

Photocatalytic Direct Conversion of Ethanol to 1,1-Diethoxyethane over Noble-Metal-Loaded TiO₂ Nanotubes and Nanorods

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As one of the most important biomass platform molecules, ethanol needs to have its product chain chemically extended to meet future demands in renewable fuels and chemicals. Additionally, chemical conversion of ethanol under mild and green conditions is still a major challenge. In this work, ethanol is directly converted into 1,1-diethoxyethane (DEE) and H₂ under mild photocatalytic conditions over platinum-loaded TiO₂ nanotubes and nanorods. The reaction follows a tandem dehydrogenation–acetalization mechanism, in which ethanol is first dehydrogenated into acetaldehyde and H⁺ ion by photo-generated holes, and then acetalization between acetaldehyde

and ethanol proceeds through promotion by H⁺ ions formed in real time. Excess H⁺ ions are simultaneously reduced into H₂ by photogenerated electrons. This photocatalytic process has a very high reaction rate over nanosized tubular and rod-like TiO₂ photocatalysts, reaching 157.7 mmol g⁻¹ h⁻¹ in relatively low photocatalyst feeding. More importantly, the reaction is highly selective, with a nearly stoichiometric conversion of reacted ethanol into DEE. This photocatalytic dehydrogenation C–O coupling of ethanol is a new green approach to the direct efficient conversion of ethanol into DEE and provides a promising channel for sustainable bioethanol applications.

Introduction

Ethanol, one of the most important bio-alcohols, can be obtained from biomass by fermentation.^[1] Bioethanol production rapidly increased over the last decade, and the total annual capacity reached 100 billion liters in 2013.^[2] Bioethanol is very important to rationally utilize for future energy and chemical industry needs.^[3] Bioethanol can be used as fuel or fuel additive and can act as a versatile platform molecule because of its rich chemistry for the production of numerous chemicals or fuels, such as ethylene, acetaldehyde, acetic acid, esters, and acetals.^[4]

Economic and environmental factors have led to the pursuit of direct, green, and efficient processes for the chemical conversion of bioethanol, and significant progress has been made. The vapor-phase dehydration of ethanol can afford ethylene with 99% selectivity and 99.5% conversion over activated alumina.^[4a] Tu et al. reported a simple and clean one-step reaction of converting ethanol into acetaldehyde using inexpensive Cu catalysts under mild conditions with 100% selectivity.^[5] The clean, selective oxidation of ethanol with molecular oxygen has also been recently reported by Christensen,^[6] who oxidized

ethanol into acetic acid using supported Au catalysts. Nearly 95% selectivity and >90% conversion are obtained at moderate temperatures (150 °C) and pressures. Beller et al.^[4b] developed a green process for a direct synthesis of ethyl acetate from ethanol through an efficient acceptorless dehydrogenation. Meanwhile, photocatalytic organic synthesis is attracting increased interest because of its great potential of using clean and abundant solar energy.^[7] Recently, photocatalytic oxidation of ethanol has been studied by Murcia et al.,^[8] who partially oxidized ethanol with O₂ into acetaldehyde over Pt/TiO₂ under ultraviolet irradiation. Sannino et al.^[9] reported that the presence of VO_x species anchored onto TiO₂/SiO₂ can enhance ethanol conversion up to 66%, with >99% acetaldehyde selectivity. Zhu et al.^[10] showed that ethanol can also exhibit dehydrogenation C–C coupling behavior under Pt/TiO₂ photocatalytic condition and selectively convert ethanol into 2,3-butanediol.

As a derivative product of selective ethanol oxidation, 1,1-diethoxyethane (DEE) is gaining attention because of its wide applications, for example, as organic solvent, starting material for organic synthesis, and fuel additive.^[11] Particularly, DEE is considered as an alternative fuel to replace ethanol fuel because of the instability of the ethanol–diesel fuel blend even at low temperatures.^[11] Compared with ethanol, DEE is miscible in diesel fuel and shows good characteristics in terms of viscosity and auto-ignition temperature. Interestingly, DEE addition to fuel can drastically reduce nitrogen oxide emission. These characteristics suggest that the conversion of bioethanol into DEE is a promising strategy for the rational utilization of bioethanol.

