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A facile one-pot hydrothermal method to produce SnS_2/reduced graphene oxide with flake-on-sheet structures and their application in the removal of dyes from aqueous solution

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ABSTRACT

In this article, we report a novel one-pot synthesis of SnS_2/reduced graphene oxide (rGO) flake-on-sheet nanocomposites via in situ reduction of graphene oxide (GO) by Sn^{2+} under hydrothermal conditions. The morphology and structure of the obtained product were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction instrument (XRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The adsorption characteristics of the SnS_2/rGO nanocomposites were examined using an organic dye Rhodamine B (RhB) as adsorbate. SnS_2/rGO exhibited superior adsorption behavior for RhB. The adsorption kinetics and adsorption isotherm were investigated. The adsorption of RhB by SnS_2/rGO was well fitted to the Langmuir isotherm model, and the resultant kinetic data were well described by pseudo-second-order model.

1. Introduction

The dyes in effluent pollution from industries based on textiles, paper, leather, food, and cosmetics have attracted considerable attention, because most of them are toxic and carcinogenic to human beings as well as the environment [1,2]. In addition, the colors of the dyes can be easily observed even at very low concentrations, making them highly undesirable. So far, many technologies have been developed for the removal of dyes from aqueous media, including biodegradation, adsorption, oxidation processes, and so on [3–6]. On the whole, the dyes could be removed mainly in two ways. One is enriching dyes through different media which are separated afterward. The other is to break down the molecular structure of the organic dyes, leading to their degradation and decoloration. In fact, most of dyes are stable to photodegradation, biodegradation, and oxidizing agents. Therefore, adsorption technique is considered as an easy, effective, and economic process for removing dyes from aqueous solution [7,8]. Thus, searching for novel, low cost, and efficient materials for the adsorption of dyes is of great importance. Recently, with the rapid development of nanotechnology, a variety of nanomaterials have been developed for the removal of hazardous dyes and pigments in consideration of their high specific surface area [9–12].

As a new kind of carbon nanomaterials, graphene (including GO and rGO) has unique two-dimensional lamellar structure of sp^2-hybridized carbon atoms, a high theoretical specific surface area of 2630 m^2/g, and strong π–π interactions with the aromatic moieties present in many dyes, which make it a good candidate as an adsorbent for the adsorption of dyes [13–16]. GO has a wide range of oxygen-containing groups, such as epoxide (C—O—C), hydroxyl (OH), carboxyl (COOH), and carbonyl groups. It is hydrophilic, negatively charged, and well dispersed in water to form a stable colloidal suspension as a result of the ionization of the carboxylic acid and phenolic hydroxyl groups. However, to the best of our knowledge, the use of GO or rGO as adsorbents for dye decontamination is still restricted by a certain factors. Firstly, it is difficult to separate GO from aqueous solutions because of their small particle size and good dispersibility. And it would bring about serious health and environmental problems once they are released into the environment [17,18]. Secondly, rGO sheets usually suffer from serious agglomeration in the process of adsorption, due to the π–π interactions between neighboring sheets, leading to reduced effective surface area and consequently lower adsorption capacity than expected.

In recent years, chemical modified graphene sheets have been developed by attaching organic groups or inorganic particles onto graphene surfaces, which can not only bring in new functional groups, but also prevent graphene from agglomeration while retaining high surface area and pore volume in the nanocomposite [19–23]. Cao's group have successfully introduced ZnO, Cu_2O, $Mg(OH)_2$,

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and Ni nanoparticles on the surface of rGO. And these graphene-based materials exhibit enhanced performance for the removal of dye solution. The incorporation of graphene with inorganic photocatalyst nanoparticles could also improve the adsorptivity of pollutants. Tin sulfide (SnS_2) has a layered hexagonal CdI_2-type crystal structure, consisting tin cations sandwiched between two layers of close-packed sulfur anions. These triple layers are stacked along the c axis and held together by van der Waals interactions, which provides the possibility to form oriented structures of 2D nanobuilding blocks similar to that of graphite sheet. Nanoflake-like SnS_2, if attached onto the surface of the graphene, could effectively serve as spacers to support adjacent graphene. Thus, we anticipate that the incorporation of SnS_2 on the surface of graphene could also improve its adsorption property. Recently, SnS_2/graphene composites have been synthesized by hydrothermal method, but they are merely used for rechargeable lithium ion batteries [24–26]. To the best of our knowledge, no graphene-SnS_2 adsorbent has been reported. In this regard, we proposed a new one-pot hydrothermal method to grow SnS_2 nanoflakes on rGO supports for dye removal. As expected, the as-prepared SnS_2/rGO nanocomposites showed enhanced adsorption ability for organic dyes.

2. Experimental

2.1. Preparation of GO and rGO

The GO was obtained from natural graphite using a modified Hummers method [27]. For the chemical conversion of GO to rGO, 100 mg GO was added into 100 ml distilled water. And a uniform dispersion was achieved by ultrasonication for 30 min. Then, 2 ml hydrazine solution (85%) was mixed with the GO aqueous suspension in a 250 ml three-necked flask. After being vigorously stirred for a few minutes, the mixture solution was put in an oil bath (~95 °C) and reacted for 6 h under stirring. The products were collected by centrifugation and washed several times with water and ethanol, respectively. Subsequently, the product was dried under vacuum at 40 °C.

