Electrochemical and Electrocatalytic Properties of a stable Cu-Based metal-organic Framework

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A redox-active Cu-based metal-organic framework (Cu-MOF) was prepared via a facile solvothermal synthesis. The electrochemical and electro-catalytic properties of the as-prepared Cu-MOF were investigated in pH 7.2 phosphate buffer solution (PBS) by casting the material on a carbon paste electrode (CPE) (Cu-MOF/CPE). The Cu-MOF exhibited high stability and well-behaved redox events. It also showed strong absorption ability towards electro-active probe ferricyanide ion (Fe(CN)₆³⁻), allowing the efficient immobilization of Fe(CN)₆³⁻ on the electrode (Fe(CN)₆³⁻/Cu-MOF/CPE). The Fe(CN)₆³⁻/Cu-MOF/CPE presented significantly enhanced electro-catalytic activity towards the oxidation of nitrite. The Cu-MOF was first demonstrated for the electrochemical sensing application in the determination of nitrite, which showed excellent sensing performances. The results indicated that the Cu-MOF offer a promising candidate applied in electro-catalysis and electro-analysis.

Keywords: metal–organic framework; potassium ferricyanide; nitrite; electro-catalysis; electrochemical sensor.

1. INTRODUCTION

Metal-organic frameworks (MOFs), a new class of highly porous crystalline materials, are constructed by assembling metal ions or metal-containing clusters with multidentate organic ligands via coordination bonds [1]. Compared with other porous materials, MOFs have some unique characteristics, such as particularly high surface area, tunable pore size, and uniform-structured cavities, which make them very promising for diverse applications in gas storage [2], separation [3], catalysis [4], and sensing [5]. In addition, in the recent years, the application of MOFs in the

4900

electrochemical field receives growing interest. Yaghi et al. studied the performance and properties of 23 porous MOFs as supercapacitors [6]. These MOFs represented a diversity of structure types and metrics, and sizes and functionalities of pore. The results showed that several of these MOFs exceed the capacitance of the benchmark materials because the special structure and functionality of some MOFs are directly involved in electrochemical processes. In addition, Awaga et al. synthesized the first microporous MOF material with independent redox active sites on both metal and ligands, and used it as a novel cathode active material for lithium batteries [7]. It was found that the proposed MOF materials have good potential for use in industrial batteries. Cu based MOF has also been presented for the electro-catalyst in oxygen reduction reaction (ORR) [8]. Furthermore, some MOFs and MOFs based composites were demonstrated for the electro-reduction of CO_2 [9] and electro-oxidation of glutathione (GSH) [10], L-cysteine (CYS) [11], ascorbic acid (AA) [12], hydrazine [13], H₂O₂ [14], methanol [15], ethanol [16], and NADH [17].

The stability of MOFs has long been considered as a major impediment in their application in electrochemistry. Therefore, stable MOFs are promising for the application in electrochemical fields. For example, zeolitic imidazolate frameworks (ZIFs), one subclass of MOFs with high chemical stability, have been reported to electro-catalyze the oxygen evolution reaction in a wide pH range [18]. Ma et al. [19] demonstrated the first application of ZIF material as a matrix for developing electrochemical biosensors. However, introducing other stable MOFs for electrochemical application is still one of the current challenging researches. For the first time, Yaghi et al. [20] used 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid (H₃BTB), copper(II) nitrate, and *N*, *N*'-dimethylformamide (DMF) to prepared a highly porous and structurally stable networks $Cu_3(BTB)_2(H_2O)_3 \cdot (DMF)_9(H_2O)_2$ named MOF-14. The compound is stable in air and insoluble in water and common organic solvents. In spite of this great potentiality, to the best of our knowledge, the exploitation of MOF-14 for electrochemical investigation has not been explored so far. Herein, we synthesized the same Cu based MOF (Cu-MOF) by a simple developed method and studied with respect to its electrochemical and electro-catalytic properties. The well-behaved redox events, high electro-catalytic activity and durable stability of the as-prepared Cu-MOF indicated that it would have great potentiality in electrochemical application.

2. EXPERIMENTAL

2.1. Chemicals and solutions

 H_3BTB , Sodium nitrite, Cu(OH)₂ and potassium ferricyanide (K₃Fe(CN)₆) were purchased from Sigma-Aldrich and used without further purification. All other chemicals used were of at least analytical reagent grade, and the aqueous solutions were prepared with doubly distilled water. All the electrochemical experiments we carried out in 0.1 M pH 7.2 phosphate buffer solution (PBS).

