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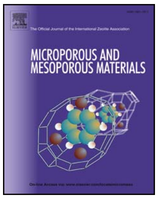

Synthesis and properties of ferrocene confined within UiO-67 MOFs

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ABSTRACT

Ferrocene was encapsulated into the cavities of the metal-organic framework UiO-67 using a solvent-free evaporation method. The obtained host-guest compounds were characterized by XRD, TEM, EDS, TG, XPS, N_2 adsorption-desorption, magnetic hysteresis and cyclic voltammetry studies. The results show that the micropores of UiO-67 are successfully occupied by ferrocene molecules and the ferrocene@UiO-67 composite shows an interesting ferromagnetic behavior at room temperature. Both the oxidation and reduction peak are observed in cyclic voltammograms due to the reversible conversion between Fe^{2+} and Fe^{3+} of ferrocene confined within UiO-67 framework. The results reveal that the novel properties of ferrocene embedded inside MOFs carries a substantial potential with regard to the synthesis of ferro-magnet or catalytic materials.

1. Introduction

Ferrocene is a sandwich compound composed of a pair of planar cyclopentadienyl ring of 6p-electrons and 6d-electrons on Fe(II) atom [1–4]. Ferrocene is capable of engaging in electron transfer processes. Therefore, ferrocene has frequently been used as an electron transfer mediator for various electro-catalytic reactions. Previous studies have demonstrated that hollow structures (cages, bowls, capsules etc.) with nanometer-sized cavities have ability to encapsulate large guest molecules and can regulate specific reactions inside the cavities. In particular, encapsulation of ferrocene in carbon nanotubes (NTs) can combine both advantages of NTs and novel properties of ferrocene. The electronic properties of ferrocene-filled NTs are greatly modified due to the charge transfer between ferrocene molecules and NTs [5]. Intercalation and exfoliation of graphene oxide using covalently attached ferrocene was achieved and the composites showed interesting magnetic behavior [1]. Recently, the organometallic host-guest chemistry of porous crystalline organic frameworks (COF) was studied by infiltration of ferrocene. The structure of the inclusion compound $(FeCp_2)_4$@COF-102 has a unique arrangement of $FeCp_2$ molecules which replicates the host structure [6]. These works extend the scope of these new classes of low dense materials for possible applications in the fields like catalysis and sensing.

Metal-organic frameworks (MOFs) with high surface areas and well-defined pore structures have been demonstrated as novel functional and robust materials because of their designable framework structures modularly built from metal clusters as nodes and organic ligands as struts [7–10]. Recent work on host-guest chemistry of MOFs is mostly focused on desorption and storage features of small gas molecules, i.e. CO_2, H_2, CH_4 and NH_3 as guests inside MOFs. In view of developing molecular-based switching systems, control of large guest molecular motions inside the cavity by external stimuli is an attractive task. $FeCp_2$($\sim$5 Å diameter) is an ideal probe molecule for adsorption studies due to its chemical and thermal robustness [11–15].

In this work, we have started a study to investigate the host-guest chemistry of MOFs by introducing volatile ferrocene using the solvent-free gas phase infiltration method. The result reveals that the redox properties of ferrocene embedded inside MOFs are very interesting and carries a substantial potential with regard to the synthesis of ferro-magnet or catalytic materials. Herein, we choose UiO-67 as the presentative example of host materials. UiO-type MOFs (UiO stands for University of Oslo), which is composed of $\{Zr_6O_4(OH)_4\}$ oxo cluster nodes and dicarboxylate linkers, are known for their excellent thermal and chemical stabilities [16–23]. Among these types of MOFs, UiO-67 crystal is based on the $Zr_6O_4(OH)_4$ building unit, forming lattices by a 12-fold connection through the biphenyl dicarboxylic acid (BPDC) linkers, resulting in a face centered cubic (f c c) structure (a = 27.1 Å). The structure of UiO-67 contains two types of cages: an octahedral cage (Φ ~18 Å) that is face sharing with 8 tetrahedral cages (Φ ~ 11.5 Å) [17,19], as showing in Scheme 1.

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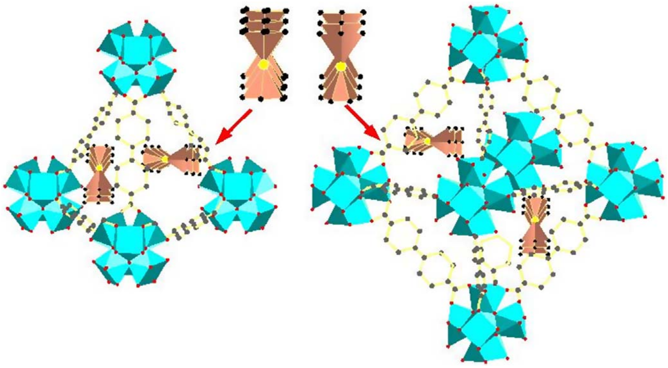

Scheme 1. Illustration of ferrocene confined in UiO-67 MOFs.

