Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers. This journal is © the Partner Organisations 2018

Ultrathin porous nanosheet-assembled hollow cobalt nickel oxides microspheres with optimized compositions for efficient oxygen evolution reaction

Jun Zhao [a], Xiao-ru Wang [a], Xiao-jing Wang [a], Yu-Pei Li [a], Xiao-dong Yang [a], Guo-dong Li [b*] and Fa-tang Li [a*]

[a]College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, China.

[b]State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, International Joint Research Laboratory of Nano-Micro Architecture Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China.

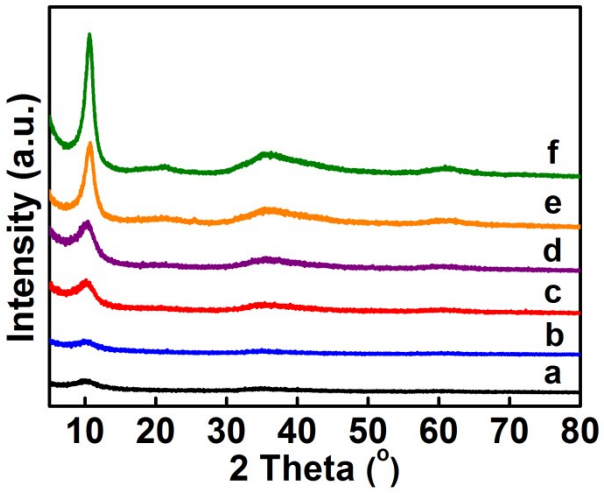

Fig. S1 XRD patterns of (a) s-CoA, (b) *s*-C_6N_1A, (c) *s*-C_2N_1A (d) *s*-C_1N_1A (e) *s*-C_1N_6A and (f) s-NiA.

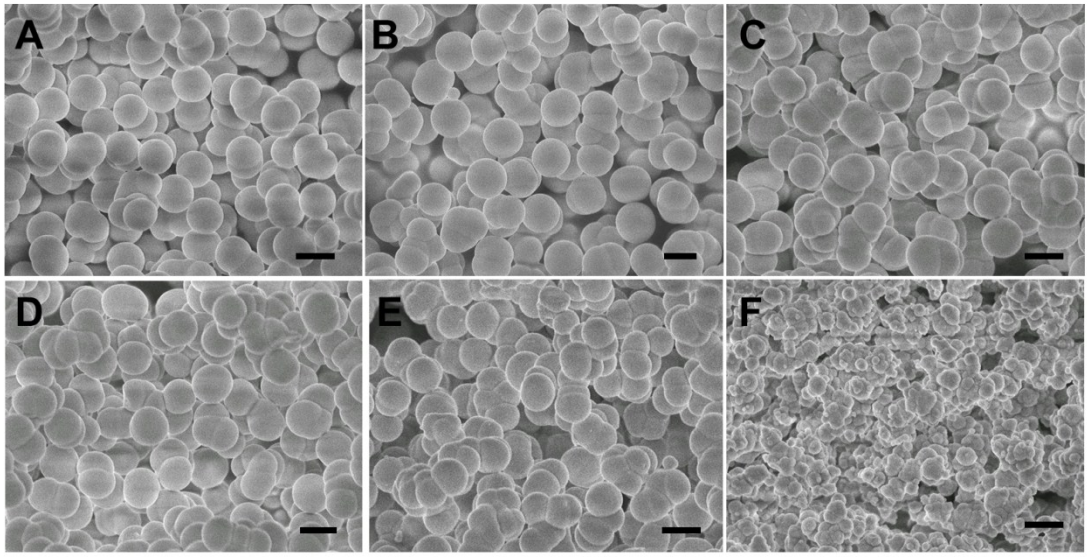

Fig. S2 SEM images of (A) s-CoA, (B) *s*-C_6N_1A, (C) *s*-C_2N_1A (D) *s*-C_1N_1A (E) *s*-C_1N_6A and (F) s-NiA. Scale bar: 1μm

