

Contents lists available at ScienceDirect

## Journal of Alloys and Compounds



journal homepage: www.elsevier.com/locate/jalcom

# Nickel-cobalt derived nanowires/nanosheets as electrocatalyst for efficient H<sub>2</sub> generation via urea oxidation reaction



### Yuanjian Liu, Jibiao Guan, Wubin Chen, Yudong Wu, Shanshan Li, Xiangheng Du, Ming Zhang\*

National Engineering Lab for Textile Fiber Materials and Processing Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China

#### ARTICLE INFO

Article history: Received 7 April 2021 Received in revised form 14 August 2021 Accepted 29 August 2021 Available online 10 September 2021

Keywords: Hydrogen evolution reaction Urea oxidation reaction Phosphide Oxide Morphology control

#### ABSTRACT

Exploring high-efficient catalysts to reduce the voltage of the electrolytic cell is pivotal for large-scale hydrogen production, and using other electrochemical reactions to replace inert oxygen evolution reaction (OER) is also a feasible way. In this paper, a series of Ni–Co precursors supported by carbon cloth (CC) were prepared by hydrothermal method and subsequently treated with phosphating and oxidation, respectively. The phosphating products and oxidation products were used for hydrogen evolution reaction (HER) and urea oxidation reaction (UOR), respectively. The materials morphology and electron configuration were also controlled by adjusting relative Ni–Co content in the precursors. Furthermore, the effects of different Ni-Co ratios on electrocatalytic activity under the same crystal structure were discussed in detail. Benefited from the optimum electron structure and maximum active sites, Ni<sub>2</sub>Co<sub>1</sub>-P/CC displayed the best HER catalytic performance, with an overpotential of 79 mV to reach 10 mA cm<sup>-2</sup>. On account of the comparatively low theoretical oxidation voltage of urea, Ni<sub>x</sub>Co<sub>3-x</sub>-O/CCs displayed a much lower working potential in urea-containing electrolyte than the urea-free electrolyte. Thereinto, Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC showed the best UOR catalytic performance, with a potential of 1.362 V at  $\eta_{10}$  in 1.0 M KOH and 0.33 M urea. With the combination of the above catalysts, it needed only 1.47 V to drive the current density of 10 mA cm<sup>-2</sup> in the electrolytic cell for hydrogen production via UOR.

© 2021 Elsevier B.V. All rights reserved.

#### 1. Introduction

With the depletion of traditional fossil fuels and the environmental pollution picking up, constructing new energy systems is significant for future sustainable development [1]. Hydrogen is one of the most promising candidates as the energy carrier, which is widely studied due to its properties of clean, renewable, widespread, and high energy density (~120 MJ kg<sup>-1</sup>)[2,3]. Among several kinds of hydrogen production methods (like fossil fuel reforming[4], electrocatalytic water splitting, photocatalytic water splitting[5-7]), electrocatalytic water splitting with high-efficiency, no emission and pure production of H<sub>2</sub> at the cathode has aroused great research interest. To improve the electrolysis efficiency and reduce the energy consumption for hydrogen production, highly efficient catalysts are applied to promote the sluggish kinetics of HER and OER[8,9]. The noble-metal-based electrocatalysts such as Pt[10,11] and IrO<sub>2</sub>[12,13] still are state-of-the-art catalysts toward HER and OER, respectively. However, the scarcity on earth limits their large-scale applications to

Corresponding author.
 E-mail address: zhangming@zstu.edu.cn (M. Zhang).

https://doi.org/10.1016/j.jallcom.2021.161790 0925-8388/© 2021 Elsevier B.V. All rights reserved. a great extent[14]. Therefore, the catalysts designed with earthabundant elements are the crux of hydrogen generation by electrolysis water splitting[15,16].

Transition metal compounds (TMCs) including phosphides [17], oxides<sup>[18,19]</sup>, sulfides<sup>[20]</sup>, carbides<sup>[21]</sup>, and alloys<sup>[22]</sup>, have been widely studied as catalysts for electrolysis water splitting because of their noble-metal liked performance and low cost. For HER, transition metal phosphides (TMPs) display extraordinary activity, because the strong electronegative P atoms are able to draw electrons from surrounding metal atoms, acting like base to trap protons in electrolytes and accelerate the dissociation of H<sub>2</sub>[23]. Over past decades, NiFeP[24,25], Ni<sub>2</sub>P[26-28], CoP[29,30], CoMoP[31], MoP[32], WP [33,34] and so on have been proven to have excellent performance. In recent years, chemicals assistant catalytic oxidation have been researched to substitute OER in the electrolytic process, including hydrazine catalytic oxidation reaction (HzOR,  $N_2H_4$  + 40H  $^{\scriptscriptstyle -}$   $\rightarrow$   $N_2$  + 4 H<sub>2</sub>O + 4e<sup>-</sup>, -0.33 V vs. RHE)[35-37] and urea oxidation reaction (UOR,  $CO(NH_2)_2 + 6OH^- \rightarrow N_2 + 5 H_2O + CO_2 + 6e^-$ , 0.37 V vs. RHE) [38,39]. Thereinto, urea is non-toxic, mild, and readily available, with a much lower theoretical oxidation potential (0.37 V) than OER (1.23 V)[40]. In particular, urea is the main pollutant in certain sewage<sup>[41]</sup>. Transition metal oxides (TMOs) are deemed as outstanding catalysts toward OER, especially nickel cobaltite  $(NiCo_2O_4)$  has been widely researched, due to their abundant active sites, rich redox reactions, and low price [42,43]. Especially, the adjustable Ni–Co ratio gives the crystal its unique chemical properties toward catalytic reaction. D. Wang et al. had confirmed that mesoporous NiCo<sub>2</sub>O<sub>4</sub> nanosheets are also active to catalyze urea oxidation [44]. L. Sha et al. synthesized NiCo<sub>2</sub>O<sub>4</sub> nanowires grown on Ni foam for urea oxidation [45]. However, the study on the activity of  $NiCo_2O_4$ crystal toward UOR by regulating its composition has not been reported yet. Moreover, the design of bifunctional catalysts used as both cathode and anode materials is the trend in the field of water electrolysis, because it can simplify the production process and reduce costs [46,47]. However, due to the difference of reaction mechanism and active site, there is almost no single-phase material that can effectively reduce cathode and anode overpotential at the same time. According to the existing literature, some attempts have been made to combine substances with high activity for hydrogen evolution and oxygen evolution respectively to achieve a bifunctional effect [48,49], but this is not sufficient from the perspective of making full use of the active sites. Therefore, the design of cathode and anode material synthesis paths involving the same synthesis steps is another idea to achieve a bifunctional effect.

