Controllable Synthesis of Co@CoO_x/Helical Nitrogen-Doped Carbon Nanotubes toward Oxygen Reduction Reaction as Binder-free Cathodes for Al–Air Batteries

Yisi Liu,^{||} Biqiong Wang,^{||} Qian Sun, Qiyun Pan, Nian Zhao, Zhong Li, Yahui Yang,* and Xueliang Sun*

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ABSTRACT: Efficient and stable electrocatalysts for oxygen reduction reaction and freestanding electrode structure were developed to reduce the use of polymer binders in the cathode of metal—air batteries. Considering the unique geometrical configurations of helical carbon nanotubes (CNTs) and improved properties compared with straight CNTs, we prepared high-purity $Co@CoO_x/$ helical nitrogen-doped carbon nanotubes ($Co@CoO_x/HNCNTs$) on a carbon fiber paper by hydrothermal and single-step in situ chemical vapor deposition strategies. Under an optimized growth time (1 h), the synthesized $Co@CoO_x/$ HNCNTs provide richer edge defects and active sites and show prominent electrocatalytic performance toward oxygen reduction reaction (ORR) under alkaline media compared with $Co@CoO_x/HNCNTs$ -0.5 h and $Co@CoO_x/$ HNCNTs-2 h. The soft X-ray absorption spectroscopy technique is used to investigate the influences of different growth times on the electronic structure and local chemical configuration of $Co@CoO_x/HNCNTs$. Furthermore, the Al–



air coin cell employing $Co@CoO_x/HNCNTs-1$ h as the binder-free cathode exhibits an open-circuit voltage of 1.48 V, a specific capacity of 367.31 mA h g⁻¹ at the discharge current density of 1.0 mA cm⁻², and a maximum power density (P_{max}) of 3.86 mW cm⁻², which are superior to those of $Co@CoO_x/HNCNTs-0.5$ h and $Co@CoO_x/HNCNTs-2$ h electrodes. This work provides valuable insights into the development of scalable binder-free cathodes, exploiting HNCNT composite materials with an outstanding electrocatalytic performance for ORR in Al–air systems.

KEYWORDS: helical carbon nanotubes, high yield and purity, oxygen reduction reaction, Al-air battery, binder-free electrode

1. INTRODUCTION

The increasing demand from energy and environment has greatly urged the research for high-efficiency and renewable energy storage and conversion technology.^{1,2} Over the past few years, in view of high theoretical voltage and energy density, low cost, and high safety properties, metal—air batteries have attracted renewed interests as a possible energy storage solution. Among numerous metal—air batteries, Al—air batteries possess broad energy application prospects because of their lowest cost and high theoretical energy density (8.1 kW h kg⁻¹), which are the second highest only to that of lithium—air batteries (13.0 kW h kg⁻¹).³ Besides, aluminum is a cheap, abundant, recyclable, and environmentally friendly metal.⁴

The oxygen reduction reaction (ORR) is the central reaction of the air electrode in an Al–air battery, but its sluggish kinetics is a pivotal factor that influences the efficiency of the air electrode, thus restricting the performance of Al–air batteries.^{5,6} Additionally, polymer binders used in traditional air electrodes, such as polytetrafluoroethylene and polyvinylidene fluoride, have brought about a series of problems including increasing nonactive electrode materials, blocking pore structure, decreasing electrical conductivity, and side reactions, which have affected the activity of electrodes. In order to solve the above problems, the conception of "binderfree" was proposed. In this design, catalytic active ingredients are combined with conductive substrates through covalent bonding or chemical adsorption to avoid using binders and facilitate transferring electrons simultaneously. Recently, some research groups have attempted to design efficient binder-free electrodes for metal—air batteries.^{7,8} For example, Qu et al.⁹ prepared a $Co_4N/CNW/CC$ three-dimensional self-supporting air electrode on a carbon fiber paper by an in situ coupling method, which showed excellent ORR and oxygen evolution reaction electrocatalytic performance, good charging and discharging performance, and cycle stability in a rechargeable

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zinc—air battery. Meng et al.¹⁰ reported porous carbon nanofiber flexible membranes with high specific surface area synthesized by the high-temperature pyrolysis of electrostatic spinning polyimide films, which were used as air electrodes in a Zn—air battery, showing a high open-circuit voltage (1.48 V) and energy density (776 W h kg⁻¹). Lu et al.¹¹ prepared silver nanoparticles on a carbon fiber paper by in situ electrodeposition and used them as air electrodes for Al—air batteries, showing superior discharge performance and stability compared to the commercial catalysts. Therefore, designing and preparing binder-free electrodes with efficient electrocatalytic activity for ORR is one of the critical technologies to improve the performance of the Al—air battery.

