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One-step synthesis of magnetic and porous Ni@MOF-74(Ni) composite

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ABSTRACT

We demonstrated a facile and efficient method for the preparation of a magnetic and porous Ni@MOF-74(Ni) [Ni_2(DOBDC), DOBDC = 2, 5-dihydroxyterephthalate] composite by one-step solvothermal reaction of Raney Ni and DOBDC. Ni in the reaction not only acted as the core of the composite, but also provided metal source for the formation of MOF-74(Ni). The Ni@MOF-74(Ni) composite exhibits both magnetic characteristics and high porosity, enabling it an efficient candidate for dye removal and target drug delivery system. The adsorption amount of rhodamine b reached up to 177.8 mg g^{-1}, and 4.1 mg g^{-1} for ibuprofen.

1. Introduction

Metal-organic frameworks (MOFs) [1–3] are an emerging class of crystalline micro- and/or mesoporous materials constructed from metal or metal clusters interconnected by organic linkers. Due to their variety of applications in gas storage [4,5], adsorption [6] and catalysis [7–9], MOFs have been intensively investigated over the last two decades. Recently, hybrids comprising nanoparticle (NP) and MOF are attracting more and more attentions. NP/MOF composite can be prepared either by using MOFs as host matrix for in-situ generation of nanoparticles in cavities of MOFs [10–12] or by encapsulating pre-synthesized NPs into cavities of MOFs [13–15]. The composites often give rise to distinct properties from the single component due to their synergistic effects. Preparation of NP/MOF composites is a promising strategy to alter and/or modify the properties of single component for various applications [16]. In particular, synergistic effects have been observed in NP core@MOF shell for hydrogen storage [17] and in a variety of organic catalytic reactions [18,19]. In point view of the separation and recycle of NP-MOF composites, tedious and laborious centrifuging or filtering in both preparations and applications limits their practical applications.

Considerable efforts have been devoted in the past few years to couple magnetic NPs with MOFs for convenient separation and recycle using magnet [20]. Among various magnetic particles, iron oxides have received the most attention owing to their strong magnetic responsiveness and biocompatibility. Several methods have been reported for the syntheses of magnetic MOF hybrids or composites by integrating magnetic iron oxide particles into MOFs. For example, Fe_3O_4@[Cu_3(btc)$_2$] and Fe_3O_4@MIL-100(Fe) [Fe^{III}_3O(OH)$(H_2O)_2${$C_6H_3(CO_2)_3$}$_2$] core-shell microspheres were synthesized using a step-by-step assembly strategy by alternately dispersing metal ions and organic ligands on the mercaptoacetic acid (MMA) modified Fe_3O_4 microspheres [21–24]. Fe_3O_4@ZIF-8 core-shell structured composite was obtained by a solvothermal method using poly(styrene sulfonate sodium salt) or polyvinylpyrrolidone as a promoter [25,26]. Very recently, Wang et al. has synthesized Fe_3O_4@MIL-100(Fe) core-shells via in situ one-step hydrothermal reaction, in which Fe_3O_4 microspheres not only serve as magnetic cores but also provide Fe(III) source for MIL-100(Fe) synthesis [27]. As seen from literature, most magnetic NP-MOF composites were synthesized using nano-structured Fe_3O_4 as magnetic component, whereas for Fe_3O_4@MOF syntheses, it still involved multi-step manipulation.

Herein, we report a one-pot solvothermal method for synthesis of magnetic and porous Ni@MOF-74(Ni) [Ni_2(DOBDC), DOBDC = 2, 5-dihydroxyterephthalate] composite using Raney Ni and DOBDC, in which metal Ni not only acts as core component, but also provides Ni^{2+} for the formation of MOF-74(Ni). To the best of our knowledge, no such one-pot synthesis of magnetic NP@MOF composite has been reported yet. It is noted that partly thermal decomposition of MOF-74(Ni) led to Ni nanoparticles incorporated inside of MOF-74 matrix [16]. As-prepared Ni@MOF-74(Ni) composite exhibited both magnetic characteristic and high porosity, making it applicable as efficient adsorbent for removal of organic pollutants, e.g. rhodamine b dye (RhB). The adsorption amount in Ni@MOF-74(Ni) was determined to be 177.8 mg g^{-1} with an adsorption rate of 10 mg g^{-1}·min^{-1}. Furthermore, the magnetism of Ni@MOF-74(Ni) makes its separation and recycling use easily. This kind of magnetic and porous NP@MOF composite exhibits potential application for targeted drug delivery.

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2. Experimental

2.1. Reagents and instruments

All reagents and solvents were purchased from commercial sources and used without further purification: Raney nickel (Raney Ni, 20–40 mesh, dispersed in water, CAS: 7440-02-0) and rhodamine b (RhB, AR, CAS: 81-88-9) were purchased from Aladdin; 2, 5-dihydroxyterephthalate (DOBDC, 98%, CAS: 610-92-4) was obtained from Macklin; methanol (CH_3OH, AR, CAS: 67-56-1), tetrahydrofuran (THF, AR, CAS: 109-99-9) and trichloromethane ($CHCl_3$, AR, CAS: 67-66-3) were purchased from Sinopharm.

2.2. Preparation of Ni@MOF-74(Ni)

A solution of DOBDC (486.3 mg, 2.45 mmol) in THF (8 mL) was added to the aqueous suspension of Raney Ni (576.2 mg, 9.82 mmol) in 8 mL deionized H_2O, followed by ultrosonicating for 10 min. After stirring for 1 h, the reactant mixture was placed in 25 mL Teflon-lined stainless steel bomb under autogenous pressure at 110 °C for 3 days. After cooling down to room temperature, the product Ni@MOF-74(Ni) composite were collected from the reaction media by a magnet, and washed with deionized water and ethanol.

