Supporting Information

Engineering Cobalt Oxide by Interfaces and Pore Architectures for Enhanced Electrocatalytic Performance for Overall Water Splitting

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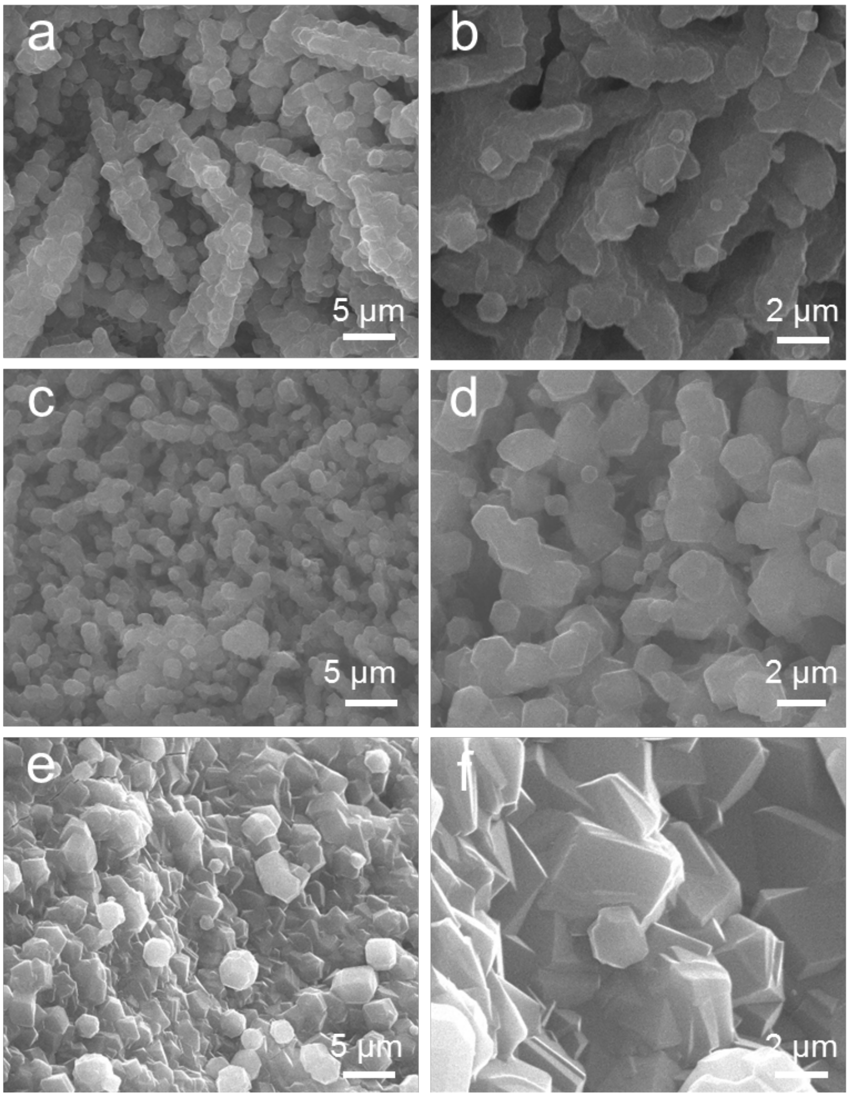

Figure S1. SEM images of $Co_2(OH)_2CO_3$@ZIF-67 CSNSAs on Ni foam with different reaction time: (a-b) 6 h, (c-d) 8 h, and (e-f) 12 h.

