechanism details of H₂ evolution and CO₂ reduction at molecular level.

High electrocatalytic activity is a necessary criterion for an excellent cocatalyst, but it is not sufficient. To let the cocatalyst work well, the electron transfer from light harvester to cocatalyst must be efficient. A good cocatalyst should match with the light harvester in many aspects, such as driving force for charge transfer (ΔG_{ET}), contact manner (interface

interaction), energy barrier for charge transfer, etc. The solar fuel production by molecular cocatalyst/semiconductor hybrid photocatalyst is regarded as a simplified model of natural photosynthesis, as shown in Figure 3. The electron transfer from photoexcited semiconductors to complexes is the reverse process to that in n-type semiconductor based dye-sensitized solar cells (in DSSCs, the electron transfer is from the excited state of dye molecules to the conduction band of semiconductors²⁷). It is predicted that the electron transfer from photoexcited semiconductors to complexes can be accomplished on the same time scale as, or even faster than, that in DSSCs.^{28–30} The fast electron transfer

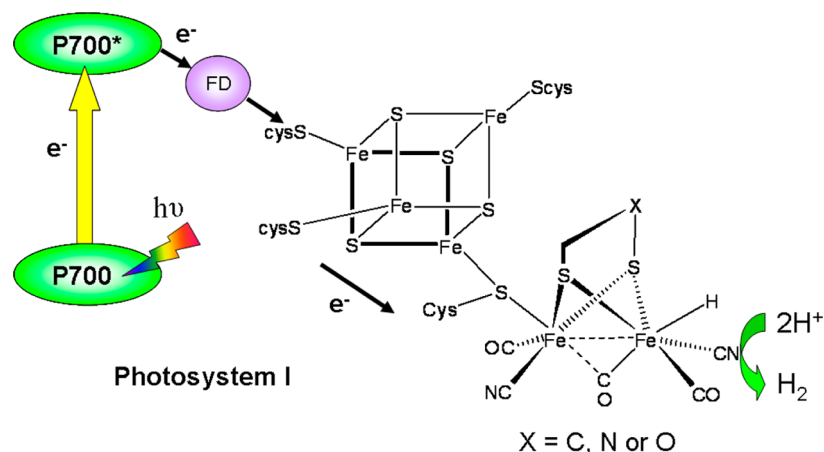


FIGURE 4. Structure of the active site in FeFe hydrogenase and the mechanism of biocatalytic H₂ evolution.

could effectively reduce the recombination of the photo-generated electrons and holes, which is essential for the high efficiency of solar fuel conversion.

The advantages of the complex/semiconductor hybrid photocatalyst could be summarized as follows: (1) as light harvester, a semiconductor is relatively stable, and the spectral absorption range is broad; (2) using a noble-metal free biomimetic complex as cocatalyst not only can facilitate charge separation but also can help us to understand the mechanisms of H₂ evolution and CO₂ reduction at the molecular level; (3) the rate of photoexcited electron transfer from the semiconductor to the complex is fast. In this Account, we will present recent progress in the hybrid photocatalyst of complex/semiconductor for solar fuel production, with more examples reported in this group. We have assembled three complex/semiconductor hybrid photocatalysts for photocatalytic H₂ evolution and transfer hydrogenation.^{31–33} All the hybrid photocatalysts show high activity, demonstrating the promising perspective of the strategy of using a semiconductor as light harvester and a biomimetic complex as molecular cocatalyst.

Requirements for Semiconductor Light Harvester

As in the case of natural photosynthesis, light capture by the light harvester is the primary step for an artificial photosynthetic system. A semiconductor light harvester with broad spectral absorption range and high stability is essential to achieve high efficiency for solar fuel conversion. Moreover, the semiconductor light harvester should possess suitable energy levels of conduction band and valence band. The bottom level of the conduction band has to be more negative than the redox potential of H⁺/H₂ or CO₂/HCOOH

(0 V and –0.19 V vs NHE at pH = 0, respectively), while the top level of the valence band must be more positive than the redox potential of O₂/H₂O (1.23 V vs NHE at pH = 0). For better loading of the molecular cocatalysts, particular surface anchoring groups on the semiconductors are usually necessary.

