Available online at www.sciencedirect.com
SCIENCE DIRECT
Sensors and Actuators B 114 (2006) 402–409
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

MCo_2O_4 (M = Ni, Cu, Zn) nanotubes: Template synthesis and application in gas sensors

Guo-Ying Zhang, Bing Guo, Jun Chen *

Institute of New Energy Materials Chemistry, Nankai University, Tianjin 300071, PR China

Received 4 March 2005; received in revised form 16 June 2005; accepted 17 June 2005
Available online 28 July 2005

Abstract

MCo_2O_4 (M = Ni, Cu, Zn) nanotubes were prepared by a porous alumina-template method. Powder X-ray diffraction (XRD), fourier transformation infrared spectroscopy (FT-IR), thermogravimetry and differential thermal analysis (TG–DTA) were employed to trace the formation of the composite oxides. The as-prepared samples were further characterized by scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Application of the MCo_2O_4 nanotubes to gas sensors displayed excellent selectivity and high sensitivity to various gases such as ethanol and SO_2 due to the one-dimensional (1D) electron-conductivity characteristic and hollow nanotube structure.

Keywords: MCo_2O_4 (M = Ni, Cu, Zn) nanotubes; Gas sensor; Template synthesis; Hollow structure

1. Introduction

Transition-metal oxides constitute an attractive class of inorganic solids due to a variety of structure, properties and phenomenon [1,2]. Among the transition-metal oxides, spinel-type AB_2O_4, where element A and B denote divalent and trivalent metallic cations, respectively, are very interesting materials with improved reactivity than the corresponding single oxides [3]. In particular, the cobalt-containing spinel oxides MCo_2O_4 (M = Ni, Cu, Zn, Mg, Mn, Cd, etc.) are technologically intriguing materials and have found many applications in the areas such as chemical sensors [4], electrode material [5], electrocatalyst [6] and pigment [7]. To date, three morphological MCo_2O_4 (M = Ni, Cu, Zn) nanostructures of nanoparticles [4–8], nanofibres [9] and films [10] have been prepared by various techniques. However, to the best of our knowledge the fabrication of MCo_2O_4 nanotubes has not yet been reported.

The synthesis of one-dimensional (1D) transition-metal composite oxides has seen success with only a few systems such as $BaTiO_3/SrTiO_3$ nanorods [11] and nanotubes [12], $La_{0.325}Pr_{0.300}Ca_{0.375}MnO_3$ nanotubes [13] and (La, Sr)MnO_3 nanorods [14]. The extension of this kind of effort is limited due to the complex compositions of transition-metal composite oxides, and most techniques developed for preparing 1D single oxides cannot be fully used because of issues such as phase separation and the lack of suitable catalysts [15].

For the formation of 1D nanotubes, a template method, which is based on porous anodic aluminum oxide (AAO) membrane [16], has been established to be a simple and effective strategy in the synthesis of various mater, such as metals [17], semiconductors [18] and polymers [19]. Furthermore, the unique hollow tubular structure on the nanoscale usually exhibits properties different from those of their bulk form [20]. Thus, the preparation of MCo_2O_4 nanotubes should be of great interest in both fundamentals and applications.

Herein, we report on the template-assisted synthesis of MCo_2O_4 (M = Ni, Cu, Zn) nanotubes. Gas-sensing experiments to various gases such as ethanol and SO_2 were carried out to investigate effects of the hollow nanotube structure on the surface-related properties with the comparison of the corresponding nanoparticles. The good selectivity and high

* Corresponding author. Tel.: +86 22 23506808; fax: +86 22 23509118.
E-mail address: chenabc@nankai.edu.cn (J. Chen).

0925-4005/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.snb.2005.06.010

sensitivity of nanotube sensors indicate that the 1D tube structure favors the electronic conductivity of semiconductors as well as the adsorption and desorption of gases.

2. Experimental

2.1. Sample preparation and characterization

Anodic aluminum oxide (AAO) membranes (Whatman, Ø 47 mm with 0.20 μm-pore and 60 μm-thickness) were used as the templates. All reagents are of analytical grade and used as received. MCo_2O_4 nanotubes were synthesized by thermal decomposition of a nitrate mixture within the AAO template, as shown schematically in Fig. 1. The preparation process mainly involves the steps that follow: (1) preparation of a homogenous precursor with the corresponding nitrate mixture; (2) precursor impregnation in the membrane channel and the surface treatment of the membrane; (3) drying and calcination of the membrane in a furnace; (4) repeating of another two cycles; and (5) template dissolution.

