P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
2022,16 (1) : 50 -54

Improved sensing properties of Zinc Oxide gas sensor to detect hydrogen gas by using ZIF-8

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ARTICLE INFO

Received: 4 /4/2022
Accepted: 23/ 5 /2022
Available online:20/7/2022

DOI: http://dx.doi.org/............................

Keywords:
Gas sensors.
Metal Oxide.
Metal−Organic Frameworks (MOFs).
ZnO thin film.
ZIF-8.

ABSTRACT

In this research, ZnO nanorods were utilized as gas sensor materials for detecting toluene vapour and hydrogen gas prior to and following the use of Zeolitic imidazolate frameworks-8 (ZIF-8) as gas filter. On porous Al_2O_3, ZIF-8 was deposited and the thickness was 200 nm. Scanning electron microscope (SEM), XRD, and gas sensing tests were used to examine the material characteristics regarding ZIF-8 and ZnO. Thin films' sensitivity and selectivity to different gases such as C_7H_8 and H_2 were also investigated. Comparing with pristine ZnO nanorods sensor, ZnO sensor is highly sensitive to C_7H_8 and H_2, whereas the nanostructure regarding ZnO with ZIF8 as sensor has significantly selective response to the hydrogen gas. The small pore aperture of the ZIF-8 explains this behavior as H_2 molecules could rapidly spread across ZIF-8 network and reach the surface of the ZnO.

1- INTRODUCTION

Metal oxide gas sensors (MOGs) have numerous benefits over other sensors, including low cost, ease of construction and simple measurement performance. The sensing method comprises gas adsorption on the surface of the sensor material that results in a change in the sensor's electric conductivity [1]. Environmental conditions (humidity, temperature), material doping, and the morphology of the thin film (roughness and grain size) all influence sensor properties, such as selectivity, sensitivity, response time, and recovery time [2, 3].

In the field of MOG sensor research, increasing sensor selectivity is one of the most difficult issues. For improving the selectivity of MOG sensor, it may be functionalized chemically, for example, with the catalytically active additions like gold [4] or platinum [5]. A recent study proposed a combination of the metal oxide-based sensors and metal-organic frameworks (MOF). Because of their uses in sensors, storage, separation, and catalysis of gas, the MOFs with a high specific surface area and well-defined porous structure had gotten huge interest [6].

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Due to their heterostructures, MOFs integrated with the metals, metal oxides, as well as other functional materials exhibit significant benefits [7]. Deposition of metal (oxide) into MOF pores and coating the MOFs as shell on the metal (oxide) can be used to integrate heterostructures [7] [8]. To improve the sensitivity for specific gases, the idea is to combine metal-oxide based sensors with the MOF-based materials either by coating the MOFs directly to the MO devices or by preparing MOF-based membranes, which are mechanically decoupled from the sensitive material of the sensors [9]. It is known that MOFs can be used as gas filters and several publications demonstrate the application in combination of MOF-based materials with MOGs. In this research we studied the effects of preparation of ZIF-8 deposited on Al_2O_3 porous used as a filter for H_2 gas to enhance the selectivity of ZnO based sensor for the H_2 gas in comparison with other gases such as toluene vapor. This material of ZIF-8/Al_2O_3 was used for first time as filter

2. EXPERIMENTAL

2.1- Chemical materials

Zinc chloride ($ZnCl_2$) was utilized as Zn source, 2-methyl-imidazole ($C_4H_6N_2$, >99%, Merck KGaA, Germany) was utilized as ligands. Sodium formate (NaCOOH, >95% Alfa Aser). Methanol (>95%).

2.2- ZIF-8 Synthesis

P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
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ZIF-8 synthesis on the porous of Al_2O_3 substrate by solvothermal method Solution was prepared by dissolving 0.538g (3.95 mM) of Zinc chloride, 0.486 g (5.92 mM) of 2-methylimidazole and 0.268 g (3.95 mM) solved by ultrasonic treatment in 100 ml of methanol. Porous of Al_2O_3 discs (1 mm thickness and 13 mm diameter) used as substrate. The disc was immersion in the solution and they loaded into autoclave thermal at 100 C° for 24h.

