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Template synthesis of two-dimensional ternary nickel-cobalt-nitrogen co-doped porous carbon film: Promoting the conductivity and more active sites for oxygen reduction

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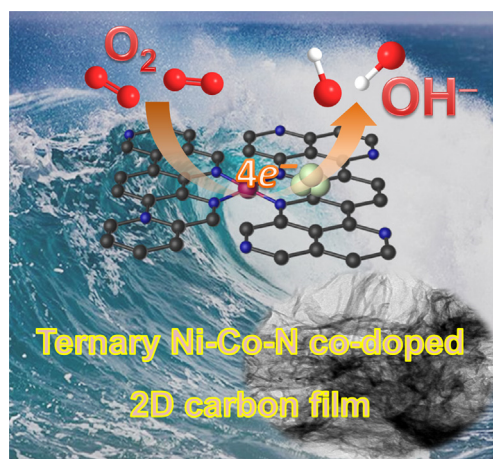
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HIGHLIGHTS

- Ternary Ni/Co/N co-doped porous carbon film (Ni-Co-N@CF) is fabricated by a simple controllable and scalable strategy.
- The Ni-Co-N@CF catalyst exhibits a large electrochemically active surface area and maximum diffusion limited current density.
- The catalyst demonstrates a superior anti-poisoning capacity and long-term stability.
- The excellent ORR activities are attributed to the synergetic interactions of ternary doping of Ni/Co/N in the film skeleton.
- The ternary Ni/Co/N in the film can enhance electron conductivity and provide more Co-N active sites.

GRAPHICAL ABSTRACT



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ABSTRACT

Rational design of a stable, highly active non-precious metal-based electrocatalysts for oxygen reduction reaction (ORR) is vitally important for industrial application of fuel cells technology. As a potential alternative of Pt/C catalyst, two-dimensional (2D) porous carbon materials are widely investigated due to the highly accessible surface area and active sites, wherein carbon films doped with a plurality of metals and non-metal elements are rarely reported due to an uncontrollable synthesis process. Here, a bi-metallic (NiCo alloy nanoparticles) and nonmetallic (N) co-doped porous carbon film (Ni-Co-N@CF) is fabricated by a simple controllable and scalable strategy comprising the synthesis of NiCo alloy nanoparticles, modification of organic molecules, and high-temperature carbonization process. The optimized Ni-Co-N@CF catalyst shows an excellent ORR electrocatalytic activity with a larger electrochemically active surface area ($2.31 \text{ m}^2 \text{ g}^{-1}$), a higher half-wave potential (0.86 V) and a lower diffusion limited current density (-4.43 mA cm^{-2}) than all the prepared control catalysts. Moreover, the designated catalyst also exhibits high durability and superior methanol tolerance in alkaline media, significantly better than the commercial Pt/C (20 wt%). The superior ORR performance is attributed to the synergetic interactions of ternary

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doping of Ni/Co/N in the 2D film skeleton, which not only greatly enhances conductivity but also provides more Co-N active sites.

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1. Introduction

Oxygen reduction reaction (ORR) is one of the cornerstone reactions for energy conversion and storage devices, such as fuel cells, metal-air batteries [1,2]. However, the commercialization of these devices has been hindered due to the sluggish reaction kinetics that require high over-potential to drive ORR and performance deterioration at the cathode. Platinum (Pt) and platinum-based materials have been recognized as state-of-the-art electrocatalysts for ORR because of a direct four-electron oxygen reduction within a relatively low overpotential [3,4]. Nevertheless, the high cost, limited reserves, and poor durability are key obstacles for its broad application in fuel cells, metal-air batteries, and industrialization [5,6]. Great endeavors have been focused on developing non-precious metal materials as cost-effective, efficient and durable ORR electrocatalysts [7–9].

Amongst these explorations, the nitrogen-doped two-dimensional (2D) carbon materials have recognized as the emerging ORR electrocatalysts since it has large surface area, high active site density, and the excellent electrical conductivity [10]. In addition, C–N composites supported Ni or Co could further improve the electrocatalytic performance due to the change of electronegativity of carbon substrate [11–13]. To date, the synthesis methods of 2D carbon materials include chemical vapor deposition (CVD) method and template assisted pyrolysis organic substances [14–17]. However, the above strategies require suitable template or structural directing agent or repeated calcinations/leaching process, which lead to complex synthesis process, time-consuming and difficult to scale up [18,19]. Therefore, besides the overcoming technical challenge, designing a simple synthesis process that is suitable for industrial application is the crucial step for the commercialization of ORR cathode technology. To our best knowledge, very few reports of bimetallic catalysts, especially Ni/Co particles, toward ORR could be found so far [20–22]. Moreover, the catalytic activity and stability of the catalysts need to be further improved compared with Pt/C. Given these, developing a simple strategy that allows cost-effective and scalable preparation of nitrogen-doped 2D carbons supported Ni/Co bimetallic catalyst is necessary.

Herein, we report a sodium chloride template assisted and scalable approach towards synthesis of Ni/Co/N ternary elements co-doped porous carbon film as ORR catalysts by direct pyrolysis of biomolecule guanine aggregates, NaCl, and NiCo₂O₄. The catalyst, labeled as Ni-Co-N@CF, exhibits highly catalytic activity, excellent durability, and superior methanol tolerance towards ORR in alkaline solution. The electrochemical test result of control sample has confirmed that the metallic NiCo alloy nanoparticles and Co-N active sites played a crucial role in enhancing the ORR activity. The synergetic interactions from the metallic Ni/Co particles, 2D N-doped carbon film and Co-N active sites are ascribed to account for the excellent ORR activity comparable to commercial 20 wt% Pt/C.

2. Experimental section

2.1. Synthesis of NiCo layered double hydroxides (LDH) and NiCo₂O₄ composites

All chemical reagents are analytical grade and used without further purification. The NiCo LDH was prepared by the previously

reported method with minor modifications [23]. In a typical synthesis, 2.5 mmol Ni(NO₃)₂·6H₂O and 4 mmol Co(NO₃)₂·6H₂O were dissolved in a mixture solvent of 37.5 mL ethylene glycol and 12.5 mL deionized water. Then, 37.5 mmol of urea was added under magnetic stirring. The resulting solution was transferred into a round-bottom flask to be refluxed under vigorous magnetic stirring for 3 h at 90 °C. The precipitates were collected by centrifugation and washed several times with distilled water until the residual solution was colorless, and then frozen and freeze-dried at –52 °C in a vacuum lyophilizer for overnight.

The NiCo₂O₄ material was obtained by calcination of NiCo-LDH in a ceramic crucible at 350 °C for 2 h with a heating rate of 2 °C min^{–1} in air.

