Supporting Information

Thin MoS_2 nanosheets grafted MOFs derived porous Co-N-C flakes grown on electrospun carbon nanofibers as self-supported bifunctional catalysts for overall water splitting

Dongxiao Ji, Shengjie Peng, Li Fan, Linlin Li, Xiaohong Qin,* and Seeram Ramakrishna**

* Email: seeram@nus.edu.sg; seeram@nus.edu.sg; mpepeng@nus.edu.sg

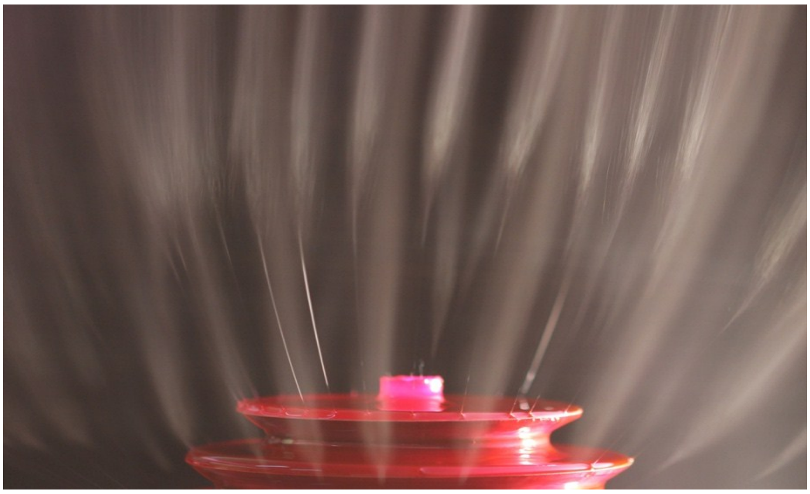

Fig. S1 Mass production of PAN nanofiber through Free-surface electrospinning

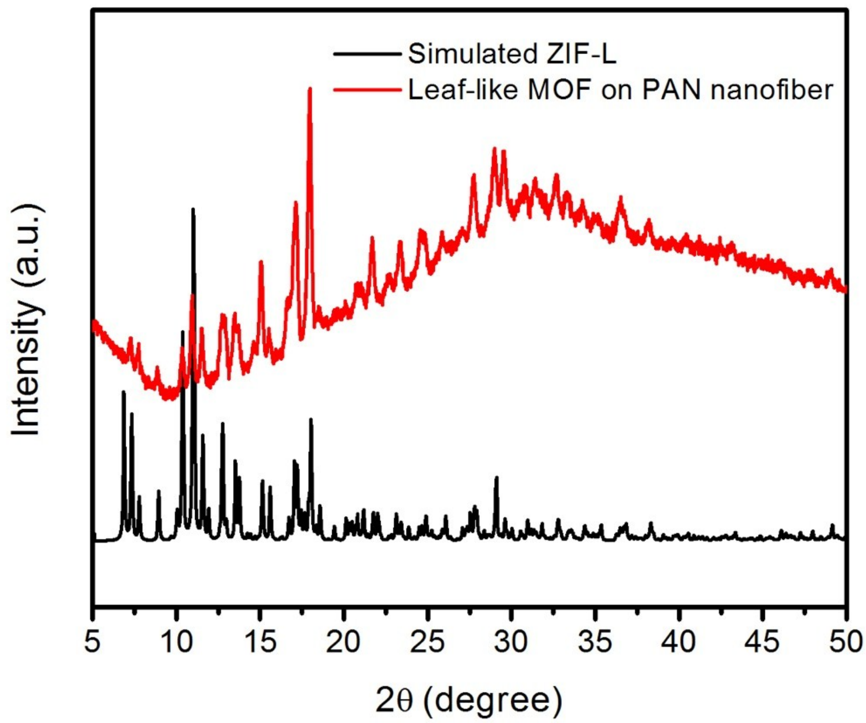

Fig. S2 XRD pattern of as-prepared ZIF-L grown on PAN nanofiber.

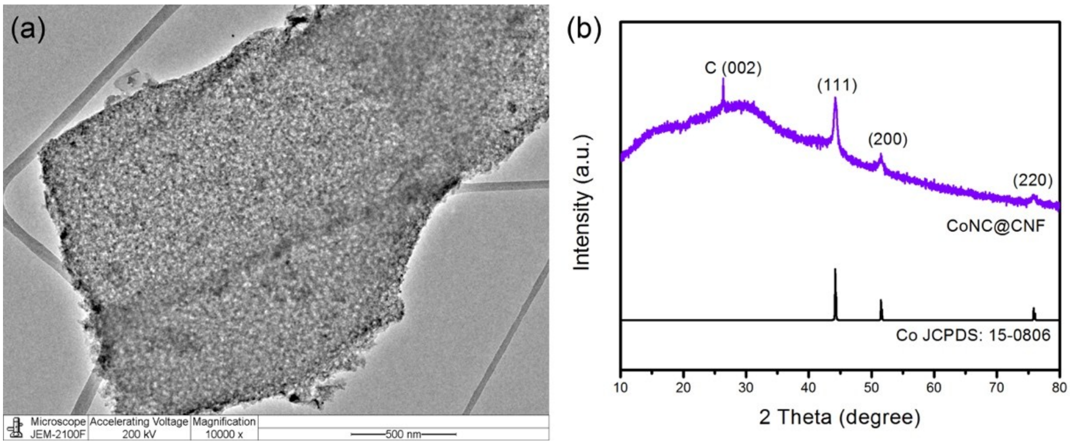

Fig. S3 a) TEM image of CoNC/CNF carbonized in N_2 at 800 °C. b) the corresponding XRD pattern of CoNC/CNF-800.

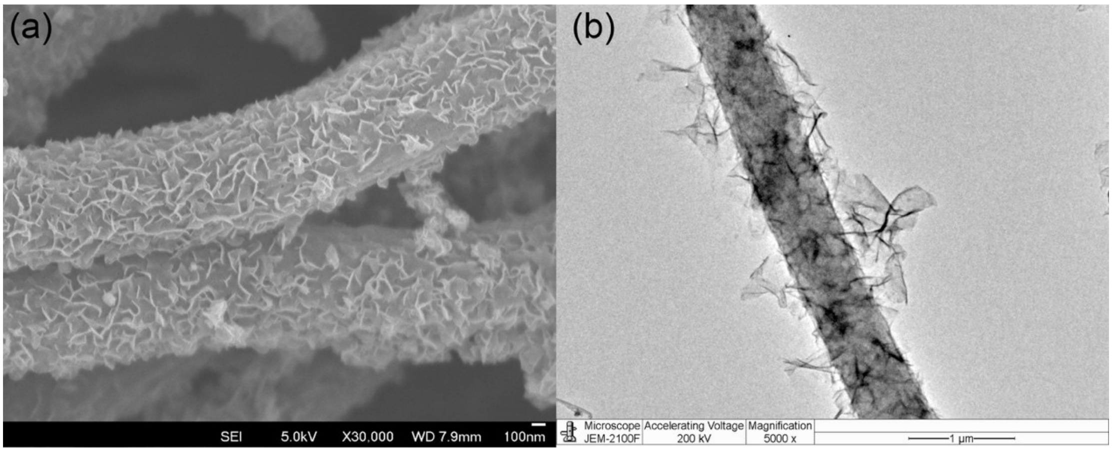

Fig. S4 a) SEM and b) TEM images of as-prepared MoS_2/CNF.

