



Surface-binding through polyfunction groups of Rhodamine B on composite surface and its high performance photodegradation

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ABSTRACT

A kind of novel composite ZnS/In(OH)₃/In₂S₃ is synthesized using zinc oxide nanoplates as zinc raw material during hydrothermal process. Although the obtained samples are composited of ZnS and In(OH)₃ and In₂S₃ phase, the samples possess different structure, morphology and optical absorption property depending on molar ratio of raw materials. Zeta potential analysis indicates different surface electrical property since various content and particle size of the phases. The equilibrium adsorption study confirms the composite ZnS/In(OH)₃/In₂S₃ with surface negative charge is good adsorbent for Rhodamine B (Rh B) dye. In addition, the degradation of Rh B over the samples with surface negative charge under visible light ($\lambda \geq 420$ nm) is more effective than the samples with surface positive charge. The samples before and after adsorbing Rh B molecule are examined by FTIR spectra and Zetasizer. It is found that the three function groups of Rh B molecule, especially carboxyl group anchors to surface of the sample through electrostatic adsorption, coordination and hydrogen-bond. It contributes to rapid transformation of photogenerated electron to conduction band of In(OH)₃ and suppresses the recombination of photogenerated carrier. The possible adsorption modes of Rh B are discussed on the basis of the experiment results.

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1. Instruction

Dyes are widely used in industries and have shown significant increase to color their final products. Meanwhile industrial dyes are becoming one of the largest groups of chemical pollutants and causing significant pollution to groundwater. To prevent environmental pollution, many treatment technologies have been developed including photocatalytic degradation under the assistant of catalyst [1–10]. Since photocatalytic reaction occurs at the surface of catalyst, then the prerequisite for degradation reactions occurrence is the adsorption of dyes on catalyst surface [11,12]. To explore high effective photocatalyst, the understanding of adsorption mode and site of dyes is an important issue. For example, Liu et al. [13] proposed defect sites affected the adsorption structure of Rh B and in the end led to different photodegradation product and efficiency. Liu et al. [14] found that sulforhodamine-B gave different degradation products when it adsorbed on TiO₂ with sulfonate or diethylamino. Several typical dyes, for example Rh B had been investigated for photodegradation on single or complex catalysts surface [15–21]. Degradation of Rh B on the surface of

catalysts was previously studied by STM, UV, ESR, X-ray diffraction, and absorption spectroscopy [22–25]. Since Rh B molecule contains three functional groups and varies adsorption mode and site depending on surface property of photocatalysts, therefore photodegradation of Rh B is a complex process and leads to different degradation products and efficiency. Moreover, two degradation mechanisms are involved, direct photodegradation reaction and the successive deethylation of the four ethyl groups [26]. Different catalysts possibly hold different degradation mechanism for Rh B under light irradiation. We have to determine the adsorption modes by analyzing in detail interaction between Rh B and catalyst surface.

In this paper, we prepared the multicomponent composite ZnS/In(OH)₃/In₂S₃ under the experimental condition and investigated the adsorption and photocatalytic degradation of Rh B in the surface of the samples under the visible light irradiation. When Rh B molecule tightly bonds onto ZnS, In₂S₃ and In(OH)₃ phase in the composite ZnS/In(OH)₃/In₂S₃ through carboxyl and amino group, photogenerated electron and hole can separate rapidly and effectively so that the sample holds high performance photocatalytic degradation activity. Meanwhile, we find one new degradation pathway that after Rh B removing one ethyl group in dark, N,N,N'-triethyl rhodamine can simultaneously remove three ethyl and transform to rhodamine rather than successive deethylation

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Table 1
Description, specific surface area and apparent rate constant of the obtained samples.

Molar ratio of Zn, In and S	1:1:3	2:1:3	3:1:3	4:1:3	5:1:3	2:1:1	2:1:2	2:1:4	2:1:5
Samples denoted as	S1	S2	S3	S4	S5	S6	S7	S8	S9
BET ($\text{m}^2 \text{g}^{-1}$)	40.50	44.89	33.79	28.34	30.66	70.42	21.97	30.16	69.44
Apparent rate constant (κ)	0.097	0.099	0.023	0.0037	0.00036	0.008	0.0013	0.088	0.076

of Rh B. Next the rhodamine is degraded into colorless little molecule. All of these are not reported up to now.

2. Experimental

2.1. Preparation of ZnO nanoplate

ZnO nanoplate was synthesized by a hydrothermal process at 95°C for 24 h using a modified literature method [27]. Typically, 40 mmol of ZnO, 80 mmol of NaOH and 0.014 mmol of sodium citrate were dissolved in 75 mL of ultrapure water. The mixture was stirred for 30 min and then transferred to a 100 mL Teflon autoclave, treated at 95°C for 24 h, and then cooled to room temperature in air. The white product was separated by filtration, washed with ultrapure water, and dried at 70°C for 6 h [28].

