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Controlled synthesis of highly ordered CuO nanowire arrays by template-based sol-gel route

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Abstract: The highly ordered CuO nanowire arrays of composite-oxides were synthesized within a porous anodic aluminum oxide(AAO) template by a citrate-based sol-gel route. A vacuum system was applied to draw the gel into the template pores, which conquers the only driving force of this technique—capillary action, then the gel was thermally treated to prepare desired CuO nanowires. The results of scanning electron microscopy(SEM) indicate that the CuO nanowires are very uniformly assembled and parallel to each other in the pores of the anodic aluminum oxide(AAO) template membranes. The results of X-ray diffraction(XRD) and the selected-area electron diffraction(SAED) indicate that the CuO nanowires are monoclinic-type crystalline structure. Furthermore, X-ray photoelectron spectroscopy (XPS) demonstrates that the stoichiometric CuO is formed.

Key words: CuO; nanowire; anodic aluminum oxide(AAO) template

1 Introduction

In the past decade, metal oxide nanowires of wide band gap n-type semiconductors, such as TiO_2[1−2], CdS[3], ZnO[4] and SiO_2[5], have attracted much attention because of their novel optical, catalytic and magnetic properties. There is considerablely scientific and technological interest in developing nanostructured metal oxides with p-type semiconductivity. Cupric oxide(CuO) is one of the most important p-type semiconductor as it exhibits a stable narrow band gap (1.2 eV) and other interesting properties[6−8]. It was demonstrated that CuO could exist in three different magnetic phases[9−10]. It also can be used potentially in gas sensors, solar cells, FE emitters, electronic cathode materials and catalysts[11−12]. Based on these applications, many methods have been developed to prepare CuO with various morphologies.

Several groups attempted to synthesize CuO nanowires. WANG et al[13] proposed that CuO nanowires might be involved as a by-product when Cu_2O nanowires were formed by reducing copper sulfate with hydrazine in a basic solution. WANG et al[14] observed the formation of polycrystalline containing both CuO and Cu_2O when Cu_2S nanowires were oxidized by O_2 at elevated temperatures. In this work, we describe a simple sol-gel template method for the synthesis of uniform CuO nanowires.

2 Experimental

2.1 Membrane preparation

High purity aluminum foil (99.999 %) employed in this experiment was electropolished in a mixed solution of $V(HClO_4)$:$V(CH_3CH_2OH)$=1:4 for 5 min to provide a smooth surface. Afterwards, the resulted clean aluminum foil was anodized at 80 V_{dc} for 2 h in 0.5 mol/L phosphoric acid solution. Each sample was then placed into a saturated $HgCl_2$ solution for 1 h to separate the

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template membrane from the aluminum substrate.

2.2 Preparation of CuO nanowire arrays

Cu^{2+} sols were prepared in advance as follows [15−17]: 6 mol/L ammonia was added dropwise at room temperature to an aqueous cupric nitrate solution (0.9 mol/L). The final pH value of the solution was about 8.5. The hydrated precipitate so formed was separated centrifugally, washed three times with distilled water and peptized with nitric acid (0.25 mol/L) to obtain a translucent, homogenous and stable sol. The final pH value was kept in the range of 2.4−2.5. The Cu^{2+} gel (about 1 mL) was placed on the top side of the template membrane (1.2 cm^2 surface area) and a vacuum (a water aspirator) was applied to the bottom of the membrane. The sol-containing membrane was then dried in air for 30 min and then this sample was annealed in air at 850 K for 7 h. As a result, the membrane with gel was obtained.

2.3 Apparatus

An atomic force microscope (SOLVER scanning probe microscope, Russia) was employed to characterize the morphology of the template membrane.

TEM images were obtained using a HATACHI−600 microscope.

The XRD patterns for CuO nanowires were recorded with a diffractometer (Rigaku, Model D/max 2400) using CuK_α radiation (λ=0.154 05 nm). XPS data were obtained with a ESCA LAB5 X-ray photoelectron spectrometer with Mg X-ray at 10 kV.

