Materials Research Bulletin 69 (2015) 116–119

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Alkaline earth metal doped tin oxide as a novel oxygen storage material

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ARTICLE INFO

Article history:
Available online 25 November 2014

Keywords:
Alkaline earth metal
Tin oxide
Hollow nanospheres
Solvothermal
Oxygen storage

ABSTRACT

Alkaline earth metal doped tin oxide (SnO_2) hollow nanospheres with a diameter of 50 nm have been synthesized successfully via a facial solvothermal route in a very simple system composed of only ethanol, acetic acid, $SnCl_4·5H_2O$ and $A(NO_3)_2·xH_2O$ (A = Mg, Ca, Sr, Ba). The synthesized undoped SnO_2 and A-doped SnO_2 hollow nanospheres were characterized by the oxygen storage capacity (OSC), X-ray diffraction, transmission electron microscopy and the Brunauer–Emmet–Teller (BET) technique. The OSC values of all samples were measured using thermogravimetric-differential thermal analysis. The incorporation of alkaline earth metal ion into tin oxide greatly enhanced the thermal stability and OSC. Especially, Ba-doped SnO_2 hollow nanospheres calcined at 1000 °C for 20 h with a BET surface area of 61 $m^2 g^{-1}$ exhibited the considerably high OSC of 457 μmol-O g^{-1} and good thermal stability. Alkaline earth metal doped tin oxide has the potential to be a novel oxygen storage material.

1. Introduction

So-called oxygen storage materials (OSMs) have become important after being applied to three-way automotive exhaust catalysts (TWCs) to compensate for the fluctuation between lean (oxidizing) and rich (reducing) conditions [1–3]. Ceria-based materials are well-known OSMs which already find application as TWCs for the removal of NO_x, CO, and hydrocarbons from automobile exhaust emissions [4,5]. Since 1990s, CeO_2–ZrO_2 solid solutions have gradually replaced pure CeO_2 as OSC materials in the TWCs to reduce the emission of toxic pollutants (CO, NO_x, hydrocarbons, etc.) from automobile exhaust, because of their enhanced OSC performance and improved thermal stability at elevated temperatures [6–9]. The redox property of CeO_2 can be greatly enhanced by incorporation of zirconium ions (Zr^{4+}) into the lattice to form a solid solution [10–12]. Nagai et al. have suggested that enhancing the homogeneity of Ce and Zr atoms in the CeO_2–ZrO_2 solid solution can improve the OSC performance [13]. Fornasiero et al. have reported that an optimum composition, like $Ce_{0.5}Zr_{0.5}O_2$ (molar ratio of Ce:Zr = 1:1) can exist as a cubic phase, which can have considerably high redox property [14]. Using density functional theory, Wang et al. found that in a series of $Ce_{1-x}Zr_xO_2$ solutions with a content of 50% ZrO_2 possesses the lowest formation energy of the O vacancy, therefore, $Ce_{0.5}Zr_{0.5}O_2$ exhibits the best OSC performance [14]. Recently, many researchers have paid much attention to prepare the new ceria-based oxygen storage materials [15–20]. For example, Singh et al. have reported a fluorite-type solid solution series, $Ce_{1-x}Cr_xO_{2+y}$, which exhibit excellent reversible oxygen release/storage properties at relatively low temperatures [21]. In our previous work, $Ce_{1-x-y}Zr_xM_yO_{2-z}$ (M = Sn, Al, Ti, Fe, Co and others) solid solutions have been prepared, which showed enhanced thermal stability and oxygen storage capacity [22–27].

Although, ceria-based oxygen storage materials have been studied extensively, there are few reports on the preparation of non-ceria-based oxygen storage materials in the literature. Moreover, by soaring price of cerium (Ce) as a rare earth element in recent years, research of decreasing Ce amount and non-ceria-based of the oxygen storage materials with the homogeneity of the composition, good dispersion of particles, narrow particle size distribution, better crystallinity and high surface area is arising much attention [28,29]. However, the complicate synthetic procedures greatly inhibit their practical applications. Therefore, it is a still challenging and promising task to prepare novel oxygen storage materials using cheaper elements instead of Ce by a simple preparation procedure. We have reported that $Ce_{0.5}Zr_{0.4}Sn_{0.1}O_2$ solid solution showed excellent thermal stability and oxygen storage capacity, and $Sn^{4+} \Leftrightarrow Sn^{2+}$ reaction can reversibly undergo at relatively lower temperature and contribute to CO oxidation [22,23]. On the basis of previous work, inhere, for the first time, we describe the preparation and characterization of alkaline earth metal (Mg, Ca, Sr, Ba) doped tin oxide hollow nanospheres with

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http://dx.doi.org/10.1016/j.materresbull.2014.11.018
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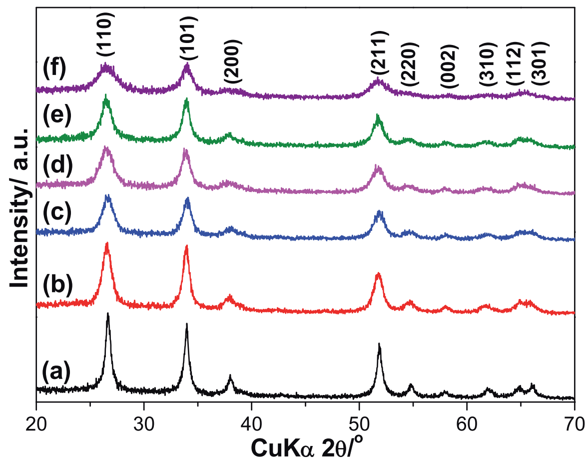

