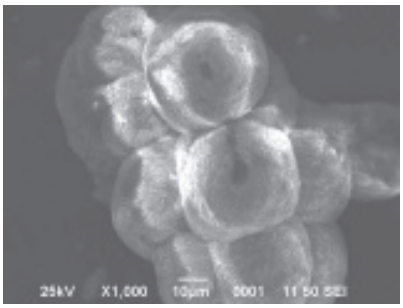
Electrochemical response of Copper Metal-Organic Frameworks for Heavy Metal Sensor application

Krishnamurthy G* and Sangeetha S
Department of Studies in Chemistry, Bangalore University
Central College Campus, Bangalore-560 001

Abstract:

MOFs can be the potential candidates for heavy metal sensor application. Synthesis of highly stableMetal-Organic frameworks(MOFs) has been achieved by precipitation method under room temperature. The prepared Copper MOFs sample was characterized by the techniques such as FTIR, Powder X-ray diffraction (PXRD), SEM, BET surface area measurement and Cyclic voltammetrytechniques. FTIR spectral analysis has confirmed the co-ordination the functional groups with metal in the compound. Surface morphology, crystalline nature and surface area of the compound were confirmed by Scanning electron microscopy, Powder diffraction X-ray, Brunauer-Emmett-Tellersurface area measurements respectively. Stability of MOFs studied by Thermo-gravimetric analysis. These MOFs are found to be stable up to 600 to 650°C temperature. Alsothe electrochemical studies have been carried out to explore electrical behavior of these MOFs for sensor application to sense the heavy metal such as Cadmium. The Cyclic voltammetry studies were made by using the working electrode prepared by the above Co-MOF sample in 0.05M $K_4Fe(CN)_6$, 0.05M KCl and 0.05M KOH solution. A significant electrochemical response has been shown by the above Copper–MOF sample.



SEM image of Cu- MOF synthesized.

Keywords: Copper- MOFs, Metal sensor, BET surface area, Cyclic Voltammetry studies.
***Corresponding author:** E-Mail: drgkmurthy.bub@gmail.com

1. Introduction

Metal-Organic Framework (MOFs) are the building blocks of metal and organic ligands. Varity of MOFs are generally prepared by different combination of metals and ligands. MOFs are quite differentfrom metal complexes by their crystalline nature with permanent porous voids. Due to the presence of porous structure in MOFs and 3D network, MOFs got importance in gas storage (Hydrogen gas storage) application, also in drug delivery, catalysis, separation technology, sensors, etc, MOFs can be synthesized by Conventional and non-conventional methods. In this work, we have used precipitation method for the synthesis of MOFs and studied the properties of MOFs in presence of chelating ligand in alkaline media. Thus, linker solubility and the crystallization/precipitation processes in which the linker is involved would be different [1]. Diamino-ethane-tetraacetic acid(EDTA) is a polyaminocarboxylic acid chelating(hexa-dentate) ligand, which donates six pair of electrons. EDTA

ligand is moderately soluble in water. So solubility is increased by increasing the pH by adding base [2-4].

This article focuses on synthesis of amorphous Cu-MOF, which has been strategically selected to prove the benefits/unique feature of this new approach in water media using chelating ligand. Also the electrochemical sensor studies on heavy metal such as [Cd^{2+}]. Presence of these heavy metal in environment causes several health disorder. Detection of toxic trace metals in the environment is a challenging analytical problem. The major existing techniques for metal trace analysis are spectroscopic and inductively coupled plasma mass spectroscopy (ICP-MS), voltammetric and chronoamperometric. In recent years, applications of chemically modified electrodes havehad great interest in various areas of research and development, such as material corrosion and inhibition, electrocatalysis, electronics, biosensors and electroanalysis [5-12]. Here, the cyclic voltammetry method is used for the study of heavy metal sensing property. The well-behaved redox event, electro-sensor activity and high stability of the as-prepared Cu-MOF indicated that it would have great potential in electrosensor application. The aim of this investigation is to highlight the potential for using synthesized metal-organic frameworks for the fabrication of electrochemical sensors. These electrodes were used for the chemical preconcentration of different heavy metals at trace levels.