2.3- Synthesis of ZnO thin film

Utilizing RF power – 200W and 60 minutes deposition time, a ZnO layer with a thickness of 200nm and a total area of $1cm^2$ x $1cm^2$ was prepared with the use of an RF sputtering plasma machine. The initial pressure in the chamber was $1x10^{-6}$ mbar which then raised to $2.3x10^{-2}$ mbar through filling it by 99% highly pure argon gas. Before starting the coating process, the highly pure ZnO target has exposed to plasma to obtain clean surface. A silicon (Si) wafer substrate has been utilized to create ZnO nanostructure. In addition, ZnO nanostructure was then heat-treated in an air environment for 2 hours at different temperatures of 350℃. A 200 nm aluminium (Al) layer has deposited, succeeded by the patterning of appropriate electrodes that have been deposited using equipment of thermal evaporation.

2.4- Characterization of the samples

The XRD measurements were performed using a Shimadzu X-ray diffractometer with a 1.54056Å wave-length. Philips XL-30 Field Emission ESEM was used to get images of samples surface. Prior to and following the use of ZIF-8/Al_2O_3, the gas sensor characteristics of ZnO nanostructure gas sensor have been measured in homemade gas sensing setup whereas being exposed to H_2 gas and C_7H_8 gas and the operating temperature was 250℃. The resistance of the ZnO films that were exposed to various environmental gases was measured inside the homemade gas sensing set-up while the flow rate of the carrier gas was calculated by using a flow meter. The gas sensor's sensitivity specified as the sensor's capacity for responding to existence of specific gas concentration. The response, S, has been mathematically characterized as

S = Rg -Rn/Rn for reduction of the gas and S= Rn -Rg/Rg for oxidizing gas, in which Rn and Rg represent sensor's resistances after and before the gas flows and reaches saturation, respectively [1, 2]. The gas sensor response was measured before and after use the ZIF-8 gas filter. The ZIF-8 gas filter was fixed in the tube supplier of gas.

Fig. 1: Shows home-made gas sensing setup.

3. Results and Discussion

3.1.Structural properties

3.1.1- XRD studies

Fig. 2 shows XRD of ZIF-8 deposited on Al_2O_3 purpose peaks of 7.349°, 10.386°, 12.66° ,14.695°, 16.459° and 18.044° were correspond to ZIF-8 (011), (002), (112),(022), (013) and (222) [10, 11].

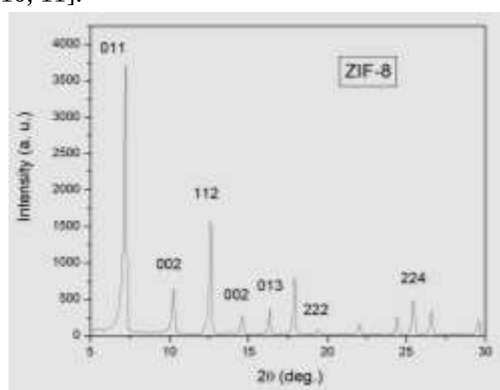

Fig.2 XRD of ZIF-8 on pores Al_2O_3

The XRD data for deposited ZnO on Si wafer has been presented in Figure (3), which shows intensity peaks at 2θ = 31.98◦, 34.63◦ and 36.50◦, respectively, corresponding to the (100), (002), and (101) planes, which indicate the hexagonal structure of the wurtzite regarding ZnO crystals [12]. The observations are nearly identical to those on standard card (JCPDS36–1451).

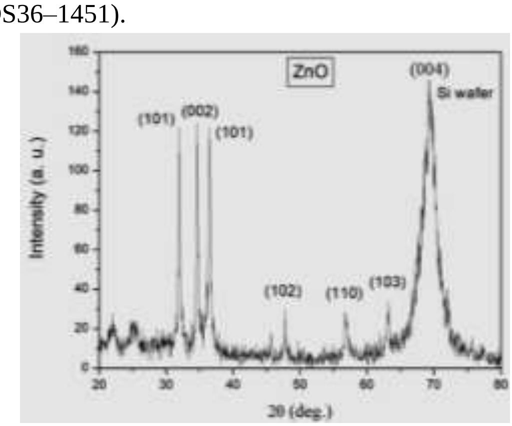

Fig. 3 XRD of ZnO deposited on Si wafer.

