



H₂- and NH₃-treated ZnO nanorods sensitized with CdS for photoanode enhanced in photoelectrochemical performance

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HIGHLIGHTS

- Effect of solid state doping of H/N in ZnO: redshift and enhanced IR absorption.
- Optimized length/diameter of ZnO nanorod for the maximum electrode performance.
- Direct measurement of electrode performance by hydrogen gas production rate.
- Discussion of the ultimate effects of the bandgap, doping, and nanostructures.

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ABSTRACT

A ZnO/CdS core-shell nanorod structure is studied for use as photoanode in photoelectrochemical cell for water splitting. The focus is to examine the effect of hydrogen and/or nitrogen doping of ZnO nanorods on its performance as photoanode. ZnO nanorods hydrothermally synthesized on ITO glass substrate are heat-treated in pure hydrogen ambient and then in atmospheric pressure of ammonia for H- and N-doping of ZnO. The H- and/or N-doped ZnO nanorod structure (N/H:ZnO) reveal an enhanced photocurrent and photo-to-current conversion efficiency in comparison to untreated ZnO nanorods by shifting the absorption edge towards visible region and increasing absorption of infrared region wavelengths. CdS sensitization of the nanorods is also studied. The morphology and properties of the samples are examined by SEM, XRD, UV–vis absorption and photoluminescence. Optimization of the ZnO nanorod growth and CdS coating processes are also undertaken. An optimized N/H:ZnO nanorods sensitized by CdS layer yields a photocurrent density of $\sim 12.61 \text{ mA cm}^{-2}$ at 0 V (vs. SCE) and photon-to-current conversion efficiency of $\sim 4.5\%$ (at -0.73 V vs. SCE) in $0.5 \text{ M Na}_2\text{S}$ solution under a simulated solar light. The H₂ gas generation with the optimal structure is about $6 \text{ mL h}^{-1} \text{ cm}^{-2}$.

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1. Introduction

Hydrogen (H₂) is considered by many to be the future of fuel because it can be produced by clean and renewable energy sources [1]. Hydrogen could provide the answer to the crisis of inevitable future energy; as such, it has come to the forefront of alternative energy research. Photo-electrochemical (PEC) water splitting in

particular has been widely recognized as one of the most promising methods for H₂ gas generation by the scientific community ever since Fujishima and Honda used a titanium dioxide (TiO₂) photoanode to electrolyze hydrogen from water in 1972 [2,3]. In recent years, much attention has also been given to zinc oxide (ZnO) as a viable semiconductor for PEC water splitting [4]. ZnO has been extensively researched due to its relative abundance, low cost, nontoxicity, and high electron mobility [4–7]. Unfortunately, ZnO like TiO₂ absorbs only the UV region of the electromagnetic spectrum, which accounts for only 4% of solar energy due to its large energy band gap ($>3.1 \text{ eV}$) [8,9]. This, in turn, yields a very low photon-to-current conversion efficiency (ABPE). Therefore, broadening the absorption spectrum of ZnO material towards the visible

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region, which accounts for about 45% of the whole solar energy spectrum, has been widely studied; for example, doping with metal [10–13] and nonmetal ions [14,15], and hydrogenation [6,16] has received extensive attention to improve light absorption and charge transport.

Attempts to enhance the STH conversion efficiency of the electrodes used in the PEC cell have led to employment of narrow band gap materials such as CdS (~2.4 eV) [7,17], CdSe (~1.7 eV), and CdTe (~1.5 eV) [18,19] as photoactive sensitizers of the photoanodes based on ZnO material due to its attractive light – harvesting characteristic, tunable band gap, easy fabrication, and low cost. The formation of a feasible band alignment with ZnO causes efficient charge separation and transportation. There have been many people studied ZnO and CdS heterojunction structures, but to the best of our knowledge, the deposition of CdS on hydrogenated and ammoniac heat-treated ZnO nanorods for the improvement of hydrogen generation efficiency has not yet been reported.

Prompted by the success of previous works [20,21], in which cost-effective ZnO/CdS nano heterojunction structures showing high photocurrent and photon-to-electron conversion efficiencies were realized, we modified the underlying ZnO template in the conductance by doping H and/or N (denoted by N/H:ZnO) for band gap narrowing and enhanced carrier transport. The reduction of charge recombination due to an increased conductance as well as the enhanced absorption ability in visible and IR light with N/H:ZnO was also expected to contribute to an enhanced conversion efficiency of the electrode. Herein, the sensitization by CdS was again used to enhance the absorption of solar spectrum over a wide wavelength range and compare with other literature reports [7,17,20,21]. For the comparison, three-electrode electrochemical set up was used.

2. Experimental procedure

2.1. Materials

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.99%, Sigma-Aldrich Co., Ltd), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Sigma-Aldrich Co., Ltd), hexamethylenetetramine (HMTA) ($\text{C}_6\text{H}_{12}\text{N}_4$, 99%, Sigma-Aldrich Co., Ltd), cadmium nitrate tetrahydrate ($(\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O})$, 98%, Aldrich Chemical Company, Inc), thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, 98%, Alfa Aesar Co., Ltd), sodium sulfate, anhydrous (Na_2SO_4 , $\geq 98\%$, Samchung Pure Chemical Co., Ltd), sodium sulfide pentahydrate ($\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$, 98%, Daejung Chemical and Metals Co., Ltd) and distilled water (18.4 M Ω /cm).

