CO₂ responses based on pure and doped CeO₂ nano-pellets


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In the present work, the study of semiconducting pure and Gd-doped cerium oxide (CeO₂) 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 CO₂ gas in temperature range from 200 to 400 °C. The Gd-doped CeO₂ gas sensor has better sensitivity, good stability and lower operating temperature, with a detection fixed concentration of 800 ppm CO₂ 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.

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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 CO₂ level in the atmosphere has brought about global warming. CO₂ detection using the infrared
(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 CO₂ 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 CO₂ 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 extensively; 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 SnO₂, Sn–Sb, ZnO₂, CuO, CuO₂, Ga₂O₃, GaN, WO₃ [11,12] have proved to be good gas sensors. Also, CeO₂ has become one of a new promising generation of gas sensors [13]. CeO₂, 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 CeO₂ 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. CeO₂ exhibits high mobility of oxygen on its surface and also, inside the lattice. Generally, metals added to CeO₂ has been proved to improve catalytic and transport properties [15]. CeO₂ 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(NO₃)₃·6H₂O), Gadolinium(III) acetate (Gd(CH₃COO)₂·H₂O), 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 CeO₂.

For synthesizing Gd-doped CeO₂ 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 CO₂ insertion. After that a calculated amount (800 ppm) of CO₂ has been introduced to the nitrogen stream and the change in the resistance value was recorded. After 5 min of CO₂ 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.
Fig. 1 – Schematic diagram of the electrical conductivity cell.

Fig. 2 – XRD pattern for pure and Gd-doped cerium oxide powder.
Table 1 – Lattice parameters and the theoretical density of pure and Gd-doped CeO₂ samples.

<table>
<thead>
<tr>
<th>Materials</th>
<th>a (Å)</th>
<th>Dₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CeO₂</td>
<td>5.4148</td>
<td>7.19</td>
</tr>
<tr>
<td>Gd doped CeO₂</td>
<td>5.4000</td>
<td>7.26</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Powder X-ray diffraction studies

Fig. 2 shows the X-ray diffraction patterns of pure and Gd-doped CeO₂ nanoparticles. Well defined peaks located at 28.5°, 33.1°, 47.5°, 56.3°, 59.1° and 69.4° are corresponding to (111), (200), (220), (311), (222) and (400) planes, respectively. All peaks of the synthesized CeO₂ can be indexed to the face centered cubic phase of CeO₂. This phase has been recorded in previously [17]. After doping with Gd no new peaks can be observed in the diffraction pattern, which insures the good solubility of the dopant in the matrix of the main oxide phase. But a significant reduction in the peaks intensities is observed with a reduction in the particle size, as will be discussed in the next section. Also a general shift in the peaks centers toward a smaller value is observed accompanied by a slight increase in the d-spacing values for all plans. Such result could be attributed to the difference in the ionic radii between the Ce⁴⁺ (ionic radii = 101 nm) and Gd³⁺ (ionic radii = 107.5 nm). Such shift will cause a stress evolution in the powder which cause the loss of the crystallinity and the reduction in the peaks intensity.

The average crystallite size of the prepared powder was calculated using Scherrer’s formula [18]:

\[ D = \frac{0.94\lambda}{\beta \cos \theta} \]

(1)

where D: crystal size, λ: X-ray wave length, β: the broadening of the diffraction peak and θ is the diffraction angle. The crystallite size was found to be 29.7 and 20.8 nm for pure and doped nanoparticles respectively.

The lattice parameters, are the physical dimensions of unit cells in a crystal lattice. It is well known that in three dimensions lattices generally have three lattice constants, nominated as a, b, and c. However, in the special case of cubic crystal structures, all of the constants are equal and that means similarly. The lattice parameter was calculated according to the lattice cubic geometry of ceria crystalline lattice. The theoretical density was calculated using Eq. (2).

\[ D_x = \frac{ZM}{NV} \]

(2)

where Z is the number of molecules/unit cell, M is the sample molecule weight, V is the unit cell volume (V = a³) and N is the Avogadro’s number. The calculated parameters are listed in Table 1, from which it was obviously observed the lattice expansion was accompanied by reduction in the particle size and this behavior related to the increase of the point defects concentrations as a result of substitution smaller cations of Ce⁴⁺ by larger cations of Gd³⁺. It is predictable that the

Fig. 3 – Raman spectra of pure CeO₂ and Gd doped CeO₂ prepared by co-precipitation method.

Fig. 4 – TEM images of (a) pure CeO₂ and (b) Gd doped CeO₂ nano-particles prepared by co-precipitation method at 160 °C and pH = 11.
trivalent 4f ion Gd$^{3+}$ enter the parent cubic lattice of ceria on the expense of Ce$^{3+}$ ions. It is clearly observed from the values of Table 1 that Gd$^{3+}$ doping decreased the lattice parameter. The direct reason is the difference between the ionic radius of Ce$^{3+}$ (1.143 Å) and that of Gd$^{3+}$ (1.053 Å) is 8f coordination. As a response of that decrease of lattice parameters, the density is increase in the cubic lattice.

