Single crystal tin nano-rod arrays electrodeposited by a soft template

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Received (in Cambridge, UK) 11th July 2005, Accepted 16th August 2005
First published as an Advance Article on the web 8th September 2005
DOI: 10.1039/b509818a

Single crystal tin nano-rod arrays were fabricated by the electrodeposition method when amphiphilic triblock copolymer P123 was used as a soft template at a concentration much lower than that for forming a liquid crystalline phase.

Metal nano-wires have been studied for their important roles as active components and/or interconnectors in fabricating nano scale electronic or optoelectronic devices. It has been known that electrodeposition is an efficient and ready technique for preparing metal nano-fibers by employing hard templates such as mesoporous silicas,[1] alumina templates,[2,3] polycarbonate membranes[4,5] and carbon nanotubes.[6,7] Although the use of physical templates may have the advantages of predefined 1D morphology and controllable wire diameters, there are also a number of intrinsic shortcomings or limitations. For example, it is very difficult to prepare single crystal nano-rods using hard templating methods. There is also another method of obtaining nano-metal particles: using soft templates such as lyotropic liquid crystalline phase materials.[8,9] However, there are very few reports on the electrochemical synthesis of nano-rod arrays of tin though mesoporous tin has been synthesized by using $C_{18}EO_{10}$ as a surfactant.[10] In this communication, we report the preparation of single crystal tin nano-rod arrays by the electrochemical deposition method when amphiphilic triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer ($EO_{20}PO_{70}EO_{20}$, P123) is used as a soft template at a concentration much lower than that required for forming a liquid crystalline phase. Comparison of the structure with those prepared without P123, shows that the presence of amphiphilic triblock copolymer P123 results in fundamental changes in the microstructures of the electrodeposited tin. The tin with a 1D nanostructure is of particular significance because the unique morphology bears several important features. Due to their array structure, tin nano-rods can be used as novel cathodes of electron emitters for field electron emission applications[11] and can shorten the Li^+ diffusion pathway and release the pressure induced by volume expansion upon lithium insertion from the viewpoint of high specific surface area and pore volume.

A typical electroplating solution was prepared as follows: 15.87 g of 0.15 M $SnSO_4$ and 0.6 M H_2SO_4 solution were mixed with 12.5 g ethanol solution of P123 (0.033 g P123 per ml ethanol). The mixed solution underwent magnetic stirring for 1 h until the solution became as turbid as milk. An electrolysis copper and a cast tin plate were used as the cathode and anode, respectively. The electrodeposition was conducted using a galvanostatic electroplating circuit. After deposition, the electrode was washed with ethanol in order to remove the surfactant. The electrode was subsequently dried in air. The microstructures of the samples were characterized by X-ray diffraction (XRD; Bruker D8 Advance X-ray diffractometer, Cu-Kα radiation at 40 kV and 40 mA), scanning electron microscopy (SEM; Philips XL30 at 30kV) fitted with an energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM; JEOL JEM 2011 at 200 kV).

The effect of experimental conditions on the growth of the plating tins was carefully studied. The electroplating solution consisted of water, ethanol, $SnSO_4$, H_2SO_4 and copolymer P123. It was found that in order to obtain tin nano-rod arrays, an aging process for the electroplating solution was necessary before adding the P123. During the aging period, a very small amount of pale yellow-white precipitate (SnO_2) was observed, which might be produced *via* an oxidation reaction by the oxygen in the air. Some Sn^{2+} ions were oxidized to Sn^{4+} as reported by Donaldson and Moser.[12] The trace amount of Sn^{4+} may influence the electrochemical deposition process strongly. The existence of P123 in the electroplating bath is also very important to obtain tin nano-rod arrays. Fig. 1 shows the morphologies of tin thin films deposited from electroplating solution with or without P123 for 60 min at current density of 3.2 mA cm^{-2} at different temperatures. At a temperature of 30 °C, the electrodeposited tin is in the form of cuboid rods (Fig. 1a), which are perpendicular to the substrate. The edge of the cross section is about 1–3 μm. But when the deposition temperature was tuned to 40 °C, large domain tin nano-rod arrays were formed as shown in Fig. 1b. It looks just like the micro sized tin cuboid rods, as observed in Fig. 1a, are divided into many uniform tin nano-rods. The diameter of the nano-rods is

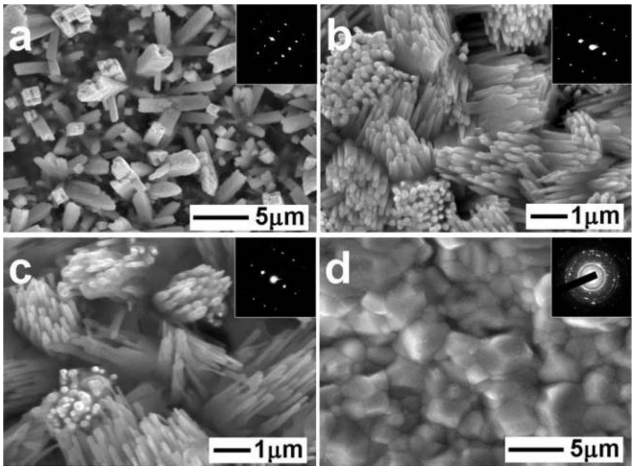

Fig. 1 SEM images and SAED patterns of tin electrodeposited from solutions with P123, at 30 °C (a), 40 °C (b), 50 °C (c), and without P123 at 30 °C (d), for 60 min.

