



Tunable interconnectivity of mesostructured cobalt oxide materials for sensing applications

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ABSTRACT

A mesostructured cobalt oxide microsensor was fabricated using a template replication method under different hydrothermal treatments, and attempts were made to enhance the response of this gas sensor. To evaluate the sensing performance, the sensing materials were deposited via the dielectrophoresis (DEP) process, on micro-hot-plate platforms with interdigitated electrodes. The resistance changed when the carbon monoxide target gas was injected at the optimum temperature. The mesostructured cobalt oxide material with high hydrothermal treatment revealed the well-ordered domains, whereas with low hydrothermal treatment it did not contain ordered domains. Moreover, the cobalt oxide high hydrothermal material had 1.5 times the response to 70 ppm carbon monoxide as the low hydrothermal treatment sample. The unobstructed interconnectivity promotes gas diffusion and increases the active surface areas.

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1. Introduction

In order to protect the environment and reduced air pollution, the monitoring of toxic gases is an important issue. In this regard, carbon monoxide (CO) sensors are widely used for measuring CO concentrations. Many materials including SnO₂, ZnO, TiO₂, MoO₃, and Fe₂O₃, have been used to create semiconducting metal oxide sensors [1–3]. Cobalt oxide is an interesting example of these semiconductor metal oxide materials. Cobalt oxide belong to the family of transition metal oxides. The most stable, cobalt oxide is an intrinsic p-type semiconductor (direct optical bandgaps at 1.48 and 2.19 eV), which has been used in application in many fields, such as for electrochromic devices, heterogeneous catalysts, and solid-state sensors [4–6]. Yamazoe et al. improved the response time of an In₂O₃-based CO sensor by the addition of 0.5 wt.% Co₃O₄ and 0.04 wt.% Au at 250 °C [7]. Co₃O₄-based films on a silicon substrate have been used in GasFETs, where the resistive method has been used for measurements at 240–460 °C and the work function method for measurements at 30 and 130 °C [8]. However, the cobalt oxide materials reported above do not usually have a well-defined porous structure and are accompanied by interconnected aggregates. Therefore, the active surface areas are restricted by the small pores, leading to sensors with poor response. With this in mind, it seemed clear that the use of a sensing material with a well-defined

structure and porosity might make it possible to increase the active surface area and the gas diffusion, thereby improving response. Literature research revealed that the interconnectivity affect the sensor response are not reported up to now. Herein, we report the synthesis of mesostructured cobalt oxide materials with tunable interconnectivity through the use of the template replication method and the tuning of the hydrothermal temperature of the templates. These sensing films were immobilized on the micro-hot-plate platform via the dielectrophoresis (DEP) method. We also compared the response of these films by exposure to different CO concentrations.

2. Experimental

2.1. Preparation of cobalt oxide-sensing materials

The SBA-15 materials were synthesized by the traditional hydrothermal method using the triblock copolymer P123 (EO₂₀-PO₇₀-EO₂₀, Aldrich) as the surfactant [9]. An 8.5 g P123 block copolymer (Sigma) was dissolved in 325 mL HCl (1.6 mol L⁻¹) and 30 mL deionized water. After complete dissolution, 18.7 g of tetraethyl orthosilicate (TEOS, Merck) was added at once. The mixture was left under stirring at 35 °C for 24 h, followed by hydrothermal treatment at 100 °C for 24 h under static conditions. The solid product was filtered off, washed with water, and calcined at 823 K for 6 h (heating rate 2 K min⁻¹). In order to tune the interconnectivity, the hydrothermal treatment temperature under static conditions was varied at 40 and 100 °C. Reaction temperature of the SBA-15 at 40 and 100 °C were denoted SBA-40d and

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SBA-100d. Mesoporous cobalt oxide materials were prepared using SBA-15 as templates. Generally, a mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.8 M) and SBA-15 (0.2 g) was dissolved in ethanol and stirred for 1 h. Further, the resultant materials were calcined at a temperature of 723 K for 6 h. Finally, the silica template was removed using 5% HF and the black-colored Co_3O_4 materials were recovered by centrifugation and dried at a temperature of 323 K overnight. The cobalt oxide materials synthesized from SBA-40d and SBA-100d were denoted Co-40d and Co-100d.

