Transformation of carbon-encapsulated metallic Co into ultrafine Co/CoO nanoparticles exposed on N-doped graphitic carbon for high-performance rechargeable zinc-air battery

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Abstract

In this work, Co-MOFs microrod structures were firstly fabricated using Co^{2+} source and trimesic acid (H_3BTC) as reaction precursors by a simple solvothermal method, followed by pyrolysis treatment at $900\text{ }^\circ\text{C}$ in N_2 atmosphere to obtain metallic Co encapsulated into graphitic carbon structure ($\text{Co}@C$) with an average Co particle size of $7.7 \pm 0.2\text{ nm}$ excluding large-sized Co particles ($>20\text{ nm}$) and a surface area of 184 g cm^{-2} . Interestingly, ultrafine Co/CoO nanoparticles with an average size of $1.8 \pm 0.2\text{ nm}$ anchored on graphitic carbon surface (Co/CoO-C) can be obtained through further acid/alkali rinsing treatment of the as-prepared $\text{Co}@C$ using HNO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$ aqueous solutions respectively, followed by thermal treatment at $900\text{ }^\circ\text{C}$ in N_2 atmosphere. The formation of Co/CoO-C with a surface area of 247 g cm^{-2} can be ascribed to the dissolution and reorganization process of carbon-encapsulated metallic Co under acid/alkali rinsing and post-thermal-treatment conditions. As the electrocatalyst, Co/CoO-C exhibits superior bifunctional electrocatalytic activities of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in alkaline media, notably better than ORR and OER activities of $\text{Co}@C$. The characterization results show that Co-N_x and N doping can be found in both $\text{Co}@C$ and Co/CoO-C due to triethylamine (TEA) as solvent providing N source during Co-MOFs synthesis, which are catalytic active species toward electrocatalytic oxygen reactions. Furthermore, the highly exposed ultrafine Co/CoO on graphitic carbon surface can provide more catalytic active sites for high-performance ORR and OER, while carbon-encapsulated metallic Co in $\text{Co}@C$ is incapable of directly contacting

the electrolyte (only influencing shell-layer carbon function work) with limitedly improved electrocatalytic performance. The fabricated Co/CoO-C with superior bifunctional ORR and OER activities as air cathode material was assembled into a rechargeable zinc-air battery, exhibiting high power density and long-term stability. Our work provides an approach to transform low catalytic active electrocatalyst to high catalytic active one for renewable energy applications.

Keywords: Co-MOFs; Co/CoO-C; Bifunctional oxygen electrocatalyst; Oxygen reduction reaction; Oxygen evolution reaction; Zinc-air battery

1. Introduction

Electrochemical energy conversion and storage devices such as fuel cells and metal-air batteries have been extensively studied in recent decades owing to their excellent conversion efficiency, high theoretical specific energy capacity, and environmentally friendly components [1-3]. For rechargeable metal-air batteries, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are two key reactions, which are highly dependent the ORR and OER activities of electrocatalysts [4-6]. Currently, the most effective ORR and OER catalysts are Pt-based and Ru/Ir-based materials respectively, but their intrinsic shortcomings such as sole oxygen reaction activity, high cost and resource scarcity, hinder their large-scale production applications [5, 7]. Therefore, development of cheap, abundant and high-performance non-precious metal catalysts with ORR and OER activities is still highly needed for future rechargeable metal-air battery applications.

