Synthesis and characterization of Cu doped cobalt oxide nanocrystals as methane gas sensors

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Abstract

In this paper, nanoparticles of copper–cobalt compound oxide have been prepared by the sol–gel technique with different mole ratios of Cu/Co (ranging from 0.05 to 0.15) for the detection of methane gas, which is chemically a very stable hydrocarbon. The structural properties and morphology of the powders were studied by x-ray diffraction (XRD), Fourier transform infrared spectroscopy and transmission electron microscopy (TEM). By XRD analysis, we confirm that Co₃O₄ and (Cu₃O₃CoO₁₋ₓ)Co₂O₄ phases are formed and mean grain size is decreased with increasing Cu doping (from 28 to 24 nm). On the basis of TEM images, it is found that these particles possess a cubic structure with nearly uniform distribution. Also, gas-sensing measurements reveal that the optimal operating temperature is 300 °C, that the use of Cu as a dopant improved the sensing properties of cobalt oxide and that the sensitivity increased considerably with Cu concentration. The best sensitivity properties of nanosensors have been found at the mole ratios of Cu/Co of 0.125 and 0.15.

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(Some figures in this article are in colour only in the electronic version.)

1. Introduction

Gas sensors have been developed recently to measure environmental pollution and hazardous events. One of these colorless and odorless gases is methane gas that has many industrial and household applications. However, the frequency of occurrence of unexpected explosions of methane gas because of leakage has been growing with its increased use, and so the ability to detect and measure methane gas leakage below the explosion limit is essential for preventing such accidents.

Various pure and doped semiconducting oxides have been used as gas sensors [1–4]. The use of nanomaterials has gained interest because of a much greater ratio of surface to bulk than bulk materials. In addition, when the grain size decreases to nanometers, especially when the dimension becomes less than twice the space-charge depth, a large fraction of atoms are present on the surface and the surface properties become dominant. Hence, materials of conduction type become materials of surface conduction type [5–7]. The sensing mechanism depends on the change in surface electrical conductivity due to a chemical reaction between target gases and the oxygen absorbed on the surface of nano-sized metal oxides. Consequently, it is important to enhance the rates of chemisorption and surface reaction. Co₃O₄ is a very active catalyst in the oxidation of methane [8], and therefore it is a good candidate for a methane gas sensor. The addition of a second component as a dopant is becoming
one of the most interesting methods for the optimization of gas-sensing properties in this type of sensor. These additives can act as catalysts in surface sites and lead to greater adsorption of oxygen or the detected gas [9].

Copper oxide has good catalytic activity for the oxidation of methane [8] and hence is used as a dopant in methane gas sensors. For this reason, in this work, nano-sized powders of Cu-doped cobalt oxide with different concentrations of the Cu dopant have been prepared by the sol–gel method for use as a methane sensor.

2. Experiment

2.1. Synthesis of compounds

Nanoparticles of copper–cobalt compound oxide were synthesized by the sol–gel method. Systematically, proper amounts of CoCl$_2$·6H$_2$O and CuCl$_2$·2H$_2$O were dissolved in deionized water and ethanol. The initial solutions were prepared with different mole ratios of Cu/Co, namely 0.0, 0.05, 0.08, 0.10, 0.125, and 0.15. Then, citric acid (as a complexing agent) was added in the mole ratio of Cu$_6$H$_{12}$O$_7$/CoCl$_2$·6H$_2$O of 5, and the primary sol was prepared by adding ethylene glycol (as a polymerizing agent) in the mole ratio of 6 to cobalt cation and stirring for 20 min. The clear mixed solution was refluxed at 120 °C in an oil bath for 6 h. The final resultant sol from the reflux process was kept at 80 °C for 17 h in an oil bath to evaporate the solvent and unstable compounds, and a wet gel was formed. To remove the other residual volatile components, the gel was heated again directly on a hot plate at 180 °C for 20 min and then dried at 220 °C for 30 min. Finally, the dry gel was annealed in 450 °C for 1 h to eliminate the organic component and obtain copper–cobalt compound oxide nanopowder.