Among the extensive research efforts dedicated to developing advanced ORR electrocatalysts, carbon nanotubes (CNTs) have attracted great attention because of high tensile modulus, high specific surface area, mesoporous structure, and good electrical properties.^{12–14} Furthermore, it is an effective method to improve their ORR catalytic activity by heteroatom doping to increase the structural disorders or form heteroatom functionalities.^{15–17} As a result, heteroatom-doped CNTs are promising electrocatalysts with excellent ORR activity in metal-air systems. CNTs have been observed in a variety of geometrical configurations, such as straight and helical, which make them suitable for various applications. The helical configurations of CNTs, which are referred to as helical CNTs (HCNTs), are essentially longer CNTs formed into spring-like shapes.^{18,19} Because of their unique helical spring-like structural shapes and exceptional properties, HCNTs hold great application potential in the field of catalyst supports, electrode materials, micro- and nanoelectromechanical devices and sensors, photoconductive materials, and structural nano-composites.²⁰⁻²⁴ The unique geometry of HCNTs makes them more flexible than straight CNTs and enable them to absorb more energy during stretching and compression.²⁵ In spite of several reports in the literature on HCNTs, effective and controllable synthesis of HCNTs with high purity and high yield remains a major challenge. Until recently, various synthetic methods have been proposed to obtain high-purity HCNTs with high yields. Tang et al. proposed a catalyst granularity-based growth strategy. Thereinto, small catalyst particles usually are available to form high-purity HCNTs, whereas large catalyst particles result in the formation of straight CNTs.²⁶ Wang et al. synthesized catalyst nanoparticles with controllable size and narrow particle size distribution by means of atomic layer deposition technology so as to produce \sim 100% pure carbon nanocoils.²⁷ Jian et al. developed a novel gas-induced method to form catalysts for the preparation of high-purity helical carbon nanofibers (HCNFs).²⁸ However, complex synthetic methods such as controlling the size and size distribution of catalytic particles limit their large-scale applications. On the other hand, synthesizing HCNTs on a carbon fiber paper as a substrate to obtain economic binderfree electrodes for metal-air systems is still a blank. Therefore, developing a convenient and controllable growth method to prepare high-purity HCNTs on substrates directly as air electrodes in Al-air batteries is significant and challenging.

Herein, we synthesized high-purity $Co@CoO_x$ /helical nitrogen-doped CNTs ($Co@CoO_x$ /HNCNTs) on carbon fiber papers by hydrothermal treatment and the single-step in situ chemical vapor deposition (CVD) method, regardless of focalizing the size control of catalytic particles, and used them as binder-free cathodes for Al-air batteries. $Co@CoO_x$ /

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HNCNTs exhibit excellent ORR electrocatalytic performance in alkaline condition and superior stability and methanol tolerance compared to the commercial Pt/C catalysts. Besides, the Al–air coin cells using $Co@CoO_x/HNCNTs$ grown on carbon fiber papers as binder-free electrodes show definite discharge performance, demonstrating that $Co@CoO_x/HNCNT$ electrodes can be prospectively applied to metal– air batteries.

2. EXPERIMENTAL SECTION

2.1. Preparation of Catalytic Precursors/Carbon Fiber Paper. 3 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 7 mmol urea were uniformly dissolved in 20 mL of deionized water by ultrasonication. The solution was then transferred into a 50 mL Teflon-lined autoclave; then, a piece of activated carbon fiber paper was immersed into the solution and hydrothermally treated at 100 °C for 12 h. After the autoclave cooled to room temperature naturally, the carbon fiber paper covered with catalytic precursors was washed with distilled water and dried in a vacuum at 60 °C for 8 h.

