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Hydrogen Photogeneration from Water on the Biomimetic Hybrid Artificial Photocatalytic Systems of Semiconductors and Earth-abundant Metal Complexes: Progress and Challenges

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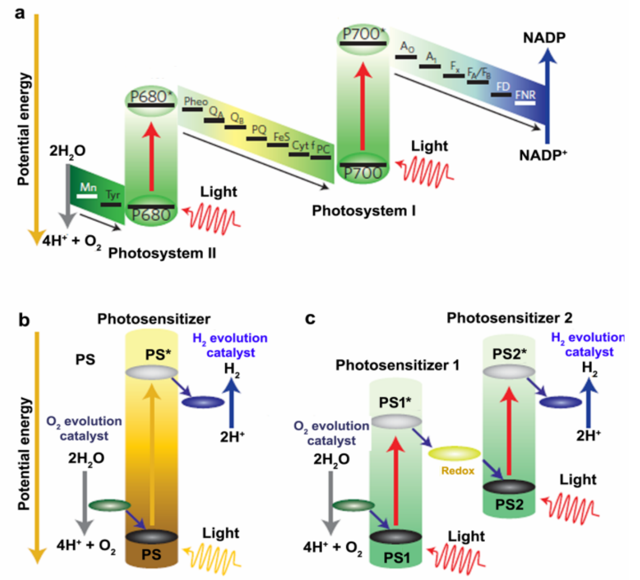
The replacement of traditional non-renewable fossil fuels by sustainable energy sources is one of the most challenging problems that must be solved in the 21st century. In this context, conversion of solar energy into stored chemical energy, especially solar driven splitting of water into molecular H_2 and O_2, has emerged as an attractive technology for solving the global energy issue. Inspired, but not constrained, by natural photosynthesis, a number of artificial systems and devices have been developed to harvest sunlight and oxidise water and reduce protons to produce useful solar fuels. This context reviews the recent significant developments in the field of hybrid artificial photocatalytic systems containing semiconductors as the photosensitizer and organometallic complexes made of earth-abundant elements (Fe, Co, Ni) as the molecular catalyst, for photogeneration of H_2 from water. A brief introduction for artificial photosynthesis and water reduction is first given, followed by an explanation of the basic principles and mechanism involved in artificial solar-driven water splitting for H_2 generation. Different series of hybrid artificial photocatalytic systems based on semiconductor photosensitizers and molecular catalysts that can be applied in photogeneration of H_2 from water are discussed in detail. Finally, the future perspective of this research field is also discussed.

1. Introduction

Energy resources human society currently relies on mainly come from non-renewable fossil fuels (*i.e.* oil, coal and natural gas), which were generated in the earth through natural photosynthesis (NPS) in the last 2.5 billion years. In the light of their current consumption rate and proven reserves, fossil fuels are assumed to be depleted within hundreds of years.[1-3] However, the worldwide energy demanding is ever-increasing due to the population explosion and economic growth. More strikingly, the combustion of the traditional carbon-based energy sources has resulted in several severe environmental issues, ranging from air and water pollution to greenhouse effect.[4-6] Therefore, considering the significant aspects including economic development, environmental protection and human health, seeking for nonpolluting and sustainable alternative energy sources will unquestionably be one of the most demanding scientific and technological challenge in a postfossil age. Among all the alternative candidates, solar energy is the most feasible one as the solar energy irradiating the earth's surface far exceeds the current global human energy consumption.[7-10] Thus, efficient utilization of solar energy to generate solar fuels could alleviate many energy and environmental issues we are now facing to a certain degree.

In the course of pursuing the sustainable production of solar fuels, NPS provides people with an excellent example as it can convert solar energy into biomass-stored chemical energy through a thermodynamically uphill ($\Delta G>0$) reaction. In NPS, carbon dioxide (CO_2) and water (H_2O) are consumed to produce O_2 and carbohydrates by using sunlight as the primary energy. In nature, these conversions are realized based on a fascinating biologic machinery consisting of two large protein complexes, the photosystem I (P700) and photosystem II (P680), assisted by various redox cofactors[11,12], as presented in **Scheme 1a**. Basically, the whole photosynthetic process of NPS involves the following three key steps: (i) initial sunlight-harvesting process and local charge separation in photosystem I and II; (ii) spatial charge separation via proton-coupled electron transfer between redox cofactors, and (iii) multielectronic redox catalysis at active sites resulting in the formation of fuel (carbohydrates) and O_2. As the largest-scale avenue for solar energy utilization on the earth, photosynthesis not only is the main source of the energy that stored in fossil fuels and that powers most of the biological world, but also can generate the earth's oxygenated atmosphere.[7]



Scheme 1 (a-c) Schematic representation of charge-separation processes in NPS and APS systems: (a) NPS systems including type I and II reaction centers; (b) single-photosensitizer APS system. (c) two-photosensitizers APS system. Reproduced with permission from ref. 11. Copyright 2012, Nature Publishing Group.

NPS provides researchers with an excellent blueprint for the design of artificial systems and devices. During the past several decades, a number of artificial photosynthesis (APS) systems have been designed and developed for the realization of sunlight utilization and efficient production of solar fuels by mimicking the key structural elements and functions of NPS. In particular, solar-driven splitting of water into molecular hydrogen (H_2) and oxygen (O_2) through APS represents one of the most important approaches to the utilization of solar energy, since H_2 is an ideal environmentally-friendly energy carrier with its high energy density (143 $MJkg^{-1}$) and benign combustion product (water).[11-20] Currently, two different types of APS systems are widely investigated, including single-photosensitizer system and two-photosensitizer system. As shown in **Scheme 1b**, the former comprises a single photosensitizer (generally dye or semiconductor) attached to O_2-evoluting catalyst on one side and H_2-evoluting catalyst on the other. Evidently, simple structure is the main advantage for this type of APS systems. However, there are two obvious drawbacks of it. On one hand, photosensitizer choice is limited because it desires materials with suitable band structure for overall water splitting. That is, an ideal photosensitizer must possess a more positive excited-state reduction potential than the water oxidation potential (+0.82V *vs.* NHE at pH 7), and meanwhile a more negative excited-state oxidation potential than he water reduction potential (-0.41V *vs.* NHE at pH 7).[11] On the other hand, even though using the materials whose excited-state energy can match the redox potential of water, only the ultraviolet light, which is a small fraction of the sun spectrum (less than 5%), can be harnessed to drive both H_2- and O_2-evolution reactions in these single-photosensitizer systems. To overcome these problems, the construction of two-photosensitizer systems with a Z-scheme configuration, which is analogous to the NPS, is an alternative technique, as shown in **Scheme 1c**. In these systems, H_2- and O_2-evoluting catalysts can be separately attached to two different photosensitizers (PS1 and PS2). Here, the excited-state oxidation potential of PS1 should be more negative than the water reduction potential level and the excited-state reduction potential of PS2 should be more positive than the water oxidation potential level. Obviously, one major advantage of this type of systems is that it can utilize visible even infrared light and greatly increase available choices for material combinations.[11] Note that the overall structure in two-photosensitizer systems is more complex than that of the single-photosensitizer ones, controlling the kinetic balance of all the electron-transfer processes to achieve high efficiency in charge separation and meanwhile reduce the energy loss through charge recombination reaction is more difficult to be realized. Currently, it is common to divide this type of systems into reductive half-reaction and oxidative half-reaction and to study them separately due to the complexity in constructing and optimizing such a complete APS system.

