

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

Zhigang Chai,[†] Ting-Ting Zeng,[‡] Qi Li,[†] Liang-Qiu Lu,[‡] Wen-Jing Xiao,^{*,‡} and Dongsheng Xu^{*,†}

[†]Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[‡]Key Laboratory of Pesticides and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, China

S Supporting Information

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}

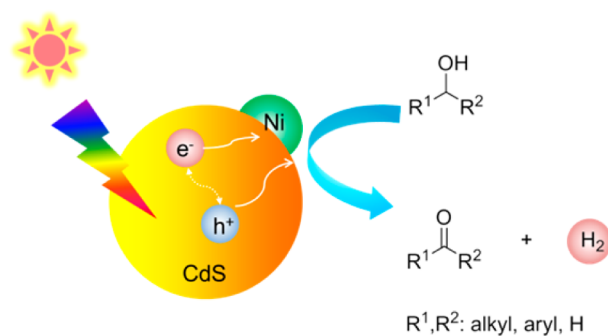
There are two ways to produce hydrogen from alcohols. The first method is conventional alcohol reforming, which produces both hydrogen and carbon dioxide under high temperatures and high pressures.^{7,8} Recently, ruthenium-catalyzed aqueous-phase dehydrogenation of methanol to hydrogen and carbon dioxide at relatively low temperatures (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 an electron acceptor, and alcohol is used as a sacrificial agent; 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 ppm) can easily poison the catalyst in proton exchange membrane fuel cells (PEMFCs).²⁰ To achieve a stoichiometric splitting of alcohol, the photocatalyst should be able to abstract hydrogen from the alcohol instead of water. Herein, we report a noble-metal-free photocatalyst (Ni nanocrystal-modified 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 light-driven 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).

Scheme 1. Visible Light-Driven Splitting Alcohol over a Ni-Modified CdS Photocatalyst



Received: July 3, 2016

Published: July 30, 2016

Modification of the surface of CdS NPs with a 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 the fact that metallic Ni nanocrystals could be oxidized by water. Therefore, a methanol solution of NiCl₂ was chosen for the photodeposition. Then we studied the concentration of NiCl₂ on the rate of hydrogen evolution. As shown in Figure S3, the rate of hydrogen evolution first increased along with an increasing amount of NiCl₂ and then reached 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

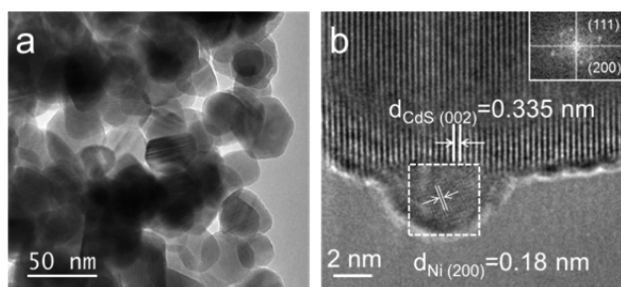


Figure 1. (a) TEM image of Ni/CdS and (b) HRTEM image of Ni/CdS (the inset image is the Fourier transform of the marked area).

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, the 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 (Figures S7 and S10); in the resultant spectrum, the peak at 852.1 eV was attributed to metallic Ni;¹⁵ and peaks at 853.3 and 856.0 eV were attributed to be NiO and NiCl₂, respectively.

Photocatalytic splitting of methanol, ethanol, and 2-propanol were performed at room temperature (20 °C) under visible light illumination ($\lambda > 420$ 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 $\lambda = 447$ nm (intensity of the incident light was 2.60 mW) for dehydrogenation of methanol, ethanol, and 2-propanol, respectively. To our knowledge, these are unprecedented AQYs of visible light-driven dehydrogenation of alcohols; the molar ratio of H₂ 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 CO and CO₂ at concentrations of less than 1 ppm were produced by all of these reactions. In addition, overoxidation 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

