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Bulk Synthesis of Single-Crystalline Magnesium Oxide Nanotubes

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Crystalline tubular magnesium oxide nanostructures were obtained through carbon-thermal evaporation of a MgO powder. Gallium oxide was added into the mixture of MgO and carbon. The reduction of gallium oxide by carbon resulted in gallium vapor at high temperatures. Condensed gallium droplets catalyzed the anisotropic growth of tubular MgO nanostructures in situ. The products were characterized by X-ray powder diffraction technique, scanning electron microscopy, and high-resolution microscopy. All the analyses indicated that the prepared tubular MgO nanostructures are, in fact, single crystals.

The discovery of carbon nanotubes in 1991[1] has stimulated comprehensive interest in the synthesis of nanometer-sized tubular forms of various materials. The formation of closed nanotubes is believed to be a generic property of materials with highly anisotropic two-dimensional (2D) layered structures. Tubular nanostructures of boron nitride and metal disulfides (MoS_2, WS_2, TiS_2, ZrS_2, and HfS_2) have been reported.[2] There is a long-standing challenge to produce tubular nanostructures from 3D compounds. Sol−gel coating and chemical vapor deposition process have been able to generate nanotubular metal oxides and metals by using carbon nanotubes or porous membranes as templates,[3] although these nanomaterials are generally polycrystalline or amorphous. Recently, Goldberger et al.[4] have reported on the synthesis of single-crystalline gallium nitride nanotubes using a chemical-vapor-deposition epitaxial casting on zinc oxide nanowires.

Magnesium oxide is a typical wide-band-gap insulator. It has found many important applications for use in catalysis, refractory material industry, paint, and superconductors.[5] One-dimensional (1D) MgO nanostuctures can display a unique capability to pin the magnetic flux lines within a high-temperature superconductor (HTSC). It has been demonstrated that the incorporation of MgO nanorods as columnar defects into HTSCs can drastically improve the HTSC performance at elevated temperatures or in intensive magnetic fields.[6] The synthesis of 1D MgO nanostructures has been reported by many groups.[7] Here we report on the bulk synthesis of single-crystalline MgO nanotubes through carbon-thermal evaporation of MgO mixed with gallium oxide.

The MgO nanotubes were synthesized in a vertical induction furnace, as described in detail elsewhere.[8] The furnace consists of a fused-quartz tube and an induction-heated cylinder made of a high purity graphite coated with a C fiber thermoinsulating layer, which has an inlet C pipe and an outlet C pipe on its top and base, respectively. A graphite crucible, containing 0.40 g of MgO, 0.18 g of activated carbon, and 0.19 g of Ga_2O_3, was placed at the center cylinder zone. After evacuation of the quartz tube to ~0.1 Torr, a pure N_2 flow was set within the carbon cylinder at a constant rate of 200 sccm. The furnace was further heated to and kept at 1200 °C (measured by an optical pyrometer with an estimated accuracy of ±10 °C) for 1 h. After the reaction was terminated and the furnace cooled to room temperature, a white product was collected from the outlet of a graphite induction-heated cylinder. The product then was characterized using X-ray powder diffraction (XRD; RINT 2200) with Cu Kα radiation and scanning electron

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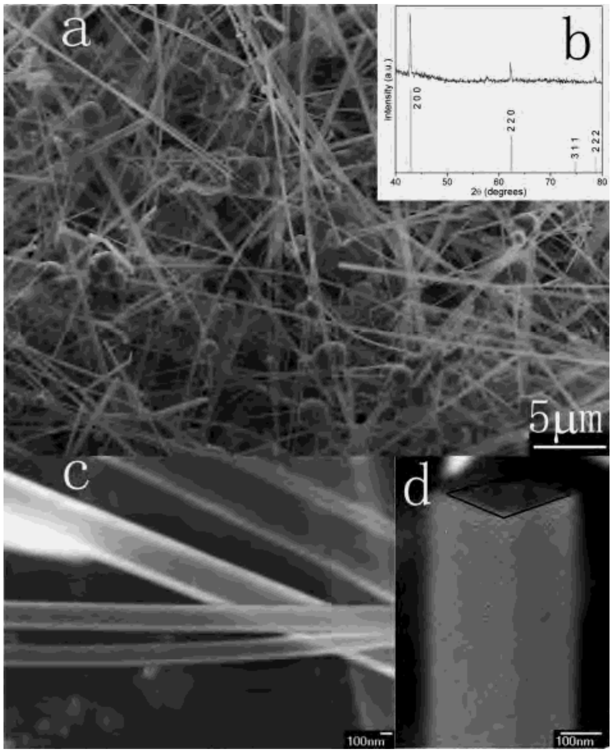

Figure 1. (a) SEM image of a product. (b) XRD pattern recorded from it. (c) High-resolution SEM image of tubular MgO nanostructures. (d) High-resolution SEM image of an individual tubular MgO nanostructure revealing the open square-like tip-end.

microscopy (SEM, JSM-6700F), and by means of a high-resolution transmission electron microscope (HRTEM; JEM-3000F) equipped with an energy-dispersive X-ray spectrometer (EDS).

