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S-doped ZnO nanorods on stainless-steel wire mesh as immobilized hierarchical photocatalysts for photocatalytic H_2 production

*Mu-Hsiang Hsu, Chi-Jung Chang**

Department of Chemical Engineering, Feng Chia University, 100, Wenhwa Road, Seatwen, Taichung 40724, Taiwan, ROC

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ABSTRACT

S-doped ZnO nanorods were grown on stainless steel mesh as immobilized hierarchical photocatalysts for hydrogen production. Properties of the photocatalysts were investigated by field-emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), photoinduced current, and photocatalytic hydrogen evolution test. Effects of polymer additive and doping on the surface texture, surface property, and H_2 production performance of the photocatalysts were studied. Polyethyleneimine helps the growth of nanorods on the entire surface of wire mesh. Photocatalytic H_2 production activity of the photocatalysts changes with dopant content and surface texture modification. Due to increased surface area of the hierarchical photocatalyst, enhanced light trapping and liquid flow among wire-mesh, the highest hydrogen evolution rate of 3640 μmol g^{-1} h^{-1} is obtained. The photocatalytic activity of photocatalyst remained at 87% of its original performance after five cycles.

Introduction

Photocatalytic hydrogen production by water splitting using solar energy is a promising way to obtain renewable and clean energy. It has advantages such as the abundant resource of seawater and light, low cost, and less pollution [1]. To achieve higher activity for photocatalytic hydrogen production, many techniques about water splitting process by semiconductor photocatalysts [2,3], including addition of sacrificial agents and surface modification of photocatalysts have been studied. The sulfide/sulfite is reported to be the most common and effective agent [4].

Because of large excitation binding energy and the wide band gap (3.37 eV) at room temperature, ZnO can be used for many applications, including photocatalysts [5–7], transparent conducting layer [8,9], solar cells [10,11], and gas sensors [12,13]. On the other hand, ZnS is also a good photocatalyst which has a wider band gap ($E_g = 3.6$ eV) than ZnO. ZnS can photodecompose many organic compounds because it possess the properties, including the rapid generation of electron–hole pairs by photoexcitation and the highly negative reduction potentials of excited electrons [14]. The photocatalytic efficiency of semiconductor oxide photocatalysts depends on the separation efficiency of electron–hole pairs

* *Corresponding author*. Tel.: +886 4 24517250x3678; fax: +886 4 24510890.
E-mail address: changcj@fcu.edu.tw (C.-J. Chang).

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and the adsorption ability. Doping can help the separation of photoinduced charge carriers in the semiconductor photocatalysts [15]. Doping cations such as Ni^{2+} [16], Ag^{+} [17], and Mg^{2+} [18] can be incorporated in photocatalysts to improve their photocatalytic activity. Because ZnS is a good photocatalyst for hydrogen production [19], we try to investigate the effect of doping S^{2-} anion into ZnO nanorods on the photocatalytic performances of the photocatalysts. Some methods for the synthesis of S-doped ZnO nanostructures have been reported [20,21]. However, photocatalytic H_2 evolution from salt water over these S-doped ZnO nanorods coated on stainless-steel wire mesh substrates has not been investigated before. We believe that the S doped ZnO based photocatalysts can enhance the photocatalytic H_2 evolution. Besides, the nanorods-based photocatalyst has large surface area. In this study, we try to investigate the photocatalytic H_2 production performance of S-doped ZnO nanorods based photocatalysts.