Traditionally, converting ethanol into DEE proceeds in two steps: selective oxidation of ethanol into aldehyde and acid-

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catalyzed aldehyde–ethanol acetalization as DEE.^[11a,12] In this indirect process, besides the process complexity, the oxidation step (currently using noxious oxidants such as manganese and chromium compounds^[13]) is highly unfriendly to the environment. Therefore, the development of a simple and green process is urgently needed. Recently, Gusevskaya^[4e] reported a tandem aerobic oxidation–acetalization of ethanol using Pd(OAc)₂/Cu(OAc)₂/p-TsOH as an efficient bifunctional catalyst. Unlike the aerobic oxidation process, Milstein^[4c] developed an acceptorless dehydrogenation coupling (ADC) to convert alcohols into acetals, which exhibits a green, atom-economic feature because hydrogen atoms obtained from alcohols are converted into useful H₂. Unfortunately, Milstein's process is unsuitable for ethanol because of its low boiling point (liquid reaction at a high temperature is required).^[4c] Recently, we found that under mild photocatalysis conditions (typically at room temperature) over Pt/TiO₂(P25), primary C2–C6 alkyl alcohols can readily undergo ADC reaction and generate acetals and H₂ with high selectivity.^[14] This process provides the possibility of directly converting bioethanol into DEE in an atom-economical green way.

In this paper, we report that TiO₂-nanotubes (NTs) and TiO₂-nanorods (NRs) loaded with platinum are highly photoactive for the dehydrogenation C–O coupling of ethanol without need for any oxidant. The reaction efficiently produces DEE and H₂ following a tandem dehydrogenation–acetalization mechanism.

Results and Discussion

TiO₂-NT and TiO₂-NR were synthesized by a hydrothermal process similar to a previously reported method.^[15] Sodium titanate NTs (NaTiO₃-NTs) were initially prepared from a hydrothermal treatment of titania powder in an aqueous NaOH solution. When excessive NaOH was used, titania powder was nearly completely assembled as NaTiO₃-NTs. These tubes were typically 800–1200 nm long and 8–10 nm in diameter (Figure 1a). To transform NaTiO₃-NT into TiO₂-NT, NaTiO₃-NT was ion-exchanged with hydrochloric acid and then calcined at desired temperatures. Clearly, the ion exchange that resulted in titanic acid NTs (HTiO₃-NTs) produced a truncation of tubes of about 100 nm (Figure 1b). After calcination of HTiO₃-NT at a relatively low temperature (300 °C), tubule structure showed no visible change (Figure 1c), whereas the phase structure transformed into anatase TiO₂-NT (Figure S1). However, calcination at a higher temperature (400 °C) led to tubule collapse and reorganization into rod-like morphology (Figure 1d; TiO₂-NRs). Compared with TiO₂-NT obtained at 300 °C, TiO₂-NRs were highly crystalline, as shown by a high-resolution TEM image (inset in Figure 1d). A lattice fringe of 3.52 Å can be clearly observed, which corresponds to the (101) lattice planes of anatase TiO₂. Improvement in crystallization degree for TiO₂-NRs was also proven by X-ray diffraction analysis (Figure S1).

Photocatalysis behaviors of the synthesized NTs and NRs were characterized for the dehydrogenation coupling reaction of ethanol, with metal co-catalysts being loaded by in situ photodeposition.^[16] We performed photocatalytic reaction in neat

