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Preparation of Nanowire Arrays of Amorphous Carbon Nanotube-Coated Single Crystal SnO_2

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Tin oxide is an important wide band n-type semiconductor as a result of its numerous potential applications in resistors, gas sensors, dye sensitized solar cells, and transparent conducting coatings for glasses and electrodes. It is also a prospective anode material for high-energy density lithium ion batteries.[1] So far much work has been conducted on one-dimensional (1-D) metal oxides because their large ratio of surface/volume, and the congruence of their carrier screening length with their lateral dimensions make them efficient electronic nanodevices. One-dimensional SnO_2 materials were recently reported to be fabricated by thermal evaporation,[2–7] solution precursor route,[8] and template method.[9,10] Up to now, synthesis of single-crystal SnO_2 nanowires is mainly focused on vapor transport processes, and the resulting nanowires are entangled. However, the thermal evaporation requires high temperature (1000–1350 °C).[2–7] Other methods mainly resulted in polycrystalline array structures.[9] Reports on successfully synthesizing large scale single-crystal SnO_2 nanowire arrays are very rare. Here we report on the development of an easy fabrication method for highly ordered tetragonal single-crystal SnO_2 nanowire arrays using anodic alumina membrane (AAM) as a template via a sol–gel route employing citric acid as a chelating complex. In addition, the as-prepared SnO_2 nanowires are coated with in situ formed amorphous carbon nanotubes (a-CNT). Such a microstructure has the advantage of regular electron screening length in the lateral direction, and its outer carbon layer supplies the electronic transportation along the nanowire axis, making it an ideal host for lithium storage.

The AAM templates were prepared by the method described in the literature,[11] and through-hole membranes were obtained with a mean pore diameter of 80 nm (See Supporting Information). The preparation process for the nanowire arrays of the amorphous carbon nanotube-coated single crystal SnO_2 is shown in Scheme 1. As to the details, please see Supporting Information.

Scheme 1. Illustration of the Synthesis Process of the Nanowire Arrays of a-CNT-Coated Single-Crystal SnO_2

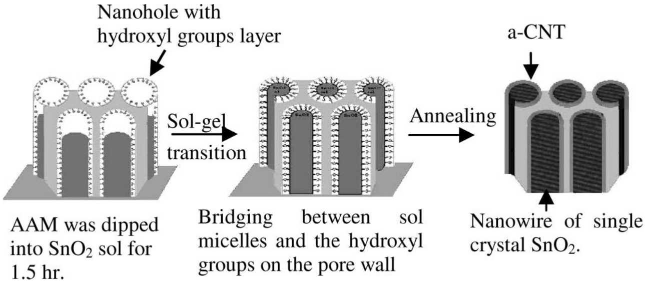

Figure 1 shows the scanning electron micrographs (SEM, Philips XL30) and transmission electron micrograph (TEM, JEOL JEM-2010) of the prepared nanowire arrays of SnO_2. In Figure 1a, SnO_2 nanowire arrays emerged after the alumina was partially removed by immersing in 0.5 M NaOH solution for 2 h. Figure 1b presents that the SnO_2 nanowires without the AAM template, which was removed by immersing in 1 M NaOH solution for 4 h, are uniform with a mean diameter of 80 nm. Figure 1c shows the image of a single SnO_2 nanowire, and the corresponding selected area electron diffraction (SAED) pattern is shown in the inset, which indicates the typical characteristics of a perfect single-crystal structure where all the diffraction spots can be indexed to the $[11\bar{2}]$ zone axis of SnO_2 with rutile structure. The high resolution TEM micrograph taken from the edge area of the nanowire shows the facets parallel to the (110) plane, as

