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ARTICLE TYPE

Fabrication of hybrid magnetic HKUST-1 and its high efficient adsorption performance for Congo red dye

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A facile and efficient strategy for the preparation of a hybrid magnetic metal-organic framework HKUST-1 via chemical bonding approach was reported. The composite features both magnetic separation characteristic and high porosity of MOF, making it an excellent adsorbent for removal of hazardous anionic Congo red dye from effluents.

As with zeolite materials,¹⁻⁴ metal-organic frameworks (MOFs) are a fascinating class of porous crystalline materials with many unique properties such as tunable pore sizes, high specific surfaces. Moreover, they can be more easily functionalized compared with zeolite materials.⁵ These outstanding features make MOFs promising for diverse applications, especially, in separation science.⁶⁻⁹ MOFs have been a focus of research concerning environmental purification.¹⁰⁻¹³ For example, the protonated ethylenediamine-grafted Cr-MIL-101 exhibited high adsorption capacity, rapid uptake and ready regeneration for the removal of methyl orange (MO).¹⁰ Fe-MOF-235 could be used as adsorbent for both cationic dye methylene blue (MB) and anionic dye methyl orange (MO).¹¹ However, these adsorbents are difficult to be separated from contaminated water, which limits their applications. Therefore, a simple and efficient synthetic method that can facilitate the separation of MOF-type adsorbent is required.

Multifunctional magnetic hybrid MOF materials have been a topic of growing interest as they involve both magnetism and porosity in one material. In this aspect, a controllable manner by using Fe₃O₄ nanoparticles as the core through a versatile layer-by-layer strategy has been reported for the synthesis of magnetic hybrid MOF material.¹⁴⁻¹⁵ However, it is difficult to control the heterogeneous growth of MOF crystals on the magnetic microparticles. Recently, Park and co-workers reported that the functional proteins can be grafted onto the surface of MOF through the bioconjugation,¹⁶ which indicates that it is possible to efficiently functionalize the MOF materials via chemical interaction with the groups exposed on the surface of the MOF.¹⁷

In this article, we demonstrated a facile method to fabricate magnetic hybrid MOF-type material through the decoration of Fe₃O₄@SiO₂ core-shell microparticles on the surface of MOF materials via chemical bonding approach. HKUST-1 was selected as an example of MOF materials due to its attractive features, such as high surface area, large pore windows, excellent chemical and solvent stability.¹⁸⁻²⁰ The Fe₃O₄@SiO₂ microparticles were

firstly functionalized with amino groups (named Fe₃O₄@SiO₂-NH₂), which can then react with the pendent carboxyl groups on the surface of HKUST-1. Figure 1 shows the fabrication process of the hybrid magnetic HKUST-1 material. The magnetic MOF composite obtained through the chemical bonding method has desired chemical uniformity, permanent magnetism, high removal efficiency for Congo red dye and could be reused for several times.

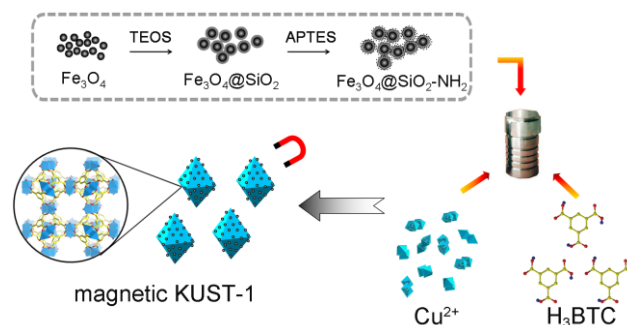


Figure 1. Schematic of fabrication process of hybrid magnetic HKUST-1 material.

Structure and phase purity were studied by powder X-ray diffraction (XRD) analysis. Figure 2a shows the simulated XRD pattern of HKUST-1 generated based on the reported crystal structure data.¹⁸ The experimental XRD pattern of the as-prepared HKUST-1 (Figure 2b) is consistent with the simulated one, indicating the as-prepared product is pure phase. In XRD pattern of Fe₃O₄@SiO₂-NH₂ microparticles (Figure 2c), the strong peaks appeared at 30.0°(220), 35.2°(311), 42.9°(400), 56.9°(511) and 62.5°(440) are characteristic peaks of Fe₃O₄ (JCPDS card, file no. 89-4319), suggesting the stability of crystalline phase of Fe₃O₄ during silica coating and surface amino modification. The broad peak at 20-30° in figure 2c can be attributed to the amorphous silica shell. In XRD pattern of hybrid magnetic HKUST-1 (Figure 2d), besides the peaks for HKUST-1, the other peaks all come from Fe₃O₄@SiO₂-NH₂, suggesting the decoration of Fe₃O₄@SiO₂ on HKUST-1 does not affect the crystal structure of the MOF. Figure 3 shows the room-temperature magnetization curve hybrid magnetic HKUST-1. The saturation magnetization values for hybrid magnetic HKUST-1 is 2.27 emu g⁻¹, which can meet the requirement for magnetic separation of the adsorbent from solution.