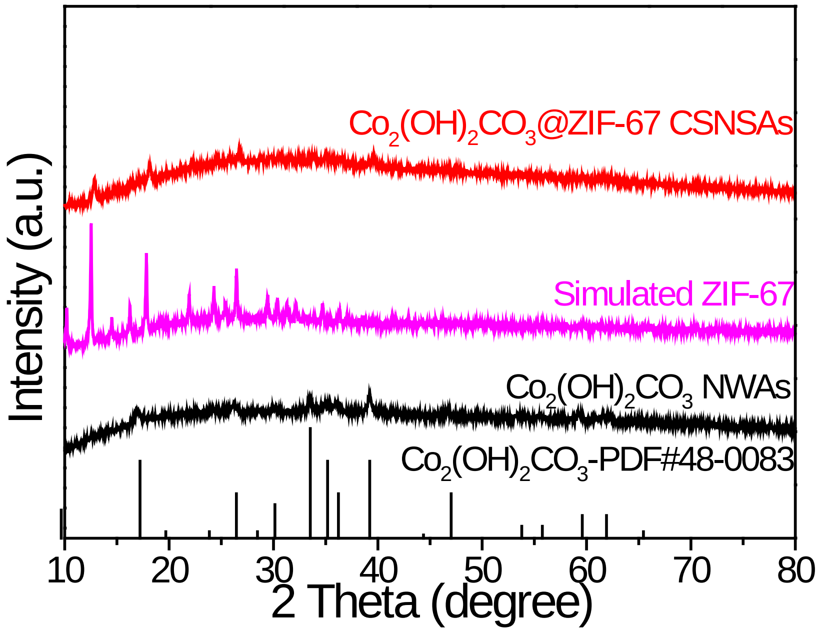

Figure S2. XRD patterns of $Co_2(OH)_2CO_3$ NWAs and $Co_2(OH)_2CO_3$@ZIF-67 CSNSAs.

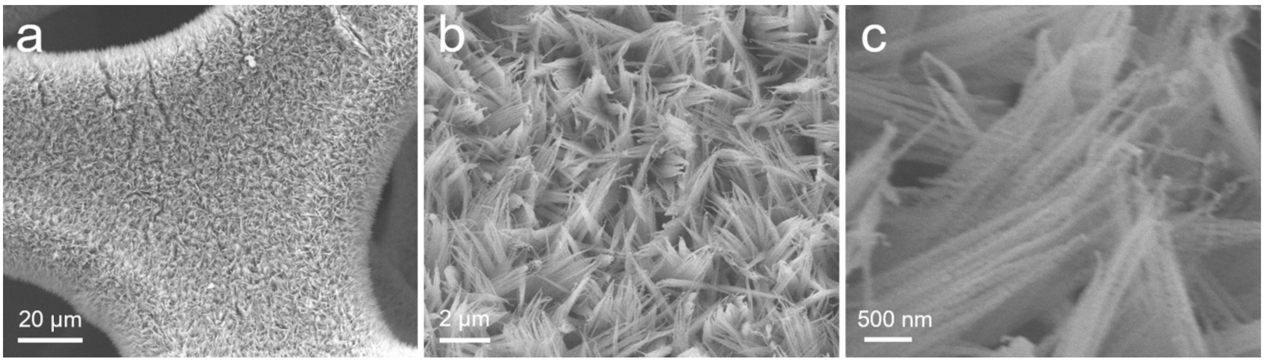

Figure S3. SEM images with different magnifications of mes-CoO NWAs on Ni foam.