3.1.2. SEM measurements

To examine the surface morphology, SEM has been used. Typical SEM images of the ZnO nanorods and ZIF-8 are shown in Fig.4. The overall morphology of the pure ZnO nanorods on the substrate is shown in Figure 4(A, B), which indicates the obtained products consist of ZnO nanorods with an average length of 7 µm.

The morphology of ZIF-8 membranes formed. After solvo-thermal preparation at 100 °C for 24hrs, a more compact deposition and growth of the ZIF-8 on porosity of Al_2O_3 discus could be clearly visible in Figure 4 (C, D,E,F), taken from top-view of membrane. A well-intergrown and continuous ZIF-8 layer composed of micro-size crystals with nano-size crystals filling inter-crystalline gaps can be seen from top view of membrane.

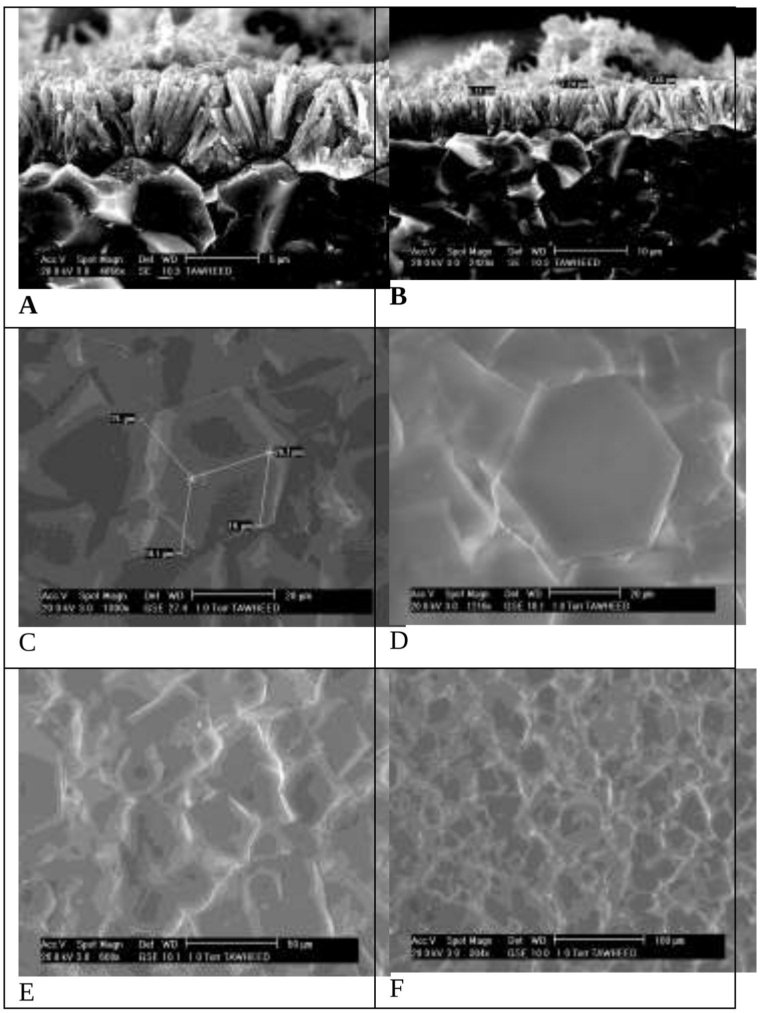

Fig. 4: A&B SEM of ZnO nanorods and C, D, E &F of ZIF-8 deposited on Al_2O_3 porous

3.2. Experimentations of Gas Sensing

To investigating gas-sensing ZnO thin film performance before and after used gas filter of ZIF-8. The fabricated ZnO based sensor were assessed for two gases: H_2 and C_7H_8 gases.

