



Short Communication

Synthesis and characterization of mesoporous CeO₂ nanotube arrays

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ABSTRACT

Mesoporous CeO₂ nanotube arrays were fabricated by the following procedure: ZnO nanorod arrays were prepared as templates, and then the templates were in turn submerged in the NaOH solution, deionized water and the Ce(NO₃)₃ solution at 60 °C for 20 times. After annealed at 500 °C for 30 min, the mesoporous polycrystalline CeO₂ nanoshells covered ZnO nanorod arrays were obtained. Through HNO₃ treatments, ZnO nanorods were dissolved, as a result, the mesoporous CeO₂ nanotube arrays were achieved. The XPS result demonstrates that the ratio of Ce³⁺ ions to Ce⁴⁺ ions is about 1:2. Nitrogen adsorption–desorption experiment results give that the specific surface area is 109 m²/g. By using the mesoporous CeO₂ nanotubes as the electrode in the H₂O₂ solution, the electrochemical experiment proves that these arrays have the reduction action. The formation mechanism of mesopores in the CeO₂ nanotubes and the origin of the reduction action were discussed in detail.

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1. Introduction

CeO₂ as an important catalytic and reduction agent has been well recognized, and it has been widely used in various application fields, such as purification of exhaust gas antioxidants in biomedicine [1–3], in three-way automotive catalytic converters [4], and solid oxide fuel cells [5,6]. Many authors have made lots of works on the synthesis of nano-CeO₂ and the study of catalytic properties [7–16]. Recently, Hua et al. [17] synthesize mesoporous CeO₂ nanotubes. It is found that these nanotubes exhibit excellent reduction ability in the process of CO → CO₂ transition. They found that this high reduction activity was closely associated with the existence of large numbers of Ce³⁺ ions in the surface of mesoporous CeO₂ nanotubes and formation of lots of Ce³⁺ ions was attributed to large numbers of oxygen vacancies and vacancy groups in these CeO₂ nanotubes. Skorodumova et al. [14] theoretically suggested that oxygen-vacancy formation could induce valence transition of Ce ions in CeO₂ from +4 to +3 because oxygen escapes from lattice sites, leaving vacancy sites with two electrons at each vacancy. Namely, this transition can be expressed as follows: 2Ce⁴⁺ + 2e → Ce³⁺. This is why mesoporous CeO₂ nanotubes possess the high reduction activity. However, easy aggregation of CeO₂ nanotubes of random distribution will lead the reduction ability to be decreased, resulting in losing repeated application value. In order to overcome the aggregation disadvantage and keep the strong reduction ability, we synthesized mesoporous CeO₂ nanotube arrays with macro-scale. In order to investigate the

reduction activity of mesoporous CeO₂ nanotube arrays, according to the literature [20], we used the mesoporous CeO₂ nanotube arrays on the ITO layer as electrode to detect trace H₂O₂. In the literature [20], Ispas et al. [20] reported that they utilized the catalytic properties of CeO₂ for the development of a highly sensitive, simple and inexpensive H₂O₂ sensor in sensing and biosensing applications.

In this paper, we used ZnO nanorod arrays as the templates and synthesized the mesoporous CeO₂ nanotube arrays. The formation mechanism of mesopores was discussed. The strong reduction ability was proved through H₂O₂ decomposition experiments. Based on this, the reduction mechanism associated with the mesoporous structure was analyzed.

2. Experimental

2.1. Synthesis

The formation process of mesoporous CeO₂ nanotube arrays is shown in Fig. 1. The ZnO nanorod arrays were fabricated as templates via the seeding layer and aqueous solution route [18,19]. The 5 mL of 0.005 M zinc acetate alcohol solution was deposited uniformly on ITO for 5 times. After annealed at 350 °C in air for 30 min, the seed layer was prepared. Then, the ITO with seed layer was put into an aqueous solution of zinc acetate (Zn(Ac)₂·2H₂O, 0.02 M) and hexamethylenetetramine (HMTA, C₆H₁₂N₄, 0.02 M), which was stirred at 75 °C for 6 h. The product was then taken out and washed using distilled water. As a result, the ZnO nanorod arrays were obtained. The assemblies of mesoporous polycrystalline CeO₂ nanoshells on the ZnO nanorod arrays were prepared

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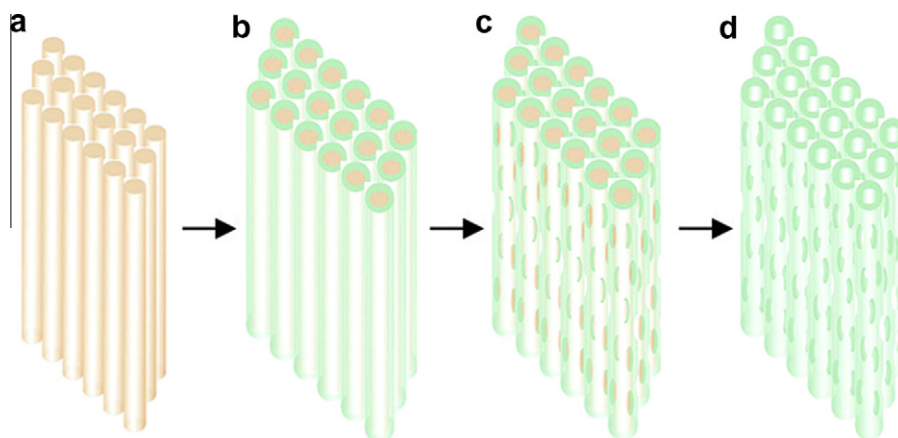


