Electronic Supplementary Information

Fabrication of practical catalytic electrodes using insulating and eco-friendly substrates for overall water splitting

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Experimental details

Materials

Nickel sulfate ($NiSO_4$▪$6H_2O$, AR), Cobaltous sulfate ($CoSO_4$, AR), dimethyl ammonium borane (Et_2NHBH_3, DMAB, AR), sodium sulfate (Na_2SO_4, AR), sodium succinate (AR), sodium phosphite (NaH_2PO_2, AR), sodium borohydride ($NaBH_4$, AR), Pt-C (10 wt% Pt), Iridium oxide (IrO_2) and Nafion (5 wt%) were purchased from Sinopharm Chemical Reagent Company. Acetone (AR, 99.5%), ethanol (AR, 99.5%), nitric acid (HNO_3, AR) and potassium hydroxide (KOH, AR) were bought from Aladdin. Filter paper about 0.1 mm in thickness was purchased from Shanghai Titan Technology Company. Polyurethane of sponge (PU) and cotton cloth was purchased from Shanhai Huayi Company. Water was purified through a Millipore system before use. All chemicals were used as received without further purification.

Preparation of Ni-P-B/Paper electrode

Firstly, filter paper (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the paper into 0.2 M $NiSO_4$ aqueous solution for 2 s and then 0.5 M $NaBH_4$ aqueous solutions for 2 s each and finally washed with water and ethanol. The weight of the activated paper was increased by about 0.2 mg cm^{-2}. The electroless plating (EP) bath for Ni-P-B was then prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g), sodium phosphite (0.094 g) and $NiSO_4$ •$6H_2O$ (2.5 g) in 100 mL water. To prepare the Ni-P-B/Paper electrode, the activated paper substrate (1 cm × 0.5 cm) was immersed in the aqueous EP bath for a period of time at 10 ^oC. After washed with water and ethanol, the as-prepared electrodes were dried at room temperature overnight. In order to study the formation process of the Ni-P-B/Paper electrode, Ni-P-B/Paper electrodes with different plating times of 0 min, 30 min, 60 min and 90 min were obtained. The amount of catalyst deposited on the paper was calculated by weighting method.

To prepare large size electrode of 100 cm^2, filter paper (10×10 cm^2) was cleaned with water and acetone, and activated by alternative dipping the paper into 0.2 M $NiSO_4$ aqueous solution and 0.5 M $NaBH_4$ aqueous solution for 2 s each and then washed with

water and ethanol. The electroless plating (EP) bath for Ni-P-B was prepared by dissolving Na_2SO_4 (7.5 g), sodium succinate (12.5 g), sodium phosphite (0.49 g) and $NiSO_4 \cdot 6H_2O$ (12.5 g) in 500 mL water. To prepare the Ni-P-B/Paper electrode, the activated paper substrate (10 cm × 10 cm) was immersed in the aqueous EP bath for 60 minutes at 10 ^oC. After washed with water and ethanol, the sheet was dried at room temperature overnight to obtain the electrode.

Deposition of Ni-P-B on a single fiber

A single fiber extracted from paper sbustrate (Diameter: 17.4 μm) was cleaned with water and acetone, and activated by alternative dipping the paper into 0.2 M $NiSO_4$ aqueous and $NaBH_4$ aqueous solutions for 2 s each and finally washed with water and ethanol. The electroless plating (EP) bath is the same to that used during Ni-P-B/Paper electrode preparation. To deposit the Ni-P-B catalyst on the fiber, the activated fiber was immersed in the aqueous EP bath for a period of time at 10 ^oC. In order to study the deposition process, the morphology of the fiber at different plating times of 0 min, 30 min, 60 min and 90 min was observed.

Preparation of other electrodes

The electrodes of Co-B/Paper, Ni-Co-B/Paper, Ni-B/Paper, Ni-P/Paper, Ni-P-B/Cloth, Co-B/Cloth, Ni-Co-B/Cloth, Ni-P-B/PU, Co-B/PU and Ni-Co-B/PU electrodes were prepared with the similar activation and EP method. Ni-P-B/Ni Foil electrode and Ni-P-B/Ni Foam electrode were prepared using EP method.

(1) Co-B/Paper electrode: filter paper (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the paper into 0.2 M $CoSO_4$ aqueous solution for 2 s and then 0.5 M $NaBH_4$ aqueous solutions for 2 s and finally washed with water and ethanol. The weight of activated paper was increased by about 0.1-0.3 mg cm^{-2}. The EP bath for Co-B was prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g), DMAB (0.72 g) and $CoSO_4$ (1.38 g) in 100 mL water. To prepare the Co-B/Paper electrode, the activated substrate (1 × 0.5 cm^2) was immersed in the aqueous EP bath for 60 min at 10 ^oC; **(2)** Ni-Co-B/Paper electrode: filter paper (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the paper into 0.1 M $CoSO_4$ and 0.1 M $NiSO_4$ aqueous solution for 2 s and then 0.5 M

$NaBH_4$ aqueous solutions for 2 s and finally washed with water and ethanol. The weight of activated paper was increased by about 0.1-0.3 mg cm^{-2}. The EP bath for Ni-Co-B was then prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g), $CoSO_4$ (0.69 g), DMAB (0.72 g) and $NiSO_4 \cdot 6H_2O$ (1.25 g) in 100 mL water. To prepare the Ni-Co-B/Paper electrode, the activated substrate (1× 0.5 cm^2) was immersed in the aqueous EP bath for 60 min at 10 °C. **(3)** Ni-B/Paper electrode: filter paper (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the paper into 0.2 M $NiSO_4$ aqueous solution for 2 s and then 0.5 M $NaBH_4$ aqueous solutions for 2 s and finally washed with water and ethanol. The weight of activated paper was increased by about 0.1- 0.3 mg cm^{-2}. The EP bath for Ni-B was prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g), $NiSO_4 \cdot 6H_2O$ (2.5 g) and DMAB (0.72 g) in 100 mL water. To prepare the Ni-B/Paper electrode, the activated substrate (1 × 0.5 cm^2) was immersed in the aqueous EP bath for 60 min at 10 °C; **(4)** Ni-P/Paper electrode: filter paper (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the paper into 0.2 M $NiSO_4$ aqueous solution for 2 s and then 0.5 M $NaBH_4$ aqueous solutions for 2 s and finally washed with water and ethanol. The weight of activated paper was increased by about 0.1- 0.3 mg cm^{-2}. The EP bath for Ni-P was prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g) and $NiSO_4 \cdot 6H_2O$ (2.5 g) and NiH_2PO_2 (1.245 g) in 100 mL water. To prepare the Ni-P/Paper electrode, the activated substrate (1 × 0.5 cm^2) was immersed in the aqueous EP bath for 60 min at 30 °C; **(5)** Ni-P-B/Cloth electrode: cloth (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the cloth into 0.2 M $NiSO_4$ aqueous solution for 2 s and then 0.5 M $NaBH_4$ aqueous solutions for 2 s and finally washed with water and ethanol. The weight of activated cloth was increased by about 0.1- 0.3 mg cm^{-2}. The EP bath for Ni-P-B was then prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g), sodium phosphite (0.094 g), DMAB (0.72 g), $NiSO_4 \cdot 6H_2O$ (1.25 g) in 100 mL water. To prepare the Ni-P-B/Cloth electrode, the activated substrate (1 × 0.5 cm^2) was immersed in the aqueous EP bath for 60 min at 10 °C. **(6)** Co-B/Cloth electrode: cloth (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the cloth into 0.2 M $CoSO_4$ aqueous solution for 2 s and then 0.5 M

$NaBH_4$ aqueous solutions for 2 s and finally washed with water and ethanol. The weight of activated cloth was increased by about 0.1-0.3 mg cm^{-2}. The EP bath for Co-B was then prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g), DMAB (0.72 g), $CoSO_4$ (1.39 g) in 100 mL water. To prepare the Co-B/Cloth electrode, the activated substrate (1 × 0.5 cm^2) was immersed in the aqueous EP bath for 60 min at 10 °C. **(7)** Ni-Co-B/Cloth electrode: cloth (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the paper into 0.1 M $CoSO_4$ and 0.1 M $NiSO_4$ aqueous solution for 2 s and then 0.5 M $NaBH_4$ aqueous solutions for 2 s and finally washed with water and ethanol. The weight of activated cloth was increased by about 0.1-0.3 mg cm^{-2}. The EP bath for Ni-Co-B was then prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g), $CoSO_4$ (0.69 g), DMAB (0.72 g) and $NiSO_4$ ▪6H2O (1.25 g) in 100 mL water. To prepare the Ni-Co-B/cloth electrode, the activated substrate (1 × 0.5 cm^2) was immersed in the aqueous EP bath for 60 min at 10 °C. **(8)** Ni-P-B/PU electrode: PU (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the PU into 0.2 M $NiSO_4$ aqueous solution for 2 s and then 0.5 M $NaBH_4$ aqueous solutions for 2 s and finally washed with water and ethanol. The weight of activated PU was increased by about 0.1-0.3 mg cm^{-2}. The EP bath for Ni-P-B was then prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g), sodium phosphite (0.094 g), DMAB (0.72 g) and $NiSO_4$ ▪$6H_2O$ (1.25 g) in 100 mL water. To prepare the Ni-P-B/PU electrode, the activated substrate (1 × 0.5 cm^2) was immersed in the aqueous EP bath for 60 min at 10 °C. **(9)** Co-B/PU electrode: PU (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the cloth into 0.2 M $CoSO_4$ aqueous solution for 2 s and then 0.5 M $NaBH_4$ aqueous solutions for 2 s and finally washed with water and ethanol. The weight of activated PU was increased by about 0.1-0.3 mg cm^{-2}. The EP bath for Co-B was then prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g), $CoSO_4$ (1.39 g) and DMAB (0.72 g) in 100 mL water. To prepare the Co-B/PU electrode, the activated substrate (1 × 0.5 cm^2) was immersed in the aqueous EP bath for 60 min at 10 °C. **(10)** Ni-Co-B/PU electrode: PU (1× 0.5 cm^2) was cleaned with water and acetone, and activated by alternative dipping the PU into 0.1 M $CoSO_4$ and 0.1 M $NiSO_4$ aqueous solution for 2 s and then 0.5 M $NaBH_4$ aqueous

solutions for 2 s and finally washed with water and ethanol. The weight of activated PU was increased by about 0.1-0.3 mg cm^{-2}. The EP bath for Ni-Co-B was then prepared by dissolving Na_2SO_4 (1.5 g), sodium succinate (2.5 g), $CoSO_4$ (0.69 g), DMAB (0.72 g) and $NiSO_4 \cdot 6H_2O$ (1.25 g) in 100 mL water. To prepare the Ni-Co-B/PU electrode, the activated substrate (1 cm × 0.5 cm) was immersed in the aqueous EP bath for 60 min at 10 °C. **(11)** Ni-P-B/Ni foil electrode: Before performing electroless plating (EP), the Ni foil (1× 0.5 cm^2) was cleaned with water and acetone, activated with acid etch in dilute nitric acid for 15 min, and finally washed with water and ethanol. The EP bath for Ni-P-B catalyst was prepared by dissolving Na_2SO_4 (1.5 g), sodium phosphite (0.094 g), sodium succinate (2.5 g) and $NiSO_4 \cdot 6H_2O$ (2.5 g) in 100 mL water followed by the addition of DMAB (0.72 g) into the solution. To prepare the Ni-P-B/Ni electrode, the pretreated substrate (1 cm × 0.5 cm) was immersed in the aqueous EP bath for 60 min at 25℃. After washed with water and ethanol, the as-prepared binder-free electrodes were dried at room temperature overnight. **(12)** Ni-P-B/Ni Foam electrode: Before performing electroless plating (EP), the Ni foam (1× 0.5 cm^2) was cleaned with water and acetone, activated with acid etch in dilute nitric acid for 15 min, and finally washed with water and ethanol. The EP bath for Ni-P-B catalyst was prepared by dissolving Na_2SO_4 (1.5 g), sodium phosphite (0.094 g), sodium succinate (2.5 g) and $NiSO_4 \cdot 6H_2O$ (2.5 g) in 100 mL water followed by the addition of DMAB (0.72 g) into the solution. To prepare the Ni-P-B/NF electrode, the pretreated Ni Foam substrate (1 cm × 0.5 cm) was immersed in the aqueous EP bath for different time at 10℃. After washed with water and ethanol, the as-prepared binder-free electrodes were dried at room temperature overnight.

Preparation of Pt-C/Paper and IrO_2/Paper electrodes

5 mg commercial Pt-C, 30 μL nafion solution and 970 μL ethanol was mixed and dispersed with ultrasonic for 30 min.[1] An aliquot of 10 μL was pipetted onto the paper (0.5 cm^2) for several times to reach a catalyst loading of 6.0 mg cm^{-2}. IrO_2/Paper, Pt-C/Ni Foil and IrO_2/Ni Foil were prepared with the same process.