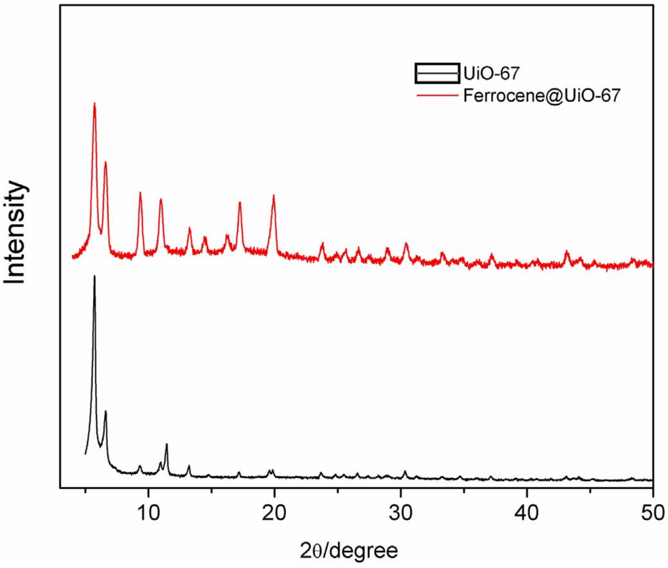

Fig. 1. XRD patterns of UiO-67 and ferrocene@UiO-67.

2. Experimental

2.1. Synthesis of UiO-67

Synthesis of UiO-67 was performed by dissolving 1.2 mmol of zirconium (IV) chloride ($ZrCl_4$), 1.2 mmol of 4,4′-Biphenyl dicarboxylic acid (H_2BPDC) and 30 equivalents of acetic acid (CH_3COOH) in 30 mL of N,N-dimethyformamide (DMF) at room temperature. The mixture was placed in a 100 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 48 h. The product was cooled to room temperature, washed three times with DMF, and dried at room temperature. Excess H_2BPDC and DMF in the pores were removed using a high temperature treatment at 300 °C for one day. A pale yellow powder was obtained.

2.2. Synthesis of ferrocene @UiO-67

150 mg of dry and activated UiO-67 and 300 mg of ferrocene were placed in two separate glass boats in a Schlenk bottle. The bottle was then evacuated to 10^{-3} mbar for 5 min and sealed. The reaction bottle was kept at 110 °C for 72 h.

2.3. Physical measurements

X-ray powder diffraction (XRPD) patterns were recorded using a PANalytical X'Pert powder diffractometer with CuKα radiation. Transmission electron microscope (TEM) measurement was performed by use of a FEI Tecnai G2 F20. Thermogravimetric analysis (TGA) were performed using a Simultaneous Thermal Analyzer (STA 449C, NETZSCH) in the temperature range between 30 °C and 800 °C in a N_2 atmosphere. X-ray photoelectron spectroscopy (XPS) was measured with Thermo Escalab 250Xi. Nitrogen adsorption/desorption isotherms were measured at 77 K using surface area and pore size analyzer (3H-2000PS2). The magnetic properties of sample were determined using a vibrating sample magnetometer (VSM, VersaLab, Quantum Design) at room temperature.

2.4. Electrochemical measurements

5 mg of ferrocene@UiO-67 powder was dispersed in a 1 mL mixture of distilled water and ethanol (3: 1 v/v). Then, 10 mL of 5 wt% Nafion was added to the above mentioned solution. The mixed solution was sonicated for at least 30 min to form a homogeneous ink. 5 mL of the mixed solution was drop-cast onto a glassy carbon electrode with a diameter of 5 mm for the electrochemical measurements. All the electrochemical measurements were performed on an electrochemical workstation (CHI 660E, CHI Instruments Inc., Shanghai) using a typical three-electrode mode with an electrolyte solution of 6 M KOH, a Pt counter electrode, an Ag/AgCl (saturated KCl) reference electrode, and a modified glassy carbon working electrode. For comparison, the electrochemical measurements of UiO-67 and blank glassy carbon electrode as work electrode were performed under the same conditions.

3. Results and discussion

Powder X-ray diffraction patterns (Fig. 1) of ferrocene@UiO-67 suggested that the crystal structure of UiO-67 is maintained without damage when ferrocene molecules are encapsulated into the cavity of UiO-67. Inspection of the PXRD-data reveals that all peaks are at the same position of the pristine powder, which indicates that no contraction or change in the symmetry of the crystals happens due to the rigidity of UiO-67. A change in Bragg peak intensity at low angle was noticed, which can be associated to the presence of ferrocene molecules within the pores of UiO-67. This is explained by taking account of scattering factors due to loading of ferrocene. Moreover, the powder pattern did not show any reflections corresponding to $FeCp_2$, which rules out the presence of crystals of $FeCp_2$ outside the framework.

TEM (Fig. 2) show that the framework of UiO-67 are maintained by the loading of ferrocene, which exhibit a well-defined mono disperse octahedral microcrystals with particle size in the range of 150–300 nm. The element composition of the sample is qualitatively determined by EDS attached to TEM. Confine of ferrocene within UiO-67 was further confirmed by EDS analysis of ferrocene@UiO-67 which showed the presence of Fe peaks in the spectrum (Fig. 2c). The relative atomic percentage of 0.19%, 90.72%, 6.34% and 1.49% for Fe, C, O and Zr respectively were obtained by the EDS analysis (Table 1). Moreover, the EDS mapping of ferrocene@UiO-67 (Fig. 2f) also confirms that the ferrocene are uniformly distributed in the frameworks.

Fig. 3 shows the thermal behavior of ferrocene in UiO-67 framework. The thermogravimetric analysis (TGA) profile of ferrocene@UiO-67 exhibits no weight drop until 110 °C. Above 110 °C, there was a 25% weight loss until temperature reached 280 °C, which was attributed to the release of ferrocene from the UiO-67 channels. The curve shows a

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