The overall water splitting reaction is very complicated because the two half-reactions are multielectron processes, as illustrated in the following equations (1-3):[21]

$$4H^+ + 4e^- \longrightarrow 2H_2 \qquad (1)$$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

$$2H_2O \longrightarrow 2H_2 + O_2 \qquad (3)$$

Harnessing solar energy for the splitting of H_2O into H_2 and O_2 therefore requires interfacing several fundamental but challenging photophysical steps with complicated catalytic transformations. To date, only a few APS systems have been reported to produce O_2 and H_2 simultaneously. The separation of water splitting reaction into reductive and oxidative half-reactions not only can facilitate the investigations and optimization of the key structural elements but also can avoid some undesired back- and side-reactions and enable detailed studies. Especially, the field of artificial photocatalytic systems for H_2 generation in both homogeneous and heterogeneous environment is undergoing an exciting development with increasing achievements in the past few decades. Of particular worthy noting is that a large number of hybrid photocatalytic systems consisting of semiconductors as photosensitizers and organometallic complexes as molecular catalysts for H_2 evolution have been described. Several recent reviews have summarized the advances in hybrid artificial photocatalytic systems.[15,16,20]

In this perspective, we will highlight the significant achievements realized in the designing of hybrid artificial photocatalytic systems based on semiconductor as photosensitizers and organometallic complexes made of earth-abundant elements (Fe, Co, Ni) as molecular catalysts for photocatalytic H_2 production. The basic principles and mechanism involved in artificial solar-driven water splitting for H_2 generation will be shown first. Different series of hybrid catalytic systems that can be used for photocatalytic H_2 production are discussed in detail based on some important and typical examples. Finally, an outlook in this research field will be presented.

2. Basic components of artificial photocatalytic systems for H_2 generation

To construct an artificial photocatalytic system for the reductive half-reaction of solar-driven water splitting, the following basic components are typically needed: a photosensitizer to absorb sunlight, a H_2 evolution catalyst to reduce aqueous protons, and a sacrificial electron donor (SED) to supply electrons for H_2 formation and regenerate the photosensitizer. Based on these basic components, the design principles for this type of artificial photocatalytic systems mainly involved: (i) using of photosensitizers that have strong light absorptivity and good photostability, (ii) the possibility to generate electronically coupled heterostructures between the photosensitizer and molecular catalyst, (iii) suitable energy alignments that would permit electrons transfer effectively from the photoexcited photosensitizer to the molecular catalyst. In addition, considering the cost factor and long-term sustainability, an ideal artificial photocatalytic system should be one not only where all the components are composed exclusively of earth-abundant elements, but also with high activity and good stability for H_2 generation. To date, the main focus in this field has been to design and synthesize ideal photosensitizers and catalysts for constructing highly efficient and stable photocatalytic systems.

2.1. Photosensitizers

As a photoactive component, the photosensitizer in an artificial photocatalytic system functions as both the light harvester and the electron deliverer to the catalyst, analogous to the photosynthetic pigments.[22,23] Generally, when the energy of the incident photons matches a possible electronic transition of the photosensitizer (e.g. molecular dyes), an electron from a low energy molecular orbital of the photosensitizer can be excited to a higher energy orbital, thus the photosensitizer is excited from the ground state to an excited state. The excited photosensitizer can serve as an electron deliverer and transfer an electron to an acceptor (H_2-evoluting catalyst or electron mediator) to create a charge-separated state. To achieve high efficiency in light harvesting, photosensitizers should possess the ability to utilize the majority of sunlight, that is, have a broad spectral absorption. Moreover, the photosensitizers should possess suitable band structure for water reductive half-reaction. A variety of photoactive materials including molecular dyes and semiconductors can induce electron transfer and have the potential to been used as photosensitizers in artificial photocatalytic systems. For most molecular dyes with few exceptions, their excited states undergo reductive quenching, resulting in unstable radical anions that easily decompose. Comparing to molecular dyes, semiconductors seem to be more promising due to their unique properties including broad and continuous spectral absorption, relatively higher photostability as well as tunable crystal structure and morphology, electronic structure, and surface chemistry, making them ideal candidates as photosensitizers in artificial photocatalytic systems.[15,16]

2.2 Catalysts

The reduction of protons to H_2 molecules has a large activation barrier, resulting in a great overpotential and a low rate. It is therefore necessary to use a catalyst, which will lower the barrier and allow for efficient generation of H_2. The catalyst for the reductive half-reaction in artificial solar-driven water splitting accepts electrons from the excited photosensitizer and catalyzes protons reduction into H_2. Although the Pt-group elements show excellent activity for photocatalytic H_2 production, the limited supply and the sky-rocketing price of these precious metals, apparently, cannot sustain scalable and economic production of H_2 by solar-driven photocatalysis. The development of catalysts relying on noble-metal-free materials is therefore significant. During the past two decades, molecular catalysts, especially biomimetic complexes composed of earth-abundant elements such as Fe, Co, and Ni, have been exploited for catalytic proton reduction for H_2 generation. The advantages of molecular complexes as the catalyst could be summarized as follows:[16,17] (i) the use of molecular catalyst not only can facilitate charge separation and improve the efficiency of electron transfer but also can provide us more mechanism details of H_2 generation at molecular level; (ii) molecular catalysts possess designable structures, tunable redox properties and possible links to semiconductor materials due to the large versatility of ligands; (iii) differing from bare semiconductor-based photocatalytic processes, the solar-driven water splitting for H_2 evolution through the integration of molecular catalysts with semiconductors typically require photogenerated charge carriers from the semiconductor to drive a multiple reduction reaction of a single molecular catalyst. Currently, the investigation of highly efficient biomimetic molecular catalysts made of earth-abundant elements is a hot topic in the field of solar-driven H_2 production.

2.3. Sacrificial electron donors

As mentioned above, the SED in the reductive half-reaction of artificial solar-driven water splitting provides electrons for protons reduction and regenerate the photosensitizer. In general, a SED material should meet two principal requirements when combining with semiconductor photosensitizers.[11] On one hand, the energy level of SED must be higher than the valence band of the semiconductor, but lower than the water oxidation potential. On the other hand, fast and efficient electron transfer from the SED to semiconductor should be realized prior to decay of the photoexcited state of the semiconductor. In some systems, the SED can also serve as the source of protons. The frequently used SED materials in reductive half-reaction of artificial solar-driven water splitting involve tertiary amines (TEA), triethanolamine (TEOA), alcohols, and ascorbic acid (H_2A).

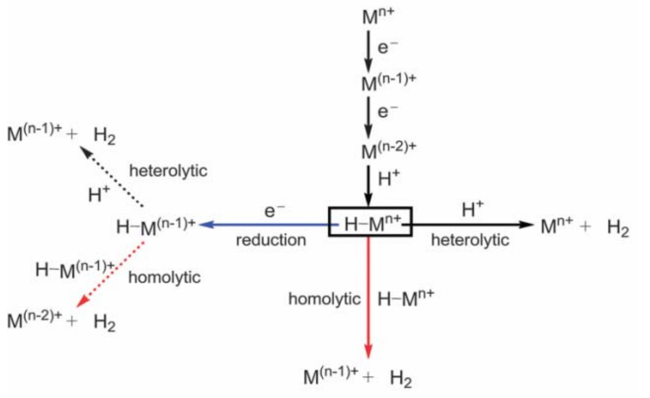
Although the components mentioned above seem not complicated, the combination of them with efficient light absorption, fast electron transfer, and ultimately efficient catalysis is not easily accomplished. The essential challenge in solar-driven H_2 production technology is to develop artificial photocatalytic systems than can orchestrate and enable all of the steps in photocatalysis to occur efficiently with marginal energy losses. Although significant advance has been made in this field, there still remains much to be done before realizing its full potential.