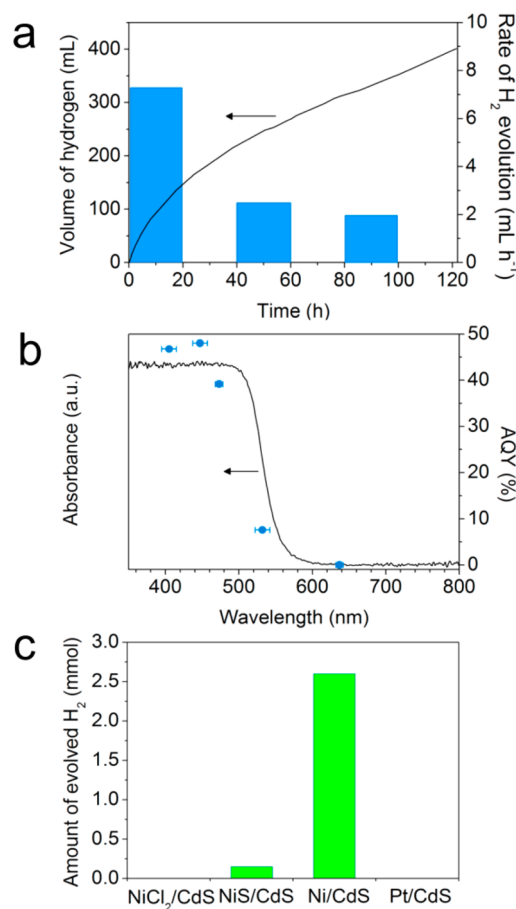


Figure 2. (a) Long-term photocatalytic splitting of 2-propanol (5 mL) under visible light ($\lambda > 420$ nm). The bars denote the rate of hydrogen evolution averaged over 20 h of illumination. (b) Ultraviolet–visible diffuse reflectance spectrum of the CdS NPs and the AQYs of hydrogen evolution from 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).

(401 mL) had been evolved which corresponded to a 25% conversion of 2-propanol to acetone. Therefore, the turnover 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. 1222 h⁻¹ for the first 6 h, which is comparable with the known state-of-the-art data (1109 h⁻¹) of a thermal catalytic system.¹⁰

The dependence of the rate of H₂ evolution from 2-propanol 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-mentioned results reveal that the dehydrogenation of 2-propanol proceeds through light absorption by CdS and exclude the possibility of direct thermal catalytic dehydrogenation by Ni.^{12,22–24}

From the viewpoint 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

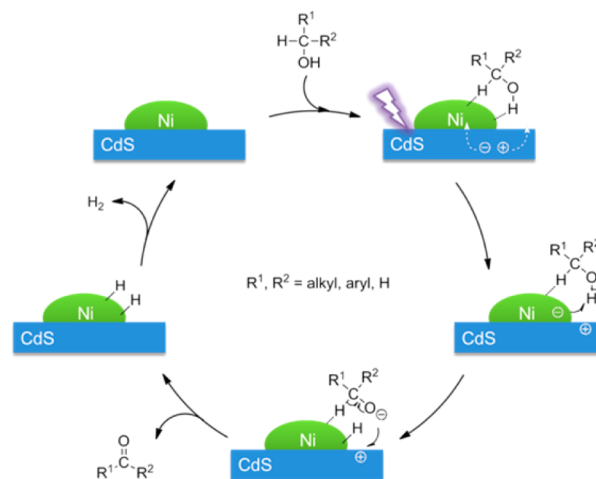
^aReaction conditions: alcohol (0.2 mmol), CdS (6 mg), NiCl₂·6H₂O (5 μmol), MeCN (3 mL), Ar atmosphere, 7 W blue LED, 20 h. ^bDetermined by GC. ^cWithout NiCl₂·6H₂O. ^dHydrobenzoin (38%) and benzoin (37%) were formed. ^eAlcohol (0.1 mmol).

To understand the mechanism of the photocatalytic splitting of alcohols, a series of experiments were 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, a much lower rate of hydrogen evolution was obtained when NiS-modified CdS NPs were employed. Platinum (Pt), which is a well-known catalyst for the 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-mentioned results strongly suggest that an interface between metallic Ni and CdS plays a key role in the reaction mechanism. Then we investigated the kinetic isotope effect (KIE) using a CH₃OH/CD₃OH (1:1 molar ratio) mixture. The ratio of the reaction rates (k_H/k_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 CD₃OD was used, D₂ was detected (see Figure S9) indicating that the source of hydrogen was indeed from the alcohol.

Based on the above-mentioned results, we propose a catalytic mechanism for the photocatalytic dehydrogenation of alcohols (Scheme 2). Initially, alcohol can be absorbed on the surface of

Scheme 2. Proposed Potential Mechanism of the Photocatalytic Splitting of Alcohols by Ni/CdS



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 photoexcited 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 adsorbed 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 the Ni nanocrystal and CdS. We believe that, after further optimization of the semiconductor and cocatalyst, efficient splitting of alcohols under sunlight will become feasible.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06860.

Experimental details and data (PDF)

Video of hydrogen gas formation during photocatalytic splitting of alcohols (AVI)

■ AUTHOR INFORMATION

Corresponding Authors

*wxiao@mail.ccnu.edu.cn

*dsxu@pku.edu.cn

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 21303004, 21133001, 21232003, and 21472057) and the National Key Basic Research Program of China (Grant Nos. 2014CB239303, 2013CB932601).

