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# Free-Standing Copper(II) Oxide Nanotube Arrays through an MOCVD Template Process

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In the past few years inorganic nanotubes and nanowires have attracted more and more attention because of their potential applications for electrical contacts in nanoelectronics, for catalytic gas detectors, solar cells, and optical devices.[1]

The physicochemical properties of inorganic nanotubes (INTs) are more easily controllable than those of carbon nanotubes (CNTs), which are strongly related to the CNTs diameter and crystal structure. In fact, the properties of INTs depend essentially on their chemical nature, even though they differ from the properties of the bulk materials.

Several studies have been reported on the synthesis of metal, oxide, halide, and chalcogenide nanotubes[2a,c] or nanowires.[2b,c] Wet chemical routes, such as sol−gel,[3] solid liquid-phase arc-discharge,[4] and electrochemical method,[5] as well as vapor-phase evaporation,[6] have been attempted.

In some cases, these techniques use a "template" to synthesize well-aligned nanostructures and for this reason they are usually reported as "template methods".[7−9]

Pioneering studies in this area have been proposed by Martin et al. using different types of hard templates (track-etch polymeric, anodic aluminum oxide membranes, and carbon nanotubes).[7,8]

Soft templates (DNA) have been also proposed to assemble conducting silver wires.[9]

Metal−organic chemical vapor deposition (MOCVD) has been already used to fabricate CNTs,[10] nickel nanowires,[11] and $TiO_2$ nanorods.[12] Nevertheless, to our knowledge no attempts have been made for an MOCVD template synthesis of metal oxides nanotubes.

In this perspective, the synthesis of copper oxide nanotubes through simple reproducible routes represents an appealing goal. CuO has been, in fact, extensively studied for several reasons from its close connection to high-Tc superconductors to its electrical and magnetic properties, from its use as a powerful heterogeneous catalyst to its potential as a cathode material in the fabrication of lithium copper oxide electrochemical cells. In particular, copper oxide based thin films have been used already in the field of heterogeneous catalysis and in gas-sensing devices. For these particular applications, the high surface−volume ratio and the nanometric size are expected to result in a tremendous improvement of chemical properties, thus rendering CuO nanotubes particularly appealing.

In this paper, we report on the preparation of ordered homogeneous arrays of copper (II) oxide nanotubes through an MOCVD template route using $Cu(tmhd)_2$ (Htmhd = 2,2,6,6-tetramethyl-3,5-heptandione) as a source. The $Cu(tmhd)_2$ has been chosen since it represents a suitable MOCVD precursor and has been widely applied for MOCVD fabrications of high $T_c$ superconductors.[13,14]

Anodic aluminum oxide (AAO) membranes consisting of ordered hole arrays of 200-nm diameter and 60-$\mu$m thickness have been used as a template. AAO membranes have been chosen due to several advantages; namely, they have uniform pores of high density, are chemically stable during the process up to at least 700 °C, can be easily removed, and are commercially available.

The nanotubes were obtained by deposition on vertically positioned membranes in conditions typically applied for the deposition of CuO thin films,[15] i.e., deposition temperature of 400 °C and oxygen partial pressure of 1.5 Torr.

These results are in accordance with data reported in the literature, since the use of low process temperatures, a common practice in nanoscale CVD, favors the precursor decomposition on the side-walls of the membrane pores, thus avoiding complete filling of the channels.[16]

The nature of fabricated nanotubes has been investigated by X-ray diffraction (XRD) before removing the AAO membrane. The XRD pattern carried out in graz-

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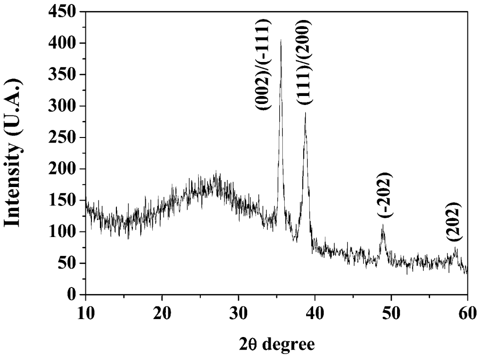

**Figure 1.** Assembled CuO nanotube array in an AAO template. X-ray diffraction pattern indicating the formation of the monoclinic CuO phase.

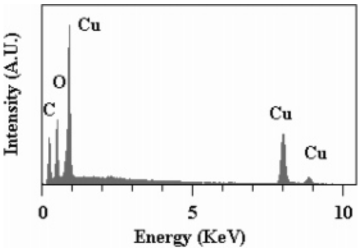

**Figure 2.** Free-standing CuO nanotube arrays. EDX spectrum corresponding to the area inside the gold grid in Figure 3a showing that no Al is present after the template removal.

ing incidence mode (Figure 1), shows several peaks at $2\theta = 35.55°$, $38.75°$, $48.85°$, and $58.35°$ corresponding to the 002/−111, 111/200, −202, and 202 reflections, respectively, of the CuO tenorite phase with a monoclinic lattice.[17] The presence of all these reflections clearly points to the polycrystalline nature of the nanotube arrays as further confirmed by transmission electron microscopy (TEM) studies.

