Ultrathin Amorphous Nickel Doped Cobalt Phosphates with Highly Ordered Mesoporous Structures as Efficient Electrocatalyst for Oxygen Evolution Reaction

*Lan Yang, Hao Ren, Qinghua Liang, Khang Ngoc Dinh, Raksha Dangol and Qingyu Yan**

L. Yang, Dr. H. Ren, Dr. Q. Liang, K. N. Dinh, R. Dangol, Prof. Q.Y. Yan

School of Materials Science and Engineering

Nanyang Technological University

Singapore 639798, Singapore

E-mail: alexyan@ntu.edu.sg

Keywords: cobalt phosphate, nickel doping, amorphous mesoporous, oxygen evolution reaction, electrocatalysts

Herein, the authors report the facile preparation of ultrathin (~ 3.8 nm in thickness) two-dimensional (2D) cobalt phosphate (CoPi) nanoflakes through an oil-phase method. The obtained nanoflakes are composed of highly ordered mesoporous (~ 3.74 nm in diameter) structure and exhibits an amorphous nature. Attractively, when doped with nickel, such 2D mesoporous Ni-doped CoPi nanoflakes display decent electrocatalytic performances in terms of intrinsic activity, and low kinetic barrier towards oxygen evolution reaction (OER). Particularly, the optimized 10 at% Ni-doped CoPi nanoflakes (denoted as Ni10-CoPi) delivers a low overpotential at 10 mA cm^{-2} (320 mV), small Tafel slope (44.5 mV dec^{-1}) and high stability for OER in 1.0 M KOH solution, which is comparable to the state-of-the-art RuO_2 tested in the same condition (overpotential: 327 mV at 10 mA cm^{-2} , Tafel slope: 73.7 mV dec^{-1}). The robust framework coupled with good OER performance enable the 2D mesoporous Ni10-CoPi nanoflakes to be promising material for energy conversion applications.

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1002/sml.201906766](#).

This article is protected by copyright. All rights reserved.

Owing to the depletion of fossil fuel and increasing concern on global warming, there is an urgent desire for sustainable and clean energy resources. Hydrogen is deemed as one to the most promising candidate, which could be produced from water electrolysis.^[1] The main challenge is that the anodic reaction of water splitting - oxygen evolution reaction (OER) exhibits sluggish kinetics and high energy barrier (overpotential) because it involves four electron-electron process and O=O bond formation. Highly active electrocatalysts are needed to fasten reaction kinetics and lower that overpotential. However, the benchmark OER catalysts so far are still based on the expensive and low-abundance noble metals such as IrO₂ and RuO₂.^[2]

The past decade has witnessed extraordinary progress on overcoming the bottleneck of OER electrocatalysis by transition metal phosphides,^[3] dichalcogenides,^[4] nitrides,^[5] and thiophosphate materials.^[6] Nevertheless, the real active sites of the above materials remain controversial because their phase, structure, and composition usually undergo obvious evolution under strong oxidation condition.^[3c, 7] It has been reported that the phosphate group plays an important role in facilitating adsorption and stabilizing catalytic centers,^[8] however transition metal phosphates are rarely explored as electrocatalysts for OER. Among the few reports on phosphate materials as OER catalyst, their performances are still far from satisfactory.^[8c, 9] As known, the electrocatalytic performance depends on many factors, such as the number of accessible active sites, mass transport efficiency, and the ability to resist corrosion in electrolytes, which are related to the internal compositional properties as well as the external structure and morphology.^[3c, 10]

Hence, there are multiple effective strategies to optimize the OER performance of transition metal phosphates. Firstly, cation doping can improve the intrinsic activity. Mixed metal cations show more favourable adsorption/desorption of oxygen-containing intermediates than

that of the single-metal counterparts.^[8b, 8c] The transition metal Fe, Co, Ni and their mixed compounds are excellent catalysts in alkaline OER reactions, and different combinations of these three elements can significantly change the properties of the catalysts. It was reported that moderate amount of Fe and Ni doping in cobalt-based catalysts yielded higher OER activity and lower overpotential, which are associated with reduction of the adsorption energy on the catalyst surface, and Fe, Ni substitutions were revealed to facilitate surface reconstruction into active Co oxyhydroxides under OER conditions.^[11] Due to the similar atomic structure of Co and Ni subgroup elements, Ni doping in CoPi is beneficial to keep the original morphology and structure. Moreover, reducing the thickness is another effective way since it can accelerate the mass transport.^[12] Mass transport is an important parameter to describe the transfer rate of electrocatalysts to the electrolyte. Faster mass transport leads to higher electrocatalysts utilization, which means better performance of the electrocatalysts for the same mass loading.^[13] Furthermore, a highly-ordered porous structure such as mesopores can offer higher surface area, which means more active sites are exposed to electrolyte.^[14] The increased effectively active surface area facilitates the adsorption/desorption process and yields better electrocatalytic activity. Besides, the design of amorphous structure has merits such as short-range structure ordering and high density of active sites density.^[15] Compared to crystallized materials, the disordered structures of amorphous electrocatalysts offer more active sites for highly efficient water oxidation.

