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# Incorporating a molecular co-catalyst with a heterogeneous semiconductor heterojunction photocatalyst: Novel mechanism with two electron-transfer pathways for enhanced solar hydrogen production

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ABSTRACT

Photocatalytic hydrogen production is considered to be a promising solution to the global energy crisis and to environmental pollution caused by fossil fuel consumption. In the present study, a core/shell cadmium sulfide/zinc oxide (ZnO/CdS) semiconductor heterojunction photocatalyst is used with a cobalt–salen molecular co-catalyst for highly enhanced photocatalytic activity. CdS nanorods were synthesized using a simple solvothermal method and a ZnO shell was grown by a solution deposition method. Under optimum conditions, the system exhibited a $H_2$ evolution rate of 725 $\mu$mol $h^{-1}$ $mg^{-1}$ with a turnover number of ~102,700 and excellent stability over 50 h in the presence of $Na_2S/Na_2SO_3$ as the electron donor under visible light. The highest apparent quantum yield of the system was 44% under monochromatic 420 nm light. The formation of ZnS during photocatalysis was proved due to surface dissolution of ZnO in alkaline sulfide solution. ZnS can enhance the photocatalytic activity of ZnO/CdS nanorods by providing increased charge transfer interfaces. The molecular cobalt co-catalyst also contributed to the enhanced activity by accepting the photogenerated electrons from the semiconductor photosensitizer. The proposed mechanism suggests that the photogenerated electrons in CdS are transferred not only to ZnO but also to the molecular co-catalysts, leading to highly improved photocatalytic activity for $H_2$ production.

## 1. Introduction

The development of inexpensive, clean, sustainable alternatives to fossil fuels is one of the most urgent needs of humanity, because the consumption of carbonaceous fuels is inextricably linked to pollution of the water, air, and land [1,2]. Solar energy has long been considered as a possible alternative – an inexhaustible, renewable, nonpolluting, and free energy source to address energy problems. Scientists are making efforts to effectively utilize solar energy by photovoltaic and solar fuel systems [3–10]. Solar electricity produced by solar cells is still expensive, difficult to store for a long time, and also affected by daily or seasonal variability in solar flux [11]. Conversion of solar energy into chemical fuels has been considered an efficient way to transform and store this abundant energy resource [12–16].

Hydrogen attracts much attention as a chemical fuel because it can be synthesized directly by solar energy via artificial photosynthesis. Furthermore, its chemical energy per mass is ~142 MJ $kg^{-1}$, which is higher than other chemical fuels, and the burning of $H_2$ results in an environmentally benign product ($H_2O$) [17,18]. In 1972, Fujishema and Honda reported water splitting over $TiO_2$ anodes under UV light [19]. Since then, numerous homogeneous and heterogeneous systems using organometallic or semiconductor photosensitizers have been studied for photocatalytic $H_2$ production [20–23]. Among semiconductor photosensitizers, CdS has proved itself an attractive candidate for $H_2$ evolution due to its narrow bandgap, low cost, and high photocatalytic activity [24,25]. However, CdS undergoes photocorrosion under long-term solar light irradiation. To overcome this drawback, various co-catalysts have been employed, including materials that use noble metals [26,27] and non-noble metals [16,28–30]. These co-catalysts enhance photocatalytic activity by accepting the photogenerated electrons and preventing charge recombination in CdS. In the literature, a few molecular co-catalysts have also been used with CdS to enhance the stability and efficiency of photocatalytic $H_2$ production systems [31–34].

