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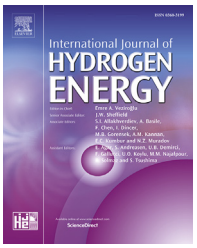

Three-dimensional nickel nanodomes: Efficient electrocatalysts for water splitting

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ABSTRACT

Highly efficient and stable three-dimensional (3D) Ni nanodome (Ni-NDs) arrays were fabricated as candidate cathode materials for alkaline water splitting. The NDs were prepared by a combined methods of soft lithography-nanosphere lithography, physical vapor deposition (PVD) and electrochemical deposition using polydimethylsiloxane (PDMS) as template. The water splitting activity of the 3D nanostructures were examined in 6 M KOH solution using polarization and electrochemical impedance spectroscopy techniques. The data obtained showed that well-structured and uniformly distributed Ni-NDs could be fabricated using this combined method. The ND arrays perform excellent hydrogen evolution activity with respect to Ni plate as a reference point since their nano-sized roughness results in larger real surface area. By comparing with Ni plate, lower hydrogen onset potential (85 mV) and charge transfer resistance (90.1%) as well as higher current density (90.4%) corresponding to the amount of evolved hydrogen were observed at the NDs. The Ni-NDs have high time-stability in the electrolysis conditions. It is believed that the Ni-ND arrays contribute to the design of novel electrocatalytic electrodes as candidate supporting materials.

Introduction

Due to many environmental issues caused by fossil fuels, hydrogen gas has been one of the most promising energy sources for replacing petroleum fuels since this gas is a clean, environmentally friendly and fully recyclable green energy carrier with high gravimetric energy density and a practically unlimited supply [1–4]. The hydrogen energy process chain consists of three major steps: hydrogen production, hydrogen storage, and repowering. All three steps are subject to ongoing research. With respect to the irreversible hydrogen storage, the production of hydrogen by hydrolysis reaction of hydrides [5–11] recently attracts increased attention because of its safe and their amenability to mild reaction conditions. Splitting of water by electrolysis is one of the simplest and the most promising production methods since sustainable hydrogen gas can be produced in large-scale and high purity by this method without any environmental pollution. However, this method is currently quite expensive for practical industrial water electrolysis systems due to high energy consumption in the cell [12–15]. The production cost of hydrogen gas by water splitting system can be lowered by improving novel and cheap electrodes with high efficiency, low anodic and cathodic overpotentials and onset potentials, large surface area/electrochemically active sites. The electrodes also have high corrosion resistance and time-stability to prolong their life time.

Pt-group metals have excellent properties for this aim and have still been candidate electrode materials. Unfortunately,

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their commercial usage has been limited in industrial applications due to low abundance on earth and high cost [16,17]. Therefore, efforts are being devoted to develop cheaper and efficient earth-abundant metals alternative to the noble metal-based electrode materials [18,19]. In this content, Ni has received great attention as non-noble electrocatalyst for hydrogen evolution reaction (HER) due to its high initial catalytic performance, good corrosion resistance in a wide pH range, appropriate hydrogen adsorption energy and abundance on earth [20–22]. However, its performance and time-stability needs to be further improved to be used in real electrolysis systems. The literature survey indicated that fabrication of metallic micro or nanostructures results with larger real surface area and electrochemically active sites, which enhance their activity of the HER [12,20,23–26]. It was reported that Ni nanostructures have superior HER activity than bulk Ni [20,24–29]. Also, nanostructured materials can be used as supporting materials for fabricating efficient and cheap electrodes in order to reduce the dosage of noble metals [12]. We have shown that Ni-modified supporting materials for loading noble metals have large spaces and perform excellent HER activity [30–34].

In literature, various Ni nanostructures have been reported [20,24–28]. To our best knowledge, the fabrication of nanodomes and their application for alkaline water splitting have not been reported yet. In this study, we demonstrate a new approach for the preparation of Ni-NDs by combining soft lithography and nanosphere lithography. This fabrication method offers many important advantages to others, *i.e.* size-controllable reproducibility, uniformity and simplicity [23]. The hydrogen evolution activities of the 3D nanostructures were examined with respect to a Ni plate in 6 M KOH solution by the current-potential (E-i) curves, semi-logharitmic current-potential curves (Tafel) and electrochemical impedance spectroscopy (EIS) techniques. We have aimed to fabricate size-controllable Ni nano arrays to contribute designing of novel electrocatalytic electrodes and candidate supporting materials to be used for further modifications.