Hybrid Photocatalysts for H₂ Evolution

In nature, photocatalytic hydrogen evolution can efficiently perform through the combination of pigment molecules with hydrogenases in PS I.³⁴ The active sites of hydrogenases can be classified into four categories, namely, NiFeSe, NiFe, FeFe, and Fe hydrogenases. The FeFe hydrogenase is the most active catalyst for H₂ evolution, with a fascinating turnover frequency (TOF) up to 6000–9000 s^{–1}.^{16,17} Since the structure of FeFe hydrogenase was resolved in 1998 (as shown in Figure 4),^{35,36} many [Fe₂S₂] hydrogenase mimics have been synthesized.^{37–41} Some of the [Fe₂S₂] hydrogenase mimics show electrocatalytic H₂ evolution activity,^{42–44} demonstrating the possibility of using hydrogenase mimics as cocatalysts for photocatalytic H₂ evolution. Besides [Fe₂S₂] hydrogenase mimics, cobaloxime is another family of widely studied molecular electrocatalyst for H₂ evolution.^{45,46} For its high activity and relatively low working potential, this type of complex has been recognized as a functional hydrogenase mimic.^{47,48} To achieve light-driven H₂ evolution, hydrogenase mimics were combined with light harvesters. So far, most hydrogenase mimics based photocatalytic systems are homogeneous systems, in which molecular dyes are employed as photosensitizers.^{46,49,50} Due to the instability of the molecular dyes, most of the reported homogeneous systems suffered from limited lifetime.

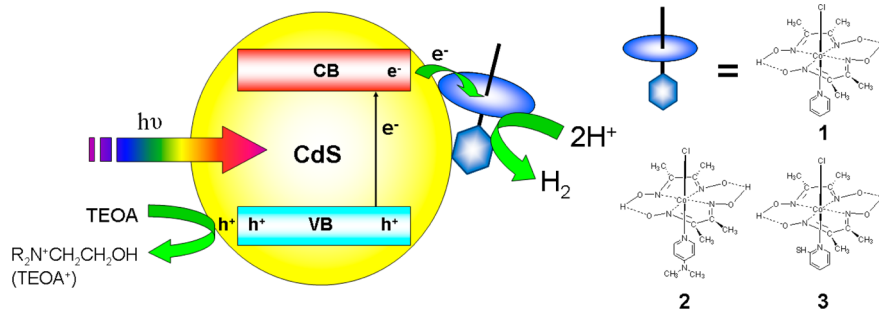


FIGURE 5. Photocatalytic H₂ evolution over Co complexes/CdS hybrid photocatalysts in the presence of TEOA as electron donor. Adapted with permission from ref 31. Copyright 2011 Elsevier.

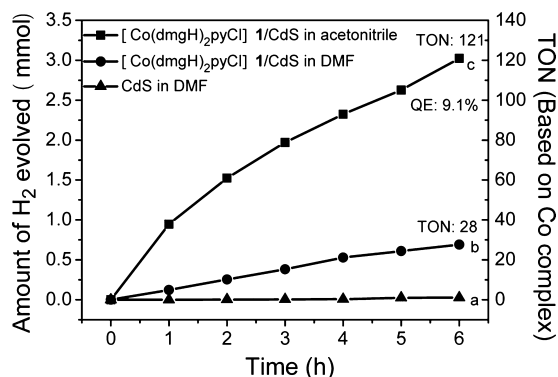


FIGURE 6. Time courses of photocatalytic H₂ evolution over CdS and **1**/CdS hybrid system in DMF solvent (lines a and b) and in acetonitrile solvent (line c) under visible light irradiation ($\lambda > 420$ nm). CdS (0.05 g); **1** (0.25 mM); 10 vol % TEOA (total solution volume 100 mL, 0.75 M); 10 vol % H₂O (total solution volume 100 mL); 80 vol % DMF or acetonitrile (total solution volume 100 mL); light source, Xe lamp (300 W). Adapted with permission from ref 31. Copyright 2011 Elsevier.

