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Supplementary material:

$Na_4Ni_3P_4O_{15}$-$Ni(OH)_2$ core-shell nanoparticles as hybrid electrocatalysts for the oxygen evolution reaction in alkaline electrolytes

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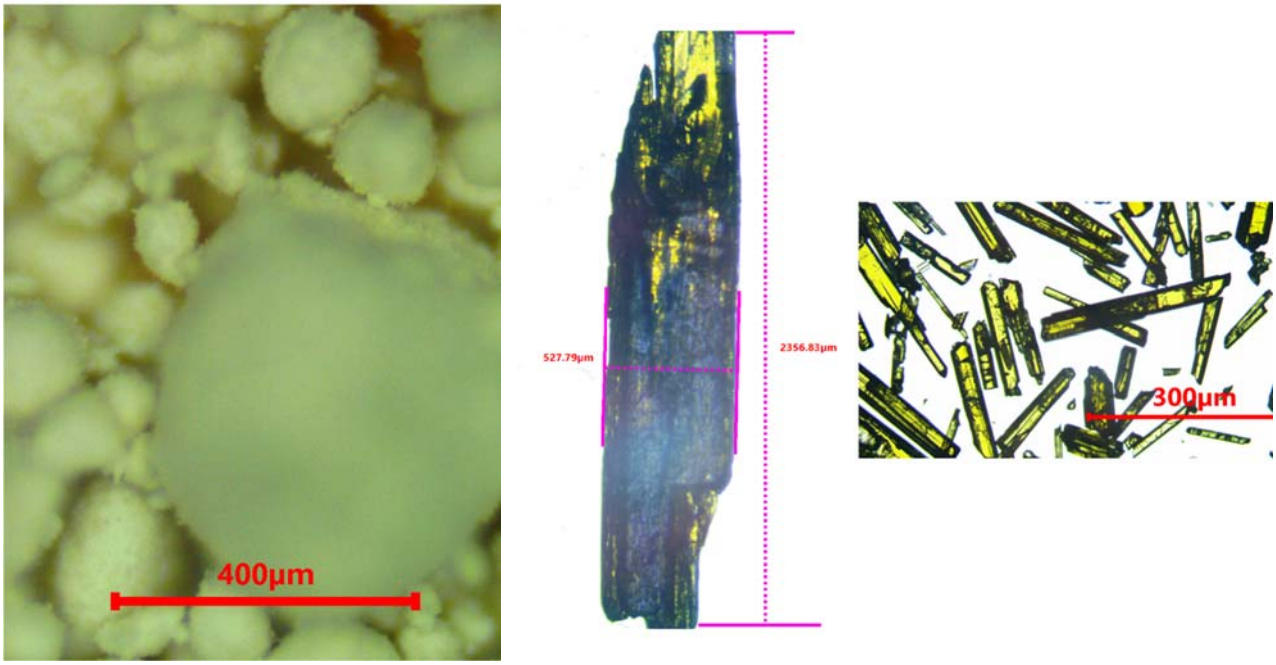


(a) **(b)**

Figure S1. Photomicrographs (a) n-NNP and (b) c-NNP of prepared samples.

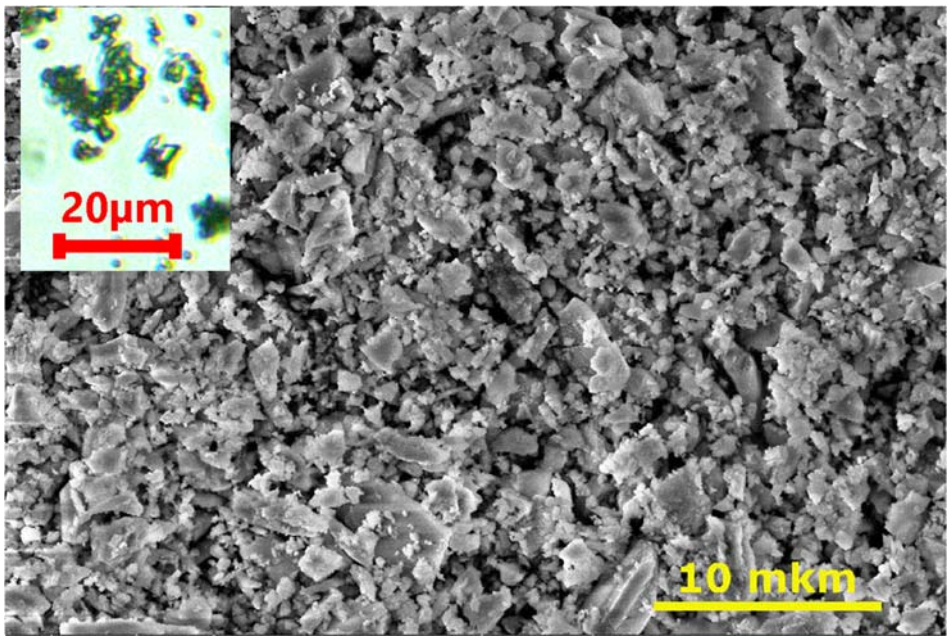


Figure S2. SEM image of powder c-NNP after milling (insert: photomicrograph of sample).

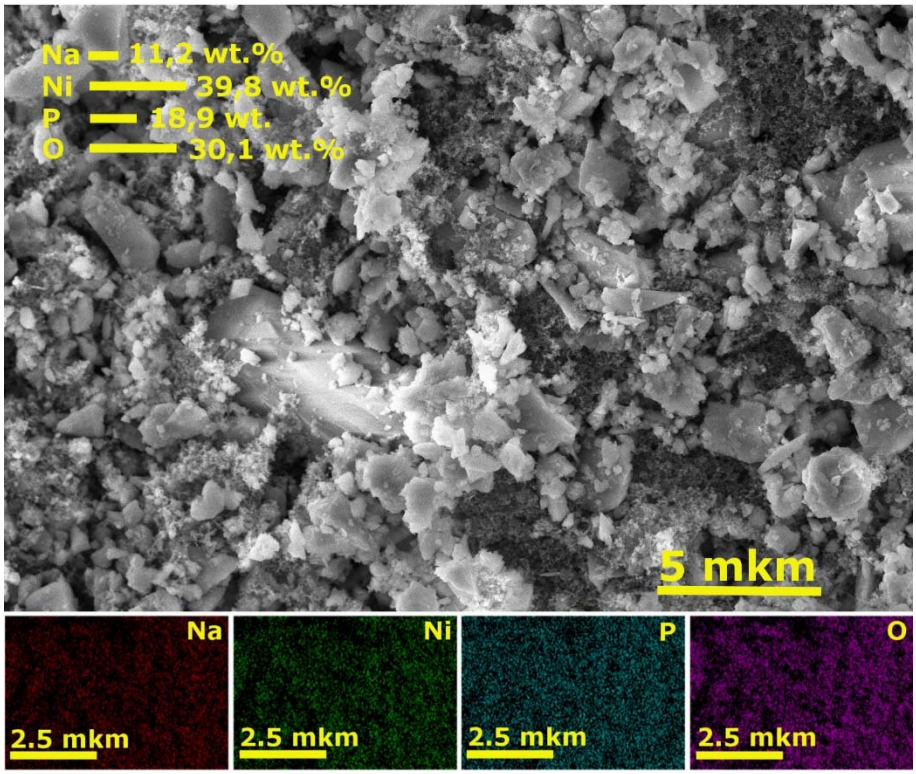


Figure S3. SEM image and elemental mapping of c-NNP/C-CC electrode.

