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Morphology-dependent electrochemical sensing performance of metal (Ni, Co, Zn)-organic frameworks

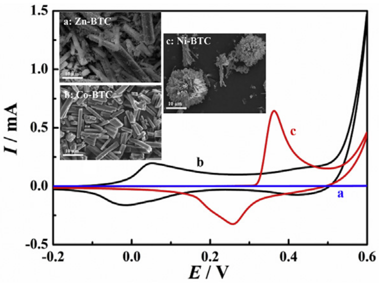
Liudi Ji [a, 1], Yunshan Jin [a, 1], Kangbing Wu [a, *], Chidan Wan [b], Nianjun Yang [c], Yong Tang [b, **]

[a] *Key Laboratory for Material Chemistry of Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, 430074, China*
[b] *Department of Hepatobiliary Surgery, Union Hospital, Tongji Medical College, Huazhong University of Science and Technology, Wuhan, 430022, China*
[c] *Institute of Materials Engineering, University of Siegen, Siegen, 57076, Germany*

HIGHLIGHTS

- Metal-organic frameworks (MOFs) with different morphology are synthesized with different metal centers.
- Electrochemistry of MOFs are dependent on their morphology.
- Sensitive and selective monitoring of Ponceau 4R on nickel MOFs.

GRAPHICAL ABSTRACT



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ABSTRACT

To clarify the morphology effect of metal-organic frameworks (MOFs) on their electrochemistry as well as to explore their electrochemical applications, three MOFs with metal centers of nickel, cobalt, and zinc are synthesized. The used organic ligand is only 1,3,5-benzenetricarboxylic acid. Characterizations using Fourier Transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, and electrochemical techniques reveal that these MOFs possess similar bonding properties, crystalline structures and phase purity, but various morphology and electrochemical activities, including their own redox behavior, electrochemical response toward redox probes and analytes in solutions. As a case study of analytes, voltammetry of Ponceau 4R is investigated on three MOFs. Its sensitive and selective monitoring is further achieved on nickel MOFs with a linear range from 0.5 to 150 nM and a detection limit of 80 pM. Therefore, the morphology of MOFs determines electrochemistry of MOFs and their electrochemical sensing applications.

1. Introduction

Metal-organic frameworks (MOFs) are newly-developing multifunctional porous materials. They have exhibited unique features, including large surface areas, tunable morphology/pore sizes, various structures, and unsaturated coordination sites. Up to date, MOFs with different metal ions and organic ligands have been widely explored for hydrogen storage [1], gas adsorption/

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* Corresponding author.
** Corresponding author.
E-mail addresses: kbwu@hust.edu.cn (K. Wu), tangyong_2222@126.com (Y. Tang).
[1] The first two authors contribute equally to this work.

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separation [2,3], chemical sensors [4,5], catalysis [6,7], drug release [8], and related applications [9–12].

It has been shown that chemical, physical, and biological features of MOFs are probably dependent on the morphology of MOFs, more exactly, the type and numbers of organic ligands and metal centers as well as synthetic strategies. For example, copper center inside MOFs plays a significant role in determining their electrochemical performances (e.g., own redox behavior, electrocatalytic ability, etc.) [5,9,10]. The organic ligands are found to affect the second building units of MOFs as well as the morphology of electrosynthesized MOFs [5]. It is expected that the metal centers will affect the morphology of MOFs and subsequently their electrochemistry (e.g., own activity, catalytic ability, and electrochemical applications). Surprisingly, such kind of studies is seldom reported.

With an aim to clarify the effect of the morphology of MOFs on their, including their own redox behavior, response toward redox probes and target compounds in solutions, three MOFs with different metal centers are synthesized. The adopted metal centers are from nickel, cobalt, and zinc ions. The used organic ligand is 1,3,5-benzenetricarboxylic acid (H_3BTC). As-synthesized MOFs, so-named in this paper as M-BTC (M = Ni, Co, Zn) frameworks were used to form carbon paste electrodes (CPEs). Their own electrochemical behavior, the response towards redox probes, and voltammetry of target compounds in solution were then studied. Ponceau 4R, a widely-used synthetic food colorant with health side effects, was selected as a case study.

2. Experimental

Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), zinc(II) nitrate hexahydrate ($(Zn(NO_3)_2 \cdot 6H_2O$), 1,3,5-benzenetricarboxylic acid (H_3BTC), sodium hydroxide (NaOH), ethanol, graphite powder (spectral reagent), and paraffin oil were purchased from Sinopharm Chemical Reagent Company (Shanghai, China) and used without purification. The aqueous stock solution of 0.01 M Ponceau 4R (Sigma, USA) was stored at 4 °C. Ultrapure water (18.2 MΩ cm) from a Milli-Q water purification system was used.

A Quanta 200 microscope (FEI Company, Netherlands), an Equinox-55 Fourier Transform infrared spectrometer (Bruker Company, Germany), and a X'Pert PRO diffractometer (Panalytical Company, Netherlands) were utilized to characterize as-synthesized M-BTC frameworks. For Fourier Transform infrared (FTIR) spectra, KBr pellets were used. For X-ray diffraction (XRD) patterns, Cu $k\alpha_1$ radiation (0.154 nm) was operated in the 2θ scan range from 5° to 50°.

