Electronic Supplementary Information (ESI)

Effect of Morphology of Electrodeposited Ni Catalysts on the Behavior of Bubbles Generated during the Oxygen Evolution Reaction in Alkaline Water Electrolysis

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A. Experimental section

A conventional three electrode cell with a potentiostat (Metrohm Autolab PGSTAT302) was used for preparing various Ni catalysts, measuring their catalytic activities and examining their electrochemical surface areas. The working electrode was a bare GC (Hochtemperatur-Werkstoffe GmbH) substrate with an exposed geometrical area of 1.32 cm^2 as the other parts were sealed by a home-made Teflon™ holder. A platinum wire and a saturated calomel electrode (SCE, Sigma Aldrich) were used as the counter and reference electrodes, respectively. Prior to the electrochemical depositions and characterizations, the dissolved oxygen in the electrolyte was removed by purging it with nitrogen at a flow rate of 50 cm^3 min^{-1} for 10 min.

The electrolyte used for Ni electrodeposition consisted of 0.50 M nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, Kanto Chemical Co., 28115-00) as the metal precursor and hydrochloric acid (HCl, Sigma Aldrich) as an adjustor of pH to 2.5. The different Ni catalysts were electrodeposited using CA at corresponding deposition potentials and time, respectively. The catalytic activities of OER on the Ni catalysts were investigated by CV with a 6.0 M of KOH solution. The CV measurement was carried out within the potential range between 0.30 V and 0.90 V at a scan rate of 50 mV s^{-1}. The results were compared with a commercial Ni catalyst (Sigma Aldrich, 7440-02-0, thickness = 0.125 mm, purity ≥ 99.9%) used as a reference.

Characterization of the Ni catalysts was carried out to investigate their surface structure. The morphologies of the Ni catalysts were analyzed using FESEM (S-4100, Hitachi) and AFM (XE-100, Park Systems). The oxidation state variation of Ni catalysts under OER condition was examined by XPS (K-alpha, Thermo U. K.). To characterize the hydrophilicity of the different Ni catalysts, a contact angle meter (FM40, KRÜSS) was used. The volume of the deionized water droplets was 1.0 μL.

B. Supporting data

Table S1. Tafel slopes in the low overpotential region and exchange current densities of various Ni catalysts for OER at 1st and 50th cycle

Catalysts	Cycle #	Tafel slope / V dec^{-1}	Exchange current density / mA cm^{-2}
Flat	1st	0.036	1.52
	50th	0.034	0.04
Smooth	1st	0.027	3.49
	50th	0.031	0.33
Cauliflower-like	1st	0.035	6.75
	50th	0.038	2.72
Needle-like:	1st	0.025	10.38
	50th	0.025	8.25

Table S2. Contact angle and solid-gas surface tension of the various Ni catalysts

Catalysts	Contact angle θ / degree		Solid-gas surface tension / mN m^{-1}		
	θ^{W}	θ^{MI}	$\gamma_{sg}{}^{d}$	$\gamma_{sg}{}^{p}$	γ_{sg}
Flat	79.79	46.69	34.45	4.68	39.13
Smooth	72.13	41.83	38.68	6.73	45.41
Cauliflower-like	42.69	18.42	48.23	18.52	66.75
Needle-like	30.24	8.64	50.23	23.69	73.92

From the experimental contact angles with water (θ^{MI}) and methylene iodine (θ^{MI})[3], solid-gas surface tensions were calculated based on the Owens-Wendt theory[3,4], where the solid-gas surface tension is divided into two components of dispersion term (superscript *d*) and polar term (superscript *p*). For each Ni catalyst, the $\gamma_{sg}{}^{d}$ and $\gamma_{sg}{}^{p}$ were determined by solving the following equation for two kinds of liquids, with the reported liqud-gas surface tensions (Table S3). Then, the solid-gas surface tensions (γ_{sg}) were obtained as the sum of $\gamma_{sg}{}^{d}$ and $\gamma_{sg}{}^{p}$.

$$\gamma_{lg}\left(1+\cos\theta\right)=2\sqrt{\gamma_{sg}{}^{d}\gamma_{lg}{}^{d}}+2\sqrt{\gamma_{sg}{}^{p}\gamma_{lg}{}^{p}}$$

Table S3. Test liquids and their liquid-gas surface tension components[1-3]

Liquids	Liquid-gas surface tension / mN m^{-1}		
	γ_{lg}	$\gamma_{lg}{}^{d}$	$\gamma_{lg}{}^{p}$
Water (W), H_2O	72.8	21.8	51.0
Methylene iodide (MI), CH_2I_2	50.8	50.8	0