REFERENCES

- (1) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353.
- (2) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127.
- (3) Dalebrook, A. F.; Gan, W.; Grasemann, M.; Moret, S.; Laurenczy, G. *Chem. Commun.* **2013**, *49*, 8735.
- (4) Sakintuna, B.; Lamari-Darkrim, F.; Hirscher, M. *Int. J. Hydrogen Energy* **2007**, *32*, 1121.
- (5) Nielsen, M.; Alberico, E.; Baumann, W.; Drexler, H.-J.; Junge, H.; Gladiali, S.; Beller, M. *Nature* **2013**, *495*, 85.
- (6) Rodríguez-Lugo, R. E.; Trincado, M.; Vogt, M.; Tewes, F.; Santiso-Quinones, G.; Grützmacher, H. *Nat. Chem.* **2013**, *5*, 342.
- (7) Palo, D. R.; Dagle, R. A.; Holladay, J. D. *Chem. Rev.* **2007**, *107*, 3992.
- (8) Haryanto, A.; Fernando, S.; Murali, N.; Adhikari, S. *Energy Fuels* **2005**, *19*, 2098.
- (9) Lokras, S. S.; Deshpande, P. K.; Kuloor, N. R. *Ind. Eng. Chem. Process Des. Dev.* **1970**, *9*, 293.
- (10) Nielsen, M.; Kammer, A.; Cozzula, D.; Junge, H.; Gladiali, S.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 9593.
- (11) Mitsudome, T.; Mikami, Y.; Funai, H.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 138.
- (12) Shimizu, K.-i.; Kon, K.; Shimura, K.; Hakim, S. S. M. A. *J. Catal.* **2013**, *300*, 242.
- (13) Kim, W.-H.; Park, I. S.; Park, J. *Org. Lett.* **2006**, *8*, 2543.
- (14) Chen, X.; Shen, S.; Guo, L.; Mao, S. S. *Chem. Rev.* **2010**, *110*, 6503.
- (15) Simon, T.; Bouchonville, N.; Berr, M. J.; Vaneski, A.; Adrović, A.; Volbers, D.; Wyrwich, R.; Döblinger, M.; Susha, A. S.; Rogach, A. L.; Jäckel, F.; Stolarczyk, J. K.; Feldmann, J. *Nat. Mater.* **2014**, *13*, 1013.
- (16) Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. *Nat. Mater.* **2009**, *8*, 76.
- (17) Okamoto, Y.; Ida, S.; Hyodo, J.; Hagiwara, H.; Ishihara, T. *J. Am. Chem. Soc.* **2011**, *133*, 18034.
- (18) Wu, G.; Chen, T.; Su, W.; Zhou, G.; Zong, X.; Lei, Z.; Li, C. *Int. J. Hydrogen Energy* **2008**, *33*, 1243.
- (19) Zou, Z.; Ye, J.; Abe, R.; Arakawa, H. *Catal. Lett.* **2000**, *68*, 235.
- (20) Oetjen, H. F.; Schmidt, V. M.; Stimming, U.; Trila, F. *J. Electrochem. Soc.* **1996**, *143*, 3838.
- (21) Yan, H.; Yang, J.; Ma, G.; Wu, G.; Zong, X.; Lei, Z.; Shi, J.; Li, C. *J. Catal.* **2009**, *266*, 165.
- (22) Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. *Science* **2003**, *300*, 2075.
- (23) Uemichi, Y.; Sakai, T.; Kanazuka, T. *Chem. Lett.* **1989**, *18*, 777.
- (24) Meng, X.; Wang, T.; Liu, L.; Ouyang, S.; Li, P.; Hu, H.; Kako, T.; Iwai, H.; Tanaka, A.; Ye, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 11478.
- (25) Tojo, G.; Fernández, M. *Oxidation of Alcohols to Aldehydes and Ketones*; Springer: New York, 2006.
- (26) Enache, D. I.; Edwards, J. K.; Landon, P.; Solsona-Espriu, B.; Carley, A. F.; Herzing, A. A.; Watanabe, M.; Kiely, C. J.; Knight, D. W.; Hutchings, G. J. *Science* **2006**, *311*, 362.
- (27) Li, Y.; Wang, H.; Xie, L.; Liang, Y.; Hong, G.; Dai, H. *J. Am. Chem. Soc.* **2011**, *133*, 7296.
- (28) Zong, X.; Yan, H.; Wu, G.; Ma, G.; Wen, F.; Wang, L.; Li, C. *J. Am. Chem. Soc.* **2008**, *130*, 7176.
- (29) Jin, Z.; Li, Q.; Zheng, X.; Xi, C.; Wang, C.; Zhang, H.; Feng, L.; Wang, H.; Chen, Z.; Jiang, Z. *J. Photochem. Photobiol., A* **1993**, *71*, 85.
- (30) Mitkina, T.; Stanglmair, C.; Setzer, W.; Gruber, M.; Kisch, H.; König, B. *Org. Biomol. Chem.* **2012**, *10*, 3556.
- (31) Su, F.; Mathew, S. C.; Lipner, G.; Fu, X.; Antonietti, M.; Blechert, S.; Wang, X. *J. Am. Chem. Soc.* **2010**, *132*, 16299.
- (32) Yamashita, M.; Dai, F.-Y.; Suzuki, M.; Saito, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 628.
- (33) Tong, H.; Ouyang, S.; Bi, Y.; Umezawa, N.; Oshikiri, M.; Ye, J. *Adv. Mater.* **2012**, *24*, 229.