N-doped porous carbon-based catalysts hold great promise for hydrogen evolution reaction (HER) due to their plentiful cavity construction, high specific surface area, and flexible metal assemblies. Nevertheless, the cumbersome synthetic process and the use of highly corrosive chemicals greatly increase the production costs and pollutions. Herein, we report a facile and eco-friendly thermal puffing strategy, which imitates the popcorn forming process, for the fabrication of N-doped hierarchical porous carbon–CoOₓ catalysts. The results indicate that the well-developed porosity and high specific surface area (696 m² g⁻¹) of CoOₓ–NC-1.0 are achieved during the thermal expansion. Impressively, the as-prepared CoOₓ–NC-1.0 with ultralow Co loading (0.67 wt %) presents admirable HER performance to drive 10 mA cm⁻² at an overpotential of 189 mV in the alkaline electrolyte. Especially, the activity of CoOₓ–NC-1.0 can be maintained for a continuous ~70 h test. Such an excellent property of CoOₓ–NC not only derives from the hierarchical porous structure but is also due to the higher ratio of graphitic-N and pyridinic-N, which promotes the better electrical conductivity and formation of more active Co⁹ for HER, respectively. Moreover, this strategy is applicable to the fabrication of other transition metal-based hierarchical porous composites, which opens new possibilities for exploring promising candidates to substituted commercial Pt/C.

1. INTRODUCTION

The gradual depletion of fossil energy and global warming have spurred intense research on eco-friendly new energy sources.¹ Hydrogen, due to its high energy density and pollution-free emission, has become a clean sustainable alternative to traditional fossil fuels.²,³ Among various synthetic technologies, electrolysis of water has been accepted as an efficient way to generate high-purity H₂.⁴,⁵ However, the practical voltage is much higher than the theoretical reaction barrier of 1.23 V for water splitting owing to the extra resistance and polarization effect. Accordingly, the catalysts are unavoidably used to significantly reduce the reaction barrier and obtain the lower overpotential. Up to now, Pt/C is considered to be the state-of-the-art electrocatalyst toward hydrogen evolution reaction (HER).⁶ Nevertheless, the commercial application of the water splitting technique is largely impeded by the high cost and scarcity of Pt. In order to conduct electrolytic water in an effective manner, it is urgent to exploit highly active catalysts based on earth-abundant elements.⁷–⁰

Co-based catalysts are considered to be the promising low-cost catalysts for HER due to their moderate Gibbs free energy of hydrogen adsorption, according to the well-known volcano plot.¹¹,¹² Recently, a large variety of Co-based electrocatalysts, including CoP,¹³–¹⁵ CoN₂,¹⁶,¹⁷ CoSe₂,¹⁸ and so forth,¹⁹–²³ have been adopted as potential candidates to substitute Pt-based catalysts. Nevertheless, the superior activity derives from the phosphorization or sulfuration process. The tedious post-treatment procedures and toxic reagents (e.g., NaH₂PO₂) inevitably increased the production costs and went against the environment protection. More importantly, the catalytic properties of the catalysts are still unsatisfactory for HER, especially in terms of stability. Therefore, development of a convenient and green strategy for the design of active and stable Co-based catalysts is extremely desirable but remains a great challenge.²⁴–²⁶

Nanoporous carbon materials are characterized by a high specific surface area (SSA), superior electrical conductivity, good acid-alkali corrosion resistance, and controllable chemical structure.²⁷–²⁹ The hybridization of porous carbon with active metals facilitated the mass transfer process and the release of hydrogen.³⁰–³² Particularly, the incorporation of heteroatoms (such as N) into porous carbon materials not only enhanced the surface hydrophilicity, conductivity, and the density of defects but also reinforced the interaction between the porous carbon skeleton and metal phases,³³ which may accelerate the electron transfer and provide more anchor sites for the metal...
components. Consequently, N-doped porous carbon has been widely applied in the field of energy conversion and storage. In general, porous carbon materials are synthesized by nanocasting or the chemical activation method. As for the former method, the introduction of templates, especially hard templates (SiO₂), greatly complicates the preparation process. Moreover, the removal of the template normally employs highly corrosive reagents (such as HF). For the latter means, whether using solid activators or gas activators, the activation processes require high-level equipment and produce much gas emissions. In this regard, the development of a simple and versatile synthesis technique for the fabrication of heteroatom-doped porous carbon-based composites is of great significance.

