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> Advance Publication on the web November 3, 2018 doi:10.1246/bcsj.20180237

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Preparation of Bimetallic Metal-Organic Framework Microflowers by Spray Method

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Abstract

The NiCo-MOF microflowers are fabricated by a rapid spray method, which are assembled by 2D NiCo-MOF nanosheets with uniform crystal morphology and homogeneous dispersion of Ni and Co. Because of their large exposed active sites and nanoscale thickness, the NiCo-MOF microflowers exhibit good catalytic performance for the reduction of 4-nitrophenol.

Keywords: bimetallic metal-organic framework, spray method, microflower

1. Introduction

Owing to large exposed surface area and convenient charge transfer, the microflower materials are highly desirable for their good applied prospects in the fields of sensing^[1],

catalysis^[2] and analytical science^[3]. The microflower structure is one of the typically hierarchical nanostructures which is formed by the integration of nanobuilding blocks with the combination of appropriate order^[4]. At present, the nanobuilding blocks of microflower materials are mainly metal-organic frameworks (MOFs), metal oxides and inorganic salts^[5]. Among them, MOFs have attracted more and more attentions, ascribing to their diverse chemical composition, coordination structure and porous architectures. MOFs are a class of organic-inorganic hybrid porous materials, which are formed by metal ions and organic ligands through coordination bonds^[6,7]. Moreover, the MOF microflowers provide a feasible means to combine the merits of both 2D and 3D materials with 2D MOF nanosheets as building blocks. Such kinds of structures not only offer a stable framework for immobilizing individual 2D nanosheets, but also inherit all the advantageous



Scheme 1. The schematic illustration of the fabrication process of NiCo-MOF microflowers by spray method.

2D MOF nanosheets as building blocks. Such kinds of structures not only offer a stable framework for immobilizing individual 2D nanosheets, but also inherit all the advantageous features of 2D materials, such as high surface-to-volume ratios, highly exposed active sites and excellent charge transport capability^[8]. For example, Yuan, Chen and co-workers reported the flower-like ferrocene confined MOFs show high sensitivity in an electrochemical immunsensor for amyloid- β detection, which is fabricated by solvothermal method^[9]. Zou, Zhao and co-workers reported the hybrid flower-like boron nitride nanosheets/MOFs show an enhanced catalytic activity in the acetalization of benzaldehyde owing to facilitated diffusion process in the hierarchical microflower structure^[10].

Benefiting from the synergistic effects of compsite materials, bimetallic MOFs with uniform dispersion of bimetallic active sites have gained considerable attention^[11]. Two species of metal are incorpotated during the crystallization process to synthesize a homogeneous bimetallic MOF, which provides excellent synergistic effects due to the uniform distribution of bimetallic nodes in integral MOF structures. According to the research of Wang's group, the NiCo-MOF catalyst showed a much better catalytic hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol comparing with individual Ni or Co MOF-derived catalysts^[12]. However, it is still a great challenge to construct bimetallic MOF microflowers by a facile method.

In this paper, a rapid and feasible spray method is presented to fabricate bimetallic MOF (NiCo-MOF) microflowers under mild conditions^[13,14]. The fabrication process is illustrated in Scheme 1, metal ion solution of two kinds of metal ions (Ni²⁺ and Co²⁺) are atomized to small droplets, then uniformly sprayed on surface of the organic ligand (1,4-benzenedicarboxylic acid, H₂BDC) solution. Bimetallic metal ions and the organic ligand were formed crystal nucleus, with the process of anisotropic growth led to the morphology of 2D MOF nanosheets and ultima flower-like structure. Owing to their large exposed surface areas with bimetallic active sites, the NiCo-MOF microflowers showed good catalytic performance in the reduction of 4-nitrophenol (4-NP).

