Supplementary material for

Wafer-scale 1-nm Ni(OH)₂ Nanosheet with Superior Electrocatalytic activity for Oxygen

Evolution Reaction

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Experimental Section

ILE Synthesis of 1.4nm Ni(OH)² **nanosheet.** In a typical synthesis process, a substrate (FTO glass or Si wafer) was placed at the bottom of a glass culture dish (1cm high and 75cm² open area). A 30mL of aqueous nutrient solution containing 2.5 mM nickel nitrate hexahydrate and 2.5 mM hexamethylenetetramine (HMT) was gently added to the dish. After 20-minute standing, 180 µL of surfactant solution with a concentration of 2 mg oleic acid in 10 mL cyclohexane was added to the water surface. After 10 minutes, the glass culture dish was covered with a glass and placed in a convection oven at 60 °C. Two hours later, the glass culture dish was removed from the oven. To deposit nanosheet onto the substrate, the nutrient solution was removed by a syringe along the side wall of dish. After natural drying, washed the nanosheet/substrate by ethanol to remove excess surfactant and precursors. Finally, the sample was naturally dried again.

Synthesis of thicker Ni(OH)₂ films. 7.0 nm Ni(OH)₂ layers were synthesized through the same ILE process as described above, where the concentrations of both nickel nitrate hexahydrate and HMT were increased to 10 mM. The 230 nm Ni(OH)₂ film was cathodically deposited from unstirred solutions of $0.1 \text{ M Ni}(\text{NO}_3)_2$. The deposition was conducted on a FTO substrate at current density of -10 mA/cm² for 20 s.

RuO₂-FTO electrode. 5 mg of commercial RuO₂ (from Aldrich-Sigma) was ultrasonically dispersed into 5 mL aqueous solution to form a catalytic ink. The aqueous solution contained 3.95mL of DI water, 1 mL of ethanol, and 50 μ L of a Nafion® solution (5 wt% in aliphatic alcohol from Aldrich-Sigma). RuO₂-FTO electrode was prepared by depositing catalytic ink onto surface of FTO, which corresponded to a loading of 0.05 mg of catalyst per cm². The ink was dried at

room temperature under air.

Characterization. SEM measurements were carried out on a Zeiss Leo 1530 field emission scanning electronic microscope. TEM characterizations were performed on a FEI TF30 transmission electronic microscope. X-ray photoelectron spectroscopy (XPS) spectra were obtained from Thermo Scientific K-alpha XPS instrument. The thickness and topographic image of Ni(OH)₂ nanosheet were measured by XE-70 atomic force microscopy (AFM) from Park Systems. TEM sample was collected by dipping a holey carbon TEM grid into the reaction solution from the side of the reactor and then lifting up. The detail process was described in our previous work.¹

Electrochemical measurements. The electrochemical measurements were conducted with a typical three-electrode setup with FTO/Ni(OH)₂ (exposed active area is about 0.3 cm²) as the working electrode, Pt wire (length of 3 cm, diameter of 0.5 mm) as the counter electrode and a Hg/HgO electrode as the reference electrode. All electrodes were emerged in a 1 M NaOH electrolyte (pH=13.6). The electrochemical measurements were conducted on an Autolab PGSTAT302N workstation. Prior to the measurements, the working electrode was soaked for 10 min in the electrolyte with N₂ bubbling, and then 25 cycles of cyclic voltammetric scans (0.2-1.0 V vs. Hg/HgO, at a scan rate of 20 mV s⁻¹) were used to activate the Ni(OH)₂ catalysts. Standard measurements for OER were taken at a scan rate of 1 mV s⁻¹ from 0.2 to 0.8 V vs. Hg/HgO. The electrochemical impedance spectroscopy (EIS) measurements were conducted at applied potential of 0.62V vs Hg/HgO by applying a 5 mV bias to the sample and sweeping the frequency from 10 kHz to 0.1 Hz. The overpotential (η) was calculated by the following relationship: $\eta = E$ (vs.

Hg/HgO) + 0.098 V + 0.0592× pH - 1.23V- iR_u . R_u was assumed to be the minimum total impedance in the frequency regime between 10 kHz to 0.1 Hz, where the capacitive and inductive impedance are negligible and the phase angle was near zero. The typical electrochemical cell had R_u =15~20 Ω in 1M NaOH. Current densities (*j*) were calculated using geometric surface areas. The *j*- η curves and Tafel slops of Ni(OH)₂\FTO electrodes were shown in Fig. S11.