In consideration of the above merits, herein, a facile oil-phase method is employed to realize the compositional, morphological, and lattice structural engineering of transition metal phosphates. Particularly, the amorphous 10 at% Ni doped CoPi nanoflakes (denoted as Ni10-CoPi) composed of highly ordered mesoporous structure were prepared as an efficient and electro-stable OER electrocatalyst. The obtained mesoporous Ni10-CoPi nanoflakes show an ultrathin thickness of ~3.8 nm and an average pore diameter of ~3.74 nm. During OER

process, the as-prepared Ni10-CoPi electrodes show a decent activity with low overpotential of 320 mV at 10 mA cm⁻² and small Tafel slope of 44.5 mV dec⁻¹.

We prepared the mesoporous CoPi nanoflakes with different Ni doping content of 0%, 5%, 10% and 15% based on a modified oil-phase method (see Experimental Section for details).^[16] The Co/Ni atomic ratio of the as-obtained CoPi, Ni5-CoPi, Ni10-CoPi and Ni15-CoPi was confirmed by individually coupled plasma-optical emission spectrometry (ICP-OES), which is close to that was used in the corresponding synthesis (**Table S1, Supporting Information**).

X-ray diffraction (XRD) patterns of the synthesized CoPi, Ni5-CoPi, Ni10-CoPi and Ni15-CoPi (**Figure 1a**) show no sharp diffraction peak, indicating the amorphous nature of the tested samples. To investigate the chemical bonds and oxidation states of the obtained materials, X-ray photoelectron spectroscopy (XPS) was performed on CoPi and Ni10-CoPi (**Figure 1b-d; Figure S1, Supporting Information**). In the high-resolution Co 2p XPS spectrum (**Figure 1b**), the spin-orbit doublets of Co 2p_{3/2} and Co 2p_{1/2} are located at binding energy of 797.4 and 781.64 eV, respectively. The spin energy interval is around 16.76 eV, suggesting the existence of Co²⁺.^[17] In the corresponding Ni 2p profile (**Figure 1c**), the main two strong peaks observed at the binding energy of 856.23 and 873.88 eV can be attributed to 2p_{3/2} and 2p_{1/2} from the Ni²⁺ species, respectively.^[18] The P 2p (**Figure 1d**) and O 1s (**Figure S1b, Supporting Information**) XPS spectra show the feature peaks at 133.7 and 531.2 eV, respectively, which matches the characteristic peaks of (PO₄)³⁻.^[19] The P 2p and C 1s (**Figure S1c, Supporting Information**) spectra revealed the existence of P-C bonding with the corresponding feature peak showing at 132.7 and 285.2 eV, respectively.^[20]

To characterize the morphology of the obtained materials, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were carried out. The low-magnification TEM images

clearly reveal the nanoflakes morphology of Ni10-CoPi with a lateral size of > 800 nm (**Figure 2a**). The low and high magnification SEM images in **Figure S2** also confirmed such 2D layered nanoflakes structure. Furthermore, the high-resolution TEM (HRTEM) images in Figure 2b-c show that there are many channels on the nanoflakes. The distance between the centres of two neighbouring channels (defines as D_{center}) is measured to be ~ 3.74 nm (inset of Figure 2c), indicating the mesoporous structure of the obtained material. The HRTEM images of CoPi, Ni5-CoPi, and Ni15-CoPi show the same mesoporous morphology and very similar pore diameters of ~ 3.42 , ~ 3.4 and ~ 3.75 nm, respectively (**Figure S3, Supporting Information**). The selected area electron diffraction (SAED) pattern further confirms the amorphous nature of the material (inset of Figure 2b), which agrees well with the XRD result above. The low-angle X-ray diffraction (XRD) in Figure 2d shows three resolved diffraction peaks. According to Bragg's law ($2d \sin \theta = n\lambda$), the d values for the three peaks are calculated to be 1.87, 1.26 and 0.94 nm. The three d values is approximately $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ of the D_{center} , thus indicating that the three peaks can be accordingly indexed as (200), (300) and (400) reflections and proves that the mesopores are highly ordered distributing along the [100] direction. The low-angle XRD patterns of Co-Pi, Ni5-CoPi and Ni15-CoPi nanoflakes (**Figure S4, Supporting Information**) also show the same correlation between the d values and D_{centre} , indicating that Ni-doping does not affect the structure and morphology of the synthesized materials. It is worth noting that the thickness of the flake measured by atomic force microscopy (AFM) (~ 3.8 nm) is very close to d and D_{center} (**Figure S5, Supporting Information**), indicating that the nanoflake may contain only one layer of the mesoporous channels. The ultrathin nature of the materials is conducive to mass transport and charge transfer, which leads to high electrocatalytic performance towards water oxidation. The Brunauer-Emmett-Teller (BET) surface area obtained from N₂ adsorption-desorption isotherms is $35 \text{ m}^2 \text{ g}^{-1}$, and the pore size distribution calculated by the Barrett-Joyner-Halenda

(BJH) method shows a narrow peak with a mean value of 4.5 nm (**Figure S6, Supporting Information**). The mesoporous structures provide a large surface area and expose more active sites. Beside, mesoporous structure has the advantages of regular channel structure and narrow pore size distribution, which is conducive to the adsorption and desorption process during OER. Moreover, the energy dispersive X-ray spectroscopy (EDX) elemental mapping confirmed the presence of P, Co, and Ni and their uniform distribution overlapping the Ni10-CoPi nanoflakes, which is consistent with the XPS results (**Figure S7, Supporting information**).

