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Three-dimensional hierarchical meso/macroporous Fe/Co-nitrogendoped carbon encapsulated FeCo alloy nanoparticles prepared without any template or surfactant: High-performance bifunctional oxygen electrodes



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ABSTRACT

Exploring highly efficient bi-functional electro-catalysts toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are critical for developing energy conversion and storage systems. Herein, for the first time, without any template or surfactant, a family of Fe/Co–N-doped three-dimensional (3D) hierarchical meso/macroporous carbon encapsulated FeCo nanoparticles (denoted as FexCo(1–x)-N/PC) have been successfully synthesized through pyrolyzing the low-cost biomass-based precursors in the NH₃ atmosphere. After optimizing the molar ratio of Fe/Co, benefiting from the collaborative advantages of the Fe/Co–N–C species, cobalt-based electro-active phases, and unique 3D electrode configuration, the resultant Fe0.5Co0.5-N/PC amazingly shows considerable ORR activity comparable with commercial Pt/C catalyst via a 4e⁻ pathway in alkaline electrolyte. When used for OER catalysis in an alkaline medium, Fe0.5Co0.5-N/PC achieves an extremely negative potential of 1.625 V vs. RHE at a current density of 10 mA cm⁻² and a low Tafel slope of 68.3 mV dec⁻¹. Furthermore, the overpotential (ΔE) between ORR and OER is just 0.813 V, which is nearly the minimum value for the non-precious metal catalysts. We believe that our present synthetic strategy can be further extended to develop other 3D hierarchical meso/macroporous carbonaceous catalysts for various applications, such as sensors, batteries, and supercapacitors.

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1. Introduction

The theoretically high energy density of regenerative fuel cells (especially the dual functionality regenerative fuel cell typically comprises a fuel cell function $(2H_2 + O_2 \rightarrow 2H_2O)$ where electricity is produced and an electrolyzer function $(2H_2O \rightarrow 2H_2 + O_2)$ where H₂ is stored) and metal-air batteries makes them very desirable for future energy conversion and storage applications. Significant efforts have been devoted to the development of practical regenerative fuel cell and metal-air systems for various applications [1]. Even so, unlike conventional secondary batteries, many scientific and technical challenges still remain to realize the potential for practical applications, one of which being the development of

* Corresponding author. E-mail address: guolp078@nenu.edu.cn (L. Guo). efficient bi-functional electro-catalysts for both oxygen reduction reaction (ORR) during the discharge process and oxygen evolution reaction (OER) during the recharge process [2]. To facilitate low over-potentials and fast kinetics in ORR/OER catalytic processes, electro-catalysts based on the precious metals have been widely explored and reported [3-8]. However, finding stable and efficient electro-catalysts which drive both reactions is also difficult, because good catalysts for ORR often tend to be poor for OER and vice versa [9,10]. For example, those platinum based catalysts are very excellent catalysts for ORR but which are poor for OER. Similarly, catalysts based on ruthenium or iridium are the state-of-art OER catalysts but are poor for ORR catalysis [11,12]. Recently, most bi-functional electro-catalysts are prepared by combining Pt (good catalysts for ORR) and Ru/Ir (good catalysts for OER) to form a composite [13,14]. Unfortunately, those materials used to synthesize these catalysts are extremely scarce and in turn demand a high price, which limit the technology from becoming a ubiquitous form of renewable energy. Therefore, commercial viability of electrochemical devices about metal-air batteries can only be achieved through the use of low-cost and abundant catalysts for ORR/OER. Developing efficient and cost-effective electro-catalysts using earth-abundant elements for ORR/OER is still highly desirable.

Some efforts have been directed towards the incorporation of excellent noble metal-free ORR and OER catalysts into a composite. in which the constituent ORR and OER catalysts retain their individual properties. This strategy has been used in the past with platinum group metals for obtaining bi-functional materials for acid media [9], and more recently by combining OER active lowcost transition metal oxides with carbon supports that provide ORR functionalities for alkaline media [15]. Fe based nanostructures have been widely explored for various kinds of electro-catalysts. To date, in most reports on iron-based catalysts they always deliver considerable electro-catalytic activities being similar to Pt-based catalysts in ORR, such as: Fe/Fe₃C-C based catalysts; FeN_xC/C based catalysts, Fe-N-C composite, etc. [16-20] However, Fe based catalysts cannot give consideration to the highly efficient OER catalytic activity [21,22]. Cobalt, on the other hand, is abundant and large amounts of Co based composites have been reported to have good OER activities, which are considerable activities even compared with RuO₂ and IrO₂ catalysts in alkaline media [23–27]. Summarizing those facts mentioned above, to design and synthesize bi-functional catalysts for both ORR and OER with merits of high activity, low-cost, and excellent stability: the incorporation of good ORR catalyst (based on Fe) and OER catalyst (based on Co) into a composite is one of the effective ways, in which the constituent Fe and Co based catalytic active sites retain their individual properties. Up to now, a material of FeCoN/rGO has been tentatively prepared as ORR/OER bi-functional catalyst. Even so, may be limited by the lack of porous structures and nonuniformity of active site dispersion, its ORR/OER activities is not so excellent, in order to further enhance the total catalytic efficiency, Ru elements have been inevitably used [28].