Fe-Rich NaOH Electrolyte. In polypropylene bottle, ~0.5mL of Fe(NO₃)₃ aqueous solution (0.1M) was added into 100 mL of 1M NaOH, stirred for at least 5 min, followed by at least 1 h of resting. The mixture was centrifuged, and the Fe-rich NaOH supernatant was collected into a clean polypropylene bottle for use.

Effective thickness. The effective thickness of $Ni(OH)_2$ layers were calculated by integrating the $Ni^{3+/2+}$ oxidation peak (as shown in Fig S12-13) according to the reported work.²⁻³

$$Thickness = \frac{Q \times M}{F \times A \times d}$$

where Q is the quantity of electric charge (A·s), which was calculated by integrating redox peak Area; M is molecular weight of material (g/mol); F is Faraday constant; A is area of electrode (cm²); d is density of Ni(OH)₂ (g/cm³). The result was listed in Table S1. It is worth mentioning that the calculated thickness (230 nm) of N3 is different from the thickness measured from SEM (1.35 µm, as shown in Fig. 4c). The main reason is the thick Ni(OH)₂ film is not dense.

Mass activity. The values of mass activity (A g^{-1}) were calculated from the mass loading (*l*) in g cm⁻² and the measured current density (*j*) in A cm⁻². The result was exhibited in Table S2

Mass activity =
$$\frac{j}{l}$$

 $l = Thickness \times 1cm^2 \times d = \frac{lcm^2 \times Q \times M}{F \times A}$

ECSA and RF

Electrochemical active surface area was calculated by the followed equation

$$ECSA = \frac{C_{dl}}{C_s}$$

In which C_s is the specific capacitance of the samples. Herein, C_s of 0.04 mF cm⁻² was used according to the previously reported value of metal oxide/hydoxides in NaOH solution.⁴ C_{dl} was calculated from the slope of the line in the plot of capacitive current density (*j_{dl}*) vs scan rates v (V/s) ^[5]. A is surface area of electrode.

$$j_{dl} = \frac{C_{dl} * \nu}{A}$$

Cyclic voltammograms (CVs) were recorded in the double-layer regime (1 M NaOH, 0 to 0.2 V vs Hg|HgO) by varying scan rates ranging from 10 to 60 mV s⁻¹ (as shown in Fig. S3). And the values of roughness factor (*RF*) was calculated from the *ECSA* and electrodes' surface area (*A*).

Reference

- 1. Wang, F.; Yu, Y. H.; Yin, X.; Tian, P.; Wang, X. D. J. Mater. Chem. A 2017, 5, 9060.
- 2. Trotochaud, L.; Ranney, J. K.; Williams, K. N.; Boettcher, S. W. J. Am. Chem. Soc. 2012, 134, 17253.

3. Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher, S. W. J. Am. Chem. Soc. 2014, 136, 6744.

Charles C. L. McCrory; Suho Jung§; Jonas C. Peters; Thomas F. Jaramillo. J. Am. Chem. Soc.,
 2013, 135, 16977

5. Xie, J. F.; Zhang, X. D.; Zhang, H.; Zhang, J. J.; Li, S.; Wang, R. X.; Pan, B. C.; Xie, Y. Adv.

Mater: 2017, 29.1604765



Figure S1. Low-magnification SEM images and an optical image of 1.4nm Ni(OH)₂ nanosheet on a Si\SiO_x substrate.



Figure S2. 1.4nm Ni(OH)² **nanosheets on FTO. (a)** and **(b)** SEM images of a Ni(OH)² nanosheet on a FTO glass. Insert of (a) is an optical image of bare FTO (1) and 1.4nm Ni(OH)² nanosheet covered FTO (2). **(c)** XPS survey spectra of Ni(OH)² nanosheet on FTO glass. **(d)** XPS of Ni²⁺ peak.



Figure S3. Characterization of 7.0 nm Ni(OH)₂ layer. (a) SEM image of Ni(OH)₂ layer on a Si wafer. (b) AFM topography image of the Ni(OH)₂ on a Si wafer. Insert is the height profile along the yellow line in (b) showing a rough film thickness of \sim 7 nm. (c) SEM image of the 7 nm Ni(OH)₂ film on FTO.(d) XPS spectra of the 7 nm Ni(OH)₂ layer.



Figure S4. Characterization of 230 nm thick Ni(OH)² **film. (a)** Low-magnification and **(b)** highmagnification SEM images of the Ni(OH)² thick film deposited on a FTO glass. **(c)** XPS spectra of the Ni(OH)² film on FTO. **(d)** XPS of the Ni²⁺ peak.



Figure S5. Characterization of commercial RuO₂ on FTO. (a) Low magnification SEM image (b) High magnification SEM image.



