

## Electronic Supplementary Information

# Hydrogen Evolution Reaction (HER) over Electroless- Deposited Nickel Nanospike Arrays

*Hitoshi Ogihara\*, Mizuho Fujii, and Tetsuo Saji*

Department of Chemistry & Materials Science, Tokyo Institute of Technology  
2-12-1, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

[ogihara@cms.titech.ac.jp](mailto:ogihara@cms.titech.ac.jp)

### Experimental Procedure

#### Electroless deposition

Electroless deposition baths were prepared according to a previous report.<sup>1</sup> The bath contains NiCl<sub>2</sub>·6H<sub>2</sub>O (0.05 M), H<sub>2</sub>NNH<sub>2</sub>·H<sub>2</sub>O (0.10 M; reductant), glycine (0.30 M; complex agent), H<sub>3</sub>BO<sub>3</sub> (0.50 M; buffer), and KOH (to adjust pH). NiCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in 250 mL of water under stirring. After adding glycine, 250 mL of water was poured into the solution. The solution was sufficiently stirred. pH of the solution was adjusted to > 9 by the addition of KOH, and then H<sub>2</sub>NNH<sub>2</sub>·H<sub>2</sub>O was added. Finally, water, KOH, and/or HCl was added to be the given mol concentration and pH = 12.

Cu plates (5×0.5 cm<sup>2</sup>) were used as the substrates for electroless deposition. The Cu substrates were polished with a metal polishing reagent (PIKAL, Nihon Maryo-Kogyo Co. Ltd.), and ultrasonicated in acetone for 10 min. The Cu plates were immersed into 10 wt% KOH aqueous solution at 333 K for 5 min, and then 10 vol. % H<sub>2</sub>SO<sub>4</sub> solution at 298 K for 30 s. Finally, the substrates were rinsed with water. Immediately after the

treatment, the substrates were immersed into the electroless deposition baths at 353 K. The electroless deposition was carried out for 2, 5, 20, and 60 min. The obtained samples were sonicated in ethanol for 10 min and then in water for 10 min, followed by drying at room temperature.

### Electrodeposition

Electrodeposition baths were prepared on the basis of a typical nickel electrodeposition bath (known as Watt's bath). An aqueous solution of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (240 g/L),  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (45 g/L),  $\text{H}_3\text{BO}_3$  (30 g/L), and saccharin (1 g/L) was prepared and its pH was adjusted to 3.5 by the addition of  $\text{NiCO}_3$  and/or  $\text{H}_2\text{SO}_4$ .

Cu plates ( $4 \times 2 \text{ cm}^2$ ) were used as the substrates for electrodeposition. The Cu substrates were polished with a metal polishing reagent (PIKAL, Nihon Maryo-Kogyo Co. Ltd.), and ultrasonicated in acetone for 10 min. The Cu substrates were masked with insulated tapes to leave  $20 \times 20 \text{ mm}^2$  of exposed area. A Ni plate was used as a counter electrode. The Cu and Ni plates were vertically immersed into 50 mL of the electrodeposition baths. The distance between the Cu and Ni plates was 20 mm. The baths were stirred with a stirring bar and their temperature was kept at 323 K using a water bath. By applying constant current density ( $0.5 \text{ A/dm}^2$ ), electrodeposition was performed on the Cu substrates. The electrodeposition time was 60 min. The resulting films were washed with water and dried in air at room temperature.

### Electrochemical analysis

Electrochemical analysis was performed using a 3 electrode system: a saturated Ag/AgCl reference electrode, a Pt wire counter electrode, and a working electrode.

Prior to the electrochemical analysis, the working electrodes (i.e., Ni electrodes) were treated by applying reduction potential. After flowing  $\text{N}_2$  gas through the measurement solution, the working electrodes were reduced at  $-1.6 \text{ V}$  vs. Ag/AgCl for 30 min using a potentiostat/galvanostat HA-151A (Hokuto Denko), and then the electrode potential was scanned until the current arrived at 0 A. After the treatment, the following electrochemical analysis was carried out using an electrochemical workstation (CV-50W, BAS, Inc.) HER activity was estimated by measuring linear sweep voltammetry (LSV) from  $-0.5$  to  $-1.5 \text{ V}$  at  $10 \text{ mV/s}$  of scan rate in  $1 \text{ M KOH}$ . Electrochemically active surface area was estimated by measuring cyclic voltammetry (CV) from  $-0.48$  to

-1.1 V at 10 mV/s of scan rate in 0.5 M NaOH.

