Journal of Solid State Chemistry 217 (2014) 87–91

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Hydrothermal synthesis of nanostructured SnO particles through crystal growth in the presence of gelatin

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ARTICLE INFO

Article history:
Received 29 March 2014
Received in revised form
27 May 2014
Accepted 27 May 2014
Available online 5 June 2014

Keywords:
Crystal growth
SnO
Hydrothermal synthesis
Nanostructure
Gelatin

ABSTRACT

Crystalline SnO particles were obtained from $Sn_6O_4(OH)_4$ by the hydrothermal treatment in aqueous solutions containing gelatin at 150 °C for 24 h, where the morphologies of the SnO products changed from blocks to layered disks, stacked plates and unshaped aggregates with increasing amount of gelatin in the solutions. Such morphological changes of SnO particles were thought to be attributed to the suppression of the growth of SnO crystals by the adsorbed gelatin.

1. Introduction

Tin monoxide (SnO) is now receiving attention as an anode material for lithium ion batteries with high theoretical specific capacity [1–4] and as p-type semiconductors with high hole mobility [5–7]. The performances of such applied materials depend on the crystallite size and shape, and the morphology of the secondary particles, and thus the control of SnO particles in nanometer scale is important for the practical applications. Crystal growth in aqueous solutions is effective synthetic route for nanostructured inorganic materials. The nucleation and growth of inorganic crystals are controlled by the adjustment of the degree of supersaturation and the addition of organic molecules, which frequently lead to the formation of architectures consisting of nanoscale crystalline units. Previously, various types of SnO particles have been prepared via aqueous routes [2–4,8–17]. Ning et al. reported the preparation of SnO nanocrystals with hierarchical structure by the heat treatment of $Sn_6O_4(OH)_4$ in aqueous solutions containing 1-octadecene and oleylamine at 90 °C [3]. Imai et al. prepared SnO plates, blocks, meshes and flowers by heating $Sn_6O_4(OH)_4$ in aqueous solutions at 25–60 °C [4,10–14]. Wang et al. obtained single-crystalline SnO nanosheets from $SnCl_2$ solutions containing poly(vinylpyrrolidone) under ultrasonic irradiation [15]. These suggest that aqueous solution process holds promise for the fabrication of nanostructured SnO particles.

Recently, biomineralization has received attention as a good model for aqueous routes assisted by organic molecules. Carbonate-based biominerals such as nacres, corals, sea urchin spines, and eggshells consist of oriented and bridged calcite nanounits of 10–50 nm, and such highly-ordered nanostructures are deduced to be formed by self-assembly and self-organization via interaction between carbonate materials and biological polymers (e.g., chitin, chitosan and gelatin) [18–28]. These indicate that biological polymers could be effective organic additives for the fabrication of nanostructured inorganic materials via aqueous routes. In this work, we address the preparation of nanostructured SnO particles through crystal growth in aqueous solutions containing gelatin. Gelatin is a biological polymer that contains many polar amino acids [29], and thus adsorbs on the surface of inorganic crystals such as ZnO [30,31], $CeCO_3OH$ [32] and $LaCO_3OH$ [33], leading to the formation of biomimetic architectures consisting of nanounits. Here, SnO particles were prepared from $Sn_6O_4(OH)_4$ by the hydrothermal treatment in aqueous solutions containing gelatin. We varied the amounts of gelatin in the solutions, and investigated the effects of gelatin on the morphology of SnO crystals.