Table S1. ICP results of s-CNA and Co-Ni Oxides

samples	**Feed ratio of Co:Ni**	**Content of Co (mg/L)**	**Content of Ni (mg/L)**	**Atom ratio (Co:Ni)**
s-C_6N_1A	6:1	24.3	4.05	5.98:1
s-C_2N_1A	2:1	19.2	9.5	2.01:1
s-C_1N_1A	1:1	14.3	14.5	1:0.98
s-C_1N_6A	1:6	7.05	43.0	1:6.12
Co_6-Ni_1-O	6:1	42.6	7.18	5.91:1
Co_2-Ni_1-O	2:1	34.5	17.0	2.02:1
Co_1-Ni_1-O	1:1	24.9	24.6	1.01:1
Co_1-Ni_6-O	1:6	7.05	43.0	1:6.12

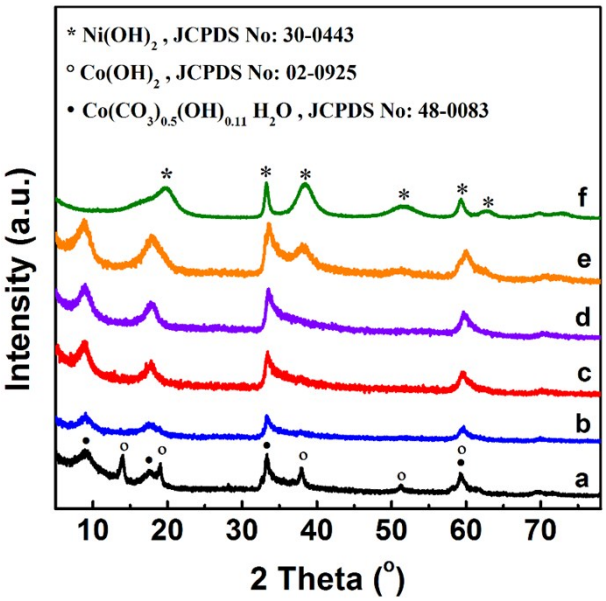

Fig. S3 XRD patterns of (a) CoI, (b) *h*-C_6N_1I, (c) *h*-C_2N_1I (d) *h*-C_1N_1I (e) *h*-C_1N_6I and (f) NiI.

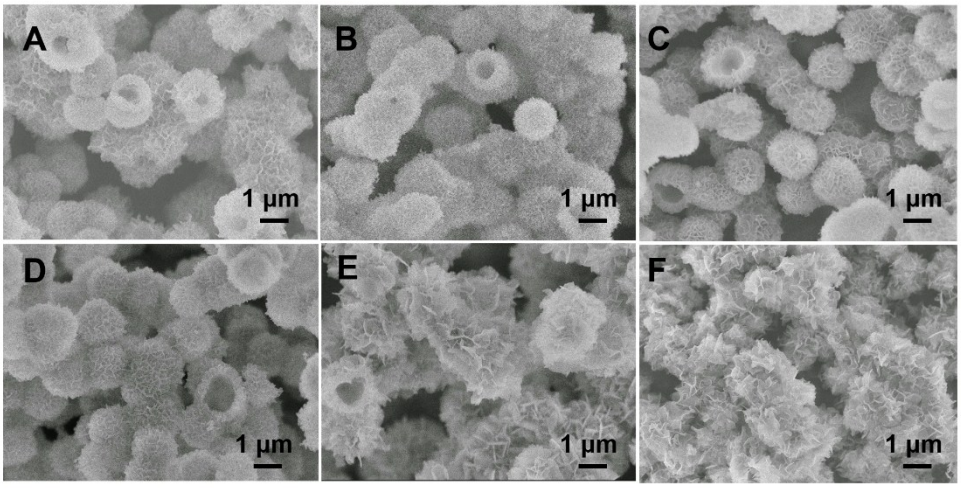

Fig. S4 SEM images of (A) CoI, (B) *h*-C_6N_1I, (C) *h*-C_2N_1I (D) *h*-C_1N_1I (E) *h*-C_1N_6I and (F) NiI.

