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Original Research Paper

$ZnCo_2O_4$ nanorods as a novel class of high-performance adsorbent for removal of methyl blue

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ABSTRACT

Spinel $ZnCo_2O_4$ nanorods were synthesized by a simple template-free hydrothermal method in the presence of zinc chloride, cobalt chloride, glucose, and urea. The phase structure, morphology and chemical composition have been characterized by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and the corresponding selected area electron diffraction (SAED). The results showed that the typically porous and poly-crystalline structure was successfully grown on the surface of $ZnCo_2O_4$ nanorods. The $ZnCo_2O_4$ nanorods were further applied to remove methyl blue (MB), which was used as a model of organic pollutants in aqueous solution. In particular, the maximum equilibrium adsorption capacity of MB in $ZnCo_2O_4$ nanorods reaches up to 2400 mg/g, which is higher than that of most adsorbents. The adsorption isotherms and kinetics followed standard Langmuir and pseudo-second-order models, respectively. MB adsorption decreased with increasing solution pH at pH > 7 implying that MB adsorption on $ZnCo_2O_4$ nanorods may via chemisorption between negatively charged MB molecular and positively charged adsorption sites on the surface of $ZnCo_2O_4$ nanorods. This study provides great promise of using $ZnCo_2O_4$ nanorods as adsorbent for removal of pollutant dyes.

1. Introduction

Along with the modern science and technology development, wastewater generated by different industries, such as textile, printing, pulp and paper, has received significant attention in recent years [1–4]. In the past, many methods have been applied for removal of contaminants from wastewaters that include adsorption [5], oxidation [6], electrolysis [7], membrane separation [8], and electrocoagulation [9]. Among these techniques, adsorption is one of the most efficient and economical method. Many nanostructural materials have attracted great interest as the adsorbents due to their many unique chemical and physical properties [10,11]. For instance, Yttrium based metal organic framework was studied for potential removal of methylene blue at specific temperature because of its crystalline porous materials [12]. Liu et al. prepared adsorbent composites using three kinds of Fe_3O_4 nanoparticles as core. The saturation adsorption capacity of these composites for Rhodamine B (RhB) exceeds 177 mg/g at relatively optimal condition [13]. However, these adsorbents have its own limitations such as specific adsorption condition and slow rates of adsorption. Thus, it is need of time to research into the convenient adsorbent for the effective removal of dyes from wastewaters.

Recently, some researchers have been focused on zinc-based compound of $ZnCo_2O_4$ as zinc is cheap, abundant, and electrochemically active toward lithium [10,14–19]. Multifarious forms of $ZnCo_2O_4$, such as nanospheres, nanoflakes and nanorods, have been fabricated and applied abundantly in supercapacitors and Li-ion batteries [20–26]. For example, Chen et al. synthesized large-scale $ZnCo_2O_4$ nanospheres on anode materials for lithium-ion batteries, exhibiting excellent lithium-storage performance [18]. In addition, $ZnCo_2O_4$ can also store hydrogen with high capacity and good cycling stability, which is attributed to its abundant adsorption sites [21]. Combined with their large specific surface area, $ZnCo_2O_4$ has the potential to use as the dye adsorbent. However, the practical application of $ZnCo_2O_4$-based materials on dye adsorption has not been studied.

In this work, one-dimensional (1D) $ZnCo_2O_4$ nanorods were prepared by a simple template-free hydrothermal method at high

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temperature in the presence of cobalt salt as cobalt source. The aim of this work is to investigate the possibility of using $ZnCo_2O_4$ nanorods for the adsorption removal of organic pollutants. Methyl blue (MB) serves as a model compound of the harmful and water-soluble organic pollutants, which are widely used in textile industries and harmful to the environment. The adsorption equilibrium and kinetics studies were carried out and the effect of various parameters such as pH and initial dye concentration has been investigated. Moreover, possible adsorption mechanism of MB in $ZnCo_2O_4$ nanorods is proposed and discussed in detail. This may provide a novel glass of high-performance adsorbent for organic pollutant in further practical application.

2. Experimental section

2.1. Materials

Zinc chloride monohydrate ($ZnCl_2$), dextrose monohydrate glucose ($C_6H_{12}O_6 \cdot H_2O$) were bought from National Reagent Corp. (Shanghai, China). Cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and urea ($CO(NH_2)_2$) were obtained from Tianjin Damao Chemical Reagent Corp. (Tianjin, China). Methyl blue (MB) was purchased from Tianjin Tanggu Chemical Reagent Corp. (Tianjin, China). All chemicals used in the experiments were of analytical grade and without further purification.

