Supporting Information

Experimental

Preparation of C-NiPAN900 and C-NiPAN900-300:

The hybrid C-NiPAN900-300 was produced by electrospining combined with subsequent heat treatments. The electropinning was performed with a similar process reported elsewhere. Typically, polymer precursor of DMF solution of mixture polyacrylonitrile and nickel acetate salt (weight ratio of 1/1) was loaded into a syringe mounted with a 22–gauge blunt needle tip. With the follow rate of the polymer precursor controlled by a syringe pump, a positive voltage of 12-19 V was applied between the syringe needle and a grounded Al foil separated by about 15-20 cm. Polymer fiber composite of polyacrylonitrile and nickel acetate (denoted as 11NiPAN) were then collected on the Al foil. The obtained 11NiPAN was carbonized in a tube furnace at 900 °C for 30 min under nitrogen protection with a ramping rate of 10 °C min⁻¹, after which the 11NiPAN was converted to nickel nanoparticles decorated carbon nanofiber and denoted as C-NiPAN900. Subsequently, the C-NiPAN900 was annealed in air at a relative low temperature of 300 °C for 2h, this process enable the majority of nickel nanoparticles decorated on the CNF to be oxided to form nickel/nickel oxides decorated CNF to improve the OER catalytic activity of the composite fiber. Thus produced final product is demoted as C-NiPAN900-300.

Material characterization

The morphological information of the electrospun fiber materials were obtained using a JMF 6700F scanning electron microscope (SEM) and a Philips CM300 transmission electron microscope (TEM). X– ray photoelectron spectroscopy (XPS) data was collected with a Theta Probe electron spectrometer (VG ESCALAB200i–XL, Thermo Scientific). The binding energies were calibrated using C 1s peak at 284.5 eV. X-ray diffraction (XRD) analyses were conducted with a Bruker D2 Phaser using a Cu K_a radiation source.

Electrochemical measurements

Electrochemical measurements including cyclic voltammetry (CV), linear sweep voltammetry (LSV), accelerated degredation test (ADT) were carried out on an Autolab potentiostat/galvanostat (PGSTAT302N) station combined with a rotating disk electrode (RDE). Pt foil, gassy carbon (GC) loaded with catalyst, and Ag/AgCl electrode (saturated with 3 M KCl) were employed as the counter, working and reference electrodes, respectively. And 0.1 M KOH was used as electrolyte unless other stated. The current density was normalized to the geometrical area of the electrode. The potential with respect to the reversible hydrogen electrode (RHE) was converted as follows: $E_{(RHE)} = E_{(Ag/AgCl)} + 0.059 \text{ pH} + 0.197$. Where $E_{(RHE)}$ is the converted potential vs. RHE, $E_{(Ag/AgCl)}$ is the measured potential against the reference electrode of Ag/AgCl. The overpotential was calculated according to the equation of $\eta = E_{(RHE)} - 1.23 \text{ V}$.

Zinc-air battery (ZnAB) assembly and tests

ZnABs were assembled according to our previous report using home-built Zn-air cells. The battery performances were evaluated by galvanostatic method at room temperature under ambient open air conditions. 6 M KOH aqueous solution containing 0.2 M ZnCl₂ was used as the electrolyte and polished zinc plates were used as the anode. The air cathodes using a hybrid material of C-NiPAN900-300 and commercial Pt/C or Ir/C as catalyst were prepared by following a previously reported method.¹ Briefly, 50 mg of catalyst and 100 μ L of 5 wt.% Nafion solution were dispersed in ethanol to form a catalyst ink solution. And then desired amount of the catalyst ink was drop-cast onto a carbon paper with pre-defined area by firmly covered Parafilm®. With descripted method, the catalyst loading is well controlled at ~1.0 mg cm⁻² for all the air cathodes.



Fig. S1. TEM images of C-NiPAN900-300. A) A typical individual C-NiPAN900-300 fiber showing many small NPs (~20 nm) are decorated on the fiber. B) High resolution TEM image of an individual NP, the lattice spacing (2.12 Å) clearly indicated is assignable to the (200) plane of NiO.



Fig. S2. XRD patterns for C-NiPAN900 and C-NiPAN900-300.



Fig. S3. SEM images of C-NiPAN900-300 before (A and B) and after (C and D) a chronoamperometric (*i-t*) test. The *i-t* test was performed for ~ 2 h on C-NiPAN900-300/GC electrode in 1M KOH. After the testing, the GC tip was gently rinsed with ethanol and dried by gentle N₂ flow, and then the C-NiPAN900-300 was transfer to a copper tape by gentle contacting for further SEM characterization.