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Another effective strategy is to functionalize the CdS surface with another semiconductor with a suitable bandgap to construct a heterojunction, which can enhance the photostability and photocatalytic activity by efficient transfer of photogenerated charge carriers [35]. Several hybrid semiconductors have been used, such as CdS/$TiO_2$ [36–38], CdS/ZnS [35,39,40], CdS/ZnO [41,42], and CdS/$Cu_2O$ [43]. Among the wide bandgap semiconductors, ZnO has attracted much attention because of its higher electron mobility, stability, and high exciton binding energy (60 mV) [44]. These properties make integration of ZnO with CdS of great interest, allowing unique physical and chemical properties in the photocatalytic reaction. Recently, CdS/ZnO hybrid semiconductors of varying size, thickness, and morphology have been reported [31]. Qureshi and co-workers synthesized an urchin-like nanostructured CdS/ZnO photocatalyst and obtained a high photocatalytic $H_2$ evolution rate [45]. Kundu and co-workers reported that CdS/ZnO nanorod structures exhibited high photocatalytic activity for hydrogen production [46]. In most studies, the photocatalytic experiments were performed under UV–visible light and CdS was deposited over ZnO. Wang and co-workers reported that a CdS shell over ZnO is not stable and suffers photocorrosion when subjected to long-term irradiation [47].

Motivated by previous studies, we report a novel photocatalytic system that incorporates the advantages of a CdS/ZnO core/shell nanorod heterojunction and a molecular cobalt–salen co-catalyst [35,48]. The system showed a highly enhanced photocatalytic $H_2$ evolution rate and great stability under visible light ($\lambda > 420$ nm). The highest $H_2$ evolution rate over 50 h was 725 $\mu mol\ h^{-1}\ mg^{-1}$ with a turnover number of ~102,700 based on the cobalt–salen co-catalyst. The average apparent quantum yield is ~41% and the highest is ~44% under monochromatic 420 nm light. Analysis of the recovered photocatalyst confirmed the formation of ZnS on the surface of ZnO/CdS NRs in the presence of a $Na_2S/Na_2SO_3$ sacrificial electron donor. The effects of ZnS formation on catalytic activity and optical absorption properties were further investigated. Based on the spectroscopic results, a proposed mechanism is discussed for this enhanced photocatalytic $H_2$ production.

## 2. Experimental

### 2.1. Materials

Ethylenediamine (99.0%), *o*-phenylendiamine (98.0%), salicylaldehyde (98.0%), cobalt(II) acetate tetrahydrate ($Co(OAc)_2\cdot 4H_2O$, 99.5%), cadmium chloride hemipentahydrate ($CdCl_2\cdot 2.5H_2O$, 99.0%), sodium sulfide nonahydrate ($Na_2S\cdot 9H_2O$, 99.0%), thiourea ($CH_4N_2S$, 99.0%), sodium sulfite ($Na_2SO_3$, 99.0%), triethanolamine (TEOA, 99%), and N,N-dimethyl formamide (DMF, 99.5%) were purchased from Alfa Aesar or Aldrich and used without further purification. Millipore water (resistivity ~18 MΩ·cm) was used to prepare aqueous solutions. The salen ligands and their corresponding cobalt complexes **1**–**4** were prepared according to reported procedures with minor modifications [49–51].

#### 2.1.1. Synthesis of 3-formyl-4-hydroxybenzoic acid

4-Hydroxybenzoic acid (7.5 g, 54.0 mmol) was added into 20 mL trifluoroacetic acid (TFA) in a 250 mL flask, followed by addition of 7.6 g hexamethylenetetramine (54.5 mmol) in 20 mL TFA under Ar. After being refluxed for 3 h, the suspension became a clear yellow solution. After this was cooled to room temperature, 4 M HCl (100 mL) was added to produce yellow precipitates and the mixture was stirred for 3 h. The precipitates were filtered, thoroughly washed with water, and dried under vacuum. Yield: 45%. $^1H$ NMR (400 MHz, DMSO): $\delta$ (ppm) 11.52 (s, 1H), 10.29 (s, 1H), 8.23 (d, $J = 2.3$ Hz, 1H), 8.03 (dd, $J_1 = 8.7$, $J_2 = 2.3$ Hz, 1H), 7.07 (d, $J = 8.7$ Hz, 1H) (Fig. S1a). Calculated $m/z$ 166.02; found 165.01 $[M-H]^-$ (Fig. S1b).