2.2. Preparation of N/H:ZnO/CdS nanorods on indium tin oxide substrate

Prior to the growth of the ZnO nanorods, a ZnO seed layer was prepared on the indium-tin oxide (ITO) substrate by Zn metal sputtering process followed by oxidation at 400 °C (at a heating rate of 15 °C/min) for 2 h. The ZnO nanorods were grown on the seeded substrate by hydrothermal method at 90 °C for 4 h using a mixture of 0.04 M of aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}:\text{C}_6\text{H}_{12}\text{N}_4 = 1:1$ ratio. The hydrothermal reaction was repeated one more time to increase the length of the ZnO nanorods. The second reaction time was varied to 0, 2, 4, and 6 h; this means the total growth time of ZnO nanorods was varied to 4, 6, 8, and 10 h followed by annealing at 500 °C for 2 h in air. The samples were then heat-treated sequentially at 350 °C for 60 min in hydrogen and at 500 °C for 20 min in NH_3 . The ammoniac treatment was carried out in a two-zone temperature controlled tube furnace. The zone I at upstream was set at 900 °C for pre-cracking of ammonia and the substrate was placed in zone I at downstream at

500 °C for N-doping (Fig. 1).

The CdS nanoparticles were directly grown on the surface of nanorod array structures of ZnO, H:ZnO, and N/H:ZnO by soaking the electrodes in an aqueous solution of 10 mM of $\text{Cd}(\text{NO}_3)_2$ and 10 mM of $\text{C}_2\text{H}_5\text{NS}$ at 80 °C. The dipping time in the solution for CdS growth was varied to obtain the highest ABPE. The electrodes were rinsed with deionized water followed by natural drying. The fabricated nanostructured films were treated in ambient argon at 400 °C for 2 h to improve the structural stability and crystallinity. The flowchart of the N/H:ZnO/CdS nanorods array fabrication process on ITO substrate was shown in Fig. 1a.

2.3. Characterization of the films

The surface morphological, structural, and optical properties of the fabricated structures were investigated by field emission scanning electron microscopy (JSM-700F, JEOL), X-ray diffraction (D/max2500, Rigaku, Japan) using Cu K α radiation with a Ni filter, and UV–vis–NIR absorption spectroscopy (Scinco S-3100). Photoluminescence (PL) measurements of the samples were carried out at room temperature using a 325 nm wavelength laser as the excitation source (Lab RAM HR-800).

2.4. Measurements of PEC property and H_2 production

PEC properties were measured in a three-electrode electrochemical system (Potentiostat/Galvanostat Model 263A) using $\text{Hg}_2\text{Cl}_2/\text{Hg}$ in saturated KCl (SCE) as the reference electrode, a platinum (Pt) grid as counter electrode, and the fabricated photoanode structure as the working electrode. The electrolyte used was 0.5 M Na_2SO_4 for the ZnO structures and that 0.5 M Na_2S for the CdS-deposited structures. A simulated sunlight source, a 150 W Xe lamp (UXL – 150MO) with an intensity of 100 mW cm $^{-2}$ coupled with an AM 1.5 G filter, was employed to evaluate the performance of the photoanodes. All the measurements were done with light illumination into the front-side of the photoanodes. The area of the working electrode exposed to the electrolyte was fixed at 0.25 cm 2 using insulating epoxy resin. The evaluation of the electrode performance was done and compared by measuring the three-electrode applied-bias photon-to-current conversion efficiency (ABPE) using the following equation [20,22],

$$\eta(\%) = 100 \frac{I(E_{\text{rev}} - E_{\text{app}})}{I_0} \quad (1)$$

where I is the photocurrent density (mA cm $^{-2}$) at the applied bias, I_0 is the irradiance intensity of the light (100 mW cm $^{-2}$ at AM 1.5G), and $E_{\text{rev}} = 1.23$ V is the standard state reversible potential for water splitting. $E_{\text{app}} = E_{\text{meas}} - E_{\text{aoc}}$ is the applied potential, where E_{meas} is the electrode potential (vs. SCE) of the working electrode at which the photocurrent was measured under illumination and E_{aoc} is the electrode potential (vs. SCE) of the same working electrode under open circuit condition or the photo-current turn-on potential. The H_2 gas generated in the PEC water-splitting process was collected in a home-made hollow glass tube of diameter 2 cm (Fig. 1b).

3. Results and discussion

3.1. Morphology and characteristics

Fig. 2(a–d) shows the SEM images of ZnO nanorods grown in various growth times. We can see that the ZnO nanorods grew quasi-vertically on the transparent conductive ITO glass substrates. The diameter and length of ZnO nanorods increased with the growth time. The lengths of the ZnO nanorods were about 1.3, 1.5,

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