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Electrodeposition of Cu_2O Nanowires Using Nanoporous Alumina Template

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We first electrodeposited highly ordered Cu_2O nanowires using a home-made alumina template. Home-made nanoporous alumina templates were prepared by a two-step anodization method and selective removal of aluminum substrate by bromine solution. Chronopotentiometry (*i.e.*, constant current method) of -0.5 mA/cm^2 was applied to deposit compact Cu_2O nanowires without disconnection into the honeycomb shaped pores of a home-made nanoporous alumina membrane. Analyzing morphological observations by scanning electron microscopy and transmission electron microscopy, we observed that the diameter of Cu_2O nanowire was *ca.* 57 nm and the length was 4 μm demonstrating an aspect ratio of 70. X-ray diffraction structural analysis indicated that $Cu_2O(200)$ was preferentially formed compared with other Cu_2O crystalline phases which may be due to an adjusted solution pH 9.

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Materials with at least one-dimension in the range of 1-100 nm have attracted steadily growing interest owing to their distinct, attractive properties, as well as their unique applications compared with bulk materials.[1-4] Nanowires, *inter alia*, should play an important role as both interconnectors and active components in fabricating nanoscale devices.

Of late, the formation of nanoporous alumina template via the electro-oxidation of aluminum is of great interest in relation to fabrication of ordered nanosized materials in biological, electronic, thermoelectric, and photonic devices.[5-7] This increasing attraction of porous alumina as a template is due mainly to an easy and low-cost manufacturing process. In addition, pore diameters between 4 and 200 nm and interpore distance between 50 and 500 nm of an anodic alumina template could be controlled by applied voltage, solution temperature, and electrolyte concentration.[8-13]

Until very recently, nanowires of metals,[14-16] semiconductors,[17-19] and polymers[20] have been made by several research groups into hexagonally ordered nanoporous alumina template. Particularly, the fabrication of nanotube of polystyrene (PS) with a cylindrical monodisperse diameter by wetting phenomena could be references in a broad range of nanotechnology. Ni nanowires made by a potential modulation mode,[21] known as an attractive tool for the modification and preparation of metal oxide films, have potential applications in high-density magnetic memories. Antimony (Sb)[16] nanowires may be used for the production of metal-semiconductor heterogeneous junction nanowire arrays. Sander *et al.* presented that thermoelectric materials, Bi_2Te_3 nanowires[17,18] array with controlled aspect ratios were deposited into a nanoporous alumina template. Nanoarrays of TiO_2[19] into commercial Al_2O_3 membrane (Whatman, Anodisc) with a small pore size of 200 nm were prepared by a simple dipping technique and they showed higher dielectric constant compared with conventional Al_2O_3 film formed in an aluminum anodizing process.

In this work, we first tried to fabricate cuprous oxide (Cu_2O) nanowires using a home-made nanoporous alumina template by electrodeposition technique. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and Energy-dispersive spectrometry (EDS) analysis clearly showed the formation of Cu_2O nanowires with a diameter of 57 nm. Cu_2O is a nonstoichiometric p-type semiconductor with a bandgap of 2.0 eV and recently was proposed as a photocatalytic material for splitting water into H_2 and O_2 via visible light irradiation.[22-24] It is also a potential material for fabrication of low-cost solar cells.[25,26]

Experimental

To create hexagonally ordered nanoporous alumina membrane, we used a two-step anodization method followed by selective dissolution of aluminum and barrier aluminum oxide (Fig. 1). A high purity aluminum sheet (Aldrich, 99.999% purity, 0.25 mm thick) was used in this experiment. The specimen was embedded in a Teflon holder with an exposed surface area of 1.18 cm^2 and electrolyte was rigorously mixed and maintained at 0°C. Pretreatment of the aluminum sheet, *i.e.*, electropolishing process was performed by constant-voltage condition of +21 V below 0°C for 4 min in a mixed solution of $HClO_4$ (Aldrich), C_2H_5OH (Aldrich), and deionized water (v/v = 8:90:2). The electropolished aluminum foil was then rinsed with isopropyl alcohol and deionized water.