Section: ***Electrochemical measurements***

In all electrochemical measurements a three-electrode cell configuration was used. Calibrated with respect to RHE Hg/HgO electrode was used as the reference electrode (the calibration was performed in the hydrogen saturated electrolyte with a Pt wire as the working electrode: CV curves were run at a scan rate of 1 $mV \cdot s^{-1}$; the average of the two potentials at which the current crossed zero was taken as the thermodynamic potential for the hydrogen electrode reactions):

$$E_{vs.RHE} = E_{vs.Hg/HgO} + 0.921 \text{ V}$$

The overpotential (η) is calculated as the following equation:

$$\eta = E_{vs.RHE} - 1.23 \text{ V}$$

Electrochemical impedance spectroscopy (EIS) results have been analyzed using the ZSimpWin software.

Section: ***Crystallization of the $Na_4Ni_3PO_{15}$ melt***

According to,[68] the mixed-anionic phosphate $Na_4Ni_3(PO_4)_2P_2O_7$ can be synthesized by crystallization of the appropriate $Na_4Ni_3PO_{15}$ melt. In this case, an interaction can be represented by the equation:

$$4NaPO_3 + 3NiO \rightarrow Na_4Ni_3P_4O_{15}$$

To achieve this scheme, the grinded mixture of $NaPO_3$ and NiO (in molar ratio 4:3) was heated up to 1000°C in platinum crucible. Then obtained homogeneous melt was slowly cooled to 400°C (as recommended in[68]). The result of powder XRD analysis showed that the basic crystalline phase in synthesized sample is target phosphate $Na_4Ni_3(PO_4)_2P_2O_7$ (PDF # 01-087-0977), but it also contains significant quantity of other complex phosphates, such as $Na_4Ni_7(PO_4)_6$ (PDF # 01- 084-0845) and $NaNi_4(PO_4)_3$ (PDF # 01-078-0111). Phase composition of samples are illustrated in Figure S4. Further heat treatment in temperature range 400-800°C did not lead to the disappearance of impurity phases. Thus, for synthesis of pure c-NNT we chose another rout, as described below.

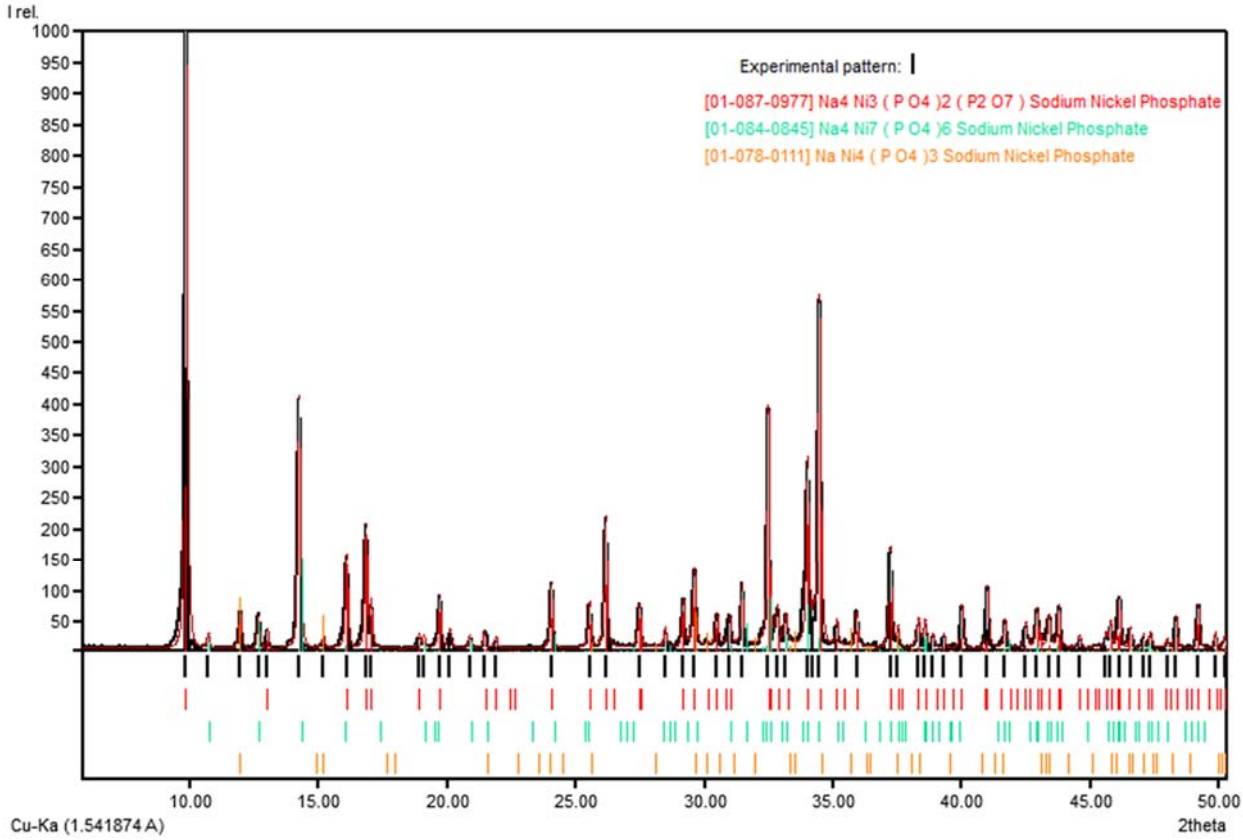


Figure S4. XRD powder data for the crystallized $Na_4Ni_3PO_{15}$ melt.

Section: ***Investigation of crystallization process from Na-Ni-P-O self-fluxes***

In work,[69] the authors applied flux-aimed method for growing the crystalline phase of $Na_4Ni_3(PO_4)_2P_2O_7$ in Na-Ni-P-O system. To develop a procedure for the synthesis of a pure compound, we have performed additional studies. The crystallization of target compound from Na-Ni-P-O flux were conducted at molar ratio of Na:P in range 1.0-1.6 (with increment 0.1 of molar ratio) and fixed value of NiO at 15 wt. %. A typical synthesis procedure was as follows: mixtures with appropriate number of components ($NaPO_3$, $Na_4P_2O_7$ and NiO) were heated to 1000°C in platinum crucibles and kept in isothermal conditions for 4 hours. Then homogeneous fluxes cooled to 700°C at a rate of $20°\times h^{-1}$ and poured out on a copper sheet to freeze the crystallization. Crystalline precipitate was washed by a plenty of hot distilled water and dried at 80°C. The phase compositions of obtained samples were determined by powder X-ray diffraction (Table S1).

Table S1.
The phase composition of samples obtained from fluxes in Na-Ni-P-O system at different molar ratios of Na:P.

