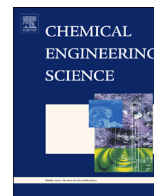




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## Scalable solvo-plasma production of porous tin oxide nanowires

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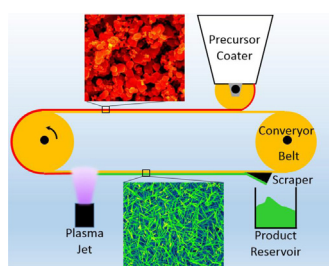
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## HIGHLIGHTS

- A fast (reaction time scale less than 1 min), scalable method for synthesizing tin oxide nanowire powder using atmospheric plasma.
- The mechanism for observed one-dimensional growth is explained through the observation of an intermediate phase involving potassium stannate.
- The conversion of potassium stannate nanowires through acid wash followed by simple annealing step resulted in porous tin oxide nanowires.
- The resulting porous tin oxide nanowire powder shows a high reversible capacity of  $848 \text{ mA h g}^{-1}$  after 55 cycles at a current density of  $100 \text{ mA g}^{-1}$ .
- A large-scale production of tin oxide nanowire powder as high as 10 g per hour has been produced and could be increased further up to 300 g per hour using a lab-scale roll-to-roll setup.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This paper reports a fast, scalable method for synthesizing tin oxide nanowire powder using cheap starting material of commercial tin oxide particles and an atmospheric microwave plasma reactor. Specifically, the synthesis concept involves plasma oxidation of tin oxide powder combined with potassium hydroxide for few seconds to a minute which is orders of magnitude lower than that using hydrothermal or vapor-liquid-solid (VLS) techniques. Even at lab scale, large-scale production of tin oxide nanowire powder as high as 10 g per hour has been produced. Systematic studies reveal nucleation and growth of  $\text{K}_2\text{SnO}_3$  nanowires from molten alloy involving KOH and tin oxide. A simple annealing step is used to convert  $\text{K}_2\text{SnO}_3$  intermediate nanowires into pure tin oxide nanowires. The extremely short reaction time of 20 s is three orders of magnitude faster than that of traditional hydrothermal method. It was shown that our tin oxide nanowire powder shows a high reversible capacity of  $848 \text{ mA h g}^{-1}$  after

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## 1. Introduction

Tin oxide nanowires is one of the most promising 1D nanostructures for advanced applications in lithium-ion batteries (Meduri et al., 2009), solar cells (Gubbala et al., 2009), sensors (Hui et al., 2006), optical devices (Chandra et al., 2008), and electronic devices (Kolmakov et al., 2008). However, the wide-spread use of nanowire based materials in to energy device applications has been limited due to the fact that there are no scalable manufacturing methods, yet. For example, the lithium-ion battery electrodes will require production on the order of kilograms even for simple pouch cell prototyping. Thus, the development of reliable, reproducible and simple techniques for production of tin oxide nanowires and their testing into energy devices is of great interest. Up to date, several approaches have been proposed to prepare tin oxide nanowires including chemical vapor deposition (Dai et al., 2002), laser ablation (Liu et al., 2003), template method (Zhang et al., 2011) and most predominantly hydrothermal technique (Wang et al., 2003).

Hydrothermal synthesis has been traditionally used to prepare nanostructured materials including nanoparticles and nanowires. However, this approach requires long time scale, high pressure, multiple steps and expensive precursors (Zhang et al., 2006). Further, in most cases, hydrothermal techniques require the use of surfactant to control the nanowire growth. Also, no clear mechanism for tin oxide nanowires have been proposed. Importantly, the hydrothermal techniques are limited to lab scale (few milligrams to hundred milligrams a batch) (Cheng et al., 2004; Jian et al., 2003). Two recent hydrothermal based approaches are microwave assisted hydrothermal and continuous flow hydrothermal method, which can increase the production rate to about 5 g/day and 10 g/h, respectively (Cabanas et al., 2000; Chung et al., 2008). However, these hydrothermal methods have been shown to work only for nanoparticles (NPs) and not to make nanowires. Another popular method for making nanowire growth is that using vapor-liquid-solid (VLS) process for many semiconductors including tin oxide (Dai et al., 2002). However, VLS processes require the use of low pressure, high temperatures, high fabrication cost and Au as catalyst.