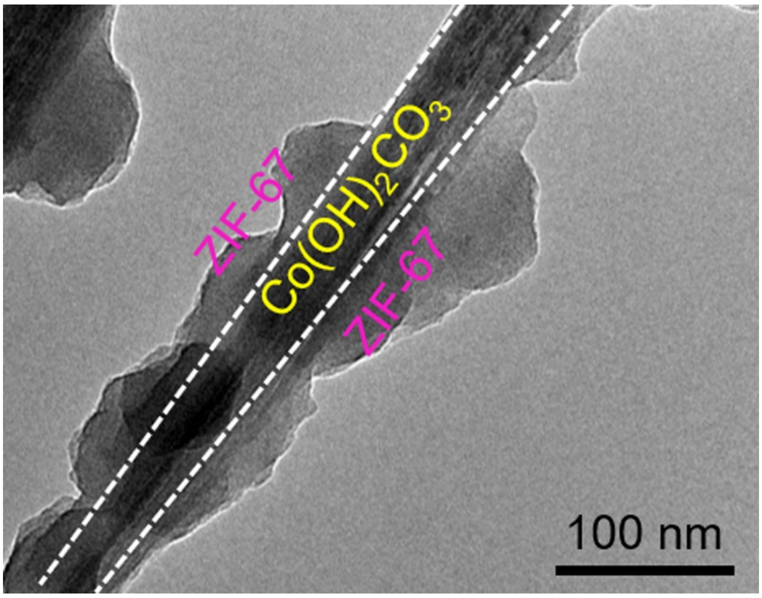

Figure S4. TEM image of a single core-shell structured $Co_2(OH)_2CO_3$@ZIF-67 nanowire.

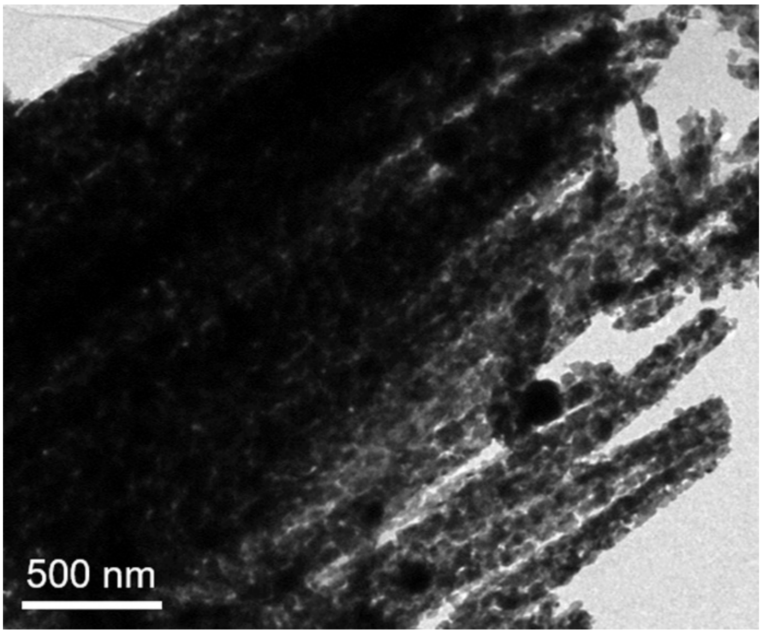

Figure S5. TEM image of mes-CoO NWAs.

