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Synthesis and LPG sensing properties of nano-sized cadmium oxide

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Abstract

This paper reports the synthesis and liquid petroleum gas (LPG) sensing properties of nano-sized cadmium oxide (CdO). The nano-sized CdO powder was successfully synthesized by using a chemical co-precipitation method using cadmium acetate and the ammonium hydroxide, as starting materials and water as a carrier. The resulting nano-sized powder was characterized by X-ray diffraction (XRD) measurements and the transmission electron microscopy (TEM). The LPG sensing properties of the synthesized nano-sized CdO were investigated at different operating temperatures and LPG concentrations. It was found that the calcination temperature and the operating temperature significantly affect the sensitivity of the nano-sized CdO powder to the LPG. The sensitivity is found to be maximum when the calcination temperature was 400 °C. The sensitivity to 75 ppm of LPG is maximum at an operating temperature 450 °C and it was found to be ∼341%. The response and recovery times were found to be nearly 3–5 s and 8–10 s, respectively. The synthesized nano-sized CdO powder is able to detect up to 25 ppm for LPG with reasonable sensitivity at an operating temperature 450 °C and it can be reliably used to monitor the concentration of LPG over the range (25–75 ppm). The experimental results of the LPG sensing studies reveal that the nano-sized CdO powder synthesized by a simple co-precipitation method is a suitable material for the fabrication of the LPG sensor.

Keywords: Nano-sized CdO; Chemical co-precipitation; LPG; Gas sensor

1. Introduction

In recent years, the synthesis of nano-crystalline oxide materials has been a focal point of research and developmental activities in the area of nano-materials owing to the quest for their various technological applications [1–10]. Semiconducting metal oxides such as SnO_2 [11], ZnO [12], WO_3 [13] and Fe_2O_3 [14] have been widely used as gas sensing materials for the detection of inflammable and toxic gases. The sensor performance is strongly dependent on the microstructural features such as crystallite size, grain boundary characteristics and thermal stability [15]. Several approaches have been explored to fabricate the sensors with an improved performance, which include nano-sized crystallites [16,17], solid solution [18,19] and additives or surface functionalization [20,21].

Out of these approaches, the successful synthesis of nano-crystalline semiconducting oxides with high surface area for gas adsorption opens up a new paradigm for sensor materials. Several research groups have systematically studied the synthesis of nano-crystalline metal oxides and their nanocomposites and investigated their gas sensing properties [1–10]. For example, more recently, Aifan et al. [4] prepared the nano-crystalline SnO_2–In_2O_3 composites using a chemically controlled co-precipitation method and studied their sensing properties for the detection of CO and NO_2. They observed that the preparation parameters are crucial in controlling the grain size and crystallinity of the nano-crystalline SnO_2–In_2O_3 composites. These nanocomposites exhibit high sensitivity and selectivity for the detection of CO and NO_2. Further, it was found that the nanocomposite composition, calcination temperature and operating temperature significantly affects the sensitivity and selectivity.

LPG is a combustible gas and it is widely used as a fuel for domestic heating and industrial use. Although it is one of the extensively used gases, it is hazardous. Hence, it is crucial to detect it in its early stages of the leakage and to perform the active suppression [22]. In order to accomplish this, more attention has been paid to develop the gas sensors for the detection

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of LPG, using several sensing materials such as Ag_2O doped γ-Fe_2O_3, Pt modified Al_2O_3 [23], $ZnGa_2O_4$ [24], Sb doped SnO_2 [25], $MgFe_2O_4$, $CdFe_2O_4$ [26] etc. Recently, the thick films of the mixed oxide of WO_3, TiO_2, In_2O_3 and SnO_2 and doped with nobel metals Au, Pd and Pt were investigated as sensing materials by Chaudhari et al. [3] for the detection of LPG. Srivastava et al. [2] studied the influence of microwave irradiation on SnO_2 powder prepared by precipitation method using water as a medium. They observed that the microwave irradiation results into the increase in LPG sensitivity.