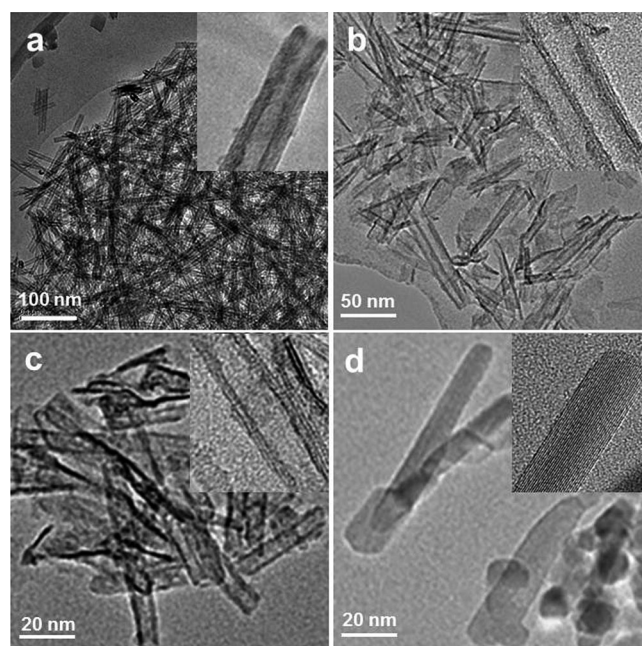


Figure 1. TEM images of the photocatalysts: a) as-synthesized NaTiO₃-NT, b) HTiO₃-NT obtained by ion exchange of NaTiO₃-NT with HCl, c) TiO₂-NT obtained by calcinating HTiO₃-NT at 300 °C, and d) TiO₂-NR obtained by calcinating HTiO₃-NT at 400 °C.

ethanol in argon atmosphere under UV irradiation at room temperature. The experimental results are presented in Table 1. Results showed that 1%Pt/NaTiO₃-NT was inactive. Only a small amount of DEE was detected after 9 h of irradiation, with a very low conversion of ethanol of about 0.83%. The simple ion exchange from Na⁺ to H⁺ dramatically activated the photocatalyst, and about 27% of ethanol conversion was achieved for 1%Pt/HTiO₃-NT. Photoactivity was further improved, and after 9 h of reaction, ethanol conversion reached about 29% for both TiO₂-NTs and TiO₂-NRs. This value was slightly higher than when using commercial 1%Pt/TiO₂ (P25).^[14] The reaction rates were high, i.e., 109.1 and 110.8 mmol g⁻¹ h⁻¹ for 1%Pt/TiO₂-NT and 1%Pt/TiO₂-NR, respectively. Notably, the rate reached 157.7 mmol g⁻¹ h⁻¹ in relatively low photocatalyst feeding, as described below. Most interestingly, the present photocatalytic reaction was highly selective, with >99% of reacted ethanol converted into DEE, or nearly a stoichiometric reaction. Only trace amounts of carbon-containing byproducts such as acetaldehyde, acetate acid, CO, CO₂, and CH₄ were detected by GC for liquid and gas sample (Figure S2). Notably, the data presented in Table 1 were obtained after 9 h of reaction, exhibiting relatively low ethanol conversion. Actually, ethanol conversion can reach 50% with increased reaction duration (Figure 2), after which the reaction was limited by thermodynamic equilibrium because the reaction-derived water (as described below) can promote the reverse reaction.^[17]

We also examined the effect of metal cocatalysts (Pt, Pd, Au, and Rh) on photocatalyst performance based on TiO₂-NRs. Blank experiments with bare TiO₂-NRs (without any metal loading) showed that it is inactive for the present reaction, with no

Table 1. Experimental data of the photocatalytic dehydrogenation C–O coupling of ethanol.^[a]

$$3 \text{ CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{Catalyst}]{h\nu} \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} + \text{H}_2$$

Entry	Catalyst	Catalyst amount [g]	Conv. [%]	Selectivity [%]	Rate ^[b] [mmol g ⁻¹ h ⁻¹]
1	1%Pt/NaTiO ₃ -NT	0.1	0.83	99.0	3.1
2	1%Pt/HTiO ₃ -NT	0.1	26.9	99.2	101.7
3	1%Pt/TiO ₂ -NT	0.1	28.9	99.1	109.1
4	1%Pt/TiO ₂ -NR	0.1	29.3	99.2	110.8
5	1%Pd/TiO ₂ -NR	0.1	23.5	99.5	89.1
6	1%Au/TiO ₂ -NR	0.1	0.9	99.5	3.4
7	1%Rh/TiO ₂ -NR	0.1	1.3	99.3	4.9
8	1%Pt/TiO ₂ -NR	0.05	20.8	99.5	157.7
9	1%Pt/TiO ₂ -NR	0.07	24.3	99.6	131.8
10	1%Pt/TiO ₂ -NR	0.15	18.4	99.3	46.4
11	1%Pt/TiO ₂ -NR	0.2	15.1	99.5	28.6
12	0.50%Pt/TiO ₂ -NR	0.1	20.1	99.2	76
13	0.75%Pt/TiO ₂ -NR	0.1	26.3	99.5	99.7
14	1.50%Pt/TiO ₂ -NR	0.1	26.4	99.4	100
15	2.00%Pt/TiO ₂ -NR	0.1	24.1	99.2	91.1
16	TiO ₂ -NR	0.1	0.59	—	2.3
17	TiO ₂ -NT	0.1	0.48	—	1.8