2.2. Preparation of Co@CoO_x/HNCNTs. Co@CoO_x/HNCNTs were prepared by the single-step CVD method. The detailed procedures are as follows: a piece of precursor/carbon fiber paper (Toray, TGP-H-60) was put over the porcelain boat in the middle of the quartz tube. A certain amount of melamine was put in the central region of the tube as the nitrogen source. A thin layer of grease was used for sealing the inlet and outlet rubber gaskets against the outside air. Before the furnace was heated, Ar (99.999% in purity) was introduced into the heating system at a flow rate of 500 sccm for 30 min to purge out the air in the tube. Next, the furnace was heated to 900 °C with an Ar gas flow of 60 sccm, and then C_2H_4 gas was fixed between 15 and 20 sccm as the carbon source for 0.5, 1, and 1.5 h, respectively. Throughout the CVD process, Ar gas was kept running. Finally, the samples were calcined in air atmosphere at 250 °C for 2 h. The as-prepared materials were denoted as Co@CoO_x/HNCNTs-0.5 h, Co@CoOx/HNCNTs-1 h, and Co@CoOx/HNCNTs-2 h. The yield of Co@CoO_x/HNCNTs is calculated by the equation⁴⁹

$$\text{Yield}_{\text{Co/n-CNTs}} = \frac{M_{\text{total}} - M_{\text{precusors}}}{M_{\text{precusors}}} \times 100 \tag{2-1}$$

2.3. Material Characterizations. The conditions and requirements of various characterizations are recorded in the Supporting Information. In particular, synchrotron-based X-ray absorption spectroscopy (XAS) was carried out at the Canadian Light Source. Carbon and nitrogen K-edge and cobalt L-edge X-ray absorption near-edge structure (XANES) measurements were carried out on a high-resolution spherical grating monochromator beamline equipped with a 45 mm planar undulator and three gratings with a photon energy range of 250–2000 eV.

2.4. Electrochemical Measurements. The electrochemical characterizations were performed in a standard three-electrode system at room temperature. A rotating disk electrode with rotation control (Pine Instruments), a platinum sheet, and Ag/AgCl (3 M KCl) were used as the work electrode, the counter electrode, and the reference electrode, respectively. The electrolyte was 0.1 mol L^{-1} KOH solution. The samples were fixed on a glassy carbon RDE by an acrylic tape, which formed the working electrode. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted by our previous method (Supporting Information).²⁹

2.5. Fabrication of Al–air Coin Cells. According to the reports of our previous work, detailed manufacturing steps are described in the Supporting Information.³⁰ An Al foil, a piece of $Co@CoO_x/$ HNCNT, a piece of glass microfiber, and KOH solution were used as the anode, the cathode, the separator, and the electrolyte, respectively. The electrode reactions can be signified as follows. Anode

$$AI + OH^{-} \rightarrow AI(OH)_{4}^{-} + 3e^{-}$$
(2-2)



Figure 1. Schematic illustration for the synthesis of $Co@CoO_r/HNCNTs$.

$$Al(OH)_4^- \to Al(OH)_3(s) + OH^-$$
(2-3)

Cathode

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
(2-4)

Overall reaction

$$Al + 3/4O_2 + 3/2H_2O \rightarrow Al(OH)_3$$
 (2-5)

3. RESULTS AND DISCUSSION

3.1. Analyses of Characterizations. Figure 1 illustrates the growth schematics of $Co@CoO_x/HNCNTs$ by combining the hydrothermal synthesis and the single-step in situ CVD method. Urea was used to release OH^- into the Co^{2+} precursor solution, leading to the formation of cobalt hydroxide $Co_2(OH)_2CO_3$. During the hydrothermal process, $Co_2(OH)_2CO_3$ is transformed into $Co_2(OH)_2CO_3$ nanosheets. The reaction mechanism was as follows

$$\mathrm{NH}_{2}\mathrm{CONH}_{2} + 3\mathrm{H}_{2}\mathrm{O} \rightarrow 2\mathrm{NH}_{4}^{+} + \mathrm{OH}^{-} + \mathrm{HCO}_{3}^{-}$$

$$(3-1)$$

$$\mathrm{HCO}_{3}^{-} \to \mathrm{CO}_{3}^{2-} + \mathrm{H}^{+} \tag{3-2}$$

$$2\text{Co}^{2+} + 2\text{OH}^- + \text{CO}_3^{2-} \rightarrow \text{Co}_2(\text{OH})_2\text{CO}_3$$
 (3-3)

Figure S1 shows the scanning electron microscopy (SEM) images of $Co_2(OH)_2CO_3$ nanosheets grown on a carbon fiber paper. The as-synthesized catalyst precursors were not spherical but ultrathin flaky, with a thickness of ~50 nm (Figure S2) and a length distribution from a few micrometers to dozens of micrometers, and they were twisted together like the strands of a rope with high density. During the CVD process, $Co_2(OH)_2CO_3$ first converted to Co as the catalyst for producing HCNTs, which was in accordance with the XRD results (Figure 2). Generally, the catalyst plays an important role in the control of helical carbon materials with a desired