To study the electrocatalytic performance of Ni10-CoPi, we tested the Ni10-CoPi nanoflakes for OER in the alkaline solution of 1.0 M KOH. A three-electrode system was used with a glassy-carbon electrode coated with catalyst as the working electrode, carbon rod and Hg/HgO as the contact and reference electrode respectively. The OER activities of CoPi, Ni5-CoPi, Ni15-CoPi, and commercial RuO₂ were also evaluated for comparison.

In the *iR*-compensated polarization curves obtained by steady-state linear sweep voltammetry (LSV), it can be seen that the Ni10-CoPi electrode exhibits an onset overpotential of 272 mV (**Figure 3a**), which is obviously lower than those of CoPi (302 mV), Ni5-CoPi (286 mV) and Ni15-CoPi (279 mV). The polarization curves without *iR*-correction (**Figure S8, Supporting Information**) show an onset overpotential of 272 mV for Ni10-CoPi, which is lower than those of CoPi (303 mV), Ni10-CoPi (287 mV) and Ni15-CoPi (280 mV). Moreover, Tafel slopes obtained from Tafel equation indicate that Ni10-CoPi electrode has faster OER kinetics with a smaller Tafel slope of 44.5 mV dec⁻¹. The Tafel slope of CoPi, Ni5-CoPi and Ni15-CoPi is 68.3, 55.1, and 51.2 mV dec⁻¹, respectively (Figure 3b). Tafel slope of CoPi is more than 60 mV dec⁻¹, indicating that the discharge of OH⁻ is the rate-determining step, while the Tafel slope of Ni-doped CoPi is in the range of 40-60 mV dec⁻¹, implying that the

adsorption of OH^{-1} on the catalysts is the rate-determining step. This revealed that Ni doping moves the rate-limiting step to the end of the multi-electron transfer reaction and speed up the OER kinetic process, which is very important for improving the catalytic activity. Besides, the performance of Ni10-CoPi also surpasses the tested OER electrocatalyst RuO_2 , which requires 327 mV to drive a current density of 10 mA cm^{-2} and the corresponding Tafel slope is 73.7 mV dec^{-1} (**Figure S9, Supporting Information**). The respective η_{10} , i.e., required overpotential to realize the current density of 10 mA cm^{-2} , for the optimized Ni10-CoPi nanoflakes is 320 mV, which is smaller than that of CoPi (354 mV), Ni5-CoPi (335 mV) and Ni15-CoPi (325 mV) (**Figure 3c**). To investigate the effect of mesoporous structure on OER, we also synthesized Ni10-CoPi nanoflakes without mesoporous structures by improving the reaction temperature (see Experimental Section) and tested the OER performance under same condition (**Figure S10, Supporting Information**). The TEM images (**Figure S10a-c, Supporting Information**) show that there is no as obvious channels as those on Ni10-CoPi with mesoporous structure, indicating that too high reaction temperature is not conducive to the formation of this morphology. In the OER polarization curve (**Figure S10d, Supporting Information**), Ni10-CoPi without mesoporous structure exhibits the performance nowhere near as good as Ni10-CoPi with mesoporous structure, showing an overpotential of 350 mV at 10 mA cm^{-2} . This contrast furtherly proved that mesoporous structure plays an important role in OER process by providing large surface area and making more active sites exposed. More importantly, the chronoamperometry test performed on carbon paper shows that a stable current density of 20 mA cm^{-2} was maintained for 20 h with ignorable change less than 5%, demonstrating the excellent durability of the electrode (**Figure 3d**). The XRD characterization shows that the Ni10-CoPi electrode still maintains the amorphous structure after 20-hour stability test (**Figure S11a, Supporting Information**), indicating the structural stability during the OER process. For TEM analysis of Ni10-CoPi after stability test, the as-