In this work, we used the hydrothermal method to grow Ni-Co precursor on carbon cloth, then calcined in different atmospheres. The precursor calcined in phosphorus-containing mixed gas (Argon and NaH<sub>2</sub>PO<sub>2</sub> thermal decomposition products) is for phosphide generation (denoted as Ni<sub>x</sub>Co<sub>3-x</sub>-P/CC, x presents the initial molar content of nickel salt in hydrothermal solution), calcined in the air is for oxides generation (denoted as Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC), respectively. We modulated the morphology and electron configuration by simply alter the ratio of Ni-Co. It is found that, with nickel content increasing, the morphology of phosphides shift from nanowires to nanosheets. The oxides' morphology keeps nanowires with wires getting shorter and smaller. Benefited from the strong synergistic effects and supreme electrochemical active surface, Ni<sub>2</sub>Co<sub>1</sub>P/CC shows the best HER catalytic performance with an overpotential of 79 mV at  $\eta_{10}$ . All corresponding oxides show nearly the same OER catalytic performance with a potential of about 1.428 V at  $n_{10}$ . But Ni<sub>15</sub>Co<sub>15</sub>O/CC shows the best UOR catalytic performance with a potential of 1.362 V at  $\eta_{10}$ . With the combination of Ni<sub>2</sub>Co<sub>1</sub>-P/ CC= |Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC, it achieves only 1.47 V for overall water splitting at  $\eta_{10}$ .

#### 2. Experimental section

#### 2.1. Chemical reagents

Cobalt nitrate hexahydrate ( $Co(NO_3)_2$ · $GH_2O$ ), nickel nitrate hexahydrate ( $Ni(NO_3)_2$ · $GH_2O$ ), urea ( $CH_4N_2O$ ), potassium hydroxide (KOH), were procured from Sigma-Aldrich. All chemicals were used without further purification. Carbon cloth (CC) was purchased from Taiwan Carbon Energy Co., Ltd. Deionized water was used throughout the experiment.

#### 2.2. Synthesis of the $Ni_xCo_{3-x}$ -P/CC

The two-step synthesis process is depicted in Fig. 1. Before the synthesis, the carbon cloth  $(1 \times 4 \text{ cm}^2)$  was cleaned in DI water, ethanol, and DI water by ultrasonication for 10 min in sequence. In a regular process, a total of 3 mM Ni(NO<sub>3</sub>)<sub>2</sub>.6 H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (the moles of Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O are 0, 0.5, 1, 1.5, 2, 2.5 and 3 mM, respectively) with 6 mM urea were added into 30 mL DI water then stirred for 30 min to obtain a homogeneous solution. Then the solution and the as-cleaned CC were transferred into a 50 mL Teflon-lined stainless autoclave to have a hydrothermal reaction at 120 °C for 6 h. When it cooled to room temperature naturally, the

precursor/CC was washed with DI water and ethanol. After drying, as-treated CC and 0.5 g NaH<sub>2</sub>PO<sub>2</sub> were placed in a corundum boat at its downstream and upstream, respectively. The boat was placed in a tube furnace, calcining at 350 °C for 2 h with a heating rate of 5 °C/ min in an argon atmosphere. As a result, the NiCoP electrocatalysts grown on CC were prepared.

The materials were denoted as  $Ni_xCo_{3-x}$ -P/CC (x = 0, 0.5, 1, 1.5, 2, 2.5, and 3), wherein x represents the initial molar of nickel salt.

#### 2.3. Synthesis of the $Ni_xCo_{3-x}-O/CC$

The synthesis process of the precursor is as same as the Ni<sub>x</sub>Co<sub>3-x</sub>-P/CC. The difference is that the Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC is obtained by calcining the precursor in the air (350 °C for 2 h).

#### 2.4. Materials characterization

Filed-emission scanning electron microscope (FESEM) and energy dispersive spectroscopy (EDS) spectrum measurements were performed on a JSM-6700 F scanning electron microscope (JEOL, Japan) with an accelerating voltage of 3 kV and 10 kV, respectively. Transmission electron microscopy (TEM) images were obtained by using a JSM-2100 transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and STEM-EDX mappings images were taken on a Tecnai G2 F30S-Twin STEM (Philips-FEI) with an accelerating voltage of 300 kV. The analysis of crystal structures of the products was detected by X-ray diffraction (XRD) on a Bruker AXS D8 DISCOVER X-ray diffractometer at a scanning rate of 5°/min<sup>-1</sup> with Cu K $\alpha$  radiation ( $\lambda$  = 0.15406 nm). X-ray photoelectron spectra (XPS) analysis was carried out using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer with an Al Kα source (1486.6 eV).

#### 2.5. Electrochemical measurements

All electrochemical measurements were operated on a CHI660E workstation (Chenghua Instrument, China) with a standard threeelectrode system. Ni<sub>x</sub>Co<sub>3-x</sub>-P/CC and Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC (cut into about 2 \*2 mm<sup>2</sup> square) were employed as the working electrode in HER and OER/UOR tests, respectively. A graphite rod and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. HER and OER tests were conducted in 1 M KOH electrolytes, UOR test was conducted in 1 M KOH and 0.33 M urea electrolytes, respectively. The potential against reversible hydrogen electrode (RHE) was calculated according to  $E_{VS RHE} = E_{VS SCE} + 0.244 + 0.059pH$ .

In all measurements, linear sweep voltammetry (LSV) was primarily used to obtain the polarization curves at a scan rate of 5 mV s<sup>-1</sup> with iR compensation. The Tafel slope was calculated following the formula:  $\eta = a + blgj$ . Then, cyclic voltammetry (CV) scans were carried out in a non-Faradaic region (0-1.23 V) at different scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mV s<sup>-1</sup>. The double-layer capacitance  $(C_{dl})$  was measured by fitting the linear relationship between scan rates and current density differences of anodic and cathodic. The electrochemically active surface areas (ECSAs) were evaluated using the following equation: ECSA  $= S_{geo} C_{dl}/C_s$ . Wherein, Cs is specific electrochemical double-layer capacitance and its value in alkaline media is 40  $\mu$ F cm<sup>-2</sup>, and the  $S_{geo}$  represents the geometric surface area of the electrode. In addition, the frequencies set to obtain the Electrochemical impedance spectroscopy (EIS) ranged from 1000 kHz to 0.1 Hz, and the stability of the Ni<sub>2</sub>Co<sub>1</sub>-P/CC and Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC was evaluated by testing current-time responses at  $\eta_{10}$  for some time.



Fig. 1. The schematic illustration of the synthesis process of Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC & Ni<sub>x</sub>Co<sub>3-x</sub>-P/CC.

#### 3. Results and discussion

A traditional hydrothermal method was applied to grow Ni–Co precursor on substrate CC, then calcined the precursor in a tube furnace. The precursor calcined with sodium hypophosphite transformed to phosphides and calcined in air transformed to oxides.