Figure 2. X-ray diffraction patterns of catalyst precursors, $Co@CoO_x/HNCNTs-0.5$ h, $Co@CoO_x/HNCNTs-1$ h, and $Co@CoO_x/HNCNTs-2$ h.

category and morphology.³⁰ High-yield Co@CoO_x/HNCNTs-1 h (yield_{Co/N-CNTs} = ca. 976.36%) can be obtained, which is much higher than most reported in the literature.³¹⁻³⁴

The X-ray diffraction (XRD) patterns of catalyst precursors, Co@CoO_x/HNCNTs-0.5 h, Co@CoO_x/HNCNTs-1 h, and Co@CoO_x/HNCNTs-2 h are shown in Figure 2. It is observed that Co@CoO_x/HNCNTs have the Co phase (JCPDS: 15-0806) and a graphite carbon phase at the characteristic diffraction peak of 25.3° (002). The characteristic diffraction peaks of the catalyst precursors are indexed to the crystal planes of Co₂(OH)₂CO₃ (JCPDS:48-0083). Furthermore, the longer growing time can facilitate the generation of the graphite phase. When the growth time is 1 h, the content of the Co phase is the highest in Co@CoO_x/HNCNTs. Remarkably, no CoO_x phase can be detected because of the coverage by plentiful Co and HNCNT phases and the restricted resolution of XRD.

The SEM image of $Co@CoO_x/HNCNTs$ (Figure S3) shows that a mass of HCNTs was uniformly grown on a carbon fiber paper surface with a high density. The morphological characterizations of $Co@CoO_x/HNCNTs$ with different growth times are shown in Figure 3. All Co@



Figure 3. SEM images of $Co@CoO_x/HNCNTs$ with different growth times at different magnifications: (a,b) $Co@CoO_x/HNCNTs$ -0.5 h, (c,d) $Co@CoO_x/HNCNTs$, and (e,f) $Co@CoO_x/HNCNTs$ -2 h.

 $CoO_x/HNCNTs$ exhibit a perfect helical shape with tough surface and uniform diameters, and high purity can be estimated by systematic field emission SEM observations. With the increasing growth time, the coil diameter of Co@ $CoO_x/HNCNTs$ increases from about 100 to 400 nm, and the coil pitch decreases from about 400 to 100 nm. The probable reason for this phenomenon is that the Co catalysts experience a growing-up process by agglomerating or recrystallizing, as the

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growth time increases. As shown in Figure 4a-d, energydispersive system elemental mapping of the red square region



Figure 4. (a–d) SEM images and elemental mapping images of C, Co, and O in $Co@CoO_x/HNCNTs$.

was conducted to study the elemental distribution of Co@ $CoO_x/HNCNTs$. The Co@ $CoO_x/HNCNTs$ -1 h electrode contains C (98.22 At %), Co (0.45 At %), and O (1.33 At %) elements. The C elemental mapping (Figure 4b) clearly confirms the formation of HCNTs. The Co elemental mapping (Figure 4c) exhibits the uniform distribution of Co species with a high density. The O elemental mapping (Figure 4d) indicates the possibility of existence of cobalt oxides and oxygen-containing functional groups.

Figure 5a-d exhibits the typical high-resolution transmission electron microscopy and scanning transmission electron



Figure 5. (a,b) TEM, (c) HRTEM, and (d) HAADF–STEM images of Co@CoO_x/HNCNTs-2 h.

microscopy (STEM) images of $Co@CoO_x/HNCNTs$. The TEM images show that the inner diameter of the $Co@CoO_x/HNCNT$ coil is about 150 nm and its outer diameter is about 300 nm, containing several graphitic layers. The pitches of the outer surface along the rod axis are observed to be around 150 nm. The results are consistent with the SEM results. The high-resolution TEM image (Figure 5c) confirms the existence of the graphitic layer according to the outer surface with amorphous carbon lattice fringes. There are three bright concentric diffraction rings from inside to outside in the selected-area electron diffraction pattern (Figure S4b,c), owing

to the polymorphism of Co or CoO_x . To confirm the distribution of Co species in detail, high-angle annular dark-field STEM (HAADF–STEM) for $Co@CoO_x/HNCNTs-2$ h was performed (Figures 5d and S5). The Co species may include metal cobalt and cobalt oxides with particle diameters of 30–50 nm existing on the edges of HNCNTs.

