Applied Clay Science 144 (2017) 115–120

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Mechanochemical synthesis of ultrafine ZnS/Zn-Al layered double hydroxide heterojunction and their photocatalytic activities in dye degradation

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ARTICLE INFO

Keywords:
Mechanochemistry
Ultraviolet-light photocatalysis
ZnS/Zn-Al LDH composite

ABSTRACT

ZnS/Zn-Al layered double hydroxide (LDH) heterostructures were synthesized by a mechanochemical method and characterized by a set of analytical methods: X-ray diffraction, Raman spectroscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy and scanning electron microscopy. The photocatalytic degradation activity for Rhodamine B (RHB) under ultraviolet light irradiation exhibited a large enhancement with the increasing ZnS content, with 94% RHB degraded in 180 min by using 2ZnS/Zn-Al LDH heterostructured composite, but only 75% by the LDH sample without ZnS. A detailed discussion was performed to understand the reason for the enhanced photocatalytic activity based on the efficient separation of photoinduced electrons and holes. This work provides an effective way to fabricate a series of LDH-based and transition metal sulfide-containing heterostructured photocatalysts.

1. Introduction

Photocatalysis technology is widely used for the disposal of organic pollutants. As one of the most important II-VI group semiconductors, ZnS with a large band-gap energy, has been deeply studied due to its application in various optoelectronic devices, such as electroluminescent displays (Kavanagh et al., 2004), laser buffer layers in solar cells and photovoltaic displays (Asenjo et al., 2008; Islam et al., 2009). ZnS crystallizes in the zinc-blende (ZB) or wurtzite (WZ) structures at room conditions with a band gap of 3.68 eV and 3.77 eV (Durandurdu, 2009), respectively. Several methods have been developed to synthesize ZnS with various phases and morphologies, such as the hydrothermal method (Demazeau, 2007), co-precipitation method (Iranmanesh et al., 2015) and solvothermal method (Mendil et al., 2016). As an effort to develop new materials with enhanced photocatalytic activity, clear improvements in optical properties have been confirmed when forming a heterostructure of transition metal sulfide including ZnS with other catalysts, such as $CuInS_2$, TiO_2, and CdSe (Lee et al., 2008; Zubair et al., 2014; Roy et al., 2016; Tian et al., 2016). However, the synthesizing methods are usually complicated and require elaborate efforts to obtain samples with the expected structure rather than a simple physical mixture. A method with low cost and giving the synthesized material standing stability is required for the development of ZnS catalyst.

Layered double hydroxides (LDHs) or anionic clays are a group of binary clay minerals, which can be represented by the general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2](A^{n-})_{x/n-}\cdot mH_2O$ (Ceckeler and Nishide, 2010; Mittal, 2010; Qu et al., 2016a,b). Multiphases of LDHs which can be manufactured by ion-exchange or hydration reconstruction processes have been researched for many years because of potential uses in nanocomposites (Vasti et al., 2017), agriculture (Bernardo et al., 2017), and catalyst (Abderrazek et al., 2016; Sobhana et al., 2016; Yuan and Li, 2017). LDH with zinc and titanium located in the sheet have been widely used as photocatalyst for photo degradation of organic pollution or photocatalytic water-splitting (Xia et al., 2014; Xu et al., 2017). ZnS and LDH are prepared into a composited state in order to enhance the photocatalytic activity through their mutual interaction during the light irradiation.

Mechanochemistry offers new challenges in the synthesis of nanocrystals. This synthetic route can be performed via simple solid-state approach using ambient pressure and room temperature (Dutková et al., 2015). Our previous researches show that, various LDHs and corresponding precursors can be synthesized through a mechanochemical route, with a solvent-free operation and the promoted adsorption capacity (Qu et al., 2016a,b; Wang et al., 2016).