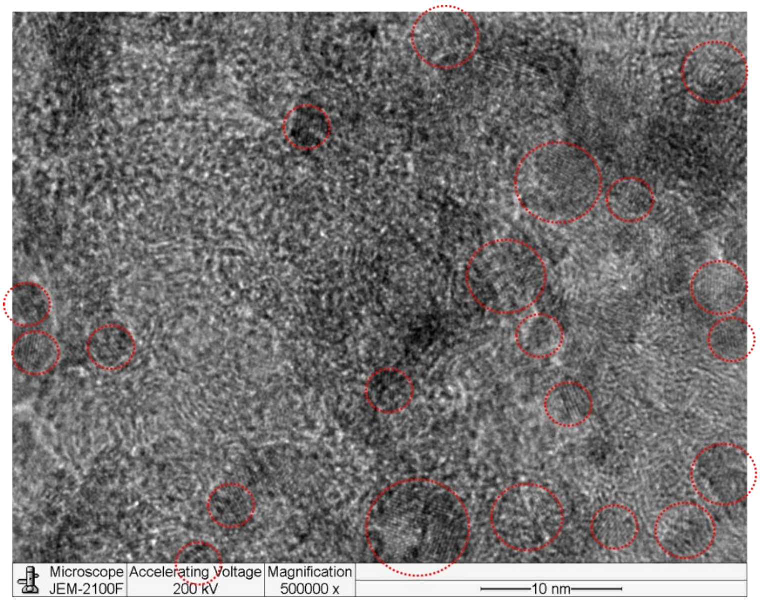

Fig. S5 TEM showing Co particle size and morphology

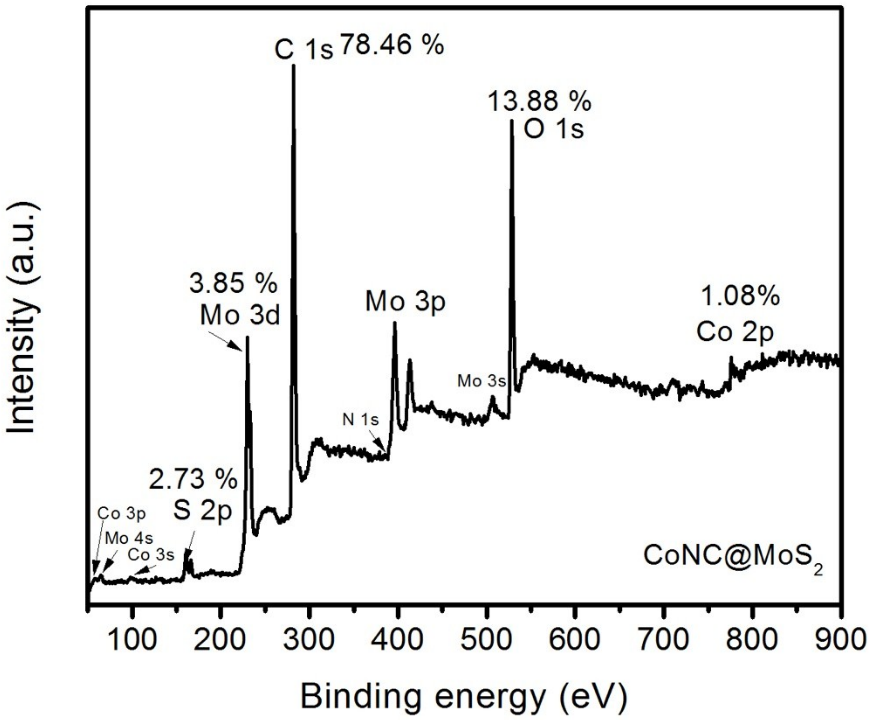

Fig. S6 Data survey spectra of CoNC@MoS_2/CNF film.

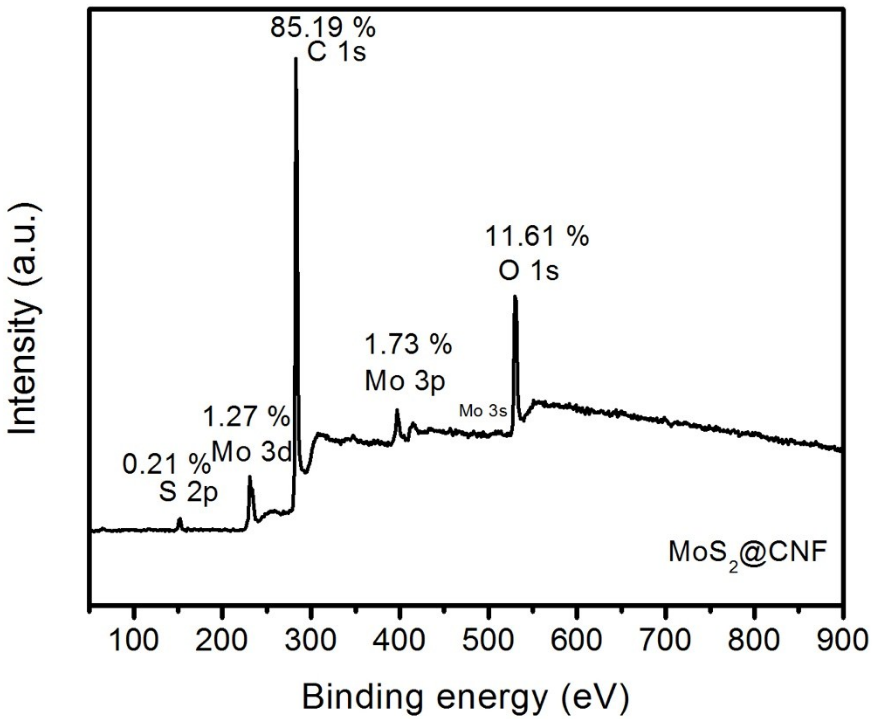

Fig. S7 Data survey spectra of MoS_2/CNF film.

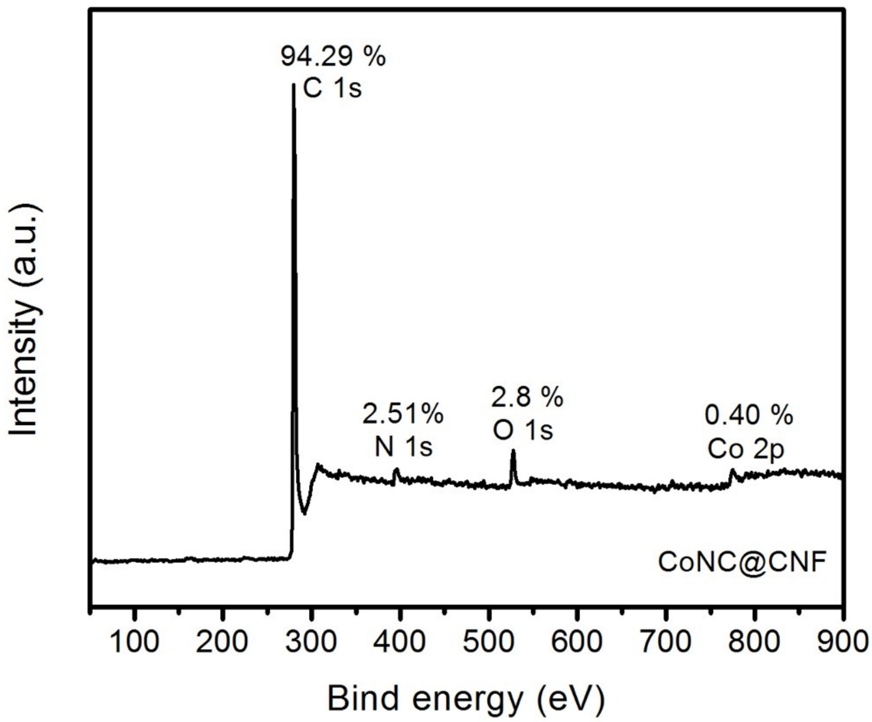

Fig. S8 Data survey spectra of CoNC/CNF film.

