

# Journal of Materials Chemistry A

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**Molecular Cobalt-Salen Complexes as Novel Cocatalysts for Highly Efficient Photocatalytic Hydrogen Production over CdS Nanorods Photosensitizer under Visible Light**

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**Abstract.** An efficient photocatalytic system is highly demanded for the production of hydrogen fuel through water splitting. Herein we report an artificial photocatalytic system made of low-cost materials for high-performance H<sub>2</sub> production in water. The new system contains semiconductor (CdS nanorods) as the photosensitizer, a cobalt-salen complex as H<sub>2</sub> evolution cocatalyst, and Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as sacrificial electron donors. Under optimal conditions, the highest hydrogen evolution turnover number reached 64700 after 37 hours and the rate was 106 μmol·h<sup>-1</sup>·mg<sup>-1</sup>, which is much higher than when using CdS NRs and also is among the best for photocatalytic systems using molecular cocatalysts for H<sub>2</sub> production. The highest apparent quantum yield (AQY) was ~29 % at 420 nm. Steady state photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) decay spectra revealed that the system allows effective electron transfer from the excited CdS NRs to the cobalt-salen complex for highly efficient H<sub>2</sub> production.

**Keywords.** Photocatalysis; Hydrogen Production; Molecular Catalyst; Cobalt-Salen Complex; Visible Light

## 1. Introduction

Efficient Hydrogen ( $H_2$ ) production via water splitting is believed to be an ideal pathway to store solar energy for a future supply of clean energy.<sup>1-2</sup> In nature, three typical iron-based hydrogenases ([FeFe] hydrogenase,<sup>3-4</sup> [FeNi] hydrogenase,<sup>3</sup> and [Fe] only hydrogenase<sup>5</sup>) serve as efficient catalysts to highly promote proton reduction for  $H_2$  production. To mimic the function of the natural process, many kinds of molecular catalysts have been reported in the literature for photocatalytic  $H_2$  production, such as cobalt (II) complexes (such as cobaloximes,<sup>6</sup> cobalt dithiolenes,<sup>7</sup> cobalt polypyridyl complexes.<sup>8</sup>), nickel (II) complexes (such as nickel phosphines<sup>9-10</sup> and nickel pyridinethiolate complexes<sup>11</sup>), and iron (II) complexes (such as iron pentacarbonyl<sup>12</sup> and iron carbonyl phosphines<sup>13</sup>). In a typical reaction system, these molecular catalysts are combined with a molecular photosensitizer and a sacrificial electron donor. The well-known molecular photosensitizers include ruthenium (II) trisbipyridyl complexes,<sup>14-15</sup> platinum terpyridyl complexes,<sup>16-17</sup> iridium (II) polypyridyl complexes,<sup>18</sup> and organic dyes.<sup>19</sup> However, only a specific wavelength or narrow region of visible light can be absorbed by these photosensitizers.<sup>20</sup> In addition, these organic photosensitizers can easily suffer degradation and instability under light illumination.<sup>9,20-22</sup>

Besides molecular photosensitizers, semiconductors have also been extensively studied as heterogeneous photocatalysts for  $H_2$  production since Honda and Fujishima reported the use of  $TiO_2$  semiconductor for photoelectrochemical water splitting in 1972.<sup>23</sup> Semiconductors have a broad and continuous spectral absorption range for

effective collection of sunlight, rendering them quite promising for photocatalytic H<sub>2</sub> production from water.<sup>24-27</sup> Many heterogeneous photocatalysts have much better photoresponse than TiO<sub>2</sub> in the visible region for H<sub>2</sub> evolution reaction (HER), such as other metal oxides (Fe<sub>2</sub>O<sub>3</sub>,<sup>28</sup> Cu<sub>2</sub>O,<sup>29</sup> etc.), metal oxynitrides,<sup>30-31</sup> and metal sulfides.<sup>19,32-34</sup> Among them, materials incorporating CdS have attracted much attention because of its low band gap (~2.4 eV), high photocatalytic activity, and low cost.<sup>4,35-38</sup> To prevent the recombination of photogenerated electron-hole pairs, loading a cocatalyst on CdS semiconductor photocatalysts is an effective approach to improve the photocatalytic activity,<sup>19,27,33,39-40</sup> resulting in photocatalysts such as CdS-Pt,<sup>41</sup> CdS-Ni,<sup>42</sup> CdS-NiO,<sup>43</sup> CdS-Cd,<sup>37</sup> and CdS-MoS<sub>2</sub>.<sup>44</sup> A few publications report molecular catalysts that are combination with CdS for photocatalytic H<sub>2</sub> production, such as cobaloximes<sup>33</sup> and ruthenium carbonyl complexes.<sup>45</sup>

In this paper, we report for the first time that cobalt-salen complexes can serve as novel low-cost and efficient catalysts in an artificial photocatalytic system for H<sub>2</sub> production using CdS nanorods (CdS NRs) as the photosensitizer. Under visible light irradiation ( $\lambda > 420$  nm), the highest turnover number (TON) achieved was ~64700 for H<sub>2</sub> production after 37 hours of visible light irradiation in aqueous solution. The highest rate of hydrogen production based on cobalt-salen complex **6** was 106  $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{mg}^{-1}$  and the highest apparent quantum yield is ~29% at 420 nm.