2. Experimental

2.1. Material Characterization

All chemicals for the synthesis were purchased commercially and were used without further purification. The analytical techniques used for the material characterization are as follows. The IR spectra were recorded on a AT-IR 170 SX (BRUKER) spectrophotometer (4000–400 cm^{-1} region) using KBr pellets. SEM images obtained by 1105SEI instrument. The TG measurements were carried out with a SDT Q600 V20.9 Build 20 thermal analyzer from room temperature to 1000 °C under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (CuKá, 1.5418 Å). The ambient pressure gas sorption isotherms were measured by using NOVA- 1000 V er.3.70 adsorption equipment. The electrochemical experiments were carried out using an Auto lab PGSTAT30 modelInstrument with pilot integration controlled by GPES 4.9 software in a three-compartment cell.

2.2. Synthesis of Cu-MOF

EDTA of about 0.125 g (1.51 mmol), which was dissolved in an aqueous NaOH solution of4.954 g (4.76 mmol), the Solution 1. On the other hand, $Cu(NO_3)_2$û 0 $6H_2O$ (0.291 g, 3.4 mmol) was dissolved in 40 mL of distilled water (Solution 2). Solution 2 was added drop wise to the Solution 1 until the formation of blue precipitation and further kept stirringfor one weekunder room temperature [1]. The blue solid was recovered by filtration, washed with distilled water (20 mL). Afterwards, it was kept in ethanol for 6 days. Small nanocrystals formed were collected by slow evaporation method of solvent but these nanocrystals were not suitable for SXRD studies.

2.3. Electrode Preparation and Electrochemical Characterization.

The working electrodes were prepared by mechanical grinding of mixture containing active electrode material (45%), carbon black (45%) and polytetrafluroethylene (10%). The obtained slurry was then coated onto nickel mesh current collectors (1 cm x1 cm) followed by drying at room temperature for 24hsubsequently, it was pressed and obtain the final electrode material [13]. All the electrochemical experiments were conducted on AUTOLAB PGSTAT302N

electrochemical workstation with a conventional three-electrode system consisting of a bare carbon paste electrode (CPE), metal-organic-frame work electrode (Cu-MOF/CPE) as working electrode, platinum coil as auxiliary or counter electrode, and saturated calomel (saturated KCl) as reference electrode. The electrochemical studies of the individual electrode were made in 0.05M

$K_4Fe(CN)_6$ and 0.05M KCl mixed electrolyte. Cyclic voltammetry (CV) tests were done within the potential range of -1.0 to 1.0 V at different scan rates. The electrochemical sensor studies were made in 0.1M KOH solution.

3. Result and Discussion

3.1. FTIR analysis

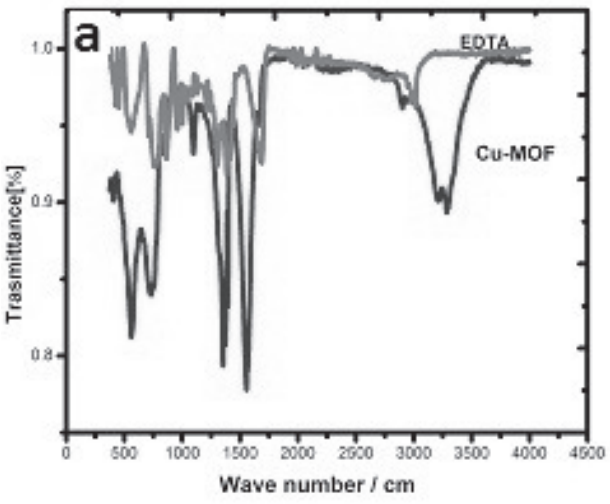


Figure. 1. a). ATR-FTIR of synthesized Cu-MOFs

Figure 1a. shows the infrared spectra of the complex, which has shown wide absorption band in the region 3200–3400cm^{-1}. Thesepeaks can be assigned to the O–H stretching vibration of the water molecules. The peaks observed at 2927 cm^{-1} are correspond to the C–H vibrations. The band at about 1632 cm^{-1}imply thatthe carboxyl groups are co-ordinated with Metal. The peak at 1092 cm-$^{-1}$ is for C-N vibrations. [14]

3.2. PXRD analysis

The Cu-MOF formed was highly crystalline and the peaks were quite different from starting materials, $CuSO_4$ and Diamino-ethane-tetra acetic acid. It is shown in figure 2a, PXRD pattern of synthesized Cu-MOF matches with PXRD pattern of Cu-MOF reference **[15].** Crystalline nature of Cu-MOF prepared at room temperature confirmed by the PXRD data. Average crystals size calculated by Scherrer's equation was found to be 30-40nm.