3 Results and discussion

3.1 AFM, SEM and TEM analysis

The AAO template with pores in a parallel arrangement throughout was fabricated using the two-step anodization process. The pore diameter depends on the anodization voltage. The pores depth of the AAO template is proportional to the second anodization time [18]. A longer anodization time favors not only increasing the pore depth but also extending the uniformity of the AAO membrane. Fig.1 shows the AFM top-view micrograph of the as-prepared AAO with pores of 70 nm in diameter. Almost perfect hexagonally arranged pore domains can be seen. The pores with a narrow size distribution are surrounded by six columnar oxides, which are interconnected to form a network structure.

Fig.2 shows SEM images of the CuO nanowires grown in the AAO template. These photographs show that the nanowires are uniformly distributed, highly ordered, parallel to each other. Fig.2(a) shows planforms from which we can find several clusters of nanowires. The clusters can result from the situation in which the

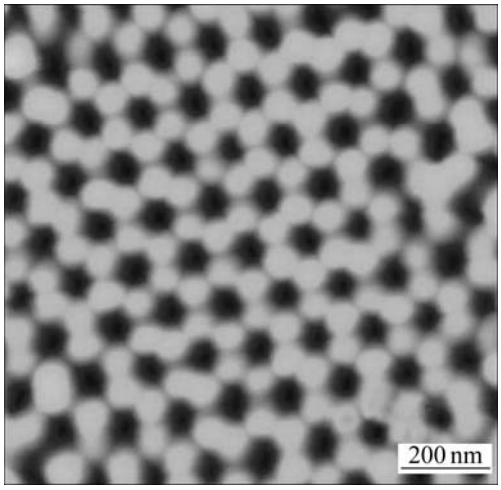

Fig.1 AFM photograph of AAO template

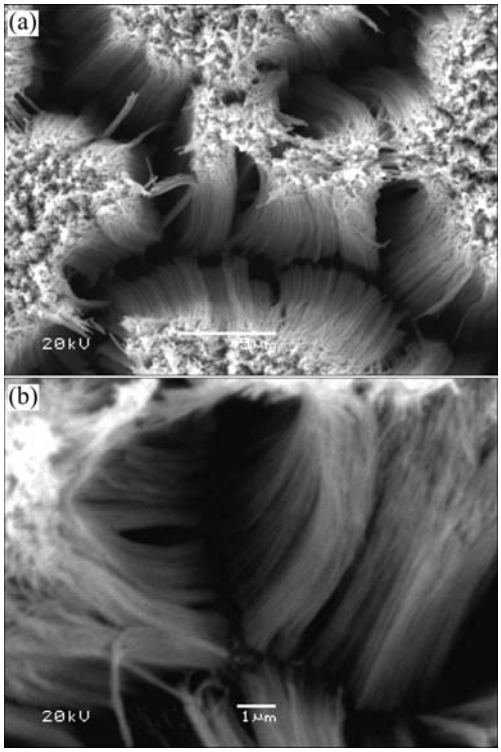

Fig.2 SEM images of CuO nanowires with AAO template partly dissolved: (a) Whole morphology of CuO/AAO composite; (b) CuO stripping from CuO/AAO composite

nanowires are uncovered from the framework of the AAO template but freestanding incompletely. When the top alumina of the AAO template is dissolved away, the nanowires embedded in the template release gradually and incline to agglutinate together. It is conceivable that the surface energy of the nanowires causes this interesting phenomenon. Fig.2(a) also shows that the CuO nanowires are abundant, uniform and highly ordered in large area. Fig.2(b) reveals a cross-section where the alumina matrix of the AAO template has been partially dissolved away. It can be seen that the

nanowires deposited inside the nanochannel of the AAO template are parallel, tidily aligned and uniformly distributed. It is correlative to that the AAO template has an array of densely parallel nanoholes arranged in a hexagonal fashion. We can see that these nanowires have a fiber-brush aspect. From these figures, the CuO nanowire arrays can be produced in large areas within the pores of the AAO template. At the same time, it also can be estimated that the length of CuO nanowires is about 50 μm, which is corresponding with the thickness of the AAO template. The outside diameters of these nanowires are about 70 nm, which are equivalent to the pore diameter of the template membrane.