Taking $NiCo_2O_4$ nanotubes as an example of a typical synthesis, the stoichiometric amount of nickel and cobalt nitrates were dissolved in deionized water to obtain a 0.3 M precursor solution, in which the AAO membrane was gently immersed for 30 min. After the precursor-containing AAO template was taken out, the excess sol on the membrane surface was wiped off carefully with laboratory tissue and then air-dried for 2 h. The nitrate-filled template was heated in air at a rate of 2 °C/s to 380 °C and maintained at that temperature for 4 h, followed by cooling to ambient temperature naturally in the muffle furnace. The off-gases were introduced to a 1 M NaOH solution before they were vented into the atmosphere. After three cycles of the 'dip-dry-calcination' procedure, the membrane was rinsed with deionized water several times and dissolved in a 6 M NaOH solution. The as-prepared solid was collected, washed and dried in vacuum at 80 °C for 2 h to obtain the nanotube products. The chemical reactions involved in the preparation process can be expressed as:

$$Ni(NO_3)_2{\cdot}6H_2O + 2Co(NO_3)_2{\cdot}4H_2O \rightarrow NiCo_2O_4 + 6NO_2\uparrow + 14H_2O\uparrow + O_2\uparrow;$$

$$2NO_2 + 2NaOH \rightarrow NaNO_3 + NaNO_2 + H_2O;$$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O.$$

For comparison, $NiCo_2O_4$ nanoparticles were prepared by a template-free calcination of the nitrate precursor under the same conditions. $ZnCo_2O_4$ and $CuCo_2O_4$ nanotubes and nanoparticles were synthesized following the similar procedure except that the concentration of the $CuCo_2O_4$ nitrate precursor was 0.2 M.

The as-prepared samples were characterized by XRD (Rigaku INT-2000 X-ray generator, Cu Kα radiation), SEM (Philips XL-30, 20 kV) equipped with EDX (Kevex Super 8000 detector.), TEM and HRTEM (Philips Tecnai F20, 200 kV), FT-IR (Bruker Tensor 27) as well as TG-DTA (Shimadzu DT-40) analysis.

2.2. Fabrication and analysis of gas sensors

The sensors of the as-prepared samples were fabricated on ceramic tubes with the connection of gold electrodes that were connected by four platinum wires [21]. The mixture of the nanotubes (or nanoparticles) and ethanol was coated as a thin film spanning across the two Au electrodes. After calcinations at 380 °C in air for 4 h to improve stability, a small Ni–Cr alloy coil was crossed through the alumina tube as a heater to provide the operating temperature by adjusting the heating power. The electrical contact was made through connecting the four platinum wires and the two coil ends with the instrument-base by silver paste. The fabricated sensors were fixed into the gas-sensing apparatus and aged at 300 °C for 96 h. Before analysis the sensors-settled chamber was kept under a continuous flow of fresh air for 30 min. The sensor structure and the testing principle were schematically shown in Fig. 2. The heating voltage (V_h) was supplied to the coils for

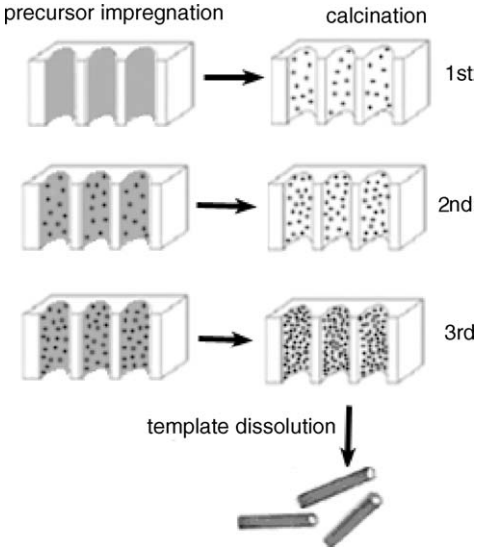

Fig. 1. Schematic diagrams showing the template preparation for MCo_2O_4 nanotubes.

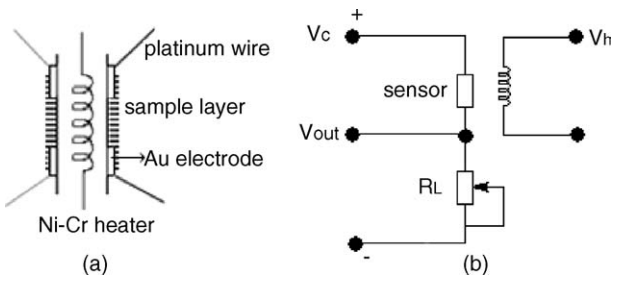

Fig. 2. Schematic diagrams of (a) the gas sensor and (b) the working principle. V_h, V_c, V_{out} and R_L represent the heating voltage, circuit voltage, signal voltage and load resistor, respectively.