3. Basic mechanistic considerations in hybrid artificial photocatalytic systems for H_2 production

Scientific understanding of the fundamental principles and mechanisms involved in the process of solar-driven water splitting for H_2 generation is of great importance in designing and constructing efficient artificial photocatalytic systems. As mentioned above, light-absorption, charge generation and separation, and catalytic transformation are three basic processes in a photosynthetic reaction. The balance of thermodynamics and kinetics of these processes jointly determines the overall efficiency. During the past decade, fundamental advance has been made in detailed mechanistic studies in solar-driven water splitting, which provides new inspiration for designs of artificial photocatalytic systems with high efficiency.

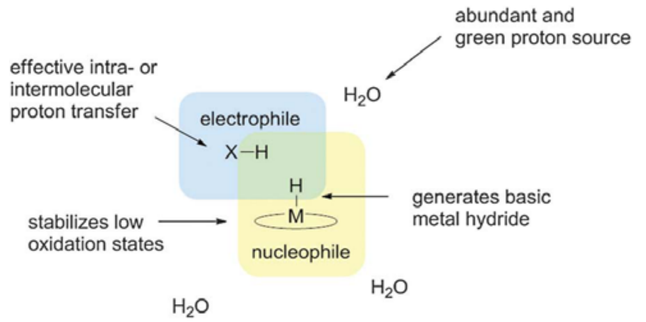
In case of a photochemical cycle occurring in hybrid photocatalytic systems comprising semiconductor photosensitizers and molecular catalysts, the semiconductor can absorb light irradiation from sunlight or an illuminated light source whose energy is equal or larger than the band gap (E_g) of semiconductor. After photoabsorption, the electrons are excited from the valence band of the semiconductor into its conduction band, while the holes are left in the valence band, thus generating photogenerated electron-hole pairs. The photoexcited electron can be transported from the photogenerated center to the surface of semiconductor and then further to the molecular catalysts adsorbed on the surface of the semicondcutors if electron transfer from semiconductor to the molecular catalyst is thermodynamically favorable. On the other hand, the photogenerated hole remaining in the valence band of semiconductor could be reduced by electron transfer from the SED. Emission quenching and flash photolysis experiments are commonly used to study the electron transfer between the semiconductor and molecular catalysts and SED.

High efficiency in electron transfer processes is essential for achieving high activity in photosynthesis. In an APS system, electron transfer reactions occur via interfaces formed between photosensitizer and various redox cofactors (e.g. catalyst, SED, and electron mediator). As mentioned above, from a photochemical point of view, electron transfer reaction within an APS system is induced by the photoabsorption of the photosensitizer, following by photoexcited photosensitizer transferring an electron to the catalyst (or an electron mediator) or accepting an electrons from the SED (or an electron mediator). Investigation reveals that a series of factors, such as the structures and surface properties of the photosensitizer, cofactor redox potential and solvent networks, jointly contribute to geometric and thermodynamic parameters that control the rates of electron transfer.[24,25] In general, the losses of energy through charge recombination reaction during different interfacial charge-transfer reactions in multicomponents photocatalytic system are the major reasons for the low conversion efficiency. For hybrid photocatalytic systems using semiconductor as photosensitizers, the recombination of charges (electrons and holes) within semiconductor is one of major pathways that lose energy and limit the quantum efficiency (QE) of H_2 production. Currently, several strategies have been developed to reduce energy losses resulting from charges recombination reaction in semiconductor, such as modifying the size and morphology of the materials to reduce the distance between the photogenerated center to the surface which charges must travel before taking part in the surface reactions, and using proper catalysts to accelerate interfacial reaction kinetics. Currently, much effort has been devoted to kinetic studies of charge carrier dynamics in bare semiconductors or homogeneous molecular systems. In contrast, there have been relatively few studies into hybrid photocatalytic systems based on semiconductors and molecular complexes until now. Many significant aspects, such as how these dynamics are related to structure and components of the photocataltic systems and how they affect the H_2 production efficiency, still need more in-depth theoretical and experimental studies in the future.



Scheme 2 Proposed mechanistic pathways for hydrogen evolution catalysis at a metallic centre M^{n+} of transition metal complexes. Reproduced with permission from ref. 17. Copyright 2014, The Royal Society of Chemistry.

Careful consideration of the mechanisms of H_2 formation is of the importance for designing active H_2 evolution catalysts. From a thermodynamic point of view, all the redox couples with a more negative reductive potential than the water reduction potential are capable of reducing protons for H_2 evolution. In fact, even though their energy level can match the water reduction potential level, proton reduction reaction on some of those materials are kinetically disfavoured and commonly require a proper catalyst to lower the activation barrier and improve the reaction rate. Transition metal complexes are suitable candidates to efficiently catalyze the reduction of protons into molecular H_2 as they are able to store electrons via multiple redox states. Although a complete understanding of the H_2 formation mechanism based on transition metal complex catalysts has not been established, the findings resulting from the studies on both homogeneous and heterogeneous molecular system could provide valuable reference for the design and synthesis of efficient molecular catalysts. A generic mechanistic proposal for H_2 evolution catalyzed by transition metallic complexes is illustrated in **Scheme 2**. When the electron transfers from the photoexcited PS to complex catalyst, metallic center (M^{n+}) experiences two separate one-electron reductions, and then protonate to generatd an intermediate hydride H-M^{n+}, which can react further in three different pathways to release H_2.[17] The first pathway involves a heterolytic mechanism, where the hydride is protonated to evolve H_2, regenerating the starting M^{n+} catalyst. In other possibility, two hydride molecules react with each other to form $M^{(n-1)+}$ and yield H_2 through a homolytic pathway. Apart from these two pathways, the third possible route involving further reduction of the hydride to generate a low valent hydride H–$M^{(n-1)+}$ followed by the heterolytic or homolytic route to genrate H_2 can occur. Distinguishing between homolytic and heterolytic mechanisms is often challenging, because the two competing pathways can occur uniquely or simultaneously, depending on a series of factors, such as the concentration of the molecular catalyst, pH value or acid concentration of the given system. In view of the above mechanistic considerations, two design criteria should be taken into account when designing and synthesizing molecular catalysts for H_2 evolution (see **Scheme 3**). On one hand, metal center in the complex should possess available open coordination sites and appropriate electronic characteristics for producing metal-hydride intermediate species.[26] This is the first and foremost criterion. On the other hand, the metallic complex should contain a ligand platform which can effectively stabilize reducing metal species.[26] To be an excellent H_2-evolution catalyst in photochemical systems, the molecular complex itself (or its converted products) must possess high electrocatalytic activity for protons reduction, but it is not sufficient. To let the molecular catalyst function well in a photochemical system, high efficiency in electron transfer from photosensitizer to molecular catalyst must be achieved, which requires the molecular catalyst matching well with the photosensitizer in many aspects, such as driving force and energy barrier for electron transfer, distance, orientation and contact manner between photosensitizer and catalyst.[16]



Scheme 3 Design parameters for an effective proton reduction catalyst that operates through a generic metal-hydride intermediate. Reproduced with permission from ref. 26. Copyright 2013, The Royal Society of Chemistry.

4. Hybrid artificial photocatalytic systems for H_2 generation

As mentioned above, compared with organic or organometallic chromophores, semiconductors have superior advantages, including broad and continuous spectral absorption and high photostability, to function as light-harvesting materials for constructing efficient APS systems. The field of APS systems for solar-driven water splitting is currently undergoing an exciting developing with increasing achievements. In this part, we will briefly review the recent developments of hybrid artificial photocatalytic systems comprising semiconductors, especially colloid semiconductor nanoscystals, as photosensitizers and earth-abundant elements (Fe, Co, Ni)-based complexes as molecular catalysts for photocatalytic H_2 production. The features, activity, and the electron transfer mechanism in each system will be discussed based on some typical and important examples extracting from the recent publications.