2.2. Synthesis of Ni-Co-N@CF composite

For the synthesis of Ni-Co-N@CF, 5.0 g sodium chloride was ultrasonically dissolved in 10 mL deionized water. After that 2.0 g guanine and 25 mg NiCo₂O₄ were added into the above solution and stirred for 0.5 h until getting a gray seriflux. Until the solvent was evaporated at 80 °C, the collected powders were grinded in a quartz mortar and then subjected to carbonizing at different temperatures (800–1100 °C) for 2 h with a heating rate of 5 °C min^{–1} under N₂ atmosphere. The resulting black powder was subsequently washed with abundant deionized water to remove sodium chloride, then ethanol for twice and finally dried at 60 °C. The products are termed as Ni-Co-N@CF (X) (X = 800, 900, 1000 and 1100 °C). If not specified, the Ni-Co-N@CF discussed in the work refers to the Ni-Co-N@CF (900 °C).

As a comparison, the products using different mass of NiCo₂O₄ (15 and 50 mg) were further explored and denoted as Ni-Co-N@CF-15 and Ni-Co-N@CF-50, respectively. Moreover, the control samples, including Ni-N@CF, Co-N@CF and N@CF, were synthesized by the similar strategy as discussed above.

2.3. Preparation of catalytic electrode

The working electrode was polished with 0.05 μm alumina powder and rinsed with water, 0.5 M H₂SO₄ and ethanol for 3 times, respectively. The catalyst inks were prepared by ultrasonically dispersing the catalyst (4 mg) in 1.0 mL mixed solvent with 490 μL isopropanol, 495 μL deionized water and 10 μL of 5 wt% Nafion. Then, 19.6 μL of inks were pipetted onto the surface of glassy carbon electrode ($\phi = 5.61$ mm) and naturally dried for use. The loading of all catalysts was calculated as 0.318 mg cm^{–2} except that the loading of commercial Pt/C (20 wt% Pt, JM) was 0.081 mg cm^{–2}.

A rotating ring-disk electrode (RRDE) of 5.61 mm in diameter separately modified by different catalysts was served as working electrode in O₂-saturated 0.1 M KOH. The kinetic parameters, kinetic current densities, hydrogen peroxide yields and electron transfer numbers for ORR were calculated and discussed in detail in supporting experimental section.

2.4. Electrochemical measurements

The LSV curves and chronoamperometric responses of the prepared catalysts and commercial Pt/C (20 wt% Pt) were recorded on an electrochemical workstation (Pine Research Instrumentation,

Inc., Durham, NC, USA) with a conventional three-electrode cell. The Ag/AgCl (sat. KCl) and a graphite plate are used as reference and counter electrode, respectively. All the potentials values were calibrated with respect to the reversible hydrogen electrode (RHE) of $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.96 \text{ V}$ (Fig. S1).

The ORR activity of these catalysts was evaluated in O_2 - or N_2 -saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1} with varying rotating speeds from 400 to 2025 rpm. The methanol crossover effects in CVs for Ni-Co-N@CF and Pt/C were recorded by adding 3.0 M methanol into the O_2 -saturated 0.1 M KOH. The methanol poisoning measurements also recorded by chronoamperometric response in O_2 -saturated KOH solution at a rotation speed of 1600 rpm with adding 3.0 M methanol at 200 s. The stability tests were carried out by chronoamperometric technique at a rotation rate of 1600 rpm in O_2 -saturated electrolyte for 35000 s.

3. Results and discussion

3.1. Synthesis, structure, and composition of materials

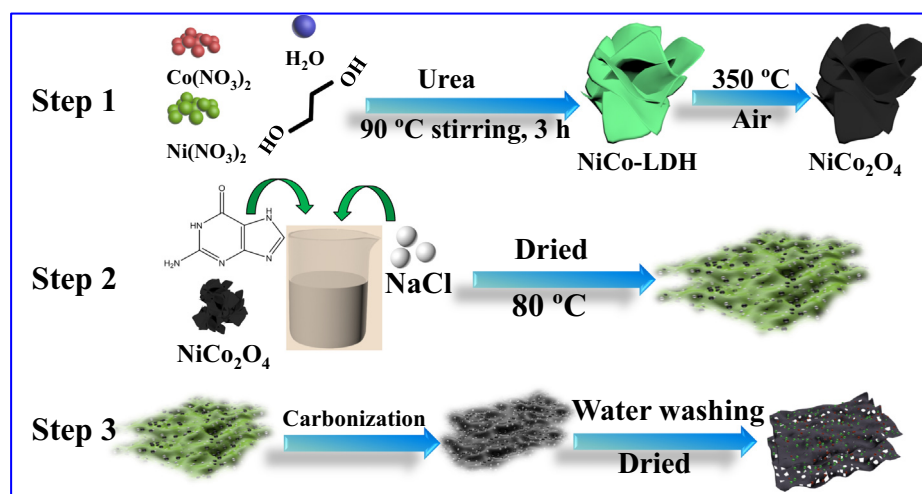
The ternary Ni/Co/N co-doped 2D porous carbon film (Ni-Co-N@CF) was prepared by a controllable three steps (Scheme 1). In the first step, the ethylene glycol molecule forms a coordination precursor with different metal cations ($\text{Ni}^{2+}/\text{Co}^{2+}$), and is gradually converted into NiCo-LDH film-like structure under the alkaline environment created by urea hydrolysis [23]. After calcination in air, a stable NiCo_2O_4 material is prepared. In the second step, the guanine molecules are uniformly and fully adsorbed on the surface of NiCo_2O_4 with the aid of saturated NaCl solution. After drying, the NiCo_2O_4 /guanine/NaCl mixed powder was obtained. In the third step, the dried mixed powder was placed in a tube furnace and carbonized at different temperatures under Ar atmosphere. After a large amount of H_2O /ethanol washing, a series of porous Ni-Co-N@CF composites were prepared. In contrast, the Ni-N@CF, Co-N@CF, and N@CF were also prepared using the similar approach as discussed above.

The phase and crystal structures of the synthesized products were first examined via X-ray diffraction (XRD) and the results were shown in Fig. 1a. Three sharp peaks at 44.3° , 51.6° , and 76.4° of Ni-N@CF sample in Fig. 1a matched well with the (1 1 1), (2 0 0), and (2 2 0) crystal planes of the face-centered cubic Ni (Ni, JCPDS: 01-1258), respectively [24,25], confirming that NiO in the precursor is effectively reduced to Ni metal nanoparticles. Moreover, the corresponding characteristic diffraction peaks of Ni-Co-N@CF are located in between those of Co (Co JCPDS:

15-0806) and Ni (Ni JCPDS: 01-1258), indicating the formation of alloyed NiCo nanoparticles (Fig. S2) [26]. The broad peak around 26° can be index to the graphitic carbon [27,28]. No typical peaks of cobalt/nickel oxides can be detected, suggesting that the oxide contents are very low or exist in an amorphous form. As shown in Fig. S3a, the diffraction peaks of NiCo-LDH centered at 11.5° , 20.9° , 35.2° and 61.5° that can be assigned to the (0 0 3), (0 0 3), (0 1 2) and (1 1 3) planes of nickel cobalt carbonate hydroxide hydrate (JCPDS: 40-0216) [29]. In addition, the as-prepared Co(OH)₂ and Ni(OH)₂ materials were in good agreement with previously reported results [23]. Fig. S3b-d show the typical diffraction peaks of Co_3O_4 , NiO and NiCo_2O_4 obtained from Co-LDH, Ni-LDH and NiCo-LDH after annealed at 350°C for 2 h in air, respectively. To clarify the NiCo_2O_4 sample from NiCo LDH only contain the NiCo_2O_4 phase, we carefully compared the XRD patterns of NiCo_2O_4 with the mixture of Co_3O_4 and NiO (molar ratio of 1.25:2) and NiCo oxide from different $n(\text{Ni}^{2+}) : n(\text{Co}^{2+})$ in the precursor. From the XRD results in Fig. S4a, we find that the two characteristic peaks of NiCo_2O_4 at 44.6° and 64.8° are different from those of the physical mixture of Co_3O_4 and NiO where the pure Co_3O_4 and NiO show the corresponding typical peaks at 44.9° & 65.3° and 43.3° & 62.9° respectively. While the more Co^{2+} in the precursor, the peaks of corresponding oxide shift to a high degree, indicating the formation of Co oxide (Co_3O_4). The peaks of the NiCo oxide shift to a low degree when the more Ni^{2+} in the precursor, suggesting the formation of NiO (Fig. S4b).

The morphologies of the as-prepared samples were further characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image shows that NiCo-LDH exhibits a rugae-like nanofilm morphology (Fig. 1b). After calcination, no visual change in morphology was detected (Fig. 1c). The ultra-thin film structure of Ni-Co-N@CF composite was subsequently confirmed by TEM image (Fig. 1d), where the Ni-Co-N@CF consists of abundant semitransparency film with wrinkled edges. The high-resolution TEM shows that the NiCo alloy nanoparticles has a single crystal structure with a lattice spacing of 0.21 nm, corresponding to the (1 1 1) crystal plane of NiCo alloy nanoparticles (Fig. 1e). The average particle size of the metallic nanoparticles is 1.3 nm, as shown in the TEM (Fig. S5). Additionally, the HAADF-STEM and corresponding elemental mappings revealed that the elements of C, N, Ni and Co were uniformly distributed on the entire architectures of Ni-Co-N@CF (Fig. 1f).

Raman spectroscopy is an efficient method for discerning the disorder and graphitic structures of carbon materials. As shown in Figs. 2a and S6, the Raman spectra of all samples display two



Scheme 1. Schematic diagram of the preparation process of ternary Ni/Co/N co-doped 2D porous carbon film (Ni-Co-N@CF).

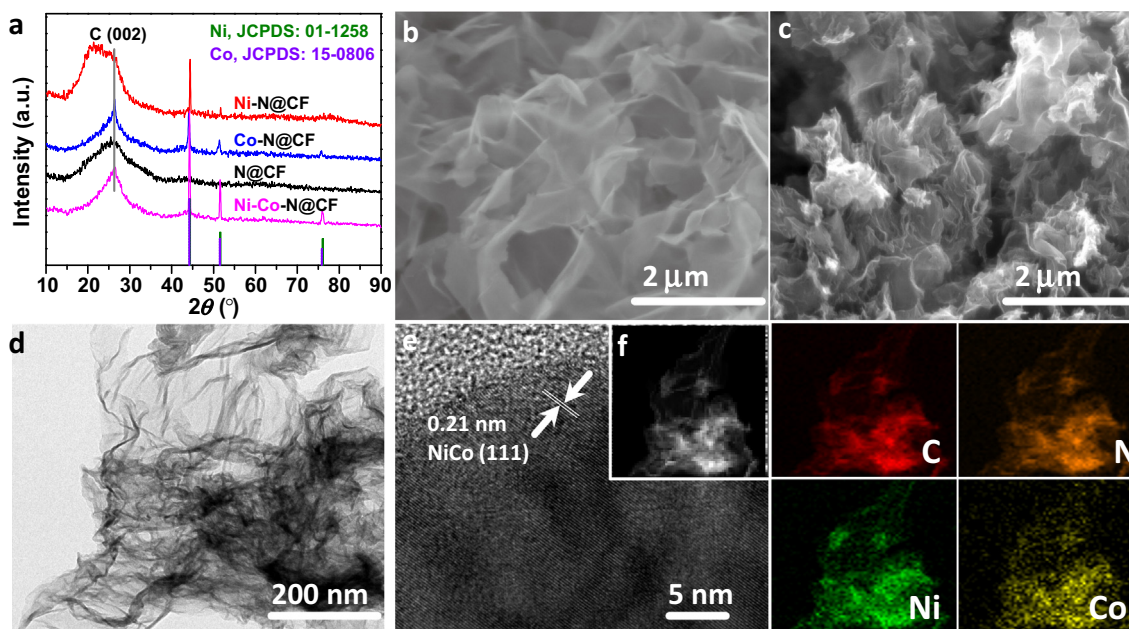


Fig. 1. (a) XRD patterns of N@CF, Ni-N@CF, Co-N@CF, and Ni-Co-N@CF. SEM images of (b) NiCo-LDH and (c) Ni-Co-N@CF. (d) TEM image, (e) high-resolution TEM image, and (f) HAADF-TEM and the corresponding EDS mappings of C, N, Ni and Co elements of Ni-Co-N@CF.

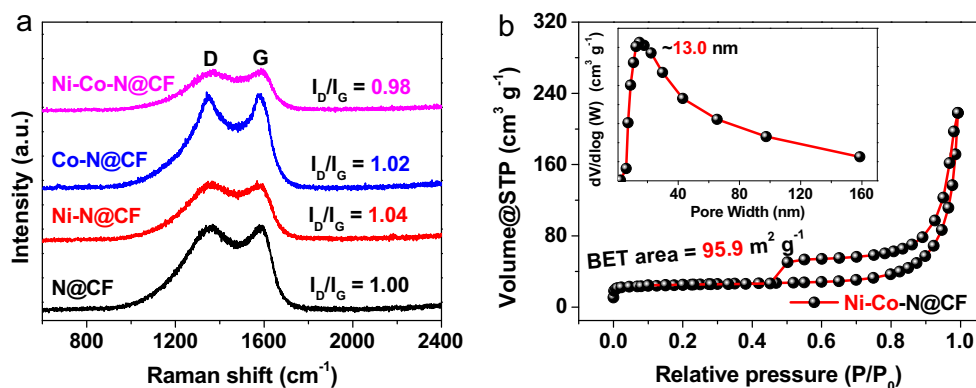


Fig. 2. (a) Raman spectra of N@CF, Ni-N@CF, Co-N@CF and Ni-Co-N@CF. (b) Nitrogen adsorption-desorption isotherms with pore width distribution curve of Ni-Co-N@CF.