From a rational design point of view, an ideal electro-catalyst should have highly active catalytic centers to facilitate a complete reversibility of the electrochemical process; meanwhile, those active catalytic sites should also be easily accessible to the electrons and reactants necessary to complete the electrochemical reactions [29]. Generally, the exposed edges are affected by the morphologies and structures of catalysts. Hence, designing ORR/OER electrocatalysts with more Fe and Co based catalytic active edge sites and better electron/proton transport efficiency is one effective strategy to enhance their catalytic activity. Since they were synthesized for the first time, porous carbonaceous materials (such as ordered mesoporous carbon, onion-like mesoporous carbon vesicles, macroporous carbon, hierarchical porous carbon foams, etc) have been paid intensive attention on their electrochemical applications [30–37]. However, for large-scale development and industrialization of these catalysts, their primary obstacles are the complex preparation processes. In fact, in recent years, for preparing porous carbonaceous catalysts, carbon materials derived from renewable biomass resources have received considerable attention because biomass is extensively available, accessible and recyclable [38–41]. Porous carbon composite membranes have been prepared using low-cost common filter papers as precursors [42]. At the same time, A4 printing papers have also been carbonized into graphene-tethered carbon fiber composite papers [43]. As shown in Fig. S1, as the different processing methods compared with those for filter papers and ordinary papers, the light transmission tests prove that paper towels show the best transmittancy, displaying a higher porosity. We conjecture this structure is very suitable for preparing porous carbons dispersed by abundant Fe/Co catalytic active sites and contain enough transport channels for electrons/reactants.

With these in mind, in this work, for the first time, we attempt to prepare novel material of three-dimensional (3D) hierarchical meso/macroporous Fe/Co-nitrogen-doped carbon encapsulated Fe/ Co nanoparticles (NPs) from low-cost common paper towels (as the carbon precursors) without any template or surfactant. The constant dosage of paper towels (2 g) were first impregnated with 30 mL of 66.7 mM $M(AC)_2$ aqueous solution (M = Fe and/or Co), and then dried at room temperature. Finally, the catalysts were prepared by temperature-programming in a tube furnace under NH₃ at a heating rate of 5 °C min⁻¹ and kept at 800 °C for 2 h. Those resultant catalysts are denoted as FexCo(1-x)-N/PC, where x values represent the molar ratios of $Fe(AC)_2$ used in the total $M(AC)_2$ and have been controlled as 1, 0.75, 0.5, 0.25 and 0 respectively. For example, the Fe0.75Co0.25-N/PC represents the usages of $Fe(AC)_2 \cdot 4H_2O$ and $Co(AC)_2 \cdot 4H_2O$ are 369 mg (50 mM) and 124.5 mg (16.7 mM) in 30 mL impregnated solution. Those 3D hierarchical meso/macropores of resultant samples will provide plenty of low-resistance channels for both electron and mass transfer. Especially, after optimizing the x values of FexCo(1-x)-N/PC in the impregnated solutions, compared with other samples, the resultant Fe0.5Co0.5-N/PC catalyst could get a better balance in both OER and ORR catalyses, accompanying the minimum overpotential between ORR and OER.

2. Experimental

2.1. Reagents and apparatus

The paper towels were afforded by 'mind act upon mind' and obtained from the local supermarket in Changchun. Fe(AC)₂·4H₂O, Co(AC)₂·4H₂O, KOH, and Nafion solution (5 wt%) were purchased from Sigma-Aldrich. The commercial 20 wt% Pt/C catalyst was obtained from Johnson Matthey Company (Shanghai, China). All these chemicals were used as delivered without further treatment. Cyclic voltammetry (CV) and rotating disk electrode (RDE, d = 5 mm) voltammetry experiments were performed with a PARSTAT 2273. Meanwhile, all electrochemical measurements were performed in a standard three-compartment cell. The modified RDE, Pt wire, and Ag/AgCl electrodes acted as working, counter, and reference electrodes, respectively.

2.2. Synthesis of catalysts and modified electrodes

The intact preparation procedures of the FexCo(1–x)-N/PC catalysts have been displayed in Supplementary Scheme S1. The detailed descriptions are placed in the supporting information (Synthesis of catalysts in the supporting information). Prior to modification, the RDE was polished carefully with alumina powders and then cleaned with HNO₃ (1: 1), ethanol, and deionized water. The catalyst ink was prepared by mixing 3 mg catalyst powders into 1 mL Nafion solution (0.5 wt%). Then 30 μ L of the catalyst ink was dropped onto the cleanly washed RDE and dried before electrochemical experiments.

2.3. Physical characterization and electrochemical measurements of the resultant catalysts

The detailed descriptions for the physical characterizations and ORR/OER electro-chemical measurements of those resultant catalysts were also located in the supporting information. It's important to note that in the electrochemical testing processes for ORR and OER, the polarization curves were plotted as potential (*E vs.* RHE) versus log $|j(mA cm^{-2})|$ to get the Tafel plots for assessing the ORR

and OER kinetics of those resultant catalysts. By fitting the linear portion of the Tafel plots to the Tafel equation ($\eta = b \log (j) + a$), the Tafel slope (b values) can be obtained. All potentials appeared in this paper are referred to reversible hydrogen electrode (the potentials recorded and referred to Ag/AgCl in each experiment were calculated using the formula $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.197 \text{ V}$, where E_{RHE} is a potential vs. reversible hydrogen electrode (RHE), $E_{\text{Ag/AgCl}}$ is a potential vs. Ag/AgCl electrode, and pH is the pH value of electrolyte. All data were reported with the typical iR compensation. All current densities are the ratios of those recorded currents to the geometric area of electrode.

