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Enhanced Photocatalytic H₂ Production on CdS Nanorods with Simple Molecular Bidentate Cobalt Complexes as Cocatalysts under Visible Light

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Abstract: Photocatalytic hydrogen production via water splitting has attracted much attention for future clean energy application. Herein we report a noble-metal-free photocatalytic hydrogen production system containing a simple bidentate cobalt Schiff base complex as the molecular cocatalyst, CdS nanorods as the photosensitizer, and ascorbic acid as the electron donor. The system shows highly enhanced photocatalytic activity compared to pure CdS NRs under visible light ($\lambda > 420$ nm). Under optimal conditions, the turnover numbers (TONs) for hydrogen production reached ~15,200 after 12 hours of irradiation and an apparent quantum yield of ~27% was achieved at 420 nm monochromatic light. Steady-state photoluminescence (PL) spectra indicated efficient charge transfer between the excited CdS NRs and the cobalt cocatalyst for improved hydrogen production. Spectroscopic studies of the photocatalytic reaction revealed the reduction of Co(II) complex to Co(I) species, which are probably active intermediates for hydrogen production. On the basis of spectroscopic studies we propose a reaction mechanism for hydrogen production in the present photocatalytic system.

Introduction

Currently, the main energy resources for humankind are carbon-based fossil fuels such as oil, coal, and natural gas.¹ The combustion of fossil fuels always releases carbon dioxide, which is not friendly to the environment.² Scientists have made extensive efforts to develop renewable and sustainable energy resources to meet the global energy demand.³⁻⁶ Hydrogen is one of the best alternatives to the carboniferous fuels but industrial hydrogen production is mainly from methane and other fossil fuels using processes that release carbon dioxide and carbon monoxide.⁷ It should be obtained from appropriate sources in an eco-friendly manner.^{4, 8}

In recent years, the development of inexpensive and efficient systems for photo- and/or electrocatalytic hydrogen production has attracted great attention than other solar fuels.⁸⁻¹⁴ Many homogeneous systems have been reported on photocatalytic hydrogen production since the late 1970s, which usually contain [Ru(bipy)₃]²⁺ as the photosensitizer, amines as the electron donor, and molecular cocatalysts (such as cobalt and nickel complexes,^{15,16} biomimetic hydrogenases,¹⁷ and bioinspired hydrogenase model complexes and clusters [Fe₂S₂].^{18,19} Besides ruthenium-based photocatalytic systems, iridium- and platinum-based photosensitizers have also been studied. Bernhard and coworkers investigated rhodium cocatalysts in combination with iridium phenylpyridine sensitizers.²⁰ Eisenberg and coworkers studied a series of cobalt dimethylglyoxime catalysts with platinum terpyridyl sensitizers.²¹ In most studies, cocatalysts or photosensitizers based on noble metals have been mainly employed. More interestingly from a practical application point of view, noble-metal-free systems involving xanthene dyes or copper(I) complexes as the photosensitizers have been studied for homogeneous H₂ production catalysis.²²⁻²⁴

In all of the above-mentioned systems, the photosensitizers are organometallic complexes or organic compounds which can only absorb a narrow band of light or light of particular wavelengths.

On the other hand, semiconductors have continuous and broad light absorption range, which is efficient for solar energy collection.²⁵⁻²⁷ Heterogeneous photocatalytic systems using metal oxides,^{26, 28} metal oxynitrides^{26, 29} and metal sulfides,^{27, 30} as photocatalysts have been extensively studied in the past four decades. Photoactive CdS material has attracted much attention because of its low cost, high photocatalytic activity, and low band gap (~2.4 eV).^{31, 32} Loading an efficient heterogeneous cocatalyst on CdS can enhance the photocatalytic activity and protect the semiconductor from photocorrosion to some extent.^{30, 33, 34} Although heterogeneous cocatalysts in combination with CdS have been widely used, only a few studies have been reported on photocatalytic systems comprising CdS in combination with molecular catalysts.^{33, 35, 36}

In this present study, we report a noble-metal-free photocatalytic system containing a simple cobalt Schiff base complex as the molecular catalyst, CdS nanorods (NRs) as the photosensitizer, and ascorbic acid (AA) as the electron donor. This system can achieve an apparent quantum yield of ~27% at 420 nm monochromatic light. The rate of hydrogen production from this system is around 45 times higher than that of pure CdS NRs under the same conditions.