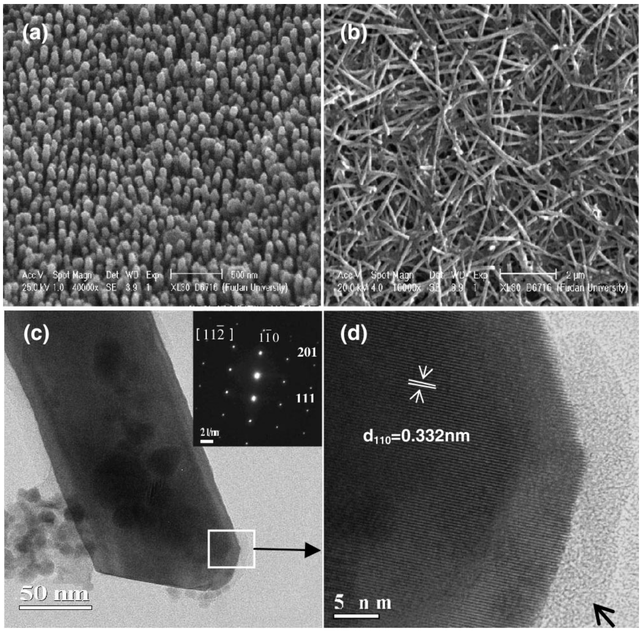

Figure 1. SEM micrographs of SnO_2 nanowires after the AAM was (a) partially and (b) totally removed by immersing in 0.5 and 1 M NaOH solution for 2 h and 4 h, respectively; (c) TEM image of single SnO_2 wire after the AAM was totally removed (inset is the corresponding SAED pattern of the single-crystal SnO_2), and (d) HRTEM micrograph of the marked area in picture (c) with a square.

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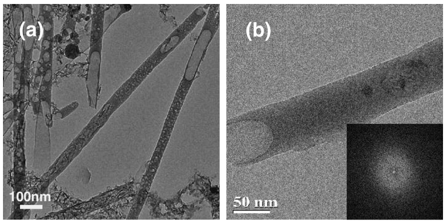

Figure 2. TEM micrographs of (a) the remains of the composite after the removal of the core SnO_2 nanowires and (b) individual tube in Figure part a with an open end (inset: fast Fourier transform of the amorphous nanotube).

marked in Figure 1d. The interplanar spacings of the nanowires were measured to be 0.332 and 0.236 nm, corresponding to the (110) and (111) planes of a tetragonal SnO_2. Analysis of the SAED pattern reveals that the tetragonal SnO_2 crystal structure is consistent with the rutile SnO_2 (*P*42/*mnm*, JPDCS No. 41-1445), which can also be identified in the X-ray diffraction (XRD) pattern (See Supporting Information).

A thin layer with an average thickness of about 7 nm was observed at the surface of SnO_2 nanowires, as marked in Figure 1d with a black arrow.

The obtained SnO_2 arrays were further immersed in hot concentrated NaOH solution to remove the core SnO_2 nanowires, and TEM micrographs of the remains are shown in Figure 2. Evidently, the remains are from the surface layer on the single crystal SnO_2 and consist of nanotubes. The fast Fourier transform pattern (the inset FFT in Figure 2b) of the nanotube suggests it is amorphous. The energy dispersive X-ray detection (EDX) (see Supporting Information) confirms that the component element of the tube is carbon. Thus, it is clearly presented that the thin layer consists of amorphous carbon nanotubes (a-CNTs). That means we successfully prepared nanowire arrays of single crystal SnO_2 coated by amorphous carbon nanotubes. As to the formation of the a-CNTs, this is due to the pyrolysis of citric acid (complexing agent) under anoxic conditions in the nanopores, even though the heat-treatment was performed in the air atmosphere, which is quite different from our original expectation.

It is thought that the citric acid coordinates with Sn^{2+} metal ions in the as-prepared sol. During the dipping process, citric acid partially coordinates with the dangling hydroxyl groups on the walls of AAM pores forming Sn−-citric acid−AAM bonds. During the annealing process, the citric acid continuously moves toward the pore walls because of phase separation between citric acid and the SnO_2 gel. Although the annealing process was taking place in air, there was an inert or reductive atmosphere inside the pores which are virtually inaccessible to oxygen. Consequently, citric acid was transformed into amorphous carbon along the walls of the pores of AAM. The carbon layer along the walls of the pores formed carbon tubes. In the meanwhile, SnO_2 nucleated and grew into a single crystal nanowire in the nanopore. Therefore, the a-CNT coated single crystal SnO_2 was obtained. This sol–gel template method provides an easy way to fabricate nanowire arrays of oxides coated with in situ formed a-CNTs.

