Roles of cocatalysts in semiconductor-based photocatalytic hydrogen production

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A photocatalyst is defined as a functional composite material with three components: photo-harvester (e.g. semiconductor), reduction cocatalyst (e.g. for hydrogen evolution) and oxidation cocatalyst (e.g. for oxidation evolution from water). Loading cocatalysts on semiconductors is proved to be an effective approach to promote the charge separation and transfer, suppress the charge recombination and enhance the photocatalytic activity. Furthermore, the photocatalytic performance can be significantly improved by loading dual cocatalysts for reduction and oxidation, which could lower the activation energy barriers, respectively, for the two half reactions. A quantum efficiency (QE) as high as 93 per cent at 420 nm for \(\text{H}_2\) production has been achieved for Pt–PdS/CdS, where Pt and PdS, respectively, act as reduction and oxidation cocatalysts and CdS as a photo-harvester. The dual cocatalysts work synergistically and enhance the photocatalytic reaction rate, which is determined by the slower one (either reduction or oxidation). This work demonstrates that the cocatalysts, especially the dual cocatalysts for reduction and oxidation, are crucial and even absolutely necessary for achieving high QEs in photocatalytic hydrogen production, as well as in photocatalytic water splitting.
1. Introduction

Photocatalytic hydrogen generation, using solar energy to produce H\textsubscript{2}, especially from water splitting, is considered to be a promising technology to address environmental crises and energy shortage [1–5]. Of all renewable energy sources, solar energy is the most abundant on Earth. Solar energy has the potential to power a significant fraction of global energy demand. Solar water splitting as a means of converting solar energy to chemical energy in the form of fuels has received much attention since the 1970s [6]. Approaches to solar water splitting have been explored through heterogeneous photocatalytic reactions based on semiconductor nanoparticles [7], molecular donor–acceptor systems [8] and photovoltaic cells coupled directly or indirectly to electrocatalysts [9]. The photocatalytic water splitting on semiconductor-based heterogeneous photocatalysts, although still with a low efficiency, is regarded as the most promising way for H\textsubscript{2} production.

For water splitting, 2H\textsubscript{2}O → 2H\textsubscript{2} + O\textsubscript{2}, where ΔG° = 237 kJ mol\textsuperscript{−1} (corresponding to a minimum energy requirement of 1.23 eV), the thermodynamically uphill reaction is a non-spontaneous process; thus, photo-energy is required both to store the solar energy in the final products and to overcome the activation energy barrier for the reaction (scheme 1). Most semiconductors act mainly as the photo-harvester, while the catalytic reactions take place usually on catalysts loaded on the semiconductor. These loaded catalysts are termed cocatalysts (a few semiconductors themselves can also show catalytic function while harvesting light). So, generally the photocatalyst is composed of the semiconductor and the cocatalysts. Much progress has been made in setting up a big library of semiconductor materials. Those materials, as light harvesters, have been extended from UV to visible-light regions for solar light usage during recent decades [4].

A photocatalytic process can be schematically described as in scheme 2. When the semiconductor material absorbs photons with energy equal to or higher than its band gap, electrons are excited from the valence band into the conduction band, leaving holes in the valence band (1.1). And then reduction half reaction (1.2), e.g. for H\textsubscript{2} evolution (1.3), and oxidation
half reaction (1.4), e.g. O₂ evolution for overall water splitting (1.5), occur on the surface of the semiconductor or cocatalyst.

\[
\text{Photoexcitation: semiconductor } \overset{h\nu}{\rightarrow} e^- + h^+ \tag{1.1}
\]

\[
\text{Reduction half reaction: } e^- + A \rightarrow A^- \text{ (where A is an electron acceptor)} \tag{1.2}
\]

\[
2e^- + 2H^+ \rightarrow H_2 \tag{1.3}
\]

\[
\text{Oxidation half reaction: } h^+ + D \rightarrow D^+ \text{ (where D is an electron donor)} \tag{1.4}
\]

\[
4h^+ + 2H_2O \rightarrow O_2 + 4H^+ \tag{1.5}
\]

\[
\text{Recombination: } e^- + h^+ \rightarrow \text{light or heat} \tag{1.6}
\]

