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A novel organic pollutants gas sensing material p-type $CuAlO_2$ microsphere constituted of nanoparticles for environmental remediation

S. Thirumalairajan*, Valmor R. Mastelaro

Instituto de Física de São Carlos (IFSC), University de São Paulo, CP 369, 13560-970 São Carlos, SP, Brazil

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ABSTRACT

In this paper, novel organic pollutants gas sensing material $CuAlO_2$ microspheres constituted of nanoparticles were successfully prepared by wet chemical route and characterized by structural (XRD, XAS), morphological (SEM, TEM, HRTEM) and thermal (TG) analysis. In addition, the oxidation (O_3 and NO_2) and reduction (NH_3 and CO) toxic gas sensing properties of the prepared $CuAlO_2$ microspheres were systematically investigated. $CuAlO_2$ microspheres exhibited real-time response for very low detection level of 200 ppb at 200 °C, with fast response (29 s), recovery (45 s) time, good reproducibility and stability to ozone gas indicating their promising application in toxic gas sensor which is better than other oxidation and reduction gases. Also comparative studies of charge-transport properties mainly ascribed to the increased proportion of ozone gas exposed surface active layers are discussed in gas sensing mechanism.

1. Introduction

Controlled size and shape dependent properties of nanomaterials have been extensively studied with the aim of enhancing the performance of toxic gas sensors for environmental remediation [1]. In recent years researchers have found that transparent conducting oxide (TCO) nanomaterials are presenting themselves as one of the most important class of materials due to their excellent exclusive properties of low electrical resistivity and high optical transparency in the visible range [2–4]. The synthesis of nanosized TCO materials with controlled morphology and texture has attracted intensive interest since these parameters play an important role in determining their optical, electrical, catalytic, and sensing properties [5]. More importantly, this type of materials might possess new physicochemical properties arising from their secondary architecture [6]. Delafossite compounds belong to a family of ternary oxides with the general formula $A^{1+}B^{3+}O_2$. In this structure, the A cation is linearly coordinated to two oxygen ions and occupied by metals such as Pd, Pt, Cu or Ag. The inter-atomic distance between cations is quite small, ranging from 2.8 to 3.0 Å for most compounds [7]. The B cation (Fe, Al and Ga) is located in distorted edge-shared BO_6 octahedral with a central metal cation. The universality of the toxic gas sensing performance of $CuBO_2$ has attracted extensive interest and attention during the last decade [8]. Recently, $CuCrO_2$ has been applied for room temperature ozone sensor, unfortunately, for the ozone concentration of 20–50 ppm the response was very poor [9]. The design and development of highly toxic gas sensing delafossite type materials with low detection level (ppb) has been a challenging research subject in the field of materials science [10]. $CuAlO_2$ is one of the p-type delafossite-type oxide having high electrical conductivity and exhibits good oxidation–reduction characteristics at wide temperature and good matched properties for sensing and catalysis behaviour. Hence, $CuAlO_2$ was chosen as a sensing material to sense different toxic gases in the present work.

Several solution routes and gas phase evaporation techniques have been developed for the preparation of $CuAlO_2$ materials [11,12]. However, most of the reported routes were related to a complex reaction process. The hard template, high-temperature and high-pressure were usually used to control the morphology of the final product, which are not beneficial for obtaining high-purity and low defect density products [13]. Among the various methods, hydrothermal method is an environmental facile dominant tool for the synthesis of nanoscale materials [14–16]. Significant advantages of this method are controlled size, low temperature growth, cost effectiveness and less complicated. In addition, polyvinyl

* Corresponding author.
E-mail address: sthirumalairajan@gmail.com (S. Thirumalairajan).

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alcohol (PVA) is a common and good chelating agent for metal ions to form coordination complexes. Metal nitrate ion and PVA ion coordination complex can easily be synthesized by hydrothermal reaction. Recently, $CuAlO_2$ nanoparticles having size in the range <100 nm, but with no interesting morphology were prepared using wet chemical methods [17,18]. In addition, the morphology and structure of $CuAlO_2$ material is the key factor in influencing the performance and enhancing the gas-sensing properties.

The toxic gas sensor detection is very important because many gases are harmful to organic life. In particular, detection of ozone (O_3) is currently the subject of extensive scientific and technological research, motivated by its deleterious impact on the environment and on human health and safety [19]. Recently, transparent conducting oxide based toxic gas sensors are used for environmental monitoring and industrial applications due to their advantages such as small dimensions, low cost and convenient operation [20,21]. Commercially available gas sensors which normally operate in the range of temperatures between 100 and 400 °C are made mainly of semiconductor based materials used for the detection of gaseous species down to several parts per million (ppm) [22]. There is a great demand to enhance the sensitivity of chemical sensors for various sensing applications such as monitoring and conditioning of air quality, detection of flammable or toxic gases, medical diagnosis, there emerges a strong motivation to develop sensors which are capable of sensing gas concentration changes down to several parts per billion (ppb) [23]. Therefore toxic gas sensor with good sensitivity, detection limit, fast response and recovery time are urgently required. To the best of our knowledge reports on oxidization and reduction gas sensing by microsphere constituted of $CuAlO_2$ nanoparticles is not available in the open literature.