4.1. Photogeneration of H_2 from water using semiconductor photosensitizers and Fe-based molecular catalysts

4.1.1 [FeFe]-hydrogenase

Hydrogenase (H_2ase) existing in many micro-organisms are natural enzymes that can catalyses the reversible reduction of protons to H_2 with high activity. In natural photosystem I, the integration of pigment molecules with H_2ases can efficiently achieve photocatalytic reduction of protons for H_2 production. The H_2ases possess catalytic sites with organometallic clusters composed of earth abundant elements, low activation energies, as well as a wide range of O_2 sensitivities, making them ideal H_2-activating catalysts. H_2ases can be classified into three categories according to their active sites, namely, [NiFe]-, [FeFe]-, and [Fe]-H_2ases. Among them, [FeFe]-H_2ase is highly active for H_2 evolution reaction, with low overpotential and a turnover frequency (TOF) as high as 6000-9000 s^{-1} per catalytic site, underscoring the enormous potential of [FeFe]-H_2ases as a promising H_2-evolution catalyst for constructing efficient photocatalytic systems.[27] During the past decade, [FeFe]-H_2ases have been widely utilized as efficient catalysts to combine with suitable semiconductor photosensitizers for artificial photocatalytic H_2 production.[28-31]

For example, King *et al.* demonstrated an efficient biomimetic strategy for coupling *Clostridium acetobutylicum* [FeFe]-H_2ase I (CaI) to CdTe nanocrystals for photocatalytic H_2 evolution.[28] It is widely recognized that, in vivo environments, electron transfer to CaI can be achieved through the redox-shuttle ferredoxin, which deeply embeds in a positively charged pocket on the enzyme. Inspired by these, they used 3-mercaptopropionate (MPA) as the ligand to functionalize the CdTe nanocrystals and enabled an electrostatic interaction between CdTe nanocrystals and CaI as the MPA molecule can attach to the CdTe nanocrystals through thiolate groups (-SH) and present negatively charged carboxylate groups ($-COO^-$) to CaI, resulting in the formation of stable, enzymatically active complexes through the molecular assembly of CdTe nanocrystals and CaI (see **Fig. 1a**). Upon illumination of these enzymatically active complexes, rapid intermolecular photogenerated electron transfer from the conduction band of CdTe to CaI led to efficient H_2 generation. The optimized CdTe-CaI system could achieve a single-wavelength quantum efficiency (QE) of 9% (λ=523 nm) and an AM 1.5G efficiency of 1.8% using ascorbic acid as a SED.

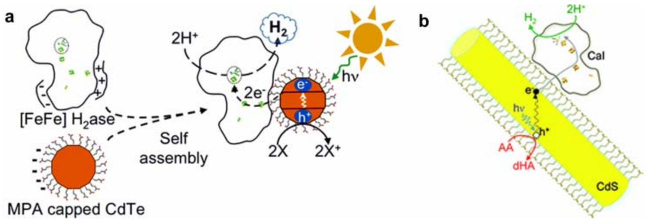


Fig. 1 (a) Schematic illustration of the self-assembly of CaI and MPA capped CdTe nanocrystals, and light-induced H_2 evolution of the self-assempled complex. (b) Schematic illustration of the photocatalytic H_2 production by the CdS:CaI complex. (a) Reproduced with permission from ref. 28. Copyright 2010, American Chemical Society. (b) Reproduced with permission from ref. 29. Copyright 2012, American Chemical Society.

Photochemical H_2 generation from water by semiconductor nanocrystal-CaI complexes were further investigated in a hybrid photocatalytic system consisting of CdS nanorod-CaI complexes.[29] In this study, King and co-workers developed complexes of MPA-capped CdS nanorods and CaI that could effectively photocatalyze reduction of protons to H_2, giving a TOF of 380-900 s^{-1} (based on H_2ase) and a QE of up to 20% under illumination at 405 nm using ascorbic acid as a SED (see **Fig. 1b**). They proposed that the high TOF relied on the directed assembly of MPA-capped CdS and CaI, in which site-specific binding of the MPA-capped CdS to a positive patch on the CaI surface facilitated rapid photoexcited electron transfer from the conduction band of CdS to the CaI.

A general trend has emerged for semiconductor–H_2ase complexes, such as CdTe-[NiFe]-H_2ase[32], dye-sensitized TiO_2-[NiFeSe]-H_2ase[33,34], suggesting the promising potential of coupling biological H_2ase with inorganic semiconductor nanoscrystals for highly efficient H_2 production.

4.1.2 [FeFe]-hydrogenase mimics

Nature has produced [FeFe]-H_2ase as a highly efficient H_2-forming catalyst. However, they do not meet the demands of practical application of solar-driven water splitting technology because of their limited stability and the difficult isolation of them from natural systems. Therefore, the development of artificial [FeFe]-H_2ase analogues that could reproduce the high activity of natural enzymes has attracted considerable interest. With reference to the active sites of natural [FeFe]-H_2ase, scientists have successfully synthesized a series of [FeFe]-H_2ase mimics on the basis of the Fe_2S_2 cluster and demonstrated their feasibility for H_2 production via either electrochemical or photochemical approaches.[35] The first artificial photocatalytic system using a [FeFe]-H_2ase analogues as the catalyst for H_2 production was reported in 2003 by Sun and Åkermark.[36] Following this pioneering work, a great deal of efforts have been directed to construct artificial photocatalytic systems based on [FeFe]-H_2ase mimics for H_2 evolution. Of particular interesting is the development of various hybrid artificial photocatalytic systems comprising of semiconductor as photosensitizers and [FeFe]-H_2ase mimics as catalysts.[37-43]

In 2012, Li *et al.* reported the construction of an efficient hybrid photocatalytic system for H_2 evolution by using a [FeFe]-H_2ase mimic, $[(\mu\text{-SPh-4-NH}_2)_2Fe_2(CO)_6]$(**1**), as the molecular catalyst, ZnS nanocrystals as a photosensitizer and ascorbic acid as an SED[37], as presented in **Fig. 2**. Study on the energy band structure of ZnS and the redox potential of the [FeFe]-H_2ase mimic **1** revealed that the electron transfer from photoexcited ZnS to the [FeFe]-H_2ase mimic **1** catalyst was thermodynamically favorable, which leading to efficient H_2 evolution. As a consequence, this hybrid catalytic system exhibited a high photocatalytic H_2 production activity, giving an initial TOF of 100 h^{-1} (based on **1)** under irradiation of a xenon lamp without cut-off filter. The photocatalytic H_2 evolution rate of this [FeFe]-H_2ase mimic **1**/ZnS system was even higher than that of Pt/ZnS system (see **Fig. 2**). Furthermore, the resultant photocatalytic system showed an excellent stability, achieving a total TON (based on **1**) of more than 2607 over 38 h of irradiation. The apparent QE of H_2 production from [FeFe]-H_2ase mimic **1**/ZnS system was 2.5% at 325 nm.

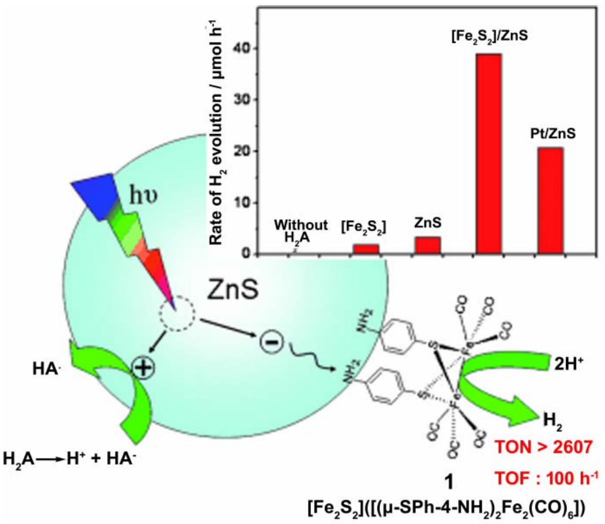


Fig. 2 Schematic diagram of the **1**/ZnS heterogeneous APS system and the rates of H_2 evolution on various photocatalytic systems. Reproduced with permission from ref. 37. Copyright 2012, John Wiley and Sons.