As shown in Fig. 1a, first anodization in 0.3 M oxalic acid (Aldrich) by applying +40 V at 0°C and alumina dissolution by dipping in chromic acid solution were performed in sequence, resulting in a prepatterned aluminum substrate (Fig. 1b). Then, the same condition of the first anodization was applied for a second anodization resulting in an ordered nanopore array (Fig. 1c). To make an alumina membrane defect-free and in the absence of an obstacle in the nanohole of the membrane, complete removal of the barrier layer and the bottom aluminum is needed. Therefore, we used the following three

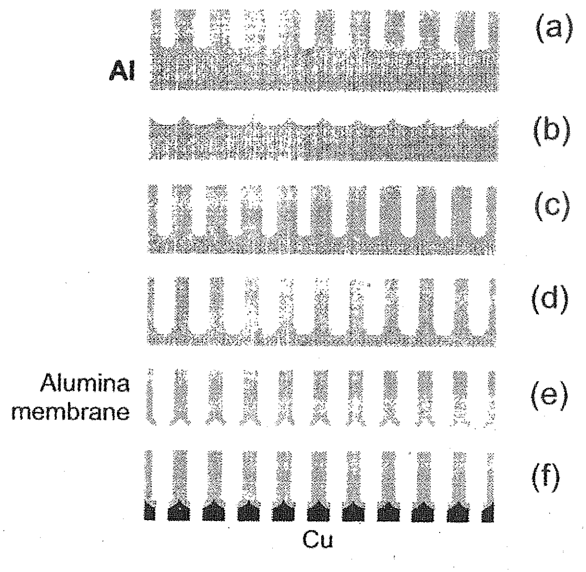

Figure 1. Schematic diagram of the fabrication of the home-made alumina membrane with well-ordered nanosize hole.

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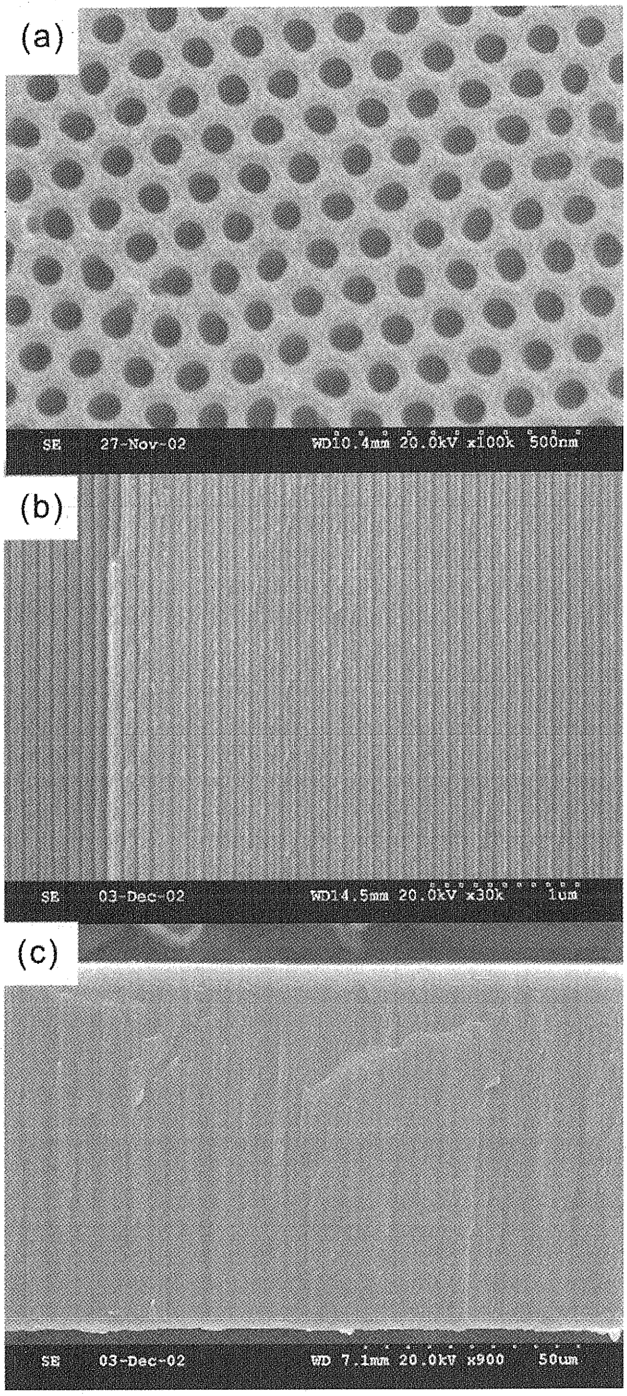