characteristic peaks, including D-band at 1350 cm^{-1} for disorder-activated edge phonon and G-band at 1580 cm^{-1} for graphitic lattice phonon [30]. The ratio of D-band to G-band (I_D/I_G) is usually utilized to evaluate a degree of disorder of the samples, wherein a smaller value of I_D/I_G indicates a higher degree of graphitization [31,32]. The structural defects of D-band in the catalysts may be caused by the N-doping and/or metal influence, resulting in the loss of some graphitized carbon atoms [33,34]. As shown in Fig. 2a, the value of I_D/I_G is 1.00, 1.04, 1.02 and 0.98 for N@CF, Ni-N@CF, Co-N@CF and Ni-Co-N@CF, respectively. Interestingly, a higher graphitization degree in Ni-Co-N@CF was obtained as compare to that of Ni-Co-N@CF- x ($x = 15$ or 50) (Fig. S6a). However, the initial degree of graphitization in all the samples are very close. Moreover, the ratios of I_D/I_G decrease from 1.06 to 0.93 when the annealing temperatures increase (Fig. S6b), indicating that a higher thermal-treatment temperature could result in a higher degree of graphitization [33,35]. Numerous studies have shown that more defects are beneficial to provide more active sites, while higher graphitization helps to enhance electron transfer properties, so they cooperatively modulate ORR catalytic activity [36,37]. Therefore, it can be considered that the higher

degree of graphitization is the key to the excellent ORR catalytic performance of Ni-Co-N@CF.

Nitrogen adsorption-desorption measurements were conducted to analysis the surface structural features of the prepared Ni-Co-N@CF catalyst. As shown in Fig. 2b, the Brunauer-Emmett-Teller (BET) surface area and total pore volumes of Ni-Co-N@CF are $95.9\text{ m}^2\text{ g}^{-1}$ and $0.33\text{ cm}^3\text{ g}^{-1}$, respectively. Notably, the isotherm curves is categorized as type IV isotherm with a pronounced hysteresis loop at P/P_0 0.4–0.9 for Ni-Co-N@CF, and the average pore-size distribution of Ni-Co-N@CF by the BJH method was 13.0 nm , proving that the composite is a typical mesoporous material [38]. The mesoporous structure helps to expose more active sites and facilitates rapid gas release and electrolyte diffusion [39,40], thereby significantly enhancing ORR catalytic activity.

Inductively coupled plasma spectroscopy (ICP) tests were performed to detect the metal contents in all the samples. As shown in Table S1, the Co and Ni contents in the optimized Ni-Co-N@CF sample is about 1.07 wt% and 1.41 wt%, respectively, showing the optimal metal content compared to all other control bimetallic ORR catalysts. Moreover, the Co/Ni ratio decreases when the temperature increases. The reason may be that the Co-N species

decompose at high temperatures faster than Ni-N and leach out from the porous carbon substrate.

X-ray photoelectron spectroscopy (XPS) measurement was performed to further understand the chemical compositions as well as elemental valence of the synthesized catalysts. As shown in Fig. S7a, the survey spectrum of Ni-Co-N@CF shows clear C, O, N, Co and Ni peaks, which is consistent with the theoretical values. The high-resolution C 1s spectrum of Ni-Co-N@CF is deconvoluted into four peaks at 284.0 eV (C=C), 284.8 eV (C–C/N), 286.0 eV (C–O) and 288.7 eV (C=O), which are further used as the standard correction reference for other elements (Fig. S7b).

Fig. 3a shows the high-resolution Ni 2p spectra of Ni-Co-N@CF and Ni-N@CF, in which the Ni 2p_{3/2} region of Ni-Co-N@CF is deconvoluted into four peaks at 852.8, 854.5, 856.8 and 862.3 eV, corresponding to the metallic Ni, Ni²⁺, Ni³⁺ and satellite peaks, respectively. It is recognized that the high-valence Ni species is mainly caused by the oxidation of air [41]. Compared with Ni-N@CF, the Ni²⁺ species in Ni-Co-N@CF material undergoes a slight negative shift (0.12 eV). In addition, the high-resolution Co 2p spectra of Ni-Co-N@CF and Co-N@CF are presented in Fig. 3b, where the Co 2p_{3/2} region of Ni-Co-N@CF is fitted to the metallic Co (778.5 eV), Co²⁺ (780.8 eV) and satellite peaks, respectively. It is generally believed that a portion of the Co²⁺ species coordinates with N to form Co-N active sites in the N-containing composite [42]. As expected, the binding energy of Co²⁺ in Ni-Co-N@CF is a little positive shift about 0.20 eV compared to Co-N@CF, indicating that the Co species have a higher electron density than the Ni species in the composite [43]. The electronic effect between Co and Ni is related to the d-electron structure of the transition metals and the Co-N active sites [44,45]. Moreover, the high-resolution N 1s spectra of Ni-Co-N@CF as well as Ni-N@CF and Co-N@CF are discussed in Fig. 3c, where the N 1s region is mainly fitted to the pyridinic N (398.0 eV), pyrrolic N (400.2 eV), and graphitic N (403.7 eV) [46]. It is believed that the binding energy of N from the Co-N active sites is very close to the pyridinic N, thereof a higher pyridinic N content often means more active sites [47,48]. The study found that the content of pyridinic N in Ni-Co-N@CF was ca. 48.2%, which was slightly higher than that of N@CF modified single Ni or Co, indicating that the introduction of bimetallic Ni-Co species can increase the content of active sites, thereby leading to a higher ORR electrocatalytic activity [20].

Moreover, the elemental analyzer test showed that the nitrogen content slowly decreased as the pyrolysis temperature increased [20,49], and the doping of the bimetal contributed to the increase of the N content relative to the that of the single metal doping (Table S2). Studies have shown that higher N doping plays an important role in forming more active sites and changing the electronegativity of adjacent carbon atoms [50], which is the key to the improved electrocatalytic performance.

3.2. Electrochemical characterization of catalysts

The electrocatalytic performance of the designed series of Ni-Co-N@CF catalysts were initially optimized by regulating the loadings of NiCo₂O₄ in the composites. As shown in Fig. 4a, as the theoretical contents of NiCo₂O₄ increase in the precursors, the half-wave potentials of Ni-Co-N@CF catalysts increased first and then decreased, whereas they had similar limiting current densities. Meanwhile, the Ni-Co-N@CF (25 mg) catalyst also showed a low H₂O₂ selectivity and nearly 4-electron electron transfer characteristics (Fig. 4b). In addition, the influence of the calcination temperatures were further optimized, and it was found that as the calcination temperatures raised, the half-wave potential and the limiting current density also increased firstly, followed by decreasing (Fig. 4c), wherein the optimized Ni-Co-N@CF (900 °C) catalyst also showed a lower H₂O₂ selectivity and close to 4 electron-transfer numbers compared to all other catalysts (Fig. 4d). Obviously, the Ni-Co-N@CF-25 obtained by annealing the precursor at 900 °C with 25 mg NiCo₂O₄ showed the best ORR activity. Such high ORR performance of Ni-Co-N@CF-25 might be ascribed to the fact that the ternary Ni/Co/N doping can greatly change the electronic structure of the material, as well as the high degree of graphitization of the carbon layers [44,45]. In addition, higher calcination temperature (1000 °C and 1000 °C) may result in the loss of nitrogen (Table S2) and decrease the nitrogen-containing active sites. Therefore, Ni-Co-N@CF-25 showed the best ORR performance. If not specified, the catalyst discussed below of Ni-Co-N@CF composite was all prepared with a precursor content of NiCo₂O₄ for 25 mg and calcined at 900 °C in Ar atmosphere.

