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A facial method to synthesize $Ni(OH)_2$ nanosheets for improving the adsorption properties of Congo red in aqueous solution

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ABSTRACT

A new and facial (low temperature and low cost) method for a direct synthesis of the stable and crystalline phase pure $Ni(OH)_2$ nanosheets was developed using cationic surfactant cetyltrimethylammonium bromide (CTAB). X-ray diffraction (XRD) analysis, Fourier transformed infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were used to examine the morphology and the microstructure of the obtained compound. The morphological study clearly revealed that obtained compounds appear in a flake-like nanosheet form with a typical length in the range of several hundreds of nanometers and a width in the range of several tens of nanometers. A possible formation mechanism is preliminary proposed for the formation of the nanostructure. The adsorption properties of $Ni(OH)_2$ nanosheets were tested by the adsorption of azo dye Congo red (CR). The results show an excellent removal capacity for organic pollutant CR from the wastewater, making them a promising candidate for wastewater treatment.

1. Introduction

The pollution of water owing to color effluents originating from various industrial capacities is a current problem worldwide [1–5]. Textile dyes and other industrial dyestuffs form one of the largest groups of organic compounds that represent an increasing environmental danger. Textile industry wastewater is known to contain considerable amounts of non-fixed dyes, azo dyes, and a quantity of inorganic salts [6]. The most of the dyes used in dyeing processes are released into the environment. For instance, azo dyes, the most important and frequently used for colorization in textile industries, endanger human health due to either toxic or mutagenic and carcinogenic effects [7]. They are very stable because of their complex aromatic structures, hence are difficult to degrade. Congo red (CR) is a typical and the first synthetic dye of anionic azo dyes, which is synthesized by coupling tetrazotised benzidine with two molecules of napthionic acid. The traditional physical and chemical pathways of the wastewater treatment often have a little or negligible removal effect on the CR azo dye pollutant. As the very promising method for the removal of azo dyes from the wastewater, adsorption and degradation are popular [8]. In the past few years, compounds such as nanoporous silica, hematite, γ-Fe_2O_3/SiO_2, $CuFe_2O_3$, mesoporous TiO_2, and activated carbon have been used to remove azo dyes [9–16]. Recently, nickel hydroxide compounds present a large interest in technical and industrial applications, for example, as a starting material to produce NiO [17], as active materials in electrochemical cycling (occurring in Ni–MH [18], Ni–Cd [19], Ni–Zn [20], Ni–Fe [21]), or as a photocatalyst to remove organic dyes [22,23] and photocatalytic H_2 [24]. Various synthesis methods for $Ni(OH)_2$ with different morphologies have been reported, such as tubes [25] and rods [26] by template synthesis, nanoribbon by hydrothermal treating [27], stacks of pancakes by a chemical precipitation method [28], hollow spheres by a simple solution chemistry method [29], sheet-like geometry by the hydrothermal method [29–31], and flower-like nanoarchitecture by a one-step mild hydrothermal reaction [32]. At the same time, materials with hierarchically multimodal pore size distributions have attached much attention, because they combine the advantages of high surface area micro- and mesoporosity with the readily accessible diffusion pathways of macroporous networks which also play a key role in the industrial processes, from adsorption to catalysis, catalytic supports, gas storage, purification, and separation [22,33–36].

In this paper, $Ni(OH)_2$ nanosheets were synthesized at room temperature using the cationic surfactant CTAB and the simple chemical reagents (hydrous nickel chloride ($NiCl_2 \cdot 6H_2O$ and NH_4OH)). This synthetic approach is a low-energy and environmentally benign green process because the post-calcinations or thermal treatments at high temperature are avoided. Comparing plentiful $Ni(OH)_2$ nanostructures synthesized with various methods, a little work has been carried out to investigate their adsorption properties so far. Consequently, additional studies are warranted in order to gain a better understanding of the factors governing the adsorption properties of $Ni(OH)_2$. With this aim, this work pays attention to the green synthesis of $Ni(OH)_2$

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nanosheets and discusses its application for removing Congo red in the wastewater treatment.