The structural compositions and defect degrees of Co@CoO_x/HNCNTs were studied by Raman spectroscopy (Figure 6). Two representative Raman peaks of carbon materials are



Figure 6. Raman spectra of $Co@CoO_x/HNCNTs-0.5$ h, $Co@CoO_x/HNCNTs-1$ h, and $Co@CoO_x/HNCNTs-2$ h.

observed at around 1360 and 1590 cm⁻¹, corresponding to the "defect-induced" D band and crystalline graphite with the $E_{2\sigma}$ vibration-mode G band, respectively. In general, the intensity ratio (I_D/I_G) of D band and G band is able to judge the disorder degree of carbon nanomaterials.³⁵ The I_D/I_G values are 0.94, 1.07, and 0.92 for Co@CoO_x/HNCNTs-0.5 h, Co@ CoO_v/HNCNTs-1 h, and Co@CoO_v/HNCNTs-2 h, respectively, indicating that the increase in the defects for Co@ CoO_r/HNCNTs-1 h is due to more Co phases introduced in the more active sites. Notably, some prominent peaks detected at 400-700 cm⁻¹ can be ascribed to the modes of spinel Co_3O_4 ,^{36,47} indicating that Co_3O_4 nanoparticles with the particle size of around 30 nm are within the scope of Raman spectroscopy detection (~ 2 nm), which can be confirmed by the HAADF-STEM images of Co@CoO_v/HNCNTs in Figure S5.

Thermogravimetric (TG) analysis was performed in air from room temperature to 900 °C to evaluate the amount of Co species. Figure S6 shows the TG-differential scanning calorimetry (DSC) curves of Co@CoO_x/HNCNTs-0.5 h, Co@CoOx/HNCNTs-1 h, and Co@CoOx/HNCNTs-2 h. Two obvious reductions of weight and two exothermic peaks are observed when the temperature is in the range of 400-650°C, which can be attributed to the oxidation of NCNTs and metallic Co. A total weight loss from 400 to 650 °C is ascribed to the combined effect of oxidation of metallic Co and carbon in $Co@CoO_x/HNCNTs$. When the temperature reaches up to around 500 °C, a gradual weight decrease and an exothermic peak are observed because of the oxidation of Co to Co₃O₄. The total weight loss between around 500 and 650 °C is 27.73 wt % for Co@CoOx/HNCNTs-0.5 h, 16.63 wt % for Co@ $CoO_x/HNCNTs-1$ h, and 18.76 wt % for $Co@CoO_x/$ HNCNTs-2, demonstrating that the content of Co species in $Co@CoO_x/HNCNTs$ follows the trend of $Co@CoO_x/$ HNCNTs-1 h > $Co@CoO_r/HNCNTs-2$ h > $Co@CoO_r/$ HNCNTs-0.5 h.

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Figure 8. (a) CV curves of $Co@CoO_x/HNCNTs-0.5$ h, $Co@CoO_x/HNCNTs-1$ h, $Co@CoO_x/HNCNTs-2$ h, and 20 wt % Pt/C electrocatalysts in O₂-saturated 0.1 M KOH aqueous solution; (b) LSV curves of $Co@CoO_x/HNCNTs-0.5$ h, $Co@CoO_x/HNCNTs-1$ h, $Co@CoO_x/HNCNTs-1$ h, $Co@CoO_x/HNCNTs-1$ h, $Co@CoO_x/HNCNTs-1$ h, $Co@CoO_x/HNCNTs-2$ h, and 20 wt % Pt/C electrocatalysts on an RDE electrode in O₂-saturated 0.1 M KOH solution at a rotation rate of 1600 rpm with a scan rate of 5 mV s⁻¹; (c) LSV curves of $Co@CoO_x/HNCNTs-1$ h in O₂-saturated 0.1 M KOH solution at various rotation rates with a scan rate of 5 mV s⁻¹; inset: corresponding Koutecky–Levich plots at different potentials; (d) mass activities at -0.199 V for all the catalysts.

