# UV-LED Assisted Ethanol Sensing Properties of NiO-Modified ZnO Thick Film at Low Temperatures

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**Abstract**

*Sensor based on thick film of ZnO hollow microspheres with average thickness about 200 µm were obtained by spin-coating technique. The surface of the film was modified by NiO through dropping solution of $Ni(NO_3)_2$ onto the film to reach mass ratio of $Ni(NO_3)_2$ to ZnO of 1 %. Subsequently, the obtained film was calcined at 500 °C for 2 h. Upon calcination, $Ni(NO_3)_2$ would reduce to NiO. Ethanol sensing properties of sensor film were investigated and compared with those of pristine ZnO hollow microspheres. The measurement was carried out under illumination of UV-LED (365 nm, 3W) at temperatures from 75 to 125 °C and ethanol vapor concentration levels 125 to 1500 ppm. The results show that the sensor with NiO-modified surface reaches significantly high response (6.5) toward 1500 ppm of ethanol vapor at 100 °C.*

Keywords: Ethanol sensing properties, UV-LED assisted, Low temperatures, ZnO hollow microspheres.

## 1. Introduction

Recently, it is known that controlling and monitoring ethanol is important in testing drunk drivers [1]. Indeed, prolonged heavy consumption ethanol can cause significant permanent damage to the brain and other organs [2]. In addition, the enduring alcohol abuse makes a major public health problem with important repercussions for individuals, the health care system, and society in general [3]. Hence, it is important to monitor and detect ethanol concentration in the environment for health and the workplace for safety [4] .

Zinc oxide (ZnO), with direct band gap of about 3.37 eV (at 300 K) and a large free exciton binding energy of 60 meV, is one of the most promising materials for gas sensors, especially for detecting ethanol vapor [5]. The sensing properties of ZnO are directly related to its morphology and operating temperature [6]. Many ZnO nanostructures were synthesized, such as nanorods [7], nanowires [8], nanoparticles [9]. Among these nanostructures, hollow microspheres have attracted larger attention due to high specific surface area even with a certain degree of the particle aggregation and highly porous microstructure which facilitates the interaction of the oxide surface with targeted gas molecules thus possibly enhancing the sensitivity [10].

Chemiresistive sensors based on metal oxide semiconductors such ZnO have been widely studied due to their simplicity of fabrication, good reproducibility and a wide variety of detected gases. However, the main drawback of these oxides is the demand for an external heater, which is used to raise the sensor temperature up to 200~400 °C for sufficient gas response activation energy [11]. The high temperature operation probably limits their applications. To reduce the operating temperature some methods were proposed as doping materials with transition elements [12] and noble metals [13] or irradiation by ultraviolet (UV) light [14]. Among these approaches, the UV illumination and composition of ZnO with other metal oxide not only enhance the gas-sensing performance but also reduce the working temperature.

In this paper, we report a catalysis free synthesis of hollow ZnO microspheres by two-step hydrothermal method without activating surfactant agents. In fact, pure NiO was reported to have excellent structural stability, high tendency toward the adsorption of oxygen, and strong catalytic activity [15]. Accordingly, two thick films of pristine and NiO-modified surface ZnO hollow microspheres were prepared. Their ethanol sensing properties under UV illumination at low temperatures were determined and compared. The ethanol sensing mechanism of the material was also discussed.

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## 2. Experimental

### *Synthesis of carbon microspheres*

Firstly, 4 g glucose was dissolved in 100 ml distilled water under magnetic stirring at room temperature to form a transparent solution. Subsequently, the obtained solution was transferred into Teflon-lined sealed stainless autoclaves and maintained at 180 ºC for 24 h under autogenous pressure. Afterwards, the solution was centrifuged to obtain the black precipitates. Then, the black precipitates was washed, filtered carefully with ethanol (99.6%) and distilled water. Finally, the last product was dried in air in laboratory oven at 80 ºC for 6 h to obtain carbon microspheres.