2. Experimental

The synthesis of $Ni(OH)_2$ nanosheets was performed at room temperature. The synthetic procedure was as follows: (1) CTAB was mixed with the distilled deionized water under vigorous stirring until a homogenous solution was obtained; (2) 10 mL NH_4OH (25 wt.% solution) was mixed with the distilled deionized water and then added into the CTAB solution under stirring; (3) when the mixing solution became homogenous, solution of $NiCl_2$ in the distilled deionized water was introduced, producing a white slurry. The molar ratio of $NiCl_2$:CTAB:H_2O was 1.0:0.5:156. The obtained mixture was further stirred for 4 h before being aged at room temperature for 48 h. The solid product was then recovered by filtration and washed with distilled water. Finally, $Ni(OH)_2$ powder was dried at 60 °C for several hours.

Powder X-ray diffraction (XRD) characterization was carried out with a Rigaku D/max-RB diffractometer using Cu K_α radiation ($\lambda = 1.5418$ Å). The sample characterized by XRD was scratched from the titanium plate. Fourier transformed infrared (FTIR) spectra, in the range of 4000–400 cm^{-1}, were recorded on a Perkin Elmer Spectrum GX infrared spectrophotometer. Scanning electron microscopy (SEM) images were recorded with an XL30ESEM-TMP microscope. The samples for SEM were prepared by dispersing the final powders in the conductive glue; such dispersion was then sprayed with carbon. Transmission electron microscopy (TEM) measurement was performed on a Zeiss EM 912Ω instrument at an acceleration voltage of 120 kV. N_2 adsorption–desorption isotherms at 77 K were recorded on a Belsorp-max automated sorption analyzer. The samples were outgassed for 20 h at 150 °C before the analysis.

Congo red ($C_{32}H_{22}N_6Na_2O_6S_2$, molecular weight: 696.67 g mol^{-1}, from Guangzhou Reagent Corporation, China) was used as a model dye to investigate the adsorption properties of $Ni(OH)_2$ nanosheets. The adsorption was carried out in an aqueous solution at ambient temperature using either as prepared $Ni(OH)_2$ nanosheets or for comparison commercial $Ni(OH)_2$ as absorbents. In a typical adsorption experiment, 5 mg of the $Ni(OH)_2$ nanosheets or commercial $Ni(OH)_2$ was added into 25 mL of Congo red aqueous solutions (CRS) with a concentration of 25 mg L^{-1} in a quartz beaker under stirring. 2 mL of the dispersion was extracted and subsequently centrifuged to separate $Ni(OH)_2$ and dye solutions at 3500 rpm for 10 min at different intervals. The changes of concentration of the centrifuged solutions were recorded by a UV-2401PC spectrophotometer. The concentration (C) of the centrifuged solution and the initial concentration (C_0) of the CR solution were monitored immediately by measuring the absorbance of the supernatant at 493 nm using a spectrophotometer (Model No. JH722N) and finally analyzed by a UV-2401PC spectrophotometer. The removal rate of the CR dye was calculated using the following relation:

$$R = \frac{C_0 - C}{C_0} \times 100\%. \tag{1}$$

3. Results and discussion

The XRD pattern of the as-synthesized $Ni(OH)_2$ compound is shown in Fig. 1(a). It reveals well-developed reflections of nickel hydroxide (ICDD PDF No. 14-0117), space group $F\bar{3}m1$ (164). No crystalline by-products such as CTAB, $NiCl_3$ or other nickel oxides are found in the pattern, indicating that the as-synthesized sample is pure $Ni(OH)_2$ with hexagonal crystal structure. FE-SEM micrograph, displayed in Fig. 1(b), clearly depicts that the morphology of $Ni(OH)_2$ compound is a nanosheet. Further investigation of $Ni(OH)_2$ morphology was performed with TEM. In Fig. 1(c), it is clear that the $Ni(OH)_2$ nanosheets are rather heterogeneous, which agrees well with FE-SEM finding. The selected area electron diffraction (SAED) pattern shown in the inset of Fig. 1(c) reveals the polycrystalline nature of $Ni(OH)_2$ nanosheet. Moreover, the well-developed lattice fringes visible in HRTEM image (Fig. 1(d)) also point to the good crystallinity of $Ni(OH)_2$ nanosheets. The space between the two adjacent lattice planes is 0.247 nm, indicating (101) lattice planes. For the sample prepared without CTAB, as shown in Fig. 1(e), the product is mainly composed of the particles. Considering the results of the above experiments, we concluded that, by this precipitation method, $Ni(OH)_2$ nanosheets could be fabricated in the presence of CTAB. CTAB plays an important role in the preparation of $Ni(OH)_2$ nanosheets.