Although [FeFe]-H_2ase mimics exhibit high H_2-evolution activity, an issue associated with these artificial [FeFe]-H_2ase analogues is their low solubility in water. For most of [FeFe]-H_2ase mimic catalysts using for photocatalytic H_2 production, they function only in pure organic solvents or in aqueous/organic solution, and thus they are not suitable for coupling with practical solar-driven water splitting technology. Several approaches have been put forward to address this issue, including encapsulating the [FeFe]-H_2ase mimic catalysts inside micelles or cyclodextrins or linking them using ligands with water affinity or water-soluble substituents, or anchoring them onto the surface of water-soluble semiconductor nanocrystals. The eventual goal is to develop efficient photocatalytic systems that can operate in aqueous media, especially in pure water, for solar-driven H_2 production from water.

In 2011, Wu and co-workers designed a robust water-soluble [FeFe]-H_2ase mimic (**2**) and achieved photocatalytic H_2 production in water.[38] Here, to modulate water solubility of the catalyst, three hydrophilic ether chains were anchored to the active site of the [FeFe]-H_2ase mimic **2** via a cyanide (CN) group (see **Fig. 3a**). With CdTe quantum dot (QD) stabilized by MPA as the photosensitizer, [FeFe]-H_2ase mimic **2** as the catalyst, and ascorbic acid as both a proton source and the SED, an efficient artificial photocatalytic system for H_2 generation from water was established. Under optimized conditions, this catalytic system could produce 789 μmol H_2 after 10 h of visible light irradiation (λ>400 nm) in pure water corresponding a TON and a TOF of up to 505 and 50 h^{-1} (based on **2**), respectively. Another important advance in constructing water-soluble [FeFe]-H_2ase mimics for photocatalytic H_2 evolution made by Wu group is the development of an interface-direct assembly strategy.[39] In this study, the [FeFe]-H_2ase mimic, $Fe_2S_2(CO)_6$ (**3**), was assembled on the surface of MPA-capped-CdSe QDs be means of a interface-directed approach in aqueous/organic solution, forming the water-soluble CdSe/**3** assembly (see **Fig. 3b**). The resulting artificial photocatalytic system was able to produce H_2 with a total TON of 8781 (based on **3)** over 82 h and an initial TOF of 596 h^{-1} in the first 4 h under visible-light illumination in water. They demonstrated that the highly efficient H_2 evolution relied on the fast electron transfer from the photoexcited CdSe to catalyst **3** owing to the close contact and strong interaction in the assembly.

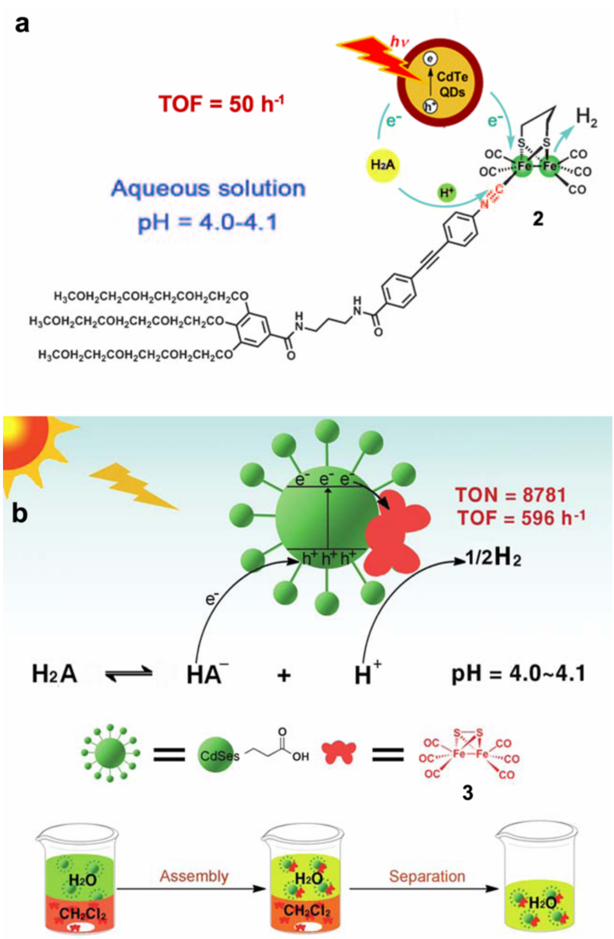


Fig. 3 (a) Schematic diagram of **2**/ CdTe hybrid system and its H_2 photogeneration. (b) Schematic diagram of **3**/CdSe hybrid system and its H2 photogeneration. (a) Reproduced with permission from ref. 38. Copyright 2011, John Wiley and Sons. (b) Reproduced with permission from ref. 39. Copyright 2013, The Royal Society of Chemistry.

Several polymers with water affinity can also be utilized to react with [FeFe]-H_2ase mimics to make them soluble in water. For instance, Wu *et al.* have succeeded in creating the first set of polymer-based [FeFe]-H_2ase mimics for photocatalytic H_2 generation.[40] The polymer-based [FeFe]-H_2ase mimics was constructed on the basis of the covalent link between a hydrophilic polymer, poly (acrylic acid) (PAA), and [FeFe]-H_2ase mimics **4** (see **Fig. 4a**), generating a water-soluble catalyst. Importantly, the key roles of the PAA chain in polymer-based [FeFe]-H_2ase mimics should be noted. First, PAA chain is a framework to bring the Fe_2S_2 active site into aqueous solution as well as an excellent stabilizer protecting the

CdSe QDs from aggregation. Secondly, it could narrow the distance between the CdSe and the grated catalyst **4,** thus promoting the photoinduced electron transfer from the excited CdSe QDs to **4**. These functions jointly contribute to a highly efficient photogeneration of H_2 from water, achieving a TON of 27135 (based on **4**) for 8 h irradiation, a TOF of 3.6 s^{-1} (based on **4**) in the initial 30 min as well as a QE up to 5.07% using ascorbic acid as both a proton source and the SED (λ=450 nm). Based on this work, Wu and co-workers further anchored [FeFe]-H_2ase mimic **5** (see **Fig. 4b**) on branched polyethylenimone (PEI) to make a water-soluble [FeFe]-H_2ase mimic and then combined with CdSe QDs to construct an efficient artificial photocatalytic system for H_2 production.[41]

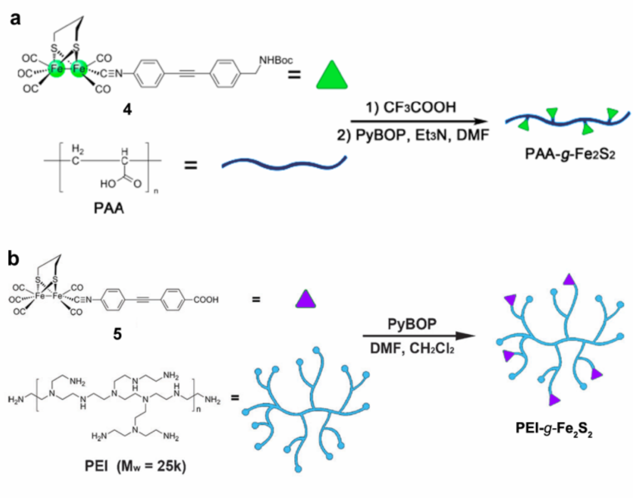


Fig. 4 (a) Schematic illustration of the synthetic route of PAA-g-Fe_2S_2 (**4**). (b) Schematic illustration of the synthetic route of PEI-g-Fe_2S_2 (**5**). (a) Reproduced with permission from ref. 40. Copyright 2013, John Wiley and Sons. (b) Reproduced with permission from ref. 41. Copyright 2015, John Wiley and Sons.