[a] Reaction conditions: 20 mL of neat ethanol, 0.05–0.2 g of catalyst with 0.5–2.0 wt% of noble metal co-catalyst, argon atmosphere, 20 °C, 300 W high-pressure Hg-lamp, 9 h of irradiation time. [b] The rates were calculated on the basis of the converted ethanol.

quite complex, mainly contributing to the separation of photo-generated electron-hole pairs. It is achieved through two micro-processes: one is the formation of surface Schottky potential between the noble metal and TiO₂ semiconductor,^[16] the other is the promotion of the H⁺-to-H₂ reduction, which linking with a chemical consumption of electrons. For optimization purposes, the loading content of platinum cocatalyst was varied from 0.5 wt%–2.0 wt%, and results showed that 1.0 wt% content was the most suitable for efficient reaction (Table 1). 1%Pt/TiO₂-NRs in different feeding amounts (0.05–0.2 g in 20 mL of ethanol) were also examined, and a significant effect of total amount of TiO₂ photocatalyst on

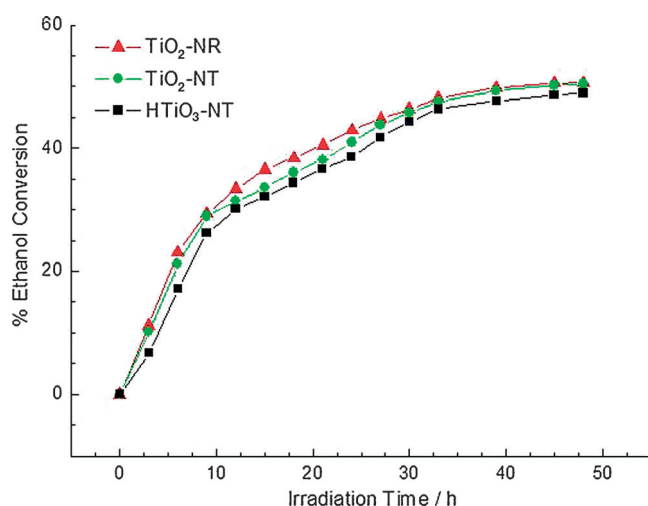


Figure 2. Ethanol conversion as a function of reaction duration over different photocatalysts. Reaction conditions: 20 mL of neat ethanol, 0.1 g of photocatalyst with 1 wt% of platinum, argon atmosphere, 20 °C, and 300 W high-pressure Hg-lamp.

any product being detected in the liquid phase after 9 h of irradiation. Alternatively, a very weak photolysis of ethanol was observed by the analysis of gas products. The presence of metal co-catalysts is necessary for the ethanol reaction. Catalysis tests showed that platinum and palladium are highly active, whereas gold and rhodium show very low activity, with <2% ethanol conversion; however, DEE selectivity remained at a high level (Table 1). As observed by TEM (Figure 3 and S2), the metals loaded on the TiO₂ nanotubes and nanorods are well dispersed on the TiO₂ surfaces as nanoparticles, with size of a few nanometer. The role of the noble metal cocatalysts is

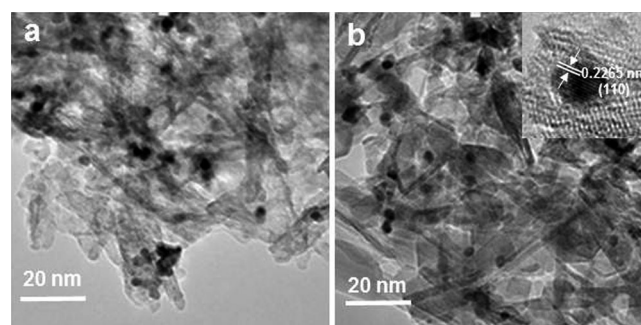


Figure 3. TEM images of metal loaded photocatalysts: a) Pt/TiO₂-NR, b) Pt/TiO₂-NT (inset: high resolution TEM image of the crystal lattice of platinum nanoparticle).

reaction efficiency was observed. Ethanol conversion displayed a peak value when 0.1 g of catalyst was used, but reaction rate per gram catalyst was clearly higher at relatively low catalyst feeding. For example, when 0.07 and 0.05 g of catalysts were used, the reaction rate reached 131.8 and 157.7 mmol g⁻¹ h⁻¹, respectively. This result indicated that the utilization efficiency of catalyst was higher at low feeding amounts, likely because of a blocking effect of catalyst on light transfer in a bulk reaction system.