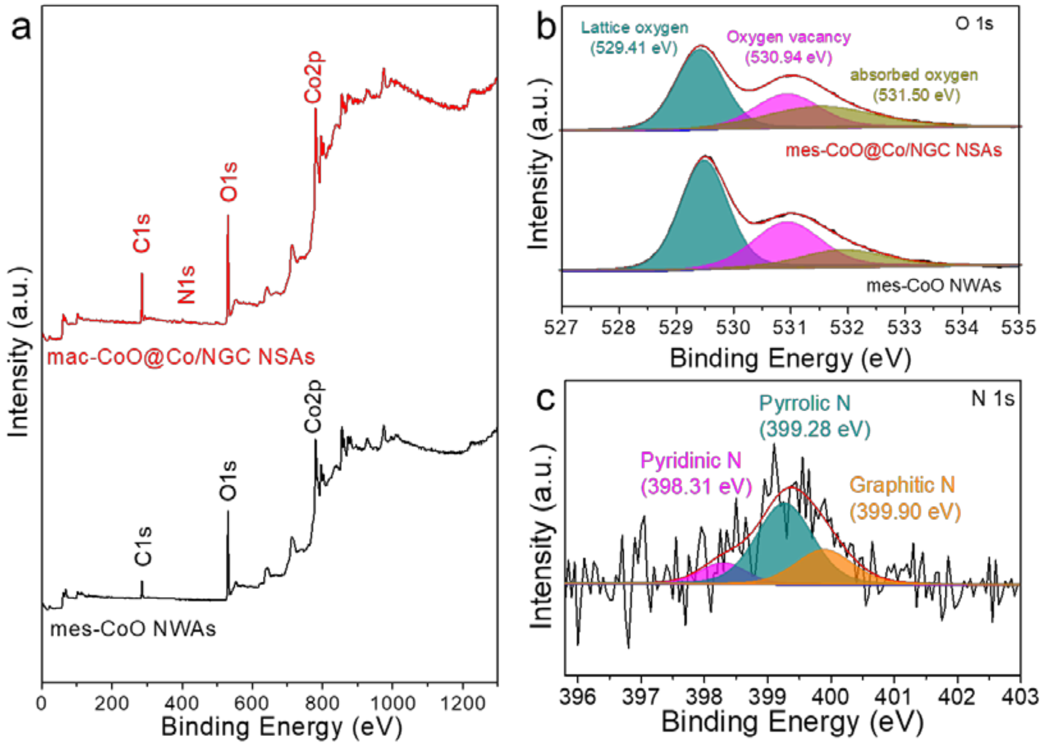

Figure S6. (a) XPS survey spectra of mes-CoO NWAs and mac-CoO@Co/NGC NSAs, and high resolution XPS spectra of (b) O 1s for mes-CoO NWAs and mac-CoO@Co/NGC NSAs, (c) N 1s for mac-CoO@Co/NGC NSAs.

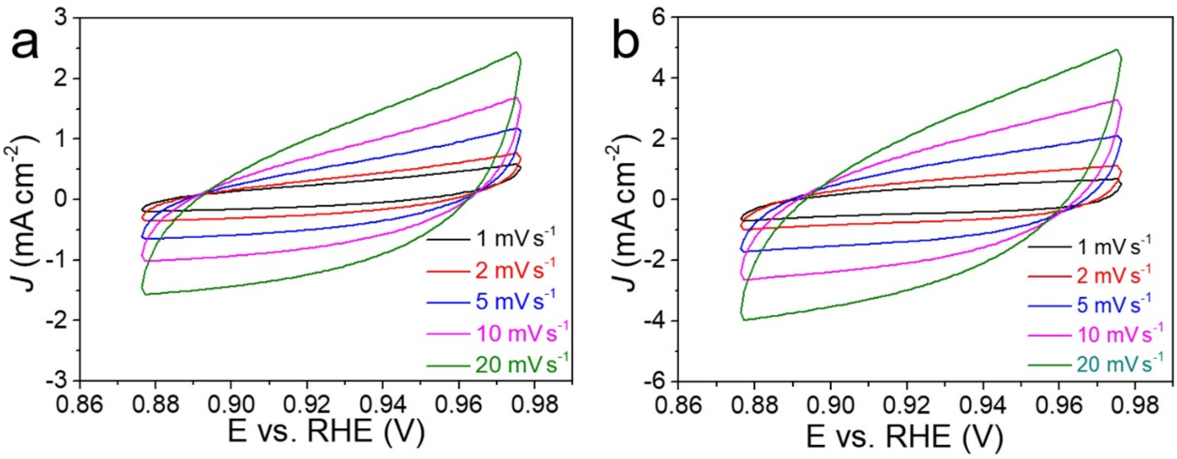

Figure S7. CVs of (a) mes-CoO NWAs and (b) mac-CoO@Co/NGC NSAs measured in 1.0 M KOH solution.

