Controlled growth of spinel CuAl2O4/Cu hybrid nanorods array by electrodeposition in porous aluminum oxide template

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1. Introduction

Template synthesis of multi-functional nanoscale device using porous aluminum oxide (PAO) has been applied in many fields [1–7]. PAO template provides an ideal mold for the formation of one-dimensional metal or semiconductor nanomaterials in large scale owning to its high pore densities in a hexagonal close packed array and the ability to tailor pore’s diameter and depth [8–11]. The use of PAO for the fabrication of spinel CuAl2O4/Cu hybrid nanorod was first proposed in our earlier work [12]. The spinel-type semiconductor/metal hybrid featuring low band-gap has been applied for degradation of organic pollutants using solar energy. Besides, owing to the particular structure and favorable charge separation at semiconductor/metal interface [13,14], the CuAl2O4/Cu hybrids could also be found important application in solar-thermal conversion and hydrogen generation [15].

The anodization of aluminum into porous honeycomb structure usually results in a dense, insulated alumina layer at the bottom, which makes the electrochemical deposition of metal using direct current (dc) into the pores difficult [16,17]. Without separating PAO from the barrier layer, electrodeposition in PAO is only possible under alternating current (ac) conditions given the barrier layer is not highly resistive, as for that prepared at low oxidation potential (15–20 V) at room temperature [18]. It is documented that aluminum, as a “valve metal” [4], allows reductions of ions in the pores during cathodic half-cycle, without reoxidation during anodic half-cycle [19–21]. So far, Ni [3], Co [22], Au [23] and other metal nanowires of several micrometer lengths have been fabricated using the PAO template.

It is also reported that metal oxide could form on the nanoparticle-termed barrier layers under alternating potentials [24]. Our previous study showed an system of metal/metal oxide could be co-electrodeposited in PAO pores of relative shorter length (0.6–0.7 μm), implying a series of much complex chemical reactions involved in the evolution of a hybrid Cu/CuAl2O4 system [12]. To identify optimal conditions that favor the growth of CuAl2O4 during electrodeposition of Cu into the PAO pores, a set of parameters including pH, applied potential and effect of “protecting ions” were evaluated in this study. Quality of pore-filling was characterized using scanning electron microscopy (SEM) of as-deposited surfaces and of pore cross sections. The structure and crystallization of the hybrids were studied using X-ray diffraction (XRD).

2. Materials and methods

High-purity aluminum foil (99.99%), 0.2 mm thick, was annealed in air at 500 °C for 4 h in furnace. Al pieces, 3 × 3 cm in size, were etched in 0.5 M sodium hydroxide at 60 °C for 2 min to remove the native oxide layer and degreased by acetone in ultrasonic for 5 min, rinsed in distilled water for several times. Prior to anodization, the back and edges of electrodes were sealed with wax to produce an electrode with only one face exposed, and each electrode was electropolished at 19 ± 1 °C in a magnetically stirred solution composed of perchloric acid and ethanol (20/80 V/V) to a mirror-like finish under potentialstatic supply.

Anodization was carried out in a 2 M phosphoric acid at 20 °C for 20 min under a voltage of 15 V against a graphite counter electrode. This procedure produces a porous AAO template of pore fraction about 40% by volume. The pore thickness was about 700 nm with mean diameter approximates to 50 nm.
Electrodeposition was carried out in a two-electrode system consisting of a graphite plate as the counter electrode and PAO as the working electrode. The electrolyte was CuSO₄ (35 g L⁻¹), MgSO₄ (20 g L⁻¹) and boric acid (pH 3–4), which was then adjusted to pH 1.5 with sulfuric acid and to pH 7 with triethanolamine to evaluate the effect of different pH value. Deposition voltage was varied from 11 Vrms to 16 Vrms at 60 Hz with a sine waveform. For all samples, the deposition duration was set for 60 s. To evaluate the role played by Mg²⁺, an electrolyte consisted of only 0.5 M CuSO₄ and H₃BO₃ (pH 3–4) was adopted. The temperature of electrolyte was kept at 20°C by water cooling system. The electrolyte was refreshed after every five samples to compensate Cu²⁺ depletion.

Phase identification was performed by X-ray diffraction (XRD) using a D8 ADVANCE X-ray Polycrystalline Diffractometer (Bruker, Germany) with Cu Kα radiation (λ = 0.154056 Å). Scanning electron microscopy (SEM) images were acquired on a SIRION 200 scanning electron microscope (FEI, USA) equipped with an INCA energy dispersive Spectrometer (EDS) system (Oxford Instrument, UK).