Initial molar ratio of Na:P	Phase composition, according to powder XRD data
1.0-1.1	$Na_2NiP_2O_7$ (PDF #00-052-1256)
1.2	$Na_2NiP_2O_7$ (PDF #00-052-1256) and $Na_4Ni_3(PO_4)_2P_2O_7$ (PDF #01-087-0977)
1.3-1.5	$Na_4Ni_3(PO_4)_2P_2O_7$ (PDF #01-087-0977)
1.6	$Na_4Ni_3(PO_4)_2P_2O_7$ (PDF #01-087-0977) and $NaNiPO_4$ (PDF #00-054-0811)

As can see from Table S1, in pure state the mixed-anionic phosphate $Na_4Ni_3(PO_4)_2P_2O_7$ was formed in range of initial limits of Na/P (1.3-1.5) in the flux. In further for electrochemical study we used the sample of c-NNT obtained at molar ratio Na:P = 1.4.

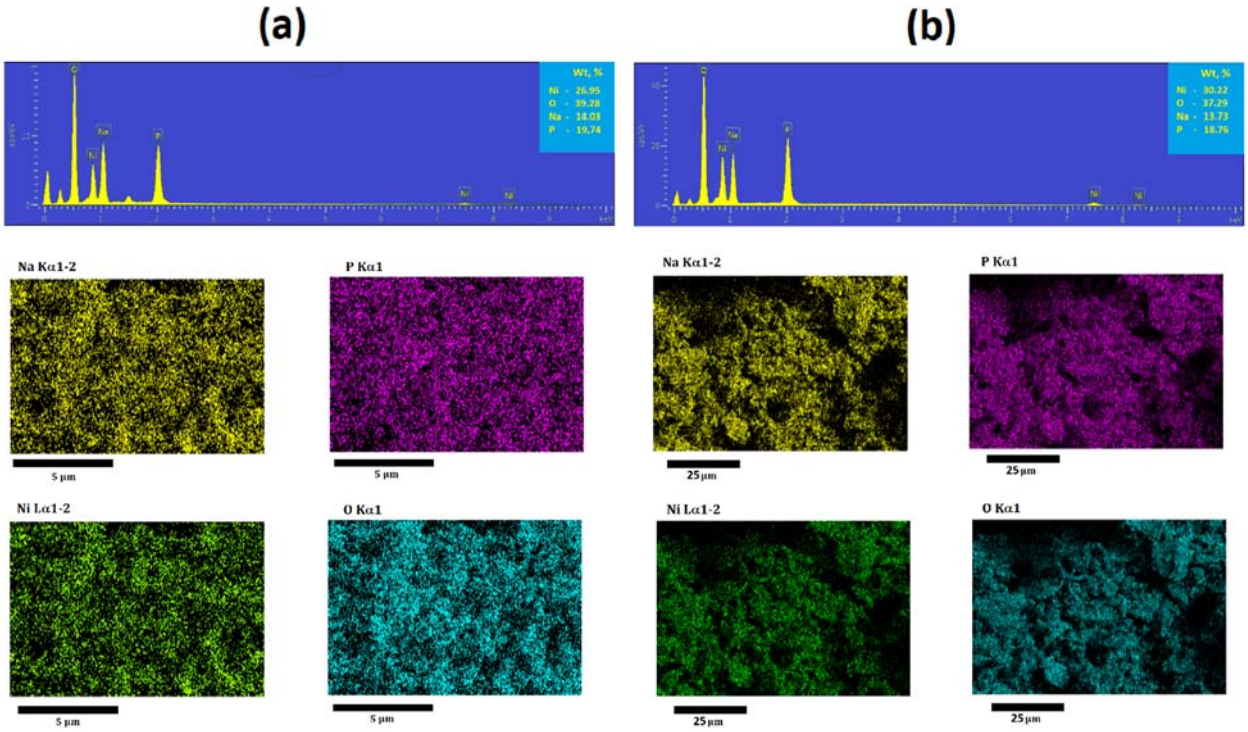
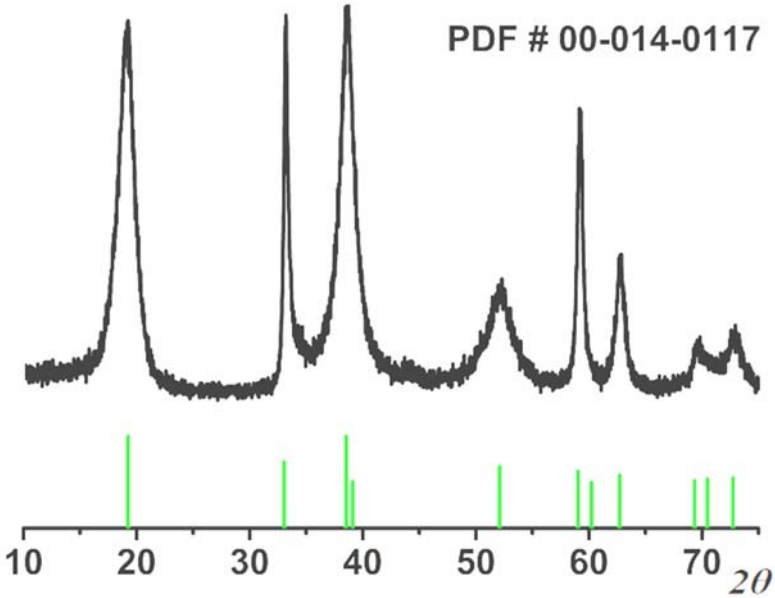
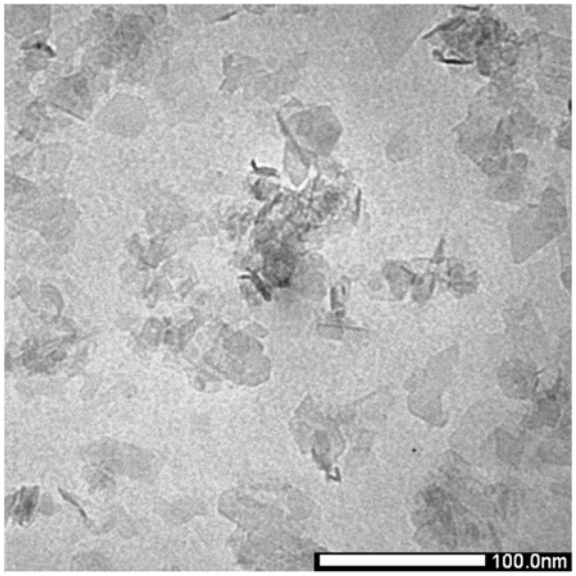


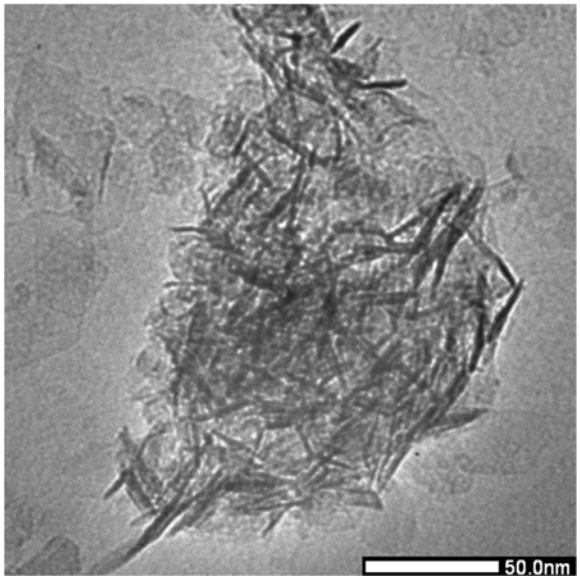
Figure S5. The results EDX and elemental mapping for (a) n-NNP and (b) c-NNP.