To study the photocatalytic reaction process, ethanol depletion rate and the formation rates of DEE, H₂, and H₂O were calculated based on their quantitative analyses by GC. Figure 4 shows that the depletion rate of ethanol was about three times as fast as the formation rate of DEE. The time courses of the formation rate of H₂O and H₂ were similar to that of DEE, maintaining a rate ratio of 1:1. These data indicated that the formation of DEE in the present photocatalytic process pro-

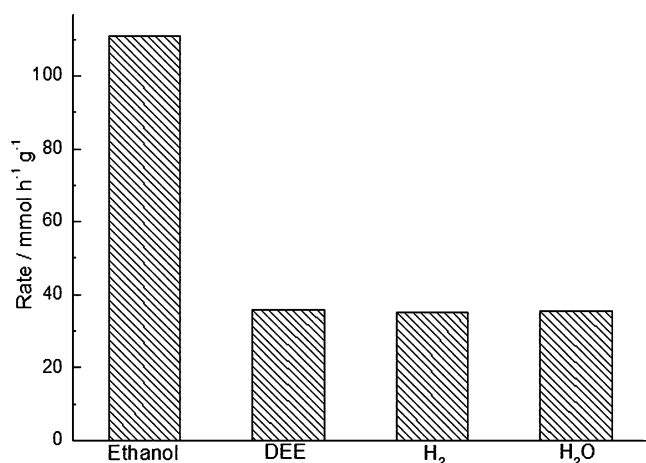
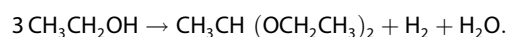


Figure 4. Depletion rate of ethanol versus formation rates of products DEE, H₂, and H₂O. Data were obtained over 1%Pt/TiO₂-NRs after 6 h of reaction, at which the reaction was still located in the kinetic region (Figure 2).

ceeded nearly stoichiometrically following the chemical equation shown below:



Such a highly selective dehydrogenation C–O coupling reaction of ethanol, with a simultaneous evolution of useful H₂, could be viewed as a perfect approach to the efficient and green conversion of bioethanol.

Interestingly, the present photocatalytic reaction over ethanol differed from our previous report,^[10] in that case, reaction is carried out in aqueous ethanol solution (volume ratio of ethanol to water is 3:10), and dehydrogenation C–C coupling into 2,3-butanediol selectively occurs with no DEE formation. The process follows a hydroxyl radical-mediated ethanol dehydrogenation, with formation of hydroxyethyl radicals and subsequent coupling into 2,3-butanediol.^[10] In the present case, reaction was performed in neat ethanol, and reacted ethanol was nearly completely converted into DEE with no 2,3-butanediol detected. This dramatic change reflected a significant difference in reaction mechanism between the two reactions.

To understand the reaction mechanism of the present dehydrogenation C–O coupling reaction of ethanol, we attempted to extract information from the by-product formed. As aforementioned, acetaldehyde was detected by GC (Figure S3 a) although in a very low content. Careful observation of the time course of acetaldehyde formation revealed that acetaldehyde initially formed but remained at a near-constant concentration over the entire reaction duration (Figure S4). This suggested that acetaldehyde likely acted as a reaction intermediate, maintaining a formation–depletion balance, strongly supported by the fact that acetals were traditionally condensed from aldehydes and alcohols. If acetalization reaction really occurred between acetaldehyde and ethanol in the present photocatalytic reaction, the next question was how the reaction proceeded without any acid catalyst fed externally because acetalization usually relies on the promotion role of acid catalysts. Inspired by the fact that, under semiconductor-based photocatalysis

condition, H⁺ ion forms from a hole-intermediated oxidation of hydrogen-rich compounds such as water and alcohols,^[16,18] we inspected the profile of H⁺-ion formation with a pH meter. We found that the concentration of H⁺ ion in bulk liquid reaction solution quickly increased within the initial 40 min of irradiation and subsequently remained at a constant level of about $6.3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ (Figure 5). In comparison, ethanol con-

