Fabrication of MOF-177 for electrochemical detection of toxic Pb^{2+} and Cd^{2+} ions

S SANGEETHA and G KRISHNAMURTHY*

Department of Studies in Chemistry, Bangalore University, Jnanabharathi Campus, Bangalore 560056, India

*Author for correspondence (drkgmurthy.bub@gmail.com)

MS received 14 March 2019; accepted 3 July 2019; published online 18 December 2019

Abstract. We have studied the electrochemical behaviour of room-temperature synthesized MOF-177. The MOF-177 sample was characterized by various techniques like Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive X-ray, powder X-ray diffraction, nuclear magnetic resonance and CHNS elemental analysis. The MOF-177 electrode was prepared and electrochemical performance was carried out to explore the electrical activity of MOF-177. Cyclic voltammetry studies were performed in 0.05 M $\text{K}_4\text{Fe}(\text{CN})_6$ solution and electrochemical sensing experiments were performed in 0.05 M H_2SO_4 and pH 7 buffer solution. A significantly increased electron transfer property has been observed and it has been explored for the electrochemical detection of heavy metal ions. The MOF-177/cp electrode has shown excellent sensitivity towards toxic heavy metal ions such as Pb^{2+} and Cd^{2+} at the limit of detection of 0.004 and 0.03 μM , respectively.

Keywords. MOF-177; electrochemical sensor; heavy metal ions; chronoamperometry.

1. Introduction

Here we report the electrochemical behaviour of MOF-177, which was earlier reported by Omar M Yaghi [1,2]. MOF-177 was chosen because it presents a cross-section of attractive properties such as highly crystalline and ultrahigh porosity [3]. Although previously published research studies [2,4] have implied and highlighted the gas adsorption property of MOF-177, much less information is available for electrochemical sensor application of MOF-177. Hence in this work we have explored the electrochemical detection of hazardous heavy metals by the MOF-177/cp electrode. The worldwide environmental related issues have been continuously increasing from past few years. Accumulation of non-biodegradable, heavy metals such as cadmium and lead, to the ecosystem through industrial activities has been increasing day by day. Kidney damage, brain damage, mental disorder, behaviour problems and development delays are severe health issues amalgamated with subject to high levels of metal ions (e.g., Cd^{2+} , Pb^{2+} and Hg^{2+}) due to their propensity to be assemble in the body, noxious and elimination rate is very low [5,6]. For instance, the biological half-life of lead in bone is more than 20 years, while that for cadmium is 10–30 years [7]. Hence detection and elimination of these metal ions is necessary to maintain healthy environment and human health. Moreover, utilization of MOF electrodes has great attention in various areas of research and development, such as electro-catalysis, biosensors and electro-analysis [8–15]. Hence we illustrate the application of simple, rapid and room temperature

synthesized MOF-177/cp electrode towards low-concentration detection of heavy metals.

2. Experimental

2.1 Materials and methods

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Sigma-Aldrich and benzene tricarboxylic acid was purchased from Spectrochem Pvt. Ltd., Mumbai (India). Other reagents were purchased from Merck Pvt. Ltd. All solvents and reagents were used without further purification. Attenuated total reflection infrared (ATR-IR) spectra were recorded with samples in KBr for the title complexes on a BRUKER-ATR-IR spectrophotometer in the range of 3500–400 cm^{-1} . Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer ($\text{CuK}\alpha$, 1.5418 Å). Electrochemical analyses were performed using an Autolab potentiostat. Scanning electron microscopy (SEM) images were collected using a Supra55 field emission SEM system (Zeiss). Elemental analysis was carried out on an Inca 2400 Series II element analyser. Nuclear magnetic resonance spectra were collected by using a VNMR5-400 'Agilent-NMR'. Thermal gravimetric analyses were carried out with a SDT Q600 V20.9 Build 20 thermal analyser from room temperature to 1000°C under a nitrogen atmosphere with a heating rate of 10°C min^{-1} . CHN elemental analysis was

performed in a Flash EA 1112 series CHN Thermo Finnigan instrument.

2.2 Synthesis of MOF-177

MOF-177 was designed according to the reported method with some modifications [1]. Benzenetribenzoic acid (0.06 g) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3 g) were stirred in 50 ml DMF for 3 h. The product formed was washed with pure ethanol and the sample was taken for PXRD analysis, which showed a strong similar pattern with simulated MOF-177 [1].

