Room Temperature Methanol Sensor Based on Ferrite Cobalt (CoFe$_2$O$_4$) Porous Nanoparticles

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ABSTRACT

In this work, porous nanoparticles of ferrite cobalt were prepared by dissolving CoCl$_2$·6H$_2$O and FeCl$_3$ in ethylene glycol in a hydrothermal process. Using ethylene glycol instead of DI water as a solvent would cause to provide porous structure of ferrite cobalt. 0.05 ml of colloidal fluid of fabricated nanostructure was injected on interdigitated electrodes (IDE) on a printed circuit board (PCB) substrate by a drop casting process. Morphological and structural characterizations of structure were investigated by X-ray diffraction and scanning electron microscopy and the obtained results of analyses show the porous nanostructure of the material. Sensor’s performance in detection of gas vapors was evaluated in different temperatures which has the best response (20.38% for 100ppm methanol vapors) for methanol vapors at room temperature. Performance of sensor in selection of methanol vapors, chemical stability and repeatability of that, makes it useful to profit it in different fields and industries.

1. INTRODUCTION

Today, emission of gases like NH$_3$, CO$_2$, CO, NO$_2$ and volatile organic compounds (VOCs) such as methanol, ethanol, formaldehyde, propanol can cause environmental pollutions and are dangerous for human’s health [1-9]. One of the VOCs that has used in pharmaceutics, dyeing, biodiesel fuels, antifreeze and primary substance to make chemical materials, is methanol [10-12]. Methanol vapors are transparent, volatile and flammable. Inhalation of vapors can cause blood anomalies, skin and eye sensitivity, fatigue, headache and central nervous system problems. Excess of these vapors in environment can start environmental destructive activities [13], [14]. Therefore, providing a sensitive sensor to detect these vapors is important. In recent decades, development of gas sensors based on semiconductor metal oxides such as ZnO, SnO$_2$, TiO$_2$, ZnFe$_2$O$_4$, CuFe$_2$O$_4$ and CoFe$_2$O$_4$, because of their chemo physical properties to detect hazardous and pollutant gases are increased [15-20]. In recent years’ ferrites with a chemical formula of AB$_2$O$_4$, because of their magnetic properties and their proper response in detection of some gases like VOCs, CO, NH$_3$ and H$_2$S are attracted much attention [21]. For example, in order to detect gases by metal oxide sensors, Li et al. [13] were deposited SnO$_2$ on silicon nonporous pillar array and provided a honeycomb porous surface to detect methanol. Their best response was 3.6% for 5ppm methanol in 320°C. In another study, Bagade et al. [22] were prepared a CoFe$_2$O$_4$ thin films by pyrolysis technique and used them to detect methanol. At 150°C for 80ppm methanal, their response was 15%. In addition, Wang et al. [23] were prepared NiFe$_2$O$_4$ nano-cubes and their best response for 200ppm methanal at 160°C was 17%. In another study, Lin et al. [10] prepared CoFe$_2$O$_4$-SiO$_2$-In$_2$O$_3$ nanocomposite by hydrothermal method and their response at 260°C for 200ppm methanal was 10%. Moreover, Feng Ji et al. [14] deposited GaN
nanostructures on silicon nonporous pillar array by chemical vapor deposition (CVD). At 350°C, their response for 5ppm methanol was 1.22%.

By investigation of the previous works in methanol sensors, it is obvious that most of sensors have the best response in high temperatures. In this study, a sensor based on ferrite cobalt porous nanoparticles are prepared by a hydrothermal method that has the best response at room temperature which optimize the energy consumption of sensor and reduce the risk of working in high temperatures. Structural and morphological characterizations of structure are examined by XRD and SEM. Response of sensor in different methanol concentrations, selectivity, repeatability and chemical stability of sensor are investigated deeply.

2. EXPERIMENTAL DETAILS

A. Preparation of CoFe$_2$O$_4$ porous nanoparticles

To prepare porous nanoparticles, first, 10 mmol of CoCl$_2$·6H$_2$O (99%, Merk) and 20 mmol of FeCl$_3$ were dissolved in 75 ml ethylene glycol and followed by 20 minutes stirring and adding 0.18 mol urea (99%, Merck). The mixture continues stirring until the completely dissolution and then poured in to the autoclave and heated at 200°C for 12 hours. Then, the autoclave was allowed to cool to room temperature and the precipitates filtered out and washed several times with water. All precipitates were dried in an oven at 80°C for 10 hours.

B. Sensor Fabrication

As shown the process of sensor fabrication in Fig. 1, after preparing cobalt ferrite porous nanoparticles, the resulting powder of nanostructure is mixed with amount of distilled water and colloidal fluid of nanostructure is obtained. First, Cu interdigitated electrodes (IDE) were printed on printed circuit board (PCB) with circuit printing board technique. Then, copper wires were connected to PCB substrate by soldering process Fig. 1(B). Afterwards, micro syringe is poured by 0.05 ml of colloidal fluid of nanostructure and is injected to PCB substrate Fig. 1(C). Furthermore, the prepared sensor was heated on hot plate at 60 °C for 15minutes as depicted in Fig. 1(D).

