Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

Monolithic metal-free electrocatalyst for oxygen evolution reaction and overall water splitting

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Experimental Section

Materials

Hydrated nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$, 99%] was purchased from Guangzhou Chemical Reagent Factory and Hexamethylenetetramine was purchased from Tianjin Damao Chemical Reagent Factory. Hydrochloric acid (98.05%) and ethanol (99.7%) were all purchased from Guangzhou Chemical Reagent Factory and used as received without further purification. Carbon textile was purchased from Fuel Cell Earth LLC, United States.

Synthesis of the Ni-based Precursor

All reagents were of analytical grade and were directly used without any purification. Firstly, Ni-based precursor was grown on the CC. In a typical synthesis, CC were cleaned carefully by immersing it into concentrated HNO_3 for 30 min. and then washed by ultrasonication in distilled water and ethanol for several times. Next, 10 mmol $Ni(NO_3)_2 \cdot 6H_2O$ and 20 mmol Hexamethylene (HMT) was dissolved in 40 mL of deionized water and vigorously stirred for 15 min., and the clean CC (6 cm^2) was immersed into solution for another 20 min. under stirring. The solution and CC were transferred to a 50 mL Teflon-lined stainless-steel autoclave and the autoclave was heated in an electric oven with a heating speed of 5 ^{o}C min^{-1} to 120 °C. The autoclave was maintained in an oven for 10 h and then naturally cooled down to room temperature. After cooling down to room temperature, the Ni precursor/CC was washed with water, ethanol for several times and dried in 60 ^{o}C oven overnight.

Synthesis of the NiC

The Ni-based precursor prepared above was then annealed in N_2 atmosphere at 900 ^{o}C for 90 mins. The Ni-based precursor was heated with a heating speed of 10 ^{o}C min^{-1} to 900 °C (1 bar, 200 sccm). After reacting for 90 mins at 900 °C, the system was allowed to cool down to room temperature naturally still under a flowing N_2 atmosphere (1 bar, 200 sccm) and Ni NPs anchored CC sample (denoted as NiC) was obtained.

Synthesis of the NiD-PCC

The NiC sample prepared above was immersed in conc. HCl for 12 hours to remove the Ni NPs and obtain N-doped porous carbon cloth (represented as NiD-PCC).

Synthesis of the HCC

Carbon cloth (CC) were cleaned carefully by immersing it into concentrated HNO_3 for 30 min. and then washed by ultrasonication in distilled water and ethanol for several times. The BCC was then immersed in conc. HCl for 12 hours to the HCl treated CC (represented as HCC).

Synthesis of the BCC/NiO and NiD-PCC/NiO

Ni-based precursor was grown on the bare carbon cloth (BCC) or NiD-PCC. In a typical synthesis, 10 mmol $Ni(NO_3)_2 \cdot 6H_2O$ 16 mmol of urea and 20 mmol Hexamethylene (HMT) was dissolved in 40 mL of deionized water. The clean BCC or NiD-PCC was immersed into solution, transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained in an oven at 120 °C for 3 h. After reaction, the autoclave was allowed to cool down to room temperature and the Ni precursor/BCC or Ni precursor/NiD-PCC was washed with water, ethanol for several times and dried in 60 ^{o}C oven overnight. The precursor products were then annealed in air at 500 ^{o}C for 180 min to form the BCC/NiO and NiD-PCC/NiO samples.

Characterization

The morphology, structure, and composition of the electrode materials were characterized by field emission SEM (JSM-6330F) and transmission electron microscope (TEM) (JEM2010-HR, 200

KV). The element identification and heteroatom functional group distribution was measured through photoelectron spectroscopy (XPS, ESCALab250). The crystallographic information and phase purity of the products were characterized by X-ray diffraction Spectrometry (XRD; Shimadzu X-ray diffractometer 6000, Cu Kαradiation, Shimadzu, Tokyo, Japan) and Raman Spectroscopy (Renishaw inVia). The nitrogen adsorption–desorption isotherms were measured using a Micromeritics ASAP 2000 system at 77K.

Electrochemical Measurements

All the electrochemical measurements were performed in a three-electrode system on an electrochemical workstation (CHI760E) using the as-fabricated NiD-PCC or NiC or BCC or HCC as the working electrode (weight of about 8 mg cm^{-2}), Ag/AgCl (3 M KCl) electrode as the reference electrode and Pt wire as the counter electrode. The active area was simply determined by the geometric area of carbon cloth. The carbon cloth we used for electrochemical characterization was sealed with epoxy resin, leaving a square with 1.0 cm^2 in area for measuring and a small area at the other end for ohmic contact. Thereby, all data were normalized by its geometric area (1.0 cm^2). All data were collected under O_2 saturation to ensure oxygen/water (O_2/H_2O) equilibrium at 1.23 V vs. RHE. Linear sweep voltammetry (LSV) was conducted in 1 M KOH solution (pH=14) with a scan rate of 10 to 100 mV s^{-1}. The Tafel plots were obtained at the scan rate of 10 mV s^{-1}. Its slope was calculated based on the Tafel equation: $\eta = b\log j + a$, where η represents overpotential (V), j stands for current density (mA cm^{-2}), and b is Tafel slope (mV dec^{-1}). The chronopotentiometric measurements were carried out also in solution of 1.0 M KOH with vigorous stirring by a stir bar for 28 h. Electrochemical impedance spectroscopy (EIS) measurements of the various catalysts were carried out using above three electrode systems at 0.607 V vs Ag/AgCl. The frequency range was 100 K Hz to 0.1 Hz, and the amplitude of the applied voltage was 5 mV.