3. Results and discussion

The detailed synthesis procedures and the macrostructures of FexCo(1-x)-N/PC electro-catalysts and corresponding precursors are presented in Scheme S1. The morphologies of resultant PC, N/ PC, and FexCo(1-x)-N/PC samples are first observed by SEM images. As shown in Fig. S2a, for PC calcined under N₂ atmosphere, lots of tubers and ravines can be obviously observed on the surfaces, increasing its specific surface area. Furthermore, for the N/PC calcined under NH₃ atmosphere, large amounts of extra meso/ macropores can be clearly observed on the surfaces (Fig. S2b). As shown in Fig. 1a-c and Fig. S2c-d), it is noteworthy that large amounts of metal NPs have encapsulated within or located on surfaces of graphitized carbons for FexCo(1-x)-N/PC samples, suggesting the efficient assembly between metal NPs and graphitized PC. Specially, the surfaces of Co-N/PC seems to be more rough than other samples, lots of embossments can be clearly observed on their surfaces, which could be the predecessors of carbon nanotubes (CNTs). As shown in Fig. S3, the low-magnification SEM of Fe0.5Co0.5-N/PC provides a visual evidence for the homodisperse of abundant metal NPs. Furthermore, Fig. 1a'-c' and Fig. S2e-f illustrate the corresponding histograms of the particle size distribution for metal NPs by counting 200 particles. One can see that the average diameters are about 37.1, 27.0, 26.7, 30.5, and 36.4 nm for the resultant Fe-N/PC, Fe0.75Co0.75-N/PC, Fe0.5Co0.5-N/PC,

Fe0.25Co0.75-N/PC, and Co-N/PC samples. It is clear that, as the synergistic effect of Fe(AC)₂ and Co(AC)₂ in the nucleation process of calcinations, Fe0.75Co0.75-N/PC, Fe0.5Co0.5-N/PC and Fe0.25Co0.75-N/PC show smaller particle sizes than Fe-N/PC and Co-N/PC. Specially, Fe0.5Co0.5-N/PC displays the minimum particle sizes. In fact, such a geometric confinement of metal NPs within graphitized carbon layers has been reported to enhance their interface contact and to suppress the dissolution and agglomeration of NPs, thereby promoting the electrochemical activity and stability of the resultant hybrids [44].

The morphologies and structures of as-prepared samples were also observed by TEM image (Fig. 2). Fig. 2a shows that N/PC is composed of hollow graphitic nanoshells with a pore size range of 2–200 nm; meanwhile, as shown in Fig. S4, abundant onion rings exhibit the open structures of N/PC, demonstrating hierarchical meso/macroporous structures have been successfully synthesized in the pyrolysis process of paper towels in NH₃ atmosphere. Fig. 2b-d reveal that those 3D hierarchical meso/macropores have been successfully reserved from the precursor even if the using of metal acetates in the impregnating solution; meanwhile, most metal NPs are encapsulated within carbon nanoshells. For Fe-N/PC (Fig. 2b) and Fe0.5Co0.5-N/PC (Fig. 2c), the main difference is that less aggregation of metal NPs is observed on the surface of Fe0.5Co0.5-N/PC. However, Co-N/PC has started to display the characteristic bamboo-like morphology of CNTs (Fig. 2d), demonstrating large amounts of embossments appeared in the SEM image of Co–N/PC is really incomplete CNTs. Nevertheless, the growth process is just remained in the first step of CNT growth. As shown in Fig. 2e, continuing to enlarge the TEM image of Fe0.5Co0.5-N/PC into a smaller scope. One can see most metal NPs are retained and encapsulated in carbon nanoshells for Fe0.5Co0.5-N/PC and abundant mesopores can also be observed. At last, a d-spacing of 2.02 Å corresponding to the (110) plane of the FeCo nanocrystal have also been found in Fig. 2f.

XRD images are carried out to display the compositions of PC, N/ PC, and FexCo(1–x)-N/PC samples. As shown in Fig. 3a, two broad peaks at 2θ values of about 26° and 43°, corresponding to the (002)



Fig. 1. SEM images of (a) Fe–N/PC, (b) Fe0.5Co0.5-N/PC, and (c) Co–N/PC. The corresponding histograms of particle size distribution for (a') Fe–N/PC, (b') Fe0.5Co0.5-N/PC, and (c') Co–N/PC.



Fig. 2. TEM images of (a) N/PC, (b) Fe–N/PC, (c) Fe0.5Co0.5-N/PC, and (d) Co–N/PC. (e) Megascopic TEM image of Fe0.5Co0.5-N/PC. (f) HRTEM image of an individual CoFe alloy NP for Fe0.5Co0.5-N/PC.

and (100) planes of carbon, respectively. However, for the FexCo(1-x)-N/PC catalysts, those peaks located at 43° for (100) planes all degrade. At the same time, five new peaks being assigned to the Fe₂N phase (JCPDS No. 89-3939) appeared in XRD curve of Fe-N/PC. XRD curve of Fe0.75Co0.25-N/PC shows three characteristic peaks located at 44.76°, 82.45°, and 65.12°, corresponding to the Co₃Fe₇ alloy (JCPDS No. 48-1618); furthermore, other diffraction peaks are assigned to the corresponding reflections of Fe₂C phases (JCPDS No. 37-0999), confirming the co-existence of Co₃Fe₇ alloy and Fe₂C phases in Fe0.75Co0.25-N/PC. Compared with Fe0.75Co0.25-N/PC, tiny diffraction peaks for Fe₂C phases could still be observed in XRD curve of Fe0.5Co0.5-N/PC accompanying a transformation of Co₃Fe₇ alloy to CoFe alloy (JCPDS No. 49-1568). The cubic CoC_x phase (JCPDS No. 44-0962) can be observed for Fe0.5Co0.5-N/PC. For Fe0.25Co0.75-N/PC, CoFe alloy continually change to the Co₇Fe₃ alloy ((JCPDS No. 48-1818); meanwhile, other strong diffraction peaks are assigned to the face centered cubic (fcc) metallic Co (JCPDS No. 15-806). Finally, only strong and sharp diffraction peaks associated with fcc metallic Co (JCPDS No. 15-806) are observed in XRD curve of Co-N/PC. Hereto, we have clearly displayed the chemical compositions of those black NPs shown in both SEM and TEM images of those FexCo(1-x)-N/PC catalysts.

