Dyes and Pigments 120 (2015) 8–14

Contents lists available at ScienceDirect

Dyes and Pigments

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

Solid-state synthesis of ZnS/graphene nanocomposites with enhanced photocatalytic activity

Fengjuan Chen [a, b], Yali Cao [a], Dianzeng Jia [a, *], Anjie Liu [a]

[a] Key Laboratory of Material and Technology for Clean Energy, Ministry of Education, Key Laboratory of Advanced Functional Materials, Autonomous Region, Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, Xinjiang, PR China
[b] School of Physics Science and Technology, Xinjiang University, Urumqi 830046, Xinjiang, PR China

ARTICLE INFO

Article history:
Received 5 February 2015
Received in revised form
25 March 2015
Accepted 26 March 2015
Available online 9 April 2015

Keywords:
ZnS
Graphene
Nanocomposites
Photocatalysis
Solid-state method
Mechanism

ABSTRACT

A simple solid-state method was employed for the first time to obtain ZnS/graphene nanocomposites. The chemical composition, morphology and properties of the products were characterized by X-ray diffraction, Raman spectroscopy, transmission electron microscopy, nitrogen absorption-desorption and UV–vis spectroscopy. The photocatalytic performances of the products were evaluated by methyl orange. The results indicated that nanocomposites exhibited superior photocatalytic activity to pure ZnS, owing to the reduction of photoinduced electron–hole pair recombination induced by the introduction of graphene. In addition, effects of solid-state synthetic conditions on photoactivity were also investigated. It was found that the nanocomposite obtained by the reduction of $NaBH_4$ exhibited higher photoactivity than that of got by the direct addition of graphene, which can be attributed to the high specific surface area and the enhanced synergetic effect between ZnS and graphene. With the help of scavengers, $\cdot O_2^-$ was proved to be the main reactive species during the degradation.

1. Introduction

Photocatalysis based on semiconductors has drawn much attention in recent years owing to increasing energy demand and growing environmental issues [1,2]. Thus, many semiconductor photocatalysts have been extensively investigated, including TiO_2, ZnO, ZnS, and so on [3–5]. Among them, zinc sulfide (ZnS) has been considered as one of the best photocatalytic materials because of the tunable electric and optical properties [6,7]. Photocatalytic activity of ZnS can be heavily affected by the ability of electron–hole pair separation under UV irradiation. When ZnS absorbs a photon, electron–hole pair can be produced, which can then reach the catalyst surface and degrade the pollutants [8]. However, the quick recombination of photo-generated electrons and holes would lead to the significant decrease of photocatalytic activity.

In respect to improve the photocatalytic activity of ZnS, many attempts have been made, such as modifying ZnS by carbonaceous material, metallic and nonmetal materials [9–11]. Recently, it was reported that carbonaceous materials played an important role in enhancing the photocatalytic activity of ZnS [12]. As an emerging carbonaceous material, graphene has attracted much attention in recent years owing to its excellent electronic transport property, high chemical stability and large specific surface area [13–15]. In addition, graphene is also expected to be served as an electron collector to enhance photoinduced charge transfer for excellent photocatalytic activity. Therefore, graphene-modified ZnS is an important study for improving the photocatalytic activity. Recently, many efforts have been devoted to prepare ZnS/graphene nanocomposites with multifunctionalities [16–18]. For example, Song et al. [19] prepared CdSe/ZnS/RGO hybrids using ionic liquids, which showed efficient photocarrier generation ability and high photocurrent. ZnS–graphene nanocomposites obtained by microwave-assisted synthesis method exhibited excellent photocatalytic activity in the degradation of organic dye [20]. That is because graphene can act as good electron acceptors to improve the interfacial electron transfer and restrain the electron/hole pair recombination of ZnS; on the other hand, graphene with high specific surface area can allow for greater photon absorption on the photocatalytic surface. Though great progress has been made in the respect, it is still imperative to adopt a simple, high yield and environmentally friendly method to synthesize ZnS–graphene nanocomposites.

In the last years, room-temperture solid-state method has emerged as a promising alternative to wet chemistry and other

* Corresponding author. Tel.: +86 0991 8583083; fax: +86 0991 8588883.
E-mail address: jdz0991@gmail.com (D. Jia).

http://dx.doi.org/10.1016/j.dyepig.2015.03.030
0143-7208/

methods in the synthesis of nanomaterials due to its simplicity, low cost, high yield and low environmental impact [21,22]. As shown in our previous work [23–25], we have synthesized a series of metal oxides, metal sulfides and composites by this method. To our knowledge, there is no report on the synthesis of ZnS/graphene nanocomposites via the above method so far. Consequently, in this work, we report for the first time the synthesis of ZnS/graphene nanocomposites by low-temperature solid-state method through two different approaches. The photocatalytic performance of the as-prepared ZnS/graphene nanocomposites was investigated. The results indicated that the nanocomposites showed enhanced photocatalytic activity in the degradation of methyl orange under UV irradiation, it was also found that the solid-state synthetic conditions of the nanocomposites play an important role in photocatalytic activity. We believe that this facile method can be extended to prepare other graphene-based composite nanomaterials for various applications such as photocatalysis.