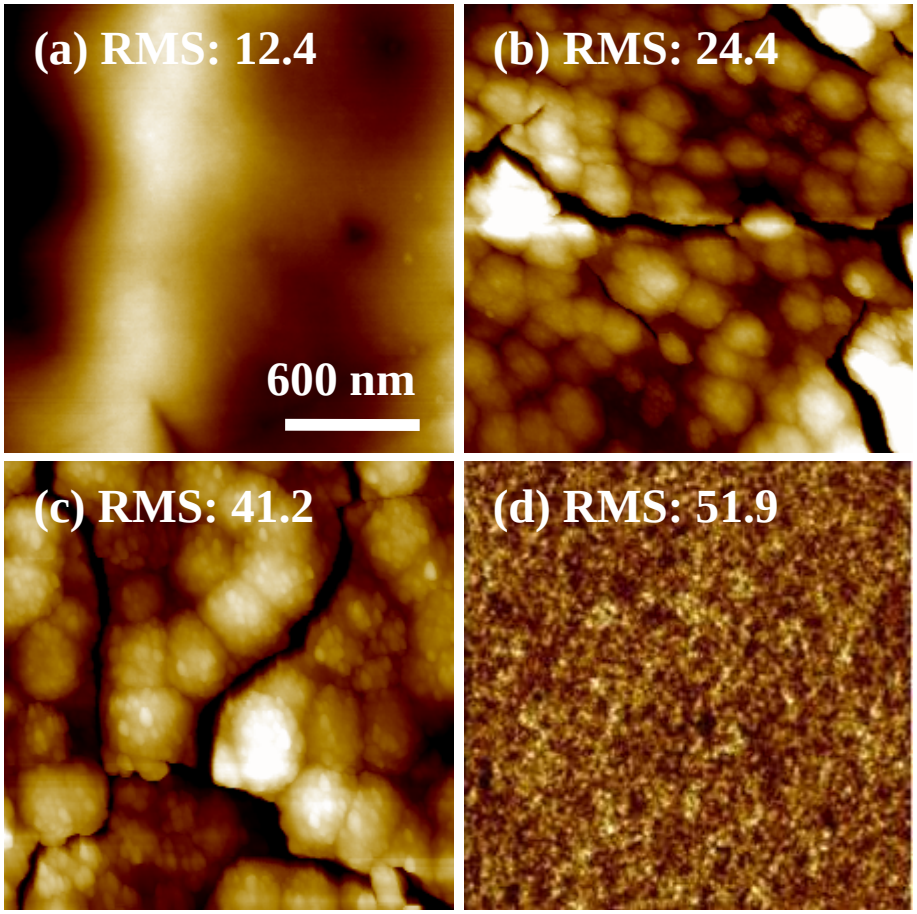

Figure S1. Scanning surface roughness: AFM images of 2 μm x 2 μm of Ni catalysts: (a) Flat: commercial (Sigma Aldrich). (b) Smooth: deposited at -1.2 V for 20 s. (c) Cauliflower-like: -1.0 V for 60 s. (d) Needle-like: -0.8 V for 180 s.

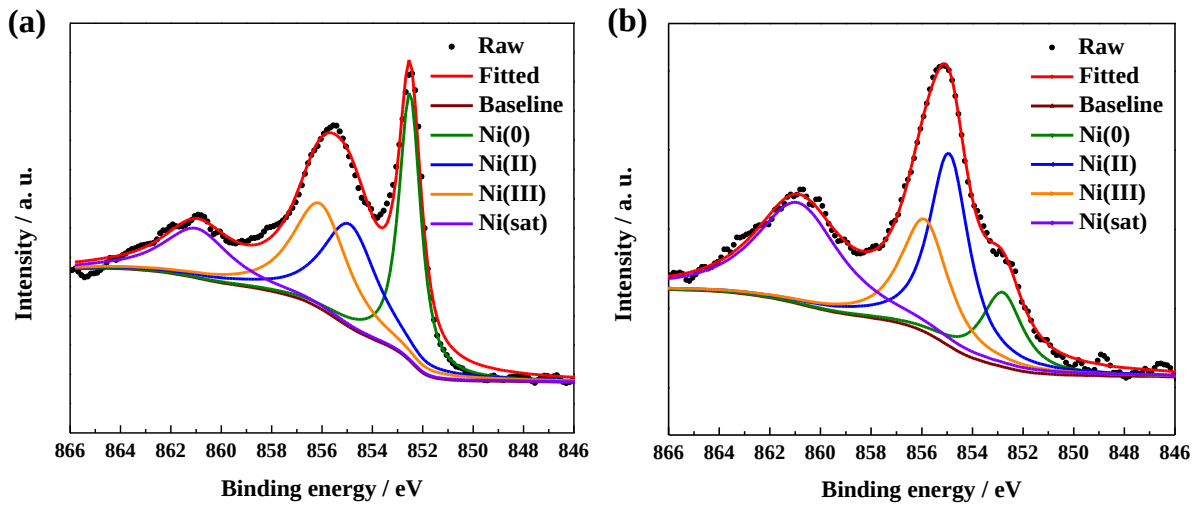

Figure S2. XPS analysis: Ni 2p3/2 spectra of smooth Ni catalyst (a) before OER and (b) after OER.