2.2. Material characterization

X-ray diffraction (XRD) patterns were obtained using a Bede/D1 diffractometer with $\text{Cu K}\alpha$ radiation (1.543 Å) at a voltage of 40 kV and a current of 40 mA. Scanning electron microscopy (SEM) was performed using a JOEL 6700F electron microscope at an acceleration voltage of 10 kV. The nitrogen adsorption–desorption isotherms were measured at a temperature of 77 K using a NOVA 1000e system in static measurement mode. The samples were measured at liquid nitrogen temperature (-196°C) with prior degassing under vacuum at 150°C for 3 h. The specific surface areas were determined by the Brunauer–Emmett–Teller method based on the adsorption branches. The pore diameter and pore size distribution (PSD) were measured from the desorption branches obtained by the Barrett–Joyner–Halenda (BJH) method. Transmission electron microscopy (TEM) was used to clarify the structure of the mesoporous cobalt oxide materials using a JOEL-2010 electron microscope at 200 kV. Sine-wave signals of 1 MHz and an amplitude (peak-to-peak) of 10 V were chosen to enable the mesoporous cobalt oxide materials to be deposited onto the electrode gap using dielectrophoresis forces. The mesoporous cobalt oxide was tested as a sensor as followed. The gas-sensing properties were characterized using a computer-controlled gas-sensing characterization system. The sensors were constantly purged by synthetic air only interrupted by the trace gases which had been diluted in synthetic air. The test gas injected into the chamber at a total flow rate of 100 sccm. After some time, the chamber was purged with air and the experiment was repeated. The electrical resistance response during testing was monitored using a precision analyzer (Keithley 2400). The sensor response (S) was defined as follows: $S = [(R_{\text{Co}} - R_{\text{air}})/R_{\text{air}}] \times 100\%$, where R_{air} and R_{Co} represent the resistance of the sensor in air and in CO gas, respectively. The average response time and recovery time, T_{90} and TR_{90} , defined as the time required for the resistance to reach 90% and the time required to return to 10% of the saturated resistance.

3. Results and discussion

Sensing materials should have certain structural, morphological, and electrical characteristics in order to have a maximum performance. The periodicity of the pore systems in mesoporous materials is important; thus, wide-angle X-ray diffraction (XRD) patterns were made of the Co-100d and Co-40d obtained from the mesoporous silica. Fig. 1(a) shows the low-angle diffraction patterns of the Co-40d and Co-100d. The (1 0 0) reflections remained for the Co-100d replica samples. The replication for cobalt oxide was almost the same as those for the SBA-15 template, suggesting that cobalt oxide replicated the mesoporous structure of the SBA-15. At Co-40d, the reflection totally disappeared. The loss of reflections in the low-angle region should not be attributed to the dilution of the guest species but to the complete filling of pores, which decreases the contrast between the walls and the pores. At a high templated temperature, the reflections were preserved, though their intensity was reduced due to the dilution of the amorphous gel. In general, the pore diameters of the templates were tuned

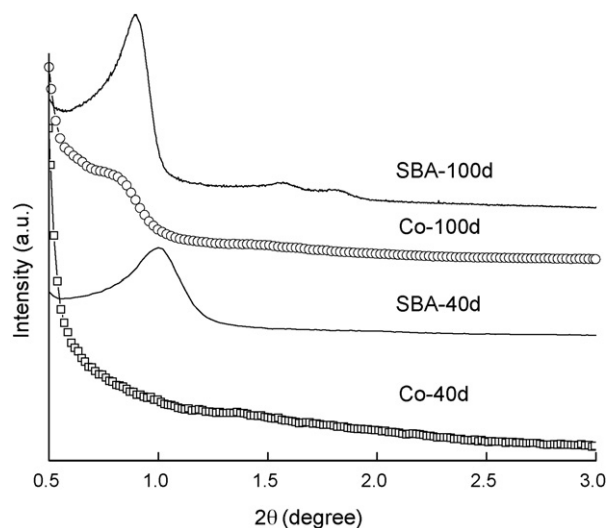


Fig. 1. The low-angle XRD patterns of mesoporous cobalt oxide at different templated temperatures.

