Electronic Supplementary Information

Ultrathin Defect-rich Nickel Cobalt Oxide Nanosheet Array for Enhanced Bifunctional Oxygen Electrocatalysis

Wanru Chen[a,§], Weikai Xiang[a,§], Wenbo Li[a], Hao Zhang[b], Fuping Du[c], Tiejun Zhao[c], Qi Xiao*[a], Xiaopeng Li*[a], Wei Luo[a]

[a.] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

[b.] Institute of Functional Nano and Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Collaborative Innovation Center of Suzhou Nano Science & Technology, Soochow University, Suzhou 215123, Jiangsu, China

[c.] Jiangsu JITRI-Topsoe Clean Energy Research and Development Co., Ltd. 2266 Taiyang Road, Suzhou 215100, Jiangsu, China

[§] Wanru Chen and Weikai Xiang contributed equally to this work.

* E-mail: qi.xiao@dhu.edu.cn; xiaopeng.li@dhu.edu.cn

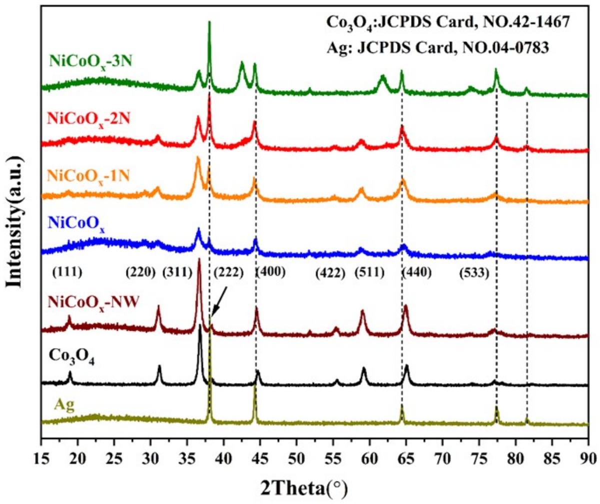

Fig. S1 XRD patterns of Ag, Co_3O_4, $NiCoO_x$-NW, $NiCoO_x$, $NiCoO_x$-1N, $NiCoO_x$-2N and $NiCoO_x$-3N.

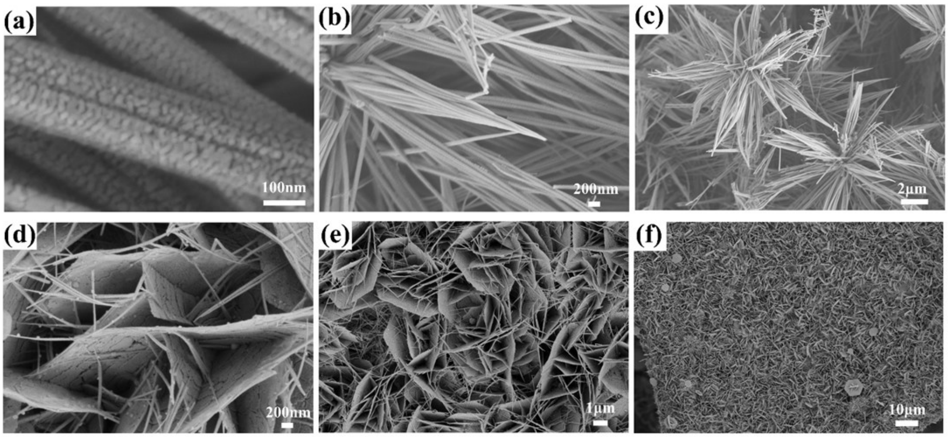

Fig. S2 (a-c) SEM images of $NiCoO_X$-NW. (d-f) SEM images of $NiCoO_X$-2N.