Template-based systems are frequently used to control the nucleation and the growth of inorganic particles. In this approach, the template simply serves as a scaffold for in situ generation of different materials with the morphology complementary to the template. The anionic surfactant cetyltrimethylammonium bromide CTAB can combine with OH^- due to the action of Coulomb force. Then the CTAB can promote the formation of $NiOH^+$ and Ni^{2+} because of the combination of CTAB and OH^-. In aqueous solution, it is expected that CTAB molecules aggregate into a layer of structural micelles. As the basic unit for the growth of $Ni(OH)_2$ crystals, the small crystals can facilely grow and form the nanosheet structures in CTAB layer structural micelle template.

Fourier transform infrared (FTIR) spectroscopy was usually employed as an additional probe to evidence the presence of major functional groups including organic and inorganic species. FTIR of CTAB and $Ni(OH)_2$ nanosheets is shown in Fig. 2. The group of peaks in the range of 1600–500 cm^{-1} is attributed to the stretching mode of ions in CTAB. The strong peaks at 2920 cm^{-1}, and 2852 cm^{-1} together with a weak peak at 3020 cm^{-1} are assigned to $-CH_2$ and $-CH_3$, respectively [37]. The narrow and sharp band at 3642 cm^{-1} is the signature of the stretching vibrational mode of non-hydrogen-bonded, free hydroxyl groups (O–H) of the brucite-like sheet structure [38], while the broad band at 3432 cm^{-1} is characteristic of the stretching vibration of hydroxyl groups hydrogen-bonded to H_2O. The band at 1638 cm^{-1} can be assigned to the adsorbed water [17]. The weak appearance of 1465 cm^{-1} bands, is indexed to the C=O vibration of the acetate ions (CH_3-COO-). The peak at 1379 cm^{-1} can be attributed to a (NH_2) twisting vibration individually. FTIR spectrum also shows the presence of carbonate anions adsorbed on the surface of $Ni(OH)_2$ originating from atmospheric CO_2, as suggested from the weak broad peak at 1379 cm^{-1} [39]. The absorption bands at 522 cm^{-1} can be attributed to the (Ni–OH) vibration [17].

BET nitrogen adsorption–desorption isotherm measurements were performed to determine the specific surface area of as-synthesized $Ni(OH)_2$ nanosheets. The Brunauer–Emmett–Teller (BET) specific surface areas of as-synthesized $Ni(OH)_2$ nanosheets and commercial $Ni(OH)_2$ are 37.8, 10.3, and 12.1 $m^2\ g^{-1}$, respectively. It is believed that adsorption performances can be improved by increasing the specific surface area of the adsorption materials. Hence, the materials with nanosheets will provide more surface sites available for adsorption–dyes contact area and interface adsorption.

In order to test the adsorption performance of $Ni(OH)_2$ nanosheets, the adsorption of CR was carried out with aqueous $Ni(OH)_2$ nanosheets. The continuous UV–vis spectra of the centrifuged solution after adsorption reactions at different intervals were used to record and contrast with that of initial CR solution, which further clarify the removal performance and mechanism of Congo red. As seen in Fig. 3(a) and (b), three absorbance peaks at 234, 343 and 493 nm can be observed from the UV–vis absorbance spectrum of CR starting solution. The absorption spectra of the original CR solutions are characterized by one main band in the visible region with its maximum absorption at 493 nm corresponding to the azo bonds of the Congo red molecule, which is responsible for the dark red color of aromatic rings pertaining to azo groups [39,40]. The other two bands in the ultraviolet region located at 236 nm and 343 nm, are attributed to the benzene ring and