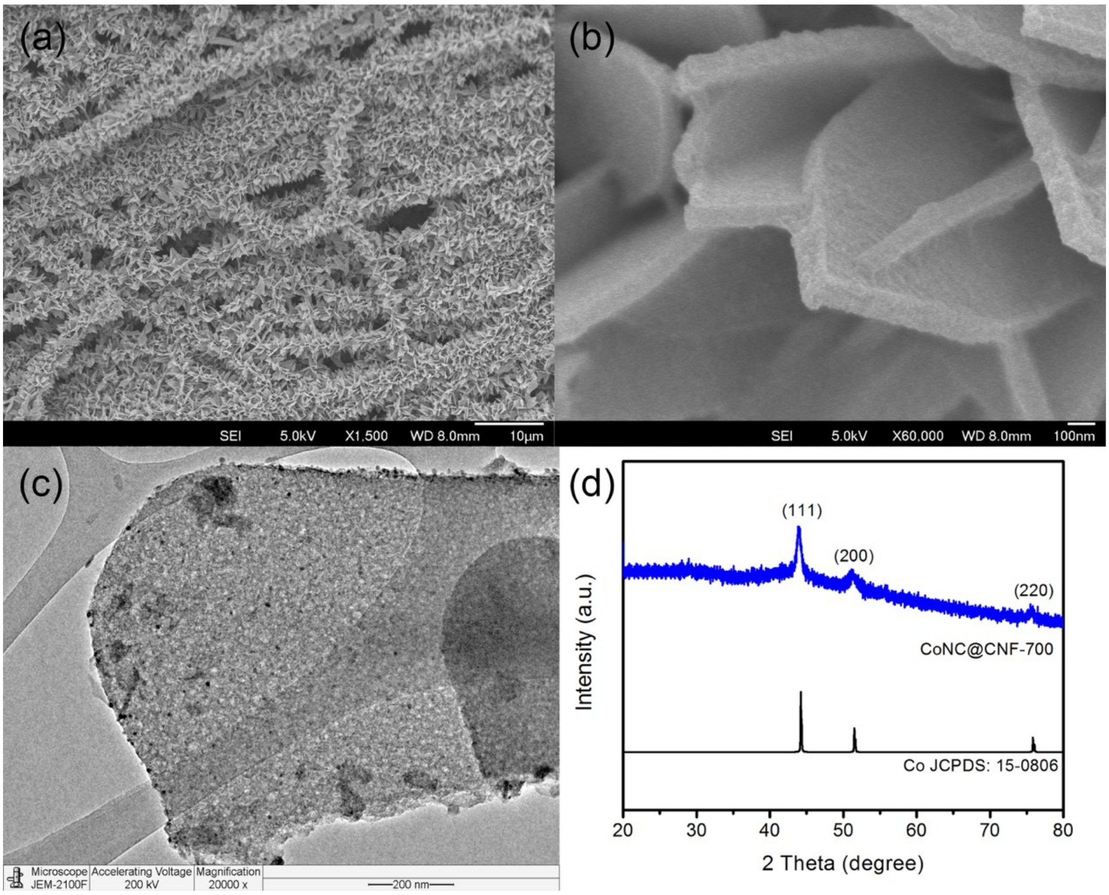

Fig. S9 a-b) SEM images of CoNC/CNF carbonized in N_2 at 700 °C. c) Corresponding TEM image. d) XRD pattern of CoNC/CNF-700.

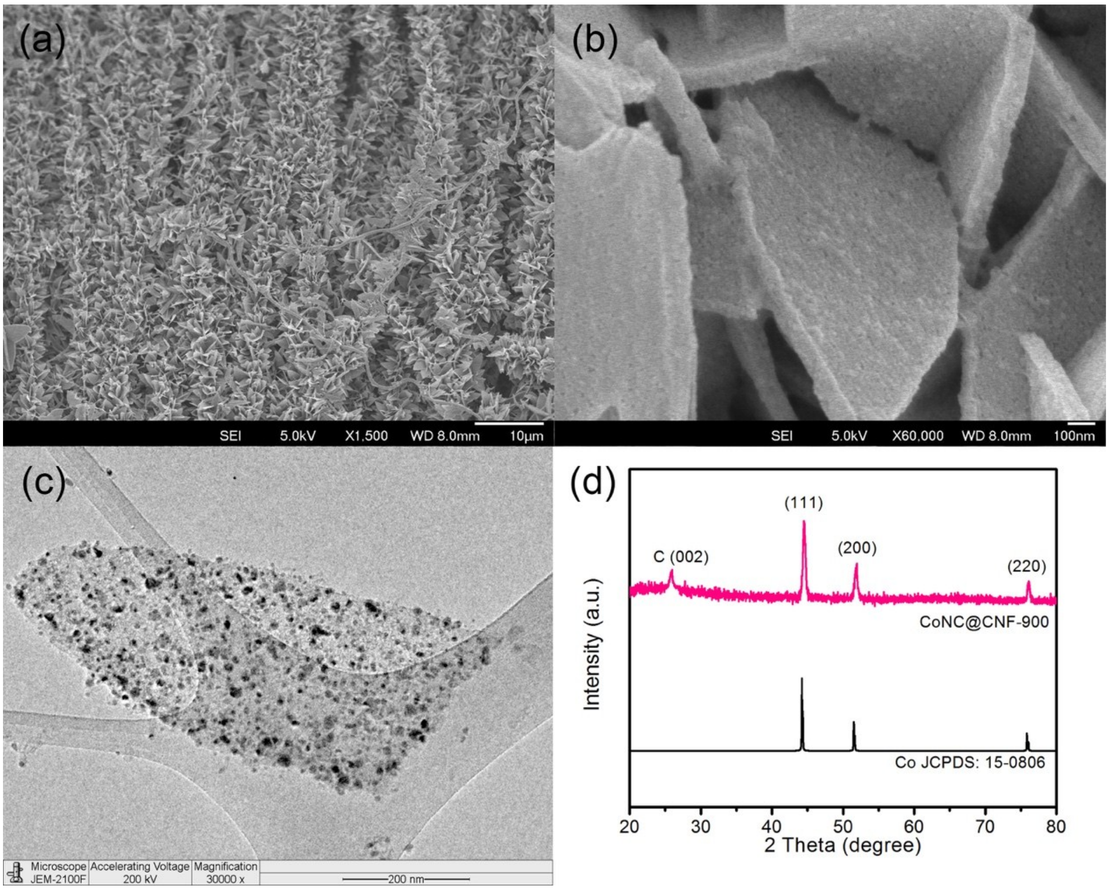

Fig. S10 a-b) SEM images of CoNC/CNF carbonized in N_2 at 900 °C. c) Corresponding TEM image. d) XRD pattern of CoNC/CNF-900.

