In Situ Preparation of CoP@CdS and Its Catalytic Activity toward Controlling Nitro Reduction under Visible-Light Irradiation

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ABSTRACT: CoP was synthesized in situ on the surface of CdS nanowires using a cobalt–amine complex as a precursor. The generated CoP@CdS photocatalyst was well characterized by X-ray diffraction, transmission electron microscopy, selected-area electron diffraction, and diffuse reflectance spectra. A more efficient charge transfer was successfully achieved owing to the close contact between CoP and CdS. The hybrid photocatalyst showed excellent activity for the reduction of nitroarenes to the corresponding anilines or azobenzene compounds in water. In present work, hydrogen evolution and nitro reduction were concurrent and with the consumption of substrate, the rate of hydrogen evolution increased. The driving force for the reduction originated from the activated hydrogen species in the photocatalytic reaction rather than from dihydrogen. The photocatalytic activity of as-prepared CoP@CdS in situ is comparable to that of the catalysts formed using a noble metal loaded onto CdS. Mechanistic investigation showed that the condensation route is the major pathway for nitro reduction in the present system, and azo compounds could be obtained with less irradiation time, while aniline will be obtained via long-time irradiation.

1. INTRODUCTION

Heterocatalysis, especially photocatalysis, with semiconductor materials has attracted considerable attention. However, most of the research on photocatalysis is largely concentrated on the photocatalytic splitting of water to H2 and O2 or the decomposition of organic pollutants to H2O and CO2 without selectivity.1–7 Nevertheless, it is a challenge to utilize semiconductor-based photocatalysts for organic transformation. The rational application of suitable semiconductor catalysts and the control of the reaction conditions can promote the conversion of reactants into target products.8 The reduction of nitroaromatics is one of the most important reactions in organic synthesis and industrial production.9,10 The traditional reduction reactions with an initial reaction rate of 132μmol h−1 g−1.11 Weiss et al. have reported that electron transfer, not proton transfer, is the rate-limiting step for nitrobenzene reduction.26 Guo et al. used Cu on graphene as a catalyst for the controlled catalysis of the reduction of aromatic nitro compounds to azo compounds.27

2. EXPERIMENTAL SECTION

2.1. Materials. All chemicals were of analytical grade and used as received without further purification. Co(OAc)2·4H2O, NaH2PO2, ethylene diamine, and sodium diethyldithiocarbamate trihydrate (C4H10NNaS2·3H2O) were obtained from...
were dried in an oven at 60 °C for 24 h and then cooled to room temperature. A yellow precipitate followed by 0.5 mL of NH₃·H₂O was added to a 250 mL eggplant-shaped bottle, followed by the addition of 3 mL of deionized water and subsequently the mixture was treated by ultrasonic wave for 20 min. Cadmium diethyldithiocarbamate (Cd(S₂CNEt₂)₂) was obtained, and then 40 mL of ethylene diamine was added into a 100 mL autoclave. The autoclave was maintained at 180 °C for 24 h and then cooled to room temperature. A yellow precipitate was collected and washed with ethanol, and the final products were dried in an oven at 60 °C overnight.

2.2. Preparation of CdS Nanowires (CdSnw’s). CdS nanowires (CdSnw’s) were synthesized via a modified method. In a typical procedure, 627.6 mg of CdCl₂·2.5H₂O and 1238.3 mg of sodium diethyldithiocarbamate trihydrate (C₅H₁₀NNaS₂·3H₂O) were added into 3 mL of deionized water and subsequently the mixture was treated by ultrasonic wave for 20 min. Cadmium diethyldithiocarbamate (Cd(S₂CNEt₂)₂) was obtained, and then 40 mL of ethylene diamine was filled into a 100 mL autoclave. The autoclave was maintained at 180 °C for 24 h and then cooled to room temperature. A yellow precipitate was collected and washed with ethanol, and the final products were dried in an oven at 60 °C overnight.

