



Highly efficient simultaneous hydrogen evolution and benzaldehyde production using cadmium sulfide nanorods decorated with small cobalt nanoparticles under visible light



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ABSTRACT

Photocatalytic hydrogen evolution coupled with selective oxidation to produce fine chemicals under mild conditions is a promising strategy for green synthesis of both fuel carriers and useful materials. Herein, we report a highly efficient catalyst, created by in-situ anchoring cobalt nanoparticles onto cadmium sulfide nanorods, for simultaneous hydrogen evolution and benzaldehyde production from photocatalytic dehydrogenation of benzyl alcohol under visible light. Two half reactions, hydrogen evolution and benzaldehyde production, are well coupled as the reductive side and oxidative side, respectively. The system can produce hydrogen and benzaldehyde with high selectivity and efficiency. The optimal selectivity for benzaldehyde production is ~94.4%. Mechanism studies indicate that the carbon-centered radical is the key intermediate during the oxidation of benzyl alcohol and plays a very important role on the selectivity for benzaldehyde production. Under optimal conditions, the rate of hydrogen evolution in the present noble-metal-free system is ~848 $\mu\text{mol h}^{-1}$ and an apparent quantum yield of 63.2% ($\lambda = 420 \pm 5 \text{ nm}$) is achieved. To the best of our knowledge, this is the highest value ever reported for hydrogen evolution from photocatalytic dehydrogenation of benzyl alcohol under visible light.

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1. Introduction

Solar driven hydrogen (H_2) evolution is a promising approach for the direct conversion of solar energy to chemical energy and has drawn great attention due to the depletion of fossil fuels and increasing environmental issues [1–9]. Photocatalytic water splitting is a well-researched way to achieve this purpose. It is generally believed that in an ideal photocatalytic system, protons are reduced to H_2 by the photogenerated electrons on the reductive side and oxygen is produced as the product of water oxidation by the holes on the oxidative side, which is so-called photocatalytic overall water splitting. Unfortunately, in most cases, the rate of total photocatalytic reaction is considerably low due to the fact that the sluggish water oxidation half-reaction does not match well with the reduction side half-reaction [10]. In addition, O_2 is not a desirable product during H_2 evolution due to the fact that uncontrolled reverse reaction of H_2 and O_2 on the photocatalyst surface reduces the performance of photocatalytic water splitting

[11]. Furthermore, it is well known that H_2 - O_2 is an explosive gaseous mixture, so system safety and gas separation thus should be taken into consideration, which still remains a great challenge in industry.

As an alternative way to solve the abovementioned problems, sacrificial reagents, which are oxidized much easier than water, are commonly added in the photocatalytic system to speed up the consumption of photogenerated holes for high-performance photocatalytic H_2 evolution [12–16]. However, the oxidation of sacrificial reagents usually involves a complicated pathway and the corresponding products have limited commercial applications. Some systems also release CO_x ($X = 1$ or 2), which will be harmful to our environment [17]. Thus, the introduction of sacrificial reagents not only greatly increases the cost but also wastes the energy of the holes [18–21]. To solve this problem, a suitable reaction substrate which can be selectively transferred to high-valued chemical products at desirable rate should be preferred for the oxidative half-reaction. Among various candidates, benzyl alcohol (BA) can meet this requirement. The selective oxidation of BA to benzaldehyde is one of the most important organic reactions due to the fact that the carbonyl derivatives are widely used in industry

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[22–24]. Traditionally, this transformation is achieved by hazardous, toxic stoichiometric oxidants under stringent conditions such as high pressure and/or high temperature [22,23,25]. Green synthetic routes have been reported, featuring photocatalytic oxidation of BA under air over semiconductors such as TiO₂ [26], C₃N₄ [27], CdS [28], and Bi₂MoO₆ [25]. However, it should be noted that, no hydrogen was reported to be produced in these systems and molecular oxygen (O₂) is essential in these photocatalytic systems for benzaldehyde production. Recent studies pointed out that superoxide radicals produced by the reaction of O₂ with the photo-generated electrons on the reductive side serve only as electron and proton acceptors, and do not participate in the BA oxidation process [25,29]. These results indicate that the energy of both electrons and protons from BA are wasted for aerobic BA oxidation reaction.

A promising approach to address the issues of the oxidation side is to design a CO_x-free photocatalytic reaction system for dehydrogenation of BA in which protons from BA are reduced to H₂ by the electrons and BA is selectively oxidized to carbonyl compounds by the photogenerated holes. As a result, the photogenerated charge carriers can be fully utilized and so such a photocatalytic approach for H₂ evolution will be more practical compared to water splitting with sacrificial reagents in terms of economic sustainability.

Herein, we report a novel efficient noble-metal-free photocatalytic system using CdS nanorods (NRs) as the photosensitizer and in-situ photodeposited tiny cobalt nanoparticles as cocatalyst for efficient visible-light driven dehydrogenation of BA for simultaneous H₂ evolution and selective benzaldehyde production. Under optimal conditions, the reaction selectivity for benzaldehyde production is as high as 94.4% and this system shows an impressive H₂ production activity (848 μmol h⁻¹) under visible light irradiation (λ > 420 nm). The average apparent quantum yield is 63.2% at 420 nm.