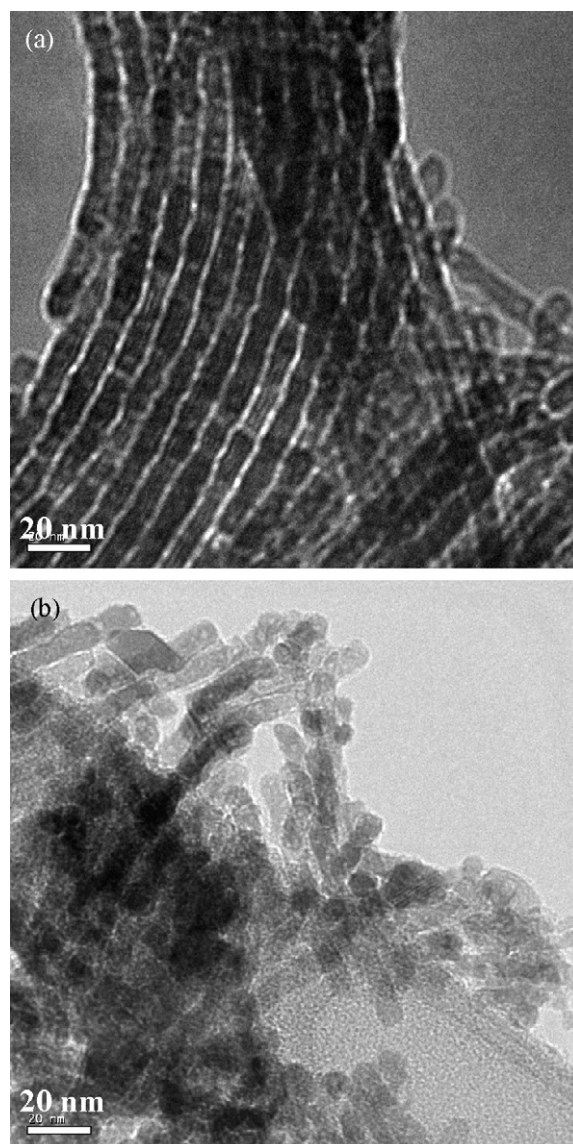


Fig. 2. TEM image with (a) full interconnectivity, and (b) poor interconnectivity of mesoporous cobalt oxide.