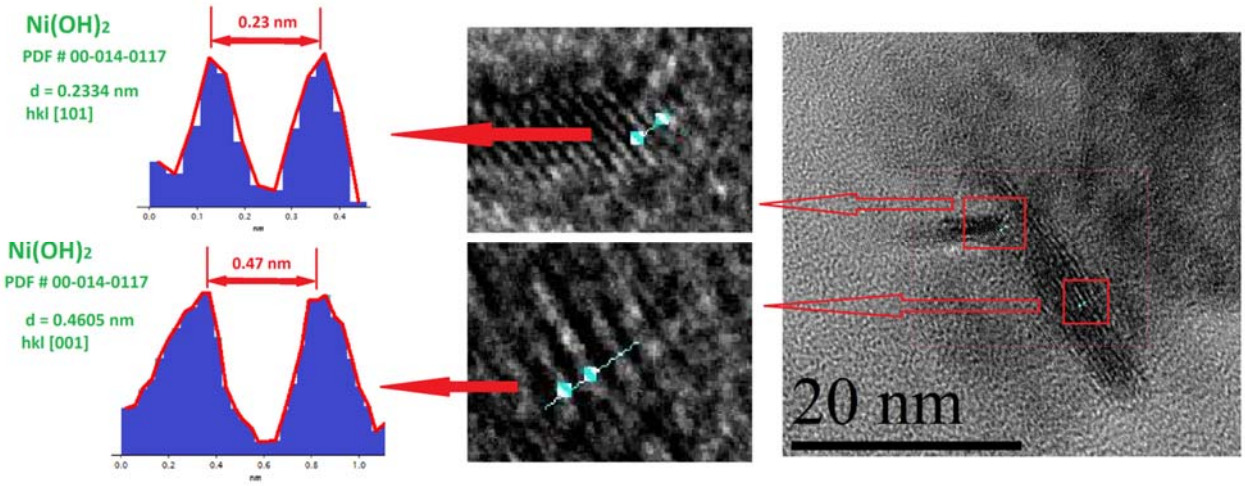
(a)



(b)



(c)



(d)

Figure S6. The results XRD (a), TEM images (b, c) and (d) TEM of high-resolution for n-NNT after treatment alkaline solution (6 M KOH, test time is 1 h).

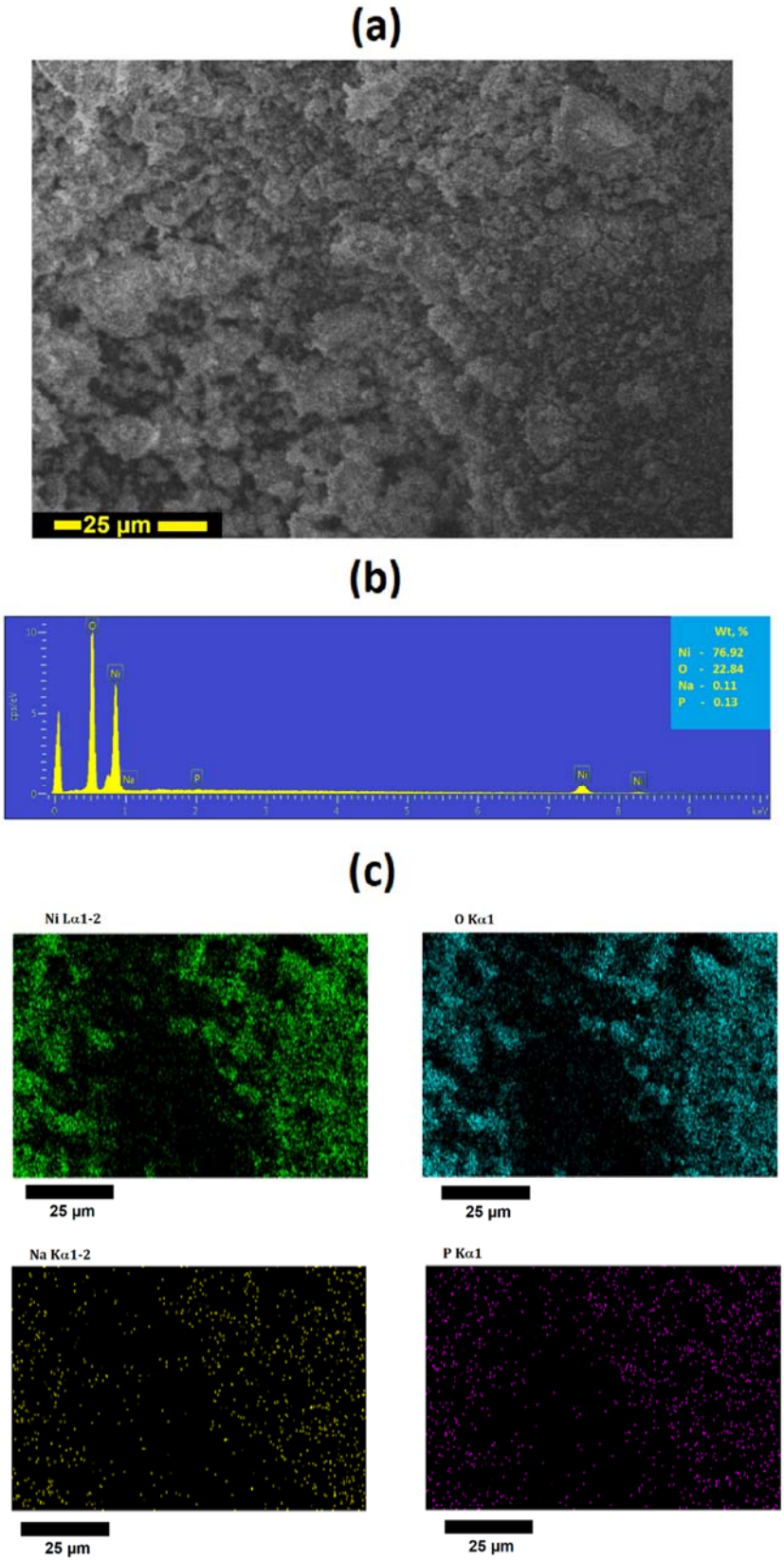


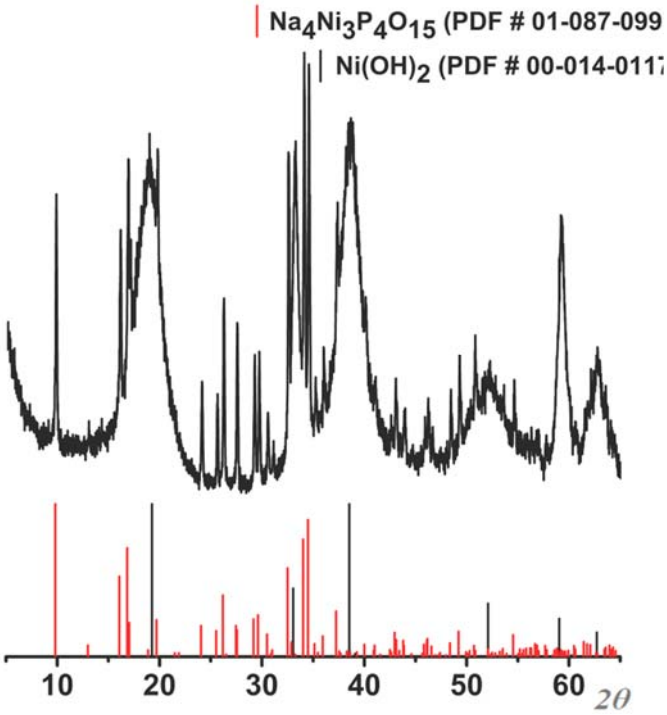
Figure S7. The results SEM (a), EDX (b) and elemental mapping (c) for n-NNT after treatment alkaline solution (1 M NaOH, test time is 1 h).

