

## Photocatalytic Dye Methyl Orange Decomposition on Ternary Sulfide (CdIn<sub>2</sub>S<sub>4</sub>) under Visible-light

Xiao Dan YU<sup>1</sup>, Xue Song QU<sup>1</sup>, Yi Hang GUO<sup>1\*</sup>, Chang Wen HU<sup>2</sup>

<sup>1</sup> Faculty of Chemistry, Northeast Normal University, Changchun 130024

<sup>2</sup> Department of Chemistry, Beijing Institute of Technology, Beijing 100081

**Abstract:** A novel and efficient photocatalyst, CdIn<sub>2</sub>S<sub>4</sub>, was simply prepared by a programmed temperature hydrothermal method. The product had a nanometer size (10-15 nm) and strong absorption in the range of 200 to 580 nm, and it exhibited visible-light photocatalytic activity to decompose dye methyl orange in aqueous system.

**Keywords:** Ternary sulfides, hydrothermal treatment, visible-light photocatalysis, methyl orange.

Heterogeneous photocatalytic destruction of organic pollutants in waste water by using sun light or light in the visible region of the spectrum as the excitation energy is an appealing field. Widely used semiconductor photocatalysts, such as anatase TiO<sub>2</sub> and ZnS, showed very low photoactivity under visible-light excitation. Therefore, several attempts have been developed to produce efficient photocatalytical materials. One approach is to use the synergy with other coupled semiconductor photocatalysts including ZnS, WO<sub>3</sub>, ZrO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> with anatase TiO<sub>2</sub>, which would permit to enhance the charge separation in the photocarriers generation process<sup>1</sup>. Another possibility is to prepare materials that had absorptions extending towards visible range, thereby allowing the use of the main part of the solar spectrum<sup>2-4</sup>. Motivated by these ideas, we thought that ternary sulfide with strong absorption in the visible region might be used as good candidates of efficient photocatalysts. Metal sulfides such as CdS also have this light-absorption characteristic, but they are unstable during photocatalytic reaction. Here, we prepared a ternary sulfide, CdIn<sub>2</sub>S<sub>4</sub>, by a simply hydrothermal method at a constant heating rate. This method is in mild condition, compared with the chemical transport method. The visible-light photoactivity of CdIn<sub>2</sub>S<sub>4</sub> was tested *via* degradation of aqueous methyl orange. Methyl orange is one of the most stable azo dyes extensively used in the textile industry, and it is resistant to biodegradation. The aqueous methyl orange solution could be degraded totally by visible-light irradiation in the presence of CdIn<sub>2</sub>S<sub>4</sub>.

---

\* E-mail: guoyh@nenu.edu.cn

## Experimental

$\text{CdIn}_2\text{S}_4$  was prepared as follows. The stoichiometric amount of  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  (1 mmol, 2 mmol, respectively) and double excess thiourea were added to a teflon-lined stainless steel autoclave. The autoclave was filled with double-distilled water up to 20 % of its volume, and then heated to 160 °C (raised 2 °C/min), kept at 160 °C for 60 h. The orange product was washed with water and ethanol and dried at 70 °C in a vacuum.

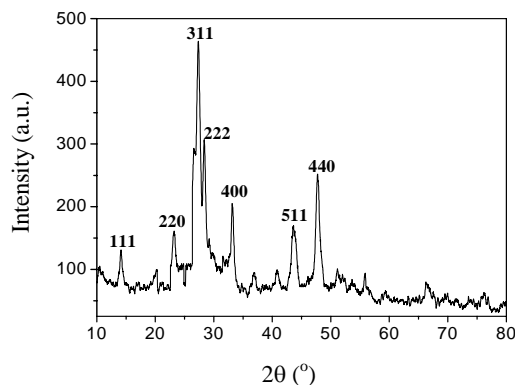
The photoreactor was a cylindrical glass cell with internal visible-light source (400 W Xe lamp) surrounded by an optical glass jacket (UV light of Xe lamp was cut by the optical glass jacket, which has complete absorption in the range of 190 to 330 nm). The suspension of the solid catalyst (0.25 g) and aqueous methyl orange (50 mg/L, 150 mL) were totally surrounded by the light source. The pH of the suspension was 7, and the temperature of the system was maintained at  $35 \pm 2$  °C by circulation water through an external cooling coil.

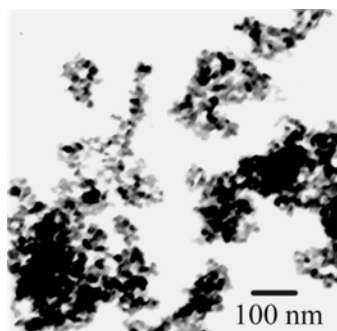
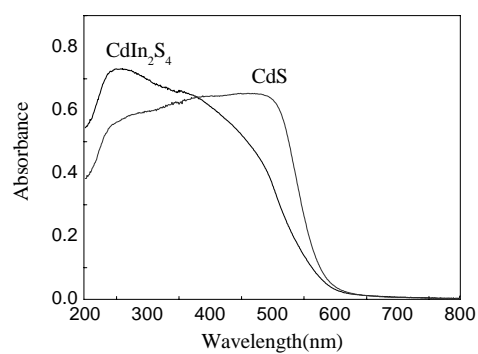
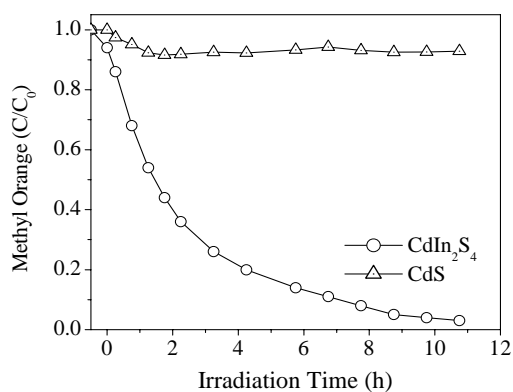
UV-Vis diffuse reflectance (DR) spectra of  $\text{CdIn}_2\text{S}_4$  and CdS were recorded on a Cary 500 UV-VIS-NIR spectrometer, and this apparatus was also used to determine the concentrations of methyl orange in the reaction system. The XRD patterns were obtained with a Japan Rigaku D/max 2000 X-ray diffractometer. TEM micrographs were obtained on a Hitachi H-7500 transmission electron microscope.