3.2. Raman spectroscopy analysis

Raman spectra of hydrothermally synthesized CeO$_2$ and Gd-doped CeO$_2$ are illustrated in Fig. 3, which confirms the formation of the polygonal fluorite phase. The intensive band at 450–470 cm$^{-1}$ corresponding to the allowed Raman mode (F$_{2g}$) of fluorite metal dioxides belonged to the O$^{1}_{h}$ (Fm3m) space group [19–21]. For pure CeO$_2$ powders, the Raman spectrum was symmetric around 464 cm$^{-1}$ and the F$_{2g}$ mode corresponded to the symmetric vibration of oxygen ions around Ce$^{4+}$ ions [21]. In the gadolinium doped CeO$_2$, the F$_{2g}$ band became asymmetrical and slightly shifted to low frequencies, due to the cell expansions resulting from the substitution of Gd$^{3+}$ ions in the CeO$_2$ lattices and the subsequent oxygen loss around cations.

3.3. Transmission electron microscope examination

Fig. 4(a) and (b) shows TEM images of pure and Gd-doped CeO$_2$, respectively. It was found that homogeneous nano-cubic structures were obtained for all prepared samples. It is clearly seen that particles by doping become more uniform, regularly distributed with smaller particle size. The average particle size of pure CeO$_2$ and Gd-doped CeO$_2$ was found to be about 24 nm and 18.6 nm, respectively. From the data obtained, the addition of Gd restrict the growth of crystallites in the CeO$_2$ nano-particles.

3.4. Gas sensing performance

As shown in Fig. 5, the resistance of pellet decreased by introducing the gas in Table 2. All ceria phases are known to be n-type semiconductor. Although, the resistance of the pellets was found to decrease as a result of CO$_2$ exposure, which is against the recorded behavior reported by Fine et al. [22]. The reduction in the resistance is observed at all operating

Table 2 – Resistivity measurements of pure and Gd-doped CeO$_2$ nano-pellets at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Resistivity for pure CeO$_2$ (Mohm)</th>
<th>Resistivity for Gd-doped CeO$_2$ (Mohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2158.8</td>
<td>1766.3</td>
</tr>
<tr>
<td>250</td>
<td>1373.8</td>
<td>510.3</td>
</tr>
<tr>
<td>300</td>
<td>176.6</td>
<td>117.8</td>
</tr>
<tr>
<td>400</td>
<td>19.6</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Fig. 5 – Gas sensing response of pure and Gd-doped CeO$_2$ nano-pellets at different temperatures (a) at 200 °C, (b) at 250 °C, (c) at 300 °C, and (d) at 400 °C.
temperatures. Hoefer et al. [22] reported a reduction in the resistance in case of n-type tin oxide films with carbon dioxide. Such behavior could be attributed to the following reasons. The poisoning effect of the gas as mentioned by Jasiński et al. [23], in the case of nitrogen dioxide with cerium oxide. This may change the structure powder sample to a higher conductive phase. In this case the resistance also decreased. The second reason was the re-oxidation of the ceria surface using CO₂ would be energetically feasible at the adsorption sites that have been sufficiently reduced. Furthermore, partial reoxidation often the reduced ceria occurs with high reaction probability even at room temperature [24].

Fig. 6 shows the sensitivity changes in pure and Gd-doped powder as a function in the operating temperature in the range from 200 to 400 °C. The sensitivity was calculated according to the following equation [13]:

\[
S = \frac{R_2 - R_0}{R_0} \times 100
\]

As observed the doping increases the sensitivity of the powder as the temperature below 400 °C. Also, for the pure ceria nano-pellets the sensitivity increases with temperature up to 400 °C. That may indicate that the optimum operating temperature may be at 400 °C or higher. In the other case (Gd-doped CeO₂) a peak of sensitivity is observed around 250 °C. Such shift of the optimum operating temperature is desirable along with the increase in the sensitivity increase. This increase in the sensitivity of the doped pellets at different temperature could be attributed to the reduction in the resistivity as a result of doping since Gd has higher atomic number than Ce. This increases the free charge carriers concentration, electrons in this case, and consequently increases the surface charge concentration. Such behavior increases the sensitivity of the powder and considered as a remarkable advantage of nano materials. This effect accompanied with the reduction on the particle size may cause the increase in the sensitivity of doped powder.

4. Conclusion

Pure and Gd-doped CeO₂ nano-powder has been successfully prepared using co-precipitation technique. The formation of single phase is confirmed by XRD and Raman spectroscopy data. The particle size was measured using Scherrer’s equation. The crystallite size decreased from about 29 nm to 20 nm as a result of doping. Finally, all powders show a reduction in the resistance value as a result of exposing the nano-pellets for carbon dioxide gas with concentration 800 ppm. The sensitivity was found to shift to lower temperature, 250 °C, by doping with Gd.

Conflicts of interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References

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