Available online at www.sciencedirect.com
SCIENCE DIRECT®
Sensors and Actuators B 109 (2005) 57–63
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Nanostructured metal oxides synthesized by hard template method for gas sensing applications

E. Rossinyol [a,*], J. Arbiol [a], F. Peiró [a], A. Cornet [a], J.R. Morante [a], B. Tian [b], T. Bo [b], D. Zhao [b]

[a] *Electronics Materials and Engineering, Electronics Department, University of Barcelona, c\Martí i Franqués, Barcelona 08028, Spain*
[b] *Molecular Catalysis and Innovative Materials Laboratory, Department of Chemistry, Fudan University, Shanghai 200433, China*

Available online 16 April 2005

Abstract

In order to increase the surface area, mesoporous oxides have been synthesized. In this work, we have used mesoporous silica SBA-15 and KIT-6 as a template for the synthesis of different semiconductor oxides: CeO_2 and WO_3. These materials show a small particle size, about 5–10 nm, and a high surface area. As required increase the sensitivity when used for gas sensing applications. XRD and HRTEM studies reveal that the silica host has been completely removed; therefore, the nanowires constitute a self-supported superlattice.

Keywords: Synthesis; Mesoporous WO_3 and CeO_2; Gas sensor; HRTEM

1. Introduction

Semiconductor gas sensors offer good advantages with respect to other gas sensor devices due to their simple implementation, low cost and good reliability for real-time control systems. As the adsorption is a surface effect, one of the most important parameter to tailor the sensitivity of the sensor material is the surface area. Li and Kawi [1] have shown that a direct relationship was found between the surface areas of SnO_2 sensors and their sensitivities to 500 ppm of H_2. According to these results, increase in the surface area involves increase in the sensitivity of the sensor. For this purpose, mesoporous oxides have been synthesized.

Nanostructured mesoporous materials have been widely studied in the development of catalytic systems [2], due to their large, controllable pore size and high surface area. The pore structure, such as pore size and channel conductivity can be designed for practical application, and a variety of synthetic pathways have been proposed for the development on these nanostructures [5]. Since the successful synthesis of MCM-41 [3–6], great efforts were made to synthesize mesoporous oxide materials other than silica. Mesoporous materials of many oxides, such as TiO_2, SnO_2, ZrO_2, WO_3, etc. synthesized by self-assembly pathway using block-copolymers as a surfactant (soft template route), present an amorphous pore wall and low thermal stability. Recently, novel methodologies for preparing nanomaterials have been developed by using mesoporous materials with pore diameter of 2–50 nm as host to accommodate different oxides [7–14]. In this synthesis pathway, known as hard template route, the voids of a preformed mesoporous solid are utilized and impregnated with desired precursors. The subsequent mineralization of these precursors and removal of the former solid templates may lead to mesostructures with other compositions and crystalline frameworks. For the preparation of ordered nanostructure arrays, a hard template has some advantages when compared with a soft template, especially in its specific topological stability, veracity, predictability and controllability.

In this work, we have used SBA-15 and KIT-6 as a template for the synthesis of two different semiconductor oxides: CeO_2 and WO_3. WO_3 is a material, widely used for the detection of NO_2, important for monitoring environmental pollution resulting from combustion or automotive emissions [15,16]. Cerium oxide is particularly interesting because of its catalytic activity and the ability to store and release oxygen depending on the redox environment. It is widely used as a promoter in three-way catalysts for the elimination of toxic

* Corresponding author.
E-mail address: erusinol@el.ub.es (E. Rossinyol).

0925-4005/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2005.03.016

auto-exhaust gases [17] and recently used as a solar cell material [29]. We have reported here the synthesis pathways of these mesoporous oxides and their structural and electronic characterization.

2. Experimental

2.1. Synthesis

Two different mesoporous silica template were synthesized: two-dimensional *p6mm* hexagonal structure, SBA-15, and three-dimensional *Ia3d* cubic mesostructure KIT-6. SBA-15 was synthesized in acidic conditions using the Pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$) as template and tetraethyl orthosilicate (TEOS, 98%, Aldrich) as a silicon source [11,12]. A solution with 6 g of P123 was dissolved in 195 g distilled H_2O and 30 g of concentrated HCl (35%) was prepared and stirred for 6 h at 35 °C. 12.49 g of TEOS was added at the mixture and stirred for 24 h at 35 °C, and then heated at 100 °C for another 24 h as a hydrothermal treatment. The solid product was filtered, washed, dried at room temperature in air atmosphere and calcined at 550 °C for 4 h. KIT-6 was also prepared in acidic conditions using a mixture of Pluronic P123 and butanol [18]. Six grams of P123 were dissolved in 220 g of distilled water and 12 g of concentrated HCl (35%). The solution was stirred for 6 h at 35 °C and 6 g of butanol was added under stirring for another hour. 12.48 g of TEOS was finally added and stirred for 24 h at the same temperature. The mixture was heated for 24 h at 100 °C under static conditions for the hydrothermal treatment and filtered, washed, dried at room temperature in air atmosphere with water, dried and calcined at 550 °C.