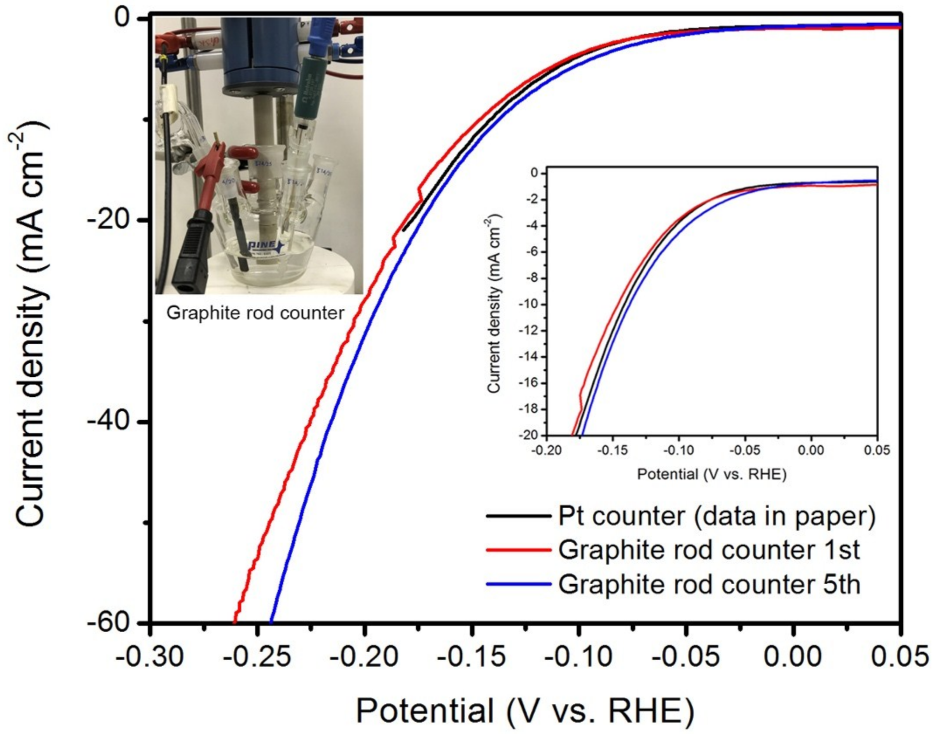

Fig. S11 The comparison of the HER performance when using Pt counter and graphite rod counter, respectively.

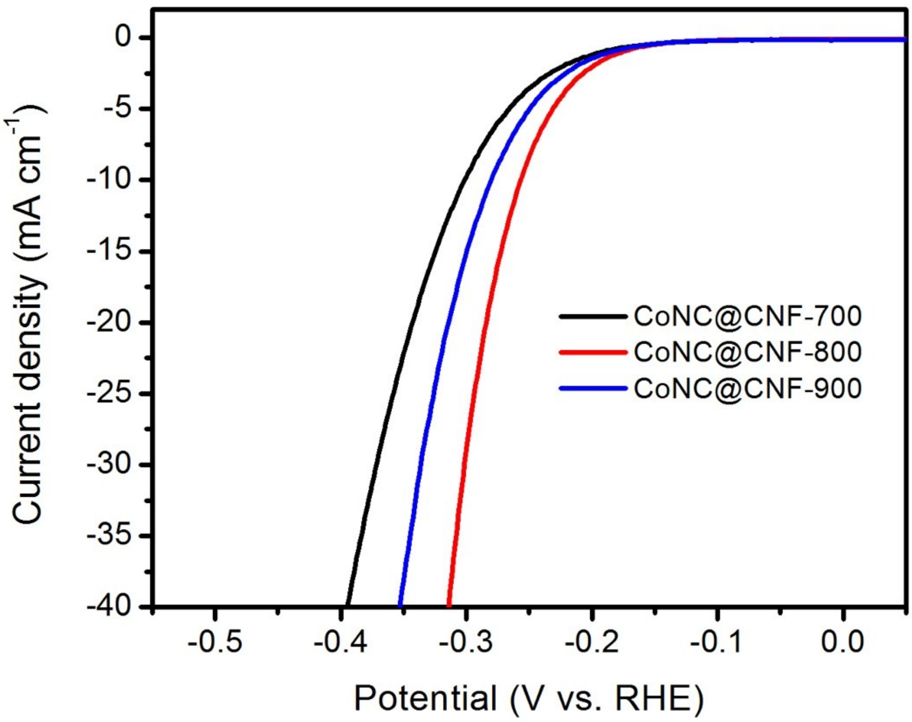

Fig. S12 The HER LSV curves of CoNC/CNF obtained from 700 °C, 800 °C and 900 °C.

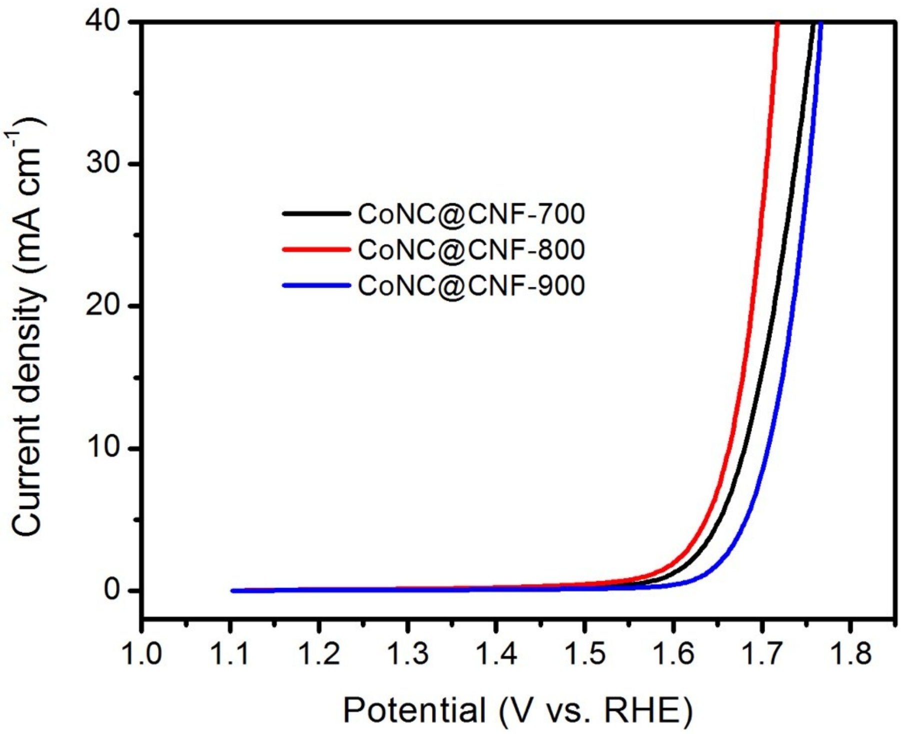

Fig. S13 The OER LSV curves of CoNC/CNF obtained from 700 °C, 800 °C and 900 °C.

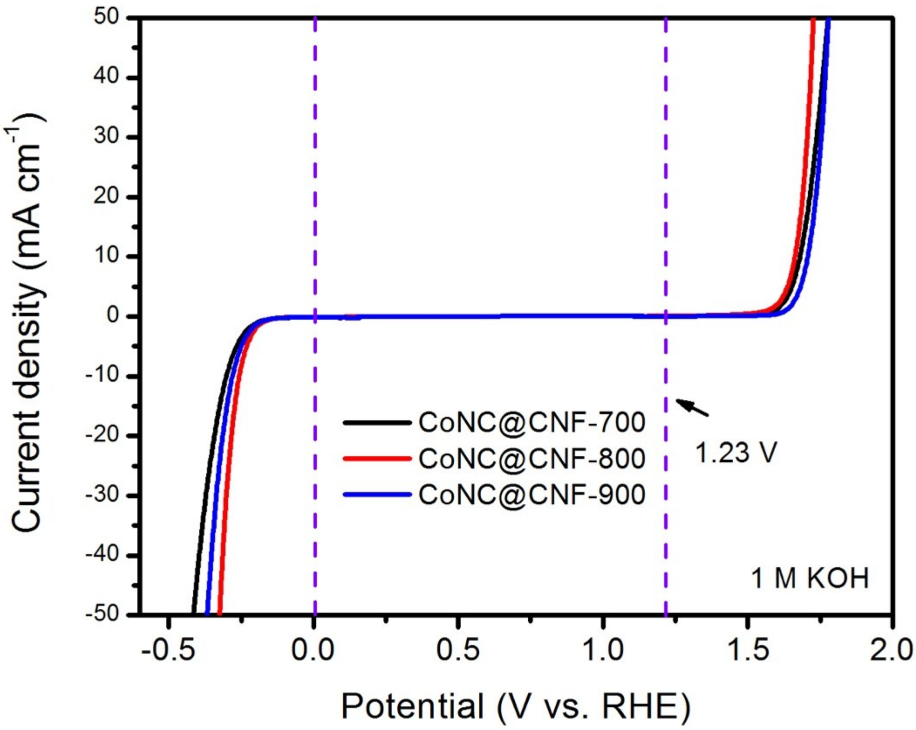

Fig. S14 The HER and OER performances of CoNC/CNF obtained from 700 °C, 800 °C and 900 °C.