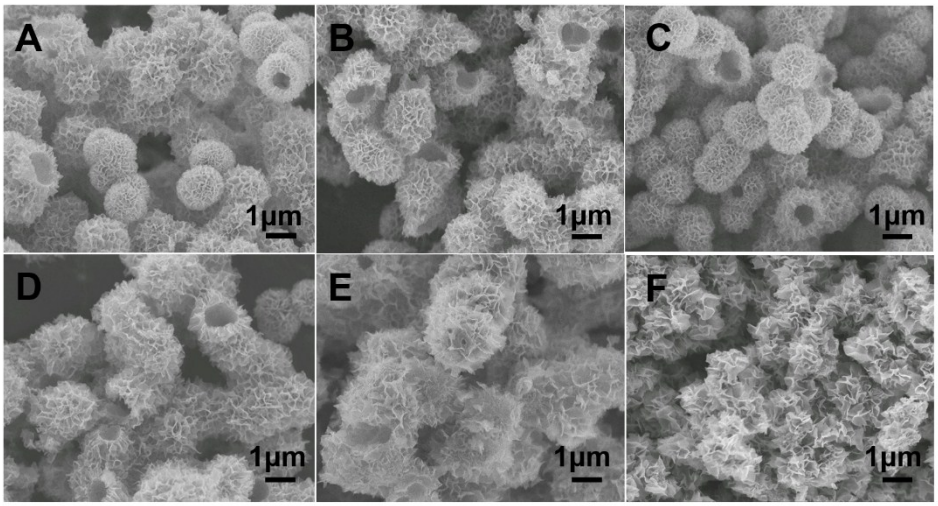

Fig.S5 SEM images of (A) Co_3O_4, (B) Co_6-Ni_1-O, (C) Co_2-Ni_1-O (D) Co_1-Ni_1-O (E) Co_1-Ni_6-O and (F) NiO.

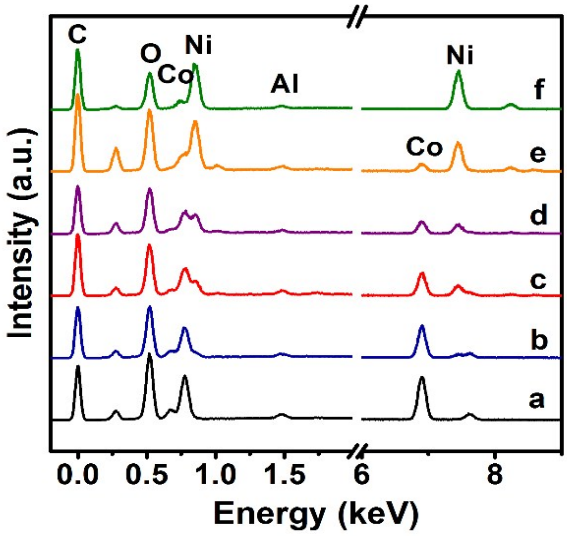

Fig.S6 EDX anlysis of (a) Co_3O_4, (b) Co_6-Ni_1-O, (c) Co_2-Ni_1-O (d) Co_1-Ni_1-O (e) Co_1-Ni_6-O and (f) NiO.

Table S2 Textural parameters of Ni_x-Co_y-O, Co_3O_4, NiO obtained by calcining intermediates at 300 °C for 2 h.

	BET surface area (m^2 g^{-1})	**Pore volume (cm^3 g^{-1})**	**Pore diameter (nm)**
Co_3O_4	160	0.71	15.7
Co_6-Ni_1-O	166	0.76	16.2
Co_2-Ni_1-O	181	0.83	23.7
Co_1-Ni_1-O	215	0.79	14.7
Co_1-Ni_6-O	159	0.68	14.9
NiO	150	0.21	5.6