The electrocatalytic activities of the optimized Ni-Co-N@CF catalyst as well as N@CF, Ni-N@CF and Co-N@CF were evaluated through CV measurements in N₂- or O₂-saturated 0.1 M KOH at a

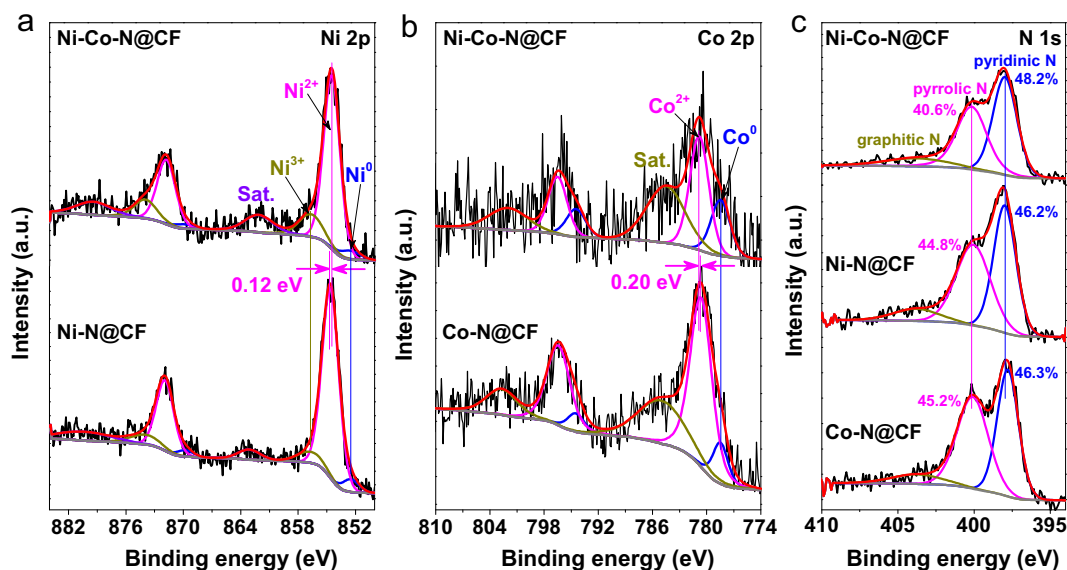


Fig. 3. High-resolution XPS spectra of (a) Ni 2p, (b) Co 2p, and (c) N 1s from Ni-Co-N@CF, Ni-N@CF and Co-N@CF, respectively.

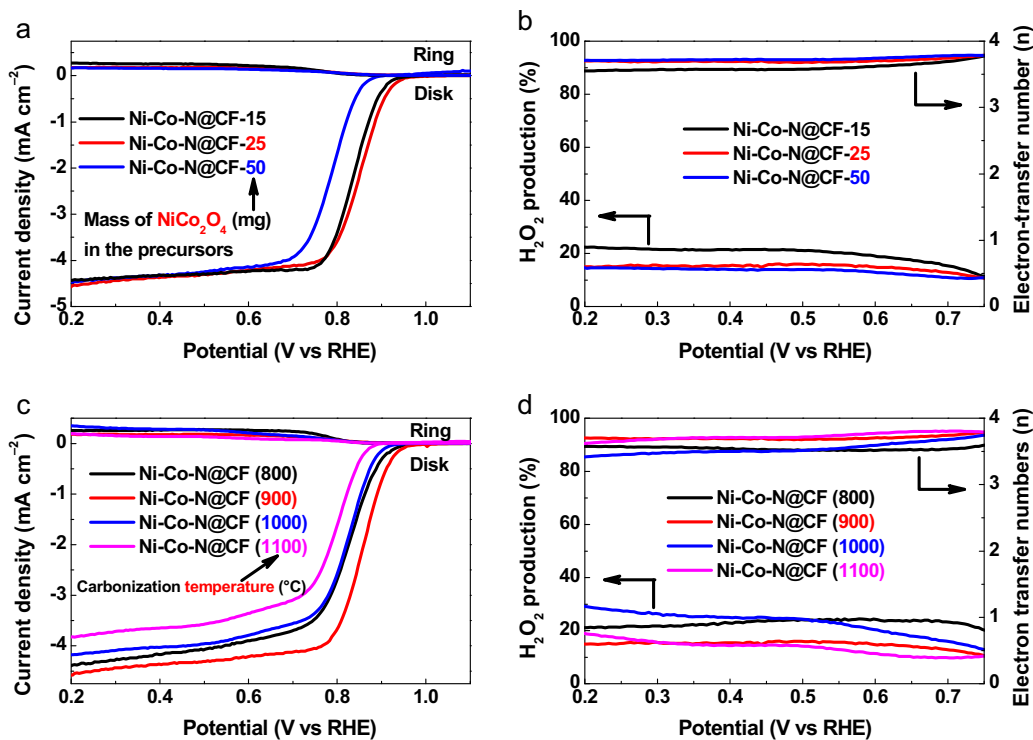


Fig. 4. (a) ORR polarization curves measured using RRDEs at 1600 rpm with scan rate of 10 mV s^{-1} of Ni-Co-N@CF catalysts with different contents of NiCo_2O_4 in the precursors. (b) The summarized selectivity of H_2O_2 and electron-transfer numbers from a. (c) ORR polarization curves of Ni-Co-N@CF catalysts prepared at different carbonization temperatures (800–1100 °C). (d) The summarized selectivity of H_2O_2 and electron-transfer numbers from c.

scan rate of 50 mV s^{-1} (Fig. 5a). Notably, an intense cathodic oxygen reduction peak appeared for all three samples in O_2 -saturated solution, while no characteristic voltammetry response was observed in N_2 -saturated solution. Such a characteristic ORR signal

of Ni-Co-N@CF centered at 0.82 V (all potential in the context are versus to RHE) is more positive than that of Co-N@CF (0.80 V), Ni-N@CF (0.76 V), and N@CF (0.71 V). The rotating ring-disk electrode (RRDE) measurements were performed to further monitor

