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Monolithic film photocatalyst and its application for hydrogen production with repeated unit structures

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ABSTRACT

Interest in the immobilized film photocatalyst for hydrogen production has been increased. In this study, a simple monolithic film system is used, and a variety of cell configurations is investigated for minimizing electron losses in the electron transport pathways. The relative area ratio of Pt and photocatalyst (CdS/TiO_2) is also an important parameter to maximize hydrogen production on a limited substrate. The relative area ratio (Pt/photocatalyst) is 0.37 for the highest hydrogen production in our photocatalyst system. Repeated unit structures generate high amount of hydrogen without decreased efficiency at large photocatalyst area, comparing to the single unit structure for the same area. Therefore, minimizing electron loss and the effective use of limited area are important factors in applications of monolithic large scale film photocatalyst.

1. Introduction

Hydrogen has long been considered as a clean and environmentally benign alternative source of energy since it leaves only water after interaction with oxygen. As an alternative energy, hydrogen can be produced from various resources. Today, about 95% of hydrogen is obtained from fossil fuels such as natural gas, liquefied hydrocarbons, and liquefied petroleum gas by a steam reforming process, and these non-renewable resources use high-energy consumption for the manufacturing processes [1–3]. In that sense, production of hydrogen from photocatalytic water splitting under solar irradiation is one of the ideal methods because of the complete consumption and regeneration cycle [4].

$$\begin{array}{l}\text{Generation}: H_2O + \text{energy(solar)} \rightarrow H_2 + 1/2O_2 \\ \text{Consumption}: H_2 + 1/2O_2 \rightarrow H_2O + \text{energy}\end{array} \quad (1)$$

This method was developed by Fujishima et al. [5] in 1972, and later many researchers have devoted to improve photocatalytic performance in various ways, for example, composite photocatalyst [6], doping [7], metal loading [8], sacrificial agent [9], and nano-structures [10] as a particulate form in an aqueous solution. In addition to the particulate forms of photocatalysts, film photocatalysts have also been studied for hydrogen production mostly as a photoelectrochemical (PEC) cell structure [11–14]. The PEC cell is composed of photo anode and cathode, and then two electrodes are electrically connected via wire. The main purpose of using the PEC cell structure is the application of bias between photo anode and cathode to increase the amount of hydrogen production. However, it would be more desirable to produce hydrogen without applying external energies because the hydrogen generation and consumption cycle is self-satisfied under solar irradiation.

Lianos et al. [15,16] proposed the use of a simple monolithic electrode system for hydrogen production without external bias. We utilized a similar monolithic system, and the schematic view including the ideal electron transport pathways (ETP) is shown in Fig. 1. The film consists of photocatalyst and Pt metal parts on a conducting fluorine-doped tin oxide (FTO) glass substrate. Basically, hydrogen molecules are generated on the Pt part by proton reductions with electrons transported from the photocatalyst part, due to the lower Fermi level of Pt than that of the photocatalyst. The different reaction sites for hydrogen and oxygen in our film structure are also advantageous to suppress the backward reaction ($H_2 + 1/2O_2 \rightarrow H_2O$) which is thermodynamically possible. Accordingly, the photocatalyst part is considered as a light active area for generating electron-hole pairs, and the Pt part is used as reaction sites for proton reduction. Thus, it is desirable to have sufficient Pt area for high proton reductions and sufficient photocatalyst area for high electron generation. However, the usable area is always limited, so it is necessary to optimize the relative area ratio of photocatalyst and Pt parts on a substrate to generate the highest amount of hydrogen. Applications of the film photocatalyst for the large scale production are strongly related to electron losses while transporting the electrons from photocatalyst to Pt. The ETP on large film area become much complex and long, and thus electron loss is generally increased in large cell cases. So, applying the large scale cell systems for various applications

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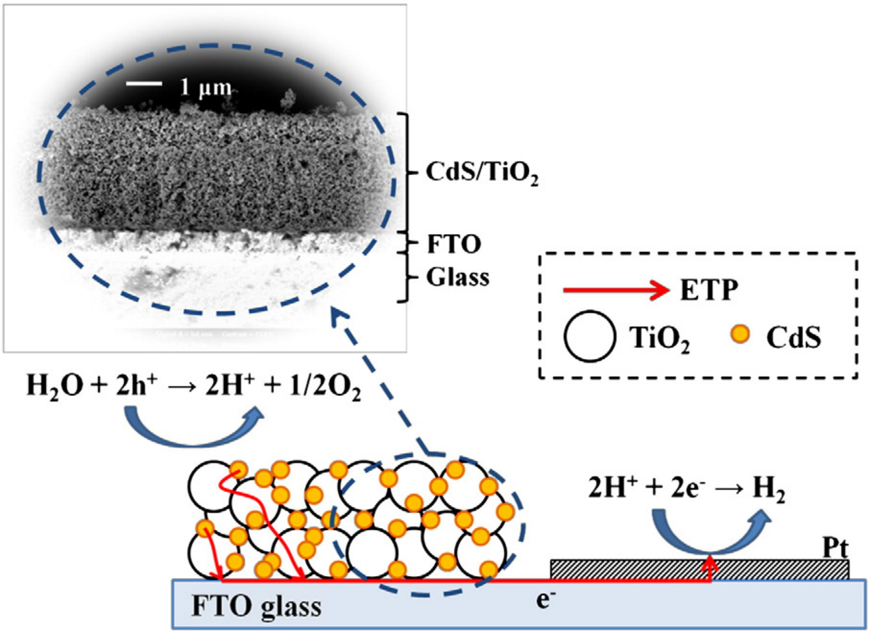