2. Experimental section

2.1. Synthesis

All reagents were of analytical purity and used without further purification. In our study, firstly, graphene oxide (GO) was synthesized by the modified Hummer's method from graphite powder [26]. Sample graphene (GR) was fabricated by calcining the as-synthesized GO at 600 °C for 2 h. Then, the ZnS/graphene nanocomposites were obtained by low-temperature solid-state method. In a typical procedure, 2.1950 g of zinc acetate was accurately weighed and ground for about 30 min. Then 2 mg of GO power and 0.7513 g of thioacetamide fine powder were added, and ground for 60 min continuously (The weight ratio of graphene to ZnS in the nanocomposite was 0.2%). After that, 1.893 g of sodium borohydride ($NaBH_4$) was added, and ground for 60 min to assure an entire reaction. The reaction started as soon as the reactants came into contact, accompanied by the release of heat and evaporation of water vapor. Finally, the mixture was washed with distilled water and ethanol several times to remove by-products, and was dried in air at 60 °C for 2 h. Then the ZnS/graphene composite was successfully obtained, which was labeled as ZG-1.

For comparison, we also prepared ZnS/graphene nanocomposites by another low-temperature solid-state approach. In a typical method, 2.1950 g of zinc acetate was accurately weighed and ground for about 30 min. Then 2 mg of GR and 0.7513 g of thioacetamide fine powder were added, and was ground for 60 min continuously (The weight ratio of graphene to ZnS was same as the nanocomposite ZG-1). Finally, the mixture was washed and dried, and the resulting product was named as ZG-2. In addition, pure ZnS was also prepared under the same conditions without the presence of graphene.

2.2. Characterization

The phase component of products was determined by X-ray diffraction (XRD, D8 Advance, Bruker Co.) under the operation conditions of 40 kV and 40 mA at scanning rate of 0.04° s^{-1} in the range of 10–80°. The morphologies of products were observed by transmission electron microscopy (TEM, JEOS, H-600). In the preparation of samples for TEM observation, the materials were first suspended in ethanol and sonicated over 10 min. Subsequently, a drop of the supernatant dispersion was dropped onto a cupper grid, which was dried in air at room temperature and kept in vacuum for 20 min before TEM observation. Raman spectra were acquired on a BRUKER VERTEX 70. Specific surface area and porosity measurements were carried out on a Micromeritics ASAP 2050 instrument at liquid-nitrogen temperature using nitrogen gas as the adsorbate, in which all samples were previously degassed at 200 °C for 6 h in flowing N_2. The Brunauer–Emmett–Teller (BET) surface area were obtained by the Brunauer–Joyner–Halenda (BJH) method. The pore size distribution was determined using the density functional theory (DFT) model based on nitrogen desorption isotherm. The UV–vis absorption spectra were conducted on Hitachi U-3100 Spectrophotometer, using BaSO4 as the reference. The fluorescence decay spectra were performed by spectrofluorometer (JY-3). The photocatalytic experiments were carried out in an XPA-1 photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China).

2.3. Photocatalytic test

The photocatalytic activities of the samples were evaluated by the degradation of methyl orange (MO) under UV irradiation using a 300 W mercury lamp. Typically, 50 mg of photocatalysts were added into 100 mL of 10 mg/L MO aqueous solution. The suspension was continuously stirred for 1 h in the dark to ensure the adsorption–desorption equilibrium between the photocatalyst and the MO. The solution was then shined under UV irradiation. At a given irradiation time, 5 mL of the suspension was collected and centrifuged to remove the photocatalyst, then analyzed by recording the UV–vis spectra of MO at the maximum absorption wavelength. All the experiments were conducted at room temperature.

3. Results and discussion

3.1. Crystal structure and chemical composition analyses

Fig. 1 showed the X-ray diffraction (XRD) patterns of ZnS/graphene nanocomposites as well as GO, GR and ZnS. As seen in Fig. 1, GO displays a sharp (001) diffraction peak at 10.4°, indicating the formation of GO [27]. After chemical reduction of GO, the diffraction peak of GO disappeared and a very broad peak at about 25.7° was observed, corresponding to (002) crystal plane of GR, suggesting that GO has been reduced to GR [28]. The characteristic diffraction peaks of ZnS are in good agreement with that of sphalerite ZnS (JCPDS card no. 05-0566), demonstrating that pure ZnS was obtained. Only ZnS diffraction peaks are observed in XRD patterns of ZnS/graphene nanocomposites, which coincide with the standard sphalerite ZnS (JCPDS card no. 05-0566). Although graphene possesses high crystallinity, no characteristic diffraction

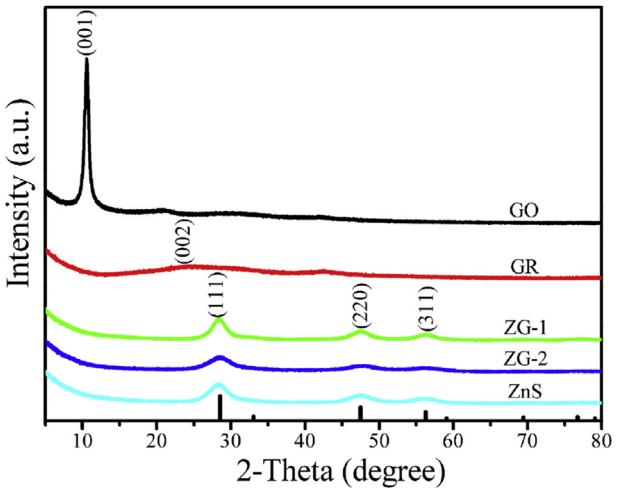

Fig. 1. XRD patterns of as-synthesized ZnS/graphene nanocomposites.