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Trilayer CdS/carbon nanofiber (CNF) mat/Pt-TiO_2 composite structures for solar hydrogen production: Effects of CNF mat thickness

Young Kwang Kim[a], Sang Kyoo Lim[a], Hyunwoong Park[b], Michael R. Hoffmann[c], Soonhyun Kim[a,*]

[a] Division of Nano and Energy Convergence Research, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, 42988, Republic of Korea
[b] School of Energy Engineering, Kyungpook National University, Daegu 41566, Republic of Korea
[c] Linde + Robinson Laboratories, California Institute of Technology (CALTECH), Pasadena, CA 91125, United States

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ABSTRACT

Solar H_2 production by photocatalytic water splitting is a promising technology that permits direct H_2 production from the clean and abundant resources of water and solar light. We successfully fabricated trilayer heterostructures of CdS/carbon nanofiber (CNF) mat/Pt-deposited TiO_2 (Pt-TiO_2) for solar H_2 production. The CNF mat was prepared by electrospinning and carbonization. CdS and Pt-TiO_2 were coated on the front and back of the CNF mat by doctor blading. Under visible-light irradiation on the CdS side, the addition of the Pt-TiO_2 coating improved the H_2 production by a factor of 3.4. This suggests that the H_2 production reaction could occur on Pt-TiO_2, which is not active under visible irradiation; therefore, the CNF mat could act as an efficient photogenerated electron-transfer mediator from CdS to Pt-TiO_2. The H_2 production rates of the trilayer CdS/CNF/Pt-TiO_2 heterostructures were strongly affected by the thickness of the CNF mat and the carbonization temperatures used in production, which affect the resistance of the CNF mat between the CdS and Pt-TiO_2 sides. The results clearly demonstrated that the CNF acted as an efficient electron-transfer mediator as well as a support material.

1. Introduction

Photocatalytic water splitting is a promising technology that permits H_2 production directly from water and solar light, which are clean, renewable, and abundant resources [1,2]. Semiconducting photocatalysts have been extensively studied for photocatalytic water splitting [3,4]. In general, multi-component systems are necessary in photocatalytic water splitting to efficiently absorb solar light, separate and transfer photogenerated electron-hole pairs, and catalyze the reduction and oxidation reactions. Many researchers have focused on enhancing the photocatalytic efficiency by developing new semiconducting materials, because low photocatalytic efficiency is a major obstacle for industrial applications of the technology [5–9]. However, cost reduction is also an important factor for industrial applications. Therefore, finding cost-effective materials is necessary for the industrial use of semiconductor-based photocatalytic H_2 production.

Carbon materials have been extensively used for photocatalytic water splitting because they possess special physicochemical properties. Carbon nanomaterials can act as supporting materials with high surface areas [10], catalysts for the reduction reaction [11], and efficient electron-transfer mediators [12–14]. Carbon nanotubes (CNTs) provide spatial confinement for TiO_2 and large surface areas that increase the rates of redox reactions. Two-dimensional graphene sheets in graphene-embedded photocatalysts promote electron transfer by the geometry, built-in electron reservoirs, and excellent charge mobility of graphene. Furthermore, modifications to the graphene surface can improve photocatalytic water splitting by enhancing the light absorption of TiO_2. Carbon nanofibers (CNFs) have useful characteristics including relatively simple fabrication, cost effectiveness, and flexibility [15,16]. Previous studies have shown the advantages of CNFs applied in composites with photocatalytic materials [17–20]. CNFs could enhance photogenerated charge separation, as they have large surface areas and good conductivities.

Previously, we studied the application of a CNF/photocatalyst composite in photocatalytic H_2 production. We first applied a flexible mat of CNFs for H_2 production under UV irradiation [21]. We further investigated the fabrication of CdS and CNF mats and applied this composite to visible light-induced H_2 production [22].

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* Corresponding author.
E-mail address: sh2358@dgist.ac.kr (S. Kim).

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In the CdS/CNF composite, most electrons reacted with water molecules to generate H_2 on the surface of CdS. However, it was possible that some electrons were transferred to the CNF mat, which would promote electron-hole pair separation; this implies that the CNF mat could function as an electron-transfer mediator as well as a support material. Therefore, to better understand the photocatalytic H_2 production system of CNF/photocatalysts, the role of CNF must be further investigated.

In this study, to investigate the role of CNF, we fabricated a trilayer heterostructure of CdS/CNF mat/Pt-nanoparticle-deposited TiO_2 (Pt-TiO_2) composite. The CNF mats were prepared by electrospinning and carbonization. CdS and Pt-TiO_2 were deposited on the front and back, respectively, of the CNF mat. CdS on the front could directly absorb the visible light and Pt-TiO_2 on the back could act as co-catalyst for H_2 production. Because the Pt particle deposited on the TiO_2 are on the back side, the visible light absorption of Pt-TiO_2 due to surface plasmon resonance (SPR) effects of Pt nanoparticles might be negligible and the effects of depositing Pt-TiO_2 on the back of the CNF mat would help to elucidate the photogenerated electron transfer occurring in the heterostructure. We studied the effects of varying the CNF mat thickness and the carbonization temperature, because these two factors could affect the resistance of the CNF mat and thus the electron-transfer process.

2. Experimental details

2.1. Materials

We used chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, ≥ 37.50% Pt basis, Sigma-Aldrich), titanium oxide (TiO_2, Degussa), cadmium acetate dihydrate (CdAc·$2H_2O$, 99%, Sigma-Aldrich), sodium sulfide pentahydrate ($Na_2S{\cdot}5H_2O$, 98%, Daejung), sodium sulfite (Na_2SO_3, 98%, Daejung), polyacrylonitrile (PAN, $M_w = 150000$, Sigma-Aldrich), *N*,*N*-dimethylformamide (DMF, 99%, Sigma-Aldrich), ethanol (99%, Daejung), methanol (99%, Daejung), nitric acid (HNO_3, 1 mol/L, Duksan), hydrochloric acid (HCl, 1 mol/L, Duksan) and distilled water to synthesize the samples.