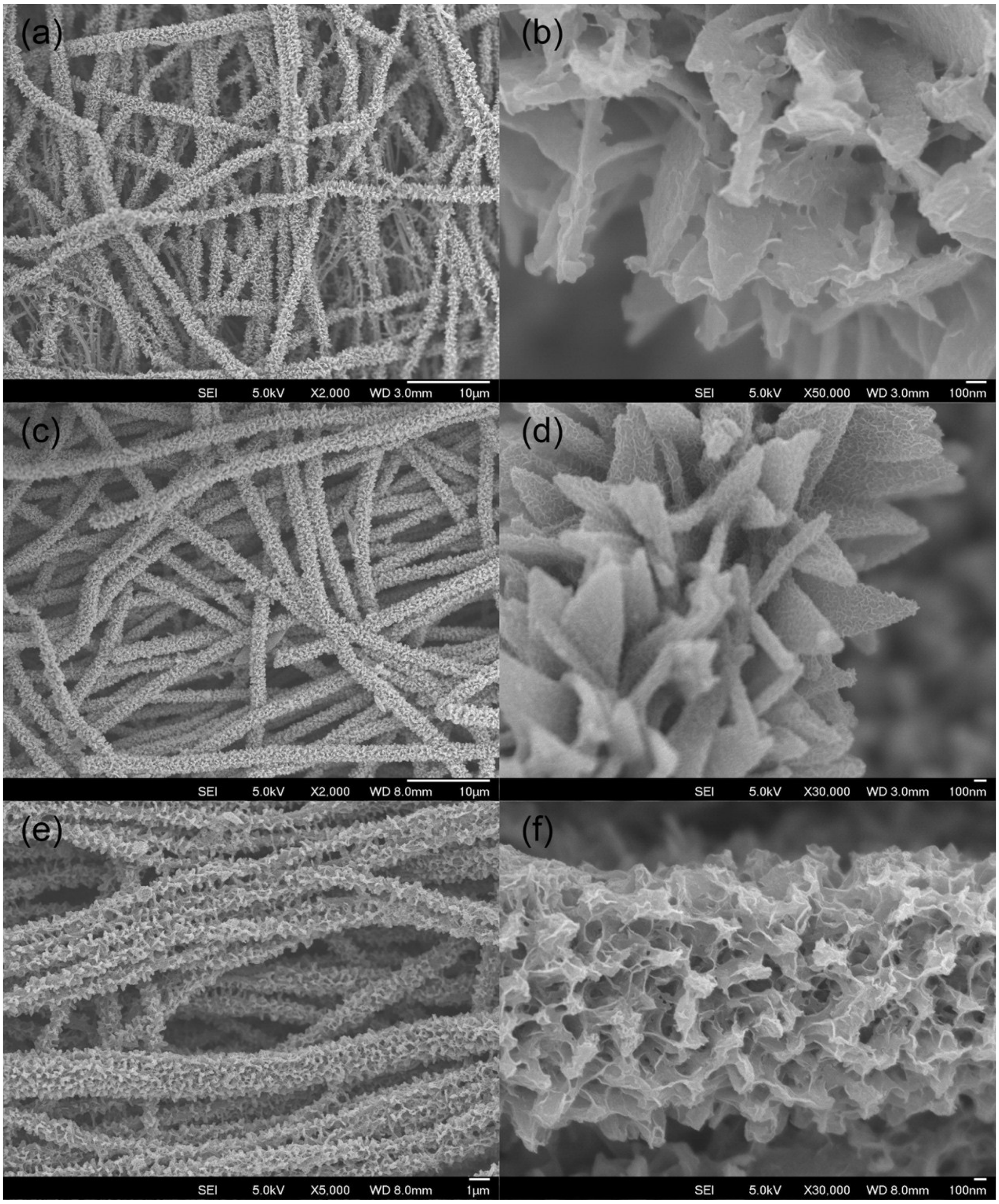

Fig. S15 SEM images of CoNC@MoS_2 obtained from different mass ratio between $(NH_4)_2MoS_4$ and CoNC/CNF. a, b) 0.2:1, c, d) 0.5:1 and e, f) 1:1.

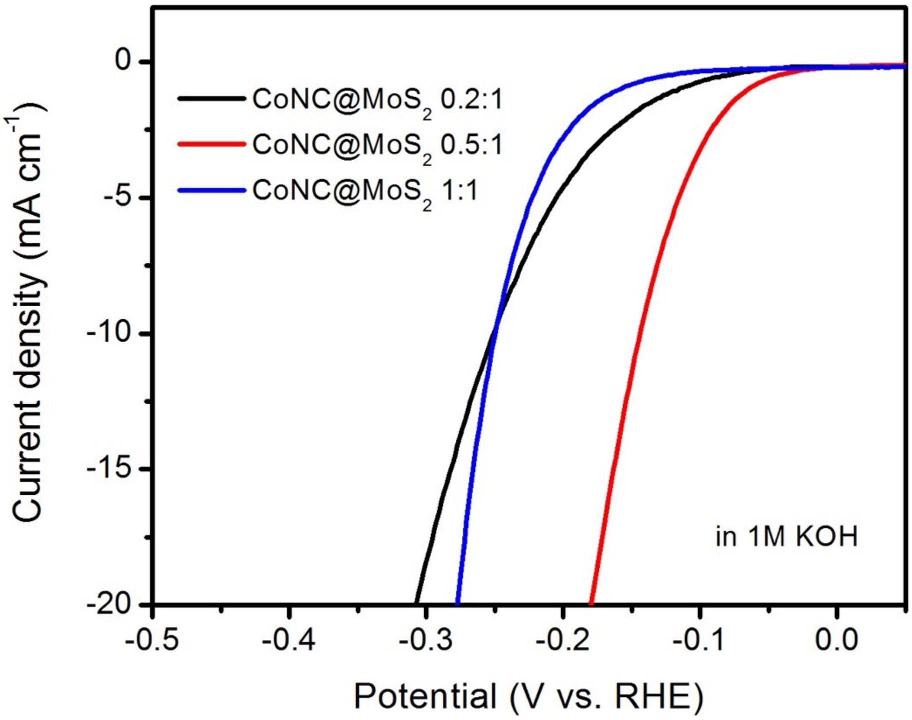

Fig. S16 The HER performances of CoNC@MoS_2 obtained from different mass ratio between $(NH_4)_2MoS_4$ and CoNC/CNF.

