Controlling the Diameter of Cu₂O Nanowires by Electrodeposition

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Abstract: Cuprous oxide (Cu₂O) nanowires were prepared by electrodeposition into a porous alumina template. To deposit the Cu₂O nanowires defect-free into the alumina membrane, a cathodic current density of -0.5 mA/cm² was constantly applied in a copper sulfate electrolyte in the presence of lactic acid. Top-view and cross-sectional observations by TEM and SEM showed homogeneous filling of the Cu₂O nanowires in the 100- and 200-nm alumina pores. The length of the Cu₂O nanowires was 4 μm. EDS data indicated pure Cu₂O and XRD analysis showed preferential growth of Cu₂O (200) and (111) nanowires in the absence of Cu metal and CuO.

Keywords: Cu₂O, electrodeposition, nanowires, alumina template

Introduction

Nanowires have received a great deal of attention because of their distinct properties and unique applications, such as interconnectors and active components in fabricating nanoscale devices [1-4]. Recently, the development of nanoporous alumina templates through a simple, low-cost manufacturing process led to great interest in the preparation of ordered nano-sized materials in biological, electronic, thermoelectric, and photonic devices [5-7]. Until now, electrochemical fabrication of nanowires of metals [8-10], semiconductors [11,12], and polymers [13] using ordered alumina templates [14-16] have all been demonstrated, but nanowire preparations of metal oxides, such as silver oxide, thallium oxide, copper oxide, and zinc oxide, in ordered arrays through electrodeposition technique have yet to be reported. Among those metal oxides, copper (I) oxide, a p-type semiconductor having a 2.0-eV band gap energy, is especially attractive, because it could be used as a photocatalytic material for splitting water into H₂ and O₂ upon visible light irradiation [17-19]; thus, Cu₂O is a potential material for the fabrication of low-cost solar cells [20,21]. The crystallinity of Cu₂O thin films prepared by the electrodeposition is strongly dependent on the electrolyte’s pH [22]. Wang and coworkers [23] introduced the fabrication of Cu₂O nanowires through a novel reduction route in the presence of polyethylene glycol (PEG).

In this study, we have succeeded in the manufacture of Cu₂O nanowires by electrodeposition. The diameters of the Cu₂O nanowires can be controlled readily by using different pore sizes of alumina template.

Experimental Section

Cu₂O nanowires were filled galvanically into a hexagonal nano-array alumina membrane using a conventional three-electrode system. Applying a direct current (DC) sputtering technique, copper metal was deposited onto one side of a commercial alumina membrane (Whatman, Anodisc 25) that had highly ordered nanopores (diameters: 100 and 200 nm), which was used as the working cathode electrode. Saturated calomel electrode (SCE) and platinum mesh were employed as the reference and counter electrodes, respectively.

The electrolyte was 0.4 M copper sulfate (Aldrich, 99,999%) dissolved in 3.0 M lactic acid (Aldrich, 88%); the copper ions were stabilized by complexing with the lactate ions. 5 M aqueous NaOH (Aldrich) solution was added to adjust the pH to 9. A potentiostat and galvanostat (EG&G PAR 273A) was used to apply the optimal current density of -0.5 mA/cm² and the temperature of

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the solution was maintained constant at 65°C during the experiments.

The surface morphology of the Cu₂O nanowires was analyzed by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4300) and transmission electron microscopy (TEM, Phillips CM200). The crystallinity and a quantitative analysis of the prepared Cu₂O nanowires were determined using X-ray diffraction (XRD, Phillips DY616) and energy dispersive X-ray spectroscopy (EDS) an coupled with the TEM equipment.

