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STUDY THE RESPONSE OF GAS SENSOR USING ZnO NANORODS SYNTHESIZED BY HYDROTHERMAL METHOD

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ABSTRACT

Low-dimensional nano structures ZnO are potential material for optoelectronicand gas-sensing applications. The syntheses of a large quantity of ZnO nanostructures play an important role for practical applications for future. In the paper, we propose hydrothermal reduction method to synthesize large quantities ZnO nanorods under atmospheric pressure and without using any catalysts. As-prepared ZnO nanorods exhibited a hexagonal wurtzite crystal structure. For sensing properties, ZnO nanorods were coated on the Pt interdigitated microelectrodes arrays and examined at operating temperatures of 200 to 350 ^oC for the detection capacity of NO_2 gas. The changes in response resistance revealed that the sensor exhibited a high sensing performance for low concentrations of NO_2 gas (0.5 ppm). Additionally, the ZnO nanowires sensors have a good performance to ethanol.

Keywords: ZnO, nanorods, gas sensor.

1. INTRODUCTION

In recent years, Zinc oxide (ZnO) is one of the first materials studied as a gas sensor [1 – 3]. This is primarily due to the high mobility of conduction electrons in the material and good chemical and thermal stability under operating conditions [4]. It is a direct band gap wurtzite type semiconductor with band gap energy of 3.37 eV at room temperature, and a very large exciton binding energy of about 60 meV. ZnO presents interesting electrical, optical, acoustic and chemical properties, which find wide applications in acoustic and short wavelength optical devices. Although ZnO is one of the earliest materials developed as a gas sensing material, because of high operating temperature (around 400 ^oC to 500 ^oC) and poor selectivity, until recently it has been less popular compared to SnO.

In recent years, several studies are going on to improve the performance of ZnO sensors in order to increase the selectivity and to lower the operating temperature. Most of the attempts are towards the use of ZnO nanoparticles to improve the sensitivity or with additives for selective sensing of H_2, H_2S or NH_3 vapor. These are mostly based on nanowire diameter, which require specific instrumentation as well as high temperature treatment. On the other hand, thick film sensors are more versatile and amenable for large - scale production. There are some reports on thick film sensors with highly claimed samples [5, 6] and a few on the sensing of ethanol (EtOH) at an operating temperature of 332 ^oC [7]. There is hardly any report on liquefied petroleum gas (LPG) sensors based on ZnO. With the aim of developing a sensor to detect LPG at comparatively low temperature, an attempt is made to synthesize nanoparticles of ZnO and study their gas sensing characteristics.

This study introduces a simple and scalable hydrothermal synthesis of single-crystal ZnO nanorods with nanovoids using Pluronic P-123 (P123) as a surfactant and structure directed agent. The asobtained nanorods with nanovoids can be used to fabricate highly sensitive NO_2 nanosensors with a relatively good response to sub-ppm concentration and satisfactory long term stability for detecting NO_2 gas in air quality monitoring. The size and morphology of the nanostructures were thoroughly examined using electron microscopy, X-ray diffraction, and Raman spectroscopy.

2. MATERIALS AND METHODS

In a typical synthesis, 1.36 g zinc chloride ($ZnCl_2$) and 1.36 g P123 were dissolved in 100 ml distilled water to obtain a clear solution. The solution was stirred and its pH was adjusted to 10 by drop wise addition of ammonium (NH_4OH). The final milky solution was then subjected to hydrothermal treatment in a Teflon-lined autoclave at 160 ^oC for 16 h. The solid precipitates were collected through centrifugation and washed with distilled water and ethanol. After drying, the collected powders were oxidized at 500 ^oC for 8 h to remove the surfactant. The crystal structure, morphologies and composition of the as-synthesized materials were investigated by using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HRTEM), selective area electron diffraction (SAED), scanning transmission electron microscopy (STEM), and dispersive X-ray analysis for elemental mapping (STEM-EDS). The optical properties of the synthesized materials were investigated by using UV–vis adsorption and photoluminescence (PL) spectra at room temperature.

Figure 1. The equipments used in the fabrication process of ZnO nanomaterials by hydrothermal method.