C. Sensor measurements

In order to measure the response of sensor, a lab made setup as shown in Fig. 2 is prepared. A power supply is used to provide required voltage in micro heater to evaporate liquid methanol that is injected in chamber A. The determined amount of methanol is injected in chamber by micro syringe to evaporate by micro heater to be exposed in chamber. Resistance of sensor before exposure of methanol ( $R_a$ ) is measured and by exposing methanol in chamber, resistance of sensor is measured again ( $R_g$ ). Response of sensor is measured as follows:

$$\text{Response (\%)} = \frac{R_g - R_a}{R_a} \times 100$$

Figure 2: The setup for measuring sensor’s resistance before and after exposing the methanol vapors.

3. RESULTS & DISCUSSION

A. Structural and morphological studies

In order to investigate the structural properties of the prepared CoFe$_2$O$_4$ nanoparticles, X-ray diffraction analysis (XRD) was done by XRD device D8 ADVANCE type (BRUKER-GERMANY) with the source of cu-κα (λ=κα-κα 0.1542nm). As the XRD pattern is shown in Fig. 3 for the structure, the 2θ range was chosen between 20° to 80° in order to show all the peaks in the structure. Peaks are obtained in 2θ=30° (200), 35° (311), 37° (222), 43° (400), 53° (511), 57° (440), 62°
(622) which show that the pattern is totally according to the pure cubic spinel structure of CoFe$_2$O$_4$ (JCPDS CARD-NO -22-1086) and [24], [25], [26] and there are no other extra impurity peaks in the pattern. To investigate the morphological characterization, scanning electron microscopy (SEM) image was achieved. As it is shown in Fig. 4, CoFe$_2$O$_4$ nanoparticles are gathered to each other and provided some pores in their structure and therefore it has a porous nanoparticle structure. To explore the composition of the structure and investigate the presented elements in the structure, the energy dispersive X-ray (EDX) analysis was provided.

![Figure 3: XRD pattern of porous nanoparticles.](image)

![Figure 4: SEM image of porous nanoparticles.](image)

As the result shown in Fig. 5, there are only three elements such as Co, Fe and O in the structure and there are no extra elements in the structure and by attention to the results of the elemental mass fraction that is shown in Table 1, it is transparent that the results are in accordance to the mass weights of the elements in CoFe$_2$O$_4$ structure. Therefore, by pursuing the results of EDX analysis, it is understood that the prepared structure contains the CoFe$_2$O$_4$ elements with the almost similar mass weights.

**B. Gas Sensing Properties**

Determining the optimum working temperature of sensor is important in the view points of power consumption and risks of working in high temperatures. Therefore, to achieve the optimum working temperature of sensor, response of that in different temperatures for 100 ppm methanol vapors are investigated. By the results that shown in Fig. 6, the best response was obtained at room temperature. By examining the sensor for 100 ppm methanol vapors at room temperature to 110°C, the process shows that by increasing temperature, the response of sensor decreases. The reason of such changes in the response toward different temperatures could be explored by the diffusion theory. Based on this theory, the temperature in which, response of sensor has the maximum value is depended on many factors such as morphology of the structure, shapes of grains, size of grains, and size of the pores in the porous structures. By attention to these factors, response has a maximum value in a special temperature and after that, it may decrease [27]. In our prepared structure, maximum response is occurred at room temperature and after that temperature, response starts to decrease. By the results, the optimum working temperature was chosen room temperature and other measurements are achieved in this temperature. Then, response of sensor in different concentrations of methanol vapors was measured. In Fig. 7, response of sensor to methanol vapors from 30 ppm to 1500 ppm is shown. As shown, by increasing in concentration of methanol vapors, response of sensor is increasing. In Table 2, responses of sensor in different methanol vapors concentrations are briefly provided. As depicted in Fig. 8, it is transparent that, increasing the concentration of methanol vapors, is the reason for increasing the response of sensor.

a) **Response time and Recovery time**

To investigate the time that takes the sensor to response the methanol vapors, another parameters are defined. In presence and absence of methanol vapors in chamber, the time that takes the sensor to change its electrical resistance by 90%, is called response time and recovery time, respectively. In Fig. 9, the process of measuring response time and recovery time of 30ppm methanol vapors are illustrated. Response time and recovery time in this sensor for each concentration of methanol vapors are briefly shown in Table 2.
b) Selectivity

To investigate the selectivity of sensor to methanol vapors, responses of sensor for 100ppm of different vapors such as ethanol, methanol, acetone, methane and LPG are compared. By the obtained result that shown in Fig. 10, sensor has the best response to methanol vapors almost twice than response to acetone and ethanol and ten times more than methane and LPG. Therefore, sensor has acceptable selectivity to methanol vapors.