For the synthesis of mesoporous oxides, these silica materials were used as a template. 0.15 and 0.2 g of SBA-15 (and the same amounts for KIT-6) was dissolved in ethanol with 0.4 g of $Ce(NO_3)_3{\cdot}6H_2O$ and 0.4 g of phosphotungstic acid, respectively. After 30 min of stirring, both solutions were dried at room temperature in air atmosphere and calcined at 350 °C for 4 h. The silica/oxide mixture was solved again in ethanol with 0.2 g of each precursor, dried at room temperature in air atmosphere and calcined at 550 °C. Finally the silica template was removed with HF for the WO_3 powders and NaOH for the CeO_2.

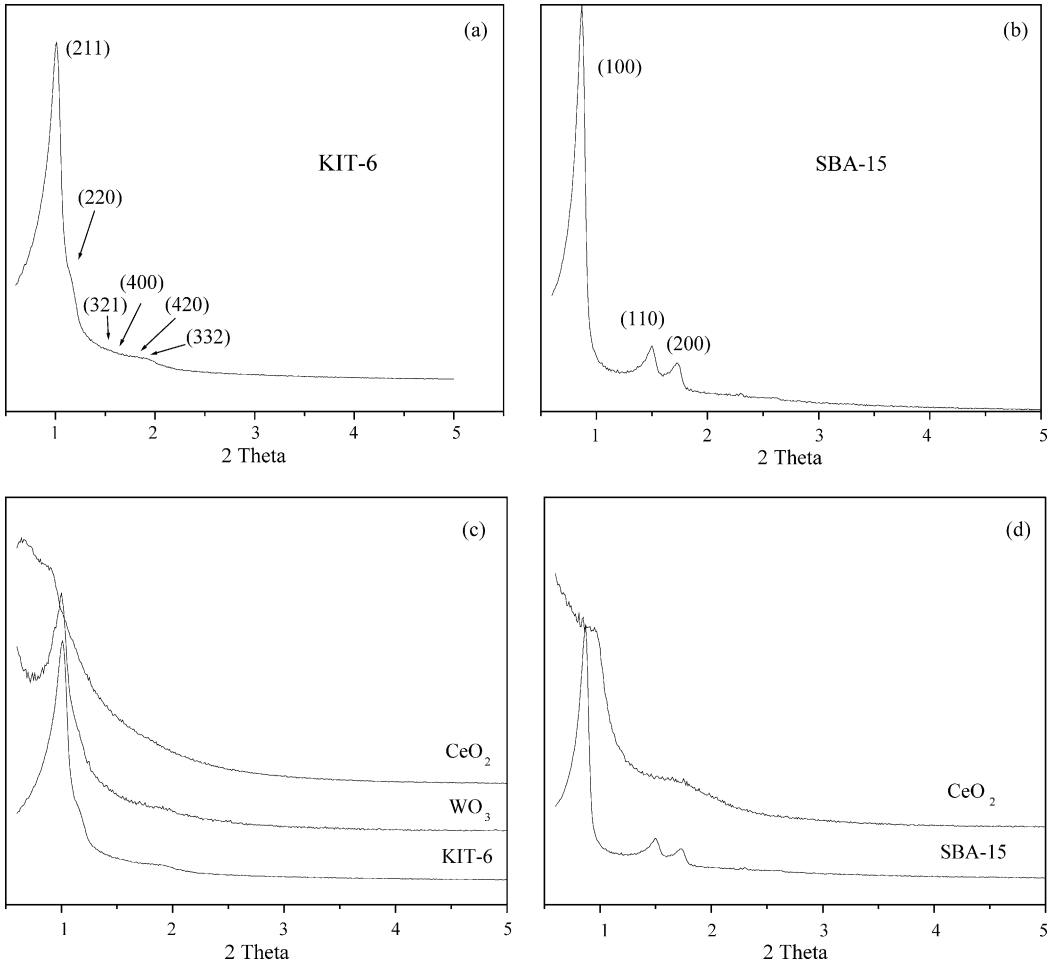

Fig. 1. Low angle XRD patterns of the two silica templates: three-dimensional *Ia3d* cubic structure (a) and two-dimensional *p6mm* hexagonal structure (b). Cerium and tungsten oxides synthesized with KIT-6 template (c) and CeO_2 with SBA-15 silica template.