



Nanoconfined nonequilibrium electrodeposition of metal-metal hydroxide one-dimensional nanostructures



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ABSTRACT

In this paper, we present a new insight into nonequilibrium electrodeposition. Owing to the nanoscale confinement effect of the template channels, the large overpotential leads to a highly nonequilibrium process and generates segmented metal-metal hydroxide one-dimensional (1D) nanostructures. The synthesized Ni-Ni(OH)_{x≈2} nanotubes vividly reflect the evolution of the local electrochemical environments, by which both the morphology and the composition have been modulated. The electrochemical mechanisms responsible for this unexpected deposition have been identified and discussed. It was exploited to obtain bi-segmented Ni nanowire-Ni(OH)_{x≈2} nanotube. This work opens the way to a versatile synthesis of metal-metal hydroxide 1D nanostructures that could be applicable for the integration of well-aligned metal-hydroxide nanostructures into large-scale energy-storage devices.

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1. Introduction

Transition metal oxides and hydroxides are promising electrode materials for batteries and pseudocapacitors [1–3]. Among them, nickel hydroxide is of particular interest because of its high theoretical capacitance, low cost and well-defined electrochemical redox activities [4,5]. Designing and establishing nanostructured systems can further improve their specific capacitance, reach multifunctionality and offer new opportunities for novel applications [6–8]. Therefore, explorations on controllable synthesis of complex nanostructures that are composed of multi-components and specific morphologies (eg., rods, wires, tubes) are of fundamental significance.

As a cost-effective and versatile technique, template-based electrodeposition has been developed to be one of the most important methods for synthesizing one-dimensional (1D) nanostructures [9–11]. Nevertheless, the poor conductivities of metal oxides and hydroxides can be a drawback, regarding the electrodeposition method. Although electrodeposition into nanoscale channels is a very complicated process, it is usually considered that the electrochemical environments, including pH value, ion concentration, local overpotential, etc., establish a rather

stable system, enabling the production of uniform, even single-crystalline 1D nanostructures [12–14]. It has also been widely accepted that the large-overpotential electrodeposition from aqueous solution into nanoporous templates would be blocked by the concurrent hydrogen reduction evolution [15,16], which indeed prohibits further explorations towards template-based nonequilibrium electrodeposition process. On the other hand, nonequilibrium electrodeposition has been employed to construct branched fractal patterns [17] and three-dimensional nanostructured architectures [18,19] on smooth (conducting) surfaces, even to coat metal on insulating substrates [20]. Recently few studies explored the high-current-density electrodeposition into nanoporous templates, by which the morphology of the products can be controlled, and metal and alloy nanotubes were directly electrodeposited into pristine (nano) porous anodic alumina membranes generally referenced as anodic aluminum oxide (AAO) templates [21–24].

Two mechanisms have been proposed to explain the formation of the tubular morphology resulting from the unconventional electrochemical conditions. On the one hand, the ring-shaped nanoelectrode within each nanopores, as a result of AAO one-side metallization by evaporation or sputtering, was primarily considered. It promotes a nonuniform electric field concentrated at the tip end of this tubular structure [21,23,25]. This enhanced electric field at the periphery of the pore channel results in the expected preferential electrodeposition [15,26]. On the other hand,

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it has been pointed out that the hydrogen gas evolution induced by the electrodeposition can partially occupy pore channels of the template, and thus suppress the lateral-direction (perpendicular to the pore channel) deposition [27,28]. Until now, however, the as-mentioned two mechanisms have never been considered in a converging approach, possibly because the electrochemical processes were still too mild to generate simultaneously some effects related to both mechanisms. Further explorations are essential not only to provide a detailed understanding on the formation of the nanotube morphology by nanoconfined electrodeposition, but also to develop new strategies for facile synthesis of complex 1D nanostructures.

Here we demonstrate that the confinement effect within nanoporous AAO template can lead to a highly nonequilibrium electrodeposition in aqueous medium. This nonequilibrium process not only generates a long nanotube structure with an inner conical profile (instead of nanowires produced by the conventional electrodeposition), but it also dramatically changes the composition of the products from nickel (bottom part) to nickel hydroxide (top part) along the nanotube. The as-synthesized bi-segmented Ni-Ni(OH)_{x≈2} nanotube structure vividly reflects the evolution of the local electrochemical environments confined in the pore channels, each pore channel serving as a nano-reactor. Beyond the new insight into the mechanisms of nanoconfined electrodeposition, this study opens up new perspectives to explore voltage-pH (also called Pourbaix) diagrams. We further carried out a one-pot synthesis of a segmented Ni nanowire-Ni(OH)_{x≈2} nanotube geometry.