Raman spectroscopy is a powerful and widely used tool for characterizing carbonaceous materials, the typical Raman spectra of PC and N/PC are first tested and shown in Fig. S5. They all display two prominent peaks, which can be ascribed to the welldocumented D-band (at approximately 1359 cm⁻¹, associated with structure defects and disorders) and G-band (observed at ca. 1590 cm⁻¹, is commonly found with all graphitic structures usually assigned to the E_{2g} phonon of sp² C atoms). The intensity ratio of Dband to G-band, namely I_D/I_G ratio, provides the gauge for the amount of structural defects and reflects the extent of graphitic crystalline in graphitic carbons. It thus evident that more defect sites have been introduced into the carbon skeletons of N/PC compared with PC, a larger I_D/I_G ratio of N/PC (1.20) compared with PC (1.09) is powerful evidence (Fig. S5). As can be seen in Fig. 3b, the further increased intensities of D-bands for all FexCo(1-x)-N/PCsamples compared with those for PC and N/PC prove that the geometric confinement of metal NPs within graphitized carbon layers has enhanced their interface contact and then afford more defect sites. The maximum I_D/I_G ratio of Fe-N/PC (1.66) indicates that abundant content of disordered carbon increases after Fe and N doping. However, once a part of $Fe(AC)_2$ are replaced by $Co(AC)_2$ in the impregnating solutions, resultant Fe0.75Co0.25-N/PC, Fe0.5Co0.5-N/PC, and Fe0.25Co0.75-N/PC samples show smaller I_D / $I_{\rm G}$ ratios compared with Fe–N/PC, demonstrating the decrease of defect sites. Specially, for Co–N/PC, the minimum I_D/I_G ratio has been calculated compared with other FexCo(1-x)-N/PC catalysts, but which is still larger than those for PC and N/PC. Combining the SEM and TEM images, we preliminary analyse that large amounts of meso/macroporous are filled by some fragmentary CNTs grown on the surfaces, which will hugely decrease the accessible meso/ macroporous structures of Co-N/PC and then decrease the defect sites

Fig. 4a–b shows the N₂ adsorption-desorption isotherms and pore size distributions of FexCo(1–x)-N/PC. All adsorptiondesorption curves belong to the type IV isotherms (based on IUPAC classification) with a hysteresis loop, indicating the existence of abundant mesopores. Meanwhile, the pore size distributions calculated by using the BJH method from desorption branches (Fig. 4b) show that all resultant samples have wide pore size distributions from 2 to 200 nm. At the same time, BET surface area of N/PC is 634.3 m² g⁻¹ with the largest total pore volume of 0.29 m³ g⁻¹ (Fig. S6). However, BET surface areas and total pore volumes have decreased down to 242.6 m² g⁻¹ and 0.23 m³ g⁻¹ (for Fe–N/PC), 254.0 m² g⁻¹ and 0.23 m³ g⁻¹ (for Fe0.75Co0.25-N/PC), 236.8 m² g⁻¹ and 0.22 m³ g⁻¹ (for Fe0.5Co0.5-N/PC), 228.9 m² g⁻¹ and 0.2 m³ g⁻¹ (for Co–N/PC) (Fig. 4c–d). One can see that all FexCo(1–x)-N/PC samples except for Co–N/PC show similar BET area and pore volumes. The slight decrease in BET area and total pore volume for Co–N/PC is mainly due to the coverage of meso/



Fig. 3. (a) XRD patterns of resultant PC, N/PC, and FexCo(1-x)-N/PC samples. (b) Raman spectra of different FexCo(1-x)-N/PC samples.

macropores by fragmentary CNTs.

X-ray photoelectron spectroscopy (XPS) was further used to analyze the composition of N/PC, Fe-N/PC, Fe0.5Co0.5-N/PC, and Co–N/PC. Survey spectra reveal the presence of C, N, and O in four samples, demonstrating that N atoms can be successfully doped into carbon skeletons after being calcined in NH₃. After the precise quantitative analysis by XPS, the total N contents are 1.2, 2.3, 2.8, and 2.5 at.% for resultant N/PC, Fe-N/PC, Fe0.5Co0.5-N/PC, and Co-N/PC samples. As shown in Fig. S7a-d, all C 1s XPS spectra are decomposed into five components, two main peaks located at ~284.5 and ~285.4 eV are assigned to sp²-hybridized graphite-like carbon (C-C sp²) and sp³-hybridized diamond-like carbon (C-C sp^3 overlapping with sp^2 carbon bound to nitrogen (N–C sp^2)). By fitting the high resolution N 1s XPS spectra of N/PC (Fig. 5a), we can assign four peaks at 398.3 \pm 0.2, 400.4 \pm 0.2, 401.7 \pm 0.2, and 399.4 ± 0.2 eV to pyridinic-N, pyrrolic-N, graphitic-N, and oxidized N species, respectively. Different from the N/PC, as shown in

Fig. 5b-d, except for the four peaks of pyridinic-N, pyrrolic-N, graphitic-N, and oxidized N species, an added peak of Fe-N/Co-N species located at about 399.4 \pm 0.2 eV also appear in the high resolution N 1s XPS spectra of Fe-N/PC, Fe0.5Co0.5-N/PC, and Co-N/PC, but there are large differences in contents of each N species. On the other hand, XPS characterization results have proved that the total metal contents are all close to 1.5 at.% for Fe-N/PC, Fe0.5Co0.5-N/PC and Co-N/PC. However, no characteristic peaks of Fe or Co elements have been observed in the binding energy range of Fe 2p and Co 2p for N/PC (Fig. S8a,b). The high resolution Fe 2p_{3/2} and Fe 2p_{1/2} spectra of Fe-N/PC (Fig. S8c) and Fe0.5Co0.5-N/PC (Fig. 5e) are fitted into three peaks severally, corresponding to the Fe(0), Fe(III)/Fe(II) ions, and satellite peaks, respectively. As shown in Fig. 5e, the Co 2p_{3/2} XPS spectrum of Fe0.5Co0.5-N/PC was fitted into four peaks located around 776.8, 780.5, 783.3, and 788.4 eV assigned to the Co(0), Co-N, Co(II) nitrate, and satellite peak, respectively. However, Co 2p_{3/2} XPS spectrum of Co-N/PC was fitted into five peaks located around 776.8, 779.8, 780.8, 783.5, and 788.3 eV assigned to the Co(0), cobalt oxide, Co-N, Co(II) nitrate, and satellite peak, respectively (Fig. S8d). Finally, the contents of pyridinic-N, metal-N, pyrrolic-N, graphitic-N, oxidized N, and pyridinic-N + metal-N species for the N/PC, Fe-N/PC, Fe0.5Co0.5-N/PC, and Co-N/PC are all calculated and recorded in Fig. 5f. It is clear that the resultant Fe0.5Co0.5-N/PC contains the maximum pyridinic-N, Fe/Co-N, and graphitic-N species.