Fig. S4. LSV curves of the C-NiPAN900-300/carbon cloth electrode (red) and the blank carbon cloth (black); inset: the current response of blank carbon cloth in much smaller current density scale. (B) i-t profiles of C-NiPAN900-300/carbon cloth electrode (red) and the blank carbon cloth (black) at fixed potential of 0.65 V (vs. Ag/AgCl) in 1M KOH. The significantly higher current density for C-NiPAN900-300/carbon cloth electrode as compared to its counterpart electrode of blank carbon cloth confirms the high OER activity of C-NiPAN900-300.



Fig. S5. A) LSV curves of the C-NiPAN900-300 at initial cycle and 500th cycle of ADT. B) and C) LSV curves of C-NiPAN900 for ADT of OER at different cycles. As compared to the initial cycle, one can see a gradually improvement of OER activity of C-NiPAN900 upon ADT. D) A comparison of C-NiPAN900 of after the ADT for 100 cycles and the C-NiPAN900-300, illustrating the similar OER catalytic activities of the two samples. Above measurements were done under a scan rate of 20 mV s⁻¹.



Fig. S6. CV curves of C-NiPAN900-300 in O₂- (red) and N₂- saturated (blue) 0.1 M KOH solution.



Fig. S7. Charge and discharge polarization curves of the Zn-air battery using C-NiPAN900-300 (blue) compared with the one using Ir/C (black) and Pt/C (red), respectively.

Catalyst	Electrolyte	[#] Potential (V vs. RHE) at 10 mA cm ⁻²	η (mV) at 10 mA cm ⁻²	Tafel slope (mv/dec)	Reference
C-NiPAN900-300	0.1 M KOH	1.662	432	123	this work
Ir/C	0.1 M KOH	1.628	398	121	this work
Ni/N-Graphene	0.1 M KOH	1.66 (at 15mA cm ⁻²)		188.6	Energy Environ Sci., 2013, 6 , 3693
NiCo ₂ S ₄ /Graphene	0.1 M KOH	1.7			ACS Appl. Mater. Interfaces, 2013, 5 , 5002
NiCo ₂ O ₄ /Graphene	0.1 M KOH	~ 1.69 1.96 (35.4mA cm ⁻²)		161	J. Mater. Chem. A, 2013, 1, 4754
NiCo ₂ O ₄ /Graphene (no PVP)	0.1 M KOH	~1.78 1.96 (21.4mA cm ⁻²)		799	J. Mater. Chem. A, 2013, 1, 4754
NiCo ₂ O ₄ (Graphene free)	0.1 M KOH	~1.82 1.96 (18.6mA cm ⁻²)		205	J. Mater. Chem. A, 2013, 1, 4754
Ni@NC	0.1 M KOH	1.62	390	40	<i>Adv. Energy Mater.</i> 2015, 5 , 1401660
Ni@C		1.65	420	44	<i>Adv. Energy Mater.</i> 2015, 5 , 1401660
Ni(OH) ₂	0.1 M KOH		595	165	J. Mater. Chem. A, 2014, 2 , 11799
MWCNTs+Ni(OH) ₂	0.1 M KOH		540	140	J. Mater. Chem. A, 2014, 2 , 11799
MWCNTs/Ni(OH) ₂	0.1 M KOH		474	87	J. Mater. Chem. A, 2014, 2 , 11799
PNG-NiCo	0.1 M KOH	1.603 (5mA cm ⁻²) 1.664 (16.5mA cm ⁻²)	373 (5mA cm ⁻²) 434(16.5mA cm ⁻ ²)	156	ACS Nano, 2013, 7, 10190
NG-NiCo	0.1 M KOH			249	ACS Nano, 2013, 7, 10190
PG-NiCo	0.1 M KOH			254	ACS Nano, 2013, 7, 10190
NA-Co ₉ S ₈ /G	0.1 M KOH		433	83	Energy Environ. Sci. 2016, 9 , 1320
Co ₉ S ₈	0.1 M KOH		602	307.2	Energy Environ. Sci. 2016, 9 , 1320
C0 ₉ S ₈ /G	0.1 M KOH		441	93.9	Energy Environ. Sci. 2016, 9 , 1320
N - C0 ₉ S ₈	0.1 M KOH		548	241	Energy Environ. Sci. 2016, 9 , 1320
N- C0 ₉ S ₈ /G	0.1 M KOH		409	82.7	Energy Environ. Sci. 2016, 9 , 1320
RuO ₂ /C	0.1 M KOH		380	157.5	Energy Environ. Sci. 2016, 9 , 1320
IrO ₂ /C	0.1 M KOH	1.54	310	97	J Am. Chem. Soc., 2014, 136 , 13925

Table S1. Comparison of OER performances of C-NiPAN900-300 to the catalysts reported recently in 0.1M KOH.