Figure 2. SEM image of the home-made alumina membrane with pore distance of 103 nm and pore diameter of 57 nm; (a) top-view and (b) and (c) cross-sectional view in the middle.

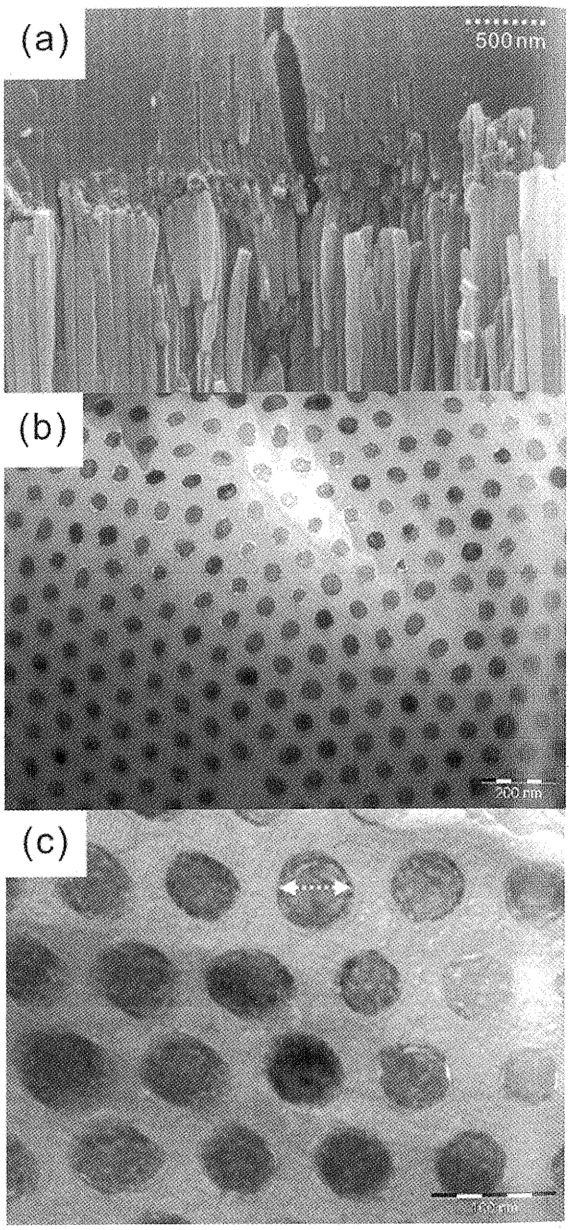

Figure 3. Morphological observations of Cu_2O nanowires array composite. (a) SEM data of the cross-sectional view, (b) and (c) TEM top view.

processes (Fig. 1d and e); (*i*) applying 40% of the anodizing voltage (*i.e.*, 16 V) for 20 min, (*ii*) dipping process in 5 wt % H_3PO_4 (Aldrich) solution at 30°C for 30 min, and (*iii*) removal of the bottom aluminum substrate with bromine solution ($Br_2:CH_3OH$(Aldrich) = 1:9, v/v). The dc sputtering technique was applied to form a conducting Cu substrate on one side of the membrane (dark area in Fig. 1f).