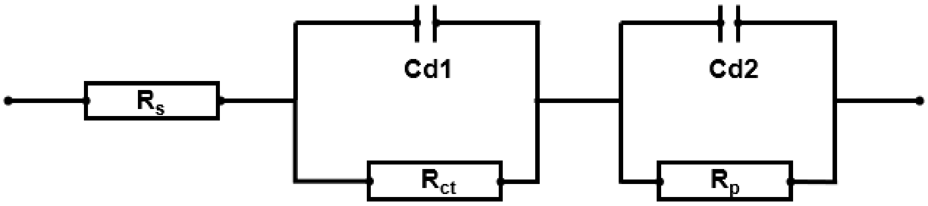

Figure S8. Equivalent circuit used for fitting the Nyquist plots, which consists of a series resistance R_s (the ohmic resistance) in series with two parallel branches: one reflecting the charge-transfer process (C_{d1}-R_{ct}) and the other related to the surface porosity (C_{d2}-R_p).

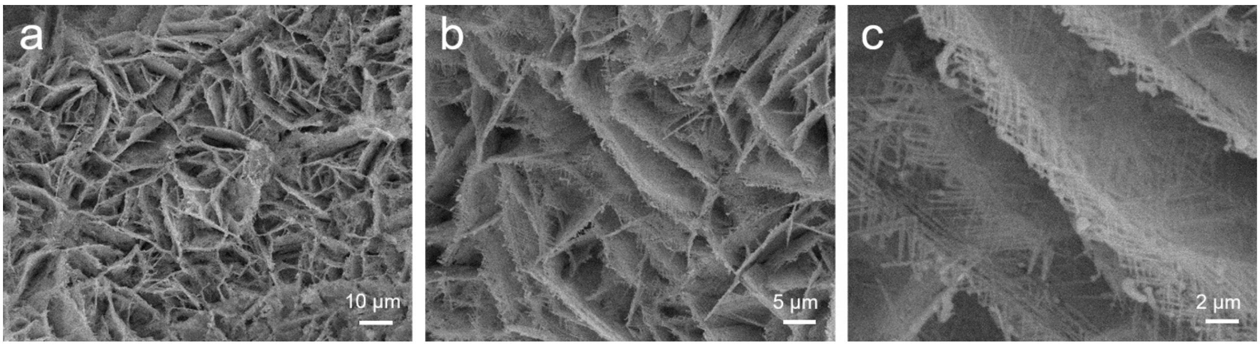

Figure S9. SEM images with different magnifications of mac-CoO@Co/NGC NSAs at anode for OER after full water splitting test for 35 h.

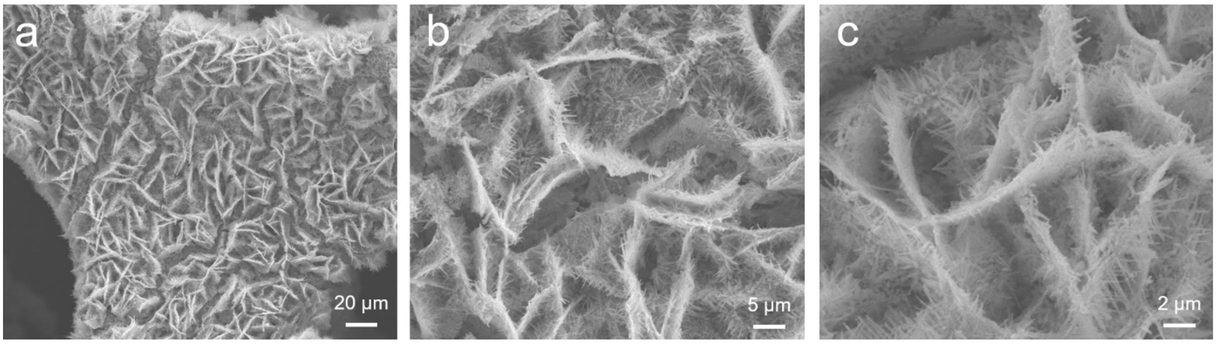

Figure S10. SEM images with different magnifications of mac-CoO@Co/NGC NSAs at cathode for HER after full water splitting test for 35 h.