Owing to low cost, abundance, high resistance to corrosion in alkaline solution

and richly variable valence states arousing catalytic activity, transition metal (e.g., Fe, Co, Ni) based materials have demonstrated great applicable potential as oxygen reaction electrocatalysts [8]. Among various synthesis approaches, utilization of metal-organic frameworks (MOFs) as precursor materials to fabricate transition metal based electrocatalysts with high oxygen reaction activities has aroused great research attention because of MOFs precursors with many advantages such as high surface area, controllable pore structure, rich composition and modifiability [9]. For instance, Zhao et al. reported the pyrolytic carbonization of monodisperse nanoscale Fe-MOFs (MIL-88B-NH₂), as electrocatalyst exhibiting superior ORR activity and high power density of 22.7 mW cm⁻² in fuel cell [10]. Recently, several groups synthesized Ni-MOFs using trimesic acid as organic linker by a simple solvothermal method, followed by pyrolytic treatment to achieve Ni@C materials [11-13]. As electrocatalysts, the prepared Ni@C materials displayed bifunctional electrocatalytic activities of ORR and OER, demonstrating great applicable potential as air cathode materials for rechargeable zinc-air batteries [11-13]. Utilization of MOFs precursors by simple pyrolysis approach to fabricate high performance transition metal based electrocatalysts could have following several advantages: (1) intrinsic crystalline structures of transition metal based MOFs mean controllable transition metal active species amount in pyrolytic carbon product with inheritable porous structure [9]; (2) transition metal carbides, nitrides and sulfides can be easily obtained by pyrolysis of N-/S-containing organic linkers constructed MOFs or MOFs synthesized in N-/S-containing solvents, accompanied with the formed N/S doping/co-doping and

M-N_x active species (M=Fe, Co, Ni) for high-efficiency electrocatalysis [14, 15]; (3) through controlling the pyrolysis conditions, carbon-encapsulated transition metal species or highly exposed transition metal active species on graphitic carbon surface can be easily achieved, possibly exhibiting different electrocatalysis activities [16]. Recently, several studies have demonstrated that carbon-encapsulated metallic Fe or Co can decrease the shell-layer carbon work function, favourable for the adsorption of O₂ and H₂O molecules on catalyst surface, thus facilitating the oxygen reaction activities [17, 18]. In their studies, carbon-encapsulated metallic Fe or Co cannot directly contact the electrolyte, significantly improving the catalysts applicable stability. However, this indirect utilization approach of Fe or Co related active species may result in a compromise of oxygen reaction activity of catalyst, which deserves a further study by developing a suitable electrocatalyst.

In this work, we choose Co-MOFs (taking trimesic acid as organic linker) as precursor to firstly fabricate graphitic carbon-encapsulated metallic Co (Co@C) by a pyrolysis approach at 900 °C in N₂ atmosphere. Subsequently, Co@C was further treated by HNO₃ and NH₃·H₂O aqueous solutions at 40 °C for 24 h respectively, followed by thermal treatment at 900 °C in N₂ atmosphere to obtain ultrafine Co/CoO nanoparticles with an average size of 1.8 ± 0.2 nm exposed on graphitic carbon surface (Co/CoO-C). The characterization results confirm the presence of Co-N_x and N doping in both Co@C and Co/CoO-C due to triethylamine (TEA) as solvent providing N source during Co-MOFs precursor synthesis. These Co-N_x, N doping active species combined with highly exposed ultrafine Co/CoO nanoparticles result in

significantly improved ORR and OER activities of Co/CoO-C compared to Co@C, displaying great potential as air cathode material for rechargeable zinc-air battery application.

2. Experimental section

2.1 Materials

All chemicals were commercially available and used without further purification: cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, 99.99%), trimesic acid (H_3BTC , Sigma-Aldrich, 99.99%), triethylamine (TEA, Sinopharm Chemical Reagent Co., Ltd, 99.99%), methanol (CH_3OH , Sinopharm Chemical Reagent Co., Ltd, >99%), ruthenium (IV) oxide powder (RuO_2 , Sigma-Aldrich), Nafion® 117 ~ wt.5% in lower aliphatic alcohols and water (Sigma-Aldrich) and potassium hydroxide (KOH, J. T. Baker). Deionized water (18 M Ω) was supplied by a Millipore System (Millipore Q, USA).