The chemical structure of the as-prepared material was characterized by FTIR and shown in Figure S1. The peak at 570 cm^{-1} is a characteristic peak of Fe_3O_4 . The peaks at 1097 cm^{-1} and 1574 cm^{-1} can be assigned to the Si-O and N-H groups. The peaks at 1374 cm^{-1} , 1451 cm^{-1} and 1645 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of carboxylate groups in 1,3,5-benzenetricarboxylic acid (H_3BTC).²¹⁻²² The results prove that the hybrid composite has been prepared successfully. A thermogravimetric (TG) analyzer was used to evaluate the thermal stability, which revealed that the hybrid magnetic HKUST-1 was stable up to $350\text{ }^\circ\text{C}$ (Figure S2). Nitrogen adsorption-desorption isotherm of HKUST-1 and hybrid magnetic HKUST-1 were measured on ASAP 2020 V3.02 micromeritics surface and porosity analyzer as shown in Figure S3. The BET surface area for HKUST-1 is calculated to be $1316\text{ m}^2\text{ g}^{-1}$ with a pore volume of $0.590\text{ cm}^3\text{ g}^{-1}$. For hybrid magnetic HKUST-1, the BET surface area and the pore volume are $1134\text{ m}^2\text{ g}^{-1}$ and $0.508\text{ cm}^3\text{ g}^{-1}$, respectively, which implies that the surface modification strategy does not affect the pore property of the MOF seriously.

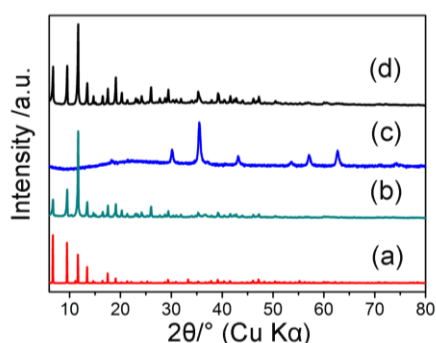


Figure 2. Powder XRD patterns of (a) HKUST-1 stimulated from crystallographic data, (b) as-prepared HKUST, (c) $\text{Fe}_3\text{O}_4@SiO_2-NH_2$ microparticles, and (d) hybrid magnetic HKUST-1.

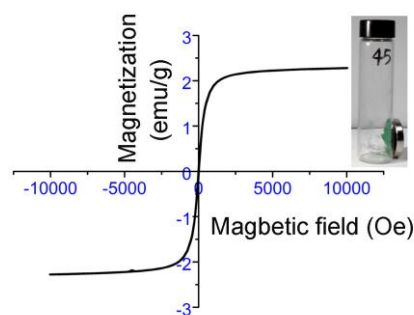


Figure 3. Magnetization curve of the hybrid magnetic HKUST-1 at room temperature.

The morphology and structure of as-prepared core-shell $\text{Fe}_3\text{O}_4@SiO_2$ microparticles were characterized by SEM (Figure 4A) and TEM (Figure 4B). The microparticles are circular-shaped with a magnetic core of about 200 nm and a thin silica layer of 20 nm . The SEM images of HKUST-1 (Figure 4C) and hybrid magnetic HKUST-1 (Figure 4D) clearly demonstrate that the surface of HKUST-1 has been decorated by $\text{Fe}_3\text{O}_4@SiO_2$ microparticles successfully. However, there are still some bare $\text{Fe}_3\text{O}_4@SiO_2$ microparticles unbound to HKUST-1 due to the incomplete reaction. Figure S4 shows the TEM image of the

hybrid magnetic HKUST-1 material.