## 2. Experimental Details

### 2.1. Materials

All the chemical reagents were purchased from Aldrich or Alfa and used without further purification, including ethylene diamine (99.0%), salicylic aldehyde (98.0%), o-phenylenediamine (99.0%), 1,2-hexamethylene diamine (98.0%), 3,5-di-tert-butylsalicylaldehyde (98.0%), cobalt acetate tetrahydrate ( $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , 99.5%), cadmium chloride hemi(pentahydrate) ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ , 99.0%), thiourea ( $\text{CH}_4\text{N}_2\text{S}$ , 99.0%), ethylenediamine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , 99.0%), ethanol (EtOH, 99.7%), acetonitrile ( $\text{C}_2\text{H}_3\text{N}$ , 99.7%), sodium sulfide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ , 99%), anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_3$ , 97.0%), sodium sulfate ( $\text{Na}_2\text{SO}_4$ , 99.0%), triethanolamine (TEOA, 99%), N, N-Dimethylformamide (DMF, 99.5%), and glacial acetic acid (HOAc, 99.0%). 5% Nafion solution (Dupont company product) was purchased from Shanghai Geshi Energy Technology Co. Ltd. CdS NRs were prepared according to a reported method.<sup>46</sup> The aqueous solutions were freshly prepared with Millipore water (resistivity:  $\sim 18 \text{ M}\Omega \cdot \text{cm}$ ).

## 2.2. Synthesis of cobalt(III)-salen complexes 1-6

The salen ligands were synthesized according to a method reported in the literature.<sup>47-50</sup> Co(II)-salen complexes, the precursor of Co(III)-salen complex, were synthesized from salen ligands and cobalt(II) acetate in ethanol according to the procedure described.<sup>47-48,50-51</sup> Co(III)-salen complexes **1-6** were prepared from the Co(II)-salen complexes by treatment with HOAc in dichloromethane: 0.5 mL acetic acid was added to the Co(II)-salen complex (200 mg) in dichloromethane (15 mL). After stirring the mixture for 50 min, the solvent of dichloromethane was removed with a rotovap and the excess acetic acid was removed under vacuum.<sup>52-57</sup> The

resulting solids were recrystallized in ethanol to obtain final products. The molecular structures of the Co(III)-salen complexes **1-6** are shown in Scheme 1.

### 2.3. Preparation of CdS NRs

CdS NRs were prepared according to a modified method.<sup>46</sup> Typically, 20.25 mmol CdCl<sub>2</sub>·2.5H<sub>2</sub>O (4.62 g) and 60.75 mmol CH<sub>4</sub>N<sub>2</sub>S (4.62 g) were added in 60 mL ethylenediamine in a 100 mL Teflon-lined stainless steel autoclave without stirring. Then the autoclave was sealed and maintained at 160 °C for ~50 h in a muffle furnace and allowed to cool down to room temperature (RT). The obtained yellow powder was washed with Millipore water and ethanol three times each to remove impurities. Finally, the powder was dried under vacuum at RT for overnight.

### 2.4. Photocatalytic H<sub>2</sub> evolution

The photocatalytic reactions were carried out in a 50 mL flask, except for the experiment on long-term hydrogen production (in which a 250 mL reaction flask was used). Generally, the reaction system contained 20 mL Millipore water, 1.0 mg CdS NRs, different amounts of cobalt-salen complexes, Na<sub>2</sub>S, and Na<sub>2</sub>SO<sub>3</sub>. The reaction mixture was stirred for 10 min in the dark and degassed by bubbling with high purity N<sub>2</sub> for 15 min to remove air. A 300 W Xe-lamp equipped with a long-pass cut-off filter ( $\lambda > 420$  nm) was used for visible light irradiation. The amounts of hydrogen produced during photocatalysis were determined by a gas chromatography (GC) equipped with a TCD detector using methane as the internal standard.<sup>16,19</sup>

### 2.5. Photoelectrochemical measurements

Analyses of the photoelectrochemical properties of CdS NRs and CdS NRs/cobalt-salen complexes were performed in a standard three-electrode system at room temperature using CHI602E potentiostat (purchased from Shanghai Chenhua Instrument Co., Ltd.). FTO plates were ultrasonicated and washed with Millipore water and ethanol three times each. The suspension of CdS NRs containing Nafion was dropped using a pipette onto the conductive surface of an FTO plate within an area of 1 cm<sup>2</sup> to form the CdS/FTO electrode (working electrode). Then, a cobalt-salen complex in acetonitrile was dropped using a pipette onto the CdS/FTO electrode and dried in air. The ratio of CdS NRs and cobalt-salen complex is the same as that used in the photocatalytic system. An Ag/AgCl electrode (3 M KCl, 0.21 V vs. NHE) was used as the reference electrode and Pt wire as the counter electrode. The photocurrents were obtained in 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution at an applied potential of 0 V under visible light irradiation ( $\lambda > 420$  nm).

## 2.6. Apparent quantum yield (AQY)

The AQY was measured under the optimal condition for photocatalysis. A 300 W Xe lamp equipped with a monochromatic band-pass filter ( $\lambda = 420$  nm  $\pm$  5 nm) was used for visible light irradiation. The value of AQY was calculated according to equation (1) and the turnover number (TON) was calculated according to equation (2):<sup>26,58-59</sup>

$$\begin{aligned} \text{AQY [\%]} &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \\ &= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100 \quad (1) \end{aligned}$$

$$\text{TON} = \frac{\text{number of product molecules}}{\text{number of cocatalyst molecules}} = \frac{\text{number of evolved H}_2 \text{ molecules}}{\text{number of cocatalyst molecules}} \quad (2)$$

### 2.7. Physical characterization

The crystalline diffraction patterns of CdS NRs were analyzed by powder X-ray diffraction (XRD, D/max-TTR III) using graphite monochromatized Cu K $\alpha$  radiation of 1.54178 Å, operating at 40 kV and 200 mA. The scanning rate was 5° min<sup>-1</sup> from 20° to 80° (2 $\theta$ ). Ultraviolet-visible (UV-vis) diffuse reflection spectra were characterized by using an UV-visible spectrophotometer (SOLID 3700 UV-vis spectrometer). Transmission Electron Microscopy (TEM) images were obtained using a JEM-2010 electron microscope, operated at an acceleration voltage of 200 kV. The steady state photoluminescence (PL) spectra were recorded using a PerkinElmer LS 55 fluorescence spectrometer and time-resolved photoluminescence (TRPL) decay spectra tests were performed by PicoHarp300 spectrometer at room temperature (RT). The chemical compositions and valence states of the photocatalysts were probed with an ESCALAB 250 X-ray photoelectron spectroscopy (XPS) instrument.

