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Electrocatalytic activity of Ni nanowires prepared by galvanic electrodeposition for hydrogen evolution reaction

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ABSTRACT

We describe an electrochemical method to prepare Ni nanowires and Ni thin film into porous alumina templates sputtered by Au and onto Au foil as well as their electrocatalytic activity of them for hydrogen evolution reaction (HER). SEM results demonstrated that the Ni nanowires were composed of uniform size with a diameter of ca. 200 nm and a length of about 20 μm, exhibiting an aspect ratio of 100. The Ni nanowires were then employed for the electrocatalysis of HER reactions and showed superior catalytic activities, four times higher than that of Ni thin film when the overpotential of −1.3 V was applied in alkaline water electrolysis.

1. Introduction

The fossil fuel sources are fast approaching an end; hydrogen energy becomes more attractive in that it can resolve the exhaustion of fossil fuels and their environmental problems. In addition, hydrogen plays an important role in many applications, such as fuel cell and steel reel out, etc. [1–4]. The key issue is how to generate hydrogen and store it. Hydrogen has been stored in tanks of compressed or liquefied H_2, in hydrogen-storing alloys, and on activated carbon or carbon nanotubes or graphite nanofiber, or in a hydrogen-adsorbing alloy. The techniques for hydrogen generation from liquid hydrocarbons (propane, methanol, gasoline, etc.) and chemical hydrides ($NaBH_4$, KBH_4, $LiBH_4$, etc.) have been extensively investigated [5]. Numerous works have also been developed for hydrogen generation from water by electrolysis [6–10]. At present, one could say that water electrolysis has been the sole commercialized technique to produce hydrogen from non-fossil fuels, since it is an environmentally friendly technique to split water into hydrogen and oxygen, so that it can be utilized without any limitation of resources.

However, high-energy consumption process delays the commercialization of water electrolysis for hydrogen generation and to reduce applied energy, high active cathode materials should be developed. Of late, many researchers have continued their efforts for cheap and effective hydrogen production. Besides platinum, the most attractive material is nickel, its alloys and compounds, since it shows good electrocatalytic activity for HER, corrosive resistance to the strongly alkaline environment and its low price [6–8]. Tremendous efforts have been made to enhance the electrocatalytic HER activity of Ni and Ni-based electrodes such as (i) to increase the surface area and (ii) from a catalytic point of view, to combine Ni with other pure metals to obtain alloys with optimized adsorption characteristics of hydrogen [9,10]. Among the methods to increase active surface area, the fabrication of nanowires using nanoporous alumina template is very promising because the nanowires have a high aspect ratio, distinct and attractive properties compared with bulk materials [11,12]. For example, they exhibit electronic properties due to quantum size effects as well as changes in chemical reactivity. Nanowires of metals and metal oxides have been synthesized in hexagonally ordered nanoporous alumina templates by several research groups [13–18].

In this work, we tried to increase the surface area of Ni and controlled electrodeposition of Ni into porous alumina template with a high surface area was carried out. X-ray diffraction (XRD) and scanning electron microscope (SEM) measurements were used to characterize the structure and morphology of Ni film and Ni nanowires. Finally, electrocatalytic activities of both Ni wires and Ni film were evaluated for hydrogen evolution reactions (HER) and their line performance were compared.

2. Experimental

Ni film and nanowires were prepared by electrodeposition. Ni film was deposited onto Au sputtered Ti foil in 1.4 M $Ni(NH_2SO_3)_2{\cdot}4H_2O$ (Aldrich) solution with 0.5 M H_3BO_3 (Aldrich) under cathodic constant current and the electrodeposition of Ni

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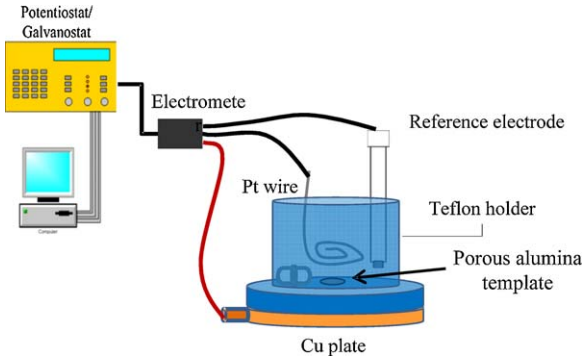

Fig. 1. Schematic diagram of experimental apparatus for Ni electrodeposition.

nanowires was carried out into the Au sputtered commercial porous alumina template (Whatman, Anodisc 25) under same conditions. The solution was stirred during the electrodeposition process. After electrodeposition, Ni nanowires could be obtained by dissolving the porous alumina template in 2 M NaOH solution for 10 h at room temperature. The HER catalytic activity of the as-prepared Ni film and nanowires was evaluated by linear sweep voltammetry (LSV).