Section: ***Chemical stability test in solutions of hydroxides***

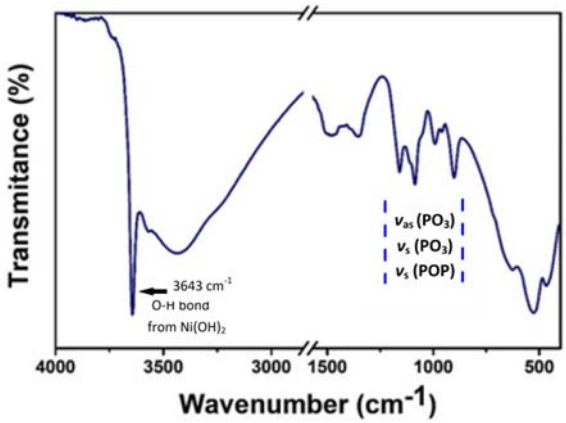
Experiment setup: Initial alkali solutions were prepared by dissolving KOH or NaOH of calculated weights in distilled water. For testing, solutions with alkali concentrations of 6M, 1M, and 0.1 M were used. Powdered samples (n-NNP or c-NNP) weighing from 0.1 to 0.2 g were placed in 10 ml of an alkaline solution and stirred. The shortest contact time of samples with an alkaline solution was 1 h, and the longest – 30 days. Precipitates were filtered off, washed several times with distilled water and dried in air. Initial evaluation of obtained samples was carried out visually (by color change), and also selectively analyzed using XRD, FTIR, SEM and TEM.

Test results for n-NNP: Upon contact of N-NNP with an alkaline solution (regardless of alkali concentration), a color transformation from yellow to light green was almost immediately observed, which indicates formation of $Ni(OH)_2$. In all cases, the quantitative formation of Ni $(OH)_2$ was observed already after 1 h testing. It was confirmed by XRD, SEM and TEM methods (as example, see Fig. S6 and S7). More longer contact of n-NNP with alkaline solutions (1 or 10 days) did not lead to any significant changes in the chemical composition, morphology and phase composition of $Ni(OH)_2$.

Test results for c-NNP: The rate of interaction of c-NNP with an alkaline solution depends on alkali concentration and reaction time. Interaction results of 6M and 1M KOH (or NaOH) differ slightly. After 1 h testing, a slight color change is observed: the yellow powder acquires a weak greenish tint. The depth of green color gradually increases and powders turn light green after about 1 day. Further visual changes do not occur within 29 days. XRD, FTIR and TEM results show that formation of $Ni(OH)_2$ shell around phosphate core ends after about 1 day, and further thickness of this shell varies little (see Fig. S8). In case of interaction of c-NNP with a 0.1 M KOH (or NaOH) solution, formation of $Ni(OH)_2$ layer on the surface of $Na_4Ni_3P_4O_{15}$ crystals is going slower. A gradual color change from yellow to light green takes place during 3 days. After 14 days of interaction, formation of $Ni(OH)_2$ shell ends, and obtained samples become identical to those previously described. Thus, a decrease in concentration of alkaline solution and a change in reaction time make it possible to control the coating thickness of $Na_4Ni_3P_4O_{15}$-$Ni(OH)_2$ core-shell structure.



(a)



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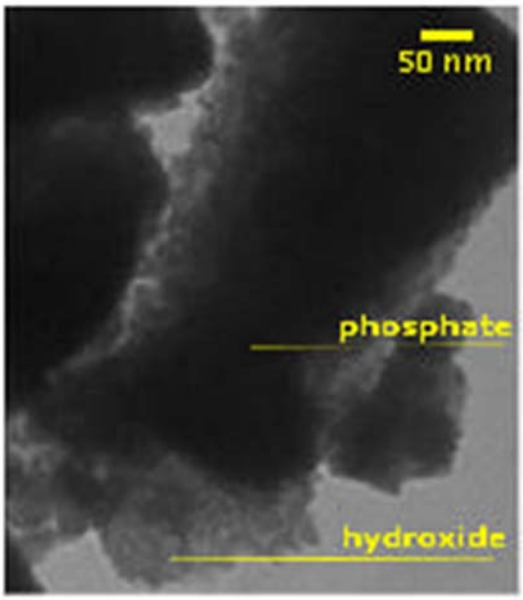

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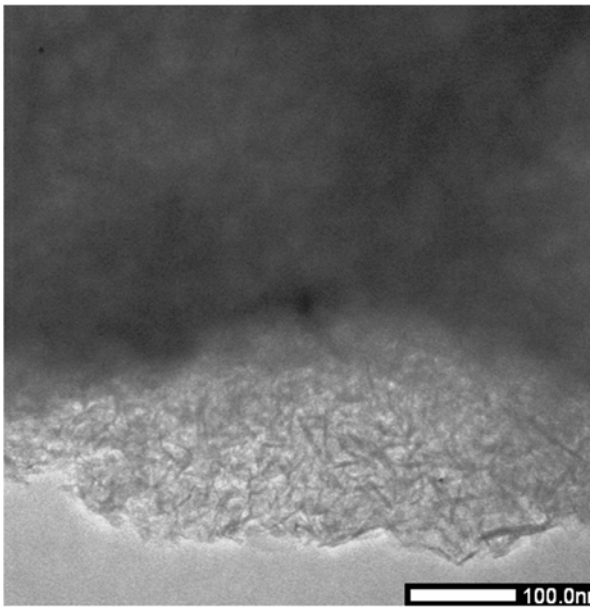

(d)

Figure S8. c-NNT alkaline test results: (a) XRD (6 M KOH, after 30 days test); (b) FTIR spectrum (6 M NaOH, after 30 days test); (c) TEM image (6 M KOH, after 10 days test); (d) TEM image (6 M KOH, after 30 days test).