For the hydrogen evolution reaction measurement, the potential values used in this study were changed to E (RHE) from E (SCE) according to the formula:

$$E\ (RHE) = E\ (SCE) + 0.2412 + 0.05916 \times pH$$

Thus, LSV was also conducted in 1 M KOH solution with a scan rate of 10 mV s^{-1} between +0.2 and -0.8 V vs RHE.

For IrO_2 comparison, we prepared IrO_2 on a glassy carbon working electrode and test it under the same condition with other electrodes. About 2 mg of IrO_2 was ultrasonically dispersed in a mixture of 1 mL water and 30 μL of 0.1% Nafion. Finally, the catalyst dispersion was transferred onto the glassy carbon electrode and dried. The loading of the IrO2 catalyst is about ~0.1 mg cm^{-2}.

Overall Water-Splitting Measurement

The NiD-PCC was employed as anode and the NiC was employed as cathode. LSV was also conducted in 1 M KOH solution with a scan rate of 10 mV s^{-1} between 0.0 and 2.0 V.

The bottle was open to the air during the testing to release the produced H_2 and O_2. The chronopotentiometric measurements were carried out also in solution of 1.0 M KOH with vigorous stirring by a stir bar for 16 h.

Supplementary Figures

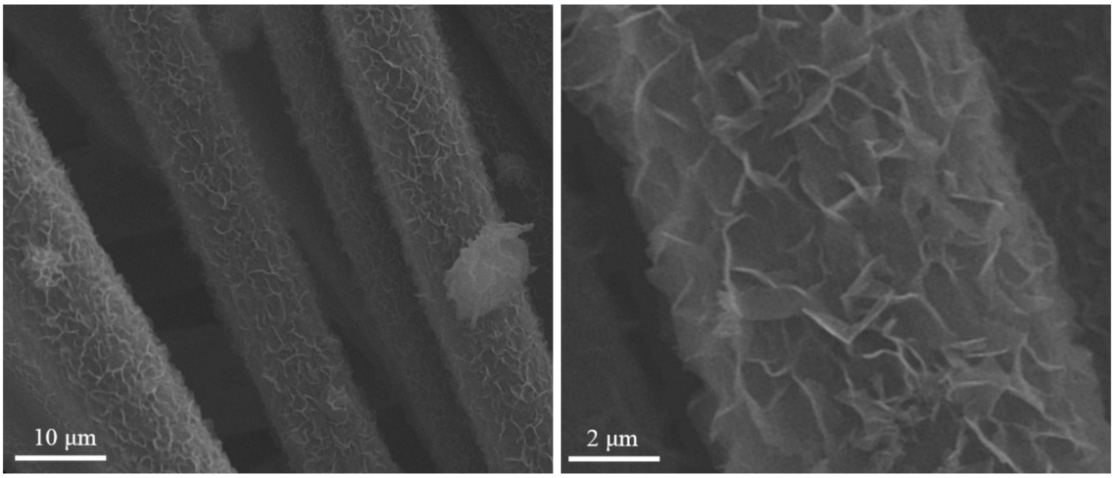

Figure S1. SEM images of the Ni-based nanosheets precursor.

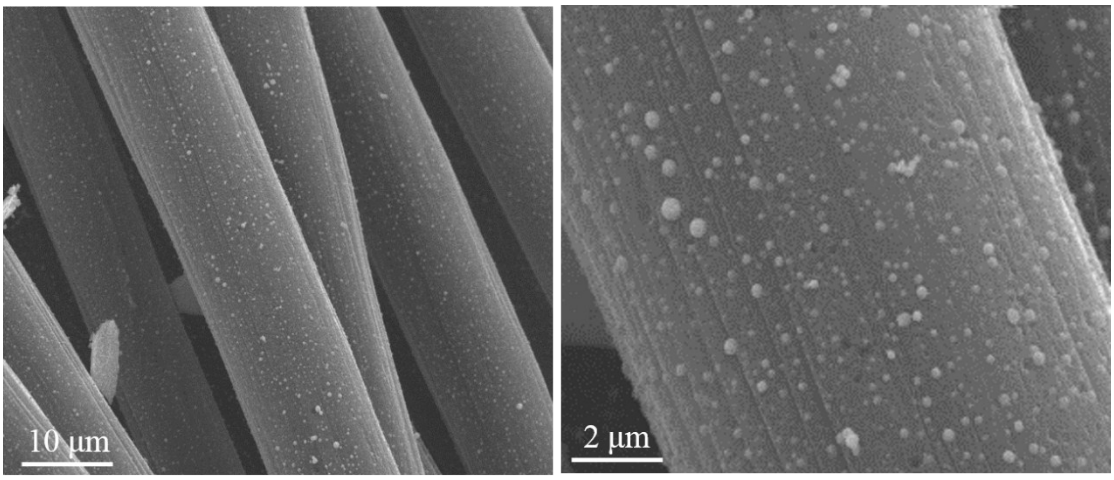

Figure S2. SEM images of the Ni NPs embedded on the carbon cloth (NiC) sample.

