Fabrication of Transition-metal (Zn, Mn, Cu)-based MOFs as Efficient Sensor Materials for Detection of H2 Gas by Clad Modified Fiber Optic Gas Sensor Technique

M Nagoor Meeran (nagoorchem@gmail.com)
Vel Tech Dr RR and Dr SR Technical University: Vel Tech Rangarajan Dr Sagunthala R&D Institute of Science and Technology https://orcid.org/0000-0002-7551-4642

S.P. Saravanan
Karuppannan Mariappan College

H.H Hegazy
Al-Azhar University

Research Article

Keywords: Metal-organic framework, Chemical sensor, High surface area, Fiber optic sensor, Hydrogen gas

DOI: https://doi.org/10.21203/rs.3.rs-250500/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License
Abstract

Recent research demonstrate that promising gas sensing materials are called metal-organic structures (MOFs) and their products due to their tunable form, elevated surface area, and extremely porous structure and physisorption towards gases with relatively low temperature.

In this report, recent developments in transition-metal (Zn, Mn, Cu)-based MOFs and their derivatives are synthesized as sensing materials. The sensors samples were analyzed by XRD, SEM, TEM, BET and XPS in order to know the textural, structural and electronic state of the samples. Fiber optic clad modified sensors were fabricated and tested gas sensing properties towards H$_2$ gas with various concentrations (0-1000 ppm). Among the three sensing material, Zn doped MOFs sensor showed outstanding selectivity with high sensitivity (115 counts/kpa) towards H$_2$ gas. Moreover, it has shown high response (20 s) and recovery time (27 s) as well as long term stability. The designed sensors may be required to apply to the production of an outstanding sensor for H$_2$ for commercial uses.

1. Introduction

Gas Sensors draw a great deal of scientific interest in remote sensing industrial processing and sensing with evolving emerging innovations protocols. They are commonly used in commercial, environmental and medical applications [1]. Often, measurement of the new area of study in nanoscience and technology has started new the confidence in the ability of metal oxides and their compounds in variety of applications. Gas sensors have been developed because of industrial development and environmental degradation. Especially, to control the poisonous and dangerous gas control in our atmosphere. Recent development in the eld of nanoscience and its synthesis methods can growth and produced a various types of novel gas sensing materials such as metal oxides, polymers, and carbaneseous based materials [2-7]. Generally, metal oxide semiconductors like, ZnO, SnO$_2$, WO$_3$, TiO$_2$ and Fe$_2$O$_3$ are investigated as sensing materials due to substantial exposure to VOC sensing as a smart semiconductor nanomaterial attributable to their outstanding electronic structure, chemical and mechanical stability.

A modern class of crystalline porous materials, nanoporous metal-organic frameworks (MOF), are derived from a mixture of metal ions (or clusters of metals) and organic binders. Due to their application potential, gained intensive coverage in diverse areas such as preservation of gas [8, 9], sensing of gas [10], catalysis [11], oxidation of water [12] and supercapacitors [13,14]. Since the first MOFs’ synthesis in the 1990s, by Yaghi and Li [15, 16], a number of MOFs with special structures were constructed by changing the middle and centre of the metal ligands of organic origin [17, 18]. Actually, 0D, 1D, 2D and 3D MOFs are effectively synthesized by various preparation processes like microwave, hydrothermal, solvothermal and mechanical methods. Most of the research work focuses on the lithium ion batteries and super capacitor based MOFs. For example, Hu et al., [19] synthesized MOFs-derived metaloxide nanomaterials electrodes and were used as energy storage applications. Zhaog et al., [20] reported electrochemical applications of nanostructures with MOFs electrode by wet chemical route. Zheng et al., [21] also derived Fe, Co, and Ni doped MOFs for electrochemical energy storage applications. Even so,
there are hardly any analyses of MOFs and their derivatives focused on Zn/Mn/Cu that is suitable for gas sensors for use as sensing materials. In this, we work on analyzing and summarizing Zn/Mn/Cu-MOFs and their derivatives and the debate and use of their properties in gas sensors. The fabricated sensor samples were exposed to various hazard gases and the results shows that Zn-based MOFs showed outstanding sensing performance than compared with other two metal based MOFs. The sensing mechanism was also discussed.