The copper oxide nanotubes were recovered by dissolving the AAO membrane in 2 M NaOH solution for 1 h at room temperature and filtering on a gold grid. The product was washed with distilled water several times and dried in air. The complete dissolution and elimination of the template has been confirmed by using energy-dispersive X-ray (EDX) analyses (Figure 2). The spectrum shows the Cu Kα, Kβ, and L peaks at 8.040, 8.900, and 0.920 keV, respectively. The use of a “windowless” detector allowed the detection of low atomic number elements. Therefore, the O Kα peak is observed at 0.520 keV while no aluminum peak can be detected, thus confirming complete removal of the AAO membrane.

The morphology of the prepared nanotubes has been probed by scanning electron microscopy (SEM). Figure 3a−c show the SEM morphology of the CuO nanotubes after removing the template. In the low-magnification image (Figure 3a and b) well- ordered nanotube arrays are clearly visible. There is therefore evidence that very wide nanotube sheets are formed simply upon removal of the template. The nanotube arrays keep memory of the nanochannels alignment in the AAO membrane, even when the template is removed. This is a relevant key issue since fabrication of free-standing aligned nanotubes generally represents a difficult task.

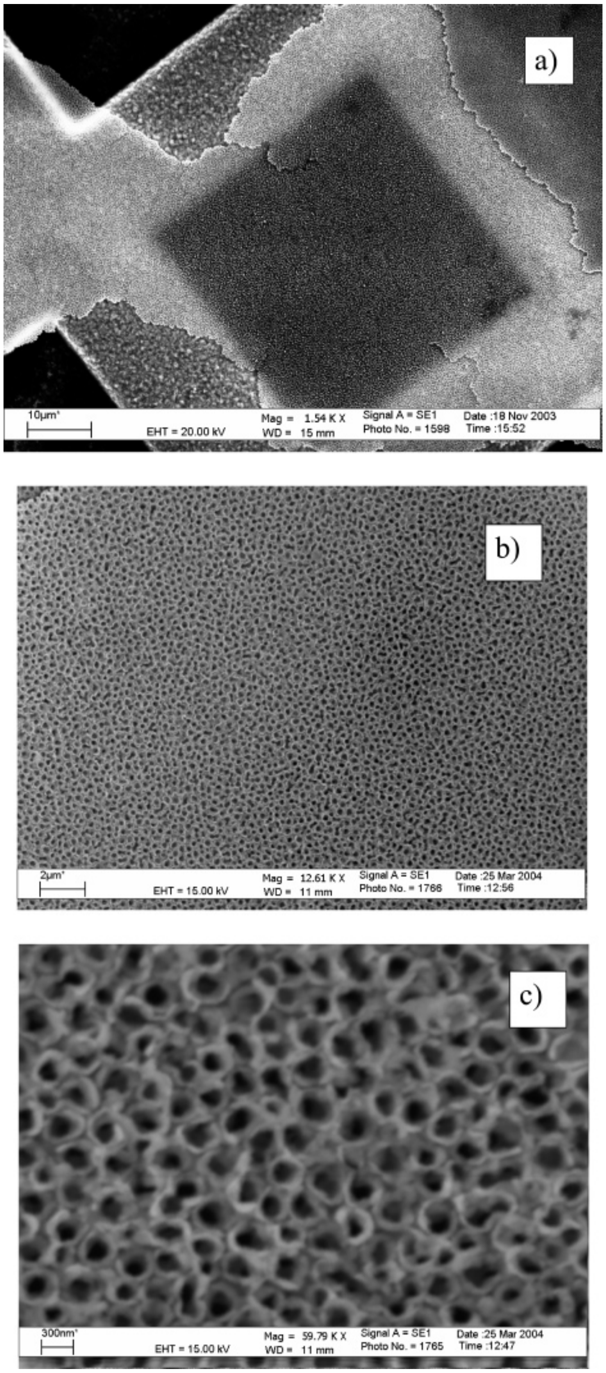

**Figure 3.** Free-standing CuO nanotube arrays: (a) and (b) low-magnification plan-view SEM images of the CuO nanotube sheet; and (c) high-magnification plan-view of the nanotube sheet.

