Nickel-doped Co₄N nanowire bundles as efficient electrocatalysts for oxygen evolution reaction

Dan Li¹, Wenbiao Zhang¹, Jiachang Zeng¹, Boxu Gao², Yi Tang² and Qingsheng Gao^{1*}

ABSTRACT Cost-efficient electrocatalysts composed of earth-abundant elements are highly desired for enhanced oxygen evolution reaction (OER). As a promising candidate, metallic Co₄N already demonstrated electrocatalytic performance relying on specific nanostructures and electronic configurations. Herein, nickel was introduced as the dopant into one-dimensional (1D) hierarchical Co₄N structures, achieving effective electronic regulation of Co₄N toward high OER performance. The amount of Co³⁺ increased after Ni-doping, and the *in-situ* formed surface oxyhydroxide during OER enhanced the electrocatalytic kinetics. Meanwhile, the 1D hierarchical structure further promoted the performances of Co₄N owing to the high electrical conductivity and abundant active-sites on the rough surface. As expected, the optimal Ni-doped Co₄N with a Ni/Co molar ratio of 0.25 provides a small overpotential of 233 mV at a current density of 10 mA cm⁻², with a low Tafel slope of 61 mV dec⁻¹, and high long-term stability in 1.0 mol L⁻¹ KOH. Following these results, the enhancement by doping the Co₄N nanowire bundles with Fe and Cu was further evidenced for the OER.

Keywords: oxygen evolution reaction, cobalt nitrides, heteroatom doping, electronic state, nanowire bundles

INTRODUCTION

As the main half-reaction of water-splitting and metal-air batteries, oxygen evolution reaction (OER) usually suffers from slow kinetics of the four-electron transfer process and is the main impediment to catalytic efficiency [1–4]. Although RuO₂ and IrO₂ have displayed high electrocatalytic activities, shortcomings such as low earth-abundance, high price, and poor stability severely restrain their industrial applicability [5–9]. Thus, it is highly desired to develop cost-efficient and durable alternatives

based on transition-metal nitrides, sulfides, phosphides, selenides, and carbides [10–15].

Among noble-metal-free candidates, the “family” of cobalt nitrides (e.g., CoN, Co₂N, and Co₄N) have attracted particular attention due to their metallic properties, exceptional corrosion resistance, and unique 3d electronic configurations [16–21]. Although important progress has been made, the rational design of catalysts with high activity and excellent stability is still challenging. It is also well-known that optimizing the electronic state of a catalyst ameliorates the binding energies between the active sites and reactive species and then cuts down the overpotential of the reaction [22,23]. For example, using V as a doping agent can downshift the d-band center, leading to optimal hydrogen binding and a comparable hydrogen evolution performance to Pt/C [24]. Meanwhile, it is supposed that the efficient electrocatalysts should possess fine-tuneable specific surface area, rich active sites and excellent electrical conductivity. Such structural peculiarities can be combined in one-dimensional (1D) nanostructures. For instance, 1D porous Co₄N nanowire arrays already expressed outstanding OER activity, requiring a relatively low overpotential of 290 mV to reach a current density of 10 mA cm⁻² in an alkaline electrolyte [25]. Regarding the role of cobalt atom in the active catalytic site of Co₄N [26–29], significant electronic modulation could be the key to further boost the OER activity intrinsically.

Herein, we prepared a transition-metal-doped M-Co₄N (M = Ni, Fe, Cu) nanowire bundles with hierarchical structures by a two-step process. As illustrated in Scheme 1, M-doped CoC₂O₄·2H₂O microwires were synthesized by a simple co-precipitation method firstly, and then they were nitrogenized in an NH₃/Ar flow to

¹ College of Chemistry and Materials Science, and Guangdong Provincial Key Laboratory of Functional Supramolecular Coordination Materials and Applications, Jinan University, Guangzhou 510632, China

² Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials and Collaborative Innovation Center of Chemistry for Energy Materials, Fudan University, Shanghai 200433, China

* Corresponding author (email: tqsgao@jnu.edu.cn)

Scheme 1 Schematic illustration for the preparation of Ni-Co₄N nanowire bundles.