In order to improve light-harvesting efficiency and stability, we employed a semiconductor as light harvester to combine with cobaloximes for photocatalytic H₂ evolution.³¹ CdS was selected as light harvester for its broad spectral absorption range and suitable conduction band potential (-0.9 V vs NHE). Three cobaloximes with different axial pyridine ligands were combined with CdS via adsorption (Figure 5). An initial TOF of 38 h^{-1} and a H₂ evolution rate of $945.6\ \mu\text{mol h}^{-1}$ were achieved for Co(dmgh)₂pyCl (**1**)/CdS hybrid photocatalyst in acetonitrile solution containing triethanolamine (TEOA) as electron donor, corresponding to a quantum efficiency (QE) of 9.1% at 420 nm. The photocatalytic H₂ evolution rate of **1**/CdS is even higher than that of Pt/CdS catalyst (Pt has been considered to be one of the most active cocatalysts for H₂ evolution). Moreover, the hybrid photocatalyst shows relatively high stability as evidenced by the TON higher than 121 (based on Co complex **1**) under irradiation for 6 h (Figure 6). The fast electron transfer from semiconductor to cobaloxime may be the main reason for the

high activity of the hybrid system. The fast photodriven electron transfer from semiconductor to cobaloxime was confirmed by Huang et al. very recently.⁵¹ Results show that the photoexcited electron transfer from CdSe/ZnS core/shell quantum dot (QD) to cobaloxime takes place with an average time of 105 ps, which is much faster than that for the charge recombination.

Using [Fe₂S₂] hydrogenase mimics as cocatalysts of H₂ evolution to incorporate with semiconductor light harvesters is highly desirable, since the structures of [Fe₂S₂] biomimetic complexes are more similar to natural hydrogenase. The investigation on this type of hybrid photocatalyst can give us more relevant information on the natural H₂ evolution process. Recently, some hybrid photoelectrocatalytic H₂ evolution systems containing semiconductors and [Fe₂S₂] hydrogenase mimics have been assembled.^{52,53} However, a hybrid photocatalytic system with high efficiency has been rarely reported.

Very recently, we constructed an efficient hybrid photocatalyst by using semiconductor ZnS as light harvester and [Fe₂S₂] hydrogenase mimic [(μ -SPh-4-NH₂)₂Fe₂(CO)₆] (**4**) as H₂ evolution catalyst (Figure 7).³² Considering the relatively negative reduction potential of the [Fe₂S₂] catalyst (the first reduction potential of Fe^IFe^I to Fe⁰Fe^I is -1.07 V vs NHE), ZnS with a conduction band potential of -1.85 V vs NHE⁵⁴ was chosen as a light harvester. When [Fe₂S₂] **4** catalyst was assembled onto ZnS via adsorption, photocatalytic H₂ evolution was efficiently achieved with an initial TOF of 100 h^{-1} (Figure 8). Moreover, this hybrid photocatalyst exhibits high stability as demonstrated by the TON of more than 2600 (based on [Fe₂S₂] **4**) after the photocatalytic reaction for 38 h (actually the photocatalyst is still active even after achieving the TON of 2600). The photocatalytic H₂ evolution rate of [Fe₂S₂] **4**/ZnS is even higher than that of Pt/ZnS catalyst. Photoluminescence (PL) spectra demonstrate that the photoexcited electron transfer from ZnS to the [Fe₂S₂] hydrogenase mimic **4** is very efficient.

