

MN and Co, Metal - organic frameworks for hydrogen gas(energy) storage and heavy metal ion sensor application for clean environment

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Abstract- Metal-organic frameworks (MOFs) are the fascinating porous materials, which are constructed by the linkage of metal ions and organic ligands. The MOFs have interesting visual structures and topological features with wide potential applications in heterogeneous catalysis, energy (H₂ gas) storage, ion sensor, bimolecular sensor, etc. We, in this work have presented on the MOF materials for clean energy (H₂ fuel storage) material and Cd²⁺ ion sensing application. The Mn-MOF, [C₁₅H₇Mn_{1.5}N₂O₆] and Co-MOF [(Co(H₂O)₅NO₂)₁₈C₁₂H₂4O₆] are synthesized by a solvothermal route. The prepared products were characterized by Single crystal X-ray diffraction (SXRD), Powder Xray diffraction(PXRD), FTIR spectroscopy and Field emission Scanning electron microscopy(FE-SEM). The high energy storage (super capacitance) of the synthesized Mn-MOFs was evaluated using cyclic voltammetry (CV) and galvanostatic charge/ discharge measurements. The Co- MOF electrode has shown the electrochemical sensing property towards Cd²⁺ ion in aqueous medium. Mn-MOFs lead to an inherent increase in conductivity and specific capacitance from 133 Fg⁻¹ to 808 Fg⁻¹. These values demonstrate the better show of all the Mn-MOFs material for energy (H₂ gas) storage application and Co-MOFs for toxic (heavy) metal sensor applications.

Keyword: Mn-MOFs, Co-MOFs, Solvothermal synthesis, Energy storage, Cadmium ion sensor.

INTRODUCTION

Emission of CO₂ gases by increased vehicular density and contamination of aqueous and soil environment by toxic (heavy) metals is a serious concern all over the world. In this connection scientists are making new materials and adopting new technology to overcome such issues. Metal-organic frameworks (MOFs) are among the new materials, which are the porous solids constructed from a variety of organic ligands and metal ions. The construction of novel MOFs is considered as one of the most important issues in coordination chemistry as they have interesting visual structures and topological features¹ with wide variety of applications. These applications include heterogeneous catalysis,² gas storage³, ion sensor, bimolecular sensor and photoluminescent property.⁴ Generally, MOFs are constructed through the coordination of metal ions and organic linkers.⁵ MOFs can be synthesized by hydrothermal, solvothermal, Microwave, etc., techniques.

In the early 80s, fundamental host-guest studies aimed to gain insights into the nature of second sphere coordination were carried out⁶ using electrochemistry and later single crystal X-ray analysis to investigate whether macrocyclic organic molecules were able to encapsulate metal ions. Recently, from a more functional point of view, perovskite-like⁷ hybrid metal-organic materials are also self-assembled using second sphere

interactions. The hydrogen adsorption on a porous MOFs have been evaluated as physisorbents for hydrogen storage applications.⁸

The Metal-organic framework, Mn-MOF and Co-MOF having second sphere interaction was prepared by solvothermal process. Co-MOF has been prepared by the reaction between the Cobalt salt and 18-Crown ether. Crown ethers exhibit an extremely versatile range of interactions with metal cations. Multidimensional metal-organic frameworks constructed by means of hydrogen bonds constitute a recent class of compounds with high current interest in various areas including in supramolecular and host-guest chemistry, material science, crystal engineering, catalysis, molecular magnetism, etc.⁹⁻¹²

Mn-MOF [Mn(bdc)(Mi)(Dmf)], has been prepared by solvothermal route using two kinds of organic ligands including Terephthalic acid and Methyl imidazole and Mn(NO₃)₂ as a manganese precursor. The Solvothermal synthetic routes described in this work allow obtaining a new Mn-MOFs and the coordination modes of the carboxylate groups that give rise to the extraordinary crystal and shows a unique 3D structure of Mn-MOF.

EXPERIMENTAL

Materials and methods

Cobalt nitrate hexa-hydrated (Co(NO₃)₂·6H₂O), Zinc nitrate hexahydrate Zn(NO₃)₂·6H₂O, were purchased from Sigma-

Aldrich and 18-crown-6-ether was purchased from Spectrochem Pvt. Ltd., Mumbai (India). Terephthalic acid, N, N-dimethylformamide (DMF) etc., used in this research work were of analytical grade, obtained from SDFCL (s d fine chem. Limited). 1-methyleimidazole All solvents and reagents were used without further purification.

