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# ZnO-ZnS Composites for Pollutant Photo-Degradation Reactions: Co-Precipitation Synthesis and Characterization

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# ABSTRACT

Co-precipitation method was employed to synthesize the ZnO-ZnS nanocomposites with different ZnO:ZnS ratios. These prepared nanocomposites were characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM) and Thermogravimetric analysis (TGA). The characterization results reveal that particles in all nanocomposites have similar size of about 30 nm. Zinc oxide may exist in the form of composite with ZnS and free from which can be seen in the XRD patterns. Though zinc oxide may exist in the different form, particles in all samples are relatively similar in size. The presence of ZnS in the composites can be seen clearly in the TGA curves.

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## Introduction

Semiconductor materials, also called photocatalysts, have been considered as potential materials due to the their in various potential application fields, such as electroluminescent panels, optical window, sensors, lasers, solar cells, emission display, hydrogen production and photodegradation of organic pollutant in aqueous solution  $\begin{bmatrix} 1 & 2 & 3 \\ 2 & 3 \end{bmatrix}$ . Therefore, semiconductors have been extensively studies in recent years. Under the solar irradiation, semiconductors can generate electron-hole pairs. These pair can react with other substances to degrade them with the oxidation-reduction processes. This photo-degradation of substances is clean and maintainable. For these reasons, different researches have been focused on the improvement of photo-activity of photocatalytic materials. Most researches concentrated on the expanding the radiation absorption range and the lengthening life of electron-holes pars. Two promising approaches have been carrying out to widen the absorption range and expand the life of generated electron-hole pairs. The first one is to develop new materials by doping new components to expand the light absorption range or shifting the absorption band to visible region. The second one is to use heterostructured materials with multi-components to separate generated electrons and holes for improving their life, and therefore improving the photocatalytic efficiency of materials [4, 5, 6, 7]. Among heterostructured materials, ZnO-ZnS material has been paid much attention due to its naturally low cost and highly photocatalytic performance compared to its pristine components. The ZnO-ZnS materials has fabricated with different methods. Jung Hyeun Kim et. al. produced ZnO-ZnS by gradually thermal treatment of ZnS with oxygen at different temperature. The obtained materials showed the significant improvement of photocatalytic performance. X. Wang et. al. reported that ZnO-ZnS was fabricated by precipitation method. Firstly,  $Zn^{2+}$  reacts with citric acid to form complexes. The complexes then was mixed with S<sup>2-</sup> solution and transferred to autoclave for hydrothermal

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treatment. The photocatalytic efficiency of the obtained materials was also higher than that of its mono-component.

Herein, the ZnO-ZnS material is fabricated by the coprecipitation method from zinc acetate, citric acid, sodium hydroxide and sodium sulfur as precursors. The ZnO to ZnS materials were produced with different ratio of ZnO to ZnS. **Experimental part** 

**Chemicals:** Moderacid Black (MDB), Zn(CH<sub>3</sub>COO)<sub>2</sub> and all other chemicals were analytical grade reagents purchased from China and used as received.

Preparation of ZnS-ZnO materials: The ZnO-ZnS composites with different molar ratios were synthesized from stock solution of 0,2 M NaOH, 0.1 M Na2S, 0.1 M Zn(CH<sub>3</sub>COO)<sub>2</sub> and 0.1 M sodium citrate Na<sub>3</sub>C<sub>6</sub>H<sub>7</sub>O<sub>5</sub>. These stock solutions were prepared from appropriate solids. ZnO-ZnS composites were synthesized as following procedure: a V1 mL of 0.1 NaOH solution was mixed with V2 mL of 0.1 M Na<sub>2</sub>S solution to form solution A. Solution B was prepared by mixing the V3 mL of 0.1 M Zn(CH<sub>3</sub>COO)<sub>2</sub> and V4 mL of 0.1 M Na<sub>3</sub>C<sub>6</sub>H<sub>7</sub>O<sub>5</sub> under the vigorous stirring at 70°C. The solution A was then slowly dropped into solution B under continuous stirring. The precipitate was finally filtered, washed, dried and calcined at 200°C under atmosphere condition. The obtained ZnO-ZnS composites with different ratio of ZnO to ZnS were denoted as ZnOXZnS (where X stands for the molar fraction of ZnO in the composites and X = 25, 50, 75, 90 and 95%).