Experimental Details

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Materials. Cobalt (II) acetate tetrahydrate (Co(OAc)₂·4 H₂O, 99.5%), *p*-hydroxybenzoic acid (99.0%), salicylaldehyde (98.0%), *p*-aminophenylacetic acid (98.0%), *p*-iodoaniline (98.0%), *p*-nitroaniline (99.0%), thiourea (CH₄N₂S, 99.0%), and cadmium chloride hemi(pentahydrate) (CdCl₂·2.5H₂O, 99.0%) were purchased from Aldrich or Alfa and used without further purification. Millipore water (Blue Water Industry, resistivity: ~18 MΩ·cm) was used for photocatalytic experiments. CdS NRs were prepared according to a reported procedure.^{37, 38}

Synthesis of 3-formyl-4-hydroxybenzoic acid. 3-formyl-4-hydroxybenzoic acid was prepared according to a reported procedure.³⁹ In a 250 mL flask, *p*-hydroxybenzoic acid (7.5 g, 54 mmol) was added into 20 mL trifluoroacetic acid (TFA). A solution of hexamethylenetetramine (7.65 g, 54.5 mmol) in 20 mL TFA was added dropwise to the flask under argon atmosphere. The resulting solution was refluxed for 3 hours. A transparent yellowish solution was obtained which was cooled to ambient temperature, after which 4 M HCl (150 mL) was added and the result stirred for 4 hours to produce a yellow precipitate. The final product was filtered, washed with an excess of water and dried in an oven under vacuum. Yield: 45%. ¹H NMR (400 MHz, DMSO): $\delta = 11.52$ (s, 1H), 10.29 (s, 1H), 8.23 (d, J = 2.3 Hz, 1H), 8.03 (dd, $J_I = 8.7$, $J_2 = 2.3$ Hz, 1H), 7.07 (d, J = 8.7 Hz, 1H) ppm.

Synthesis of ligand L-1, 2-(4-((2-hydroxybenzylidene)amino)phenyl)acetic acid. *p*aminophenylacetic acid (1.5 g, 10 mmol) was dissolved in 15 mL mixture of methanol:water (2:1, v/v). Methanolic solution (10 ml) of salicylaldehyde (10 mmol) was added dropwise to the solution of *p*-aminophenylacetic acid. After its addition, the solution turned yellow and it was then heated to reflux for 3 hours. The resulting solution was allowed to stand and evaporate slowly at room temperature. After 24 hours, yellow crystals were collected, washed with cold ethanol, and dried under vacuum. Yield: 85%. ¹H NMR (400 MHz, DMSO): $\delta = 13.16$ (s, 1H), 8.97 (s, 1H), 7.64 7.64 (dd, J_1 = 7.6, J_2 = 1.7 Hz, 1H), 7.46-7.36 (m, 5H), 7.01-6.96 (m, 2H), 3.62 (s, 2H) ppm. C₁₅H₁₃NO₃: calculated C 70.58, H 5.13, N 5.49; found C 70.48, N 5.31, H 5.07.

Synthesis of complex 1, Co(L-1)₂. Schiff base ligand L-1 (0.51 g, 2 mmol) was dissolved in methanol. Then 0.24 g Co(OAc)₂·4 H₂O (1 mmol) was dissolved in methanol and the solution was added dropwise to the above L-1 solution. The mixture was heated to reflux for 2 hours. Precipitates were collected by filtration, washed with water then ethanol, and finally dried under

vacuum. Yield: 55%. C₃₀H₂₄N₂CoO₆: calculated C 63.52, H 4.26, N 4.94; found C 63.79, H 4.73, N 4.49.