3. Results and discussion

In order to get a well filling ratio and efficiency, proper electrodeposition voltage was tried using potential-current scan in the electrolyte of CuSO₄ and MgSO₄ at pH 3. It showed that the electrodeposition began at 6 Vrms, and the current density reached to as high as 28 mA/cm² at 15 Vrms (Fig. 1).

At high deposition current density, abundant bubbles spilled at the cathodes, suggesting the over vigorous chemical reaction and evolution of H₂. Accordingly, three electrodeposition voltages were applied, 11 Vrms, 13 Vrms and 15 Vrms. Fig. 2a showed a scanning electron microscope (SEM) image of the as-electrodeposited PAO under 11 Vrms. As can be seen, the growth of nanorods in alumina pores is quite slow, few pores are fully filled. Cross section (Fig. 2b) showed that the nanorods were around 500 nm long. When the applied potential was increased to 13 Vrms, considerable pore-filling quality was obtained (Fig. 2c and d). Since the growth rate of nanorods in porous alumina varies according to the different resistances of the barrier layer resulted from the previous anodic oxidation of aluminum, over growth of nanorods into nearly submicron-octahedral crystallite on the surface of PAO template was seen (Fig. 2c). Continued increase of voltage to 15 Vrms resulted in template pitting and random agglomeration of nanoparticles on the surface of PAO template (Fig. 2e and f).

Fig. 3 showed the X-ray diffraction patterns of electrodeposited PAO under different deposition potentials corresponding to SEM images. For all the samples, diffraction lines due to a spinel phase were observed. The crystal structure of CuAl₂O₄ is consistent with that of cubic spinel aluminate (JCPDS/ICSD number 061454). For sample a (11 Vrms), peak corresponding to (012) plane of CuAlO₂ was also observed in addition of CuAl₂O₄ and Cu crystallites. Compared with that of sample a, the XRD pattern exhibited much stronger and sharper (311) reflection (2θ = 36.82°) of the spinel form of CuAl₂O₄ for the sample b and peaks of CuAlO₂ disappeared. When the applied potential is raised to 15 V, a broader and weaker peak of (311) plane of spinel CuAl₂O₄ is witnessed, which is accompanied by the arisen sharper and stronger peak of copper crystals. This can be explained from SEM images (Fig. 2e and f) that dimensional confinement did not exist any more due to destruction of the PAO structure. The deposited copper together severed as cathode for preferential growth of copper crystallite that was similar with the dc electrodeposition.
The influence of electrolyte pH level on the crystallite structure was also investigated by adjusting the electrolyte to pH 1.5 and to pH 7, which were originally studied as proper conditions for the deposition of metallic Cu or cupric oxide (CuO), respectively. At pH 1.5, the resulted nanorods were purely copper crystallites; at pH 7, the peaks were much weaker and corresponded to planes of CuO, in accordance with that of Jamine et al. [25], as shown in Fig. 4.

The role played by Mg2+ in the deposition of CuAl2O4/Cu hybrid was also concerned in this work. As a protection ion of the barrier layer, Mg2+ was found to improve the deposition of Cu into PAO pores [26]. Although there was not efficient evidence for direct relation of Mg2+ to the formation of CuAl2O4, the results implied that Mg2+ must have some impact on the activity of Cu2+, since only Cu2O was detected in the filled PAO template in a simple solution of CuSO4 at pH 3–4, as shown in Fig. 5.

Mechanism on the hybrid’s evolution can be proposed in terms of the applied potential and proper chemical environment in this case. The whole process is illustrated by Scheme 1.

When an anodic bias is applied, electric field is focused at the bottom of the pores, as depicted in Scheme 1a. Pores begin to nucleate at the tips based on the field-enhanced oxide dissolution mechanism [27–29], and Al3+ ions were released into the electrolyte (Scheme 1b). During the cathodic reaction, Cu2+ is reduced to Cu+ by gaining one electron or to Cu by gaining two electrons and hydrogen gas is generated at this stage. In the subsequent anodic reactions, part of the reduced Cu+ is re-oxidized into Cu2+. Cupric ions, with the dissolved Al3+ in an acidic environment and in situ generated OH−, co-precipitate to form hydroxide compound, presumably in the form of Cu[Al(OH)4]2. The Cu[Al(OH)4]2 hydroxide is further decomposed to CuAl2O4 by external applied power. The whole process can be generalized by chemical reaction as follows.