CdO is degenerate, n-type semiconductor and it has interesting properties like large band gap, low electrical resistivity, high transmission in the visible region etc; which make it useful for a wide range of applications such as photodiodes [27], phototransistors [28], photovoltaic cell [29], transparent electrodes [30], liquid crystal displays, IR reflectors and anti-reflection coatings [31]. To the best of our knowledge, there are no reports in the literature dealing with the use of CdO as sensing material for the fabrication of the gas sensors. However, it was reported that the CdO can be used as the dopant to improve the sensor performance. Xiangfeng et al. [32] studied the influence of CdO dopant on the gas sensing properties of zinc ferrite ($ZnFe_2O_4$) to C_2H_2OH. It was shown that the CdO improves the sensitivity, selectivity, response and recovery times of $ZnFe_2O_4$.

With the objective to search for new sensing materials for the detection of LPG, we have made an attempt to synthesize nano-sized CdO by a simple chemical co-precipitation method and to investigate the LPG response of the resultant nano-sized CdO.

2. Experimental

The nano-sized powder of CdO was prepared by a simple co-precipitation method. In this method, a diluted ammonium hydroxide solution was used to hydrolyze the metal salt precursors at a certain solution pH value. Fig. 1 is a schematic representation of the synthesis procedure. In this work, the aqueous solution of 0.5 M cadmium acetate was prepared in double distilled water. To this solution the ammonium hydroxide was added drop-wise under stirring until the final solution pH value of about 8 was achieved. The resulting precipitate was filtered and washed three to four times using double distilled water to remove impurities. The hydroxide, thus formed was dried at 100 °C and grinded into a powder, which is the precursor. The precursor was calcined in air at different temperatures of 300 °C, 400 °C, 500 °C and 600 °C for 2 h to produce nanocrystalline powders with different grain size. During the calcinations, the as-prepared powder was decomposed as follows:

$$(CH_3COO)_2Cd \cdot H_2O + 2NH_4OH \rightarrow Cd(OH)_2 + 2H_2O + 2CH_3COONH_4$$

$$Cd(OH)_2 \xrightarrow{400^\circ C} CdO + H_2O$$

The structure of the calcined powder 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 K_α ($\lambda = 0.1542$ nm). The crystalline size was estimated from the broadening of CdO (111) diffraction peak ($2\theta = 32.2^\circ$) using Debye-Scherrer's formula. The transmission electron microscopy (TEM) was used to determine the particle size and the morphology of the nano-sized powder with JEOL 1200 EX.

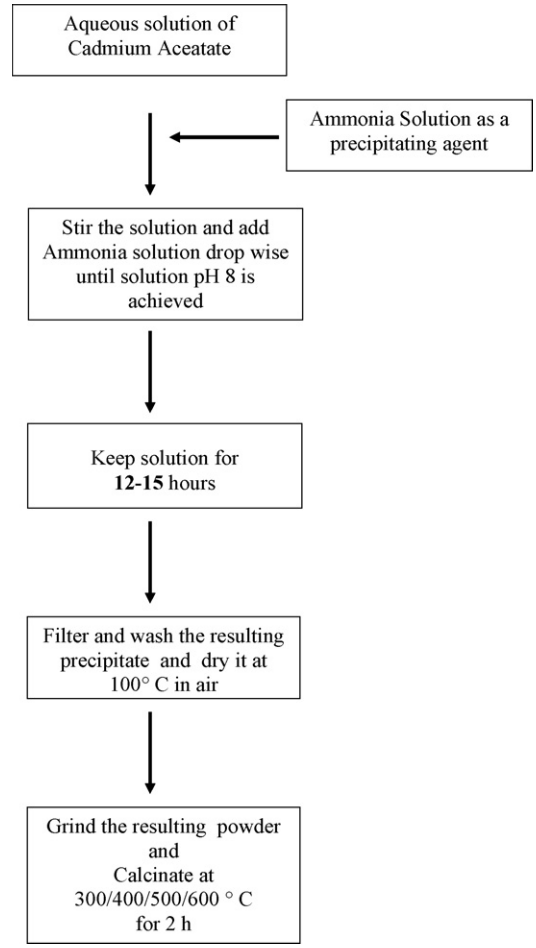

Fig. 1. Schematic diagram of the synthesis procedure for nano-sized CdO.

The nanocrystalline CdO 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 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 500 °C. The temperature of the sensing element was monitored by chromel-alumel thermocouple placed in contact with the sensor. The known volume of the 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 multi meter (METRAVI 603). The sensitivity (S) of the sensing element is defined as:

$$S(\%) = \frac{R_g - R_a}{R_a} \times 100$$

where R_a and R_g are the resistance values of the sensor element in air and in the presence of LPG.