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Synthesis of SnO_2 Nanoribbons by Direct Oxidation of Tin Powders

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A new method has been successfully developed to synthesize SnO_2 nanoribbons in a large scale by direct oxidation of tin powders. The lengths of the nanoribbons were up to several hundreds of micrometers, and the width and thickness were in the range of 20–150 nm and 10–50 nm, respectively. The as-synthesized SnO_2 nanoribbons had preferred [001] growth direction.

The rutile form of tin dioxide is an n-type semiconductor with a wide band gap ($Eg = 3.6\,\text{eV}$, at 300 K) and well-known for its potential applications in gas sensors,[1] dye-based solar cells,[2] transparent conducting electrodes[3] and catalyst supports.[4] Recently, one-dimensional (1D) nanoscale materials have stimulated great interest because of their unique physical properties and their potential applications in nanodevices. The newly distinct 1D nanostructures with beltlike (or ribbonlike) morphology, which has a rectangular cross section, have been successfully prepared for semiconducting metal oxides.[5–10] It has been found that individual SnO_2 nanoribbons are small, fast and sensitive devices for detecting ppm-level NO_2 at room temperature under UV light.[11] SnO_2 nanoribbons have been synthesized by evaporating SnO_2 powders at 1400 °C or SnO powders at $\geq$1000 °C, and the yield of products was only about 20–30%.[6] In addition, it has been reported that SnO_2 nanowires, nanotubes and SnO diskettes can also be synthesized at different place downstream of the alumina tube,[12,13] so the products may be a mixture of above-mentioned nanostructures. These disadvantages limited the application of the SnO_2 nanostructures. So the synthesis of SnO_2 nanoribbons with high purity is very important. In this paper, we report a simple route for large-scale preparation of SnO_2 nanoribbons on the source place.

The experimental apparatus consists of a horizontal tube furnace, an alumina tube ($\phi 4 \times 100\,\text{cm}$), a rotary pump system, and a gas supply and control system. The alumina tube was mounted inside the horizontal high-temperature tube furnace. Both ends are sealed by rubber plug. The Ar gas comes in from the left end of the alumina tube and is pumped out at the right end. The pressure in the alumina tube can be controlled by a needle valve. Commercial elemental tin powders (5 g, 100 mesh, 99.9%) were used as source material. The source material was placed on an alumina boat (40 mm × 10 mm × 10 mm). After transferring the boat to the center of the alumina tube, the tube was sealed by the rubber plug and evacuated by a mechanical rotary pump to a pressure of 6×10^{-2} Torr, then a constant flow of wet Ar (about 1% H_2O) was maintained at a flow rate of 80 standard cubic centimeters per minute (sccm), and the pump continually evacuated the system so that the pressure inside the tube was kept at 100 Torr. The temperature of the furnace was increased to 880 °C from room temperature for 1 h and kept at 880 °C for 2 h. After the furnace was cooled to room temperature, white wool-like products were found in a high yield on the source place. The morphologies and crystal structure of the products were characterized using scanning electron microscopy (SEM; Philips XL 30 FEG), X-ray diffraction (XRD; Bruker D8 with Cu Kα radiation), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) (Hitachi Model H-800 at 200 kV).

A typical SEM image (Figure 1) shows that the synthesized products consist of a large quantity of nanometer beltlike structures. The widths of these nanoribbons ranged from 20 to 150 nm, and lengths were up to several hundreds of micrometers, some of them even have lengths on the order of millimeters. The XRD results show that all of the diffraction peaks can be indexed to the tetragonal rutile structure of SnO_2, no characteristic peaks of impurities, such as metal Sn or other tin oxides, were observed (XRD support). It can be found that the yield of nanobelts was very high, ~80%, according to the amount of tin powders used, the other was SnO_2 powders, so several grams of SnO_2 nanoribbons can be prepared once a time.

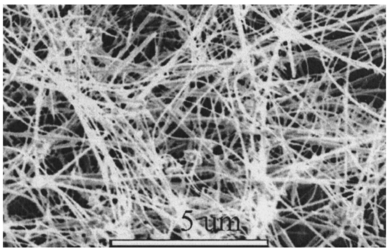

Figure 1. SEM images of the Tin oxide nanoribbons.

The typical TEM image of the as-prepared products was shown in Figure 2. Each ribbon has a uniform width and thickness along its entire length. Every nanoribbon displays the rectangle-

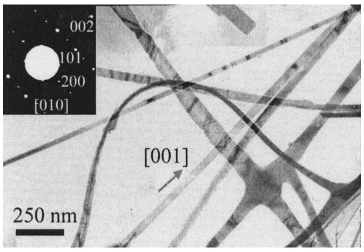

Figure 2. TEM image of SnO_2 nanoribbons. (Inset was the SAED pattern.)

like cross section. The typical widths and thickness of the ribbons are in the range of 20–150 nm and 10–50 nm, respectively. From TEM image, it can be seen that the nanoribbons have many streak contrasts on their observed faces and these may be bending contours because of lattice bending in thin TEM samples. The SAED pattern of the nanoribbon shown in Figure 2 was recorded with the electron beam along the [010] zone axis. It demonstrated that this particular ribbon was a single crystal with a growth direction of [001].

In addition, there were no products collected in the region downstream away from the source place in our experimental, and most of the metal Sn powders have been changed into SnO_2 nanoribbons, so the new method is advantageous for the synthesis of SnO_2 nanoribbons in large scale. For there is no temperature gradient on the zone where the source materials was placed, we can conclude that the temperature gradient may not be a driving force for the growth of SnO_2 nanoribbons in our experiment.

By variation of the experimental temperature, we can get nanoribbons even the temperature reaches as high as 1100 °C. The as-synthesized products are not sintered together, but the width of the SnO_2 nanoribbons increases significantly. On the other hand, if the temperature is lower than 880 °C, for example, 830 °C, the products were just particles and sintered together. Growth of SnO_2 nanoribbons was not observed in dry Ar, so H_2O might play an important role for the growth of nanoribbons. If air flew through the alumina tube, the products were just SnO_2 particles.

The source materials used in our experimental is elemental tin powders and it will be molten into liquid droplets at elevated temperature (mp 232 °C, bp 2260 °C). The liquid tin could react with H_2O to yield tin oxides. The XRD analysis demonstrated the products were just SnO_2. Based on these results, the reaction as follows would occur at high temperature:

$$\mathrm{Sn\ (liq.)} + 2H_2O \rightarrow SnO_2\ \mathrm{(s)} + 2H_2$$

The nucleation and growth mechanisms of nanobelts are unclear now. Further study is in progress in our lab. We believe that this high temperature synthetic route based on simple reactions with no participation of catalysts or templates, requiring no expensive equipments, and ensuring higher purity and uniformity of the products, will greatly reduce the production cost and offer great opportunity for large scale synthesis of such one dimension nanostructure materials.

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