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# Photocatalytic H<sub>2</sub> evolution from NaCl saltwater over ZnS<sub>1-x-0.5y</sub>O<sub>x</sub>(OH)<sub>y</sub>-ZnO under visible light irradiation

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## ABSTRACT

Photocatalytic hydrogen production was investigated over ZnS<sub>1-x-0.5y</sub>O<sub>x</sub>(OH)<sub>y</sub>-ZnO using sulfide ion (Na<sub>2</sub>S-Na<sub>2</sub>SO<sub>3</sub>) as an electron donor from NaCl saltwater. NaCl can affect markedly the activity for photocatalytic hydrogen production, depending on NaCl concentration. When NaCl concentration is lower, the activity is lower than that in pure water, whereas when NaCl concentration is higher, the activity is higher than that in pure water. NaCl decreases not only the surface charge of ZnS<sub>1-x-0.5y</sub>O<sub>x</sub>(OH)<sub>y</sub>-ZnO but also the surface hydration. When ZnS<sub>1-x-0.5y</sub>O<sub>x</sub>(OH)<sub>y</sub>-ZnO was impregnated with the electron donor (Na<sub>2</sub>S-Na<sub>2</sub>SO<sub>3</sub>), ZnO was transformed partly into ZnS. The impregnated ZnS<sub>1-x-0.5y</sub>O<sub>x</sub>(OH)<sub>y</sub>-ZnO exhibits higher activity than the non-impregnated one. The possible mechanisms were discussed.

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## 1. Introduction

Hydrogen is an ideal energy carrier. Photocatalytic hydrogen production (PHP) using a heterogeneous photocatalyst has been studied extensively as a potential method to supply hydrogen from sunlight and water [1–21]. Although water is abundant on the earth, pure water is scarce because 93% of the earth's water is present in oceans and inland seas [22]. Although PHP from seawater would be important to practical application, few studies on PHP from seawater have been made. Domen et al. have investigated effects of some electrolytes including NaCl on the photocatalytic activity of (Ga<sub>1-x</sub>Zn<sub>x</sub>)(N<sub>1-x</sub>O<sub>x</sub>) for overall water splitting under visible light ( $\lambda > 400$  nm) [23]. Lee et al. reported PHP from seawater over La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> under ultraviolet light, and over CdS/TiO<sub>2</sub> under visible light [22]. Our group has recently investigated PHP from

NaCl saltwater over Pt/Cd<sub>0.5</sub>Zn<sub>0.5</sub>S using glucose as an electron donor under visible light [24], and over Pt/TiO<sub>2</sub> using various pollutants as electron donors under ultraviolet light [25].

To achieve higher efficiency for PHP, many researches in this field have involved electron donors as sacrificial agents, which can react irreversibly with the photoinduced holes. From the viewpoint of practical application, the electron donors for PHP should be cheap and easy to obtain. Pollutants in pure water as electron donors have been utilized for PHP over various photocatalysts [11,26–30]. H<sub>2</sub>S occurs widely in natural gas fields and is produced in large quantities as an undesirable byproduct in the coal and petroleum industry. The release of sulfur compounds can badly pollute the environment. The conversion of H<sub>2</sub>S with photocatalysis has been extensively investigated [31–33]. In this process, H<sub>2</sub>S is dissolved in a basic aqueous solution, such as NaOH, to produce sulfide ions (S<sup>2-</sup>

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and  $\text{HS}^-$ ), and then the sulfide ions are used as sacrificial agents for PHP from pure water. Usually, sulfite ( $\text{SO}_3^{2-}$ ) is used together with the sulfide ions to maintain the catalytic activity by producing  $\text{S}_2\text{O}_3^{2-}$  instead of elemental sulfur.

It is significant to develop visible-light driven photocatalysts with high activity, because visible light accounts for ca. 45% of the incoming solar energy. In previous work, we prepared a basic zincoxysulfide photocatalyst which is in fact a composite of  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y$  and ZnO, and found that the former is visible light active [34]. The photocatalyst exhibits a good visible light activity for hydrogen production without noble metal as a cocatalyst using sulfide ion ( $\text{Na}_2\text{S}-\text{Na}_2\text{S}_2\text{O}_3$ ) as an electron donor.

It is expected that with appropriate photocatalyst and/or reaction system, more efficient PHP from seawater can be achieved. In this work, we have investigated PHP over  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y-\text{ZnO}$  using sulfide ion ( $\text{Na}_2\text{S}-\text{Na}_2\text{S}_2\text{O}_3$ ) as an electron donor from NaCl saltwater, because NaCl is a major component of natural seawater and sulfide ion is a common pollutant. The hydrogen evolution increases markedly in concentrated NaCl saltwater compared to that from pure water. Moreover,  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y-\text{ZnO}$  impregnated with the electron donor ( $\text{Na}_2\text{S}-\text{Na}_2\text{S}_2\text{O}_3$ ) exhibits higher activity than the non-impregnated one. The possible mechanisms were discussed.