Electrochemical measurements were conducted on a CHI 660E electrochemical workstation (Chenhua Instrument, Shanghai, China) with a three-electrode system. The reference and counter electrodes were a saturated calomel electrode (SCE) and a platinum wire, respectively. A CPE acted as the working electrode. A modified CPE was fabricated in two steps. In the first step, 8 mmol H_3BTC was dissolved in the mixture of 200 mL ethanol and water (V:V = 1:1). Then, 12 mmol $Ni(NO_3)_2 \cdot 6H_2O$ (or $Co(NO_3)_2 \cdot 6H_2O$, or $Zn(NO_3)_2 \cdot 6H_2O$) was added. The resultant mixture was stirred till a transparent solution was obtained. Further addition of 24 mmol NaOH and continuous stirring for more than 30 min led to the precipitation of light green, pinkish-purple, and white material, which was subsequently collected, washed with water and ethanol copiously. It was finally dried in vacuum for 12 h at 50 °C. In the second step, 0.10 g M-BTC, 0.90 g graphite powder, and 0.20 mL paraffin oil were mixed homogeneously in a carnelian mortar. Such paste was tightly pressed into the end cavity of a copper electrode body. After polished on a smooth paper, a modified CPE was formed. The modified CPEs are denoted as Ni-BTC/CPE, Co-BTC/CPE, and Zn-BTC/CPE. The unmodified CPE was prepared only with 1.00 g graphite and 0.20 mL paraffin oil.

3. Results and discussion

3.1. Characterization of M-BTC frameworks

The synthesized M-BTC frameworks were characterized, including their bonding properties using FTIR, their crystal structures and phase purities using XRD, and their morphology using SEM. Fig. 1A compares their FTIR spectra with that of used organic ligand. Similar infrared spectra of M-BTC frameworks are noticed, suggesting similar bonding properties. The absorption bands of the asymmetric and symmetric stretching vibrations of carboxylate group appear at 1375 and 1563 cm^{-1}, respectively [13–15]. The disappearance of the adsorption of C-OH at 1278 cm^{-1} in H_3BTC indicates its deprotonating and coordination to metal centers.

Fig. 1B shows XRD patterns of M-BTC frameworks. Similar XRD patterns are seen, expect their intensity difference. These frameworks are thus crystallized and have iso-structures. Their XRD patterns agree also well with the reported ones [16], confirming their high purity.

Fig. 1C–E are SEM images of M-BTC frameworks. From them, one can tell that Ni-BTC frameworks are separated and have flower-like hierarchical architectures, consisting of abundant nanoplates (Fig. 1C). The Co-BTC frameworks own uniform columns or of rod-like structures (Fig. 1D). Differently, Zn-BTC frameworks have similar columns as Co-BTC frameworks (Fig. 1E). Their surfaces are heavily coated with cloud-like fragments.

Consequently, the metal centers inside M-BTC frameworks affect significantly the morphology of MOFs. The exposed ratio and numbers of metal centers are probably different and then morphology-dependent electrochemistry of MOFs is expected.

3.2. Electrochemistry of M-BTC frameworks

Electrochemistry of three M-BTC frameworks, including their own redox behavior, response toward redox probes and analytes in solutions, was then investigated by means of voltammetry, impedance, and chronocoulometry.

Fig. 2A–D shown cyclic voltammograms of three M-BTC frameworks recorded in 1 M KOH. Within the scanned potential range, no redox waves are found for a CPE and Zn-BTC frameworks. In both cases, the background currents are low (Fig. 2A). For both Ni-BTC and Co-BTC frameworks, a couple of sharp redox waves is seen (Fig. 2B). These waves obviously originate from the redox activities of metal centers inside MOFs, namely cobalt and nickel. Then, cyclic voltammograms of Ni-BTC (Fig. 2C) and Co-BTC (Fig. 2D) were recorded at different scan rates. For both MOFs, their redox peaks are proportionally enhanced with the scan rates (the inset in Fig. 2C and D), indicating adsorption-controlled electrode processes. The charges for wave (I) in both MOFs were then integrated to estimated their active-center densities, which are 6.49 and 3.22 $\mu mol\ cm^{-2}$ for Ni-BTC and Co-BTC, respectively. Moreover, the magnitude of the redox currents of Ni-BTC frameworks is much higher than Co-BTC frameworks. This probably originates from their different morphology. In other words, the flow-like Ni-BTC frameworks might have more open and electroactive sites than column-like Co-BTC frameworks. The difference of electron transfer rates for the redox reaction of cobalt and nickel metal centers is another possible source for such varied redox behavior.

To further study electrochemistry of three MOFs, redox probes (e.g., K_3/K_4 $[Fe(CN)_6]$) were employed. Fig. 2E shows the related cyclic voltammograms of K_3 $[Fe(CN)_6]$ on different CPEs. On all

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