Synthesis of ligand L-2, 4-hydroxy-3-(((4-iodophenyl)imino)methyl)benzoic acid. 3-Formyl-4-hydroxybenzoic acid (1.66 g, 10 mmol) was dissolved in 15 mL ethanol. 2.19 g p-iodoaniline (10 mmol) was dissolved in 10 mL ethanol and the solution was added dropwise to the solution of 3-formyl-4-hydroxy-benzoic acid. The resulting solution turned to an orange color under reflux and stirring was continued for 3 hours. When the solution was cooled to room temperature, a yellow solid product was obtained by filtration, washed with cold ethanol, and dried under vacuum. Yield: 80%.¹H NMR (400 MHz, DMSO): δ = 13.51 (s, 1H), 9.08 (s, 1H), 8.33 (d, J = 2.2 Hz, 1H), 7.97 (dd, $J_1 = 8.6$, $J_2 = 2.2$ Hz, 1H), 7.83 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 8.78.6 Hz, 1H) ppm. C₁₄H₁₀INO₃: calculated C 45.80, H 2.75, N 3.82; found C 45.86, H 3.08, N 3.73. Synthesis of complex 2, Co(L-2)₂. 0.24 g Co(OAc)₂·4 H₂O (1 mmol) was dissolved in 10 ml methanol and was added dropwise to a freshly prepared solution of Schiff base ligand L-2 (0.73g, 2 mmol) in methanol at room temperature. The yellowish green precipitate appeared rapidly. The reaction mixture was stirred for 3 hours. The solid product was filtered, washed with cold ethanol and water, and dried under vacuum. C₂₈H₁₈I₂N₂CoO₆: calculated C 42.52 H 2.29, N 3.54; found C 42.10, H 2.64, N 3.78.

Synthesis of ligand L-3, 4-hydroxy-3-(((4-nitrophenyl)imino)methyl)benzoic acid. 1.38 g *p*nitroaniline (10 mmol) was dissolved in 10 mL ethanol in a 50 mL round bottom flask. 1.66 g 3formyl-4-hydroxy-benzoic acid (10 mmol) in ethanol (15 ml) was added dropwise to the flask. The solution turned yellow rapidly and was heated to reflux for 2 hours. The reaction mixture was cooled to room temperature for slow evaporation. The yellow solid product was filtered, washed with cold ethanol, and dried in vacuum. Yield: 75%. ¹H NMR (400 MHz, DMSO): $\delta = 12.87$ (s,

1H), 9.10 (s, 1H), 8.42 (d, *J* = 2.3 Hz, 1H), 8.33 (d, *J* = 9.1 Hz, 2H), 8.01 (d, *J* = 10.9 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 1H) ppm. C₁₄H₁₀N₂O₅: calculated C 58.74, H 3.52, N 9.79; found C 58.81, H 3.49, N 9.17.

Synthesis of complex 3, Co(L-3)₂. 0.24 g Co(OAc)₂·4 H₂O (1 mmol) was dissolved in 10 mL methanol and added dropwise to 20 mL solution of Schiff base ligand L-3 (0.57 g, 2 mmol) in methanol. The solution became translucent after stirring for 3 hours. The volume of solution was reduced to half under reduced pressure. The resulting precipitate was filtered, washed with methanol and water, and dried under vacuum. Yield: 65%. C₂₈H₁₈N₄CoO₁₀: calculated C 53.48, H 2.88, N 8.91; found C 53.79, H 3.24, N 8.62.

Synthesis of ligand L-4, 3-(((4-(tert-butyl)phenyl)imino)methyl)-4-hydroxybenzoic acid. The Schiff base ligand was prepared by the method as described above for L1-L3. Yield: 80%. ¹H NMR (400 MHz, DMSO): $\delta = 14.03$ (s, 1H), 9.09 (s, 1H), 8.32 (d, J = 2.2 Hz, 1H), 7.96 (d, J = 10.9 Hz, 1H), 7.45 (dd, $J_1 = 39.1$, $J_2 = 8.7$ Hz, 4H), 7.04 (d, J = 8.6 Hz, 1H).

Synthesis of complex 4, Co(L-4)₂. 0.58 g Schiff base ligand L-4 (2 mmol) was dissolved in 20 mL mixed solution of DMF:ethanol (1:1) and heated at 60 °C for 30 min. 0.24 g Co(OAc)₂·4 H₂O (1.0 mmol) solution was dissolved in ethanol and added slowly to the hot solution of L-4. The resulting mixture was heated to reflux for 2 hours. Precipitates were filtered and washed with ethanol and water. The solid product was dried under vacuum. Yield: 70%. $C_{36}H_{36}CoN_2O_6$: calculated C 66.36, H 5.57, N 4.30; found C 66.78, H 5.32, N 4.63.