### 3. Results and discussion

The CdS NRs material was successfully synthesized by a modified solvothermal method.<sup>46</sup> The morphology of the obtained product was investigated by TEM, which confirmed the formation of nanorods shape with lengths of 0.5~2  $\mu$ m and diameters of 40-90 nm, as shown in Figure 1a. The powder XRD diffraction pattern of the CdS NRs was also collected (Figure 1b), in which all the different peaks of CdS NRs are well indexed as hexagonal CdS (JCPDS No.77-2306).<sup>19,38</sup> The molecular structures of

cobalt-salen complexes **1-6** are displayed in scheme 1. Figure S1 shows the UV-vis diffuse reflectance spectra of pure CdS NRs, complex **6**, and mixed complex **6**/CdS NRs samples. Pure CdS material has good absorption in the visible region with a band gap at  $\sim 2.4$  eV. When mixing complex **6** with CdS NRs, the band gap of CdS remains unchanged.

When mixing a cobalt-salen complex with CdS NRs, the TEM image of the composite is similar to the image of pure CdS NRs (Figure S2). No obvious cobalt-salen complex could be observed probably because of its low content in the composite. Figure 1b shows XRD pattern of complex **6**/CdS composite, in which all the different peaks are also well matched with the pattern of hexagonal CdS (JCPDS No.77-2306), indicating that the loading cobalt-salen complex does not affect the crystallinity of CdS NRs.

The photocatalytic activities of  $H_2$  production of CdS NRs and CdS/cobalt-salen complexes **1-6** were studied in aqueous solution, as shown in Figure 2a. The solution contained 1.0 mg CdS photosensitizer, a cobalt-salen complex ( $1 \times 10^{-5}$  M),  $Na_2S$  (0.25 M),  $Na_2SO_3$  (0.35 M), and 20 mL Millipore water. All the complexes can promote  $H_2$  production under the same conditions, indicating that cobalt-salen complexes are active cocatalysts for proton reduction. Pure CdS NRs showed low photocatalytic activity ( $\sim 12 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{mg}^{-1}$ ). Complexes **1**, **3**, and **5** showed slight enhancement for  $H_2$  production. Impressively, the photocatalytic activities of **2**, **4**, and **6** are much higher than pure CdS NRs, yielding  $H_2$  evolution rates of  $\sim 37$ ,  $\sim 51$ , and  $\sim 73 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{mg}^{-1}$ , respectively. It is not very clear why complex **6** has the highest

activity to promote photocatalytic H<sub>2</sub> production in the present system. Comparing the structural differences, complexes **1**, **3**, and **5** have bulky *tert*-butyl groups but complexes **2**, **4**, and **6** are more planar. The bulky *tert*-butyl groups may significantly decrease the water solubility, causing aggregation of **1**, **3**, and **5** in aqueous solution. However, due to their good solubility in alkaline solution, complexes **2**, **4**, and **6** probably have better contact with CdS NRs than the complexes with *tert*-butyl groups, which will help transport the photogenerated electrons. The combination of complex **6** and CdS NRs may be highly preferable, resulting in the highest H<sub>2</sub> evolution rate in the present photocatalytic system.

It was found that the photocatalytic activities are dependent on the concentrations of cobalt-salen complexes and the sacrificial donors. Figure 2b shows the H<sub>2</sub> evolution rates in the complex **6**/CdS NRs system with different concentrations of complex **6**. With the initial increasing concentration of complex **6**, an improvement of photocatalytic activity was clearly observed. When its concentration reached more than 0.015 mM, the H<sub>2</sub> evolution rate decreased. The optimal rate was achieved at a concentration of 0.015 mM complex **6** (106 μmol·h<sup>-1</sup>·mg<sup>-1</sup>), which is ~9 times higher than pure CdS NRs without a cobalt-salen complex. A further increase in concentration of complex **6** resulted in a decrease of the rate for photocatalytic H<sub>2</sub> evolution, probably a result of the fact that more cobalt-salen molecules per unit area can shield the visible light absorption of CdS NRs and lead to a decrease of photons passing through the photocatalysts. A comparison of Co<sup>2+</sup> and complex **6** was further explored. When complex **6** in the system was replaced by Co<sup>2+</sup> with the same

concentration, the system did produce H<sub>2</sub>, but only with lower photocatalytic activity than complex **6** (Figure S3).

The photocatalytic activities of H<sub>2</sub> evolution over different amounts of sacrificial electron donors are shown in Table 1. The concentration ratio of Na<sub>2</sub>S:Na<sub>2</sub>SO<sub>3</sub> was fixed at 5:7. With increasing concentrations of the sacrificial electron donors from 0.25 M:0.35 M to 1.25 M:1.75 M (Na<sub>2</sub>S:Na<sub>2</sub>SO<sub>3</sub>), the catalytic turnover numbers (TONs) based on complex **6** increased from ~1200 to ~6360 after 3 hours of visible light irradiation, corresponding to the amounts of H<sub>2</sub> from 355 μmol to 1872 μmol. When the sacrificial reagents were oversaturated in aqueous solution with a concentration of 1.5 M Na<sub>2</sub>S and 2.1 M Na<sub>2</sub>SO<sub>3</sub>, the amount of evolved H<sub>2</sub> decreased (1777 μmol, TONs = 6040). During photocatalysis, protons are reduced to produce H<sub>2</sub> by photogenerated reducing species accompanied by oxidation of sacrificial electron donors. A higher concentration of sacrificial electron donors can oxidize more photogenerated holes to prevent the recombination of electron-hole pairs on CdS NRs semiconductor under visible light, and subsequently increase the photocatalytic activity for H<sub>2</sub> production. In an oversaturated solution, a large number of the solid crystals may also shield the visible light absorption of CdS NRs, resulting in a lower H<sub>2</sub> evolution rate.