2. Experimental Procedure

In the synthesis of Zn doped MOFs, 2.5 g of Zn(NO$_3$)$_2$ and 1.1 g of 1,3,5-benzenetricarboxylic acid (BTC) were diluted with 50 mL of ethanol and N,N-dimethylformamide (DMF). The volume of ethanol and DMF is 1:1. Then the solutions were transported into an autoclave of Teflon-lined stainless steel. The combination was made of hydrothermally heated at 150 °C for 10h. After steadily cooling, the resulting blue crystals were purified and methanol removed overnight. The solved DMF can be extracted using the Soxhlet extractor. They then dried the substance at room temperature. In the process of Mn and Cu doped MOFs, 2.5 g of Mn(NO$_3$)$_2$ and Cu(NO$_3$)$_2$ were diluted with BTC. Then hydrothermal process was adapted under same experimental conditions. Zn, Mn and Cu doped MOFs samples were named as Zn-MOF, Mn-MOF and Cu-MOF, respectively.

2.1. Gas sensor set up and preparation of sensor region

The sensor set up and sensor region preparation method was described in already reported work [22]. The configuration of the fibre optic gas sensor to detect VOC was seen in Fig. 1. A cable light source (SLS201/M halogen lamp) was installed at one end of the bulb. The other end was attached to the fibre and optical spectrometer (CCS200/M) to analysis the spectral response of the prepared samples. Room temperature and the relative humidity spectrum were carried out in the dark room for the entire sensing test. The scale using the hygrometer was about 60-65%. The concentration gas is varied from 0-500 ppm. The sensitivity was calculated by the following formula [23], Sensitivity $S = \frac{dI}{dC}$ Where $dI$ is the rate of change of spectral intensity and $dC$ is the rate of change of vapour concentration.

3. Results And Discussion

3.1. Structural analysis

Figure 2 shows the XRD pattern of Zn-MOF, Mn-MOF and Cu-MOF, respectively. The hexagonal crystalline structure of Zn-MOF is indexed to all peak positions with diffraction planes and the findings are precisely affiliated with previously published works [24, 25]. Although the monoclinic crystalline phase was exposed to the Mn-MOF and Cu-MOF samples, the findings are ideally suited to the works already published [26, 27]. A sharp diffraction pattern could be found in the Zn-MOF sample than compared with others, this may due to the high crystalline nature of the samples. Moreover, all the three sensor samples
were crystalline with high purity due to the absence of any impurity peaks in their respective diffraction patterns.

### 3.2. Morphological analysis

To analyse the morphological identity of the samples, SEM and TEM photographs were carried out. Figure 3 (a-c) shows the SEM images of Zn-MOF, Mn-MOF and Cu-MOF samples and the relative morphologies are nanotubes, nanosheets and nanoparticles, respectively. Further, the TEM image of Zn-MOF clearly shows that nanotubes with length around 200-300 nm and diameter of 10-20 nm (Fig. 3d). The clear sheets with wrinkle type with average diameter of around 120-180 nm was identified in the Mn-MOF sample (Fig. 3e). The individual and less collected spherical nanoparticles (30-35 nm) were found in the Cu-MOF samples (Fig. 2f). Further, the elemental mapping of the sensor samples results exhibit the main elements are zinc, manganese, copper, nitrogen and their distribution are uniform (Fig. 3 g-j).

### 3.3. Textural and elemental composition studies

Figure 4 (a) and (b) shows the N\textsubscript{2} adsorption curves of Zn-MOF, Mn-MOF and Cu-MOF samples, respectively. Type IV isotherm with H3 hysteresis loop in the range (0.6-1.0, P/P\textsubscript{0}) confirms that mesoporous characteristics of the samples [28-30]. The BET surface area of Zn-MOF, Mn-MOF and Cu-MOF samples were 102.4 m\textsuperscript{2}/g, 87.4 m\textsuperscript{2}/g and 67.4 m\textsuperscript{2}/g, respectively. The corresponding pore diameter values are 13.4, 22.5 and 31.2 nm, respectively. To detect the chemical composition, XPS was carried out and the wide range survey spectrum illustrates that Zn, Mn and Cu elements are evenly distributed on the metal-metal organic framework system (Fig 5 a). Fig. 5b) display the HR XPS of Zn 2p, which exposed two BE at 1014.1 and 1021. eV is due to the Zn 2p\textsubscript{1/2} and Zn2p\textsubscript{3/2}, respectively. The Mn XPS spectrum (Fig. 5c) presents the BE at 651.1 and 642.1 eV that correspond to the valence states of Mn 2p\textsubscript{1/2} and Ni 2p\textsubscript{3/2}, respectively.