For overall water splitting ((1.1), (1.2) and (1.5)), the most efficient photocatalytic system in the visible light region reported so far is Rh₂₋ₓCrₓO₃ loaded (Ga₁₋ₓZnₓ)(N₁₋ₓOₓ) [10], with a quantum efficiency (QE) of 5.9 per cent at 410 nm. The corresponding energy conversion efficiency is less than 1 per cent. So, there is still a long way to go for the practical application of solar energy to chemical energy conversion. Fundamental researches are urgently needed for this technology to attain its full potential. Sacrificial donors are usually used for mechanistic study since they allow one to examine the individual light-driven half reaction, reduction or oxidation, respectively. High QE for H₂ production (e.g. even higher than 90% [11]) was found with sacrificial electron donors, such as EDTA, methanol, sulfide and sulfite (1.4). To achieve a high QE, undesirable photogenerated electron–hole recombination (1.6) must be prohibited. In addition to the necessary superior quality of the semiconductor, cocatalysts are considered to be indispensable for a high QE. This article presents our recent progress in developing cocatalysts for photocatalytic H₂ production, a half reaction of water splitting. The principles also hold true for overall water splitting and general artificial photosynthesis.

2. Experimental

(a) Preparation of photocatalysts

CdS nanoparticles were synthesized according to [11] by a facile and mild approach, in which the primary nanocrystalline CdS was obtained by precipitation and a subsequent hydrothermal treatment.

Y₂Ta₂O₅N₂ was obtained by nitriding YTaO₄ powder under a flow of ammonia gas (flow rate: 40 ml min⁻¹) at 1123 K for 15 h in a quartz tube. YTaO₄ was synthesized by a solid-state reaction method [12]. Y₂O₃ and Ta₂O₅ powder were mechanically mixed in stoichiometric quantities, and then calcined at 1073 K for 2 h and 1473 K for 10 h in air. The Y₂Ta₂O₅N₂ powder was yellowish-green in colour.
Colloidal MoS\textsubscript{2} was prepared by solvothermal treatment of (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} dissolved in methanol in the presence of polyvinylpyrrolidone (PVP, K27–33) as a protecting polymer and N\textsubscript{2}H\textsubscript{4} \cdot H\textsubscript{2}O (50\%) as a reductant \[13\]. In a typical process, (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} (2.5–12.5 mmol) was dissolved in methanol (25 ml) containing N\textsubscript{2}H\textsubscript{4} \cdot H\textsubscript{2}O (0.02–0.1 ml) and an appropriate amount of PVP. The solution was added to a Teflon-lined stainless steel autoclave with a capacity of 30 ml and then heated at temperatures from 373 to 473 K for 3 h to obtain the colloidal MoS\textsubscript{2}.

Co(\text{III})(\text{dmgH})\textsubscript{2}pyCl was synthesized as follows \[14\]: to a hot solution (343 K) of 2.5 g (0.0105 mol) of CoCl\textsubscript{2} \cdot 6H\textsubscript{2}O, 2.75 g (0.0235 mol) of dimethylglyoxime (dmgH) and 0.42 g (0.0105 mol) of NaOH in 100 ml of 95 per cent ethanol, 0.86 g (0.0105 mol) of pyridine was added under N\textsubscript{2} atmosphere. After cooling to 293 K, a stream of air was blown through the solution for 30 min. The reaction mixture was then allowed to stand for 60 min at 293 K, and during this period the product was crystallized in the solution. The brown crystals were collected by filtration, washed successively with water, ethanol and diethyl ether, and extracted with acetone.

The loading of metals on CdS was made through photodeposition or impregnation at room temperature and reduction in H\textsubscript{2} stream at 473 K for 2 h \[11\]. The loading of metal sulfide (Ru\textsubscript{2}S\textsubscript{3}, Rh\textsubscript{2}S\textsubscript{3} and PdS) was made by an \textit{in situ} addition of M\textsuperscript{n+} (M = Rh, Ru, Pd) solution into a dispersion of CdS in Na\textsubscript{2}S aqueous solution. The co-loading of Pt and these metal sulfides on CdS was through a similar way except for an extra addition of an H\textsubscript{2}PtCl\textsubscript{6} aqueous solution (0.0019 M). The co-loading of metals with PdS was done by an \textit{in situ} deposition of PdS on M/CdS. MoS\textsubscript{2} was loaded on CdS by an impregnation method from aqueous solution of (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4}, followed by a treatment at temperatures from 443 to 773 K in H\textsubscript{2} for 2 h \[15\].

Pt and Ru were photodeposited on the Y\textsubscript{2}Ta\textsubscript{2}O\textsubscript{5}N\textsubscript{2} catalyst \textit{in situ} from precursors of H\textsubscript{2}PtCl\textsubscript{6} \cdot 6H\textsubscript{2}O and RuCl\textsubscript{3} \cdot 3H\textsubscript{2}O.

