

Communication

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Efficient Visible Light-Driven Splitting of Alcohols into Hydrogen and Corresponding Carbonyl Compounds over a Nimodified CdS Photocatalyst

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Photocatalysis, splitting of alcohol, visible light, semiconductor, hydrogen production

ABSTRACT: Splitting of alcohols into hydrogen and corresponding carbonyl compounds has potential applications in hydrogen production and chemical industry. Herein, we report that a heterogeneous photocatalyst (Ni-modified CdS nanoparticles) could efficiently split alcohols into hydrogen and corresponding aldehydes or ketones in a stoichiometric manner under visible light irradiation. Optimized apparent quantum yields of 38%, 46% and 48% were obtained at 447 nm for dehydrogenation of methanol, ethanol and 2-propanol, respectively. In the case of dehydrogenation of 2-propanol, a turnover number of greater than 44,000 was achieved. To our knowledge, these are unprecedented values for photocatalytic splitting of liquid alcohols under visible light to date. Besides, the current catalyst system functions well with other aliphatic and aromatic alcohols, affording the corresponding carbonyl compounds with good to excellent conversion and outstanding selectivity. Moreover, mechanistic investigations suggest that an interface between Ni nanocrystal and CdS plays a key role in the reaction mechanism of the photocatalytic splitting of alcohol.

As a promising form of clean energy, hydrogen energy has attracted increasing attention, focusing on the highly efficient conversion of chemical energy into electricity. The storage and transportation of hydrogen is a key but challenging technology for mobile applications of proton exchange membrane fuel cells (PEMFCs).¹⁻⁴ Alcohols, such as methanol and ethanol, are regarded as potential carriers for hydrogen production and storage.3,5,6

There are two ways to produce hydrogen from alcohols. The first method is conventional alcohol reforming, which produces both hydrogen and carbon dioxide under high temperatures and high pressures.^{7,8} Recently, ruthenium-catalyzed aqueous-phase dehydrogenation of methanol to hydrogen and carbon dioxide at relatively lowtemperatures (65-95°C) and ambient pressure has been reported.⁵ The second method of producing hydrogen from alcohols is the direct catalytic dehydrogenation of alcohols, which generates hydrogen and corresponding aldehydes or ketones. The reported direct dehydrogenation reactions of alcohols were conducted at reflux or an even higher temperature signifying that extra energy is essential.9-13





A sustainable way to drive the splitting of alcohols is to utilize solar energy. Photocatalytic hydrogen generation from water using alcohols as hole scavengers has been mostly studied.¹⁴⁻¹⁷ Notably, in this system, water is used as electron acceptor and alcohol is used as a sacrificial agent and its primary oxidation products, such as aldehydes, could be further oxidized to carboxylic acid, carbon monoxide (CO) or carbon dioxide because of the presence of water.^{14,15,17-19} In particular, even a small concentration of CO (10 parts per million, p.p.m.) can easily poison the catalyst in proton exchange membrane fuel cells (PEMFCs).²⁰ To achieve a stoichiometric splitting of ACS Paragon Plus Environment

alcohol, the photocatalyst should be able to abstract hydrogen from the alcohol instead of water. Herein, we report a noble-metal-free photocatalyst (Ni nanocrystalmodified CdS nanoparticles (NPs), Ni/CdS) which could efficiently split alcohols into hydrogen and corresponding aldehydes or ketones in a stoichiometric manner using visible light (Scheme 1). To our knowledge, such an efficient heterogeneous photocatalyst for the visible lightdriven splitting of alcohol has not been reported to date.

Well-crystallized hexagonally structured CdS NPs prepared according to a previously described method²¹ were employed as photocatalysts (see Supporting Information, Figure S₅). Modification of the surface of CdS NPs with Ni nanocrystal was performed by in situ photodeposition in which methanol acts as an electron donor and NiCl₂ serves as an electron acceptor (Figure S1). The influence of solvent on the photodeposition is shown in Figure S2, which reveals that the photodepositions performed in the absence of water were more favorable for the hydrogen evolution. We attribute this to that metallic Ni nanocrystals could be oxidized by water. Therefore, methanol solution of NiCl₂ was chosen for the photodeposition. Then we studied concentration of NiCl₂ on the rate of hydrogen evolution. As shown in Figure S₃, the rate of hydrogen evolution firstly increased along with increasing amount of NiCl, and then reached to a plateau. The optimized weight ratio of Ni and CdS was 1.6 wt% determined by inductively coupled plasma-atomic emission spectroscopy (ICP) analysis. Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images of the Ni/CdS NPs are provided in Figure 1a and Figure 1b, respectively, which indicate that a ca. 5 nm Ni nanocrystal was deposited on the CdS surface. The lattice distances measured for the Ni nanocrystals are 0.20 and 0.18 nm, which correspond well with lattice distances of (111) and (200) of a metallic Ni (the Powder Diffraction File, PDF#04-0850), respectively. However, Ni nanocrystal does not show any obvious peaks in the X-ray diffraction (XRD) pattern (Figure S6), which can be attributed to its low loading amount and small crystalline size. X-ray photoelectron spectroscopy (XPS) was performed (Figure S7 and Figure S10); in the resultant spectrum, peak at 852.1 eV was attributed to metallic Ni;15 peaks at 853.3 and 856.0 eV were attributed to be NiO and NiCl₂, respectively.