ATRIR spectra were obtained with samples in KBr for the title complexes on BRUKER-ATRIR spectrophotometer in the range 3500–400 cm^{-1} . Single crystals of $\text{C}_{24}\text{H}_{72}\text{Co}_2\text{N}_4\text{O}_{36}$ were collected on a Xcalibur, Nova diffractometer at 298K. Electrochemical analysis was made using Auto lab potentiostat. Field emission scanning electron microscopy (FESEM) images were collected using a Supra 55 field emission SEM system (Zeiss). The elemental analysis (C, H, and N) was carried out on a Inca 2400 Series II element analyzer.

Synthesis of Mn-MOF and Co-MOF

The Mn-MOF was prepared by mixing the solutions of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 gm) and Benzene 1,4 dicarboxylic acid (0.70gm) dissolved separately in DMF. About 0.5 ml of 1-methylimidazole was added to get a clear solution. The resulting solutions were transferred to a Teflon-lined stainless steel autoclave and heated in an oven at 120°C for 72 hours. The Co-MOF was obtained by the reaction of 18-Crown ether (0.26 g, 0.01 mol) dissolved in DMF and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.29 g, 0.1mol) dissolved in deionised water. The resulting solution was then heated at 100°C for 6 h in a Teflon-lined stainless steel bomb. After cooling to room temperature, the solutions were kept for crystallization about 1 week to 1 month.

RESULTS AND DISCUSSION

Crystal structures of the MOFs

Single-crystal X-ray crystallography study has given the details that, the asymmetric unit consists of two Mn^{2+} ions: one H2BDC ligand, which is coordinated with DMF molecules in Mn-MOF. The entire cluster designed by interconnection of crown ether, one nitrate ion and water molecule through hydrogen bonding in Co-MOF. Crown ether linked through second sphere coordination by hydrogen atom of water molecules and acts as a bridging linker between two neighbouring molecule.

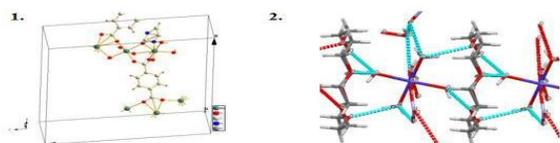


Figure 1 (a) Crystal structure of Mn-MOFs and (b) Crystal structure of Co-MOFs.

FT-IR spectral, PXRD and SEM analyses

The FTIR spectral study of Mn-MOF has shown the broad absorption band centred at 3250–3000 cm^{-1} indicating the hydrogen-bonding interactions in the framework. The strong bands at 1513 cm^{-1} and 1369 cm^{-1} of the asymmetric stretching vibrations(OCO) and stretching vibrations (OCO) of the H₂BDC ligand. The IR spectrum of Co-MOF, has shown wide absorption band in the region 3200–3400 cm^{-1} for O–H stretching vibration of the water molecules. The C–O–C (s) peak was observed at 1345 cm^{-1} and the bands at about 1632 and 1390 cm^{-1} implied us the presence of NO₂ group.

The X-ray powder diffraction pattern (Fig.2a and 2b.) for the product was obtained by employing the monochromatic high-intensity $\text{CuK}\alpha$ radiation ($\lambda = 0.1541874 \text{ nm}$). The sharpness of the peaks in the pattern indicates the crystalline nature of the product. The presence of prominent metallic peak at the Mn-MOFs and Co-MOFs 2 θ values at 10.43, 20.97 and 15.27, 29.09 indicate the coordination of metal with the ligands to form complex.

FE-SEM images of Co-MOFs and Mn-MOF that are presented enable the study of the microstructure and surface morphology of the products. The Fig.2 (c) shows the SEM micrographs of a Co-MOFs sample, which are formed by square shaped and micro-sized particles, having particles size between 1- 4 μm . Fig.2 (d) shows the distribution of particles in Mn-MOF in a range of dimensions arranged as diamond shaped crystals. The FE-SEM images were viewed under high and low (such as 100 μm and 20 μm) magnifications. The images show the stacks of well-aggregated diamond like crystals with attractive smooth surfaces.

Electrochemical (CV and Charge–discharge) studies:

The working electrodes were prepared by taking a mixture of 80 wt% of Mn-MOF and Co-MOF samples (~ 4 mg), 15 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) binder with ethanol as a solvent. The above slurry was subsequently pressed onto nickel foam under a pressure of 20 MPa, serving as the current collector. Here,

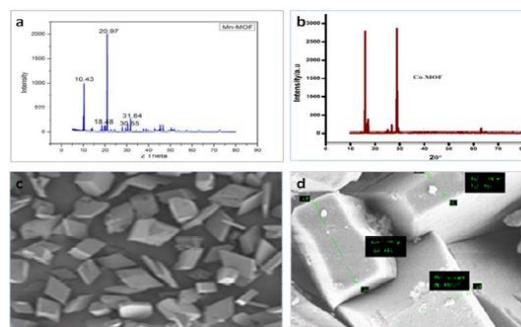


Fig.2: (a) and (b) are the PXRD patterns of Mn-MOFs and Co-MOFs (c) and (d) are the FE-SEM images correspond to Co-MOFs and Mn-MOFs respectively at different magnifications

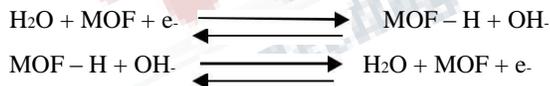
the prepared electrode, platinum foil and saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively.

