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Fast and selective Cu_2O nanorod growth into anodic alumina templates via electrodeposition

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ABSTRACT

The fast and selective growth of cuprous oxide (Cu_2O) nanorods into anodic aluminum oxide (AAO) templates is achieved under optimized alkaline conditions via electrochemical deposition. The growth rate of Cu_2O nanorods at room temperature reached 360 nm/min, the fastest rate reported to date. The synthesis of Cu_2O nanorods by applying a constant current by using Cu_2O nanotubes as a transition state is extensively discussed; a Pt pottery-shaped layer played a key role as a seed layer for the fast Cu_2O growth. We report here the existence of regions of nanostructured Cu_2O based on our studies and previous relevant works, which include potential-pH curves for Cu^{2+}-lactate solutions.

1. Introduction

The synthesis of nanostructures, in the ranges of only a few hundred nanometers, such as nanowires, −rods, and −tubes, has generated great interest owing to their distinct properties and unique applications, as compared to bulk materials [1,2]. For such nano-objects, template-based approaches are one of the most common fabrication methods for mass production and alignment [3]. In particular, anodic aluminum oxide (AAO) templates have been widely employed in the production of nanostructures due to their relatively uniform pore distribution, as well as their thermal and chemical stability [4,5]. Electrochemical deposition is generally used for the growth of metals and conducting metal oxides because of the following advantages: (i) the thickness and morphology of the nanostructure can be precisely controlled by adjusting the electrochemical parameters, (ii) relatively uniform and compact deposits can be synthesized in template-based structures, (iii) higher deposition rates are obtained, and (iv) the equipment is inexpensive due to the non-requirements of either a high vacuum or a high reaction temperature [6,7]. Note that our previous studies have demonstrated the fabrication of nanostructures such as Ni [8,9], Bi_2Te_3 [10], Pb−CeO_2 [11] nanowires, and V_2O_5 agglomeration [12]. Thus, it is expected that the preparation of nanosized materials via electrodeposition into an AAO template can be a powerful fabrication method.

Copper (I) oxide (Cu_2O) is one of the best photovoltaic p-type semiconducting materials, with a direct band gap of ca. 2.0 eV [13]. Furthermore, Cu_2O has been attracting considerable attention not only due to its potential applications for splitting water into H_2 and O_2 upon visible light irradiation, but also for its application in cost-effective solar cell production and non-toxic devices [14–16].

Recently, we have extensively reported the preparation of Cu_2O nanowires or −rods via electrodeposition into AAO templates [17–20]. The electrodeposition of Cu_2O is available from an alkaline solution of copper lactate, according to the following reactions [20]:

$$2Cu^{2+} + 2e^- \rightarrow 2Cu^+ \quad (1)$$

$$2Cu^+ + 2OH^- \rightarrow 2Cu(OH)_s \quad (2)$$

$$2Cu(OH)_s \rightarrow Cu_2O + H_2O \quad (3)$$

however, such reactions typically take place under optimized electrochemical preparative conditions, which includes the presence of sufficient OH^- ions (pH > 8) and a solution temperature of ca. 65 °C. If the solution is unsuitable for this optimized condition, the formation of Cu metal could be the dominant reaction into the porous template [19,21]:

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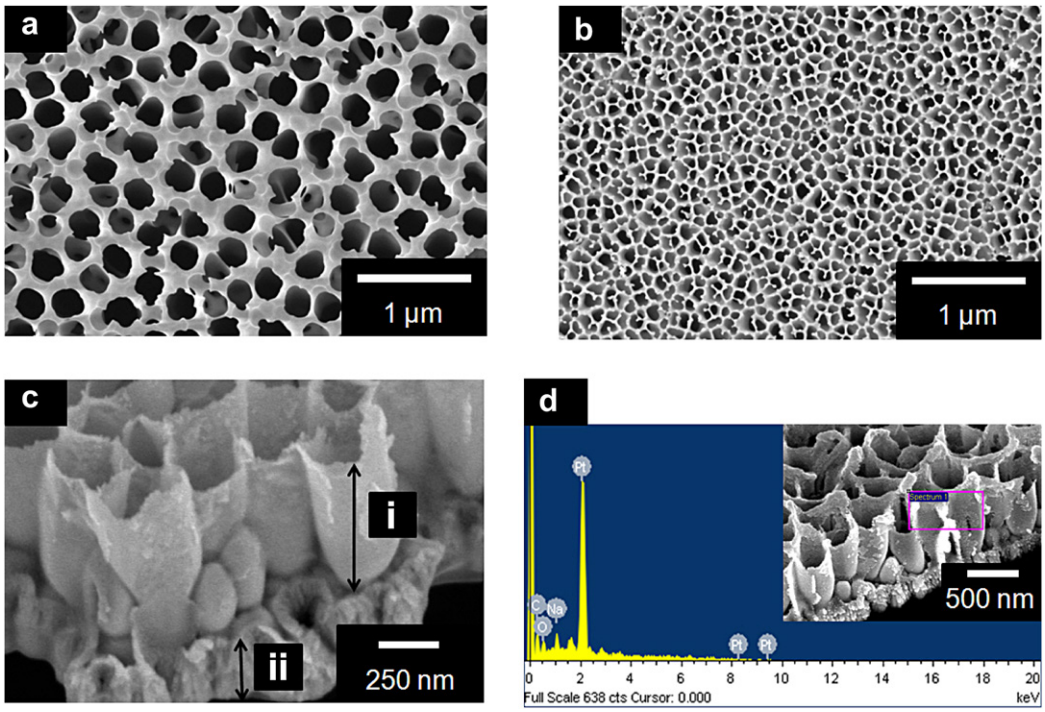