Figure 1. (a) TEM image of Ni/CdS and (b) HRTEM image of Ni/CdS (the inset image is the Fourier transform of the marked area).



Figure 2. (a) Long-term photocatalytic splitting of 2propanol (5 mL) under visible light (λ >420 nm). The bars denote the rate of hydrogen evolution averaged over 20 h of illumination. (b) Ultraviolet-visible diffuse reflectance spectrum of the CdS NPs and the AQYs of hydrogen evolution from 2-propanol under different incident lights. The error bars refer to the wavelength range of the incident light. (c) Photocatalytic splitting of 2-propanol using different photocatalysts (after 6 h).

Photocatalytic splitting of methanol, ethanol and 2propanol were performed at room temperature (20°C) under visible light illumination (λ >420 nm). The generation of hydrogen gas from these alcohols when Ni/CdS was used as a photocatalyst was clearly observed (see Supplementary Video 1). In contrast, no activity was found using CdS NPs alone. Figure S4 displays quantities of hydrogen that evolved as a function of irradiation time. The rate of hydrogen evolution for 2-propanol was 46.6 mmol h^{-1} g⁻¹ CdS, which is comparable with reported data of a water-alcohol system.¹⁵ Optimized apparent quantum yields (AQYs) of 38%, 46% and 48% were achieved at λ =447 nm (intensity of the incident light was 2.60 mW) for dehydrogenation of methanol, ethanol and 2propanol, respectively. To our knowledge, these are unprecedented AQYs of visible light-driven dehydrogenation of alcohols, the molar ratio of H, and the expected aldehyde or ketone was calculated to be *ca*. 1.0, indicating a stoichiometric dehydrogenation reaction. Analysis of the evolved gas by gas chromatography (GC) reveals that 1

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59 60 CO and CO₂ at concentrations of less than 1 part per million (ppm) were produced by all of these reactions. In addition, over-oxidation products in solution, such as carboxylic acids, were not detected in GC-MS analysis.

To test the stability of the photocatalyst, long-term continuous evolution of H₂ from 2-propanol using Ni/CdS (6 mg) was performed (Figure 2a). After 121 h, 16 mmol of H₂ (401 mL) had been evolved which corresponded to 25% conversion of 2-propanol to acetone. Therefore, the turn-over number (TON) based on the amount of metallic Ni was calculated to be *ca*. 44,465 after 121 h, clearly indicating the high stability of the photocatalyst. The turnover frequency (TOF) was *ca*. 1,222 h⁻¹ for the first 6 h, which is comparable with the known state-of-the-art data (1,109 h⁻¹) of a thermal catalytic system.¹⁰

The dependence of the rate of H_2 evolution from 2propanol on the wavelength of incident light was investigated. As indicated in Figure 2b, the AQY trend corresponds well to the absorption spectrum of CdS NPs. The above results reveal that the dehydrogenation of 2propanol proceeds through light absorption by CdS and exclude the possibility of direct thermal catalytic dehydrogenation by Ni.^{12,22-24}

From the view point of chemical science and industry, the conversion of alcohols to aldehydes and ketones is a fundamental process.^{11,25,26} To demonstrate the synthetic utility of our catalyst system, we examined the feasibility of visible-light photocatalytic dehydrogenative oxidation of other alcohols in acetonitrile (MeCN). To our delight, the current catalyst system functions well with aromatic and cyclic aliphatic alcohols, affording the corresponding carbonyl compounds with moderate to excellent conversion and outstanding selectivity (see Table 1). In the case of long-chain aliphatic alcohols, their conversions were low but the selectivity of dehydrogenative products was high (entries 9 and 10, Table 1).