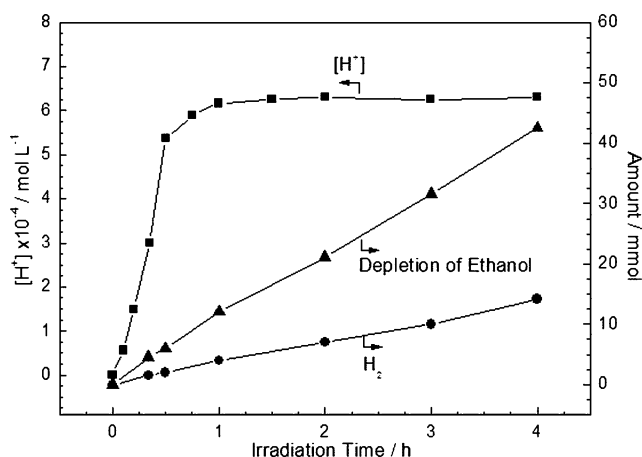


Figure 5. Evolution profiles of H⁺ ions in bulk liquid during the photocatalytic dehydrogenation coupling of ethanol. Conditions: catalyst, 1%Pt/TiO₂-NR; amount, 0.1 g; others are the same as in Figure 2.

version and H₂ evolution continuously proceeded throughout the entire reaction duration (Figure 5). These observations suggested that H⁺ ions generated from the hole-induced ethanol dehydrogenation on photocatalyst surface can move into and store in bulk solution and serve as acid catalysts for acetalization between acetaldehyde and ethanol.

To confirm this conjecture, we performed acetaldehyde–ethanol acetalization under similar acidic conditions created by feeding external HCl acid at a concentration of $6.3 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, which showed that this acidic condition was sufficient to support acetalization at a very high rate (Figure 6 a). We also performed acetalization between acetaldehyde and ethanol (with a molar ratio of 1:2) over 1%Pt/TiO₂-NRs, with no feeding of external acid catalyst. In darkness, no reaction was observed; however, under UV irradiation, DEE formed selectively (selectivity = 99.6%) as expected, and the reaction was quite fast, reaching an equilibrium state within a short duration of typically 40 min (Figure 6 b).

The observations described above indicated that the present direct conversion of ethanol into DEE followed a tandem dehydrogenation–acetalization mechanism, as shown in Scheme 1. In this mechanism, ethanol was first dehydrogenated into acetaldehyde and H⁺ ion by photogenerated holes, and then acetalization between acetaldehyde and ethanol proceeded through promotion by real-time formed H⁺ ions. Excess H⁺ ions were simultaneously reduced into H₂ by photogenerated electrons.

Additionally, we determined whether acetalization occurred in bulk liquid phase and not only on photocatalyst surfaces.

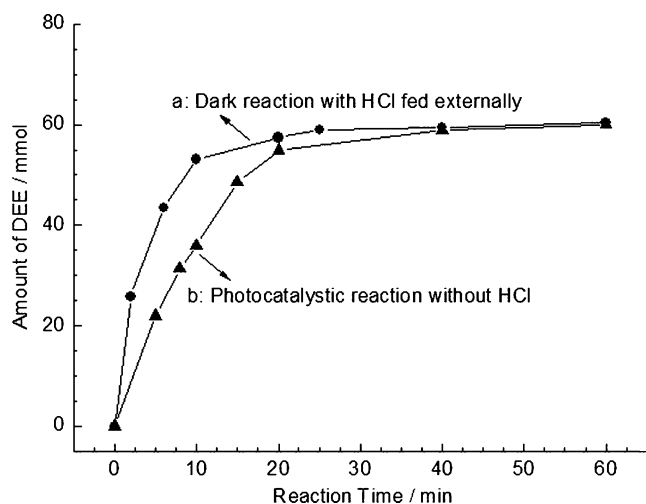
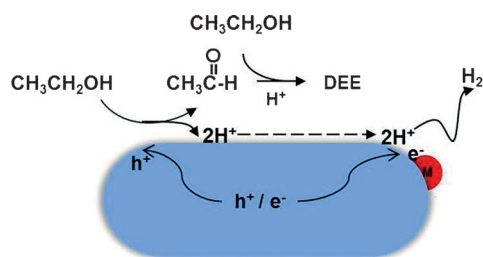


Figure 6. DEE production from the reaction between 20 mL of ethanol and acetaldehyde fed externally (molar ratio of ethanol to acetaldehyde = 2:1) under different conditions. (a) Reaction was performed in darkness by feeding external HCl catalyst ($[HCl] = 6.3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$). (b) Reaction was performed over 1%Pt/TiO₂-NRs under UV irradiation without HCl feeding.