**b) Characterization of photocatalysts**

High-resolution transmission electron microscopy (HRTEM) images were obtained on Tecnai G\textsuperscript{2} F30 S-Twin (FEI Company) microscope with an accelerating voltage of 300 kV. The photoluminescence spectra were recorded on a FLS 920 fluorescence spectrometer (Edinburgh Instruments). A 355 nm continuous-wave laser (~8 mW) was used as the excitation source. The photocurrent–voltage measurements were performed at room temperature on an EG&G 2273A potentiostat/galvanostat with a standard three-electrode configuration connected with a 100 W Xe lamp. The as-prepared films were used as the working electrode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. 0.5 M Na\textsubscript{2}S–0.5 M Na\textsubscript{2}SO\textsubscript{3} aqueous solution (pH = 13.6) was used as the supporting electrolyte. The illuminated area of the working electrode was about 0.5 \times 0.5 cm\textsuperscript{2}. The photoelectrochemical properties for the CdS/fluorine-doped tin oxide (FTO) and M/CdS/FTO electrodes were evaluated by linear sweep voltammetry with a sweeping rate of 20 mV s\textsuperscript{-1}.

**c) Photocatalytic H\textsubscript{2} production**

The photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. Photocatalyst was dispersed in 200 ml of aqueous solution containing sacrificial reagents (e.g. Na\textsubscript{2}S and Na\textsubscript{2}SO\textsubscript{3}, lactic acid, triethanolamine (TEOA)) or H\textsubscript{2}S dissolved in TEOA non-aqueous solution. The suspension was then thoroughly degassed and irradiated by a 300 W Xe lamp (ILC Technology; Cermax LX-300), which is equipped with an optical filter (HOYA, \lambda > 420 nm) to cut off the light in the ultraviolet region. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the photocatalytic reaction. The amount of hydrogen evolved was determined with on-line gas chromatography (Agilent 7890A, MS-5 A column, TCD, Ar carrier).

The apparent QE was measured under the same photocatalytic reaction condition with irradiation light at 420 nm by using combined band-pass (Kenko) and cut-off filters (HOYA) and
a 300 W Xe lamp and the QE was calculated according to

\[
\text{QE} (\%) = \frac{\text{no. reacted electrons}}{\text{no. incident photons}} \times 100 = \frac{\text{no. evolved H}_2 \text{ molecules} \times 2}{\text{no. incident photons}} \times 100. \tag{2.1}
\]

The number of incident photons was \(3.54 \times 10^{17}\) photons s\(^{-1}\), which was measured using a calibrated Si photodiode (Hamamatsu S2281).

3. Results and discussion

(a) Noble metals as reduction cocatalysts for photocatalytic H\(_2\) production

In heterogeneous photocatalytic systems, typically semiconductors loaded with noble metals, each semiconductor particle can be pictured as a ‘short-circuited’ micro-electrochemical cell in which noble metals are the cathode where protons from solution combine with electrons to form hydrogen atoms and then H\(_2\) at the metal surface. Oxidation reaction often occurs on the semiconductor itself as the anode. Noble metals are usually loaded as the cocatalysts because of their better conductivity, lower overpotential and higher catalytic activity for H\(_2\) evolution than the semiconductors.

The work functions of the noble metals (e.g. those of Pt, Pd, Au, Rh, Ru and Ag are 5.65, 5.55, 5.10, 4.98, 4.71 and 4.64 eV, respectively) are usually greater than the work functions of many semiconductors (e.g. TiO\(_2\), 4.2 eV)\([16]\). Taking TiO\(_2\), as an example, a Schottky barrier can be formed at the metal/TiO\(_2\) interface when TiO\(_2\) is loaded with these metals. The barrier could reduce the possibility of \(e^-\)–\(h^+\) recombination. CdS is one of the well studied semiconductors for its relatively narrow band gap, 2.4 eV, being able to absorb a wide range of solar light, and a flat-band potential, \(-0.9\) V versus normal hydrogen electrode, negative enough to reduce H\(^+\).