Cu_2O nanowires were deposited galvanically into a hexagonal nanoarray alumina membrane using the three-electrode system. Counter electrode and reference electrode were Pt mesh and saturated calomel electrode (SCE), respectively. A total of 45 g of 99.9995% $CuSO_4$ (Aldrich) was dissolved in 75 mL of 88% latic acid (Aldrich) and the copper ions stabilized by complexing with lactate ion. 5 M NaOH (Aldrich) aqueous solution was added to adjust the pH to 9. Potentiostat and galvanostat (PAR 273A) was used to apply a current density of -0.5 mA/cm^2 and the solution temperature of 65°C was constantly maintained during the experiments.

The surface morphology of Cu_2O nanowires was analyzed by field-emission scanning electron microscopy (FESEM, Hitachi, S-4300) and TEM (Philips CM200). The crystallinity and quantitative analysis of prepared Cu_2O nanowires was carried out using XRD (Philips DY616) and EDS coupled with the TEM equipment.

Results and Discussion

Figure 2a and b shows the top view and cross-sectional view of the home-made alumina membrane with highly ordered nanopores.

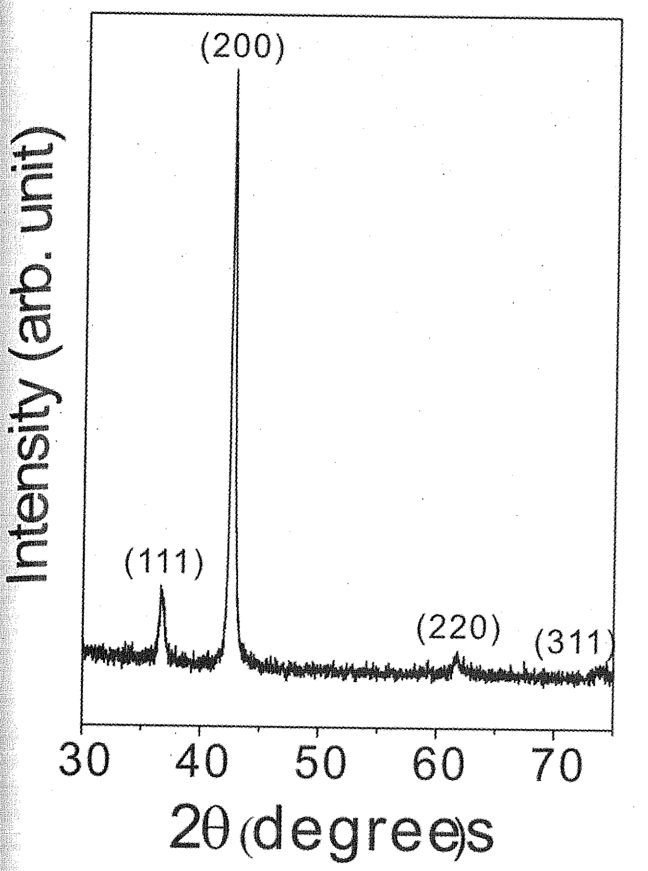

Figure 4. XRD pattern of a sample of Cu_2O nanowires in the alumina template prepared by the electrodeposition method at 65°C.

The diameter, an interpore distance, and the thickness of aluminum oxide are 57 nm, 103 nm, and 60 μm, respectively. It clearly shows homogeneous and defect-free structures.

According to the Pourbaix diagram,[27] theoretically, Cu_2O could be formed in a broad range of pH values between 5 and 12, while to apply optimal low current is more important, because Cu metal could be electrodeposited at high cathodic current.[28]