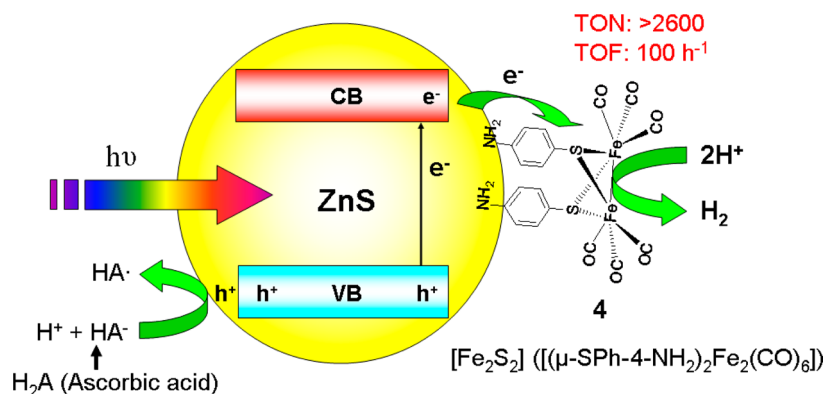


FIGURE 7. Photocatalytic H₂ evolution over [Fe₂S₂] **4**/ZnS hybrid photocatalyst in the presence of ascorbic acid as electron donor. Adapted with permission from ref 32. Copyright 2012 Wiley.

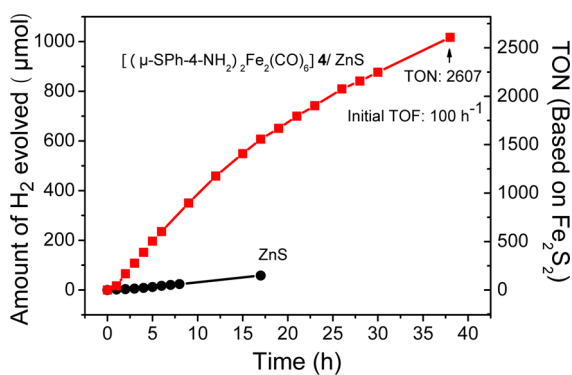


FIGURE 8. Time courses of photocatalytic H₂ evolution over ZnS and [Fe₂S₂] **4**/ZnS hybrid photocatalyst in DMF solution. ZnS (0.2 g); [Fe₂S₂] **4** (3.9×10^{-3} mM); ascorbic acid (8.52×10^{-2} M); 10 vol % H₂O; 90 vol % DMF (total solution volume 100 mL); light source, Xe lamp (300 W). Adapted with permission from ref 32. Copyright 2012 Wiley.

When CdTe quantum dot light harvesters were incorporated with an aqueous soluble [Fe₂S₂] hydrogenase mimic, the efficient electron transfer from photoexcited semiconductor CdTe to the [Fe₂S₂] catalyst was observed too.⁵⁵ The high photocatalytic activity for the hybrid system is mainly due to the efficient electron transfer from semiconductor to [Fe₂S₂] catalyst on which protons are reduced to H₂.

Besides the cobaloximes and [Fe₂S₂] hydrogenase mimics, some nickel-based molecular cocatalysts were also integrated with semiconductors in recent years.^{56,57} One of the remarkable results is the achievement of a TON of more than 600 000 (based on nickel catalyst) in 110 h and an initial TOF of 7000 h⁻¹ photocatalyzed by a Ni²⁺-DHLA (dihydrolipoic acid)/CdSe QD hybrid system.⁵⁷ This result demonstrates that by taking the advantages of both molecular cocatalyst and semiconductor, hybrid artificial photosynthetic systems could approach comparable performance to natural PS I.

Hybrid Photocatalysts for Transfer Hydrogenation

Visible light driven organic synthesis under mild conditions has attracted much attention from organic chemists.^{58–60} However, the direct electron transfer between photoexcited photosensitizers or semiconductors and reactants is usually difficult. It needs a suitable molecular cocatalyst to accept the photogenerated electrons from the semiconductor. Then the major function of the molecular cocatalyst is to reduce the activation energy barrier of the reaction and consequently accelerate the catalytic reactions. Considering the broad spectral absorption of semiconductors, the strategy of hybrid photocatalyst by incorporating a molecular cocatalyst with a semiconductor light harvester should be very promising for various photocatalytic reactions in addition to water splitting and CO₂ reduction.

