



Highly sensitive and fast responding CO sensor based on Co_3O_4 nanorods

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ABSTRACT

Co_3O_4 nanorods (diameters $\sim 6\text{--}8$ nm and lengths $\sim 20\text{--}30$ nm) were synthesized for the first time through a simple co-precipitation/digestion method by calcination of cobalt hydroxyl carbonate in air and their CO gas sensing properties were investigated. The Co_3O_4 nanorods exhibited outstanding gas sensing characteristics such as, higher gas response ($\sim 6.55\text{--}50$ ppm CO gas at 250°C), extremely rapid response ($\sim 3\text{--}4$ s), fast recovery ($\sim 5\text{--}6$ s), excellent repeatability, good selectivity and lower operating temperature ($\sim 250^\circ\text{C}$). Furthermore, the Co_3O_4 nanorods are able to detect up to 5 ppm for CO with reasonable sensitivity (~ 3.32) at an operating temperature 250°C and they can be reliably used to monitor the concentration of CO over the range (5–50 ppm). The experimental results clearly demonstrate the potential of using the Co_3O_4 nanorods as sensing material in the fabrication of CO sensors. Plausible CO sensing mechanism of the Co_3O_4 nanorods is also discussed.

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1. Introduction

Carbon monoxide (CO) is one of the most harmful pollutants, which presents significant health risks [1–3] and studies have shown that it interacts with the haemoglobin and damages the human body by producing a reduction in cellular respiration [4]. This has stimulated considerable interest for scientific research to develop simple and cost-effective chemical sensors for the detection of CO in recent years and many efforts, in this field, are today devoted to the synthesis of novel sensing materials with enhanced performance [1,4–7]. Up till now, the metal oxide semiconductors have been widely investigated in the past decades as gas sensing materials because of their low cost and power consumption, simplicity of fabrication and use, versatility in detecting a wide range of toxic/flammable gases, and stability in harsh environments [8,9]. The metal oxide semiconductors such as SnO_2 [4], In_2O_3 [5] and ZnO [10] have been investigated as CO sensing materials.

Recent studies reveal that the nanostructured metal oxides with reduced dimensionality (i.e. in the form of nanoparticles, nanorods, nanotubes, nanowires and nanoribbons) have ultrahigh sensitivity to different gases due to their small grain size and large surface-to-volume ratio [11–16]. Various nanostructured metal oxide materials like CdO nanoparticles [11], $\alpha\text{-Fe}_2\text{O}_3$ nanorods [12],

SnO_2 nanotubes [13], In_2O_3 nanowires [14], CuO nanoribbons [15] and ZnO nanorods [16] have been evaluated as gas sensing materials during the past few years.

Cobalt oxide (Co_3O_4), an important magnetic p-type semiconductor, has received considerable attention in the past few years due to its application potential in many technological areas such heterogeneous catalysis, anode material in lithium rechargeable batteries, sensors, electrochromic devices, solar energy absorber, etc. [17–19]. Consequently, different methods for synthesizing the Co_3O_4 nanostructures with various morphologies have been reported [20–22]. For example, Dong et al. [20] prepared the Co_3O_4 nanowires having the diameters of $\sim 20\text{--}100$ nm and physical lengths of about $10\text{--}20$ μm by directly heating pure cobalt foils in air. Lakshami et al. [21] synthesized the Co_3O_4 nanofibers using the sol gel method combined with a template synthesis technique. Nam et al. [22] demonstrated the feasibility of employing the viruses to synthesize and assemble the Co_3O_4 nanowires as an electrode material for lithium ion batteries. Although, different methods for synthesizing the nanostructured Co_3O_4 in the form of nanowires and nanofibers were reported, there are only few reports on the gas sensing properties of nanostructured Co_3O_4 [23,24]. A two-step polyol process to synthesize nanostructured Co_3O_4 with different morphologies such as nanoplates, well-organised cabbage like structures and microspherical composites was reported recently by Cao et al. [23]. These authors investigated the CO and alcohol sensing properties of the synthesized nanostructured Co_3O_4 . The synthesized nanostructured Co_3O_4 exhibited good sensitivity ($>8\text{--}50$ ppm), response and recovery times (<10 s), remarkable selectivity and high stability to alcohol at an operating temperature

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of 300 °C. However, it was found to be insensitive to 50 ppm CO at 300 °C and the resistance change was still at a much lower level for 1000 ppm CO. Li et al. [24] prepared the Co₃O₄ nanotubes by a thermal decomposition of Co(NO₃)₂·6H₂O within an ordered porous alumina templates and investigated the gas sensing characteristics of these nanotubes exposed to H₂ and alcohol. The prepared Co₃O₄ nanotubes exhibited an excellent sensitivity to hydrogen and alcohol at room temperature.

Herein, we report for the first time a successful synthesis of Co₃O₄ nanorods by using a simple and low cost coprecipitation/digestion route without any template or a capping agent. Sensing characteristics of the Co₃O₄ nanorods to CO gas were systematically investigated.