The single-crystal ZnO nanorods powders were dispersed in an ethanol solution by using an ultrasonicator and were then dropped onto a platinum interdigitated electrode for gas sensor fabrication. The sensor resistance was automatically recorded during gas sensing characterization by using a digital source meter (Keithley model 2700) interfaced with a computer

3. RESULTS AND DISCUSSION

After fabrication are nanomaterials, we surveyed the surface morphology of the material. SEM and HRTEM images as well as the SAED pattern were used to investigate the orphologies and the crystal structure of the synthesized nanorods, as shown in Fig. 2. The SEM image (Fig. 2A) indicates the successful fabrication of homogenous nanorods that have an average length and diameter of about 900 nm and 23 nm, respectively. The HRTEM image (Fig. 2B) shows the nanorods having several nanovoids with an average size of less than 5 nm. The convex and concave surfaces of the Nanorods are due to the formation of the nanovoids (Fig. 2C). The high-magnification HRTEM image in Fig. 2D reveals a highly crystallized nanorod with a lattice spacing of 0.52 nm, which corresponds to the distance between the (001) planes of ZnO crystal structure. None of the grain sizes were observed in the HRTEM image, which indicates that the nanorods has a single crystal structure. This result is consistent with the SAED pattern (Fig. 2F) in which the diffraction spots are arranged on the (010) and (001) directions in the hexagonal ZnO structure [8].

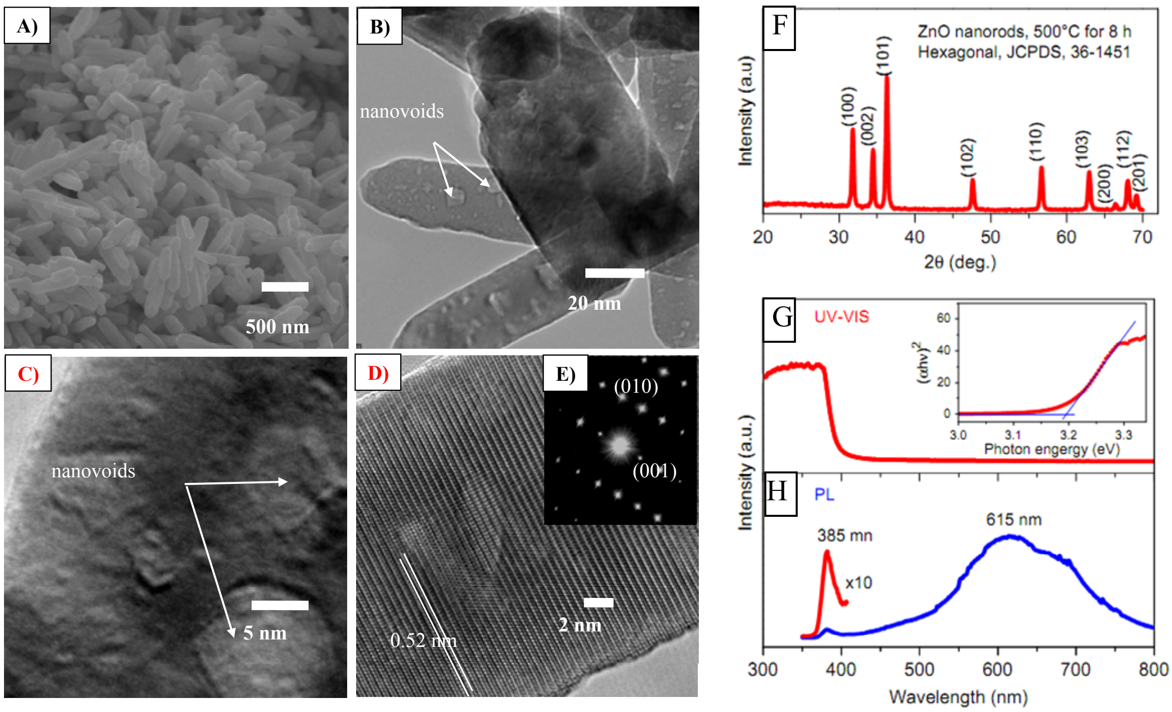

Figure 2. (A) Typical SEM and (B)–(D) HRTEM images of the as-synthesized ZnO nanorods; the inset of (D) depicts the SAED pattern of single crystal ZnO, (E) STEM image and (F)–(H) EDS mapping of the ZnO Nanorods. (F) XRD pattern, (G) UV adsorption, and (H) PL spectra of the fabricated ZnO nanorods.