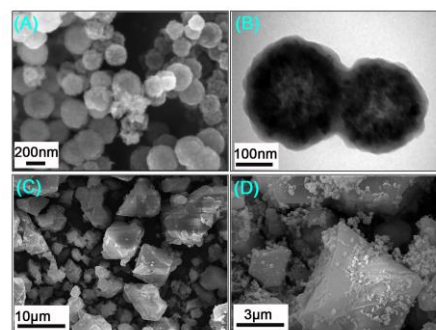


Figure 4. (A) SEM image and (B) TEM image of $\text{Fe}_3\text{O}_4@SiO_2$; (C) SEM images of HKUST-1 and (D) hybrid magnetic HKUST-1 materials.

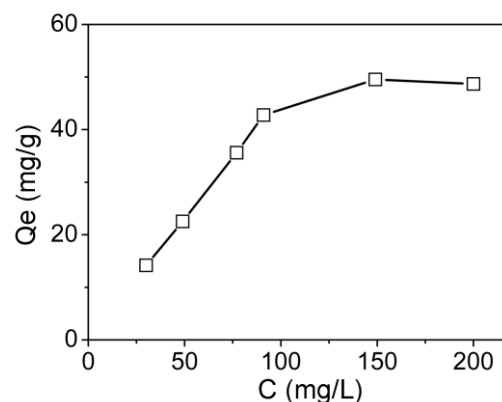


Figure 5. Adsorption isotherm of hybrid magnetic HKUST-1 for various concentrations of Congo red.

The Congo red adsorption performance of the hybrid magnetic HKUST-1 was analyzed by UV-visible spectrophotometer at the wave length of 497 nm . The maximum adsorption capacity of hybrid magnetic HKUST-1 is 49.5 mg/g (Figure 5), which lies between the maximum adsorption capacity of pure HKUST-1 (58.3 mg/g , Figure S5A) and amino functionalized $\text{Fe}_3\text{O}_4@SiO_2$ (45.5 mg/g , Figure S5B). Figure 6 shows the results of the sorption and desorption circulatory experiments. The maximum adsorption amount of Congo red at the end of 15 min was 98% at pH of 7 (Figure 6A), indicating that Congo red was almost completely removed from the aqueous solution. The hybrid magnetic HKUST-1 material could keep high removal efficiency (above 90%) for Congo red for at least four cycles (Figure 6B). The results of the recycling experiments confirm that the as-prepared hybrid magnetic HKUST-1 is an efficient adsorbent for the removal of Congo red pollutant and can be reused for several times. The diameter of Congo red molecule is estimated to be approximately 21 \AA ,²³ which is much greater than the pores of HKUST-1 (9 \AA).¹⁸ Therefore, the Congo red dye is mainly adsorbed on the surface of HKUST-1. The XRD patterns of hybrid magnetic HKUST-1 dispersed in water and ethanol without Congo red for different time are shown in Figure S6, revealing that the structure of hybrid magnetic HKUST-1 is chemically stable in pure water and ethanol. The XRD patterns of hybrid magnetic HKUST-1 before and after sorption and desorption circulatory experiments are shown in Figure S7, which indicate that part of HKUST-1 framework in the hybrid magnetic HKUST-1 material collapses.

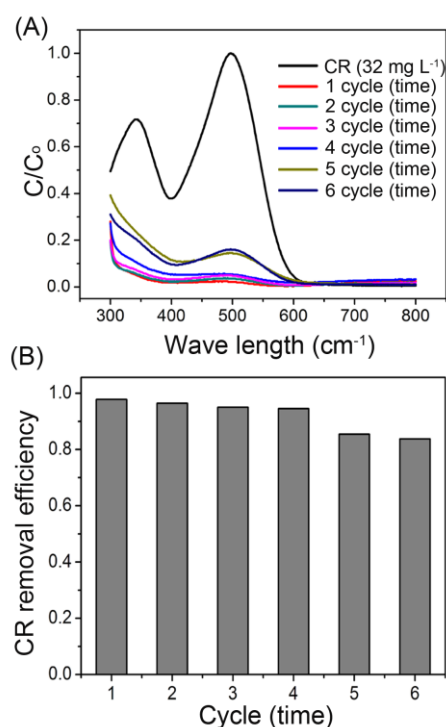


Figure 6. (A) UV-vis adsorption spectra of Congo red containing solution at different stage; (B) Cycle measurements of hybrid magnetic HKUST-1 for the adsorbent of Congo red. ($T = 298 \text{ K}$, Congo red = 32 mg L^{-1} , time = 15 min, $\text{pH} = 7$).