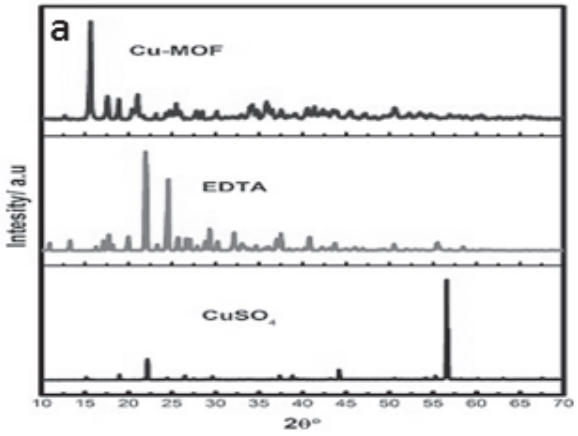


Figure.2.a) Powder x-ray diffraction (PXRD) of synthesized Cu-MOFs.

3.3. SEM analysis.

Cu-MOF particles prepared at room temperatureexhibit the morphology of semi pressedspheres, which areaggregatedby smaller needle like structures shown in figure 3a. The estimated averagesize of these sphere are 40-50µm. The smaller particles might be of nano size.

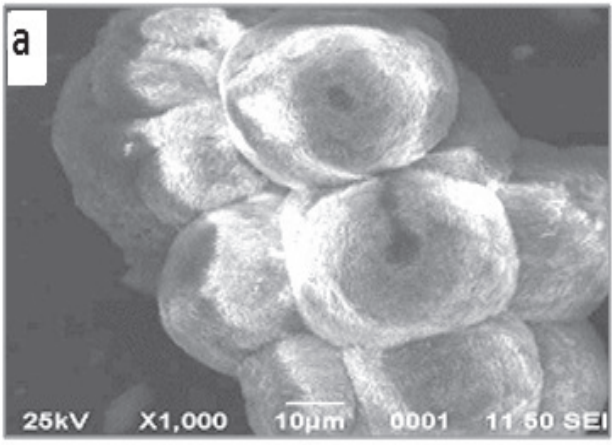


Figure.3.a) SEM of Cu-MOFs prepared at room temperature.

3.4. BET analysis

Figure.4.a) compares the N_2 adsorption/ desorption isotherms of the calcined sample Cu-MOF prepared at room temperature.The total surface area and specific surface area estimated

using the BET method are 380.7 $m^2 g^{-1}$ and 95.185 $m^2 g^{-1}$ respectively. We havefound that surface area ofCu-MOF is more thanthe estimated surface area of MOFs synthesized at room temperature. The adsorbed volume, which corresponds to an external surface area is 83.424 m^2/g^1, with the average pore diameter 96.94 Å. This lightly lower surface area of the Cu-MOF prepared at room temperature can be explained bythe presence of impurities in it. PXRD and TG analysis give supporting information for the presence of impurities. The other notable feature of this isotherm is the amount of N_2adsorbed at P/P° beyond 0.01g. Supporting this interpretation, above shows the N_2adsorption isotherms of the MOF material.

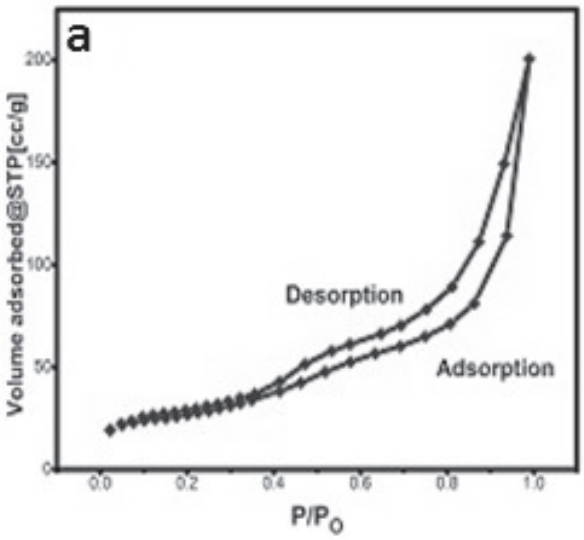


Figure.4. a) N_2 adsorption/desorption isotherm of the calcined Cu-MOF materials prepared at room temperature.

