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A single-step approach to create nano-pottery structures for efficient water electrocatalysis

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ABSTRACT

We have introduced a simple fabrication process to create Ni nano-pottery structure using a well-controlled electrodeposition process into a nanoporous alumina template. The nanostructures were then applied as a stable and effective cathode catalyst for hydrogen evolution reaction (HER) in alkaline water electrolysis. Their catalytic activity was compared to that of the Ni nano-rod and film and the result shows that the HER activity was greatly enhanced when using the Ni nano-pottery structure which mainly resulted from both larger and higher numbers of surface reactive sites.

1. Introduction

Metallic nanomaterials have been widely applied for nanoscale devices, magnetic memories, chemical sensors and catalysts. There have thus been extensive efforts to synthesize different metallic nanostructures such as nano-rod/-wire and nanotube into nanoporous templates. However, the creation of metallic nanopore structures (e.g. nanotubes) using alumina template still requires complexed processes; (i) pre-treatment processes including chemical modification and addition of surfactants [1–3] which both can cause purity issues of the nanostructure [4] and (ii) atomic layer deposition [5] followed by electroless deposition [6] can be employed, which can be expensive and also very sensitive to produce well-defined nanotube structures [7,8]. Recent research are directed towards developing simpler fabrication methodologies to create nanostructures and nanomaterials in conjunction with extending their applications [4,7].

The metallic nanostructures have emerged as a superb electrocatalyst in a wide range of electrochemical processes since it offers a larger active area to enhance the catalytic activities due to inherent effects of their quantum size as well as changes in physicochemical and electronic properties [9,10]. The higher active sites can usually be obtained by controlling the metal structure and fabrication of nanostructures with a porous metal oxide template. In particular, Ni and Ni alloys nanostructures have received great attention in the use of electrocatalytic cathode materials for hydrogen evolution reaction (HER), since it possesses relatively high initial electrocatalytic activity, corrosive resistance to strongly alkaline environments, and cost-effective [11–13].

In this communication, we describe a simple and single-step approach to fabricate Ni nanostructures, mainly nano-pottery and nano-rod into a porous alumina template by electrodeposition. The electrocatalytic activities of the nanostructures in HER are compared to that of Ni films in terms of the polarization measurement.

2. Experimental

An alumina template (Whatman, Anodisc 25) with a diameter of 200 nm was used to fabricate Ni nanostructure. Before electrodeposition, a 200 nm-thick gold nano-bowl gold layer was deposited on one side of the template by applying DC sputtering.

To compare with the Ni nanostructures formed by the alumina template, Ni film was electrodeposited onto a gold quartz crystal. The Ni electrolyte solution consisted of 1.4 M $Ni(NH_2SO_3)_2{\cdot}4H_2O$ (Aldrich) and 0.5 M H_3BO_3 (Aldrich) at a pH of 3.5. Ni was then electrodeposited under a current density of -10 mA/cm^2. A Pt wire was used as counter electrode and Ag/AgCl, 3 M KCl as reference electrode. After electrodeposition, Ni nanostructures were obtained by dissolving the alumina in a 2.0 M NaOH for 10 h. Finally, electrochemical evaluation of HER catalytic activity of the Ni nanostructures and film were carried out using linear sweep voltammetry in 1.0 M NaOH.

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The surface morphology of the electrode was analyzed using FE-SEM (Hitachi S-4700) and TEM (JEOL JEM-2100). The crystal structure of electrodeposited materials was investigated by XRD (Rigaku, D/MAX Uitima III).

3. Results and discussion

A schematic in Fig. 1 shows a single-step fabrication to form Ni nano-pottery. Before the electrodeposition, we have one side of the template by sputtering of gold (Fig. 1a) to provide good electrical contacts for the electrodeposition. Then, the top hole of the Ni nano-pottery was formed by further galvanic electrodeposition (Fig. 1b). This single-step process can further be utilized to form a Ni nano-rod by filling the open hole of the nano-pottery if the electrodeposition time increased (Fig. 1c). The complete filling of the open hole of Ni nano-pottery for obtaining nano-rod is followed (Fig. 1d).

The key parameter in the formation of different shapes of Ni nanostructures ranging from nano-potteries to nano-rods is the potential transit from −0.95 to −1.05 during the electrodeposition

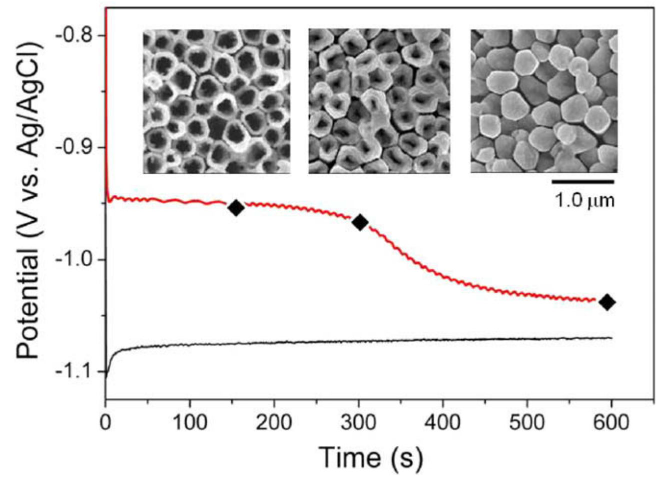

Fig. 2. A plot of potential variation at a current of −10 mA/cm^2 and inset shows the corresponding top-view of SEM images.

