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

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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 field of nanoscience and its synthesis methods can growth and produced a various types of novel gas sensing materials such as metal oxides, polymers, and carbanesous based materials [2-7]. Generally, metal oxide semiconductors like, ZnO , SnO_2 , WO_3 , TiO_2 and Fe_2O_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 $\text{Zn}(\text{NO}_3)_2$ 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 $\text{Mn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ 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 $S = dI/dC$ 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 analyses 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 N₂ 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/P₀) 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 m²/g, 87.4 m²/g and 67.4 m²/g, respectively. The corresponding pore diameter values are 13.4, 22.5 and 31.2 nm, respectively. To detection of 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 frame work 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_{1/2} and Zn2p_{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_{1/2} and Ni 2p_{3/2}, respectively.

There are two BE at 943.3 and 960.8 eV is assigned to Cu 2p_{3/2} and Cu 2p_{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 H₂ 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-MFO 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

(d-f). Due to the higher light output intensity, the Zn-MOF sensor exhibits high sensitivity of 115 counts/k Pa than compared with Mn-MOF (92 counts/k Pa) and Cu-MOF (69 counts/k Pa) 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_2CO_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/k Pa than compared with Mn-MOF (92 counts/k Pa) and Cu-MOF (69 counts/k Pa) 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

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Table

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

Figures

Figure 1

Schematic diagram of the gas sensor set up

Figure 2

XRD pattern of the sensor samples

Figure 3

SEM images of (a) Zn-MFO; (b) Mn-MFO; (c) Cu-MFO; TEM images of (d) Zn-MFO; (e) Mn-MFO; (f) Cu-MFO; Elemental mapping of (g) Zn (h) Mn; (i) Cu and (j) N

Figure 4

(a) N₂ adsorption and desorption analysis and (b) corresponding pore size distribution of Zn-MFO, Mn-MFO, Cu-MFO, samples

Figure 5

XPS spectra of APG-50 sample (a) survey; (b) Zn2p; (c) Mn 2P; (d) Cu 2p

Figure 6

Output spectral response curves of (a) Zn-MFO; (b) Mn-MFO; (c) Cu-MFO; Sensitivity plot of (d) Zn-MFO; (e) Mn-MFO; (f) Cu-MFO;

Figure 7

(a) Sensitivity as function of RH; Response and recovery curve of (b) Zn-MOF; (c) Mn-MOF; (d) Cu-MOF;

Figure 8

(a) Selectivity; (b) stability diagram for Zn-MFO, Mn-MFO, and Cu-MFO sensor samples; (c) gas sensing mechanism of the proposed sensor

Supplementary Files

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