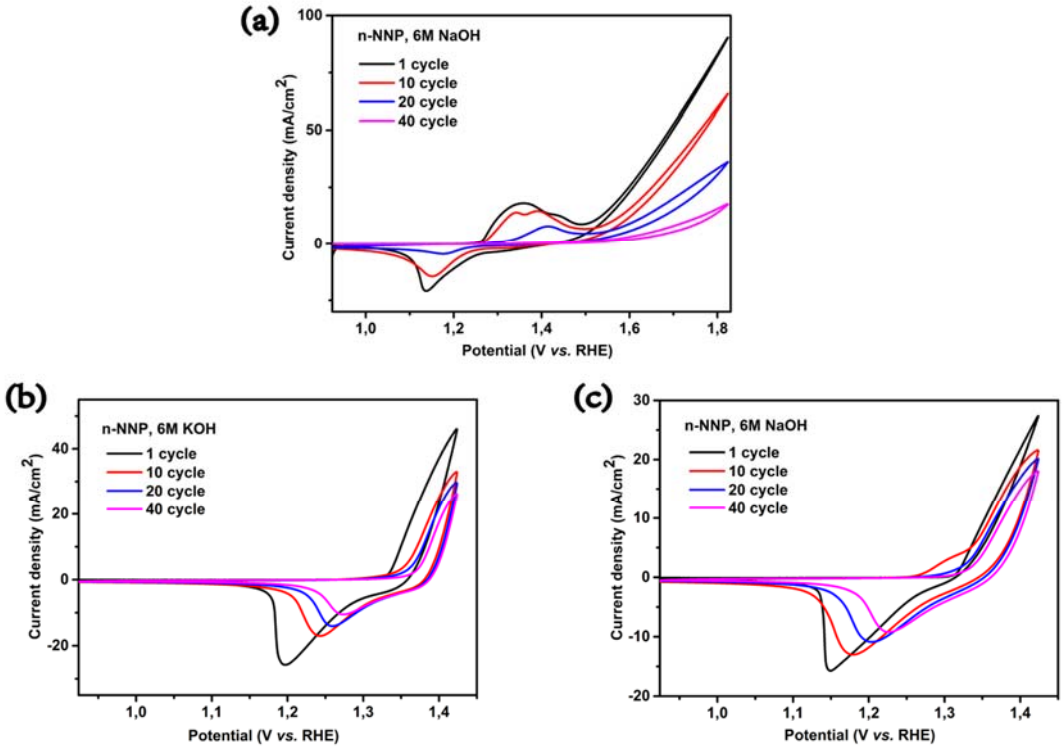

Figure S9. CV curves for n-NNP: (a) 1st, 10th, 20th and 40th cycles in 6 M NaOH (potential window from 0.9 to 1.85 V *vs* RHE); (b) 1st, 10th, 20th and 40th cycles in 6 M KOH (potential window from 0.85 to 1.45 V *vs* RHE); (c) 1st, 10th, 20th and 40th cycles in 6 M NaOH (potential window from 0.85 to 1.45 V *vs* RHE).

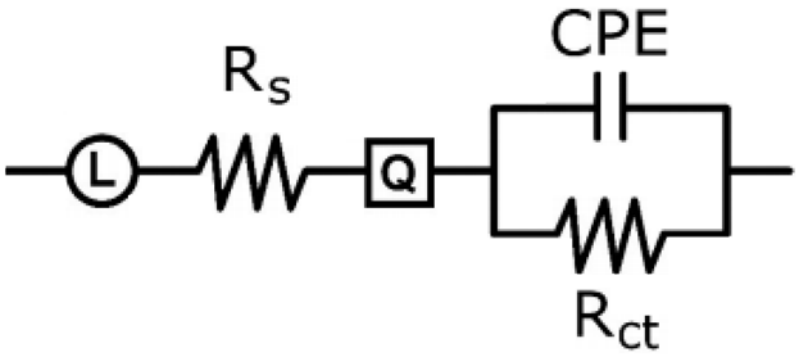

Figure S10. The equivalent scheme for EIS measurement.

Table S2.

Interpretation of components derived from EIS measurements.

Parameters	6M KOH		6M NaOH	
	n-NNP	c-NNP	n-NNP	c-NNP
L x10^{-6} (H·cm^{-2})	8.16	8.45	8.45	9.39
R_s (Ω·cm^{-2})	0.99	1.784	1.457	1.659
Y_o (S·sec^n·cm^{-2})	2.372	6.067	2.328	1.454
Freq power, n (0<n<1)	0.1847	0.2195	0.2855	0.7208
CPE x10^3 (F·cm^{-2})	4.806	4.846	2.517	2.218
R_{ct} (Ω·cm^{-2})	4.025	4.605	6.36	6.84

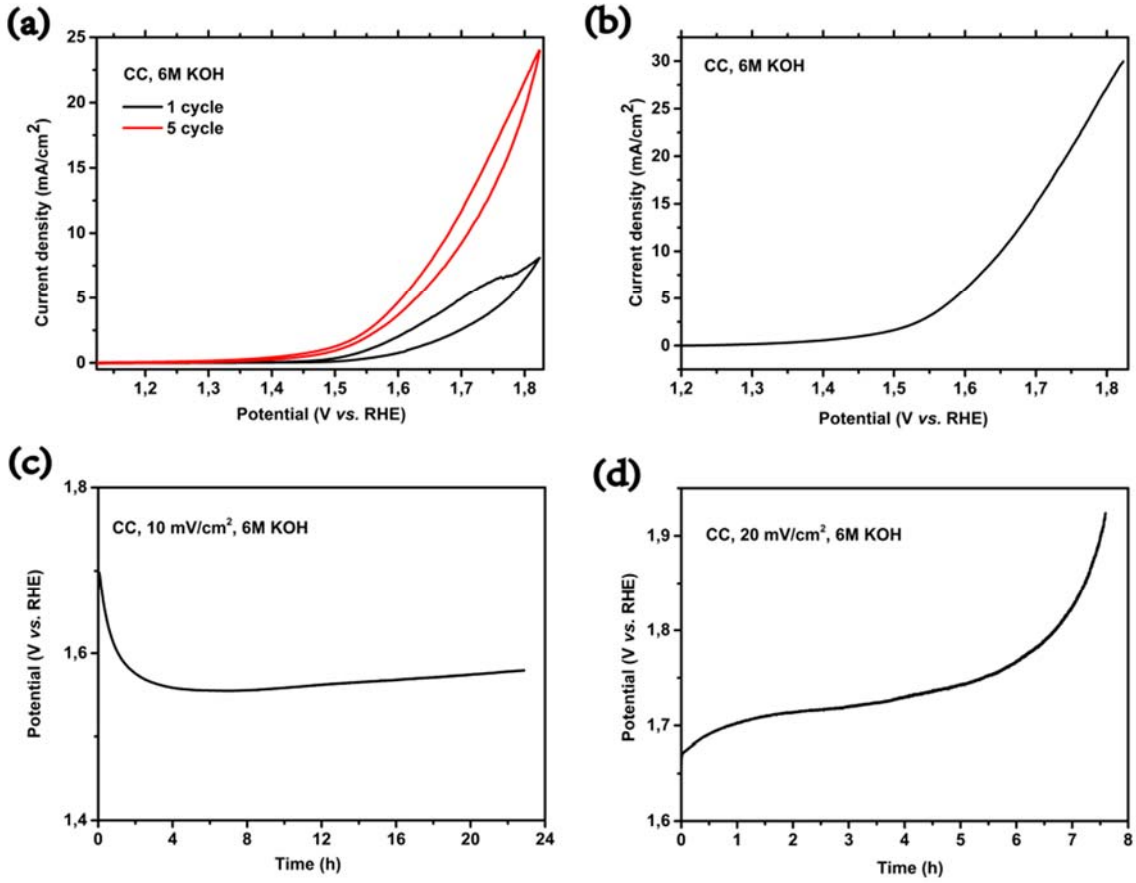

Figure S11. Electrochemical measurements for CC electrode: (a) 1st and 5th CV cycles in 6 M KOH; (b) LSV curve at a scan rate of 1 mV·s^{-1} in 6 M KOH; (c) time dependencies of potential under a constant current density of 10 mA·cm^{-2} in 6 M KOH; (d) time dependencies of potential under a constant current density of 20 mA·cm^{-2} in 6 M KOH.

