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Synthesis of α-tellurium dioxide nanorods from elemental tellurium by laser ablation ☆

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Abstract

Elemental tellurium was evaporated by laser ablation, the vapor of which was condensed and deposited on the surface of the heated glass surface and then formed α-tellurium dioxide nanorods with uniformly size distribution by oxidation in the chamber with hot air atmosphere. TEM images and Electron diffraction (ED) pattern confirm the crystallinity of α-phase tellurium dioxide. The formation process of the nanorods involves a vapor–liquid–solid (VLS) following a chemical oxidation in the hot air atmosphere, in which the low melting point tellurium serves as a liquid-forming reagent.

Keywords: Nanorod; Tellurium dioxide; Laser ablation

As a class of optical materials, tellurium oxide (TeO_2) commands interest in terms of fundamental theory and engineering applications [1–5], for example, TeO_2-based glasses find application in laser devices and nonlinear optics [6–11]. The α-phase of tellurium dioxide exhibits excellent acousto-optical properties arising from its elastic behavior and high birefringence [12–15]. Large crystals of tellurium dioxide [16] are easy to grow, and device-quality tellurium dioxide can be grown by the Czochralski process [2,17]. Recently, it was reported that nanoparticles of tellurium dioxide can be synthesized by sol–gel process [18]. However, to our knowledge, no one-dimensional nanostructures of tellurium dioxide have been reported. Herein, we present an account of the synthesis of nanorods of tellurium dioxide by using a laser assisted growth route.

High-purity tellurium powder was placed in an unstoppered 25 cm quartz tube, which was set vertically in a tube furnace (4 × 38 cm) [19]. The 1064 nm pulse-laser from a Q-switched Nd:YAG system (Quantary DCR 130) of 7 ns pulse width was focused onto the tellurium powder for about 20 min. During the laser ablation, the tube was heated to a given temperature. After the laser ablation, the tube was cooled down to the room temperature and the white material that deposited on the walls was collected.

At approximately 500 °C of the furnace temperature, the white deposit consisted almost entirely of nanorods; moreover, the nanorods were uniformly spread over a narrow range of diameter (20–80 nm) only and they grew to several microns long (Fig. 1). The elemental composition of the nanorods (34.1% Te, 65.9% O) was measured by the EDX spectrum, indicating the presence of TeO_2. X-ray diffraction of the as-prepared products was further carried out, which showed that the products belong to the tetragonal $P4_12_12$ phase of α-TeO_2. In the diffraction pattern, no possible impurities such as pure Te can be found.

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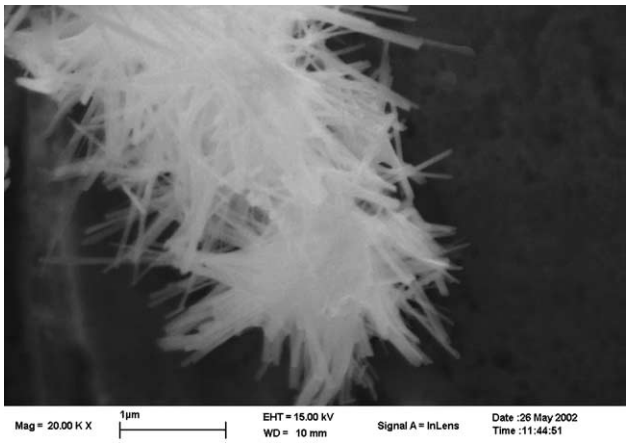

Fig. 1. SEM image of the product of laser-ablated tellurium heated in air at 500 °C.

That the TeO_2 nanorods are single crystals is illustrated by the high-resolution TEM image of a selected nanorod with a diameter of 31 nm (Fig. 2(a)). The lattice planes separated by 0.762 nm in the HRTEM image (Fig. 2(b)) correspond to the (0 0 1) plane. Those lattice planes in the perpendicular direction separated by 0.488 nm corresponds to the (1 0 0) plane. The ED pattern (Fig. 2(c)) also supports the presence of the tetragonal phase and shows that the long axis of the nanorod (i.e., the growth direction) orientates along the [1 0 1] direction.

When the temperature of the furnace was set to less than 400 °C, only nanoparticles of elemental tellurium or partially oxidized tellurium were formed (Fig. 3(a)). At the temperature of about 450 °C, the melting point of tellurium, wedge-shaped nanorods appeared (Fig. 3(b)),

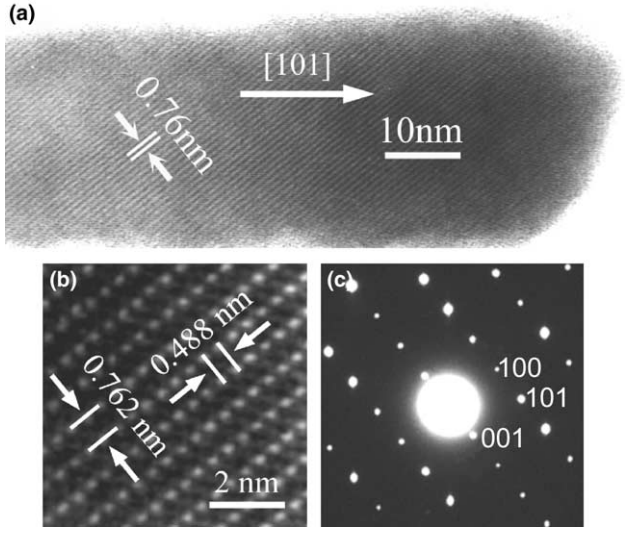

Fig. 2. (a) TEM image of the tip part of one TeO_2 nanorod. (b) Enlarged TEM image. (c) The corresponding electron diffraction pattern.