The SEM image, shown in Figure 1a, indicates that the product is composed of one-dimensional nanostructures of a high aspect ratio. Their length reaches up to 50 μm. These nanostructures can be identified as magnesium oxide by XRD (Figure 1b). The semitransparent appearance of these one-dimensional nanostructures, as revealed by the higher resolution SEM image in Figure 1c, clearly suggests a tubular form. Figure 1D shows that a typical nanotube has an open square-like end, as indicated by the dark line.

The nanostructures were further examined using transmission electron microscopy. Figure 2a depicts a typical TEM image of these nanostructures. The walls of tubes are so thin that they are transparent to an electron beam, and thus, the carbon film of a TEM grid beneath the nanostructures can be clearly seen. Microscopic examination on the tubular MgO nanostructures displays that the average tube width is ∼200 nm, the wall thickness ∼20 nm, and the cavity width ∼160 nm. EDS analysis revealed that all tubular nanostructures are made of pure MgO. X-ray peaks of carbon and copper originate on the TEM grid. An overall ratio of magnesium to oxygen is 1:1.08, as verified by the EDS analysis. A typical ED spectrum is shown in Figure 2b. Figure 2c depicts a TEM image of a single MgO nanotube with the wall thickness ∼15 nm and the cavity width ∼100 nm. The corresponding electron diffraction pattern is shown in Figure 2d. The pattern can be indexed as that recorded along the [010] zone axis of a cubic MgO crystal. Electron diffraction patterns taken from various domains of the tube were exactly same even without any need to tilt the sample. This clearly suggests its single-crystal nature. Other tubular nanostructures were also confirmed to be single crystals. Streaking of the reflections on the underfocused electron diffraction pattern (Figure 1e) implies the preferred growth along the [001] orientation. ED patterns recorded on various nanotubes are identical along the [010] zone axis, which suggests that a

