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Synthesis, characterization and performance of zinc ferrite nanorods for room temperature sensing applications

Archana Singh [a], Ajendra Singh [a], Satyendra Singh [b,*], Poonam Tandon [a], B.C. Yadav [c], R.R. Yadav [b]

[a] Macromolecular Research Laboratory, Department of Physics, University of Lucknow, Lucknow 226007, U.P., India
[b] Department of Physics, University of Allahabad, Allahabad 211002, U.P., India
[c] Department of Applied Physics, School for Physical Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow 226025, U.P., India

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ABSTRACT

In the present communication, nanorods of zinc ferrite was synthesized and fabricated by employing sol–gel spin coating process. The synthesized material was characterized using X-ray diffraction, scanning electron microscopy, acoustic particle sizer, atomic force microscopy, UV–visible absorption and infrared spectroscopic techniques. Thermal properties were investigated using differential scanning calorimetry. The XRD reveals cubic spinel structure with minimum crystallite size 10 nm. SEM image of the film shows porous surface morphology with uniform distribution of nanorods. The band gap of the zinc ferrite nanorods was found 3.80 eV using the Tauc plot. $ZnFe_2O_4$ shows weak super paramagnetic behavior at room temperature investigated using the vibrating sample magnetometer. Further, the liquefied petroleum gas (LPG) and carbon dioxide gas (CO_2) sensing properties of the fabricated film were investigated at room temperature (25 °C). More variations in electrical resistance were observed for LPG in comparison to CO_2 gas. The parameters such as lattice constant, X-ray density, porosity and specific surface area were also calculated for the better understanding of the observed gas sensing properties. High sensitivity and percentage sensor response, small response and recovery times, good reproducibility and stability characterized the fabricated sensor for the detection of LPG at room temperature.

1. Introduction

A gas sensor is a device which receives a stimulus (physical/chemical) and converts into measurable electrical/optical signal. The prominence is currently being placed on the development of sensor materials for the detection of LPG that offer high sensitivity, short response and recovery times, superior reproducibility and long-term stability [1,2]. However, most of the sensors developed so far are kinetically slow with a limited sensitivity for the detection below the permissible level of LPG and operate above room temperature; although the detection of LPG at room temperature will be very helpful for the chemical industries and research laboratories [3–5]. The sensing response would be more effective for the material with high surface area and porosity [6,7].

Nanostructured materials may present new opportunities for improvement in the performance of gas sensors because they have a high specific surface area and a nano-scale structure that provides a large number of active sites at which gases may react [8–11]. They also possess a large fraction of the surface atoms per unit volume. The total surface energy of nanostructured materials increases with the overall surface area, which is strongly dependent on the dimensions of the material. One dimensional (1-D) nanostructures have attracted great attention because of their remarkable properties and potential applications in various devices. 1-D nanostructures have a high surface-to-volume ratio, which can overcome the limitations of the commercial sensors, such as their operation at high temperatures and lack of long-term stability of the prepared sensors.

Spinel-type oxides (ferrites) are an alternative for inexpensive and robust detection systems because of their better chemical and thermal stability under operating conditions [12,13]. Particularly, $ZnFe_2O_4$ nanostructure has generated a lot of interest owing to their potential applications in gas sensor, magnetic behavior, electrical characteristics and semiconductor photo catalysis [14–17]. For these applications the surface morphology of $ZnFe_2O_4$ plays a vital role to tune their chemical and physical properties to the appropriate ones. Nowadays, various $ZnFe_2O_4$ nanostructures such as nanoparticles, nanotubes, nanosheets, nanoflowers and nanowalls are widely used in the fabrication of various devices [18–22] due to their pronounced characteristics.

* Corresponding author. Tel.: +91 9651276364.
E-mail address: satyendra_nano84@rediffmail.com (S. Singh).