Table 1. Visible light-driven splitting of alcohols^[a]

Entry	Alcohol	Conv.(%) ^[b]	Sel.(%) ^[b]
1	Benzyl alcohol	96	96
2 ^[c]		50	9 ^[d]
3	4-chlorobenzyl alcohol	99	96
4	1-phenylethanol	97	97
5	Diphenylmethanol	94	93
6	Cinnamyl alcohol	63	98
7 ^[e]	Cyclooctanol	93	99
8	Cyclopentanol	30	98
9	1-octanol	3	97
10	2-octanol	15	99

[a] Reaction conditions: alcohol (0.2 mmol), CdS (6 mg), NiCl₂· $6H_2O$ (5 µmol), MeCN (3 mL), Ar atmosphere, 7 W blue LED, 20 h. [b] Determined by GC. [c] Without NiCl₂· $6H_2O$. [d] Hydrobenzoin (38%) and benzoin (37%) were formed. [e] Alcohol (0.1 mmol).

To understand the mechanism of the photocatalytic splitting of alcohols, a series of experiments was conducted. We initially investigated the influence of NiCl₂ and NiS on the photocatalytic splitting of 2-propanol (Figure 2c). No activity was found when NiCl₂-modified CdS NPs were employed as photocatalysts. Compared with Ni/CdS, much lower rate of hydrogen evolution was obtained when NiS-modified CdS NPs were employed. Platinum (Pt), which is a well-known catalyst for hydrogen evolution reaction (HER),^{27,28} was also modified on the surface of CdS. However, no hydrogen was evolved when it was used for the photocatalytic splitting of alcohol (Figure 2c), indicating Pt could not abstract hydrogen from alcohol which is consistent with previous literature.²⁹ It was determined that the Ni/CdS was deactivated for the photosplitting of simple alcohols when this catalyst was exposed to air and thoroughly oxidized (similar to Raney Ni). Moreover, in the absence of Ni, only moderate conversion (50%) was observed for benzyl alcohol (see entry 2, Table 1), and the selectivity for benzaldehyde was poor (9%). The main products were hydrobenzoin and benzoin owing to the coupling of benzyl radicals.³⁰ However, when Ni/CdS was used, benzyl alcohol was converted to benzaldehyde with high conversion and excellent selectivity (see entry 1, Table 1). This result indicates that the initial radical formation may be on the oxygen atom which immediately forms the C=O bond³¹ through Ni-assisted C-H activation. The above results strongly suggest that an interface between metallic Ni and CdS plays a key role in the reaction mechanism. Then we performed kinetic isotope effect (KIE) using a CH₃OH/CD₃OH (1:1 molar ratio) mixture. The ratio of the reaction rates $(k_{\rm H}/k_{\rm D})$ was estimated to be ca. 5.1, indicating that the rate-limiting step involves the activation of an α C-H bond. In addition, when CD₂OD was used, D₂ was detected (see Figure S₉) indicating that the source of hydrogen was indeed from the alcohol.



Scheme 2. Proposed potential mechanism of the photocatalytic splitting of alcohols by Ni/CdS.

Based on the above results, we propose a catalytic mechanism for the photocatalytic dehydrogenation of

alcohols (Scheme 2). Initially, alcohol can be absorbed on the surface of Ni particles, a phenomenon similar to a step in the mechanism of thermal catalytic dehydrogenation.³² When CdS is illuminated by a photon with energy greater than its band-gap energy, a photo-excited electron and hole are generated, and the electron is localized from the conduction band (CB) of CdS to the deposited Ni NPs.^{15,33} A proton abstracted from the OH group of the alcohol absorbed on Ni surface is reduced by this electron, resulting in a Ni-H hydride and an alkoxide anion. Subsequently, this alkoxide anion is oxidized by the hole,³¹ and the Ni-assisted homolytic cleavage of α C-H occurs,¹² affording another Ni-H hydride and the corresponding aldehyde or ketone. Finally, two Ni-H hydrides afford one molecule of hydrogen. Given the KIE results and the difference in dissociation energy between C-H and O-H,³² the oxidation half-reaction is a rate-limiting step.

In conclusion, we demonstrated that the efficient, visible light-driven dehydrogenation of alcohols under ambient conditions can be achieved. Key to success is the interface between Ni nanocrystal and CdS. We believe that after further optimization of the semiconductor and cocatalyst, efficient splitting of alcohols under sunlight will become a feasible way.

ASSOCIATED CONTENT

Supporting Information.

Experimental details and data. This material is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.

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The authors declare no competing financial interest.

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