From the biomimetic point of view, both inorganic cofactor of H_2ase and the biological environments where enzyme-like reaction proceeds should be taken into account when design and construct artificial photocatalytic systems. It is well recognized that [FeFe]-H_2ases are buried within the protein matrix in nature. To more closely mimic the biological environment of H_2ase, Wu and co-workers have successfully constructed a chitosan-confined [FeFe]-H_2ase mimic for photocatalytic H_2 production (see **Fig. 5**).[42] In this study, they selected a [FeFe]-H_2ases mimic (**6**) as the molecular catalyst, MPA-stabilized CdTe QDs as the photosensitizer, and ascorbic acid as the proton source and SED to construct a hybrid photocatalytic system. Here, [FeFe]-H_2ases mimic (**6**) was incorporated in the chitosan-confined environment via the chelation and electrostatic interactions between them, and the MPA-stabilized CdTe QDs with negatively charged surface can also interact with cationic chitosan. Under optimal conditions, the resultant self-assembled system was able to produce H_2 with TON of up to $(5.28\pm0.17)\times10^4$ and initial TOF of 1.40 ± 0.22 s^{-1} (based on **6**) under visible light irradiation from a methanol/water mixture solution. Both the catalytic activity and stability was much higher than those of the same system without chitosan. The results suggest that the environment surrounding the catalytic center plays a crucial role on the photocatalytic H_2 production. Thus, when design active photocatalytic systems based on [FeFe]-H_2ase mimics for H_2 production, both the structure of the active center of the natural [FeFe]-H_2ase and biological environmental surrounding them should be taken into account.

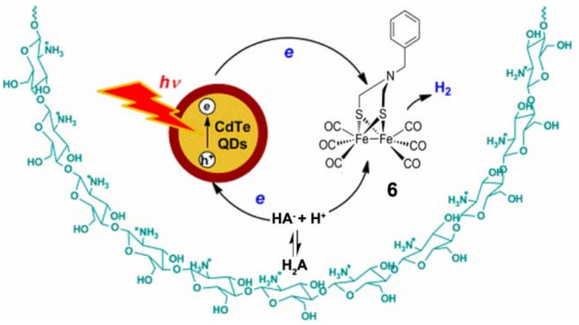


Fig. 5 Schematic illustration of H_2 photogeneration of of a chitosan-confined **6** in the presence of CdTe quantum dots and H_2A. Reproduced with permission from ref. 42. Copyright 2013, Nature Publishing Group.

4.2. Photogeneration of H_2 from water using semiconductor photosensitizers and Co-based molecular catalysts

Co-based complexes are another family of molecular catalysts for photocatalytic H_2 production. In 1981, Krishnan and Sutin explored the first attempt to construct a photocatalytic system using a Co-based complex ($[Co(bpy)_n]^{2+}$ (n=undefined)) as the catalyst in combination with $[Ru(bpy)_3]^{2+}$ as the photosensitizer and ascorbic acid as the proton and source and SED.[44] Since this pioneering work, the concept has been extended to designing and constructing a series of artificial photocatalytic systems based on Co-based complexes. In particular, Co complexes with diglyoxime ligands (cobaloximes), which comprise a coordinated Co^{III} ion as the metal center and an –OH group in the second coordination sphere as the ligand platform, have been widely studied in hybrid photocatalytic systems in combination with semiconductors for H_2 evolution.[45-51]

For instance, Li *et al.* described the combination of CdS nanoparticles and cobaloximes for efficient photocatalytic H_2 evolution.[45] Three cobaloximes **7-9 (Fig. 6a-c)** with different axile pyridine ligands, as the molecular catalyst, were coupled with CdS nanocrystals via the physical adsorption. The adsorption ability of cobaloximes on CdS was found to influence the photocatalytic activity. They demonstrated that the interfacial electron transfer from photoexcited CdS to cobaloximes was efficient through the weak adsorption of cobaloximes on CdS, which was essential for H_2 production. The cobaloxime **7**/CdS hybrid system could achieve a TON of 171 for H_2 generation in H_2O/CH_3CN solution over 15 h of irradiation (λ>420 nm) using TEOA as the SED, corresponding a QE of 9.1% at 420 nm. In another example, Chen and co-workers constructed a hybrid system containing CdSe/ZnSe core/shell QDs and a cobaloxime **10** and investigated the photodriven charge-transfer dynamic and catalytic properties **(Fig. 6d)**.[46] In this study, they successfully archored the complex **10** onto the surface of CdSe/ZnS QDs via a phosphonate linkage to created a hybrid photocatalytic system. Study on the photodriven charge-transfer dynamic by optical transient absorption spectroscopy revealed that electron transfer from the photoexcited CdSe/ZnSe QDs to **10** occurred much faster than the charge recombination, leading to the generation of long-lived catalytically active sites. As a result, the cobaloxime **10**/ CdSe/ZnSe system was capable of catalyzing H_2 generation photochemically in the presence of a proton source (triethylamine hydrochloride) and a SED (TEOA) with a TON more than 10000 H_2 per QD in 10 h. Except for inorganic semiconductor photosensitizer, some organic polymeric semiconductor materials, such as carbon nitride (g-C_3N_4), can also been used as photosensitizer coupled with cobaloximes for photocatalytic H_2 production. Xue group demonstrated an cost-effective, efficient and noble-metal-free artificial photocatalytic systems, consisting of g-C_3N_4 nanosheets as a photosensitizer and cobaloximes **11 (Fig. 6e)** as molecular catalyst for H_2 evolution.[47]

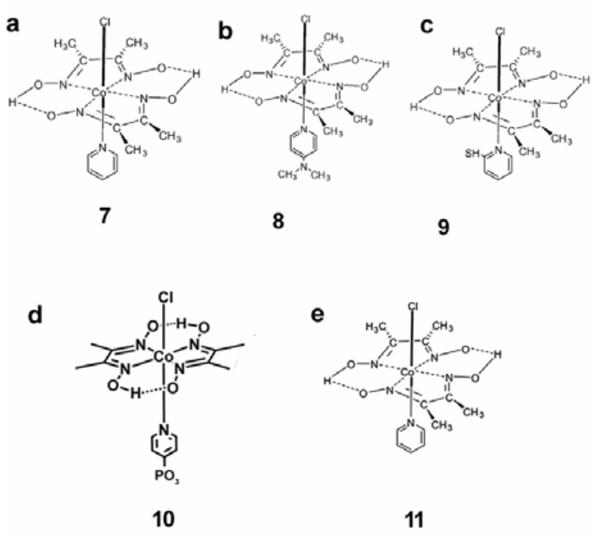


Fig.6 (a-e)Structures of various cobaloximes **7-11** used as molecular catalysts for photocatalytic H_2 production in combination with semiconductor PSs. (a-c) Reproduced with permission from ref. 45. Copyright 2011, Elsevier. (d) Reproduced with permission from ref. 46. Copyright 2012, American Chemical Society. (e) Reproduced with permission from ref. 47. Copyright 2013, The PCCP Owner Societies.