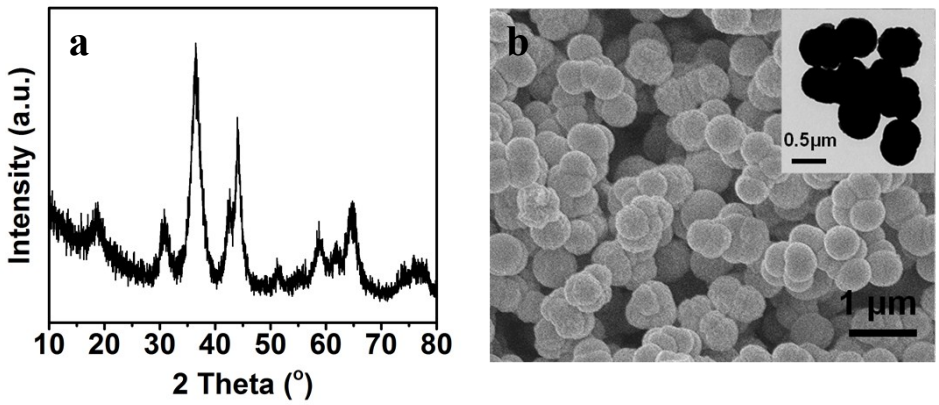

Fig.S7 (a) The XRD pattern and (b) SEM image of the obtained *s*-Co_2-Ni_1-O (solid spheres), the inset is the corresponding TEM image. As shown in Fig. S7a, XRD pattern shows the *s*-Co_2-Ni_1-O can be indexed to spinel $NiCo_2O_4$, SEM and TEM images shown in Fig. S7b reveal that *s*-Co_2-Ni_1-O is composed of solid spheres with size of 0.5-0.8 μm.

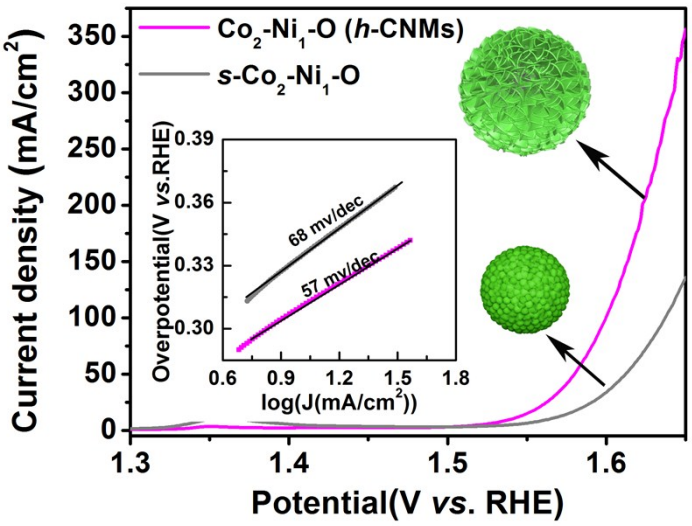

Fig. S8 LSV curves of Co_2-Ni_1-O and *s*-Co_2-Ni_1-O, the inset is the corresponding Tafel slopes.

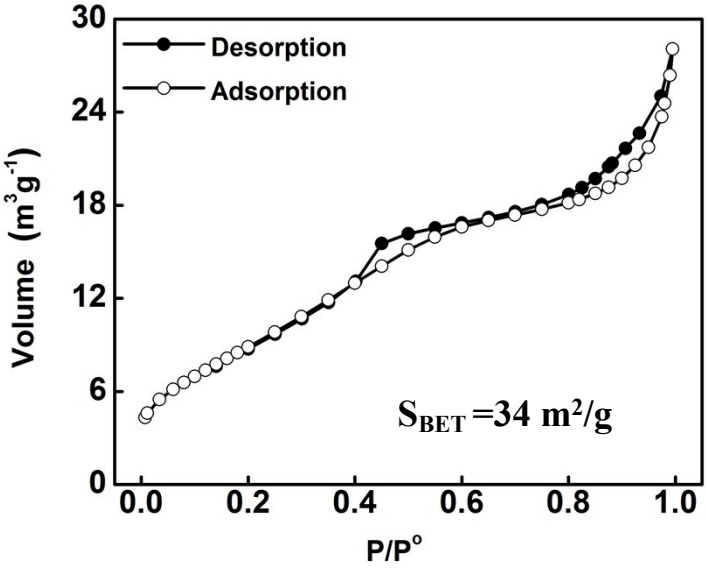

Fig. S9 N_2 adsorption-desorption isotherms of *s*-Co_2-Ni_1-O.

