## Supporting Information

## **Electrospun Cobalt Embedded in Porous Nitrogen Doped Carbon Nanofibers as an Efficient Catalyst for Water Splitting**

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Figure S1. Low and high magnification SEM images of nitrogen doped CNFs (NCNFs).



**Figure S2**. SEM image of Co-NCNFs (before acid treatment), showing the cobalt nanoparticles on the surface of CNFs.



**Figure S3**. SEM image and EDS elemental mappings of Co-PNCNFs. (a) SEM image of Co-PNCNFs. (b) Element distribution of O. (c) Mixed EDS mapping of all elements.



**Figure S4**. SEM image and EDS elemental mappings of NCNFs, (a) SEM image of NCNFs. (b) EDS profile. (c) Mixed EDS mapping of C, N, O. Individual mapping of elements (d) C, (e) N, and (f) O.



Figure S5. Thermogravimetric analysis of Co-PNCNFs in air.



Figure S6. (a) XPS spectrum of pure NCNFs. (b) High resolution XPS spectrum of N 1s.



Figure S7. Nitrogen sorption isotherm of NCNFs



**Figure S8.** Cyclic voltammograms (CV) of (a) Co-PNCNFs, and (b) NCNFs, both in 1 M KOH solution in a potential window without faradaic processes. (c) Scan rate dependence of the average capacitive current densities at open circuit potential for Co-PNCNFs and NCNFs.



**Figure S9.** (a) The chronoamperometric stability test of Co-PNCNFs at the fixed potentials (1.52 V *vs.* RHE) in alkaline solution for 60 h. (b) SEM image of Co-PNCNFs after stability test (60 h), displaying the carbon matrix and porous structure were maintained. (c) XRD spectra of Co-PNCNFs before and after stability test, showing the cobalt still exists as metallic state after the stability test.



Figure S10. Thermogravimetric analysis of Co-, Ni- and Fe-PNCNFs in air.



**Figure S11.** Catalytic activities of (a) Co-PNCNFs, Ni-PNCNFs, Fe-PNCNFs and pure NCNFs, and (b) Co-PNCNFs, Co-PCNFs and NCNFs. All these catalytic activity of CNFs based materials towards OER were tested in 1 M KOH solution, showing the electrocatalytic improvements promoted by metal or N functionalization.



**Figure S12** Cyclic voltammograms (CV) of (a) Co-PNCNFs, (b) Ni-PNCNFs, and (c) Fe-PNCNFs, in 1 M KOH solution in a potential window without faradaic processes. (d) Scan rate dependence of the average capacitive current densities at center potential (1.13 V *vs*. RHE) for Co-, Ni- and Fe-PNCNFs.



**Figure S13.** Polarization curves of initial and 1000th cycles towards hydrogen evolution in 1 M KOH solution, showing excellent electrocatalytic stability towards HER.



**Figure S14.** Electrochemical performance test of Co-PNCNFs deposited on nickel foam towards (a) OER and (b) HER in 1 M KOH solution.

Materials	Potential for 10 mA cm <sup>-2</sup>	Reference
Co-PNCNFs	1.66 V	This work
EG/Co <sub>0.85</sub> Se/NiFe-LDH	1.67 V	Energy Environ. Sci., 2016, 9, 478-483
NiCo <sub>2</sub> O <sub>4</sub> hollow		
microcuboids	1.65V	Angew. Chem. Int. Ed. 2016, 55, 6290-6294
CP/CTs/Co-S	1.743 V	ACS Nano 2016, 10, 2342–2348
NiS/Ni foam	1.64 V	Chem. Commun., 2016, 521,486-1489
Ni/Ni <sub>8</sub> P <sub>3</sub>	1.61 V	Adv. Funct. Mater. 2016, 26, 3314–3323
PNC/Co	1.64 V	J. Mater. Chem. A, 2016, 4, 3204-3209
Co-P/NC	~1.71 V	Chem. Mater., 2015, 27, 7636–7642
ONPPGC/OCC	1.66 V	Energy Environ. Sci., 2016, 9, 1210-1214.

## Table S1 The comparison of the catalysts for overall water splitting