There are two BE at 943.3 and 960.8 eV is assigned to Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2}, in the HR XPS of Cu 2p (Fig. 5d).

### 3.4. Gas sensing test

Figure 6 (a-c) depicts the output spectral response of Zn-MOF, Mn-MOF and Cu-MOF samples, respectively. The concentration of H\textsubscript{2} gas is varied from 0-1000 ppm with the help of mass flow controller (MFC). There are three visible peaks are situated at 687, 775 and 954 nm, indicating the optical fibre characteristic peak recruited. All three peaks demonstrate the major difference in intensity after adjustable gas concentration (0-500 ppm). It can be found, from the spectral graph, Zn-MOF sensor demonstration much better difference in the output intensity as a function gas concentration with respect to other sensor materials. The sensitivity curve of all the three sensor samples was displayed in Figure 6.
Due to the higher light output intensity, the Zn-MOF sensor exhibits high sensitivity of 115 counts/kPa than compared with Mn-MOF (92 counts/kPa) and Cu-MOF (69 counts/kPa) sensor samples. Humidity has a great effect on the identification of gas sensing effects. In sequence to examine the effect of humidity on the identification of ammonia, different saturated solutions such as MgCl$_2$, MgNO$_3$, NaCl and Na$_2$CO$_3$ with differing relative RH values (30%, 50, 70 and 90%). The humidity dependent response curve is shown in Figure 7 (a). The constructed sensor shows better sensitivity towards H$_2$ gas with a lower RH (up to 50% RH) value. The time response curves of the sensor samples were shown in Figure 7 (b-d). The Zn-MOF sensor demonstrate that high response (20 s) and recovery time (27 s). The overall gas sensing parameters of H$_2$ gas is displayed in Table 1. Different types of vapor gases like NO$_2$, NH$_3$, CO$_2$ and SO$_2$ gases were passed through the sensing materials in order to know the selectivity performance of the sensors. Figure 8 (a) shows bar diagram of the selectivity gas test for all the sensors. The results clearly noticed that all the sensors exhibit higher sensitivity towards H$_2$ gas than compared with other gaseous species. The findings showed that good selective response of H$_2$ gas for the fabricated sensors. Another important feature of validating gas sensing is stability. The durability of the sensors was tested for 100 days at 1000 ppm of H$_2$ gas with a steady period of 200 days (Fig. 8b). Remarkably, the sensors does not change their sensing response (steady state) even at long period (100 day) and it can be predictable for making performance H$_2$ gas sensor based devices. As the gases to be defined interfere with these oxygen ions, chemisorption of oxygen occurs, leading in a transition in the real characteristics of the sensing medium. The mechanism of the proposed gas sensors are shown schematically in Figure 8c). Gases help contribute to the absorption spectrum as the desorption of oxygen happens, or embrace, because of it and, the index of refraction index of the clad-modified region increases when the refractive index of a substance is linked to the electronic structure. Variations in the refractive index of the absorption spectrum are suspected. The air and the existence of charged particles will absorb such evanescent wave. The findings of the analysis indicate that the detector performance is inclined to refractive index associations by charged particles at the clad-modified-air interface then the refractive index shifts in the changed cladding. Thus, the strength of the entirely internally light reflected may change. This means that the quality of the sensor depends mostly on the diffusion of the evanescent wave than on variations in the refractive index.