2. Experimental details

2.1. Materials

Ethylenediamine (99.0%), cobalt chloride hexahydrate (CoCl₂·6H₂O, 99.5%), thiourea (CH₄N₂S, 99.0%), cadmium chloride hemipentahydrate (CdCl₂·2.5H₂O, 99.0%), acetonitrile (CH₃CN, 99.0%), BA (C₇H₈O, 99.0%), and benzaldehyde (C₇H₆O, 99%) were purchased from Alfa-Aesar or Aldrich and used without further purification. Millipore water (resistivity: ~18 MΩ cm) was used when needed.

2.1.1. Synthesis of Co/CdS photocatalysts

CdS NRs were synthesized according to our previous reports [30,31]. 10.125 mmol (4.62 g) of CdCl₂·2.5H₂O and 30.375 mmol (4.62 g) of thiourea (CH₄N₂S) were dissolved in 60 mL of ethylenediamine. The mixture was transferred into a Teflon-lined autoclave with a volume of 100 mL, sealed, and maintained at 160 °C for 48 h. Then the autoclave was allowed to cool down to room temperature. The resulting yellow solid products were collected by centrifugation, washed with distilled water and ethanol three times each to remove any residue of organic solvent. The final product was then dried at 60 °C overnight.

The Co/CdS composite was prepared by an in-situ photodeposition method. Typically, a certain amount of CoCl₂·6H₂O was added to a suspension of CdS NRs photocatalysts (5.0 mg) in BA solution and then the suspension was irradiated under visible light. The sample prepared using 0.3 mg/mL CoCl₂·6H₂O was then

centrifuged and stored under argon after the photocatalytic experiments for further physical characterization.

2.2. Characterization methods

The crystal diffraction patterns of the photocatalyst samples were investigated by powder X-ray diffraction (XRD, D/max-TTR III) using graphite monochromatized Cu Kα radiation of 1.54178 Å, operating at 40 kV and 200 mA. The scanning rate was 10° min⁻¹ from 20° to 80° (2θ). Scanning electron microscopy (SEM) was performed on a JSM-6700F microscope. Transmission electron microscopy (TEM) images were collected on a JEM-2010 electron microscope, operated at an acceleration voltage of 200 kV. The UV-Vis diffuse reflectance spectra were obtained using a UV-visible spectrophotometer (SOLID 3700 UV-vis spectrometer). X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 250 X-ray photoelectron spectrometer. The steady state photoluminescence (PL) spectra were obtained on JY Fluorolog-3-Tou fluorescence spectrometer, and time-resolved photoluminescence (TRPL) spectra were recorded on a PicoHarp 300 (PicoQuant) instrument. The spin trapping experiments were performed in deoxygenated solutions using a JES-FA200 ESR spectrometer at room temperature. The irradiation experiments were carried out with a Xe lamp (500 W, USHIO Optical Modulex SX-U1501XQ) equipped with a UV cutoff filter (λ > 420 nm).

2.3. Photocatalytic dehydrogenation of BA

The experiments were carried out in a 50 mL round-bottom flask at ambient temperature. A 300 W Xe-lamp equipped with a 420 nm cut-off filter was used to provide the visible light irradiation. In a typical photocatalytic reaction, the photocatalyst powder sample was dispersed in a 20 mL pure benzyl alcohol or a mixture of benzyl alcohol and acetonitrile depending on the concentration of benzyl alcohol used for the photocatalytic reactions. Before irradiation, the solution was bubbled with high purity nitrogen for 15 min to remove the air. Methane was added in the reactor as the internal standard. The amount of evolved H₂ was determined by gas chromatography (GC) equipped with a TCD detector. After reaction, the catalyst powders were removed by centrifugation (10 min at 12000 rpm), and the supernatants containing BA and products were injected into GC (JieDao 1690) with a flame-ionization detector using a PEG-20M 0.25 mm × 0.25 μm × 30 m capillary column (GC conditions: front inlet temperature: 280 °C, FID temperature: 300 °C, carrier gas: Ar, oven temperature: first kept at 60 °C for 3 min, and then increased to 230 °C at a rate of 15 °C/min, sample injection volume: 2 μL). Calibration curves were used to determine the yields of benzaldehyde (Fig. S1). Qualitative analysis of catalytic mixture was characterized by using proton nuclear magnetic resonance (¹H NMR) spectroscopy on a Bruker DPX 400 spectrometer at 298 K using CD₃CN as solvent. The chemical structures of the products were confirmed by GC-MS (Trace 1300, Thermo scientific). The apparent quantum yield (AQY) was measured using a 300 W Xe-lamp equipped with a 420 nm (±5 nm) bandpass cut filter. The light intensity was ca. 7.3 mW/cm² and the illuminated area for the reactor was about 1.44 cm². The AQY was calculated based on the following equation:

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

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