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Rapid and Template Free Synthesis of ZnO Nanorods and Analysis of their LPG Sensing Properties

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Abstract: ***ZnO nanorods (diameters~25 nmand lengths~145-150 nm) were synthesized by using a simple solochemical method and their LPG sensing properties were investigated. The ZnO nanorods exhibited outstanding gas sensingcharacteristics such as, higher gas response (~502 to 50ppm LPG at 300 ◦C), extremely rapid response(~6-7 s), fast recovery (~6–7 s), excellent reproducibility, good sensing selectivity and relatively lower operating temperature(~300◦C). The experimental results clearly demonstrate the potentialof using the ZnO nanorods as sensing material in the fabrication of LPG sensors.***

Keywords: ZnO nanorods, LPG sensor, Semiconductor gas sensors, TEM, XRD.

1. Introduction

Over the last decade, considerable attention has been focused on the synthesis and characterization of nanostructured metal oxides for the fabrication of low cost, selective and low temperature operative gas sensors [1].Nanostructured metal oxides such asundoped SnO_2 [2], SnO_2 doped with nobel metals [3], CdO [4], WO_3 [5], Al doped ZnO [6] and $BaTiO_3$[7] have been investigated in the past decades as liquid petroleum gas (LPG) sensing materials because of their low cost, ease of synthesis, versatility in detecting a wide range of toxic/flammable gases and stability in harsh environments. In particular, ZnO is extensively used in the fabrication of gas sensors for detecting various toxic and flammable gases.

Various techniques have been used to prepare ZnO nanostructures such as hydrothermal synthesis [8], co-precipitation [9], solochemical method [10], sol-gel method [11] etc. Out of these recently used solochemical is a simple, quick, template free and inexpensive route to synthesize the ZnO nanorods at relatively low temperature.

LPG is a clean source of energy therefore it is widely used as a fuel in domestic and industrial heating [12]. It becomes hazardous due to its high possibility of explosion accidents caused by leakage or human error. Therefore to detect it in early stages, continuous efforts have been made in the development of reliable, efficient, simple, low cost sensors to monitor LPG having good response and sensing selectivity.

In the present work experiments have been carried out for the fabrication of rapid and selective LPG sensor based on ZnO nanorods. The ZnO nanorods were synthesized by solochemical method without any template, using zinc chloride ($ZnCl_2$) and NaOH as precursors at 70°C. LPG sensing properties of the ZnO nanorods were systematically investigated.

2. Experimental

2.1. Synthesis of ZnO nanorods

The synthesis of ZnO nanorods was carried out using analytical grade zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH) without further purification. In a typical synthesis, 1 M aqueous solution of NaOH was kept at 70 °C with continuous stirring. Then to this solution, 0.3 M aqueous solution of $ZnCl_2$was slowly drop-wise added for 1 h with a continuous stirring at 70 °C till another 2 h. The resulting precipitate produced in the reaction was harvested by filtration and washed repeatedly with methanol and doubled-distilled water. Finally, the filtered product was dried at 80 °C under vacuum for 5 hto obtain the end-product for further characterization..

2.2. General characterization

The structural analysis of the zinc hydroxyl carbonate precursor and as-synthesized product was carried out using X-ray diffractometer (XRD, D8 Advance, Bruker AXS) with CuK_α radiation (λ=1.5418 A°). The surface morphology and microstructure of the products were observed using a transmission electron microscope (TEM, Tecnai G^2 U20, FEI, USA) operating at an accelerating voltage of 200 kV.

2.3. LPG sensing measurements

The spin coated ZnO films were used for the evaluation of LPG gas sensing performance. 1g of ZnO powder was dispersed slowly to a surface modifier consisting of a mixture of acetyl-acetone and ethanol in ratio 1:10 to produce the suspension. Then, 0.1 g of p-hydroxy benzoic acid was added and the suspension was sonicated using ultrasonic probe for 1 h to achieve a homogeneous suspension of ZnO. The mixed suspension was then spin coated using Spin Coater (SPN 2000, Milman Thin film systems, Pvt. Ltd., Pune, India) on to the alumina substrates at 2000 rpm for 12 s to form ZnO films. After spin coating, the ZnO films were dried at 80°C for 12 h and used as sensing element to evaluate the LPG sensing characteristics.

The electrical contact leads were fixed at 0.7 cm apart with the help of silver paste on the surface of the ZnO film.