3.2. NEXAFS Analysis. To further investigate the electronic structure and local chemical configuration of the $Co@CoO_x/HNCNT$ catalysts, XAS measurements were carried out. It can effectively reveal the local chemical environment of target elements in the sample microdomain and characterize the electronic structures of the selected element. The XANES of Co L-edge in $Co@CoO_x/HNCNTs$ was acquired using the total electron yield (TEY) and fluorescence yield (FLY). TEY can be used to analyze the chemical state of elements on the surface or near the surface film (5 nm), whereas FLY can be used to analyze the chemical state of elements within the bulk material. The L_2 , L_3 absorption edges of cobalt are generated by the inner-shell $2p_{1/2}$ and $2p_{3/2}$ electron transitions.

As shown in Figure 7a,b, the soft X-ray absorption Co $L_{2,3}$ edge spectra (770–810 eV) of Co@CoO_x/HNCNTs-0.5 h, Co@CoO_x/HNCNTs-1 h, and Co@CoO_x/HNCNTs-2 h are basically consistent without obvious changes and shifts, indicating that Co exists in similar chemical environments in the three samples. The widening of the peaks certifies the nanoparticle morphology of Co species. Compared to the spectra of the standard samples, the edge jump of the spectra is similar to that of Co metal.⁴⁸ The spectral shape of Co $L_{2,3}$ edge spectra changes drastically with the Co oxidation states (Co²⁺ and Co³⁺), as predicted by Raman results.^{37,38} The redox reaction between Co species can be regarded to assist the charge transfer for ORR processes.⁴⁴ In addition, the consistency between the TEY and FLY spectra suggests the uniform chemical nature of Co throughout the sample. The Co L_{2,3}-edge features in the TEY spectra are more sensitive to the spin configuration of CoO in the ground state and more sensitive to the spin configuration of Co_3O_4 in the FLY spectra, which suggests that CoO exists on the surface or near the surface film, whereas Co_3O_4 is located in the interior of Co@ $CoO_x/HNCNTs.$

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Figure 9. (a) Configuration of an Al–air coin cell; discharge curves of the Al–air coin cells assembled with $Co@CoO_x/HNCNTs-0.5$ h, $Co@CoO_x/HNCNTs-1$ h, and $Co@CoO_x/HNCNTs-2$ h under ambient conditions at a current density of 1.0 mA cm⁻²; (b) voltage–time (*V*–*t*) curves; (c) voltage–specific capacity (*V*–*Q*) curves; power–current density curves for the Al–air coin cells with (d) $Co@CoO_x/HNCNTs-0.5$ h, (e) $Co@CoO_x/HNCNTs-1$ h, and (f) $Co@CoO_x/HNCNTs-2$ h electrodes.

As shown in Figure S7a, the C K-edge spectra of Co@ CoO_x/HNCNTs-0.5 h, Co@CoO_x/HNCNTs-1 h, and Co@ CoO_x/HNCNTs-2 h are relatively similar, suggesting the existence of uniform carbon structure environments. The excitations of π^* at 287.6 eV (peak C1) and 290.8 eV (peak C2) are attributed to C=C and C-N or C-O-C, respectively. The excitation of σ^* at 293.8 eV (peak C3) suggests the formation of sp² C–C species.³⁹⁻⁴¹ Under a high CVD temperature, the oxygen-containing functional groups decompose and a part of nitrogen atoms run off; so, the intensity of peak C2 from Co@CoOx/HNCNTs-0.5 h to Co@ CoO_x/HNCNTs-2 h decreased. In the N K-edge near-edge Xray absorption fine structure (NEXAFS) spectra (Figure S7b), the resonances of π^* at around 400.1 and 402.0 eV are attributed to pyridinic N and graphitic N, respectively.⁴¹ The peak intensity of graphitic N in Co/N-CNTs-1 h is stronger, which means better electrocatalytic activity. 42,45,46 The excitations of σ^* at 407–408 eV are ascribed to C–N.⁴ The presence of N species improves the charge mobility of the carbon matrix and the electrocatalytic activity of carbon in the electron-transfer reactions by introducing electron-donor characteristics.43