prepared electrode was dispersed into ethanol by vigorous sonication and then dropped onto the copper grid. TEM characterizations show that the mesoporous structure can be still maintained after 20h OER testing (Figure S11b-c, Supporting Information). On the other hand, it is undeniable that the morphology of the Ni10-CoPi electrode was mostly damaged, which can be attributed to the formation of oxyhydroxide under highly oxidizing OER condition. To specify, post mortem XPS was carried out. As shown in Ni 2p XPS profile (**Figure S12a, Supporting Information**), the two separate peaks at the binding energy of 855.15 and 861.83 eV correspond to the Ni^{2+} and Ni^{3+} states, respectively.^[21] The corresponding peaks of Co^{2+} and Co^{3+} in Co 2p spectrum (Figure S12b, Supporting Information) appear at 781.50 and 779.80 eV, respectively.^[22] Noteworthy, the atomic ratio of $\text{Ni}^{3+}/\text{Ni}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ are all 5:4, indicating that the doped Ni were equally oxidized as Co during OER and played as important role as Co in the electrocatalytic process. Figure S12c in Supporting Information shows the loss of P after OER. In contrast, the O content increases after 20h OER, as revealed by the O 1s spectrum (Figure S12d, Supporting Information). The atomic ratio of P/Co is 0.84:1.69 after OER test from XPS analysis, comparing to the ratio of 16.14:64.4 before OER test. Moreover, P spectrum shifted to higher binding energy, indicating the oxidation of P in the P-C bonding. Furthermore, the two corresponding peaks in the O 1s profile indicate that the ratio of OH^- (531.3 eV) and O^{2-} (533.2 eV) is 2:1, which supports the oxyhydroxide formation during OER.^[23]

The electrochemically effective surface area (ECSA) was estimated to better understand the electrocatalytic properties of the Ni10-CoPi catalyst toward OER by conducting cyclic voltammetry (CV) at various scan rate (**Figure S13, Supporting Information**). The linear fit results in **Figure 4a** reveal that the Ni10-CoPi has a double layer capacitance (C_{dl}) value of $262.8 \mu\text{F cm}^{-2}$, which is comparable with that of CoPi ($277.7 \mu\text{F cm}^{-2}$), Ni5-CoPi ($259.2 \mu\text{F cm}^{-2}$) and Ni15-CoPi ($317.2 \mu\text{F cm}^{-2}$). Based on the C_{dl} values, the symbolic ECSA was

calculated as well.^[24] The Ni10-CoPi nanoflakes displays an ECSA of 6.57 mECSA^2 , which is comparable with that of CoPi (6.94 mECSA^2), Ni5-CoPi (6.48 mECSA^2) and Ni15-CoPi (7.93 mECSA^2). Furthermore, the specific activity from the normalization of ECSA were also calculated to elucidate the origin of the superior performance of Ni10-CoPi (**Figure S14, Supporting Information**). Among the four electrodes, the Ni10-CoPi sample shows the highest specific activity of $0.91 \text{ mA cmECSA}^{-2}$ at the 380 mV OER overpotential, which outperforms those of CoPi ($0.17 \text{ mA cmECSA}^{-2}$), Ni5-CoPi ($0.37 \text{ mA cmECSA}^{-2}$) and Ni15-CoPi ($0.41 \text{ mA cmECSA}^{-2}$). The higher specific activity indicates that Ni10-CoPi has a higher intrinsic activity, which contributes to the better electrochemical performance. On the other hand, RuO₂ tested within the same potential window and test condition exhibits a huge C_{dl} value of 3 mF cm^{-2} (**Figure S15, Supporting Information**), and yields a specific activity of only $0.09 \text{ mA cmECSA}^{-2}$, which furtherly stands out the superior intrinsic activity of Ni10-CoPi. We also tested the electrochemical impedance spectroscopy (EIS) of the four samples (Figure 4b) to investigate the charge transfer ability of the materials. The charge transfer resistance (R_{ct}) of the Ni10-CoPi electrode is only 38.59Ω , which is much smaller than those of CoPi (190.5Ω), Ni5-CoPi (92.17Ω) and Ni15-CoPi (44.25Ω). The smaller R_{ct} indicates its faster charge transfer kinetics of the optimised Ni10-CoPi electrode. Comparing with CoPi, the smaller R_{ct} of Ni doped CoPi indicates that the introduction of Ni enhances the electro conductivity of the cobalt phosphate materials.

To investigate the origin of the enhanced OER performance of Ni10-CoPi, attention was driven to the pre-oxidation of Co (II) in the synthesized materials. Earlier studies have revealed the importance of the pre-oxidation of Co (II) for OER in Co-based catalysts, where Co (II) is inclined to be oxidized to Co (III) or higher oxidation state, which is believed to be a critical step to generate active oxyhydroxide sites for OER.^[11b, 25] To study this behaviour, the cyclic voltammetry (CVs) of the four samples were explored. We found that the

oxyhydroxide formation here displays different pseudocapacitive behaviours depending on the presence or not of Ni. **Figure 5** reveals the first and second cycle of the CV profiles. For both CoPi (Figure 5a) and Ni10-CoPi (Figure 5c), the first cycle displays a larger pseudocapacitive charge corresponding to the peak at 1.29 V and 1.27 V, respectively. For Ni10-CoPi, significant changes are observed between the first and second cycles in the oxidation peak and the pseudocapacitive charges from 1.27 V to 1.12 V, indicating a change in surface chemistry, while no such obvious contrast observed on CoPi. Thus, a more thorough reconstruction may happen on the surface of Ni10-CoPi and then lowered the overpotential. The CV profiles exhibit negligible changes during the subsequent cycles (**Figure S16, Supporting Information**), indicating the surface reconstruction might be irreversible evolving oxyhydroxide serving as stable active sites for OER. Similar changes can also be observed on Ni5-CoPi from 1.24 V to 1.11 V (Figure 5b) and Ni15-CoPi from 1.31 V to 1.23 V (Figure 5d), while the change on Ni15-CoPi is not as huge as Ni10-CoPi, indicating that surface reconstruction almost saturated with 10% of Ni substituting Co.