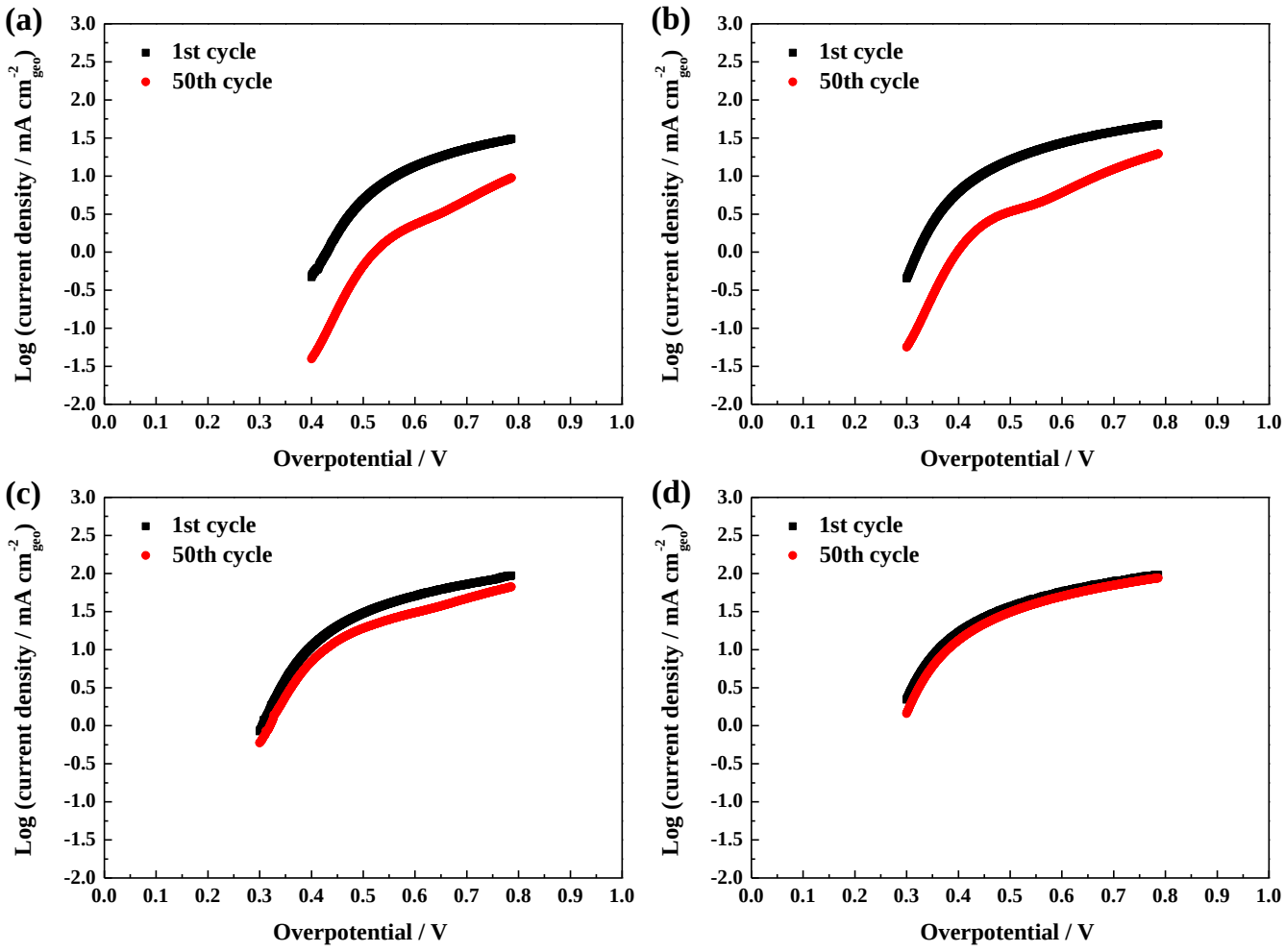

Figure S3. Tafel plots of the various Ni catalysts for OER: (a) Flat: commercial (Sigma Aldrich). (b) Smooth: deposited at -1.2 V for 20 s. (c) Cauliflower-like: -1.0 V for 60 s. (d) Needle-like: -0.8 V for 180 s.