Thermal puffing technology has been widely applied in the production of puffed food, which was made from starch-based feedstock (e.g., potato, rice, and corn). Benefitting from the high temperature and instantaneous release of large pressure, the expanded three-dimensional porous materials with increased volume and surface area are obtained. Herein, we constructed a series of CoOₙ−N-doped hierarchical porous carbon-based composites via a simple thermal expansion strategy, which is characterized by facile operation and speediness without environmental pollution. During the thermal expansion process, the cross-linked structure of the “starch strips” was destroyed, so the synthesized materials exhibited a hierarchical porous structure. Impressively, the CoOₓ−NC catalyst delivered superior catalytic activity and stability toward HER due to the unique structural features. In 1.0 M KOH solution, the overpotential of CoOₓ−NC-1.0 with ultralow Co loading (0.67 wt %) was as low as 189 mV at a current density of 10 mA cm⁻². Furthermore, the CoOₓ−NC-1.0 catalyst showed negligible loss of activity for ~70 h in a continuous catalytic process.

2. RESULTS AND DISCUSSION

The synthetic process of CoOₓ−NC composites is schematically illustrated in Scheme 1. Commercial “starch strips”, ingredients for the production of puffed food, served as a carbon source. Generally, the fabrication of CoOₓ−NC followed two steps: (i) The pretreatment of “starch strips”. “Starch strips” were first impregnated in a homogenous solution containing cyanamide and Co(NO₃)₂ during which the color of “starch strips” transferred from yellow to pink (Figure S1). Then, the adsorbed “starch strips” were moved to an oven and dried at 60 °C. (ii) Thermal puffing. The treated “starch strips” were calcined via a two-step pyrolysis procedure under an inert atmosphere to build the N-doped hierarchical porous morphology. The obtained catalysts are denoted as CoOₓ−NC-ₓ (ₓ represents the dosage of cyanamide). The experimental process is elaborated in the Supporting Information. During the first temperature interval, the moisture in the “starch strips” was rapidly heated and gasified, and then, pressure-increased expansion was carried out. By the expansion force of vapor, the dense, cross-linked structure of “starch strips” was destroyed and abundant hierarchical pores were formed. Meanwhile, the N atoms from the decomposition of the cyanamide polymer (CₓNₓ) doped into the carbon skeleton and substituted part of carbon atoms. Owing to the anchoring effect of N atoms, CoOₓ nanoparticles were tightly attached to the porous carbon. More importantly, the introduction of N atoms not only regulated the electronic structure and promoted the adsorption of protons on the metal surface but also enhanced the strong interaction between the d orbital of the metal and the p orbital of N atoms, further improving the material stability. Followed by the second stage of high-temperature treatment, the graphitization degree of this composite was further enhanced, which was favorable to improve the electrical conductivity.

The scanning electron microscopy (SEM) image of the hierarchical porous structure of CoOₓ−NC-1.0 is illustrated in Figure 1a. It disclosed that CoOₓ−NC-1.0 was featured with a well-developed pore structure, which was advantageous for the rapid transport of gas and the electrolyte on the catalyst surface. More importantly, the abundant pores could expose more active sites, thus increasing the catalytic activity. In addition, transmission electron microscopy (TEM) was further employed to confirm the existence of the porous structure. From Figures 1b and S2, it was clearly observed that CoOₓ−NC-1.0 was equipped with dense pores, which was in accordance with the SEM image. Moreover, a small amount of Co-based nanoparticles were attached to the porous carbon surface. Because of the high atomic surface energy of non-noble transition metals and the high-temperature pyrolysis treatment, the Co-based particles were inclined to generate local agglomeration. As the high-resolution transmission electron microscopy (HRTEM) images shown in Figure 1c,d, the lattice fringes were measured with interplanar spacings of 0.205, 0.248, and 0.464 nm, corresponding to the (111) plane of Co, the (111) plane of CoOₓ, and the (111) plane of Co₃O₄, respectively. Besides, energy-dispersive X-ray spectroscopy (EDX) mappings further marked a relatively homogenous distribution of C, N, O, and Co species in the selected region (Figure 1f–i).