2. Experimental

Materials. Cobalt acetate tetrahydrate [Co(OAc)₂·4H₂O], nickel acetate tetrahydrate [Ni(OAc)₂·4H₂O], 1,4-benzenedicarboxylic acid (H₂BDC), N,N-dimethylformamide (DMF) and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. Sodium borohydride (NaBH₄) and 4-nitrophenol (4-NP) were purchased from Alfa Aesar. Pure water was purchased from Shenyang Wahaha Group Co. Ltd. All reagents and solvents were used without further purification.

Characterization. The scanning electron microscopy (SEM) images and the energy-dispersive X-ray (EDX) elemental mapping images were obtained by Hitachi SU8010. X-ray diffraction (XRD) patterns were recorded by Shimadzu XRD-6000 with Cu K α 1 ($\lambda = 1.54$ Å) radiation. Fourier transform infrared spectra (FT-IR) were recorded by a Bruker VERTEX 70. Thermogravimetric analysis (TGA) was carried out with a thermobalance (TGA-2050, TA Instruments) under N₂ from room temperature to 800 °C with a temperature ramp of 10 °C/min. The ultrasonic generator (DP30) and the nozzle (ZPQ-S-95) were manufactured by Siansonic Technology Ltd. The UV-Vis spectra were obtained by Maya2000 pro optic spectrometer.

Preparation of NiCo-MOF. The NiCo-MOF

macroflowers were fabricated by spray method under mild conditions. Bimetallic salts and H₂BDC were respectively dissolved in а ternary mixed solvent of N.N-dimethylformamide (DMF), ethanol and water (V:V:V=16:1:1), the concentrations of $Ni(OAc)_2 \cdot 4H_2O$, Co(OAc)2·4H2O and H2BDC were 0.028 mol·L-1, 0.056 mol·L⁻¹, 0.083 mol·L⁻¹, respectively. The NiCo-MOF microflowers were obtained by sparying 0.6 mL bimetallic solutions onto the 4.5 mL H₂BDC solution in a glass culture dish at the flow rate of 36 µL/min. The purple precipitate was washed with DMF and ethanol for three times, then heated under vacuum at 120 °C for 10 h.

The NiCo-MOF bulk crystals were fabricated according to literature^[15]. The bimetallic salts and H₂BDC dissolved in a ternary mixed solvent of DMF, ethanol and water (V:V:V=8:1:1), respectively. The two solutions were mixed and reacted at 140 °C for 48 h. After being washed with DMF and ethanol for three times, the products were heated under vacuum at 120 °C for 10 h.

Catalytic Test. The catalytic performance of NiCo-MOFs in the reduction 4-NP was tested. The NaBH₄ aqueous solution (2.5 mL, 0.1 M), 4-NP (20 μ L, 5 mM) and NiCo-MOFs aqueous solution (20 μ L, 0.125 mg/mL) were mixed. The reaction progress was monitored by UV-Vis spectrometry.

3. Results and Discussion

The morphology of NiCo-MOF microflowers prepared by spray method is characterized by scanning electron microscopy (SEM). The SEM image shows the morphology of NiCo-MOF is uniform flower-like microspheres (Figure 1a). 2D nanosheets are observed in NiCo-MOF microflowers, which are staggered and superimposed to form flower-like structure (Figure 1b). Moreover, the thickness of NiCo-MOF nanosheets is 50-80 nm and the length is a few microns (Figure 1c), which is identical to the typical 2D structures. The average diameter of NiCo-MOF microflowers is 5.6 \pm 0.7 μm by measuring one hundred of individual microflowers, and the low relative standard deviation of 12.4% suggests the good monodispersity of NiCo-MOF microflowers (Figure 1d). The SEM image and its corrsponding energy-dispersive X-ray (EDX) elemental mapping images of microflowers (Figure 1e and 1f, Figure S1b, S1c and S1d) show that the ratio of Co/Ni in NiCo-MOF microflowers is approximately 1:1, and Ni and Co elements are uniformly dispersed throughout entire NiCo-MOF microflowers.