Table 1.	Volumes	of stock	solution	used	to	prepared
	ZnS-	ZnO cor	nposites.			

Zilo-Zilo composites.							
ZnO:ZnS	<b>V</b> <sub>1</sub>	$V_2$	<b>V</b> <sub>3</sub>	$V_4$			
Molar ratio	mL	mL	mL	mL			
95:5	116.2	6.1	122.3	244.5			
90:10	109.0	12.1	121.1	242.2			
75:25	88.3	29.4	117.7	235.3			
50:50	56.1	56.2	112.4	224.7			
25:75	26.9	80.6	107.5	215.0			

The value of V1, V2, V3 and V4 varies according to the ratio of ZnO to ZnS and reaction coefficients in the reaction

of NaOH and Na<sub>2</sub>S with  $Zn(CH_3COO)_2$ . These values are listed in the Table 1.

#### **Characterization:**

Scanning electron microscope (SEM) was performed by a Hitachi S-4800 field emission scanning electron microscope at 5 kV. X-ray diffraction (XRD) patterns of the samples were measured on a Bruker-D5005 powder X-ray diffractometer using copper K<sub> $\alpha$ </sub>-radiation with  $\lambda = 1.5406$  Å. Fourier transform infrared spectroscopy (FT-IR) was performed on NEXUS-670, Nicotet–USA. Thermogravimetric analysis (TGA) was carried out on a Shimazu DTG-60H instrument at a heating rate of  $10^{\circ}$ /min under air flow.

#### **Results and discussion**

*X-ray Diffraction (XRD):* the synthesized ZnOXZnS composites were characterized by X-ray diffraction. The XRD patterns of ZnOXZnS composites are displayed in Figure 1. As can be seen, figure 1 shows dominate peaks at 31.7, 34.4, 36.3, 56.6 and 62.9° indexed to (100), (002), (101), (110) and (103) crystallographic planes of hexagonal ZnO, characteristic of only ZnO in the form of hexagonal wurtzite, and peaks at 47.6° indexed to (102) crystallographic plane of ZnS [8,9]. At the molar fraction of ZnO  $\geq$  75%, characteristic peaks of ZnO are sharp with high intensity. However, when when the molar fraction of ZnO is less than 75%, no sharp peak of ZnO can be seen. The presence of ZnS in the sample creates the diffraction peaks of ZnS (at around 28° in the ZnO50ZnS and ZnO25ZnS) which dominate the peaks of ZnO in the samples.



nanocomposites.

# Thermogravimetric analysis:

The composition and structure of the ZnOXZnS composites were studied by thermogravimetric analysis in which the total content of ZnS can be estimated based on the oxidation of ZnS at high temperature. As shown in Figure 2, all the materials show a small portion loss at the temperature less than 200°C due to the evaporation of adsorption water and de-intercalation of H<sub>2</sub>O from materials [10]. The mass of samples continues to decrease slowly in the range from 200°C to 450°C. This loss may be explained due to the decomposition of small amount of Zn(OH)<sub>2</sub> present in the sample. It is interestingly that at the temperature greater than

470°C, the mass of the sample starts to increase slightly before continuous decreasing. This increase can be explained due to the formation of zinc sulfurous from reaction between oxygen and zinc sulfide. At higher temperature, due to the decomposition of zinc sulfurous zinc sulfate, the mass of the sample continues to decrease. When temperature reaches around 700°C, mass of composite one more time increases then decreases rapidly. The second mass increase of the samples can be interpreted as a result of the formation of zinc sulfate from the reaction between residue zinc sulfide and zinc sulfurous and oxygen. The change in the mass of the composite revealed that zinc sulfide may exist in the composites with two types, chemically and physically combined with zinc oxide. This observation can be clearer in the composite with higher molar fraction of zinc sulfide.