Figure 1. ATR-IR spectrum of synthesized MOF-177 at room temperature.

2.3 Electrode preparation and electrochemical characterization

Typical cyclic voltammetry (CV) experiments were carried out on a classical three-electrode cell configuration with a platinum auxiliary electrode and a MOF-177 electrode as the working electrode (surface area = $1 \times 1 \text{ cm}^2$) and a saturated calomel as the reference electrode using an Autolab PGSTAT-30 electrochemical workstation [16]. The working electrodes were constructed by mechanical grinding of the mixture containing the MOF-177 crystal (40%), graphite powder (40%) and polytetrafluoroethylene (20%). The obtained plaster was then overspread on the surface of the nickel mesh ($1 \times 1 \text{ cm}^2$) followed by drying at room temperature for 24 h [17]. Subsequently, it was pressed and the final electrode (MOF-177/cp) material was obtained. The electrochemical activity of the electrode was tested in a 0.05 M H_2SO_4 and 0.05 M $\text{K}_4\text{Fe}(\text{CN})_6$ electrolyte separately. Electrochemical sensor performance was studied in buffer solution (pH 7) and H_2SO_4 solution separately.

3. Results and discussion

3.1 ATR-IR analysis

Figure 1 shows the IR spectra of synthesized MOF-177 and analysis shows strong similarity with the simulated IR pattern of MOF-177 [18]. The appearance of bands at around 1581 to 1367 cm^{-1} is attributed to $\text{mas}(\text{COO})$ and $\text{ms}(\text{COO})$, respectively. The characteristic bands below 1500 cm^{-1} of the included precursor molecules are more or less superimposed by MOF-177 absorptions [19].

Figure 2. (a) PXRD pattern of synthesized MOF-177 and (b) TG curve of MOF-177.

Figure 3. (a) High-magnification SEM images of as-synthesized MOF-177 after grinding. (b) EDS of MOF-177 with (inset) percentage composition.

Figure 4. (a) NMR spectrum of as-synthesized MOF-177 and (b) CHNS analysis of MOF-177 with percentage composition of C, N, and H.

3.2 PXRD and thermogravimetric (TG) analysis

In order to confirm the product formation, crystalline nature and diffraction patterns of synthesized MOF-177, we performed PXRD. Our PXRD pattern results show strong similarities and agree with reported MOF-177 (figure 2a) [1]. The

main peaks at 4.7, 6.2 and 10.1 are well identified, as shown in the figure. However, a significant weight loss (~45.7 wt%) was observed at temperatures from 330 to 420°C for the oxygen-treated sample (figure 2b). Hence MOF-177 synthesized at room temperature is stable till 330°C and shows similarities with simulated MOF-177 [3].

Figure 5. Cyclic voltammograms of (a) the MOF-177 electrode at different scan rates (v). Inset: plot of redox peak current vs. $v^{1/2}$ and (b) the MOF-177/cp electrode at different scan rates in 0.05 M H_2SO_4 .

Figure 6. Cyclic voltammograms obtained by the MOF-177/cp electrode at 50 mV s^{-1} for (a) different concentrations of the cadmium ions in 0.05 M H_2SO_4 , (b) the cadmium ions in pH 7 phosphate buffer, (c) the lead ions in 0.05 M H_2SO_4 and (d) the lead ions in pH 7 phosphate buffer.

Figure 7. CVs of MOF-177/cp electrode response at different temperatures: (a) 20 μM Cd²⁺ in pH 7 phosphate buffer and (b) Pb²⁺ in sodium phosphate buffer. Also the plots (c) and (d) show the effect of temperature on the current response upon addition of 20 μM of Cd[II] and Pb[II] ions in pH 7 phosphate buffer respectively.

3.3 SEM and elemental analysis

SEM was used to characterize the morphology of the MOF-177 material. Figure 3a shows the SEM image of the MOF-177 sample after grinding. The shapes of the synthesized particles look like aggregation of elongated needles. Energy dispersion X-ray analysis mapping in figure 3b shows percentage composition and exhibits signals of carbon Kα (1.1 keV), oxygen Kα (1.25 keV) and zinc Kα (1.5 keV).