An earlier report on CdS as photocatalyst for H\(_2\) evolution was in 1981\([17]\), when H\(_2\) could be produced from EDTA aqueous solution with \(\text{QE} = 4\) per cent on Pt/CdS powder under visible light irradiation. In 1984, Reber and co-workers showed that the QE of CdS for H\(_2\) production could be increased to 37 per cent in aqueous Na\(_2\)S/Na\(_2\)SO\(_3\) by doping CdS with 15 mol\% ZnS and using Pt as cocatalyst. Bao et al.\([18]\) realized a QE of about 60 per cent at 420 nm for H\(_2\) evolution from Na\(_2\)S/Na\(_2\)SO\(_3\) solution by loading 13 wt\% of Pt on nanoporous CdS. The activity depends on the Pt-loading content, the amount of catalyst and the concentration of sacrificial regents, and was attributed to an efficient charge separation, a fast transport of the photogenerated carriers and a fast photochemical reaction at the CdS/electrolyte interface\([18]\). Subsequently, we reported a QE of 50 per cent at 420 nm for H\(_2\) evolution from Na\(_2\)S/Na\(_2\)SO\(_3\) solution on CdS synthesized by a hydrothermal method through loading less than 1 wt\% of Pt\([11]\).

The loading of two noble metals as cocatalysts together sometimes shows a synergistic effect in photocatalysis. The rate of H\(_2\) evolution in the presence of methanol over Y\(_2\)Ta\(_2\)O\(_5\)N\(_2\) displayed an enhancement when Pt was photodeposited on Ru/Y\(_2\)Ta\(_2\)O\(_5\)N\(_2\) (figure 1)\([12]\). Although Pt generally functions as a cocatalyst for photocatalytic reduction of protons to H\(_2\), 0.15 wt\% Pt/Y\(_2\)Ta\(_2\)O\(_5\)N\(_2\) exhibited very low H\(_2\) evolution activity. In contrast, H\(_2\) evolution was remarkably enhanced by the addition of 0.25 wt\% Ru to Y\(_2\)Ta\(_2\)O\(_5\)N\(_2\). The activity of H\(_2\) evolution was further increased by co-loading both Pt and Ru on the Y\(_2\)Ta\(_2\)O\(_5\)N\(_2\) catalyst, increasing with the amount of Pt to a maximum for a catalyst of Y\(_2\)Ta\(_2\)O\(_5\)N\(_2\) with 0.15 wt\% Pt and 0.25 wt\% Ru. This rate is 22 times greater than that for 0.15 wt\% Pt/Y\(_2\)Ta\(_2\)O\(_5\)N\(_2\). The remarkably high activity for photocatalytic H\(_2\) evolution achieved by the presence of both Pt and Ru as noble metal cocatalysts is attributable to facile electron migration from the conduction band of Y\(_2\)Ta\(_2\)O\(_5\)N\(_2\) to the Pt–Ru cocatalysts, thereby retarding the possibility of electrons recombining.
Figure 1. Dependence of the rate of H₂ evolution from an aqueous ethanol solution on the atomic ratio of Pt to Ru on Y₂Ta₂O₅N₂ catalyst under visible-light irradiation. Catalyst, 0.3 g; ethanol solution (20% v/v), 200 ml; light source, 300 W Xe lamp (λ > 420 nm). (Online version in colour.)

with holes in the valence band and improving the charge separation efficiency. This promoting effect is much greater when both Pt and Ru are present as cocatalysts compared with each single cocatalyst.

(b) Heterojunctions between cocatalyst and light harvester enhancing the H₂ production activity

By loading MoS₂ as a cocatalyst, the rate of H₂ evolution under visible light irradiation on CdS is significantly enhanced when using lactic acid solution as the sacrificial reagent [15]. The activity of MoS₂/CdS is even higher than that of Pt/CdS under the same reaction conditions (table 1). The HRTEM images show that the cocatalyst MoS₂ deposited on the CdS surface has a typical layered structure (figure 2). The number of the MoS₂ slabs deposited on CdS is about 1–6, and the MoS₂ slabs are intimately deposited on the surface of CdS. Surprisingly, MoS₂ (0.0005 g)/CdS (0.1 g) shows much higher activity than the mixture of CdS (0.1 g) and MoS₂ (0.005 g) even though the amount of MoS₂ deposited on CdS is much less (table 2). This fact indicates that the intimate contact between CdS and MoS₂ is beneficial for the charge transfer from semiconductor (CdS) to the cocatalyst (MoS₂). Although Pt usually shows superior performance than MoS₂ for the activation of H₂ in electrochemical system [19,20], the rate of H₂ evolution for 0.2 wt% Pt/CdS is still lower than that for 0.2 wt% MoS₂/CdS, suggesting that the junction formed between cocatalyst and CdS is crucial for the electron transfer from CdS to MoS₂, consequently enhancing the photocatalytic activity. The good matching between the structures and electronic configurations of MoS₂ and CdS together with the high H₂ activation ability of MoS₂ is responsible for the high activity of MoS₂/CdS catalyst. The junction between MoS₂ and CdS is readily formed because both components have the common S²⁻ on the interface, which might bridge the MoS₂ and CdS in the interface. Similar results were found for WS₂/CdS, which also shows high activity in H₂ production where WS₂ was used as a cocatalyst for H₂ production [21].