2.2. Sensor preparation

For measuring gas sensing, usually nanopowders are screen-printed on electrodes. Therefore, for the use of a component as a binder, in many cases ethylene glycol is necessary. Choi and Min [8] reported that the sensitivity of a Co$_3$O$_4$ sensor decreases with an increase in ethylene glycol concentration. Therefore, sensors were fabricated by adding ethylene glycol (as a polymerizing agent) in the mole ratio of 6 to cobalt cation and stirring for 20 min. The clear mixed solution was refluxed at 120 °C in an oil bath for 6 h. The final resultant sol from the reflux process was kept at 80 °C for 17 h in an oil bath to evaporate the solvent and unstable compounds, and a wet gel was formed. To remove the other residual volatile components, the gel was heated again directly on a hot plate at 180 °C for 20 min and then dried at 220 °C for 30 min. Finally, the dry gel was annealed in 450 °C for 1 h to eliminate the organic component and obtain copper–cobalt compound oxide nanopowder.

2.3. Characterization

The phase-structure formation and crystallinity of nanopowders were studied by x-ray diffraction (XRD) using the Bruker D8 Advance apparatus with Cu Kα radiation (λ = 0.15405 nm) in the 2θ range of 15°–85° with steps of 0.05°. The atomic link was investigated using Fourier transform infrared (FTIR) spectroscopy on a Bomem MB-154 spectrometer. Transmission electron microscopy (TEM) micrographs of the prepared nanopowders for the determination of particle shape and size were obtained using an LEO 912 AB system operating at 120 kV. As-prepared samples were placed in the sensing chamber for gas-sensing characterization. Sensitivity measurements were carried out in the temperature range 200–300 °C with a fixed quantity of trial gas of methane in the range 3000–6000 ppm. The electrical resistance of the sensor was monitored using a digital multimeter. The sensitivity was defined as $(R_{\text{gas}} - R_{\text{air}})/R_{\text{air}} \times 100$%, where $R_{\text{air}}$ and $R_{\text{gas}}$ are the electrical resistances in clean air and in the presence of the gas at the same temperature, respectively.

3. Result and discussion

XRD patterns of copper–cobalt compound oxide nanopowders with different mole ratios of Cu/Co are shown in figure 1, which reveals the polycrystalline structure of Co$_3$O$_4$ with cubic phase (a = 8.08400 Å) in all the samples and the mix phase of (CuO$_0.3$CoO$_0.7$)Co$_2$O$_4$. The main XRD peak in the preferred orientation corresponds to the (3 1 1) plane at 36.9°, and its intensity does not change evidently by adding copper in samples, but it does become slightly wider. Besides the preferred peak, other peaks corresponding to the (2 2 0) and (4 0 0) planes also become wider. It is clearly identified that copper as a dopant decreases the crystallinity and enhances the amorphous state that leads to a decrease in crystalline size. No other phase has been created in samples with different mole ratios of Cu/Co, and this demonstrates that the formed phases are stable and that their formation is independent of copper quantity. The mean grain size is calculated from the major peak using Sherrer’s equation

$$D = \frac{k \lambda}{\beta \cos \theta},$$

where $k$ is a constant that depends on the crystal morphology in the range of 0.89–1.39, and it is 0.9 in this calculation, $\gamma$ and $\beta$ are the wavelength and width at half-maximum of the strongest peak, respectively, and $\theta$ is the Bragg’s angle of the XRD peak. Grain size values are given in table 1. They
Table 1. The x-ray parameters and mean size of Cu–Co oxide nanoparticles at different mole ratios of Cu/Co prepared by the sol–gel method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mole ratio of Cu/Co</th>
<th>$2\theta$ (°)</th>
<th>$B$ (FWHM)</th>
<th>$D$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>0.00</td>
<td>36.95</td>
<td>0.295</td>
<td>28</td>
</tr>
<tr>
<td>$S_2$</td>
<td>0.05</td>
<td>36.95</td>
<td>0.337</td>
<td>27</td>
</tr>
<tr>
<td>$S_3$</td>
<td>0.08</td>
<td>37.025</td>
<td>0.304</td>
<td>27</td>
</tr>
<tr>
<td>$S_4$</td>
<td>0.10</td>
<td>37.075</td>
<td>0.314</td>
<td>26</td>
</tr>
<tr>
<td>$S_5$</td>
<td>0.125</td>
<td>37.125</td>
<td>0.328</td>
<td>25</td>
</tr>
<tr>
<td>$S_6$</td>
<td>0.15</td>
<td>37.00</td>
<td>0.335</td>
<td>24</td>
</tr>
</tbody>
</table>

Figure 2. FTIR intensity results for Cu–Co oxide nanocrystals with different mole ratios of Cu/Co.