In this article, ZnS/Zn-Al LDH heterostructures were prepared by simply milling zinc carbonate hydroxide hydrate, aluminum hydroxide and sodium sulfide hydrate. Different molar ratios of ZnS/LDH hetero-

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http://dx.doi.org/10.1016/j.clay.2017.05.015
Received 31 January 2017; Received in revised form 2 May 2017; Accepted 12 May 2017

structures could be easily prepared by altering the dosage of reactants. Many characterization techniques were used to study the morphology, structure and composition of the samples. The ultraviolet light photocatalytic activity is embodied as the degradation of RHB and is significantly improved with the content increase of ZnS. The composite structure is characterized and the mechanism of enhanced photocatalytic activity is investigated. It demonstrates that the formation of heterostructures containing ZnS and LDH can indeed greatly enhance photocatalytic performance. More importantly, this method could be further extended to synthesize a series of highly efficient light active LDH-based transition metal sulfide-containing heterojunction photocatalysts, offering a new easy approach for the synthesis of photocatalyst with some specific structures.

2. Experimental

2.1. Materials and methods

Zinc carbonate hydroxide hydrate ($Zn_4CO_3(OH)_6{\cdot}H_2O$), aluminum hydroxide ($Al(OH)_3$), sodium sulfide hydrate ($Na_2S{\cdot}9H_2O$) and RhB were purchased from Sinopharm Group Co Ltd., Shanghai, China, Analytical reagent. All chemicals were used without further purification. A planetary ball mill (Pulverisette-7, Fritsch, Germany), which has two mill pots (45 cm^3 inner volume each) made of zirconium dioxide with 7 zirconium dioxide balls of 15 mm in diameter, was used to conduct the ball-milling operation. The milling intensity was fixed at 600 rpm for 2 h.

A two-step operation was involved for synthesizing the Zn-Al LDH. In the first dry grinding process, 2 g of zinc carbonate hydroxide hydrate and $Al(OH)_3$ (Zn/Al molar ratio fixed at 2/1) mixture were ground to obtain the LDH precursor. In the second agitation step, 1 g of the precursor was put into a capped erlenmeyer flask filled with 100 ml of distilled water and stirred for 4 h on the magnetic stirring apparatus (524G, Meiyingpu, Shanghai, China) at 1200 rpm. ZnS was synthesized by grinding 2 g of zinc carbonate hydroxide hydrate and $Na_2S{\cdot}9H_2O$ at a molar ration according to Eq. (1). After grinding, all the powder was put into a capped erlenmeyer flask filled with 150 ml of distilled water and stirred for 2 h on the magnetic stirring apparatus at 600 rpm, filtered and dried with light shut, in order to remove the sodium impurities in the product.

$$ZnCO_3{\cdot}3Zn(OH)_2{\cdot}H_2O + 4Na_2S{\cdot}9H_2O = 4ZnS + Na_2CO_3 + 6NaOH + 37H_2O \tag{1}$$

ZnS/LDH composites were synthesized by grinding 2 g of zinc carbonate hydroxide hydrate, $Al(OH)_3$ and $Na_2S{\cdot}9H_2O$ (ZnS/LDH molar ratio varied at 0.5/1, 1/1 and 2/1). After grinding, sodium impurities were also removed as above mentioned.

2.2. Characterizations

Phases and phase changes of the samples were identified by the XRD analysis on a Rigaku Max-RB RU-200B diffractometer using CuKα radiation (λ = 1.5403 Å) at 2θ between 5° and 70°, with a rated power at 12 kW. A SEM (JSM-5610LVJEOL) spectroscopic measurement with EDS accessory (Phoenix, EDAX) was used to observe the microstructures and the distribution of ZnS on LDH matrix of the as-prepared composites. TG-DSC analysis was performed by a simultaneously thermal analyzer (STA449F3, NETZSCH) in air flowing from 30 °C to 1000 °C at a heating rate of 10 °C/min. A UV/VIS/NIR Spectrometer (Lambda 750 S, PerkinElmer) was used to record the UV–Vis diffusive reflectance spectra of the prepared sample, with a 6° relative specular reflection accessory. The wavenumber (nominal resolution) can be regulated from 0.17 nm to 5 nm. A Raman Spectrometer (Raman, RENISHAW, INVIA, UK) with spectral resolution at 1–2 cm^{-1} was used to analyze the property change of the ground sample. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi system.