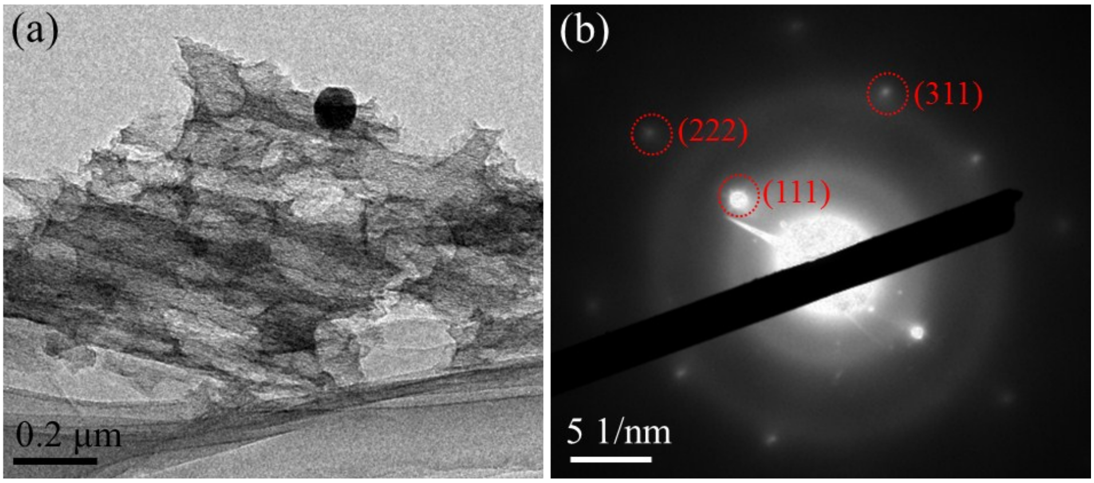

Figure S3. (a) TEM image of the NiC showing the Nickel NP anchored on the carbon cloth. (b) SAED pattern collected at the edge of the Ni NP and the carbon cloth from the NiC TEM in a).

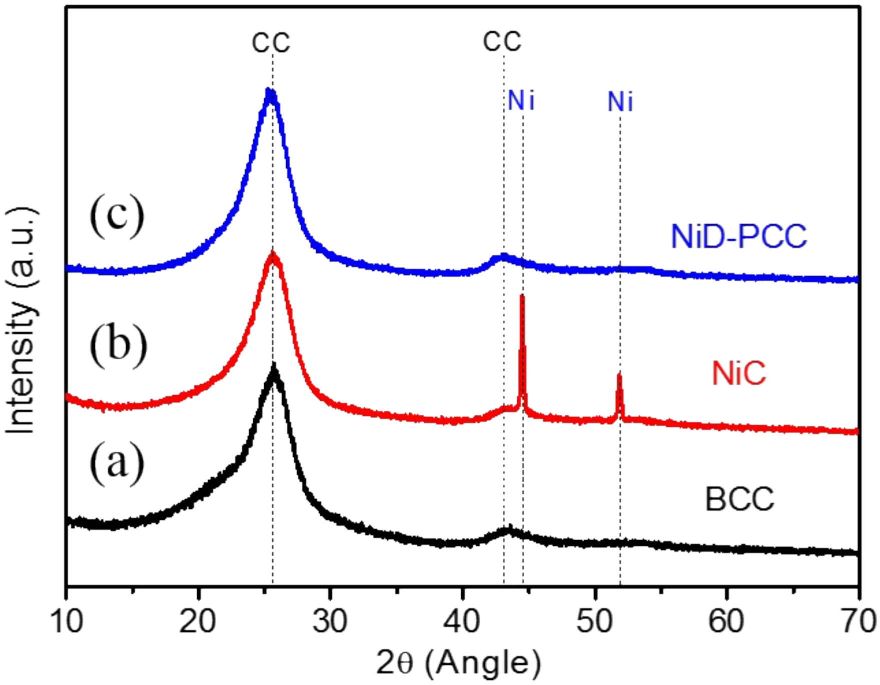

Figure S4. XRD pattern of the a) BCC, b) NiC and c) NiD-PCC.

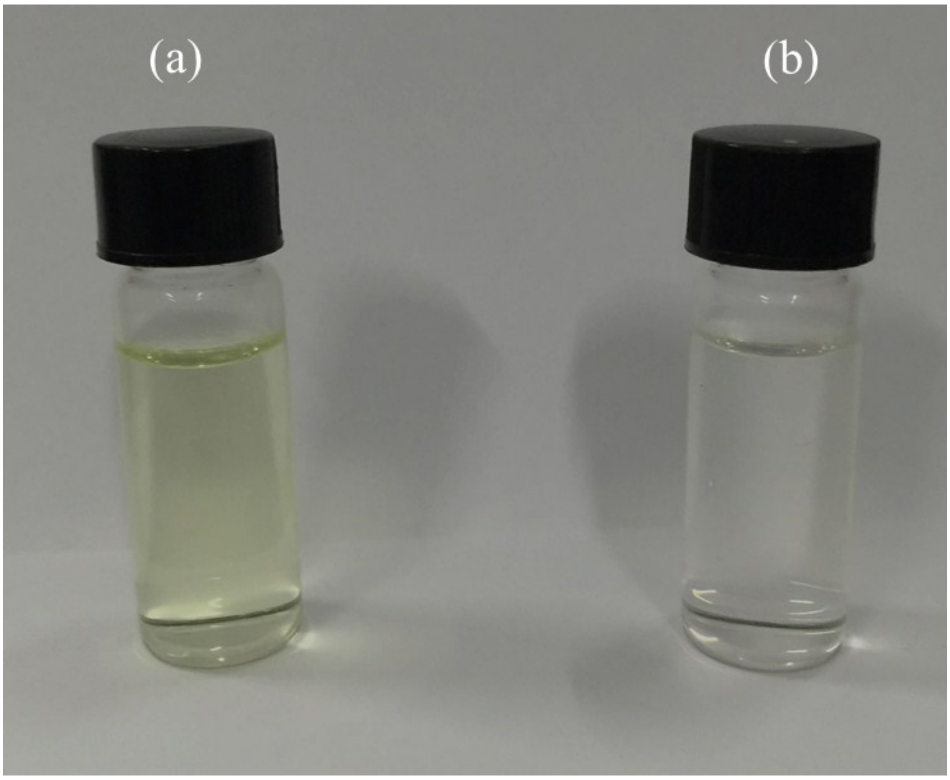

Figure S5. Digital images of the a) dissolved NiC in conc. HCl overnight and b) dissolved NiD in conc. HCl overnight. After the dissolution of the NiC in conc. HCl overnight, the conc. HCl solution becomes greenish yellow indicating that Ni has been dissolved and NiD-PCC was formed as shown in

Figure S7a. To further confirm that the NiD-PCC is Ni-free, the NiD-PCC formed was further immersed into conc. HCl overnight and Figure S7a shows that the solution are very clear suggesting that the as-prepared NiD-PCC are metal free.