Very recently, MoS₂ was reported by Frame et al. [22] to be an effective cocatalyst for H₂ evolution from aqueous sodium sulfite/sulfide solution over CdSe nanoribbon photocatalyst
Figure 2. (a) HRTEM image of 1 wt% MoS$_2$/CdS prepared at 773 K and (b) magnified HRTEM image of the selected frame from image (a).

Table 1. The rate of H$_2$ evolution on CdS loaded with 0.2 wt% of different cocatalysts. Catalyst (0.1 g); 10 vol% lactic solution (200 ml); light source, Xe lamp (300 W).

<table>
<thead>
<tr>
<th>cocatalyst</th>
<th>MoS$_2$</th>
<th>Pt</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>activities ($\mu$mol h$^{-1}$)</td>
<td>550</td>
<td>420</td>
<td>360</td>
<td>250</td>
<td>200</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 2. The rate of H$_2$ evolution on MoS$_2$, CdS, MoS$_2$/CdS and mechanical mixture of MoS$_2$ and CdS under visible light ($\lambda > 420$ nm). 10 vol% lactic solution (200 ml); light source, Xe lamp (300 W).

<table>
<thead>
<tr>
<th>photocatalyst</th>
<th>MoS$_2$ (0.005 g)/CdS (0.1 g)</th>
<th>MoS$_2$ (0.05 g) + CdS (0.1 g)</th>
<th>CdS (0.1 g)</th>
<th>MoS$_2$ (0.1 g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>activities ($\mu$mol h$^{-1}$)</td>
<td>500</td>
<td>30</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

under visible light irradiation, with a QE of 9.2 per cent at 440 nm. When the nanoribbons are chemically linked to MoS$_2$ nanoplates that were obtained by exfoliation and ultrasonication of bulk MoS$_2$, the activity increases by almost four times, depending on the loading amount of MoS$_2$. Cyclic voltammetry reveals that the enhancement from the MoS$_2$ nanoplates is owing to a reduction of the H$_2$ evolution overpotential by the cocatalyst MoS$_2$. In contrast, chemical linkage of Pt nanoparticles to the nanoribbons does not increase the photocatalytic activity.

(c) Colloidal or molecular complexes as H$_2$ evolution cocatalysts

MoS$_2$ was then successfully applied to molecular systems by preparing colloidal nanoparticles [13]. Molecular systems usually consist of a transition metal complex such as Ru(bpy)$_2^{2+}$ (bpy = 2,20-bipyridine) as photosensitizer, an electron transfer relay and a H$_2$ evolution catalyst. The catalysts used in these systems are usually colloidal Pt or Pt complexes. Here, inexpensive colloidal MoS$_2$ nanoparticles have been shown as an efficient H$_2$ evolution cocatalyst in a Ru(bpy)$_3^{2+}$-based molecular system (scheme 3). Under visible light irradiation, catalytic H$_2$ generation with a turnover number of 100 based on Ru(bpy)$_3^{2+}$ has been successfully realized in a system consisting of colloidal MoS$_2$, Ru(bpy)$_3^{2+}$ and ascorbic acid (H$_2$A). Colloidal MoS$_2$ nanoparticles exhibit superior efficiency than the supported MoS$_2$/Al$_2$O$_3$ catalyst in catalysing H$_2$ evolution in the molecular system, which has shown excellent catalytic activity in traditional heterogeneous catalysis. The superior catalytic activity of colloidal MoS$_2$ nanoparticles could be owing to its small particle size and high dispersibility leading to facile efficient charge transfer between MoS$_2$ and the reactant. This result also suggests the facile transfer of electrons from light harvester to nanoparticle cocatalysts is important for achieving the high photocatalytic activity.
In recent years, molecular photocatalytic systems based on biomimetic hydrogenase have been assembled for H\textsubscript{2} evolution, where a molecular catalyst actually acts as the cocatalyst. Cobaloximes, which possess high electrocatalytic hydrogen evolution activity, were studied as functional models of hydrogenases [23,24]. We employed cobaloximes (Co(III) complexes) as H\textsubscript{2} evolution cocatalysts in heterogeneous photocatalytic H\textsubscript{2} production by using semiconductor (CdS) as the light-harvester in the presence of TEOA as sacrificial electron donor [14]. This artificial photocatalytic system shows high hydrogen evolution activity (turnover number up to 171 based on Co(III)(dmgH)\textsubscript{2}pyCl) under visible light irradiation. The apparent QE for the hybrid photocatalytic system in acetonitrile solution is estimated to be 9.1 per cent at 420 nm. The interfacial electron transfer from photoexcited CdS to Co(III) complexes is very efficient although Co(III) complexes are just physically adsorbed on CdS. The efficient electron transfer, the broad electronic absorption character of CdS, as well as the H\textsubscript{2} evolution ability of Co(III) complexes account for the high photocatalytic activity of this hybrid photocatalytic system. The strategy of using a semiconductor to replace the traditional dyes or organometallic complexes as light-harvesters can overcome the drawbacks of narrow spectral absorption and poor stability of the organometallic complex photosensitizers. The results show that biomimetic molecular catalysts display high activities even fabricated in the inorganic photocatalytic system.