Further structural details of CoOₓ−NC-1.0 were gained from X-ray photoelectron spectroscopy (XPS). As seen from Figure 2a, the high-resolution C 1s spectrum of CoOₓ−NC-1.0 exhibited three C species, corresponding to C−C (∼284.5 eV), C≡C (∼285.4 eV), and C≡N−C (∼287.0 eV). The presence of C≡N−C suggested that the N atoms were successfully doped into the carbon texture rather than the residues of precursors. Furthermore, the powder X-ray diffraction (XRD) patterns (Figure 2b) were also operated to reveal the crystallographic structure of CoOₓ−NC-1.0. The characteristic peaks of the graphite-type lattice (C, PDF #14-184), Co, and CoO (Co, PDF #15-0806, CoO, PDF #43-1004) were recorded, which was consistent with the results of HRTEM. The detailed pore structure information of CoOₓ−NC-1.0 was obtained by the N₂ adsorption–desorption isotherms (Figure 2c). According to the N₂ absorption–
desorption isotherms, the SSA was calculated to be 696 m² g⁻¹. Additionally, the Barrett–Joyner–Halenda (BJH) PSD diagram (Figure 2d) further demonstrated the hierarchical porous feature of CoOₓ−NC-1.0, especially concentrating in the mesoporous range, which was believed to facilitate the mass transfer. All the investigations manifested that N-doped hierarchical porous carbon–CoOₓ composites were successfully synthesized through the one-pot thermal puffing strategy.

Based on the characteristics of the materials, the performance of the samples was tested through a typical three-electrode system in 1.0 M KOH. Above all, the effect of different components on the HER activity was explored. For comparison, graphitic carbon (C), obtained from the pyrolysis of “starch strips”⁵, N-doped carbon (NC), and CoOₓ−C were also constructed. As presented in Figure 3a, CoOₓ−C displayed a much better HER activity than that of C and NC. In sharp contrast, once the cyanamide was added, CoOₓ−NC-1.0 manifested superior performance toward HER, which required a small overpotential of 189 mV driving a cathodic current density of 10 mA cm⁻². Compared with commercial Pt/C (20 wt %), CoOₓ−NC-1.0 exhibits lower catalytic activity owing to the ultralow Co loading (Figure S3a). However, the mass activity of CoOₓ−NC-1.0 is comparable to that of Pt/C, implying that it has the potential to replace commercial Pt/C (Figure S3b). Moreover, electrochemical impedance spectroscopy (EIS) was further employed to reveal the electronic conductivity of samples. From the Nyquist plots, it is demonstrated that CoOₓ−NC-1.0 had the smallest semicircle diameter than that of C, NC, and CoOₓ−C (Figure S3c).

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metallic species. As a result, the diluted CoOx species could synergistically promote the catalytic process. More information about the effects of the two components on the HER activity would be discussed as follows.

In order to investigate the effect of the N doping level on the catalytic performance, a series of CoOx−NC composites with diverse N amounts were synthesized by changing the additive content of cyanamide. According to the results of elemental analysis (Table S2), the N content reached 2.13 wt % for CoOx−NC-1.0 and then slightly reduced with the increase in cyanamide concentration. It has been reported that N doping can activate the nearby C atoms to increase the number of active sites. Meanwhile, owing to the lone electrons in N atoms, they can provide extra electrons to the carbon skeleton, thus improving the conductivity. Among the CoOx−NC with different N contents, CoOx−NC-1.0 with the highest N content (2.13 wt %) exhibited the best catalytic performance. However, although the N content in CoOx−NC-1.5 was higher than that of CoOx−NC-0.8, the activity of the former attenuated slightly. It indicated that the N content was not the main factor influencing the activity, but the bonding configuration of N might have an arresting effect on the performance.