The morphology of the samples was firstly characterized by FESEM. Fig. S1 and Fig. 2 represent the low and high-resolution FESEM images of all the samples, respectively. Fig. 2a-e display the morphology of Ni<sub>x</sub>Co<sub>3-x</sub>-P/CC with incremental Ni content. When x was less than 1.5, nanowires can be observed and the size of the wires gradually shrank with x increasing. When the Ni-Co ratio was 2, nanowires transformed to nanosheets, which may be caused by the changes in the preferred orientation of crystal growth [50,51]. When the x value was higher, the nanosheets got thicker and agminated. Fig. 2f-j show the morphology of Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC, nanowires grow evenly on the CC. Notably, the size of the nanowires shrank with the increasing content of Ni. The FESEM images of precursor are shown in Fig. S2, sharing the same morphology change with Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC, which indicated the nanowires-nanosheets transformation was caused by phosphorization and specific Ni-Co ratio. The monometallic compounds (Ni<sub>3</sub>-P/CC, Ni<sub>3</sub>-O/CC, Co<sub>3</sub>-O/CC, Co<sub>3</sub>-P/ CC) in Fig. S3 also conform to the change. EDS was further applied to detect the element relative content of Ni<sub>2</sub>Co<sub>1</sub>-O/CC, Ni<sub>1</sub>Co<sub>2</sub>-O/CC, Ni<sub>2</sub>Co<sub>1</sub>-P/CC, and Ni<sub>1</sub>Co<sub>2</sub>-P/CC (Fig. S4). All the Ni-Co relative contents accord with the initial ratio in hydrothermal solutions, which proves the feasibility of the experimental strategy to modulate composition.

TEM images show that the nanosheets of Ni<sub>2</sub>Co<sub>1</sub>-P/CC were composed of numerous nanoparticles (Fig. 3a). The diameter of the particles was 5 ~ 10 nm and lattice fringes of 0.209 nm and 0.197 nm correspond to the (111) and (201) facets of NiCoP (Fig. 3b), respectively. Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC was also characterized by TEM, and the single nanowire can be observed (Fig. 3d). It's also composed of nanoparticles with diameters of 10 ~ 15 nm and lattice fringes of 0.253 nm

correspond to the (111) facets of NiCo<sub>2</sub>O<sub>4</sub> (Fig. 3e). The two samples presented good crystallinity and specific morphology of nanosheets (Ni<sub>2</sub>Co<sub>1</sub>-P/CC) and nanowires (Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC). Besides, EDX element mappings (Fig. 3c and f) also revealed the uniform dispersion of Ni, Co, O, and Ni, Co, P in Ni<sub>2</sub>Co<sub>1</sub>-P/CC and Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC, respectively, indicating the fine generation of single-phase compound. In Fig. S5, EDS in TEM also confirmed the element ratio in accord with the initial solution mixture ratio.

The crystal structure and phase purity were primarily detected by XRD. As shown in Fig. 4a, Ni<sub>3</sub>-P/CC, Ni<sub>2</sub>Co<sub>1</sub>-P/CC, and Co<sub>3</sub>-P/CC were tested. The XRD spectrums of Ni<sub>3</sub>-P/CC, Ni<sub>2</sub>Co<sub>1</sub>-P/CC, Ni<sub>1.5</sub>Co<sub>1.5</sub>-P/CC, and Co<sub>3</sub>-P/CC matched with hexagonal Ni<sub>2</sub>P (JCPDS 74-1385), hexagonal NiCoP (JCPDS 71-2366, both of the nickel-cobalt binary phosphides), and monoclinic Co<sub>2</sub>P (JCPDS 74-0287), respectively. Additionally, Ni<sub>3</sub>-P/CC also displayed some peaks point to hexagonal Ni<sub>5</sub>P<sub>4</sub> (JCPDS 18-0883), which may be caused by excess sodium hypophosphite [52]. It also shows that the Ni<sub>2</sub>Co<sub>1</sub>-P/CC and Ni<sub>15</sub>Co<sub>15</sub>-P/CC maintain the same crystal structure of NiCoP, although they have different morphologies. For the oxides (Fig. 4b), the XRD spectrums of Ni<sub>3</sub>-O/CC, Ni<sub>2</sub>Co<sub>1</sub>-O/CC, Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC, and Co<sub>3</sub>-O/CC matched with cubic NiO (JCPDS 71-1179), cubic NiCo<sub>2</sub>O<sub>4</sub> (JCPDS 73-1702, both of the nickel-cobalt binary oxides), cubic Co3O4 (JCPDS 74-1656), respectively. It is worth noting that the diffraction peaks progressively shift toward a higher angle with Co doping concentration increasing. That is because the unit cell shrinks as a result of Ni substitution by Co [53], which could indicate the successful composition modulation of the samples.

XPS was further applied to analyze the chemical states and electronic structure of the materials. Table. S1 presents the numerical details of XPS peaks. Fig. S6a–c present the XPS survey spectrum of Ni<sub>3</sub>-O/CC, Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC, Co<sub>3</sub>-O/CC, respectively, indicating the formation of corresponding oxides. Fig. S6d–f show the XPS survey spectrum of Ni<sub>3</sub>-P/CC, Ni<sub>2</sub>Co<sub>1</sub>-P/CC, Co<sub>3</sub>-P/CC. In addition to the peaks match with Ni, Co, and P, the peaks corresponding to O 1 s were also detected, which is caused by the surface oxidation of the



Fig. 2. (a-e) High-resolution FESEM of Ni<sub>x</sub>Co<sub>3-x</sub>-P/CC (X = 0.5, 1, 1.5, 2, 2.5, respectively) and (f-j) Ni<sub>x</sub>Co<sub>3-x</sub>-O /CC (X = 0.5, 1, 1.5, 2, 2.5, respectively). All the images share the same scaleplate.



Fig. 3. Ni<sub>2</sub>Co<sub>1</sub>-P/CC's (a) low-resolution TEM image, (b) high-resolution TEM image, (c) STEM-EDX elemental mapping of Ni, Co, and P, respectively. Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC's (d) low-resolution TEM image, (e) high-resolution TEM image, (f) STEM-EDX elemental mapping of Ni, Co, and O, respectively.

samples. Fig. 5a shows the core-level spectra of Ni 2p in Ni<sub>3</sub>-P/CC and Ni<sub>2</sub>Co<sub>1</sub>-P/CC, respectively. For Ni<sub>2</sub>Co<sub>1</sub>-P/CC, the binding energy peak at 852.2 eV was assigned to Ni  $2p_{3/2}$  of Ni<sup> $\delta^+$ </sup> in the Ni-P compound [54]. The peaks at 855.7 eV and 873.6 eV could be consigned to the Ni  $2p_{3/2}$  and Ni  $2p_{1/2}$  spin-orbital splitting of Ni<sup>2+</sup>[55,56]. Besides, the satellite peaks for Ni 2p were also detected. Compared with Ni<sub>3</sub>-P/CC, the corresponding peaks red-shifts to lower energy. In Co 2p spectrum, as shown in Fig. 5b, the peak at 774.8 eV was consigned to Co-P [57], the peaks at 781.2 eV and 797.3 eV were assigned to Co<sup>2+</sup>[58], the red-shift phenomenon was also observed. The changing Binding energy of Co and Ni was caused by the electron transfer from Co to Ni, due to the highly electronegative of Ni (1.91) vs. Co (1.88)[59], indicating that alter Ni-Co ratios could modulate electron configuration. In the P 2p spectrum (Fig. 5c), the binding energy peaks at 129.5 eV and 130.4 eV were assigned to P  $2p_{3/2}$  and P  $2p_{1/2}$  in the form of metal phosphide 60. It is worth noting that, no matter the Ni/Co relative content, the binding energy of P 2p<sub>1/2</sub> was still 130.4 eV. However, the Ni<sub>2</sub>Co<sub>1</sub>-P/CC presents the lowest binding energy of P  $2p_{3/2}$ , which is favorable for the adsorption and the desorption of products [61]. As shown in Fig. 5d, two chemical states of Ni are detected in Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC, the peaks

