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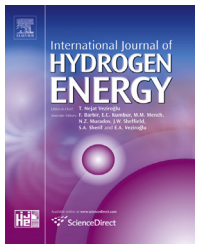

Photocatalytic hydrogen production over CuO and TiO_2 nanoparticles mixture

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ABSTRACT

Cheap and efficient photocatalysts were fabricated by simply mixing TiO_2 nanoparticles (NPs) and CuO NPs. The two NPs combined with each other to form TiO_2/CuO mixture in an aqueous solution due to the opposite surface charge. The TiO_2/CuO mixture exhibited photocatalytic hydrogen production rate of up to 8.23 mmol h^{-1} g^{-1} under Xe lamp irradiation when the weight ratio of P25 to CuO was optimized to 10. Although the conduction band edge position of CuO NPs is more positive than normal hydrogen electrode, the TiO_2/CuO mixture exhibited good photocatalytic hydrogen production performance because of the inter-particle charge transfer between the two NPs. The detailed mechanism of the photocatalytic hydrogen production is discussed. This mixing method does not require a complicated chemical process and allows mass production of the photocatalysts.

1. Introduction

Since the first discovery by Fujisima and Honda in 1972 [1], photocatalytic water splitting to produce hydrogen has been widely studied because it provides a clean and renewable method of hydrogen production based on solar energy and water [2]. Various photocatalysts have been developed for the photocatalytic water splitting, but titanium dioxide (TiO_2) is still most widely used as a photocatalysts because of its high resistance to photo-corrosion, stability in aqueous solution, and low cost as well as high hydrogen production rate [3].

Illumination of sunlight produces electron–hole pairs in TiO_2. Photo-generated electrons reduce water to produce hydrogen, while holes oxidize water to generate oxygen. However, these photo-generated electron–hole pairs tend to rapidly recombine with each other and disappear [1]. Therefore, to increase the hydrogen production rate by photocatalysis, the suppression of electron–hole recombination is crucial. Generally, metals are deposited on TiO_2 because the metals act as electron acceptors that induce a separation of the electrons and holes [4–7]. Expensive noble metals such as Pt, Au, Pd, and Ag are mostly used for this purpose [8–11]. Considering the practical application of the photocatalytic water splitting, low-cost acceptor materials showing effective charge separation characteristics should replace the noble metals. Moreover, existing metal deposition methods have limitation in the practical applications. For example, photodeposition is most popularly used to load noble metal on photocatalyst [12]; however, the limited size of UV light for photodeposition is inappropriate to mass-produce the metal-loaded photocatalysts. Other metal deposition methods such as impregnation and deposition-precipitation require more than a day to load metals on the catalysts, and these methods also require a high temperature process [5].

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Therefore, a cheap and mass-producible method to suppress the charge recombination is necessary to realize the practical application of the photocatalytic hydrogen production beyond lab-scale researches.

Here, we present a simple and effective approach to induce charge separation in TiO_2 and to produce hydrogen by photocatalytic water splitting. Only by mixing commercialized copper (II) oxide (CuO) nanoparticles (NPs) with TiO_2 NPs in an aqueous solution, stable and high hydrogen production rate can be achieved. No pre-deposition process is necessary and the two NPs aggregated with each other in the aqueous solution work as good photocatalysts for water splitting. CuO NPs are much cheaper than noble metal NPs and this simple mixing process does not limit the scale-up of the CuO-loaded TiO_2 production.

2. Experimental

2.1. Chemicals and materials

P25 TiO_2 with the average diameter of 25 nm was purchased from Degussa, Germany. Commercialized CuO NPs from Sigma Aldrich was used. The average size of the CuO NPs was 50 nm, which was the smallest commercialized NPs that we can achieve. Methanol (purity $>$ 99.9%) was obtained from Merck. Distilled water (DI water, $\geq$18.3 MΩ cm) obtained from a water purification system (Human Power I+, Human Corporation) was used in the experiments. All the chemicals and materials were used in their as-received form without further purification.

