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# Ni-doped ZnS decorated graphene composites with enhanced photocatalytic hydrogen-production performance

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## ABSTRACT

This study investigated the abilities of photocatalytic H<sub>2</sub> production by Ni-doped ZnS-graphene composite photocatalysts. Undoped or Ni-doped ZnS was loaded on the surface of graphene to prepare a series of composite photocatalysts. Properties of the photocatalysts were characterized by field-emission scanning electron microscope (FESEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), ultraviolet–visible diffuse reflectance spectroscopy (DRS), photoinduced current, and photocatalytic hydrogen evolution test. The as-prepared graphene@Ni-doped ZnS nanocomposites are highly active photocatalysts for hydrogen evolution and the highest photocatalytic activity reaches 8683 μmol h<sup>-1</sup> g<sup>-1</sup>. Effects of introducing graphene, doping, and decorated ZnS on the surface chemistry, crystalline property, optical property, surface morphology, and photocatalytic hydrogen production performance were studied. Ni-doping and decorated ZnS on graphene improved the photocatalytic H<sub>2</sub> production activity because of improved dispersing property, increased surface area, increased absorption, and enhanced transfer of photogenerated electrons.

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## Introduction

Photocatalytic hydrogen production from water splitting has attracted much attention because it can convert light energy to hydrogen energy. In the hydrogen production procedure, energy gap of photocatalyst has to cross H<sub>2</sub>O reduction potential to decompose water and generate the oxygen. Semiconductor materials have been used for H<sub>2</sub> production [1,2],

photocatalytic degradation [3,4], and gas sensor [5,6] applications. Materials with a more negative conduction band than the reduction potential of protons, such as TiO<sub>2</sub>, SrTiO<sub>3</sub>, ZnS, CdS, are promising photocatalysts for H<sub>2</sub> production [7–10]. Among them, chalcogenide nanomaterials are attractive candidates for the photocatalytic H<sub>2</sub> production applications [11,12]. ZnS exhibits relatively high activity for hydrogen production performance [13]. Decreasing the band gap and increasing the light absorption are very important for the

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development of photocatalysts. Band gaps of the photocatalysts can be tuned by doping with dopants such as N, B, Cr, Fe, and Ce [14–17]. Quick recombination of photoexcited charge carriers will deteriorate the quantum efficiency of photocatalysis. A lot of researchers have been devoted to reduce the recombination of photogenerated electron–hole pairs by hybridizing the photocatalysts with other materials, such as semiconductors [18], noble metals [19], and graphite-like carbon [20]. Because of the superior electrical conductivity, large specific surface area, high adsorption and the two-dimensional nature of graphene, fabrication of composites with graphene is also a promising way to enhance the photocatalytic activity of traditional semiconductor photocatalysts [21–26]. Graphene is an excellent electron-transport material which helps to transfer the photogenerated electrons from the semiconductor to graphene, and also participates in the photocatalysis process of  $H_2$  generation [27–29]. Graphene can act as an ideal support of photocatalyst materials for environmental and energy applications, such as photocatalytic degradation of pollutants, photocatalytic hydrogen generation [30–32]. Ng et al. [33] showed incorporation of graphene oxide can enhance the photocurrent generation and photoelectrochemical water oxidation of  $BiVO_4$  thin film. Ye et al. [34] reported that introducing graphene helped to enhance the activity of the composite photocatalyst. The  $H_2$  evolution rate for the CdS–graphene composite photocatalyst reached  $700 \mu\text{mol h}^{-1} \text{g}^{-1}$ . Graphene–metal sulfide nanocomposites can be used as efficient photocatalysts for  $H_2$  production [35,36].

In this study, efficient photocatalytic  $H_2$  production can be achieved using the Ni-doped ZnS-decorated graphene photocatalysts. The roles of decorated ZnS and  $Ni^{2+}$ -doping on the surface chemistry, crystalline property, optical property, surface morphology, and photocatalytic hydrogen production of the ZnS-graphene based photocatalysts were investigated.