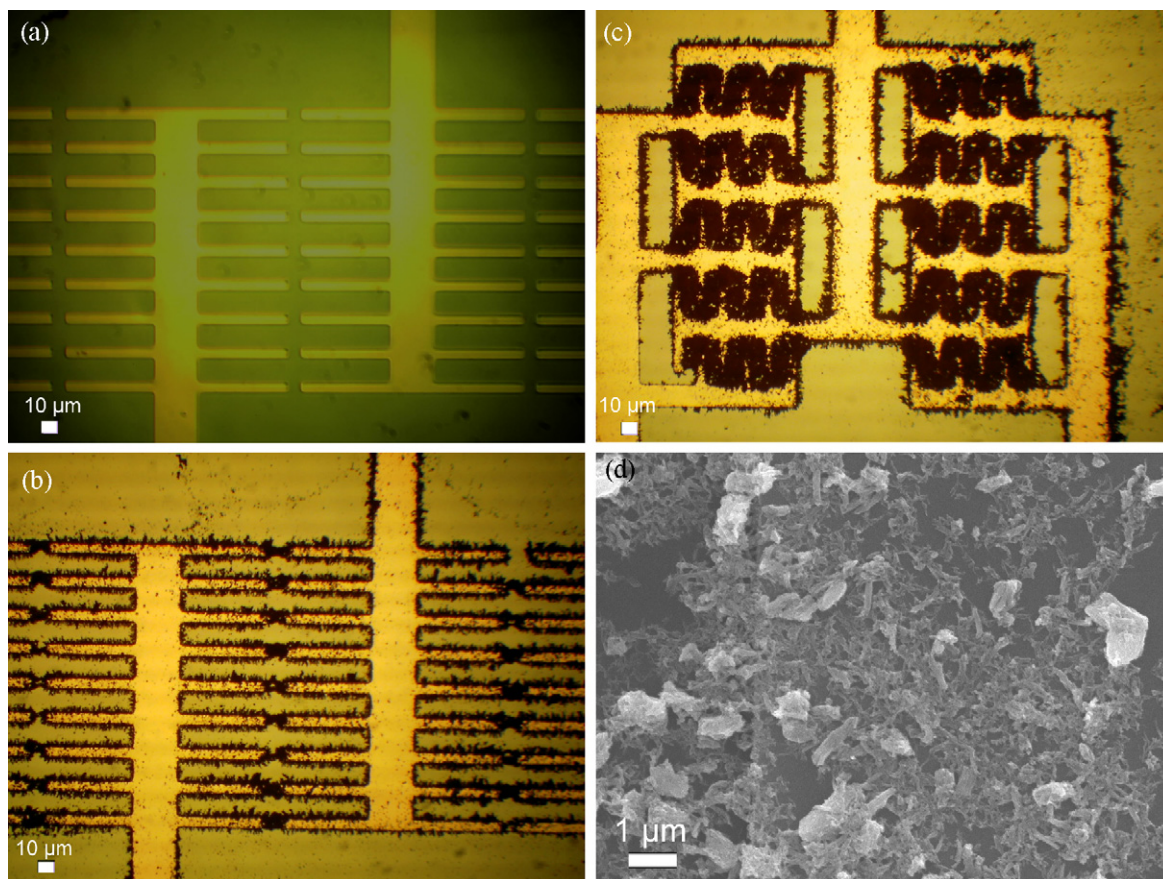


Fig. 3. OM images (a) before DEP immobilization, (b and c) after DEP immobilization of the Co-100d and Co-40d, and (d) high-magnification SEM image of mesostructured cobalt oxide.

by changing the temperature of the hydrothermal treatment after the synthesis of the mesoporous silica. Fig. 2 shows TEM images of the mesostructured cobalt oxide materials prepared from SBA-15 with different pore diameters. As can be seen, it is possible to cast the mesopore structure from different SBA-15 silicas, resulting in cobalt oxide materials of different diameters. Moreover, the use of cobalt oxide allowed the differences in network interconnectivity to be imaged. Nevertheless, the cobalt oxide preparation at a low templated temperature of 40 °C did not contain ordered domains, whereas the Co-100d sample predominantly featured well-ordered domains, with cobalt oxide arrays reaching several nanometers in length. Arrays of mesostructured cobalt oxide materials may arise from the bridge between the mesopores in SBA-15, as demonstrated in the cases of mesoporous carbon, noble metals, and other metal oxide nanowires [10]. According to the TEM images, the mesopore diameters of the mesostructured cobalt oxide materials were close to 7.0 nm for all of the samples. Fig. 3 shows the cobalt oxide-sensing materials before and after immobilization via the DEP process. Fig. 3(a) shows an optical image of the interdigitated electrodes. The distance between the two electrodes was 2 μm. The cobalt oxide materials were immobilized after the DEP process, as shown in Fig. 3(b). In a comparison with Fig. 3(a), it can be seen that the cobalt oxide samples were immobilized around the electrodes. It is evident that the cobalt oxide materials were successfully immobilized on the interdigitated electrodes via the DEP process. Fig. 3(c) shows higher magnification SEM images of the region with the cobalt oxide materials. Overall, all of them showed a silk-like structure and some regions had aggregates. N₂ sorption isotherm measurements showed that the Co-100d had a surface area of 175.4 m² g⁻¹, and an average pore radius of 2.7 nm. On the other hand, the Co-40d had a surface area of 122.3 m² g⁻¹, and an

average pore radius of 1.5 nm. It is interesting that the surface area and pore radius of the Co-100d is 1.5 times higher than for the Co-40d. The different textural properties of the cobalt oxide materials might further influence the electrical properties of sensing materials. For our cobalt oxide-sensing materials, all of the performance parameters were detected at different CO concentrations and an elevated temperature of 200 °C. Fig. 4 shows the typical response changes of the cobalt oxide materials to different CO concentrations. The tests were performed by measuring the changes in resistance at different CO concentrations of 10–70 ppm. They showed that the resistance increased while the CO gas was being injected and then