Fig. 1. SEM images of AAO template and Pt pottery-shaped layer. Top view of AAO template: (a) the ordered side and (b) the solution side. Cross-sectional view of Pt pottery-shaped layer after the selective dissolution of AAO templates in 1 M NaOH for 5 h: (c–i) remaining Pt pottery-shaped layer, (c-ii) bottom of the Pt layer film, and (d) EDX analysis of Pt pottery-shaped layer. Source: H. Ju et al.

$$Cu^{2+} + 2e^{-} \rightarrow Cu \quad (4)$$

In particular, a Pourbaix diagram shows that the Cu_2O domain exists in a very narrow potential range at all pH levels [22]. Moreover, Switzer and co-workers [23–25] have already reported that the co-deposition of Cu and Cu_2O nanostructures was also observed due to the mass transfer limitation of OH^- ions and the increase of resistance. For this reason, previous studies have shown that the co-deposition of Cu_2O/CuO or Cu_2O/Cu into AAO templates or onto thin films [26–28]. In addition, a few reports demonstrated the fabrication of selective Cu_2O nanorods using AAO templates, but with a very low deposition rate; between 33.3 nm/min [20] and 10.3 nm/min [29], at a deposition temperature of 60 °C. Note that Cu_2O nanorods are generally deposited layer-by-layer through a filling of pores in the AAO template via electrodeposition because most templates are insulators [30]. Thus, to overcome the low yield of the deposition rate, it is necessary to sufficiently increase the deposition interface.

In this study, Cu_2O nanorods and nanotubes were electrochemically deposited into AAO templates at a 10–20 times faster growth rate with high selectivity at room temperature by providing the Cu_2O nucleation site with a seed layer. Furthermore, our results provide a new insight into the mechanism affecting fast electrochemical Cu_2O deposition, based on a pE–pH diagram.

2. Experimental

A platinum metal layer with a thickness of a few hundreds of nanometers was sputtered onto one side of a commercial AAO membrane (Whatman, Anodisc 25) having a nominal pore size of 200 nm by direct current (DC) sputtering (GS NanoTech Inc.). The Pt-sputtered layers acted as a working electrode to provide nucleation sites of Cu_2O, as shown in Fig. 1. During sputtering, a Pt pottery-shaped layer was formed at the bottom of the AAO pores and along the wall surfaces of the AAO channels. However, the non-Pt pottery-shaped layer had a potential effect that was unsuitable for shortcut formation due to the breakdown of metal oxides, which commonly leads to a disturbed growth rate [20]. Therefore, having a Pt pottery-shaped layer as a starting seed metal layer was able to increase the electroactive surface. This phenomenon suggests that metal ions favorably migrate to a conduction substrate placed onto the boundary of AAO template during the initial stages of electrochemical growth of Cu and Ni [31,32].

Here, Ag/AgCl, 3 M KCl and Pt wires were employed as the reference and counter electrodes, respectively. The electrolyte consisted of 45 g of 99.99% $CuSO_4$ (Aldrich) and 75 mL of 88% lactic acid (Aldrich). By complexing with lactate ions, Cu^{2+} ions were stabilized and the pH was raised to alkaline values [13]. An

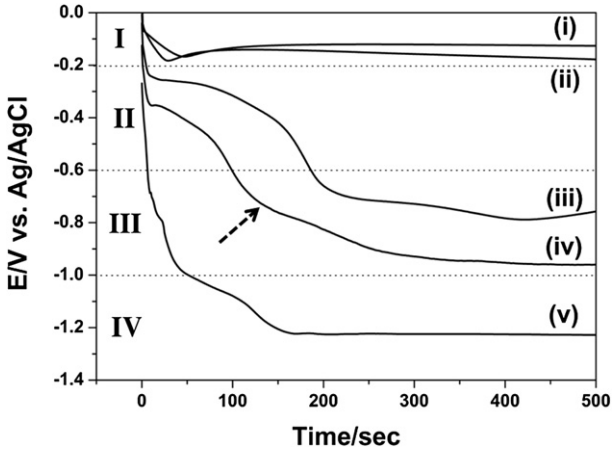

Fig. 2. Corresponding potential profiles during electrochemical deposition performed at room temperature and pH 9 at various applied current densities for 500 s: (i) −0.5 mA/cm^2, (ii) −1 mA/cm^2, (iii) −3 mA/cm^2, (iv) −5 mA/cm^2, and (v) −10 mA/cm^2. Source: H. Ju et al.