### *Synthesis of ZnO hollow microspheres*

Firstly, 2.97 g $Zn(NO_3)_2.6H_2O$ was dissolved in 160 ml absolute ethanol and 20 ml distilled water. The mixture was magnetically stirred at room temperature to form a transparent solution. Subsequently, 6 g urea was added into this solution. Afterwards, 1 g of previously synthesized carbon microspheres was added. The mixture was magnetically stirred about 5 minutes and was transferred into Teflon lined sealed stainless autoclaves and maintained at 60 ºC for 12 h under autogenous pressure. After that, the mixture was centrifuged to attain the grey precipitates. The grey precipitates was washed, filtered several times with ethanol (99.6 %) and distilled water. Finally, the last product was dried in air in laboratory oven at 60 ºC for 4 h and calcined at 500 ºC for 10 h to obtain ZnO hollow microspheres.

### *Preparation of pristine and NiO-modified surface ZnO thick films*

For the ethanol sensing measurement, these sensor films were prepared following procedure: at first, 0.1 g obtained ZnO powder was dispersed with assistance of polyethylene glycol (PEG, 4000) into 1 ml distilled water at room temperature and magnetically stirred to form slurry. Then 0.6 µL slurry was coated onto self-generating template which was deposited on Pt-interdigitated electrodes (the electrode gap is 20 µm). During the film preparation the amount of ZnO was controlled for prevention of loss. These sensor films were dried in air at 80 °C for 24 h and heated at 500 °C for 2 h to evaporate organic species. For preparation of sensor film with NiO-modified surface, the $Ni(NO_3)_2$ solution was obtained by dissolving 0.01 g $Ni(NO_3)_2$ onto 10 ml distilled water. Then 0.6 µL $Ni(NO_3)_2$ solution was dropped slowly onto the film surface by micro-pipette. The $Ni(NO_3)_2$ solution volume was also controlled carefully. Afterward the film was calcined at 500 ºC for 2 h to reduce $Ni(NO_3)_2$ to NiO [16]. The film prepared from pristine ZnO hollow microspheres is referred to as M1 and the film prepared from ZnO hollow microspheres with NiO-modified surface as M2, respectively.

### *Ethanol sensing measurement*

The both sensor films obtained previously were placed in a plate of external electric heater inside a glass chamber one by one. A UV LED (wavelength of 365 nm, power of 3 W) was placed in the opposite direction above these samples. The response of these sensor films at temperatures from 75 to 125 °C and ethanol concentration levels from 125 to 1500 ppm was tested using a static gas-sensing system. Gas response ($S$) is defined as ratio of their resistance in air to their resistance in presence of ethanol vapor. The $S$ formula is expressed as follows:

$$S = \frac{R_a}{R_g} \quad (1)$$

where, $R_a$, $R_g$ are resistances of these sensor films in air and in presence of ethanol vapor, respectively.

## 3. Results and discussion

FESEM image in Fig. 1a depicts that ZnO hollow microspheres have been synthesized with average diameter and thickness about 1.5 µm and 40 nm, respectively. It shows that the shell is formed of closely packed nanoparticles with average diameter of 40 nm. More details can also be observed in Fig. 1a, some openings in the spheres can be seen clearly, implying the hollow structure of the spheres. This porous network is believed to be favorable for gas sensor, which can facilitate the inward and outward diffusion.

The typical XRD pattern of the ZnO hollow microspheres (Fig. 1b) depicts that all the diffraction peaks can be assigned to the hexagonal wurtzite structure of ZnO with lattice constants of $a = b =$ 0.3249 nm and $c$ = 0.5206 nm (JCPDS 36-1451). The strong and narrow diffraction peaks indicate that the material possesses good crystallinity. The crystallite size of the microsphere is 24.8 nm, which is calculated for the most intense peak (101) by using the Scherrer equation [17]:

$$D = \frac{0.89\lambda}{\beta \cos\theta} \quad (2)$$

where $D$ is the crystallite size (nm), $\beta$ is the full width of the diffraction line at half of the maximum intensity i.e. (101) in radians, $\lambda$ = 1.54065 Å is the X-ray wavelength of CuK$\alpha$ and $\theta$ is the Bragg's angle.