2. Experimental

The nanostructured Co₃O₄ was synthesized by a simple coprecipitation/digestion method. In this method, equal volumes of aqueous solutions of Co(NO₃)₂·6H₂O (0.0339 M) and K₂CO₃ (0.0627 M) were added drop-wise to 200 ml of double distilled water kept at 70 °C with continuous stirring, under argon atmosphere to achieve precipitation of cobalt hydroxyl carbonate. The necessary pH value between 7 and 8 required for supersaturation was instantly reached by this process. The precipitation obtained after completion of addition was digested in mother liquor at the same temperature for duration of 8 h. The cobalt hydroxyl carbonate precursor obtained were thoroughly washed with distilled water several times to avoid K⁺ ion contamination and further dried in an oven at 70 °C. The as-dried sample is named as D-8 corresponding to 8 h digestion time. The thermogravimetric analysis (TGA) showed that the hydroxyl carbonate decomposes to give the corresponding oxide at 250 °C. The composition of the hydroxyl carbonate was found to be Co(OH)(CO₃)_{0.5}·0.11H₂O as revealed from TGA and CH analysis. Hence, a part of the as-dried sample was calcined in air at 300 °C for 5 h to obtain the powder of nanostructured cobalt oxide. The calcined sample is named as C-8 corresponding to 8 h digestion.

The structure of the calcined sample C-8 was investigated by using X-ray diffraction (XRD) technique. The X-ray diffraction patterns were recorded with a Rigaku diffractometer (Miniflex Model, Rigaku, Japan) having Cu Kα (λ = 0.1542 nm). The high resolution transmission electron microscopy (HRTEM) was used to determine the particle size and the morphology of the nano-sized powder with JEOL 1200 EX. The X-ray photoelectron spectroscopy (XPS) analysis was carried out using a V.G. Microtech Scientific spectrometer, ESCA 3000, U.K. equipped with two ultrahigh vacuum chambers. The pressure in the chambers during the experiments was about 10⁻⁹ Pa. The XPS spectra were recorded with un-monochromatized Mg Kα radiation (photon energy = 1253.6 eV) at a constant 50 eV pass energy. The core level binding energies were corrected with the C 1s binding energy of 284.9 eV.

The nanostructured Co₃O₄ powder was pressed into pellets under a pressure of 15 MPa and the ohmic contacts were made with the help of silver paste to form the sensing element. The gas sensing studies were carried out on these sensing elements in a static gas chamber to sense CO in air ambient. The sensing element was kept directly on a heater in the gas chamber and the temperature was varied from 50 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 the CO 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 CO using a sensitive digital multi-meter (METRAVI 603). The performance of the sensing element is presented in terms of gas response (*S*), which is defined

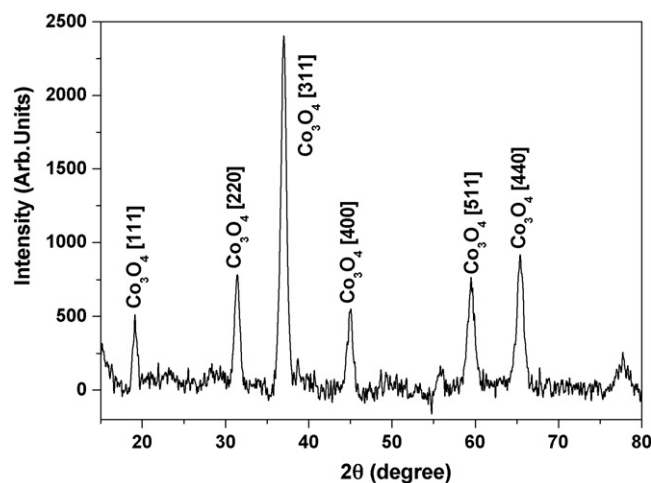


Fig. 1. XRD pattern of nanostructured Co₃O₄ prepared with 8 h digestion time.

as:

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

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

3. Results and discussion

3.1. XRD results

Fig. 1 shows the XRD pattern of the calcined sample C-8. It exhibits the diffraction peaks at 2θ values of 19.08°, 31.36°, 36.97°, 45.02°, 59.42° and 65.37°, which are attributed to the formation of spinel oxide Co₃O₄ with cubic lattice parameter of $a = 8.083$ Å. This is in good agreement with the reported value for Co₃O₄ powder ($a = 8.084$ Å; JCPDS #9-418). The crystallite size was estimated by using the Scherrer formula:

$$t = \frac{k\lambda}{B \cos \theta} \quad (2)$$

where t is the average size of the crystallite, assuming that the grains are spherical, k is 0.9, λ is the wavelength of X-ray radiation, B is the peak full width at half maximum (FWHM) and θ is the angle of diffraction. The crystalline size of the calcined sample C-8 is found to be in the range of 10–20 nm.

3.2. Surface morphology

The HRTEM images of the calcined sample C-8 are shown in Fig. 2. As can be seen from Fig. 2(a), mostly the Co₃O₄ particles are in the form of rods (diameter = 6–8 nm, length = 20–30 nm) with presence of few spherical crystallite particles of size ~2–3 nm in the calcined sample C-8. The parallel lattice fringes across almost all the primary particles are clearly visible (Fig. 2(b)) which confirms the perfectly oriented aggregation of the nanoparticles of Co₃O₄. It is clearly seen that the aggregated Co₃O₄ rod like particles are composed of many small Co₃O₄ nanoparticles. In order to confirm further the formation of the nanorods, we have calculated the surface area of both the rods and spherical particles by taking the dimensions from the HRTEM images. The calculated surface area of the nanorods is around 100 m²/g and the surface area of the spherical particle is around 187 m²/g. However, the observed surface area is 95 m²/g. If we consider only the presence of spherical particles the surface area value would have been nearly equal to 187 m²/g. Thus, the experimentally observed surface area value

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