2.2 Preparation of Co-MOFs, Co@C and Co/CoO-C

In a typical procedure, a mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.0 mmol, 0.582 g) and H_3BTC (1.0 mmol, 0.210 g) was first dissolved in 20 mL of solution containing H_2O and TEA ($V_{\text{H}_2\text{O}}:V_{\text{TEA}}=9:1$) under stirring, and then transferred into a 25 mL of Teflon-lined stainless-steel autoclave. The solvothermal reaction was performed at 120 °C for 24 h. Then, the autoclave was naturally cooled to room temperature and the product was collected and washed with water to obtain pink Co-MOFs powder with a yield of 85%. Subsequently, the as-prepared Co-MOFs as precursor was pyrolytically treated at 900 °C in N_2

atmosphere for 2 h with a heating rate of 5 °C min⁻¹ to obtain graphitic carbon-encapsulated metallic Co (Co@C). Subsequently, the obtained Co@C was sequentially rinsed with HNO₃ (1.0 M) and NH₃·H₂O (6.0 M) at 40 °C for 24 h respectively, to remove the large metallic Co and carbon-encapsulated metallic Co nanoparticles, followed by further thermal treatment at 900 °C in N₂ atmosphere for 2 h with a heating rate of 5 °C min⁻¹ to obtain ultrafine Co/CoO nanoparticles anchored on graphitic carbon (Co/CoO-C).

2.3 Characterizations

The crystalline structures of samples were identified by X-ray diffraction analysis (XRD, Philips X'pert PRO) using Ni filtered monochromatic Cu K_α radiation (K_α= 1.5418 Å) at 40 kV and 40 mA. The morphology and structure of samples were characterized by field emission scanning electron microscopy (FESEM, SU8020) and transmission electron microscopy (TEM, Philips TecnaiG2 F20) with an energy dispersive X-ray spectrometer (EDS Oxford, Link ISIS) operated at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis of the samples was performed on ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al K_α monochromatized radiation at 1486.6 eV X-ray source and the C1s peak at 284.8 eV as internal standard. The nitrogen (N₂) adsorption-desorption isotherms were measured at 77 K using an automated adsorption apparatus (Ommishop 100CX). The Brunauer-Emmett- Teller (BET) equation was used to determine the specific surface area, and the Barrett-Joyner-Halenda (BJH)

methods were utilized to calculate the pore size distribution. Thermogravimetric analysis (TGA) was performed on a Pyris 1 instrument under a N₂ atmosphere at a heating rate of 10 °C min⁻¹.

2.4 Electrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (CHI 760D, CH Instruments, Shanghai, China) coupled with a PINE rotating disk electrode (RDE) system (Pine Instruments Co. Ltd. USA). A standard three-electrode electrochemical cell equipped with gas flow system was employed during measurements. Prior to measurements, rotating disk electrode (RDE, 5.0 mm in diameter) was first polished with 5.0, 3.0 and 0.05 μm alumina slurry sequentially and then washed ultrasonically in water and ethanol for 30 s, respectively. The cleaned electrode was dried with a high-purity nitrogen gas. The Co-MOFs derived Co@C and Co/CoO-C catalyst inks were prepared by dispersing catalyst powder (2.0 mg) into a mixture including 40 μL of Nafion solution (0.5 wt.%), 40 μL of H₂O and 420 μL of ethanol, followed by ultrasonic treatment for 5 min. After that, 20 μL of catalyst ink was cast onto glassy carbon (GC) electrode surface, leading to a catalyst loading amount of 407 μg cm⁻². For comparison, commercial Pt/C and RuO₂ catalyst inks were also made as the same procedure as Co@C and Co/CoO-C catalyst inks. The ORR performance of catalysts was investigated by cyclic voltammogram (CV) and linear sweep voltammogram (LSV) measurements in O₂ (or N₂)-saturated 0.1 M KOH solution. CV curves were measured at a scan rate of 50 mV s⁻¹.