The evolution of ORR performances for PC. N/PC, and series of FexCo(1-x)-N/PC catalysts are shown in Fig. 6. All the RDE curves recorded at a rotation rate of 1600 rpm in O₂-saturated 0.1 M KOH solution are self-consistent, and display an obvious ORR activity with different catalytic performances (Fig. 6a). The pure PC in 0.1 M KOH is sluggish for ORR, evident by the low onset potential (E_{onset}) and half wave potential $(E_{1/2})$; after doping N atoms into the skeletons of PC, the resultant N/PC will show more positive E_{onset} (0.77 V vs. RHE) and $E_{1/2}$ (0.67 V vs. RHE) accompanying a obvious increase of limited diffusion current densities $(j_{\rm L})$. But these performances are still not on the same level as commercial Pt/C. Specifically, with constantly changing the composition of precursors, both the E_{onset} and $E_{1/2}$ (Fig. 6b) will decrease from Fe–N/PC (0.939 and 0.822 V vs. RHE) to Fe0.75Co0.25-N/PC (0.933 and 0.820 V vs. RHE) to Fe0.5Co0.5-N/PC (0.925 and 0.813 V vs. RHE) to Fe0.25Co0.75-N/PC (0.911 and 0.805 V vs. RHE) and then to Co0.75-N/PC (0.839 and 0.779 V vs. RHE). One can see that, except for the Co–N/PC, ORR catalytic activities (viewing from E_{onset} and $E_{1/2}$) of samples contain Fe atoms are comparable to those for the commercial 20%Pt/C (0.957 and 0.817 V vs. RHE). As shown in Fig. 6c, the high ORR electro-catalytic activities of these Fe based catalysts are also gleaned from their much larger current densities (at 0.6 V vs. RHE).

The ORR catalytic performances of FexCo(1-x)-N/PC were further evaluated for mechanistic and kinetic performances using Tafel plots (Fig. 6d). Tafel slopes in low current density region are 63.5 mV decade⁻¹ on Fe-N/PC, 65.7 mV decade⁻¹ on Fe0.75Co0.25-N/PC, 67.3 mV decade⁻¹ on Fe0.5Co0.5-N/PC, 70.6 mV decade⁻¹ on Fe0.25Co0.75-N/PC, and 57.2 mV decade⁻¹ on Co-N/PC. All these data are close to and even surpass that recorded on a Pt/C surface (67.6 mV decade⁻¹). From a mechanistic point of view, these results imply the ORR mechanisms on FexCo(1-x)-N/PC and Pt-based catalysts are similar in alkaline medium and reveal the transfer of the first electron on these FexCo(1-x)-N/PC catalysts are all the rate determining step under Temkin conditions for the adsorption of intermediates. Overall, the ORR catalytic activities briefly decrease by an order of Fe-N/PC > Fe0.75Co0.25-N/PC > Fe0.5Co0.5-N/ PC > Fe0.25Co0.75-N/PC > Co-N/PC. Thus, we can draw a conclusion that the doping of Co atoms into the catalytic systems cannot



Fig. 4. (a) N₂ adsorption/desorption isotherms for FexCo(1-x)-N/PC samples. (b) The corresponding pore size distributions calculated by using the BJH method from the curves displayed in Fig. 4a. (c) BET surface area distribution histograms of the N/PC and other FexCo(1-x)-N/PC samples. (d) The corresponding pore volume distribution histograms of different samples.



Fig. 5. High resolution XPS spectra of N 1s for N/PC (a), Fe–N/PC (b), Fe0.5Co0.5-N/PC (c), and Co–N/PC (d) samples. (e) High resolution XPS spectra of Fe 2p and Co 2p for resultant Fe0.5Co0.5-N/PC sample. (f) The contents of N-bonding configurations of N/PC, Fe–N/PC, Fe0.5Co0.5-N/PC, and Co–N/PC.

further promote the ORR activity, superabundant Co atoms doped into the Fe–N/PC even result in inferior ORR catalysis. By viewing the N₂ adsorption results shown in Fig. 4c–d, surface area and pore volume are the main drawbacks accounting for the inferior ORR performance.

Finally, the ORR mechanisms occurred on the electrodes were determined by RDE measurements at various rotation speed (Fig. 7a–b and Fig. S9a-d), based on which the Koutecky-Levich (K-L) plots at different potentials were also obtained for each catalyst (Fig. 7c–d and Fig. S9a'-d'). One can see that the K-L plots at



Fig. 6. (a) RDE polarization curves of ORR for pure PC, N/PC, FexCo(1-x)-N/PC, and Pt/C in O₂-saturated 0.1 M KOH with a scan rate of 5 mV s⁻¹ at a rotation speed of 1600 rpm. (b) Coresponding *E*_{onset} and *E*_{1/2} values of different catalysts tested in Fig. 6a. (c) Coresponding current densities recorded at 0.6 V vs. RHE from the LSV curves shown in Fig. 6a. (d) Tafel plots of the FexCo(1-x)-N/PC and Pt/C catalysts derived and calculated from the corresponding RDE data shown in Fig. 6a.