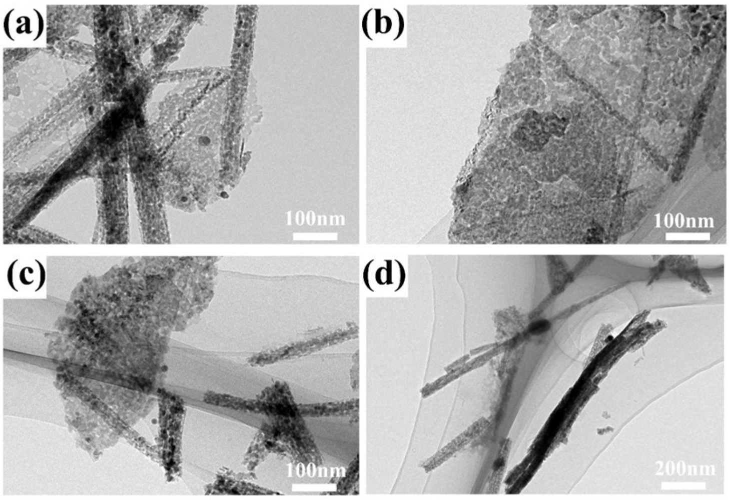

Fig. S3 HRTEM images of $NiCoO_X$-2N.

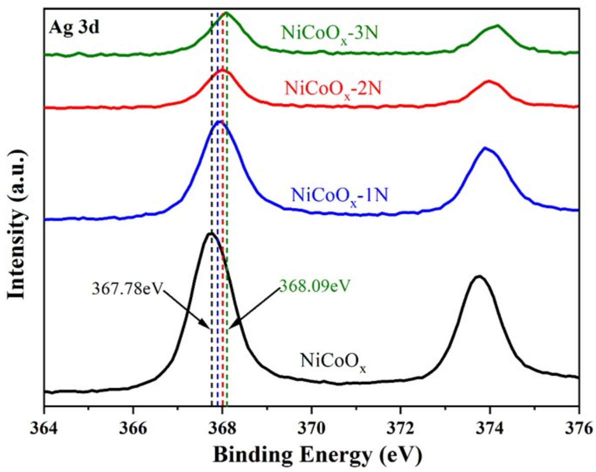

Fig. S4 XPS spectra of Ag 3d for $NiCoO_x$, $NiCoO_x$-1N, $NiCoO_x$-2N and $NiCoO_x$-3N.

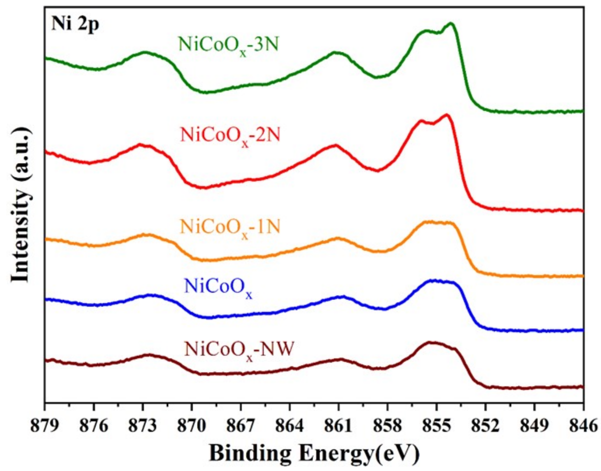

Fig. S5 XPS spectra of Ni 2p for $NiCoO_x$-NW, $NiCoO_x$, $NiCoO_x$-1N, $NiCoO_x$-2N and $NiCoO_x$-3N.

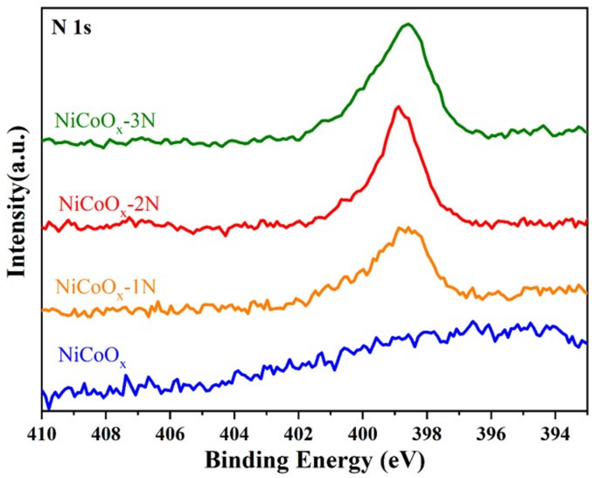

Fig. S6 XPS spectra of N 1s for $NiCoO_x$, $NiCoO_x$-1N, $NiCoO_x$-2N and $NiCoO_x$-3N.