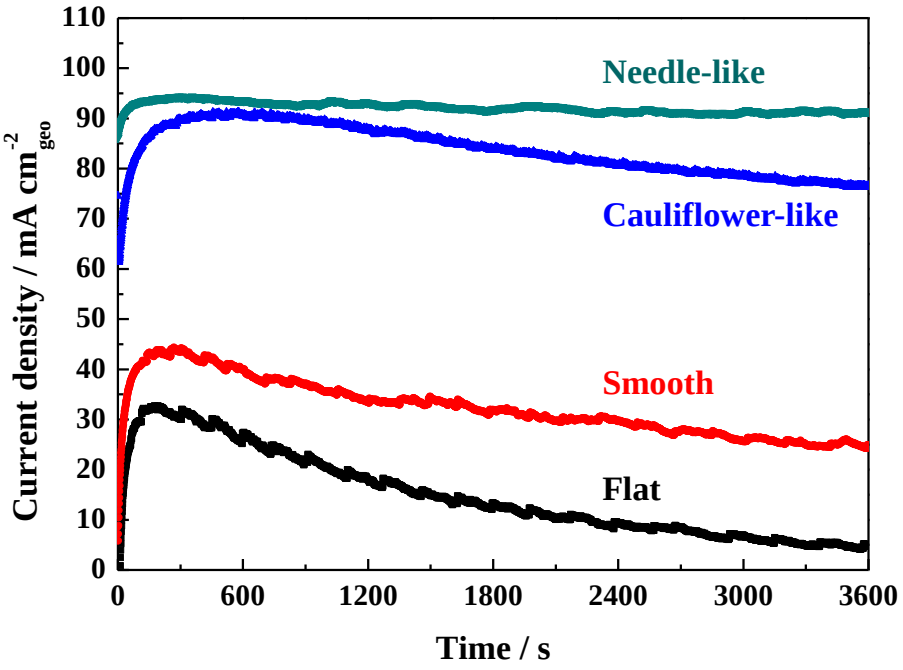

Figure S4. CA curves of the various Ni catalysts with 0.90 V in 6.0 M KOH during 3600 s at 298 K.

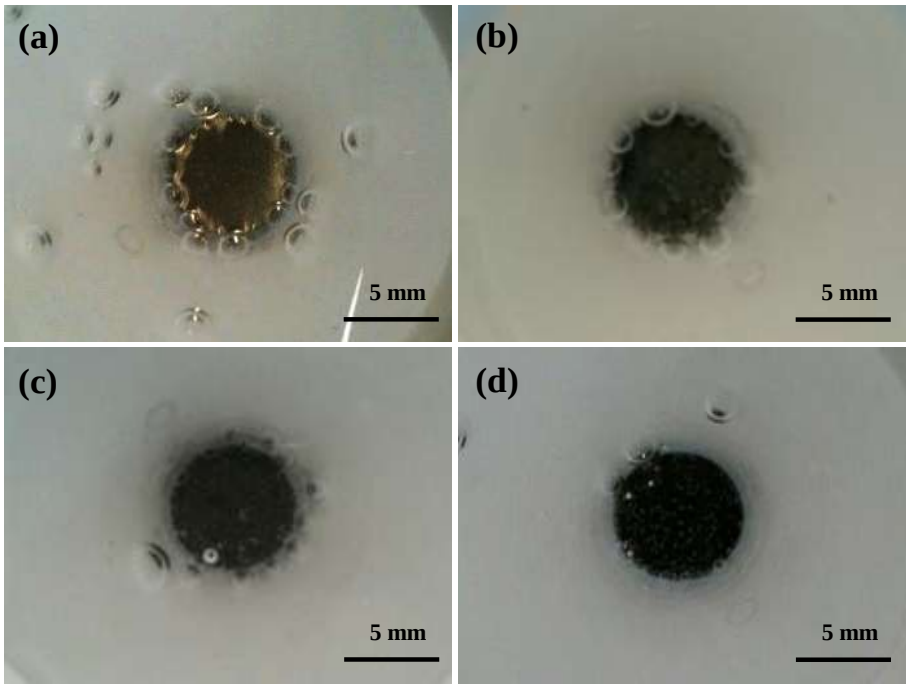

Figure S5. Photographs of bubbles that remained on the surface of Ni catalysts right after the CA measurements: (a) flat, (b) smooth, (c) cauliflower-like, and (d) needle-like.

References

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