A Novel Example of Molecular Hydrogen Generation from Formic Acid at Visible-Light-Responsive Photocatalyst

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ABSTRACT The photocatalytic decomposition of formic acid (HCOOH) into dihydrogen and carbon dioxide was found to occur at Cu_2O, particularly without the contamination by CO from the organic acid. This work first demonstrated that the stoichiometric and selective decomposition of HCOOH is induced by a visible-light-responsive photocatalyst.

KEYWORDS: cuprous oxide • formic acid • hydrogen generation • photochemistry • photolysis

INTRODUCTION

Since Honda and Fujishima reported the photoelectrochemical water splitting using a TiO_2 electrode (1), considerable efforts have been made to fabricate photocatalysts responsive to visible-light energy, especially for efficient uptake of solar energy into output (1, 2). However, among the conventional visible-light-responsive photocatalyst materials, there has been an issue of its stability during photoinduced reaction. For example, in the case of CdS, the holes photogenerated in the compound cannot react with water, and therefore, its photocorrosion usually occurs to involve the elution of highly toxic cadmium ions (3, 4). This may be associated with the consumption rate of the photogenerated holes, thus leading to the photocorrosion kinetically faster than the oxidation of water. As recently reported by the authors (5), Cu_2O also exhibited characteristics for water oxidation similar to those of CdS under visible-light irradiation. However, in a water phase containing alcohol, those compounds exhibited stable photocatalysis without photocorrosion because of the kinetically swift consumption of the holes by alcohol (3−6). Although such oxidation of organic matter involves the emission of CO_2 that contributes to the greenhouse effect, CO_2 can return into the biosphere through photosynthesis in nature (7). Therefore, if organic matter can be produced from biomass resources with respect to carbon neutral, the H_2 generation from organic matter at visible-light-responsive photocatalyst may be one of the promising and reasonable approaches.

Formic acid (HCOOH) is one of the major products formed in biomass processing such as fermentation, pyrolysis, and supercritical reaction (8, 9). HCOOH can undergo the direct decomposition into H_2 and CO_2 without the formation of any other stable intermediates (eq 1) (10); in other words, the organic acid is a terminal intermediate in the decomposition of more complicated organic matter.

$$\mathrm{HCOOH} \rightarrow \mathrm{H_2} + \mathrm{CO_2} \tag{1}$$

Thus, the photocatalytic evaluation of the decomposition of HCOOH is meaningful in terms of the prospective utilization of biomass resources as well as the H_2 generation. Although CdS and TiO_2 have been applied in the photocatalytic decomposition of HCOOH (3, 4, 11), the formation of CO from HCOOH in the dark (eq 2) was also recognized to occur along with the photodecomposition (eq 1) (3).

$$\mathrm{HCOOH} \rightarrow \mathrm{H_2O} + \mathrm{CO} \tag{2}$$

The dark reaction resulted in a decrease in the efficiency of H_2 formation. In addition, the gaseous contaminant of CO causes the poisoning of Pt catalyst during the operation of a fuel cell (12). Therefore, the production of CO-free H_2 is desirable. In the present work, we examined the photocatalysis of Cu_2O in an aqueous solution of HCOOH. As shown in Scheme 1, the band edges of Cu_2O (band gap 2.0−2.3 eV) are available for H_2 generation along with the oxidative decomposition of HCOOH (6, 13). Here we show that the stoichiometric and selective decomposition of HCOOH can be induced at the photofunctional interface of Cu_2O, according to eq 1. The details are described in the following section.

EXPERIMENTAL SECTION

Cu_2O powder was prepared through the reduction of Cu^{2+} ion in the presence of sodium thiosulfate, according to the reported procedure (5). Ten cubic centimeters of 1.0 mol dm^{-3} $CuSO_4 \cdot 9H_2O$ (Kanto Chemical) aqueous solution was dropped into 100 cm^3 of 1.0 mol dm^{-3} $Na_2S_2O_3$ aqueous solution, and subsequently, the mixture solution was dropped into 200 cm^3 of 1 mol dm^{-3} NaOH solution at 80 °C. The resulting reddish-brown precipitate (Cu_2O) was separated by filtration and washed