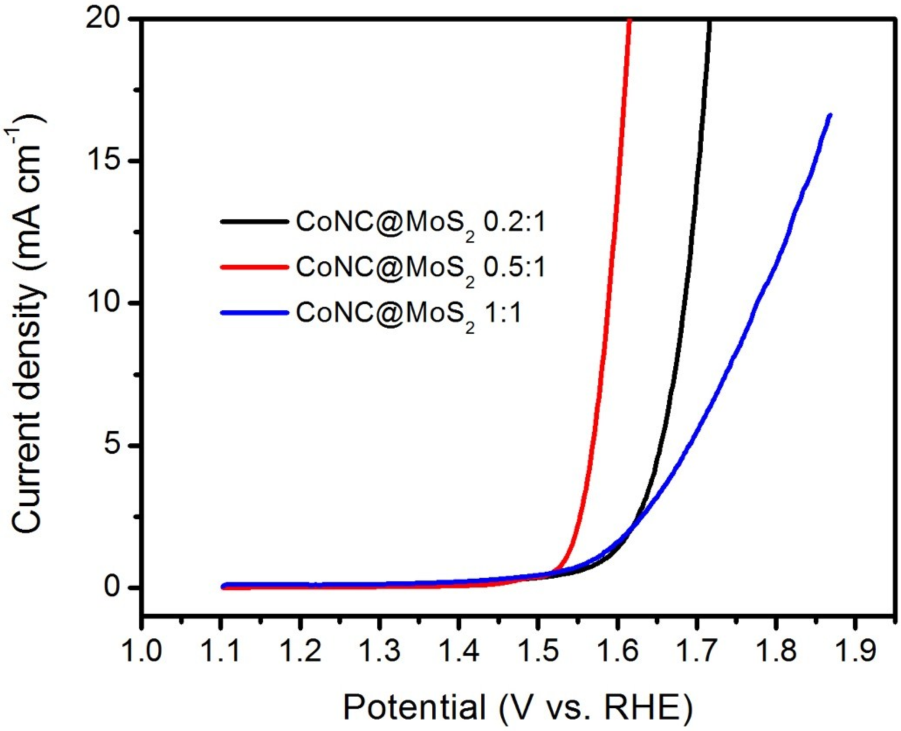

Fig. S17 The OER performances of CoNC@MoS_2 obtained from different mass ratio between $(NH_4)_2MoS_4$ and CoNC/CNF.

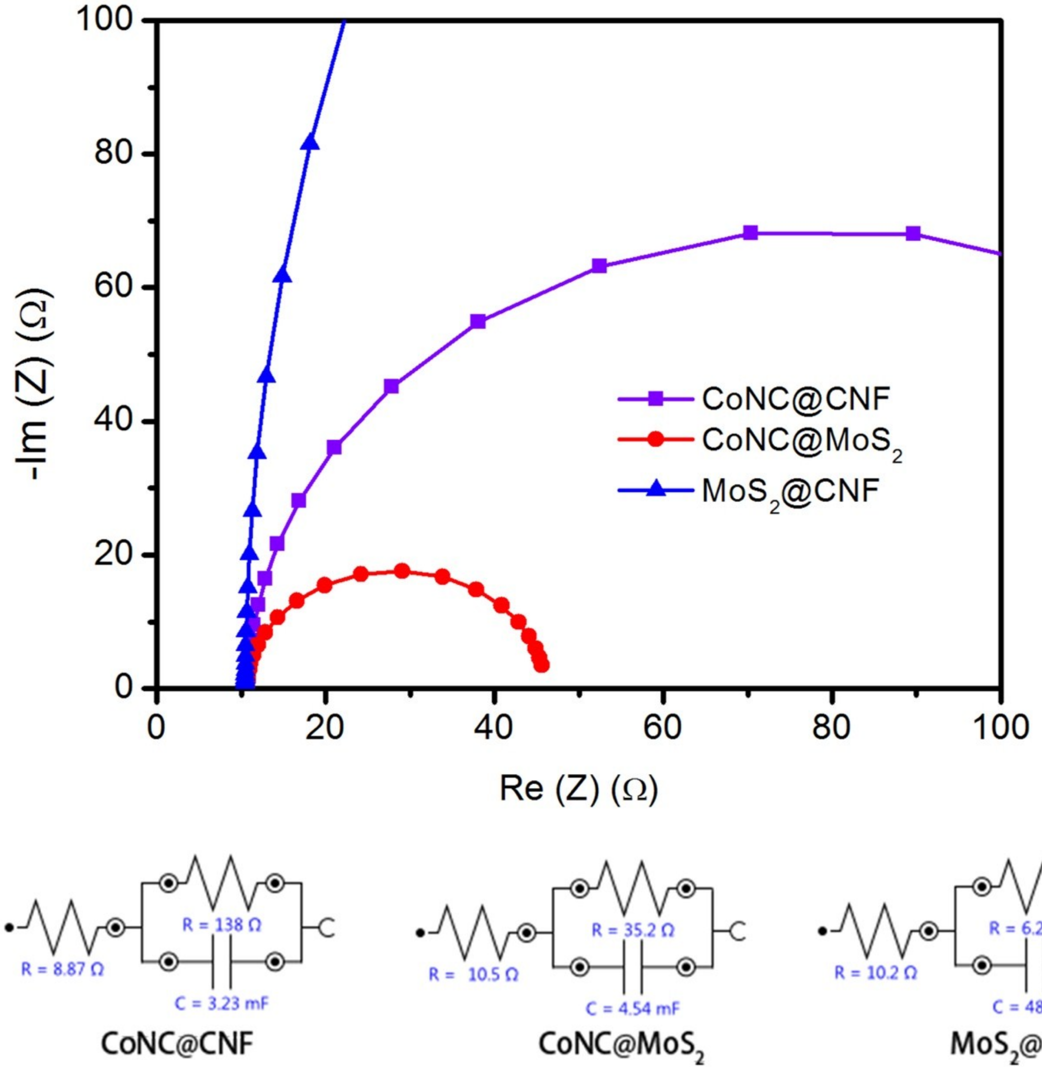

Fig. S18 HER EIS and Corresponding equivalent circuit that fits the electrochemical impedance spectroscopy (EIS) data for HER: a) CoNC/CNF, b) CoNC@MoS2 and c) MoS2/CNF.

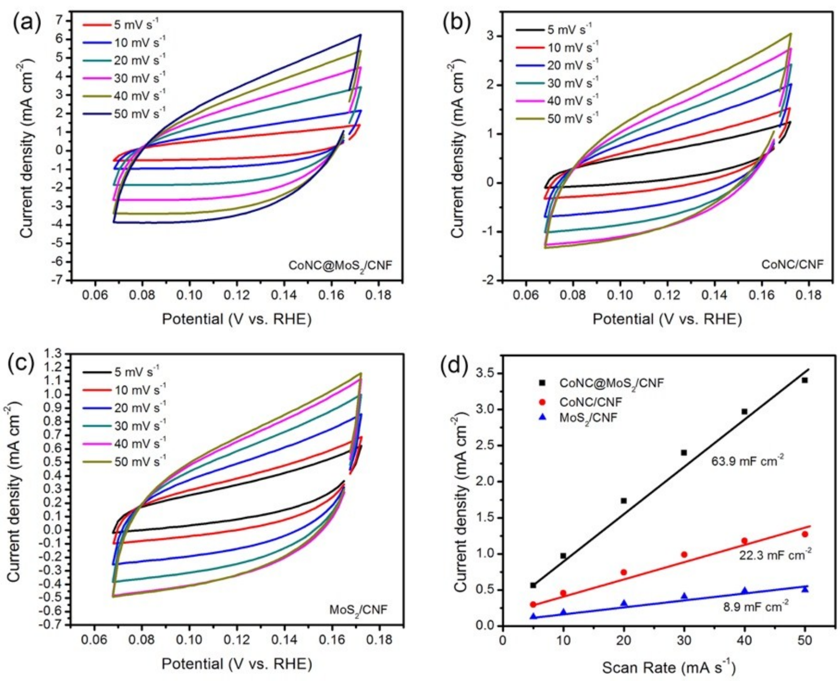

Fig. S19 CVs and Cdl of CoNC@MoS2/CNF, CoNC/CNF and MoS_2/CNF, respectively.