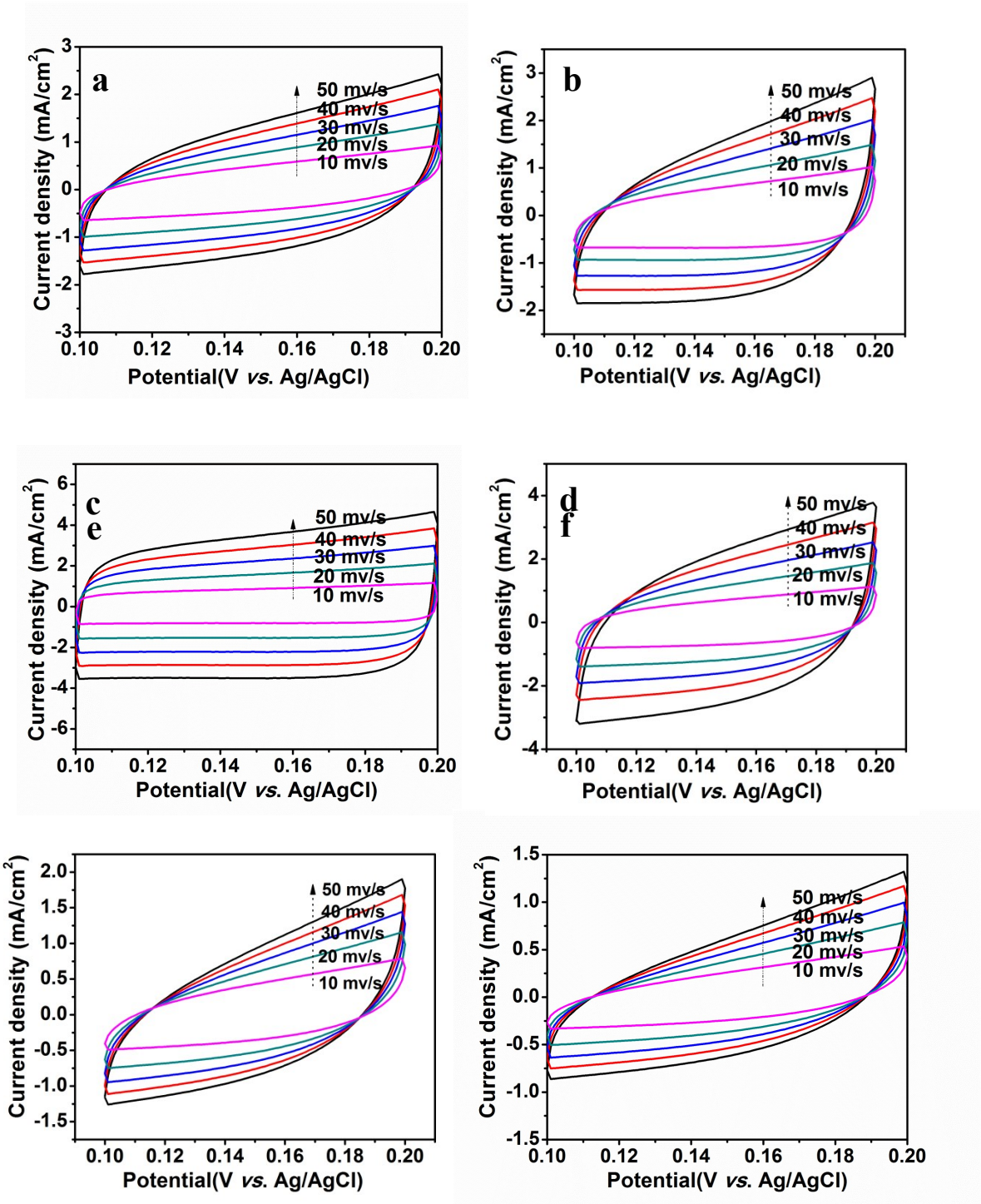

Fig.S10 Cyclic voltammetry (CV) curves of (a) Co_3O_4, (b) Co_6-Ni_1-O, (c) Co_2-Ni_1-O (d) Co_1-Ni_1-O (e) Co_1-Ni_6-O and (f) NiO tested at various scan rates from 10 to 50 mV s^{-1}.