Characterization. ¹H NMR measurements were recorded in DMSO with a 400 MHz Bruker AV400 spectrometer at room temperature. Powder X-ray diffraction (XRD, D/max-TTR III) was used to analyze the crystalline diffraction patterns of the CdS nanorods, using graphite monochromatized Cu K α radiation of 1.54178 Å, operating at 40 kV and 200 mA. The scanning

rate was 5° min⁻¹ from 20° to 80° in 20. Elemental analyses were carried out on Elementar Vario EL Cube. Electronic spectra were obtained with a UNICO SQ-3802 spectrometer. The steady-state photoluminescence (PL) spectra were recorded using a Perkin-Elmer LS55 fluorescence spectrometer. UV-Vis diffuse reflectance spectra were recorded using a Solid Spec-3700 UV–vis spectrometer. Scanning electron microscopy (SEM) was performed on a JSM-6700F microscope. TEM images were obtained with a transmission electron microscope JEM-2010. XPS spectra were recorded on an ESCALAB 250 X-ray photoelectron spectrometer.

Photocatalytic hydrogen production. All the photocatalytic experiments were performed in a 50 mL flask using Xe lamp (300 W) with a longpass cut-off filter ($\lambda > 420$) at ambient temperature. A gas chromatograph (SP-6890) equipped with a thermal conductivity detector was used for the measurement of hydrogen gas. Nitrogen was used as the carrier gas. A typical sample for photocatalytic experiment was prepared in a 50 ml round bottom flask sealed with rubber septum. A suspension of the molecular cocatalyst, photosensitizer, and ascorbic acid was prepared in 20 mL water. The pH value of reaction mixture was adjusted with solution of NaOH or 2 M HCl. The sample was ultrasonicated for 10 min and purged with nitrogen gas for 15 min to remove the air. After that, 5 mL methane gas was added as the internal standard.^{21,40}

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Apparent Quantum Yield (AQY). The apparent quantum efficiency was calculated using a 300 W Xe lamp with a band pass filter ($\lambda = 420$ nm). Calculations for AQY and TON were done by using equations (1) and (2).^{33, 41}

$$AQY (\%) = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100$$
$$= \frac{\text{number of evolved H}_2\text{molecules} \times 2}{\text{number of incident photons}} \times 100 \quad (1)$$
$$TON = \frac{\text{number of product molecules}}{\text{number of cocatalyst molecules}}$$

 $= \frac{\text{number of evolved H}_2 \text{ molecules}}{\text{number of cocatalyst molecules}}$

(2)

Results and discussion

All the cobalt Schiff base complexes were successfully prepared and their molecular structures **1-4** are shown in Figure 1a. CdS NRs were synthesized by a modified solvothermal process³⁸ and characterized by TEM (Figure 1b) and powder XRD (Figure 1c). The TEM image confirmed the nanorod morphology of CdS with diameters of 40-90 nm and lengths of 0.5-2 μ m. The powder XRD diffraction patterns showed that all the peaks were well indexed as hexagonal CdS (JCPDS No. 77-2306).^{30, 42} The diffraction peaks at 24.81°, 26.51°, 28.18°, 36.62°, 43.7°, 47.84°, and 51.82° correspond to the (100), (002), (101), (102), (110), (103), and (112) faces, respectively.⁴³ After mixing with a molecular cobalt complex, the XRD diffraction patterns had no significant changes, indicating that the complex did not change the crystalline structure of CdS. Moreover, no obvious cobalt complex was observed in the TEM image when complex **1** was added, probably due to low content of the cobalt complex in the composite (Figure S1).

Figure 2a shows the UV-Vis absorbance spectra (converted from UV-Vis diffuse reflectance spectra) of CdS NRs, complex **1**, and the mixture of CdS NRs and complex **1**. Pure CdS NRs exhibited good absorption in the visible region with a band gap at ~2.4 eV, which is consistent with previous studies.^{34,44} The absorption region of CdS NRs remained unchanged when it is mixed with complex **1**, suggesting that there is no variation of the band gap in the presence of complex **1** (Figure S2).

The photocatalytic activities of CdS NRs and CdS/complexes **1-4** for H₂ production in aqueous solution were examined under visible light irradiation ($\lambda > 420$ nm). The reaction mixture