In conclusion, the amorphous Ni10-CoPi nanoflakes composed of highly ordered mesoporous structures were prepared by a facile oil-phase method and demonstrated for the application of OER. The amorphous structure and mesoporous morphology provides high active sites density and large exposed surface area. Ni doping improves the synergistic work and facilitates the surface reconstruction evolving into active oxyhydroxide sites under OER. The materials displayed its decent OER performance, delivering a durable current density of 10 mA cm⁻² at 320 mV. Its reaction kinetics is comparable to noble metal based electrocatalyst such as Ir/RuOx with a gentle Tafel slope of only 44.5 mV dec⁻¹. The mesoporous Ni10-CoPi shows promise as a low-cost alternative due to its abundance as compared to Ru and Ir.

Experimental section

Materials. Cobalt (II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 98%), Nickel (II) Chloride Hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 98%), sodium oleate (NaOA , $\geq 82\%$ fatty acids (as oleic acid) basis powder), 1-Octadecene (ODE, technical grade, 90%), Tetradecylphosphonic acid (TDPA, 97 %) and Nafion®117 solution (5%, in a mixture of lower aliphatic alcohols and water) were purchased from Sigma-Aldrich. The isopropyl alcohol (IPA, technical grade, 99%), ethanol absolute (99.9%), hexane (99.9%) and methanol (99.9%) were purchased from Aik Moh. All chemicals and materials were used without further purification.

Synthesis of Co(OA)_2 and Ni-doped Co(OA)_2 Precursor: The synthesis of Co(OA)_2 and Ni-doped Co(OA)_2 precursor was followed by thermal decomposition. According to a typical method,^[26] different molar ratio of Co/Ni solution (1:0, 95:5, 90:10, 85:15 for the synthesis of Co(OA)_2 and 5%, 10 %, 15% Ni-doped Co(OA)_2 , respectively) were obtained by adding $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 20mmol NaOA in a mixture solution of 16 mL ethanol absolute, 12 mL DI water and 28 mL hexane. The total amount of metal cations (Co^{2+} and Ni^{2+}) were kept at 10 mmol. Then the solution was heated at 70 °C for 4 hours with vigorous stirring. The obtained products were firstly dissolved into hexane and then washed with deionized water (DI water) for 3 times and subsequently washed with methanol for 3 times. The pure brown Co(OA)_2 and Ni-doped Co(OA)_2 precursors were then dried at 80 °C in an vacuum oven overnight.

Synthesis of Amorphous CoPi and Ni-doped CoPi nanoflakes with highly Ordered Mesoporous Structure: The synthesis is based on a slightly modified oil-phase method.^[16] To start, 5mL of ODE was heated to 300 °C under Ar protection in a three-neck flask. Next, 0.9mmol Co(OA)_2 precursor and 0.6mmol TDPA were added into the hot oil and kept heating at 300 °C for 1.5 hours. Then cooled to room temperature naturally. Ni-doped CoPi was conducted with similar procedure by replacing Co(OA)_2 with Ni-doped Co(OA)_2 . The

obtained products were washed by hexane and IPA for 5 to 6 times and collected by centrifuging and dried in air. Synthesis of the amorphous 10% at Ni doped CoPi nanoflakes is similar except heat ODE to 320 °C.

Characterizations: The morphology of the samples was characterized with the transmission electron microscope (TEM) system (JEOL 2010 UHR) operating at 200 kV, field emission scanning electron microscopy (FESEM, JEOL, JSM-7600F). X-ray diffraction was performed to characterize the samples on a Bruker D8 Advance powder X-ray diffraction (XRD) at the 2θ range of 10° to 80° with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The scanning rate is 2° min^{-1} with a step size of 0.01° . Low-angle X-ray diffraction (XRD) was tested by Panalytical XPert Pro at the 2θ range of 3° to 10° with Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scientific) using monochromatic Al K α X-ray beam (1486.6 eV). The voltage step size was 1 eV for survey spectra and 0.1 eV for high resolution scan. The energy-dispersive X-ray spectroscopy (EDX) mapping was tested on a transmission electron microscopes (TEM, JEOL 2100HR). The composition of the synthesized materials was confirmed by the PerkinElmer Optima 8000 ICP-OES. AFM Asylum Research Cypher S was used to confirm the thickness of the obtained materials. The Brunauer-Emmett-Teller (BET) surface areas were obtained from N₂ adsorption-desorption isotherms (ASAP Tri-star II 3020).