2.2. Preparation of ZnS-In(OH)₃-In₂S₃ photocatalyst

The ZnS-In(OH)₃-In₂S₃ photocatalyst was synthesized via a hydrothermal method. Typically, 1.0 mmol of In₂(SO₄)₃·6H₂O, a amount of thioacetamide (TAA) and ZnO nanoplates were added to 75 mL of ultrapure water. The mixture was stirred for 30 min and then transferred to a 100 mL Teflon autoclave. The mixture was heated to 120°C and maintained at this temperature for 6 h and then cooled to room temperature in air. The product was separated by filtration, washed with ultrapure water and ethanol, and dried at 70°C for 6 h. The obtained samples were denoted in Table 1 depending on molar ratio of raw materials.

2.3. Characterization

XRD patterns were acquired with a Bede D1 system multifunction X-ray diffractometer employing Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation. The voltage and current were 40 kV and 40 mA, respectively. Scanning electron microscopy (SEM) images were taken with a JSM 6701F field emission scanning electron microscope. Brunauer–Emmett–Teller (BET) surface was determined by nitrogen adsorption–desorption using a Micromeritics ASAP 2020C analyzer. UV–vis diffuse reflectance spectra were obtained using a Hitachi U-4100 spectrophotometer. UV–vis absorption spectra were obtained using a Shimadzu UV-250 1PC spectrophotometer. Fourier transform infrared spectra were recorded at room temperature with a KBr pellet on Nicolet 5700 spectrometer. Zeta potential and conductivity values of the samples in ultrapure water were determined on nano ZS 90 Malvern Zetasizer.

2.4. Catalyst evaluation

Photocatalytic reaction was conducted in a 400 mL Pyrex cell. A 300 W Xe lamp was used as the light source removing the ultra-violet light with a 420 nm cutoff filter. A water bath was used to keep constant temperature. In a typical photocatalytic experiment, 50 mg of the as-prepared photocatalyst was added to 250 mL 11.2 mg L^{-1} of Rh B (Rh B) solution. Prior to illumination, the suspension was magnetically stirred in the dark for 1 h to reach the adsorption–desorption equilibrium of Rh B on the photocatalyst surface. During the visible light irradiation, 5 mL of the reaction suspension was sampled at intervals of 5 min and separated by the

filter membrane of a syringe to remove the catalyst particles. The concentration of Rh B in the clear supernatant solution was determined by measuring the absorbance at ca. 554 nm with UV–vis spectrophotometer.

3. Result and discussion

3.1. Characterization of the samples synthesized

Fig. 1 shows the XRD patterns of the samples obtained with different molar ratio of zinc and indium and TAA. From Fig. 1a, changing the molar ratio of zinc and indium, the obtained samples are composed from the cubic phase ZnS (PDF No. 77-2100) and tetragonal phase In₂S₃ (PDF No. 73-1366) and cubic phase In(OH)₃ (PDF No. 85-1338). Compared with the intensity and width of diffraction peaks, when the molar ratio of zinc and indium and TAA was 2:1:3, the crystallinity and particle size of In(OH)₃ phase are higher than the other four samples. Moreover, when the molar ratio of zinc and indium and TAA was 4:1:3 and 5:1:3, the obtained samples present a new obvious diffraction peak at ca. 12.40 degree,

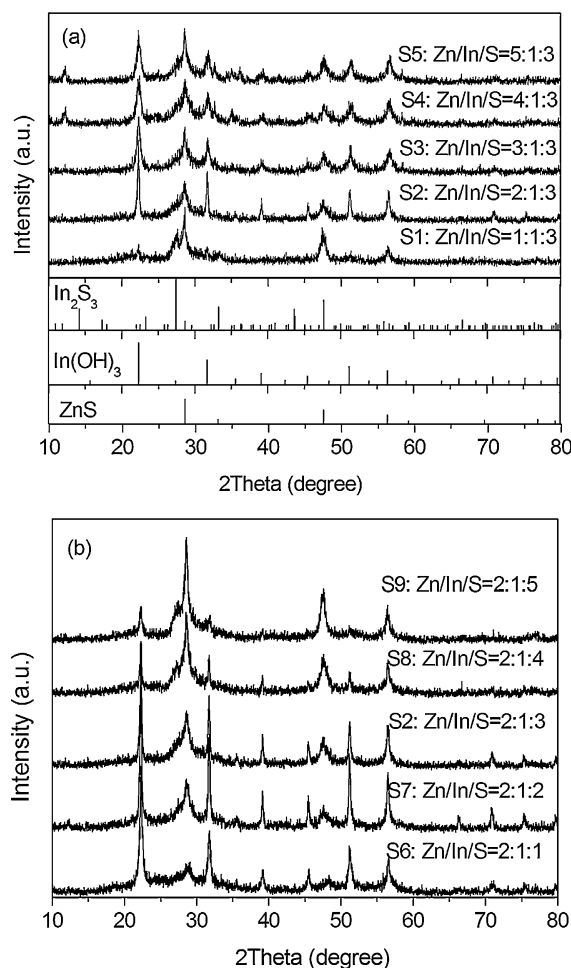


Fig. 1. XRD patterns of the obtained samples with different molar ratio of zinc and indium and thioacetamide.

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