Subsequently, a systematic analysis of the distribution of N species in each sample was obtained from the high-resolution XPS data. As described in Figure 4a, three typical peaks at ~398.4 eV, ~400.0 eV, and ~401.0 eV were observed in CoOx−NC-0.8, CoOx−NC-1.0, and CoOx−NC-1.5, which belong to the pyridinic-N (N3), pyrrolic-N (N2), and graphitic-N (N1), respectively. Based on the semiquantitative analysis of each N species (Figure 4b), we found that the activity of CoOx−NC-1.0, CoOx−NC-0.8, and CoOx−NC-1.5 was positively correlated with graphitic-N and pyridinic-N content. Considering that graphitic-N enables more electrons to be introduced into the layers of graphite, this would improve the electronic conductivity of the carbon support. Furthermore, doping N atoms induces a decrease in the spin density, which prevents the deep oxidation of metal particles. In particular, pyridinic-N is beneficial to increase the ratio of metallic species.

In addition, the semicircle diameter of each catalyst in EIS (Figure 3b) was gradually reduced from CoOx−NC-0.8 and CoOx−NC-1.5 to CoOx−NC-1.0, which had almost the same changes as the activity trend. Such a result indicated that CoOx−NC-1.0 had a faster charge transfer rate, thus delivering the optimal catalytic ability. Furthermore, Raman spectra were carried out to investigate the degree of graphitization of the materials. The results suggested that CoOx−NC-1.0 had the highest degree of graphitization because of the minimum I_D/I_G value (Figure S4), implying its excellent conductivity. The SSA and pore structure are the key factors influencing the exposure of catalytic sites and mass transfer. Although both CoOx−NC-0.8 and CoOx−NC-1.5 exhibited hierarchical pores to some extent (Figures S5, S6), the degree of pore formation was worse than that of CoOx−NC-1.0. Based on the analysis of Brunauer−Emmett−Teller (BET) results (Figures 2c and 5b,d), the SSA of CoOx−NC-1.0 (696 m² g⁻¹) was obviously higher than that of CoOx−NC-0.8 (635 m² g⁻¹) and CoOx−NC-1.5 (605 m² g⁻¹). The high SSA was conducive to exposing more active sites and thus promoted the reactivity. It was worth noting that CoOx−NC-1.0 presented wide PSD, especially concentrating at ~15 nm. The large pore size facilitated the mass transfer and H₂ diffusion. Additionally, as an important factor affecting the catalytic performance, the electrochemical active surface area (ECSA) was obtained by measuring the double-layer capacitance (C_dl). The large C_dl manifested the high ECSA and further presented the superior catalytic activity. The C_dl of CoOx−NC-0.8, CoOx−NC-1.0, and CoOx−NC-1.5 was calculated via CV curves. As illustrated in Figure S6, it could be seen that the C_dl of CoOx−NC-1.0 was 218.4 mF cm⁻², which was larger than that of CoOx−NC-0.8 (161.9 mF cm⁻²) and CoOx−NC-1.5 (159 mF cm⁻²).