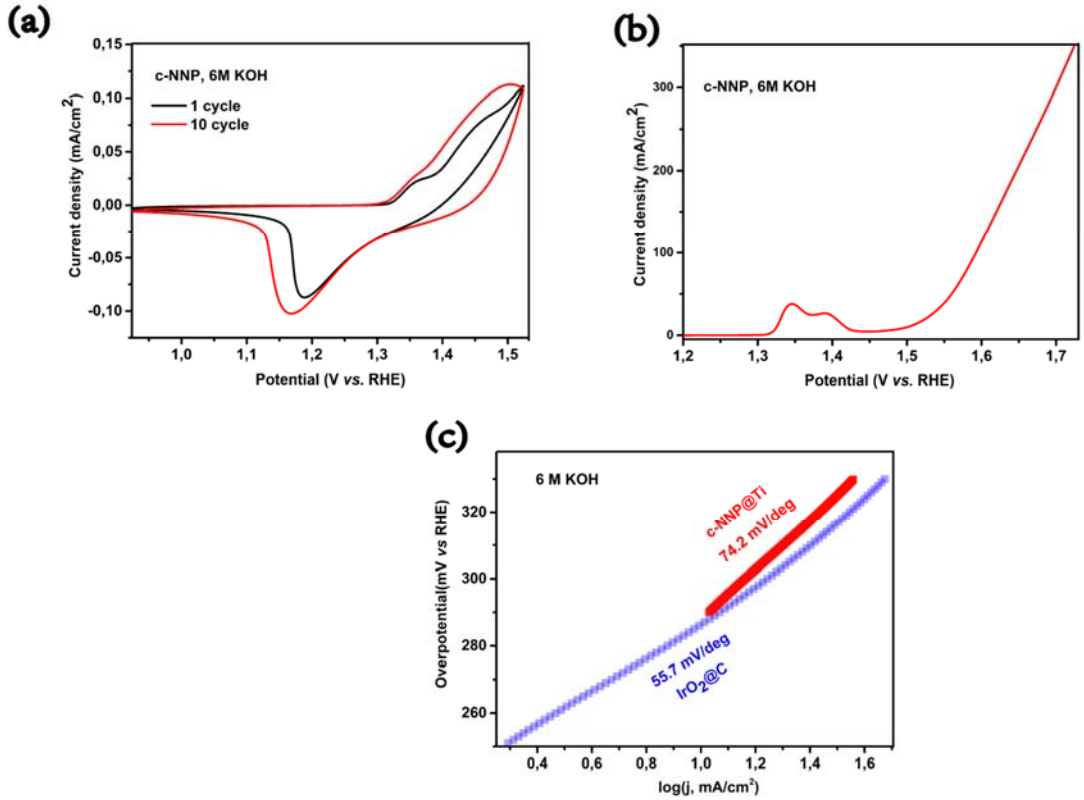

Figure S12. Electrochemical measurements for c-NNP/Ti* electrode in 6 M KOH: (a) 1st and 10th CV cycles; (b) LSV curve at a scan rate of 1 mV·s^{-1}; (c) Tafel plots of c-NNP/Ti and IrO_2/CC at a scan rate of 1 mV·s^{-1}.

*Comment to manufacture of c-NNP/Ti electrode: PVDF, carbon black ("Super P") and c-NNP fine powder (weight ratio of 5:10:85) were alternately added to NMP with stirring. The mixture was vigorously stirred for 1 hour to the resulting viscous suspension. Then a thin layer of the suspension was applied on a titanium mesh and dried at 100 ° C for 24 hours in a vacuum oven. The amount of c-NNP was about 1.8 mg·cm^{-2}.

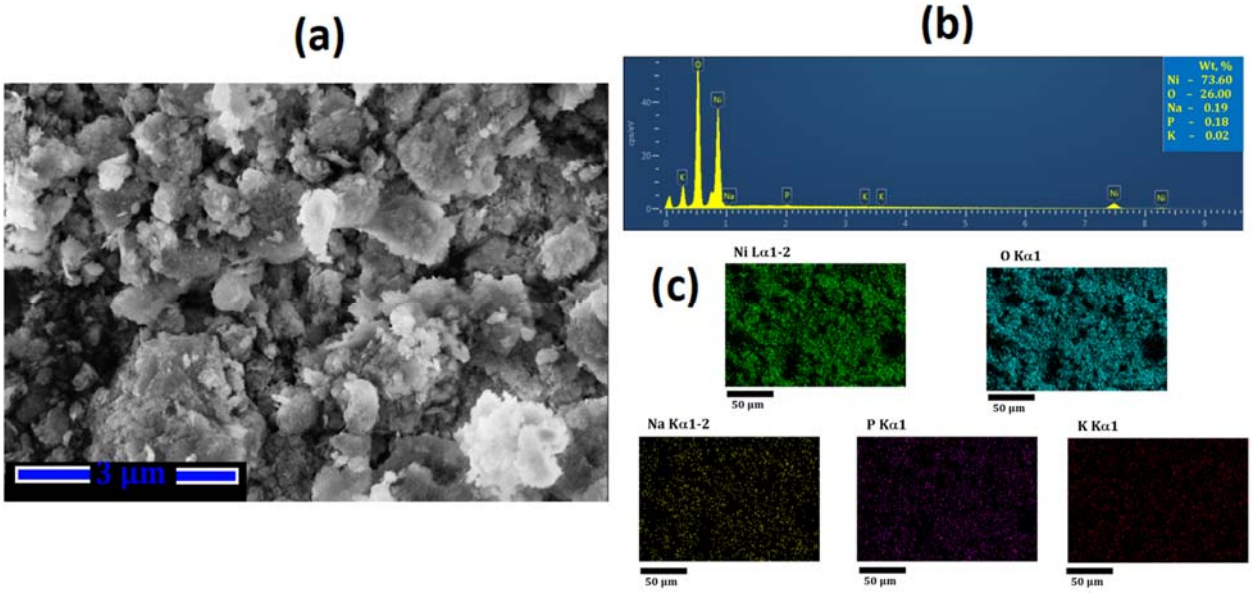

Figure S13. The results SEM for n-NNP-C/CC electrode after CP test in 6 M KOH: (a) SEM image; (b) EDX analysis; (c) elemental mapping.

