Effect of Zn(O,S) Synthesis Temperature to Photocatalytic Hydrogen Evolution Performance

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Abstract. About 80% of global energy demands had been fulfilled with the utilization of fossil fuels and accordingly, CO\textsubscript{2} amount in the air had been increased to 406 ppm (\~{}40\% higher than pre-industrial level). Therefore, to find clean, renewable, and carbon-free alternative energy sources such as hydrogen energy is greatly needed. In this work, hydrogen was photocatalytically evolved with Zn(O,S) nanoparticles (NPs) in 10\% ethanol as a hole scavenger reagent without Pt as a co-catalyst under low UV light illumination. To find out the optimum processing temperature, Zn(O,S) NPs were prepared in three different temperatures (50, 70, and 90 \textdegree{}C) with 4-h reactions in aqueous solution. The as-prepared catalysts were tested for their capabilities to evolve hydrogen and the experimental data revealed the produced hydrogen amounts were enhanced as the processing temperature increased. It was also found that the as-prepared catalysts were reusable and stable, although the colour of catalyst was changed from white to grey during the photocatalytic hydrogen evolution reaction (HER) and was changed back to white colour after HER was accomplished. The change in catalyst colour indicated the formation of oxygen vacancy on catalyst which further enhanced the HER. The highest amount of evolved hydrogen achieved 2.7 mmol/gh.

Keywords: Oxygen vacancy, hydrogen evolution, Zn(O,S) NPs, and photocatalyst

1. Introduction
As the worldwide energy demands heavily depend on fossil energy which is not a sustainable energy source, many environmental problems such as air pollution, global climate change have emerged and become more serious nowadays.\textsuperscript{1,2,3} Therefore, to find renewable, clean and carbon-free alternative energy sources is considerably needed. Among various kinds of renewable energy sources, solar energy is the most abundant one. By only harnessing 0.01\% energy of sunlight in one second illumination is adequate for one-year energy consumption of human living.\textsuperscript{4,5} However, to convert and store the sunlight energy for future use is a significant challenge for the world.\textsuperscript{6,7} Hydrogen as energy carrier is believed to be a best future energy source to replace fossil energy due to the environmental consideration, since the by-product of hydrogen combustion is only water which is totally clean for environment. Renewable and sustainable hydrogen fuel by using water as a source is very promising alternative for future energy resource to provide carbon-free and storable energy. Global hydrogen production is classically obtained from petroleum and natural gas steam reforming process which is
not sustainable for long term application.\textsuperscript{8,9} Only 4\% of the production is originated from water electrolysis. Most of the hydrogen production is still based on raw fossil materials.\textsuperscript{40}

In this work, hydrogen was photo-catalytically evolved with Zn(O,S) nanoparticles (NPs) in 10\% ethanol as a hole scavenger reagent without Pt as a co-catalyst under low UV light illumination. To find out the optimum processing temperature, Zn(O,S) NPs were prepared in three different temperatures (50, 70, and 90 °C) with 4-h reactions in aqueous solution. The as-prepared catalysts were tested their capabilities to evolve hydrogen and the results revealed the evolved hydrogen amounts were enhanced as the processing temperature increased.

2. Experimental procedure

2.1. Materials

All the materials in this work were commercially available and utilized without any purification treatment.

2.2. Synthesis of Zn(O,S) powders

In a typical powder preparation, 4.4 g Zn(Ac)\textsubscript{2}H\textsubscript{2}O and 0.75 g C\textsubscript{2}H\textsubscript{5}NS were dissolved in a beaker glass containing 500 mL distilled water and heated at a specific temperature (50, 70, and 90 °C) for 4 h as shown in Fig. 1. The obtained precipitate was collected and washed with ethanol for three times, then dried in vacuum oven at 80 °C for 12 h.

Fig. 1 Experimental procedure to prepare Zn(O,S) at different temperatures

3. Results and discussions

3.1. XRD pattern analysis

XRD patterns in Fig. 2 show the as-prepared Zn(O,S) powders at 50, 70, and 90 °C have the same patterns with the major peaks are located between those of ZnO (PDF #65-2880) and ZnS (PDF #05-0566). The results indicating the formation of Zn(O,S) solid solution. As compared to the standard PDF file of ZnS, all the peaks shifted to higher angles, since the smaller oxygen anions occupied sulfur anion sites, thus shrinking the lattice parameter of Zn(O,S).
3.2. Transmission electron microscopy (TEM) analysis