TEM images of CuO nanowires formed within the AAO template are shown in Fig.3. Fig.3(a) shows several CuO nanowires, in which some of these nanowires cross and overlap with each other. This image also shows that the diameter of CuO nanowires is about 70 nm, which approximately equals to those of the nanochannels of the employed AAO template. Although the length of nanowires is much less than 50 μm, it does not mean that the nanowires are only so short, because during the preparation of samples for TEM observation, the nanowires are easily broken by the ultrasonic stirring. These nanowires are uniformly distributed, which indicates that the alumina matrix is dissolved completely. In Fig.3(b) there is only a single one, the image shows that these nanowires are, in fact, microporous, resulting in a large surface area. Longer sintering time (up to 18 h) does not remove this microporosity[19]. The corresponding electron diffraction pattern shows continuous rings that are indexed to monoclinic CuO (insert of Fig.3(b)). The rings are sharp and continuous, which shows that although the nanowires are highly crystalline, they are not single crystals, and the various crystalline domains show no preferred orientation.

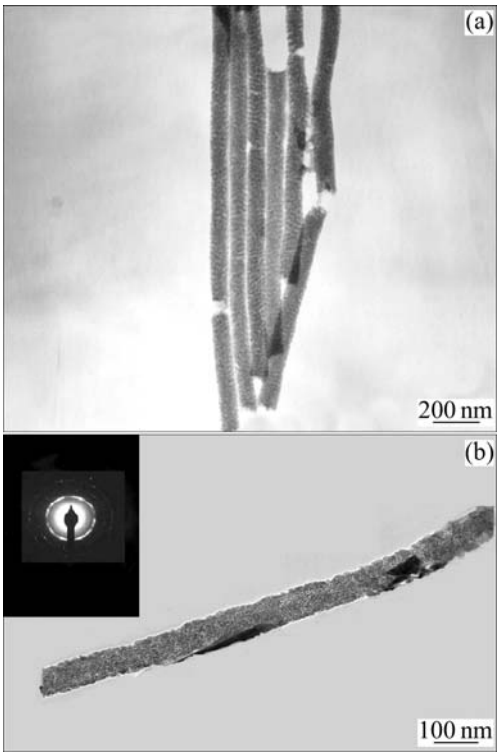

Fig.3 TEM image of dispersed CuO nanowires (a) and single CuO nanowires and corresponding selected area diffraction pattern (b) of nanowires

3.2 XRD analysis

Fig.4 shows XRD pattern of CuO nanowires. Although the background diffraction peaks of the Al_2O_3 template exist, the major diffraction peaks of CuO are observed. Four observed peaks with 2θ values of 35.57°, 38.75°, 49.01°, 66.44° and 67.92° correspond to diffraction from the $(\bar{1}11)$, (111), $(\bar{2}02)$, $(\bar{3}11)$ and (220) planes of crystalline CuO, respectively. The reason for weaker diffraction peaks of CuO is the relatively small quantity of CuO in the template and the lack of CuO on the surface of the template. The XRD results not only reveal that the nanowires of CuO are crystalline as anticipated from the annealing temperatures, but also show no additional impurity diffraction from cubic Cu_2O, indicating the phase purity of these nanowires[20].