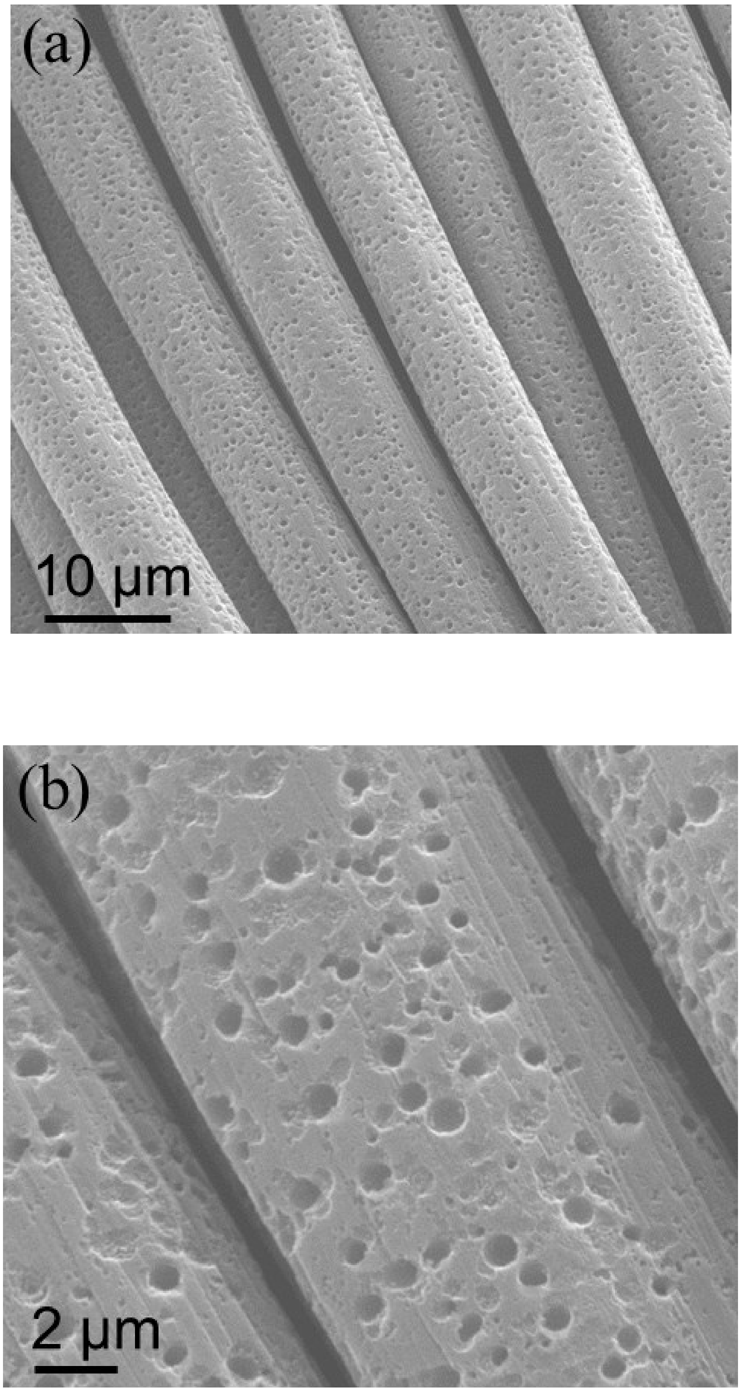

Figure S6. Enlarged SEM images of the NiD-PCC sample. (a) Low magnification from Figure 1c and (b) high magnification from Figure 1d.

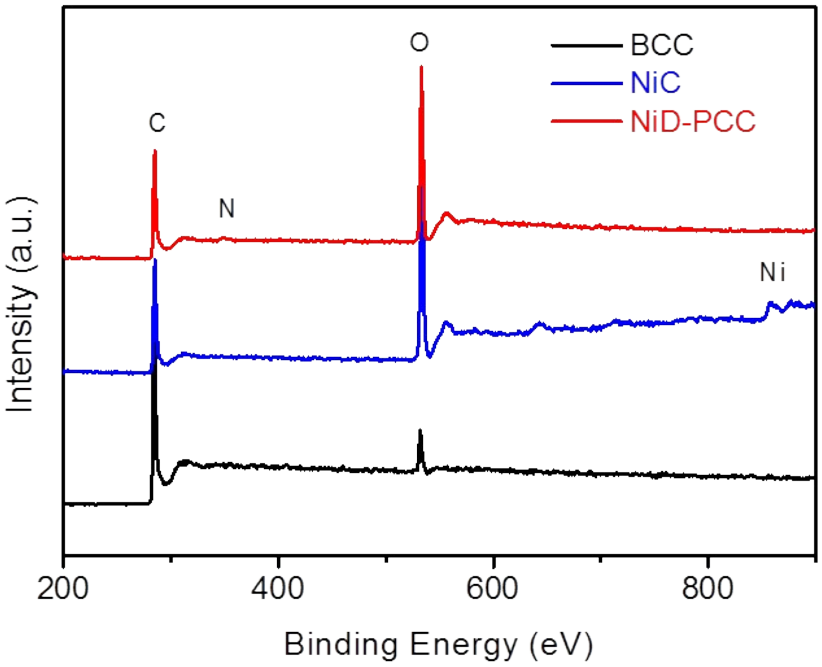

Figure S7. XPS spectra of all the samples.