3.3. Electrocatalytic Performance of Co@CoO_x/ HNCNTs for Oxygen Reduction Reaction. To evaluate the electrocatalytic performance of Co@CoO_x/HNCNTs, CV and LSV measurements on a rotating disk electrode in O₂saturated 0.1 M KOH solution were comparatively performed. The CV curves (Figure 8a) exhibit a more positive peak potential for Co@CoO_x/HNCNTs-1 h (-0.23 V vs Ag/AgCl) than that of Co@CoO_x/HNCNTs-0.5 h (-0.34 V vs Ag/ AgCl) and Co@CoO_x/HNCNTs-2 h (-0.36 V vs Ag/AgCl) but negative than that of commercial Pt/C (-0.13 V vs Ag/ AgCl). The LSV curves at a rotating rate of 1600 rpm of different catalysts were acquired to further investigate their ORR catalytic performance (Figure 8b). Remarkably, Co@ CoO_x/HNCNTs-1 h shows a more positive onset potential ($E_{onset} \approx -0.11$ V vs Ag/AgCl) along with a higher half-wave potential ($E_{1/2} \approx -0.19$ V) than that of Co@CoO_x/HNCNTs-0.5 h ($E_{\text{onset}} \approx -0.18$ V, $E_{1/2} \approx -0.31$ V vs Ag/AgCl) and Co@ CoO_x/HNCNTs-2 h ($E_{\text{onset}} \approx -0.18$ V, $E_{1/2} \approx -0.33$ V vs Ag/ AgCl), which is comparable with the that of 20 wt % Pt/C catalyst ($E_{\text{onset}} \approx -0.10$ V, $E_{1/2} \approx -0.18$ V vs Ag/AgCl). The more positive peak potentials, E_{onset} and $E_{1/2}$, portend higher ORR electrocatalytic activity. Thus, the results of electrochemical testing demonstrate that the better electrocatalytic activity of Co@CoO_x/HNCNTs-1 h toward ORR may be because of the more Co species and graphitic N introducing more active sites on the surface structure.

The electron-transfer number (n) for ORR was determined from the LSV studies (Figure 8c) in the O₂-saturated 0.1 M KOH electrolyte at different rotation rates from 400 to 1600 rpm according to the Koutecky-Levich (K-L) equation (for details, see the Supporting Information). The corresponding Koutecky-Levich (K-L) plots at different potentials are shown in Figure 8c, inset. The *n* value of $Co@CoO_r/$ HNCNTs-1 h is calculated to be about 3.36, which is higher than that of Co@CoO,/HNCNTs-0.5 h (3.12) and Co@ $CoO_r/HNCNTs-2$ h (3.16) and lower than that of the 20 wt % Pt/C catalyst (4.0, Figure S8), suggesting that $Co@CoO_x/$ HNCNTs-1 h favors a priority for the four-electron ORR pathway. Co@CoO_x/HNCNTs-1 h shows a much higher ORR mass activity (76.07 mA g^{-1}) at -0.199 V than Co@ CoO_x/HNCNTs-0.5 h and Co@CoO_x/HNCNTs-2 h, which is still below the level of Pt/C (111.00 mA g^{-1}) (Figure 8d). The long-term stability of Co@CoOr/HNCNTs-1 h was investigated by linear cyclic sweeping tests in the O2-saturated 0.1 M KOH electrolyte before and after continuous 2000 cycles (Figure S9a). The LSV curve shows no obvious changes in the onset potential and half-wave potential and a slight change in the diffusion-limiting current after continuous 2000 cycles, indicating the high stability of Co@CoO_x/HNCNTs-1 h. Additionally, 3 mol L^{-1} methanol was added into the O₂saturated $0.1 \text{ mol } L^{-1}$ KOH solution in the process of chronoamperometric test at a rotation rate of 900 rpm to study

the methanol crossover effect. Figure S9b exhibits that the ORR current density of $Co@CoO_x/HNCNTs-1$ h almost remains stable in contrast to the significant decay for the Pt/C catalyst, which should be ascribed to the incomplete methanol oxidation on the electrode surface, demonstrating its higher tolerance of crossover effect against methanol.