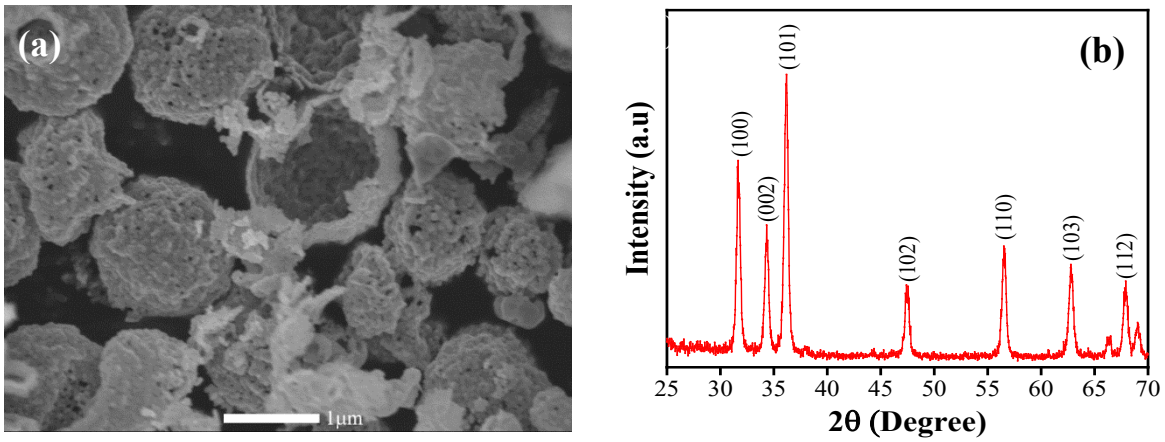


**Fig. 1**. SEM images (a) and XRD pattern (b) of ZnO hollow microspheres.

Fig. 2 depicts the formation mechanism of ZnO hollow microspheres. The surface of obtained carbon microspheres is hydrophilic. Therefore, the embedding of zinc precursor $Zn(OH)_4^{2+}$ into the hydrophilic shell of carbon microspheres takes place. The main reactions joining in the creation of ZnO hollow microsphere in ethanol/water mixer can be described by the following equations [18][4]:

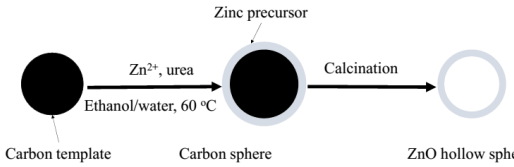


**Fig. 2**. Schematic illustration of the formation of ZnO hollow microspheres.

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + NH_3 \quad (3)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (4)$$

$$Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2+} \quad (5)$$

$$Zn(OH)_4^{2+} \rightarrow Zn(OH)_2 + 2OH^- \quad (6)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (7)$$

The energy dispersive X-ray and elemental mapping are used to detect Ni concentration and distribution. The EDX spectrum is shown in Fig. 3a, which demonstrated that Ni has been presented in the M2 sensor film. The composition obtained from EDX spectrum is roughly consistent with desired weight ratio of NiO and ZnO. All the three elements Zn, O, Ni are homogeneously distributed over the sensor film (Fig. 3b). We can also observe the shape of the M2 sensor film (inset, Fig. 3a).

Typical response transient of the M2 sensor film is shown in Fig. 4a. We note that it shows an n-type semiconductor properties. In the dark, the M2 sensor film shows no response to ethanol vapor at 100 ºC all concentration levels (Fig. 4b).

Fig. 5 depicts their response to ethanol vapor with concentration levels 125 to1500 ppm at temperatures of range from 75 to125 ºC under UV illumination. We can observe that the response of the M2 sensor film is always higher than the M1 sensor film. The optimal temperature of the both is 100 ºC. At this condition, the response of these sensor films to 1500 ppm ethanol vapor is 6.5 and 4.5, respectively.