obtain target products. To determine the most favorable doping content, a series of Ni-Co₄N catalysts were prepared with varied molar ratios of Ni/Co ($R_{\text{Ni/Co}}$). The samples were denoted accordingly as Ni-Co₄N- $R_{\text{Ni/Co}}$. It was found that after Ni-doping, the ratio of Co³⁺ increases, and the oxyhydroxide *in-situ* formed on the surface during OER was a benefit for electrocatalytic kinetics. Besides, Ni-doping also influenced the morphology of the products, which evolved from microwires to nanowire bundles with more exposed surface active-sites and porous microspheres with excessive Ni dosage. Serving as OER electrocatalysts, the optimal Ni-Co₄N-0.25 nanowire bundles require an overpotential (η_{10}) of only 233 mV to reach a current density of 10 mA cm⁻² and a Tafel slope of merely 61 mV dec⁻¹ in 1.0 mol L⁻¹ KOH. Meanwhile, after a long-term test with 40,000 s, they are proved remarkably durable. The OER performance proves that the as-optimized electronic state and the structure of unique nanowire bundles promote the efficient electrocatalytic performance.

EXPERIMENTAL SECTION

Catalyst preparation

All reagents were of analytical grade and used without further purification. The M-Co₄N catalysts were prepared using a simple co-deposition process and a high-temperature nitridation under a 5% NH₃/Ar gas flow. The synthesis of Ni-Co₄N-0.25 is detailed as an example. Typically, Co(NO₃)₂·6H₂O (2.07 g, 8 mmol), Ni(CH₃-COO)₂·4H₂O (0.53 g, 2 mmol) and oxalic acid dihydrate (~1.26 g, 10 mmol) were added into 100 mL deionized water in a beaker and stirred for 2 h at room temperature. The product was washed with deionized water and absolute ethanol several times and dried at 70°C in a vacuum dryer. The as-obtained Ni-CoC₂O₄·2H₂O (0.30 g) was heated at 500°C for 2 h under an NH₃/Ar gas flow to get the targeted Ni-Co₄N-0.25. The content of Ni dopant in Ni-Co₄N was tuned by adjusting the dosage of

Ni(CH₃COO)₂·4H₂O (the amount of Co and Ni sum up to 10 mmol) during precursor synthesis (with similar parameters as described above). In control experiments, Fe-Co₄N and Cu-Co₄N nanowire bundles were synthesized *via* a similar procedure except replacing the Ni(CH₃COO)₂·4H₂O with FeSO₄·2H₂O and Cu(CH₃-COO)₂·4H₂O, respectively.

Physical characterization

The crystal structures were characterized by X-ray diffraction (XRD) on a Bruker D8 diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) was measured using a Thermo Scientific Escalab 250Xi, using C 1s (284.6 eV) as a reference. The morphologies were observed by field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) on a ZEISS ULTRA55 and a JEOL JEM-2100F, respectively. The Co and M (M = Ni, Fe, Cu) contents in the M-Co₄N catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Electrochemical measurements

Electrocatalysts were loaded onto a glassy carbon electrode (GCE) as a working electrode. Typically, 5 mg of catalyst and a solution of 50 μL of 5 wt% Nafion were dispersed in 950 μL of isopropyl alcohol using a 30 min sonication to form a homogeneous ink. Then 10 μL of the catalyst ink was loaded onto the GCE with a diameter of 3 mm.

Linear sweep voltammetry (LSV) was conducted with a scan rate of 2 mV s⁻¹ in 1.0 mol L⁻¹ KOH on a CHI760 (CH Instruments) potentiostat, using a Hg/HgO electrode as the reference electrode and a graphite rod as the counter electrode. All the potentials reported in this paper were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.098 + 0.059 pH) V. Electrochemical impedance spectra (EIS) measurements were carried out in an electrochemical setup with the same configuration at $\eta = 244 \text{ mV}$ from 0.1 to 10⁵ Hz. iR correction was manually performed for every electrode to remove the influence of solution and instrument resistance (R_s). We got R_s value according to the EIS data and calculated the “real” potential by the formula: $E_{\text{real}} = E_{\text{test}} - iR_s$.

