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Highly-ordered mesoporous nanocrystalline yttria-stabilized zirconia synthesized through evaporation-induced self-assembly method

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Abstract

An ordered tetragonal mesoporous 16 mol% yttria-stabilized zirconia (8YSZ) has been successfully prepared by evaporation-induced self-assembly (EISA) using tri-block copolymer Pluronic F127 as a structure-directing agent and inorganic chlorides as precursors in a non-aqueous medium. The arrangement of mesopores was identified by small-angle X-ray diffraction and transmission electron microscopy (TEM). A distinct face-centered tetragonal lattice was able to describe such an ordered mesopore arrangement. The structure and crystallite size of pore-walls were determined by wide-angle X-ray powder diffraction and high-resolution TEM. The well-ordered face-centered tetragonal mesoporous 8YSZ with average pore size of 4.3 nm and high specific surface area of 134 m^2/g and the pore-wall is composed of ~4.8 nm nanocrystalline 8YSZ domains.

Keywords: Ceramics; Powder technology; Mesoporous; Tri-block copolymer; Nanocrystalline

1. Introduction

Since the discovery of M41S following the supramolecular template approach introduced by the scientists in Mobil Corp, the silica-based mesoporous materials have been well investigated [1,2]. Related synthesis methods and applications have been described in detail in several excellent reviews [3,4]. In recent years, the preparation and application of mesoporous materials has been extended from silica-based materials to transition metal (TM) oxides materials [5] because they have great potential in a wide range of applications, such as photovoltaic [6], biochemical [7], lithium-ion battery [8], solid oxide fuel cell (SOFC) [9] and sensor [10]. Mesoporous TM oxides are more difficult to synthesize [11] than that of silica-based materials attributed to the complexity of TM chemistry, such as their variable valence and coordination number, and high hydrolysis/condensation reactivity. In addition, in most cases, the mesoporous structure collapsed because metal-oxo polymers tend to form crystalline phase during the subsequent calcinations for mesoporous TM oxides [12,13].

Ozin et al. [14] were first to extend supramolecular template approach to the synthesis of mesoporous YSZ using cetyltrimethylammonium bromide ($[CH_3(CH_2)_{15}N^+(CH_3)_3Br^-]$, CTAB) as the template and using glycolate-modified inorganic solution as the metal ion precursors. Liu et al. [15] reported the preparation of YSZ/NiO using Pluronic P103 as a structure-directing agent and inorganic chlorides as precursors in a non-aqueous medium. Gedanken et al. [16] reported that mesoporous YSZ was obtained when octanoic acid ($C_7H_{15}COOH$) was used as a templating agent and $Zr(i\text{-}OPr)_4$ and Y_2O_3 were used as metal ion sources. However, these mesoporous YSZ consisted of crystallized particles in a wormhole-like mesoporous structure, which suggest that the wormhole structure is formed during the crystallization of TM oxides. Until recently, based on our best knowledge, only a few articles about the synthesis and characterization of periodically organized mesoporous YSZ were reported [17,18].

In the present work, we report the reproducible synthesis of thermally stable YSZ presenting a periodically organized

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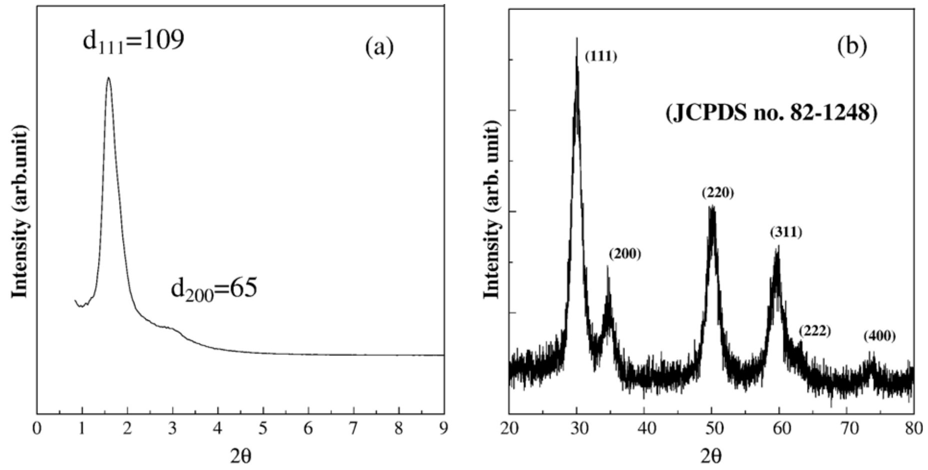

Fig. 1. (a) SAXD and (b) wide-angle powder XRD patterns of ordered mesoporous YSZ calcined at 500 °C for 2 h.

mesoporosity with high surface area associated with nanocrystalline inorganic walls by well-controlled calcination. SAXD, HR-TEM, EDX and nitrogen absorption/desorption isotherm were employed to analyze the crystal structure, pore arrangement and surface properties of mesoporous YSZ.