at 872.9 eV and 855.7 eV were assigned to Ni<sup>3+</sup>, the peaks at 871.3 eV and 854.2 eV were assigned to Ni<sup>2+</sup>, respectively. Ni<sub>3</sub>-O/CC displayed the same peak position with peak area changing. In Co 2p spectrum (Fig. 5e), the peaks at 796.7 eV and 781.2 eV were consigned to Co<sup>2+</sup>, the peaks at 779.7 eV and 794.9 eV were consigned to Co<sup>3+</sup>, respectively [62]. Co<sub>3</sub>-O/CC also displayed the same peak position with peak area changing. In the O 1 s region (Fig. 5f), the peak at 529.6 eV corresponded to metal-oxygen bonds of Co-O and Ni-O in the metal oxide, the peak at 531.4 eV was attributed to OH<sup>-</sup>[63]. It is notable that the binding energy of O2 and O1 gradually blue-shifted to higher energy with Co content increasing, which is the result of the stronger OH<sup>-</sup> adsorption capacity of Ni [64], indicating that varying Ni-Co relatively content not only influence the surface hydroxylation but also change the lattice O atoms' chemical environment.

To understand the effects of the Ni-Co relatively content to the catalytic performance of Ni<sub>x</sub>Co<sub>3-x</sub>-P/CC, linear sweep voltammetry (LSV) with 95% iR-correction was firstly evaluated in 1.0 M KOH electrolyte. As shown in Fig. 6a, Ni<sub>2</sub>Co<sub>1</sub>-P/CC needed 79 mV to drive 10 mA cm<sup>-2</sup> current density, which was only 28 mV larger than the 20 wt% Pt/C catalyst, indicating an outstanding HER performance. While other samples all showed higher overpotential at  $\eta_{10}$ 



Fig. 4. XRD patterns of (a) Ni<sub>3</sub>-P/CC, Ni<sub>1.5</sub>Co<sub>1.5</sub>-P/CC, Ni<sub>2</sub>Co<sub>1</sub>-P/CC and Co<sub>3</sub>-P/CC (b) Ni<sub>3</sub>-O/CC, Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC, Ni<sub>2</sub>Co<sub>1</sub>-O/CC and Co<sub>3</sub>-O/CC.



Fig. 5. XPS spectrum of (a) Ni 2p of Ni<sub>2</sub>Co<sub>1</sub>-P/CC and Ni<sub>3</sub>-P/CC (b) Co 2p of Ni<sub>2</sub>Co<sub>1</sub>-P /CC and Co<sub>3</sub>-P /CC (c) P 2p of aforementioned three phosphides samples (d) Ni 2p of Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC and Ni<sub>3</sub>-O/CC (e) Co 2p of Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC and Co<sub>3</sub>-O/CC (f) O 1 s of aforementioned three oxides samples.

(Ni<sub>0.5</sub>Co<sub>2.5</sub>-P/CC (104 mV), Ni<sub>1</sub>Co<sub>2</sub>-P/CC (113 mV), Ni<sub>1.5</sub>Co<sub>1.5</sub>-P/CC (81 mV), Ni<sub>2.5</sub>Co<sub>0.5</sub>-P/CC (92 mV)), confirming the improved HER activity was related to the optimal Ni-Co ratio of bimetallic phosphides. In addition, the HER kinetics and mechanism can be reflected by the Tafel slope values. Fig. 6b reveals that the calculated Tafel slopes of Ni<sub>x</sub>Co<sub>3-x</sub>-P/CC were 64.44, 82.72, 63.89, 59.51, and 65.86 mv dec<sup>-1</sup>, (x = 0.5, 1, 1.5, 2, 2.5, respectively). Ni<sub>2</sub>Co<sub>1</sub>-P/CC also showed the lowest Tafel slope values (59.51 mv dec<sup>-1</sup>), which indicated that the HER proceeding on Ni<sub>2</sub>Co<sub>1</sub>-P/CC followed a Volmer-Heyrovsky mechanism (Volmer reaction: H<sub>2</sub>O + e<sup>-</sup>  $\rightarrow$  H<sub>abs</sub> + OH<sup>-</sup>; Heyrovsky reaction: H<sub>abs</sub> + H<sub>2</sub>O+ e<sup>-</sup>  $\rightarrow$  H<sub>2</sub> + OH<sup>-</sup>[65]), in which the

Heyrovsky reaction was considered as the rate-determining step, and the Volmer reaction was much faster. The overpotential and Tafel slope of Ni<sub>2</sub>Co<sub>1</sub>-P/CC was also compared with other non-precious catalysts. As shown in Table. S2, Ni<sub>2</sub>Co<sub>1</sub>-P/CC has good performance among transition metal catalysts. To estimate the inherent activity of the samples, electrochemical surface area (ECSA) was taken into consideration, which is linear positive correlate to its double-layer capacitance (C<sub>dl</sub>). Hence, Cyclic Voltammetry (CV) was applied in a non-Faradaic window with incremental scan rates from 10 mV s<sup>-1</sup> to 100 mv s<sup>-1</sup> (Fig. S7). As shown in Fig. 6c, with the content of Ni increasing from 0.5 to 1.5, the C<sub>dl</sub> of the samples decreases



Fig. 6. HER performance in 1.0 M KOH. (a) Polarization curves of HER for (insert of corresponding overpotentials at  $\eta_{10}$ ). (b) The corresponding Tafel plots. (c) Capacitive current at 0.4 V vs. scan rates for the determination of C<sub>d1</sub> values. (d) The corresponding Nyquist plots.



**Fig. 7.** OER performance in 1.0 M KOH. (a) Polarization curves of OER for different Ni-Co oxides (insert of corresponding overpotentials at η<sub>10</sub>). (b) The corresponding Tafel plots. (c) Capacitive current at 1.17 V vs. scan rates for the determination of C<sub>dl</sub> values. (d) The corresponding Nyquist plots.

