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Nickel nanotube array via electroplating and dealloying

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ABSTRACT

Ni nanotube arrays are fabricated using a facile, one-pot, and template-free method by electroplating Cu-Ni core-shell microcolumns followed by electrochemical dealloying of Cu. Well-separated Cu-Ni core-shell microcolumns are first formed as a result of controlled electrodeposition rates of Ni and Cu and the existence of miscibility gap for Ni-Cu alloys. Cu is more rapidly deposited onto the substrate forming cores that serve as the template to be coated with less rapidly deposited Ni species, producing Cu-Ni core-shell microcolumns. Ni nanotube arrays are then generated by selectively etching away the Cu cores. The Ni nanotube arrays thus obtained possess attractive anti-reflection, superhydrophobicity, and magnetic properties.

1. Introduction

Nickel-based porous nanomaterials are very attractive for wide-ranging applications, which include use in supercapacitors [1], lithium batteries [2], catalysts [3], biosensors [4], and electronic devices [5]. Arrays of one-dimensional Ni nanostructures consist of oriented nanowires or nanotubes are particularly attractive for the benefits of their large surface area, high electrical conductivity, mechanical reinforcement, and interesting magnetic properties. Various bottom-up methods have been explored for use in constructing aligned metallic nanostructures, such as metal-organic chemical vapor deposition [6], electrochemical deposition [7], and atomic layer deposition [8]. Notably, nanotemplates with ordered nanochannels (e.g. anodic aluminum oxide, polycarbonate membranes) are generally required for these methods to achieve metallic nanowires arrays [9,10]. With various techniques developed for promoting higher metal deposition rate along nanochannel walls [11–14], more complex repetitive template strategies have also been developed, e.g., repetitive structural replicating from template A to material B which serves as a new template for material C and so on [15–17]. In general, the use of template entails extra fabrication steps and leads to higher degrees of complexity.

By advancing island-formation mechanism for Ni-Cu electrodeposition [18–20], this study reports a template-free method with Ni-Cu first electrodeposited and then dealloyed to selectively remove Cu, resulting in a self-ordered Ni nanotube array. Dealloying selectively etches away the more active metal component from an alloy for

generating porous metals [21]. Ni with chaotic porous structures has been fabricated by dealloying Ni-based alloys such as Ni-Al [22] Ni-Cu [23], and Ni-Mn [24]. Notably, dealloying lacks morphological control, and usually is not suitable for rendering one-dimensional metallic nanostructures, particularly in template-free synthetic approaches. The method reported here fully takes advantage of the simplicity and convenience of electrochemical techniques, and offers desirable morphological control, providing a remarkably facile route to ordered metal nanotube arrays.

2. Experimental details

2.1. Sample fabrication

Electrochemical fabrication of samples was carried out at room temperature via a three-electrode cell configuration with controlled potentiostat (HEKA, PG310). A $1.5 \times 1 \text{ cm}^2$ piece of indium-tin-oxide (ITO) glass (CSG PVTech Co., Ltd) was used as the working electrode, a platinum ring as the counter electrode, and a saturated calomel electrode (SCE, 0.244 V vs. standard hydrogen electrode) as the reference electrode. The Cu-Ni alloy films were electrodeposited in a deionized water-based electroplating bath containing 0.05 M copper (II) sulfate pentahydrate (Riedel-Dehaën), 0.5 M nickel (II) sulfamate tetrahydrate (Aldrich, 98%), 0.6 M boric acid (Riedel-Dehaën), and 0.001 M saccharin (International Laboratory), with the deposition charge kept at 10 C cm^{-2} . The alloy samples deposited at -0.9 V , -1.0 V and -1.1 V

