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Detection of carbon dioxide with a novel HPTS/NiFe-LDH nanocomposite

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ABSTRACT

Carbon dioxide (CO_2) is a major greenhouse gas, which is considered as a leading contributor to global warming and climate change. Therefore, the detection of CO_2 is highly important and beneficial for many applications. Layered double hydroxide (LDH) is considered as a good adsorbent for CO_2 with high adsorption selectivity and capacity. However, the adsorption capacities of CO_2 on LDH are usually investigated at high temperatures. And CO_2 adsorption is measured with bulky instrumentation, which exist the problems of high cost, long cycle, complicated test processes and unsuitability for real-time measurements of CO_2 gas. Herein, a new approach to rapid CO_2 detection is introduced using a novel HPTS/NiFe-LDH nanocomposite (8-hydroxypyrene-1,3,6-trisulfonicacid trisodium, HPTS) through a facile fluorescence technology at room temperature. In this paper, HPTS/NiFe-LDH nanocomposite was firstly synthesized through a facile one-step hydrothermal method. The HPTS/NiFe-LDH nanocomposite had no fluorescence with anionic dye HPTS intercalated into the cationic interlayer of NiFe-LDH. When CO_2 gas was gradually bubbled into the above system, $CO_3{}^{2-}$ ions were then intercalated into the interlayer of NiFe-LDH and anionic dye was released from NiFe-LDH, thereby leading to the fluorescence recovery of HPTS. The results indicated that fluorescence intensity was linearly related to the bubbling volumes of CO_2, suggesting that the HPTS/NiFe-LDH nanocomposite can be used as a sensor to selectively discriminate CO_2 gas, which provided not only a new route to rapidly detection of CO_2 but also a new application field of the hybrid LDH composites.

1. Introduction

Carbon dioxide (CO_2) is naturally present in the atmosphere, which is a major greenhouse gas. In recent years, the combustion of fossil fuels (coal or natural gas) releases large volumes of CO_2 into the environment, resulting into pollution problem, which have both acute and long-term toxicity to humans. The increasing atmospheric CO_2 concentration is of great concern to mankind, which is considered as a leading contributor to global warming and climate change [1,2]. Therefore, the detection of CO_2 is highly important and beneficial for many applications, including environmental monitoring, medical diagnosis, food packaging, agricultural production, and so on [3–6].

Layered double hydroxides (LDH), a family of two-dimensional anionic layered materials, have shown potential applications in catalysts, flame retardants, acid absorbents, drug delivery, anion sorbents, electro- and photoactive materials, and so on [7–10]. LDH have a host-guest structure, consisting of positively charged mixed metal hydroxide layers and anions located in the interlayer. Given their tunable layer composition, high chemical versatility and anionic exchange property, different types of anionic guest can intercalate into the cationic interlayer of LDH to form a hybrid LDH-based composite, which can enhance the thermal, optical, and physicochemical properties of LDH materials [11–14].

$CO_3{}^{2-}$ ions have a very strong affinity to LDH [15,16]. Thus LDH have been widely studied and used as adsorbents for CO_2 with high adsorption selectivity and capacity to prevent the emission of CO_2 into the ambient atmosphere [17–19]. However, the adsorption capacities of CO_2 on LDH are usually investigated at high temperatures. And CO_2 adsorption is measured with large instruments, which exist the problems of relatively long cycle, complicated test processes and unsuitability for real-time measurements of CO_2 gas [20,21]. How to find a facile, rapidly and low cost approach to rapidly detect CO_2 at room temperature condition?

On the basis of this hypothesis, herein, we developed a new approach to rapidly detection of carbon dioxide with a novel HPTS/NiFe-LDH nanocomposite through a facile fluorescence

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technology at room temperature. To the best of our knowledge, research on the detection of carbon dioxides applications of LDH-based nanocomposites has never been reported so far. The HPTS/NiFe-LDH nanocomposite was firstly synthesized through a facile one-step hydrothermal method. The obtained nanocomposite was systematically characterized. Then, the HPTS/NiFe-LDH nanocomposite was employed as a sensor to discriminate CO_2 gas selectively. The results indicated that fluorescence intensity was linearly related to the bubbling volumes of CO_2. Thus, the HPTS/NiFe-LDH nanocomposite could be employed as a sensor to discriminate CO_2 gas selectively. These findings showed that the proposed fluorescent method provided a facile, rapid, low-cost and powerful approach to detect CO_2 rapidly by using a novel HPTS/NiFe-LDH nanocomposite at room temperature. The proposed method could provide not only a new route to rapidly detection of CO_2 but also a new application field of the hybrid LDH composites.

2. Experimental

2.1. Materials

All the chemicals are of analytical grade and were used without further purification. 8-Hydroxypyrene-1,3,6-trisulfonicacid trisodium (HPTS) (Fig. 1) was purchased from Sigma Chemical Co. Ultrapure Milli-Q water ($\rho > 18.0\,\mathrm{M\Omega\,cm}$) was used throughout the fluorescence experiments.