The coordination interaction in NiCo-MOF is confirmed by Fourier transform infrared spectroscopy (FT-IR) (Figure 2a). The characteristic peak of 1508 cm⁻¹ ascribes to the vibration absorption of benzene ring in organic ligand H2BDC. There are two characteristic absorption peaks at 1388 and 1588 cm⁻¹, which are corresponded to the symmetrical stretching vibration and anti-symmetrical stretching vibration absorption peak of carboxylate groups, respectively. The characteristic absorption peaks C=O and O-H of carboxyl groups in H₂BDC are not found at 1710 and 1245 cm⁻¹, which indicate H₂BDC has been deprotonated and coordinates with Ni²⁺ and Co²⁺ successfully. All these indicate the existing of coordination bonds between metal ions and BDC. The thermal stability of NiCo-MOF microflowers is confirmed by thermogravimetric analysis (TGA), which is performed under a N2 atmosphere with heating rate of 10 °C·min⁻¹ from ambient temperature up to 800 °C (Figure 2b). The TGA curve of NiCo-MOF microflowers shows a distinct weight loss at 410 °C, ascribing to the decomposition of NiCo-MOF, which indicates good thermal stability of NiCo-MOF microflowers.



Figure 1. (a-c) Different magnifications SEM images of NiCo-MOF microflowers. (d) The histogram of NiCo-MOF microflowers diameter distribution. (e) SEM image of NiCo-MOF microflower and (f) its corresponding EDX elemental mapping images of Co, Ni, O and C element distribution.

The crystalline structures of MOFs are also investigated by X-ray diffraction (XRD). The XRD pattern (Figure 2c) has four peaks at 9.08°, 14.30°, 15.82° and 17.98° corresponding to the [200], [001], [201] and [201] crystallographic planes of the NiCo-MOF structure. None of the additional Bragg diffractions of the bulk crystals are detected due to the special 2D nanosheet structures of NiCo-MOF. Moreover, the XRD pattern of NiCo-MOF microflowers is similar to the 2D NiCo-MOF nanosheets as reported in Tang's work^[15], which further proves that the NiCo-MOF microflowers are consisted of 2D NiCo-MOF nanosheets. According to Tang's work^[15], 2D bimetallic layers separated by BDC molecules are formed by both the Co and Ni atoms octahedrally coordinated by six O atoms and these pseudo octahedra are further edge/corner connected with each other along the [010]/[001] direction in the (200) crystallographic plane (Figure 2d).



Figure 2. (a) FT-IR spectrum of NiCo-MOF microflowers. (b) The thermogravimetric profile of NiCo-MOF microflowers. (c) XRD pattern of NiCo-MOF microflowers and the simulated XRD pattern of NiCo-MOFs. (d) 3D crystalline structures of NiCo-MOF microflowers. Nickel, cobalt, oxygen, carbon and hydrogen are shown in green, purple, red, grey and white, respectively.