In this work, we report a facile, fast "solvo-plasma" production of tin oxide nanowires using tin oxide particles as a low-cost source. This study demonstrates, for the first time, the direct conversion of tin oxide particles to tin oxide nanowires with reaction time scales on the order of a minute or lower. More importantly, various experimental studies are used to understand the underlying principle of nucleation and growth of tin oxide nanowires in the presence of alkali hydroxides. Thin films made using the resulting tin oxide nanowire powders are also investigated for their performance as high capacity anodes in lithium ion batteries.

## 2. Experimental

Tin oxide nanowires are synthesized in an upstream microwave plasma reactor whose details have been described in detail elsewhere (Kumar et al., 2011). Briefly, tin oxide particles ( $1 \div 5 \mu\text{m}$  size, Atlantic Equipment Engineer, Inc) are mixed with KOH powder in a 3:1 ratio by weight and water is added to make the

precursor paste. The precursor paste is then sprinkled on the top of a  $1 \times 1$  in. quartz substrate (Fig. 1a), which is then carefully exposed to the plasma flame at power of 1.0–1.4 kW, 8 l pm of Air flow for 10 s to 5 min. The as-synthesized materials are dispersed in 0.1 M HCl solution for 1 h to facilitate ion exchange, washed with deionized water, and annealed by exposure to plasma flame for 1–5 min. The samples are characterized using a scanning electron microscope (SEM) (FEI Nova 600), X-ray diffraction (Bruker D8 Discovery with Cu  $K\alpha$  radiation), and a transmission electron microscope (TEM) (Tecni F20 FEI TEM operating at 200 kV).

The electrochemical measurements are performed using a battery tester (16 Channel Arbin Instruments, USA). The electrode materials were prepared using 70 wt% active materials with 20 wt% AB (acetylene black) and 10% PVDF binder in NMP. The well-mixed slurry was casted onto a copper foil using a doctor blade. The electrode is dried at  $180^\circ\text{C}$  for 4 h under vacuum. The typical loading of active materials is  $0.2\text{--}0.5 \text{ mg/cm}^2$ . The CR-2032 coin-type assembling is performed in a dry argon-filled glove box. The electrodes are separated by two pieces of glass fiber filter. The electrolyte solution was 1 M  $\text{LiPF}_6\text{-EC:DMC}$  (1:2 by volume).

## 3. Results and discussion

All experiments are performed using inexpensive, commercial tin oxide particles without any further purification by mixing them with KOH and exposing to atmospheric plasma flame for 15 s to 1 min. Using a 1-in. square substrate, we were able to demonstrate production of tin oxide nanowires at a scale of 10 g in one hour (Fig. 1b). The exposure time used here is less than a minute which is about 3.5 orders of magnitude faster than that using a hydrothermal method. Fig. 2a shows SEM images of the resulting tin oxide nanowires that are  $2 \mu\text{m}$  in length and about 50–100 nm in diameter. The TEM images of tin oxide nanowires show highly porous structures of tin oxides, which is due to HCl ion exchange and plasma annealing step (Fig. 2b, and c). The BET surface area of the porous tin oxide nanowires turned out to be  $37 \text{ m}^2/\text{g}$ . The BET surface area could be increased further by controlling the ion exchange and annealing parameters. The phase transformation of intermediate nanowires to tin oxide nanowires created the porous structures where potassium and water vapor are removed. The porous structures consisted of interconnected tin oxide nanoparticles. The underlying mechanism for porous structure formation seems to be similar to that suggested in many other reports using hydrothermal synthesis with additional annealing step (Wang et al., 2003). However, the actual mechanism is not completely clear in terms of how phase transformation leads to porous nature within the nanowires. Fig. 2c also revealed the twinning effect where the boundary in the top left corner clearly showed merging of two nanowires. The merging maybe due to the high surface diffusion of tin atoms on nanowire surface under plasma exposure (Ostrikov et al., 2010). The HR-TEM image in Fig. 2d shows the match of interplanar lattice spacing of  $3.35 \text{ \AA}$  and  $2.64 \text{ \AA}$  for the plane (110) and (101), respectively.

The powder XRD pattern of tin oxide nanowires after annealing in plasma is shown in Fig. 3. The diffraction peaks revealed that tin oxide nanowires have tetragonal crystal structure with lattice

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