Figure 3a shows the apparent quantum yields (AQYs) of the photocatalytic system for H<sub>2</sub> production. The reaction system was irradiated for 10 hours under monochromatic light with a band-pass filter ( $\lambda = 420 \text{ nm} \pm 5 \text{ nm}$ ). Initially, the AQY was ~25% in the first hour. After the first hour, the AQYs increased. The average

value of AQY was calculated to be ~29% after 10 hours of irradiation. Such a high AQY is comparable with or even higher than those in the reported studies based on molecular cocatalysts, such as, cobalt dithiolenes (AQY ~24%),<sup>60</sup> cobalt bipyridyl complexes (AQY ~13%),<sup>61</sup> and cobaloxime (AQY ~9%).<sup>33</sup>

To test the photocatalytic stability during H<sub>2</sub> production, a long-term photocatalytic experiment was performed in a solution containing 1.0 mg CdS NRs, 0.006 mM complex **6**, 1.25 M Na<sub>2</sub>S, and 1.75 M Na<sub>2</sub>SO<sub>3</sub> (Figure 3b). The result demonstrates good stability for H<sub>2</sub> production for more than 37 hours, with a nearly linear relationship between the reaction time and the amount of H<sub>2</sub>, indicating good stability for this system. The highest TON was achieved at 64700, corresponding to a TOF number of ~1748 h<sup>-1</sup>.

For photocatalytic H<sub>2</sub> production systems based on a metal complex, one may wonder if the metal complex actually decomposed to form metal(0) as the real catalyst for proton reduction. Therefore, more physical characterizations (such as TEM and XPS) were performed after long-term visible light irradiation. After 10 hours of photocatalysis, the reaction solution was centrifuged to collect CdS NRs, followed by washing with acetonitrile and water three times each to remove molecular cobalt complexes and inorganic salts. The recovered CdS NRs material was examined by TEM (Figure S4a), which still showed morphology and shape similar to the CdS sample before photocatalytic reaction. No obvious cobalt(0) nanoparticles were observed from the TEM image. These results indicate that the cobalt-salen complex did not decompose to form cobalt(0) in 10 hours, but the observation does not

guarantee no cobalt(0) formation after a much longer time of irradiation. The EDX spectrum of CdS NRs after reaction is shown in Figure S4b, confirming no cobalt species deposited on CdS NRs during 10 hours of photocatalysis. Similar result was previously reported that there was no Co(0) species on the surface of CdS after short-term photocatalysis.<sup>33</sup>

The photocatalyst samples were further investigated by X-ray photoelectron spectroscopy (XPS) (Figure 4). Figure 4a shows the survey spectra of the samples. The black plot is the spectrum of a mixed complex **6**/CdS NRs sample and the red plot is for the sample washed by acetonitrile and water after photocatalysis. Both survey spectra are quite similar, with the presence of Cd, S, O, and C elements. The difference lies in that the mixed sample clearly shows the presence of a Co peak. Before photocatalysis, the high resolution XPS spectra of S 2p and Cd 3d are exhibited in Figures 4b and 4c. Two main peaks are located at 162.52 and 161.31 eV, which can be attributed to S 2p in CdS.<sup>19,62-64</sup> Figure 4c demonstrates two obvious Cd 3d peaks located at 404.42 eV and 411.15 eV, which are consistent with the Cd character in CdS materials.<sup>62</sup> After photocatalysis, both S 2s and Cd 3d peaks only have slight changes of binding energies but not significant. The broadening of the peaks in Cd 3d and S 2s before photocatalysis could be due to the presence of cobalt-salen complexes (poor conductivity for XPS measurement). The high resolution XPS spectrum of Co 2p in a mixed complex **6**/CdS NRs sample is shown in Figure 4d. Before irradiation (black plot), two appreciable Co 2p peaks are observed at 780.3 eV and 794.5 eV, indicating the presence of a highly oxidized state of cobalt.

In contrast, no apparent Co 2p peaks can be seen in the sample after irradiation, further confirming no metallic cobalt formation during photocatalytic H<sub>2</sub> production over a period of 10 hours.

To gain more insights into the photocatalytic reaction mechanism, the photophysical properties were studied by both steady state photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) decay spectra (Figure 5). Under an excitation wavelength of 405 nm, pure CdS NRs show an intense luminescence band centered at ~506 nm and a weak luminescence band at ~712 nm (Figure 5a), which is consistent with the previous reports.<sup>45,65</sup> The intense luminescent band can be assigned to near-band-edge emission and the weak band may be attributed to defects of the CdS NRs surface. The luminescence intensities of pure CdS NRs are readily quenched by adding cobalt-salen complex **6**. This phenomenon probably results from efficient electron transfer in the complex **6**/CdS NRs hybrid system from CdS to cobalt complex, leading to the spatial separation of electrons and holes. Therefore, the cobalt-salen complex could serve as an electron acceptor and transporter, which will prevent fast recombination of electron-hole pairs upon irradiation. The fast electron transfer process can be further confirmed by TRPL spectra, as shown in Figure 5b. The PL intensity of the complex **6**/CdS NRs composite system decayed much faster than that of pure CdS, indicating that the composite system has shorter PL lifetimes and better charge transfer capability to facilitate photocatalytic H<sub>2</sub> production. The data of complex **6**/CdS NRs can fit to a biexponential decay kinetics,  $F(t) = A_1 \cdot \exp(-t/\tau_1) + A_2 \cdot \exp(-t/\tau_2)$ , where A<sub>1</sub>, and A<sub>2</sub> are preexponentials related to the

concentration of emitting species,  $\tau_1$ , and  $\tau_2$  are the corresponding lifetimes,  $t$  is the measurement time, and  $F(t)$  is the photon counts at time  $t$ . The PL lifetimes of complex **6**/CdS NRs are  $\sim 59$  ps and  $\sim 360$  ps, which are significantly shorter than for pure CdS NRs ( $\sim 500$  ps and  $\sim 7700$  ps).