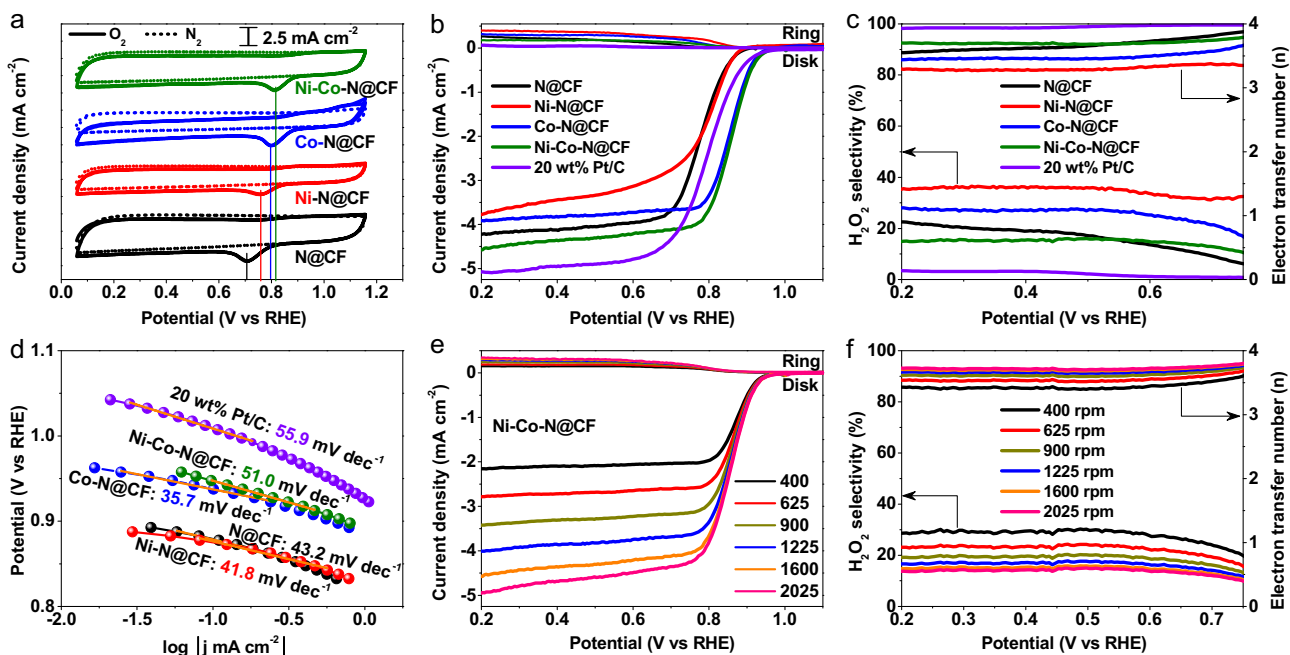


Fig. 5. (a) CV curves of different catalysts in N_2 - and O_2 -saturated 0.1 M KOH at a scan rate of 50 mV s^{-1} . (b) RRDE voltammograms of different catalysts at a rotation rate of 1600 rpm in an O_2 -saturated 0.1 M KOH solution at 10 mV s^{-1} . (c) RRDE tests for H_2O_2 selectivity and corresponding electron transfer number (n). (d) Tafel plots of different catalysts. (e) RRDE voltammograms of Ni-Co-N@CF in O_2 -saturated 0.1 M KOH with a sweep rate of 10 mV s^{-1} and (f) the summarized the electron transfer number and H_2O_2 selectivity at various rotation rates.

Table 1The summarized ORR catalytic performance parameters of different catalysts in O₂-saturated 0.1 M KOH.

| Catalyst | E _{1/2} (V vs RHE) | J _L @0.3 V (mA cm ⁻²) | H ₂ O ₂ selectivity (%) | Electron-transfer number (n) | Tafel slope (mV dec ⁻¹) |
|-------------|-----------------------------|--|---|------------------------------|-------------------------------------|
| Ni-Co-N@CF | 0.86 | -4.43 | 10.4–15.0 | 3.70–3.79 (3.75) | 51.0 |
| Co-N@CF | 0.85 | -3.84 | 16.4–28.1 | 3.44–3.67 (3.56) | 35.7 |
| Ni-N@CF | 0.78 | -3.59 | 32.4–35.5 | 3.29–3.35 (3.32) | 41.8 |
| N@CF | 0.77 | -4.16 | 6.1–22.6 | 3.54–3.88 (3.71) | 43.2 |
| 20 wt% Pt/C | 0.87 | -4.82 | 1.2–5.4 | 3.78–3.79 (3.79) | 55.9 |

the electrocatalytic activity of the synthesized catalysts for ORR in O₂-saturated KOH solution. As shown in Fig. 5b, the E_{1/2} (0.86 V) and diffusion limited current density (J_L = -4.43 mA cm⁻² at 0.3 V) of Ni-Co-N@CF catalyst were obviously higher than that of all control catalysts except that of 20 wt% Pt/C (Table 1), wherein the more positive E_{1/2} and larger J_L of Ni-Co-N@CF catalyst than Ni-N@CF and Co-N@CF signified the important role of bimetallic synergy in enhancing the ORR catalytic performance. The H₂O₂ selectivity and electron transfer-number (n) calculated from RRDE tests demonstrated a nearly four-electron pathway of Ni-Co-N@CF catalyst during the ORR process where the O₂ was transformed straightforward into OH⁻, similar to that of 20 wt% Pt/C, over a wide potential range from 0.2 to 0.75 V (Fig. 5c). The result mentioned above indicated that bimetallic co-doping could not only improve the reactivity, but also optimize the ORR selectivity of the catalyst. Tafel slope is another pivotal parameter to evaluate the electrocatalytic activity of catalysts. As showed in Fig. 5d, the Tafel slope of Ni-Co-N@CF is calculated to be 51.0 mV dec⁻¹, slightly lower than that of 20 wt% Pt/C (55.9 mV dec⁻¹), suggesting a faster ORR kinetic in alkaline medium. It should specially point out that the ORR catalytic activity of Ni-Co-N@CF is not only comprehensively superior to all control catalysts, but also much better than most of the previously reported Co-based catalysts (Table S4).

We also carried out RRDE measurements at different rotation rates varying from 400 to 2025 rpm to further determine the electron-transfer kinetics of Ni-Co-N@CF. As show in Fig. 5e, the current densities increased sharply with increasing the rotation speeds [51]. The corresponding Koutecky–Levich (K–L) plots presented in Fig. S8 showed a good linearity within the potential ranges from 0.3 V to 0.6 V, suggesting first-order reaction kinetics for ORR [52]. It can see that the electron transfer number gradually approaches 4 electrons with a gradual decrease in the selectivity of H₂O₂ as the rotation rate increases, and they are substantially constant when the rotational speed reaches 1600 rpm and above (Fig. 5f).