Figure 2 shows the FTIR spectra of copper–cobalt compound oxide nanoparticles with different mole ratios of Cu/Co, namely 0.0, 0.05, 0.10 and 0.15 ($S_1$, $S_2$, $S_3$ and $S_6$, respectively). The bands at 576 and 668 cm$^{-1}$ are attributed to vibration of the Co–O bond due to Co$_3$O$_4$. No peak corresponding to the Cu–O bond was identified. It is probable that the Co–O peaks overlap the Cu–O peak, because they are seen to have very close wavelengths. There is no peak that could be assigned to C–H, which suggests that the carbonate component was removed completely from the samples.

TEM images of cobalt oxide nanoparticles ($S_1$) and copper–cobalt compound oxide nanoparticles with a mole ratio of Cu/Co of 0.15 ($S_6$), prepared by the sol–gel method, with different magnifications are presented in figure 3. It is found that the particles have cubic morphologies, with a nearly uniform distribution. The average particle size is about 30 nm in $S_1$ and 15 nm in $S_6$, which decreases with an increase in dopant concentration. It is in agreement with the result of Sherre’s formula from XRD patterns.

Sensitivities are greatly affected by the operating temperature and gas concentration. Figures 4(a)–(c) show the sensitivity versus operating temperature plots for different sensors in 3000, 4500 and 6000 ppm of methane gas that are below its lower explosive limit (LEL). The temperature was kept constant during each measurement at 200, 250 and 300 °C. It is shown that the sensitivities increase with temperature in this temperature range and the maximum sensitivities occur at 300 °C in all sensors. Wollenstein et al [10] investigated the sensitivity of pure Co$_3$O$_4$ in 3000 ppm methane at 240 and 460 °C and illustrated that the sensitivity significantly decreases with an increase in temperature to 460 °C. Hence, it is expected that the optimal operating temperature of this sensor is around 300 °C or slightly higher in a broad range of temperatures. Comparing figures 4(a)–(c) reveals that sensitivities change with the gas concentration for all the sensors. An increase in the mole ratio of Cu/Co considerably improved the sensitivity in general. The maximum sensitivity was that of the sensor with a mole ratio of Cu/Co of 0.15 at 300 °C and 6000 ppm of methane gas.
Figure 4. Effect of operating temperature on the sensitivity of sensors at (a) 3000, (b) 4500 and (c) 6000 ppm methane gas concentrations.

4. Conclusion

Copper–cobalt oxide nano-sized powders with different mole ratios of Cu/Co (ranging from 0.0 to 0.15) were prepared by the sol–gel technique for use as a gas sensor. Cubic Co$_3$O$_4$ and (CuO$_{0.3}$CoO$_{0.7}$) Co$_2$O$_4$ phases were firmly formed. The mean grain size varied from 28 to 24 by changing the mole ratio of Cu/Co from 0.0 to 0.15. The gas-sensing performances of sensors were investigated in the presence of methane gas. The results showed that the optimal operating temperature is 300$^\circ$C in all sensors. Doping Co$_3$O$_4$ with copper altered the sensing behavior by influencing the defect chemistry and decreasing the particle size. Therefore, a comparison with sensors under the same operating conditions indicated that the sensitivity increases significantly with an increase in Cu doping and the sensitivity of a sensor with a mole ratio of Cu/Co of 0.15 was considerably higher than that of a pure Co$_3$O$_4$ sensor.

References

[8] Choi S-D and Min B-K 2001 Co$_3$O$_4$-based isobutane sensor operating at low temperatures Sensors Actuators B 77 330–4