Measurements of the photocurrent responses of CdS NRs and complex **6**/CdS NRs were performed in 0.5 M Na<sub>2</sub>SO<sub>4</sub> under chopped visible light irradiation ( $\lambda > 420$  nm), as shown in Figure S5. When no light irradiation existed, both samples showed very low dark current densities ( $j < 10^{-6}$  mA/cm<sup>2</sup>). In contrast, much higher photocurrent was obtained under irradiation, indicating good photoresponse to visible light. Meanwhile, the photocurrent response for complex **6**/CdS NRs was higher than that of pure CdS NRs under the same conditions, indicating that cobalt-salen complex can highly enhance transport of the photoexcited charge carriers under visible light illumination.

UV-vis absorption spectra of the reaction solution during photocatalysis were studied to examine the reaction mechanism in detail. Inspired by previous studies,<sup>16-17</sup> a Pt chromophore (platinum terpyridyl phenylacetylide complex) was chosen as the photosensitizer. The solution contained  $1.6 \times 10^{-2}$  M triethanolamine (TEOA),  $1.1 \times 10^{-5}$  M Pt chromophore and  $3.0 \times 10^{-4}$  M cobalt-salen complex **6** in 20 mL DMF (5% water). The results are shown in Figure 6. Prior to photocatalysis, the color of the solution was light yellow and the absorption spectrum exhibited two peaks located at 334 nm and 403 nm (black plot), which is in agreement with previous study.<sup>66</sup> After one hour of irradiation, the solution color had turned to dark yellow and the

absorption spectrum has had significant changes (red plot). New absorption bands are clearly seen. One absorption band maximized at 500 nm can be attributed to the formation of Co(II) species.<sup>16,66</sup> Another new broad absorption band centered at ~800 nm is consistent with Co(I) species absorption.<sup>67-68</sup>

Based on all of the above results, a reaction mechanism for photocatalytic H<sub>2</sub> production based on cobalt-salen complex/CdS NRs is proposed in Scheme 2. Upon visible light irradiation, CdS NRs absorb photons and generate electron-hole pairs. The holes can be scavenged by the Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> electron donors. The decomposition mechanism of these donors has been well studied in the literature.<sup>32,69-70</sup> The photogenerated electrons are powerful electron reducing reagents, which are capable of reducing Co(III) ions in a cobalt-salen complex to generate Co(II) species. The conversion of Co(II) to Co(I) is probably achieved by further electron transfer from the photosensitizer to Co(II) after the initial reduction of complex **6**. The Co(III) hydride generated from Co(I) is probably the key reaction intermediate for H<sub>2</sub> production. Subsequently, our proposed mechanism for the H<sub>2</sub>-forming contains a bimolecular reaction of two Co(III) hydrides to produce H<sub>2</sub> + 2Co(II) and a monometallic reaction of one Co(III) hydride and protons to produce H<sub>2</sub> + Co(II). The regenerated Co(II) is probably the dominant Co species in the system during photolysis. A nearly linear relationship (Figure 7) can be obtained from Figure 2b when the concentrations of cobalt-salen complex **6** increase from zero to 0.015 mM, probably indicating that the H<sub>2</sub> generation process is a monometallic process. A schematic illustration of the proposed reaction mechanism is shown in Scheme 3.

#### 4. Conclusions

In summary, we have studied the cobalt-salen complex as a highly efficient and inexpensive molecular catalyst for photocatalytic H<sub>2</sub> production in aqueous solution. Our system combines CdS NRs as the photosensitizer, a cobalt-salen complex as the catalyst, and Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as the sacrificial electron donors. Under visible light irradiation ( $\lambda > 420$  nm), photocatalytic H<sub>2</sub> production was successfully achieved with a highest TON of ~64700 under optimal conditions. The average AQY was ~29 % after 10 hours of irradiation with 420 nm monochromic light. The efficient interfacial electron transfer from photoexcited CdS NRs to the cobalt-salen complex is proposed as the reason for the high photocatalytic activity.

**Supporting Information Available.** Experimental details are available including UV-vis spectra, comparison of hydrogen evolution rates of Co<sup>2+</sup> and complex **6**, EDX spectrum and TEM image of photocatalyst after reaction, and current immediate effect data. This material is available free of charge via the Internet at <http://www.rsc.org>.

#### Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (21271166, 21473170), the Fundamental Research Funds for the Central Universities (WK3430000001, WK2060140015, WK2060190026), the Program for

New Century Excellent Talents in University (NCET), and the Thousand Young Talents Program. We appreciate the kind help from Prof. X. Y. Wang at Nanjing University for assistance with the photoluminescence (PL) spectra and the time-resolved photoluminescence (TRPL) spectra.