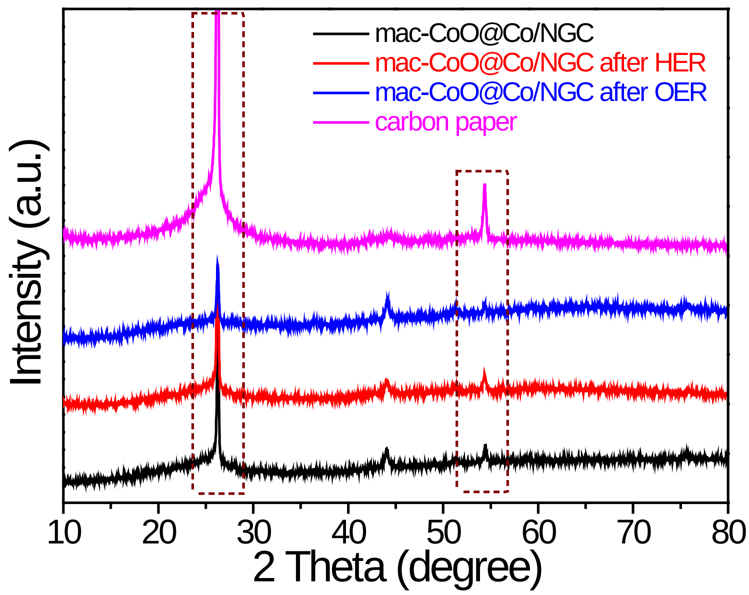

Figure S11. XRD patterns of mac-CoO@Co/NGC before and after electrolysis test. The peaks indicated by dotted line come from carbon paper electrode.

Table S1. Comparison of representative cobalt-based OER electrocatalysts in alkaline electrolyte (1.0 M KOH solution).

Catalysts	**η@*J* (mV@mA cm^{-2})**	**Tafel slope (mV dec^{-1})**	References
mac-CoO@Co/NGC NSAs	300@50	38	This work
Co_3O_4/graphene	310@10	67	*Nat. Mater.* **2011**, *10*, 780
Co_3O_4/C NWAs	290@10	70	*J. Am. Chem. Soc.* **2014**, *136*, 13925
Co_3O_4/$NiCo_2O_4$ nanocages	340@10	88	*J. Am. Chem. Soc.* **2015**, *137*, 5590
CoMn-LDH	324@10	43	*J. Am. Chem. Soc.* **2014**, *136*, 16481
$Zn_xCo_{3-x}O_4$ NWAs	320@10	51	*Chem. Mater.* **2014**, *26*, 1889
Hollow Co_3S_4 NSs	355@10	40	*Angew. Chem. Int. Ed.* **2015**, *127*, 11383
CoCo LDH	380@10	59	*Nat. Commun.* **2014**, *5*, 4477
N-doped graphene-CoO	340@10	67	*Energy Environ. Sci.* **2014**, *7*, 609
Co-PNCNFs	285@10	73	*J. Mater. Chem. A* **2016**, *4*, 12818
Co@N-C	400@10	N.A.	*J. Mater. Chem. A* **2014**, *2*, 20067
Fe-Ni(OH)$_2$/NF	267@10	51.5	*Chem. Commun.* **2018**, *54*, 463
Co(S_xSe_{1-x})$_2$	283@10	65.6	*Adv. Funct. Mater.* **2017**, *27*, 1701008
CoFePO/NF	274.5@10	51.7	*ACS Nano*, **2016**, *10*, 8738
F-Co_2B	320@10	32	*Energy Environ. Sci.* **2019**,*12*, 2443

Table S2. Comparison of representative cobalt-based HER electrocatalysts in alkaline electrolyte (1.0 M KOH solution).