The gas sensing studies were carried out on these sensing elements in a static gas chamber to sense LPG in air ambient. The sensing element was kept directly on a heater in the gas chamber and the temperature was varied from 150 to 400°C . The temperature of the sensing element was monitored by chromel-alumel thermocouple placed in contact with the sensor. The known volume of LPG was introduced into the gas chamber pre-filled with air and it was maintained at atmospheric pressure. The electrical resistance of the sensing element was measured before and after exposure to LPG using a sensitive digital multimeter (2000 Digital multimeter, Keithley) controlled by the test software supplied by Biotronic systems, Mumbai, India.

The performance of the sensing element is presented in terms of gas response(S), which is defined as

$$S = \frac{R_{air}}{R_{gas}} \qquad (1)$$

where $R_{air}$and R_{gas} are the electrical resistance values of the sensor element in air and in the presence of LPG gas, respectively.

3. Results and Discussion

Fig.1(a) shows the XRD pattern of the as-synthesized ZnO nanorods. It exhibits the diffraction peaks at 2θ values of 31.80◦, 34.40◦, 36.30◦, 47.50◦, 56.60◦, 62.80°, 68°and 69.10◦, which are attributed to the formation of hexagonal phase of ZnO (JCPDS No. 75-1533). No peaks of any other phase were detected, indicating the high purity of the as-synthesized ZnOand confirming that the used synthesis route method gives pure ZnO.

The TEM image [Fig. 1(b)] of the as-synthesized ZnO powder exhibits a smooth and rod like morphology. The nanorods have an aspect ratio (ratio between the diameter ~25 nm and length ~145-150 nm of the nanorod) of~6 as evidenced from the TEM image. The selected area electron diffraction (SAED) pattern [Fig.1(c)] confirms the random orientations of the ZnO nanorods and that no secondary phase exists.

The LPG sensing experiments were performed at different temperatures in order to find out the optimum operating temperature for LPG detection. The response of the as-synthesized ZnO nanorods to 50 ppm LPG as a function of operating temperature is shown in Fig.2(a).The LPG response increases with an increase in the operating temperature and attains a maximum at ~300 ◦C (S ~502), followed by a decrease with a further increase of the operating temperature. Thus, the optimum operating temperature for the as-synthesized ZnO nanorods to detect LPG was at300 ◦C, which is the modest from the viewpoint of semiconducting oxide gas sensors. Hence, the optimum operating temperature300 ◦C was chosen in order to investigate the LPG sensing propertiessuch as response and recovery characteristics, reproducibilityand selectivity.

The response and recovery times are defined as the time required for the sensor-resistance to change by 90% of the final resistance. Fig.2(b) represents the response and recovery characteristics of the as-synthesized ZnO nanorods to 50 ppm LPG at 300°C. Five samples were tested from each batch and each sample was tested three times.It was observed that the response increases when exposed to the LPG (reducing gas) gas, which suggests that as-synthesized ZnO nanorods behaves as a n-type semiconductor. The sensor responds very rapidly after introduction of LPG and recovers immediately when it is exposed to air. The as-synthesized ZnO nanorods have response time of ~6-7 s and the recovery time of ~6-7 s. The reproducibility of the as-synthesized ZnO nanorods was measured by repeating the test three times. The gas response of the as-synthesized ZnO nanorods upon periodic exposure to 50ppm LPG at an operating temperature of 300◦C is shown in the inset of Fig.2(b). The as-synthesized ZnO nanorods show good reproducibility and reversibility upon repeated exposure and removal of LPG under same conditions. Thus, the as-synthesized ZnO nanorods exhibit an excellent reproducibility of the response.

Fig. 2(c) depicts the LPG response of the as-synthesized ZnO naorods as a function of LPG concentration at 300°C.It is observed thatthe gas response increased with an increase in the LPG concentration. The gas response changed from 3 to 680.49 in the investigated range of 5–60 ppm. The LPG concentration dependence of the response can be seen to follow a power law, which expresses as [13] :

$$\text{Gas response} = aC^{b} \qquad (2)$$

where a is a concentration independent factor, C is the LPG concentration and b is the exponent of power law related to the sensor materials and target gas ambient. In our case, the values of a and b are calculated to be 0.38 and 1.85, respectively. The dashed curve shows the fit to the experimental data, illustrating clearly good quality of the fit. Thus, the as-synthesized ZnO nanorods can be reliably used to monitor the concentration of LPG in the range 5–60 ppm.

