



Characterization and optical properties of pole-like nano-CeO₂ synthesized by a facile hydrothermal method



Leini Wang^a, Fanming Meng^{a,b,*}, Kangkang Li^c, Fei Lu^d

^a School of Physics and Materials Science, Anhui University, Feixi Road, Hefei 230039, PR China

^b Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, PR China

^c Lab of SoC, Department of Microelectronics, Peking University, Beijing 100871, PR China

^d Baotou Research Institute of Rare Earths, Baotou 014030, PR China

ARTICLE INFO

Article history:

Received 23 May 2013

Received in revised form 6 September 2013

Accepted 11 September 2013

Available online 20 September 2013

Keywords:

Ceria

Hydrothermal method

Oxygen defect

Optical property

ABSTRACT

CeO₂ nanopoles have been successfully synthesized by a hydrothermal method using CeCl₃·7H₂O as cerium source, NaOH as mineralizer, and ethylenediamine as complexant. The pole-like nano-CeO₂ was examined by XRD, TEM, XPS, UV–vis, PL, and Raman scattering. The results show that the crystallinity of the nanopoles is not so good, and the main valence of cerium is +4. The estimated direct band gaps are 3.014, 3.099, 2.931, and 2.927 eV for the samples synthesized within 2, 18, 50, and 100 h, respectively. These band gaps are smaller than bulk CeO₂. Oxygen vacancies and Ce³⁺ ions result in an effective red shifting of the band gap. The visible luminescence exhibits similar emission peaks of room temperature photoluminescence and the emission intensity increases with the increase of concentration of oxygen vacancies and Ce³⁺ ions.

© 2013 Elsevier B.V. All rights reserved.

Introduction

Ceria (CeO₂), one of the most reactive rare-earth metal oxides, has attracted considerable interest, and its distinctive properties enable it to function widely as catalysis, UV blocking, fuel cells, adsorbing pollutants, and polishing materials [1,2]. The usability of CeO₂ for most of the applications depends on its ability of release or uptake oxygen. Ceria has large oxygen storage capacity depends on Ce³⁺–Ce⁴⁺ redox cycles which in turn depends on the concentration and types of oxygen vacancies, more efficient it is for storing oxygen [3]. XPS spectroscopy is useful to investigate the oxidation state of ceria. Raman spectroscopy is a valuable tool to understand the presence of oxygen vacancy results in asymmetry and peak shifting of active mode peak [4]. The formation of Ce³⁺ has effect in the red shifting of band gap for CeO₂ nanostructures [5]. Photoluminescence in ceria arises due to strong light absorption through the charge transfer between O²⁻ and Ce⁴⁺ [6]. Ceria with nanostructures such as octahedral [7], cubes [8], wires [2], rods [9], cauliflowers [10], square [11], and hollow spheres [12] have been fabricated. In spite of these successes, there still exist some challenges to prepare one-dimensional (1D) nanostructured

ceria materials. Although several surfactant-assisted and template methods have been reported to successfully prepare 1D CeO₂ nano-materials [13–15], the addition of surfactant in these methods means a much more complicated procedure and gives rise to an increase of the cost, and in most of the cases a usual calcination step is inevitable [16–18].

In this paper, 1D long-thin pole-like nano-CeO₂ was successfully synthesized by a facile hydrothermal method without surfactant and template. The effect of reaction time on the morphology, microstructure and optical properties of nano-CeO₂ were investigated in detail by measuring XRD, SEM, TEM, XPS, UV–vis absorbance, PL and Raman spectra.

Experimental

Synthesis of CeO₂ nanopoles crystals

All the reagents were of analytical grade purity and used without further purification. Typically, 1.49032 g of cerium chloride (CeCl₃·7H₂O) and 2.3998 g of NaOH were dissolved in 10 mL of deionized water, respectively. The NaOH aqueous solution was added gradually to the CeCl₃ aqueous solution to form lavender colorless precipitation. After continuous stirring for 15 min, 5 mL of ethylenediamine was added dropwise to the CeCl₃ solution, the solution was further stirred for 0.5 h. The mixed solution was transferred into a 50 mL Teflon-lined autoclave and heated at 180 °C for

* Corresponding author at: School of Physics and Materials Science, Anhui University, 111 Jiulong Road, Hefei 230601, PR China.