(Ni<sub>0.5</sub>Co<sub>2.5</sub>-P/CC (38.83 mF cm<sup>-2</sup>), Ni<sub>1</sub>Co<sub>2</sub>-P/CC (29.21 mF cm<sup>-2</sup>), Ni<sub>1.5</sub>Co<sub>1.5</sub>-P/CC (19.5 mF cm<sup>-2</sup>)), corresponding to the shrunken nanowires' size. For Ni<sub>2</sub>Co<sub>1</sub>-P/CC, it leapt to 50.61 mF cm<sup>-2</sup>, which was the largest among the samples. Moreover, it matched with the nanowires-nanosheets transformation, proving that the generation of nanosheets exposes more active sites. EIS tests were also applied to study the electrode kinetics and charge transfer rate in – 1.12 V. Nyquist plots in Fig. 6d were fitted by the equivalent circuit, which was consist of two parts: R<sub>1</sub> for contact resistance and solution resistance; R<sub>2</sub>-C<sub>1</sub> for charge-transfer. Ni<sub>2</sub>Co<sub>1</sub>-P/CC represents the lowest charge transfer resistance (R<sub>ct</sub>) of 7.62  $\Omega$ , indicating the fastest charge transfer and substance transport during H<sub>2</sub> evolution.

The OER performance of Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC was also investigated in 1.0 M KOH. The polarization curves with 95% iR-correction are shown in Fig. 7a. Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC (X = 0.5–2.5) showed a near coincidence of the polarization curves, except a raise of oxidation peak in Ni<sub>2.5</sub>Co<sub>0.5</sub>-O/CC. The potentials of Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC (x = 0.5, 1, 1.5, 2, 2.5) at  $\eta_{10}$  were 1.59 V, 1.595 V, 1.58 V, 1.58 V, and 1.58 V, respectively. The Tafel slope values are shown in Fig. 7b. Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC (x = 0.5, 1, 1.5, 2), the Tafel slope of Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC (x = 0.5, 1, 1.5, 2), the Tafel slope of Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC (x = 0.5, 1, 1.5, 2) was 90 mV dec<sup>-1</sup> around ( $\pm 2$  mV dec<sup>-1</sup>). However, Ni<sub>2.5</sub>Co<sub>0.5</sub>-O/CC performs the largest Tafel slope of 120.1 mV dec<sup>-1</sup>. In addition, ECSA was evaluated from CV curves (Fig. S8). As shown in Fig. 7c, it is regular that C<sub>dl</sub> values decrease along with the reduction of nickel content, corresponding to the shrunken nanowires' size. Fitted by the equivalent circuit (Fig. 7d), Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC showed the minimum R<sub>ct</sub> of 10.81  $\Omega$ , indicating its faster charge transfer.

The UOR performance of the catalysts was tested in 1.0 M KOH with 0.33 M urea. Fig. 8a shows the polarization curves of  $Ni_xCo_{3-x}$ -O/CC. It is worth noting that  $Ni_{1.5}Co_{1.5}$ -O/CC presented the lowest potential of 1.435 V to reach 50 mA cm<sup>-2</sup> among  $Ni_xCo_{3-x}$ -O/CC, indicating its remarkable UOR catalytic performance. The Tafel slopes obtained from LSV curves are shown in Fig. 8b. Obviously, Tafel slopes varied with the Ni-Co ratio, showing a trend of decreasing firstly, and then increase. Consequently,  $Ni_{1.5}Co_{1.5}$ -O/CC presented

the lowest Tafel slope of 59.68 mV dec<sup>-1</sup>, indicating the most efficient reaction kinetics upon Ni15Co15-O/CC to proceed UOR. The UOR performance of Ni15Co15-O/CC was compared with other reported catalysts (Table, S3), proving Ni-Co oxide has great potential as UOR catalysts. Fig. 8c showed the C<sub>dl</sub> value of the samples for UOR which is calculated from the corresponding CV curves (Fig. S9). And it showed the same change in the OER test (C<sub>dl</sub> decreases with the X increasing in Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC). In Fig. 8d, Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC showed the minimum  $R_{ct}$  of 5.388  $\Omega$ , indicating much more fast kinetics than OER. In Fig. S10a, Ni<sub>2</sub>Co<sub>1</sub>-P/CC presented the coincident polarization curves in 1.0 M KOH with or without 0.33 Urea, confirming the presence of urea does not affect the progression of HER. Fig. S10b shows the polarization curves of Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC working as an anode in 1.0 M KOH with or without 0.33 M urea. It clearly shows that the electrode potential in the electrolyte that contains urea was 220 mV less than 1.0 M KOH at  $\eta_{10}$ , proving it's a feasible way to replace OER to reduce power consumption. The two electrode electrolytic cell with Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC as the anode and Ni<sub>2</sub>Co<sub>1</sub>-P/CC as the cathode was also assembled to proceed electrochemical reactions. As shown in Fig. S11, in 1.0 M KOH and 0.33 M urea, it needed only 1.47 V and 1.666 V to reach the current density of 10 and 50 mA cm<sup>-2</sup>, respectively. It's much less than in the 1.0 M KOH. To explore the rate of hydrogen production, we adopted a simple drainage and gas collection method. Fig. S12a presents the gas collected on a  $0.5 \text{ cm}^{-2}$  cathode (Ni<sub>2</sub>Co<sub>1</sub>-P/CC). The volume of the hydrogen is 15.02 mL in 40 min Fig. S12b shows that the electrolysis was carried out under the potential of driving 10 mA cm<sup>-2</sup>. And the Fluctuations in the curve correspond to the formation and separation of bubbles. By integrating the curve, we got the theoretical value of hydrogen generation, which agrees well with the experimental values. So the actual hydrogen production rate is 0.751 mL min<sup>-1</sup> cm<sup>-2</sup>. Fig. S13 showed the stability of the Ni<sub>2</sub>Co<sub>1</sub>-P/CC and Ni<sub>15</sub>Co<sub>15</sub>-O/CC. The current density of Ni<sub>2</sub>Co<sub>1</sub>-P/CC maintains 87.5% current density in 40 h, and Ni<sub>15</sub>Co<sub>15</sub>-O/CC kept nearly the same current in the first 22 h, then sharply declines to 80.7% current



**Fig. 8.** UOR performance in 1.0 M KOH with 0.33 M urea. (a) Polarization curves of UOR for different Ni-Co oxides (insert of corresponding overpotentials at  $\eta_{50}$ ). (b) The corresponding Tafel plots. (c) Capacitive current at 0.1 V vs. scan rates for the determination of C<sub>d1</sub> values. (d) The corresponding Nyquist plots.

density, which was corresponding to the depletion of urea in the electrolyte. Therefore,  $Ni_2Co_1$ -P/CC and  $Ni_{1.5}Co_{1.5}$ -O/CC both showed outstanding stability to process HER and UOR, respectively.

