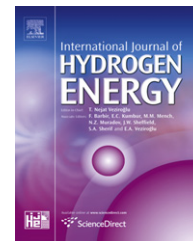


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The use of products from CO₂ photoreduction for improvement of hydrogen evolution in water splitting

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ABSTRACT

CuO/TiO₂ photocatalysts were prepared and shown to enhance the rate of CO₂ photoreduction and the production of total organic carbon (TOC), including HCOOH, HCHO and CH₃OH. Resulting TOC could act as electron donors for enhancing visible light hydrogen evolution from Pt/TiO₂ photocatalysts. The impacts on CO₂ photoreduction were investigated including the effect of Cu dopant, pH, irradiation time and using Na₂SO₃ as a sacrificial agent, and those on hydrogen evolution was also studied including TOC concentration and Pt doping. The CO₂ photoreduction mechanisms with respect to pH and CO₂ reduction potentials were discussed. CuO/TiO₂ and Pt/TiO₂ photocatalysts were characterized by X-ray diffraction, Raman spectroscopy and diffuse reflection UV–vis spectrophotometry. Both photocatalysts showed a visible light response in comparison with pure TiO₂. The photocatalytic experiments and FT-IR spectra indicated that photo-product desorption was the rate-limiting step in the CO₂ photoreduction.

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1. Introduction

The transformation and storage of solar energy into chemical energy is a promising approach for providing renewable energy. Solar radiation can induce transitions between electronic energy levels, which can be utilized in the photocatalytic reduction of carbon dioxide and water splitting for hydrogen production. Efficient conversion of sunlight to hydrogen by splitting water through direct photocatalysts is a major milestone for a viable hydrogen economy. However, photocatalysts generally suffer from low intrinsic hydrogen production efficiency due to the facile recombination of photo-generated electron-hole pairs. In addition, water oxidation by holes is also a slower process than its reduction by electrons [1]. Therefore, organic sacrificial electron donors have been widely used to reduce recombination and enhance

hydrogen evolution [2]. However, organic sacrificial electron donors require an additional energy input, and hence water is now considered the best choice as a hole scavenger [3].

Photoreduction of CO₂ has also been attracting the increasing research attention due to its potential in mitigating the greenhouse effects and fossil fuel shortages. Moreover, it is also a promising future technology since CO₂ can be reduced to useful compounds by solar energy at room temperature and ambient pressure. Possible reduction products including CO, HCOOH, HCHO, CH₃OH or CH₄, have been obtained by photoreduction of CO₂ or aqueous carbonate. Anpo [4,5] indicated that CH₄, CH₃OH, and CO were the major CO₂ photocatalytic products with highly dispersed titanium oxide anchored onto Vycor glass. In the presence of CO₂ and H₂O, Ikeue et al. [6] reported that Ti-containing porous silica thin films catalysed the formation of CH₄, CH₃OH and CO as

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a minor product under UV irradiation. Tseng et al. [7] showed that copper doping on TiO₂ promoted CO₂ photoreduction efficiency and improved the product selectivity toward methanol.

There are other factors influencing selectivity and efficiency of CO₂ photoreduction, including solvent, dissolved CO₂ concentration, pH and selection of sacrificial agent. In a study investigating the role of solvent [8], increasing the dissolved CO₂ concentration led to the major reduction products of formate and carbon monoxide. The product ratio could be controlled by the solvent dielectric constant. In a study of pH effect, Ku et al. [9] reported that carbonate photoreduction proceeded faster in acidic solutions than in alkaline solutions. Concerning sacrificial agent, Yoneyama [10] demonstrated that negative charges favored CO₂ photoreduction to formate, while positive charges favored CO production. Conditions affecting the charge of sacrificial agents influence the CO₂ photoreduction behavior.

Different pathways have been investigated to enhance CO₂ photoreduction efficiency and the transfer of inorganic carbon to organic carbon by solar energy. How to separate the various by-products and put them to practical use remains an important question. A logical but challenging approach is the photoproduct of HCOOH, CH₃OH and HCHO from CO₂ photoreduction, which could be utilized as sacrificial electron donors for enhancing hydrogen evolution. This is the main theme of the current study.