2.3. Preparation of CoP@CdS. In the first step, 600 mg of as-prepared CdSnw’s was added to a 250 mL eggplant-shaped bottle, followed by the addition of 24 mL of ethanol and 0.5 mL of deionized water. The mixture was ultrasonicated for 30 min at room temperature, and then 0.6 mL of Co(OAc)₂·4H₂O (87.2 mg) aqueous solution was dropwise added into the mixture, followed by 0.5 mL of NH₃·H₂O. After 30 min of stirring, 95 mL of ethanol was poured into the bottle and stirred for another 30 min. The obtained suspension was heated to 80 °C for 22 h. Then, the suspension was transferred into a 100 mL autoclave of 80% capacity and heated to 150 °C for 3 h. A brown-yellow product (Co₃O₄@CdS) was collected by centrifugation and washed with ethanol three times. In the second step, 281 mg of NaH₂PO₂ was placed at the upstream of a quartz boat and the dried Co₃O₄@CdS was placed at the downstream of the boat with a distance of 4 cm. Afterward, the boat was directly heated to 300 °C for 2 h under an Ar atmosphere in a tube furnace. Subsequently, after cooling to room temperature naturally in continued Ar flow, the obtained brown solid (CoP@CdS(5%)) was washed with water and ethanol several times and dried in a vacuum oven. The weight percentages of CoP (theoretical value) in the various composites produced were 1, 2.5, and 7.5, and pure CoP nanoparticles were also synthesized without CdSnw’s by a similar method.

2.4. Characterization. The samples were characterized by powder X-ray diffraction (XRD) on a Bruker AXS D8 X-ray diffractometer with Cu Kα (λ = 1.54056 Å) to identify their phases. The particle size and lattice fringes of the samples were analyzed on a transmission electron microscope (TEM; JEM 2100F) with an accelerating voltage of 200 kV. UV–vis reflectance spectra (DRS) were recorded on a spectrophotometer (Varian Cary 5000) using BaSO₄ as a reference. The chemical structure and quantity of the products were determined by ¹H nuclear magnetic resonance (NMR) spectroscopy (Bruker Avance 400 spectrometer). The produced hydrogen was measured by a gas chromatograph (GC-2014C, Shimadzu, with argon as a carrier gas) with a 5 Å molecular sieve column (3 × 2 m²) and a thermal-conductivity detector. Thermogravimetric analysis was performed on a TA Instrument Q600 SDT from room temperature to 500 °C.

2.5. Photoelectrochemical Measurements. Photocurrent measurements were conducted on a CHI 660e electrochemical workstation (Chenhua Instrument, China) using a conventional three-electrode configuration. A catalyst electrode served as the working electrode, with a platinum foil as the counter electrode and an Ag/AgCl (saturated KCl) electrode as the reference electrode. Then, 0.2 M Na₂SO₄ aqueous solution was used as the electrolyte, through which nitrogen was bubbled for 20 min prior to measurement. The white light-emitting diode (LED) (30 × 3 W, λ ≥ 420 nm) light source was used for irradiation. The working electrodes were prepared as follows: 3 mg of sample was dispersed in 40 μL of isopropanol with 5 μL of Nafion by sonication for 20 min. The slurry was then evenly spread onto a 3.0 cm × 1.0 cm × 0.1 cm indium tin oxide (ITO) glass substrate with an active area of about 1.0 cm². The film was dried in air. The photoresponses of the samples at light on and off were measured at 0.1 V.

2.6. Photocatalytic Test. Typically, 5 mL of water containing 0.1 mmol of substrate, 2 mmol of HCOONH₄, and 4 mg of the CoP@CdS photocatalyst was added to a 15 mL cuvette sealed with a rubber septum placed on top of a magnetic stirrer. A stream of Ar was then passed into the reaction system for 10 min. White light-emitting diodes (LEDs) (30 × 3 W, λ ≥ 420 nm) were used as the irradiation light source. The LEDs were positioned 3 cm away from the sample, which was kept under continuous stirring at room temperature. The mixture was stirred for 10 min before irradiation.
In the cycling tests, the used photocatalyst was recycled by centrifugation, washed with ethanol and deionized water, and dried at 60 °C in a vacuum oven. Dichloromethane was used as the extraction agent and extracted three times in a row.

3. RESULTS AND DISCUSSION

One-dimensional semiconducting materials, such as CdS nanowires, have drawn widespread attention because of their inherent structure, a large surface area with a high length-to-diameter ratio, which can reduce the transportation distance of photoinduced charge carriers as well as reduce the defects and...
impurities in CdS nanocrystals. However, their photocorrosion is a major drawback. A cocatalyst can improve the photogenerated electron−hole pair separation efficiency and enhance the activities and stabilities of photocatalysts. Crystalline metal phosphides, serving as efficient and robust cocatalysts, can produce H₂ at a high rate under sunlight irradiation, as reported in our previous work. Du and co-workers prepared a core−shell amorphous CoPₓ/CdS photocatalyst in situ. Nevertheless, CoPₓ showed no diffraction peaks, which indicated that this material could be amorphous. Herein, we report a moderate and controllable method for the preparation of CoP in situ. Cobalt acetate was combined with ammonium hydroxide to produce a yellow cobaltous hexammonate salt; subsequently, the solution was heated to 80 °C to generate a trivalent orange-yellow hexaaaminocobalt salt. After solvothermal treatment, Co₃O₄ was uniformly dispersed on the surface of the CdS nanowires and phosphorized with NaH₂PO₂ at 300 °C to form the CoP nanoparticles in situ (Figure 1).