2. Experimental

The mesoporous YSZ was prepared by EISA method [19]. The molar ratio of Y/Zr was 0.175. In a typical synthesis, 0.0596 mol of zirconia chloride (99.9%, Alfa) and 0.0104 mole yttrium chloride (99.5%, Alfa) were added to the surfactant ethanol solution where 4.16 g of poly(alkylene oxide) block copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) (where EO is ethylene oxide and PO is propylene oxide) was dissolved in 130 g of ethanol (EtOH). Water was added to this mixture solution (molar ratio of H_2O/metal is 20), which results in very acidic solution to prevent precipitation. The solutions contain 1 (Zr+Y):0.047 F127:40 EtOH:20 H_2O. The resulting sol solution was gelled in an open Petri dish and underwent solvent evaporation under controlled relative humidity at 40 °C in air for 3 days, during which the inorganic precursor hydrolyses and polymerizes into a metal oxide network. The as-made bulk samples were then calcined at 500 °C for 2 h with heating rate of 1 °C/min.

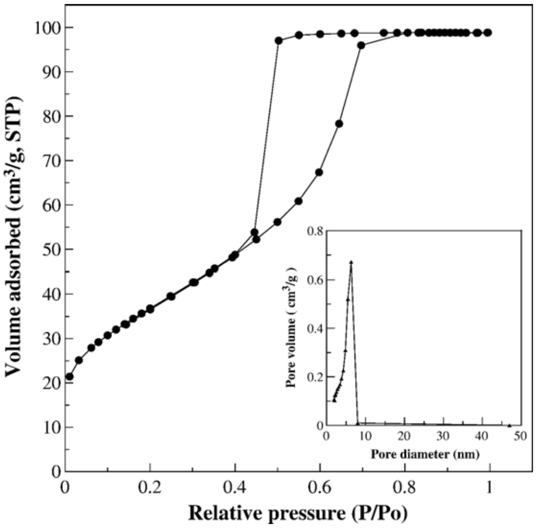

Fig. 2. Nitrogen adsorption/desorption isotherms and BJH pore-size distribution (inset) of mesoporous YSZ calcined at 500 °C for 2 h.

Small-angle X-ray diffraction (SAXD) was determined using an 18 kW rotating anode X-ray generator equipped with a rotating anode Cu target (Cu $K_{\alpha1}$ radiation, $\lambda=1.5406$ Å), that was operated at 200 mA and 40 kV.

The phase identification was performed by wide-angle X-ray diffraction (XRD) using a Rigaku, Model Rad II diffractometer with Cu K_α radiation ($\lambda=1.5406$ Å) and Ni filter, operated at 30 kV, 20 mA with scanning rate of 1°/min. The average crystallite size was calculated from the (111) diffraction peak of YSZ using Scherrer's equation [20]. High-resolution transmission electron microscopy (HR-TEM) was collected using a FEI E.O Tecnai F20 G2 MAT S-TWIN Field Emission Gun Transmission Electron Microscope. The nitrogen adsorption/desorption isotherms were measured using a Micromeritics ASAP 2010 system at 77 K after the samples were vacuum-dried at 200 °C overnight.

3. Results and discussion

The SAXD and wide-angle XRD patterns of 500 °C-calcined sample are shown in Fig. 1(a) and (b). The wide-angle XRD trace clearly shows very broad, low intensity peaks corresponding to a typical fluorite structure. The broadness of such peaks also indicates that the inorganic framework may consist of nanocrystalline oxide domains. The average size of the nanocrystals in the calcined materials is estimated to be 5.4 nm by applying the Scherrer equation on the (111) diffraction peak of YSZ.

In SAXD pattern, the calcined YSZ sample also shows two diffraction peaks, located at 1.625° and 2.728° of 2θ angles. A large and repeated lattice usually contributes the presence of reflections at pseudo-small angles. The presence of these reflections suggests that this sample may consist of a highly regular or ordered structure. The identification of this large structure will be discussed later with the assistance of TEM analysis.