Scheme 1. Proposed mechanism for the photocatalytic dehydrogenation coupling of ethanol into DEE over TiO₂ loaded with noble metal.

Ethanol dehydrogenation certainly occurred on TiO₂ surfaces because it was driven by photogenerated holes on TiO₂ surfaces.^[16,18] Acetalization on TiO₂ surfaces was also possible because the related reactants (ethanol and acetaldehyde) and acid catalyst (H⁺ ions) would theoretically appear at the same site. However, another possibility exists: acetaldehyde and H⁺ produced from ethanol dehydrogenation desorbed from TiO₂ surfaces and moved into bulk liquid phase to react with ethanol. The presence of acetaldehyde and H⁺ in bulk liquid phase as described above gave preliminary evidence for reaction in bulk liquid phase. We verified it by a transient-response experiment under a light-on/off-switching condition (Figure 7), with a measurement of DEE formation rate. In the initial stage, we carried out the direct coupling of ethanol (20 mL) over 1%Pt/TiO₂-NRs under UV irradiation. After 1 h of reaction, at which the concentration of H⁺ ions in bulk liquid phase reached a constant value (Figure 5), a small amount of acetaldehyde (1 mL) was added into the reaction system, and the reaction was allowed to proceed in darkness (with no help from photocatalyst). Obviously, DEE formation rate for the photocatalytic direct coupling of ethanol was relatively low because it was limited by the hole-driven ethanol dehydrogenation step.

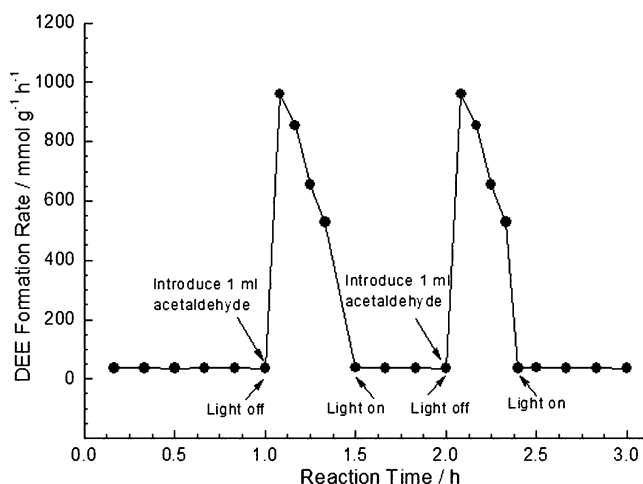


Figure 7. Transient response of DEE formation rate to an external introduction of acetaldehyde into the reaction system of photocatalytic ethanol coupling under a lights-on/off-switching condition. Other conditions are the same as in Figure 2.

Upon adding acetaldehyde, DEE production became fast even in darkness. This observation provided additional support for the role that acetalization played in bulk liquid phase, not only on photocatalyst surfaces. The high rate of the acetalization step can also explain why only a trace amount of acetaldehyde was detected in the present photocatalytic ethanol dehydrogenation system and why DEE selectivity was so high even under the high-rate-reaction condition. It would be interesting to note that under our photocatalytic reaction condition, the formed acetaldehyde does not display an aldol condensation reaction, although it can also occur theoretically with the help of acidic catalysis.^[19] A possible reason is that acetaldehyde produced from ethanol dehydrogenation has quite a low concentration under the neat ethanol condition; one could imagine that it might display a high reaction probability with rich ethanol for acetalization, while showing a low probability for reacting with itself in aldol condensation.

Conclusions

We demonstrate that platinum-coated TiO₂ nanotubes and nanorods are highly active under UV irradiation for ethanol dehydrogenation coupling into DEE. In this process, hydrogen atoms generated from ethanol dehydrogenation are simultaneously converted into useful H₂. This process for ethanol-to-DEE conversion is efficient and atom economic. Mechanism studies show that photocatalytic reaction follows a tandem dehydrogenation–acetalization mechanism. Ethanol is first dehydrogenated into acetaldehyde and H⁺ ion by photogenerated holes, and then acetalization between acetaldehyde and ethanol proceeds both on photocatalyst surfaces and in bulk liquid phase. The acid catalyst required for acetalization is derived from the H⁺ ions formed in real time, which can avoid environment pollution existing in traditional acid-catalyzed acetalization processes.