DFT calculations

CASTEP package implemented in Materials Studio was used for density functional theoretical (DFT) calculations. Generalized gradient approximation (GGA) with Perdew-

Burke-Ernzerhof (PBE) functional was used for the DFT exchange-correlation energy. Furthermore, a kinetic energy cut-off of 450.0 eV was assigned to the plane-wave basis set to calculate the density of state and electron density difference. The self-consistent field (SCF) tolerance was 1×10^{-5} eV atom⁻¹. The Brillouin Zone *k*-point was set by a $5 \times 5 \times 1$ Monkhorst-Pack grid. The core electrons were replaced with ultrasoft pseudo-potentials. For the Gibbs free energy of the OER process on the CoOOH and Ni_{0.2}Co_{0.8}OOH surface, the (100) facet was modeled with vacuum widths of 12 Å, using a single-layer 3×1 surface slab. The Gibbs free energies (*G*) of OH*, OOH*, O* species were calculated according to the following equations:

$$G = E - TS, \quad (1)$$

where *E*, *T* and *S* are the enthalpy, temperature and entropy, respectively. The changes in free energy (ΔG) were calculated as:

$$\Delta G = \Delta E - T\Delta S. \quad (2)$$

For the evaluation of the whole OER process, the change in free energy (ΔG) of each step was calculated as:

$$\Delta G_1 = G_{\text{OH}^*} + \frac{1}{2}G_{\text{H}_2} - G^* - G_{\text{H}_2\text{O}}, \quad (3)$$

$$\Delta G_2 = G_{\text{O}^*} + \frac{1}{2}G_{\text{H}_2} - G_{\text{OH}^*}, \quad (4)$$

$$\Delta G_3 = G_{\text{OOH}^*} + \frac{1}{2}G_{\text{H}_2} - G_{\text{O}^*} - G_{\text{H}_2\text{O}}, \quad (5)$$

$$\Delta G_4 = 4.92 - (\Delta G_1 + \Delta G_2 + \Delta G_3). \quad (6)$$

RESULTS AND DISCUSSION

In the XRD patterns of the precursor (Fig. 1a), all the diffraction peaks match well with CoC₂O₄·2H₂O (JCPDS No.: 25-0250). After nitridation at 500°C, a cubic phase of Co₄N (JCPDS No.: 15-0806) was observed (Fig. 1b). The peaks at $2\theta = 44.5^\circ$, 51.7° , and 76.0° are attributed to the (111), (200) and (220) planes of Co₄N, respectively [24,29]. No other diffraction peaks appear after Ni-doping, indicating the successful preparation of the pure-phase Co₄N.

The morphology of the precursor and M-Co₄N nanostructures were investigated by SEM and TEM. As

Figure 1 XRD patterns of (a) the CoC₂O₄·2H₂O precursor and (b) Ni-Co₄N-R_{Ni/Co} samples. (c) SEM, (d) TEM, (e) HR-TEM images, (f) SAED pattern, and (g) elemental mapping of Ni-Co₄N-0.25 nanowire bundles.

shown in Fig. S1, the $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precursor displays a microwire-based architecture with a length of several microns and a smooth surface. Interestingly, after the nitridation process, the $\text{Ni-Co}_4\text{N-0.25}$ maintains the 1D structure but splits into nanowire bundles with a porous and rough surface (Fig. 1c). This unique hierarchical architecture could be beneficial for electrolytes approaching the active sites and enhancing the catalytic efficiency. The TEM image of $\text{Ni-Co}_4\text{N-0.25}$ in Fig. 1d reveals that the nanowires have a diameter of ~ 100 nm and are composed of nanoparticles. The high-resolution TEM (HR-TEM) image (Fig. 1e) shows lattice fringes with d -spacings of 0.17 and 0.21 nm, corresponding to the (200) and (111) planes of Co_4N , respectively. Accordingly, the selected area of electron diffraction (SAED) pattern also reveals that the $\text{Ni-Co}_4\text{N}$ has a polycrystalline structure (Fig. 1f). Furthermore, the high annular dark-field scanning TEM (HAADF-STEM) image and the corresponding elemental mapping (Fig. 1g) verify the homogeneous distribution of Co, Ni, and N elements within the whole nanowire. It is indicated that Ni is uniformly dispersed into the structure of the nanowires.