3.4. Performance of Al-air Coin Cells Using Co@ CoO_x/HNCNTs as Binder-free Cathodes. To this end, we further explored the possibility of using Co@CoO_x/HNCNTs as binder-free cathodes in Al-air batteries. The interior structure of Al-air coin cells is shown in Figure 9a. Figure 9b presents the discharge behaviors under the atmospheric environment of coin cells using Co@CoO_x/HNCNTs-0.5 h, Co@CoOx/HNCNTs-1 h, and Co@CoOx/HNCNTs-2 h as binder-free air electrodes at a constant current density of 1.0 mA cm⁻². The coin cell with the Co@CoO_x/HNCNTs-1 h air electrode shows a higher open-circuit voltage of 1.48 V than that with Co@CoO_x/HNCNTs-0.5 h (1.38 V) and Co@ $CoO_x/HNCNTs-2$ h (1.36 V) electrodes. Moreover, the coin cell with the Co@CoO_x/HNCNTs-1 h air electrode displays a higher specific capacity of 367.31 mA h g^{-1} (Figure 9c) and a higher power density of 1.39 mW cm⁻² than that with Co@ $CoO_x/HNCNTs-0.5$ h (277.62 mA h g⁻¹ and 1.30 mW cm⁻²) and Co@CoO_x/HNCNTs-2 h (301.02 mA h g⁻¹ and 1.33 $mW cm^{-2}$) electrodes when consuming an identical mass of Al. Such a better performance of the Co@CoO_x/HNCNTs-1 h electrode confirms more excellent electrocatalytic activity of Co@CoO_x/HNCNTs-1 h, which is due to its more active sites.

In order to further evaluate the properties of the binder-free electrodes, the power–current density curves of coin cells with $Co@CoO_x/HNCNTs-0.5$ h, $Co@CoO_x/HNCNTs-1$ h, $Co@CoO_x/HNCNTs-2$ h were recorded, as shown in Figure 9d–f. The $Co@CoO_x/HNCNTs-1$ h electrode possesses a higher maximum power density (P_{max}) of 3.86 mW cm⁻² than $Co@CoO_x/HNCNTs-0.5$ h (3.38 mW cm⁻²) and $Co@CoO_x/HNCNTs-2$ h (2.64 mW cm⁻²) electrodes, which suggests the great potential of $Co@CoO_x/HNCNTs-1$ h as the air electrode for practical applications in Al–air batteries.

4. CONCLUSIONS

In summary, high-purity Co@CoOr/HNCNT-based binderfree electrodes were fabricated by a facile method combining hydrothermal treatment and single-step in situ CVD over a carbon fiber paper substrate. The synthesized Co@CoOx/ HNCNTs with a growth time of 1 h exhibit better ORR electrocatalytic performance than the samples with growth times of 0.5 and 2 h, which can be attributed to more defects and active sites from more Co species on the surface structure and graphitic N dopants of Co@CoO_x/HNCNTs-1 h. Because of the superior catalytic activity of the $Co@CoO_x/HNCNTs-1$ h binder-free electrode, the Al-air battery exhibited a higher open-circuit voltage, specific capacity, and power density. This work not only proposes an innovative and general strategy for preparing high-purity Co@CoO_x/HNCNTs on a substrate with ultrahigh specific surface area and abundant edge defects but also provides valuable guidance for designing and developing Co@CoOx/HNCNTs as binder-free electrodes in Al-air batteries, which can be further extended to be used in various metal-air systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c01603.

SEM images of catalyst precursors at different magnifications; HAADF–STEM images of Co@ CoOx/HNCNTs; TG–DSC curves of Co@CoOx/ HNCNTs-0.5 h, Co@CoOx/HNCNTs-1 h, and Co@ CoOx/HNCNTs-2 h; C K-edge and N K-edge spectra of Co@CoOx/HNCNTs on a carbon paper; LSV curves and the corresponding KL plots of Co@CoOx/ HNCNTs-0.5 h, Co@CoOx/HNCNTs-2h, and 20 wt % Pt/C; and durability test and chronoamperometric response of Pt/C and Co@CoOx/HNCNTs-1 h (PDF)

AUTHOR INFORMATION

Corresponding Author

Xueliang Sun – Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada; o orcid.org/0000-0003-0374-1245; Email: xsun@eng.uwo.ca

Authors

- Yisi Liu Institute of Advanced Materials, Hubei Normal University, Huangshi 415000, China
- Biqiong Wang Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada; orcid.org/0000-0002-3903-8634
- **Qian Sun** Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada
- **Qiyun Pan** Institute of Advanced Materials, Hubei Normal University, Huangshi 415000, China
- Nian Zhao Institute of Advanced Materials, Hubei Normal University, Huangshi 415000, China
- **Zhong Li** Institute of Advanced Materials, Hubei Normal University, Huangshi 415000, China
- Yahui Yang National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c01603

Author Contributions

^{II}Y.L. and B.W. have contributed to this work equally and should be regarded as co-first authors.

Notes

The authors declare no competing financial interest.

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