In summary, we demonstrated a simple and efficient strategy for the fabrication of a hybrid magnetic metal-organic framework HKUST-1 via chemical bonding formed between the amino functionalized $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ microspheres and the surface of metal-organic framework. The hybrid HKUST-1 material possesses desired chemical stability and permanent magnetism, which also features superior adsorption capacity for Congo red dye, magnetic separation ability and could be reused six times with little or no loss in adsorption performance. This method provides a promising way for designing and synthesizing novel kind of adsorbent for environmental purification.

Experimental

Preparation of monodisperse Fe_3O_4

Magnetic Fe_3O_4 microparticles were prepared by one-pot hydrothermal method.²⁴ 0.54 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2 mmol), 1.03 g of sodium citrate ($\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$) (4 mmol) and 0.36 g of urea (6 mmol) were dissolved in 40 mL distilled water. Then 0.3 g of polyacrylamide (PAM) was added under continuous stirring until a clear solution was obtained. The solution was then sealed in a 50 mL Teflon-lined autoclave and heated at $200 \text{ }^\circ\text{C}$ for 12 h. The black precipitation was collected with a magnet, washed with distilled water and absolute ethanol for several times, and dried overnight at $60 \text{ }^\circ\text{C}$ under an air atmosphere.

Preparation of magnetic $\text{Fe}_3\text{O}_4@/\text{SiO}_2$

The silica-coated magnetic Fe_3O_4 microspheres were synthesized according to the modified stöber method.²⁵ 0.5 g of the as-prepared Fe_3O_4 microspheres was first treated with 100 mL 0.1 M

HCl aqueous solution under ultrasonication, then washed with ultrapure water for three times. The collected Fe_3O_4 microspheres were re-dispersed in a mixture of ethanol (160 mL), ultrapure water (40 mL) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (2.5 mL, 25–28%). After ultrasonication for 10 min, 1 mL TEOS was added to the solution, and the reaction was allowed to proceed under mechanical stirring for another 12 h. The obtained particles were collected with a magnet, washed with ethanol and ultrapure water.

Preparation of the amino functionalized $\text{Fe}_3\text{O}_4@/\text{SiO}_2$

Amino functionalized $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ ($\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-NH}_2$) microparticles were obtained by surface modification using APTES as the silylation agent.²⁶ 0.3 g of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ was dispersed in ethanol (60 mL). Then APTES (600 μL) was added under ultrasonication, and the reaction was allowed to proceed under mechanical stirring for 7 h at room temperature. The resulting functionalized $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ samples were collected with a magnet, washed with ethanol and ultrapure water for several times, and drying at $60 \text{ }^\circ\text{C}$ overnight under an air atmosphere.

Preparation of hybrid magnetic HKUST-1

0.217 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.90 mmol) was dissolved in 3 mL ultrapure water and 0.105 g of H_3BTC (0.50 mmol) was dissolved in 3 mL ethanol. The two solutions were mixed and stirred for 20 min. 0.01 g of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ was dispersed in the above solution under ultrasonication for 20 min. Then the homogeneous mixture was sealed in a 15 mL Teflon-lined autoclave and heated at $120 \text{ }^\circ\text{C}$ for 12 h. The obtained blue crystals were filtered, washed several times with ultrapure water and ethanol, and then dried overnight at $60 \text{ }^\circ\text{C}$ under an air atmosphere.

Sorption and desorption circulatory experiments

Water and ethanol were used as solvent for the sorption and desorption of Congo red, respectively. For the sorption experiment, 10 mg of as-prepared hybrid magnetic HKUST-1 was placed in a 15 mL glass vial, then 5 mL of Congo red aqueous solution (32 mg L^{-1}) was added to the vial. The mixture was sonicated for 15 min at room temperature, then a magnet was attached to the glass vial so that the adsorbent can be separated and the solution was removed out to analyze. For the desorption of Congo red, the adsorbent was redispersed in 2 mL of ethanol under sonication for 30 s, separated with a magnet and washed with distilled water. The adsorbent was finally separated and dried, and reused for adsorption experiment. The removal efficiency was calculated according to the following equations:

$$\text{removal efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 and C are the initial and final concentrations of Congo red. In order to determine the maximum adsorption capacities of pure HKUST-1, amino functionalized $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ and hybrid magnetic HKUST-1, 10 mg of the different adsorbent was added to Congo red solution with various concentrations (30 mg L^{-1} , 49 mg L^{-1} , 77 mg L^{-1} , 91 mg L^{-1} , 150 mg L^{-1} , and 200 mg L^{-1}).

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Notes and references

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