2.2. Synthesis of $ZnCo_2O_4$ nanorods

One-dimensional $ZnCo_2O_4$ nanorods were synthesized using a simple hydrothermal method [27,28]. Typically, 0.01 M $ZnCl_2 \cdot H_2O$ and 0.02 M $CoCl_2 \cdot H_2O$ were added into 50 ml distilled water. Then, 0.01 M $C_6H_{12}O_6 \cdot H_2O$ and 0.1 M $CO(NH_2)_2$ were co-dissolved in the above solution, followed by vigorous magnetic stirring for 30 min. The derived solution was transferred into a 100 ml capacity autoclave followed by hydrothermal treatment at 180 °C for 20 h. After the autoclave cooled to room temperature, the obtained products were filtered and washed several times with deionized water and absolute ethanol, and then vacuum-dried at 60 °C for 12 h. Finally, the as-prepared precursor was calcined at 550 °C in air for 3 h with a heating rate of 1 °C min^{-1} to fabricate one-dimensional $ZnCo_2O_4$ nanorods.

2.3. Characterization

X-ray diffraction (XRD) measurement was conducted using an X-ray diffractometer (XRD, Rigaku D/Max 2500) with Cu Kα radiation (λ = 0.1540598 nm) from 5° to 80°. The particle size and microstructure of the samples were observed with a transmission electron microscope (TEM, FEI Tecnai G^2 F20 S-TWIN). The solid-state and chemical-state were measured using a Raman spectrometer (Renishaw, Invia Reflex) and Fourier transform infrared (FTIR, Nicolet6700). The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method based on the adsorption data.

2.4. Adsorption measurements

The adsorption property of $ZnCo_2O_4$ nanorods was investigated using MB as a representative dye. Each batch experiment was performed as follows: firstly, different concentrations of MB solutions (120–560 mg/L, 50 ml) were prepared and its pH value was adjusted to be in the range of 2–12 using HCl or NaOH solutions; secondly, the adsorbing material (5 mg) was added into MB solution with agitation for a certain time. During the adsorption process, the supernatant was withdrawn from the system by spinning them and the dye concentrations were monitored using an Ultraviolet–visible (UV–vis) spectrophotometer at the wavelengths of 601 nm. The equilibrium adsorption capacity (Q_e) was calculated using the following equation:

$$Q_e = \frac{(C_0 - C_e) \cdot V}{W} \quad (1)$$

where C_0 is the initial and equilibrium concentration of MB solution, V is the volume of MB solution, and W is the mass of MB. In this experiment, the solution volume V is 50 ml and the adsorbent mass W is 5 mg.

To further analysis the adsorption kinetics of $ZnCo_2O_4$ nanorods, the adsorption capacity at different times (Q_t) was calculated using the following equation:

$$Q_t = \frac{(C_0 - C_t) \cdot V}{W} \quad (2)$$

where C_t is the MB concentration at different times. In this experiment, the initial MB concentration C_0 is 180 mg/L, the MB solution volume V is 50 ml and the MB dosage W is 5 mg.

3. Results and discussion

The phase structures of synthesized $ZnCo_2O_4$ nanorods were measured by XRD and Raman spectrum, as displayed in Fig. 1. All reflection peaks are indexed to the standard XRD pattern for the spinel $ZnCo_2O_4$ (JCPDS 23-1390). The characteristic peaks corresponding to (2 2 0), (3 1 1), (4 0 0), (5 1 1), and (4 4 0) planes of cubic $ZnCo_2O_4$ are located at 2θ = 31.31°, 36.81°, 44.18°, 59.23°,

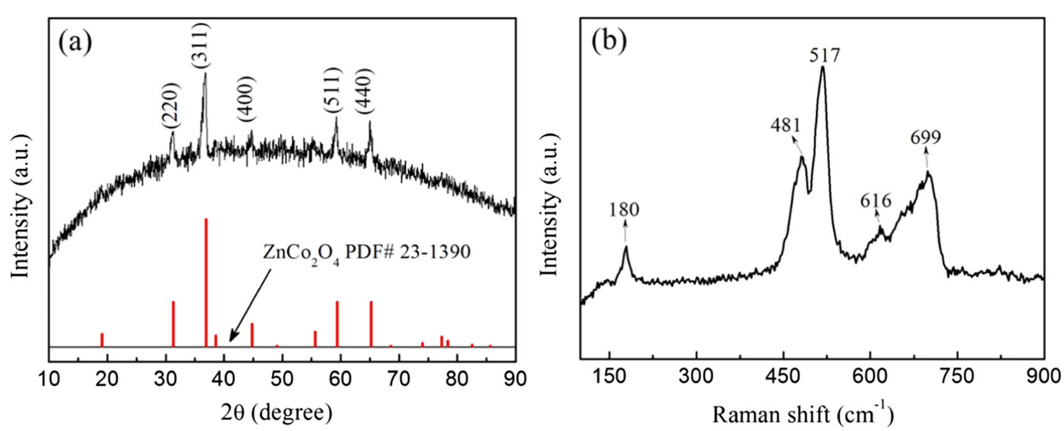

Fig. 1. (a) XRD pattern and (b) Raman spectra of $ZnCo_2O_4$ nanorods.