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Gas sensing properties of zinc ferrite are already reported in the literature for nanopowders [23], thick and thin films [17–19], nanorods [20], core–shell microspheres [21] and nanotubes [22]. Li et al. [24] reported the synthesis of spinel zinc ferrite nanospheres having diameter ~212 nm via a general, one-step and template-free solvothermal route. Zhang et al. [22] reported $ZnFe_2O_4$ nanotubes as a gas sensing material to organics such as ethanol and acetone, due to their unique interconnected channel structure and small size. Arshak and Gaidan [16] investigated the use of iron and zinc oxide nanocomposite films for the sensing applications (methanol, ethanol and propanol vapors). Sutka et al. [23] demonstrated that the gas sensing properties of a spinel ferrite complex metal oxide semiconductor can be improved by controlling iron stoichiometry. Rahman et al. [25] made the considerable effort for the growth and development of face-centered-cubic spinel zinc ferrite nanorods using hydrothermal method at room condition. Sutka et al. [26] presented an easy development of cheap, sensitive and integrable spinel zinc ferrite thin film gas sensors for the detection of ethanol. Thus most of the studies reported in the literature present the sensing response at relatively high temperatures [20–26].

However, in the present study, we have synthesized $ZnFe_2O_4$ nanorods by employing sol–gel spin coating method with almost controlled rod-shape structure. The LPG sensing characteristics of $ZnFe_2O_4$ thin film were investigated at room temperature which is more reliable, stable and robust in comparison to the earlier investigated sensors [20–26]. Detection of LPG at room temperature is very helpful for the chemical industries and research laboratories.

The objective of our work is to fabricate a LPG sensor having high sensitivity, small response and recovery times, good reproducibility and stability. Herein, for the first time, we report the LPG and CO_2 sensing performance of nanorods of zinc ferrite thin film at room temperature. To explain the interaction mechanism of the fabricated LPG and CO_2 sensors, their structural, surface evolution and optical properties were studied using XRD, SEM and UV–visible absorption, respectively.

2. Experimental details

$ZnFe_2O_4$ was synthesized via sol–gel method using stoichiometric amounts of the starting materials such as zinc sulphate [$ZnSO_4{\cdot}7H_2O$] and ferric nitrate [$Fe(NO_3)_3{\cdot}9H_2O$] taken in 1:2 M ratios respectively. These reagents were of analytical grades and used without further purification. The flow chart for the synthesis of zinc ferrite nanorods is depicted in Scheme 1. In brief, $Fe(NO_3)_3{\cdot}9H_2O$ and $ZnSO_4{\cdot}7H_2O$ were dissolved separately in appropriate amount of ethanol to form 0.1 M solution. The obtained precursors were magnetically stirred at 80 °C for 2 h to get homogeneous precursor solution. Further, both as prepared precursors were mixed together and the resulting precursor was magnetically stirred for 6 h. After that, 20 ml of polyethylene glycol (PEG) was added drop by drop, that works as a capping agent.

For the formation of the powder, ammonium hydroxide solution was added drop by drop to the prepared precursor solution under continuous stirring until the reddish brown solution was appeared. Again above solution was magnetically stirred at 80 °C for 6 h. The process of precipitation is depicted by the chemical reactions as below:

$$Fe(NO_3)_3 \cdot 9H_2O + 3NH_4OH \xrightarrow{80\,^{\circ}C} Fe(OH)_3 + 3NH_4NO_3 + 9H_2O \quad \text{(i)}$$

$$ZnSO_4 \cdot 7H_2O + 2NH_4OH \xrightarrow{80\,^{\circ}C} Zn(OH)_2 + (NH_4)_2SO_4 + 7H_2O \quad \text{(ii)}$$

The resulting solution was dried at 120 °C for 6 h and then annealed at 500 °C for 3 h to obtain the powder of $ZnFe_2O_4$. The crystalline powder annealed at 500 °C was crushed into fine powder using a pestle and mortar. The resulting powder was pressed uniaxially under a pressure of 616 MPa in a stainless steel dies for the fabrication of the pellet of $ZnFe_2O_4$. The thin film of the precursor was fabricated on alumina substrate ($12 \times 18\ mm^2$) using spin coater (Metrex Scientific Instruments, India) at 2000 rpm for 60 s. The fabricated film was dried at 120 °C for 6 h. This drying process stabilizes the film. Further, it was annealed at 500 °C for 3 h. This process converts the film as a sensing material. The synthesized material in the form of powder, solid state pellet and thin film were used for various characterizations to explore the parameters of interest. Further the fabricated film was investigated with the exposure of LPG and CO_2 in the concentration range 1000–2000 ppm at room temperature.