Besides these cobaloxime-type catalysts, other Co-based complexes, especially those can function in aqueous media, have also been examined as effective molecular catalyst to combine with semiconductors for photogeneration of H_2 from water.[52-54] For instance, Chang, Yang, Long and co-workers demonstrated photogeneration of H_2 from water using a Co pentapyridine complex, $[(CF_3PY_5Me_2)Co(H_2O)]^{2+}$ (**12**) (see **Fig. 7a**), as the catalyst in combination with GaP nanowire photosensitizer in the presence of methanol as the SED.[52] In a recent example, Llobet *et al.* have constructed a hybrid system consisting of CdTe QDs and a molecular cobalt catalyst (**13**) (see **Fig. 7b**) and analyzed all the thermodynamics and kinetics involved in the H_2 evolution catalysis in this system.[53] They found that the electron transfer from the photoexcited CdTe QDs to the molecular catalyst take place fast enough and efficiently, while the back electron transfer and catalysis were much slower, resulting in efficient light-induced proton reduction to molecular H_2.

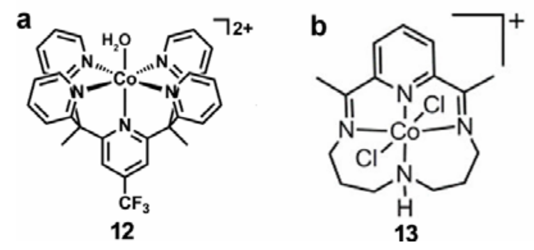


Fig.7 (a, b)Structures of Co-based complexes **12**-**13** used as molecular catalysts for photocatalytic H_2 production in combination with semiconductor PSs. (a) Reproduced with permission from ref. 52. Copyright 2013, The Royal Society of Chemistry. (b) Reproduced with permission from ref. 53. Copyright 2014, American Chemical Society.

4.3. Photogeneration of H_2 from water using semiconductor photosensitizers and Ni-based molecular catalysts

Beside Fe- and Co-based complexes, some Ni-based molecular catalysts were also used to integrate with semiconductor for photocatalytic H_2 evolution in recent years. Despite [NiFe]-H_2ases are the most abundant group of H_2ases in the nature, Ni-based complexes used for photochemical H_2 generation, especially in combination with semiconductor, were relatively less reported compared with Fe- and Co-based complexes.[55-58]

Reisner *et al.* reported an artificial photocataltic system for solar-light-driven H_2 evolution from water by employing a bioinspired synthetic Ni-based complex, $[Ni^{II}(PPh_2\{NPhCH_2P(O)(OH)_2\}_2)_2]Br_2$, (**14**) NiP (see **Fig. 8a**), as catalysts and a heptazine carbon nitride polymer, melon (CN_x), as the photosensitizer.[55] The resultant NiP **14**/CN_x system showed efficient catalytic activity for H_2 production during solar light irradiation with a TON of approximately 155 (based on **14**) in redox-mediator-free aqueous EDTA solution at pH 4.5. In another example, we demonstrated the efficient photocatalytic H_2 production from a noble-metal-free artificial photocatalytic system, consisting of ultrathin CdS nanosheets as the photosensitizer and Ni-based complexes (**15-18**) (see **Fig.8b**) as the molecular catalysts.[56] In this study, we found that the enhancement in the CdS/Ni-based complexes hybrid system relied on their unique morphological and structural features, which not only can offer a high specific surface area and a large number of active sites for harvesting more photons and absorbing the catalyst molecules, but also can enhance the reducing power for proton reduction and facilitate the transfer and separation of photogenerated charge carries. Under optimal conditions and visible light irradiation (λ>420 nm), the CdS/Ni-based complex **15** hybrid system can generate over 28000 TON of H_2 (with respect to complex **15**) with a stability of over 90 h in the ethonal/water mixture solution (pH 12.5) in the presence of triethylamine as the SED.

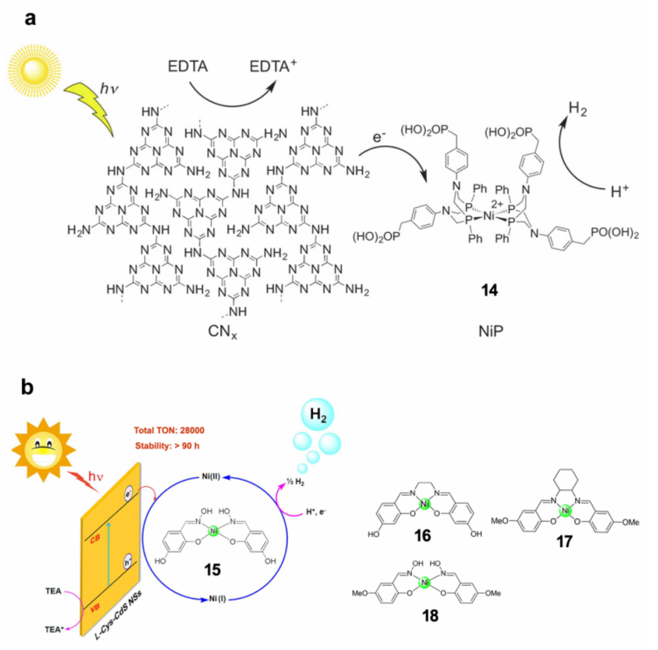


Fig. 8 (a) Schematic representation of the photo-H_2 production with CN_x and NiP **14** in aqueous EDTA solution. (b) Schematic representation of the photo-H_2 production with CdS nanosheets and Co-based commplexes **15-18** in the presence of TEA. (a) Reproduced with permission from ref. 55. Copyright 2014, John Wiley and Sons. (b) Reproduced with permission from ref. 56. Copyright 2015, John Wiley and Sons.

Some Ni-based complexes with water-soluble organic ligands could be generated through the *in situ* coordination reaction between Ni^{2+} ions and the ligand molecules in purely aqueous solution without needing a large amount of toxic organic solvent and complicated procedures. These *in situ* formed Ni-based complexes can be directly used as molecular catalysts for photocatalytic H_2 generation by introduction of suitable semiconductor photosensitizers.[59-61]

One important example of coupling *in situ* formed Ni-based molecular catalysts to semiconductor photosensitizer was reported in 2012 by Krauss and co-workers, in which a water-soluble Ni-based complex, Ni^{2+}-DHLA (DHLA=dihydrolipoic acid), could be synthesized through *in situ* coordination reaction between Ni^{2+} precursor and DHLA molecules in water.[59] With the use of DHLA stabilized CdSe nanocrystals as the photosensitizer, Ni^{2+}-DHLA as the catalyst, and ascorbic acid as the SED, the resulting catalytic system exhibited high efficiency and good stability for photocatalytic H_2 generation (see **Fig. 9**). In optimal conditions, this photocatalytic system can give a TON of more than 600000 (based on Ni catalyst) in 110 h irradiation and an initial TOF of 7000 h^{-1}. Moreover, this system exhibited an excellent stability with a lifetime of over 360 h and achieved QE in water of over 36 % at 520 nm. In another example, Sun *et al.* reported the construction of an efficient photocatalytic system by using organic semiconductor g-C_3N_4 as the photosensitizer and *in-situ* generated complex $[Ni(TEOA)_2]Cl_2$ as the catalyst for visible-light-driven H_2 generation in aqueous solution, without the need for organic solvent or Brønsted acid.[60] Similar studies have been carried out by Chen group by using g-C_3N_4 as a photosensitizer.[61] In their study, the Ni-thiourea-triethylamine molecular catalyst *in situ* formed on the g-C_3N_4 photosensitizer. The resulting hybrid photocatalytic system exhibited a comparable H_2 production with a *g*-C_3N_4-Pt photocatalytic system and a long-term photocatalytic activity.