The powder XRD pattern (Fig. 2F) of the synthesized materials exhibits typical diffraction peaks at 31.8, 34.6, 36.2, 47.5, 62.9, and 67.9 which belong to the (100), (002), (101), (102), (103), and (112) reflections of the hexagonal ZnO, respectively (JCPDS, No. 36-1451). The average crystal size calculated by using the Scherrer formula was found to be about 27 nm. The optical properties of the synthesized materials characterized by using UV adsorption and PL emission are shown in Fig. 2G, respectively. The UV adsorption spectrum exhibits strong adsorption at a wavelength of about 400 nm, which corresponds to the band-to-band ZnO adsorption (Fig. 2G). The plots of $(\alpha(h\nu)^2)$ versus hv which can be derived from the UV adsorption data are shown in the inset of Fig. 2G. The intercept of the tangent to the plot gives a good approximation of the band gap energy of about 3.2 eV [9, 10]. The room-temperature PL spectrum of the ZnO nanorods excited by using a 325 nm He–Cd laser displays an emission band at 385 nm (3.2 eV) and another at 615 nm (Fig. 2F). The former is attributed to the near-band-edge emission agreeing with the band gap value found from the absorption spectra. The latter peak is related to the deep-level defects formed by the oxygen vacancy and zinc interstitials in the ZnO crystal [10, 11]. The intensity of the visible band is much higher (12-fold) than that of the ultraviolet, which indicates the high-level defect of the ZnO nanorods that results from surface oxygen vacancies in the small-diameter nanorods with nanovoids. Compared with the ZnO nanorods fabricated by using thermal evaporation, the nanorods in this study have a significantly higher level of defects, possibly due to the presence of nano voids [12,13].

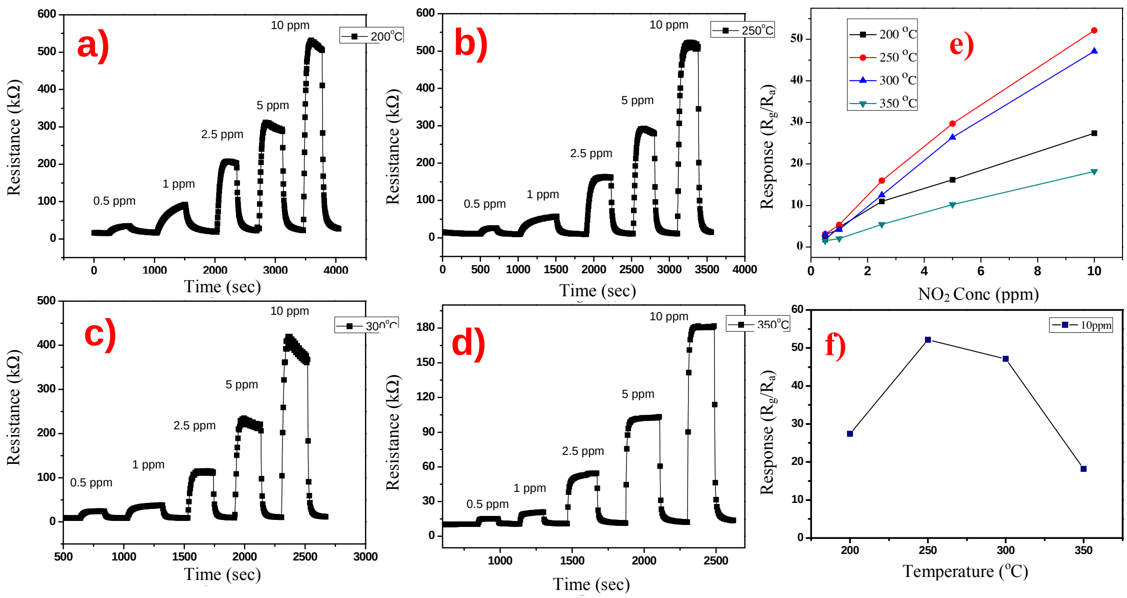

Figure 3. (a)–(d) Dynamic sensing transient of ZnO nanorods sensors measured with NO_2 gas (0.5–10 ppm) at temperatures of 200, 250, 300, and 350 °C, (e) sensor response (R/Ro) as a function of NO_2 concentration and (e) sensor response (R_g/R_a) as a function of working temperature with 10 ppm NO_2.