Recently, this model was extended to hydrogenase mimic [(\mu-SPh-4-NH\textsubscript{2})\textsubscript{2}Fe\textsubscript{2}(CO)\textsubscript{6}] (referred to as [Fe\textsubscript{2}S\textsubscript{2}]) as the cocatalyst for H\textsubscript{2} evolution, when semiconductor (ZnS) acts as a light-harvester and H\textsubscript{2}A as the electron donor [25]. Photocatalytic H\textsubscript{2} production with more than 2607 turnovers (based on [Fe\textsubscript{2}S\textsubscript{2}]) and an initial turnover frequency of 100 h\textsuperscript{−1} can be achieved through the efficient transfer of photogenerated electrons from ZnS to [Fe\textsubscript{2}S\textsubscript{2}] complex. This is the highest H\textsubscript{2} evolution efficiency based on [Fe\textsubscript{2}S\textsubscript{2}] catalysts so far. The activity keeps stable even after an irradiation of 38 h. The present work further demonstrates the feasibility of using semiconductor as light-harvester and hydrogenase mimics as H\textsubscript{2} evolution cocatalyst.

\textbf{(d) Dual cocatalyst for reduction and oxidation half reactions}

As mentioned above, metal sulfides could be employed as cocatalysts on sulfide semiconductors (e.g. CdS) because they both have the common S\textsuperscript{2−}. The effects of different noble metals and noble metal sulfides or their combinations as cocatalysts on CdS semiconductor for photocatalytic H\textsubscript{2} production were investigated in the presence of sulfide and sulfite [26]. CdS alone exhibited negligible photocatalytic activity for H\textsubscript{2} evolution [11], while significant activities were exhibited when various noble metals (Pt, Ru, Rh, Au) and noble metal sulfides (PdS, Rh\textsubscript{2}S\textsubscript{3}, Ru\textsubscript{2}S\textsubscript{3}) were loaded as cocatalysts (figure 3). Pt/CdS shows the highest activity among the noble metals investigated as cocatalysts. This could be explained in terms of the large work function and low overpotential of Pt for proton reduction (i.e. low activation energy) [27]. The loading of noble metal sulfides also shows marked enhancement, with PdS/CdS showing the highest. It is even
higher than that of Pt/CdS. Interestingly, the combination of Pt with other metal sulfides and PdS with other noble metals as dual cocatalysts show further enhancement in activity compared with any single cocatalyst loaded. Among them, the co-loading of Pt and PdS displays the most effective combination, achieving a QE of 93 per cent at 420 nm for H₂ production [11].

In order to understand well why the dual cocatalysts can give extremely high QE, systematic investigation was conducted. The properties of the dual cocatalysts obtained from band potential analyses [11] and photoelectrochemical features (figure 4) indicate that the hole transfer from CdS to PdS and electron transfer from CdS to Pt are favourable processes. Particularly speaking, PdS acts as an oxidation cocatalyst, i.e. supplying CdS with electrons through oxidizing the sacrificial reagents of S²⁻ and (or) SO₂³⁻. Therefore, the simultaneous existence of PdS acting as an oxidation cocatalyst and Pt acting as a reduction cocatalyst is supposed to be synergistically working for the efficient separation and transfer of the photoexcited electrons and holes, thus contributing to the extremely high QE. X-ray photoelectron spectroscopy results showed that part of the PdS is reduced to metallic Pd during photocatalytic reactions [11]. Hence, the high activity of PdS/CdS (figure 3) is owing to the coexistence of PdS and Pd acting as oxidation and reduction cocatalysts, respectively.