Thermogravimetric analysis gives valuable information on the stability, extra impuritiesor percentage of unreacted linker molecule present in metal-organic framework and alsotheratio of Cu/liker. Figure.4a is the TGA curve for the decomposition of Cu-MOF prepared at room temperature, whichgives the decomposition of H_4EDTA (40 w%) with average decomposition temperature (centered at 350 °C in the range 330–450 °C).

3.5. TGA analysis

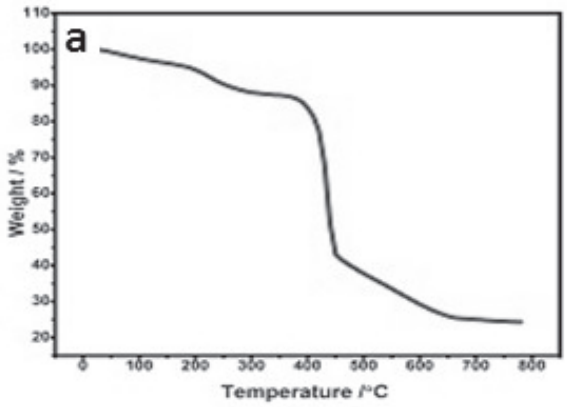


Figure.5.a) Thermogravimetric of Synthesized Amorphous Cu-MOF.

Presence of very less amount of unreacted H_4EDTA can be seen as just 4 w% (centered at 250°C and in the range 200-300°C). Thisshows that the as-synthesized Cu-MOF sample prepared in water as sole solvent at room temperature having higher stability. These values give the information of presence of very less amount of un reacted state of linker or isolated EDTA. The decompositionmust be attributed to isolated crystals of H_4BDC within nonconventional or precipitated method Cu-MOF as they were detected by XRD as well-defined peaks (Figure 5a). In support of this assignment, the decomposition of Cu-MOFstarts at 350 °C (centered at 350 °C and in the range 350–650°C) is more than the decomposition temperature of un reacted H_4EDTA is (centered at 250°C in the range 250-300°C), and an even higher than the decomposition temperature of the pure commercial organic linker H_4EDTA (200°C-300)[16].So, the presence of unreacted H_4EDTA confirmed by the decomposition at range between 200-300°C and TG analysis has confirmed thatthe decrease in weight loss attributed to the isolated H_4EDTA with reaction time. Very less amount of water contentwas lost from this sample (2w%) at100 °C, which suggests that either water or some residual solvated Na^+ cations can play a similar role to that of H_4BDC molecules.

3.6. Electrochemical Properties and Sensor Application

The electrochemical studies on heavy metal sensor application were made by conducting Cyclic voltammetric (CV) experiments by using theworking electrode made of our MOF. Preliminary CV experiments were performed to study the behavior of bare carbon paste electrode (CPE) and Cu-MOF/CPE with in an electrochemical cell containing 0.005M $K_4Fe(CN)_6$, 0.5M KCl (supporting electrolyte) solution. Then the electrode performance was observed at different scan rate 10mV to 90 mV. Comparing the two voltamogram, that recorded by the bare carbon paste electrode and that obtained from the Cu-MOF-CPE (Figure 6a), Cu-MOF/CPE having higher current density than the CPE. Again CV experiment recorded for two Cu-MOF/CPE having different concentration of Cu-MOF, Figure 6b, which reveals that redox current increases on increasing concentration of prepared Cu-MOF, which shows redox peaks between -0.3 V to 0.1 V. The redox current increase with the increasing scan rate from 10 mV to 90 mV/s (figure 6c) and are proportional to square root of the scan rate indicating that the electrochemical processes are diffusion controlled. [17]

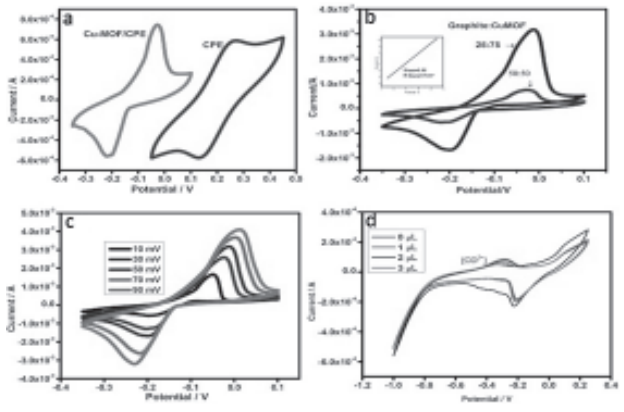


Figure. 6.a) Cyclic voltammograms comparison of Bare CPE and Cu MOF. b) Cyclic voltammograms obtained by different concentration of Cu-MOF, c) CVs of Cu-MOF/CPE at different scan rate ($\tilde{o}$),The inset figurequadratic plot of redox peak current versus $\tilde{o}^{1/2}$and d) Cyclic voltammograms obtained by Cu-MOF/CPE at 50mV/s for different concentrations of cadmium, in KOH solution.