A series of $\text{Ni-Co}_4\text{N-}R_{\text{Ni/Co}}$ ($R_{\text{Ni/Co}} = 0.01, 0.05, 0.25, 0.43, 1.0$) were examined by SEM to reveal the influence

of Ni on the $\text{Ni-Co}_4\text{N}$ nanostructures. It is clear that with the increase of the Ni content, the $\text{Ni-Co}_4\text{N}$ gradually changes from nanowire bundles to microspheres (Fig. 2 and Figs S2, S3). Regarding that similar microspheres were formed only when Ni was introduced (Fig. S4), we assumed that the morphology evolution with the increase of Ni dopant stemmed from the varied growth of Ni-related nanocrystals. The as-obtained microsphere structures could reduce the exposure of the active surface.

XPS was performed to analyze the chemical states of Co_4N and $\text{Ni-Co}_4\text{N}$ samples (Fig. 3). In the Co 2p profile of Co_4N nanowire bundles (Fig. 3a), the peaks located at 779.7 and 781.4 eV are attributed to the Co 2p_{3/2} of Co^{3+} and Co^{2+} , respectively. Furthermore, the peaks centered at 795.2 and 797.0 eV are assigned to the Co 2p_{1/2} of Co^{3+} and Co^{2+} , while the two peaks at 786.0 and 802.7 eV belong to satellite signals. The relative amount of Co^{3+} in $\text{Ni-Co}_4\text{N}$ (55.7%) is higher than that of Co_4N (48.1%). According to the previous reports [26], the existence of Co^{3+} active sites could be beneficial for the OER kinetics. Thus, the increasing proportion of Co^{3+} suggests the favored OER activity of $\text{Ni-Co}_4\text{N}$. Additionally, the XPS N 1s spectrum (Fig. 3b) verifies the presence of metal-N species [30,31], further confirming the successful pre-

Figure 2 SEM images of $\text{Ni-Co}_4\text{N}$ with various Ni doping contents: (a) Co_4N , (b) $\text{Ni-Co}_4\text{N-0.01}$, (c) $\text{Ni-Co}_4\text{N-0.05}$, (d) $\text{Ni-Co}_4\text{N-0.25}$ (e) $\text{Ni-Co}_4\text{N-0.43}$, and (f) $\text{Ni-Co}_4\text{N-1.0}$. (g) Schematic illustration of morphological evolution relying on the Ni content.

Figure 3 High-resolution XPS spectra of (a) Co 2p and (b) N 1s of Co_4N and $\text{Ni-Co}_4\text{N-0.25}$, and (c) Ni 2p of $\text{Ni-Co}_4\text{N-0.25}$.

paration of $\text{M-Co}_4\text{N}$ structures. Fig. 3c shows the XPS Ni 2p spectrum of $\text{Ni-Co}_4\text{N-0.25}$ nanowire bundles, which can be deconvoluted into two peaks located at 852.7 and 856.0 eV, assigned to the $\text{Ni 2p}_{3/2}$ of Ni-N and Ni^{2+} species, respectively [32].

The OER performance of the as-prepared catalysts was tested in 1.0 mol L^{-1} KOH at room temperature using a standard three-electrode configuration compared with commercially available IrO_2 for reference. LSV curves are shown in Fig. 4a. With the increasing Ni content, the OER activity of $\text{Ni-Co}_4\text{N}$ catalysts enhances at first and then decreases. The $\text{Ni-Co}_4\text{N-0.25}$ shows the best OER performance that even outperforms the commercial reference. Meanwhile, the Tafel plot was analyzed to evaluate the OER kinetics (Fig. 4b). Although IrO_2 possesses the smallest Tafel slope (53 mV dec^{-1}), the $\text{Ni-Co}_4\text{N-0.25}$ delivers a value of 61 mV dec^{-1} , lower than in the case of Co_4N (86 mV dec^{-1}), $\text{Ni-Co}_4\text{N-0.05}$ (68 mV dec^{-1}), $\text{Ni-Co}_4\text{N-0.43}$ (64 mV dec^{-1}), and $\text{Ni-Co}_4\text{N-1.0}$ (84 mV dec^{-1}). The smaller Tafel slope indicates a rapid increase of O_2 generation rate with the applied overpotential, following the polarization curves. Fig. 4c further summarizes the η_{10} and η_{50} criteria of Co_4N and $\text{Ni-Co}_4\text{N}$. The $\text{Ni-Co}_4\text{N-0.25}$ nanowire bundles show the lowest overpotential of 233 and 290 mV, reaching a current density of 10 and 50 mA cm^{-2} , respectively. It is also indicated that changing the Ni content can efficiently regulate the electronic state on the catalyst surface, and the optimal molar ratio of Ni to Co is 0.25. When surpassing a certain ratio, the electronic configuration deviates from the optimal state, and the morphology also evolves from nanowires bundles into microspheres (Fig. 2), resulting in poor contact between the catalyst and reactants. Besides, even compared with other Co_4N -based oxygen generation catalysts (Fig. 4d), the $\text{Ni-Co}_4\text{N-0.25}$ nanowire bundles still feature a very low overpotential at