We demonstrated a hybrid photocatalyst for transfer hydrogenation by using semiconductor CdS as light harvester and a series of iridium complexes as molecular cocatalysts (Figure 9).³³ Reduction of cyclohexanone was chosen as a model reaction. When iridium complex **5** with a hydroxyl group was used as the cocatalyst, a TON of 541 and an initial TOF of 103 h⁻¹ were achieved based on the complex molecule (Figure 10). When the substituted group of iridium complexes was switched from –OH to –OMe, lower activity was observed, delivering a TON of 251 and an initial TOF of 51 h⁻¹. When the substituted group was changed to –H and –COOH, the reactions were completely prohibited. The adsorption interaction between the CdS surface and the iridium complexes with different substituted groups may be the main reason for the different photocatalytic activity.

Hybrid Photocatalysts for CO₂ Reduction

Electrocatalytic CO₂ reduction over molecular catalysts has been widely studied.^{61,62} The merits of molecular catalysts

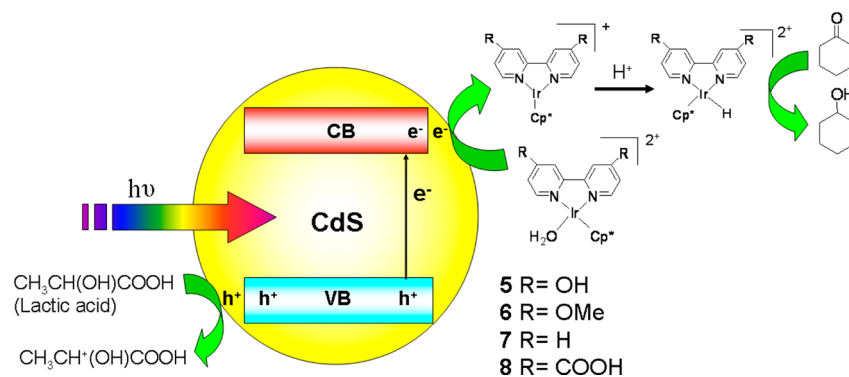


FIGURE 9. Visible light driven transfer hydrogenation over Ir complexes/CdS hybrid photocatalysts in the presence of lactic acid as electron donor. Adapted with permission from ref 33. Copyright 2011 Royal Society of Chemistry.

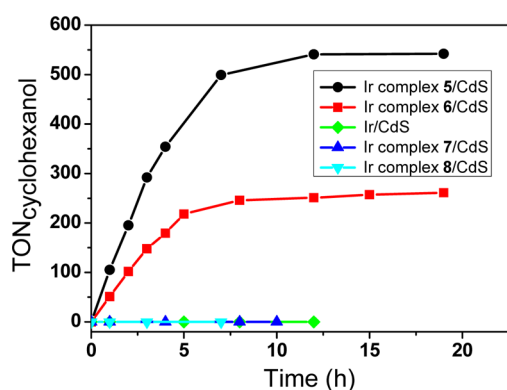


FIGURE 10. TON for cyclohexanol formation as a function of irradiation time. The reactions were performed in 5 mL H₂O (containing 1 mL lactic acid) at 313 K using Xe lamp with a cutoff filter ($\lambda > 400$ nm). The concentrations of complex and substrate are 0.4 mM and 0.4 M, respectively. CdS is 10 mg. The loading of Ir/CdS is 0.3 wt %. Adapted with permission from ref 33. Copyright 2011 Royal Society of Chemistry.

include their high efficiency and excellent selectivity. For example, the Ni(cyclam)²⁺ complex was shown to electrochemically reduce CO₂ to CO with 100% current efficiency and selectivity ratio of CO/H₂ over 100.⁶³ The complex [Co(v-tpy)₂]²⁺ was shown to have good selectivity for formic acid,⁶⁴ while the complex K₂Fe^{II}[Fe^{II}(CN)₆] showed good selectivity for methanol.⁶⁵ When the molecular cocatalysts for CO₂ reduction were assembled on semiconductor light harvesters, good selectivity was also achieved for the hybrid photocatalysts.^{66,67}