3.4 NMR and CHN analysis

NMR spectrum (figure 4a) shows the absence of peak at around 10–12 indicates the deprotonated co-ordination of the carboxylic acid group to the metal. A complex singlet observed at 7.2 to 7.9 ppm is attributed to the aromatic protons. CHN analysis is shown in figure 4b which indicates that the percentage composition of C is 62.43, H is 5.89 and the percentage of carbon matches with the composition of reported MOF-177. A trace amount of nitrogen might be present in the precursor that is 0.08% found in analysis.

4. Electrochemical studies

4.1 CV experiments

The MOF-177/cp electrode was used as the working electrode in a three electrode electrolytic cell and the redox behaviour of it was examined separately in a 0.05 M K₄Fe(CN)₆ and 0.05 M H₂SO₄ electrolyte. The electro-activity surface area can be calculated using the following equation:

$$I_p = 2.69 \times 10^5 n^{3/2} A C_0 D_R^{1/2} V^{1/2} \quad (1)$$

where I_p is the anodic peak current, C_0 is the concentration of [Fe(CN)₆]^{3-/4-}, D_R is the diffusion coefficient ($3.6 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$), V is the scan rate, A is the electrode surface area, n is the number of electron transfer. The electro-active surface area of the MOF-177/cp electrode is calculated as $0.50 \times 10^5 \text{ cm}^2$. Figure 5a and b displays the electrochemical activity of the MOF-177/cp electrode in different electrolytes. It shows the redox peaks at around 0.1 to 0.3 V in 0.05 M K₄Fe(CN)₆ and -0.3 to 0.2 V in 0.05 M H₂SO₄ electrolytes (figure 5a and b) at different scan rates, respectively. There is an increase in peak current with an increase in the scan rate from 10 to 100 mV s⁻¹ (figure 5a) and is proportional to the square root of the scan rate. This implies

Figure 8. (a) Amperometric sensing of Cd[II] upon successive addition at the MOF-177/cp electrode at 0.3 V in pH 7 phosphate buffer, (b) log–log plot of amperometric response vs. the concentration of the cadmium ion from 10 to 120 μM , (c) amperometric sensing of Pb[II] upon successive addition at the MOF-177/cp electrode at 0.3 V in pH 7 phosphate buffer and (d) log–log plot of amperometric response vs. the concentration of the lead ion from 10 to 170 μM .

that the electrochemical processes are diffusion controlled [20]. The corresponding log current–log potential calibration plot in figure 5a is plainly visible, which indicates the activity of the MOF-177/cp electrode and it corresponds to a good linear relationship ($R^2 = 0.92$). The anodic peak appears at around 0.25 V and the cathodic peak at about 0.15 V, which could be due to the conversion between different oxidation states Zn to Zn(II). The counter redox reaction associated with the electrolyte is given in equation (2).

4.2 Detection of Cd^{2+} and Pb^{2+} ions

Figure 6a and b illustrates the comparison between the CV responses of the MOF-177 electrode in two different electrolytes on addition of Cd^{2+} solution. However, in the presence of 10 μM Cd^{2+} a pair of well-defined redox peaks could be observed (figure 6a) at the MOF-177/cp electrode in a 0.05 M H_2SO_4 electrolyte. The anodic peak potential was -0.25 V, cathodic peak potential was -0.45 V and peak-to-peak separation ΔE_p was equal to 160 mV, which indicates that the electrode process of Cd^{2+} in the acidic

electrolyte was quasi-reversible [21]. A much higher anodic current response was recognized on increasing concentration of Cd^{2+} . A significant increased anodic peak on lower concentration of 10 μM was observed. On other hand, anodic current at -0.7 V increased on successive addition of Cd^{2+} ions and a prominent peak recognized at 30 μM in phosphate buffer (figure 6b). While peak-to-peak separation ΔE_p was equal to 260 mV, indicating that the electrode process of Cd^{2+} in the buffer solution electrolyte was irreversible. Signal enhancement in 0.05 M H_2SO_4 was found to be 40%, which is greater than that obtained in pH 7 phosphate buffer (15%). Upon comparison between two electrolytes, signal enhancement is greater in a 0.05 M H_2SO_4 electrolyte. Figure 6c and d illustrates the effects of different electrolytes at the MOF-177/cp electrode on successive addition of Pb^{2+} . The result indicates that a significant increased anodic peak at 0.5 V with anodic current 2.8×10^{-3} A in a 0.05 M H_2SO_4 electrolyte is higher than the anodic peak with anodic current 2.5×10^{-4} A in buffer solution at -0.3 V. While peak-to-peak separation ΔE_p was equal to 260 mV, which indicates that the electrode process of Pb^{2+} in the buffer solution electrolyte was irreversible. A signal enhancement in 0.05 M H_2SO_4 was found to be 76% which is greater than that obtained with phosphate buffer (pH 7), which is about 56%. A signal enhancement was found to be

Table 1. Comparison of analytical characteristics of the MOF-177/cp electrode with some previously reported Cd[II] and Pb[II] voltammetric sensors.