Characterizations

X-ray diffractometer (XRD) was tested on a Rigaku D/MAX 2550 with Cu Kα radiation. Scanning electron microscopic (SEM) measurements were performed on a HitachiS-4800 field at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM, JEOL Ltd., JEM-2100F) with scanning transmission electron microscopy (STEM, Bright-field, lattice resolution: 0.2 nm) was employed to analyze the morphology and composition of the Ni-P-B catalyst. The crystal structure was confirmed from the selected area electron diffraction (SAED) pattern. X-ray photoelectron spectrometer (XPS) data and energy dispersive spectroscopy (EDS) spectrum were collected on an ESCALABMK II using Mg as the exciting source. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis was measured on Model ARCOS FHS12 (SPECTRO Analytical Instruments Inc, Germany). Electrochemical measurements cyclic voltammetry (CV) and linear-sweep voltammetry (LSV) were conducted using a CHI760E (CH Instruments, Inc., Shanghai). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area (SBET) using the adsorption data. The pore size distribution (PSD) was derived from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) model (Veeco, USA). The sheet resistance (Rs) of the electrode was measured using four-point method on a resistivity measurement system (RTS-8, China). Typically, six measurements were performed at different positions and Rs was an average of the corresponding values.

Electrochemical Measurements

A three-electrode cell system was employed incorporating a Ni-P-B/Paper (Paper: 1.0 * 0.5 cm^2) as working electrode, a carbon rod as the counter-electrode and saturated calomel electrode as reference electrode. All potentials were recorded with respect to the RHE. In all measurements, the saturated calomel electrode reference electrode was calibrated with respect to the RHE. High-purity anhydrous nitrogen (N_2) gas and oxygen (O_2, 99.99%) was used to purge the system for 30 minutes before hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), respectively. LSV measurements were conducted in 1.0 M KOH at a scan rate of 2 mV s^{-1} with *iR*-

correction (80%). All potentials reported were calibrated to the RHE. In 1.0 M KOH, E (RHE) = E (SCE) + 0.245 V+0.0596 pH, where E was the potential of the electrode.[2] The commercial reference electrode had been calibrated with respect to RHE before used. The potentials measured with respect to the calomel electrode were converted to RHE by the equation of 0.245 + (0.05916*pH).

Turnover frequency (TOF) determination

TOF was calculated from the equation TOF = j/(n·F·m/M) (n=2 for HER and n=4 for OER), where *j*, F, m and M represent the current density (mA cm^{-2}) at a certain overpotential, the faraday constant (~96485 C mol^{-1}), the mass loading of the catalyst (mg cm^{-2}) and the molecular weight of the catalyst, respectively. The molecular of the catalyst was assumed to be NiP_xB_y, where its metal and boron contents were calculated from the ICP-AES data.

Electrochemically active surface area (EASA) determination

The double-layer capacitance (C_{dl}), which is in proportion to EASA, was obtained by deriving from the cyclic voltammery (CV) curves versus the scan rates.[3] The potential was swept between 0.02 and 0.12 V versus RHE at different scan rates (10, 30, 50, 70 and 90 mV s^{-1}) for HER of Ni-P-B/Ni Foil, Ni-P-B/Paper and Ni-P-B/Ni Foam, where no faradic reaction occur. The potential was swept between 0.7 and 0.9 V versus RHE at different scan rates (10, 30, 50, 70 and 90 mV s^{-1}) for OER of Ni-P-B/Ni Foil, Ni-P-B/Paper and Ni-P-B/Ni Foam. Meanwhile, before performing the OER test, the electrode was continuously cycled between 1.0 V and 1.4 V vs RHE at 2 mV s^{-1} until reproducible voltammograms were obtained. The measured capacitive currents were plotted as a function of scan rate.

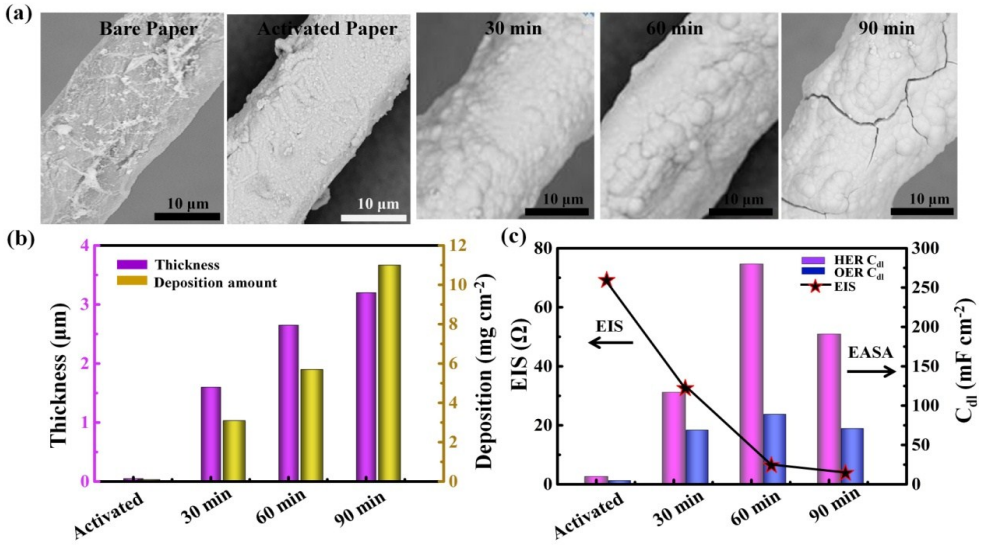

Figure S1. (a)The FESEM images of a single fiber during its formation process at 10°C; (b) the thickness of the Ni-P-B layer deposited on the single fiber and the deposition amount of Ni-P-B on the paper substrate at different plating times; (c) EIS and EASA of the Ni-P-B/Paper electrode during its formation process at 10°C.

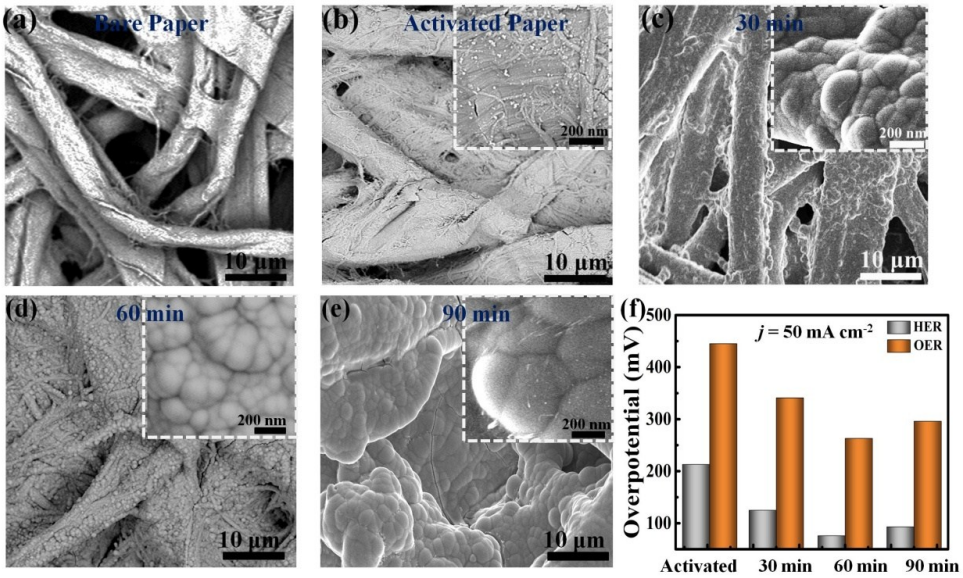

Figure S2. The FESEM images of Ni-P-B/Paper electrode during its formation process at 10°C for (a) bare paper, (b) activated paper, and electroless plating for (c) 30 min, (d) 60 min and (e) 90 min; (f) the HER and OER overpotentials to achieve a current density of 50 mA cm^{-2} for the Ni-P-B/Paper electrode at different electroless plating times.

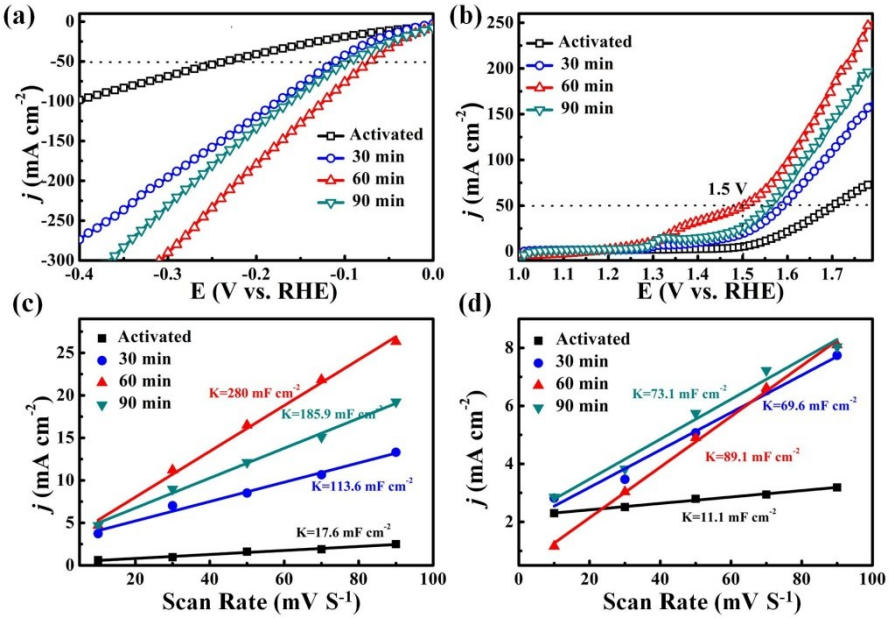

Figure S3. The LSV of HER (a) and OER (b) for the Ni-P-B/Paper electrode at different electroless plating times without *iR*-correction. (c) The capacitive currents at 0.08 V as a function of scan rate for Ni-P-B/Paper. (d) The capacitive currents at 0.8 V as a function of scan rate for Ni-P-B/Paper.

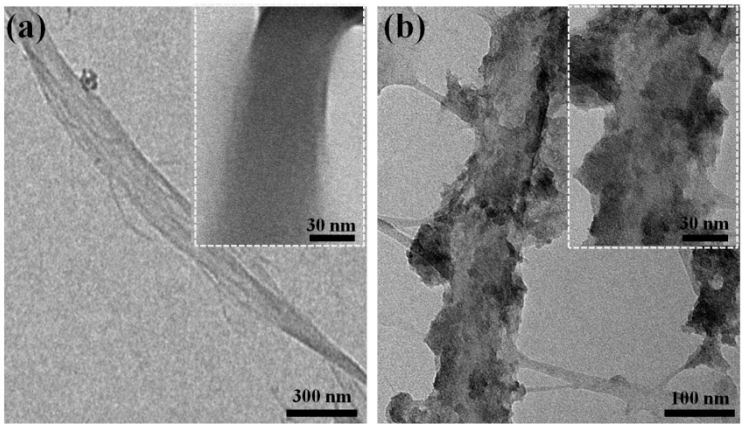

Figure S4. TEM image of a fiber drew from (a) the paper substrate and (b) the Ni-P-B/Paper electrode.

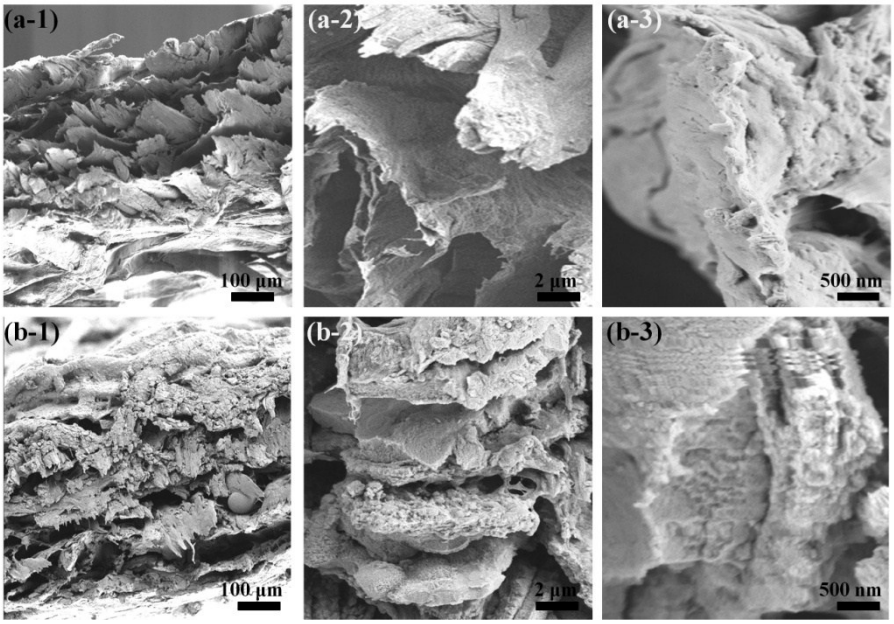

Figure S5. SEM images of the cross section of the bare paper (a-1, a-2 and a-3) and Ni-P-B/paper electrode (b-1, b-2 and b-3) cut by seizer.