The hexagonal CdSnw's (JCPDS No. 77-2306) were prepared according to a reported procedure. The as-synthesized CdS was robust at 300 °C under Ar (Figure 2d) and was stable below 320 °C, as confirmed by thermogravimetric analysis (Figure S1). The intensity of CdS is extremely high in XRD, and this is ascribed to the lower content of CoP compared to that of CdS in the CoP@CdS(5%) catalyst; therefore, the pattern of CoP cannot be observed from Figure 2d. The XRD patterns of CdSnw's and CdS(300 °C) show no difference, suggesting that CdS is stable when heated to 300 °C.

The TEM images revealed that the crystalline CoP nanoparticles (JCPDS No. 29-0497) were coated on the CdSnw's with intimate contact (Figures 2a and S2). In addition, bare CoP and Co₃O₄ nanoparticles were also prepared in the same way but in the absence of CdSnw's (Figure S3). The high-resolution TEM (HRTEM) image (Figure 2b) of CoP@CdS shows that the CoP nanoparticles were less than 10 nm in diameter. The strong reflection of the (211) plane corresponded to lattice fringes with a d-spacing of 0.19 nm, and a lattice spacing of 0.27 nm corresponded to the (002) plane, which confirmed that the CoP nanoparticles were successfully anchored to the surface of the CdSnw's. Energy dispersive X-ray (EDX) mapping images (Figure 2c) showed that Co and P were uniformly distributed over the whole surface of the CdSnw's. In addition, selected-area electron diffraction indicated that the obtained sample contained intense diffraction peaks, which were attributed to single-crystalline CdS nanowires (Figure S4), and weak diffraction peaks, which were assigned to CoP. The reason for the weak diffraction peaks of CoP may be the very strong peaks of CdSnw's and the relatively small amount of CoP coated on the surface of the CdSnw's. Figure 2e depicts the UV−vis DRS of CoP@CdS. The band gaps of the samples were obtained using the Tauc/Davis−Mott model, as shown in Figure 2f. Compared with bare CdS, with increasing content of CoP broad background absorption progressively increased in the visible light range.

| entry | catalyst | conv (%) | sel (%)     |
|-------|----------|----------|-------------|
|       |          | a        | b           | c           | d           |
| 1     | CoP@CdS(1%) | 92.9     | 7.4         | 3.2         | 56.2        | 33.2        |
| 2     | CoP@CdS(2.5%) | 92.1     | 8.6         | 2.0         | 39.3        | 50.1        |
| 3     | CoP@CdS(5%) | 93.1     | 8.4         | 1.3         | 11.6        | 78.7        |
| 4     | CoP@CdS(7.5%) | 90.6     | 10.4        | 2.0         | 36.8        | 50.8        |
| 5     | CdSnw     | 87.7     | 14.0        | 19.6        | 53.1        | 13.3        |
| 6     | CoP/CdS(5%) | 83.0     | 21.1        | 4.3         | 32.9        | 41.7        |
| 7     | Co₃O₄@CdS(5%) | 79.7     | 25.4        | 6.0         | 41.5        | 27.1        |
| 8     | Au@CdS(1.1%) | 90.7     | 9.7         | 17.5        | 3.1         | 69.7        |
| 7     | Pt@CdS(0.6%) | 95       | 5.7         | 18.5        | 28.0        | 47.8        |
| 9     | CoP@CdS(5%) | 0        | 0           | 0           | 0           | 0           |
| 10    | CoP@CdS(5%) | 0        | 0           | 0           | 0           | 0           |

*aReaction conditions: 0.1 mmol of 4-nitrotoluene, 4 mg of catalyst, 5 mL of H₂O, 2 mmol of HCOONH₄, degassed with Ar, 10 h irradiation with white LED, at room temperature. *bCoP/CdS(5%) was prepared by grinding. *cWithout photocatalyst. *dIn the dark. *eWithout HCOONH₄.
The band-gap value of CoP@CdS was smaller than that of CdS; the smallest band gap was 2.38 eV for CoP@CdS(5%). Figure 2g shows the transient photocurrent responses of CdS and CoP@CdS(5%) during several on-off cycles. The generated photocurrent mainly originated from the photoinduced electrons diffusing to the indium tin oxide (ITO), which suggested that a more efficient charge transfer was successfully observed through the formation of the heterojunction.