Catalysts	**η@10 mA cm^{-2} (mV)**	**Tafel slope (mV dec^{-1})**	**References**
mac-CoO@Co/NGC	140	94	This work
CoP/CC	67	129	*J. Am. Chem. Soc.* **2014**, *136*, 7587
CoO_x@CN	232	N.A.	*J. Am. Chem. Soc.* **2015**, *137*, 2688
Co-P film	94	42	*Angew. Chem. Int. Ed.* **2015**, *54*, 6251
Co/N-doped carbon	260	91	*ACS Nano* **2016**, *10*, 684
$NiCo_2S_4$ nanowires	N.A.	141	*Nanoscale* **2015**, *7*, 15122
Co-PNCNFs	249	92	*J. Mater. Chem. A* **2016**, *4*, 12818
Co@CN	210	108	*J. Mater. Chem. A* **2014**, *2*, 20067
$Co_{0.59}Fe_{0.41}P$	99	72	*Nanoscale* **2015**, *7*, 11055
NiCoP/CNT	80	62	*Electrochim. Acta.* **2017**, *252*, 101
CoP_2/RGO	88	50	*J. Mater. Chem. A.* **2016**, *4*, 4686
Co-NRCNTs	370	N.A.	*Angew. Chem. Int. Ed.* **2014**, *53*, 4372
CoP-MNAs	54	51	*Adv. Funct. Mater.* **2015**, *25*, 7337
Mo_5N_6	94	66	*ACS Nano* **2018**, *12*, 12761
Cu-CoP NRAs/CC	81	102	*ACS Appl. Energy Mater.* **2018**, *1*, 3835

Table S3. Comparison of overall water splitting performance of mac-CoO@Co/NGC NSAs with recently reported bi-functional electrocatalysts in alkaline electrolyte (1.0 M KOH solution).

Catalysts	**$E_{J=10}$ (V)**	**References**
mac-CoO@Co/NGC NSAs	1.62	This Work
CoO-CNF	1.63	*Nat. Commun.* **2015**, *6*, 7261
CoP-MNA	1.62	*Adv. Funct. Mater.* **2015**, *25*, 7337
Ni_2P	1.63	*Energy Envoiron. Sci.* **2015**, *8*, 2347
NiSe-NWs	1.63	*Angew. Chem. Int. Ed.* **2015**, *32*, 9483
NiFe-LDHs	1.7	*Science* **2014**, *345*, 1593
Co_3O_4-MTAs	1.63	*Angew. Chem. Int. Ed.* **2017**, *56*, 1324
Co-PNCNFs	1.66	*J. Mater. Chem. A* **2016**, *4*, 12818
EG/$Co_{0.85}$Se/NiFe-LDH	1.67	*Energy Environ. Sci.* **2016**, *9*, 478
$NiCo_2O_4$	1.65	*Angew. Chem. Int. Ed.* **2016**, *55*, 6290
CP/CTs/Co-S	1.74	*ACS Nano* **2016**, *10*, 2342
NiS/Ni foam	1.64	*Chem. Commun.* **2016**, *521*, 486
PNC/Co	1.64	*J. Mater. Chem. A* **2016**, *4*, 3204
Co-P/NC	1.71	*Chem. Mater.* **2015**, *27*, 7636
Co–Se1//Co–Se4	1.84	*Adv. Energy Mater.* **2018**, *8*, 1801926
MoS_2/NiFe LDH superlattice	1.57	*Nano Lett.* **2019**, *19*, 4518
Pt-CoS_2/CC	1.55	*Adv. Energy Mater.* **2018**, *8*, 1800935

η: Overpotential (mV);

J: Current density (mA cm^{-2});

CNF: Carbon nanofiber;

CNT: Carbon nanotube;

MNA: Mesoporous nanorod arrays;

NWs: Nanowires;

MTAs: Microtube arrays;

NWAs: Nanowire arrays;

NRAs: Nanorod arrays;

NSs: Nanosheets.

PNCNFs: Porous nitrogen doped carbon nanofibers;

NC/CN: N-doped carbon.

CC: Carbon cloth;

NRCNTs: Nitrogen-rich carbon nanotubes;

MNAs: Mesoporous nanorod arrays.