Figure 2: Thermogravimetric Analysis curves of graphite, ZnOXZnS.

# Morphology analysis:

The morphology of ZnOXZnS composites were characterized using scanning electronic microscope (SEM). As shown in Fig. 3, particles of composites are relatively uniform with the size of around 30 nm. The calculation of particle size using the Image software shows that size of particles in all sample are approximately similar with the average size of around 30 nm.







Figure 3. SEM images of (a) ZnO95Zn, (b) ZnO90ZnS, (c) ZnO75ZnS, (d) ZnO50ZnS and (e) ZnO25ZnS.

In general, the photocatalytic performance of any material depends much on its particle size. Though there are two components present in the composites, there is no difference in size of particles in the composites. This may be due to the combination of ZnO and ZnS to form ZnO-ZnS composite which mainly presents in the obtained materials.

Table 2. Size of particles in ZnOXZnS composites.

Sample	Size/nm
ZnO95ZnS	33.55
ZnO90ZnS	34.56
ZnO75ZnS	33.53
ZnO50ZnS	31.84
ZnO25ZnS	32.81

# Conclusion

In this paper, we report the preparation and characterization of ZnO-ZnS composites from zinc acetate, sodium sulfide and sodium hydroxide as precursors using coprecipitation method. SEM images show that in all composites particles are similar with the size of about 30 nm. XRD patterns reveal that there is still an existence of ZnO particles in the form of hexagonal wurtzite. These characteristics of obtained materials will help us to interpret clearer their photo-catalytic activity in the photo-degradation reaction of organic pollutants. **References** 

1. E. Hong, T. Choi, J. H Kim, Application of content optimized ZnS-ZnO-CuS-CdS heterostructured photocatalyst for solar water splitting and organic dye decomposition, Korean. J. Chem. Eng., 2015, 32, 424-428.

2. E. Hong, J. H Kim, Oxide content optimized ZnS-ZnO heterostructureds via facile thermal treatment process for enhanced photocatalytic hydrogen production., International J. Hydrogen energy. 2014, 39, 9985-9993.

3. J. Zhao, L. Zhao, Z. Wang, *Preparation and characterization of ZnO/ZnS hybrid photocatalysts via microwave-hydrothermal method*, Fron. Environ. Sci. Engin. China., 2008, 2(4), 415-420.

4. I. Bedja, S. Hotchandani, P. V. Kamat. *Photosensitization* of composite metal oxide semiconductor films. Berichte der Bunsengesellschaft/Physical Chemistry Chemical Physics, 1997, 101(11), 1651–1653.

5. C. H. Li, Y. H. Hsieh, W. T. Chiu, C. C. Liu, C. L. Kao. Study on preparation and photocatalytic performance of  $Ag/TiO_2$  and  $Pt/TiO_2$  photocatalysts. Separation and purification Technology, 2007, 58(1): 148–151.

6. Y. Xie, Y. Z. Li, X. J. Zhao. Low-temperature preparation and visible-light-induced catalytic activity of anatase F-Ncodoped TiO<sub>2</sub>. Journal of Molecular Catalysis A: Chemical, 2007, 277(1-2): 119–126.

7. D. Aaron, M. Allann, S. Martin. *Mechanochemical* synthesis of nanocrystalline SnO<sub>2</sub>-ZnO photocatalysts. Nanotechnology, 2006, 17(3): 692–698.

8. X. Liu, L. Pan, Q. Zhao, T. Lv, G. Zhu, T. Chen, Ting Lu, Z. Sun, C. Sun, UV-assisted photocatalytic synthesis of ZnOreduced graphene oxide conposites with nhance photocatalytic activity in reduction of Cr(VI)., Chem. Eng. J., 2012, 183, 283.

9. X. Zhao, M. Li, X. Lou. *Enhanced photocatalytic activity* of zinc oxide synthesized by calcination of zinc sulfide precursor. Mater Sci Semicond Process 2012;16, 489-494.

10. K. Zhang, L. L. Zhang, X. S. Zhao, J. Wu, J. Chem. Mater., 2010, 22(4), 1392.