2.2. Photocatalytic hydrogen production

The experimental procedure of the photocatalytic H_2 production over mixture of CuO and P25 TiO_2 is schematically displayed in Fig. 1. A closed-loop photocatalytic hydrogen production device was used to measure the photocatalytic hydrogen production rate. The reaction chamber was made of pyrex and the volume of the chamber was 250 mL. A 500 W Xe lamp was used as a light source. The Xe lamp with 1.5 mW cm^{-2} power density was installed on the top of the reaction chamber for the illumination of light into water. The distance from Xe lamp to the top surface of reaction chamber was fixed to 30 cm. The reaction chamber was cooled by water to remove heat produced during the Xe lamp illumination.

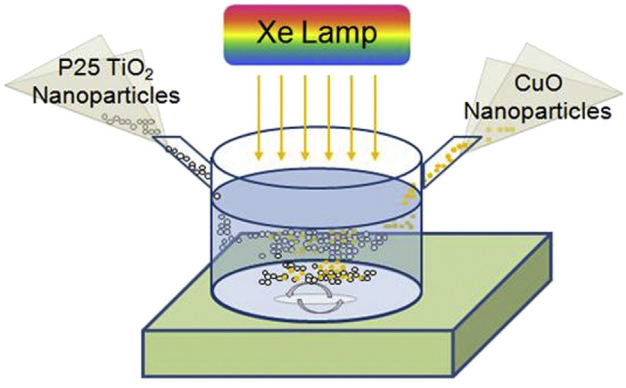

Fig. 1 – Schematic diagram of experimental procedure of photocatalytic H_2 production over mixture of CuO and P25 TiO_2.

100 mg of P25 TiO_2 was used with varying amount of CuO NPs. 25 mL of methanol was added into 100 mL of DI water as a sacrificial reagent. P25 and CuO NPs were dispersed in the 20% aqueous methanol solution without pre-deposition and sonicated for 10 min before hydrogen production experiment. After sonication, the aqueous methanol solution containing photocatalysts was poured to the closed reaction chamber and stirred by a magnetic stirrer throughout whole experiment.

The reaction chamber was evacuated prior to the hydrogen production experiment and this evacuation process removes not only air inside the reaction chamber but also dissolved gases in the aqueous solution. The production rate of hydrogen was characterized by measuring the pressure change in the reaction chamber using a pressure gauge (PIZ100, Ilmvac Gmbh). The recorded pressure change was converted to hydrogen production rate via the ideal gas law. When the aqueous solution was irradiated with a Xe lamp, the pressure was slightly increased at the initial stage even though no photocatalysts were added into the solution. This might be attributed to the increase of the water temperature. Although the reaction chamber was cooled with water, we observed that water temperature was increased by ~5 °C when the water was illuminated with a Xe lamp. The dissolved gases in the solution could be almost removed by the evacuation process, but some gases can be remained in water. This remained gas might be released into the vacuum when the water temperature was increased. Therefore, the hydrogen production rate was calculated by subtracting this initial pressure increase from the measured pressure change.

2.3. Characterization

Hydrogen evolution was confirmed by gas chromatography (GC, hp 5890) equipped with a thermal conductivity detector. The surface morphology of NPs was observed by a field-emission transmission electron microscope (FETEM, Tecnai G2 F30). Energy dispersive spectroscopy (EDS) mapping was obtained to reveal the adhesion and the distribution of CuO NPs on the P25 surfaces. In order to analyze aggregation behavior of the NPs, zeta potentials of P25 and CuO NPs were measured by a zeta-analyzer (ELS-Z2, Otsuka electronics Co., Ltd.). The NPs were dispersed in 20% aqueous methanol solution for the zeta potential measurement.

3. Results and discussions

3.1. Photocatalytic activities of the TiO_2/CuO NPs mixture

It is well known that TiO_2 alone can hardly produce hydrogen by photocatalytic water splitting. Our experiments also confirmed this: P25 did not almost produce hydrogen from aqueous methanol solution under Xe lamp illumination (Fig. 2a) . In addition, CuO alone didn't exhibit hydrogen production (Fig. 2a), although CuO is a semiconductor material with a small band gap of ~1.2 eV that can absorb broad light

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