Experimental Section

Catalyst preparation and characterization

All chemicals were analytical-grade reagents and used without further purification. TiO₂ photocatalysts were prepared by a hydrothermal process.^[15] In a typical synthesis, titania powder (1 g) and an aqueous solution of NaOH (10 M, 100 mL) were mixed under magnetic stirring. After stirring for a short time, the resulting milk-like suspension was transferred to a Teflon-lined autoclave, kept at 140 °C for 24 h, and then allowed to cool down to room temperature. The resulting precipitate was separated in a centrifuge, washed with deionized water, and then dried at 60 °C to obtain sodium titanate NTs (NaTiO₃-NTs) as crude white precipitates. NaTiO₃-NTs were washed with deionized water and ion exchanged with 0.1 mol L⁻¹ hydrochloric acid until a pH value near 8 was reached, thereby producing titanic acid NTs (HTiO₃-NTs). The HTiO₃-NTs were dried and treated at 300 or 400 °C for 0.5 h to obtain TiO₂-NTs and TiO₂-NRs, respectively. Noble metal co-catalysts were loaded onto the catalyst by in situ photodeposition,^[16] in which H₂PtCl₆·6H₂O, PdCl₂, RhCl₃·3H₂O, or HAuCl₄·3H₂O were used as precursors. Typically, 0.2 mL of ethanol solution of the precursor with desired concentration was introduced into the reaction system with ethanol and photocatalyst TiO₂ and allowed to perform a photoreduction reaction under an irradiation of 300 W UV lamp for 30 min, during which the precursors were reduced into metallic nanoparticles and deposited on the TiO₂ surfaces. Phase structure was characterized by X-ray diffraction on a D8 Advance power X-ray diffractometer with CuK_α (λ = 0.15406 nm) radiation. The morphology and microstructure of samples were examined using a transmission electron microscope (JEM-2010).

Photocatalytic experiments and analysis

All experiments were performed in a tubular quartz photoreactor containing 20 mL of ethanol and a desired amount of photocatalyst, with pure Ar continuously bubbling. A 300 W high-pressure Hg lamp was used as light source and was cooled by 20 °C water circulation. The reaction course was monitored by periodically sampling the liquid from a sampling valve, and the catalyst was immediately separated from the solution by centrifugation. Liquid products were analyzed using a gas-chromatograph (GC-950 equipped with a flame ionization detector (FID) and Rtx-5 column from Alltech) and a gas chromatograph–mass spectrometer (Shimadzu GCMS-QP2010 with a mass spectrometer and DB-5 ms column from Alltech). The following temperature program was used in the analysis: 40 °C (5 min), increased at a rate of 8 °C min⁻¹ to 180 °C. The carrier gas was nitrogen. The detected reaction product was found to be DEE (retention time = 4.10 min). Sample analysis was confirmed by comparing the mass spectrum and retention time of pure DEE. Quantitative analyses of DEE and ethanol were performed with a GC system using cyclohexane as internal standard. A GC-9790 system (equipped with a thermal conductivity detector and FID) was used to detect CH₄, CO, CO₂, and H₂. The concentration of H⁺ ion was detected from a water-diluted reaction solution using a Leici PHSJ-3F pH meter.

Acknowledgements

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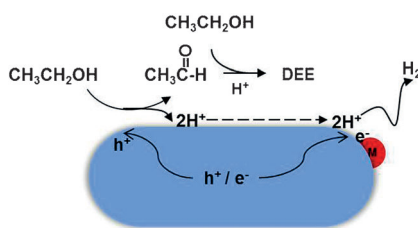
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Direct conversion: TiO₂ nanotubes and nanorods loaded with platinum can efficiently promote the direct conversion of ethanol into 1,1-diethoxyethane and H₂ under UV irradiation through a tandem reaction process consisting of a photocatalytic dehydrogenation step and a self-feeding H⁺-catalyzed acetalization step.



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Photocatalytic Direct Conversion of Ethanol to 1,1-Diethoxyethane over Noble-Metal-Loaded TiO₂ Nanotubes and Nanorods