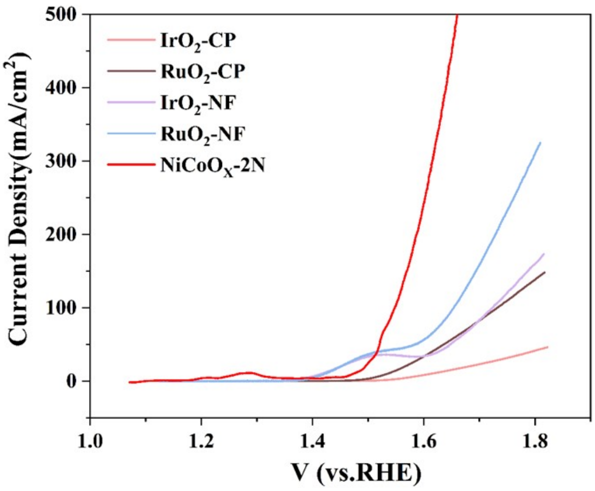

Fig. S7 Comparison of OER performance of $NiCoO_x$-2N with commercial supported RuO_2 and IrO_2 catalysts.

Supplementary Note to **Figure S7**:

We purchased commercial RuO_2 and IrO_2 from Damas-beta, Sigma Aldrich, respectively. The RuO_2 or IrO_2 powder (5.0mg) was dispersed in a solution of isopropanol and water with a volume ration of 1:3 (1mL). 20µl of Nafion solution was added as a binder. The mixture was subjected to ultrasonication for more than 30 min to obtain a homogenous catalyst ink. The ink was drop casted onto the nickel foam (NF) or carbon paper (CP) in a geometric area of 1cm^{-2}. The catalyst loading was controlled at approximately 1.0 mg cm^{-2}. The dried nickel foam or carbon paper electrode was then subjected to electrochemical measurements. The reason of using carbon paper as electrode is that carbon paper has very low OER activity. Nickel foam itself has some OER activity, and therefore nickel foam loaded with electrocatalysts performs better than the carbon paper loaded ones. There is one oxidation peak cantered at ~1.5V in the LSV curve in nickel foam loaded with RuO_2 or IrO_2, which is caused by the electrooxidation of Ni species to higher valence.

