



# Template-Free Synthesis of Tin Oxides with a Dual Pore Structure

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## ARTICLE INFO

### Article history:

Received 9 December 2015

Received in revised form 18 February 2016

Accepted 8 March 2016

Available online 16 March 2016

### Keywords:

Anodic oxidation

Sn oxide

Dual pore structure

Stress

## ABSTRACT

In this study, we report electrochemical synthesis of Sn oxides with dual-pore structure by employing anodic oxidation without the use of a porous template. As-prepared Sn oxide layers contain hemispherical micropores of less than 2  $\mu\text{m}$  diameters and nanopores of less than 50 nm diameters. The formation and size of the micropores strongly depended on the thickness of the Sn layer and the type of the underlying substrate. A two-step anodic oxidation process produced a completely open pore structure, resulting in robust interconnections between the micropores and nanopores. The tensile stresses originating from the anodized Sn oxide and the associated local distortion of the Sn metal underneath it are the likely driving forces for the formation of micropores.

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## 1. Introduction

Metal oxides that contain nano-channelled structures with large active surface area are attracting much attention as promising electrode materials for high-performance electrochemical devices because of their capability to significantly reduce potential loss due to activation polarisation of electrodes. Since the initial report on the synthesis of nano-channelled Sn oxides by anodic oxidation [1], many fundamental and applied research works have been performed to clarify their formation mechanism [2,3] and to promote their applications as functional electrode materials [4–9]. Some applications are as follows. (1) gas sensors that show high sensitivity toward specific substances [4–6]; (2) anodes that extend lifetimes of Li secondary batteries to efficiently relieve the stress induced in Li-Sn alloys during cycling and hence to increase the battery's lifetime [7]; (3) supercapacitors with high specific capacitance and long cycle life [8]; and (4) photo-electrochemical material with broad photoresponse characteristics, which can be tuned according to thermal annealing conditions [9].

Despite the popularity of nanoporous metal oxide as electrode materials, scaling up mass transfer rates through nanopores remains a challenge. When the overall rate of electrode reactions is governed by mass transfer, the performance of the electrode (or the electrochemical device) will be limited by concentration

polarisation due to the depletion of electroactive reactants and the accumulation of reaction products [10,11].

To minimize or eliminate the effect of mass transfer on electrode performance, an effective approach is to create hierarchically porous electrode structures consisting of both micropores and nanopores [12,13]. Although the volumetric surface area of such dual-porous electrodes may be reduced (relative to that of electrodes with simple nanoporous structures) by the formation of micropores, the network of micrometre-sized pores connected to numerous nanopores would significantly facilitate the rapid transport of reactants and products through the porous electrodes and thereby support high rate capability.

Here, we report the synthesis of anodic Sn oxide with dual-porous structure of nanopores and micropores without the use of any porous template. The effects of the thickness of the pre-anodized Sn layer and the type of substrate material on the size and density of the micropores were investigated. A two-step anodic oxidation process was used to produce completely open dual-porous Sn oxide. In addition, by using experimental results, the formation mechanism of micropores was analysed in terms of the mechanical stress generated during anodic oxidation.

## 2. Experimental procedure

### 2.1. Sample preparation for anodic oxidation

Three different types of substrates were used in the anodic oxidation experiments. These were prepared as follows:

**Substrate 1**—Si wafer (<100>, p-type, LG Siltron) coated by sequential deposition of Ti (5 nm), Au (100 nm), Cu (100 nm), and Sn

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(1, 20, 100, or 300  $\mu\text{m}$ -thick) layers. Here, the Au and Ti layers function as the conducting layer and the buffer layer to enhance the adhesion to the Si, respectively. The Cu layer provides a surface of superior adhesion for Sn plating.

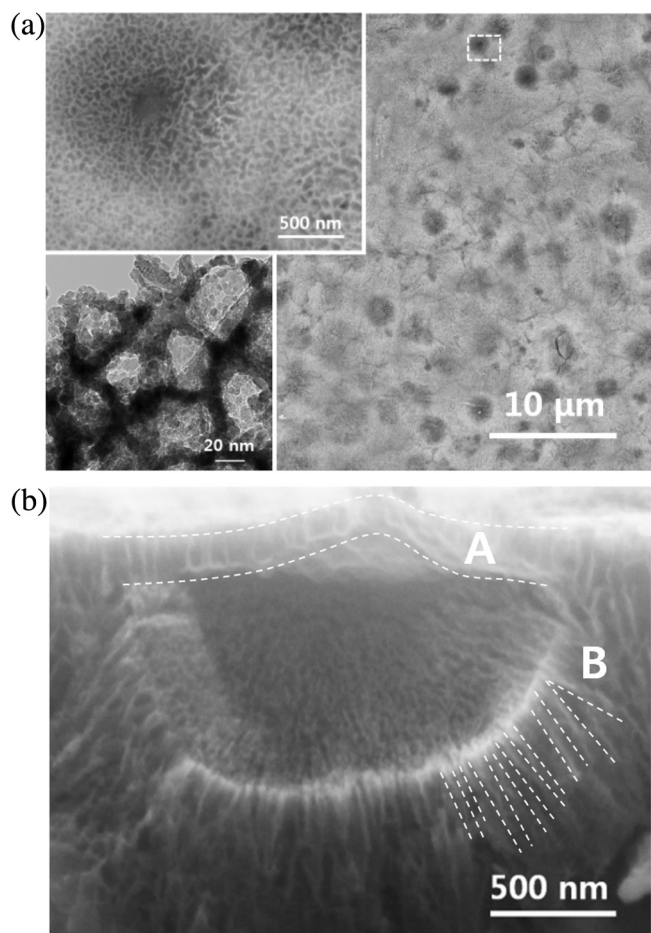
**Substrate 2**—Cu foil (99.8%, Alfa Aesar) coated with a Sn layer (1  $\mu\text{m}$  thick). The Cu foil was, first, pre-treated in 25 vol%  $\text{H}_2\text{SO}_4$  to remove the native oxide film, then washed with deionised water, and, finally, dried before Sn plating.