2. Experimental

NaOH solutions of pH 13.5 were prepared by dissolving NaOH (Wako Pure Chemical Industries, Osaka, Japan) with purified water. 1.25 g of SnF_2 (Wako Pure Chemical Industries, Osaka, Japan) were added into a 40 cm^3 NaOH solution under stirring at

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http://dx.doi.org/10.1016/j.jssc.2014.05.023
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room temperature ([SnF_2]=0.2 M), where white precipitates were immediately produced. After stirring the solution for 1 h, the white precipitates were removed from the solutions by centrifugation. Gelatin solutions were prepared separately by an addition of 0–16 g of gelatin (Wako Pure Chemical Industries, Osaka, Japan) in a 40 cm^3 purified water ([gelatin] (C_{ge})=0–400 g L^{-1}), and were mixed with the white precipitates. (The typical structure of gelatin is shown in Supporting information Fig. S1.) The suspensions thus obtained were hydrothermally treated at 150 °C in a Teflon-lined stainless steel autoclave (75 cm^3, Flon Industry, Tokyo, Japan) for 24 h, resulting in the formation of black precipitates. The black precipitates were washed with purified water and dried at 60 °C for 24 h.

The crystalline phases were identified by X-ray diffraction (XRD) measurement in ordinary $2\theta/\theta$ mode using an X-ray diffractometer (Model Rint 2550 V, Rigaku, Tokyo, Japan) with Cu*K*α radiation operated at 40 kV and 300 mA. The microstructure of the products was observed using a field emission scanning electron microscope (FE-SEM) (Model JSM-6500F, JEOL, Tokyo, Japan) and a field-emission transmission electron microscope (FE-TEM) (JEM-2000EX, JEOL, Tokyo, Japan). Infrared (IR) absorption spectra were measured with a Fourier transform infrared (FTIR) spectrophotometer (FT/IR-410, Jasco, Tokyo, Japan), using the KBr method. The chemical compositions were determined by X-ray photoelectron spectroscopy (XPS) analysis (PHI 5000 Versa Probe, ULVAC-PHI, Kanagawa, Japan).

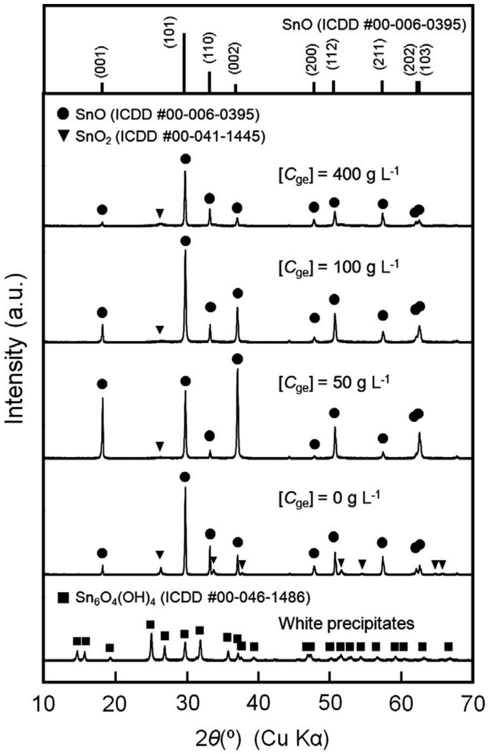

Fig. 1. XRD patterns of the white precipitates as a precursor and the black precipitates prepared at C_{ge}=0–400 g L^{-1}.

3. Results and discussion

White precipitates as a precursor were immediately produced by an addition of SnF_2 into NaOH solutions of pH 13.5 at room temperature ([SnF_2]=0.2 M), and then black precipitates were obtained from the white precipitates by the hydrothermal treatment in gelatin solutions at 150 °C for 24 h ([gelatin] (C_{ge})= 0–400 g L^{-1}). Residual fluoride ions below 3 mol% were detected in the precipitates by XPS analysis. (The chemical compositions of the precipitates obtained at C_{ge}=0 and 100 g L^{-1} are shown in Supporting information Table S1.) Fig. 1 shows the XRD patterns of the white and black precipitates. The diffraction peaks attributed to $Sn_6O_4(OH)_4$ were observed for the white precipitates. On the other hand, tetragonal SnO was detected for the black precipitates irrespective of C_{ge}, where the peak intensity of the (0 0 1) and (0 0 2) planes observed for the precipitates at C_{ge}=50–100 g L^{-1} was higher than those described in the ICDD card (SnO: #00-006-0395). Moreover, the diffraction peaks attributed to SnO_2 were slightly observed for the black precipitates irrespective of C_{ge}. The peak intensity of SnO_2 weakened by the addition of gelatin, which suggests that the nucleation of SnO_2 crystals was suppressed by gelatin.