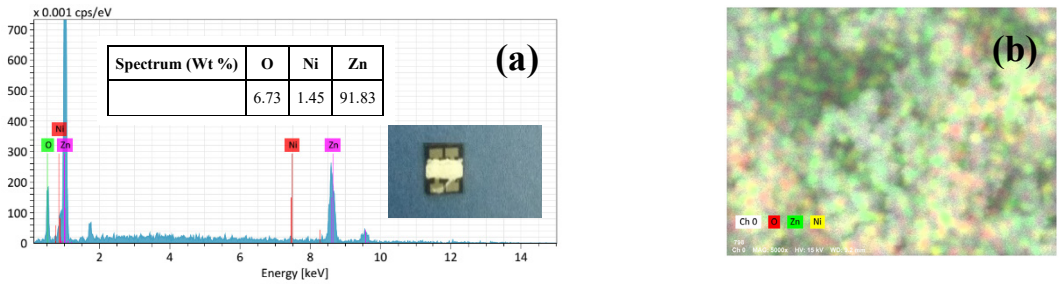


**Fig. 3**. EDX spectrum (a) and elemental mapping (b) of the M2 sensor film.

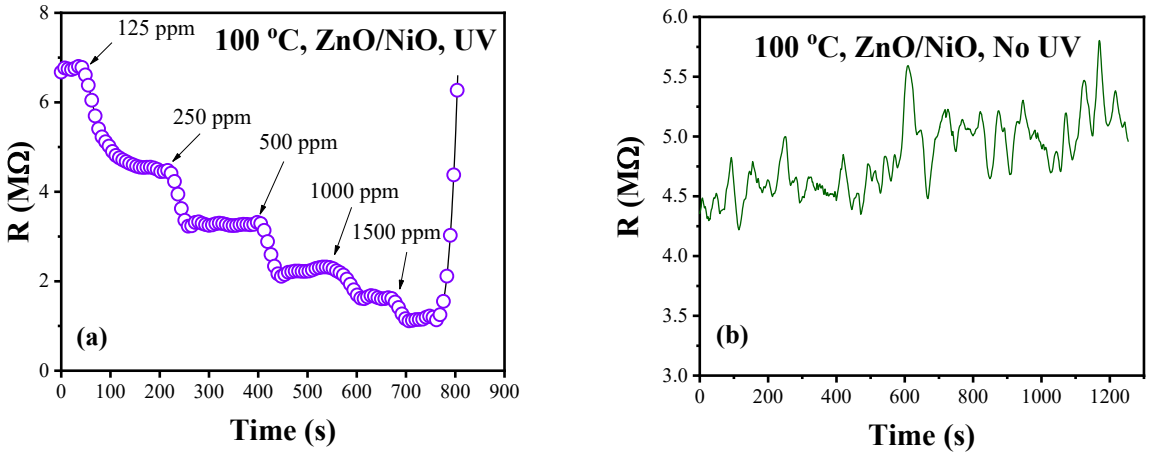


**Fig. 4**. Transient response of the M2 sensor film to ethanol vapor (125-1500 ppm) at 100 °C under UV illumination (a) and in the dark (b).