#### 2.1.2. Synthesis of Co complex 1

3-Formyl-4-hydroxybenzoic acid (0.332 g, 2 mmol) was dissolved in 15 mL ethanol, followed by addition of 15 mL ethanolic solution of ethylenediamine (66.76 μL, 1.0 mmol). The solution was stirred for 1 h at room temperature to produce yellow precipitates as the salen ligand. The product was then collected by filtration, washed with ethanol, and dried under vacuum. To synthesize Co complex 1, 0.249 g $Co(OAc)_2\cdot 4H_2O$ (1.0 mmol) in 10 mL methanol was added dropwise to 10 mL of methanolic solution of the above ligand (0.35 g, 1 mmol). During refluxing for 3 h, dark red precipitates appeared and were finally collected by filtration and thoroughly washed with methanol and water. The solid product was dried under vacuum overnight. Calculated $m/z$ 413.02; found 413.01 (Fig. S2a). Elemental analyses: calculated C 52.32, H 3.41, N 6.78; found C 52.40, H 3.83, N 6.81.

#### 2.1.3. Synthesis of Co complex 2

Ethylenediamine (133.6 μL, 2.0 mmol) in 15 mL ethanol was added dropwise into 15 mL ethanolic solution of salicylaldehyde (0.48 g, 4 mmol). Refluxing for 3 h produced a yellow precipitate. The mixture was then cooled to room temperature and the solid salen ligand was collected by filtration, washed with cold ethanol, and dried in vacuum. To synthesize Co complex 2, 0.249 g Co$(OAc)_2\cdot 4H_2O$ (1.0 mmol) in 10 mL methanol was added to 10 mL methanolic solution of the above salen ligand (0.268 g, 1 mmol). The resulting mixture was refluxed for 2 h, during which reddish brown precipitates appeared. The final product was collected by filtration, washed with methanol and water, and dried under vacuum overnight. Calculated $m/z$ 325.04; found 325.03 (Fig. S2b). Elemental analyses: calculated C 59.09, H 4.34, N 8.61; found C 58.55, H 4.22, N 9.04.

#### 2.1.4. Synthesis of Co complex 3

3-Formyl-4-hydroxybenzoic acid (0.332 g, 2 mmol) in 15 mL ethanol was added dropwise to 15 mL ethanolic solution of *o*-phenylendiamine (0.11 g, 1 mmol). After 2 h of stirring at room temperature, orange yellow precipitates were collected by filtration, washed with cold ethanol, and dried under vacuum to obtain the salen ligand. To synthesize Co complex 3, 0.40 g salen ligand (1.0 mmol) was dissolved in 10 mL methanol, followed by addition of 0.248 g $Co(OAc)_2\cdot 4H_2O$ (1.0 mmol) in 10 mL methanol. The resulting mixture was refluxed for 1 h and brown precipitates appeared. The final product was collected by filtration, washed with methanol and water, and dried under vacuum overnight. Calculated $m/z$ 460.02; found 461.01 (Fig. S2c). Elemental analyses: calculated C 57.31, H 3.06, N 6.08; found C 57.81, H 3.43, N 5.73.

#### 2.1.5. Synthesis of Co complex 4

*o*-Phenylendiamine (0.22 g, 2 mmol) was dissolved in 15 mL ethanol in a 50 mL round-bottom flask, and 0.48 g salicylaldehyde (4 mmol) in 15 mL ethanol was added dropwise into the flask. After 3 h of refluxing, orange yellow precipitates appeared. Then 0.496 g $Co(OAc)_2\cdot 4H_2O$ (2.0 mmol) in 10 mL methanol was added to this reaction solution. The resulting solution was further refluxed for 2 h. Brown precipitates of the complex were collected by filtration, washed with methanol and water, and dried under vacuum overnight. Calculated $m/z$ 373.04; found 373.03 (Fig. S2d). Elemental analyses: calculated C 64.35, H 3.78, N 7.50; found C 64.72, H 3.54, N 6.92.