The electrodeposition and the electrochemical analysis were performed in a conventional three-electrode electrochemical cell. Shown in Fig. 1, Au sputtered Ti foil and porous alumina template were used as the working electrode and Pt wire and Ag/AgCl/3 M KCl were employed as the counter electrode and the reference electrode. A potentiostat/galvanostat (Autolab, PGSTAT1287N) was used for electrochemical measurements.

The surface morphology of the prepared electrode was analyzed by FE-SEM (Hitachi, S-4700). The crystal structure and the chemical state of electrodeposited materials were observed using HR-XRD (Rigaku, D/MAX Uitima III) and XPS (SSK, MULTILAB 2000 SYSTEM).

3. Results and discussion

The electrodeposition of Ni onto Au sputtered Ti foil and into porous alumina template was employed for the fabrication of highly active electrodes. The Ni electrodeposition condition was first characterized using LSV on Au sputtered Ti foil and porous alumina template in 1.4 M $Ni(SO_3NH_2)_2{\cdot}4H_2O$ + 0.5 M H_3BO_3 (see Fig. 2). From the LSV data, the optimal current density for Ni electrodeposition was determined as -10 mA/cm^2 which will be used throughout the paper. In case of -1.5 mA/cm^2 (not shown here), the hydrogen evolution was reduced but the electrodeposition rate was also diminished. When applying to -10 mA/cm^2, the hydrogen bubbles were increased on electrode surface and the potential was suddenly gone up. In order to avoid the bubble layer on electrode surface and potential increase, the solution was stirred during Ni electrodeposition. As soon as the solution was stirred, the bubble layer was removed on electrode surface and the potential was stable.

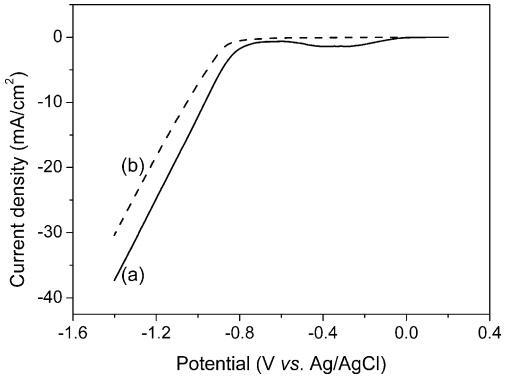

Fig. 2. Polarization curves recorded on (a) Au sputtered Ti foil and (b) Au sputtered porous alumina template in 1.4 M $Ni(NH_2SO_3)_2{\cdot}4H_2O$ + 0.5 M H_3BO_3 at room temperature. Scan rate: 10 mV/s.

The activity of Pt electrodes depends on the real surface area for HER, while in case of non-precious metals like nickel, it is difficult to determine the real surface area. Therefore, SEM can be used at least for a qualitative estimation of the real surface of the electrodeposited Ni structures. Fig. 3 shows SEM images of Ni film (a) and nanowires (b and c). It was found that Ni film was consisted of comparatively small particles having the particle size of about 10–15 nm (see Fig. 3(a)). As Ni electrodeposition was progressed, however, the electrodeposited particles were agglomerated as a lump. For the case of Ni wire as can be seen from SEM images of Fig. 3(b) and (c),