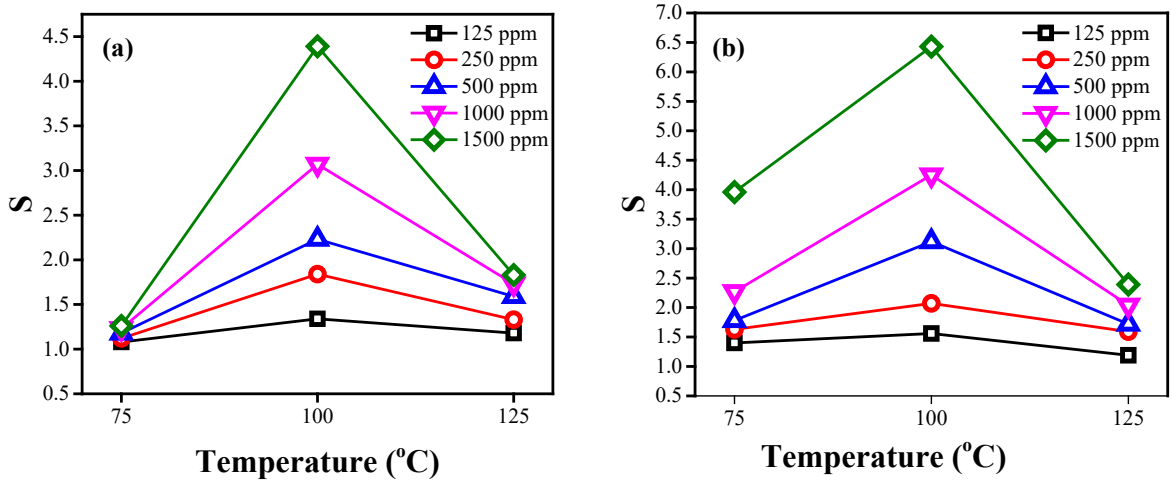


**Fig. 5**. Sensitivity of M1 (a) and M2 (b) at temperatures range 75-125 °C. All measurements were realized under UV illumination.

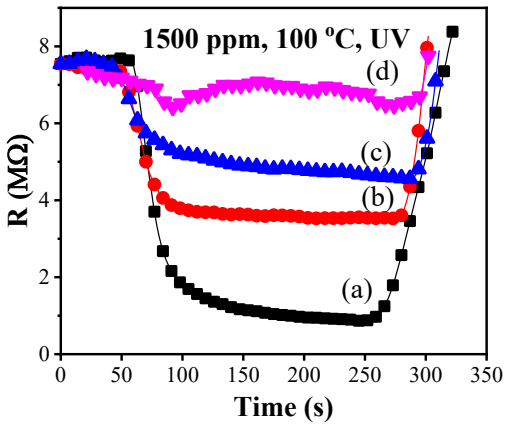


**Fig. 6**. Response of the M2 sensor film to 1500 ppm a) ethanol, b) $NH_3$, c) acetone, d) LPG at 100 °C under UV illumination.

Fig. 6a, 6b, 6c, 6d show the selectivity of the M2 sensor film at 100 °C to ethanol vapor. It can be seen that its response to 1500 ppm ethanol vapor is the highest in comparison with other VOCs. As mentioned above, this value is 6.5 while its response to $NH_3$, acetone, LPG is lower, which are 2.1, 1.6 and 1.2 respectively. Fig. 7 shows the transient response of the M2 sensor film to 1500 ppm ethanol vapor after 5 months. It should be noted that the sensor film exhibited good stability to ethanol vapor.

In this work, M2 sensor film response has been compared to the previously published reports as seen in Table 1. It shows the high performance of NiO-modified surface sensor film under UV illumination when it was exposed toward ethanol vapor at low temperatures.

**Table 1.** List of ethanol sensor based on ZnO nanostructures.

| Sensor Material | Working Temperature (°C) | Ethanol (ppm) | Response | Ref. |
|---|---|---|---|---|
| ZnO nanorods/NiO nanosheets | 200 | 500 | 375 % | [21] |
| NiO hollow hemispheres | 400 | 100 | 4 | [22] |
| NiO/ZnO nanotubes | 215 | 200 | <5 | [23] |
| ZnO microspheres/NiO | 100 | 500 | 3.0 | This work |

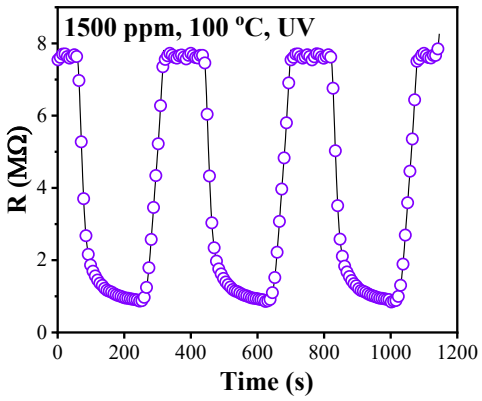


**Fig. 7**. Response of the M2 sensor film to 1500 ppm ethanol after 5 months at 100 °C under UV illumination.

In M1, before introducing ethanol, the ZnO hollow microspheres absorb $O_2$ from air, and the adsorbed oxygen molecules are converted into oxygen ions ($O_2^-, O^-, O^{2-}$) capturing free electrons from conduction band of ZnO and photoinduced electron. This action results in the formation of a depletion layer in the oxide surface region and an increase in the resistivity of the oxide. The reactions kinetics can be described as follows [14]:

$$O_{2,g} \leftrightarrow O_{2,ads}, \quad (8)$$

$$O_{2,ads} + e^- \leftrightarrow O^-_{2,ads}, \quad (9)$$

$$O^-_{2,ads} + e^- \leftrightarrow 2O^-_{ads}, \quad (10)$$

$$O^-_{ads} + e^- \leftrightarrow O^{2-}_{lat} \quad (11)$$

where the subscripts "g", "ads", and "lat" mean gas, adsorbed and lattice, respectively.

Under UV illumination, the free electron–hole pairs could be generated by reaction (12). Besides, the photoinduced hole may interact with chemisorbed oxygen ion, causing the oxygen to be desorbed from the ZnO film surface by reaction (13) [19]:

$$h\nu \rightarrow h^+ + e^- \quad (12)$$

$$h^+ + O^-_{2,ads} \rightarrow O_{2,g} \quad (13)$$

Photogenerated oxygen ions are created due to the reaction of ambient oxygen molecules with photoelectrons, as follows:

$$O_2 + e^- (h\nu) \rightarrow O_2^- [h\nu] \quad (14)$$

In contrast to the chemisorbed oxygen ions, which are strongly attached to the ZnO surface, these photogenerated oxygen ions $O_2^- [h\nu]$ are weakly bound to ZnO and can be easily removed [20]. When ethanol vapor is introduced, the ethanol molecules react with the adsorbed oxygen species to form $H_2O$ and $CO_2$ by equations:

$$C_2H_5OH_{ads} + 6O^-_{ads} \rightarrow 2CO_2 + 3H_2O + 6e^- \quad (15)$$

$$C_2H_5OH + 3O_2^- [h\nu] \rightarrow 2CO_2 + 3H_2O + 3e^- \quad (16)$$

This process releases the captured electrons back to the conduction band of the ZnO, thinning the electron-depletion layer and expanding the conduction channel. Therefore, resistance of M1 sensor film is decreased. In contrast to the M1, more significant radial modulation occurs in M2 sensor film. Electrons flow from *n*-ZnO hollow microspheres to *p*-NiO nanoparticles and holes flow in opposite direction until the flows are stopped by build-up potential. As a result, electron–hole compensation will appear in the *p–n* heterojunction region. Thus, the hole concentration in the *p*-NiO nanoparticles and the electron concentration in the *n*-ZnO hollow microspheres will decrease. Accordingly, in the M2 sensor sample, in air, the electron-depletion layer in the surface will be further expanded in the radial direction, which shrinks its conduction channel further. The electron-depletion layer on the *n*- ZnO hollow microspheres side and the hole accumulation layer on the *p*-NiO side formed due *p-n* heterojunction are overlapped onto the electron depletion layer of the pristine *n*-ZnO hollow microspheres, resulting in additional suppression of the conduction channel. It should be pointed out that the hole accumulation layer on the *p*-NiO side cannot play as a conduction channel for discretely contribution of NiO nanoparticles. When ethanol gas is introduced, the captured electrons are released and the depletion layer will be reduced and the conduction channel will be expanded. Consequently, further modulation in the resistivity of *n*-ZnO hollow microspheres and thereby the enhanced response to ethanol occurs in the decorated microspheres. The enhanced electrical response of the M2 sensor film induced by NiO modification can be explained by a radial modulation of the conduction channel described above [24].

## 4. Conclusion

ZnO hollow microspheres with average diameter of 1.5 µm and wall thickness of 40 nm were successfully synthesized by the glucose-mediated hydrothermal technique. The obtained material has wurtzite crystal structure and good crystallinity. Under UV LED (365 nm, 3 W) illumination the response of sensor film based on this material increased further in the NiO-modified surface. The observed ethanol sensing of sensor films at low temperature is attributed to influence of UV illumination. This result suggests that sensor based on NiO-modified ZnO hollow microspheres can be applied in areas where working at high temperatures is difficult, thereby significantly enhancing its applicability. .

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