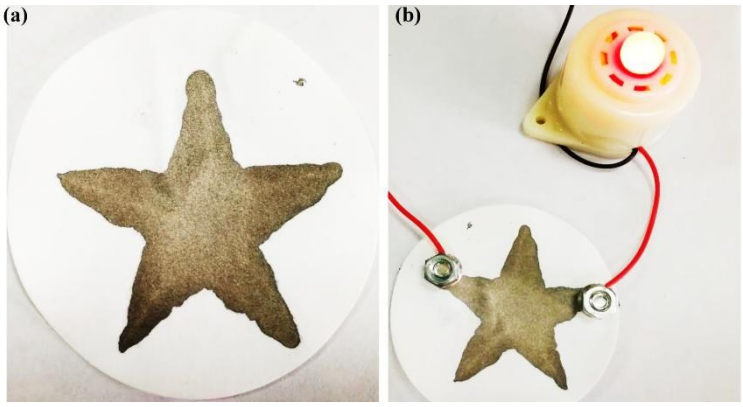

Figure S6. Photographs of the conductive Ni-P-B/Paper electrode.

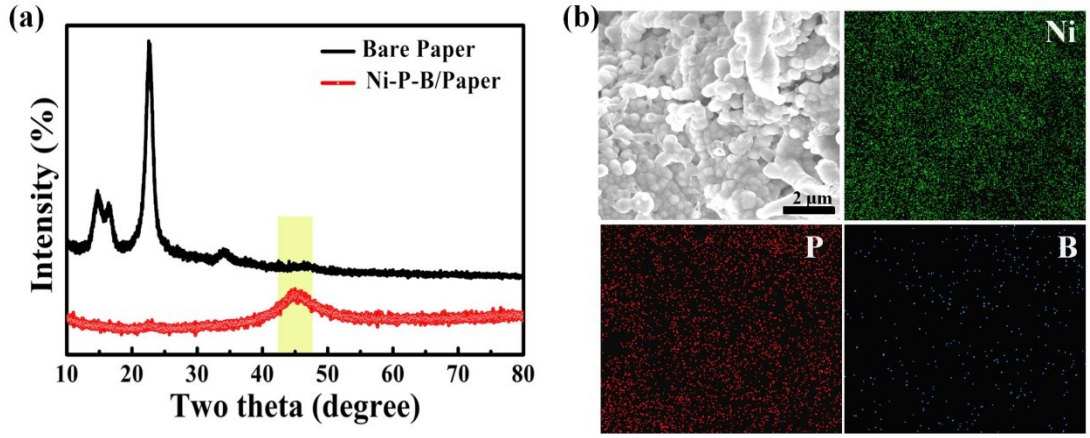

Figure S7. (a) XRD patterns of bare paper and Ni-P-B/Paper electrode. (b) SEM images of Ni-P-B nanoparticle on Ni-P-B/Paper electrode, and the EDS elemental mapping images for nickel (green), phosphorus (red), and boron (blue).

Table S1. ICP-AES analysis of the electrocatalyst on different electrodes.

Catalysts	**Ni**	**Co**	**P**	**B**	**Atomic ratio**
			(wt %)		
Ni-P-B/Paper	86.03		2.88	2.11	Ni:P:B=16:1:2.1
Ni-P-B/Paper Post-HER	81.91		2.39	1.66	Ni:P:B=18.1:1:2.0
Ni-P-B/Paper Post-OER	83.45		2.51	1.84	Ni:P:B=17.5:1:2.1
Ni-P-B/Ni Foil	81.1		3.42	1.19	Ni:P:B=12.5:1:1.9
Ni-P-B/Ni Foam	83.1		3.13	1.15	Ni:P:B=14:1:1.1
Co-B/Cloth	-	88.4	-	1.36	Co:B=11.9:1
Co-B/PU	-	86.5	-	1.46	Co:B=10.8:1
Co-B/Paper	-	89.8	-	1.48	Co:B=11.1:1
Ni-P-B/PU	85.9	-	2.93	2.65	Ni:P:B=15.5:1:2.6
Ni-P-B/Cloth	85.4	-	3.19	2.56	Ni:P:B=14.1:1:2.3
Co-Ni-B/Cloth	56.5	18.3	-	1.79	Co:Ni:B=5.77:1.85:1
Co-Ni-B/Paper	51.4	33.8	-	2.24	Co:Ni:B=4.23:2.77:1
Co-Ni-B/PU	61.5	25.8	-	1.82	Co:Ni:B=6.22:2.6:1

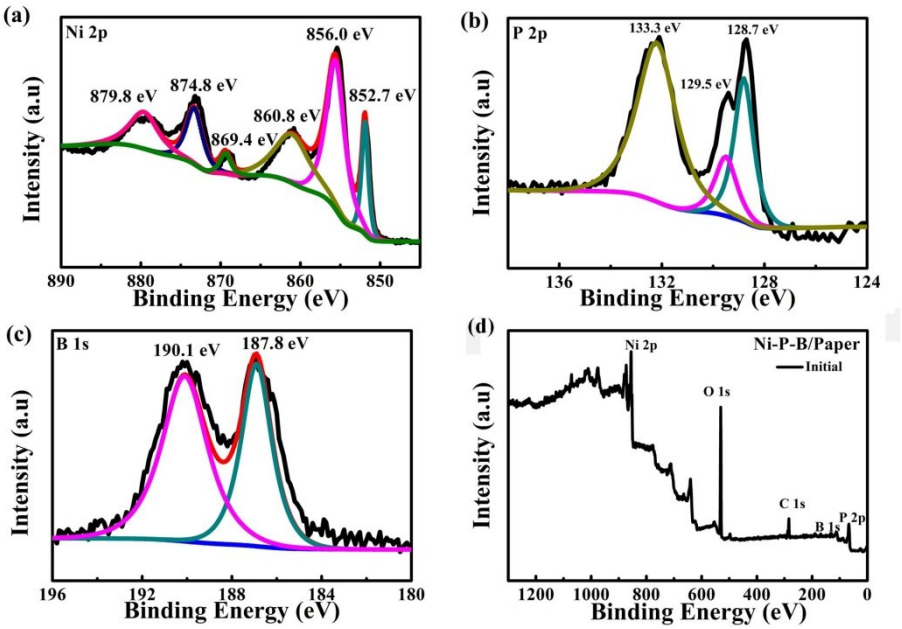

Figure S8. (a) Ni 2p, (b) P 2p and (c) B 1s core-level XPS spectra of Ni-P-B/Paper. (d) XPS survey spectrum of the Ni-P-B/Paper sample.

Table S2. The sheet resistance (Rs) of Ni-P-B/Paper sample at different deposition times.

Catalyst	**Rs (Ω▪sq^{-1})**			
	0 min	30 min	60 min	90 min
Ni-P-B/Paper	-	0.71	0.42	0.12

Table S3. Comparison of the HER performance of Ni-P-B/Paper with other electrocatalysts in 1.0 M KOH.

Catalysts	**Loading amount (mg cm^{-2})**	***j*** **(mAcm^{-2})**	**η (mV)**	**Reference**
Ni-P-B/Paper	**5.63**	**50**	**76**	**This work**
		500	**276**	
Co-Ni-B/ Ni Foam(NF)	5.0	10	205	J. Mater. Chem. A, 2017, **5**, 12379–12384
LiCoBPO/NF	3.0	10	245	Energy Environ. Sci. DOI: 10.1039/c8ee01669k

Co-O@CoB/TM	4.87	50	102	Small.2017, **13**, 1700805
Co-Ni-B/GC	2.1	10	131	Applied Catalysis B: Environmental 2016,**192**,126-133
Ni-B0.54/Cu Foil	1.4	10	135	Nano Energy. 2016, **19**, 98–107
MoB	2.5	10	210	Angew. Chem. Int. Ed. 2012, **51**, 12703 -12706
MoB_2	-	10	149	J. Am. Chem. Soc. 2017, **139**, 12370-12373
FeB_2/NF	0.2	10	61	Adv. Energy Mater. 2017, **7**, 1700513
Co_2B	0.21	10	155	Adv. Energy Mater. 2016, **6**, 1502313
Co-Mo-B/GC	2.8	10	66	Electrochimica Acta. 2017, **232**, 64–71
Ni-B/NF	12.3	20	125	Nanotechnology. 2016,**27**,12LT01
FeS_2/CoS_2 NSs	0.2	10	78.2	Small.2018, **14**, 1801070
Co-MoS_2	2.0	10	48	Adv. Mater. 2018, **30**, 1801450
Fe-Ni@NC-CNTs	0.5	10	202	Angew. Chem. Int. Ed. 2018, **57**, 8921 –8926
Fe-Doped Ni_2P	2.0	10	114	Adv. Funct. Mater. 2017, **27**, 1702513
MoP/Ni Foam(NF)	0.3	10	110	Small Methods.2018, **2**, 1700369
Co-Ni_3N	-	10	160	Adv. Mater. 2018, **30**, 1705516
Pt-CoS_2/CC	3.89	10	24	Adv. Energy Mater. 2018.**8**.1800935
Co-Ni/MoS_2	1.0	10	70	Nat. Commun. 2017, **8**, 14430
Cu@CoSx/CF	3.9	10	134	Adv. Mater. 2017, **29**, 1606200
FeMnP/NF	2.6	10	100	Nano Energy. 2017, **39**, 444
NiFe LDH-NS@DG_{10}	2.0	20	115	Adv. Mater. 2017, **29**, 1700017
MoS_2-Ni_3S_2	13.0	10	98	ACS Catal. 2017, **7**, 2357-2366
Ni/Mo_2C-P	-	10	179	Chem. Sci., 2017, **8**, 968-973

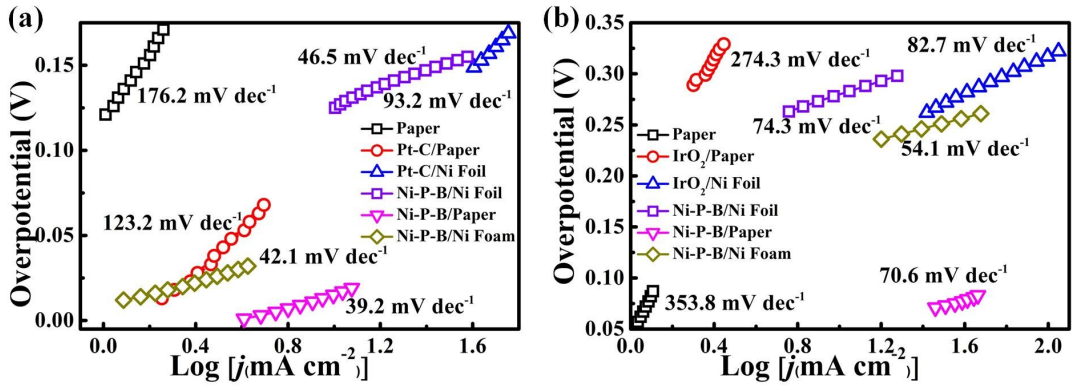

Figure S9. (a) The Tafel plots of bare paper, Pt-C/Paper, Pt-C/Ni Foil, Ni-P-B/Ni Foil, Ni-P-B/Ni Foam and Ni-P-B/Paper for HER. (b) The Tafel plots of bare paper, IrO_2/Paper, IrO_2/Ni Foil, Ni-P-B/Ni Foil, Ni-P-B/Ni Foam and Ni-P-B/Paper for OER.