Tel.: +86 551 63861637/+86 158 56983919; fax: +86 551 63861992.

E-mail addresses: mrmeng@ahu.edu.cn, mrmeng@tom.com (F. Meng).

2, 18, 50, and 100 h. After the autoclave was cooled to room temperature naturally, fresh precipitates were washed with deionized water and ethanol for three times, and then dried at 70 °C overnight.

Characterization

The crystal phases of the products were analyzed by X-ray diffractometer (XRD) with Cu K_{α} radiation ($\lambda=0.154$ nm). The morphologies, sizes and crystalline structure were characterized by scanning electron microscope (SEM, S-4800), transmission electron microscopy (TEM, JEM-2100), and selected area electron diffraction (SAED). X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was used to assess the chemical state and surface composition of the deposits. The Raman spectra was recorded by a Raman spectrometer system (in Via-Reflex) using a laser with 532 nm excitation at room temperature. The UV–vis absorption spectroscopy was measured by ultraviolet–visible–near infrared spectrophotometer (U-4100). Room-temperature photoluminescence (PL) spectra were measured by a fluorescence spectrophotometer (HORIB FluoroMax-4P) using excitation light of 340 nm.

Results and discussion

Structure and morphology analysis

Fig. 1 shows the XRD patterns of CeO₂ samples synthesized within different reaction time. It can be seen that, in each case, the direct product has been crystallized and all the characteristic diffractions corresponding to CeO₂ with the fluorite crystal structure (JCPDS Card #81-0792). The obtained CeO₂ samples are pure phase products, no obvious peaks corresponding to cerium chloride or other cerium oxides were observed in the powder patterns, indicating that pure CeO₂ is synthesized. The lattice parameter calculated from XRD spectra is about 0.5431, 0.5424, 0.5462, and 0.5463 nm, for the CeO₂ nanopoles synthesized within 2, 18, 50, and 100 h, respectively. These lattice constants are slightly higher than bulk CeO₂ (0.5411 nm), a similar lattice relaxation phenomenon was previously observed from CeO₂ nanocrystallites at decreased size [5,18]. For nanocrystalline CeO₂, which generally possesses high redox capabilities, the potential reason for the observed lattice expansion is the presence of oxygen vacancies in the crystal lattice, which could create larger Ce³⁺ ions for charge compensation (Ce³⁺ and Ce⁴⁺ have their respective ionic radii of 0.1034 and 0.092 nm) [19]. A schematic view of fluorite structure CeO₂ along with oxygen vacancies and Ce³⁺ ions in the lattice site is shown in Fig. 2. We can calculate the total concentration of oxygen vacancies in CeO₂

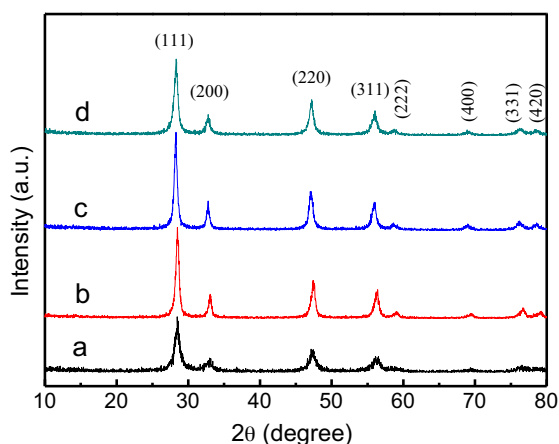


Fig. 1. XRD patterns of CeO₂ nanopoles synthesized within different reaction times: (a) 2 h, (b) 18 h, (c) 50 h, and (d) 100 h.