Electrochemical Measurement: For OER testing, 2.5 mg of the catalyst materials was dispersed in 0.5 mL of solution containing 485 μL of IPA and 15 μL of 5 wt% Nafion followed by ultrasonication for 30 minutes. Then, 5 μL of the prepared suspension was pipetted onto a pre-polished glassy carbon (GC) disk electrode (3 mm in diameter), followed by drying at room temperature for 5 minutes. Electrochemical measurements were performed in a typical three-electrode system on an electrochemical station (Solartron). A Graphite rod

and Hg/HgO served as the counter electrode and the reference electrode, respectively. The catalyst-loaded GC electrode was used as the working electrode. All measurements were carried out in 1.0 M KOH electrolyte under room temperature. Cyclic voltammetry (CV) was performed within a potential window of 0.8~1.8 V (vs. RHE) at a scan rate of 100 mV s⁻¹. Linear sweep voltammetry (LSV) was conducted at a scan rate of 2 mV s⁻¹. In all measurements, Hg/HgO RE was calibrated: $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.059\text{pH} + 0.098$. All LSV curves were corrected with 90% iR -compensation. By plotting overpotential η vs. logarithm of current density from polarization curves, Tafel slopes were obtained.

EIS measurements were carried out at a potential of 1.57 V (vs. RHE) in the frequency range from 100 KHz to 0.1 Hz in 1.0 M KOH solution. The electrochemically effective surface area (ECSA) was estimated from the electrochemical double-layer capacitance (C_{dl}) of the materials. The C_{dl} was determined by a simple CV method. The CV was conducted in a potential window of -0.1~0 V (vs. Hg/HgO reference electrode) at various scan rate of 10, 20, 40, 60, 80 and 100 mV s⁻¹. Then by plotting capacitive current difference $\Delta j = j_a - j_c$ at -0.05V against scan rates, an obtained linear slope is equivalent to twice of the double layer capacitance (C_{dl}) value. ECSAs were obtained from C_{dl} values divided by 40 $\mu\text{F cm}^{-2} \text{cm}_{\text{ECSA}}^{-2}$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This study was financially supported by Singapore MOE AcRF Tier 1 Grant 2016-T1-002-065, and Tier 2 under Grant Nos. 2017-T2-2-069 and 2018-T2-01-010. The authors greatly thank the Facility for Analysis, Characterization, Testing and Simulation (FACTS) of Nanyang Technological University, Singapore, for using their TEM, SEM, and XRD equipment.

References

- [1] a) S. Chu, A. Majumdar, *Nature* **2012**, 488 (7411), 294-303; b) T. R. Cook, D. K. Dogutan, S. Y. Reece, Y. Surendranath, T. S. Teets, D. G. Nocera, *Chem. Rev.* **2010**, 110 (11), 6474-6502; c) J. A. Turner, *Science* **2004**, 305 (5686), 972-974; d) Y.-P. Deng, Y. Jiang, D. Luo, J. Fu, R. Liang, S. Cheng, Z. Bai, Y. Liu, W. Lei, L. Yang, J. Zhu, Z. Chen, *ACS Energy Lett.* **2017**, 2 (12), 2706-2712.
- [2] a) R. Frydendal, E. A. Paoli, B. P. Knudsen, B. Wickman, P. Malacrida, I. E. L. Stephens, I. Chorkendorff, *ChemElectroChem* **2014**, 1 (12), 2075-2081; b) Y. Lee, J. Suntivich, K. J. May, E. E. Perry, Y. Shao-Horn, *J. Phys. Chem. Lett.* **2012**, 3 (3), 399-404; c) T. Reier, M. Oezaslan, P. Strasser, *ACS Catal.* **2012**, 2 (8), 1765-1772; d) M. Vuković, *J. Appl. Electrochem.* **1987**, 17 (4), 737-745.
- [3] a) C. G. Read, J. F. Callejas, C. F. Holder, R. E. Schaak, *ACS Appl. Mater. Interfaces* **2016**, 8 (20), 12798-12803; b) J. Masud, S. Umapathi, N. Ashokaan, M. Nath, *J. Mater. Chem. A* **2016**, 4 (25), 9750-9754; c) N.-T. Suen, S.-F. Hung, Q. Quan, N. Zhang, Y.-J. Xu, H. M. Chen, *Chem. Soc. Rev.* **2017**, 46 (2), 337-365.
- [4] a) J. Wu, M. Liu, K. Chatterjee, K. P. Hackenberg, J. Shen, X. Zou, Y. Yan, J. Gu, Y. Yang, J. Lou, P. M. Ajayan, *Adv. Mater. Interfaces* **2016**, 3 (9), 1500669; b) X. Duan, J. Xu, Z. Wei, J. Ma, S. Guo, H. Liu, S. Dou, *Small Methods* **2017**, 1 (11), 1700156.
- [5] a) J. Xie, Y. Xie, *Chem. Eur. J.* **2016**, 22 (11), 3588-3598; b) A. K. Tareen, G. S. Priyanga, K. Khan, E. Pervaiz, T. Thomas, M. Yang, *ChemSusChem* **2019**, 12 (17), 3941-3954; c) M. S. Balogun, Y. Huang, W. Qiu, H. Yang, H. Ji, Y. Tong, *Mater. Today* **2017**, 20 (8), 425-451.
- [6] a) P. Liu, R. N. Ali, J. Li, G. Hu, X. Zhu, Y. Lu, B. Xiang, *Appl. Surf. Sci.* **2019**, 484, 54-61; b) Q. Liang, L. Zhong, C. Du, Y. Luo, Y. Zheng, S. Li, Q. Yan, *Nano Energy* **2018**,

47, 257-265; c) Q. Liang, L. Zhong, C. Du, Y. Luo, J. Zhao, Y. Zheng, J. Xu, J. Ma, C. Liu, S. Li, Q. Yan, *ACS Nano* **2019**, *13* (7), 7975-7984.