Figure 11 shows that three Ru complexes, **9**, **10** and **11**, with different types of carbonyl linkage were adsorbed on the surface of p-type N-doped Ta₂O₅ (N-Ta₂O₅) semiconductor. A selectivity of more than 75% in HCOOH was obtained for [Ru-dcbpy] **11**/N-Ta₂O₅ hybrid photocatalyst.⁶⁶ The pyridinium/p-GaP hybrid electrode shows high selectivity in methanol production, a solar-to-methanol efficiency of 44% was achieved at -0.5 V vs SCE and under 365 nm

illumination.⁶⁷ The successful applications of hybrid photocatalysts to CO₂ reduction, transfer hydrogenation, and H₂ production demonstrate the feasibility and versatility of the strategy of using a semiconductor as light harvester and a biomimetic complex as molecular cocatalyst.

Factors Influencing Electron Transfer

Efficient photoexcited electron transfer from semiconductors to molecular cocatalysts is essential for high activity of hybrid photocatalysts. Study of the factors influencing the electron transfer can help us to rationally construct more efficient hybrid photocatalysts.

By comparing the photocatalytic H₂ evolution activities of different cobaloximes/CdS hybrid photocatalysts, we found that close contact between the molecular cocatalysts and the semiconductors has great influence on electron transfer.³¹ The H₂ evolution potentials for Co(dmgh)₂pyCl (**1**), Co(dmgh)₂(4-(Me₂N)py)Cl (**2**), and Co(dmgh)₂(2-(SH)py)Cl (**3**) are -0.78, -0.79, and -0.80 V vs NHE respectively (structures of cobaloximes are shown in Figure 5). The driving forces (ΔG_{ET}) for photoexcited electron transfer from CdS to cobaloximes are in the order of **1** > **2** > **3** (0.12 > 0.11 > 0.10 eV). However, **2** and **3** are more active than **1** (Figure 12). The difference in photocatalytic activity may be ascribed to the different adsorption of Co complexes on CdS. The adsorption strengths of these three Co complexes are in the order of **3** > **2** > **1**, which is consistent with the order of photocatalytic activity. The stronger adsorption may facilitate the photoexcited electron transfer from CdS to Co complexes.

That close contact of molecular cocatalyst on semiconductor through chemical interaction or strong physical adsorption can facilitate the electron transfer was also observed in photocatalytic CO₂ reduction.⁶⁸ Since phosphonate can provide a stronger linkage with N-Ta₂O₅,

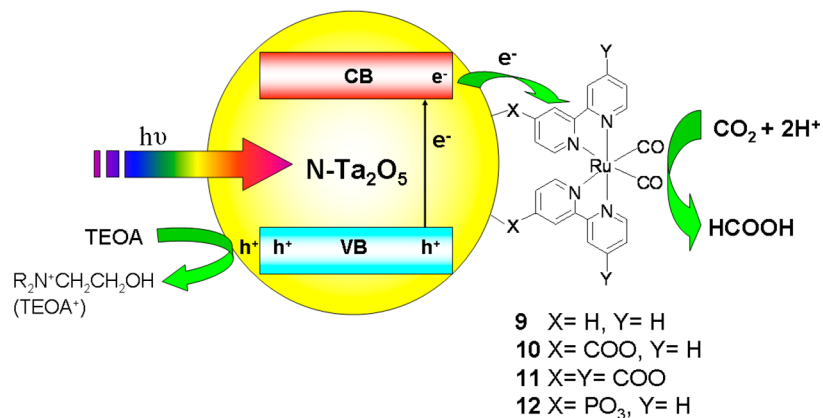


FIGURE 11. Photocatalytic CO₂ reduction over Ru complexes/N-Ta₂O₅ hybrid photocatalysts in the presence of TEOA as electron donor. Adapted with permission from ref 30. Copyright 2011 American Chemical Society.