Most aromatic nitro compounds are harmful to the environment, but its hydrogenated aromatic amino compounds are important industrial intermediates. Therefore, it is of great practical significance to develop an effective and cheap catalyst for the reduction of aromatic nitro compounds. NiCo-MOFs could be used as catalysts for the reduction of 4-NP to produce its hydrogenated compound 4-aminophenol (4-AP). The UV-Vis absorption peak of the nitro group in 4-NP is at 317 nm. After adding sodium borohydride (NaBH4) solution, the absorption peak is red shifted to 400 nm due to the deprotonation of 4-NP (Figure S2a)^[16]. In the absence of NiCo-MOFs, the absorption peak of deprotonated 4-NP is almost unchanged after 10 h (Figure S2b). When NiCo-MOFs are added to the mixed solution, the absorption peak intensity of the solution at 400 nm decreases with the increase of reaction time. Simultaneously, the absorption peak of the amino group appears near 300 nm. The reduction of 4-NP is completed after 5 min with the addition of NiCo-MOF microflowers (Figure 3a). For a better comparation, the NiCo-MOF bulk crystals are also synthesized to catalyze the reduction of 4-NP, whose structures are comfirmed by SEM and XRD (Figure S3 and Figure S4). The reduction of 4-NP takes longer for 11 min with the same amount of NiCo-MOF bulk crystals (Figure 3c). Moreover, the rate constant (k) of the NiCo-MOF microflowers is 0.663 min⁻¹ and the turnover frequency (TOF) value is 137.9 h^{-1} , while the k of NiCo-MOF bulk crystals is 0.252 min⁻¹ and the TOF value is 67.5 h⁻¹, which is calculated according to Figure 3b and Figure 3d. The linear relationships between $ln(c_0/c_t)$ and reaction time t are shown in Figure 3b and Figure 3d, while the rate constant (k) is the fitting line slope. Comparing with the NiCo-MOF bulk crystals, the NiCo-MOF microflowers are composed of 2D nanosheets, which provides more exposed surface areas with active metal sites. So the k and TOF of NiCo-MOF microflowers are two times higher than NiCo-MOF bulk crystals. The ¹H NMR spectrum of 4-AP obtained by the catalytic reduction from 4-NP confirms that the conversion rate of 4-NP to 4-AP can reach to 100% (Figure S5). What is more, the excellent synergistic effect arised from the homogeneous distribution of Ni and Co of NiCo-MOF microflowers, leads to the higher catalytic efficiency of NiCo-MOF microflowers than

the previously transition metal nanoparticles^[17-19].

The Co-MOF microflowers have also been fabricated by spray method, which are characterized by SEM, FT-IR, XRD and TGA. The SEM images show that the morphology of Co-MOFs is microflower, but the diameter of Co-MOF microflowers is two times longer than that of NiCo-MOF microflowers (Figure S6). The FT-IR spectrum of Co-MOF microflowers is similar to the NiCo-MOFs (Figure S7a), which indicates H2BDC has been deprotonated and coordinates with Co²⁺ successfully. The XRD pattern of Co-MOF microflowers have two sharp peaks at 8.88° and 15.73°, corresponding to the two crystal faces of [-200] and [-011] in MOF-71 (Figure S7b). The TGA curve of Co-MOF microflowers shows a distinct weight loss at 410 °C, ascribing to the decomposition of Co-MOF microflowers (Figure S7c). The Co-MOF microflowers are also used to catalyze the reduction of 4-NP. The reduction of 4-NP is completed after 15 min with Co-MOF microflowers (Figure S8a). The k of Co-MOF microflowers is 0.126 min⁻¹ and the TOF value is 52.86 h⁻¹ (Figure S8b). It proves that the synergistic effect between bimetallic MOF accelerates the catalytic reaction.



Figure 3. UV-Vis absorption spectra of the 4-NP reduction versus reaction time under the catalysis of (a) NiCo-MOF microflowers and (c) NiCo-MOF bulk crystals. Plots of $ln(c_0/c_t)$ versus reaction time for the 4-NP reduction with (b) NiCo-MOF microflowers and (d) NiCo-MOF bulk crystals.

4. Conclusion

In summary, bimetallic NiCo-MOF microflowers with uniform crystal structures have been fabricated by spray method, which are consisted of 2D nanosheets. The Ni and Co are homogeneous dispersed throughout the whole NiCo-MOF microflowers. Owing to the larger exposed surface areas and synergistic effect, the *k* and TOF value of NiCo-MOF microflowers, as catalysts for the reduction of 4-NP, are 0.663 min⁻¹ and 137.9 h⁻¹, which are two times higher than NiCo-MOF bulk crystals. The good catalytic performance of NiCo-MOF microflowers will inspire the development of bimetallic MOFs with hierarchical nanostructures for advanced applications.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (21503037), Fundamental Research Funds for the Central Universities (N160504002, N170503010) and Open Project of State Key Laboratory of Supramolecular Structure and Materials (sklssm201804, sklssm201822).

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