a current density of 10 mA cm^{-2} .

The electrocatalytic properties of materials generally depend on their electrochemically active surface areas (ECSAs) that are directly related to the double-layer capacitance (C_{dl}). The C_{dl} could be evaluated by cyclic voltammetry (CV) in a non-faradic region. As shown in Fig. S5, CVs of Co_4N and $\text{Ni-Co}_4\text{N}$ catalysts were recorded at different scan rates, ranging from 40 to 200 mV s^{-1} . The C_{dl} value of $\text{Ni-Co}_4\text{N-0.25}$ is 13.7 mF cm^{-2} , higher than that of the Co_4N (4.7 mF cm^{-2}), $\text{Ni-Co}_4\text{N-0.05}$ (7.3 mF cm^{-2}), $\text{Ni-Co}_4\text{N-0.43}$ (9.8 mF cm^{-2}), and $\text{Ni-Co}_4\text{N-1.0}$ (6.5 mF cm^{-2}). The difference of C_{dl} between various catalysts implies that the structure and morphology could also play a vital role in the catalytic performance.

To investigate the OER kinetics process, the Nyquist plots of Co_4N and $\text{Ni-Co}_4\text{N}$ were tested from 0.1 to 10^5 Hz (Fig. 4e). The data were fitted by using the equivalent circuit (shown in the inset of Fig. 4e). The charge-transfer resistance (R_{ct}) of $\text{Ni-Co}_4\text{N-0.25}$ is lower than that of Co_4N and other $\text{Ni-Co}_4\text{N}$ catalysts, indicating a faster electron transport during OER (Fig. S6). The long-term durability could be another key criterion for the applicability of the electrocatalysts. Herein, the prolonged electrolysis at a fixed overpotential of 279 mV was conducted on the $\text{Ni-Co}_4\text{N-0.25}$ nanowire bundles (Fig. 4f). The catalytic current remains at around 25 mA cm^{-2} for over 40,000 s without noticeable degradation.

To understand the differences of OER between the Co_4N and $\text{Ni-Co}_4\text{N-0.25}$, XPS and TEM investigations were performed after the OER test. Fig. 5a presents the Co 2p curves of the used Co_4N and $\text{Ni-Co}_4\text{N-0.25}$. Noticeably, the $\text{Ni-Co}_4\text{N-0.25}$ exhibits a higher Co^{3+} content (74.2%) in comparison with the Co_4N (56.5%), indicating more Co^{3+} species in the *in-situ* reconstructed $\text{Ni-Co}_4\text{N-}$

Figure 4 (a) *iR*-corrected OER polarization curves and (b) the corresponding Tafel plots, (c) summary of the η_{10} and η_{50} values, and (d) comparison of η_{10} of Ni-Co₄N-0.25 nanowire bundles with some recently reported cobalt nitride electrocatalysts (samples 1: Co₄N-VN_{1-x}O_x [33], 2: Co-Mo-N-PHP [34], 3: NC-Co/CoN_x nanoarrays [18], 4: NC@CuCo nitride nanosheet networks [35], 5: FeCo-Co₄N/N-C [21], 6: NiCo-nitrides/NiCo₂O₄/GF [36], 7: Co₄N porous nanowire arrays [25], 8: CoN nanowire arrays [20], 9: CoN/Ni₃N-coupled nanograsses [37], 10: Co_xFe_yN/graphene [38], 11: Co₄N/CNW/CC [39], 12: Co/CoN/Co₂P-NPC [40], 13: Co_{5.47}N/Co₃N alloy [41], 14: Co₄N [42]). (e) Nyquist plots of Co₄N, Ni-Co₄N and the commercial IrO₂ catalysts recorded in a 1.0 mol L⁻¹ KOH solution, and (f) time dependence of the current density for Ni-Co₄N-0.25 at a static overpotential of 279 mV in 1.0 mol L⁻¹ KOH.