Fig. 7. RDE voltammograms of Fe0.5Co0.5-N/PC (a) and Pt/C (b) catalysts in O₂-saturated 0.1 M KOH at various rotation speeds with a scan rate of 5 mV s⁻¹. Koutecky-Levich (*K*-*L*) plots of the Fe0.5Co0.5-N/PC (c) and Pt/C (d) catalysts at different potentials derived from RDE measurements shown in Fig. 7a,b. (e) RRDE test of ORR on Fe0.5Co0.5-N/PC and 20 wt % Pt/C in an O₂-saturated 0.1 M KOH electrolyte at a rotation rate of 1600 rpm. (f) H₂O₂ yields and electron transfer numbers tested in 0.1 M KOH (calculated from the corresponding *I*_D and *I*_R values displayed in Fig. 7f).

various potentials exhibit good linearity and parallelism for Fe-N/ PC, Fe0.75Co0.25-N/PC, Fe0.5Co0.5-N/PC, Fe0.25Co0.75-N/PC, Co-N/PC, and Pt/C catalysts, indicating the first-order reaction kinetics for ORR with respect to the concentration of dissolved oxygen. Particularly, the K-L plots of various catalysts at 0.6 V vs. RHE are shown in Fig. S10a. The K-L plots at 0.6 V vs. RHE exhibit good linearity and parallelism for Fe-N/PC, Fe0.75Co0.25-N/PC, Fe0.5Co0.5-N/PC, and Pt/C. After assessing the apparent number (n)of electrons transferred during ORR according to the equation expressed as Eq. S(1) and Eq. S(2), the four samples all display the predominantly 4e⁻ transfer pathways at this potential. However, the slopes of K-L plots of Fe0.25Co0.75-N/PC and Co-N/PC are much larger than other samples, demonstrating the smaller nvalues. Fig. S10b displays the calculated average *n* values between 0.2 and 0.6 V vs. RHE got from K-L plots, which are ~4.05, ~4.01, ~3.96, ~3.92, ~3.79, and ~3.72 for Pt/C, Fe-N/PC, Fe0.75Co0.25-N/ PC, Fe0.5Co0.5-N/PC, Fe0.25Co0.75-N/PC, and Co-N/PC catalysts. In conclusion, The RDE technique demonstrates the predominantly 4e⁻ transfer pathways for Fe-N/PC, Fe0.75Co0.25-N/PC, and Fe0.5Co0.5-N/PC; similar to ORR catalyzed by the high-quality commercial Pt/C catalyst. Meanwhile, the selectivity of fourelectron reduction of oxygen of Fe0.5Co0.5-N/PC and commercial Pt/C catalysts were further tested by RRDE technique as shown in Fig. 7e. Both the H₂O₂ yields (%) and electron transfer number were determined by the equations shown in Eq. S(3) and Eq. S(4). Surprisingly, the peroxide yields of Fe0.5Co0.5-N/PC and commercial Pt/C catalysts remain below 8.0% and 6.0% at potentials from 0.8 to 0.2 V vs. RHE: meantime, the electron transfer numbers derived from the RRDE test (Fig. 7f) were calculated to be 3.80–3.95 and 3.95-4.02 for Fe0.5Co0.5-N/PC and commercial Pt/C catalysts between 0.2 and 0.6 V vs. RHE respectively, revealing the intrinsic four-electron-transfer process.

Prior to assessing the OER catalytic activities of FexCo(1-x)-N/PC, cyclic voltammograms (CVs) of N/PC and FexCo(1-x)-N/PC are recorded in N₂-saturated 0.1 M KOH solution (Fig. S11). As the largest BET surface area, the N/PC displays the largest background current. Fe-N/PC shows a bland CV curve with the minimum background currents. However, with adding Co atoms into the catalytic systems, all Co-based samples show a pair of redox characteristic peaks for Co(II)/Co(III) between 0.9 and 1.1 V vs. RHE [45]. Specially, the peak intensities will increase with increasing the Co percentage in catalysts. OER catalytic activities of Pt/C and N/PC were firstly investigated in 0.1 M KOH, their polarization curves for OER are recorded at a scan rate of 5 mV s^{-1} (Fig. 8a). It is clear the commercial Pt/C and N/PC catalysts present very poor OER electrocatalytic activities. In contrast, under identical test conditions, the resultant FexCo(1-x)-N/PC catalysts all show acceptable performances for OER. Furthermore, the OER catalytic kinetics of FexCo(1-x)-N/PC were explored by using corresponding Tafel plots. Tafel slopes are calculated to be 126.8 mV decade⁻¹ on Fe–N/ PC, 114.9 mV decade⁻¹ on Fe0.75Co0.25-N/PC, 68.3 mV decade⁻¹ on Fe0.5Co0.5-N/PC, 74.5 mV decade⁻¹ on Fe0.25Co0.75-N/PC, and 111.5 mV decade⁻¹ on Co–N/PC, indicating the most favorable kinetics of Fe0.5Co0.5-N/PC catalyst during OER in alkaline medium.