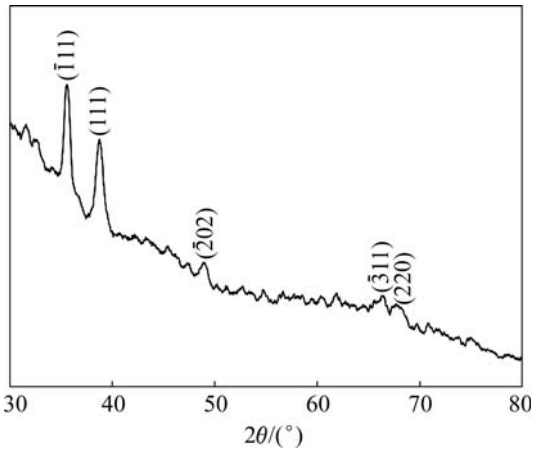

Fig.4 XRD pattern of CuO/alumina composite membrane

3.3 XPS analysis

Fig.5(a) shows XPS data for the CuO nanowires. The chemical composition of CuO nanowires (within the AAO template for a CuO/AAO composite) is obtained by XPS measurements. In order to see clear data, the AAO is partly removed. The C1s peak lies at 297.4 eV, which should be corrected to 285.0 eV. All the other peaks are corrected accordingly. No peaks of other elements except C, Cu and O are observed in the picture, indicating the high purity of the product. In the high-resolution XPS spectra (Figs.5(b) and (c)) of the as-prepared CuO nanowires, the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks lie at 933.7 eV and 953.6eV with a satellite feature

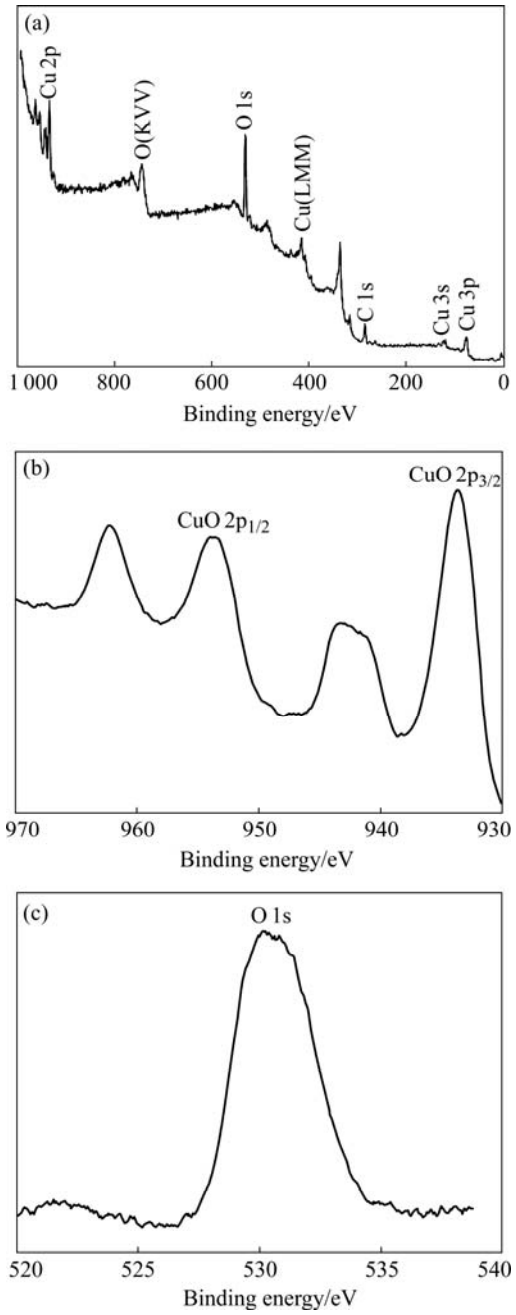

Fig.5 XPS spectra of CuO/alumina composite membrane wide spectrum (a), high-resolution Cu 2p (b) and high-resolution O1s (c)

respectively, the broad peak that lies at 530.9 eV is assigned to O 1s. No impurity peaks are observed in the XPS results for CuO, and this is in accordance with the XRD analysis.

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