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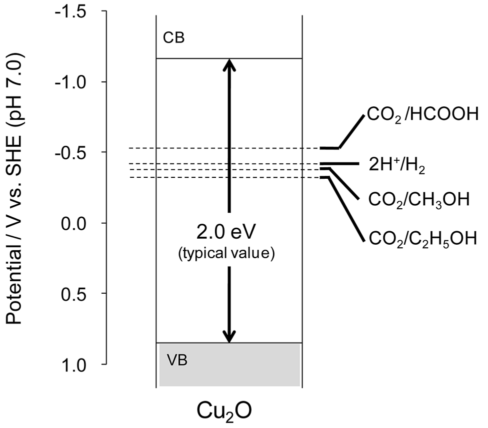
Scheme 1. Overview of the Redox Potentials of Relevant Reactions with Respect to the Position of the Cu_2O Band Edges (pH 7); With Regard to the Potentials of Alcohols, the Cases of CO_2 Formation from Organic Matter Are Listed



with deionized water, after which the precipitation was dried at 40 °C in an Ar atmosphere. In addition, platinum particles were photochemically deposited on the Cu_2O, where a visible-light irradiation was carried out for 12 h with 10 cm^3 of 2.5 mol dm^{-3} methanol aqueous solution containing 0.12 μmol of H_2PtCl_6 (Kanto Chemical) and 10 mg of Cu_2O in an Ar atmosphere (cf., the additive amount of H_2PtCl_6 was adjusted to be 0.5 wt.% Pt against the amount of Cu_2O), following which the obtained Pt-deposited Cu_2O (denoted as Pt–Cu_2O) was washed with deionized water and dried at 40 °C in an Ar atmosphere. In addition, 99.999% CdS powder (Mitsuwa Chemicals) was also employed as a reference photocatalyst. The photocatalytic experiment was conducted in a glass vessel (volume: 20 cm^3) containing 10 cm^3 of 2.5 mol dm^{-3} HCOOH and a known amount of photocatalyst (cf., the amount of photocatalysts employed: 10 mg (ca. 70 μmol) in both Cu_2O and Pt–Cu_2O) in Ar atmosphere with stirring. The pH of the HCOOH solution was adjusted to 5.0 by the addition of NaOH solution. A halogen lamp was used as the light source (light intensity: 280 mW cm^{-2}) along with a sharp-cut filter (S76-L42, Suruga Seiki Co. Ltd.), using which the samples were irradiated with light of wavelength λ >420 nm. Gaseous products were analyzed by a thermal conductivity detector (TCD) gas chromatograph (Shimadzu, GC-14B) with a packed column (SHINCARBON ST) and Ar carrier gas.

RESULTS AND DISCUSSION

The structural and optical characteristics of Cu_2O were identified from scanning electron microscope (SEM) images, XRD patterns, diffuse reflectance spectrum, and specific surface area. Using an SEM equipped with an energy dispersive X-ray fluorescence spectrometer, it was confirmed that Cu_2O particles had diameters of 100–500 nm (see the Supporting Information, Figure S1); moreover, there was no confirmation of sulfur compounds from thiosulfate (see Figure S2 in the Supporting Information). Cu_2O particles have usually been prepared by the employment of an oxidative atmosphere (e.g., calcination of metallic Cu), where CuO was involved in the product (14); however, all the peaks in the resulting XRD patterns (Figure 1a) were assigned to Cu_2O (15). Therefore, the above-mentioned procedure of Cu_2O fabrication did not involve the formation of other Cu species. From the measurement of diffuse reflectance spectrum, the band gap energy of Cu_2O was estimated to be 2.22 eV (Figure S3 in the Supporting Information). The specific surface area of Cu_2O and Pt–Cu_2O was ca. 27 and ca. 31 m^2 g^{-1}, respectively.

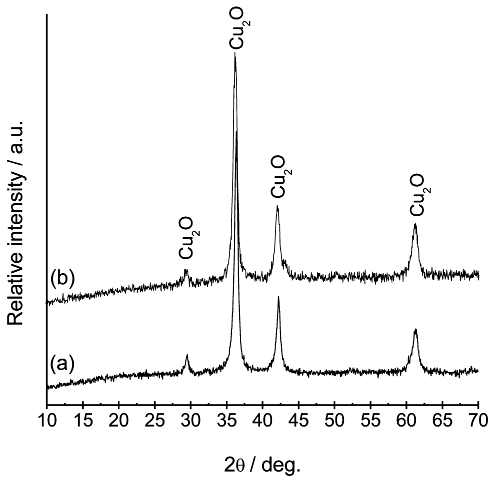


FIGURE 1. XRD patterns of Cu_2O photocatalyst. (a) Before irradiation and (b) after irradiation for 60 h in formic acid solution.