C0 ₃ O ₄ /C-NA	0.1 M KOH	1.52	290	70	J Am. Chem. Soc., 2014, 136 , 13925
Pt/C	0.1 M KOH		580		<i>Adv. Energy Mater.</i> 2015, 5 , 1401660
IrO ₂	0.1 M KOH		350	55	<i>Adv. Energy Mater.</i> 2015, 5 , 1401660
Pt/C	0.1 M KOH	1.78	550	338	ACS Appl. Mater. Interfaces, 2015, 7, 11991
IrO ₂ /C	0.1 M KOH	1.6	370		Nat. Commun., 2013, 4 , 2390

#10 mA cm⁻² is roughly the current density of a solar-to-fuel device with 10% of solar efficiency.

Table S2. Comparison of OER overpotential of C-NiPAN900-300/Ni foam to the catalysts reported recently in 1M KOH or 1M NaOH.

Catalyst	Electrolyte	η (mV) at 10 mA cm ⁻²	Reference
C-NiPAN900-300 on Ni foam	1 M KOH	277	this work
Amorphous Fe-Ni-O	1 M KOH	286	Angew. Chem., Int. Ed. 2014, 53, 7547
Ni ₃ N nanosheets grown on carbon cloth	1 M KOH	256	J Am. Chem. Soc. 2015, 137 , 4119
NiFe-LDH/CNT on Carbon fiber paper	1 M KOH	247	J. Am. Chem. Soc. 2013, 135, 8452
NiFe-LDH nanosheets	1 M KOH	302	Nat. Commun. 2014, 5, 4477
NiFe-LDH nanosheets	1 M KOH	334	J. Am. Chem. Soc. 2014, 136 , 16481
NiP	1 M KOH	300	Energy Environ. Sci. 2016, 9, 1246
Ni(OH) ₂	1 M KOH	360	Energy Environ. Sci. 2016, 9, 1246
NiO	1 M KOH	430	Energy Environ. Sci. 2016, 9, 1246
IrO ₂ /C on Cu foil	1 M KOH	250	J. Am. Chem. Soc. 2014, 136 , 13925
Co ₃ O ₄ /N-doped-graphene	1 M KOH	310	Nat. Mater. 2011, 10, 780
Amorphous Ni-Co binary oxides nanoporous layers	1 M NaOH	325	ACS Nano, 2014, 8, 9518
IrO _x	1 M NaOH	320	J. Am. Chem. Soc. 2013, 135, 16977
Ir	1 M NaOH	390 ± 10	J. Am. Chem. Soc. 2015, 137, 4347
Ru-(a)	1 M NaOH	290 ± 30	J. Am. Chem. Soc. 2015, 137, 4347
Ru-(b)	1 M NaOH	340 ± 30	J. Am. Chem. Soc. 2015, 137, 4347
NiCe	1 M NaOH	450 ± 30	J. Am. Chem. Soc. 2015, 137, 4347
NiCo-(b)	1 M NaOH	420 ± 20	J. Am. Chem. Soc. 2015, 137, 4347
NiCo-(c)	1 M NaOH	380 ± 10	J. Am. Chem. Soc. 2015, 137, 4347
NiCr	1 M NaOH	390 ± 20	J. Am. Chem. Soc. 2015, 137, 4347
NiFe-(b)	1 M NaOH	340 ± 20	J. Am. Chem. Soc. 2015, 137, 4347
NiFe-(c)	1 M NaOH	380 ± 10	J. Am. Chem. Soc. 2015, 137, 4347
NiMoFe-(b)	1 M NaOH	340 ± 20	J. Am. Chem. Soc. 2015, 137, 4347

Reference:

1. B. Li, X. Ge, F. W. T. Goh, T. S. A. Hor, D. Geng, G. Du, Z. Liu, J. Zhang, X. Liu and Y. Zong, Nanoscale, 2015, 7, 1830-1838.