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Effect of ZnO Electrodeposited on Carbon Film and Decorated with Metal Nanoparticles for Solar Hydrogen Production

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In this study, we prepared horn-like ZnO structures on carbon films (ZnO/CF) by electrodeposition and decorated the ZnO horns with different metals (Ag, Au, and Pt) *via* photodeposition (M–ZnO/CF). Using M–ZnO/CF as photocatalysts, we examined ways to enhance solar hydrogen production from various points of view, such as modifying the intrinsic physical properties and thermodynamics of the materials, and varying the chemical environment during M–ZnO/CF fabrication. In particular, we focused on the effects of the carbon film and metals in M–ZnO/CF hybrid photocatalysts on solar hydrogen production. The type of metal nanoparticles is an important factor in solar hydrogen production because the deposition rate and electrical conductivity of each metal affect the proton–water reduction ability.

1. Introduction

Photocatalyst-based solar-hydrogen (H_2) production (SHP) is a promising strategy to address increasing global energy demand because the high energy capacity (e.g. $\Delta G^\circ = 237.1$ kJ mol^{-1}) and low cost of transportation of hydrogen make it an ideal energy carrier to replace petroleum. H_2 is nontoxic and SHP is sustainable, leading to extensive study on the SHP using photocatalysis over several decades[1].

Among the investigated photocatalysts, ZnO is one of the most outstanding materials for SHP because of its wide bandgap (3.37 eV), large exciton binding energy (60 meV), superior electrochemical stability, non-toxicity, suitability for doping, and low cost. Therefore, it is also intensively used for non-SHP applications like photonics, solar cells, sensors, and piezoelectric devices[2–5]. Despite these advantages of ZnO as a semiconductor photocatalyst, it is difficult to obtain adequate efficiency for commercialization of ZnO-based SHP. To solve this problem, the structure and morphology of ZnO have been modified in many studies to improve its photocatalytic activities. For example, the effect of one-dimensional (1D) or two-dimensional (2D) ZnO morphologies (i.e., nanowires[6], nanorods[7], and nanoflowers[8]) have been studied, and the results indicate that the photocatalytic activity of ZnO is significantly affected by its structure and crystallinity. Meanwhile, the effect of substrate, which might offer electron pathways and good support for the catalyst structure, has also been widely studied in recent years. Because the immobilization of a photocatalyst on a substrate maintains the stability of the proton-reduction reaction in SHP, it could lead to high SHP efficiency. The photocatalyst can be immobilized on the substrate by electrodeposition[9], hydrothermal[10], or CVD techniques[11] on ITO[12], FTO[13], Al_2O_3 substrates[14], and so on. Among them, carbon film is a promising substrate for SHP[15,16] because it has high electrical conductivity, outstanding chemical stability, high specific surface area, and suitable porosity for improving SHP efficiency[17–20].

In our previous study, ZnO rods with different shapes were fabricated on carbon nanofibres (ZnO/CNF), and the effect of ZnO morphology on SHP was examined[21]. The results suggested that the SHP efficiency was governed by the ZnO edge morphology because it determined the light-absorption ability of ZnO/CNF. Furthermore, we also fabricated horn-like ZnO structures on carbon films. We found no significant difference in SHP on account of the carbon structures (nanofibres and film). Meanwhile, using a CNF mat as a substrate enhanced the SHP efficiency in ZnO/CNF when compared to the SHP efficiency of ZnO nanoparticles because of the higher electrical conductivity of CNFs. However, the quantitative enhancement of SHP was found to be very low. Therefore, it is necessary

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to introduce another strategy (*e.g.* metal deposition) to improve SHP efficiency and investigate its contribution to SHP. Various studies showed that metals act as electron sinks owing to the Schottky barrier at the metal–semiconductor interface[22,23], which might lead to higher photocatalytic activity of ZnO–metal hybrid photocatalysts for SHP when compared to bare ZnO nanoparticles[24–27]. Chen *et al.* suggested that hybrid nanomaterials consisting of carbon nanotubes and metal-doped ZnO had high photocatalytic activity for methyl orange degradation, which was attributed to the excellent electrical properties of carbon nanotubes and Mg-doped ZnO[28]. Zhang *et al.* suggested that the enhanced photocatalytic activity of CuS/ZnO/CF heterostructures could be attributed to the effective electron–hole separation and improved utilization of visible light[29]. Consequently, the excellent photo-response of metals, the effect of metal–ZnO hybrid materials, and the efficient electron-transfer properties of carbon materials all play supporting roles in inhibiting the charge recombination, and thus enhancing hydrogen production.

However, there have been no studies comparing the effects of different types of metals on SHP using metal-decorated electrodeposited-ZnO on carbon films. Therefore, in the study reported here, we deposited ZnO horns on carbon films using electrodeposition and then decorated the ZnO horns with three different metals (Ag, Au, and Pt) *via* photodeposition[30,31]. We investigated the effect of the metals on SHP in terms of the intrinsic physicochemical properties of the metals and the chemical environment in which M–ZnO/CF fabrication occurred. The optimal conditions of M–ZnO/CF preparation for SHP were also investigated.