0.25 during OER [43–46]. Accordingly, the Ni-Co₄N-0.25 presents a distinct larger peak area at 529.6 eV corresponding to M–O in the O 1s profile (Fig. 5b), further confirming the higher ratio of Co³⁺ after OER [47–49]. In the Ni 2p XPS spectra (Fig. S7a), the satellite peak at 861.8 eV related to the Ni³⁺ proves the oxidation reaction during the OER [50,51]. The N 1s XPS peak (Fig. S7b) becomes weaker after the OER test, which should be ascribed to the amorphous CoO_x(OH)_y layer formation on the catalyst surface. We also investigated the TEM images of the catalysts after the OER process (Fig. S8). Both Co₄N and Ni-Co₄N-0.25 catalysts maintain the original nanowire structure after the extensive oxidation reaction. HR-

TEM images of the post-OER Co₄N and Ni-Co₄N-0.25 are displayed in Fig. 5c, d, respectively. Following the previously reported results [52,53], the crystalline surface of the catalysts is oxidized to an amorphous CoO_x(OH)_y layer with a thickness of about 3–5 nm. Interestingly, under the thin amorphous layer, the Co₄N exhibits high crystallinity; in contrast, there are many disordered small grains, amorphous domains, and rich interfaces in the Ni-Co₄N-0.25. Thus, this structure can be considered efficient to promote OER performance [54].

To unveil the effect of Ni doping and further explore the theoretical background of the high catalytic activity of Ni-Co₄N-0.25, DFT calculations were performed. At first,

Figure 5 (a) Co 2p and (b) O 1s XPS profiles, and HR-TEM images of (c) Co₄N and (d) Ni-Co₄N-0.25 after the OER test in 1.0 mol L⁻¹ KOH. Free-energy diagram of the OER on (e) CoOOH and (f) Ni_{0.2}Co_{0.8}OOH models in an alkaline solution.

the electronic configurations of Co₄N and Ni-Co₄N-0.25 were queried (Fig. S9). The density of states (DOS) of Ni-Co₄N and Co₄N are continuous at the Fermi level, indicating that the inherent metallic properties of Co₄N are not destroyed after the introduction of Ni atoms [55,56]. Ni-Co₄N further exhibits a slightly increased density below the Fermi level compared with Co₄N, which suggests the enriched d electrons and easier oxidation on Ni-Co₄N [57]. This consideration is consistent with the XPS and TEM results of the used electrocatalysts (Fig. 5a–d).

Therefore, the *in-situ* formed surface oxyhydroxides should be studied as active species during the OER process [58]. Herein, the models of CoOOH and Ni_{0.2}Co_{0.8}OOH were taken to analyze the Gibbs free energy diagram of the OER. Generally, the OER process consists of four steps [59]. As shown in the results (Fig. 5e), the potential determining step (PDS) of the OER on CoOOH is from OOH* to O₂, with a ΔG as high as 1.89 eV. By contrast, the Ni-doping into Ni_{0.2}Co_{0.8}OOH results in another PDS from OH* to O*, with a ΔG of 1.71 eV,

Figure 6 (a) XRD patterns of Co₄N, Cu-Co₄N, and Fe-Co₄N, (b) *iR*-corrected OER LSV curves, (c) summary of the η_{10} and η_{50} values, and (d) the corresponding Tafel plots of Co₄N, Cu-Co₄N and Fe-Co₄N recorded in 1.0 mol L⁻¹ KOH.

which can be lower than that of the PDS on the CoOOH. It is clear that the Ni-doping promotes the OER, and thereby the overall electrocatalytic performance.