2.2. Apparatus

Scanning electron microscopy (SEM) measurements were performed using a Hitachi SU8010 instrument. Powder X-ray diffraction (XRD) measurements were operated on a Philips X'pert Pro X-

ray diffractometer with Cu Ka radiation and operated at 40 kV and 40 mA. All the electrochemical experiments were conducted on A CHI 842C electrochemical workstation (Austin, TX, USA) with a conventional three-electrode system consisting of a bare carbon paste electrode (CPE) or modified CPE as working electrode, platinum coil as auxiliary electrode, and Ag/AgCl (saturated KCl) as reference electrode. Bare CPE was prepared by mixing graphite powder and liquid paraffin with a mass ratio of 75:25. The paste was thoroughly hand-mixed in a mortar and then packed firmly into an electrode cavity of a glassy tube (1.8 mm inner diameter). The electrical contact was established via a copper wire connected to the paste in the inner hole of the tube. For electrode modification, 2 mg Cu-MOF was dispersed into 1 mL of water to give a suspension by sonication. A 5.0 μ L of Cu-MOF suspension was drop coated onto CPE to form Cu-MOF modified CPE (Cu-MOF/CPE). In order to fabricate Fe(CN)₆³⁻ modified Cu-MOF/CPE (Fe(CN)₆³⁻/Cu-MOF/CPE), Cu-MOF/CPE was immersed in 10 mM K₃Fe(CN)₆ for 30 min to adsorb Fe(CN)₆³⁻. The electrode was then washed and dried under room temperature.

2.3. Synthesis of Cu-MOF

Cu-MOF was synthesized by a modified published procedure [20]. In brief, 3.9 mg (0.04 mmol) Cu(OH)₂, 17.6 mg (0.04 mmol) H₃BTB, 0.5 mL DMF, 0.5mL DMSO, 0.5 mL deionized water and HNO₃ (0.3 mL, 2.7 M in DMA) were mixed in a 20 mL vial, and then treated with a solvothermal method at 100 °*C* for 48 h. Octahedral-shaped crystals were obtained in ca. 62% yield based on Cu, and was washed with free DMF and dried at 70 °C under vacuum. Crystallographic parameters for Cu-MOF: a = 26.948(3)Å, Cubic, *I*m-3.

3. RESULTS AND DISCUSSION

3.1. Characterization

Single crystals from the as-prepared product were characterized by XRD, and the crystallography analysis shows that the Cu-MOF crystallize in cubic space group of *I*m-3, which was constructed of Cu(II) paddle-wheel units and tritopic BTC ligands, as shown in Fig. 1. The paddle-wheel units consist of two water molecules in the axial positions and four carboxylate groups in equatorial positions. As a result, each paddle-wheel unit is composed of two five-coordinated Cu(II) ions with slightly distorted square pyramidal polyhedra. Each Cu dinuclear unit is linked with four carboxylate group ends from four BTB^{3–} ligands, which can be simplified into a 4-connected inorganic building unit, while each ligand is linked with three dinuclear units to form a 3-connected triangular node, resulting in an extended 3D (3, 4)- connected pto-a network [29-31]. The cavities of the MOF are occupied by water molecules and DMF. The product was also examined by powder XRD (Fig. 1d). It was can be seen that the peak positions of the experimental and simulated patterns are in accordance with each other, and no other peaks were observed, suggesting the pure phase of the as-prepared

product. Fig. 2 depicts the optical microscopic image of crystal of the Cu-MOF. It was found that the size of the crystal is about $200 \ \mu m$.



Figure 1. Single-crystal structure of **a** the coordination environment of each Cu paddle-wheel unit can be simplified as a 4-connected node; **b** the organic ligand, BTB³⁻, coordinates four Cu₂ units and can be simplified into a 3-connected node; **c** 3D framework built from Cu₂ units and 3-connected ligands along the [111] direction. Color code: Cu, green; O, red; C, gray. (Hydrogen atoms and guest molecules have been omitted for clarity.); **d** Powder X-ray diffraction patterns of the simulated and as-prepared Cu-MOF.



Figure 2. Optical microscopic image of Cu-MOF crystals.

3.2. Electrochemical property



Figure 3. SEM images of a bared CPE and b Cu-MOF/CPE.