2.2. Preparing CNF with varying thickness

CNF mats were prepared using electrospinning and carbonization, as previously reported [20]. A 10 wt.% PAN solution was prepared by dissolving PAN in DMF and heating the mixture at 85 °C while stirring for 4 h, followed by cooling to room temperature and stirring for another 12 h. A viscous yellow-brown solution was thus obtained. PAN nanofibers were prepared by electrospinning, in which the PAN solution was fed at a constant rate of 20 μL/min. An electric field of 20 kV was applied, and the distance between the needle and the collector plate was 15 cm. The PAN nanofibers were stacked in different numbers of layers (1, 2, 4, 6, and 8 layers) prior to calcination to control the thickness of the final CNF mats. The collected PAN nanofibers were annealed by raising the temperature at a rate of 5 °C/min for 50 min and holding at 250 °C for 20 min under atmospheric conditions, followed by 10 min in N_2 gas. The N_2 gas was in continuous flow. The temperature was raised at a rate of 5 °C/min for 100 min and held at 750 °C for another 60 min. Following this, the temperature was raised at 5 °C/min for 130 min (or 70 min to achieve a carbonizing temperature of 1100 °C) and then held at 1400 °C (or 1100 °C) for 60 min. The CNF mats were collected after annealing. The obtained samples were acid-treated by submersion in 1 L aqua regia (HNO_3:HCl = 1:3 v/v) per g of CNF mat for 30 min [23].

2.3. Preparing trilayer heterostructured CdS/CNF mat/Pt-TiO_2 composite

CdS nanoparticles were fabricated by a precipitation method [24]. Fifty mL 0.2 mM $Na_2S{\cdot}5H_2O$ solution was slowly added to 50 mL 0.2 mM CdAc solution with vigorous stirring. Pt-TiO_2 nanoparticles were synthesized through the photodeposition of Pt on the surface of TiO_2 [25]. A stock solution of chloroplatinic acid hexahydrate and 0.5 g/L TiO_2 was briefly dispersed in 10 vol.% methanol with vigorous stirring for 30 min. The Pt:TiO_2 weight ratio was 0.005:1. The suspension color changed from white-yellow to white-gray following irradiation by ultraviolet light for 30 min under N_2 purging gas. The suspension was filtered using 0.45-μm polytetrafluoroethylene (PTFE) filters (Millipore) and dried at 80 °C in an oven.

Trilayer CdS/CNF/Pt-TiO_2 composite structures were synthesized by the doctor blade method. CdS nanoparticles were loaded on one side of the CNF mat by mixing 20 mg of CdS powder with 260 mg of polyethylene glycol solution (H_2O:PEG = 2:1 by weight). This CdS paste was loaded with a thickness of 0.48 μm onto one side of the CNF mat surface using one layer of 3 M tape. After the loading process, calcination was performed at 400 °C for 30 min, before the CdS-deposited mat was cooled to room temperature. Pt-TiO_2 loading was performed on the other side of CNF by the same process, using as-prepared Pt-TiO_2 instead of CdS.

2.4. Characterization of CdS/CNF/Pt-TiO_2

Scanning electron micrographs were obtained on a field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectrometer (EDS, Hitachi, S 4800). The electrical conductivities of the samples were analyzed by a four-point probe (CMT-SR3000, AIT) on samples of 1 cm × 1 cm in size to determine the relationship between electrical conductivity and annealing temperature. The electrical resistances and calculated conductivities between the CdS and Pt-TiO_2 sides of the trilayer electrode were measured by a digital multimeter. The thickness of the CNF mat was measured using digital Vernier calipers (Mitutoyo, Japan) and the side-view SEM images. X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (Panalytical, Empyrean, 40 kV, 30 mA) using Cu-Kα_1 radiation ($\lambda = 1.54178$ Å) and a quartz monochromator. Raman spectra of the samples were analyzed by a Raman spectrophotometer (Thermo Scientific, Nicolet Almega XR) in the wavenumber range of ~100–4000 cm^{-1} using a 532-nm laser. The elemental binding energies and oxidation states were determined using an X-ray photoelectron spectroscope (XPS, Thermo Fisher Scientific, Theta Probe AR-XPS System) fitted with a monochromated Al Kα source ($h\nu = 1486.6$ eV).

2.5. Photocatalytic H_2 production and photocurrent measurement

The photocatalytic H_2 production was determined experimentally using two sacrificial reagents of 0.1 M Na_2S and Na_2SO_3 in distilled water. The rectangular quartz reactor held 4 mL of reagent and was similar to the cell used for analysis in UV–vis spectrophotometry. The head volume was 2.4 cm^3. All samples were formed as 3 cm × 0.5 cm rectangular mats with weights of ~38 mg. The light source was a 150-W Xe arc lamp (Abet Technologies) with a 420-nm cutoff filter. The distance between the reactor and light source was 15 cm N_2 gas was bubbled through the reagents for 30 min before irradiation. The H_2 produced was inspected every 30 min for 3 h using a gas chromatograph (GC, HP6890, Agilent) equipped with a thermal conductivity detector (TCD). A photocurrent measurement was performed with a three-electrode system in a 1 M Na_2SO_3 buffer (pH = 12). The working electrode is CdS/CNF/Pt-TiO_2