Selectivity is an important parameter of gas sensors and the gas response toward a specific gas needs to be markedly higher than those to other gases for selective gas detection. To study the selective behavior of the as-synthesized ZnO nanorods to LPG at300◦C, the gas responses towards H_2, CO, CO_2 and ethanol with concentration 50ppm each were also measured. The histogram of the responses of the as-synthesized ZnO nanorods toward 50 ppm of LPG, H_2, CO, CO_2 and ethanol at 300°C is depicted in Fig.2(d). The as-synthesized ZnO nanorods exhibit higher response to LPG (502), whereas it shows a considerably lower response (≤54.71) to H_2, CO, CO_2 and ethanol. In order to quantify the selectivity to LPG, the selectivity coefficient (K) was calculated further according to the definition[14]:

$$\mathbf{K} = \frac{\mathbf{S_{LPG}}}{\mathbf{S_B}} \qquad (3)$$

where S_{LPG} and S_B are the responses of sensors in LPG and B gas, respectively. The selectivity coefficients for the as-synthesized ZnO nanorods were 150.5 to H_2, 164.26 to CO_2, 159.40 to CO, 158.24 to NH_3 and 7.90 to ethanol. Higher K value imply the more selective detection to LPG in the presence of other gases. For example, K = 150.5 for H_2indicatesthat the gas response to LPG is 150.5 times higher than that to H_2. Thus, the experimental results indicate that the as-synthesized ZnO nanorods has a good sensing selectivity to LPG.

4. Conclusions

The ZnO nanorods (diameters~25 nm and lengths~145-150 nm) were successfully synthesized through a simple and low cost solochemical method. The gas response to 50ppm of LPG is maximum at an optimum operating temperature 300 ◦C and it is found to be～502. The response time was nearly 6-7 s and the recovery time was found to be 6-7 s. Further, the as-synthesized ZnO nanorods has a high gas response of3-680.49to 5–60ppm LPG, excellent reproducibility and good sensing selectivity when operating at 300 ◦C. The cost-effective and simple synthesis of ZnO nanorods at low temperature and its novel application in LPG sensing are of great significance in real time practical application.

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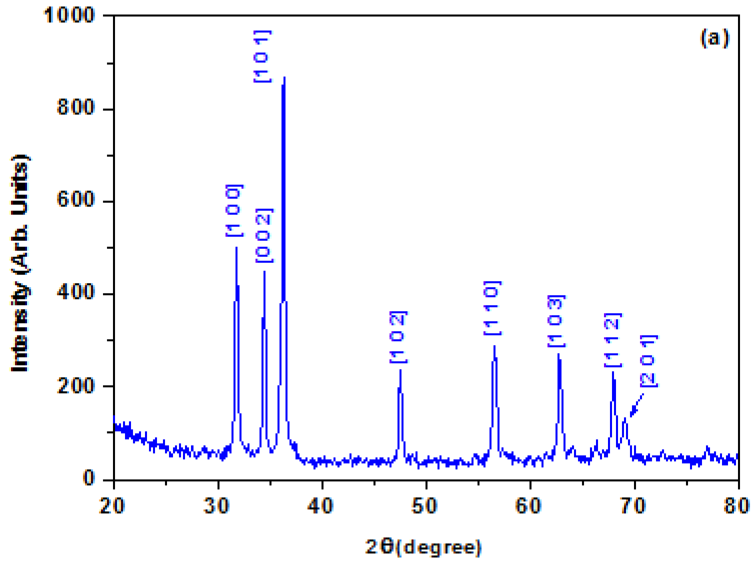

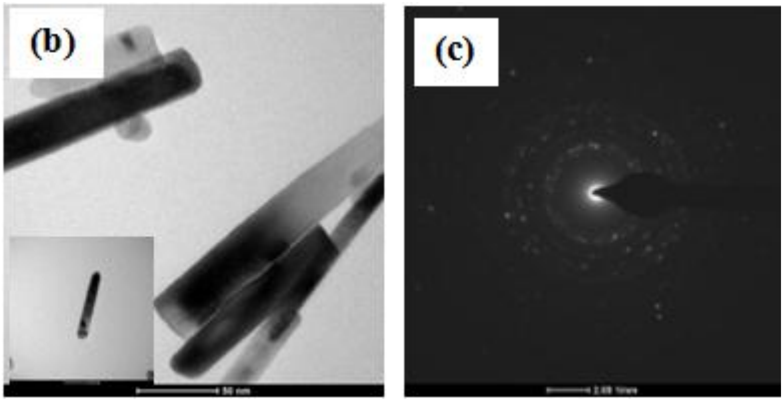

Figure 1: (a) XRD pattern, (b) TEM image and (c) the corresponding SAED pattern of ZnO nanorods.