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contained 1.0 mg CdS NRs, 0.5 M ascorbic acid, and 0.02 mM cobalt complex in 20 mL water at pH 4. Pure CdS NRs without a cocatalyst showed a low H₂ evolution rate (~12 μ mol h⁻¹ mg⁻¹). Impressively, when complex **1** was added, the H₂ evolution rate increased by a factor of 45 (~550 μ mol h⁻¹ mg⁻¹). Photocatalytic experiments were also performed for other cobalt bidentate Schiff base complexes. When cobalt complexes **2**, **3**, and **4** were used to replace complex **1**, various enhanced H₂ evolution rates were observed, yielding evolution rates of 260, 390, and 240 μ mol h⁻¹ mg⁻¹ for complex **2**, **3**, and **4**, respectively. These results show that the present system with CdS NRs semiconductor as the photosensitizer and cobalt Schiff base cocatalysts is highly active for photocatalytic H₂ production in water (Figure 2b), further confirming the important role of these molecular cocatalysts. Complexes **2** and **4** showed a relatively low rate of H₂ production compared with complexes **1** and **3**, which can be attributed to their low solubility in water.³⁵ The decreased water solubility of complexes **2** and **4** probably causes aggregation of the complex and poor contact with CdS NRs (Figure S3 and S4). Hence, less photogenerated electrons on CdS NRs would be transferred to the molecular cocatalyst, resulting a lower H₂ evolution rate.

Further experiments were performed to clarify the role of complex **1** in photocatalysis, as shown in Table S1. In the absence of CdS NRs, H₂ production was not detected, which indicates the important role of CdS in light harvesting for photocatalysis. No appreciable H₂ gas was observed in the absence of ascorbic acid, indicating that the sacrificial reagent is compulsory for reduction of protons. In the literature, various sacrificial reagents have been used to significantly improve the photocatalytic activity of the photocatalytic system.⁴⁵ Further experiments were performed to investigate the effect of different sacrificial reagents on photocatalytic efficiency of CdS/complex **1** (Table S3). It can be clearly seen that the highest H₂ evolution rate of 540 μ mol·h⁻

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reagents showed lower H_2 evolution rate, indicating that ascorbic acid is a suitable sacrificial reagent in the present system.

The pH effect on photocatalytic activity was then carried out when other conditions were fixed (Figure 2c). The highest rate of H₂ production was achieved at pH 4, which is consistent with the literature.^{46, 47} For a higher pH value, a sharp decrease in photocatalytic activity was observed, which might be the result of unfavorable protonation of complex **1**. On the other hand, the rate of H₂ production was less at a lower pH value, probably because the ability of ascorbic acid as the electron donor decreases at a lower pH resulting from suppressed equilibrium from HA to A⁻ and H⁺.⁴⁸

To optimize the reaction conditions for photocatalytic H₂ production, more experiments were performed using complex **1** as the cocatalyst. It has been previously observed that concentration of the cocatalyst has a great influence on the rate of H₂ evolution.^{35, 49} As shown in Figure 2d, at a low concentration of the cocatalyst less than 0.02 mM, the rate of H₂ evolution decreased. The maximum rate of H₂ evolution was achieved at 0.02 mM complex **1**. A considerable decrease in rate of H₂ evolution was observed for further increases in the concentration of complex **1**, indicating that a higher concentration of the cocatalyst would be unfavorable in the photocatalytic system.

Apparent quantum yields (AQYs) were calculated using monochromatic light with band pass filter ($\lambda = 420 \text{ nm} \pm 5 \text{ nm}$) for 6 hours (Figure 3a). Initially, the reaction system showed an AQY at ~26%. After first hour, a slight enhancement in AQYs was observed. The highest AQY achieved during 6 hours was ~28% and the average AQY was ~27%. The present AQY for photocatalytic H₂ production is among the best reported AQYs for molecular photocatalytic systems consist of cobalt cocatalysts (see supporting information for details, Table S3).³³ Under optimum conditions, the stability of the photocatalytic system was examined for longterm photocatalysis, as shown in Figure 3b. The results show that the system has good stability over 12 hours and only a slight decrease in the rate of H₂ production was observed, which is probably due to photocorrosion under acidic conditions. The highest TON of 15200 vs. cocatalyst was achieved after 12 hours. For comparison, a controlled experiment was performed without complex **1** while other conditions were maintained. As shown in Figure S5a, significant decrease of H₂ evolution rate was observed during 12 hours irradiation, indicating the key role of complex **1** for CdS to achieve efficient photocatalytic performance. Furthermore, time course of H₂ production was done to confirm the reusability of the photocatalyst. As shown in Figure S5b, the flask was purged with nitrogen to evacuate the produced H₂ at the end of each cycle, and no significant decrease in H₂ evolution rate was observed after 4 cycles, suggesting that complex **1**/CdS photocatalyst can efficiently catalyze H₂ production with good durability.