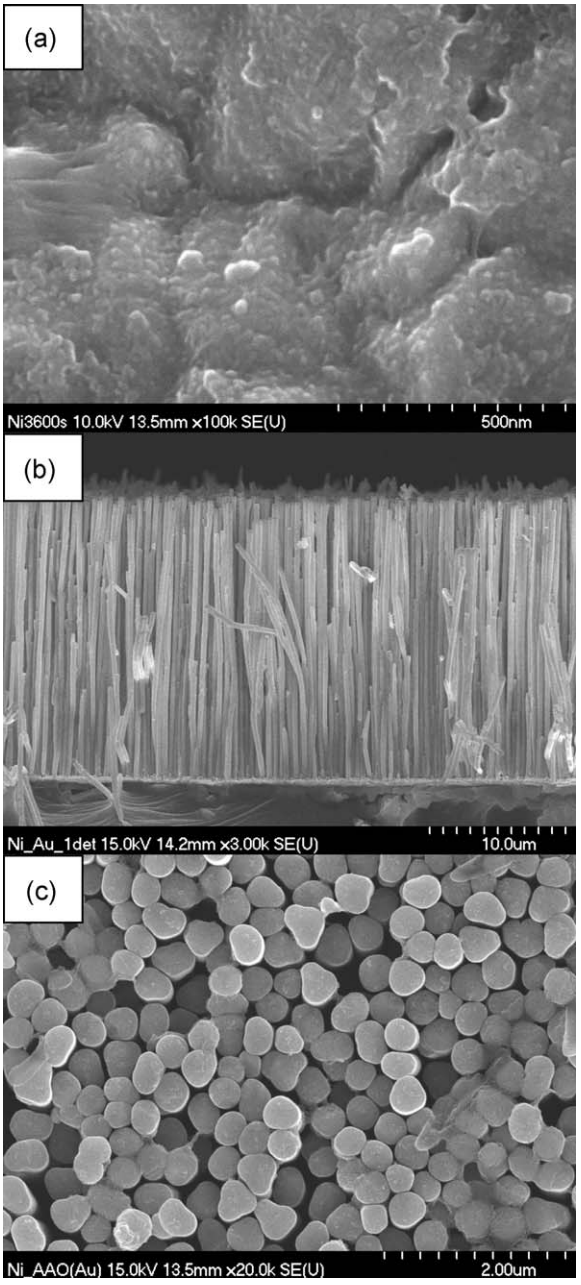

Fig. 3. SEM images of (a) Ni film electrodeposited on Au sputtered Ti foil, (b) and (c) Ni nanowires electrodeposited into Au sputtered porous alumina template. Applied current is -10 mA/cm^2 for 60 min.

electrodeposition method was successfully applied to fabricate regular arrays of Ni wires. Once the formation of Ni nanowires was confirmed by SEM (namely "as-obtained Ni nanowires"), the wire sample was then dissolved partly by chemical etching in 2 M NaOH solution for 10 h at room temperature to expose the nanowires. The as-obtained Ni nanowires have a diameter of about 200 nm and a length of about 20 μm. The aspect ratio of Ni nanowires is about 100. SEM observation can confirm the successful formation of Ni nanowires into porous alumina template as well as the size uniformity of Ni nanowires.

In addition to the size characterization of Ni nanowires, the structure of the electrodeposited Ni onto Au sputtered Ti foil and into Au sputtered porous alumina template was characterized using X-ray diffraction. The resulting diffraction patterns are shown in Fig. 4. The range of variation of the diffraction angle was between 30° and 90°. The spectrum presents pure Ni that the electrodeposited materials are crystalline. The peaks recorded correspond, in increasing order of 2θ, to the (1 1 1), (2 0 0) and (2 2 0) reflections of the face-centered-cubic (fcc) structure of nickel [19]. XRD results imply that the electrodeposition onto Au sputtered Ti foil mainly form Ni(2 0 0) and Ni(1 1 1) is a dominant orientation in Ni nanowires prepared by the electrodeposition into Au sputtered porous alumina template. We observed different initial potential transients for the preparation of Ni film and Ni nanowire applying same current density of $-10\ mA/cm^2$ (not shown in this study). The cathodic potential of ca. −1.03 V for Ni film is larger than −0.95 V of Ni nanowire. We understood that the electrodeposited Ni film could be dominantly grown with the orientation of (2 0 0) at applied potential of −1.05 V according to previous study [20], while Ni nanowire at a lower potential of −0.95 V might be mainly formed into alumina template.

As a final demonstration, electrocatalytic activities of three different electrodes prepared using Ni nanowires, Ni films and Au substrates on hydrogen evolution reactions were evaluated. Fig. 5 presents their corresponding polarization curves measured in an alkaline solution (1 M NaOH) at room temperature. The higher overpotential was reported on Ni film electrode (about −1.15 V), while the comparably lower overpotential (about −0.85 V) was observed on Ni nanowires electrode. Note that large variations in the electrocatalytic activity can also be seen. At an overpotential of −1.3 V, the current density of the Ni film was measured to be $-7.5\ mA/cm^2$ and that of the Ni nanowires was $-29.0\ mA/cm^2$ (see Fig. 6). The electrocatalytic activity of Ni nanowires is four times higher than that of Ni film in −1.3 V. We assume that the high electrocatalytic activity of Ni nanowires might be due to larger