As a typical result, photocatalytic H_2 generation was found to occur when employing Cu_2O and Pt–Cu_2O as photocatalysts in the presence of HCOOH in Ar atmosphere. In a control experiment, the decomposition of HCOOH was not observed in the dark, particularly with and without Cu_2O; therefore, in the present study of Cu_2O, the decomposition of HCOOH into H_2 and CO_2 evidently occurs through a photocatalytic process (cf., in the absence of Cu_2O, the photodecomposition of HCOOH cannot also occur). Figure 2a shows the time course of the H_2 evolved at both photocatalysts, where the solution of HCOOH was substituted every 24 h. In each system, the H_2 amount exhibited a linear dependence on the irradiation time. The photocatalytic activity of Pt–Cu_2O was superior to that of Cu_2O. The increasing efficiency of the photocatalytic H_2 formation is attributable to the loading of Pt onto the Cu_2O surface. The details of the loading effect of Pt are described below. After irradiation for 48 h in the Pt–Cu_2O system, the cumulative amount of H_2 exceeded ca. 70 μmol corresponding to turnover number (TON) of 1 (TON = [the number of H_2 molecules evolved]/[the total number of photocatalysts employed]). Although the XRD measurement of Cu_2O was also performed after irradiation for 60 h, the formation of other Cu species such as CuO (oxidative species) and metallic Cu (reductive species) cannot be confirmed (Figure 1b). In a separate experiment, the transmission electron microscope (TEM) observation of Cu_2O was conducted before and after irradiation for 60 h. The analyses of the resulting electron diffraction patterns confirmed that no other Cu species were formed (see Figure S4 in the Supporting Information). Those results evidently support the stable photocatalysis of Cu_2O for H_2 generation.

In addition to the H_2 generation, CO_2 was concurrently yielded as the oxidation product; in other words, the Cu_2O photocatalyst was effective for H_2 generation through the overall decomposition of HCOOH under visible-light irradia-

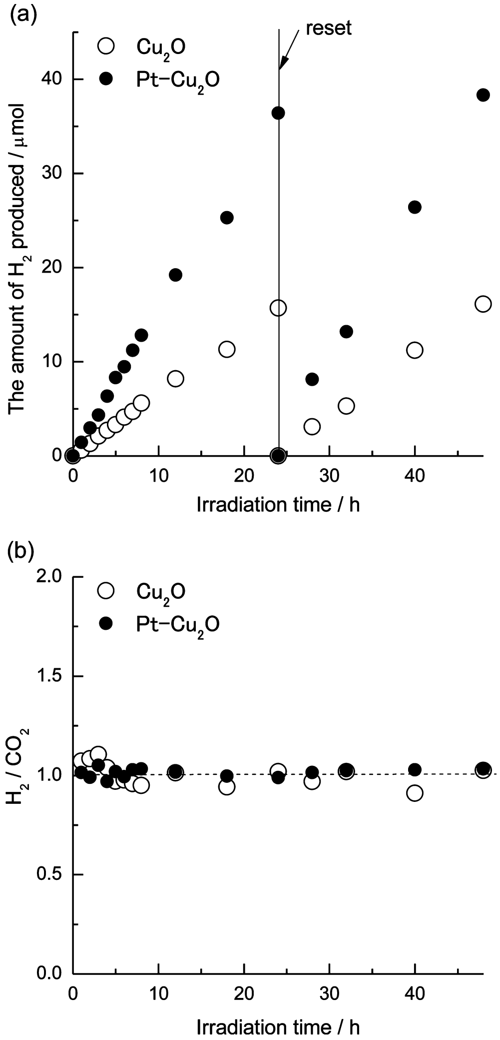


FIGURE 2. (a) Time-course of H_2 produced at Cu_2O and Pt−Cu_2O in the presence of 2.5 mol dm^{-3} formic acid (pH 5) and (b) that of the ratio of H_2 produced to CO_2 produced (H_2/CO_2). In a, when substituting HCOOH solution after irradiation for 24 h, the Cu_2O powder was quantitatively recovered by means of centrifugation.

tion. The mechanism of photocatalytic HCOOH decomposition can be represented as follows (also refer to Scheme 1) (6):