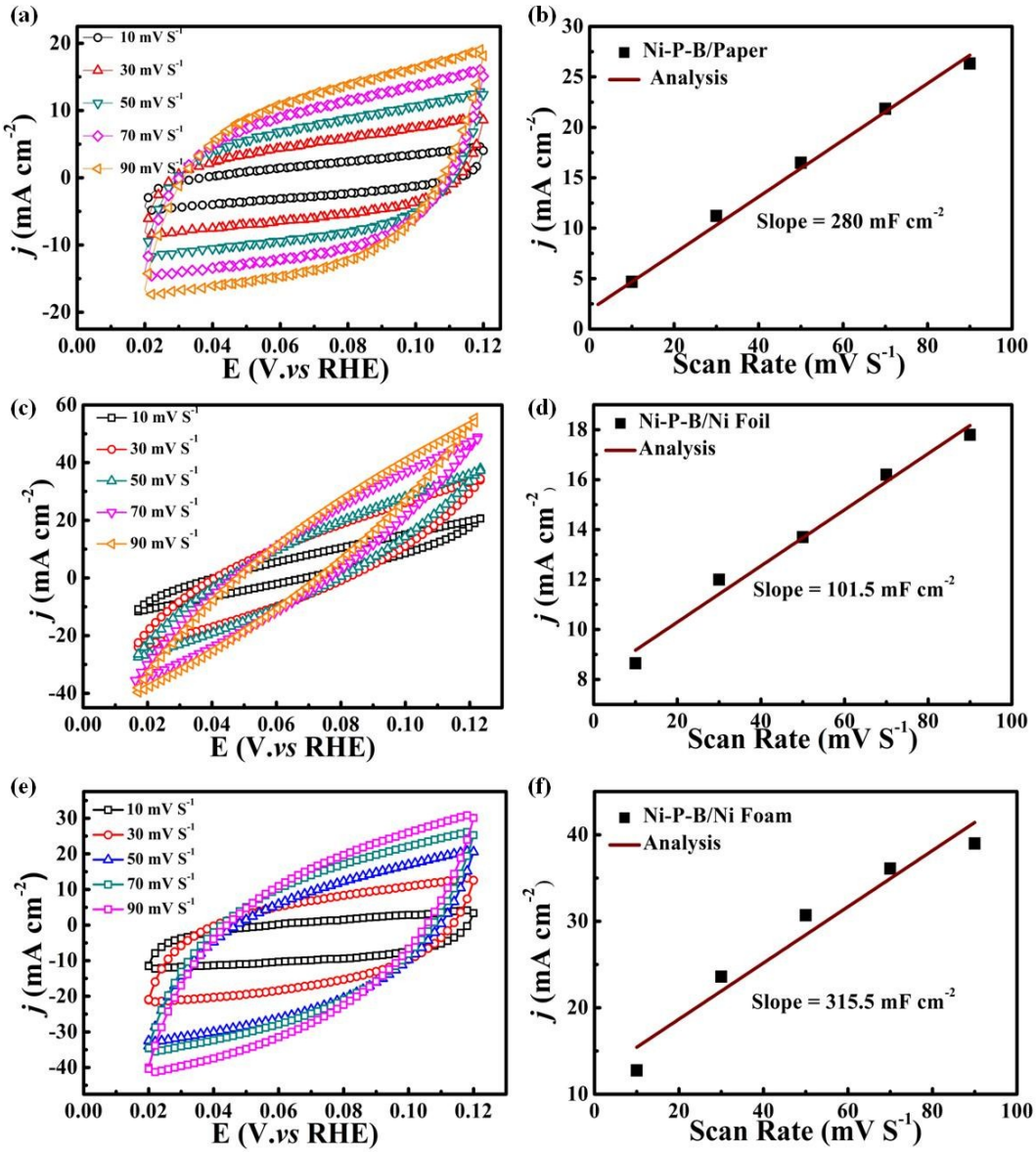

Figure S10. (a) Cyclic voltammograms (CVs) of Ni-P-B/Paper in the non-Faradaic

current range at scan rates of 10, 30, 50, 70 and 90 mV s^{-1}. (b) The capacitive currents at 0.08 V as a function of scan rate for Ni-P-B/Paper. (c) Cyclic voltammograms (CVs) of Ni-P-B/Paper in the non-Faradaic current range at scan rates of 10, 30, 50, 70 and 90 mV s^{-1}. (d) The capacitive currents at 0.08 V as a function of scan rate for Ni-P-B/Ni Foil. (e) Cyclic voltammograms (CVs) of Ni-P-B/Ni Foam in the non-Faradaic current range at scan rates of 10, 30, 50, 70 and 90 mV s^{-1}. (f) The capacitive currents at 0.08 V as a function of scan rate for Ni-P-B/Ni Foam.

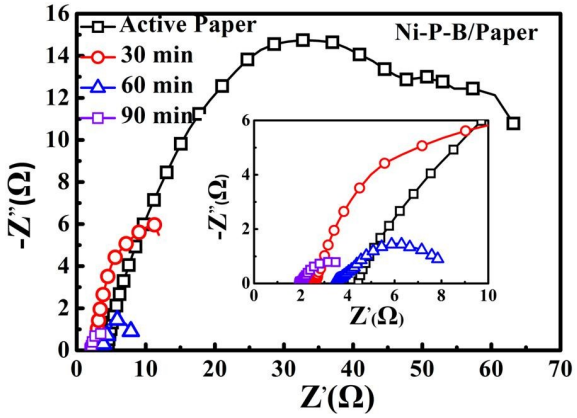

Figure S11. Nyquist plots of Ni-P-B/Paper electrode during its formation process at 10°C for activated paper, and electroless plating for 30 min, 60 min and 90 min at overpotential of 100 mV for HER.

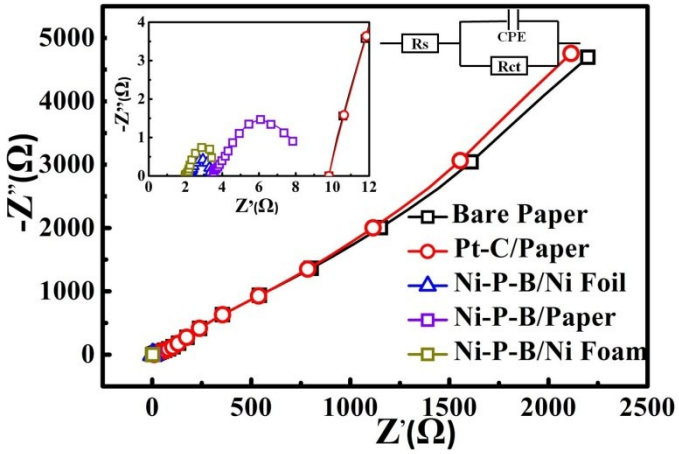

Figure S12. Nyquist plots of bare paper, Pt-C/Paper, Ni-P-B/Ni Foil, Ni-P-B/Ni Foam

and Ni-P-B/Paper measured at overpotential of 100 mV for HER.

Table S4. The OER performances of the as-prepared Ni-P-B/Paper electrode and other electrodes with non-noble-metal electrocatalysts in 1.0 M KOH.

Catalysts	**Loading Amount ($mgcm^{-2}$)**	***j*** **($mAcm^{-2}$)**	**η (mV)**	**Reference**
Ni-P-B/Paper	**6.15**	**50**	**263**	**This work**
		500	**375**	
Co-Ni-B/NF	5.0	50	400	J. Mater. Chem. A, 2017, **5**, 12379-12384
LiCoBPO/NF	3.0	10	293	Energy Environ. Sci. 2019,**12**, 988-999
Mo_2B_4	-	3.5	270	J. Am. Chem. Soc. 2017, **139**, 12915-12918
RuB_2/GCE	0.281	10	28	Adv. Energy Mater. 2018, 1803369
Co-O@CoB/TM	4.87	50	290	Small.2017, **13**, 1700805
FeB_2/NF	0.2	10	296	Adv. Energy Mater. 2017, **7**, 1700513
Co_2B-500/NG	0.21	10	360	Adv. Energy Mater. 2016.**6**, 1502313
Ni_3B-rGO	2.0	10	290	Electrochemistry Commun. 2017,**17**,30337
Co-Mo-B	2.8	10	320	Electrochimica Acta. 2017, **232**, 64–71
Ni-B/NF	12.3	100	360	Nanotechnology. 2016,**27**,12LT01
FeS_2/CoS_2 NSs	0.2	10	250	Small 2018, **14**, 1801070
Co-MoS_2	2.0	10	260	Adv. Mater. 2018, **30**, 1801450
Fe-Ni@NC-CNTs	0.5	10	274	Angew. Chem. Int. Ed. 2018, **57**, 8921 –8926
Fe-Doped Ni_2P	2.0	10	190	Adv. Funct. Mater. 2017, **27**, 1702513
MoP/ NF	0.3	10	280	Small Methods. 2018, **2**, 1700369
$Ni_{11}(HPO_3)_8(OH)_6$/NF	3.0	10	232	Energy Environ. Sci. 2018,**11**, 1287-1298
Pt-CoS_2/CC	3.89	10	300	Adv. Energy Mater. 2018.**8**.1800935
Co-Ni/MoS_2	1.0	10	235	Nat. Commun. 2017, **8**, 14430
Cu@CoSx/CF	3.9	10	169	Adv. Mater. 2017, **29**, 1606200

FeMnP	2.6	10	120	Nano Energy.2017, **39**, 444
Co-Ni/MoS_2	1.0	10	235	Nat.Commun.2017, **8**, 15377
NiFe LDH-NS@DG10	2.0	10	210	Adv. Mater. 2017, **29**, 1700017
MoS_2-Ni_3S_2	13.0	10	249	ACS Catal. 2017, **7**, 2357-2366
NiCoP/Ni	5.0	50	308	Nano Research 2016, **9**, 2251-2259

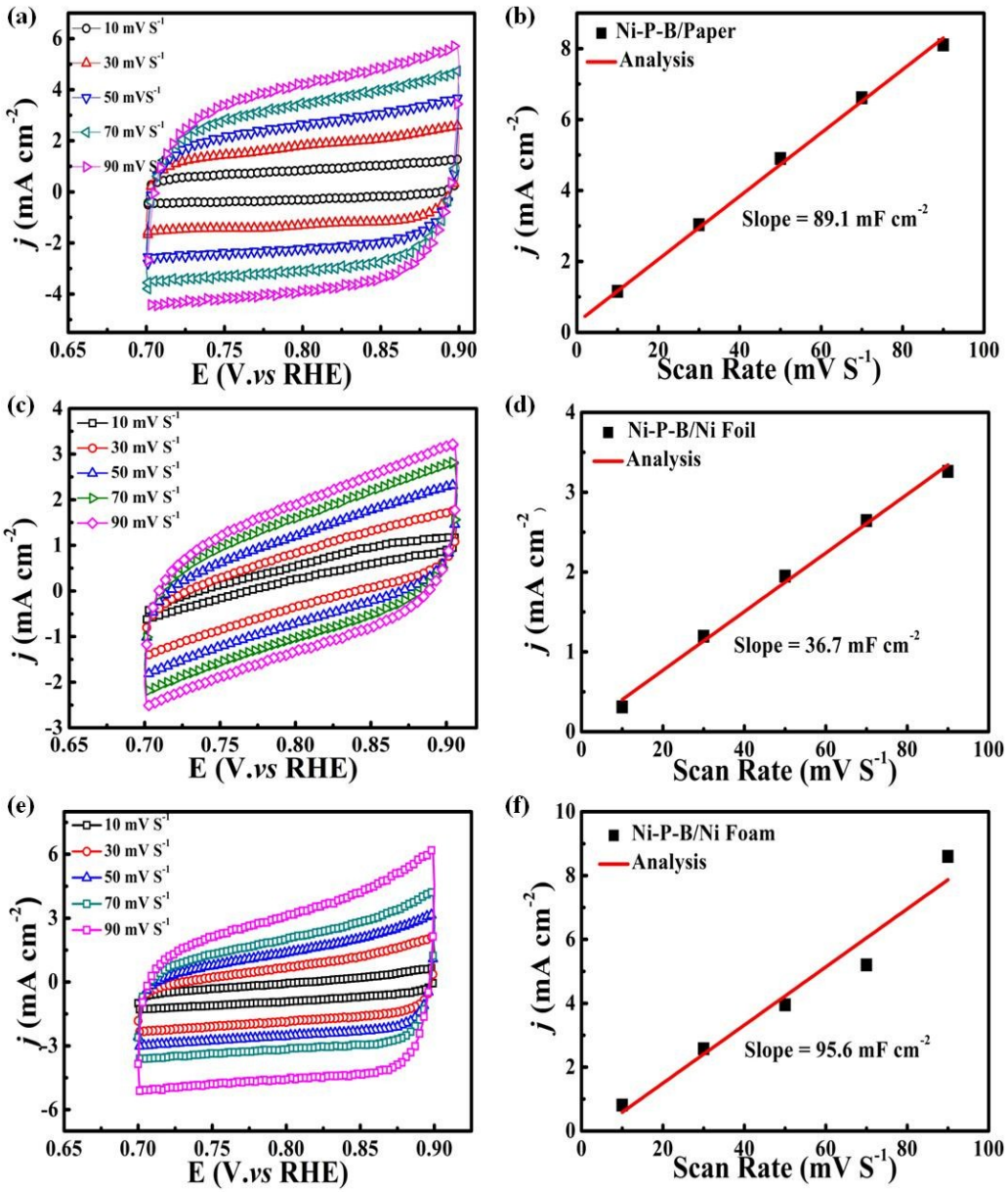

Figure S13. (a) Cyclic voltammograms (CVs) of Ni-P-B/Paper in the non-Faradaic current range at scan rates of 10, 30, 50, 70 and 90 mV s^{-1} for OER. (b) The capacitive currents at 0.8 V as a function of scan rate for Ni-P-B/Paper. (c) Cyclic voltammograms

(CVs) of Ni-P-B/Ni Foil in the non-Faradaic current range at scan rates of 10, 30, 50, 70 and 90 mV s^{-1} for OER. (d) The capacitive currents at 0.8 V as a function of scan rate for Ni-P-B/Ni Foil. (e) Cyclic voltammograms (CVs) of Ni-P-B/Ni Foam in the non-Faradaic current range at scan rates of 10, 30, 50, 70 and 90 mV s^{-1} for OER. (f) The capacitive currents at 0.8 V as a function of scan rate for Ni-P-B/Ni Foam.