2.3. Test of calibration curve

The calibration curve was obtained from the UV-Vis spectra of standard solutions prepared by dilution of stock solution, which was used to determine the residual concentration of adsorbate in solution. For the interval, the calibration curve obeys the Beer-Lambert low:

$$A = 0.0989c_1 + 0.041 \quad (1)$$

$$A = 0.10096c_2 + 0.02817 \quad (2)$$

$$A = 2.97713c_3 \quad (3)$$

Where A is the absorbance, c_1 is the RhB concentration ($mg{\cdot}L^{-1}$) dissolved in $CHCl_3$ (Eq. (1), Fig. S1), c_2 is the RhB concentration ($mg{\cdot}L^{-1}$) dissolved in CH_3CH_2OH (Eq. (2), Fig. S2) and c_3 is the ibuprofen concentration ($mg{\cdot}mL^{-1}$) dissolved in $CHCl_3$ (Eq. (3), Fig. S3).

2.4. Adsorption experiments

The as-prepared Ni@MOF-74(Ni) composite was evaluated as an adsorbent towards dye pollutants by choosing RhB as a model molecule. All the spectra were recorded in a range of 220–650 nm with a UV-Vis spectrophotometer, in a 1 cm quartz cuvette. The strongest absorption peak of RhB at 553 nm was used as the reference wavelength. As-synthesized Ni@MOF-74(Ni) composite (10 mg) was immersed in 2.5 mL 20 mg L^{-1} solution of RhB in trichloromethane without any stirring and optical absorption spectra were recorded versus time. Upon uptake of RhB by the porous composite, the intensity of peak measured in solution decreased until it reached a plateau as adsorption equilibrium state. The adsorption process towards ibuprofen followed the same procedures as above, except that the adsorbate concentration was changed to 0.465 mg mL^{-1} in trichloromethane.

2.5. Desorption experiment

The solvent desorption was tested to evaluate the feasibility of regeneration the RhB saturated Ni@MOF-74(Ni). The Ni@MOF-74(Ni) composite (10 mg) after adsorption reached to equilibrium, was separated by magnet and washed with eluent to evaluate its reusability. In our experiment, ethanol was used as the eluent to regenerate Ni@MOF-74(Ni) composite.

2.6. Characterization

PXRD patterns were measured on a Rigaku MiniFlex 600 X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å). Gas adsorption isotherms were measured on a BEL sorp-max machine, BEL, Japan. Air-dried sample was activated in vacuum at 100 °C for 3 h. Both N_2 and H_2 sorption isotherms were measured at 77 K. SEM images were measured with a field emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV). The sample was pre-treated with Au-coating to improve conductivity. UV-Vis spectra of the solution for adsorption experiments were obtained using TU-1810 UV-Vis spectrometer.

3. Results and discussions

3.1. Discussion of system selection

In order to generate a magnetic MOF-based hybrid composite, the system selection was considered as following. With respects to the choice of Ni, as an inexpensive and active metal, metal Ni is easy to react with the mildly acidic ligand (DOBDC) to form Ni-based MOF. Porous Raney Ni is produced by leaching aluminum or zinc precursor (Ni-Al or Ni-Zn) alloy using caustic solution. It has been widely used as catalyst for industrial applications for decades [28]. With regards to the choice of framework materials, MOF-74 series is one of the most popular classes of MOFs with various properties and applications [29–31]. These MOFs are synthesized by combining M^{2+} ions (M = Zn, Mg, Ca, Ni, Fe, etc.) with DOBDC ligands. The resulting framework consists of a honeycomb-like structure with a large, cylindrical, one-dimensional channel (diameter of 11 Å) [32]. We expected that synergistic effect of magnetic active Raney Ni and porous properties of the MOF endowed the hybrid composite new properties and applications [16,18].

3.2. Structure and morphology characterization

3.2.1. XRD analyses

Powder X-ray diffraction (PXRD) pattern of the as-synthesized Ni@MOF-74(Ni) composite is shown in Fig. 1. All of the diffraction peaks of Ni@MOF-74(Ni) sample can be indexed to crystalline MOF-74(Ni) and metal Ni, in which the peak positions of Ni was noted by asterisks. And no peak of impurity can be detected in the PXRD patterns, confirming high purity of the obtained Ni@MOF-74(Ni) composite. The magnetic separability of the Ni@MOF-74(Ni) composite was examined in aqueous solution by approaching the vial with a magnet; we can see that the yellow powder was attracted toward the magnet immediately (Fig. S4).

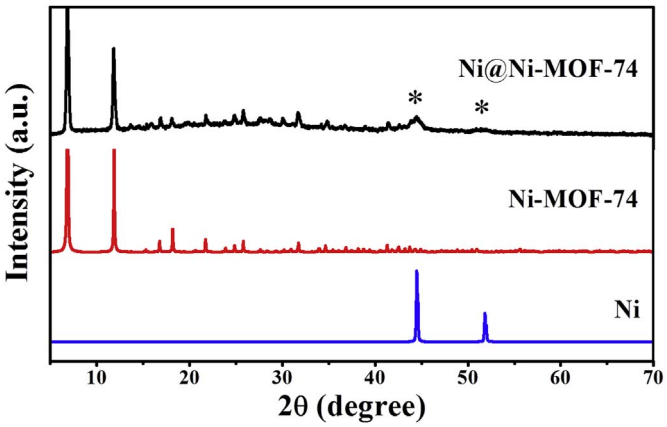

Fig. 1. PXRD patterns of as-synthesized Ni@MOF-74(Ni) (black), MOF-74(Ni) (red) and Raney Ni (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)