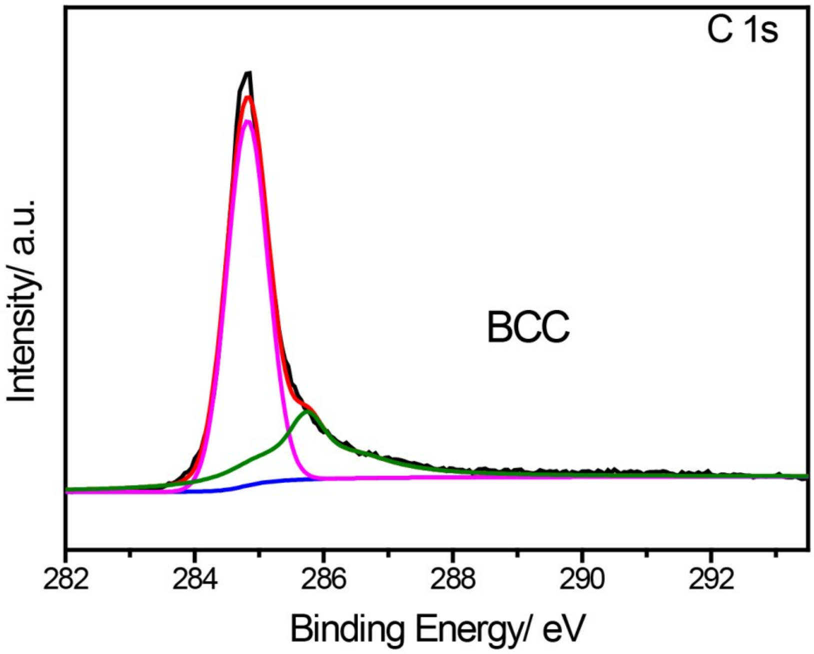

Figure S8. C 1s XPS spectra of the BCC sample.

Table S1. Elemental composition (atomic percentage) obtained from XPS analysis.

Samples	C (atomic %)	O (atomic %)	Ni (atomic %)	N (atomic %)
BCC	87.17	12.83	0.00	0.00
NiC	84.02	13.14	2.74	0.1
NiD-PCC	90.53	7.55	0	1.92

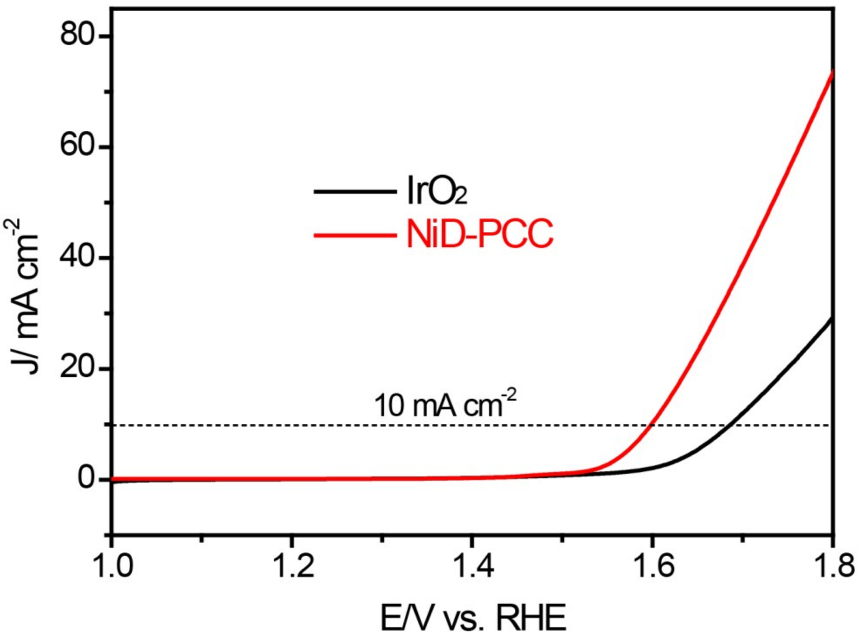

Figure S9. LSV plots recorded of the NiD-PCC and the noble metal benchmark electrode IrO$_2$. The onset overpotential of the NiD-PCC (250 mV) is lower than that of the noble metal catalyst (IrO$_2$, 300 mV). Also, the NiD-PCC delivers the current of 10.0 mA cm^{-2} at a relatively low overpotential of 360 mV when compared to the IrO$_2$ at 450 mV.

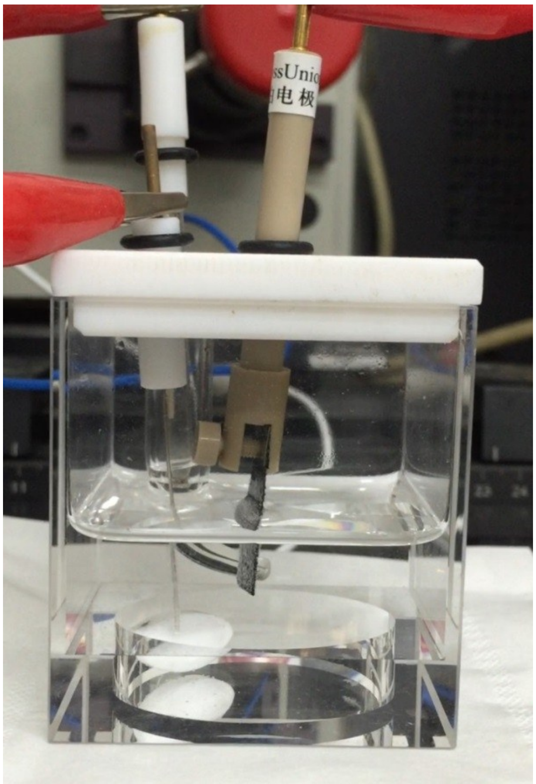

Figure SV1. Digital video displaying the evolution of O$_2$ from the 3D NiD-PCC anode, respectively.