A high contact area between the catalysts and electrolyte is favorable for a high catalytic activity. To estimate the effective surface areas of the obtained samples, the C_{dl} at the solid–liquid interface is measured by CV. The CVs are evaluated in the potential range from 0.06 V to 0.16 V vs. RHE, where the current responses are only generated from the charging of the double-layers. The double-layer charging current as a function of the scan rate is plotted, and the slopes are calculated as the C_{dl}. As can be seen, the C_{dl} of CoNC@MoS_2/CNF is 64 mF cm^{-2}, which is almost three times more than the C_{dl} of CoNC/CNF (22 mF cm^{-2}). The electrochemically active surface area (ECSA) is proportional to the C_{dl} of the materials. Due to the growth of abundant thin MoS_2 on CoNC flakes, CoNC@MoS_2/CNF demonstrates a larger ECSA in comparison with that of CoNC/CNF and MoS_2/CNF catalysts, again confirms the superiority of the thin MoS_2 grown on CoNC flakes hybrid structure to achieve high catalytic activities for electrochemical reactions.

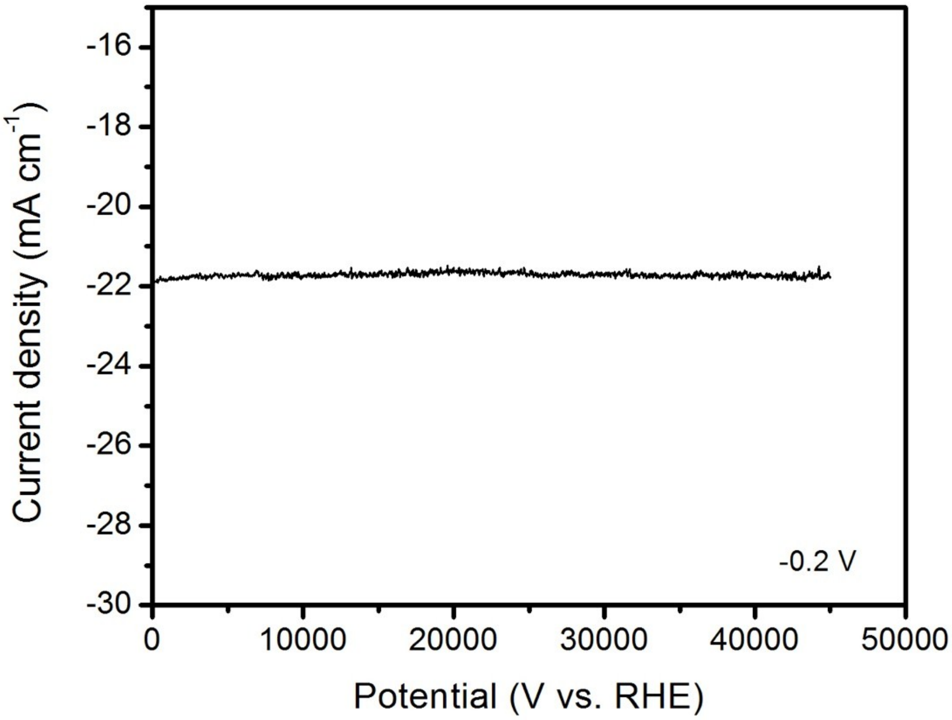

Fig. S20 The long-term stability performance of CoNC@MoS_2 for HER.

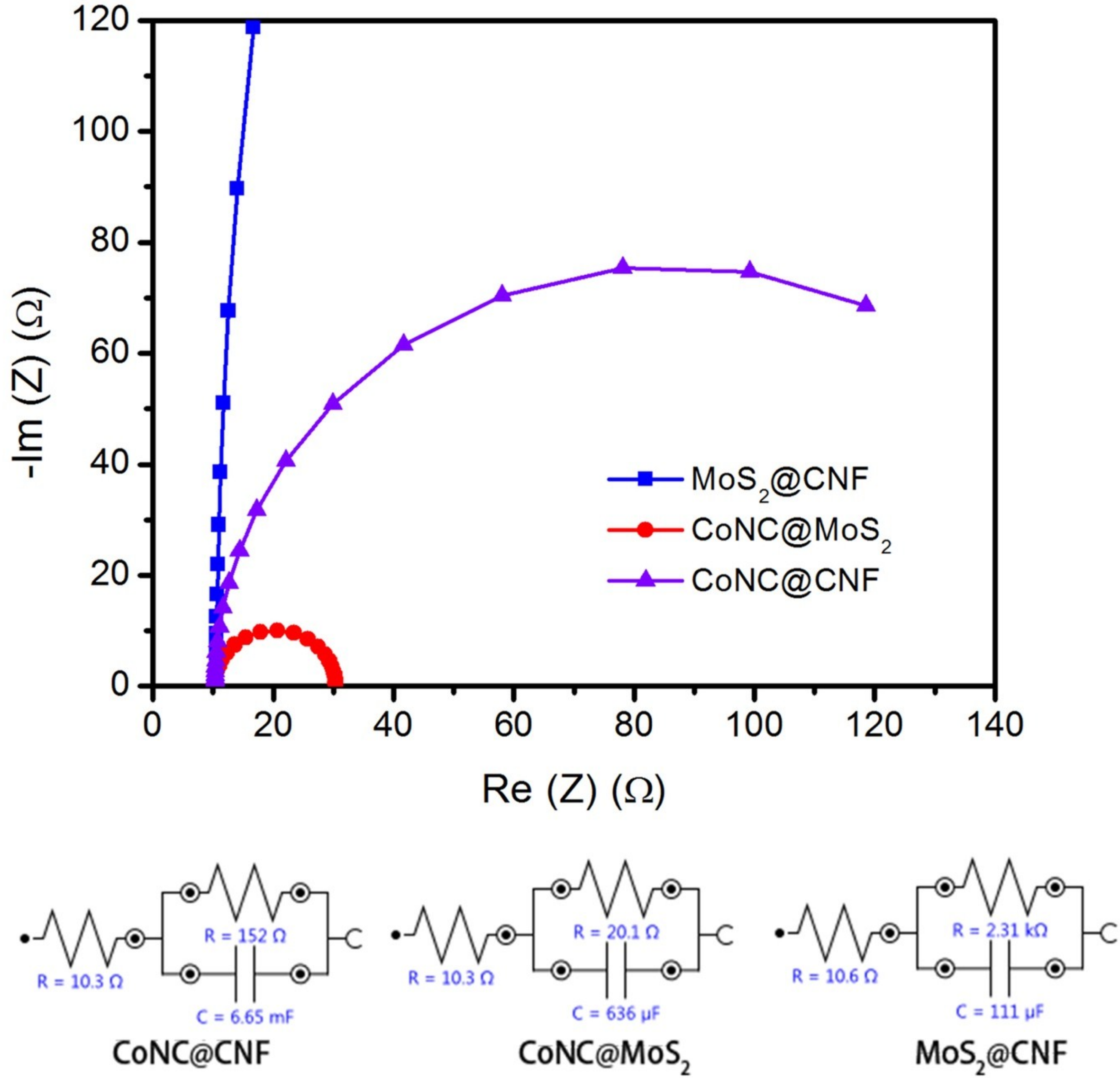

Fig. S21 Corresponding equivalent circuit that fits the electrochemical impedance spectroscopy (EIS) data for OER: a) CoNC/CNF, b) CoNC@MoS_2 and c) MoS_2/CNF.