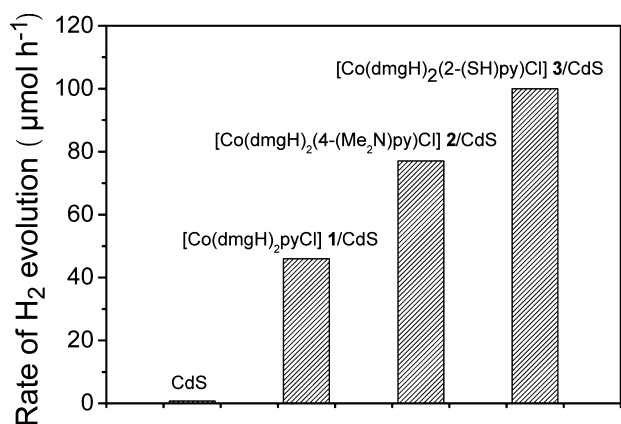


FIGURE 12. Rate of photocatalytic H₂ evolution over different Co complexes/CdS hybrid photocatalysts. CdS (0.1 g); Co complexes (1.0 mM); 10 vol % lactic acid (1.33 M); 10 vol % H₂O; 80 vol % DMF (total solution volume 100 mL); light source, Xe lamp (300 W); irradiation time, 3 h. Adapted with permission from ref 31. Copyright 2011 Elsevier.

Ru complex **12** with a phosphonate anchor group shows higher activity than that with carbonyl one. These results demonstrate that besides the thermodynamic driving force of photoexcited electron transfer, other factors such as close contact between molecular cocatalysts and semiconductors must be taken into account for constructing efficient hybrid photocatalysts.

Summary and Outlook

This Account highlights the strategy of hybrid photocatalyst, namely, using a semiconductor as light harvester and a biomimetic complex as molecular cocatalyst, mainly for reduction reaction (analogues to PS I). This strategy has been successfully applied in many reactions such as photocatalytic H₂ production, photocatalytic CO₂ reduction, and light-driven transfer hydrogenation. As demonstrated by several

examples, the merits of the hybrid photocatalyst are mainly from the broad spectral absorption of semiconductor (efficient light harvesting), the high selectivity and tunable structure of molecular complexes, the efficient electron transfer from photoexcited semiconductors to molecular cocatalysts, and improved stability for molecular cocatalysts.

The strategy of hybrid photocatalyst provides a promising approach for rational design of efficient and stable artificial photosynthetic systems. It has both scientific significance and potential application advantages. However, the research in this direction is still in an early stage and thereby leaves a much room for further development. This Account only highlights the reduction reaction (half reaction of water splitting). The application of hybrid photocatalysts in water oxidation is urgently needed, because the light-driven water oxidation plays a central role in artificial photosynthetic reactions. Considerable effort has been made to develop efficient biomimetic catalysts for O₂ evolution, and some catalysts exhibit promising activity.⁶⁹ One of the recent breakthroughs is the achievement of a TOF of more than 300 s⁻¹ catalyzed by a Ru complex in the presence of Ce^{IV}, which is moderately comparable with the reaction rate of PS II.⁷⁰ It is predictable that by rational immobilization of the active molecular catalysts on the surface of suitable semiconductor light harvesters, photocatalytic O₂ evolution with a reaction rate close to that of PS II would be achieved.

Finally, by incorporation of the reduction half reaction with the water oxidation reaction, the artificial photosynthesis would be realized over hybrid photocatalysts through either two-step photoexcitation (Z-Scheme)⁷¹ or one-step as introduced in this Account. Taking the advantages of biomimetic cocatalysts and the semiconductor nanoparticles

with efficient harvesting of solar light, a hybrid biomimetic system showing comparable or superior performance to natural photosynthesis is expected.

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BIOGRAPHICAL INFORMATION

Fuyu Wen received his M.S. degree in Inorganic Chemistry in 2006 from Liaoning University, China. He is a Ph.D. candidate at the Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences, under the direction of Professor Can Li. His work is focused on photocatalysis based on complex/semiconductor hybrid photocatalyst systems.

Can Li received his Ph.D. degree in 1989 from Dalian Institute of Chemical Physics and was promoted to full professor in 1993. 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 the 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

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