The Mn-MOF specific capacitance is calculated by different scan rates 10, 50, 100, 150, 200 mvs⁻¹ has reported a highest specific capacitance of 270 F g⁻¹ for 10 mvs⁻¹ in 6 M KOH solution. The specific capacitance values are found to decrease with increase in scan rate. The specific capacitance is greatly dependent on the ion diffusion in the electrolyte, the surface adsorption of ions on the electrode materials and the charge transfer in the electrode. At higher scan rate, any of the three process may be fairly slow, which lowers the specific capacitance.

Galvanostatic charge–discharge (GCD) analysis was performed in the potential range of 0.0 to 0.6 V at different current densities (1A g⁻¹, 2A g⁻¹, 3A g⁻¹, 5Ag⁻¹, 10 A g⁻¹) to estimate the specific capacitance and cyclic stability of Mn-MOF. Fig. 6 (c) shows the charge- discharge curves of Mn-MOF. The specific capacitance was calculated using the following equation.

$$C_{sp} = It/m\Delta V$$

Where Csp (F/g) is the specific capacitance, I is the constant current (A) of the charge-discharge processes, t is the discharge time (s), m is the mass of the electro active material on the electrode (g), and ΔV (V) is the potential window respectively. The hydrogen storage capacity of Mn-MOF was estimated from the charge passed during the discharge process until a cut off potential was reached. The charge - discharge reactions can be as follows.



This voltage is about 1Ag⁻¹ to 10 Ag⁻¹ and the corresponding specific capacitance values are 808(F/g⁻¹) 683(F/g⁻¹),

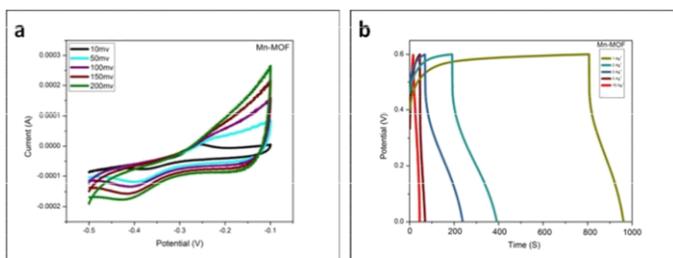


Fig.3 (a) Cvs of Mn-MOF electrode in a 0.6 M KOH solution at different scan rates such as 10, 50, 100, 150, 200 mVs⁻¹, (b) Galvanostatic Charge/ discharge curves of Mn-MOF with different current densities (1A g⁻¹, 2 A g⁻¹, 3A g⁻¹, 5Ag⁻¹, 10 A g⁻¹)

577(F/g⁻¹), 288(F/g⁻¹) and 133(F/g⁻¹) respectively. The specific capacitance decreases with increase in current density. This is due to a high IR drop and slow rate of redox reactions at higher current densities.

Electrochemical Cadmium ion sensing.

Fig. 4(a) shows the cyclic voltammograms recorded for the bare carbon electrode (BCE, in the absence of MOF) and for Co-MOF electrode in Fe(CN)₆⁴⁻/ Fe(CN)₆³⁻ electrolyte solution. The anodic peak at around 0.42 V and the cathodic peak at about 0.04 V might correspond to the conversion between different oxidation states of

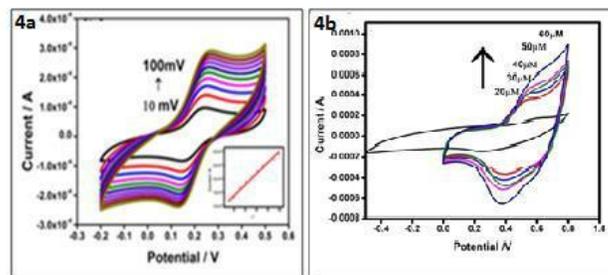
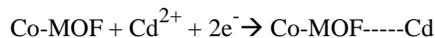


Fig.4(a)CVs of Co-MOF electrode at different scan rate (v). Inset: plot of redox peak current versus v^{1/2} and 4(b) Cyclic voltammograms obtained by Co-MOF electrode at 100 mV/s for different concentrations of Cadmium ion at pH 7.