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After 10 hours of visible light irradiation, CdS NRs were separated from the reaction mixture by centrifugation and thoroughly washed by ethanol and water. The separated photosensitizer was examined again using XRD, TEM, and energy dispersive X-ray spectroscopy (EDX). XRD patterns were well indexed to hexagonal CdS (JCPDS No. 77-2306), confirming that the crystallinity of CdS is not changed and it is stable after photocatalysis under the present conditions (Figure S6). The TEM results confirmed that the surface of the CdS NRs is smooth and no attached particles can be observed (Figures S7a-S7b). EDX data proved the absence of Co⁰ species as no signal of cobalt was detected in the spectrum (Figure S7c).

X-ray photoelectron spectroscopy (XPS) was used for further analysis before and after photocatalytic H₂ production. Figure 4a shows XPS spectra before (red plot) and after (black plot) light irradiation. XPS peaks (red plot) confirm the presence of Cd, S, C, O, and Co elements. After

irradiation (black plot), the Co peak was not observed after washing by ethanol and water. The high resolution spectrum of S 2p shows two peaks at 161.32 eV and 162.51 eV, which can be attributed to S $2p_{3/2}$ and S $2p_{1/2}$, respectively (Figure 4b).⁵⁰ As shown in Figure 4c, the binding energies of Cd $3d_{5/2}$ and Cd $3d_{3/2}$ appear at 404.73 eV and 411.25 eV, respectively, which are similar to the reported values in CdS.^{30, 51, 52} The high resolution XPS spectrum of Co 2p exhibits two peaks (red plot) at 780.62 eV and 796.45 eV (Figure 4d), corresponding to cobalt in the complex.^{53, 54} After washing, the high resolution XPS spectrum of Co 2p (black plot) does not show any significant peaks. Hence, the XPS results also confirm the absence of metallic cobalt and suggest that the enhanced H₂ evolution is due to complex **1** and no colloidal cobalt species are involved in the present photocatalytic reaction, but this will not exclude that the cobalt complex will be decomposed after long-time irradiation.

The photophysical properties were studied to understand the mechanism of this photocatalytic reaction by using steady-state photoluminescence (PL) spectroscopy (Figure 5). CdS NRs shows two PL bands, centered at ~506 nm and ~712 nm. The intense band at ~506 nm can be attributed to near-band-edge emission and the weak band at ~712 nm can be assigned to defects of the surface of CdS NRs.⁵⁵ A decrease in luminescent intensity is observed for the mixed complex 1/CdS (red plot), which probably indicates the efficient transfer of electrons from the excited CdS NRs to complex 1. The results suggest that complex 1 can prevent rapid recombination of electron-hole pairs in the excited CdS NRs and subsequently promote H₂ production.

To obtain a more mechanistic insight of the present photocatalytic reaction using complex **1** as the cocatalyst, UV-Vis spectrum in aqueous solution was examined during the photocatalytic reaction. Motivated by previous reports,^{21,35,56} a Pt chromophore (platinum terpyridylphenylacetylide complex) was chosen as the photosensitizer. The experiment was

performed using complex **1** (2×10^{-5} M) as the cocatalyst, Pt chromophore (1.11×10^{-5} M) as the photosensitizer, and TEOA (1.6×10^{-2} M) as the electron donor in a mixed acetonitrile:water (1:1, v/v) solution at pH 13. The results are shown in Figure 6a. Before visible light irradiation, the absorption spectrum was simply the sum of the components of the reaction mixture. After 30 min of irradiation, the solution color clearly turned from greenish yellow to brick red (Figure 6b), indicating that a chemical reaction had occurred during irradiation. Accordingly, a new broad absorption band appeared in the range of 550-820 nm in the absorption spectrum, which could be assigned to Co(I) formation.^{22, 57}

Based on the above results, we propose a mechanism for photocatalytic hydrogen production in the complex 1/CdS catalytic system. The mechanisms involving monometallic and bimetallic pathways have been reported in numerous studies for molecular cobalt complexes.^{56, 58} For mononuclear mechanisms, the rate of hydrogen production shows a linear dependence on concentration of cobalt catalyst. On the other hand, the H_2 production rate is proportional to the squared concentration of cobalt catalyst $[Co]^2$ for binuclear mechanisms. A nearly linear dependence of H₂ production rate on cobalt concentration can be perceived in the present system, as shown in Figure S8. Therefore, a mononuclear mechanism is suggested (Scheme 1). In detail, the visible light photons excite CdS NRs to generate electrons and holes. The photogenerated holes are filled by oxidation of ascorbic acid, which leads to dehydroascorbic acid, protons, and electrons. The ascorbic acid can also serve as a buffer due to formation of a conjugate base, which maintains the acidic pH even after the reduction of protons to H₂.⁵⁹ Complex **1** accepts the photogenerated electrons and is reduced to Co(I) species. In the next step, a proton can bind to Co(I) and yield Co(III)-H species. Further transfer of electrons will reduce the Co(III)-H species to Co(II)-H species. Binding of another proton to Co(II)-H species results in the formation of hydrogen.