The high-magnification SEM image (Figure 3c) shows that nanotubes have an outer diameter of about 250 nm while the nanotube walls are about 40 nm thick. Nanotubes are about 1 µm long. The diameter of nanotubes is controlled by the characteristic pore dimension of the template membrane, whereas their length depends on the process conditions. Nanotubes are opened on both sides and this feature becomes clearly discernible in the TEM micrographs reported in Figure 4a and b. The low-resolution plan TEM micrographs show several nanotubes of 250-nm diameter, which corresponds to the pore size of the template used. The wall thickness of 37 nm is clearly visible in the higher-

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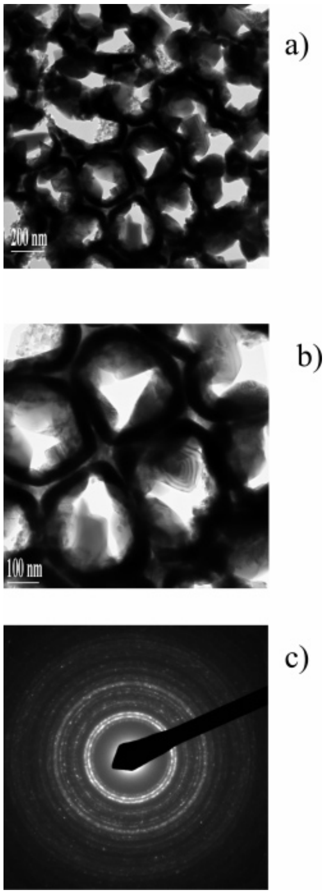

**Figure 4.** TEM micrographs of a free-standing CuO nanotube array: (a) low and (b) high magnification plan-views of the CuO nanotube sheet; and (c) SAED pattern of the CuO nanotubes.

magnification micrograph (Figure 4b). Through performing a selected-area electron diffraction (SAED) analysis on the nanotube arrays, a clear electron diffraction pattern composed of several rings is obtained. At least three diffraction rings can be distinguished, with average *d* spacings (distance between adjacent planes with any given Miller indices (*hkl*) within the crystals) of 2.530 and 2.523 Å associated with the 002 and −111 reflections, 2.323 and 2.312 Å associated with the 111 and 200 reflections, and 1.866 Å associated with the −202. The SAED result, in accordance with XRD data, demonstrates that the nanotube arrays are polycrystalline of the tenorite phase.

This simple and straightforward approach to oxide nanotubes can be compared to that previously reported for the deposition of ruthenium oxide nanotube arrays by atomic layer deposition.[18] The present approach, however, avoids the use of any intermediate template such as the C−NT arrays prepared on AAO membranes, and it is well-known that higher growth rates are associated with MOCVD processes.

Focus point of the present strategic approach to CuO nanotube arrays is the application of standard MOCVD processing conditions usually applied for CuO film depositions. Therefore, we feel confident that the present "transfer" of a well-assessed MOCVD procedure for the deposition of CuO films to analogue nanotubes could open-up new viable routes to nanotube arrays of various oxides. Note in this context that the MOCVD template route represents an actually challenging approach to the fabrication of nanoscale mixed, multielement oxides (e.g., copper based high-Tc superconductors), since the MOCVD technique has been widely and successfully applied to depositions of multielement oxide films. On the other hand, nanotube arrays of these complex systems would be very difficult to obtain with techniques such as sol−gel, electrochemistry, or evaporation, up to now essentially applied to single element oxides.

In summary, CuO nanotubes have been grown through a template MOCVD route. The synthesized nanotubes can be used either directly embedded in the template or in a free-standing mode since the template can be easily removed using a selective chemical etching.

In addition, present data indicate that this approach has the potential advantage of being a very simple method for the easy production of nanostructures such as free-standing CuO nanotube arrays on large-area.

To our knowledge this represents the first example of a regularly packed nanotube array, obtained after removal of the template, through a rather easy, user-friendly, and strategic technique. Activities are in progress to combine other assessed MOCVD procedures with AAO to simply prepare free-standing nanotube arrays of several oxide system.

## Experimental Section

The AAO membranes used as a template were purchased from Whatman. This template exhibits a precise, nondeformable structure, with pores of 200-nm diameter arranged in a hexagonal array.

The membrane was positioned in a horizontal hot-wall reactor and maintained at 400 °C. Oxygen and argon were used as reaction gas and carrier gas, respectively. The $Cu(tmhd)_2$ source, purchased from Aldrich, was sublimed at 100 °C. The deposition was carried out for 3 h at a total pressure of 2 Torr.

X-ray diffraction spectra (XRD) were recorded in grazing incidence mode with a Bruker AXS D5005 diffractometer, using a Göebel mirror to parallel the Cu Kα radiation operating at 40 kV and 30 mA. The morphology of the arrays was examined using a LEO Iridium 1450 scanning electron microscope. The chemical composition was assessed through energy-dispersive X-ray analyses using the windowless IXRF detector. Nanotube arrays were examined using a transmission electron microscope (TEM, Hitachi S4500 FE).

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