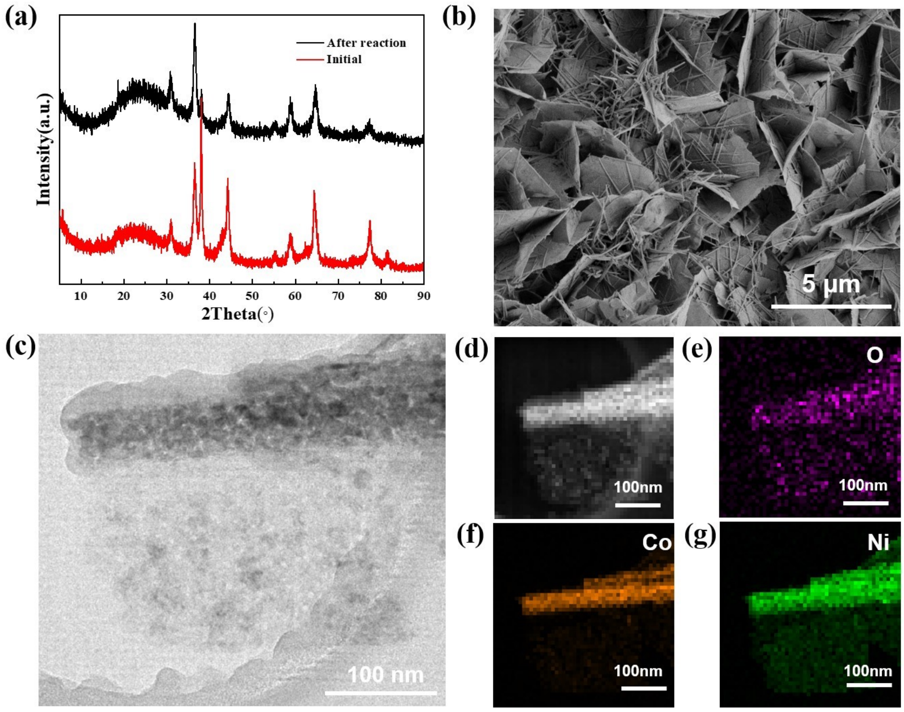

Fig. S8 (a) XRD patterns of $NiCoO_x$-2N catalyst before and after reaction. (b) SEM image of $NiCoO_x$-2N catalyst after reaction. (c) TEM image of $NiCoO_x$-2N catalyst after reaction. (d-g) STEM image and corresponding EDS element mapping of $NiCoO_x$-2N catalyst after reaction.

Supplementary Note to **Figure S8**:

After reaction, as shown in the XRD pattern, the major phase of $NiCoO_x$-2N nanosheet was retained, while the intensity of Ag peak at ~38° decreased, this could be due to the partial detachment of Ag particles from the nanosheet during OER. SEM and TEM images of the spent $NiCoO_x$-2N (**Figure S8b,c**) show the nanosheet array remained structurally stable after OER. The EDS mapping shows the co- existence of Co, Ni and O in the nanosheet. The above results prove that the NiCoOx-2N nanosheet array are robust for long-term OER and ORR.

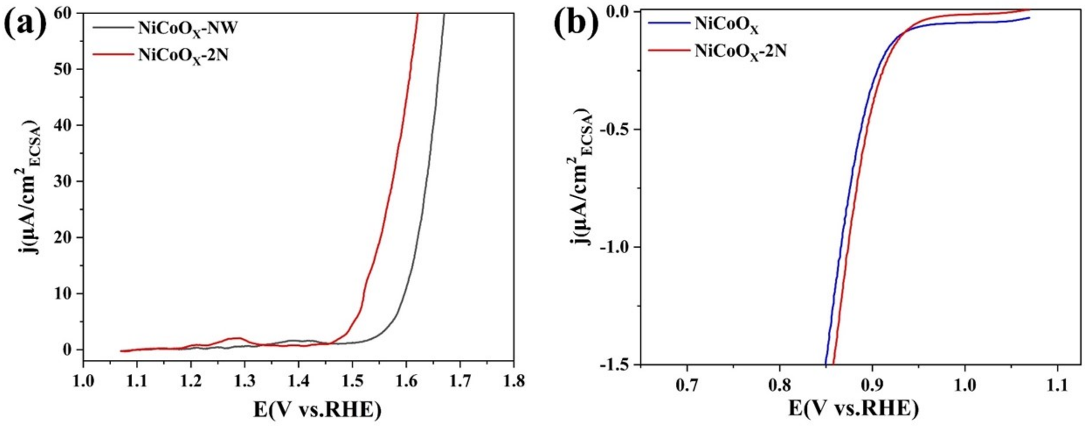

Fig. S9 (a)The activity of $NiCoO_x$-2N for OER normalized by ECSA in 1 mol L^{-1} KOH. (b) The activity of $NiCoO_x$-2N for ORR normalized by ECSA in 1 mol L^{-1} KOH. Note: iR correction was not applied in (a) and (b).

Table S1. Comparison of OER catalytic performances of recent reported nanostructure arrays.

Catalyst	C_{dl} (mF/cm^2)	Tafel slope (mV/dec)	Stability (h)	Ref.
$NiCoO_x$-2N	217	29	200	This
NiFe/$NiCo_2O_4$	-	45.5	10	29
Fe-Co-S/CC	61.2	23.87	48	28
$NiCo_2O_4$-NC	10	77	-	26
Co-$FeSe_2$	41	78	9	27

Table S2. The ECSA of various nanosheet array catalysts in 1 mol L^{-1} KOH.

Catalyst	$NiCoO_x$-2N	$NiCoO_x$-3N	$NiCoO_x$-1N	$NiCoO_x$-NW	$NiCoO_x$
ECSA	5425.0	4792.5	4812.5	2322.5	4137.5