### Characterization

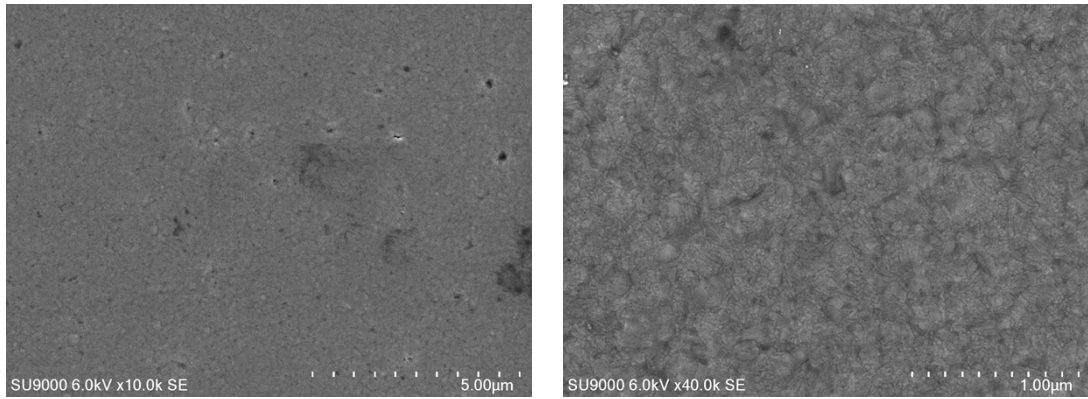
X-ray diffraction (XRD) patterns were measured with a Rigaku RINT 2500 V diffractometer using Cu-K $\alpha$  radiation at room temperature. Scanning electron microscopy (SEM) images were obtained using S-4700 (Hitachi) instruments and SU-9000 (Hitachi) equipped with EDAX (AMETEK, Genesis).

### Reference

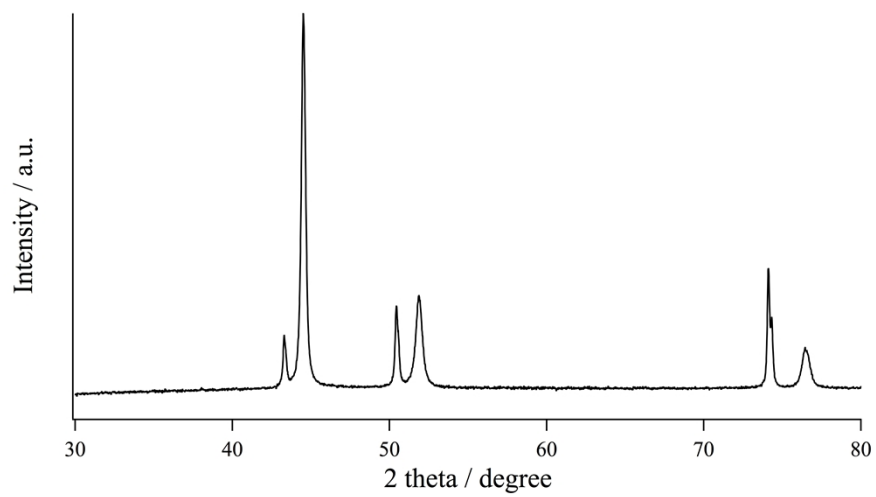
(1) K. Tashiro, T. Watanabe, H. Inaba and H. Honma, *J. Surf. Finish. Soc. Jpn*, 2000, **51**, 606.



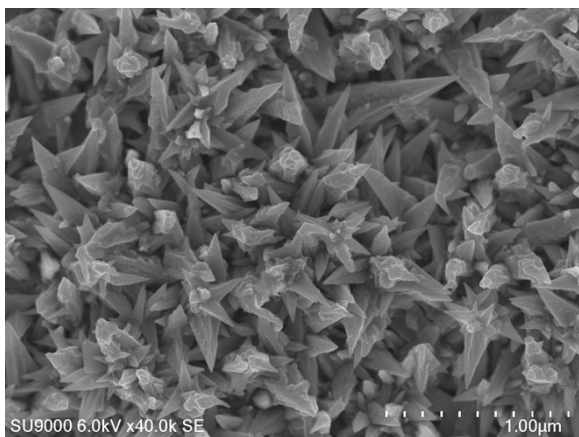
**Fig. S1** Photograph of electrodeposited Ni (left) and electroless deposited Ni (right).



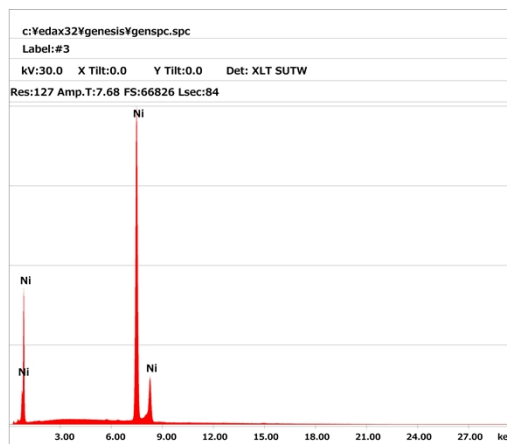
**Fig. S2** SEM images of electrodeposited Ni.