The synthesized material was characterized using X-ray diffraction, scanning electron microscopy, acoustic particle sizer, infrared spectroscopy, UV–visible absorption and atomic force microscopy for their structural, surface morphological evolution, particle size distribution, absorption band, optical and three-dimensional topographical information's, respectively. The X-ray diffraction pattern was recorded using X-ray diffractometer (X-Pert PRO PANalytical) with CuK_α radiation source having wavelength 1.54 Å. Fourier transform infra-red spectra was recorded using a FTIR spectrometer (TENSOR-27, resolution 4 cm^{-1}, region 400–4000 cm^{-1}). Surface morphology was analyzed using scanning electron microscope (SEM, LEO). Particle size distributions were investigated by acoustic particle sizer (APS-400). The optical absorption spectrum was recorded by a UV–visible spectrophotometer (Varian Carry 50 Bio, 200–800 nm, 1×10^{-5} M ethanol). Synthesized material was also characterized by NT-MDT solver TS 150, atomic force microscopy in semi-contact mode. The magnetization with applied magnetic field was measured by vibrating sample magnetometer (VSM, Lakeshore 7410) at room temperature.

For the study of the sensing properties, the sensors were fabricated in the form of rectangular (12 mm × 18 mm) thin film deposited on an alumina substrate by spin coating process. Silver electrodes were grown on two opposite ends of the film for the measurement of the resistance. Further the film was inserted into sensing chamber for the measurements of temporal resistance for different concentrations of the gas. The sensitivities of CO_2 and LPG sensors were defined as [2]:

$$(S)_{CO_2} = \frac{R_g}{R_a} \quad \text{(iii)}$$

$$(S)_{LPG} = \frac{R_a}{R_g} \quad \text{(iv)}$$

where R_a is the stabilized value of resistance in air, and R_g, the resistance in the presence of the gas. The percentage sensor responses of CO_2 and LPG sensors were defined by the Eqs. (v) and (vi), respectively given as below [2]:

$$(\%S.R.)_{CO_2} = \frac{|R_g - R_a|}{R_a} * 100 \quad \text{(v)}$$

$$(\%S.R.)_{LPG} = \frac{|R_a - R_g|}{R_g} * 100 \quad \text{(vi)}$$

Eqs. (iii)–(vi) are used for the estimation of the gas sensing characteristics.

3. Results and discussion

3.1. Surface morphological evolution

Surface morphology of $ZnFe_2O_4$ film is shown in Fig. 1(a–d). Fig. 1(a and b) depicts the morphology at nanoscale for two different locations whereas Fig. 1(c and d) depicts the morphology at microscale for two different locations of the film surface. From these images it is visible that the nanorods/ellipsoidals of $ZnFe_2O_4$ are randomly oriented throughout the whole surface of the film. The diameters of these rods are in the range 30–40 nm, whereas the lengths are in the range 100–120 nm. Such type of surface morphology possesses special features in view of rod like structures. These rods produce a number of active sites for the interaction of the target gas. The interaction between the gas and the sensitive layer is limited to the surface itself. Surface to volume ratio of such nanorods is high due to its special rods/ellipsoidals type morphology. Therefore, these short nanorods are reactive to the exposed gas under investigation. This is one of the reasons that $ZnFe_2O_4$ film produces high sensing response. In particular, this type of structure is appropriate for the gas sensing applications, because the smaller size and larger porosity increase the reactive surface area of the sensing film. It is recognized that the materials with higher surface area have larger oxygen adsorption ability that enhances the rate of reaction between the sensing gas and adsorbed oxygen. Due to the enhanced rate of reaction at room temperature the response and recovery times of the sensor may decrease significantly, that is a good indication for fabrication of a sensing device.