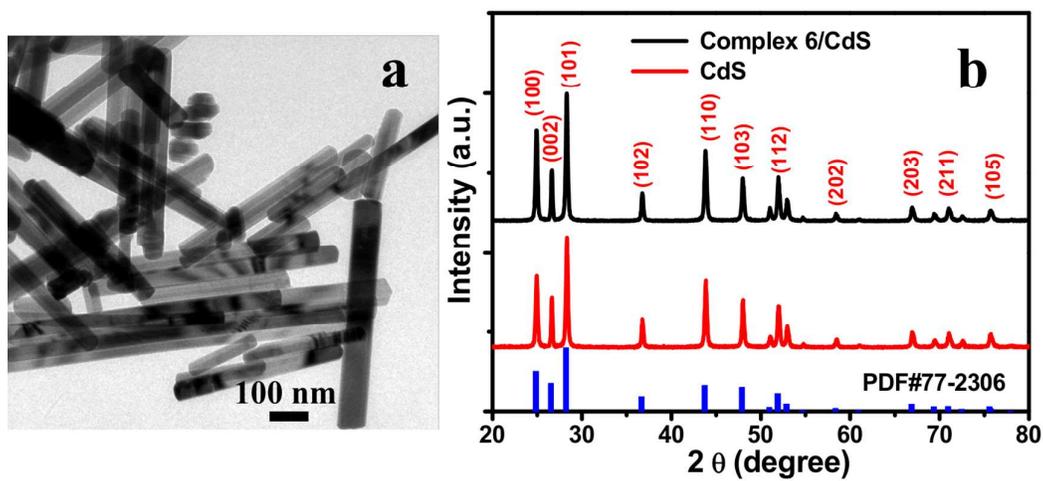
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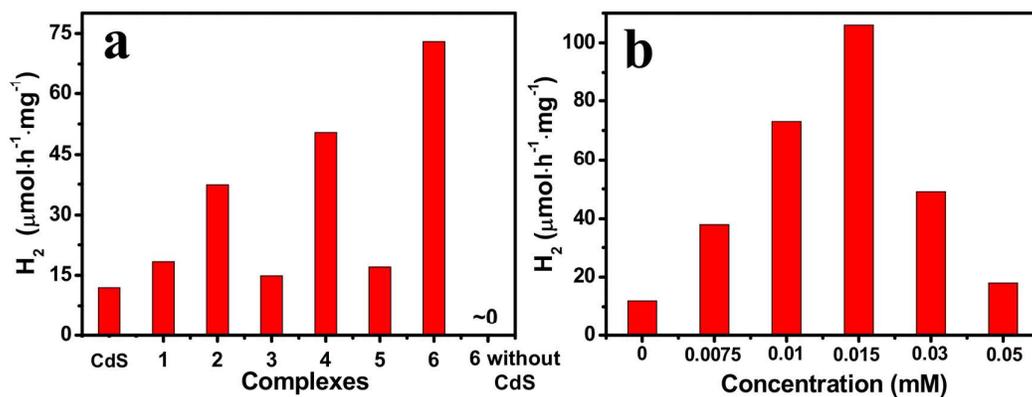
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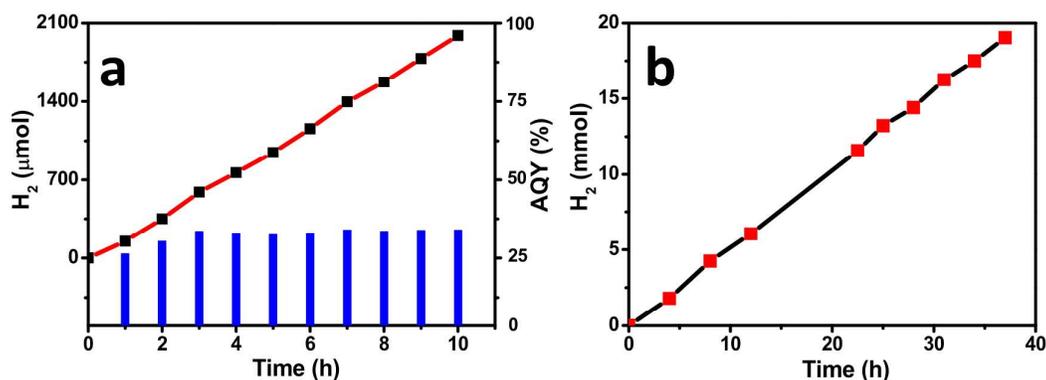
**Figure 1.** (a) TEM image of CdS NRs; (b) Powder XRD pattern of CdS NRs (red plot) and cobalt-salen complex **6** mixed with CdS NRs (1.4 wt % of cobalt in the composite). Blue plot is the standard XRD pattern, CdS-PDF#77-2306.



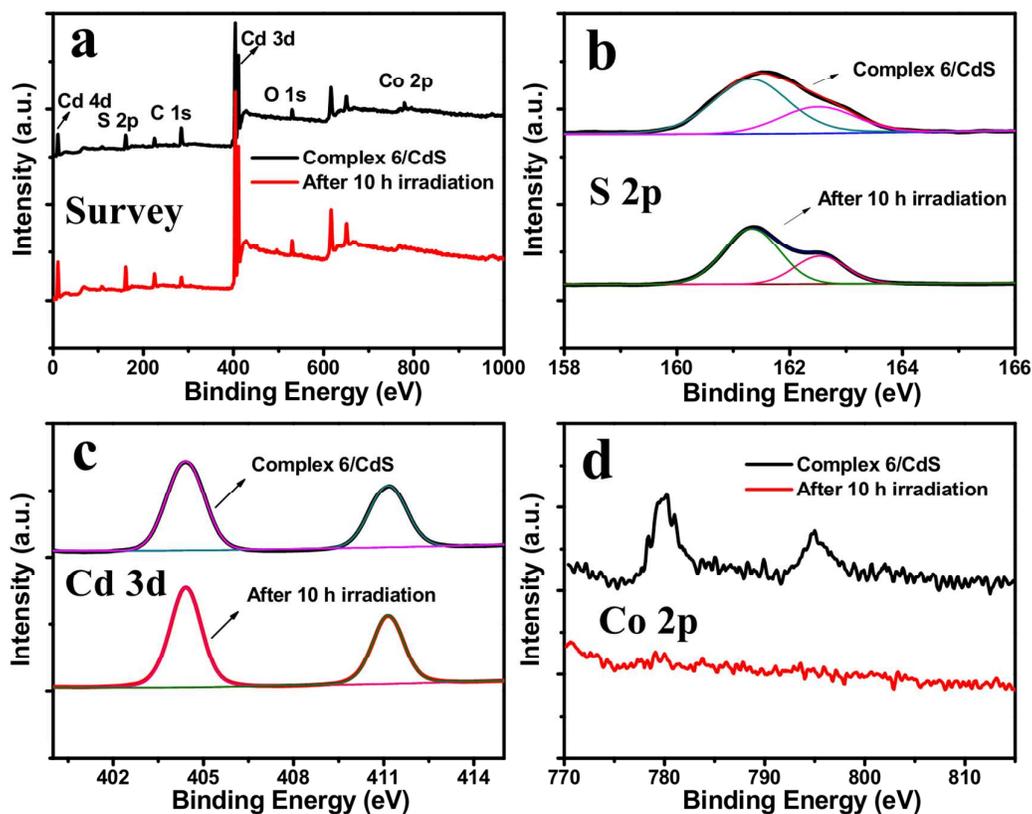
**Figure 2.** (a) Comparison of H<sub>2</sub> production rate of the cobalt-salen complexes **1-6** (0.01 mM) under visible light. The systems contained 1.0 mg CdS NRs, Na<sub>2</sub>S (0.25 M), and Na<sub>2</sub>SO<sub>3</sub> (0.35 M) in 20 mL Millipore water. Pure CdS and complex **6** were used for comparison. (b) Influence of the concentration of complex **6** on photocatalytic H<sub>2</sub> production in a system containing 1.0 mg CdS NRs, Na<sub>2</sub>S (0.25 M), and Na<sub>2</sub>SO<sub>3</sub> (0.35 M) in 20 mL Millipore water.