2.2. Preparation of the HPTS/NiFe-LDH nanocomposite

HPTS/NiFe-LDH nanocomposite was prepared via a facile one-pot homogenously precipitation method. Typically, 98 mg of the sodium salt of HPTS was dissolved in 85 mL of decarbonated water. Then, $Ni(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, urea and trisodium citrate (TSC) were added into the aforementioned dye solution to give the final concentration of 16, 4, 35 and 2 mM, respectively. After purging with nitrogen gas for 20 minutes, the mixture was sealed in a Teflon-lined stainless steel autoclave and hydrothermally treated at 150 °C for 2 days. The resulting product was filtered and washed thoroughly with decarbonated water until the filtrate is colorless and the fluorescence of the filtrate was almost quenched. The product was then dried in air.

The HPTS/NiFe-LDH nanocomposite with different HPTS amounts was also prepared through the same procedure by changing the HPTS amount. The added HPTS amount was 11, 26, 98, 204 and 491 mg, and the composites were denoted as HPTS(11)/NiFe-LDH, HPTS(26)/NiFe-LDH, HPTS(98)/NiFe-LDH, HPTS(204)/NiFe-LDH and HPTS(491)/NiFe-LDH, respectively. For comparison, pure NiFe-LDH was also prepared followed the same procedure using $Ni(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, urea and trisodium citrate (TSC) but without addition HPTS.

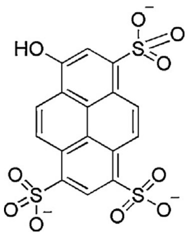

Fig. 1. The molecular structure of HPTS.

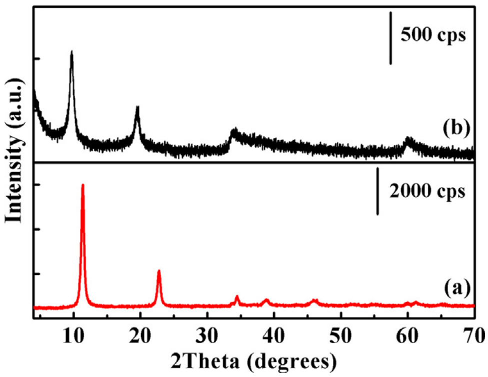

Fig. 2. XRD patterns of (a) pure NiFe-LDH and (b) the HPTS(98)/NiFe-LDH nanocomposite.

2.3. Characterization

X-ray diffraction (XRD) analysis was carried out with a D/Max2550VB+/PC X-ray diffractometer with Cu Kα ($\lambda = 0.15406$ nm), using an operation voltage and current of 40 kV and 30 mA, respectively. Fourier transform infrared (FT-IR) spectra were obtained on a Brucher EQUINX55 FT-IR spectrophotometer by a standard KBr disk method over the range of 400–4000 cm^{-1}. The surface morphologies of the obtained materials were observed by a field emission scanning electron microscope (FESEM, Hitachi, S-4800). The absorption and emission spectra were collected using a Shimadzu 1750 UV–visible spectrometer and a RF-5301 fluorescence spectrometer (Japan), respectively.

2.4. Fluorescence experiments

The as-prepared HPTS/NiFe-LDH nanocomposite was dispersed in ultrapure water and sonicated for 2 h until the composite dispersed homogeneously in the solution. Then, CO_2 gas was gradually bubbled into the aforementioned suspension at a constant rate of 3 mL/min. The sample was bubbled with CO_2 gas for 0.2 mL each time, and the supernatant was determined with fluorescence spectrophotometer. In all of the titration experiments, the total volume was maintained not exceed 5% of the original volume.

3. Results and discussion

3.1. X-ray diffraction analysis

The XRD patterns of pure NiFe-LDH and the as-prepared HPTS/NiFe-LDH nanocomposite are presented in Fig. 2. As shown in Fig. 2a, the XRD pattern of pure NiFe-LDH showed an obvious layered structure with a basal spacing of 0.78 nm, and no peaks of impurities were discerned, indicating the high purity of the product. The interlayer spacing of 0.78 nm is in accordance with the reported value for NiFe-LDH with CO_3^{2-} ions as interlayer anion [22,23]. In the case of the HPTS/NiFe-LDH nanocomposite, the XRD pattern also showed a layered structure, but the basal reflection (0 0 3) of the composite shifted to a low angle and the basal spacing increased from 0.78 to 0.91 nm (Fig. 2b). The increase of the basal spacing suggested that anionic dye HPTS was intercalated into the gallery of LDH and the HPTS-intercalated LDHs possess a larger interlayer distance compared to that of NiFe-CO_3^{2-} LDH.

3.2. FTIR spectra analysis

As shown in Fig. 3, the FTIR spectrum of NiFe-LDH exhibited the absorption bands at 3445 and 1641 cm^{-1}, which could be assigned to the stretching and bending vibrations of O—H, respectively. The