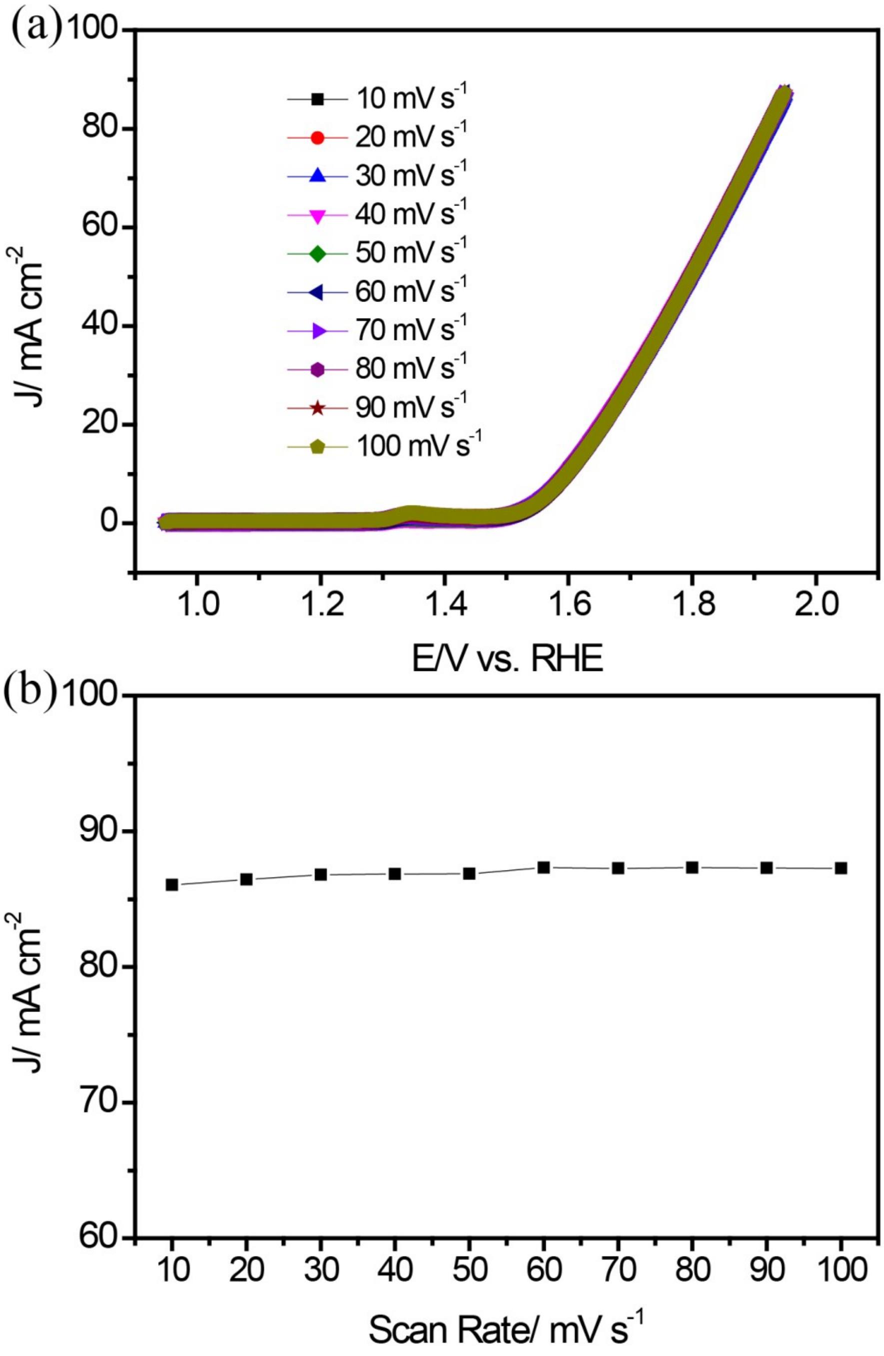

Figure S10. (a) LSV plots recorded at different scan rates. (b) Corresponding data re-plotted as the current density (at 1.0 V vs. Ag/AgCl) vs. scan rates.

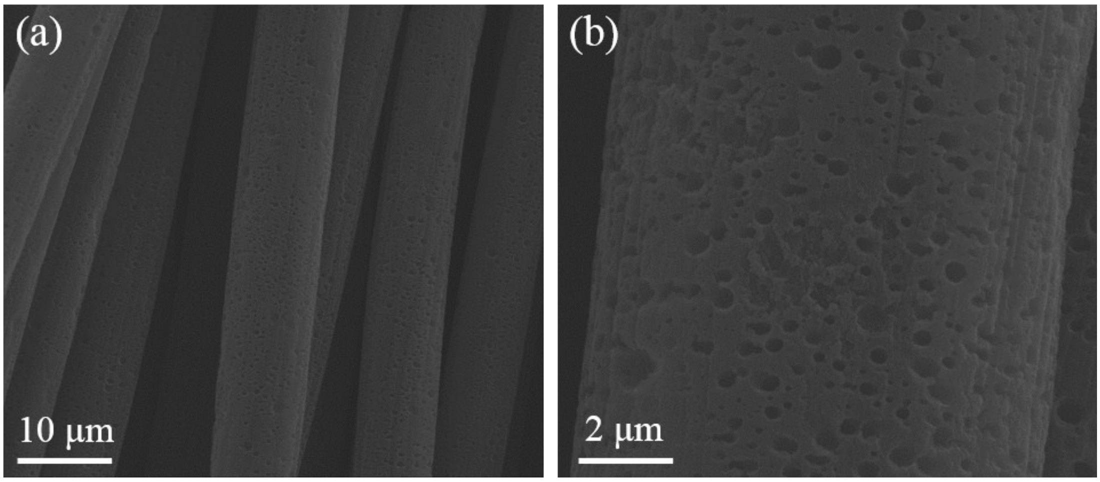

Figure S11. SEM images of the NiD-PCC electrocatalyst after 28 h durability test.