TEM analysis indicated Zn(O,S) NPs consisted of tiny particles with the size about 3 nm as confirmed with Scherrer equation. The tiny particles aggregated and formed larger particles as shown in Fig. 3a due to the nature of nanoparticles. Lattice fringe values of Zn(O,S) which located between those of ZnO and ZnS at (111) revealed the formation of solid solution as shown in Fig. 3b. In addition, the selected area electron diffraction pattern (SAEDP) obviously showed the broad ring pattern at (111)
was located between depicted-ring patterns of ZnO and ZnS as shown in Fig. 3c. Furthermore, to confirm all the elements were present in Zn(O,S) NPs, the elemental mapping of Zn(O,S) NPs was examined and it revealed all the elements were present and uniformly distributed as shown in Fig. 4.

**Fig. 4** HAADF image and the elemental mapping of (b) Zn, (c) O, and (d) S on Zn(O,S) NPs.

### 3.3. Diffuse reflectance spectra (DRS) analysis

Optical property of as-prepared Zn(O,S) NPs was analysed with UV-vis spectroscopy. Fig. 5 shows the as-prepared Zn(O,S) at 90 °C has the bandgap energy value (Eg= 3.6 eV) located between those of ZnO and ZnS, which also indicates the formation of Zn(O,S) solid solution. Based on the optical property of Zn(O,S), the blacklight-UV lamp with the average wavelength of 352 nm was used in photocatalytic experiment to match the light absorbance of Zn(O,S) NPs.

**Fig. 5** UV-vis absorbance spectra of ZnO, ZnS, and Zn(O,S) NPs.

### 3.4. Photocatalytic HER
The photocatalytic HER was carried out in 450 mL ethanol solution under 4 x 6 W UV blacklight lamp illumination. Fig. 6 shows the photocatalytic hydrogen evolution activities increase with the increasing processing temperature. Each of the catalyst with different synthesis temperature were evaluated for three runs without solution evacuation after the end of each session. The best hydrogen amount was achieved at 13535 µmol/g in 10% ethanol solution with Zn(O,S) NPs prepared at 90 °C. This reusability testing indicated the as-prepared catalysts were stable and could be possibly used for long term application.

![Graph showing photocatalytic hydrogen evolution rates in the presence of Zn(O,S) NPs prepared at different temperature for three consecutive runs without solution evacuation procedure.](image)

**Fig. 6** Photocatalytic hydrogen evolution rates in the presence of Zn(O,S) NPs prepared at different temperature for three consecutive runs without solution evacuation procedure.

### 3.5. Photocatalytic mechanism

Photocatalytic mechanism of HER was based on the solution colour change during the reaction. HER activity was actually initiated with water oxidation in the presence of photo-generated hole to produce oxygen vacancy which caused the solution colour changed from white to grey colour as shown in Fig. 7. However, the solution colour changed back to white after the light illumination was turned off. The produced oxygen vacancy then would reduce water with photo-generated electron to evolve hydrogen. The availability of surface oxygen on catalyst was generated from Schottky defect due to the relatively low temperature processing at 50 – 90 °C. During the photocatalytic hydrogen evolution reaction, 10% ethanol played an important role to enhance oxygen vacancy sites to further boost the water reduction. It was observed that more oxygen vacancy sites were generated in ethanol solution compared to that in pure water. Therefore, the evolved hydrogen amount was much higher in ethanol solution. Ethanol in solution also contributed to photo-generated hole and electron separation by consuming holes in the valence band to provide sufficient lifetime of electrons in conduction band to reduce water to hydrogen.
Fig. 7 Kinetic mechanism of photocatalytic CO$_2$ reduction to form ethanol in water

4. Conclusions
The as-prepared Zn(O,S) NPs at different temperatures have been synthesized and characterized. XRD patterns revealed the formation of Zn(O,S) solid solution, in which the major Zn(O,S) peaks were located between those of ZnO (PDF#65-2880) and ZnS (PDF#05-0566). TEM analysis indicated there were many lattice fringe values located between ZnO and ZnS at (111) supported with broad ring of diffraction patterns in SAED, which implied the solid solution formation. In addition, the DRS data also indicated the bandgap value of Zn(O,S) was located in the range between ZnO and ZnS. All the as-prepared catalysts were stable and reusable as shown in the experimental data. The best hydrogen evolution rate of 2.7 mmol/gh was achieved with the Zn(O,S) powder prepared at 90 °C. The optimum synthesis temperature was achieved at 90 °C, which was related to a better crystallinity of Zn(O,S) NPs.

5. References
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