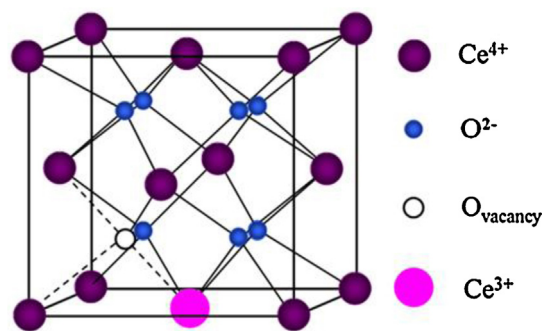


Fig. 2. Schematic representation of cubic fluorite structure of CeO₂.

nanocrystallites by adopting the equation proposed by Zhou and Huebner [20].

$$\frac{\sqrt{3}}{4} (a' - a_0) = c \left[r_{\text{Ce}^{3+}} - r_{\text{Ce}^{4+}} + \frac{1}{4} (r_{\text{V}_{\text{O}^{\cdot\cdot}}} - r_{\text{O}^{2-}}) \right] \quad (1)$$

where $r_{\text{Ce}^{3+}}$ is the radius of Ce³⁺ (0.1283 nm), $r_{\text{Ce}^{4+}}$ is the radius of Ce⁴⁺ (0.1098 nm), $r_{\text{V}_{\text{O}^{\cdot\cdot}}}$ is the radius of oxygen vacancy (0.138 nm), and $r_{\text{O}^{2-}}$ is the radius of O²⁻ (0.124 nm). In our case a' is lattice parameter calculated from XRD spectra and a_0 is the lattice parameter of bulk CeO₂ (0.5411 nm). In the above equation the parameter c is equation to the ratio of Ce³⁺/Ce⁴⁺ (the ratio of the number of Ce³⁺ and Ce⁴⁺ ions in the lattice structure of CeO₂). Now placing the values of the parameter in Eq. (1), we got the values of c are 0.03936, 0.02559, 0.10038, and 0.10235, for the CeO₂ nanopoles synthesized within 2, 18, 50, and 100 h, respectively. Ce³⁺ is formed by reduction of Ce⁴⁺ by the electrons left behind when an oxygen vacancy is created in the lattice, so the values of c can reveals the concentration of oxygen vacancies and more oxygen vacancies can induces more Ce³⁺ ions. Our results of XPS and Raman shown below reveal the existence of an appreciable amount of oxygen vacancies, which imply that the observed lattice relaxation can be attributed to increased oxygen vacancies and Ce³⁺ ions [5].

Fig. 3 shows the SEM images of the obtained CeO₂ samples. To reveal the formation mechanism of CeO₂ nanopoles, the detailed time-dependent morphology and crystal phase evolution process are investigated. It can be seen that CeO₂ nanopoles of 10–30 nm in diameter and 100–300 nm in length were synthesized within 2 h, and mingled with little nanoparticles and not developmental nanopoles. When the reaction time is 18 h, the CeO₂ nanopoles become thicker and longer and the nanoparticles increase and become larger. Within the reaction time of 50 h, the nanoparticles disappear. Uniform and long-thin CeO₂ nanopoles of 15–25 nm in diameter and 400–800 nm in length were synthesized within 100 h. obviously, the morphology of CeO₂ nanostructure is sensitive to reaction time, and suitable time is beneficial for the growth of homogeneous CeO₂ nanopoles. Ethylenediamine coordinate Ce³⁺ ions to form [Ce(NH₂CH₂CH₂NH₂)₂]³⁺ and control the release of Ce³⁺. Therefore, the Ce³⁺ ions react with hydroxyl to form Ce(OH)₃ [21], then oxidation and dehydration to Ce(OH)₄ and CeO₂ [22], respectively. The reaction mechanism may be expressed:



Fig. 4 presents TEM and HRTEM images of CeO₂ nanopoles. The TEM image in Fig. 4a indicates that the sample synthesized within 100 h reveals a mixture of morphologies mainly composed of nanopoles of 15–25 nm in diameter and 400–800 nm in length,

Download English Version:

<https://daneshyari.com/en/article/5352105>

Download Persian Version:

<https://daneshyari.com/article/5352105>

[Daneshyari.com](https://daneshyari.com)