#### 4. Conclusion

In summary, Ni<sub>x</sub>Co<sub>3-x</sub>-P/CC and Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC were successfully prepared by the hydrothermal method and subsequent calcine process. The morphology variation of the samples with different Ni-Co relative content was observed, including a nanowires-nanosheets transformation when  $N_{Ni}:N_{Co}=2:1$  in Ni<sub>x</sub>Co<sub>2-x</sub>-P/CC and the shrinking nanowires volume with Ni content increasing in Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC. Furthermore, we studied the catalytic performance of Ni<sub>x</sub>Co<sub>3-x</sub>-P/CC toward HER, and the performance of Ni<sub>x</sub>Co<sub>3-x</sub>-O/CC toward OER and UOR, respectively. According to the experimental results, Ni<sub>2</sub>Co<sub>1</sub>-P/CC presented the best HER performance among other Ni<sub>x</sub>Co<sub>3-x</sub>-P/CCs because of its enlarged electrochemically active surface area and fast kinetics, needing an overpotential of 79 mV to reach  $\eta_{10}$ . Additionally, Ni<sub>x</sub>Co<sub>3-x</sub>-O/CCs nearly showed the same performance toward OER. But Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC presented the best UOR performance, needing a potential of 1.435 V to reach  $\eta_{50}$  in 1.0 M KOH and 0.33 M urea. Notably, Ni1.5Co1.5-O/CC needs 218 mV less to reach  $\eta_{10}$  with UOR (1.362 V) than simple OER (1.58 V), indicating the feasibility of utilizing UOR to replace OER in the cell. Therefore, a concurrent two-electrode electrolyzer (Ni\_{1.5}Co\_{1.5}-O/CC=|Ni\_2Co\_1-P/CC) is used to operate the catalyst, showing a potential of 1.47 V at  $\eta_{10}$ . In addition, Ni<sub>1.5</sub>Co<sub>1.5</sub>-O/CC also performed long-term stability of keeping a changeless current density at  $\eta_{10}$  for at least 22 h. The preparation method and catalysts utilization strategies developed in this work are inspirational to the electrolytic cell design for efficient hydrogen generation.

#### **CRediT authorship contribution statement**

Yuanjian Liu: Conceptualization, Methodology, Formal analysis, Validation, Investigation, Data curation, Writing – original draft, Writing – review & editing. Jibiao Guan: Validation, Investigation. Wubin Chen: Writing – original draft. Yudong Wu: Writing – review & editing. Shanshan Li: Writing – review & editing. Xiangheng Du: Resources. Ming Zhang: Conceptualization, Methodology, Resources, Writing – review & editing, Supervision.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.161790.

#### References

- S. Chu, A. Majumdar, Opportunities and challenges for a sustainable energy future, Nature 488 (2012) 294–303.
- [2] G. Nicoletti, N. Arcuri, G. Nicoletti, R. Bruno, A technical and environmental comparison between hydrogen and some fossil fuels, Energy Convers. Manag. 89 (2015) 205–213.
- [3] M. Yue, H. Lambert, E. Pahon, R. Roche, S. Jemei, D. Hissel, Hydrogen energy systems: a critical review of technologies, applications, trends and challenges, Renew. Sustain. Energy Rev. 146 (2021) 111180.
- [4] M.A. Habib, A. Harale, S. Paglieri, F.S. Alrashed, A. Al-Sayoud, M.V. Rao, M.A. Nemitallah, S. Hossain, M. Hussien, A. Ali, M.A. Haque, A. Abuelyamen, M.R. Shakeel, E.M.A. Mokheimer, R. Ben-Mansour, Palladium-alloy membrane reactors for fuel reforming and hydrogen production: a review, Energy Fuels 35 (2021) 5558–5593.