Fig. 5 shows response of a ZnO-based sensor for H_2 gas was 80%. The response time was 40 s. while the recovery time was 50 s. Sensor response time is the time taken to attain a maximum change of 90% in resistance when exposed to the gas. Recovery time equals the time required by the sensor to revert.

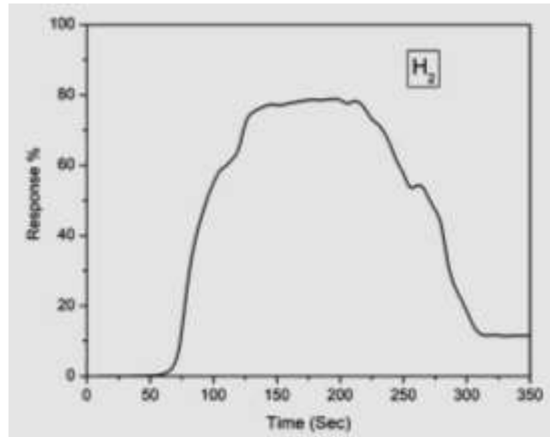

Fig. 5: ZnO based sensor response for H_2 gas.

Fig. 6 illustrates ZnO thin films gas sensor response for H_2 gas after used ZIF-8 filter. It has been found that the ZnO gas sensor response has been increased and the response time increased. This behaviour could be due to small pore aperture regarding ZIF-8 cavity (3.4Å kinetic diameter) [1, 13]. At the same time, H_2 molecules (2.89Å kinetic diameter), can easily diffuse through the network of ZIF-8 and reach the surface of ZnO. It is found that the response time was 60 s. While recovery time was 50 s. the gas response to H_2 gas decreased after used the ZIF-8 membrane as a gas filter, which certainly reduced the accessibility of target gas molecules to the ZnO gas sensor.

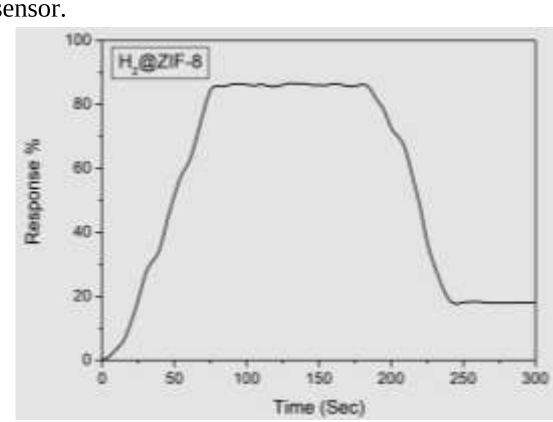

Fig. 6: ZnO based sensor with ZIF-8 filter gas response for H_2 gas.

Fig.7 Shows response of ZnO gas sensor for C_7H_8 gas. The response of ZnO gas sensor was 40%. The response time was 46 s. and the recovery time was 50 s.

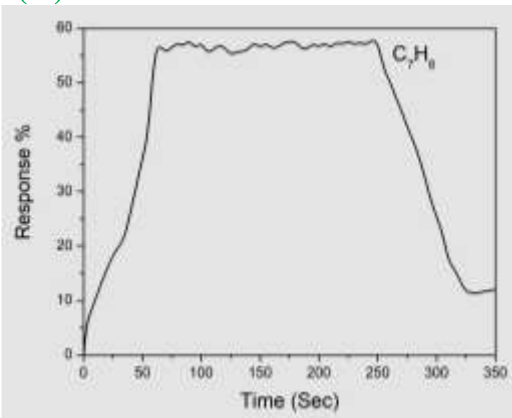

Fig. 7: The response of ZnO based sensor for C_7H_8 gas.

Fig.8: indicates that the response regarding ZnO gas sensor for C_7H_8 after used ZIF-8 filter was fairly vanished, approaching 1.0. It must be noted that response value regarding "1" does not show any change in the resistance prior to and following gas supply, specifying a 0 gas sensing response. As it has been anticipated, because of the effect of size exclusion through small size of the portal of the ZIF-8 cavities (3.4Å) molecular sieving ability of the ZIF-8 membrane layer results in the prevention of C_7H_8 gas molecules (5.92 kinetic diameter) from accessing ZnO thin film surface, thereby leading to virtually 0-gas sense response [14, 15].