Fig. 1. XRD patterns of (a) commercial SnO_2 and as-prepared (b) undoped SnO_2, (c) Mg-doped SnO_2, (d) Ca-doped SnO_2, (e) Sr-doped SnO_2 and (f) Ba-doped SnO_2.

high surface area via a facile solvothermal route. The further experimental results show that A-doped SnO_2 (A = Mg, Ca, Sr, Ba) exhibits the excellent thermal stability and OSC even after calcination at 1000 °C for 20 h. Besides undoped SnO_2 prepared by the same method, the OSC performances of the commercial SnO_2, CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ were also evaluated for comparison. The results indicated that alkaline earth metal doped tin oxides have the potential to be a novel oxygen storage material.

2. Experimental

2.1. Reagents

$SnCl_4·5H_2O$, $Mg(NO_3)_2·6H_2O$, $Ca(NO_3)_2·4H_2O$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, ethanol and acetic acid of analytical grade (purity 99.999%) were purchased from Kanto Chemical Co., Inc., Japan and used without further purification.

2.2. Sample preparation

2.2.1. Preparation of Ba-doped SnO_2

After dissolving the stoichiometric amounts of $SnCl_4·5H_2O$ (0.5 mmol) and $Ba(NO_3)_2$ (0.05 mmol; the molar ratio of Sn^{4+}:Ba^{2+} = 10:1) in a 45 ml ethanol 5 ml acetic acid mixed solution, the solution was introduced in a 100 ml Teflon®-lined autoclave, and maintained at 200 °C for 12 h, then cooled to room temperature naturally. The obtained products were washed with distilled water three times, and dried in air at 100 °C for 12 h. In order to evaluate the thermal stability, the as-prepared samples were calcined in air atmosphere at 1000 °C for 20 h.

The similar synthesis route was employed for the preparation of undoped SnO_2, Mg-doped SnO_2, Ca-doped SnO_2 and Sr-doped

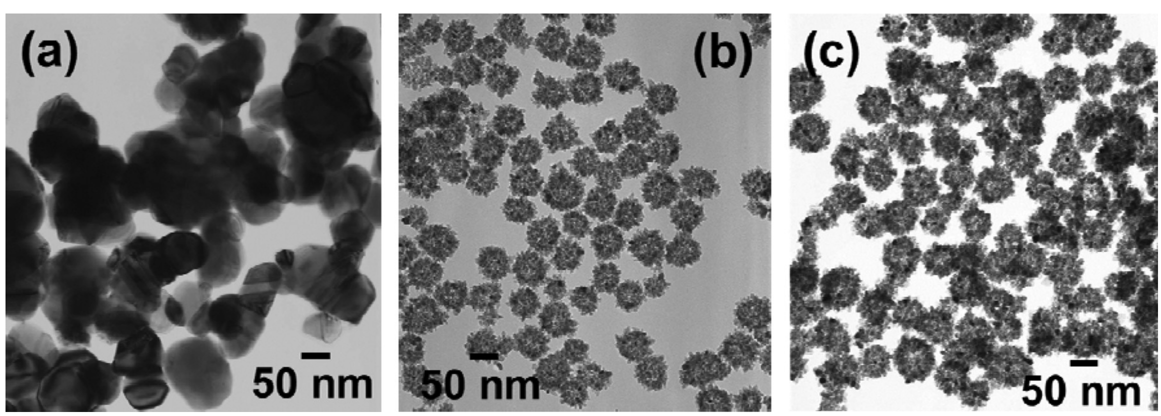

Fig. 2. TEM images of (a) commercial SnO_2, and as-prepared (b) undoped SnO_2 and (c) Ba-doped SnO_2.

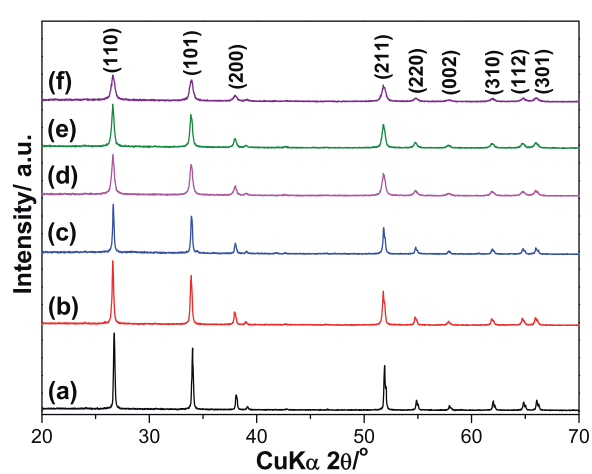

Fig. 3. XRD patterns of (a) commercial SnO_2 and calcined (b) undoped SnO_2, (c) Mg-doped SnO_2, (d) Ca-doped SnO_2, (e) Sr-doped SnO_2 and (f) Ba-doped SnO_2.