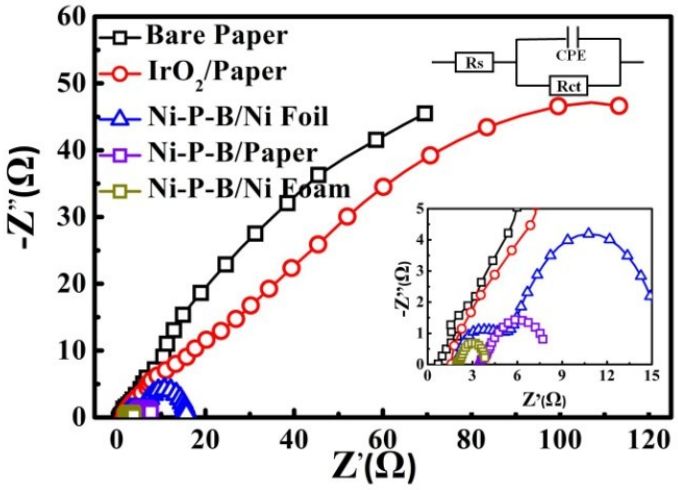

Figure S14. Nyquist plots of bare paper, Pt-C/Paper, Ni-P-B/Ni Foil, Ni-P-B/Ni Foam and Ni-P-B/Paper measured at overpotential of 300 mV for OER.

Table S5. Comparison between Ni-P-B/Paper, Ni-P-B/Paper and Ni-P-B/Ni Foam electrode.

	Deposition amount (mg ▪ cm^{-2})	**Weight (mg▪cm^{-2})**		**EIS (Ω)**	**C_{dl} mF▪cm^{-2}**	**η_{50} (mV)**	**η_{500} (mV)**	**Tafel slope mV dec^{-1}**
Ni-P-B/Paper	6.15	21.5	HER	4.0	280.0	76	276	39.2
			OER	5.0	89.1	263	375	70.6
Ni-P-B/Ni Foil	9.5	108.5	HER	2.1	101.5	141	372	46.5
			OER	4.1	36.7	323	471	74.3
Ni-P-B/Ni Foam	6.10	44.2	HER	1.7	315.5	94	251	42.1
			OER	2.0	95.6	261	335	54.1

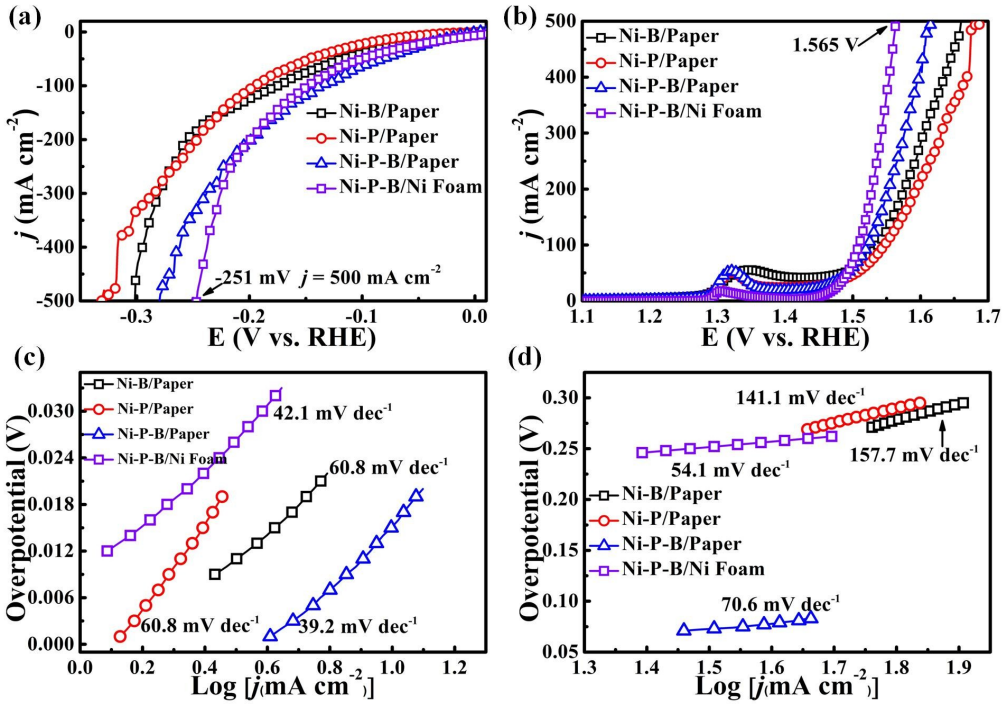

Figure S15. With *iR*-corrected polarization curves of Ni-B/Paper, Ni-P/Paper, Ni-P-B/Paper and Ni-P-B/Ni Foam electrodes at a scan rate of 2 mV s^{-1} for HER (a) and OER (b). The Tafel plots Ni-B/Paper, Ni-P/Paper, Ni-P-B/Paper and Ni-P-B/Ni Foam electrodes for HER (c) and OER (d).

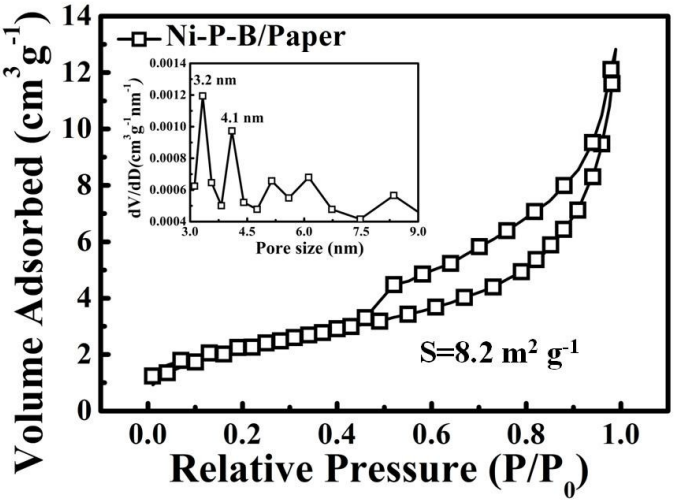

Figure S16. Nitrogen isotherms and pore size distributions of the Ni-P-B/Paper electrode in nitrogen.

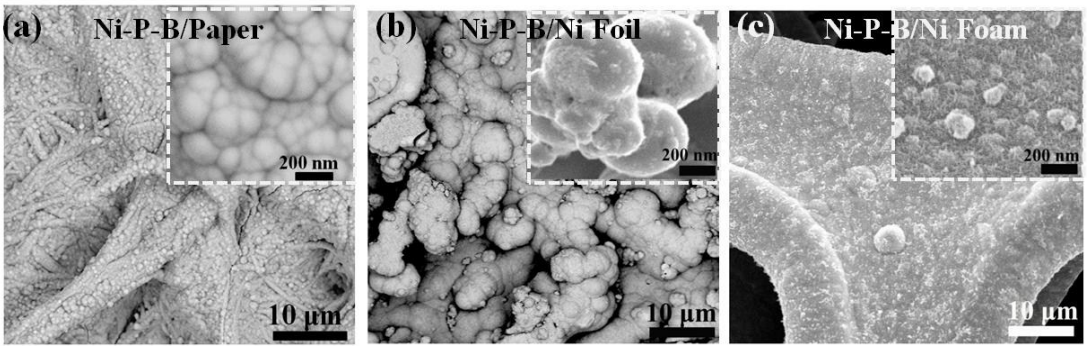

Figure S17. FESEM images of (a) Ni-P-B/Paper, (b) Ni-P-B/Ni Foil and (c) Ni-P-B/Ni Foam electrode.

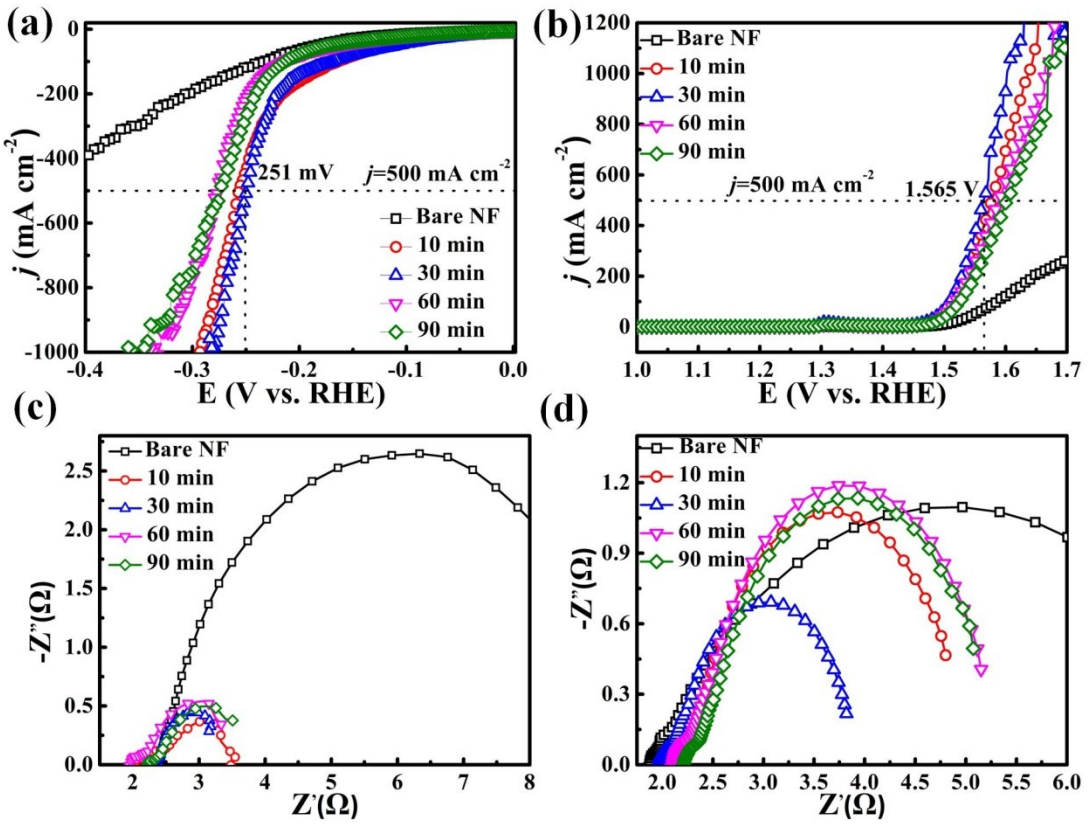

Figure S18. (a) Nyquist plots of bare Ni Foam, Ni-P-B/Ni Foam (10 min, 30 min, 60 min and 90 min) measured at overpotential of 100 mV for HER; (b) Nyquist plots of bare Ni Foam, Ni-P-B/Ni Foam (10 min, 30 min, 60 min and 90 min) measured at overpotential of 300 mV for OER.

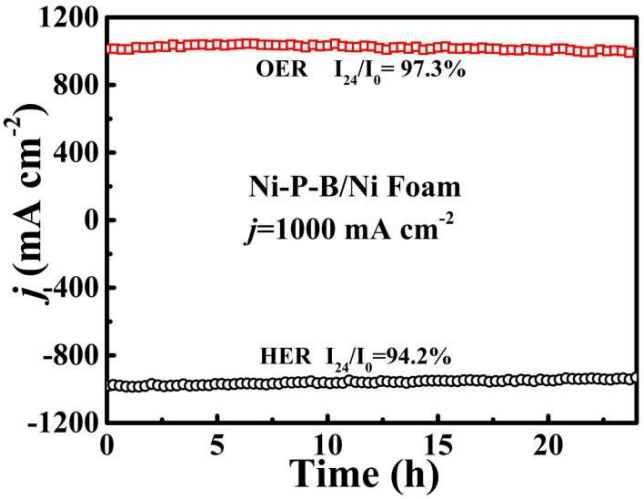

Figure S19. Chronopotentiometric measurements of long-term stability of Ni-P-B/Ni Foam at the current density of 1000 mA cm^{-2} for 24 h.