The potential required for the current density of 10 mA cm⁻² (E_{10}) is an essential parameter relevant to solar fuel cells, which is widely used to evaluate the OER activity of catalysts. The OER E_{onset} and E_{10} values for Fe0.5Co0.5-N/PC are as low as 1.564 and 1.625 V



Fig. 8. (a) IR-corrected RDE polarization curves of OER for N/PC, FexCo(1–x)-N/PC, and Pt/C in 0.1 M KOH with a scan rate of 5 mV s⁻¹ at a rotation speed of 1600 rpm. (b) Tafel plots of OER for FexCo(1–x)-N/PC and Pt/C catalysts derived by the mass-transport correction of the corresponding RDE data in Fig. 8a. (c) Coresponding OER E_{onset} values of different catalysts. (d) Coresponding OER catalytic potentials recorded at 10 mA cm⁻².

vs. RHE, being much more negative than those for the Pt/C (1.698 and 1.926 V vs. RHE), N/PC (1.742 and 1.895 V vs. RHE), Fe–N/PC (1.629 and 1.743 V vs. RHE), Fe0.75Co0.25-N/PC (1.588 and 1.693 V vs. RHE), Fe0.25Co0.75-N/PC (1.574 and 1.637 V vs. RHE), and Co–N/PC (1.589 and 1.662 V vs. RHE) (Fig. 8c–d). All these results display that there is a large change in the intrinsic OER catalytic activity of Fe0.5Co0.5-N/PC.

In order to get more information concerning the OER mechanisms involved on FexCo(1–x)-N/PC catalysts, electrochemical impedance spectroscopy (EIS) measurements have also been carried out. Fig. 9a–e shows the typical Nyquist plots for five catalysts at different potentials from 1.54 to 1.64 V vs. RHE. It can be firstly observed that the charge transfer resistances (R_{ct}) for OER on the

as-prepared FexCo(1–x)-N/PC catalysts are normally decreasing with the increasing of over-potentials according to the expected evolution regarding Butler Volmer kinetics. Furthermore, the slightly depressed semi circles observed on five materials originate from non-ideal capacitive behaviors related to the catalyst structures themselves (*i.e.* abundant hierarchical meso/macroporous structures have induced the large porosities and the obvious capacitance distributions along the materials). On the other hand, we can also compare OER catalytic activities of different catalysts from EIS characterization results. As shown in Fig. 9a, R_{ct} values of Fe–N/PC decrease significantly with increasing the over-potentials from 773.7 Ω at 1.54 V vs. RHE to 418.1 Ω at 1.56 V vs. RHE, to 237.4 Ω at 1.58 V vs. RHE, to 137.2 Ω at 1.60 V vs. RHE, to 78.4 Ω at 1.62 V vs.



Fig. 9. Nyquist plots of the Fe–N/PC (a), Fe0.75Co0.25-N/PC (b), Fe0.5Co0.5-N/PC (c), Fe0.25Co0.75-N/PC (d), and Co–N/PC (e) catalysts modified electrodes recorded at various OER potentials from 1.54 to 1.64 V vs. RHE. (f) Nyquist plots of different catalysts examined at 1.6 V vs. RHE.

RHE, and then to 44.2 Ω at 1.64 V vs. RHE. These results suggest the faster OER process of Fe–N/PC when potentials are above 1.62 V vs. RHE. However, Fe0.75Co0.25-N/PC (Fig. 9b), Fe0.25Co0.75-N/PC (Fig. 9d), and Co–N/PC (Fig. 9e) have displayed faster OER catalytic processes once the potentials are above 1.60 V vs. RHE, which are all 20 mV less than 1.62 V vs. RHE of Fe–N/PC, demonstrating the much more efficient OER catalysis. Furthermore, for Fe0.5Co0.5-N/PC (Fig. 9c), when applied potentials are larger than 1.58 V vs. RHE, the trends of EIS plots and recorded R_{ct} values from 1.58 to 1.64 V vs. RHE (Fig. 9f), Fe0.5Co0.5-N/PC gives the smallest semicircle, which still indicates that there is a smaller charge transfer resistance for Fe0.5Co0.5-N/PC. In a word, the Fe0.5Co0.5-N/PC catalyst is a promising candidate as a cathode OER catalyst.

For evaluating the bi-functional electro-catalytic activity of these given catalysts, the overpotential (ΔE) between ORR and OER is a very important parameter, which means the loss in efficiency for a cathodic catalyst. In general, the figure of merit used to quantify ORR activity is the $E_{1/2}$ value and OER activity is judged by E_{10} value, thus, $\Delta E = E_{10} - E_{1/2}$. In general, the smaller ΔE for the same cathode between ORR and OER, the better the catalyst serves as a reversible oxygen electrode. Measured by this method, as shown in Fig. 10, Δ*E* of Fe–N/PC, Fe0.75Co0.25-N/PC, Fe0.5Co0.5-N/ PC, Fe0.25Co0.75-N/PC, and Co-N/PC catalysts are found to be 0.922, 0.873, 0.812, 0.833, and 0.883 V, respectively. Compared with the ΔE data of Pt/C, Ir/C, Ru/C, and other catalysts reported previously (as shown in Table S1), a ΔE value of 0.812 V for the 0.5Co0.5-N/PC is still the minimum, once again displaying the high efficiency of 0.5Co0.5-N/PC for ORR/OER catalyses. Combining with the respective ORR and OER catalytic activities of these resultant samples, we can see that the ORR catalytic activities briefly decrease by an order of Fe-N/PC > Fe0.75Co0.25-N/ PC > Fe0.5Co0.5-N/PC > Fe0.25Co0.75-N/PC > Co-N/PC. However, the OER catalytic activities will firstly increase: Fe-N/ PC < Fe0.75Co0.25-N/PC < Fe0.5Co0.5-N/PC and then decrease: Fe0.5Co0.5-N/PC > Fe0.25Co0.75-N/PC > Co-N/PC. It is clear that 0.5Co0.5-N/PC shows the best ORR/OER total catalytic activity. As shown in Fig. 5f, compared with Fe-N/PC, the 0.5Co0.5-N/PC has



Fig. 10. (a) Oxygen electrode activities of the Fe–N/PC, Fe0.75Co0.25-N/PC, Fe0.5SCo0.5-N/PC, Fe0.25Co0.75-N/PC, and Co–N/PC catalysts in 0.1 M KOH with a sweep rate of 5 mV s⁻¹ at 1600 rpm, **(b)** the oxygen electrode activities (ΔE) of the Fe–N/PC, Fe0.75Co0.25-N/PC, Fe0.5Co0.5-N/PC, Fe0.25Co0.75-N/PC, and Co–N/PC catalysts.