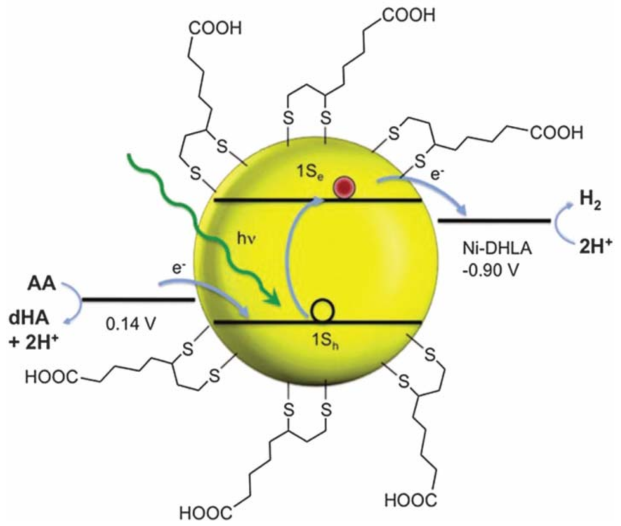


Fig. 9 Schematic diagram of the relevant energies for H_2 production. AA and dHA indicate ascorbic acid and dehydroascorbic acid, respectively. Potentials are shown versus that of an NHE at pH = 4.5. Reproduced with permission from ref. 59. Copyright 2012, The American Association for the Advancement of Science.

Indeed, many other Ni-based complexes have been recently reported for homogeneous photocatalysis for H_2 evolution.[62-69] It is highly worthy to expect that coupling these Ni-based complex molecular catalysts to appropriate semiconductors may create efficient artificial photocatalytic systems for H_2 production.

5. Conclusions and future perspective

H_2 generated from water by artificial solar-driven water-splitting technology possesses enormously promising potentials to be an ideal carbon-neutral energy source in the future, which has fascinated scientists and researchers from the fields of materials science, physical and chemistry. Inspired, but not constrained, by NPS, a variety of artificial photocatalytic systems have been designed and constructed; some of them have shown great promise for photogeneration of H_2 from water. Within this perspective, we have discussed some of the recent progress of artificial photocatalytic systems, especially those comprising semiconductors (including inorganic and some organic polymeric semiconductors) as photosensitizers and earth-abundant transition metal (Fe, Co, Ni)-based complexes as molecular catalysts, for the reductive half-reaction of solar-driven water splitting. As demonstrated by a series of representative examples, these hybrid photocatalytic systems can integrate the advantages of both semiconductor and molecular catalysts and display some unique merits, including the broad and continuous spectral absorption and long durability of semiconductor photosensitizers, the high selectivity, and the tunable structure and high catalytic activity of molecular catalysts, thus achieving efficient H_2 photonegeration. The advances provide promising strategies for rational design and preparation of efficient and stable artificial photocatalytic systems for producing H_2, which has important scientific significance and potential economic and environmental benefits.

Despite the exciting progress made in the past decade, there are still several serious challenges and issues need to be addressed. Firstly, the current state-of-art for photogeneration of H_2 from water using semiconductor photosensitizers and molecular catalysts is still far from being commercially feasible. Thus, it remains a great challenge to construct highly efficient hybrid artificial photocatalytic systems capable of producing molecular H_2 fuel at a scale and production/operating cost that are comparable to conventional fossil fuels. Secondly, stability and durability is another key issue, with reported lifetimes for artificial hybrid catalytic systems ranging from several hours to several days during photocatalytic reactions. Despite using semiconductor to replace organic dyes as the photosensitizer may overcome the poor stability of photosensitizers, molecular catalysts also typically suffer from decomposition or degradation during reaction, resulting in the deactivation of the catalytic systems. Thirdly, the air-sensitivity is an important concern for many reported transition metal complexes serving as water reducing catalysts. In catalytic reaction processes, the reduced intermediates of H_2-evolving molecular catalysts generated after accepting one electron from photoexcited photosensitizer are generally air-sensitive due to atmospheric O_2 can rapidly oxidize these intermediates. Therefore, in order to avoid decomposition or deactivation, ideal H_2-evolving molecular catalysts should be able to catalyze proton reduction much faster than oxygenation of the intermediates species. Fourthly, poor water-tolerance and insolubility in water is another issue for many H_2-evolving molecular catalysts. Evidently, water should be the solvent for solar-driven water splitting technology. However, some reported molecular catalysts that exhibit high activities in organic solvents become lowly active even suffer inactivation in the presence of even small amounts of water due to their poor water-tolerance and water solubility, which are not applicable for coupling with practical solar-driven water splitting technology. On the other hand, for the semiconductor photosensitizers, good aqueous dispersion is also a key concern to construct artificial photocatalytic systems that can be operated in aqueous conditions. Fifthly, despite that some experimental and computational studies have been carried out to reveal the detailed mechanism involved in artificial photocatalytic processes, scientific understanding of charge transfer dynamic and mechanism of H_2 formation in these systems are still not fully clear. Sixthly， for these hybrid artificial photocatalytic systems, some key interface reactions, such as the contact between catalyst molecular and semiconductor, and the adhesion behavior of as-formed gas bubbles, which greatly influence the efficiency of the system, received limited attention. For example, the adhesion of as-formed gas bubbles on the semiconductor's surface may block the contact between molecular catalyst and semiconductor, impeding charge transfer between them, and thus compromising the H_2 generation performance. In this regard, the development of superaerophic materials[70-71] seems to be a promising strategy to solve these problems. However, the application of superaerophic materials for artificial H_2 photogeneration is still in its infancy. Additionally, some other issues, such as the toxicity of the raw materials and by-products to human health and the environment, production/operating costs as well as the translation of laboratory-scale investigations into scalable technologies for practical applications, should be taken into accounted when developing artificial photocatalytic systems for H_2 production.

The research in the field of artificial solar-driven water splitting for H_2 generation is still in an early stage. It is well recognized that high efficiency in all of the light absorption, spatial charge separation and catalytic reaction processes is the essential for constructing efficient photocatalytic systems for H_2 generation. Considerably more efforts need to be done to extend the activity, stability and robustness of the artificial photocatalytic systems in the future. Further work should focus on the following aspects: (i) optimize the geometry, composition and structure of the reported organic semiconductor materials to improve their light absorption ability and photostability, and to reduce electron-hole recombination losses; in this regard, several colloid semiconductor materials with quantum-confined shapes, such 0D quantum dots, 1D ultrathin nanowires, and 2D ultrathin nanosheets, are excellent photosensitizer candidates as they usually possess high photoluminescence quantum yields and quantum confinement effects; (ii) some low-cost, earth-abundant, environmentally friendly metal-free organic polymeric semiconductor materials, such as C_3N_4[55, 72-73], deserve more attention; (iii) design and synthesize economically viable biomimetic complexes made of earth abundant elements as molecular catalysts, especially those with high catalytic activity, good water solubility, and excellent oxygen- and water-tolerance; (iv) in-depth theoretical and experimental studies are necessary to reveal the charge carrier dynamics and the H_2 formation mechanism; a good understanding of the charge carrier dynamics will lead to better design of the relative structural factors that result in efficient electron transfer; (v) take the relative interface reactions such as the adsorption of catalyst molecules and the adhesion behavior of as-formed gas bubbles into account when constructing heterogeneous hybrid catalytic systems; (vi) design robust photocatalytic systems for oxidizing water and couple the reductive and oxidative half-reaction to fulfill the removal of the sacrificial donor and to constitute complete artificial photosynthetic water splitting systems for solar energy to chemical energy conversion. It is worthy believing that such achievements in this field will accelerate the development of artificial solar-driven water splitting and contribute to global energy crises and environmental issues in the future, bringing about an energy revolution.

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