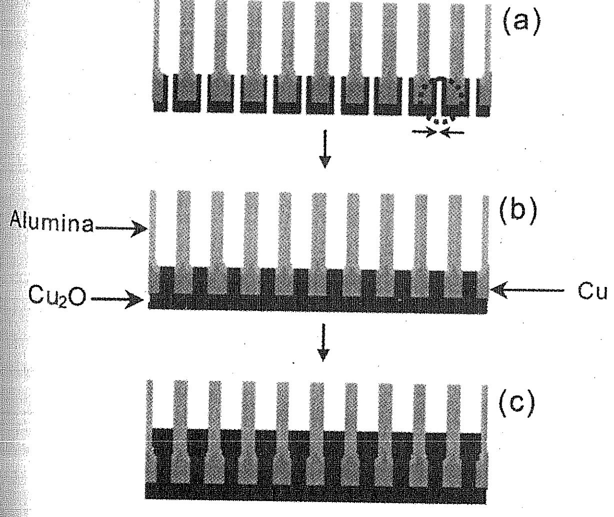

Figure 5. Schematic diagram of the production of Cu_2O nanowire by applying constant current on a porous anodic alumina membrane.

In this work, to deposit pure Cu_2O nanowires in the absence of Cu and CuO into the home-made nanoporous alumina template, an appropriate cathodic current of -0.5 mA/cm^2 was applied constantly for 4 h. For the confirmation of complete filling of Cu_2O into an alumina template with uniform orientation, SEM and TEM analysis were performed. For the TEM measurement, ion milling was applied to make an ultrathin film of Cu_2O nanowires/Al_2O_3 templates via removal of a blank alumina membrane with the oxide thickness of 55 μm at the upper part and Cu substrate deposited at the bottom part. Figure 3 is a morphological observation of cross-sectional view (a: SEM image) and top-view (b, c: TEM image) of the Cu_2O deposited in the alumina template. In Fig. 3a, one can clearly see Cu_2O nanowires filling the alumina membrane. To confirm that Cu_2O had completely filled the alumina template with a uniform orientation, TEM analysis was performed. Compact filling of defect-free Cu_2O nanowires of the pores is clearly shown in Fig. 3b and c. The diameter of Cu_2O nanowires marked with dotted arrow (Fig. 3c) is *ca.* 57 nm. Because the length of Cu_2O nanowires is 4 μm, the aspect ratio and the deposition rate is *ca.* 70 and 1 μm/h, respectively. EDS coupled with TEM instrument analyzed atomic concentration of nanowires of internal pore and the atomic percent of Cu is twice the atomic percent of O, confirming the fabrication of Cu_2O nanowires.

Figure 4 shows the XRD analysis of the Cu_2O nanowires deposited into an ordered alumina membrane. Cu_2O was preferentially grown with a [100] fiber texture. Generally, JCPDS card file 5-667 for chemically prepared Cu_2O[29] presents different relative intensity patterns of Cu_2O crystalline peaks. When the relative intensity of the 111 peak is 100%, the 200 peak has only 37% relative intensity value. Interestingly, our observations are different, *i.e.*, the 200 peak has the highest intensity, with lower intensity 111, 220, and 311 peaks. We assume that this phenomenon is strongly affected by the preparation method, especially the solution pH. Recently, Golden *et al.*[30] demonstrated that films of Cu_2O with a strong (200) sheet texture are selectively formed in pH 9, while a higher pH value of 12 induced a (111) sheet texture. Therefore, our observations are in agreement with previous work. However, a complete understanding of the deposition behavior of single-crystalline Cu_2O is still lacking and, therefore, further investigation should be undertaken.

Figure 5 shows a schematic diagram of the electrodeposition of single-crystalline Cu_2O with [100] fiber texture on an alumina template. Cu lactate solution was placed in contact with the Cu thin-film substrate located at the bottom of the porous alumina membrane. Cu_2O was first deposited at both conducting Cu edges of the membrane hole (see dotted circle in Fig. 5a) and then Cu_2O coalesced as shown in Fig. 5b. Cu_2O grew continuously to the open top pore (Fig. 5c).

At present, we succeeded only in the production of Cu_2O nanowires with a length of 4 μm and this would limit its application in solar cells and sensors. Thus, we will try to prepare longer Cu_2O nanowires with higher aspect ratio and improved compactness. We expect that this paper will be a reference for the development of better nanoscale solar cell systems.

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