Fig. 2 shows the SEM images of the SnO products obtained at C_{ge}=0–400 g L^{-1}. (Low-magnification SEM images of the SnO products including those prepared at intermediate conditions of C_{ge}=25, 200 and 300 g L^{-1} are shown in Supporting information Fig. S3.) Block-like SnO particles of 10–20 μm in width and 5–10 μm in thickness were obtained from $Sn_6O_4(OH)_4$ by the hydrothermal treatment in purified water (C_{ge}=0 g L^{-1}) (Figs. 2a and b). The addition of gelatin led to the morphological change of SnO particles. Layered disks were observed at C_{ge}=50 g L^{-1}, where a few disk-like units of ca. 10 μm in width and ca. 500 nm in thickness made up such layered secondary particles (Fig. 2c and d). Stacked architectures consisting of plate-like units of ca. 2–5 μm in width and ca. 500 nm in thickness appeared with increasing C_{ge} to 100 g L^{-1} (Fig. 2e). Fig. 3 shows the TEM images of the fraction of the stacked plates obtained at C_{ge}=100 g L^{-1}. The selected area electron diffraction (SAED) patterns show that the stacked plates consist of single-crystalline units (Fig. 3a). Moreover, fine particles of ca. 5 nm in size were partly observed in the fraction, where the lattice fringes identified to the (1 1 0) planes of tetragonal SnO were clearly found in such particles (Fig. 3b). The layered disks and stacked plates obtained at C_{ge}=50 and 100 g L^{-1}, respectively, exhibited the intense diffraction peaks of the (0 0 1) and (0 0 2) planes in the XRD patterns (Fig. 1), which indicates that the flat face of the disk- and plate-like units is the (0 0 1) plane of SnO crystals. The further increase in C_{ge} to 400 g L^{-1} led to the formation of unshaped aggregates of fine particles with inhomogeneous size and shape (Fig. 2f).

Fig. 4 shows the IR absorption spectra of the SnO products obtained at C_{ge}=0 and 100 g L^{-1}. In both cases, absorption bands were detected at around 580 and 3400 cm^{-1}. The broad band at 3400 cm^{-1} is assigned to the stretching vibrations of O–H. The broad band at around 580 cm^{-1} may be attributed to the Sn–O bonds [34]. The absorption bands at around 1250, 1380, 1450, 1650, 2850 and 2900 cm^{-1} were detected in the spectrum of the products obtained at C_{ge}= 100 g L^{-1}. The bands at 1250 and 1650 cm^{-1} are assigned to carboxylate groups that act as the monodentate ligands of metal ions, and the bands at 1380, 1450 cm^{-1} are assigned to that act as the bidentate ligands [35,36]. The bands at 2850 and 2900 cm^{-1} are assigned to the symmetric and asymmetric stretches of methyl groups. These absorption bands attributed to carboxylate and methyl groups suggest the adsorption of gelatin on the SnO products. On the other hand, the carbon contents in the product at C_{ge}= 100 g L^{-1} measured by XPS analysis was smaller than that at C_{ge}=0 g L^{-1} (Supporting information Table S1), which indicates that the amount of gelatin remaining in the precipitates was very low.

In this work, crystalline SnO particles were obtained from $Sn_6O_4(OH)_4$ by the hydrothermal treatment in gelatin solutions at 150 °C for 24 h. Here, SnO crystals are thought to be produced via the dissolution-reprecipitation from $Sn_6O_4(OH)_4$ during the hydrothermal treatment, because the size and shape of the SnO products were different from those of $Sn_6O_4(OH)_4$ as the precursor