In the anodic bias,

\[ \text{Al} - 3e^- \rightarrow \text{Al}^{3+} \]  \hspace{1cm} (1)

\[ \text{Cu}^+ - e^- \rightarrow \text{Cu}^{2+} \]  \hspace{1cm} (2)

In the cathodic bias,

\[ \text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \] \hspace{1cm} (3)

\[ \text{Cu}^+ + e^- \rightarrow \text{Cu} \] \hspace{1cm} (4)

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \] \hspace{1cm} (5)

Accompanied by the precipitation of Cu2+ and Al3+,

\[ \text{Cu}^{2+} + 2\text{Al}^{3+} + 8\text{OH}^- \rightarrow \text{Cu[Al(OH)4]}_2 \] \hspace{1cm} (6)

The crystallization of CuAl2O4 was supposed to be excited by the focused electric power instantaneously, unlike the traditional chemical synthesis rout [30,31],

\[ \text{Cu[Al(OH)4]}_2 \rightarrow \text{CuAl}_2\text{O}_4 + 4\text{H}_2\text{O} \] \hspace{1cm} (7)

It should be noticed that proper potential favors the formation of CuAl2O4 crystallites. As discussed previously, under 11 Vrms sine wave potential, not only CuAl2O4 and Cu crystallite were produced, but also CuAlO2, which can be deduced from incapable re-anodization of the reduced Cu+ into Cu2+ at this level of potential. The intermediate Cu+ reacted with hydroxyl ions and Al3+ to form CuAlO2 by the following simplified reactions.

![Fig. 4. X-ray diffraction patterns of electrodeposited PAO at different pH levels of: (a) pH 7, (b) pH 1.5 and standard patterns for CuO (round heads) and Cu (square heads).](image1)

![Fig. 5. X-ray diffraction patterns of electrodeposited PAO template in a simple solution of CuSO4 at pH 3 and standard patterns for Cu2O (square heads).](image2)

![Scheme 1. The mechanism of the evolution of CuAl2O4/Cu hybrids in the PAO template using electrodeposition. (a) Electric field is focused at the center of the pore tips (anodic bias), (b) electrical field enhanced dissolution of Al3+, (c) reduction of Cu2+ to Cu+ or to Cu and evolution of hydrogen at the cathodic bias, (d) re-oxidation of Cu+ and formation of CuAl2O4 spinel.](image3)
Cu$^{3+}$ + Al$^3+$ + OH$^-$ → CuAl(OH)$_4$

CuAl(OH)$_4$ → CuAlO$_2$ + 2H$_2$O

When the anodic potential was too high, at 15 V$_{\text{rms}}$ (21 V$_{\text{peak}}$), no intermediate cuprous oxides were generated, but the potential was too high for the porous alumina pattern to withstand, structure damage was caused and the resulted hybrid was not rod-like anymore, but clusters of hybrid nanoparticles. It is held that the proper potential was 13 V$_{\text{rms}}$ in this case, favors the formation of CuAl$_2$O$_4$/Cu hybrids without causing damage of PAO structure.

4. Conclusion

Variables including applied potential, electrolyte pH value and protection ions that affected the electrochemical deposition of CuAl$_2$O$_4$ were discussed in this work. Applied potential was found critical not only for the pore filling, but for the preferential growth of crystallite planes. It showed that the best filling efficiency and crystallization of CuAl$_2$O$_4$ were obtained under a sine wave 13 V$_{\text{rms}}$. For pH level, CuAl$_2$O$_4$ was only detected at pH 3; more acidic (pH 1.5) or neutral (pH 7) environment resulted in pure production of metallic Cu or cupric oxide (CuO). Mg$^{2+}$ was necessary for the formation of CuAl$_2$O$_4$/Cu hybrid. Mechanism on the evolution of this hybrid was investigated through a series of chemical reaction. Compared with the chemical synthesis route of CuAl$_2$O$_4$, including hydrolysis of precursor and crystallization by calcinations, the applied potential was supposed to provide energy for the final crystallized product. This study is helpful to unveil the complex electrochemical reaction involved in the evolution of CuAl$_2$O$_4$/Cu hybrid using PAO template synthesis method.

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References