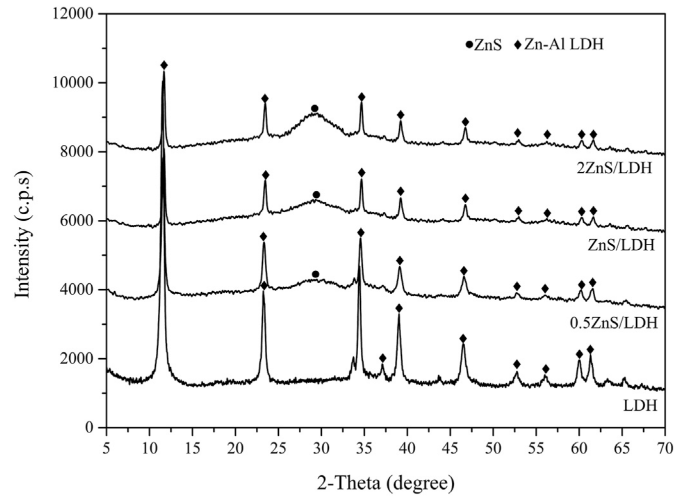

Fig. 1. XRD patterns of as-prepared Zn-Al LDH and nZnS/LDH (n = 0.5, 1 and 2).

2.3. Photocatalytic activity

The photocatalytic activity of the as-prepared samples was evaluated by the ultraviolet light irradiation of RHB in aqueous solutions on a PLS-LAM254 photocatalytic reaction equipment, in which the wavelength of the UV light was 254 nm. 0.25 g of the as-prepared samples were continuously stirred in 250 ml 4 mg/g RHB solutions respectively with irradiation. 4 ml suspension was collected and centrifuged to remove the photocatalyst at given time intervals. The absorbance of the centrifuged solutions at 556 nm for RHB was recorded on a SHIMADZU UVmini-1240 UV/VIS spectrometer for the measurement of remaining RHB concentration in the solutions.

3. Results and discussion

3.1. Characterizations of the prepared samples

The comparison of the XRD patterns of the as-synthesized nanostructures is presented in Fig. 1. The Zn-Al LDH sample exhibited intense diffraction peaks located at 11.54, 23.24, 34.44 39.04, 46.50, 60.00 and 61.32°, which corresponded to the (003), (006), (012), (015), (018), (110) and (113) diffraction plane of Zn-Al LDH, respectively (JCPDS: 48-1023, space group: R, cell constants: a = b = 3.072 Å, c = 22.650 Å). The 0.5ZnS/LDH composite revealed similar diffraction peaks corresponding to planes of Zn-Al LDH since LDH accounted for more than 80% of the total mass ratio of the reaction products. A broader peak indexed to ZnS were discovered in 0.5ZnS/LDH composite, due to the very low percentage of ZnS amount in the composite. When the molar ratio of zinc sulfide gradually increased, the XRD characteristic peaks of ZnS was becoming more obvious, particularly with 2ZnS/LDH sample and the peak intensity was getting higher. Compared with zinc sulfide prepared by other methods, mechanochemically synthesized ZnS showed typically broader XRD characteristic peaks with low crystallinity. On the other hand, the easily homogeneous dispersibility of the nanoparticles uniformly on LDH matrix might be beneficial to the improvement in photocatalysis.

The bonding nature and interactions of the prepared ZnS and 2ZnS/LDH were examined with the aid of laser Raman spectroscopy. Fig. 2 shows the Raman spectrum of ZnS and 2ZnS/LDH composite. The characteristic peaks observed at 260 cm^{-1} and 350 cm^{-1} were attributed to the A_1/E_1 transverse optical modes and the A_1/E_1 longitudinal optical phonons modes, respectively. The small peaks at 1082 cm^{-1} were due to the Zn-S vibration from ZnS nanoparticles (Mendil et al., 2016; Thangavel et al., 2016). The observed Raman modes of mechan-