Table S2. Summary of the various metal-free and self-supported-based and some carbon-based electrocatalysts for OER.

Catalyst	Onset η (mV)	η *at* 10 mA cm^{-2}	Overall Current (mA cm^{-2}) at 1.85 V	Tafel Slope (mV dec^{-1})	Ref
NiD-PCC **This work**	**250**	**360**	**91**	**98**	
NiC **This work**	**250**	**420**	**34**	**155**	
N,O-dual doped graphene-CNT	315	368 at 5 mA cm^{-2}	~15	141	[1]
MOF-CNT Frameworks	240	370	~62 at 1.7 V	93	[2]
Nickel NPs- N-doped graphene film	320	~400	~75	188.6	[3]
N-doped Carbon Materials	290	380	~55	-	[4]
g-C_3N_4/graphene	314	539	~40	68	[5]
Graphene-C_3N_4	387	414.5	~80	128	[6]
OCC-8	328	477	~25	82	[7]
g-C_3N_4–CNT NSs	300	370	~47 at 1.7 V	83	[8]
N-doped G/single-walled CNT hybrids	290	400	~20 at 1.8 V	83	[9]
3D Ni/porous carbon/Ni (NF/PC/AN)	-	400 at 5 mA cm^{-2}	~15	-	[10]

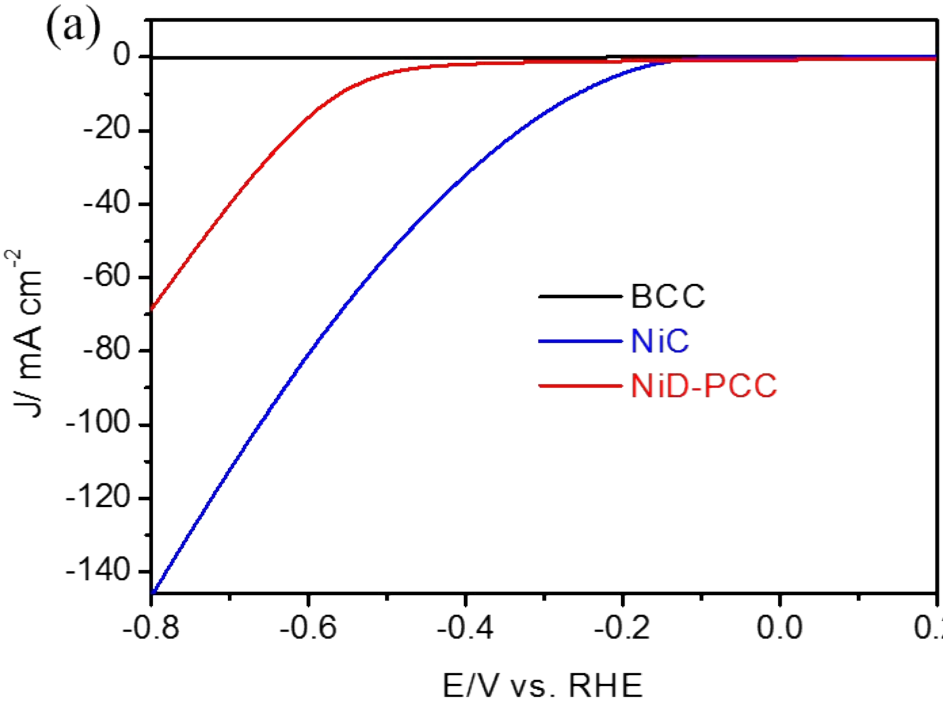

Figure S12. HER activities of the BCC, NiC and NiD-PCC electrocatalysts in 1 M KOH at a scan rate of 10 mv s^{-1}.

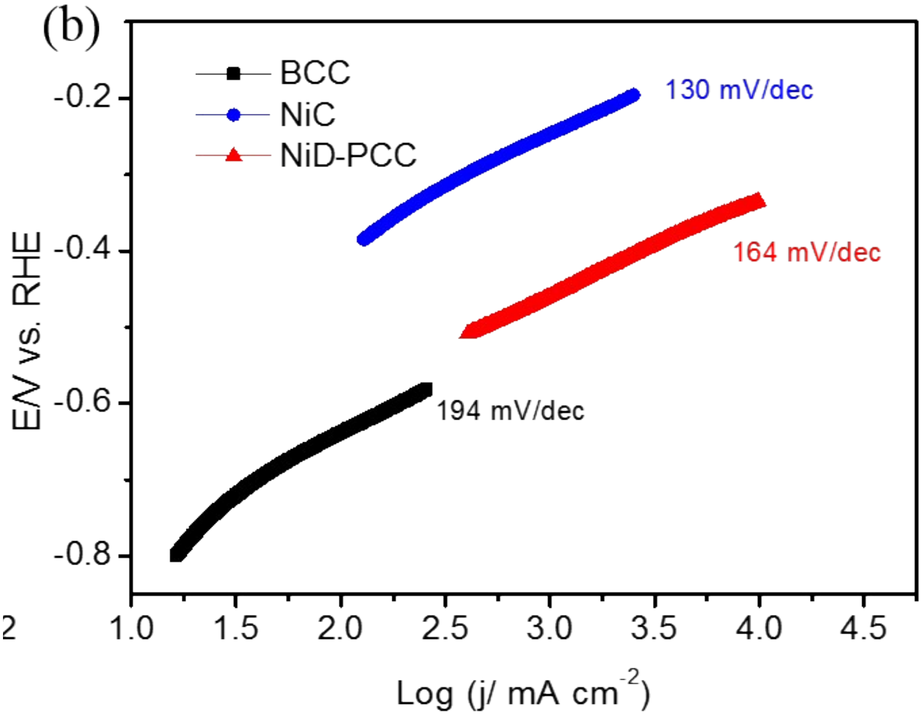

Figure S13. Tafel plots of the BCC, NiC and NiD-PCC electrocatalysts.