Semiconductors absorb photons to produce electron and hole pairs. The electrons then migrate to the cocatalyst, and the protons combine with electrons to produce atomic hydrogen. However, prior to the generation of hydrogen, the atomic hydrogen formed on the metallic CoP may reduce the nitro group. The reduction is a stepwise process via nitroso and hydroxylamine intermediates, which may condense to coupling products, as reported by Haber. Therefore, we could utilize the reaction to study the photocatalytic ability of the prepared CoP@CdS.

The reduction of nitroaromatic compounds was carried out in anaerobic water under white LED irradiation at room temperature. Previous work with the Ni2P/CdS hybrid material obtained by grinding the raw CdS and Ni2P nanoparticles showed that Na2S/Na2SO3 can be used as a reductant in the

### Table 2. Photocatalytic Reduction of Nitroarenes Containing Various Substituents

| Entry | Substrate | Time (h) | Conv. (%) | Sel. (%) |
|-------|-----------|----------|-----------|----------|
| a     |           |          |           |          |
| b     |           |          |           |          |
| c     |           |          |           |          |
| d     |           |          |           |          |

| Entry | Substrate | Time (h) | Conv. (%) | Sel. (%) |
|-------|-----------|----------|-----------|----------|
| 1     | OHC       | 12       | 95.0      | 3.8      |
|       |           |          |           | 3.0      |
| 2     | OHC       | 14       | 96.3      | 3.6      |
|       |           |          |           | 0        |
| 3     | Cl        | 16.5     | 95.0      | 4.7      |
|       |           |          |           | 0        |
| 4     | Br        | 16.5     | 95.9      | 4.4      |
|       |           |          |           | 0        |
| 5     | NO2       | 16.5     | 96.2      | 79.8     |
|       |           |          |           | 0        |
| 6     | NO2       | 16.5     | 94.6      | 5.7      |
|       |           |          |           | 0        |
| 7     | NO2       | 14       | 90.2      | 5.4      |
|       |           |          |           | 0        |
| 8     | NH2       | 14       | 69.8      | 0        |
|       |           |          |           | 0        |
| 9     | NO2       | 16.5     | 44.8      | 0        |
|       |           |          |           | 14.8     |

*a* Reaction conditions: 0.1 mmol of nitroarene, 4 mg of catalyst, 5 mL of H2O, 2 mmol of HCOONH4 degassed with Ar, irradiation with white LED, at room temperature.
In the present study, cheap and stable ammonium formate was used as an electron donor. The content of CoP had a significant influence on photocatalytic transformation. As shown in Table 1, as the CoP concentration increased from 1 to 5%, a gradual improvement in the yield of aniline was achieved, whereas the amount of the azo and hydrazo intermediates decreased rapidly. This was attributed to the higher amount of cocatalyst CoP, which provided more active sites for the reduction of the nitro groups. When the CoP content was increased to 7.5%, the selectivity to aniline dropped, whereas the conversion of nitroarene changed slightly. This could be because an excess of CoP nanoparticles coated on the surface of CdS shielded the incident light and could also merge together and reduce the amount of catalytic active sites. Therefore, the optimal loading amount of CoP was 5%. In contrast, the yield of aniline obtained with CoP/CdS(5%), which was prepared by grinding the two pure phases, was much lower than that obtained with CoP@CdS prepared in situ. The reactions with the CoP/CdS(5%) catalyst generated more azoxy and hydrazo derivatives (Table 1, entry 6), which indicated that compactness and dispersivity had a significant effect on the catalytic activity of the catalyst. Furthermore, plasmonic metals such as Au have been studied for intense absorption in the visible region because of surface plasmon resonance effects. The combination of Au and CdS could remedy their drawbacks such as low photocatalytic efficiency and photocorrosion. For comparison, Au@CdS(1.1%) was prepared by photo-deposition, and its catalytic ability for nitro reduction reached 63.2% yield of the final reduction product in 10 h, which was slightly less than that of CoP@CdS(5%) (conversion yield of 73.3%). It is well known that Pt is also an efficient hydrogen-generating catalyst. We further measured the reduction ability of 0.6% Pt@CdS under identical conditions. The results demonstrated that the catalytic activity of Pt@CdS was not better than that of the CoP@CdS(5%) sample. The photocatalytic activity of CoP@CdS prepared in situ was comparable to that of catalysts formed using noble metals loaded onto CdS. Control experiments showed that the photocatalyst, light, and sacrificial agent were indispensable (Table 1, entries 8–10).