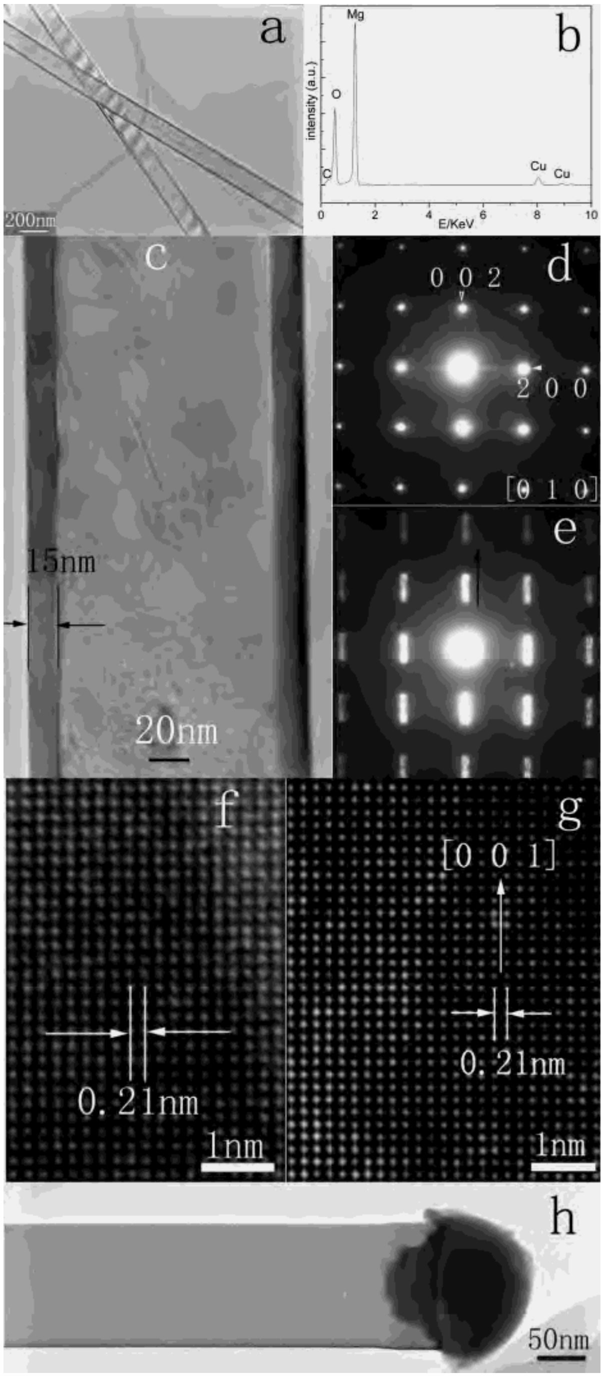

Figure 2. (a) Typical TEM image of tubular MgO nanostructures. (b) EDS spectrum of tubular MgO nanostructures. (c) TEM image of a single MgO nanotube. (d) SAED pattern of a MgO nanotube. (e) Underfocused SAED pattern of a MgO nanotube recorded along the [010] zone axis. (f) HRTEM image taken on the tube wall. (g) HRTEM image taken within the tube cavity. (h) A typical TEM image of a tubular MgO nanostructure capped with a gallium droplet.

tubular nanostructure is enclosed by four {020} crystal planes. HRTEM images taken on the tube wall and tube cavity are, respectively, shown in Figure 2f,g. The former image is a bit more diffuse than the latter one due to a larger object thickness. As seen in the images, the tubular nanostructures are structurally uniform and have no dislocations or other defects. The clearly resolved interplanar distance ($d_{200} = 0.21$ nm) can be seen in the HRTEM images. Typically, one tip-end of a given single-crystalline tubular MgO nanostructure is capped with a gallium droplet, as shown in Figure 2h.

MgO has a cubic NaCl-type crystal lattice (space group $Fm3m$ (No. 225), $a = 4.2112$ Å). Solid one-dimensional MgO nanowires or nanobelts were typically obtained via a vapor-phase reaction.[6,7] It is reasonable to assume here that the formation of single-crystalline tubular MgO nanostructures is related to capped gallium droplets at the tip-ends of nanotubes. The possibility of forming stable tubular MgO has been predicted using a compressible-ion interaction model.[9] Recently, it has been reported that magnesium can reduce gallium oxide vapor to form a Ga−MgO composite,[10] but MgO was doped with gallium. In addition to the vapor−solid growth,[11] the vapor−liquid−solid (VLS)[12] mechanism is generally attributed to the growth of one-dimensional nanostructures. The key feature for the VLS growth is that one end of a one-dimensional nanostructure is capped with an alloy droplet promoting the anisotropic crystal growth. Gallium has been reported to catalyze growth of silica nanowires.[13] Gallium droplets at the ends of MgO nanotubes may catalyze the anisotropic growth of MgO via VLS mechanism: in fact, gallium is a good solvent for magnesium. During the present synthetic process, a gallium vapor condensed to form droplets in a lower temperature reactor region (about 800 °C). The vapor resulted from a reaction between gallium oxide and carbon in a higher temperature region (about 1200 °C). Then, an evaporated magnesium oxide condensed at the gallium droplets to initiate the anisotropic crystal growth of MgO. The formation of a tubular form may be attributed to the interplay of some kinetic factors. Since the growth temperature is ~800 °C, the mobility of atoms is high enough to let newly arriving atoms rapidly adjust themselves to the growing edge and promote the fast growth of tubular forms. The growth process is schemed in Figure 3. In order to avoid the formation of MgO nanowires, an excessive amount of gallium oxide was added. Recently, it has also been reported that InP nanotubes can grow from a liquid InP−Au phase via VLS mechanism.[14]

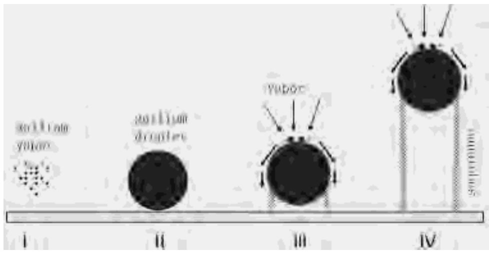

Figure 3. Growth scenario for the formation of tubular MgO nanostructures: (I) vaporization of gallium, (II) condensation of gallium vapor to form gallium droplets, (III) condensation of MgO vapor and crystal nucleation, (IV) crystal growth.

In summary, we report on the bulk synthesis of single-crystalline MgO nanotubes via a carbon-thermal evaporation method. Gallium plays a crucial role in the present formation of MgO nanotubes. These nanotubes made of one of the most chemically and thermally tough refractory materials may find novel technological applications in nanocapillary or other advanced processes. Moreover, the results indicate that gallium is able to catalyze the growth of not only inorganic solid nanowires but also crystalline tubular nanostructures. Gallium-promoted growth of other tubular nanostructures in various solids is also envisaged.

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