The electrochemical double-layer capacitances (C_{dl}) of Ni-Co-N@CF and each control catalysts are firstly estimated by cyclic voltammetry in a potential window without faradaic processes, which are considered to be proportional to the electrochemically active surface area (EASA) of the catalysts. As shown in Figs. 6a and S9, we can observe that the current densities of CV curves increase regularly as the scan rates increasing from 4 to 40 mV s⁻¹. A linear correlation can be obtained through plotting each current density against the scan rate, where the C_{dl} can be estimated from the slope [53,54]. As depicted in Fig. 6b, the Ni-Co-N@CF catalyst features the largest C_{dl} value in KOH electrolyte (2.86 mF cm⁻²),

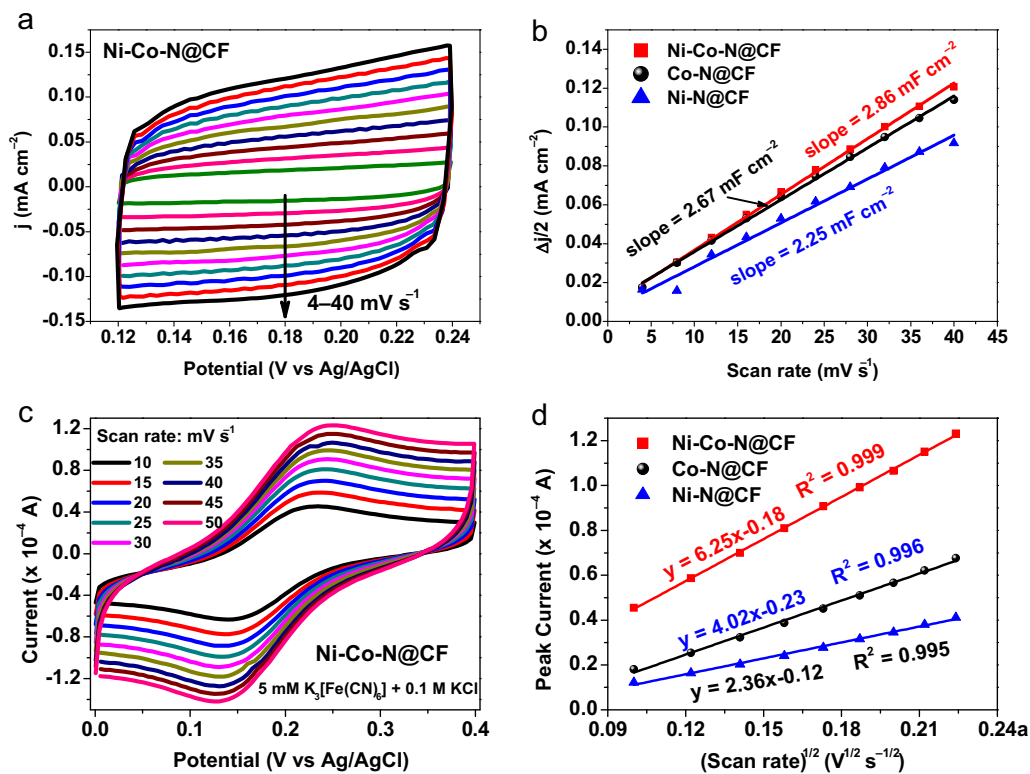


Fig. 6. (a) CV curves of Ni-Co-N@CF catalyst measured in a potential window without faradaic processes in O₂-saturated 0.1 M KOH. (b) Linear correlation of current density variation against CV scan rate in O₂-saturated 0.1 M KOH. (c) CV responses of Ni-Co-N@CF catalyst in 0.1 M KCl containing 5 mM K₃[Fe(CN)₆] solution as a function of scan rate from 10 to 50 mV s⁻¹. (d) Linear dependence of peak current versus square root of scan rates for Ni-Co-N@CF, Co-N@CF and Ni-N@CF, respectively.

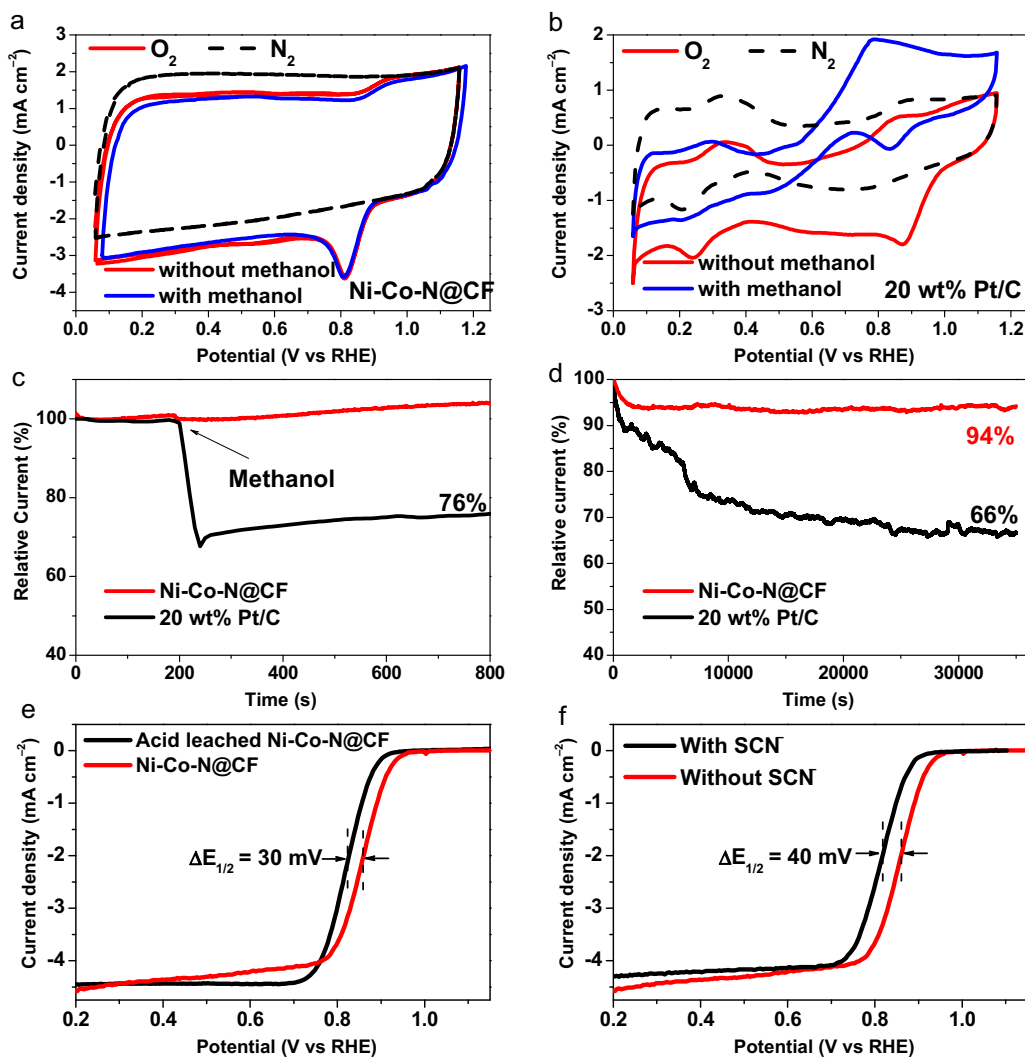


Fig. 7. Cyclic voltammetry curves of (a) Ni-Co-N@CF and (b) 20 wt% Pt/C in 0.1 M KOH measured before and after addition of 3.0 M methanol. (c) Methanol crossover tolerance measurement of Ni-Co-N@CF and 20 wt% Pt/C by adding 3.0 M methanol at 200 s. (d) Current-time (*i*-*t*) chronoamperometric response of the Ni-Co-N@CF and 20 wt% Pt/C at 0.65 V vs RHE in O₂-saturated 0.1 M KOH with a rotation rate of 1600 rpm. LSV curves of (e) the acid-leached and as-synthesized Ni-Co-N@CF catalysts and (f) Ni-Co-N@CF before and after the addition of 0.01 M KSCN in O₂-saturated 0.1 M KOH with a rotate speed of 1600 rpm at a scan rate of 10 mV s⁻¹.