It is interesting that the reduction of the nitro group in the present system was accompanied by hydrogen evolution. Figure 3 shows the \( H_2 \) evolution process with ammonium formate as the sacrificial agent in the absence of nitroarene. However, when 4-nitrotoluene was introduced into the system, the rate of hydrogen production became very slow. After 4-nitrotoluene was almost consumed, the hydrogen production rate increased after 14 h. The conversion was 76.2% after the first 2 h, whereas the selectivity for aniline was only 16.8% and the main product was the azo compound. Subsequently, the selectivity of aniline gradually increased with time, whereas the conversion increased slowly. This indicated that the nitro group was easy to reduce to an azo group and the amount of product controlled by the dynamics process was more important at the initial stage of the reaction. Therefore, we can conclude that the condensation route was the major pathway for nitro reduction in the present system (Figure S5) and the major reduction products can be tuned by controlling the reaction time. For comparison, azobenzene was used as a substrate; after 10 h of irradiation, the main product was hydrazobenzene and a small amount of aminobenzene was obtained. The result showed that hydrazo compounds were a big hurdle for obtaining aniline. However, when nitroarene was used as a substrate, the produced azo compound was converted to aniline faster than similar azo derivative was used as the substrate, which suggested that oxazobenzene generated in the condensation reaction plays an important role in the formation of aniline. A detailed investigation of this reaction is underway. In addition, 1 atm of hydrogen instead of ammonium formate was utilized to reduce the nitroarene under the same conditions, but no product was detected. Furthermore, when 2,2,6,6-tetramethyl-1-piperidinylxoy was employed to trap atomic hydrogen in the reaction system, the conversion of the substrate dropped greatly. Therefore, the activated hydrogen species, rather than the produced dihydrogen, drives the reduction reaction. The kinetic isotope effect was investigated in water and deuterated water (Figure S6). The ratio between \( k_{H} \) and \( k_{D} \) was determined to be 1.37, which suggested that the O–H(D) bond cleavage was critical to the whole reduction.

The reduction reaction induced by visible light was further extended to other nitroarenes (Table 2). From a synthesis perspective, it is challenging to selectively reduce a nitro group while keeping other reducible groups unchanged. Vulnerable functional groups such as aldehydes, ketones, alkynyls, and cyano were introduced into this photocatalytic system. The nitro group was reduced selectively, and the vulnerable groups remained unchanged. As reported by other research groups, halogenated nitroarenes were expected to dehalogenate during nitro reduction. Nevertheless, in the studied system, dehalogenation was suppressed and halogenated anilines were observed with high selectivity. In addition, a high conversion efficiency was obtained with nitroarenes containing electron-withdrawing groups, whereas high selectivity for aniline was obtained with nitroarenes containing electron-donating groups. After a long irradiation time (>12 h), azo compounds nearly disappeared and the main byproduct was a hydrazo compound, except for the case of 4-nitrophenylacetylene.

The durability of the CoP@CdS photocatalyst was examined through the reduction of 4-nitrotoluene to 4-toluidine. The used photocatalyst was recycled by centrifugation, washed with ethanol and deionized water, and dried at 60 °C in a vacuum oven. The activity of the photocatalyst in this system remained the same after eight successive runs (Figure 4).
4. CONCLUSIONS

In summary, CoP@CdS was used as an efficient and robust photocatalyst for the reduction of nitroarenes. The catalyst was fabricated using hexamminecobalt salt to produce Co₅O₆ in situ and phosphorized by a solid-state thermal reaction. Crystalline CoP was coated on the CdS nanowires with close contact and even dispersion. The nitro reduction was driven by hydrogen species originating from the photocatalytic reaction rather than by dihydrogen. The photocatalytic reduction of the nitro group proceeded through a condensation pathway, and the desired products azobenzene and aniline were obtained by controlling the irradiation time. Vulnerable functional groups remained unchanged during the reduction.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01592.

Figures S1–S11 and Table S1 (PDF)

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Notes
The authors declare no competing financial interest.

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