As for the metal components, the XRD patterns (Figure S7) confirm that the Co and CoO are the main phases, excluding the influence of the metal phase on the catalytic performance. Afterward, the chemical state of Co was analyzed according to the Co 2p-XPS spectra to deeply explore the activity origin. It can be observed from Figure 6a that only satellite and Co⁰ peaks are detected in CoOx−C. However, a new peak located at ~778.5 eV, corresponding to Co⁰, appeared after introducing N atoms in CoOx−NC (Figure 6b−d). The results suggested that the N doping was conducive to the formation of metallic Co, which was consistent with the abovementioned results. It is worth mentioning that the content of Co⁰ decreased in the order CoOx−NC-1.0, CoOx−NC-0.8, and CoOx−NC-1.5, however with the increased overpotential (Figure 6e). From the XPS analysis, we speculate that the good performance of CoOx−NC-1.0 may be derived from the high Co⁰ content. In order to clarify the role of each
component, we varied the composition of CoO–NC-1.0. Specifically, CoO–NC-1.0-H2 was prepared by H2 reduction of CoO–NC-1.0 to increase the metallic Co content. Moreover, CoO–NC-1.0-acid was achieved by acid treatment of CoO–NC-1.0 to remove the CoO and Co3O4 species. XRD data (Figures S8 and S9) revealed that only the diffraction peaks assigned to metallic Co appeared in CoO–NC-1.0-acid and CoO–NC-1.0-H2. Based on the activity analysis, the performance of CoO–NC-1.0-acid was obviously attenuated upon removing CoO and Co3O4 with an acid (Figure S10). The results showed that CoO and Co3O4 jointly contributed to the catalytic performance for HER. Furthermore, the activity of CoO–NC-1.0-H2, where the CoO and Co3O4 converted to metallic Co, outperformed that of CoO–NC-1.0 (Figure S10). Although the decrease in cobalt oxides caused the decline in activity to some extent, the increase in Co0 content not only compensated for the decrease in activity but also further optimized the catalytic performance. The results revealed the crucial effect of Co0. According to the previous reports, the researchers proposed that metal Co possessed moderate H binding energy, and CoO and Co3O4 could be hydroxylated to promote H2O splitting and act as OH– adsorption sites because of the strong electrostatic affinity by the locally positively charged Co2+/Co3+. Therefore, we speculated that Co, CoO, and Co3O4 synergistically prompted the Volmer process, and metallic Co exhibited higher reactivity than that of CoO and Co3O4.

We further changed the calcination temperature to 800 °C to study the effect of temperature on the structure of the catalyst. It was found that the pyrolysis temperature played a vital role in the pore structure of the catalyst. Based on the SEM and TEM images, it can be seen that CoO–NC-800 presents a certain pore structure (Figure S11). Compared with CoO–NC-1.0, however, the pore structure is not well developed. According to the result of BET analysis (Figure S12), the SSA of CoO–NC-800 (422 m² g⁻¹) is relatively smaller than that of CoO–NC-1.0 (696 m² g⁻¹). In addition, the value of I₀/I₁, obtained from the Raman spectrum is much higher than that of CoO–NC-1.0 (Figure S13). The result indicates the poor graphitization degree of CoO–NC-800, which is not conducive to the electrocatalytic reaction. Furthermore, the catalytic activity of CoO–NC-800 is measured under 1.0 M KOH. The experiment result shows that the overpotential of CoO–NC-800 is 355 mV to reach 10 mA cm⁻², much larger than that of CoO–NC-1.0 (Figure S14). It is worth noting that the pyrrolic-N is the dominant species, and correspondingly, the content of Co0 decreased for CoO–NC-800 (Figures S15 and S16). The abovementioned results further indicated that the low SSA, the poor electrical conductivity, and the low graphitic-N, pyridinic-N, and Co0 content lead to the unsatisfactory catalytic performance.

Tafel plots, fitting to the LSV curve, were used to further explore the reaction kinetics of HER. In Figure 7d, the Tafel slope of CoO–NC-1.0 (140 mV dec⁻¹) is smaller than that of CoO–NC-0.8 (150 mV dec⁻¹) and CoO–NC-1.5 (158 mV dec⁻¹). The low Tafel slope value manifested the fast electrode reaction kinetics. Since the Tafel slope of CoO–NC-1.0 is close to 120 mV dec⁻¹, the Volmer reaction is the rate-determining step. Additionally, the long-term stability of the catalysts is an important index to evaluate the performance in commercial applications. The I−t test showed that the current density basically had no variation during the continuous 70 h period (Figure 3e). The strong interaction between the N-doped carbon framework and metal components is beneficial to anchor and stabilize the metal phase, which ensured its ultrahigh stability.