![Figure 5: EDX analysis of porous nanoparticle.](image)

**Table 1: Mass Elemental Fractions of CoFe2O4 Porous Nanoparticles**

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass weight in (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>25.91</td>
</tr>
<tr>
<td>Fe</td>
<td>46.10</td>
</tr>
<tr>
<td>Co</td>
<td>27.99</td>
</tr>
</tbody>
</table>

![Figure 6: Response of methanol sensor to different temperature for 100ppm methanol vapors in room temperature to 110°C.](image)

![Figure 7: Response of sensor in different methanol vapors concentrations (30ppm to 1500 ppm).](image)

c) Repeatability and Stability

Repeatability of sensor for 100 ppm of methanol vapors was pursued in 3 cycles. As it is obvious in Fig. 11, sensor has the same response for each cycle and the shape of response for each cycle is almost the same. Consequently, this sensor has a good repeatability in methanol vapors. To investigate the chemical stability of sensor, response of that in 24 days was measured. As the results show in Fig. 12, sensor in each 6 days in these 30 days has almost the same responses, from 21.53% in day 0 to 20.19%, 20.71%, 20.72%, 20.83%, and 20.12 in day 6, day 12, day 18, day 24 and day 30, respectively. These results show that, this sensor is stable and reliable to work with in long times of working.

![Figure 8: Response of sensor in different methanol concentrations in 30 ppm to 1500 ppm at room temperature.](image)
**C. Sensing Mechanism**

This nanostructure provides high surface area due to its porous structure that can produce high adsorption sites for methanol vapors. In attention to surface charge model that is proposed to sensing mechanism of sensor, changing in resistance is due to species and amount of oxygen adsorbed by the chemical process on the surface [13]. When the sensor is exposed to air, oxygen molecules are absorbed by the chemical process on the surface. Electrons in the layers of the nanostructure are absorbed by the oxygen and oxygen ions \( (O_2^-, O^-, O_2^{2-}) \) are provided. At the room temperature, the process of reaction is as follows:

\[
\text{CH}_3\text{OH} + O_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + e^- \tag{4}
\]

**Table 2**

<table>
<thead>
<tr>
<th>Methanol concentration (ppm)</th>
<th>Sensor parameter</th>
<th>Response (%)</th>
<th>Response time (s)</th>
<th>Recovery time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>9.9</td>
<td>244</td>
<td>336</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>14.95</td>
<td>199</td>
<td>488</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>20.38</td>
<td>293</td>
<td>481</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>24.69</td>
<td>323</td>
<td>540</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>26.27</td>
<td>308</td>
<td>492</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>28.62</td>
<td>421</td>
<td>524</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>30.89</td>
<td>413</td>
<td>521</td>
<td></td>
</tr>
</tbody>
</table>

Therefore, resistance is increasing. By exposing sensor to methanol vapors, vapor molecules react with surface oxygen molecules and reduce the oxygen concentrations. Therefore, oxygen electrons are transferred to nanostructure and the following reaction is occurred and resistance is decreasing:

By exposing sensor to fresh air again, resistance of sensor is back to initial value. Using of porous structure in this sensor provides more sites and extra layers to absorb more oxygen molecules in these sites and layers that cause absorbing more electrons by oxygen molecules. Then, more oxygen ions and reactions between oxygen molecules and methanol vapor molecules are provided and more changes in resistance.

**Figure 9:** Response and Recovery time of sensor for 30ppm methanol vapors.

**Figure 10:** Response of sensor to 100ppm methanol, acetone, ethanol, methane and LPG at room temperature.

**Figure 11:** Repeatability of sensor to 100ppm methanol vapors at room temperature.
is achieved which shows an improvement in the response. Table 3 is provided to compare the prepared methanol sensor to previous provided methanol sensors in the view points of response, response time, and recovery time.

![Figure 12: Response of sensor to 100 ppm methanol vapors in 30 days.](image)

4. CONCLUSION

Porous nanoparticles of CoFe$_2$O$_4$ were prepared by a hydrothermal process. By benefiting of XRD analysis and SEM images, porosity of nanostructure was approved. Response of sensor in different temperatures was measured. At room temperature, it has the best response of 21.38\% for 100 ppm methanol vapors.

Room temperature working of sensor causes reducing in power consumption and decreasing risks of working in high temperatures. This sensor has a good selectivity to methanol vapors in presence of ethanol, acetone, methane and LPG vapors. Repeatability and chemical stability of sensor in long times of working were approved. By its room temperature working and all its features in sensing methanol vapors, this sensor is a good candidate to use in different industries and fields to detect methanol vapors.

5. REFERENCES


**Biographies**

**Peyman Halvae** was born in 1993. He started Electrical Engineering in 2012 and finished B.Sc. in 2016 and then started Nanoelectronics Engineering in Shiraz University in M.Sc till now. His interests are in fabrication of Nano sensors and Nano biosensors.

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