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Original Article

CO_2 responses based on pure and doped CeO_2 nano-pellets

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ABSTRACT

In the present work, the study of semiconducting pure and Gd-doped cerium oxide (CeO_2) nanostructures with application to gas sensors is addressed. Nanostructured powders were prepared by means of the co-precipitation technique. The powder has been examined using X-ray diffraction, transmission electron microscope and Raman spectroscopy to estimate the effect of Gd-doping on the properties of ceria. The particle size has been decreased by doping which indicates that the growth restriction rule of Gd in the ceria matrix. Also, a small shift in the peak position accompanied with more broadening in Raman analysis. Finally, the gas response of all powders has been tested for CO_2 gas in temperature range from 200 to 400 °C. The Gd-doped CeO_2 gas sensor has better sensitivity, good stability and lower operating temperature, with a detection fixed concentration of 800 ppm CO_2 gas. The powder sensitivity was found to be maximum at 250 °C for Gd-doped ceria where the pure powder maximum response is predicted to be beyond 400 °C.

1. Introduction

In all fields of industrial ecology the air quality is topical problem, including operation safety, fire alarm safety, ventilation and air conditioning of rooms, control of the technological parameters on plants and industry, exhaust control and analysis of modern car engines on a diluted mixture, air quality control in home appliances of enterprises and companies, and in all organizations whose activity is aimed at the solution of ecological, medical, and environmental goals.

Increasing the CO_2 level in the atmosphere has brought about global warming. CO_2 detection using the infrared

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(IR) technology has been widely used, but due to the disadvantageous of this technology because IR instruments are usually large and expensive. Thus, we need a simple and cheap method for CO_2 detection. Gas sensors based on measuring potentiometric [1–3] or amperometric [4] responses, or measuring capacitance [5,6] or resistance change [7] are considered as a potential methods for CO_2 detection.

Recently, for improving the sensitivity, response time and reduce the working temperature of chemosensors, nanocrystalline films, and ceramic composites based on transition metal oxides are studied extremely; this is resulting from the presence of the complex of effects in the electrophysical properties of these materials, which are related to the interface and grain sizes [8–10]. Semiconductor materials such as SnO_2, Sn–Sb, ZnO_2, CuO, CuO_2, Ga_2O_3, GaN, WO_3 [11,12] have proved to be good gas sensors. Also, CeO_2 has become one of a new promising generation of gas sensors [13]. CeO_2, a member of the rare-earth metal oxides, has been explored on a large scale for several advanced applications, such as electronics, optics and heterogeneous catalysis, thanks to their peculiar properties arising from the availability and mobility of their 4f shell [14]. The followed CeO_2 gas detection mechanism is different to those of common sensors usually based on semiconductors. For semiconducting materials, the detection process is based on reactions at surface level. Usually, the available oxygen (from the target gas) is adsorbed to the surface dangling-bonds. Thus, an electron of the conduction band is transferred and the electrical conductance of the material faces a reduction. CeO_2 exhibits high mobility of oxygen on its surface and also, inside the lattice. Generally, metals added to CeO_2 has been proved to improve catalytic and transport properties [15]. CeO_2 has a unit cell oxygen face centered cubic fluorite-type. The extremely open structure of fluorite tolerates a high level of atomic disorder [16], which can be produced either by reduction or dopant insertion, as proposed in the present work.

In the current work nano-particles of pure and 7% Gd-doped particles has been successfully prepared using co-precipitation techniques. The powders have been characterized and the effect of the doping on the structure has been estimated. Finally the response of the prepared powder for carbon dioxide has been recorded at different temperatures in the range of 200–400 °C.

2. Materials and methods

2.1. Samples preparation

Cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$), Gadolinium(III) acetate ($Gd(Ac)_3{\cdot}xH_2O$), and sodium hydroxide (NaOH) solutions have been used as a starting materials for the powder preparation process. All the reagents were of analytical grade and were used without further purification. In a typical experimental a solution of 0.116 M cerium salts was prepared in 100 ml distilled water. Then, NaOH (6 M) was added drop by drop under stirring for 30 min till complete precipitation of cerium hydroxide. By the end of this process, pH level was adjusted to be 11. The precipitate were filtered, washed and dried overnight. Next, the precipitated hydroxide were calcinated in a muffle furnace at 700 °C for 2 h, the obtained material was identified as CeO_2.

For synthesizing Gd-doped CeO_2 nanoparticles, the previously described synthesis process was exactly repeated with the addition of specific concentration of gadolinium (III) acetate was mixed with cerium nitrate solution before precipitation using NaOH solution.

2.2. Physical measurements

X-ray diffraction experiments were conducted on a PANalytical (Empyrean) X-ray diffraction using Cu Kα radiation (wave length 0.154 cm^{-1}) at an accelerating voltage 40 kV, current of 35 mA, scan angle 20–70° range and scan step 0:02°. FT-Raman spectra were recorded with a Bruker (Vertex 70 FTIR-FT Raman, Germany) spectrometer with laser beam of 1064 nm power. Transmission Electron microscope images were taken by JEOL-JEM 2100 (Japan) with an acceleration voltage of 200 kV.

2.3. Pellets preparation

The synthesized powders were grinded well in a mortar to bind inhomogeneous crystals. The homogeneous powders get wetted by careful addition of few drops of distilled water. A stainless steel cylindrical compacts with 1 cm diameter and 0.5 cm thickness was used to press inside an equal weights of the wetted powders at the same conditions (5 bar pressure for 3 min). The pellets adhesion enhanced by the calcinations in muffle furnace at 500 °C for 2 h.

2.4. Sensing measurements

Homemade gas sensing unit has been designed to measure the resistance change upon exposing the pellets to a fixed concentration of carbon dioxide gas (800 ppm) as indicated in Fig. 1. The pellets have been placed between two stainless steel rods mounted between two ceramic circular bases. Silver past coating has been introduced to both surfaces of the pellets to ensure the good electrical contact with the external electrodes. The whole structure has been placed inside a digital vertical furnace attached with a temperature controller in order to adjust the temperature at fixed value. The pellets have been tested at temperatures 200, 250, 300, 350 and 400 °C and the variation in the resistance has been recorded using computerized digital multimeter (Protex506).

In a highly purified nitrogen stream the pellets have been heated from the room temperature to the operating temperature where the resistance was recorded for few minutes before CO_2 insertion. After that a calculated amount (800 ppm) of CO_2 has been introduced to the nitrogen stream and the change in the resistance value was recorded. After 5 min of CO_2 insertion the gas value is switched off and the resistance value continued to be recorded until the resistance return to its original value. This process of was repeated many times to confirm the behavior and stability.

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