When Pt alone was loaded as the reduction cocatalyst, the oxidation reaction may take place on CdS surface, but CdS itself is not an active catalyst for the oxidation of sulfide. So one expects to obtain higher activity when alternative oxidation active sites are introduced to the Pt/CdS. The result just shows that the activity is remarkably enhanced when Pt is co-loaded with metal sulfides, e.g. Rh₂S₃, Ru₂S₃ and PdS. These results further demonstrate that the dual cocatalysts, Pt and metal sulfides show a strong synergistic effect on the photocatalytic activity.

A main shortcoming for CdS (and other sulfide or nitride semiconductors) photocatalyst is the photo-instability, which is owing to photocorrosion (CdS + 2h⁺ → Cd²⁺ + S) [18]. The reaction time courses (figure 5) for H₂ evolution showed that the rate of H₂ production over
Figure 4. Current density–potential ($J$–$E$) curves in the dark (solid line) and under illumination (dashed line). Light source: 100 W Xe lamp. (Online version in colour.)

Figure 5. Time courses of $\text{H}_2$ evolution under visible irradiation over Pt/CdS, PdS/CdS, and Pt–PdS/CdS. 0.5 M Na$_2$S–0.5 M Na$_2$SO$_3$ aqueous solution (200 ml); light source: Xe lamp (300 W) with an optical filter ($\lambda > 420$ nm). (Online version in colour.)

Pt/CdS gradually decreases and an evident drop in the activity is found after an irradiation for 7 h [11]. However, PdS/CdS and Pt–PdS/CdS exhibit very stable activities during irradiation for at least 25 h. Actually, lifetime experiments showed that PdS/CdS and Pt–PdS/CdS exhibit stable activity even after the photocatalytic reaction for longer than 100 h. X-ray diffraction, TEM and fluorescence characterizations show that the physical properties of the photocatalysts keep unchanged after long time reactions [26]. Thus, PdS as the oxidation cocatalyst can protect CdS from photocorrosion, and can make the PdS/CdS and Pt–PdS/CdS very stable under the photocatalytic reaction conditions. This might be general for most photocatalysts, where the semiconductors are easily oxidized by the photogenerated holes, while efficient oxidation
The cocatalyst can protect the semiconductor from photo-oxidation by efficiently removing holes from the semiconductor via the oxidation cocatalyst. The idea was verified recently on GaN:ZnO by prior co-loading of RuO2 and on TaON photoanode by loading highly dispersed CoOx nanoparticles as water oxidation cocatalysts, which results in a stable photocatalytic water splitting activity and a stable photocurrent, respectively [28,29].

The photoexcited energy/electron transfer and recombination processes can be investigated by photoluminescence (PL) spectroscopy [30]. We then employed PL spectra to verify whether the cocatalyst can prohibit the charge recombination. In the present work, PL features of CdS with or without cocatalysts were investigated aiming to study their properties under actual photocatalytic reaction conditions [26]. Figure 6 shows the PL spectra of CdS, Pt/CdS, PdS/CdS and Pt–PdS/CdS powder samples. The CdS powder samples display an intense emission band centred at 522 nm and a weak emission band centred at 739 nm. The bands at 522 and 739 nm are attributed to band-edge emission and trap state-related luminescence, respectively [31]. The fact that the band at 739 nm is much weaker than the band at 522 nm clearly suggests that the CdS prepared under optimized conditions has very few defects. The fluorescence intensities are quenched dramatically by loading individual Pt or PdS cocatalyst and even further by co-loading both cocatalysts, Pt and PdS, on CdS. These results suggest that the cocatalysts can effectively reduce the recombination processes of photogenerated carriers. In situ PL shows a similar change trend after loading the Pt and PdS cocatalysts, namely the cocatalysts reduce the fluorescence efficiently in the reaction solution [26].

Figure 7 displays the quenching efficiency of fluorescence intensity of CdS after loading with cocatalysts in comparison to that of CdS without cocatalysts. The QE is also shown for comparison. It is interestingly found that the quenching efficiency of fluorescence intensity owing to band-edge emissions varying with cocatalysts shows a parallel trend with the QE of the photocatalytic hydrogen production. Amazingly, about 94 per cent of band-edge emission of CdS is quenched by loading Pt–PdS dual cocatalysts, which corresponds to 93 per cent of QE. This correlation leads us to the conclusion that the high QE of the Pt–PdS/CdS photocatalyst is essentially owing to the effective prohibition of the recombination processes with the cocatalysts. The fact that the quenching efficiency of PdS/CdS is greater than that of Pt/CdS might imply that the oxidation reaction is more efficient than reduction for prohibiting the recombination of photogenerated carriers. In addition, it can be seen from the comparison with the normalized PL spectra that the bands for the intrinsic fluorescence of PdS/CdS and Pt–PdS/CdS become narrower than those of Pt/CdS and CdS (figure 8) [26]. This means that luminescence processes...
related to shallow trap states of CdS are also efficiently quenched when PdS is loaded on CdS, and that might be an additional contribution to the high QE in photocatalytic H₂ production.