Figure 4. CVs of Cu-MOF/CPE in pH 7.2 PBS at different scan rate (*v*). Inset: plot of redox peak current versus $v^{1/2}$.

The bared CPE and Cu-MOF/CPE were characterized by SEM, as shown in Fig. 3. Flat surface was observed on bare CPE (Fig. 3a), however, rough and wrinkle surface was found on Cu-MOF/CPE (Fig. 3b), indicating that Cu-MOF was modified on the CPE surface. Fig. 4 shows the cyclic voltammograms (CVs) of Cu-MOF/CPE in pH 7.2 PBS at different scan rate. It seems that a couple of redox peaks appear between -0.2 V and 0.3 V at the Cu-MOF/CPE. In fact, two redox events occur and overlap with each other, which can be separated at low scan rate. This results show that the redox events are assigned to the electrochemical conversion among Cu(II) species, Cu(I) and Cu metal [21]. The redox currents increase with the increasing scan rate from 0.01 to 0.5 V/s, and are proportional to square root of the scan rate, indicating that the electrochemical processes are diffusion controlled.



Figure 5. CVs of Fe(CN)₆³⁻/Cu-MOF/CPE in pH 7.2 PBS at different scan rate. Inset: quadratic plot of redox peak current versus $v^{1/2}$.

 $[Fe(CN)_6]^{3^{-/4^-}}$ redox couple with excellent electrochemical properties has been so widely used in electro-catalysis, electrochemical sensor, and biosensor [22-24]. However, the redox couple is highly water-soluble, limiting its use in electrochemistry. The immobilization of the $[Fe(CN)_6]^{3^{-/4^-}}$ redox couple have consequently received much attention. We found that $Fe(CN)_6]^{3^-}$ could be easily immobilized in Cu-MOF through the absorption interaction. The electrochemical properties of the $Fe(CN)_6]^{3^-}$ incorporated in Cu-MOF are investigated by CV in pH 7.2 PBS at different scan rate (Fig. 5). As can be seen in Fig. 5, a couple of well-defined redox peaks, associated with the electrochemical event of $Fe(CN)_6^{3^{-/4^-}}$, is observed in the range of 0.4 to 0.8 V in which the relationship between current and $v^{1/2}$ exhibits a quadratic equation, suggesting that the electrochemical processes between $Fe(CN)_6^{3^-}$ and $Fe(CN)_6^{4^-}$ are surface and diffusion mixed controlled. This results shows that $Fe(CN)_6^{3^-}$ was incorporated into the pores of Cu-MOF. The introducing of electroactive $Fe(CN)_6^{3^-}$ is bound to accelerate the electron transfer rate in Cu-MOF, and consequently increase its electro-catalytic activity [22].

3.3. Electrocatalytic property



Figure 6. CVs of bare CPE (*a*, *b*), Cu-MOF/CPE (*c*, *d*), and $Fe(CN)_6^{3-}/Cu-MOF/CPE$ (*e*, *f*) in the absence (dotted line) and presence (solid line) of 5 mM nitrite in pH 7.2 PBS, respectively. Scan rate: 0.1 V/s.

The potential application of the Cu-MOF was evaluated for electro-oxidation and the detection of nitrite. The electro-catalytic activity of different modified electrodes was investigated by CV in the presence of nitrite (Fig. 6). As it can be seen, in comparison with bare CPE (~1.0 V), the overpotential of nitrite decreases to ~0.9 V at the Cu-MOF/CPE, indicating that Cu-MOF has electrocatalytic ability towards the oxidation of nitrite, which may be attributed to the interaction between nitrite and the cavity or functionality in Cu-MOF. However, the oxidation current of nitrite at the Cu-MOF/CPE is much lower than that at bare CPE. This is because that the limited electrical conductivity of Cu-MOF results in a low electron transfer rate. When the surface of the electrode was modified with Fe(CN)₆³⁻, an enhanced oxidation current was observed, indicating that the introducing of Fe(CN)₆³⁻ increases the rate of the electron transfer process [22-24].



Figure 7. Amperometric sensing of nitrite uppon successive addition of nitrite at $Fe(CN)_6^3/Cu-MOF/CPE$ at 0.9 V in pH 7.2 PBS. Inset: Log-log plot of amperometric response versus the concentration of nitrite from 40 nM to 1.1 mM.