which is 1.07- and 1.27-fold higher than that of Co-N@CF and Ni-N@CF respectively, implying a better ORR activity in alkaline solution. The higher C_{dl} value of the bimetallic Ni-Co-N@CF catalyst in comparison with the single-metal counterparts further validates a synergistic effect between different components.

It is reported that a larger electrochemically active surface area (EASA) supports higher electrocatalytic activity [55,56]. Here, the EASA values of Ni-Co-N@CF, Co-N@CF and Ni-N@CF catalysts are further evaluated in 5 mM K₃[Fe(CN)₆] + 0.1 M KCl solution by using Pt foil as counter electrode. The CV curves in Figs. 6c and S10 show a pair of redox peaks in which the oxidation peaks are plotted against the square root of the scan rates (Fig. 6d) and is used to calculate the EASA values by the Randles-Sevcik equation as follows [57]:

$$i_{peak} = (2.68 \times 10^5) n^{3/2} \nu^{1/2} A D^{1/2} C_0 \quad (1)$$

where i_{peak} is the peak current, n is the number of electrons involved in the reaction ($n = 1$, Fe³⁺ to Fe²⁺). ν is the scan rate. A is the EASA (cm²) of the working electrode. D is the diffusion coefficient of ferricyanide (6.67×10^{-6} cm² s⁻¹). C_0 is the concentration of ferricyanide in the bulk solution (mol cm⁻³).

The EASA of Ni-Co-N@CF catalyst is ca. 2.31 m² g⁻¹, which is 1.56- and 2.69-fold higher than these of Co-N@CF (1.48 m² g⁻¹) and Ni-N@CF (0.86 m² g⁻¹), consistent with its higher ORR catalytic activity.

An excellent cathode catalyst should combine high electrochemical activity with good stability. First, the methanol crossover tolerance was investigated by the cyclic voltammetry method and chronoamperometry method. As shown in Fig. 7a, no obvious change could be observed in the current density on Ni-Co-N@CF after adding 3.0 M methanol into the solution, while the oxygen reduction peak decreased rapidly and characteristic peak of the methanol oxidation emerged in CV for 20 wt% Pt/C (Fig. 7b). As shown in Fig. 7c, the Ni-Co-N@CF showed almost no negative shift during *i*-*t* measurement after adding 3.0 M methanol, while a sharp jump of current density appeared due to the methanol oxidation occurs on the 20 wt% Pt/C. All these result firmly suggest that the Ni-Co-N@CF displayed remarkable methanol resistance than that of Pt/C. Moreover, the Ni-Co-N@CF catalyst also showed an excellent stability with only 6% decreased in current density after a 35000 s *i*-*t* test while only 66% relative current retained for 20 wt% Pt/C (Fig. 7d). This result demonstrates that the Ni-Co-N@CF displays superior durability for ORR than that of Pt/C.

The above mentioned measurement results strongly confirm the outstanding electrocatalytic activity of Ni-Co-N@CF in alkaline

solution. This may be ascribed to the cooperative effects among the NiCo alloy nanoparticles, N-doped carbon film, and the formed Co-N species. It is known that the alloy nanoparticles can enhance the electrical conductivity (Table S3) and adjust the work function of the composite, thereby promoting the adsorption of O₂ and improving the catalytic performance [45]. To verify the role of the formed NiCo alloy nanoparticles and Co-N active sites in ORR catalysis, we designed two sets of control experiments. Firstly, the Ni-Co-N@CF was leached in 0.5 M H₂SO₄ at 90 °C for 3 h to remove the NiCo alloy nanoparticles. The XRD result showed only a peak centered at 26° corresponding to the (0 0 2) plane of graphitic carbon (Fig. S11), indicating that most of the NiCo alloy nanoparticles have been removed after acid leaching. Related LSV curves (Fig. 7e) showed that the E_{1/2} of the acid leached Ni-Co-N@CF sample shifted negatively 30 mV compared with the original Ni-Co-N@CF catalyst. This result confirmed that the NiCo alloy nanoparticles are crucial for assisting the active sites to catalyze the ORR. Secondly, it is also reported that the SCN⁻ ion can poison M-N_x (Co-N_x) active sites and hinder the ORR performance of the catalysts [58]. Therefore, another contrast experiment was measured in 0.1 M KOH containing 0.01 M KSCN. The result in Fig. 7f indicated that the E_{1/2} of Ni-Co-N@CF decreased by 40 mV after the addition of 0.01 M KSCN, suggesting that the Co-N species is of great importance in enhancing the ORR activity of Ni-Co-N@CF catalyst. Both the contrast experiments indicated that the Ni/Co particles and Co-N active sites are both the reasons for the excellent ORR performance.

4. Conclusion

In summary, we have reported a facile, low-cost and scalable approach of preparing ternary Ni/Co/N co-doped 2D carbon film as a highly active and durable ORR electrocatalyst in alkaline media. The hybrid catalyst with suitable amount of Ni/Co/N loading exhibits the optimized ORR electrocatalytic activity, where the half-wave potential is 0.86 V, and the limited current density is -4.43 mA cm⁻² at 0.3 V. Besides, the Ni-Co-N@CF shows a similar Tafel slope for ORR (51 mV dec⁻¹) as compare to Pt/C (55.9 mV dec⁻¹). The excellent ORR performance is ascribed to the synergetic effects of ternary Ni/Co/N co-doped carbon film, which not only improves the electron conductivity, but also provides more Co-N active sites. In addition, the Ni-Co-N@CF catalyst also demonstrate a highly efficient and stable properties on the stability and methanol-tolerance measurements, suggesting a great potential applications in various devices, including fuel cells, metal–air batteries, etc.

CRedit authorship contribution statement

Mancai Qian: Investigation and methodology. **Meijiao Xu:** Data curation. **Shuqing Zhou:** Formal analysis. **Jianniao Tian:** Supervision. **Tayirjan Taylor Isimjan:** Writing-original draft. **Zhongfeng Shi:** Supervision. **Xiulin Yang:** Writing-review & editing.

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.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2019.12.089>.

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