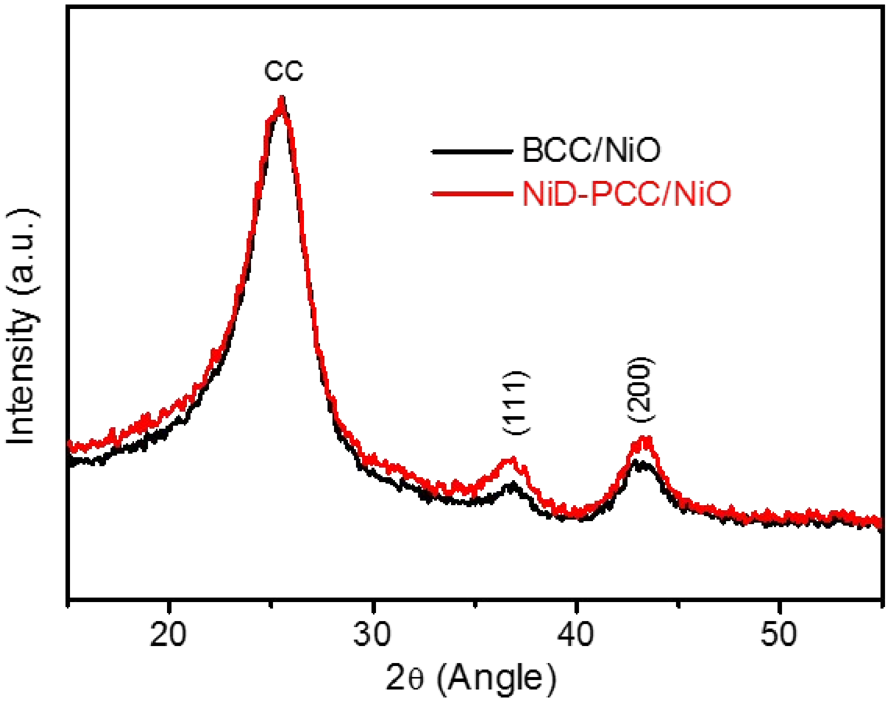

Figure S14. XRD spectra of the BCC/NiO and NiD-PCC/NiO electrocatalysts.

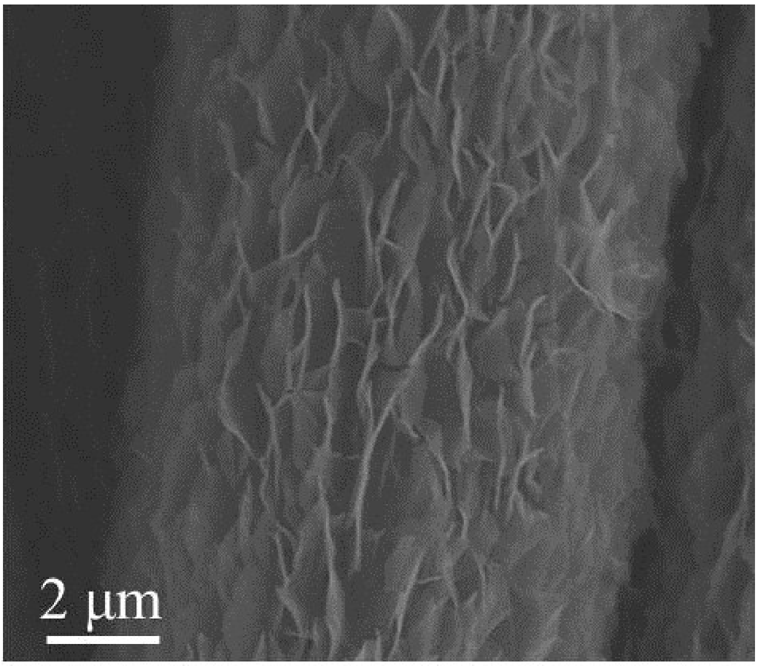

Figure S15. SEM images of the BCC/NiO electrocatalysts.

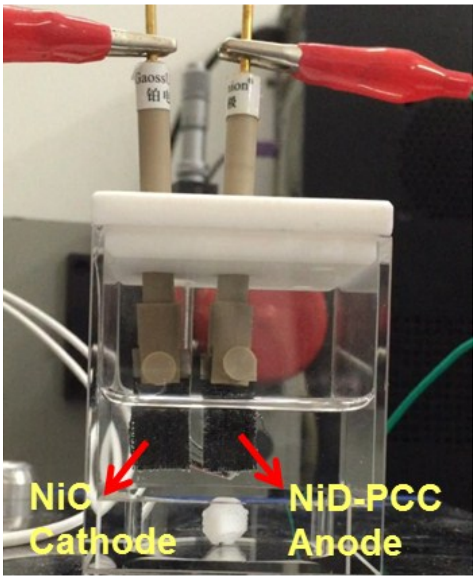

Figure SV2. Digital video displaying the evolution of H_2 and O_2 from the NiC cathode and NiD-PCC anode, respectively.

References

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