Complex	Na <sub>2</sub> S (M)	Na <sub>2</sub> SO <sub>3</sub> (M)	H <sub>2</sub> (μmol)	TONs
<b>6</b>	<b>0.25</b>	<b>0.35</b>	<b>355</b>	<b>1200</b>
	<b>0.50</b>	<b>0.70</b>	<b>588</b>	<b>2000</b>
	<b>0.75</b>	<b>1.05</b>	<b>975</b>	<b>3310</b>
	<b>1.00</b>	<b>1.40</b>	<b>1422</b>	<b>4830</b>
	<b>1.25</b>	<b>1.75</b>	<b>1872</b>	<b>6360</b>
	<b>1.50</b>	<b>2.10</b>	<b>1777</b>	<b>6040</b>

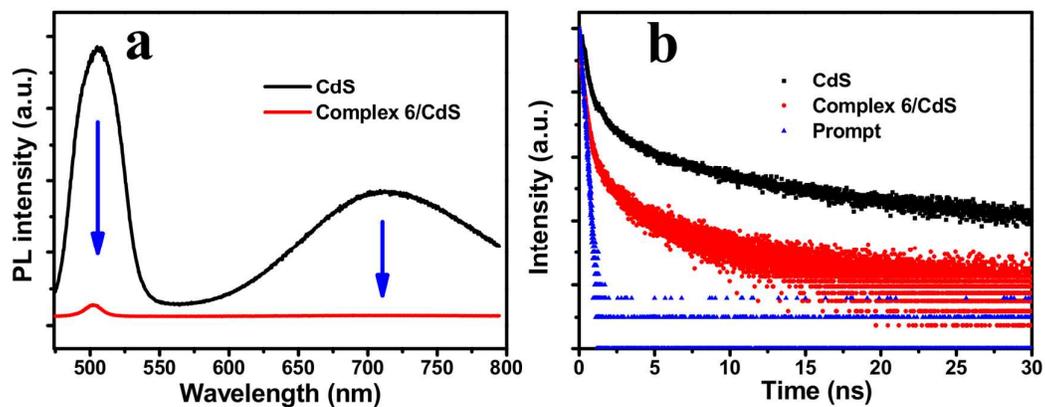
**Table 1.** Influence of the concentrations of sacrificial electron donors on photocatalytic H<sub>2</sub> production in 3 hours under visible light irradiation ( $\lambda > 420$  nm). The system contained 1.0 mg CdS NRs, 0.015 mM complex **6**, and 20 mL Millipore water.



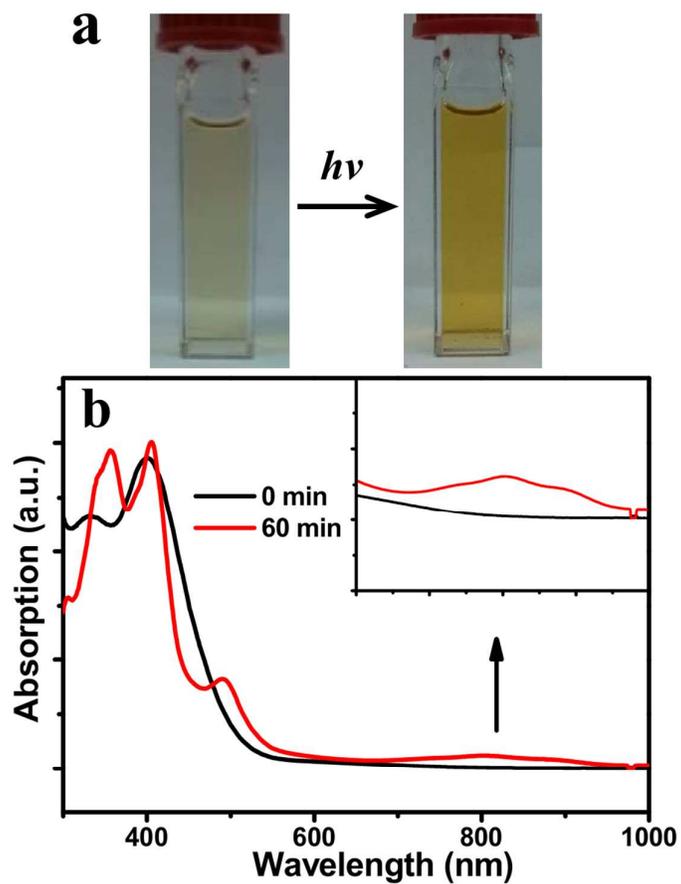
**Figure 3.** (a) Photocatalytic H<sub>2</sub> production of complex **6** under visible light ( $\lambda > 420$  nm) and apparent quantum yield (AQY) of complex **6** under monochromatic light ( $\lambda = 420$  nm). The reaction system contained 1.0 mg CdS NRs, 0.015 mM complex **6**, 1.25 M Na<sub>2</sub>S, 1.75 M Na<sub>2</sub>SO<sub>3</sub> and 20 mL deionized water. (b) Long-term H<sub>2</sub> production performance under visible light ( $\lambda > 420$  nm) irradiation. The system contained 1.0 mg CdS NRs, 0.006 mM complex **6**, 1.25 M Na<sub>2</sub>S, 1.75 M Na<sub>2</sub>SO<sub>3</sub>, and 50 mL Millipore water in a 250 mL reaction flask.