The effect of Pt and PdS co-loaded on other sulfide semiconductors shows that the photocatalytic activities are all in the order of Pt/MS < PdS/MS < Pt–PdS/MS, with the trend similar to those for CdS [26]. Other combinations of metals and metal sulfides acting as reduction cocatalysts and oxidation cocatalysts on CdS do not exhibit so high an enhancing effect as Pt and PdS. Therefore, a proper combination of reduction cocatalyst and oxidation cocatalyst to work in harmony is absolutely necessary for high QE.

This work demonstrates a successful strategy to improve the photocatalytic activity and stability by loading dual cocatalysts, respectively, for reduction and oxidation. In the work on H₂ production from photocatalytic splitting of H₂S (H₂S → H₂ + S), the activity of Pt–PdS/CdS was even greater than that for the simple sum of Pt/CdS and PdS/CdS [32]. A similar case was reported by Zhang et al. [33] that modification of oxysulfides, such as Sm₂Ti₂S₂O₅ and Gd₂Ti₂S₂O₅, with nanoparticulate Rh or Pt (reduction cocatalyst) and Ag₂S (oxidation cocatalyst) resulted in enhanced H₂ production activity using Na₂S and Na₂SO₃ as electron donors,
compared with that using catalysts modified with Rh, Pt or Ag$_2$S. This strategy has also been applied to GaN:ZnO co-loaded with Rh/Cr$_2$O$_3$ and Mn$_3$O$_4$, which shows an enhancement in water splitting activity [34]. Reece et al. [2] reported that solar water splitting at an efficiency of 2.5 per cent was achieved for a cell consisting of a triple junction, amorphous silicon photovoltaic interfaced to hydrogen- and oxygen-evolving catalysts. The cocatalysts for reduction and oxidation reactions are made from an alloy of Earth-abundant metals (NiMoZn) and a cobalt|borate catalyst, respectively.

### 4. Conclusion and prospects

A highly active photocatalyst, particularly for water splitting, generally requires photo-harvester and dual cocatalysts, where efficient cocatalysts should be in harmony with semiconductors including compatible structure and suitable Fermi level and band level. During the photo-excitation of semiconductor, the electrons are rapidly trapped by the reduction cocatalyst and might eventually recombine with a photogenerated hole in the catalytic system. On the one hand, the cocatalyst loaded on the semiconductor can provide a built-in electric field between cocatalyst and semiconductor because of the chemical potential difference. The built-in electric field can thus facilitate the separation of electron–hole pairs, induce faster carrier transfer, prohibit the recombination and promote the redox reactions. On the other hand, the cocatalysts can act as trapping sites for photogenerated carriers, i.e. electrons for reduction cocatalysts and holes for oxidation cocatalysts (transferring electrons from external electron donors to semiconductor). The major role of cocatalysts is to make chemical reactions happen at lower activation energy, as most catalysts do in chemical reactions. This is also the strategy implemented in natural photosynthesis, where water oxidation is catalysed by the Mn$_4$O$_x$Ca cluster of photosystem II at low overpotentials [35].

Noble metals have extensively been investigated as reduction cocatalysts for photocatalytic H$_2$ production, with the effects depending on the ‘matching’ of semiconductors and the cocatalysts, and the reaction systems. Exploring cheap, Earth-abundant materials instead of noble metals is required for the wide application of photocatalysis. Several successful examples have demonstrated the possibility. Biomimetic molecular catalysts have shown potential for application in heterogeneous photocatalysis as cocatalysts. The employment of oxidation cocatalysts and especially the co-loading of reduction and oxidation cocatalysts simultaneously have shown remarkable improvement for photocatalytic activity. As demonstrated for Pt–PdS/CdS, a QE approaching that of the primary course of the natural photosynthesis (usually more than 95%) can be achieved by loading dual cocatalysts.

Compared with the H$_2$ production half reaction, the four-electron water oxidation to O$_2$ is a more challenging task and is often the rate-determining step of overall water splitting. Water oxidation usually has quite high overpotential. And the low efficiency over visible-light-driven semiconductors for overall water splitting is expected to be improved through assembling suitable oxidation cocatalysts. Exploration of active cocatalysts for water oxidation is urgently needed to achieve a highly efficient visible-light-driven water splitting.

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