2. Material and methods

2.1. Preparation of photocatalysts

2.1.1. TiO₂

TiO₂ nanoparticles were prepared by the sol–emulsion–gel method [11] using tetrabutyl titanate (Ti(OC₄H₉)₄) as the precursor, cyclohexanol as the oil phase, distilled water as water phase, cetyltrimethyl ammonium bromide (CTAB) as surfactant and triethylamine as the gelling reagent. TiO₂ was calcined at 500 °C for 2 h.

2.1.2. CuO/TiO₂

An aqueous TiO₂ suspension containing Cu(NO₃)₂ was sonicated for 1 h. The temperature was increased to 95 °C and the suspension stirred for a further 4 h. The powder was collected by filtration and heated to 150 °C at a rate of 3 °C/min. It was then calcined at 500 °C with a heating rate change of 3 °C/min. After 2 h calcination, the sample was cool to the ambient temperature.

2.1.3. Pt/TiO₂

An aqueous-methanol solution (H₂O:MeOH = 99:1 by vol) TiO₂ suspension containing PtCl₂ (Pt:TiO₂ = 0.5%) was sonicated for 20 min and then heated to 75 °C [12]. After stirring for 1 h, the suspension was irradiated by a Hg lamp for 20 h under sonication [13], whereby Pt ion nanoparticle was deposited onto the TiO₂ surface. The powder was collected by filtrating, washed twice with distilled water, and heated to 200 °C for 2 h to remove any residual methanol.

2.2. Photocatalytic reactions

TiO₂ or Cu/TiO₂ photocatalyst powder (50 mg) was dispersed in 100 ml of distilled deionised water containing Na₂CO₃ (0.05%) and Na₂SO₃ (0.1%) and sonicated for 10 min. The pH was adjusted to 3 by hydrochloric acid and the suspension placed in a quartz glass reactor (210 ml) and saturated with CO₂ by bubbling for a period of 30 min and then the reactor was sealed and irradiated using a 250 W Hg lamp with one-sixth of the lamp irradiation being utilized, as shown in Fig. 1. All reactors with lamps were immersed in a sonication tank with circulating water for cooling purpose. After 6 h irradiation and then filtering for recovery of CO₂ reduction photocatalyst, Pt/TiO₂ powders (50 mg) were dispersed in filtered solution (100 ml) from CO₂ photoreduction within a pyrex glass reactor (210 ml). The reactor was then thoroughly deoxygenated with argon and sealed, and the suspension irradiated using the side of a 300 W Xe lamp with a 420 nm filter.

Formic acid and formaldehyde concentration in the liquid were analyzed by gas chromatography (GC, DX ICS3000). Hydrogen and methane concentrations in the gas, and methanol and formaldehyde concentrations in the liquid were all analyzed by gas chromatograph (HP7890). TOC concentration was analyzed by TOC instrument (SHIMADZU TOC-VWP).

2.3. Sample characterization

Crystalline size and crystal structure of the prepared doped TiO₂ samples were determined by X-ray diffraction (XRD) using a Philips X-PERT Pro Alpha 1 diffractometer, operated with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a tube current of 40 mA and a voltage of 45 kV. Data were collected over a 2θ range from 20° to 80° at a speed of 1°/min. Diffuse reflectance UV–vis spectra were recorded with a UV–vis spectrophotometer (U-3310) equipped with an integrating sphere. Laser Raman spectra were obtained using a Perkin–Elmer Ramanstation 400F Raman spectrometer. FT-IR spectra were obtained on a NICOLET 560 Fourier transform infrared spectrophotometer in the range of 4000–400 cm⁻¹ at 0.1 cm⁻¹ resolution.

3. Results and discussion

3.1. Factors effecting CO₂ photoreduction

CO₂ is a thermodynamically stable molecule. Its photoreduction mechanism is quite complex with a multi-electron transfer process, and results in several by-products with one to eight electrons transferred. Potentials of possible reaction products versus normal hydrogen electron are shown in Fig. 2 [14,15].

The photo activity of TiO₂ as a semiconductor is controlled by its band gap, band potentials and charge transfer efficiency. The potential of the electron acceptor is thermodynamically required to be lower than TiO₂ conduction band potential, while the potential of the electron donor should be greater than that of TiO₂ valence band. Moreover, the photoexcited electron-hole pairs require the rapid transfer of charge to photocatalyst active surface sites to minimize their recombination. The driving force for the electron transfer is the energy

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