which consists of α-TeO_2 as checked by XRD. An ambient temperature of 500 °C appears to be optimal for the formation of single-crystalline tellurium dioxide nanorods (see Figs. 1 and 3(c)) as at 600 °C, only micron-sized crystals were formed instead (Fig. 3(d)).

The model for laser-assisted synthesis, particularly of nanowires, to explain the growth mechanism involves the participation of vapor–liquid–solid phases (VLS) in the growth process [20–22] and the central theme of VLS growth concerns the existence of a liquid-forming agent. Indeed, the growth consists of two distinct stages, the formation/nucleation liquid droplets and the growth of nanowires from supersaturation droplets. The present study uses laser to evaporate solid tellurium to its vapor phase. Hot air atmosphere (that is supplied externally by the furnace) allows the tellurium vapor firstly to aggregate into nanodroplets on the glass surface and secondly to give the droplets enough time for the growth process to complete itself. In the absence of this external heat, the vapor rapidly condenses to black elemental tellurium nanoparticles. At a sufficiently high temperature, the tellurium vapor remains in the droplet phase during which time nanodroplets can be partially or even completely oxidized. Those droplets condensing on the glass surface serves as the nucleating point for the one-dimensional growth of the nanorods. The relatively low melting point of the element parallels that of gallium, which can be conveniently evaporated into droplets, that catalyze the growth of silica nanowires [23] and that of selenium, which catalyzes the growth of zinc oxide nanowires [24]. The molten tellurium probably also behaves similarly to self-catalyze the growth. This suggestion is supported by our observation, that when tellurium dioxide was used in place of elemental tellurium, nanorods were not formed.

Our study shows, that a temperature range (450–600 °C) must be used for the growth of the TeO_2 nanorods by using the laser ablation method, a general feature of VLS growth, that has been proposed to be responsible for the mechanism of TeO_2 nanorods formation. The temperature range must cover the melting points of the starting reagents, so that droplets can be easily formed. At the lower edge of this range, e.g., 450 °C, wedge-shaped nanorods could be found in the products, the formation of which can be rationalized in terms of a spheroidization process [25,26], that results from the well-known tendency of a small-bore cylinder to grow irregularly under the influence of the effects of capillary action or surface tension. On the other hand, at temperatures exceeding 600 °C, the TeO_2 nanostructures might melt and on cooling process the melt formed micro-size rods (Fig. 3(d)).

The inclusion of a chemical conversion to the VLS appears to be practical complementary method for the controlled growth of tellurium dioxide nanorods, having

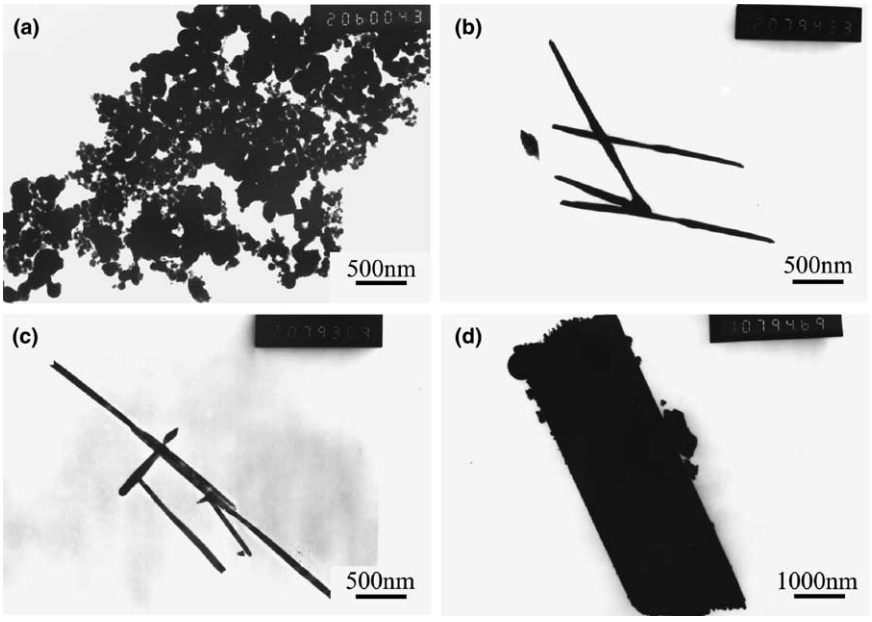

Fig. 3. TEM images of the products prepared at: (a) 350 °C; (b) 450 °C; (c) 500 °C; (d) 600 °C.

a linear morphology and uniform diameter and the combination may be easily adapted for the generation of relatively large quantities such material.

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