In order to further confirm the role of Co0 and N doping toward HER, we varied the N sources to adjust the concentration of N and Co species. As displayed in Figure 7a, urea as a N source exhibited poor activity, while the activity increased when the N source changed to dicyandiamide (DCDA). As evidenced from Figure S17, both CoO–NC–urea and CoO–NC–DCDA exhibited porous morphologies. EIS analysis (Figure 7b) showed that variation of the N source had a significant impact on the Rct. The Rct of CoO–NC–urea, CoO–NC–DCDA, and CoO–NC–1.0 gradually decreased. From the result of elemental analysis (Table S2), CoO–NC–urea possessed the equivalent N content as CoO–NC–DCDA, excluding the influence of N content on...
the properties. Nevertheless, the distribution of N species in the products was obviously different (Figure S18). The ratios of graphitic-N and pyridinic-N increased in the order CoO$_x$−NC−urea, CoO$_x$−NC−DCDA, and CoO$_x$−NC-1.0 (Figure 7c). Corresponding to this, the content of Co$^0$ increased gradually, and a low overpotential was observed when the Co$^0$ was the dominant phase (Figures 7d and S19). This conclusion further confirmed that the high graphitic-N and pyridinic-N promoted the better electrical conductivity and the high Co$^0$ proportion, which was the key factor to govern the catalytic activity.

Finally, we changed the types of metals to explore the universality of the thermal puffing method. The experimental results showed that the hierarchical pores could be constructed when Fe(NO$_3$)$_3$·9H$_2$O and WCl$_6$ are metal sources (Figures S20 and S21). This general method provides the possibility for designing promising alternatives.

3. CONCLUSIONS

In conclusion, we proposed a convenient and efficient protocol for the fabrication of hierarchical porous carbon composites. Thermal puffing instantly stimulates the "starch strips" blasting to form the hierarchical porous structure. Such an open and porous structure of the carbon substrate not only exposes more active sites but also accelerates the mass transfer process. The high graphitic-N and pyridinic-N proportions promote the excellent conductivity and the high Co$^0$ ratio, which plays a decisive role in improving the catalytic performance. Benefitting from the unique structures, the CoO$_x$−NC-1.0 presented a low overpotential of 189 mV at an ultralow metal loading (0.67 wt %) and showed almost no loss of activity for 70 h. Moreover, this thermal puffing method can be scalable to Fe and W systems. This work paves a new pathway for the preparation of hierarchical porous carbon composites, which have the opportunity to be commercially available on a large scale.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. Co(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and WCl$_6$ were purchased from Shanghai Macken Biochemical Technology Co., Ltd. Cyanamide, DCDA, and urea were used as the N source from Sigma-Aldrich Trading Co., Ltd. "Starch strips", in which starch and wheat flour are the main ingredients, were used to produce puffed food. Here, "starch strips" were selected as a source of carbon purchased from supermarkets. All the chemicals are of reagent grade and have not been further purified. All solutions were prepared with deionized water.

4.2. Synthesis of CoO$_x$−NC-0.8, CoO$_x$−NC-1.0, CoO$_x$−NC-1.5, and Other Contrast Samples. Taking the fabrication of CoO$_x$−NC-1.0 as an example, 20 mL of deionized water was added to a clear beaker; afterward, 0.1 g of Co(NO$_3$)$_2$·6H$_2$O was dissolved in the water. Then, 1.0 g of cyanamide was added to the abovementioned solution and stirred to form a uniform solution. Subsequently, about 4 g "starch strips" was impregnated into the mixture for 1 h at room temperature. After carefully removing the "starch strips" into a watch glass, the prepared precursor dried in an oven at 40 °C. Finally, the dried "starch strips" were placed in a tube furnace and calcined to 1000 °C under a N$_2$ atmosphere (see Scheme S1). After it cooled down to room temperature, the black solid (CoO$_x$−NC-1.0) was obtained. The synthetic process of other samples was similar to that of CoO$_x$−NC-1.0. The contrast samples could be synthesized by varying the dosage of cyanamide and Co(NO$_3$)$_2$·6H$_2$O. The corresponding parameters of the preparation process of the contrastive samples are shown in Table S1.

The synthetic process of CoO$_x$−NC−DCDA was similar to that of CoO$_x$−NC-1.0. Briefly, ~4 g “starch strips” were impregnated in the mixed solution of dicyandiamide (1.0 g) and Co(NO$_3$)$_2$·6H$_2$O (0.1 g) for 1 h. After drying under 40 °C, the treated "starch strips" were transferred in a tube furnace and calcined to 1000 °C under N$_2$ flow (see Scheme S1). CoO$_x$−NC−urea was fabricated via the same procedure except for urea as a nitrogen source.