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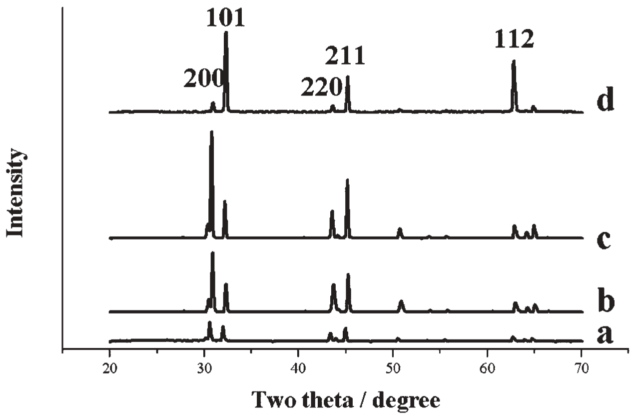

Fig. 2 XRD patterns of tin samples electrodeposited from solutions with P123 at 30 °C (a), 40 °C (b) and 50 °C (c), and without P123 at 30 °C (d).

about 140 nm. However, with the temperature increasing to 50 °C, the tin nano-rods became thinner and more irregular with a diameter of about 120 nm (Fig. 1c). For comparison purposes, we also tried the deposition of tin at 30 °C from a similar electrolyte but without surfactant P123. The electrodeposited tin film shows a rough granular structure as shown in Fig. 1d, and no tin nano-rods can be observed.

Selected area electron diffraction (SAED) patterns (inset in Fig. 1) show that the tin nano-rods prepared with P123 at 30, 40 and 50 °C are in a single crystalline structure. The diffraction pattern doesn't change as the electron beam scans across individual rods, suggesting that these tin nano-rods are single crystalline with the same lattice structure. However, SAED patterns also show that without P123 the electrodeposited tin is in polycrystalline structure, further suggesting that the copolymer P123 plays a significant role in the formation of the single-crystalline structure. The single crystalline structure of tin nano-rods was further confirmed by high-resolution TEM image (not shown here).

The X-ray diffraction (XRD) patterns of the tin thin films electrodeposited with P123 at temperatures of 30, 40 and 50 °C are presented as curves a–c in Fig. 2, respectively. Curve d is the one for the sample electrodeposited without P123 at a temperature of 30 °C. The peaks can be assigned to the diffraction from (200), (101), (220), (211) and (112) crystal planes of tetragonal tin as labelled on the curves. For curve b, using Bragg's equation, the lattice interplanar *d*-spacing constants for those planes are calculated as 2.90, 2.78, 2.08, 2.01, and 1.48 Å respectively, which are in agreement with the report of Powder Diffraction Standards file No.01-0926. Furthermore, the value of 2.90 Å agrees with the fringe spacing measured from the HRTEM image. It is worth noting that the intensity ratios between the (200) and (101) peaks, and between the (200) and (112) diffraction peaks of the tin nano-rods (2.12 and 6.17 for curve b, 2.87 and 8.18 for curve c, respectively) are much higher than those for the corresponding bulk materials (1.25 and 4.17 respectively, JCPD 01-0926). This may suggest that the {100} planes are the most abundant planes of the single crystalline tin nano-rod samples. It can be proposed that the amphiphilic species P123 tends to suppress the growth rate of the other planes more than that of the {100} planes, leading to the preferential growth rate, which is of essential importance for the growth of 1D nano-materials. A similar special characteristic of the surfactant was also observed for the chemical synthesis of gold and silver nanoparticles using poly(vinylpyrrolidone) (PVP) as a surface active additive by Xia.[13]

We also investigated the relationship between the morphology of tin and various experimental parameters including electrodeposition time, the distance *d* between the two electrodes, and current density. At 30 °C and a fixed current density of 3.2 mA cm^{-2}, we found that the morphologies of the tin nano-rods at electrodeposition times of 30, 60, 90, 120 and 180 min were similar to each other but that uniformity decreased as the deposition time increased. The electrodeposited tin was the same as that obtained without P123 under similar conditions when the distance *d* increased to 5 cm. When changing the current density, various tin nano-rods with different dimensions could be obtained with current densities higher than 3.2 mA cm^{-2}. These phenomena could be explained by the influence of the electric field on the orientation of the P123 micelles in the liquid phase and at the surface of the electrode.[14]

In brief, well ordered single crystal tin nano-rod arrays have been prepared *via* electrodeposition by using P123 as a soft template. The precipitate of SnO_2 and P123 are suggested to be essential for the growth of the tin nano-rods. Due to the defined morphology and crystal planes, tin nano-rods can be employed as electrodes for various applications such as in the field of batteries and field emission devices.

This work is supported by the Natural Science Foundation of China (NSFC No.20333040).

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