2.2. Preparation of flake-on-sheet structured SnS_2/rGO composites via a hydrothermal reaction

GO (40 mg) in 40 ml water was ultrasonicated for 30 min to give a homogeneous suspension, followed by adding 0.5 mmol citric acid. Then, 0.5 mmol $SnCl_2{\cdot}2H_2O$ and 1 mmol thioacetamide (TAA) were added to the above mixture under stirring. The mixture was kept stirring for 10 min to ensure the complete dissolution of the added chemicals. The mixture was transferred into a Teflon lined autoclave and subjected to hydrothermal treatment at 120 °C for 12 h. After cooling to room temperature naturally, the resultant solid products were collected by centrifugation at 4000 rpm and washed several times with water and ethanol, respectively. Finally, the product was dried under vacuum at 40 °C.

2.3. Materials characterization

The ultrasonic experiments were carried out by an ultrasonic disperser (KQ 50 B, Kunshan ultrasonic Instrument Co. Ltd. 40 kHz, 50 W). The structure of the as-prepared composites was investigated using TEM. TEM experiments were performed on a JEOL JEM-1200EX with an acceleration voltage of 100 kV. Analysis of XPS was performed on an ESCALAB 250 measurement. FT-IR Spectra of KBr powder-pressed pellets were recorded on a BRUKER VECTOR 22 Spectrometer. XRD patterns were obtained with a Siemens D5005 diffractometer using Cu Kα radiation (λ = 1.5418 Å). The Raman spectrum was recorded on a HORIBA Jobin Yvon-LabRAM ARAMIS. Thermogravimetric analysis (TGA) was carried out under a flow of air with a temperature ramp of 10 °C min^{-1}.

2.4. Adsorption experiments

The adsorption experiments were conducted with SnS_2/rGO as adsorbent for RhB in a conical flask at room temperature. The removal of RhB from aqueous solutions was carried out following the experimental procedure bellow: 100 mg SnS_2/rGO was added to 50 ml distilled water and then subjected to 30 min of ultrasonication to get homogeneous stock suspension. In a typical adsorption procedure, 10 ml SnS_2/rGO stock suspension (2 mg/ml) was added into 10 ml of RhB solution in the concentration range from 40 to 600 mg/L with stirring in dark. Thus, the concentration of RhB in the mixture (denoted as the initial concentration of RhB below) was in the range of 20–300 mg/L. At certain time intervals, a certain amount of mixture was withdrawn and the adsorbent was removed from the solution by centrifugation. The concentration of RhB was measured with a UV–vis recording spectrophotometer (Japan Shimadzu UV-2501 PC) at the wavelength 554 nm. With rGO and SnS as adsorbents, the similar process was conducted. The amount of adsorbate adsorbed per unit weight of adsorbent at time t (q_t, mg/g) was calculated by the following equation:

$$q_t = \frac{C_0 - C_t}{m} V \tag{1}$$

where C_0 (mg/L) represents the initial dye concentration, C_t (mg/L) is the concentration of the dye remaining in the solution at time t, V (L) is the volume of the aqueous solution, and m (g) is the weight of the adsorbent.

3. Results and discussion

3.1. The formation mechanism of SnS_2/rGO composite and XRD analysis

The hydrothermal synthesis of SnS_2/rGO nanocomposites was carried out using $SnCl_2{\cdot}2H_2O$ as both reductive agent and Sn resource, TAA as S resource. Because of negatively charged surface of GO in the suspension, Sn^{2+} can tightly adsorb onto GO surface via the electrostatic interaction. Then, the starting GO sheets were converted to rGO due to the strong reductivity of Sn^{2+}, which converted to Sn^{4+}. In the following process, the hydrolysis/dissociation reactions of TAA in the aqueous solution would generate sulfur ions and proceed faster at high temperature. The released S^{2-} will combine with Sn^{4+} in the acid aqueous solution, leading to the in situ formation of SnS_2 precipitate on graphene sheets (As shown in Scheme 1). The introduction of citric acid is to provide acid environment and control the size of SnS_2 [28]. The XRD pattern of the as-prepared product depicted in Fig. 1a shows diffraction peaks at 15.01°, 28.40°, 31.69°, 42.00°, and 50.08°, which corresponds to crystal indexes of (001), (100), (101), (102), and (110), respectively. All these diffraction peaks can be indexed to the hexagonal phase SnS_2 (JCPDS card No. 23-677). These results proved the formation of the SnS_2 in the nanocomposites. The weak additive peaks at 18.31° and 39.04° can be attributed to rGO and a small amount of SnS (JCPDS card No. 39-354), respectively. For comparison, the solid product prepared in a similar process except for GO is almost pure SnS with bits of SnS_2 (Fig. 1b), indicating that GO plays an important role for the formation of SnS_2.