In this article, we report for the first time the shape controlled synthesis of microsphere constituted of $CuAlO_2$ nanoparticles via a facile one stop hydrothermal route. The morphology can be controlled by merely changing the hydrothermal reaction and calcination time. The prepared $CuAlO_2$ morphology was used for fabricating toxic gas sensor device. We detected oxidation gases (O_3 and NO_2) and reduction gases (NH_3 and CO) at various concentrations in order to obtain a relation between the sensor response and the working temperature of all these gases. Finally, comparative studies of charge-transport properties mainly ascribed to the increased proportion of exposed surface active layers and gas molecules are discussed in gas sensing mechanism.

2. Experimental

2.1. Materials

Copper (II) nitrate trihydrate (Cu $(NO_3)_2{\cdot}3H_2O$), aluminium nitrate nonhydrate (Al $(NO_3)_2{\cdot}9H_2O$), polyvinyl alcohol (PVA), ethylene glycol (EC) and sodium hydroxides (NaOH) were used in the present experiment. All chemicals purchased were of analytical pure grade and used without further purification.

2.2. Synthesis of microspheres constituted of $CuAlO_2$ nanoparticles

In a typical hydrothermal method, 0.1 mol of $Cu(NO_3)_2{\cdot}3H_2O$ and 0.12 mol of $Al(NO_3)_2{\cdot}9H_2O$ precursors were dissolved in 50 mL of distilled water, followed by the addition of 0.2 mol surfactant PVA dissolved in 25 mL double distilled water with magnetic stirring, along with the addition of 5 mL EG and 2 g NaOH as a mineralizar to form homogeneous blue coloured solution, which was then transferred into a 110 mL Teflon autoclave. The autoclave was sealed and maintained at 200 °C for 24 h. After cooling down to room temperature naturally, the obtained products were filtered by centrifugation and washed several times with distilled water and anhydrous ethanol. The products were dried in an oven at 80 °C for 12 h. Finally, the powder was calcinated at different time (0.5, 1, 2, 4 and 5 h) for 1100 °C to obtain $CuAlO_2$ powder and used for further characterization.

2.3. Characterization analysis

The crystal phase and purity of the prepared $CuAlO_2$ samples were identified by X-ray powder diffraction (XRD), CuKα1 radiation (K = 1.5406 Å, Rigaku diffractometer, model DMax-2500 PC) in the 2θ range from 20 to 80 °C. The thermal stability was investigated using a thermogravimetric analyzer (Diamond TG/DTA, PerkinElmer Instruments). Scanning electron microscopy (SEM) measurements were carried out on a F50 INSPECT scanning microscope to investigate the morphology and surface structure of the samples. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were recorded on a TECNAI F20 microscopy at an acceleration voltage of 200 kV. A trace amount of the sample was suspended in ethanol solution followed by sonication for 10 min. Carbon-coated copper grids were used as the sample holders. Cu K-edge X-ray absorption spectra were collected at the LNLS (National Synchrotron Light Laboratory) facility using the D04B-XAS2 beam line. The LNLS storage ring was operated at 1.36 GeV and 100–160 mA. X-ray absorption spectra were collected at the Cu K-edge (8979 eV) in transmission mode using an Si(1 1 1) monochromator. All the XAFS data were collected at room temperature. X-ray absorption near edge structure (XANES) spectra at the Cu K-edge were record between 8920 and 9100 eV using an energy step of 0.3 eV around the edge. To provide good energy reproducibility during the XANES data collection, the energy calibration of the monochromator was checked during the collection of the sample data using a Cu metal foil. The Cu K-edge extended X-ray absorption fine structure (EXAFS) spectra were collected between 8890 and 9800 eV using an energy step of 2.0 eV. The XANES normalization and the extraction of EXAFS spectra were performed using the multi-platform applications for X-ray absorption (MAX) software package [24].

2.4. Fabrication of $CuAlO_2$ sensing film and detection of various gases

Microspheres constituted of $CuAlO_2$ nanoparticle powders (10 mg) were dispersed in 1 mL isopropyl alcohol by an ultrasonic cleaner for 30 min and the suspension was dropped onto a Si/SiO_2 substrate containing 100 nm thick Pt electrodes separated by a distance of 50 μm. The substrates were then heated to 90 °C for 10 min to evaporate the solvent, followed by calcination at 500 °C for 3 h in an electric furnace in air to stabilize the sample before the gas sensing measurements were performed. The sensor sample was inserted into a test chamber at controlled temperature under different gases like O_3, CO, NO_2 and NH_3. The electrical resistance was measured using Keithley (model 6514) electrometer at an applied dc voltage of 1 V. The sensing response (S) of p-type materials for oxidation gas (O_3 and NO_2) is defined as $S = R_{air}/R_{gas}$, and for reduction gas (CO and NH_3) $S = R_{gas}/R_{air}$. Here electric resistance of the sensor is exposed to the resistance in the air (R_{air}) and to the target oxidizing or reduction gas (R_{gas}). The response time of the sensor is defined as the time required for a change in the electrical resistance to reach 90% of the initial value when exposed to ozone gas. Similarly, the time required for the electrical resistance of the sensor to reach 90% of the initial value after the ozone gas has been turned off is the recovery time. During the measurements the humidity was under controlled condition within the range 50–60% RH.