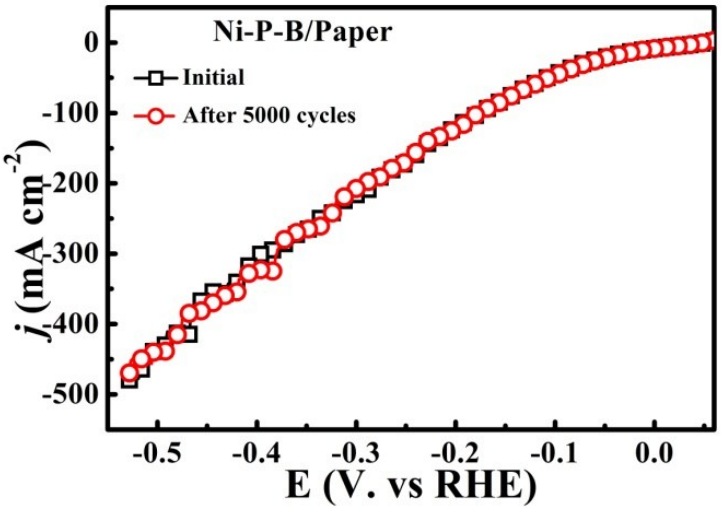

Figure S20. Polarization curve of initial Ni-P-B/Paper electrode and the electrode after 5000 CVs scans for HER.

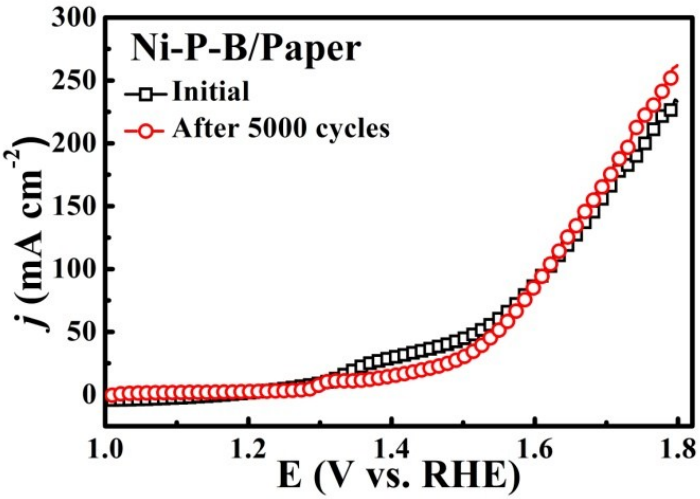

Figure S21. Polarization curve of initial Ni-P-B/Paper and the electrode after 5000 CVs scans for OER.

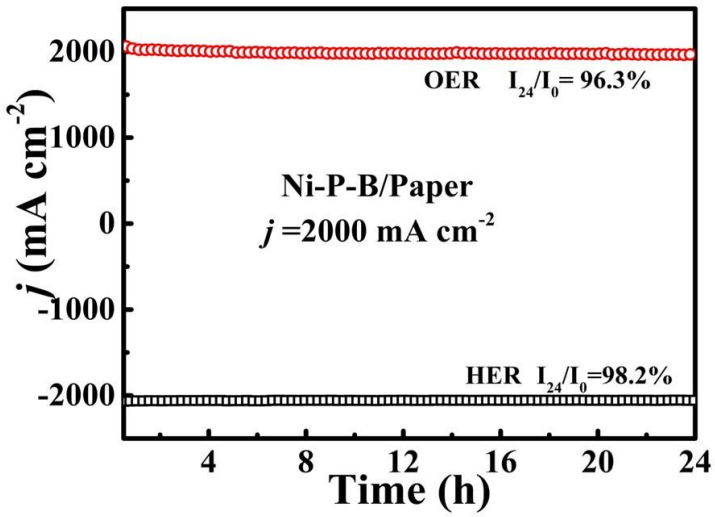

Figure S22. Chronopotentiometric measurements of long-term stability of Ni-P-B/Paper at the current density of 2000 mA cm^{-2} for 24 h.

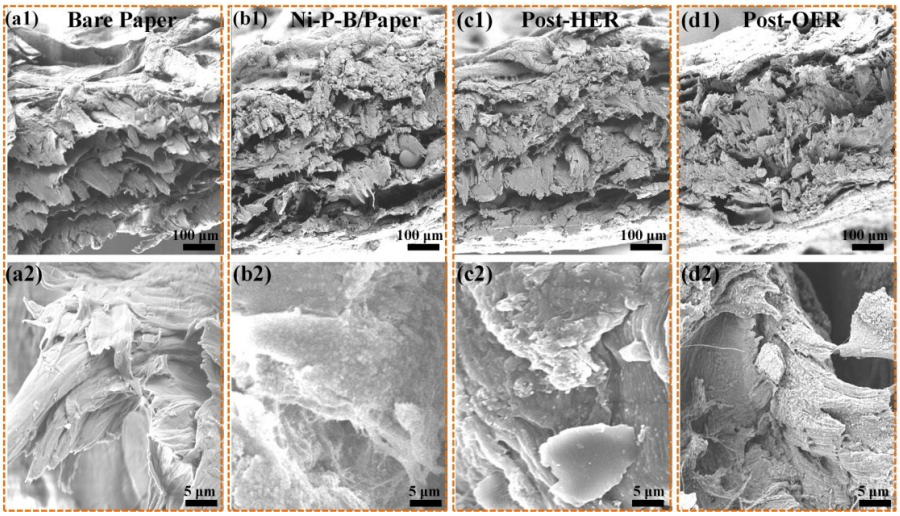

Figure S23. Cross-section SEM images of bare paper (a1), as prepared (b1), post-HER (c1) and post-OER (d1) Ni-P-B/Paper electrode. SEM images of the fiber inside the bare paper (a2), as prepared (b2), post-HER (c2) and post-OER (d2) Ni-P-B/Paper electrode after stability test at 1000 mA cm^{-2} for 24 h**.**

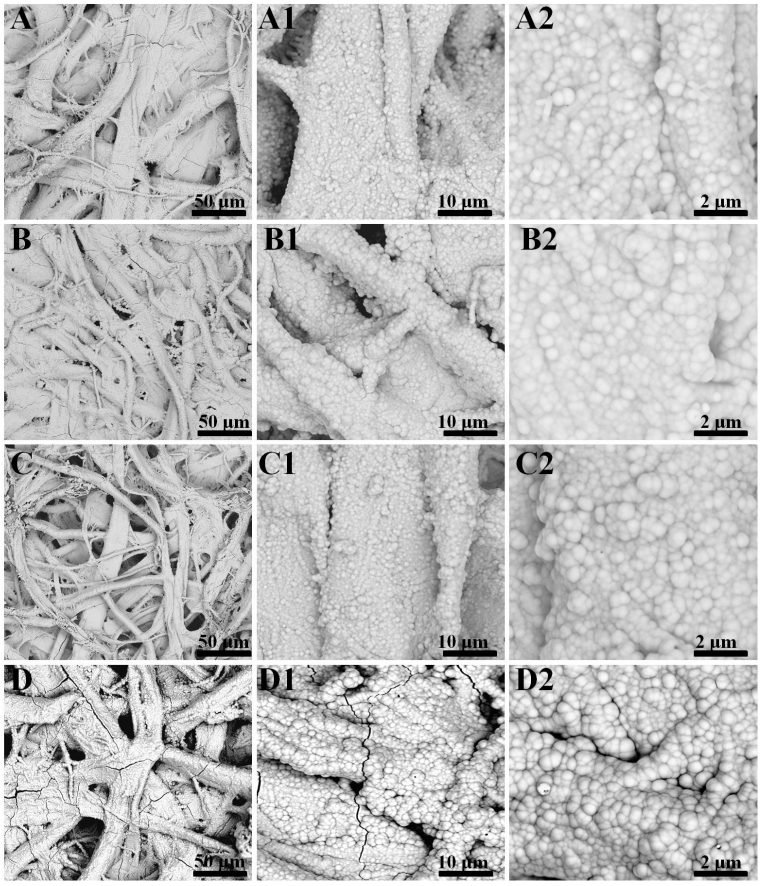

Figure S24. SEM images of the Ni-P-B/Paper electrodes before (A-A2) and after long-term HER stability tests at 1000 mA cm^{-2} in 1.0 M KOH for 5 h (B-B2), 15 h (C-C2) and 24 h (D-D2).

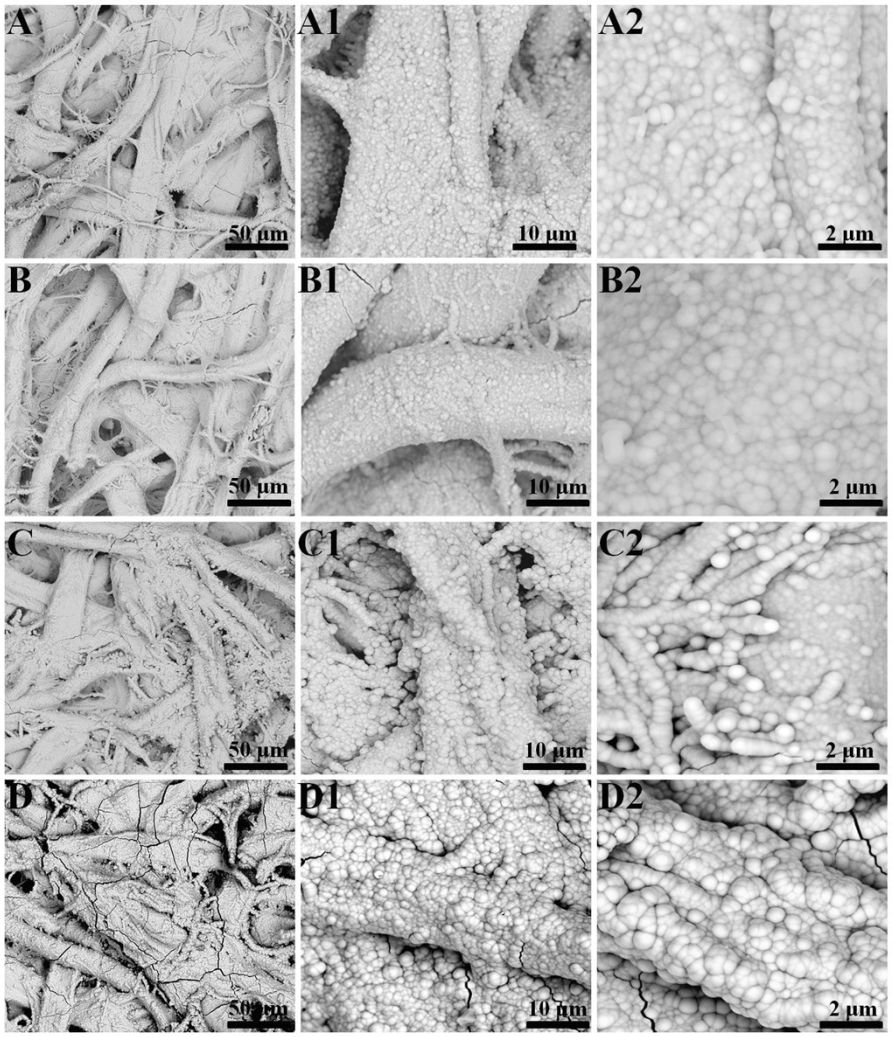

Figure S25. SEM images of Ni-P-B/Paper electrodes before (A-A2) and after long-term OER stability tests at 1000 mA cm^{-2} in 1.0 M KOH for 5 h (B-B2), 15 h (C-C2) and 24 h (D-D2).

Table S6. The weight of Ni-P-B catalyst deposited on the Ni foil, Ni foam and paper substrate**.**

Catalysts			**Weight (g)**		
1*1 cm²	0 min	Activated	30 min	60 min	90 min
Ni-P-B/Paper	0.0092	0.0094	0.0155	0.0215	0.0312
Ni-P-B/Ni Foil	0.0895	0.0894	0.0988	0.1085	0.1145
Ni-P-B/Ni Foam	0.0320	0.0380	0.0442	0.0462	0.0498

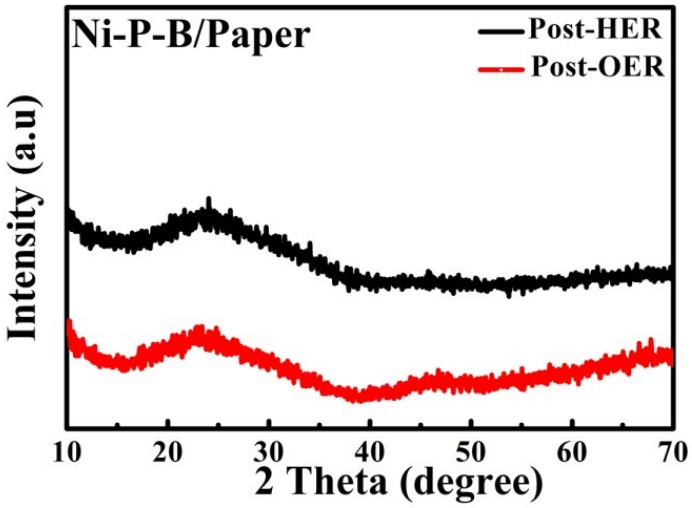

Figure S26. The XRD of post-HER and post-OER Ni-P-B/Paper electrode after operation at 1000 mA cm^{-2} for 24 h.