**Substrate 3**—Sn foil (99.9985%, Alfa Aesar). The Sn foil was polished using #2000A SiC paper followed by treatment with 0.1 M HCl to remove the native oxide film. After washing with deionised water, the Sn foil was used for anodic oxidation without further coating.

For the Sn plating of substrates 1 and 2, two-electrode cells were constructed using the pre-Sn-coated plates and Pt wire as the working and counter electrodes, respectively. The distance between the two electrodes was set to 1 cm. Sn layers of different thicknesses were deposited by applying a current density of 30  $\text{mA}/\text{cm}^2$  for various periods of time in a plating solution of Sn ( $\text{CH}_3\text{SO}_3$ )<sub>2</sub>,  $\text{CH}_3\text{SO}_3\text{H}$ , and additives (Incheon Chemical, South Korea). Sn was electrodeposited at the rate of 1  $\mu\text{m}/\text{min}$ . Plating was performed using a potentiostat/galvanostat, EG&G 263A.

## 2.2. Anodic oxidation and analyses

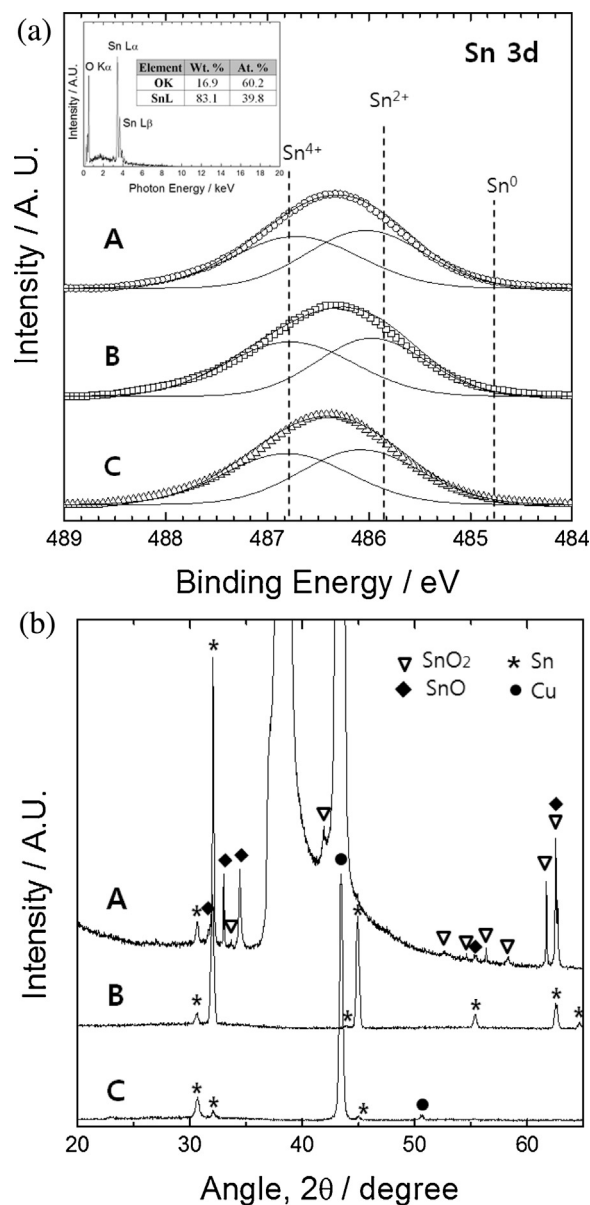
For the synthesis of porous Sn oxides, the substrates prepared as described in Section 2.1 were used as the working electrode, and Pt wire was used as the counter electrode. In an aqueous oxalic acid



**Fig. 1.** (a) Surface (top inset: magnified SEM image, bottom inset: TEM image) and (b) cross sectional views of the porous structure of Sn oxide, created from a 1- $\mu\text{m}$ -thick Sn layer on a Si wafer, after 600 pulse-anodisation cycles.

solution (0.5 M), IviumStat (Ivium Technologies, The Netherlands) was used to apply anodic pulse voltage to the working electrode to carry out anodic oxidation. A constant voltage condition was originally used in the authors' previous paper that first reported the synthesis of anodic oxides with nano-channelled structure [1]. However, such anodic Sn oxides were found to contain a large number of horizontal cracks, leading to discontinuous porous channels. In the author's recent work [14], pulsed anodisation was proposed as a method to mitigate the convective force of the  $\text{O}_2$  gas generated during anodisation, and thus, it could be a feasible way of eliminating fracture of the inner oxide layers. Since well-defined nano-channelled structures were needed in this work to more clearly analyse the formation of micropores in the oxide layer, the method of pulsed anodisation was employed.

For pulsed anodisation of tin, an anodic voltage of 8 V with a square waveform was applied. The "on-time" and "off-time"



**Fig. 2.** (a) XPS Sn 3d spectra of the anodic Sn oxides, created from a 1- $\mu\text{m}$ -thick Sn layer on a Si wafer (A), a flexible Sn foil (B), and a 1- $\mu\text{m}$ -thick Sn layer on a flexible Cu substrate (C), after 600 pulse-anodisation cycles, and (b) their X-ray diffraction patterns. Inset of (a) is the EDS spectrum obtained from the anodic Sn oxide formed on a Si wafer.

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