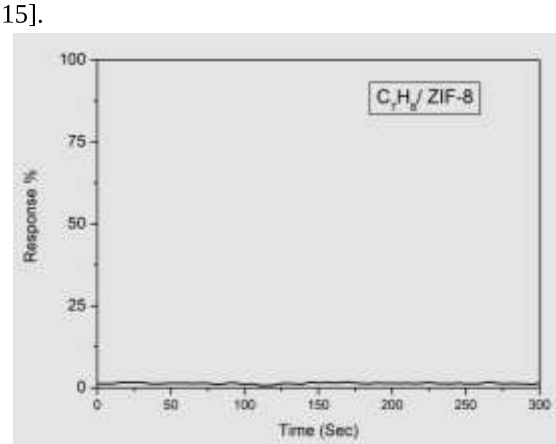

Fig. 8: Response of ZnO based gas sensor with ZIF-8 gas filter for C_7H_8 gas.

Khudiar et al [1] have reported that the response time and recovery time of the ZnO gas sensor towards H_2 and C_6H_6 gases at the operating temperature of 275 °C were 25.3 s and 50 s. , for H_2, and 26 s and 53 s for C_6H_6, respectively.

Khudiar et. al. [1] have reported that when ZIF-8 deposited on ZnO nanorods to fabrication of ZnO@ZIF-8 gas sensor it was noted that the response and recovery times for H_2 of 50 s and 130 s, respectively, are obtained. In contrast to the pure ZnO-based sensor material no sensor response can be detected for benzene in the case of the ZIF-8 coated sensor material. This behaviour can be attributed to the small pore aperture of the ZIF-8 cavity (kinetic diameter 3.4 Å), which avoids the diffusion of the C_6H_6 gas molecules (kinetic diameters 5.27 Å) to the interface with ZnO. On the other hand,H_2 molecules (kinetic diameter 2.89 Å), can diffuse easily through the ZIF-8 network and reach the ZnO surface.

In this research work, ZIF-8 was deposited on Al_2O_3 to be used as a gas filter for H_2 gas to improve the gas selectivity towards H_2 gas for ZnO gas sensor. Therefore, we note that there is a difference in the response time and recovery time of the previous gas sensor of ZnO@ZIF-8 because ZIF-8 is deposited on the Al_2O_3.

4. CONCLUSION:

In conclusion, a viable technique has been developed for increasing the selectivity regarding metal oxide sensors for H_2 gas. This method entails creating an innovative design for a MOF functional material depending on Al_2O_3 porous with molecular sieving capabilities that can be utilized as a gas filter. Compared with the pristine ZnO sensor, the ZnO gas sensor with MOF membrane has a much higher selectivity for H_2 than C_7H_8. This novel method is extremely adaptable since it could be utilized to make sensors with MOF molecular sieves that might be precisely tuned for improving the selectivity regarding metal oxide sensors to various gas mixes. This method also paves the way for the production of a vast class of the nonmaterial with more complicated 3D models that can be used for gas selectivity applications.

5. REFERENCES

[1] Khudiar A.I., Elttayef A.K., Khalaf M.K. and Oufi A.M. (2019) Fabrication of ZnO@ZIF-8 gas sensors for selective gas detection, Mater. Res. Express 6 126450.

[2] Korotcenkov G, Blinov I, Brinzari V and Stetter J R (2007) Effect of air humidity on gas response of SnO2 thin film ozone sensors Sensors Actuators B 122 519–26.

[3] Wang X, Yee S S and Carey P (1995) Transition between neck-controlled and grain- boundary-controlled sensitivity of metal-oxide gas sensors Sens Actuators B Chem 25 454–7

[4] Bhuiyan M M H, Ueda T, Ikegami T and Ebihara K (2006) Gas sensing properties of metal doped WO3 thin film sensors prepared by pulsed laser deposition and DC sputtering processJapanese journal of applied physics 45 8469–72.