Nitrogen dioxide (NO_2) is a common and highly toxic gaseous pollutant that harms the environment and human health even at extremely low concentrations in the sub-ppm level [12, 14]. Fig. 3a–d shows typical resistance transient of the fabricated nanosensor measured with NO_2 (0.5–10 ppm) at different temperatures. The sensors exhibited good response recovery characteristics regardless of the measured temperatures and target gas concentrations. This result indicates that the as-prepared nanosensors can be used for a wide working temperature range. The increase in sensor resistance can be attributed to the formation and expansion of the electron depletion layer on the nanorod surface caused by the NO_2 molecule adsorption on the surface of the n-type semiconducting ZnO [11, 15, 16].

The sensor response (R_g/R_a) as a function of NO_2 concentration at different working temperatures is shown in Fig. 3E. The sensor exhibits a nearly linear dependence of response on the gas concentration, which indicates that the sensor was not yet saturated in the measured range. The sensor responses (R_g/R_a) to 0.5, 1, 2.5, 5, and 10 ppm NO_2 at an optimal working temperature of 250 ^oC were 2.58, 5.68, 16.13, 29.04, and 51.25, respectively. These values are relatively higher compared with the maximum response of the pristine ZnO and the Au decorated ZnO nanorods (1.62) to 5 ppm NO_2 [13]. The significantly high response obtained in this study is attributed to the presence of the nanovoids along the nanorods, which provide large sensing sites for NO_2 gas molecule adsorption and enhance sensing capability.

Fig. 3e is the response of the sensor depends on ZnO nanorods operating temperature at 1 and 10 ppm of NO_2. I noticed that the line response the temperature dependent activity curve with a maximum at 250 ^oC. Eugene and colleagues [17] also pointed out that at temperatures of 250 °C using nanorods for NO_2 gas sensor has the highest response. This may be related to the adsorption properties of the nanorods O^- ions in the temperature range 100-300 ° C. When the high temperature adsorption process O^{2-} be increased and prevailed so can the response of the sensor reduces. Furthermore the process of desorption of all O^- ions, O^{2-} faster. Therefore, it is possible at 250 ^oC temperature sensor ZnO nanorods have great responsiveness [17] .

4. CONCLUSIONS

A simple hydrothermal method for fabricating single-crystal ZnO nanorods with nanovoids for effective NO_2 gas nanosensor applications was demonstrated. The single crystal ZnO nanorod has an average 900 nm length and 47 nm width, and has several nanovoids less than 5 nm along the nanorods. The nanorods exhibited a high response to sub ppm NO_2 gas concentration and excellent stability, and fulfilled the practical application of a sensor for monitoring toxic gases.

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TÓM TẮT

NGHIÊN CỨU ĐỘ ĐÁP ỨNG KHÍ CỦA CẢM BIẾN SỬ DỤNG THANH NANO ZnO CHẾ TẠO BẰNG PHƯƠNG PHÁP THỦY NHIỆT

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Vật liệu nano ZnO có cấu trúc một chiều đang có nhiều ứng dụng cho lĩnh vực quang điện tử và cảm biến khí. Tổng hợp vật liệu ZnO với cấu trúc nano đóng vai trò quan trọng trong việc phát triển những ứng dụng mới mẻ. Trong bài báo này chúng tôi tổng hợp vật liệu nano Zno bằng phương pháp thủy nhiệt với số lượng lớn dưới áp suất khí quyển, không cần mầm kết tinh. Thanh nano được tạo ra có cấu trúc tinh thể lục giác. Sử dụng vât liệu nano chế tạo được để chế phủ lên vi điện cực Pt để khảo sát sự phụ thuộc của điện trở theo nông độ khí tương tác. Cảm biến có hiệu năng tốt với nồng độ thấp (0,5 ppm) khí NO_2.

Từ khóa: ZnO, thanh nano, cảm biến khí.