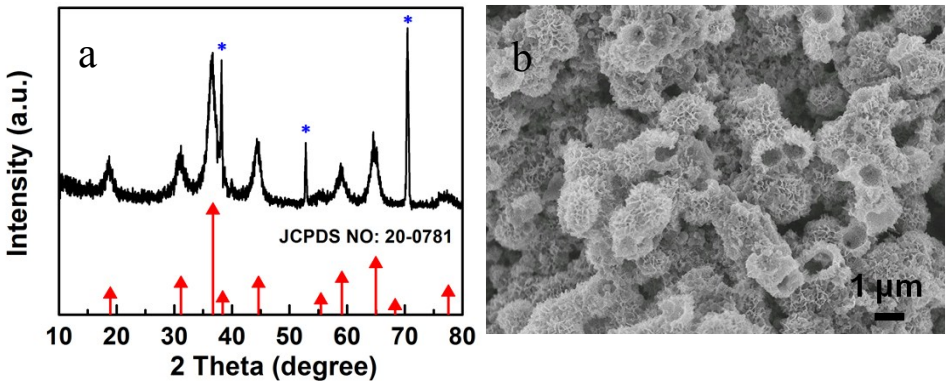

Fig. S11 (a) The XRD pattern and SEM image of Co_2-Ni_1-O after long-term durability test under a static overpotential of 310 mV. To investigate the structure and component of Co_2-Ni_1-O after OER for 12 h, 5 mg Co_2-Ni_1-O suspensions were loaded on the polished Ti plate to conduct OER. After the durability test, the catalyst on the Ti plate was used for XRD measurement. The three diffraction peaks labeled "*" were indexed to Ti.

Table S3 Comparison of OER activities for some cobalt nickel oxides catalysts in basic solution.

Catalyst	Electrolyte	Substrate	Overpotential	Tafel slope /mV dec^{-1}	Ref.
Co_2-Ni_1-O	**1M KOH**	**Ni**	**310 mV at 10 mA cm^{-2} 370 mV at 100 mA cm^{-2}**	**57**	**This work**
Core-ring $NiCo_2O_4$	1M KOH	Ni	315 mV at 100 mA cm^{-2}	54	*Adv. Funct. Mater.* **2008**, 18, 1440.
$NiCo_2O_4$	1M KOH	Ni	438 mV at 100 mA cm^{-2}	59	*Adv. Funct. Mater.* **2008**, 18, 1440.
$Ni_xCo_{3-X}O_4$ nanowire (Ni/Co= 1:0.3)	1M NaOH	Ti foils	-	54	*Adv. Mater.* **2010**, 22, 1926.
Ni-Co 3D nanosheets	1M NaOH (pH13.6)	FTO	340 mV at 10 mA cm^{-2}	51	*Adv. Energy Mater.* **2015**, 5, 1500091.
Bulk $NiCo_2O_4$	1 M KOH	GCE	420 mV at 10 mA cm^{-2}	57	*Angew. Chem. Int. Ed.* **2015**, 54, 7399
$NiCo_2O_4$	1M NaOH	-	290 mV at 10 mA cm^{-2}	53	*Angew. Chem. Int. Ed.* **2016**, 55, 1
N-doped graphene $NiCo_2O_4$ film	KOH	Graphene films	373 mV at 5 mA cm^{-2}	156	*ACS Nano* **2013**, 7, 10190.
Needle like $NiCo_2O_4$	1 M NaOH	-	370 mV at 10 mA cm^{-2}	65.46	*ACS Appl. Mater. Interfaces* **2017**, 9, 44567.
Ni-Co_2-O	0.1 M KOH	GCE	362 mV at 10 mA cm^{-2}	64.4	*Chem. Commun.* **2015**, 51, 7851
$NiCo_2O_4$ nanostructures	0.1 M KOH	GCE	340 mV at 10 mA cm^{-2}	75	*Dalton Transactions* **2015**, 44, 4148
$NiCo_2O_4$ nanoneedles	1M KOH	FTO	323 mV at 10 mA cm^{-2}	292	*J. Phys. Chem. C* **2014**, 118, 25939
$NiCo_2O_4$ nanosheets	1M KOH	FTO	-	393	*J. Phys. Chem. C* **2014**, 118,

					25939.
Hierarchical hollow urchins of $NiCo_2O_4$	1 M NaOH	RDE	419.3 mV at 10 mA cm^{-2}	51.3	*J. Power Sources* **2014**, 268, 341
$NiCo_2O_4$ nanowires arrays	1 M KOH	FTO	460 mV at 10 mA cm^{-2}	-	*J. Mater. Chem. A* **2014**, 2, 20823
$NiCo_2O_4$ core-shell nanowire	1 M NaOH	Carbon cloth	320 mV at 10 mA cm^{-2}	63.1	*Nano Energy* **2015**, 11, 333