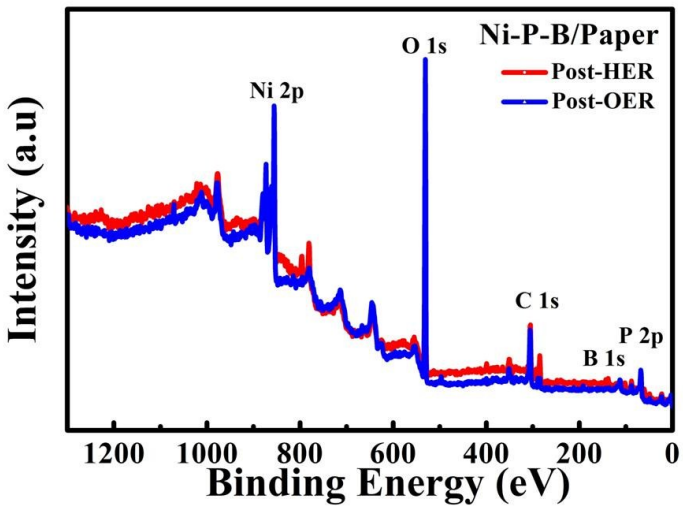

Figure S27. XPS survey spectrum of Post-HER and Post-OER Ni-P-B/Paper electrode.

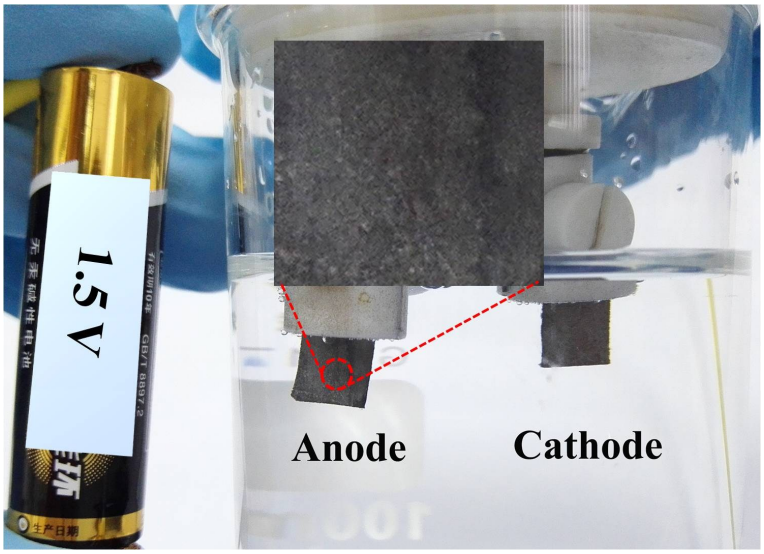

Figure S28. Photograph of Ni-P-B/Paper ||Ni-P-B/Paper two-electrode system driven by 1.5 V commercial battery.

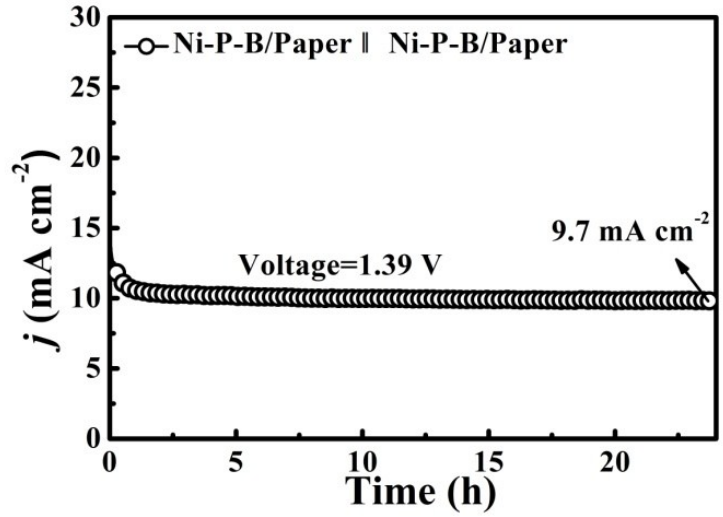

Figure S29. The overall water splitting performance of Ni-P-B/Paper ‖ Ni-P-B/Paper at 10 mA cm^{-2}.

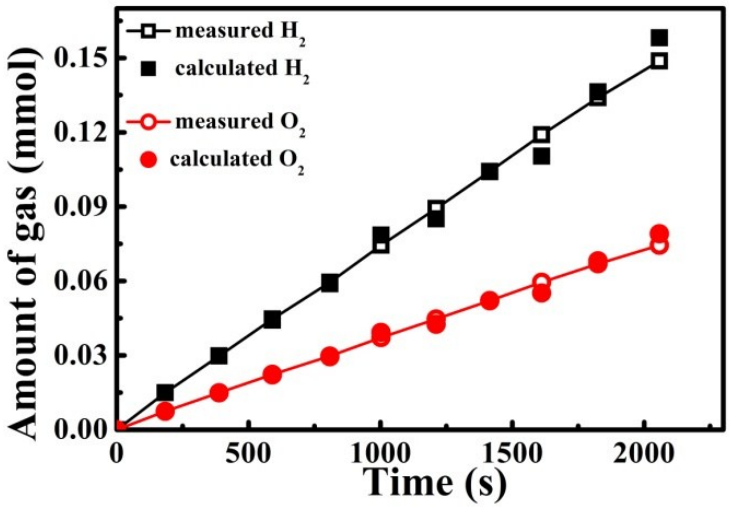

Figure S30. Generated (lines) and calculated (symbols) volumes of H_2 and O_2 as a function of time.

Figure S31. Recovery and recycle of the Ni-P-B/Paper electrode.

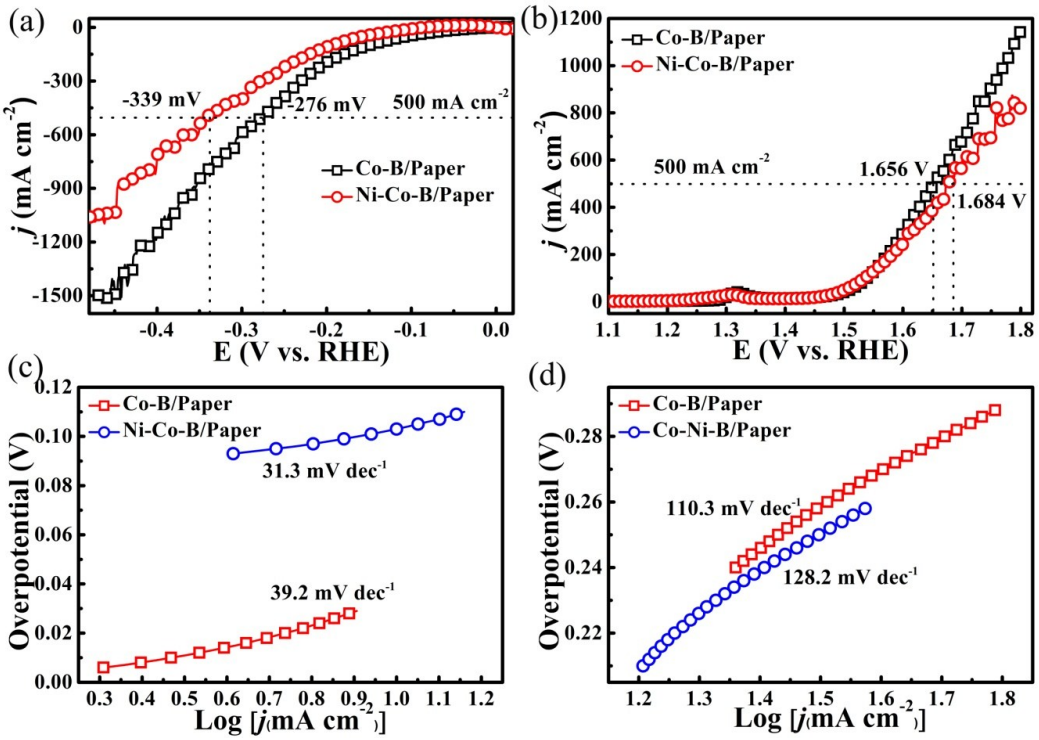

Figure S32. Electrocatalytic activity characterization of Co-B/Paper and Ni-Co-B/Paper electrodes. The HER (a) and OER (b) polarization curves in 1 M KOH at scan rate of 2 mV s^{-1} with iR-correction. Tafel plots of HER (c) and OER (d).

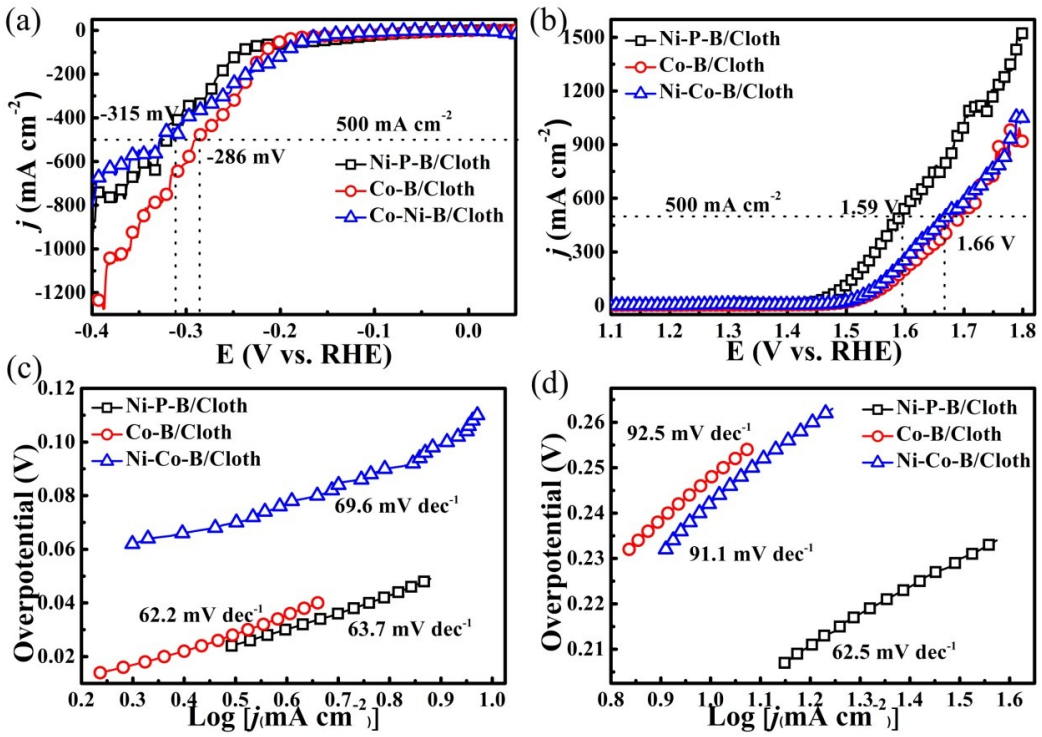

Figure S33. Electrocatalytic activity characterization of Ni-P-B/Cloth, Co-B/Cloth and Ni-Co-B/Cloth electrodes with iR-correction. The HER (a) and OER (b) polarization curves in 1 M KOH at scan rate of 2 mV s^{-1}. Tafel plots of HER (c) and OER (d).