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Conclusions

In summary, we showed that simple cobalt bidentate Schiff base complexes are highly active and noble-metal-free cocatalysts for photocatalytic H₂ production in water without any other organic solvents at ambient temperature. This efficient photocatalytic system uses CdS NRs as the photosensitizer, ascorbic acid as the electron donor, and Co(II) complexes as the molecular cocatalysts. Under optimum conditions, the system presented a TON of 15200 with good stability after 12 hours under visible light irradiation. An average apparent quantum yield of ~27% was achieved under irradiation with visible light ($\lambda = 420$ nm). The enhanced photocatalytic H₂ production is probably due to efficient transfer of electrons from CdS NRs to the cobalt complex cocatalyst. PL spectra and mechanistic studies suggested that the present cobalt molecular cocatalyst can accept the photogenerated electrons from CdS NRs, which probably prevents the recombination of photogenerated electrons and holes in the CdS NRs, thereby promoting the photocatalytic H₂ production.

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Supporting Information Available. Experimental details are available including NMR spectra

of ligands, powder XRD patterns, UV-Vis spectra of complexes in water, and additional figures

detailing solubility. This material is available free of charge via the Internet at http://pubs.rsc.org.

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Figures



Figure 1. (a) Molecular structures of cobalt bidentate Schiff base complexes **1-4**. (b) TEM image of CdS NRs (c) Powder XRD pattern of CdS NRs and mixed complex **1**/CdS. The bottom black plot is the standard XRD pattern, CdS-PDF#77-2306.



Figure 2. (a) UV-Vis absorbance spectra (converted from diffuse reflectance spectra) of CdS NRs, complex 1/CdS, and complex 1. (b) Comparison of H_2 production rates of cobalt complexes 1-4 (0.02 mM) under visible light at pH 4 after 5 h of irradiation. Photocatalytic systems contained 1.0 mg CdS NRs and 0.5 M ascorbic acid as electron donor in 20 mL water. (c) Influence of pH on H_2 evolution rate. (d) Effect of concentration of complex 1 on H_2 evolution rate at pH 4. The system contains 0.5 M ascorbic acid and 1.0 mg CdS NRs in 20 mL water.



Figure 3. (a) H₂ evolution of complex **1** under visible light ($\lambda > 420$ nm) and apparent Quantum Yield using monochromatic light ($\lambda = 420$ nm) (b) Long-term H₂ production under visible light ($\lambda > 420$ nm) containing 0.02 mM complex **1**, 0.5 M ascorbic acid, and 1.0 mg CdS NRs in 20 mL water.



Figure 4. (a) XPS survey spectra of mixture of Complex **1** and CdS NRs (red plot) and after 10 h of photocatalytic reaction (washed by ethanol and water, black plot). (b) High resolution XPS spectrum of S 2p. (c) High resolution XPS spectrum of Cd 3d. (d) High resolution XPS spectrum of Co 2p.



Figure 5. Photoluminescence spectra of CdS NRs (black plot) and complex 1/CdS (red plot) excited at the wavelength of 405 nm.



Figure 6. (a) UV-Vis absorption spectra of system containing Pt chromophore $(1.11 \times 10^{-5} \text{ M})$, TEOA (1.25% v/v), and complex **1** (2 × 10⁻⁵ M) in a mixture of acetonitrile and water (1:1) at pH 13 before and after irradiation ($\lambda > 420 \text{ nm}$) under an inert atmosphere. (b) Color change under visible light irradiation.



Scheme 1. Mechanism of the photocatalytic system with complex 1/CdS NRs under visible light ($\lambda > 420$ nm).



Scheme 2. The reaction process for photocatalytic H₂ production.

TOC

A noble-metal-free photocatalytic hydrogen production system containing a simple bidentate cobalt Schiff base complex as the molecular cocatalyst, CdS nanorods as the photosensitizer, and ascorbic acid as the electron donor was reported.