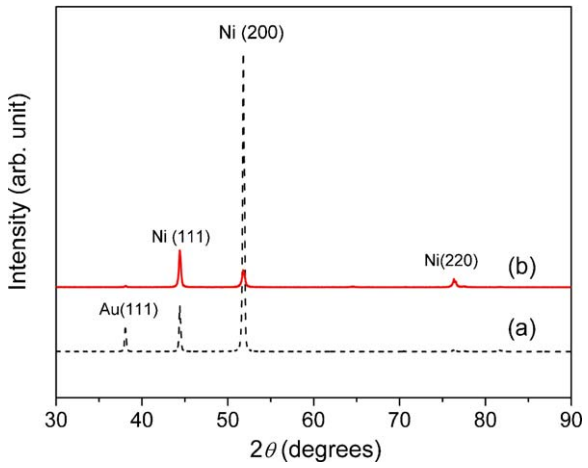

Fig. 4. XRD patterns of (a) Ni film electrodeposited on Au sputtered Ti foil and (b) Ni nanowires electrodeposited into Au sputtered porous alumina template. Applied current is $-10\ mA/cm^2$ for 60 min.

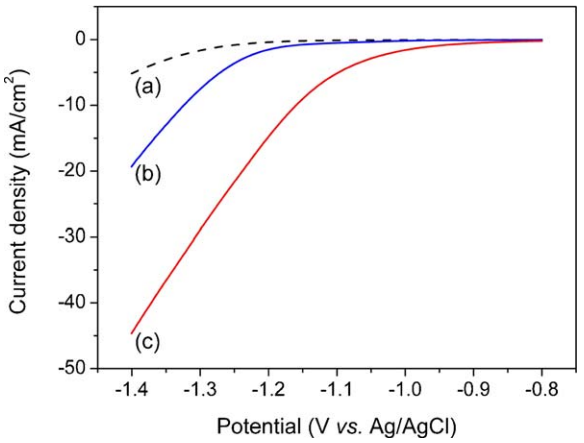

Fig. 5. Polarization curves of (a) Au sputtered Ti foil, (b) Ni film and (c) Ni nanowires for hydrogen evolution in 1 M NaOH. Scan rate: 10 mV/s.

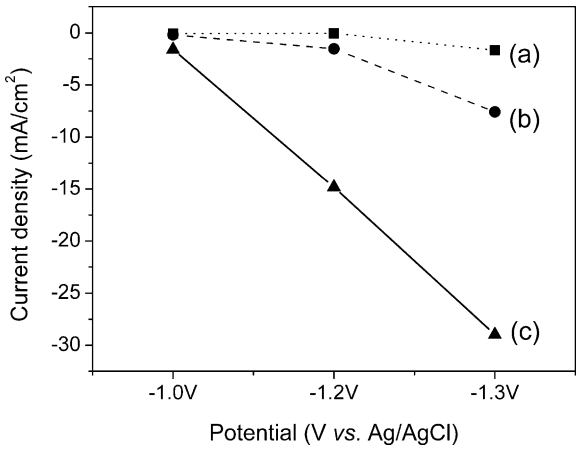

Fig. 6. Comparison of the electrocatalytic activity of (a) Au substrate, (b) Ni film and (c) Ni nanowires at overpotential of −1.0 V, −1.2 V and −1.3 V.

active surface area. Moreover, according to Hu et al., the Ni(1 1 1) preferred orientation also possesses a higher activity for hydrogen and oxygen evolution due to having a larger amount of active sites [21]. Shown in Fig. 4, our method provides a dominant orientation of Ni nanowires is Ni(1 1 1) and that of the Ni films is Ni(2 0 0). Therefore, it was found that the HER activity of Ni nanowires are superior to Ni film because of having larger surface area and preferred orientation for HER.

4. Conclusions

Ni film and uniform nanowires were successfully fabricated onto Au sputtered Ti foil and into Au sputtered porous alumina template using controlled electrodeposition technique. The as-obtained Ni nanowires have an aspect ratio of 100. Ni nanowires showed an attractive electrocatalytic activity in HER due to the fact that Ni nanowires possess larger surface area than that of Ni film and is mainly formed Ni(1 1 1) increasing the HER. Therefore, the electrocatalytic activity of Ni nanowires was improved and the overpotential was reduced for HER.

Acknowledgements

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