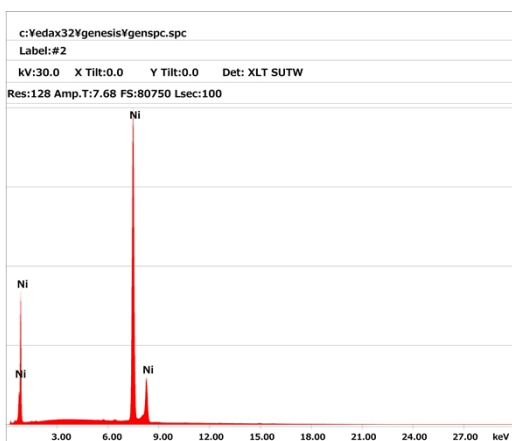
**Fig. S3** XRD pattern of the Ni nanopike arrays after HER (electroless deposition time: 60 min).



(a)

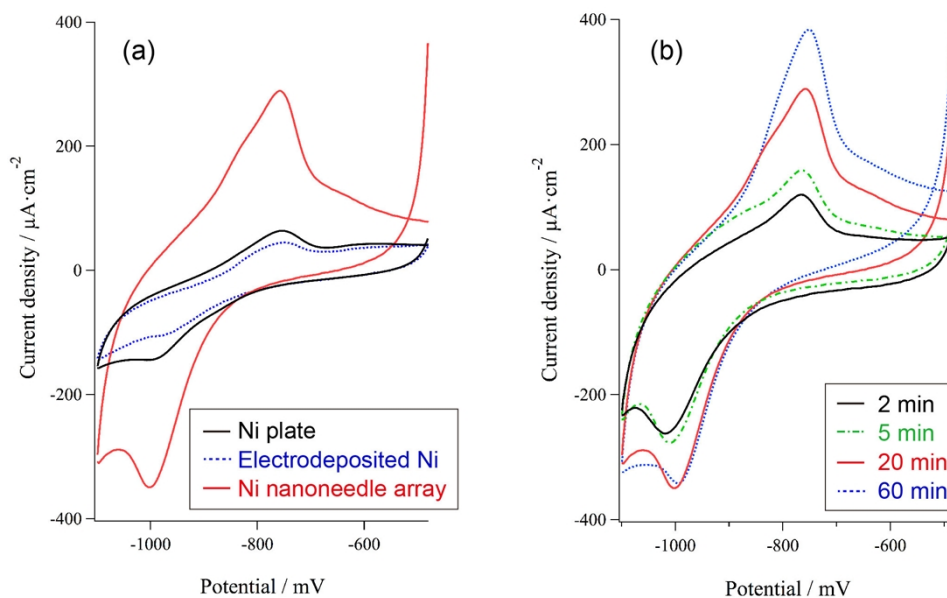


(b)



(c)

**Fig. S4** (a) SEM image and (b) EDS analysis of the Ni nanospike array after HER (electroless deposition for 60 min). (c) EDS analysis of the Ni nanospike array before HER.



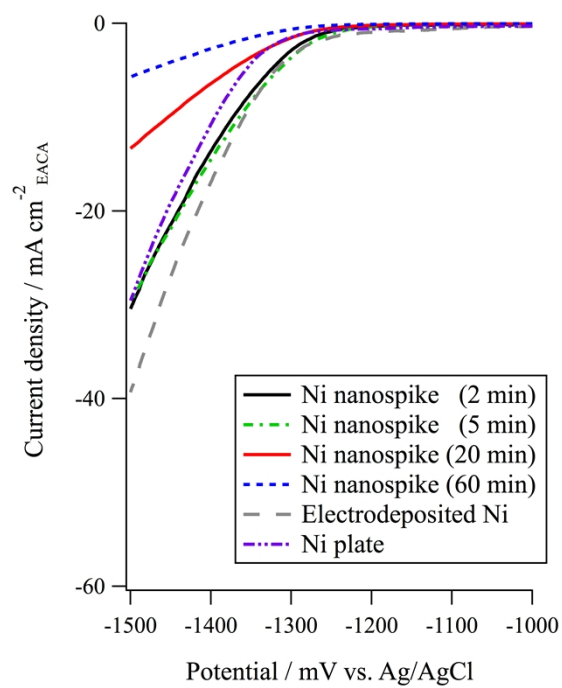
**Fig. S5** CV in 0.5 M NaOH aqueous solution at 10 mV/s of scan rate. Electrodes: (a) Ni plate, electrodeposited Ni, and Ni nanospike array; and (b) Ni nanospike arrays prepared from electroless deposition for 2, 5, 20, and 60 min.

**Table S1** EASA of Ni plate, electrodeposited Ni, and Ni nanospike arrays

Electrode	Electroless deposition time / min	Electrochemically active surface area (EASA) <sup>a)</sup> / cm <sup>2</sup>
Ni plate	-	1.10
Electrodeposited Ni	-	0.89
Ni nanospike array	2	1.73
Ni nanospike array	5	1.88
Ni nanospike array	20	4.63
Ni nanospike array	60	7.09

<sup>a)</sup> EASA was calculated by using the anodic peak in CVs shown in Fig S5. EASA was normalized by of the geometric surface (1 cm<sup>2</sup>) of the electrodes.





**Fig. S6** LSV in 1 M KOH aqueous solution at 10 mV/s of scan rate over Ni nanospike arrays prepared from electroless deposition for 2, 5, 20, and 60 min. The current density was normalized by EASA shown in Table S1.