To further demonstrate the universality of this approach, we also tested Cu- and Fe-doped Co₄N nanowire bundles for the OER. As shown in Fig. 6a, after Cu/Fe doping, the diffraction peaks of the nitrated samples correspond to the pure phase of Co₄N without any impurity. The SEM micrographs of Co₄N doped with Fe (Fig. S10) and Cu (Fig. S11) identify the consistent morphology of nanowire bundles. We further used ICP measurement to determine the Co/M ratio in the samples (Table S1), following the initial feeding ratio. As shown in XPS results (Fig. S12), the Cu 2p profile shows two main peaks at 932.8 and 952.7 eV corresponding to the Cu 2p_{1/2} and Cu 2p_{3/2} of Cu⁰, respectively [60]. The Fe 2p_{3/2} region includes two main peaks at 712.4 and 717.5 eV corresponding to Fe²⁺ and Fe³⁺, respectively [61]. Fig. 6b shows the LSV curves of the products. As expected, both Cu and Fe doping improve the OER performance in comparison with pure Co₄N. Furthermore, we summarized the η_{10}

and η_{50} values of the catalysts (Fig. 6c), which verify the improvement of OER after transition-metal doping. As shown in Fig. 6d, the Tafel slopes of Cu-Co₄N and Fe-Co₄N are lower than in the case of the Co₄N sample. These results prove that doping with transition-metals could be an efficient way to enhance the OER activity.

CONCLUSIONS

We have proved that Ni doping can effectively adjust the surface electronic properties and the morphology of the Co₄N catalyst. The Ni-Co₄N-0.25 displays an improved OER activity and long-term durability, benefiting from the optimized electronic configurations and unique nanostructures. Moreover, it shows a low η_{10} of 233 mV and a low Tafel slope of 61 mV dec⁻¹ in 1.0 mol L⁻¹ KOH. The similar enhancement of Co₄N by Cu or Fe doping suggests a universal and efficient way toward cost-effective OER. This work is anticipated to provide a useful reference for the design of novel, doping-based catalysts.

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Author contributions Gao Q and Li D designed the experiments and wrote the manuscript; Li D synthesized the catalysts and tested the electrochemical performance. Zhang W performed the DFT calculations and XRD measurement. Zeng J performed the TEM investigation. Tang Y and Gao B involved in the discussion and gave constructive suggestions. All authors participated in the revision of the paper.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Dan Li obtained his PhD degree in microelectronics and solid states electronics from Lanzhou University in 2016. After that, he continued his research as a post-doctor under the supervision of Prof. Dan Wang at the State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences. Then, he proceeded his work under the supervision of Prof. Qingsheng Gao as a post-doctor at the College of Chemistry and Materials Science, Jinan University. His research interest focuses on high-performance electrocatalysts and catalytic mechanism.

Qingsheng Gao is a professor of chemistry at Jinan University. He received his BSc degree in 2005 and PhD degree in 2010 from Fudan University under the supervision of Prof. Yi Tang. Then, he moved to the Max-Planck Institute for Colloids and Interfaces in Germany to carry out his postdoctoral research with Prof. Markus Antonietti and Dr. Cristina Giordano. His current research interests focus on cost-efficient nanostructures used in catalysis and energy conversion.

镍掺杂Co₄N纳米线束作为高效产氧电催化剂

李丹¹, 张文彪¹, 曾家昌¹, 高伯旭², 唐颐², 高庆生^{1*}

摘要 发展储量丰富、高性价比的非贵金属产氧(OER)催化剂十分必要. 具有金属特性的Co₄N是极具潜力的候选催化剂之一; 其性能受催化剂形貌和表面电子结构的影响. 本文将镍掺杂到具有一维层级结构的Co₄N纳米线束中, 实现了对催化剂形貌和电子结构的有效调控. XPS结果表明, Ni掺杂可以提高Co³⁺的比例, 而表面原位生成的羟基氧化物有利于OER反应进行. 此外, 该材料优良的导电性和一维层级结构有利于活性位点的充分暴露, 使得材料的电催化性能显著提高. 在1.0 mol L⁻¹ KOH溶液中测试OER性能, Ni/Co摩尔比为0.25的催化剂表现最佳, 只需233 mV的过电势就达到10 mA cm⁻²电流密度, Tafel斜率仅为61 mV dec⁻¹, 且稳定性优异. 本工作进而验证了Fe和Cu掺杂对Co₄N催化剂OER性能的增强作用.