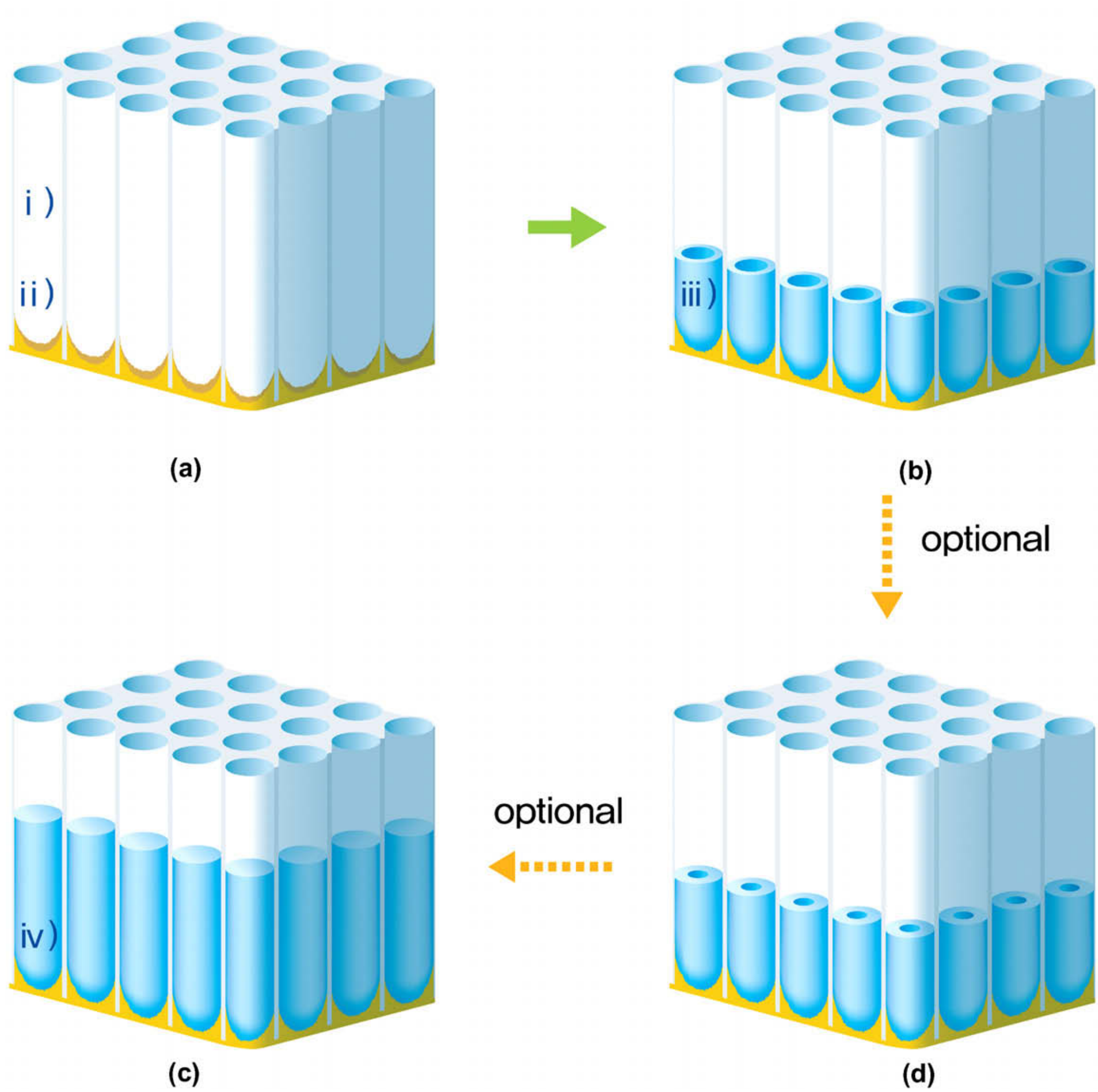

Fig. 1. Conceptional diagram of Ni nano-pottery formation. (a) The formation of gold nano-bowl into alumina template, (b) the electrodeposition of Ni nano-pottery. Optional process to create both Ni nano-pottery structures with smaller diameter holes in them (c) and nano-rod (d) by increasing electrodeposition time. (i) Alumina template, (ii) gold nono-bowl, (iii) nano-pottery and (iv) nano-rod.