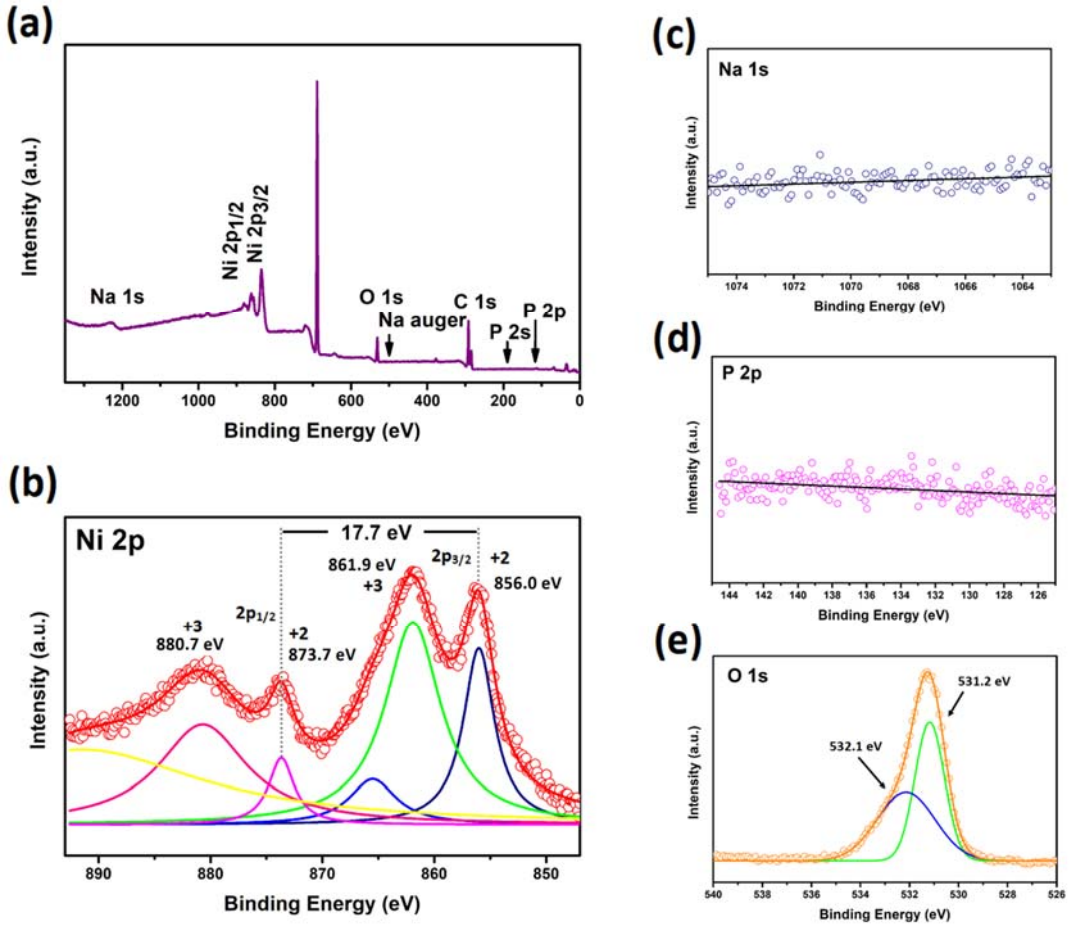

Figure S14. XPS spectra of n-NNP-C/CC electrode after CP test in 6 M KOH: (a) overall spectra and high-resolution for (b) Ni 2p, (c) Na 1s, (d) P 2p, (e) O 1s.

Table S3.
Comparison of morphology, transformation features, OER activity, and stability of the $Na_4Ni_3P_4O_{15}$-C/CC with that of some recently reported Ni (or/and Co)-phosphate-based catalysts tested at current density of 10 mA·cm^{-2} in alkaline media.

Catalyst	Morphology	Electrolyte	Transformation to	Overpotential (mV)	Stability (over)	Reference
FeNi-Pi/NF	NPs	1M KOH	$FeNiO_x(OH)_y$	206	50 h	[77]
NiFe-Pi/NF	AF	1M KOH	$NiFeO_x(OH)_y$	220-230	10 h	[31]
		5 M KOH			10 h	
$Ni_2P_2O_7 \cdot 8H_2O$/SS	MPs	1M KOH	No reported	239	9 h	[47]
NiFe-OH-PO_4/NF	NS	1M KOH	Stable	249*	20 h	[53]
Li(Ni,Fe)PO_4/rGO	NPs	0.1 M KOH	No reported	274-291	24 h	[35]
		1M KOH		258-277		
$Ni_2P_4O_{12}$/CC	NCs	1M KOH	NiOOH doped of PO_4^{3-}	270	100 h	[52]
$(Co_{0.5}Ni_{0.5})_3(PO_4)_2$/NF	3D MFs	1M KOH	No reported	273	30 h	[41]
		6M KOH		246		
Co-Fe-Pyro/GCE	Porous NS	1M KOH	$CoFeO_x(OH)_y$ doped of Co-Fe-Pyro	276	8 h	[79]
$Co_{2-x}Ni_xP_2O_7$-C/rGO	NPs and C	0.1 M KOH	$NiCoO_x(OH)_y$	283-309	8 h	[48]
$Co_3(PO_4)_2 \cdot 8H_2O$	MFs/MPs	1M KOH	No reported	292	10 h	[46]
$LiNi_{0.75}Fe_{0.25}PO_4$-rGO/CC	NPs and rGO	1M KOH	No reported	295	8 h	[49]
Co-Pi-CoP/Ti	NR, C@S	1M KOH	$CoO_x(OH)_y$	310	8 h	[80]
2D-CoH-Pi-C/GCE	MFs and C	1M KOH	$CoO_x(OH)_y$	314	6 h	[81]
$Co_3(PO_4)_2$@N-C/GCE	NPs and N-C	1M KOH	No reported	317	7 h	[45]
$Ni_{12}P_5$@$Ni_3(PO_4)_2$	NPs, C@S	1M KOH	Stable	318	10 h	[59]
$NaCo(PO_3)_3$	NCs and C	1M KOH	No reported	340	12 h	[54]
$Na_4Co_3P_4O_{15}$-C/CC	G, GC or PCs and C	1 M NaOH	$CoO_x(OH)_y$	326–369	50 h	[58]
$Na_4Ni_3P_4O_{15}$-C/CC	GrCs (c-NNP) and C	6 M KOH	HC C@S (c-NNP @$NiO_x(OH)_y$)	250	80 h	This work
		6 M NaOH		280	24 h	This work
	NPs (n-NNP) and C	6 M KOH	$NiO_x(OH)_y$ $NiO_x(OH)_y$	260	24 h	This work
		6 M NaOH		290	24 h	This work

*** - at current density of 20 mA·cm^{-2}**

Abbreviations:

Pi – phosphates
Pyro – pyrophosphate
G – glass
GC – glass-ceramic
PCs – polycrystalline
HC – hybrid composite
GrCs – ground crystals
N-C – N-doped graphitic C layer
SS – stainless steel
NF – nickel foam
GCE – glassy carbon electrode
CC – carbon cloth
rGO – reduced graphene oxide
AF – amorphous film
NPs – nanoparticles
NCs – nanocrystals
NR – nanorods
NS – nanosheets
MPs – micropetals
MFs – microflowers
C@S – core@shell structure