[7] a) Y. Jiao, Y. Zheng, M. Jaroniec, S. Z. Qiao, *Chem. Soc. Rev.* **2015**, *44* (8), 2060-2086; b) P. F. Liu, X. Li, S. Yang, M. Y. Zu, P. Liu, B. Zhang, L. R. Zheng, H. Zhao, H. G. Yang, *ACS Energy Lett.* **2017**, *2* (10), 2257-2263; c) Y. Jiang, Y.-P. Deng, R. Liang, J. Fu, D. Luo, G. Liu, J. Li, Z. Zhang, Y. Hu, Z. Chen, *Advanced Energy Mater.* **2019**, *9* (24), 1900911.

[8] a) K. Jin, J. Park, J. Lee, K. D. Yang, G. K. Pradhan, U. Sim, D. Jeong, H. L. Jang, S. Park, D. Kim, N.-E. Sung, S. H. Kim, S. Han, K. T. Nam, *J. Am. Chem. Soc.* **2014**, *136* (20), 7435-7443; b) Y. Li, C. Zhao, *Chem. Mater.* **2016**, *28* (16), 5659-5666; c) Y. Zhan, M. Lu, S. Yang, C. Xu, Z. Liu, J. Y. Lee, *ChemCatChem* **2016**, *8* (2), 372-379; d) H. Kim, J. Park, I. Park, K. Jin, S. E. Jeong, S. H. Kim, K. T. Nam, K. Kang, *Nat. Commun.* **2015**, *6* (1), 8253.

[9] a) M. Pramanik, C. Li, M. Imura, V. Malgras, Y.-M. Kang, Y. Yamauchi, *Small* **2016**, *12* (13), 1709-1715; b) Y. Zhou, H. C. Zeng, *Small* **2018**, *14* (21), 1704403.

[10] Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov, T. F. Jaramillo, *Science* **2017**, *355* (6321), eaad4998.

[11] a) D. Friebe, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, A. M. Wise, M.-J. Cheng, D. Sokaras, T.-C. Weng, R. Alonso-Mori, R. C. Davis, J. R. Bargar, J. K. Nørskov, A. Nilsson, A. T. Bell, *J. Am. Chem. Soc.* **2015**, *137* (3), 1305-1313; b) T. Wu, S. Sun, J. Song, S. Xi, Y. Du, B. Chen, W. A. Sasangka, H. Liao, C. L. Gan, G. G. Scherer, L. Zeng, H. Wang, H. Li, A. Grimaud, Z. J. Xu, *Nat. Catal.* **2019**, *2* (9), 763-772.

[12] C. Tan, X. Cao, X.-J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G.-H. Nam, M. Sindoro, H. Zhang, *Chem. Rev.* **2017**, *117* (9), 6225-6331.

[13] L. Su, H. Du, C. Tang, K. Nan, J. Wu, C. Ming Li, *J. Colloid Interface Sci.* **2018**, *528*, 36-44.

- [14] Y. Wan, H. Yang, D. Zhao, *Acc. Chem. Res.* **2006**, 39 (7), 423-432.
- [15] a) W. Liu, H. Liu, L. Dang, H. Zhang, X. Wu, B. Yang, Z. Li, X. Zhang, L. Lei, S. Jin, *Adv. Funct. Mater.* **2017**, 27 (14), 1603904; b) M. W. Kanan, D. G. Nocera, *Science* **2008**, 321 (5892), 1072-1075; c) R. D. L. Smith, M. S. Prévot, R. D. Fagan, S. Trudel, C. P. Berlinguette, *J. Am. Chem. Soc.* **2013**, 135 (31), 11580-11586.
- [16] D. Yang, Z. Lu, X. Rui, X. Huang, H. Li, J. Zhu, W. Zhang, Y. M. Lam, H. H. Hng, H. Zhang, Q. Yan, *Angew. Chem. Int. Ed.* **2014**, 53 (35), 9352-9355.
- [17] F. B. Noronha, M. Schmal, B. Moraweck, P. Delichère, M. Brun, F. Villain, R. Fréty, *J. Phys. Chem. B* **2000**, 104 (23), 5478-5485.
- [18] a) J. Yan, Z. Fan, W. Sun, G. Ning, T. Wei, Q. Zhang, R. Zhang, L. Zhi, F. Wei, *Adv. Funct. Mater.* **2012**, 22 (12), 2632-2641; b) Y. Zhang, W. Sun, X. Rui, B. Li, H. T. Tan, G. Guo, S. Madhavi, Y. Zong, Q. Yan, *Small* **2015**, 11 (30), 3694-3702.
- [19] Y. Yin, P. Wu, H. Zhang, C. Cai, *Electrochem. Commun.* **2012**, 18, 1-3.
- [20] P. Zhu, Z. Yang, H. Zhang, J. Yu, Z. Zhang, J. Cai, C. Li, *J. Alloy. Compd.* **2018**, 745, 164-171.
- [21] A. P. Grosvenor, M. C. Biesinger, R. S. C. Smart, N. S. McIntyre, *Surf. Sci.* **2006**, 600 (9), 1771-1779.
- [22] C. Yan, Y. Zhu, Z. Fang, C. Lv, X. Zhou, G. Chen, G. Yu, *Adv. Energy Mater.* **2018**, 8 (23), 1800762.
- [23] C. S. Lim, C. K. Chua, Z. Sofer, K. Klímová, C. Boothroyd, M. Pumera, *J. Mater. Chem. A* **2015**, 3 (22), 11920-11929.
- [24] a) D. Voiry, M. Chhowalla, Y. Gogotsi, N. A. Kotov, Y. Li, R. M. Penner, R. E. Schaak, P. S. Weiss, *ACS Nano* **2018**, 12 (10), 9635-9638; b) C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.* **2013**, 135 (45), 16977-16987.