The redox current increases with the increasing scan rate from 10 mV to 100 m V/s (Fig.4a) and the current values are proportional to square root of the scan rate, which indicates that these electrochemical processes are diffusion controlled. The corresponding inset calibration plot, log current versus log potential clearly indicates that the Co-18CREMOF electrode displays a good linear relationship (R² = 0.95).

Sensing of cadmium ions by the Co-MOF electrode is shown in Fig.4b, which displays the prominent oxidation peak at 0.5 V and cathodic peak around 0.3 - 0.4 V. This might be due to reduction of cadmium ions and deposition during cathodic scan and this deposition favours the oxidation process in reverse and hence the anodic current peak. The increased current response was observed on increasing concentration of Cd(II) from 20 μM to 60 μM. This shows that the hybrid Co-MOF electrode has electrocatalytic ability towards the oxidation-reduction of

cadmium/cadmium ions. This electroactive response of the MOF material could also be due to the interaction between cadmium(II) and the active sites on the available larger surface areas or functionality of the hybrid Co-18- crownether MOF. The electrochemical redox events can be given as follows.



CONCLUSIONS

The Mn-MOF [C₁₅H₇Mn_{1.5}N₂O₆] and Co-MOF were successfully synthesized by simple environmentally benign solvothermal method at low temperature of about 120°C. These MOFs are crystalline in nature and quite stable in the aqueous medium. As these materials are microporous in nature the surface areas are larger and hence these can be harnessed for Energy (H₂ gas) storage application. Thus the MOF was tested conventionally for H₂ storage capacity for CO_x free energy application in fuel cells. We found that the specific capacitance up to 808(F/g). The as-synthesized hybrid Co-MOF has exhibited well-behaved redox events and excellent electrochemical sensor activity towards Cadmium ion. Hence, this Co-MOF could be harnessed as a material for metal ion detection.

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REFERENCES

- (a) J. Pang, E. J. P. Marcotte, C. Seward, R. S. Brown, S. Wang, *Angew. Chem Int. Ed.*, 2001, 40, 4042; (b) J. Y. Lu, M. A. Li, Lawandy, *J. Inorg. Chem.*, 1999, 38, 2695;
- I. J. Dance, *Am. Chem. Soc.*, 2007, 129, 1076;
- T. K. Maji, G. Mostafa, H. C. Chang, S. Kitagawa, *Chem. Commun.*, 2005, 2436;
- J. Jin, W. Y. Wang, Y. H. Liu, H. W. Hou, Y. T. Fan, *Chem. Commun.*, 2011, 47, 7461;
- (a) K. S. Murray, *Adv. Inorg. Chem.*, 1995, 43, 261; (b) R. E. P. Winpenny, *Adv. Inorg. Chem.*, 2001, 52, 1;
- (a) B. Moulton, M. J. Zaworotko, *Chem. Rev.*, 2001, 101, 1629; (b) H. M. Colquhoun, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 39, 847–849.
- H. M. Colquhoun, S. M. Doughty, J. F. Stoddart and D. J. Williams, *Angew. Chem. Int. Ed. Engl.*, 1984, 23, 235–236.
- (a) B. Dietrich, M. W. Hosseini, J. M. Lehn and R. B. Sessions, *J. Am. Chem. Soc.*, 1981, 103, 1282–1283 (c) H. F. Zeng, T. H. Li, Z. W. Yan, S. J. Luo, F. Li, *Cryst. Growth Des.* 2010, 10, 475.
- (a) Fang Guo, Javier Martí-Rujas, *Dalton Trans.*, 2016, 45, 13648–13662; (b) A. Y. Robin, K. M. Fromm, *Coord. Chem. Rev.*, 2006, 250, 2127–2157.
- (a) G. Krishnamurthy, B. M. Omkaramurthy, *JECSE*, 2016, ISSN-0013-466X; (b) D. M. P. Mingos (Ed.), Springer, 2005.
- (a) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem, Int. Ed.*, 2004, 43, 2334–2375; (b) C. Janiak, *Dalton Trans.*, 2003, 0, 2781–2804; (c) A. M. Beatty, *Coord. Chem. Rev.*, 2003, 246, 1–354.
- (a) B. H. Ye, M. L. Tong, X. M. Chen, *Coord. Chem. Rev.*, 2005, 249, 545; (b) S. Kitagawa, K. Uemura, *Chem. Soc. Rev.*, 2005, 34, 109–119.