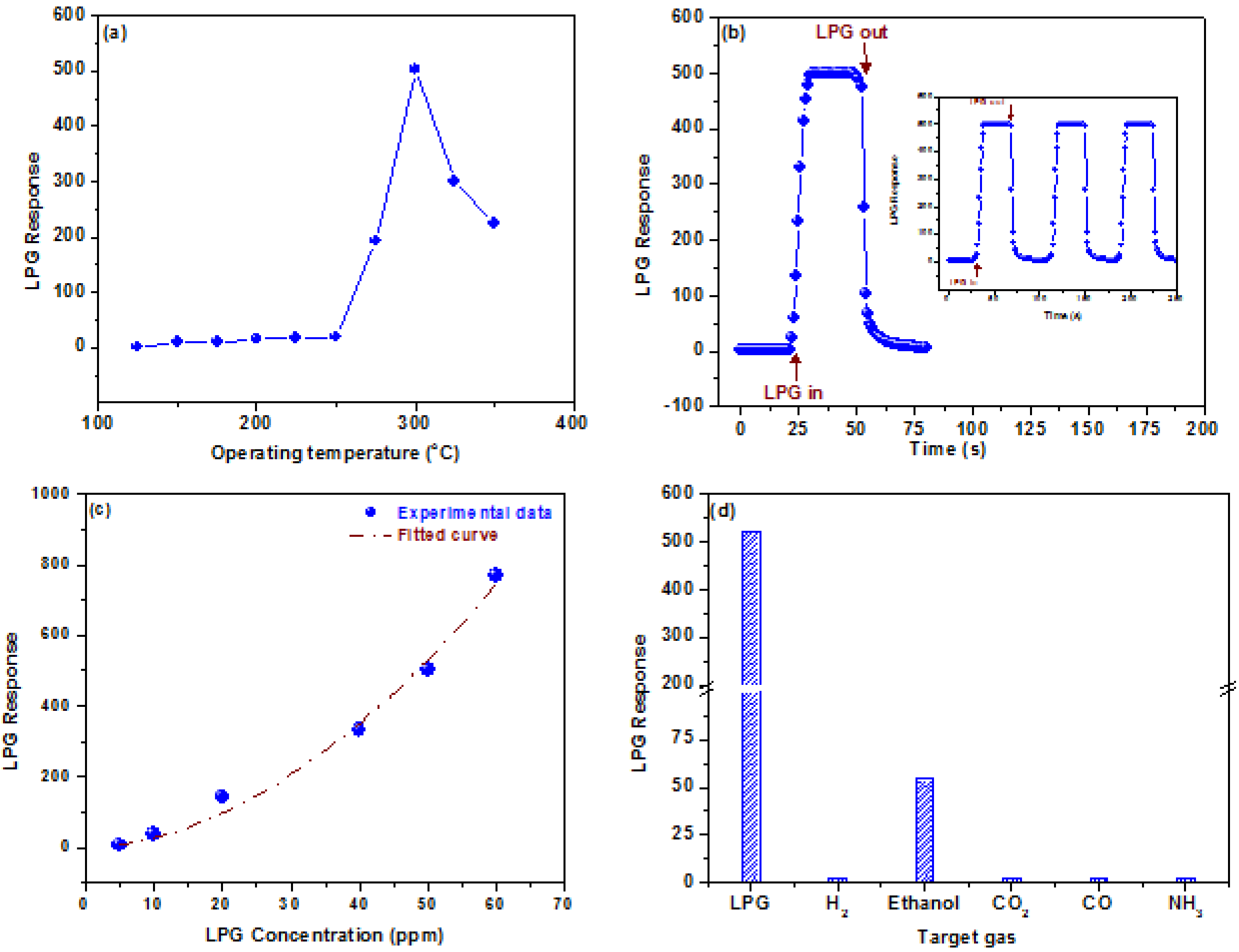

Figure 2: (a) Effect of operating temperature on the LPG response of ZnO nanorods to 50 ppm LPG, (b) Response and recovery characteristics of ZnO nanorods to 50 ppm LPG gas at 300 °C (Inset depicts the repetitive response to 50 ppm LPG gas at 300 °C), (c) LPG response of ZnO nanorodsas a function of LPG concentration at 300 °C and (d) Bar chart showing the gas response of ZnO nanodrods for different gases. The gas concentration and operating temperature in all cases were 50 ppm and 300°C, respectively.