Figure S6. Cyclic voltammograms curves of bare FTO (a), 1.4 nm Ni(OH)₂ (b), 7.0 nm Ni(OH)₂ (c), 230 nm Ni(OH)₂ (d) and commercial RuO₂ (e). The scan rates were varied from 10 to 60 mV s⁻¹.



Figure S7. EIS curve of bare FTO (a) and RuO₂-FTO (b) at potential of 0.62 vs Hg//HgO in 1 M NaOH solution. (c) Equivalent circuit.



Figure S8. Tafel slope of FTO.



Figure S9. Electrocatalytic performance of the 1.4 nm Ni(OH)₂ nanosheet in untreated (red) and Fe-rich (black) 1M NaOH electrolyte. (a) j- η curves. (b) Tafel slopes. (c) Mass activity - η curves. (d) TOF- η curves



Figure S10. The low-magnification (a) and high-magnification (b) SEM images of 1.4nm Ni(OH)₂/FTO after 15h OER in 1M NaOH.



Figure S11. Electrochemical stability evaluation. (a) Current density measured at η = 300 mV (vs. RHE) as a function of time. (b) SEM image of 1.4 nm Ni(OH)₂/FTO after 5 h OER in Fe-rich 1M NaOH.



Figure S12. Electrocatalytic performance of Ni(OH)₂ with different thickness (as shown in table S1) measured in 1 M NaOH solution for OER. (a-c) j- η curves. (d-f) Tafel slopes.



Figure S13. Example for determining integrated charge associated with Ni(OH)₂ oxidation. The shaded region shows the integration area for charge calculation.



Figure S14. Current density-time curves showing the oxidation peak of Ni(OH)₂ to NiOOH transmission.

sample	Thickne	ss(nm)
N1-1	1.4	
N1-2	1.5	1.4±0.1
N1-3	1.3	-
N2-1	7.0	
N2-2	8.4	7.7±0.8
N2-3	6.9	_
N3-1	230	
N3-2	290	240±50
N3-3	190	_

Table S1 Thickness measured by electrochemical method

Table S2 OER	R performance	comparison	of the Ni((OH)2 e	lectrodes	in this	work.
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G 1		η (mV)		Loading		Mass activity		TOF (s ⁻¹)	
Sai	Sample @10mA/cm ² (µg/cm		g/cm ²)	(A/g)		@300mV			
	-1	328		0.576		4662		1.12	
N1	-2	327	324±4	0.615	0.57±0.04	4496	5058±562	1.08	1.22±0.13
	-3	320		0.533		5620		1.35	
	-1	328		2.87		1016		0.244	
N2	-2	333	334±6	3.44	3.14±0.3	1057	951±106	0.254	0.244±0.04
	-3	340		2.84		845		0.203	
	-1	339		94		37.2		0.00894	
N3	-2	332	335±5	78	98±20	48.7	40.7±8	0.0117	0.01±0.0002
	-3	334		119		32.7		0.00787	

Table S3. Comparison of ECSA and RF

Sample	ECSA	RF
FTO	0.038 cm^2	0.120
1.4nm Ni(OH)2	0.037 cm^2	0.127
7.0nm Ni(OH) ₂	0.039cm^2	0.112
230nm Ni(OH) ₂	0.025 cm^2	0.0767
commercial RuO ₂	1.64 cm^2	5.45

Table S4 Equivalent Circuit Parameters

Sample	$\mathrm{R}_{\mathrm{u}}\left(\Omega ight)$	$R_{ct}(\Omega)$
Bare FTO	15.6	15052
RuO2	14.0	381
1.4nm Ni(OH)2	18.9	71.6
7.0nm Ni(OH) ₂	17.0	72.4
230nm Ni(OH) ₂	16.5	68.8

Materials	η (mV) @ 10mA/cm ²	j (mA/cm ²) @ η=350mV	Reference
1.4 nm Ni(OH) ₂	328	-	Our work
Fe doped 1.4 nm Ni(OH) ₂	294	>20	Our work
2 nm NiO _x NPs	350	10	1
FNC-WE/NiO _x	-	14.54±0.03	2
FNC-WE/NiFeO _x	-	16.28±0.04	2
NiFeOx	381	-	3
Co ₉ S ₈ @NOSC	370	-	4
Ti@Co _{0.85} Se	500	-	5

Table S5 Comparison of overpotential from different electrocatalysts

- [1]Adv. Funct. Mater. 2017, 27, 1605121
- [2]ACS Catal. 2017, 7, 4786
- [3]ACS Appl. Mater. Interfaces 2017, 9, 13132
- [4] Adv. Funct. Mater. 2017, 27, 1606585
- [5] Nano Energy, 2017, 39, 321