The modified electrode was soaked in solutions containing different concentration of studied heavy metal for about ten minutes, removed, then rinsed with pure water. The electrodes were then, respectively, transferred into the electrochemical cell only containing 0.1M KOH solution for cyclic voltammetry. Figure.6d shows the CVs for Cd^{2+} solutions obtained at Cu-MOF/CPE. The cathodic scan produces the reduced species of cadmium, which is deposited on the electrode. This deposition favors the oxidation process and hence the current peak of this signal (i.e., the anodic peak). The peak current increased with an increase in Cd^{2+} concentration. This suggest that the Cu-MOF/CPE has strong affinity through surface co-ordination with metal ions.

4. Conclusion

This work reports excellent electrochemical and electro-sensor properties of stable and redox-active Cu-MOF prepared by a simple, inexpensive widely applicable, environmentally friendly method. As a consequence, the industriallydemanded preparation of MOF materials at room temperature and using water as the sole solvent could be achieved for recently. So as-synthesized Cu-MOF, leading to high-quality, nanocrystalline materials possessing high stability upto 600-650°C, a notable external surface area 380.7 m^2 g^{-1} and a limited or even negligible amount of unreacted linker within the pores. The as-synthesized Cu-MOF exhibited well-behaved redox events and high electrosensing activity towards. The Cu MOF based electrode was demonstrated for the application in electrochemical sensor of Cadmium ion, and good analytical performances were obtained. The results indicated that the presented Cu-MOF have a potential application in electrochemistry. Further hydrogen storage capacity by electrochemical method have to study in future work.

REFERENCES

1. Manuel Díaz-García, Yonas Chebudeb and Isabel Díaza, *Green Chem.*,**2015**.17.1500

2. L.M.Huang, H. T. Wang, J. X. Chen, Z. B. Wang, J. Y. Sun,D. Y. Zhao and Y. S.Yan, *Microporous*

Mesoporous Mater.,**2003**, 58, 105.

3. T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille and G. Ferey, *Chem. –Eur. J.,* **2004**, 10,1373.

4. G. Calleja, J. A. Botas, M. G. Orcajo and M. Sanchez- Sanchez, J. *Porous Mater.,* **2010**, 17, 91.

5. Mouchrek VEM, Chierice GO, Marques, *Quím Nova,*.**1999**,22,314.

6. Murray RW Bard AJ, *Ed., Dekker M*, **1984**.191.

7. Abruña HD,J. *Coord Chem,*. Rev **1988**: 135-189.

8. Murray RW, *AccChem*.,**1980.**135-141.

9. Kutner W, Wang J, L'her M, Buck BP, *Pure ApplChem,*. **1998**.70.1318.

10. Arrigan DW, *Analyst*,.**1994**.1953-1966.

11. Kalcher K, *Electroanalysis*,.**1990.**419-433.

12. Kalcher K, Kauffmann JM, Wang J, Svancara I, Vytras K, *Electroanalysis,*. **1995**.7.22.

13. Yang Jiao, Jian Pei, Chunshuang Yan, Dahong Chen, Yongyuan Hu and Gang Chen, *J,RSC,*.**2016**. 10.1039.

14. Di Li and Guo-Qing Zhong, *Bioinorganic Chemistry and Applications,*. **2014.**10.1155.

15. Atsushi Kondo,Chin ChinTiew, Fumiaki Moriguchi and Kazuyuki Maeda,J,*RSC,*.**2013.**10.39.

16. Hitoshi nishizawa. Takuhiro,Tani and Kiyoshi Matasuoka, J,*ACS*,.**2006**.10.1111.

17. Baiqing Yuan, Jingchao Zhang, Renchun Zhang, Huaizhong Shi, XiuliGuo, YuanyuanGuo, XueyingGuo, ShunshouCai, Daojun Zhang, *Electrochemical science,*.**2015.**10.4899.