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were labeled as A-0.9 V, B-1.0 V and C-1.1 V, respectively. The dealloying treatment was carried out at 0.5 V for 20 min immediately after the electroplating in the same electrolyte bath. The samples were rinsed with deionized water and ethanol, and dried under nitrogen gas flow before characterization and tests.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected using an X-ray diffractometer (Bruker, D2phaser) with a radiation source of Cu K α ($\lambda = 0.15406$ nm). Sample morphologies and chemical compositions were examined with a scanning electron microscope (SEM, Philips XL 30FEG) and equipped energy dispersive X-ray spectrometer (EDX). Cyclic voltammetry (CV) was performed on multi-functional electrochemical analyzer (CHI, 660E) at room temperature in various electrolytes. A three-electrode system was used, with a 1.5×1 cm 2 piece of ITO glass as the working electrode, a 2×2 cm 2 piece of platinum foil as the counter electrode, and a SCE as the reference electrode. The vertical UV–vis reflection spectra were measured on a charge-coupled spectrometer equipped with a tungsten halogen lamp (Ocean Optics). The contact angles were measured on a goniometer (Ramé-hart 500) equipped with a charge-coupled device camera at room temperature. A vibrating sample magnetometer (VSM, Lake Shore 7410) was used to record magnetic hysteresis loops at 273 K.

3. Results and discussion

Samples are prepared following the procedures and parameters in Table 1, and the atomic compositions are determined by SEM equipped EDX. Ni-Cu alloys are obtained through constant voltage electroplating in Step 1. Ni content increases with more negative deposition potential, and compositions of Ni $_{28}$ Cu $_{72}$, Ni $_{44}$ Cu $_{56}$ and Ni $_{55}$ Cu $_{45}$ are obtained successively. After dealloying in Step 2, Ni $_{44}$ Cu $_{56}$ and Ni $_{55}$ Cu $_{45}$ become Ni $_{67}$ Cu $_{33}$ and Ni $_{65}$ Cu $_{35}$ respectively. Despite that Ni-Cu alloys usually form solid solutions due to the same FCC crystal structures, according to the Cu-Ni phase diagram, there is a miscibility gap existing at lower temperatures, where two separated phases co-exist, i.e., a Cu-rich phase and a Ni-rich phase [25]. Dealloying of the Cu-rich phase can only take place with Cu content within this miscibility gap [23]. Therefore, the Ni-Cu films electroplated at room temperature are inhomogeneous alloys. As the Cu content drops to the boundary of miscibility gap in the dealloying process, Ni-Cu alloys gradually become single-phased that cannot be dealloyed, and the dealloying reaction ceases [23]. Therefore, over 30% of residual Cu is left within as-dealloyed Samples B-1.0 V and C-1.1 V. Interestingly, Ni $_{28}$ Cu $_{72}$ becomes Ni $_{99}$ Cu $_1$, indicating deeper etching of Cu within as-dealloyed Sample A-0.9 V.

In XRD patterns (Fig. 1), Cu $\langle 111 \rangle$ ($2\theta = 43.317^\circ$, JCPDS No. 85–1326) and Ni $\langle 111 \rangle$ ($2\theta = 44.505^\circ$, JCPDS No. 04–0850) peaks are indicated in dashed lines. For the as-electroplated samples, the overlapping peaks represent the co-existence of a Cu-rich phase and a Ni-rich phase. From Sample A-0.9 V to C-1.1 V the overlapping peak set right-shifts due to reduced Cu content and increased Ni content, in agreement with the composition change from Ni $_{28}$ Cu $_{72}$, Ni $_{44}$ Cu $_{56}$, to

Table 1

Sample preparation details and compositions.

| Sample | Step 1: electroplating | | | Step 2: electrochemical dealloying | | |
|---------|------------------------|------------------------|-----------------------|------------------------------------|------------|-----------------------|
| | Voltage (V vs SCE) | Charge (C cm $^{-2}$) | Atomic ratio (%) | Voltage (V vs SCE) | Time (min) | Atomic ratio (%) |
| A-0.9 V | −0.9 | 10 | Ni $_{28}$ Cu $_{72}$ | 0.5 | 20 | Ni $_{99}$ Cu $_1$ |
| B-1.0 V | −1.0 | 10 | Ni $_{44}$ Cu $_{56}$ | 0.5 | 20 | Ni $_{67}$ Cu $_{33}$ |
| C-1.1 V | −1.1 | 10 | Ni $_{55}$ Cu $_{45}$ | 0.5 | 20 | Ni $_{65}$ Cu $_{35}$ |