Fig. 1. Schematic illustration of formation process of the mesoporous CeO_2 nanotube arrays via ZnO nanoarray template synthesis together with ultrasonic assisted SILAR covering method. (a) ZnO nanorod array; (b) ZnO/ CeO_2 nanorod array; (c) Mesoporous ZnO/ CeO_2 nanorod array; and (d) Mesoporous CeO_2 nanotube array.

by the successive ionic layer adsorption and reaction (SILAR) method, along with annealing treatment. The detailed procedure is as follows: ZnO nanorod arrays were submerged in a 0.05 M NaOH solution for 20 seconds. Subsequently, the nanorod arrays were further submerged in deionized water for 10 seconds. Then, the nanorod arrays were further submerged in a 0.05 M $\text{Ce}(\text{NO}_3)_3$ solution for 20 seconds. After that, the ZnO nanorod arrays were submerged in deionized water for 10 seconds. The above operations were taken in 60 °C in the thermostatic water tank, and the process is referred to as one deposition cycle. To obtain the ideal CeO_2 nanoshells covered ZnO nanorod arrays, the above deposition cycle was repeated for about 20 times. As a result, the $\text{Ce}(\text{OH})_3$ covered ZnO nanorod arrays were obtained. This deposition product was annealed at 500 °C for 30 min to get mesoporous polycrystalline CeO_2 nanoshells covered ZnO nanorod arrays. Then they were treated by 5% HNO_3 solution to remove the ZnO nanorod array core and were purged in deionized water several times to obtain final products. Characterization by several techniques proves that the finally obtained product is mesoporous CeO_2 nanotube arrays.

2.2. Characterization

Phase identification was performed with a powder X-ray diffractometer (XRD, Philips X'Pert) using $\text{Cu-K}\alpha$ (0.15419 nm) radiation. Field emission scanning electron microscopy (FESEM, Sirion 200) was used to observe the morphologies. Transmission electron microscopy (TEM JEM-2010) was used to examine microstructures. The nitrogen adsorption–desorption experiment was carried out on a Surface Area and Porosity Analyzer (Omnisorp 100X), and from obtained adsorption–desorption isotherms, the specific surface area and the pore size distribution in the CeO_2 nanotube walls, and inner diameters of the CeO_2 nanotubes were obtained by calculation. Energy dispersive X-ray (EDX, Inca Oxford) analysis was conducted to determine the element composition. High resolution X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250. Thermal analysis was performed on a Thermogravimetry/Differential thermal analyzer (TGA–DTA, DTG-60H) and a Differential scanning calorimeter (DSC-60) to analyze the formation process of mesoporous CeO_2 nanotube arrays from the $\text{Ce}(\text{OH})_3$ covered ZnO nanorod arrays.

2.3. Reductive activity measurement

The reductive activity measurements were conducted in the H_2O_2 solution with electrochemical workstation (Zahner IM6ex, Germany). A 1/15 M phosphate buffer (PB) solution was prepared

by mixing stock solutions of Na_2HPO_4 and KH_2PO_4 . The mesoporous CeO_2 nanotube array was used as the working electrode. All the potentials were recorded and reported vs. a saturated calomel electrode and all the experiments were carried out at room temperature. Cyclic voltammetry experiments were performed in unstirred air-saturated solutions at room temperature at a scan rate of 50 mV/s. Scanning range from -1.5 V to 1.5 V.

3. Results and discussion

X-ray diffraction patterns of the products obtained are shown in Fig. 2, it is found that the ZnO nanorod arrays are of the wurtzite structure, furthermore, the obtained mesoporous CeO_2 nanotube

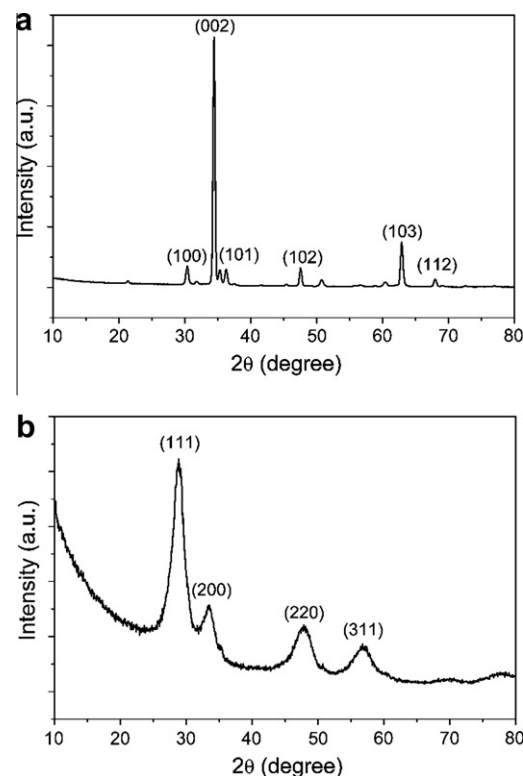


Fig. 2. X-ray diffraction patterns of ZnO nanorod arrays obtained by the seeding layer and aqueous solution route and the mesoporous CeO_2 nanotube arrays after the removal of ZnO nanorod arrays, respectively.

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