## Experimental

### Preparation of photocatalysts

All reactants and chemicals were used as received. Nickel acetate, zinc acetate, and ethylene glycol were supplied by Alfa-Aesar, Showa, and Sigma–Aldrich, respectively. Thiourea, sodium sulfide, sodium sulfite, and sodium chloride were provided by Fisher scientific, Acros Organics, Wako, and Uniregion Bio-tech, respectively. Graphene was prepared by a method reported by Tsai [37]. In this experiment, ZnS particles were formed on the graphene surface by a solvothermal process. At first, 6.18 mmol of zinc acetate  $Zn(CH_3COO)_2$  and 0.05 g graphene were dissolved or dispersed in 80 ml of ethyl glycol. The solution was kept stirring with magnetic stirring for 60 min. Then, 6.18 mmol thiourea  $SC(NH_2)_2$  were added and stirred for another 20 min. The solution was kept at  $150^\circ\text{C}$  for different period of time for the growth of ZnS nanoparticles. Then, the solution was cooled to room temperature and then filtered and washed with distilled water to prepare the composite photocatalyst. Similar procedures were applied for the preparation of Ni-doped ZnS decorated graphene composite photocatalyst,

except that different concentration of  $Ni(CH_3COO)_2$  precursor were mixed with  $Zn(CH_3COO)_2$  precursor during the solvothermal process.

### Photocatalytic hydrogen production

A 300 W mercury lamp is used as the UV light source. Photocatalytic hydrogen production was carried out in a 100 ml quartz cell with 100 ml sacrificial aqueous solution which consisted of 0.1 M  $Na_2S$ , 0.040 M  $Na_2SO_3$  and 3 M  $NaCl$  as electron donors in 100 ml water. Undoped and Ni-doped ZnS-graphene composite were used as photocatalysts. The rate of  $H_2$  evolution by 0.1 g photocatalyst in 100 ml sacrificial aqueous solution under UV light irradiation was monitored. The top of the Pyrex cell was sealed with a silicone rubber septum. Sampling was made through the septum during experiments. The concentration of  $H_2$  within the gas product was determined by a gas chromatography (with 5 Å molecular sieve column and Ar carrier) equipped with a thermal conductivity detector.

### Characterization

XRD studies were carried out with a MAC SCIENCE MXP3 diffractometer. The morphology of the samples was determined by a HITACH S-4800 field emission scanning electron microscope (FESEM). The UV–vis diffuse reflection spectra of the photocatalysts were measured by the multifunctional spectrometer (Labguide Co.). X-ray photoelectron spectroscopy (XPS) was performed using a VG ESCA scientific theta probe spectrometer in constant analyzer energy mode with a pass energy of 28 eV and  $Al K\alpha$  (1486.6 eV) radiation as the excitation source. BET surface area measurements were carried out by  $N_2$  adsorption at 77 K on a high resolution surface area and porosimetry analyser (Micromeritics ASAP2000 instrument). HRTEM experiments were performed on a Transmission Electron Microscope (JEOL JEM-2010).

The photoelectrochemical (PEC) measurements were carried out in a cell with 0.2 M NaOH electrolyte solution using PC-controlled PEC-SECM (photoelectrochemical scanning electro-chemical microscopy, CHI model 900C, CHI Instruments). A total of 0.2 g synthesized composite sample was added into a mixed solution with 2 ml anhydrous ethanol and 0.2 ml acetylacetone. After being stirred for a period of time, the dispersion was coated on a  $1.5 \times 2 \text{ cm}^2$  ITO glass substrate by spin-coating method for 3 times. After liquid volatilization, the electrode was calcinated at  $150^\circ\text{C}$  for 3 h. The photocatalyst coated ITO glass were used as the working electrode (irradiation area of  $2.25 \text{ cm}^2$ ). The Pt electrode and Ag/AgCl electrode were used as the counter and reference electrodes, respectively.

### Nomenclature

GZS1h, GZS2h, GZS3h mean the graphene@ZnS composite photocatalysts prepared with ZnS growth time 1, 2 and 3 h. GZS2hN1, GZS2hN2, GZS2hN3 mean the graphene@Ni-doped ZnS composite photocatalysts prepared with Zn/Ni precursor concentration ratio ( $Ni(CH_3COO)_2/Zn(CH_3COO)_2$ ) of 0.001, 0.00125, and 0.00167.

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