Electrode	Potential range (V)		Current (A)		LOD (μM) of		References
	Cd	Pb	Cd	Pb	Cd	Pb	
BiNPs/SPE SPEMWCNTs bismuth pl Nafion	−0.7 to −0.8	—	8.5×10^5		0.003	—	[22]
C/polyL modified electrodes	−0.1 to −0.9	0.85–0.75	6×10^{-6}	1×10^{-6}	0.2	0.2	[23]
Carbon paste electrode impregnated with $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	−0.9 to −0.8	−0.85 to −0.65	50×10^{-3}	50×10^{-6}	1×10^{-8}	7×10^{-6}	[24]
IIP modified carbon paste electrode	—	—			0.004	—	[25]
$\text{TiO}_2/\text{ZrO}_2$ carbon paste composite electrode	−0.9 to −0.6	−0.55 to 0.5			0.77 ppb	0.48 ppb	[20]
MOF-177	−0.9 to −0.6	−0.55 to 0.5			0.004	0.003	This work

greater in a 0.05 M H_2SO_4 electrolyte. The obtained results show that the parameters such as current density, response behaviour of the electrode and potential shift are influenced by the type of the electrolyte used. The above results highlight the excellent electrochemical response observed in 0.05 M H_2SO_4 for both Cd^{2+} and Pb^{2+} ions. The possible mechanism at a cathodic scan and anodic peak current is shown in following equations (3, 4 and 5).

The response of the sensor to ions was evaluated by calculating the % signal enhancement (%SE) and limit of detection (LOD) using the following equations (6 and 7):

$$\%SE = (I - I_0)/I_0 \times 100 \quad (6)$$

where I is the MOF-177/cp electrode peak current in the presence of analyte and I_0 is the MOF-177/cp electrode peak current in the absence of analyte. It was found to be around 60 to 70%.

$$\text{LOD} = 3S_a/b \quad (7)$$

where S_a is the standard deviation and b is the slope. The calculated LOD was 0.004 μM for the cadmium ion and 0.03 μM for the lead ion.

4.3 Effect of temperature on electrode sensing

To explore the effect of temperature on the electrode response to the metal ions, we have performed the CV at different temperatures for the buffer solution which contains 10 μM of Cd^{2+} ions and 30 μM of Pb^{2+} ions, separately. The obtained

results are illustrated in figure 7a and b. It could be seen that the higher electrode response achieved at temperature in between 45–50°C for sensing of metal ions. This should be ascribed to the following factors: (1) collision of metal ions increases on the electrode surface on increasing the temperature. (2) But current density decreases on further increase in the temperature which might be predicted due to an increase in the resistance of the electrode [26]. Hence, it is clear that particular temperature notably affects the response behaviour of the electrode with respect to the current density.

4.4 Amperometric sensing of Cd^{2+} and Pb^{2+}

Chronoamperometry measurements of the MOF-177/cp electrode were made upon the consecutive supply of Cd^{2+} and Pb^{2+} in pH 7 phosphate buffer solution. It can be shown that the MOF-177/cp electrode responded very rapidly for the low concentration of Cd^{2+} and Pb^{2+} . The calibration curves of the concentrations of Cd^{2+} and Pb^{2+} ions and current response are shown in figure 8a and b, respectively. A linear relationship was noticed in the range of 10 to 120 μM .

The corresponding linear equation for Cd^{2+} and Pb^{2+} ions can be expressed as: $I(\mu\text{A}) = 0.312C_{\text{Cd(II)}}(\mu\text{M}) + 7.55$ and $I(\mu\text{A}) = 0.00070C_{\text{Pb(II)}}(\mu\text{M}) + 8.532$, with a correlation coefficient of 0.98 and 0.97, respectively. The detection limit calculated was 0.004 μM for the cadmium ion and 0.03 μM for the lead ion at the signal to noise ratio of 3 ($S/N = 3$). Table 1 indicates the collation of our proposed Cd[II] and Pb[II] sensor with several reported electrochemical sensors. The results revealed that the detection linear range of the detection limit of Cd^{2+} and Pb^{2+} using the MOF-177/cp electrode is comparable with other reported electrochemical sensors. Therefore, the MOF-177/cp electrode can be used for the detection of the Cd[II] and Pb[II] ions in real environmental samples.