The Cu-MOF was also presented for the application in electrochemical sensor of nitrite. Fig. 7 shows the amperometric *i-t* curve of the $Fe(CN)_6^{3-}/Cu-MOF/CPE$ in pH 7.2 PBS at 0.9 V with successive addition of nitrite. As shown, immediately after the injection of nitrite, the $Fe(CN)_6^{3-}/Cu-MOF/CPE$ responded quickly to the oxidation of nitrite and achieved the steady-state current within 6 s after every addition. The corresponding log current-log concentration calibration plot in Fig. 7A also clearly show that the $Fe(CN)_6^{3-}/Cu-MOF/CPE$ displays a good linear relationship in the range of 40 nM-1.1 mM ($R^2 = 0.9982$) with a detection limit of 40 nM at a signal-to-noise ratio of 3 which is much lower than those of rGO/MCNT/GC (25 μ M) [25], graphene/cobalt (84 nM) [26], rGO/GC (1 μ M) [27], Potassium-doped graphene/GC (0.2 μ M) [28], GC/H⁺-bt/Fe(phen)_3^{2+} (1 μ M) [29], PMBT/GC (0.3 μ M) [30], Au-CA/IL/Hb/CPE (1.3 μ M) [31] and 3D-PEDOT/GC (0.2 μ M) [32] electrodes.

The reproducibility, operational stability, and long-term storage stability of the proposed $Fe(CN)_6^{3-}/Cu-MOF/CPE$ were further investigated by the amperometric *i*-*t* technique. For successive measurements of 40 µM nitrite, the response kept stable after twelve measurements and the relative standard deviation (RSD) was 4.1%, as shown in Fig. 8. The operational stability of the electrode was also examined by continuous analysis for nitrite (Fig. 9). It was found that the amperometric response of the sensor to nitrite still retained 97% of its original current responses after operating for 2500 s. In addition, the Fe(CN)₆³⁻/Cu-MOF/CPE also possessed good storage stability. The sensor was also able to retain 89% of its original response after two weeks storage at room temperature. The high stable response of the senor might be owing to the high stability and strong absorbing ability of the Cu-MOF.



Figure 8. Repeatable test of $Fe(CN)_6^3/Cu-MOF/CPE$ by successive addition of 40 μ M nitrite. Conditions are the same as in Fig. 7.



Figure 9. Long-term amperometric test of $Fe(CN)_6^3/Cu-MOF/CPE$ with 60 µM nitrite. Conditions are the same as in Fig. 7.



Figure 10. Amperometric response of the $Fe(CN)_6^3/Cu-MOF/CPE$ upon successive additions of 8 μ M nitrite and 1 mM of each of KCl, NaAc, KNO₃, MgSO₄, CaCl₂, and NaClO₄. Conditions are the same as in Fig. 7.

The influences of interferences on the determination of nitrite were further evaluated. As can be seen in Fig. 10, the $Fe(CN)_6^{3-}/Cu-MOF/CPE$ shows obvious amperometric response towards 8 μ M nitrite. When successive injection of 1 mM of of KCl, NaAc, KNO₃, MgSO₄, CaCl₂, and NaClO₄, no noteworthy amperometric responses were observed from the additions of 125-fold KCl, NaAc, KNO₃, MgSO₄, CaCl₂, and NaClO₄. Further 8 μ M nitrite addition still produced the same response as previous addition, indicating that the presence of these substances did not interfere with nitrite detection.

Lake water spiked with nitrite was assayed to demonstrate the practical application of the sensor. For 10 and 30 μ M spiked water samples, the determined concentrations were 10.3 (n=5) and 28.8 μ M (n=5), with average recoveries of 103% and 96%, respectively. The good recoveries achieved shows that the presented sensor has a potential application towards real sample analysis.

4. CONCLUSIONS

In summary, the electrochemical and electro-catalytic properties of stable and redox-active Cu-MOF prepared by a simple developed method were investigated in detail. The as-synthesized Cu-MOF exhibited well-behaved redox events and high electrocatalytic activity towards nitrite, which also showed strong absorption ability for electroactive $Fe(CN)_6^{3-}$, and immobilization of $Fe(CN)_6^{3-}$ was successfully achieved. The introducing of $Fe(CN)_6^{3-}$ greatly accelerated the electron transfer rate occurred in Cu-MOF, and the electro-catalytic ability was consequently increased. The Cu-MOF based electrode was demonstrated for the application in electrochemical sensor of nitrite, and good analytical performances were obtained. The results indicated that the presented Cu-MOF have a potential application in electrochemistry.

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