enough M-N-C species for maintaining considerable ORR catalytic activity. On the contrary, the Co-N/PC possesses more inactive oxidized-N species with a relatively low specific surface area, directly leading to a huge decrease in ORR catalytic activity of Co–N/PC. For OER catalysis, as the OER catalytic efficiency of Fe–N/ PC is far better than those for the N/PC and Pt/C, naturally demonstrating the function of M-N-C in enhancing OER catalytic activity. As introducing Co elements into the Fe–N/PC. OER catalytic efficiencies of 0.75Co0.25-N/PC and 0.5Co0.5-N/PC show great improvement, that is because when the presence of numerous Co phases, Co(II) is formed with extra OH⁻ species in alkaline solution, resulting in the formation of Co(III). The Co(III) reacts with OHspecies producing Co(IV)-O₂ and H₂O subsequently. Finally the OER occurs, in which the absorbed O₂ to Co(IV) species is desorbed from Co(IV) [46]. It is worth to note that immoderately using Co in the catalysts has led to an obvious decline in OER catalytic activity. Because the coverage of meso/macroporous structures by those fragmentary CNTs (Fig. 2d) leads to a decrease in BET area and total pore volume of Co-N/PC, simultaneously decreasing the exposed active sites such as M-N, pyridinic-N, etc. As the Fe0.5Co0.5-N/PC catalyst get a balance in both structural and elemental compositions, it affords the best total cathodic activities for ORR/OER catalysis.

In addition to the catalytic activities, the durability of electrocatalytic activity for ORR/OER catalysis is another major concern in constructing bi-functional cathodic catalysts for metal-air batteries. Satisfactorily, the Fe0.5Co0.5-N/PC catalyst is highly sustainable in the test as shown in Fig. 11. One can see that the $E_{1/2}$ value of the Fe0.5Co0.5-N/PC catalyst just negatively shifts 5 mV after 3000 CV scanning cycles. At the same time, the E_{10} value only shows an 8 mV of negative shift. From the above comparative analyses, we then draw the conclusion that the ORR/OER catalytic activity of our Fe0.5Co0.5-N/PC catalyst is quite stable. Meanwhile, the characteristics of the hierarchical meso/macroporous structures can still be clearly observed by TEM visualization even after stability test (Fig. S12).

Above all, as a noble metal-free ORR/OER catalyst, the unique elemental and structural characteristics of 3D hierarchical porous Fe0.5C00.5-N/PC are favorable for boosting its best ORR/OER activity in alkaline solution. (1) The numerous 3D hierarchical meso/macropores (~2–200 nm) and defects on Fe0.5C00.5-N/PC make proton efficiently transferred. For instance, for ORR catalysis, unique large pores (~10–200 nm) on the surface can facilitate the O_2 diffusion and the migration of superoxide and hydroxyl; meanwhile, those small mesopores located on the surfaces (~4 nm) are favorable for the adsorption of O_2 molecules, which are rate-determining for the whole reaction. Furthermore, in an aspectant OER catalytic process, the 3D hierarchical meso/macropores can



Fig. 11. IR-corrected polarization curves of Fe0.5Co0.5-N/PC for both ORR and OER before and after 3000 CV cycles in 0.1 M KOH solution.

also facilitate the hydroxyl diffusion and enable the facile release of evolved O₂ gas bubbles to further improve the reaction interface. (2) Abundant hollow graphitic nanoshells supported on the walls of hierarchical meso/macropores will prompt the rapid transfer of e⁻ to catalytic active sites. (3) The 3D hierarchical meso/macropores can afford a larger surface area: this feature contributes to introducing more exposed plane edges and catalytic active sites for ORR/ OER catalyses. (4) The abundant electro-active chemical compositions (M-N-C) afford it enough active sites for ORR/OER catalysis. Meanwhile, in the OER catalysis, the doping of Co-based phases into the total system will further enhance the OER catalytic efficiency of Fe0.5Co0.5-N/PC. On the other hand, the encapsulated CoFe alloy NPs into the 3D porous Fe0.5Co0.5-N/PC can activate the surrounding graphitic layers, which also act as active sites towards the ORR/OER. Thus, the superior ORR/OER catalytic performances of Fe0.5Co0.5-N/PC catalysts can be ascribed to the multiple synergistic effects of the M-N-C species, some cobalt-based electroactive phases, and unique 3D electrode configuration.

4. Conclusions

In summary, for the first time, we have successfully prepared the 3D hierarchical meso/macroporous FeCo-N/PCs from inexpensive paper towels, $Fe(AC)_2$, and $Co(AC)_2$ without using any template, surfactant or etching procedures. After being calcined in ammonia atmosphere at 800 °C for 2 h, the resultant samples all show the typical 3D hierarchical meso/macroporous structures, affording high specific surface areas. Continuing to optimize the molar ratio of $Fe(AC)_2/Co(AC)_2$ in the impregnating solution, the resultant Fe0.5Co0.5-N/PCs show excellent electro-catalytic activity for both ORR and OER in alkaline electrolytes, including a electron transfer number of ~4 for ORR, a much more negative E_{10} value for OER, the best total cathodic activity ($\Delta E = 0.813$ V), and excellent durability. The advantages in structure, elemental content, and ORR/OER catalytic activity potentially make Fe0.5Co0.5-N/PCs a promising nonnoble metal based cathode catalyst for metal-air batteries. We believe that our present synthetic strategy can be further extended to develop other 3D hierarchical meso/macroporous materials for applications, such batteries, various as sensors. and supercapacitors.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jallcom.2016.06.060.

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