

# Fabrication of Porous ZnS and ZnO Nanoplates by Calcination of ZnS(en)<sub>0.5</sub> Precursor and Their Photocatalytic Activity

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## Introduction

The solvothermal method using ethylenediamine as a liquid medium has been regarded as an economic and convenient route to obtain nanostructured materials [1,2]. Zinc sulfide (ZnS) is a wide-bandgap semiconductor of 3.80 eV for hexagonal wurtzite phase and of 3.66 eV for cubic zinc-blend phase. Similarly ZnO is one of the most important functional oxides for optoelectronics and photocatalysis due to its bandgap energy of 3.20 eV. Its potential applications were demonstrated as nanosized sensors and field-effect transistors based on ZnO nanobelts, and for photocatalytic degradation of organic dyes [3]. A few studies have recently been done to fabricate nanostructured ZnS and ZnO with high surface-to-volume ratios for improved performance. It is interesting to note the result of Hue et al. that nanoporous ZnS nanoparticles prepared via a low-cost and self-assembly route, can have high ratio of surface to volume and aggregation of nanoparticles during photocatalytic reaction of dyes [4]. Nevertheless the fabrication of porous ZnS and ZnO nanoplates has not been reported yet.

In this contribution we prepared the ZnS(en)<sub>0.5</sub> complex precursor by solvothermal routes using ethylenediamine as a single solvent and obtained porous ZnS and ZnO nanoplates through thermal treatment of the complex. In particular, the local structures confined in the nanoplates were elucidated with synchrotron radiation techniques of powder XRD and XAFS. Photocatalytic water splitting and photocatalytic degradation of organic dye were performed in order to measure the catalytic performance of the synthesized ZnS(en)<sub>0.5</sub> complex and its derivatives.

## Materials and Methods

An appropriate amount of  $16.2 \times 10^{-3}$  mol Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and  $48.6 \times 10^{-3}$  mol NH<sub>2</sub>CSNH<sub>2</sub> was added into a teflon-lined stainless steel autoclave which had been filled with NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> to 70% of its volume. The autoclave reactor was maintained at 160 °C for 12h and allowed to cool to room temperature. A color precipitate was filtered and washed with absolute ethanol and deionized water to remove the residue of impurities such as organic solvent and dried in oven at 80 °C for 12h. The ZnS(en)<sub>0.5</sub> complex precursor was calcined at 400, 500, 550, and 600 °C for 2h in an electrical furnace under ambient air.

## Results and Discussion

The solvothermal reaction of zinc precursor with thiourea in ethylenediamine (en) solvent yielded the ZnS(en)<sub>0.5</sub> complex having orthorhombic structure. Figure 1 showed SEM and TEM images of the ZnS(en)<sub>0.5</sub>-derivatives (Zn500 and Zn600) calcined at 500 °C and 600 °C. The apparent features of all samples are similar in that they have stacks of nanoplates with a

lateral size of 1-2 μm. The plane surfaces, however, appear to be different: smooth for Zn400, a little porous for Zn500, very porous for Zn550 and Zn600. The rate of hydrogen evolution for the sample calcined at 500 °C for 2h was higher than those of photocatalysts calcined at different temperatures (400 °C, 550 °C, 600 °C) as shown in Figure 2A. ZnO nanocrystallites in Zn550 and Zn600 did not produce hydrogen under visible light. ZnS(en)<sub>0.5</sub>-derivatives calcined at 400-500 °C showed narrowed band-gap by forming the absorption shoulders and thus, could have photocatalytic activity under visible light. Zn500 having the highest surface area exhibited the highest hydrogen production rate. The catalytic performance under uv-light irradiation ( $\lambda \geq 324$  nm) was also examined using photocatalytic degradation of azo dye acid red 14 (AR14), which would gauge the oxidation capability of photocatalysts. The absorption peaks of AR14 gradually decreased and finally disappeared during the photocatalytic reaction. The degradation rates of AR14 over Zn550 and Zn600 are high enough that only less than 10% of AR14 remains after uv-irradiation for 100 min. Therefore, the ZnS(en)<sub>0.5</sub> derivatives calcined at 550-600 °C are plausible candidates for the degradation of toxic organic materials.

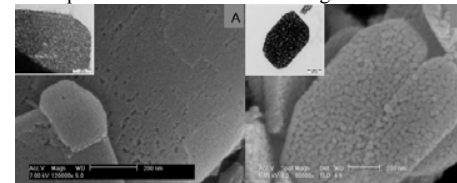


Fig. 1. SEM and TEM images of the materials calcined at 500 °C and 600 °C: (A) Zn500 and (B) Zn600.

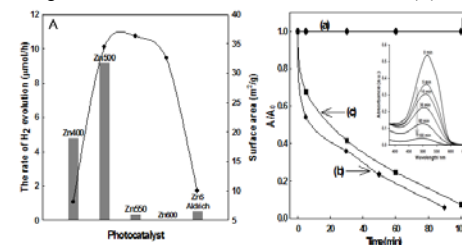


Fig. 2. A. Hydrogen production rates of the ZnS(en)<sub>0.5</sub>-derivatives calcined at different temperatures. Catalysts: 0.1g loaded 1wt% Pt, Electrolyte: 0.1 M Na<sub>2</sub>S + 0.02M Na<sub>2</sub>SO<sub>3</sub>, Light source: Hg-arc lamp (500 W) equipped with IR liquid filter and with UV cut-off filter ( $\lambda \geq 420$  nm). BET surface area is also plotted as the solid line. B. Photocatalytic decomposition of azo dye acid red 14 (AR 14) under uv light: (a) no catalyst, (b) Zn550, (c) Zn600. Catalysis : 50 mg, AR 14 solution : A 100 mL of 50 μM AR 14, Light source : Hg-arc lamp (500 W) equipped with IR liquid filter and with UV cut-off filter ( $\lambda \geq 324$  nm). Inset figure indicates spectral change with irradiation time of sample.

## References

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