2. Experimental

2.1. Preparation of carbon films

Polyacrylonitrile (PAN) films were fabricated from the PAN polymer (Mw ≈ 150,000; Aldrich, USA) *via* solution casting. A solution of 10 wt% PAN was used as the carbon precursor; it was prepared by dissolving PAN in dimethyl sulphoxide (DMSO; Duksan Pure Chemicals Co., Korea) to form a saturated solution under constant mechanical stirring for 12 h. The PAN solution was then drop-casted on an alumina plate, and an iron bar was used to spread the PAN layer to reach a constant thickness of 2 mm. After casting of the film, it was dried at 60 °C in a vacuum oven to remove the solvent. To prepare the carbon film, the prepared PAN films were carbonized by heating at a rate of 5 °C min^{-1} for 1 h and maintained at 300 °C for 2 h in a furnace under a nitrogen atmosphere. The temperature was then increased at a rate of 5 °C min^{-1} for 100 min and maintained at 800 °C for 2 h. Hereafter, the as-prepared carbon films are referred to as CFs.

2.2. Electrodeposition of ZnO on carbon film

For the electrodeposition (ED) of ZnO on CFs, a three-electrode system was used with an as-prepared CF as the working electrode (size: 1 cm × 3 cm), a KCl saturated silver chloride electrode (Ag/AgCl; Princeton Applied Research, USA) as the reference electrode, and a platinum wire as the counter electrode. ZnO horns were electrodeposited on each CF by holding a constant potential of –1 V (*vs.* the Ag/AgCl reference electrode) for 30 min at 60 °C with a potentiostat (VSP; Princeton Applied Research, USA) in a 0.5 mM zinc acetate (ZnAc, $Zn(CH_3COOH)_2 \cdot 2H_2O$; Aldrich, USA) solution containing 0.1 mM potassium chloride (KCl; Daejung Chemicals & Metals Co., Ltd., Korea). The total solution volume was 50 mL. The obtained samples were washed with distilled water and dried in air. Hereafter, the electrodeposited ZnO horn on a CF is referred to as ZnO/CF.

2.3. Photodeposition of metals on electrodeposited ZnO on carbon film

To determine the best combination of metal–semiconductor hybrid for solar-hydrogen production, three different metals—Ag, Au, and Pt—were photodeposited on the ZnO/CF using the metal precursors silver nitrate ($AgNO_3$; Junsei Chemical Co., Japan), hydrogen tetrachloroaurate hydrate ($HAuCl_4 \cdot 3H_2O$; Kojima Chemicals Co., Ltd., Japan), and hydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6 \cdot 6H_2O$; Kojima Chemicals Co., Ltd., Japan). The amount of photodeposited metal was optimized in each case by experimenting with different concentrations (0.1, 0.5, 1, and 2 mM) of each metal precursor. The as-prepared ZnO/CF (1 cm × 3 cm) samples were pre-irradiated with light (300-W Xe-arc lamp; Newport, USA) for 10 min to improve their hydrophilicity, and then immersed in each metal precursor solution (4 mL) for 10 min to allow the adsorption of metal cations on the ZnO horn surface. After that, each sample was exposed to the 300-W Xe lamp for 10 min to reduce the metal cations. Finally, different types of metal-decorated electrodeposited-ZnO on CF (M–ZnO/CF) were obtained. The three different metal-decorated ZnO/CFs are referred to as Ag–ZnO/CF, Au–ZnO/CF, and Pt–ZnO/CF, respectively. Fig. 1 shows a scheme of the M–ZnO/CF preparation. To investigate the effects of metal concentration on M–ZnO/CFs, Ag–ZnO/CFs were fabricated using Ag precursor concentrations of 0.1, 0.5, 1, and 2 mM. Hereafter, the Ag–ZnO/CFs fabricated with different Ag precursor concentrations are referred to as Ag–ZnO/CF (0.1 mM), Ag–ZnO/CF (0.5 mM), Ag–ZnO/CF (1 mM), and Ag–ZnO/CF (2 mM).

2.4. Hydrogen production behaviour of metal decorated electrodeposited ZnO on carbon film (M–ZnO/CF)

To perform the hydrogen-production experiment, the as-prepared ZnO/CF, M–ZnO/CFs (1 cm × 3 cm), and ZnO nanoparticles (0.139 mg, diameter < 30 nm; Aldrich, USA) were placed in a quartz reactor (volume = 6.4 mL) with a solution (4 mL) containing 0.1 M of sodium sulphide pentahydrate ($Na_2S \cdot 5H_2O$; Daejung Chemicals & Metals Co., Ltd., Korea) and anhydrous sodium sulphite (Na_2SO_3; Daejung Chemicals & Metals Co., Ltd, Korea). The amount of ZnO NPs used (0.139 mg = 0.566 μmol cm^{-2} × 3 cm^2 × 81.38 g mol^{-1}) was calculated in units of mg using the following equation:

$$\text{Amount of ZnO NPs} = [Zn^{2+}]_{ads} \times A_{ZnO/CF} \times MW_{ZnO} \quad (1)$$

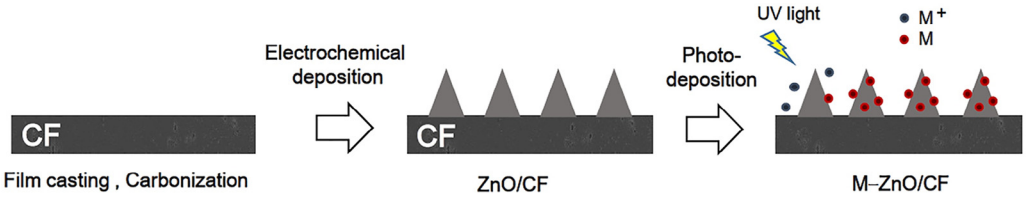

Fig. 1. Schematic fabrication illustration of ZnO/CF photodeposited with metal (Ag, Au, and Pt) nanoparticles.

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