## 2. Experimental

All chemicals were of analytic reagent grade and were used without further purification. Composite photocatalyst  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y-\text{ZnO}$  was prepared through a co-precipitation process [34,35]. Briefly, 17.85 g  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 2.4 g NaOH, and 7.2 g  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  were dissolved in 90 mL, 200 mL, and 900 mL of distilled water, respectively, and they were stirred for 1 h. The NaOH solution was poured into the  $\text{Na}_2\text{S}$  solution and stirred for 1 h (solution A).  $\text{Zn}(\text{NO}_3)_2$  solution was added dropwise into solution A under vigorous stirring at 373 K. Resulting precipitate (precursor) was aged for 12 h, filtered and then washed with distilled water. The precursor was dried at 333 K for 12 h and calcined at 673 K for 2 h under  $\text{N}_2$  atmosphere to obtain the yellow photocatalyst.

1.0 g of the as-prepared photocatalyst was impregnated with a 500 mL of aqueous solution containing  $0.10 \text{ mol L}^{-1}$   $\text{Na}_2\text{S}$  and  $0.040 \text{ mol L}^{-1}$   $\text{Na}_2\text{SO}_3$  for different times. After filtration, washing with distilled water and then drying at 333 K for 12 h, the impregnated sample was obtained. The as-prepared and impregnated  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y-\text{ZnO}$  were characterized on a Bede D1 System multifunction X-ray diffractometer, employing Cu  $K\alpha$  radiation  $\lambda = 0.15406 \text{ nm}$ . XPS spectra were measured on a Thermo Scientific K-Alpha-surface Analysis X-ray photoelectron spectroscope equipped with X-Ray Monochromatisation. The specific surface areas of the samples were determined on a ST-08A analyzer by the volumetric BET method using nitrogen as adsorbent. The transmission electron microscopy (TEM) images were taken on a JEOL JEM-2010 (TEM) working at 200 kV.

0.010 g of the as-prepared  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y-\text{ZnO}$  was added to a 10 mL of aqueous solution containing  $0.10 \text{ mol L}^{-1}$   $\text{Na}_2\text{S}$ ,  $0.040 \text{ mol L}^{-1}$   $\text{Na}_2\text{SO}_3$  and a given concentration of NaCl.

The catalyst was dispersed in an ultrasonic bath for 30 min and  $\text{N}_2$  was bubbled through the reaction mixture for 15 min to remove oxygen. Zeta potential of the obtained suspension was measured on a Malvern NANO ZS90 Zetasizer.

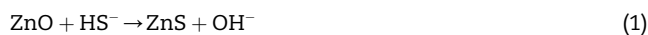
In situ infrared absorption spectra were measured on a BRUKER TENSOR 27 FT-IR spectrometer equipped with a ZnSe crystal horizontal unit. 10 mL aqueous suspension containing 0.050 g  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y-\text{ZnO}$  was obtained by 30 min sonication. For the preparation of  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y-\text{ZnO}$  film, 50  $\mu\text{L}$  the above suspension was distributed onto the surface of the ZnSe crystal and allowed to dry in air at room temperature. 50  $\mu\text{L}$  aqueous solution containing  $0.10 \text{ mol L}^{-1}$   $\text{Na}_2\text{S}$ ,  $0.040 \text{ mol L}^{-1}$   $\text{Na}_2\text{SO}_3$  and a given concentration of NaCl was added onto the film. Spectra were obtained via subtraction of the spectrum of pure water. All spectra were calculated from 300 scans at a resolution of  $4 \text{ cm}^{-1}$ .

Photocatalytic reaction was conducted in a 190 mL Pyrex cell with a flat side window for illumination. A 400 W high-pressure mercury lamp was used as the light source. The IR fraction of the beam was removed by a water-cooling jacket outside the lamp. The visible light irradiation was obtained with a cutoff filter ( $\lambda \geq 420 \text{ nm}$ ) to remove radiation below 420 nm. 0.100 g of the catalyst was suspended in 100 mL aqueous solution containing  $0.10 \text{ mol L}^{-1}$   $\text{Na}_2\text{S}$ ,  $0.040 \text{ mol L}^{-1}$   $\text{Na}_2\text{SO}_3$  and a given concentration of NaCl. Prior to irradiation, the catalyst was dispersed in an ultrasonic bath for 5 min and  $\text{N}_2$  was bubbled through the reaction mixture for 25 min to remove oxygen. The top of the cell was sealed with a silicone rubber septum. Sampling was made intermittently through the septum during experiments. The photocatalytic activity was determined by measuring the amount of hydrogen production on a gas chromatography (TCD, 13X molecular sieve column,  $\text{N}_2$  as gas carrier).

## 3. Results and discussion

### 3.1. XRD analysis of the impregnated photocatalyst

Fig. 1 shows the XRD patterns of the impregnated and non-impregnated  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y-\text{ZnO}$ . The non-impregnated (as-prepared) photocatalyst is a composite of cubic  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y$  and hexagonal ZnO (Fig. 1a), in good agreement with our previous result [34] and JCPDS Card No.36-1451. For 1 h impregnated  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y-\text{ZnO}$  (Fig. 1b), diffraction peak intensity of hexagonal ZnO decreases markedly, whereas diffraction peak intensity of cubic  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y$  keep almost constant. These indicate that ZnO would react with sulfide ions such as  $\text{HS}^-$ , whereas  $\text{ZnS}_{1-x-0.5y}\text{O}_x(\text{OH})_y$  would not. The reaction can be expressed as follows.



Because diffraction peaks of hexagonal ZnO can still be observed after the impregnation, one can assume that only a part of ZnO of the sample reacts via reaction (1) (shown in Scheme 1). The formed ZnS would be amorphous, because no diffraction peaks of ZnS were observed from Fig. 1b.

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