Materials and methods

The NDs were fabricated according to published procedure [23,35] by combining nanosphere lithography and soft lithography. In summary, the following four steps were applied.

i) Spherical latex particles having 1000 nm diameter were assembled uniformly on a regular glass slide with convective assembly method to obtain PDMS template for the preparation of nanovoids [36,37]. The volume of the suspension, concentration of the particles and the stage velocity were 40 μL, 0.8% and 1 μm/s, respectively.
ii) PDMS elastomer was poured on the assembled latex particles and put in an oven for 1 h at 70 °C. Then, the polymerized PDMS was peeled off from the glass peeled surface and bowl-shaped nanovoids on the PDMS surfaces were obtained. In order to remove any latex residues, the surface of PDMS template was washed sufficiently with dichloromethane.
iii) The nanovoids on the PDMS template were filled with Ni using PVD technique (a pure Nickel target was used) until obtaining a 100 nm thin Ni film.
iv) For the practical applications thicker plates are required. Unfortunately, we could not further thicken the Ni layer by PVD technique. Therefore, we finally transferred the Ni-NDs filled-PDMS template to a Ni deposition bath, which composed of 30% $NiSO_4 \cdot 7H_2O$ + 1% $NiCl \cdot 6H_2O$ + 1.25% H_3BO_3 at room temperature. To avoid excess hydrogen gas evolution at the cathode and removing the deposited metal from the PDMS template, a constant lower (5 mA) was initially applied to the electrolysis system for 1800 s, and followed a constant 25 mA for 2 h by multi-current step technique. A Ni plate was used counter electrode during the deposition. In this way, a thick and mechanically stable Ni film was prepared on the nanovoid containing PDMS template. The back-side thickened Ni-NDs were peeled off from the PDMS surface, washed with distilled water to remove any residues of bath chemicals and unattached particles, washed sufficiently with absolute ethanol and dried with nitrogen gas. The electrodes were stored in a desiccator before measurement.

The thin Ni-NDs sheets were cut using a lancet in dimensions of 2 mm × 10 mm. The tip of the samples was attached to a stainless steel forceps and coated with poly ester except 2 mm × 2 mm surface area that having NDs. In order to obtain reproducible electrode surfaces, the pores of Ni-NDs working electrode were electrochemically cleaned and activated by applying a constant 100 mA cm^{-2} cathodic current density for 3600 s in 6 M KOH solution.

The assembled latex particles on glass slides, nanovoids on the PDMS template and Ni-NDs were characterized by SEM (JEOL 6510 instrument) and AFM (non-contact mode) (Park Systems XE-100E instrument).

The HER activity of the NDs was evaluated by current-potential (*E-i*) curves, semi-logharitmic current-potential curves (Tafel) and electrochemical impedance spectroscopy (EIS) techniques. The test solution was 6 M KOH at 298 K. A computer-controlled CHI6096E Electrochemical Analyzer with a three-electrode configuration was used for electrochemical measurements. Counter and reference electrodes were Pt (having 2 cm^2 exposed surface area) and Ag/AgCl, KCl (3 M), respectively. All potentials given in this paper were relative to this reference electrode. The polarization and EIS experiments were performed as described previously [23,38]. In the EIS measurements, the frequency range was from 100 kHz to 0.01–0.1 Hz (depending on the applied potential). The amplitude was 0.005 V peak to peaks. The EIS data analysis was performed with a ZView software package. As a reference point, the similar measurements were repeated for a Ni plate having 2.52 cm^2 exposed surface area to show superiority of NDs.

A constant −200 mV overpotential was applied to the electrolysis system for 86400 s. After the electrolysis, EIS measurements were performed and the results were compared to those of before electrolysis to evaluate electrochemical stability of the NDs.

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