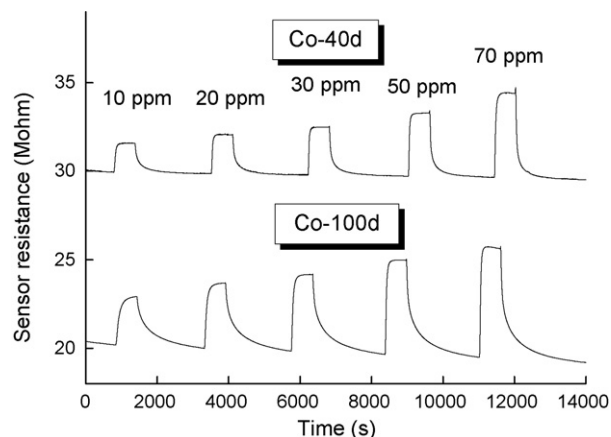


Fig. 4. The sensor resistance change of the mesostructured cobalt oxide at different templated temperatures.

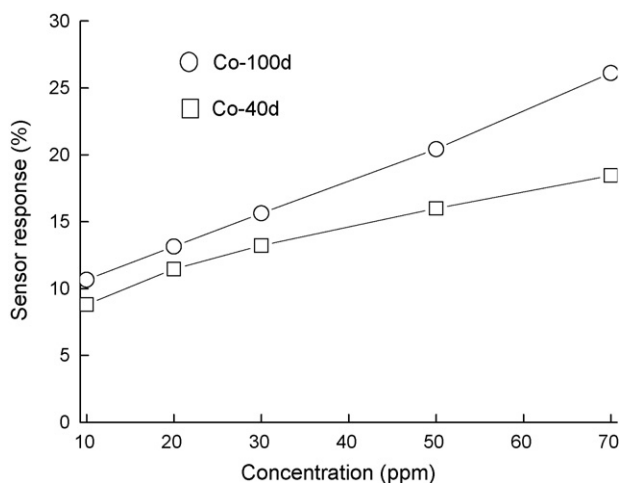


Fig. 5. Gas response curve for different CO concentrations of mesostructured cobalt oxide at different templated temperatures.

decreased to the base line once the gas was turned off. The response and recovery times of Co-100d were 75 and 585 s which were higher than Co-40d (107 and 830 s). Therefore, the surface area and interconnectivity of the mesostructured cobalt oxide influence most directly the sensor response and response/recovery times. It was also seen that these materials exhibited good repeatability during the testing. The sensor response of the Co-40d and Co-100d could be compared directly, since they were fabricated with the same method. Fig. 5 shows the sensor response of the Co-40d and Co-100d materials to different CO concentrations. Overall, all of the samples showed the same response curve dependence on the CO concentrations. However, the main difference between the samples was that the Co-100d showed a higher response than Co-40d. The Co-100d had a significant 1.5 times higher response than the Co-40d at 70 ppm CO. The enhanced response of the Co-100d material is attributed to its good-interconnectivity structure. On the other hand, the pore radius of cobalt oxide materials has a large effect on the gas diffusion. According to the Knudsen equation [11]:

$$D_k = \frac{2r}{3} \left(\frac{8RT}{\pi M} \right)^{1/2} \quad (1)$$

where D_k is the Knudsen diffusion coefficient in a porous medium, r is the pore radius, R is the gas constant, and M is the mass. The gas diffusion is directly proportional to the porosity and pore radius of the cobalt oxide materials. A poor porosity and small pore radius limit gas penetration into the internal surface of the cobalt oxide materials. In addition, it should be noted that a higher porosity and pore radius should facilitate gas diffusion into the interior of samples. The continuous channel of a material with full interconnectivity would also assist the gas diffusion and cause a higher response compared to a material with poor interconnectivity. This is evident in the higher response of Co-100d compared to Co-40d.

4. Conclusion

Cobalt oxide-sensing materials with different amount of interconnectivity was synthesized by the template replication method. An examination of their structural properties showed that sensing materials that had a higher hydrothermal treatment had full

interconnectivity, whereas those that had a lower hydrothermal treatment, had poor interconnectivity. Both the structural and textural properties of Co-100d were excellent compared with Co-40d. The Co-100d also offered a sensor response that was the 1.5 times that of the Co-40d. This gain in sensor response was attributed to a good porous architecture, which promoted CO gas diffusion and increased the available active surface areas. Finally, the template replication method offers the possibility of fabricating mesostructured sensing materials with excellent sensing performance.

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