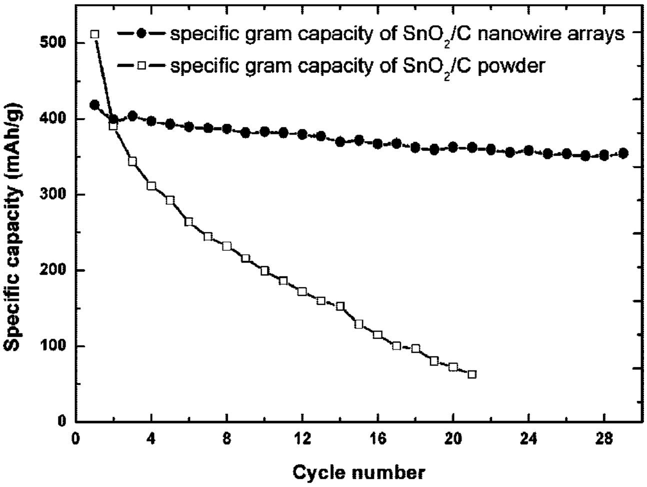

Figure 3. Cycling curves of the as-prepared SnO_2 nanowire arrays coated with a-CNT.

SnO_2 has been suggested as an alternative anode material with high reversible capacity in lithium ion batteries.[1] To demonstrate lithium insertion, a thin layer of Au was sputtered beforehand on to one side of the membrane. Then the a-CNT coated single-crystal SnO_2 nanowires embedded in the AAM were directly put into a test cell as a working electrode. The amount of the active SnO_2 was determined by ICP measurement. For comparison, a working electrode was also fabricated by mixing SnO_2 powder prepared by the sol–gel method, carbon black, and PVDF binder.

The SnO_2 nanowire array exhibits a reversible capacity of 418 mA h/g based on the weight of SnO_2 in the first cycle. Its cycling performance was greatly enhanced, as seen in Figure 3. After 30 cycles the discharge capacity still remained 353 mA h/g, while the specific capacity of the SnO_2 powder on the first discharge was 511 mA h/g, dropping rapidly to 62 mA h/g after 23 cycles. The main reason for this phenomenon is that a large volume expansion of the SnO_2 material occurs during the cycling, leading to the pulverization of the electrode.[12] In the case of the as-prepared SnO_2 nanowire arrays coated with a-CNT, the dimensional confinement of the nanowires by the surrounding a-CNT and AAM limit the volume expansion upon lithium insertion, which is consistent with carbon-coated porous SnO_2.[13] Hence, the stress formed during the process of lithium insertion was avoided. Even though the volume expansion has happened, the electrode was not pulverized. Furthermore, the in situ obtained a-CNT coating supplied electronic conductive channels and improved the conductivity of this material, and its electrochemical performance was greatly enhanced as anode in lithium ion batteries.

In summary, nanowire arrays of single-crystal SnO_2 coated with amorphous carbon nanotubes can be easily fabricated by drying and annealing the anodic alumina membrane filled with SnO_2 sol supported by citric acid chelating agent. Such nanowire arrays show great promise for application. For example, when they are used as anodes in lithium ion batteries, the cycling performance is greatly improved. In

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addition, other nanowire arrays of a-CNTs coated oxides can also be prepared by this process.

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Supporting Information Available: Synthesis details, SEM image of AAM, electrochemical preparation and electrochemical testing, XRD pattern of SnO_2 wires and SnO_2 powder, EDX of the a-CNT in Figure 2b, and additional TEM images of the single crystal nanowires (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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