[5] Srivastava A and Jain Rashmi K (2007) Study on ZnO-doped tin oxide thick film gas sensors Mater. Chem. Phys. 105 385–90.

[6] Drobek M, Kim J, Bechelany M, Vallicari C, Julbe A and Kim S S (2016) MOF- based membrane encapsulated ZnO nanorodes for enhanced gas sensor selectivity Appl. Mate. Interfaces 8 8323–8.

[7] Hassan H S, Kashyout A B, Morsi I, Nasser A A A and Raafat R (2014) Fabrication and characterization of gas sensor micro-arrays Sens Biosensing Res. 1 34–40.

[8] Yu B. , Wang F., Dong W., Hou J., Lu P., Gong J.(2015) Self-template synthesis of core–shell ZnO@ZIF-8 nanospheres and the photocatalysis under UV irradiation, Materials Letters 150 50-53.

[9] Pradeep N., Eva B., Klaus-Viktor P. (2016) Polymer supported ZIF-8 membranes by conversion of sputtered zinc oxide layers, ct Microporous and Mesoporous Materia220, 215-219.

[10] Nair S S (2019) ZnO@ZIF-8: gas sensitive core–shell hetero-structures show reduced cross-sensitivity to humidity Sensors Actuators B: chemical 304 127184.

[11] Lai L S, Yeong Y F, Lau K K and Shariff A M (2016) Effect of synthesis parameters on the formation of ZIF-8 under microwave-assisted solvothermal Procedia Eng. 148 35–42.

[12] Ausama I. Khudiar, Attared M. Ofui (2021) Effect of pulsed laser deposition on the physical properties of ZnO nanocrystalline gas sensors, Optical Materials 115, 111010.

[13] Heinke L, Tu M., Wannapaiboon S., Fischer R., Woll C., (2015) Surface-mounted metal-organic frameworks for applications in sensing and separation, Microporous and Mesoporous Materials 216 200-215.

[14] Fernando C. B., Beatriz S., Carlos T., Joaquín C., (2014) ZIF-8 continuous membrane on porous polysulfone for hydrogen separation, Journal of Membrane Science 464, 119-216.

[15] Qiang Ren, Yan-Qiang Cao, Daniel Arulraj, Chang Liu, Di Wu, Wei-Ming Li and Ai-Dong Li, (2021) Review—Resistive-Type Hydrogen Sensors Based on Zinc Oxide Nanostructures, J. Electrochem. Soc. 167 067528.

تحسين خصائص التحسسية الغازية للمتحسس أوكسيد الزنك لاستكشاف غاز الهيدروجين باستخدام ZIF-8

أسامة اسماعيل خضير

دائرة بحوث المواد – وزارة التعليم العالي والبحث العلمي والعلوم والتكنولوجيا – بغداد – العراق

الخلاصة:

في هذا البحث ، تم استخدام ZnO nanorods كمواد استشعار غاز للكشف عن بخار التولوين وغاز الهيدروجين قبل وبعد استخدام أطر إيميدازولات الزيوليت 8 (ZIF-8) كمرشح غاز والمرسب قواعد من الالومينا المسامية ، تم ترسب (ZIF-8) وكان سمكه 200 نانومتر. تم اجراء اختبارات المجهر الإلكتروني الماسح (SEM) و XRD واستشعار الغاز لفحص خصائص المواد المتعلقة بـ ZIF-8 و ZnO. كما تم فحص حساسية وانتقائية الأغشية الرقيقة للغازات المختلفة مثل C_7H_8 و H_2. بالمقارنة مع مستشعر ZnO النانوي الأصلي ، فإن مستشعر ZnO حساس للغاية لـ C_7H_8 و H_2 ، في حين أن البنية النانوية المتعلقة بـ ZnO مع ZIF8 كمستشعر لها استجابة انتقائية بشكل كبير لغاز الهيدروجين. تشرح فتحة المسام الصغيرة لـ ZIF-8 هذا السلوك حيث يمكن لجزيئات H_2 أن تنتشر بسرعة عبر شبكة ZIF-8 وتصل إلى سطح ZnO.