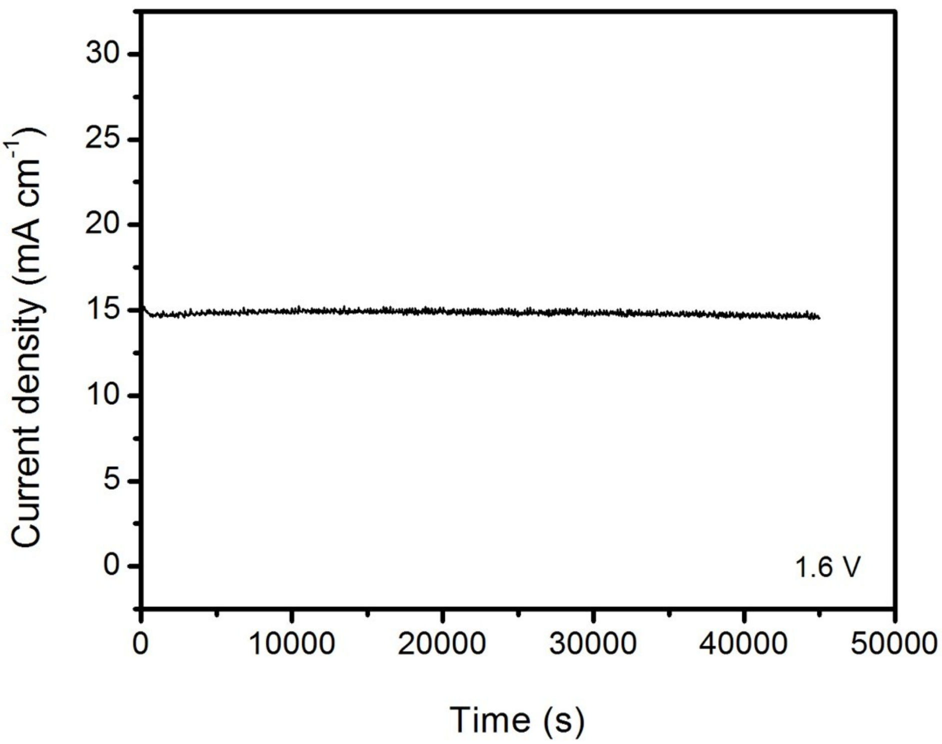

Fig. S22 The long-term stability performance of CoNC@MoS_2 for OER.

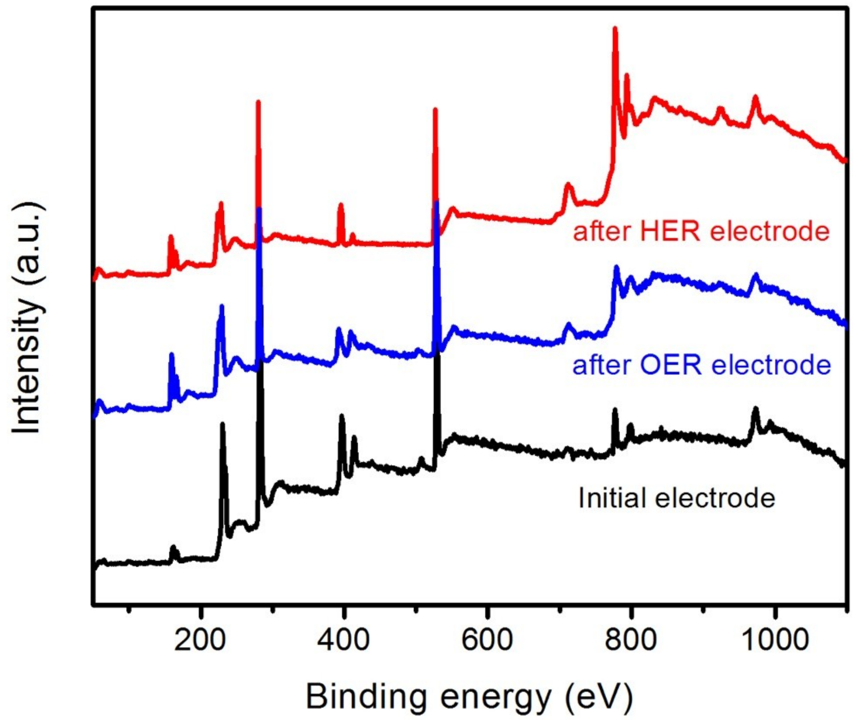

Fig. S23 Data survey spectra of initial electrode, after OER electrode and after HER electrode.

Table S1. Comparison of the HER performance of as-prepared materials with other reported Co and MoS_2 based HER electrocatalysts.

Catalyst	$\eta_{10\ mV}$	Tafel slope mV dec^{-1}	Electrolyte	reference
CoNC@MoS_2/CNF	143	68	1 M KOH	This work
CoNC/CNF	257	79	1 M KOH	This work
$NiCo_2S_4$ NW/NF	210	58.9	1M KOH	Adv. Funct. Mater. 2016, 26, 4661.
Co_9S_8@MoS_2/CNFs	190	110	0.5 M H_2SO_4	Adv. Mater. 2015, 27, 4752.
NiFe/nanocarbon	219	110	1M KOH	ACS Catal. 2016, 6, 580.
MoS_2/graphene/Ni foam	>600	98	1M KOH	Adv. Funct. Mater. 2014, 24, 6123.
MoS_{2+x} nanoparticles	310	84	1M KOH	Angew. Chem. Int. Ed., 2015, 54, 664.
Co/N-doped carbon	260	91.2	1M KOH	ACS Nano 2016, 10, 684.
Mo_2C nanoparticles	190	60	1M KOH	Angew. Chem. Int. Ed. 2012, 51, 12703.
MoS_2/CoS_2 nanorods/cc	87	73.4	0.5 M H_2SO_4	*J. Mater. Chem. A* **2015**, *3*, 22886
Co_9S_8-10@MoS_x/CC	134	70.6	0.5 M H_2SO_4	*Nano energy, 2017, 32,470*

Table S2. Comparison of the OER performance of as-prepared materials with other reported Co and MoS_2 based OER electrocatalysts.

Catalyst	$\eta_{10\ mV}$	Tafel slope mV dec^{-1}	Electrolyte	reference
CoNC@MoS_2/CNF	350	51.9	1 M KOH	This work
CoNC/CNF	430	89.7	1 M KOH	This work
CoS-$Co(OH)_2$@aMoS_{2+x}/ ni foam	380	68	1 M KOH	Adv. Funct. Mater. 2016, 26, 7386.
Co_9S_8@MoS_2/CNFs	430	61	1 M KOH	Adv. Mater. 2015, 27, 4752.
MoS_2-Ni_3S_2 HNRs/NF	249	66	1 M KOH	ACS Catal. 2017, 7,2357
CoNi-LDH/Fe-porphyrinlayer-by-layer	264	37.6	1 M KOH	J. Mater. Chem. A 2016, 4, 11516.
$Co(OH)_2$	450	62	0.1 M KOH	ACS Appl.Mater.Interfaces 2015, 7, 12930.
Co monolayer array	390	-	0.1 M KOH	J. Am. Chem. Soc., 2015,137
Co/N-C-800	370	61.4	0.1 M KOH	Nanoscale, 2014, 6, 15080
PNC/Co	370	48	1M KOH	J. Mater. Chem. A, 2016, 4, 3204

Table S3. Comparison of the water splitting performance of as-prepared materials with other reported Co and MoS_2 based water splitting electrocatalysts.

Catalyst	$\eta_{10\ mV}$	Loading mg cm^{-2}	Electrolyte	reference
CoNC@MoS_2/CNF films	1.62	2.0(CNF+ CoNC@MoS_2)	1M KOH	This work
CP/CTs/Co-S	1.743	-	1M KOH	ACS Nano 2016, 10, 2342.
$NiCo_3O_4$ hollow microcuboids	1.65	1.0	1M NaOH	Angew. Chem. Int. Ed. 2016, 55, 6290.
Co_xMn_yCH/NF	1.68	-	1M KOH	J. Am. Chem. Soc. 2017, 139, 8320.
N/Co-doped PCP//NRGO	1.66	0.714	0.1M KOH	Adv. Funct. Mater. 2015, 25, 872.
a-CoSe/Ti	1.65	3.8	1M KOH	Chem. Commun. 2015, 51, 16683.
EG/$Co_{0.85}$Se/NiFe-LDH	1.67	4.0	1M KOH	Energy Environ. Sci. 2016, 9, 478.