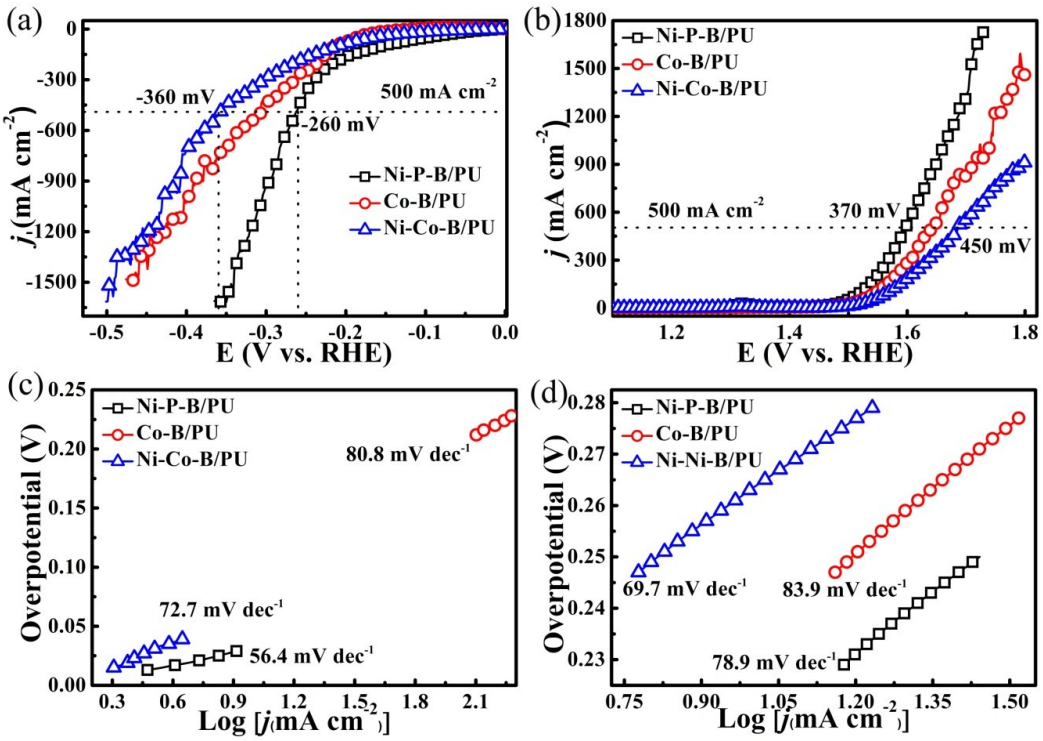

Figure S34. Electrocatalytic activity characterization of Ni-P-B/PU, Co-B/PU and Ni-Co-B/PU electrodes with iR-correction. The HER (a) and OER (b) polarization curves in 1 M KOH at scan rate of 2 mV s^{-1}.Tafel plots of HER (c) and OER (d).

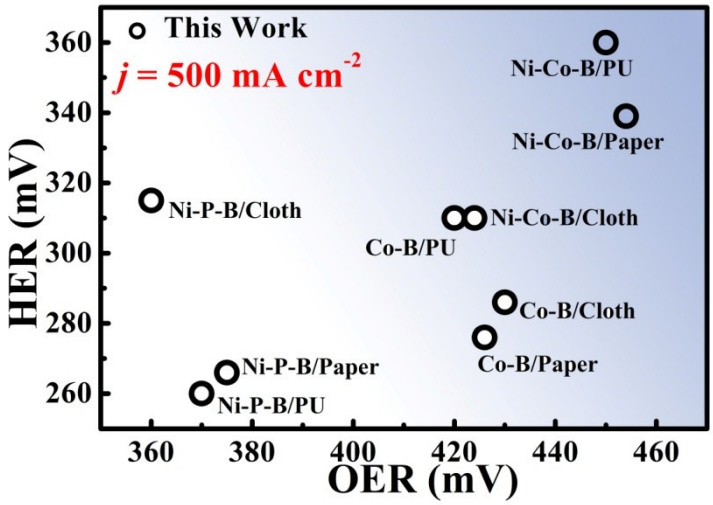

Figure S35. The HER and OER overpotentials of the as-prepared boride-based electrodes to achieve 500 mA cm^{-2} water-splitting current in alkaline (1M KOH) electrolyte.

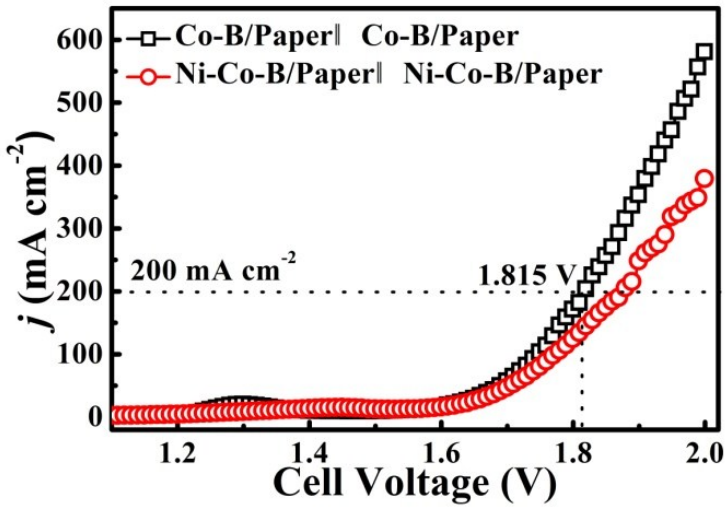

Figure S36. Polarization curve recorded at a scan rate of 2 mV s^{-1} in a two-electrode configuration of Co-B/Paper ‖ Co-B/Paper and Ni-Co-B/Paper ‖ Ni-Co-B/Paper.

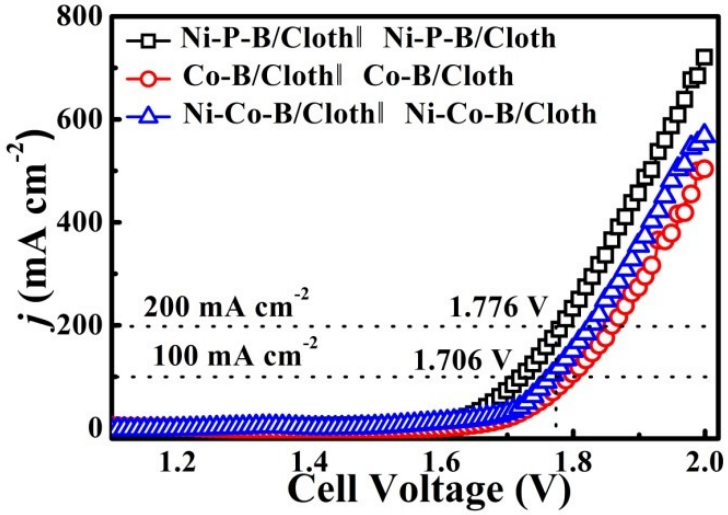

Figure S37. Polarization curve recorded at a scan rate of 2 mV s^{-1} in a two-electrode configuration of Ni-P-B/ Cloth ‖ Ni-P-B/ Cloth, Co-B/Cloth ‖ Co-B/ Cloth and Ni-Co-B/ Cloth ‖ Ni-Co-B/ Cloth.

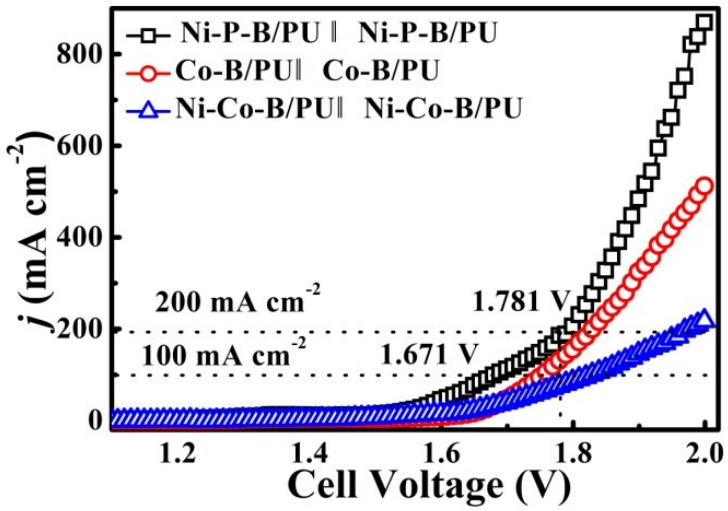

Figure S38. Polarization curve recorded at a scan rate of 2 mV s^{-1} in a two-electrode configuration of Ni-P-B/PU ‖ Ni-P-B/PU, Co-B/PU ‖ Co-B/PU and Ni-Co-B/PU ‖ Ni-Co-B/PU.

Table S7. The overall water splitting performance for Ni-P-B/Paper electrode and other electrodes with non-noble-metal electrocatalysts in 1.0 M KOH.

Catalysts	***j*** **(mAcm^{-2})**	**Voltages (V)**	**Reference**
Ni-P-B/Paper	**50**	**1.661**	This work
	200	**1.796**	
FeCoNi/NF (Ni Foam)	10/100	1.429/1.73	Nat. Commun. 2018. **9**.2452
N-Ni_3S_2/NF	10/100	1.48/1.81	Adv. Mater. 2017, **29**, 1701584
$Fe_{0.09}Co_{0.13}$-$NiSe_2$/CFC	10/100	1.52/1.71	Adv. Mater. 2018, 1802121
Ni_3N-NiMoN/CC	10/100	1.54/1.75	Nano Energy. 2018.**44**. 353–363
$CoSn_2$/NF	10/100	1.55/1.69	Angew. Chem. 2018, **130**, 15457 – 15462
$Ni_{0.8}Fe_{0.2}$LDH/NF	10/100	1.55/1.73	Small 2018, **14**, 1800759
N-CoNiPS/C	10/100/200	1.56/1.73/1.86	Adv. Funct. Mater. 2018, 1805075

NC/NiCu/NiCuN	10/100	1.56/1.92	Adv. Funct. Mater. 2018, 1803278
G-Ni_4Fe/GF	10/100	1.58/1.72	Adv. Energy Mater. 2018, 1800403
Ni-Co-P HNBs	10/100	1.62/1.94	Energy Environ. Sci. 2018,**11**,872-880
NiFeSP/NF	10	1.58	ACS Nano 2017, **11**, 10303−10312
Pt-CoS_2/CC	10	1.55	Adv. Energy Mater. 2018, **8**, 1800935
$F_{0.25}C_1CH$/NF	10	1.45	Adv. Energy Mater. 2018, 1800175
FeS_2/CoS_2 NSs	10	1.47	Small . 2018, **14**, 1801070
Co-MoS_2	10	1.45	Adv. Mater. 2018, **30**, 1801450
MoP/Ni Foam (NF)	10	1.62	Small Methods .2018, **2**, 1700369
FCCH/NF	10	1.45	Adv. Energy Mater. 2018, 1800175
Co-Mn carbonate	10	1.68	J. Am. Chem. Soc. 2017.**139**, 8320-8328.
Se-(NiCo)Sx/(OH)x	10	1.6	Adv. Mater. 2018, **30**, 1705538
Pt/Ni/Ru nanocrystal	10	1.52	Adv. Mater. 2018, 1805546
$NixCo_{3-x}S_4/Ni_3S_2$	10	1.53	Nano Energy, 2017, **35**, 161-170
FeCoNi HNTAs/NF	10	1.429	Nat.Commun.2018.**9**.2385
Ni-Mo-O nanorod/NF	10	1.38	Energy Environ. Sci., 2018, **11**, 1890-1897
Fe-Ni@NC-CNTs	145	1.98	Angew. Chem. Int. Ed. 2018, **57**, 8921-8926
$FeSe_2$	10	1.72	Angew. Chem. Int. Ed. 2017.**56**, 10506.
Co-B@CoO/TM	50	1.67	small 2017, **13**, 1700805
$Fe_{0.09}Co_{0.13}$-$NiSe_2$	10	1.52	Adv. Mater. 2018, 1802121
Fe-Doped Ni_2P	10	1.49	Adv. Funct. Mater. 2017, **27**, 1702513
FeB_2/NF	10	1.57	Adv. Energy Mater. 2017, **7**, 1700513
$Ni_{11}(HPO_3)_8(OH)_6$/NF	10	1.6	Energy Environ. Sci. 2018,**11**, 1287-1298

Ni-BCD/NF	10	1.6	Energy Environ. Sci.2018.**11**.2363
FeB_2/NF	10	1.57	Adv. Energy Mater. 2017, **7**, 1700513
N-Ni_3S_2/NF	10	1.48	Adv. Mater. 2017, **29**, 1701584.
Co-Mo-B	10	1.69	Electrochimica Acta 2017, **232**. 64-71
NiFe LDH-NS@DG_{10}	20	1.50	Adv. Mater. 2017, **29**, 1700017.
Ni@NC-800/NF	10	1.6	Adv. Mater. 2017, **29**, 1605957.
Fe-CoP	10	1.60	Adv. Mater. 2017, **29**, 1602441.
$Co_{1-x}Fe_xP$/CNT	10	1.5	Adv. Funct. Mater. 2017, **27**,1606635
Cu@NiFe LDH	10	1.54	Energy Environ. Sci. 2017, **10**,1820.
NiO/Ni-CNT	20	1.50	Nat. Commun. 2014,**5**,5695.

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