4. Conclusions

In summing up, recent developments in transition-metal (Zn, Mn, Cu)-based MOFs and their derivatives are synthesized as sensing materials. Due to the higher light output intensity, the Zn-MOF sensor exhibits high sensitivity of 115 counts/kPa than compared with Mn-MOF (92 counts/kPa) and Cu-MOF (69 counts/kPa) sensor samples. The Zn-MOF sensor demonstrate that high response (20 s) and recovery time (27 s). Remarkably, the sensors does not change their sensing response (steady state) even at long period (100 day) and it can be predictable for making performance H$_2$ gas sensor based devices. Owing to their high porosity, large specific surface area, controllable structure, and simple preparation process, Zn-MOFs are promising sensing materials for high performance H$_2$ gas based devices.
Declarations

Acknowledgement

The authors would like to express their gratitude to the Deanship of Scientific Research at King Khalid University for funding this work through the Research Groups Program under Grant No. R.G.P2/115/41. Author T. Alshahrani would like to express her gratitude to Deanship of Scientific Research at Princess Nourah bint Abdulrahman University for funding this research through the Fast-track Research Funding Program.

References

1. L. Zhu, Y. Li, Wen Zeng, Hydrothermal synthesis of hierarchical flower-like ZnO nanostructure and its enhanced ethanol gas-sensing properties, Appl. Surf. Sci. 427 (2018) 281–287.
2. L. Zhu, W. Zeng, Room-temperature gas sensing of ZnO-based gas sensor: A review, Sens. Actuators, A 267 (2017) 242–261.
3. P.S. Kolhe, P.M. Koinkar, Namita Maiti, K.M. Sonawane, Synthesis of Ag doped SnO\textsubscript{2} thin films for the evaluation of H\textsubscript{2}S gas sensing properties, Physica B 524 (2017) 90–96.
4. Z. Zhang, Mahmood haq, Z. Wen, Z. Ye, L. Zhu, Ultrasensitive ppb-level NO\textsubscript{2} gas sensor based on WO\textsubscript{3} hollow nanosphers doped with Fe, Appl. Surf. Sci. 434 (2018) 891–897.
5. O. Krsko, T. Plecenik, T. Roch, B. Granci, L. Satrapinskyy, M. Truchly, P. Durina, M. Gregor, P. Kús, A. Plecenik, Flexible highly sensitive hydrogen gas sensor based on a TiO\textsubscript{2} thin film on polyimide foil, Sens. Actuators, B 240 (2017) 1058–1065.
6. M.M. Arafat, A.S.M.A. Haseeb, S.A. Akbar, M.Z. Quadir, In-situ fabricated gas sensors based on one dimensional core-shell TiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} nanostructures, Sens. Actuators, B 238 (2017) 972–984.
7. W. Tan, J. Tan, L. Fan, Z. Yu, J. Qian, X. Huang, Fe\textsubscript{2}O\textsubscript{3}-loaded NiO nanosheets for fast response/recovery and high response gas sensor, Sens. Actuators, B 256 (2018) 282–293.
8. N.L. Rosi, Hydrogen storage in microporous metal-organic frameworks, Science. 4 (2003) 1127–1129.
9. L.J. Murray, M. Dincă, J.R. Long, Hydrogen storage in metal–organic frameworks, Chem. Soc. Rev. 38 (2009) 1294–1314.
10. Y. Lü, W. Zhan, Y. He, Y. Wang, X. Kong, Q. Kuang, Z. Xie, L. Zheng, MOF8 templated synthesis of porous Co\textsubscript{3}O\textsubscript{4} concave nanocubes with high specific surface area and their gas sensing properties, ACS Appl. Mater. Interfaces. 6 (2014) 4186–4195.
11. L. Ma, J.M. Falkowski, C. Abney, W. Lin, A series of isoreticular chiral metalg organic frameworks as a tunable platform for asymmetric catalysis, Nat. Chem. 2 (2010) 838–846.
12. C.W. Kung, J.E. Mondloch, T.C. Wang, W. Bury, W. Hoffeditz, B.M. Klahr, R.C. Klet, M.J. Pellin, O.K. Farha, J.T. Hupp, Metal-organic framework thin films as platforms for atomic layer deposition of...
cobalt ions to enable electrocatalytic water oxidation, ACS Appl. Mater. Interfaces. 7 (2015) 28223–28230.