- [25] a) M. W. Kanan, J. Yano, Y. Surendranath, M. Dincă, V. K. Yachandra, D. G. Nocera, *J. Am. Chem. Soc.* **2010**, *132* (39), 13692-13701; b) B. S. Yeo, A. T. Bell, *J. Am. Chem. Soc.* **2011**, *133* (14), 5587-5593.
- [26] D. Ge, J. Wu, G. Qu, Y. Deng, H. Geng, J. Zheng, Y. Pan, H. Gu, *Dalton. Trans.* **2016**, *45* (34), 13509-13513.

Figure 1. a) XRD patterns of CoPi (in black), Ni5-CoPi (in red), Ni10-CoPi (in blue) and Ni15-CoPi (in green). XPS spectrums of CoPi and Ni10-CoPi in b) Co 2p region, c) Ni 2p region and d) P 2p region.

Figure 2. a) TEM image, b,c) HRTEM images, and d) Low-angle XRD pattern of Ni₁₀-CoPi. The inset in (b) is the SAED pattern of Ni₁₀-CoPi. The inset in (c) is the enlarged TEM image, showing the distance between neighboring channels is 3.74 nm.

Figure 3. a) iR -corrected OER polarization curves of CoPi, Ni5-CoPi, Ni10-CoPi, and Ni15-CoPi in 1.0 M KOH at scan rate of 2 mV s⁻¹ and their corresponding b) Tafel Slope. c) The overpotentials of above samples at the current density of 10 mA cm⁻². d) The chronoamperometric measurements of Ni10-CoPi electrode under static overpotential (η =330 mV) for 20h.

Figure 4. a) The charging current density differences ($\Delta j = j_{\text{anodic}} - j_{\text{cathodic}}$) plotted against scan rates of the as-prepared CoPi, Ni5-CoPi, Ni10-CoPi and Ni15-CoPi electrodes. b) EIS spectrum measured at 340 mV overpotential of CoPi, Ni5-CoPi, Ni10-CoPi and Ni15-CoPi.

Figure 5. Pseudocapacitive behavior in the first and second cycles of a) CoPi, b) Ni5-CoPi, c) Ni10-CoPi and d) Ni15-CoPi during CV cycling.

The ultrathin amorphous 10 at% Ni-doped CoPi nanoflakes with highly ordered mesoporous structures display decent performances towards oxygen evolution reaction, delivering a current density of 10 mA cm^{-2} at 320 mV and small Tafel slope of 44.5 mV dec^{-1} .

Energy conversion

*Hao Ren, Qinghua Liang, Khang Ngoc Dinh, Raksha Dangol and Qingyu Yan**

Ultrathin Amorphous Nickel Doped Cobalt Phosphates with Highly Ordered Mesoporous Structures as Efficient Electrocatalyst for Oxygen Evolution Reaction

Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:

Yang, L;Ren, H;Liang, Q;Dinh, KN;Dangol, R;Yan, Q

Title:

Ultrathin Amorphous Nickel Doped Cobalt Phosphates with Highly Ordered Mesoporous Structures as Efficient Electrocatalyst for Oxygen Evolution Reaction.

Date:

2020-02

Citation:

Yang, L., Ren, H., Liang, Q., Dinh, K. N., Dangol, R. & Yan, Q. (2020). Ultrathin Amorphous Nickel Doped Cobalt Phosphates with Highly Ordered Mesoporous Structures as Efficient Electrocatalyst for Oxygen Evolution Reaction.. Small, 16 (7), pp.e1906766-. <https://doi.org/10.1002/sml.201906766>.

Persistent Link:

<http://hdl.handle.net/11343/275305>