5. Conclusion

In summary, we have successfully fabricated an MOF-177 metal organic framework. The synthesized MOF-177 was highly crystalline. The excellent sensing nature of MOF-177 has been unraveled. To the extent of our literature survey, a room temperature synthesized MOF-177/cp electrode rarely reported as electrochemical sensors. The as-synthesized MOF-177/cp electrode has exhibited well-behaved redox events and good electrochemical sensor activity towards cadmium and lead ions with a LOD of 0.004 and 0.03 μM , respectively. An excellent electrochemical sensing response of the MOF-177/cp electrode has been found in H_2SO_4 media, even at very low concentrations of the samples. Hence, MOF-177 is a promising material for electro-analytical application.

References

- [1] Tranchemontagne D J, Hunt J R and Omar Y M 2008 *Tetrahedron* **64** 8553
- [2] Chae H K, Siberio-Pérez D Y, Kim J, Go Y B, Eddaoudi M, Matzger A J *et al* 2004 *Nature* **427** 523
- [3] Saha D and Deng S 2010 *J. Phys. Chem. Lett.* **1** 73
- [4] Li Y and Yang R T 2007 *Langmuir* **23** 12937
- [5] Buica G-O, Ungureanu E M, Liviu B, Razus A C and Mandoc L-R 2013 *J. Electroanal. Chem.* **693** 67
- [6] Goyer R A and Klaassen C D (ed) 1996 *Progress in drug research* **25** 958
- [7] Mouchrek V E M, Chierice G O and Marques A L B 1999 *Quím Nova* **22** 312
- [8] Murray R W (ed) 1984 *Elements of molecular and biomolecular electrochemistry* (New York: Marcel Dekker) **3** 191
- [9] Alizadeh S, Nematollahi D, Alizadeh S and Nematollahi D 2017 *J. Am. Chem. Soc.* **151** 139
- [10] Abruña H D 1988 *Coord. Chem. Rev.* **86** 135
- [11] Murray R W 1980 *Acc. Chem. Res.* **13** 135
- [12] Utner W, Wang J, L'her M and Buck B P 1998 *J. Pure Appl. Chem.* **70** 1301
- [13] Arrigan D W (ed) 1994 *Electroanalysis in biomedical and pharmaceutical sciences* (USA: F. Scholz) 119 1953
- [14] Kalcher K 1990 *Electroanalysis* **2** 419
- [15] Furukawa H, Miller M A and Yaghi M 2007 *J. Mater. Chem.* **17** 3197
- [16] Jiao Y, Pei J, Yan C, Chen D, Hu Y and Chen G 2016 *J. Mater. Chem. A* **4** 13344
- [17] Yuan B, Zhang J, Zhang R, Shi H, Guo X, Guo Y *et al* 2015 *Int. J. Electrochem. Sci.* **10** 4899
- [18] Saha D and Deng S 2010 *J. Phys. Chem. Lett.* **1** 73
- [19] Müller M, Lebedev O I and Fischer R A 2008 *J. Mater. Chem.* **18** 5274
- [20] Ruslan N I, Lim D C K, Alang Ahmad S A, Abdul Aziz S F N, Supian F L and Yusof N A 2017 *J. Electroanal. Chem.* **799** 497
- [21] Fan G, Zhai D and Zou D 2016 *J. Electrochem. Sci.* **11** 4362
- [22] Mandil A and Pauliukaite R 2012 *Anal. Lett.* **45** 395
- [23] El Mhammedi M A, Achak M, Najih R, Bakasse M and Chtaini A 2009 *Mater. Chem. Phys.* **115** 567
- [24] Alizadeh T, Ganjali M R, Nourozi P, Zare M and Hoseini M 2017 *Int. J. Electrochem. Sci.* **12** 5243
- [25] Nguyen P K Q and Lunsford S K 2013 *JSM Chem.* **1** 1001
- [26] http://www.learnaboutelectronics.org/Resistors/resistors_01a.php