Fig. 1. Schematic view of the film structure including the ideal ETP. The inset is a cross sectional image of the photocatalyst.

[17–19] such as dye sensitized solar cell, quantum dot sensitized solar cell, and PEC cell is a challenging problem. Therefore, electron losses during electron transport should be minimized through circuits.

In this study, we examined various arrangements of cell configurations to see the effects of relative area ratio between photocatalyst and Pt parts on hydrogen production for large scale application. For photocatalyst synthesis, titanium dioxide (TiO_2) nanoparticles were conjugated with cadmium sulfide (CdS) quantum dots. All experimental variables such as photocatalyst, Pt, electrolyte solution, and illumination condition were kept constant for this study.

2. Experimental details

2.1. Materials and cell fabrication

All materials were purchased from Aldrich unless otherwise specified and used without further purification. Commercial nanocrystalline titanium dioxide was Degussa P25. Fluorine-doped tin oxide (about 6–9 Ω/cm^2, Pilkington) glass was used as a transparent conducting oxide substrate. The substrates were cut to make various types of samples (all dimensions are explained in the Results and discussion section). All substrates were carefully rinsed with ethanol after sonication in de-ionized water.

The cell system consists of photocatalyst and Pt parts on a substrate (FTO coated side was used), and they are next to each other as shown in the schematic view of Fig. 1. For preparing Pt part on the substrate, 0.7 mM $H_2PtCl_6 \cdot 6H_2O$ in 2-propanol solution was slowly dropped (about 3–4 drops) on the substrate, and it was sintered at 500 °C for 20 min after drying at room temperature. The photocatalyst part was fabricated from TiO_2 nanoparticles combined with CdS quantum dots. The same procedure for fabricating photocatalyst films was used as in our previous report [20]. Briefly, the doctor-blade method was used for fabricating the TiO_2 film and then chemical bath deposition (CBD) process was used to combine CdS quantum dots with TiO_2. The band gap energy of the CdS/TiO_2 photocatalyst film was 2.27 eV from the UV–vis spectrum measurement. For preparing TiO_2 porous films by the doctor blade method, TiO_2 paste was formed with 5 g TiO_2 (P25), 1.25 g of molecular weight of 10^5 g/mol polyethylene oxide, 25 g de-ionized (DI) water, 0.1 mL acetyl acetone. After the doctor-blade and CBD processes, the film was also sintered at 500 °C for 30 min. Materials for CBD process were 0.1 M $Cd(CH_3COO)_2 \cdot 2H_2O$ and 0.1 M $Na_2S \cdot 9H_2O$ aqueous solutions.

2.2. Material characterization

The cross sectional image of the photocatalyst film was observed by a field emission scanning electron microscope (FESEM, Carl Zeiss, Supra 55VP) with an acceleration voltage of 2 kV. Scanning transmission electron microscopy (STEM) image was taken by a FEI COMPANY microscope (Tecnai G2 F30 ST) operated at 300 kV equipped with energy-dispersive X-ray spectroscope (EDS). The crystalline structures of the film photocatalyst on a FTO substrate were analyzed by an X-ray diffractometer (XRD, Rigaku, DMAX-2500) with Cu Kα radiation at 40 kV and 300 mA, and the specimen dimension was 1 cm × 3 cm.

2.3. Hydrogen production

The reactor for hydrogen production was a cylindrical shape with total volume of 330 mL and it was made of Pyrex glass. Cut-off wavelength of the Pyrex glass was measured at 300 nm and below. Before doing the hydrogen production experiment, the reactor was deaerated completely with N_2 gas for about 1 h. Photocatalytic reaction for hydrogen production was carried out in 150 mL 40 mM $Na_2S \cdot 9H_2O$ aqueous solution. The film photocatalyst was immersed in the solution and continuously stirred during the reaction. A solar simulator (Peccell Technologies, PED-L11) equipped with 150 W Xe lamp and AM 1.5 G filter was used as a light source with the intensity of 1000 W/m^2. Total reaction time was 150 min, and evolved gas was collected every 30 min with a gas-tight syringe and analyzed by a gas chromatograph (Chrompack, CP9001) equipped with a thermal conductivity detector and a molecular sieve column. During the experimental period (for 150 min), there is no decrease in efficiency observed on the amount of evolved hydrogen. The apparent energy conversion efficiency (AECE) was defined as the percentage ratio of