- [6] N. Roy, N. Suzuki, C. Terashima, A. Fujishima, Recent improvements in the production of solar fuels: from CO<sub>2</sub> reduction to water splitting and artificial photosynthesis, Bull. Chem. Soc. Jpn. 92 (2019) 178–192.
- [7] K. Maeda, T.E. Mallouk, Two-dimensional metal oxide nanosheets as building blocks for artificial photosynthetic assemblies, Bull. Chem. Soc. Jpn. 92 (2019) 38–54.
- [8] Y. Zhou, Z. Yijun, Y. Chen, A perovskite nanorod as bifunctional electrocatalyst for overall water splitting, Adv. Energy Mater. 7 (2017) 1602122.
- [9] Z. Li, M. Hu, P. Wang, J. Liu, J. Yao, C. Li, Heterojunction catalyst in electrocatalytic water splitting, Coord. Chem. Rev. 439 (2021) 213953.
- [10] J.N. Hansen, H. Prats, K.K. Toudahl, N. Mørch Secher, K. Chan, J. Kibsgaard, I. Chorkendorff, Is there anything better than Pt for HER? ACS Energy Lett. 6 (2021) 1175–1180.
- [11] S. Anantharaj, P.E. Karthik, B. Subramanian, S. Kundu, Pt nanoparticle anchored molecular self-assemblies of DNA: an extremely stable and efficient HER electrocatalyst with ultralow Pt content, ACS Catal. 6 (2016) 4660–4672.
- [12] C. Ma, W. Sun, W. Qamar Zaman, Z. Zhou, H. Zhang, Q. Shen, L. Cao, J. Yang, Lanthanides regulated the amorphization–crystallization of IrO2 for outstanding OER performance, ACS Appl. Mater. Interfaces 12 (2020) 34980–34989.
- [13] J. Lim, D. Park, S.S. Jeon, C.-W. Roh, J. Choi, D. Yoon, M. Park, H. Jung, H. Lee, Ultrathin IrO2 nanoneedles for electrochemical water oxidation, Adv. Funct. Mater. 28 (2018) 1704796.
- [14] Y. Fang, T. Zhang, Y. Wu, Y. Liu, M. Zhang, Stacked Co6W6C nanocrystals anchored on N-doping carbon nanofibers with excellent electrocatalytic performance for HER in wide-range pH, Int. J. Hydrog. Energy 45 (2019) 1901–1910.
- [15] W. Li, C. Wang, X. Lu, Integrated transition metal and compounds with carbon nanomaterials for electrochemical water splitting, J. Mater. Chem. A 9 (2020) 3786–3827.
- [16] S. Dutta, A. Indra, Y. Feng, H.S. Han, T. Song, Promoting electrocatalytic overall water splitting with nanohybrid of transition metal nitride-oxynitride, Appl. Catal. B: Environ. 241 (2018) 521–527.
- [17] J. Su, J. Zhou, L. Wang, L. Cong, Y. Chen, Synthesis and application of transition metal phosphides as electrocatalyst for water splitting, Sci. Bull. 62 (2017) 633–644.
- [18] Y. Zhu, X. Liu, S. Jin, H. Chen, W. Lee, M. Liu, Y. Chen, Anionic defect engineering of transition metal oxides for oxygen reduction and evolution reactions, J. Mater. Chem. A 7 (2019) 5875–5897.
- [19] P. Sivakumar, D. Vikraman, C.J. Raj, S. Hussain, J. Park, H.S. Kim, H. Jung, Hierarchical NiCo/NiO/NiCo2O4 composite formation by solvothermal reaction as a potential electrode material for hydrogen evolutions and asymmetric supercapacitors, Int. J. Energy Res. 1 (2021).
  [20] Y. Guo, T. Park, J.W. Yi, J. Henzie, J. Kim, Z. Wang, B. Jiang, Y. Bando, Y. Sugahara,
- [20] Y. Guo, T. Park, J.W. Yi, J. Henzie, J. Kim, Z. Wang, B. Jiang, Y. Bando, Y. Sugahara, J. Tang, Y. Yamauchi, Nanoarchitectonics for transition-metal-sulfide-based electrocatalysts for water splitting, Adv. Mater. 31 (2019) 1807134.
- [21] Q. Gao, W. Zhang, Z. Shi, L. Yang, Y. Tang, Structural design and electronic modulation of transition-metal-carbide electrocatalysts toward efficient hydrogen evolution, Adv. Mater. 31 (2019) 1802880.
- [22] Chen Linlin, Yang Saisai, Qian Kun, Wei Wei, Sun Cheng, In situ growth of Ndoped carbon coated CoNi alloy with graphene decoration for enhanced HER performance, J. Energy Chem. 29 (2019) 129–135.
- [23] Y. Shi, B. Zhang, Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction, Chem. Soc. Rev. 45 (2016) 1529–1541.
- [24] D.-W. Wang, Y.-D. Zhu, S. Lei, S.-M. Chen, Z.-G. Gu, J. Zhang, Epitaxial growth of prussian blue analogue derived NiFeP thin film for efficient electrocatalytic hydrogen evolution reaction, J. Solid State Chem. 293 (2021) 121779.
- [25] R.-Q. Li, B.-L. Wang, T. Gao, R. Zhang, C. Xu, X. Jiang, J. Zeng, Y. Bando, P. Hu, Y. Li, X.-B. Wang, Monolithic electrode integrated of ultrathin NiFeP on 3D strutted graphene for bifunctionally efficient overall water splitting, Nano Energy 58 (2019) 870–876.
- [26] P. Liu, J.A. Rodriguez, Catalysts for hydrogen evolution from the [NiFe] hydrogenase to the Ni2P(001) surface: the importance of ensemble effect, J. Am. Chem. Soc. 127 (2005) 14871–14878.
- [27] L. Xiong, B. Wang, H. Cai, H. Hao, J. Li, T. Yang, S. Yang, Understanding the doping effect on hydrogen evolution activity of transition-metal phosphides: Modeled with Ni2P, Appl. Catal. B: Environ. 295 (2021) 120283.
- [28] Q. Wang, Z. Liu, H. Zhao, H. Huang, H. Jiao, Y. Du, MOF-derived porous Ni2P nanosheets as novel bifunctional electrocatalysts for the hydrogen and oxygen evolution reactions, J. Mater. Chem. A 6 (2018) 18720–18727.
- [29] J. Wang, H. Cheng, S. Ren, L. Zhang, L.-X. Ding, H. Wang, In situ coupling of CoP with MoO2 for enhanced hydrogen evolution, J. Mater. Chem. A 8 (2020) 16018–16023.
- [30] X. Du, Y. Fang, J. Guan, T. Zhang, L. Yi, L. Wang, M. Zhang, Urchin-like Co0.8-Mn0.2-P/CC nanowires array: a high-performance and cost-effective hydrogen evolution electrocatalyst, Int. J. Hydrog. Energy 45 (2020) 18976–18984.
- [31] D. Li, D. Liu, S. Zhao, S. Lu, Y. Ma, M. Li, G. Chen, Y. Wang, G. Zhou, C. Xiao, Tuning of metallic valence in CoMoP for promoting electrocatalytic hydrogen evolution, Int. J. Hydrog. Energy 44 (2019) 31072–31081.
- [32] Z. Mu, T. Guo, H. Fei, Y. Mao, Z. Wu, D. Wang, Mn-doped porous interconnected MoP nanosheets for enhanced hydrogen evolution, Appl. Surf. Sci. 551 (2021) 149321.