CoO$_x$−NC-1.0-acid was obtained by acid treatment of CoO$_x$−NC-1.0. In detail, 100 mg of CoO$_x$−NC-1.0 was dispersed in 0.5 M H$_2$SO$_4$ and stirred under room temperature. Then, the sample was washed with deionized water until the filtrate was neutral.

CoO$_x$−NC-1.0-H$_2$ was prepared by H$_2$ reduction using CoO$_x$−NC-1.0 as raw materials. CoO$_x$−NC-1.0 (80 mg) was placed in a tube furnace and heated to 450 °C for 2 h under a hydrogen atmosphere.

Fe−NC and W−NC were synthesized by a similar synthetic process of CoO$_x$−NC-1.0. Using Fe−NC as an example, 0.1 g of Fe(NO$_3$)$_3$·9H$_2$O and 1.0 g of cyanamide was dissolved in 20 mL of deionized water. Then, about 4 g "starch strips" was immersed in the abovementioned solution for 1 h. Subsequently, the "starch strips" dried off and calcined to 1000 °C under N$_2$ flow (see Scheme S1). The other samples were prepared through the same process, in which the metal source was varied to WCl$_6$.

4.3. Characterizations. SEM was used to observe the morphology, which was performed on a JSM-IT500HR microscope. HRTEM was operated on a Tecnai G2 F30 S-Twin at an acceleration voltage of 300 KV. The metal phase of samples was tested with a slit width of 5 mm on a D/tex Ultima TV wide-angle X-ray diffractometer equipped with Cu Kα radiation (1.54 Å) and a phase of 10° to 90° sweep data at a sweep rate of 5°/min. The Raman spectra were performed on a Raman spectrometer (Renishaw, Invia). The specific surface area and PSD plot were calculated by the conventional BET and BJH method, respectively. The Thermo ESCALAB 250xi spectrometer was employed to obtain X-ray photoelectron spectra for the bonding states. The Co content was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) (PerkinElmer, Optima 5300DV), and aqua regia was used to dissolve the sample. Measuring from the ICP-OES, the Co content of CoO$_x$−NC-1.0 was as low as 0.67 wt %.

4.4. Electrochemical Measurements. The electrochemical experiments were tested with a typical three-electrode system at room temperature on an electrochemical workstation of CHI760E. The glassy carbon electrode (5 mm in diameter), graphite rod, and saturated calomel electrode served as the working electrode, counter electrode, and reference electrode, respectively. The catalyst (3 mg) was weighed and then mixed with 20 μL of NaF ion and 300 μL of ethanol. A uniform slurry was obtained after ultrasonication for 25 min. Whereafter, the as-obtained ink (30 μL) was coated onto the surface of the glassy carbon electrode, yielding a catalyst loading of 1.4 mg cm$^{-2}$ after drying at room temperature. The LSV was tested under 1.0 M KOH solution with a scan rate of 5 mV s$^{-1}$. The Tafel slope was fitted using the Tafel equation ($\eta = a + b \log(j)$). EIS measured frequencies from 0.01 Hz to 100 kHz.
To determine the ECSA of the samples, a series of cyclic voltammetry (CV) curves were tested at various scan rates (10−50 mV s\(^{-1}\)) in the potential window between 0.1 and 0.2 V versus RHE. The geometric double-layer capacitance (\(C_{dl}\)) was calculated by plotting the difference of current density \(\Delta j = \left( j_{\text{mod}} - j_{\text{ath}} \right)/2\) at 0.149 V versus RHE against the scan rate, and the slope of the linear trend was the twice of \(C_{dl}\).

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00184.

Preparation parameters of different samples; calcination program; elemental analysis data; photographs of feedstock and product; TEM images of CoO\(_x\)-NC-1.0; activity comparison of CoO\(_x\)-NC-1.0 and Pt/C; Raman spectra; SEM images; double-layer capacitance measurements; XRD pattern; SEM, TEM, and other analyses of CoO\(_x\)-NC-900; TEM images, XPS data of CoO\(_x\)-NC-DCDA and CoO\(_x\)-NC-urea; and SEM images of Fe-NC, W-NC (PDF)

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### Notes

The authors declare no competing financial interest.

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