## Results and Discussion

XRD pattern of the photocatalyst was shown in **Figure 1**, and its characteristic diffraction peaks of  $2\theta$  values is at 14.1 (111), 23.2 (220), 27 (311), 28.3 (222), 33.2 (400), 43.6 (511), and 47.5° (440), respectively. These are the characteristic of the cubic spinel phase of  $\text{CdIn}_2\text{S}_4$  (JCPDS 31-0229), indicating that the product is the target compound. Using the Scherrer formula for the (hkl) peaks (311) and (440), the average diameter of the  $\text{CdIn}_2\text{S}_4$  was estimated to be *ca.* 13 nm. The result was consistent with the TEM observation (**Figure 2**), *i.e.*,  $\text{CdIn}_2\text{S}_4$  is sphere-like particles with a size of 10-15 nm.

**Figure 1** XRD patterns of cubic spinel  $\text{CdIn}_2\text{S}_4$



**Figure 2** TEM image of cubic spinel  $\text{CdIn}_2\text{S}_4$ **Figure 3** UV-Vis/DR spectra of bulk CdS and  $\text{CdIn}_2\text{S}_4$  prepared by Programmed temperature hydrothermal method**Figure 4** In the presence of  $\text{CdIn}_2\text{S}_4$  or CdS (0.25g) visible-light photocatalytic degradation of an aqueous methyl orange ( $C_0 = 50 \text{ mg/L}$ ).

UV-Vis /DR spectra (**Figure 3**) showed that both  $\text{CdS}$  and  $\text{CdIn}_2\text{S}_4$  exhibited broad and strong absorption in the range of 200 to 580 nm. The absorption edge of  $\text{CdIn}_2\text{S}_4$  was at 580 nm, with a little blueshift compared to that of  $\text{CdS}$ . The estimated band gap of  $\text{CdS}$  and  $\text{CdIn}_2\text{S}_4$  were 2.25 and 2.3 eV, respectively. The blueshift and widening of

this band gap is due to the contribution of the In 5s orbital to the conduction band of CdIn<sub>2</sub>S<sub>4</sub>. The steep shape in the visible edge and strong absorption band of CdIn<sub>2</sub>S<sub>4</sub> is ascribed to the transition between its valence band to the conduction band.

We selected the degradation of aqueous methyl orange as a model reaction to investigate the visible-light photocatalytic activity of CdIn<sub>2</sub>S<sub>4</sub>. Changes in the concentrations of methyl orange were shown in **Figure 4**. It can be seen that CdIn<sub>2</sub>S<sub>4</sub> exhibited much higher visible-light photocatalytic activity to the degradation of aqueous methyl orange. That is, in the presence of CdIn<sub>2</sub>S<sub>4</sub>, the conversion methyl orange reached 96 % after visible-light irradiation of the reaction system for 8h, while the conversion was only 8 % after 8 h invisible-light irradiation in the presence of CdS. The visible-light photocatalytic activity of CdIn<sub>2</sub>S<sub>4</sub> is mainly due to its narrow band gap, therefore, it was excited with relatively lower energy, *e.g.* by light radiation in the visible region. On the other hand, nanometer size of the product also played a role for degradation of methyl orange, which would permit to enhance the charge separation in the photocarriers generation process. Very low activity of CdS may be due to its instability during the photocatalytic reaction<sup>5</sup>. Further confirmation work is in progress.

## Conclusion

We here demonstrated a new method to prepared a photoactive ternary sulfide, CdIn<sub>2</sub>S<sub>4</sub>, *i.e.*, programmed temperature hydrothermal treatment. Compared with the conventional preparation method of solid-state reaction, this method is mild, convenient and easy to handle. As-prepared CdIn<sub>2</sub>S<sub>4</sub> was found to be active for dye methyl orange degradation under visible light irradiation. No deactivation was observed during 3 times' catalytic cycling (the conversion of methyl orange in 3 times' catalytic cycling was 97.43%, 97.14%, 96.69%, respectively). It implied that CdIn<sub>2</sub>S<sub>4</sub> is stable. The present studies indicated that it was feasible to prepare stable ternary sulfide photocatalysts with hydrothermal method.

## Acknowledgments

This work was financially supported by NNSFC (No. 20271007).

## References

1. J. Engweiler, J. Harf, A. Baiker, *J. Catal.*, **1996**, *159*, 259.
2. J. C. Yu, L. Wu, J. Lin, P. Li, Q. Li, *Chem. Commun.*, **2003**, 1552.
3. W. Choi, A. Termin, M. R. Hoffmann, *J. Phys. Chem.*, **1994**, *98*, 13669.
4. I. Justicia, P. Ordejón, G. Canto, *et al.*, *Adv. Mater.*, **2002**, *14*, 1399.
5. Z. B. Lei, W. S. You, M. Y. Liu, *et al.*, *Chem. Commun.*, **2003**, 2142.

Received 18 November, 2004