Using a support for the photocatalysts helps to maintain the dispersion of the photocatalysts. Moreover, some supports can influence the catalytic process of catalyst. For example, electric conductive supports induce the charge separation in the photocatalysts. Porous supports favor the contact between reactants and the photocatalysts. There are many literature which report the synthesis of zinc oxide on different supports such as indium tin oxide (ITO) [22], copper plates [23], and polyethylene fibers [24]. These materials with various morphologies can be synthesized by changing the type of structure-directing agent [25], including hexamethylenetetramine, polyethylene glycol, polyethyleneimine, etc. ZnO nanoparticles can be synthesized on stainless steel wire mesh [26]. Wire mesh-supported materials have recently been used as monolithic catalysts for some reactions (e.g., the preferential oxidation of CO [27], methanol decomposition [28] and N_2O decomposition [29]). Technology related to the recovery of the nanostructured photocatalysts is important for repeated hydrogen production. For the powdered photocatalysts, the separation of the particles from the reaction medium is necessary for repeated uses. These separation processes can be skipped for immobilized photocatalysts made of forming nanostructured photocatalytic materials on stainless-steel wire mesh substrates.

Fabrication of nanostructured metal oxide materials on stainless-steel wire mesh substrates as immobilized hierarchical photocatalysts for photocatalytic H_2 production application has not been reported yet. In this study, a series of S-doped ZnO nanorods were grown on stainless-steel mesh as immobilized hierarchical photocatalysts for photocatalytic H_2 production. The surface texture, surface property, photoinduced current, and photocatalytic hydrogen production performance from salt water under UV light irradiation in a reactor loaded with these immobilized hierarchical photocatalysts were examined.

Experimental

All of the chemical reagents were of analytical grade and used without further purification.

Preparation of mesh-supported hierarchical photocatalysts

Seed solution

At first, 0.01 M zinc acetate was dissolved in ethanol at 60 °C for 2 h, and then cooled to 0 °C. n-hexadecyltrimethyl ammoniumhydroxide (HTAOH) was added (Zn^{2+}/HTAOH = 1/2) into the solution and stirred for 30 min. The resulting mixture was then agitated at 60 °C for 30 min to yield a colloidal seed solution. After being coated with the seed solution, the stainless-steel mesh substrates were dried at room temperature and then annealed at 300 °C for 1 h.

Preparation of S-doped ZnO nanorods based photocatalysts on mesh

Different amounts of Na_2S precursor were added to a solution containing polyethyleneimine (PEI), equimolar aqueous solutions of zinc nitrate hydrate and hexamethylenetetramine. The Na_2S precursor concentrations were fixed at 5, 10, and 15 mM, respectively. The concentrations of both the zinc nitrate hydrate and hexamethylenetetramine are 0.1 M. S-doped ZnO nanorod arrays were grown at 95 °C by immersing the modified substrates in the aqueous solution with different ZnO growth times (3, 6, and 9 h). After that, the substrate was removed and rinsed with distilled water several times. Then, the substrate was dried at room temperature. The process is similar to that reported in our previous study [6].

Nomenclature

The samples are denoted as MwTxPSy. Mw represents the distance between edges of adjacent wires of stainless steel meshes is w μm. Tx indicates that the hydrothermal reaction time for the growth of S-doped ZnO nanorods is x h. P indicates that polyethyleneimine (PEI) is added during the growth of the nanorods on the wire mesh substrates. Sy represents the Na_2S dopant precursor concentration. The Na_2S precursor concentrations for S1, S1.5, S2, S2.5 and S3 are 5, 7.5, 10, 12.5, and 15 mM, respectively.

Characterization

X-ray Diffraction (XRD) studies were carried out on a MAC SCIENCE MXP3 diffractometer. The morphology was determined by energy dispersive X-ray (EDX) with a HITACH S-4800 field emission scanning electron microscope (FESEM). The absorbance of the dye solution of the catalyst film was measured with the PL 2006 multifunctional spectrometer (Labguide Co.). The photoinduced current of the photocatalyst was measured by scanning the photocatalyst pattern using PC-controlled PEC-SECM (photoelectrochemical scanning electrochemical microscopy, CHI model 900C, CHI Instruments). The contact angle is measured on the contact angle meter (CAM-100, Creating-Nanotech Co.).

Photocatalytic reaction

The photocatalytic reactions of hydrogen production from salt water were carried out on the mesh supported hierarchical catalysts (It is a 2 cm × 4 cm strip and the weight of catalyst layer is about 3–3.5 mg.) in a gas-closed system illuminated by