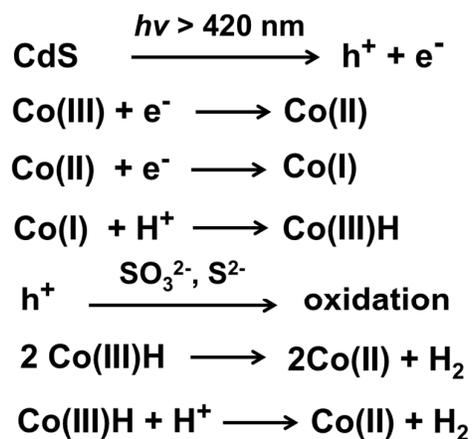
**Figure 4.** (a) XPS survey spectra of the photocatalyst samples. Black plot is for the mixture of CdS NRs and complex **6**. Red plot is the photocatalyst after H<sub>2</sub> production reaction, which was centrifuged and washed by acetonitrile and water after 10 hours of irradiation. (b) High resolution spectra of S 2p. (c) High resolution spectra of Cd 3d. (d) High resolution spectra of Co 2p.



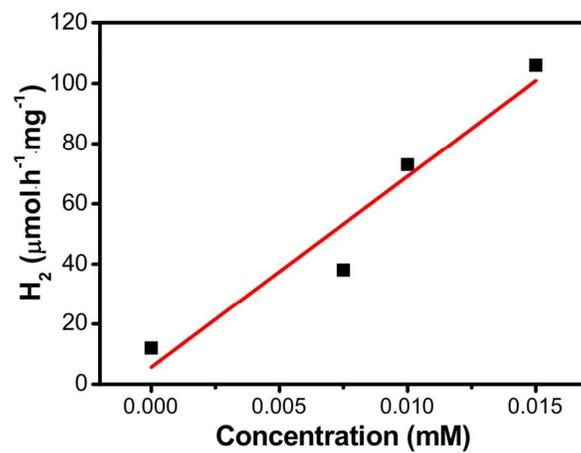
**Figure 5.** (a) Photoluminescence spectra and (b) time-resolved photoluminescence decay spectra of CdS NRs (black plot) and complex **6**/CdS NRs (red plot) excited at a wavelength of 405 nm. The complex **6** and CdS NRs were dissolved in acetonitrile and then dropped using a pipette onto a glass plate to form a film.



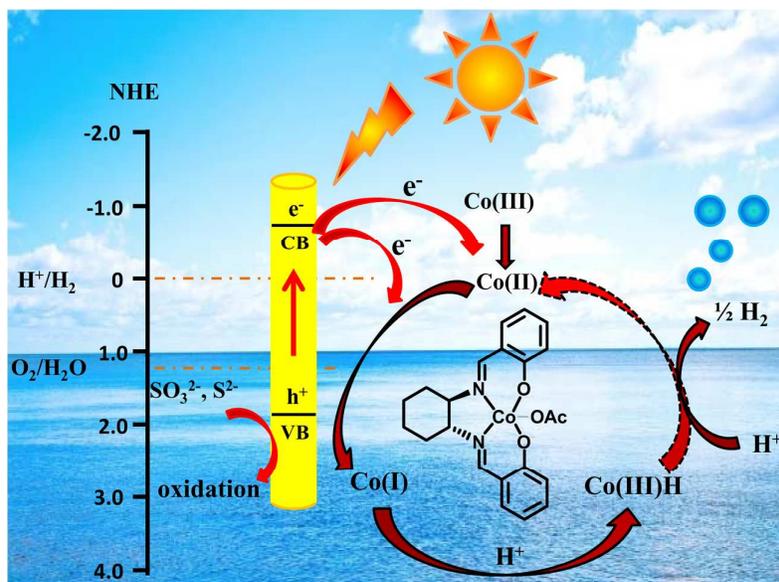
**Figure 6.** (a) Color change and (b) UV-vis absorption spectra of a solution containing  $1.6 \times 10^{-2}$  M TEOA,  $1.1 \times 10^{-5}$  M Pt chromophore, and  $3.0 \times 10^{-4}$  M complex **6** in DMF (5% water) under inert atmosphere. Black plot is from the solution without irradiation and red plot is from the solution after photocatalysis for 60 min. After 1 hour illumination, the color of the solution had turned from light yellow to dark yellow.



**Scheme 2.** Proposed mechanism of photocatalytic H<sub>2</sub> production using complex **6** and CdS NRs under visible light ( $\lambda > 420 \text{ nm}$ ).



**Figure 7.** Hydrogen production rates under different concentrations of cobalt-salen complex **6** (obtained from Figure 2(b)).



**Scheme 3.** A possible mechanism for  $\text{H}_2$  production in the present reaction system.

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