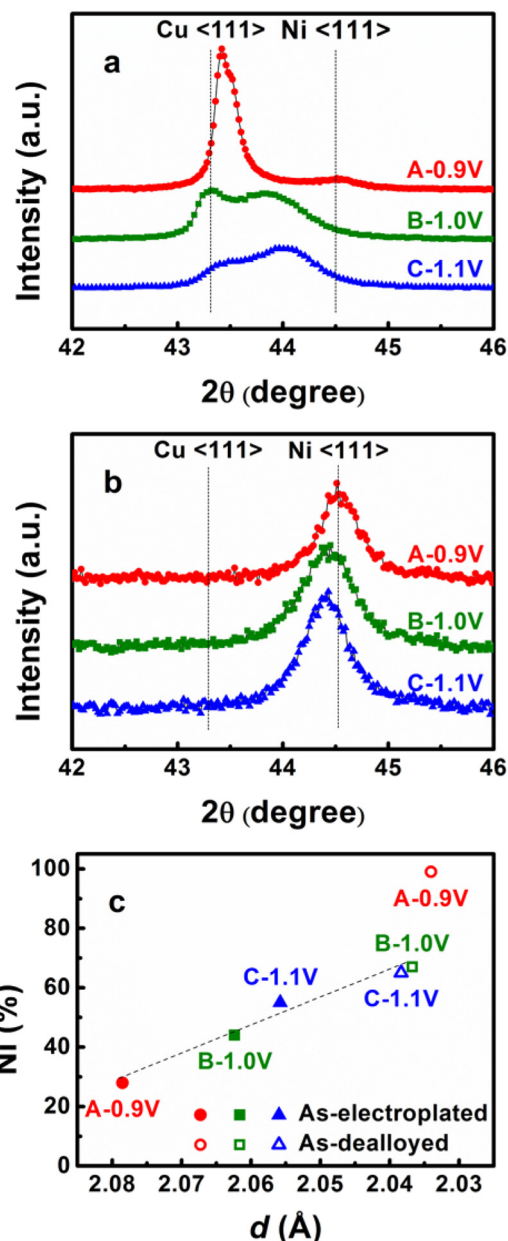


Fig. 1. XRD patterns of as-electroplated (a) and as-dealloyed (b) Samples A-0.9 V, B-1.0 V and C-1.1 V, and Ni contents within the as-electroplated and as-dealloyed samples plotted as a function of Ni-rich $\langle 111 \rangle$ interplanar spacing (c).

Ni $_{55}$ Cu $_{45}$. For the as-dealloyed samples, single peaks are observed, indicating a single phase. The single-peak set right-shifts compared to the overlapping peak set, because of decreased Cu content. Single peaks of Samples A-0.9 V, B-1.0 V and C-1.1 V left-shift successively as a result of more residual Cu, also in agreement with composition change from Ni $_{99}$ Cu $_1$, Ni $_{67}$ Cu $_{33}$, to Ni $_{65}$ Cu $_{35}$. In both as-electroplated and as-dealloyed Sample A-0.9 V, the small peaks located at the Ni $\langle 111 \rangle$ peak indicate the formation of a pure Ni phase. The Ni contents within the as-electroplated and as-dealloyed samples are plotted as a function of Ni-rich $\langle 111 \rangle$ interplanar spacing (d). The Ni contents of the first five alloy compositions are in linear relationship with d , consistent with the nature of alloys. By contrast, Ni $_{99}$ Cu $_1$ is far off the line with d value of 2.034 Å, very close to that for pure Ni (2.035 Å, JCPDS No. 04–0850). This probably hints the formation of pure Ni instead of Ni-Cu alloy after complete removal of Cu in the as-dealloyed Sample A-0.9 V.

In the SEM images of as-electroplated samples (Fig. 2), Sample A-0.9 V consists of well-separated Cu-Ni core-shell alloy microcolumns of

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