Results and Discussion

Very recently, Choi and coworkers [11] presented the first example of fast silver infiltration into monodomain porous alumina having large pore diameters (between 180 and 400 nm) by electrodeposition. They explained that the preparation of metal nanowires with large diameter, i.e., over 100 nm, into the nano-ordered alumina template is not easy because of the thick barrier layer on the bottom of the alumina template. Therefore, a high energy (potential or current) should be applied for the deposition of materials via the breaking of the barrier layer. According to previous studies and the Pourbaix diagram [22,24,25], Cu₂O could be formed theoretically in range of pH between 5 and 12 and, thus, the value of the cathodic current is important parameter. Appropriate low currents induced the electrodeposition of pure Cu₂O, whereas high cathodic currents resulted in the deposition of pure Cu and/or Cu/Cu₂O composite [25,26]. To overcome the problem of the thick oxide barrier mentioned above, an alternative method was used. A commercial alumina membrane (Whatman, Anodisc) lacking the barrier oxide was selected and one side of the membrane was then blocked by copper DC sputtering. In this case, applying high energy (potential or current) is not required to remove the barrier oxide during Cu₂O formation and, thus, pure Cu₂O nanowires could be prepared without the formation of any other Cu complexes.

In this study, to obtain pure Cu₂O nanowires into the nanoporous alumina template, an optimal cathodic current of -0.5 mA/cm² was applied continuously for 4 h. Figure 1 provides a morphological observation of the cross-sectional view and the top-view of Cu₂O nanowires of 200-nm diameter. To confirm that Cu₂O had completely filled the alumina template in a uniform orientation, a TEM analysis was performed. Figures 1(a) to
1(c) show the cross-sectional and top views of the 200-nm Cu$_2$O nanowires deposited into the alumina template and the array of Cu$_2$O nanowires after the selective dissolution of the alumina template through the use of NaOH solution, respectively. In Figure 1(a), we complete filling of the Cu$_2$O nanowires having lengths of 4 μm. Defect-free Cu$_2$O nanowires having 200-nm diameters are clearly shown in Figure 1(d).

To acquire data for the atomic concentration of the deposited material, we performed EDS analysis of the 100-nm nanowire presented in Figure 2(a). Analysis of the EDS data in Figure 2(b) suggests that the atomic percentage of Cu is twice that of O, which provides convincing evidence for the fabrication of the Cu$_2$O nanowires. Because the analysis area of the sample was about 10 nm, the peak corresponding to aluminum was not detected.

Figure 3 shows the XRD analysis of the Cu$_2$O nanowires deposited into the ordered alumina membrane. Cu$_2$O was grown preferentially with distinct orientations of [100] and [111] relative to other growing orientations, i.e., Cu$_2$O (200) and Cu$_2$O (111) are dominant when compared with the other Cu$_2$O crystallines [(220) and (311)]. We assume that this phenomenon might be a result of the preparation method, especially the solution pH.

Figure 4 shows a schematic diagram of the electrodeposition of single-crystalline Cu$_2$O into an alumina template. The Cu lactate solution came in contact with the Cu thin film [Figure 4(a)] substrate placed at the bottom of porous alumina membrane; Cu$_2$O first deposited on both of the conducting Cu edges of the membrane hole [see dotted circle in Figure 4(b)] and then Cu$_2$O coalesced as shown in Figure 4(c). Cu$_2$O continuously
grew into the open top pore [see Figure 4(d)]. At present, we have succeeded in preparing 4-μm Cu2O nanowires, but they are rather short, which limits their applications in solar cells and sensors. Thus, the preparation of longer Cu2O nanowires, presenting higher aspect ratios and greater compactness, remains to be performed.

In summary, we have electrodeposited highly ordered Cu2O nanowires using a commercial alumina template. Chronopotentiometry (i.e., constant current method) was applied to deposit compact Cu2O nanowires without any disconnection into the honeycomb-shaped pores of a nanoporous alumina membrane. Analyzing the structural and morphological properties, we determined that the Cu2O (200) and Cu2O (111) nanowires we prepared had large aspect ratios (20 and 40) depending on the pore diameter of the alumina template used. We expect that this procedure will be a useful one for the development of improved nano-scale solar cell systems.

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References