2. Experimental

2.1. Materials and Methods

AAO templates used in this study were purchased from the Whatman Company (Anodisc 13, with a nominal pore diameter of 200 nm). Before the experiments, an Au layer was deposited on one side of the template, serving as the working electrode. The samples were electrochemically synthesized in a conventional three-electrode cell. A piece of platinum sheet was used as the counter electrode, and a saturated calomel electrode (SCE) served as the reference electrode. The electrolyte used in the experiments consisted of 1 M NiSO₄·6H₂O and 0.75 M H₃BO₃ in deionized water, with a pH value of 3.8. The electrodeposition was carried out in the potentiostatic mode under a cathodic potential ranging from -1.0 to -5.0 V/SCE.

2.2. Characterization

The morphology of the as-synthesized samples was characterized by scanning electron microscopy (SEM, JEOL JSM-6400F), and their structures was analyzed by X-ray diffraction (XRD, Bruker AXS D8 Advance). Samples were also characterized by transmission electron microscopy (TEM, Hitachi HNAR9000, 300 kV and Hitachi HF2000, 100 kV) both equipped with energy-dispersive X-ray spectroscopy (EDX, Thermoelectron). Electron energy loss spectroscopy (EELS) measurements were carried out at 100 kV on the Hitachi HF2000 transmission electron microscope equipped with a GATAN

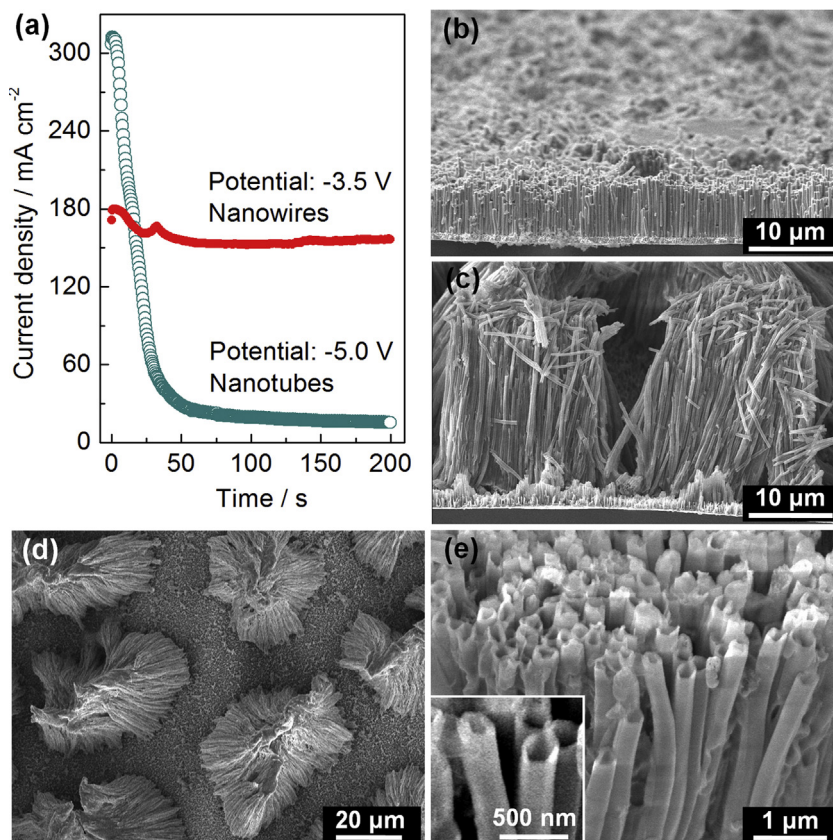


Fig. 1. (a) Current density transient curves for Ni-based electrodeposition into AAO templates at cathodic potentials of -3.5 and -5.0 V/SCE, which produce Ni nanowires and bi-segmented Ni-Ni(OH)_{x≈2} nanotubes, respectively. Side-view SEM images of the synthesized (b) Ni nanowire arrays (cathodic potential: -3.5 V/SCE) and (c) Ni-Ni(OH)_{x≈2} nanotube arrays (cathodic potential: -5 V/SCE) after the AAO templates have been dissolved by NaOH aqueous solution, showing distinct morphologies. (d) Top-view SEM image of the synthesized Ni-Ni(OH)_{x≈2} nanotubes, which self-assemble to form multiple isolated arrays. (e) SEM image of the bottom side of the nanotubes peeled off from the Au layer (serving as working electrode) revealing the nanotube structure has been well constructed. Inset: higher magnification SEM image.

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