13. D. Sheberla, J.C. Bachman, J.S. Elias, C.J. Sun, Y. Shao-Horn, M. Dincă, Conductive MOF electrodes for stable supercapacitors with high areal capacitance, Nat. Mater. 16 21 (2017) 220–224.

14. J. Yang, P. Xiong, C. Zheng, H. Qiu, M. Wei, Metal–organic frameworks: a new promising class of materials for a high performance supercapacitor electrode, J. Mater. Chem. A. 2 (2014) 16640–16644.

15. X. Cao, Hybrid micro-/nano-structures derived from metal-organic frameworks: preparation and applications in energy storage and conversion, Chem. Soc. Rev. 46 (10) (2017) 2660–2677.

16. C.H. Hendon, Grand challenges and future opportunities for metalorganic frameworks, ACS Cent. Sci. 3 (2017) 554–563.

17. N. Stock, S. Biswas, Synthesis of metal-organic frameworks (MOFs): routes to various MOF topologies, morphologies, and composites, Chem. Rev. 112 (2012) 933–969.

18. S. Dang, Q.-L. Zhu, Q. Xu, Nanomaterials derived from metal–organic frameworks, Nat. Rev. Mater. 3 (1) (2017) 17075.

19. L. Hu, Q. Chen, Hollow/porous nanostructures derived from nanoscale metalorganic frameworks towards high performance anodes for lithium-ion batteries, Nanoscale 6 (2014) 1236–1257.

20. M. Zhong, Synthesis of MOF-derived nanostructures and their applications as anodes in lithium and sodium ion batteries, Coord. Chem. Rev. 388 (2019) 172–201.

21. S. Zheng, Transition-metal (Fe Co, Ni) based metal-organic frameworks for electrochemical energy storage, Adv. Energy Mater. 7 (2017) 1–27.

22. S. Azad, E. Sadeghi, R. Parvizi, A. Mazaheri and M. Yousefi, Sensitivity optimization of ZnO clad-modified optical fiber humidity sensor by means of tuning the optical fiber waist diameter, Opt. Laser Technol. 90 (2017) 96–101.

23. S. Mohamed Manjoor Shaib Maricar, D. Sastikumar, P. Reddy Vang, M. Ashok, BiFeO₃ clad modified fiber optic gas sensor for room temperature applications, Materials Today: Proceedings. (https://doi.org/10.1016/j.matpr.2020.07.038)

24. M. Sánchez-Sánchez, N. Getachew, K. Díaz, M. Díaz-García, Y. Chebude, I. Díaz, Synthesis of metal–organic frameworks in water at room temperature: salts as linker sources, Green Chem. 17 (2015) 1500–1509.

25. T. Grant Glover, G.W. Peterson, B.J. Schindler, D. Britt, O. Yaghi, MOF-74 building unit has a direct impact on toxic gas adsorption, Chem. Eng. Sci. 66 (2011) 163–170.

26. A. Wang, Y. Zhou, Z. Wang, M. Chen, L. Sunc and X. Liu, RSC Adv., 2016, 6, 3671

27. H. Hu, X. Lou, C. Li, X. Hu, T. Li, Q. Chen, M. Shen, B. Hu, A thermally activated manganese 1,4-benzenedicarboxylate metal organic framework with high anodic capability for Li-ion batteries. New J Chem. 40 (2016) 9746–9752
28. R Boopathi Raja, M Parthibavarman, *Hetero-structure arrays of MnCo$_2$O$_4$ nanoflakes@ nanowires grown on Ni foam: Design, fabrication and applications in electrochemical energy storage*, J. Alloy. Compd. 811 (2019) 152084

29. R. Boopathi Raja, M. Parthibavarman, A. Nishara Begum, *Hydrothermal induced novel CuCo$_2$O$_4$ electrode for high performance supercapacitor applications*. Vacuum. 165 (2019) 96-104

30. M. Parthibavarman, M. Karthik, S. Prabhakaran, *Facile and one step synthesis of WO$_3$ nanorods and nanosheets as an efficient photocatalyst and humidity sensing material*, Vacuum 155 (2018) 224-232

**Table**

Due to technical limitations, table 1 is only available as a download in the Supplemental Files section.