Oxidation of formic acid:

$$HCOOH + 2h^+ \rightarrow CO_2 + 2H^+ \qquad (3)$$

Hydrogen generation:

$$2h^+ + 2e^- \rightarrow H_2 \qquad (4)$$

The valence band edge of Cu_2O [+0.844 V vs SHE (pH 7)] is capable of oxidizing HCOOH (eq 3), whereas the conduction band edge [−1.16 V vs SHE (pH 7)] is available for H_2 generation (eq 4). In both photocatalyst systems employed, the ratio of H_2 amount to CO_2 (H_2/CO_2) was ca. 1 (Figure 2b), implying that Cu_2O is capable of photocatalysis for the stoichiometric decomposition of HCOOH (eq 1). Moreover, the generation of CO from HCOOH was not confirmed in the present case of Cu_2O photocatalyst, resulting in the selective and total decomposition of HCOOH into H_2 and CO_2. As a reference, the amount of CO in Cu_2O was examined relative to that in the conventional CdS photocatalyst (see Figure S4 and Table S1 in the Supporting Information). In the case of irradiation of CdS for 24 h, CO was detected; however, CdS was much more active for HCOOH decomposition than Cu_2O. In the CdS system, the profile of the products was also in good agreement with the earlier report (3).

Table 1. Amount of H_2 Produced in the Presence of Formic Acid, Methanol, and Ethanol[a]

	H_2 amount (μmol)		
photocatalyst	formic acid[b]	methanol[c]	ethanol[c]
Cu_2O	5.6	5.4	5.1
Pt−Cu_2O	12.4	11.9	13.1

[a] Donor concentration = 2.5 mol dm^{-3}, Light intensity = 280 mW cm^{-2}, and irradiation time = 8 h. [b] The pH was adjusted to 5.0 by the addition of NaOH solution. [c] The alcohol solutions at pH 5 were prepared using 30 mmol dm^{-3} phosphate buffer as solvent.

To gain insights into the photocatalysis of Cu_2O from the viewpoints of kinetic aspects, the photocatalytic activities of Cu_2O were investigated with the types of electron donors (i.e., alcohols and formic acid) for a constant donor concentration (i.e., 2.5 mol dm^{-3}). Table 1 shows the amount of H_2 produced after irradiation for 8 h. The H_2 amount in each photocatalyst system was almost independent of the types of electron donors employed although the energy positions of the organic matter differ from each other (Scheme 1) (16, 17). Recently, the authors reported the photocatalysis of the reductively prepared Cu_2O on kinetic aspects (18). When employing experimental conditions (high-intensity irradiation, photocatalyst amount, and pH) similar to those in the present work, the photocatalytic activity for H_2 formation by Cu_2O was constant with methanol concentration of >1 mol dm^{-3}, which was also independent of the type of alcohols (i.e., methanol, ethanol, *n*-propanol, and butanol). In addition, the specific surface area of Pt−Cu_2O was almost the same as that of a neat Cu_2O (vide supra). Therefore, as also supported by the previous results and knowledge, the results listed in Table 1 may imply that the photocatalyses of Pt−Cu_2O as well as Cu_2O are kinetically dominated by H_2 evolution (eq 4) rather than by the oxidation of electron donors; that is, the rate-limiting stage was inferred to be the H_2 generation. Thus, Pt acted as a cocatalyst for enhancing the rate of H_2 generation.

In conclusion, the present work demonstrated that Cu_2O is suitable for the photocatalytic decomposition of HCOOH. This is the first instance in which the stoichiometric and selective decomposition of HCOOH into H_2 and CO_2 has been induced using a visible-light-responsive photocatalyst. Recently, the authors have revealed that Cu_2O is inactive for the overall photolysis of water into H_2 and O_2 (5). This was because the photogenerated holes can be advantageously consumed through the self-oxidation of Cu_2O into CuO, particularly because of the kinetically slow oxidation of water. However, organic matter can swiftly undergo oxidation in the presence of Cu_2O photocatalyst, preventing the oxidation of Cu_2O itself. Thus, the rate-limiting H_2 generation took place to originate in a stable photocatalysis of Cu_2O. Nowadays, chemicals originating from biomass (e.g., ethanol, formic acid, acetic acid, etc.) are attracting attention as alternative energy resources to fossil fuels (8). In particular, HCOOH can be expected as a promising source of hydrogen in terms of its low flammability and high transportability (as formate) (14, 19). Therefore, the molecular hydrogen made from HCOOH will contribute to an establishment of a renewable energy system featuring biomass resources.

Supporting Information Available: The details of the structural and optical characteristics of Cu_2O employed in the present study are provided. The results of the photocatalysis study by CdS are also shown relative to those by Cu_2O (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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