- [33] X. Zhang, T. Guo, T. Liu, K. Lv, Z. Wu, D. Wang, Tungsten phosphide (WP) nanoparticles with tunable crystallinity, W vacancies, and electronic structures for hydrogen production, Electrochim. Acta 323 (2019) 134798.
- [34] L. Wu, Z. Pu, Z. Tu, I.S. Amiinu, S. Liu, P. Wang, S. Mu, Integrated design and construction of WP/W nanorod array electrodes toward efficient hydrogen evolution reaction, Chem. Eng. J. 327 (2017) 705–712.
- [35] L. Gao, J. Xie, S. Liu, S. Lou, Z. Wei, X. Zhu, B. Tang, Crystalline cobalt/amorphous LaCoOx hybrid nanoparticles embedded in porous nitrogen-doped carbon as efficient electrocatalysts for hydrazine-assisted hydrogen production, ACS Appl. Mater. Interfaces 12 (2020) 24701–24709.
- [36] P. Tang, H. Wen, C. Chen, X. Lin, P. Wang, Hierarchically nanostructured (Ni,Co) phosphides for hydrazine electrooxidation, Electrochim. Acta 387 (2021) 138492.
- [37] W. Liu, J. Xie, Y. Guo, S. Lou, L. Gao, B. Tang, Sulfurization-induced edge amorphization in copper-nickel-cobalt layered double hydroxide nanosheets promoting hydrazine electro-oxidation, J. Mater. Chem. A 7 (2019) 24437–24444.
- [38] H. Liu, S. Zhu, Z. Cui, Z. Li, S. Wu, Y. Liang, Ni2P nanoflakes for the high-performing urea oxidation reaction: linking active sites to a UOR mechanism, Nanoscale 13 (2021) 1759–1769.
- [39] K. Ye, G. Wang, D. Cao, G. Wang, Recent advances in the electro-oxidation of urea for direct urea fuel cell and urea electrolysis, Top. Curr. Chem. (Cham) 376 (2018) 42.
- [40] Y. Tong, P. Chen, M. Zhang, T. Zhou, L. Zhang, W. Chu, C. Wu, Y. Xie, Oxygen vacancies confined in nickel molybdenum oxide porous nanosheets for promoted electrocatalytic urea oxidation, ACS, Catalysis 8 (2017) 1–7.
- [41] W. Xu, Z. Wu, S. Tao, Urea-based fuel cells and electrocatalysts for urea oxidation, Energy Technol. 4 (2016) 1329–1337.
- [42] X. Gao, H. Zhang, Q. Li, X. Yu, Z. Hong, X. Zhang, C. Liang, Z. Lin, Hierarchical NiCo2O4 hollow microcuboids as bifunctional electrocatalysts for overall watersplitting, Angew. Chem. Int Ed. Engl. 128 (2016) 6398–6402.
- [43] H. Wang, H.W. Lee, Y. Deng, Z. Lu, P.C. Hsu, Y. Liu, D. Lin, Y. Cui, Bifunctional nonnoble metal oxide nanoparticle electrocatalysts through lithium-induced conversion for overall water splitting, Nat. Commun. 6 (2015) 7261.
- [44] D. Wang, S.H. Vijapur, Y. Wang, G.G. Botte, NiCo2O4 nanosheets grown on current collectors as binder-free electrodes for hydrogen production via urea electrolysis, Int. J. Hydrog. Energy 42 (2017) 3987–3993.
- [45] L. Sha, K. Ye, G. Wang, J. Shao, K. Zhu, K. Cheng, J. Yan, G. Wang, D. Cao, Hierarchical NiCo2O4 nanowire array supported on Ni foam for efficient urea electrooxidation in alkaline medium, J. Power Sources 412 (2019) 265–271.
- [46] Y. Yan, B.Y. Xia, B. Zhao, X. Wang, A review on noble-metal-free bifunctional heterogeneous catalysts for overall electrochemical water splitting, J. Mater. Chem. A 4 (2016) 17587–17603.
- [47] L. Hang, T. Zhang, Y. Sun, D. Men, X. Lyu, Q. Zhang, W. Cai, Y. Li, Ni0.33Co0.67MoS4 nanosheets as a bifunctional electrolytic water catalyst for overall water splitting, J. Mater. Chem. A 6 (2018) 19555–19562.
- [48] T. Zhang, L. Hang, Y. Sun, D. Men, X. Li, L. Wen, X. Lyu, Y. Li, Hierarchical hetero-Ni3Se4@NiFe LDH micro/nanosheets as efficient bifunctional electrocatalysts with superior stability for overall water splitting, Nanoscale Horiz. 4 (2019) 1132–1138.
- [49] R. Bose, V.R. Jothi, K. Karuppasamy, A. Alfantazi, S.C. Yi, High performance multicomponent bifunctional catalysts for overall water splitting, J. Mater. Chem. A 8 (2020) 13795–13805.
- [50] T. Li, N. Dang, W. Zhang, W. Liang, F. Yang, Determining the degree of [001] preferred growth of Ni(OH)2 nanoplates, Nanomaterials (2018) 911.
  [51] Z. Cai, A. Wu, H. Yan, Y. Xiao, C. Chen, C. Tian, L. Wang, R. Wang, H. Fu,
- [51] Z. Cai, A. Wu, H. Yan, Y. Xiao, C. Chen, C. Tian, L. Wang, R. Wang, H. Fu, Hierarchical whisker-on-sheet NiCoP with adjustable surface structure for efficient hydrogen evolution reaction, Nanoscale 10 (2018) 7619–7629.
- [52] J.-Y. Kim, H. Park, W. Joo, D.-H. Nam, S. Lee, H.G. Kim, I.-K. Ahn, H.-Y. Kang, G.-B. Lee, I.-h Jung, M.-Y. Kim, G.-D. Lee, Y.-C. Joo, Predictive fabrication of Ni phosphide embedded in carbon nanofibers as active and stable electrocatalysts, J. Mater. Chem. A 7 (2019) 7451–7458.
- [53] I. Abidat, C. Morais, C. Comminges, C. Canaff, J. Rousseau, N. Guignard, T.W. Napporn, A. Habrioux, K.B. Kokoh, Three dimensionally ordered mesoporous hydroxylated NixCo3-xO4 spinels for the oxygen evolution reaction: on the hydroxyl-induced surface restructuring effect, J. Mater. Chem. A 5 (2017) 7173–7183.
- [54] D. Cheng, Y. Lan, F. Yang, G. Cheng, L. Wei, Nest-like NiCoP for highly efficient overall water splitting, ACS Catal. 7 (2017) 4131–4137.
- [55] S. Surendran, S. Shanmugapriya, A. Sivanantham, S. Shanmugam, R. Kalai, Electrospun carbon nanofibers encapsulated with NiCoP: a multifunctional electrode for supercapattery and oxygen reduction, oxygen evolution, and hydrogen evolution reactions, Adv. Energy Mater. 8 (2018) 1800555.
- [56] J. Liu, Z. Wang, J. David, J. Llorca, J. Li, X. Yu, A. Shavel, J. Arbiol, M. Meyns, A. Cabot, Colloidal Ni2-xCoxP nanocrystals for the hydrogen evolution reaction, J. Mater. Chem. A 6 (2018) 11453–11462.
- [57] M.F. Delley, Z. Wu, M.E. Mundy, D. Ung, B.M. Cossairt, H. Wang, J.M. Mayer, Hydrogen on cobalt phosphide, J. Am. Chem. Soc. 141 (2019) 15390–15402.
- [58] D. Zhu, L. Wang, M. Qiao, J. Liu, Phosphate ion functionalized CoP nanowire arrays for efficient alkaline hydrogen evolution, Chem. Commun. 56 (2020) 7159–7162.
- [59] B. Cao, Y. Cheng, M. Hu, P. Jing, Z. Ma, B. Liu, R. Gao, J. Zhang, Efficient and durable 3D self-supported nitrogen-doped carbon-coupled nickel/cobalt phosphide electrodes: stoichiometric ratio regulated phase- and morphology-dependent overall water splitting performance, Adv. Funct. Mater. 29 (2019) 1906316.
  [60] H. Cao, Y. Xie, H. Wang, F. Xiao, A. Wu, L. Li, Z. Xu, N. Xiong, K. Pan, Flower-like
- [60] H. Cao, Y. Xie, H. Wang, F. Xiao, A. Wu, L. Li, Z. Xu, N. Xiong, K. Pan, Flower-like CoP microballs assembled with (002) facet nanowires via precursor route:

Efficient electrocatalysts for hydrogen and oxygen evolution, Electrochim. Acta 259 (2018) 830-840.

- [61] C. Liu, G. Zhang, L. Yu, J. Qu, H. Liu, Oxygen doping to optimize atomic hydrogen binding energy on NiCoP for highly efficient hydrogen evolution, Small 14 (2018) 1800421.
- [62] Z. Chen, B. Zhao, Y.C. He, H.R. Wen, X.Z. Fu, R. Sun, C.P. Wong, NiCo2O4 nano-frames with a nanosheet surface as efficient electrocatalysts for the oxygen evolution reaction, Mater. Chem. Front. 2 (2018) 1155–1164.

- [63] L. Zhang, Y. Li, J. Peng, K. Peng, Bifunctional NiCo2O4 porous nanotubes electrocatalyst for overall water-splitting, Electrochim. Acta 318 (2019) 762–769.
  [64] M. Cui, X. Ding, X. Huang, Z. Shen, T.-L. Lee, F.E. Oropeza, J.P. Hofmann, E.J.M. Hensen, K.H.L. Zhang, Ni3+-induced hole states enhance the oxygen evolution reaction activity of NixCo3-xO4 electrocatalysts, Chem. Mater. 31 (2019) 7618–7625.
  [65] J.A. Bau, H. Haspel, S. Ould-Chikh, A. Aguilar-Tapia, J.-L. Hazemann, H. Idriss, K. Takanabe, On the reconstruction of NiMo electrocatalysts by operando spectroscopy, J. Mater. Chem. A 7 (2019) 15031–15035.