LSV curves were measured at a scan rate of 5.0 mV s⁻¹ under different disk rotation rates of 225, 400, 625, 900, 1225, 1600 and 2025 rpm. All the potentials in this work were recorded with respect to the Ag/AgCl reference electrode. The electron transfer number (*n*) per oxygen molecule in the ORR process was calculated by the Koutecky-Levich (K-L) equation [19]:

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_D} = \frac{1}{j_K} + \frac{1}{B\omega^{1/2}} \quad (1)$$

$$B = 0.62nFA(D_0)^{2/3}\nu^{-1/6}C_0 \quad (2)$$

$$j_K = nFKC_0 \quad (3)$$

where *j*, *j_K* and *j_D* correspond to the measured, kinetic and diffusion limiting current, respectively, *B* is the slope of K-L plots, *ω* is the electrode rotating angular velocity (*ω*=2π*N*, *N* is the linear rotation speed), *n* is the electron number transferred, *F* is the Faraday constant (*F*=96485 C mol⁻¹), *A* is the geometric electrode area (*A*=0.196 cm²), *D₀* is the diffusion coefficient of oxygen (*D₀*=1.9×10⁻⁵ cm² s⁻¹), *ν* is the kinetic viscosity of electrolyte (*ν*=0.01 cm² s⁻¹), and *C₀* is the saturated oxygen concentration in 0.1 M KOH solution (*C₀*=1.2×10⁻³ mol L⁻¹) [14].

The OER activities of all catalysts were investigated by the LSV method at a scan rate of 5.0 mV s⁻¹ in 0.1 M KOH solution. The durability test for OER was performed by cycling the electrode potential between 1.0 and 1.65 V at 200 mV s⁻¹ for 1000 cycles. All the potentials reported in this study were all quoted against the Reversible Hydrogen Electrode (RHE) using eq. (4) [20]:

$$E(RHE) = E(Ag / AgCl) + 0.059 \times pH + 0.197 \quad (4)$$

2.5 Zinc-air battery test

To prepare an air cathode, a mixture of activated carbon and polyvinylidene fluoride (PVDF) emulsion in 1-methyl-2-pyrrolidone with a ratio of 5:6:1 was coated onto one side of carbon fiber paper as a hydrophobic layer. Then, 5.0 mg of the electrocatalysts and 40 μL of 0.5 wt.% Nafion solution were dispersed in 0.96 mL of water. After sonication for 1 h, the catalyst ink was drop-cast onto the other side of the treated carbon fiber paper with a loading amount of 1.0 mg cm^{-2} for all samples. A polished Zn foil and 6.0 M KOH with 0.2 M of zinc acetate solution were used as the anode and electrolyte, respectively. The current-voltage (i-v) curve was subsequently measured with a scan rate of 50 mV s^{-1} .

3. Result and discussion

In this work, Co-MOFs was first fabricated using Co^{2+} source and H_3BTC as reaction precursors in $\text{H}_2\text{O}/\text{TEA}$ ($V_{\text{H}_2\text{O}}:V_{\text{TEA}}=9:1$) solution through a solvothermal method. The obtained Co-MOFs product shows pink color (inset in Fig. 1a) and microrod structures, as shown in Fig. 1a. Fig. 1b shows the XRD patterns of as-prepared Co-MOFs, matched well with the simulated XRD pattern from the crystal structure reported by Fu *et al.* (CCDC #681478) [21]. As shown in Fig. 1c, the H_3BTC organic linkers are bridged by Co-centered secondary building units (SBUs) including Co^{2+} atom binds to four oxygen atoms from four water molecules and two oxygen atoms from two H_2BTC^- ligands to form a regular CoO_6 Octahedron. In such an open framework structure, the selective inclusion of incoming molecular guests is

dependent not only on their size and shape but also their electronic affinity for the metal center. Fig. 1d shows the formed small channels in the packed structure of Co-MOFs along *a*-axis. These small channels in Co-MOFs contribute its porous property, favourable for the formation of porous structure carbon product with high surface area after pyrolysis of Co-MOFs for electrocatalysis applications.

Fig. 1

The as-prepared Co-MOFs were used as precursor to fabricate Co-based carbon product by a pyrolysis method. Fig. 2a shows the TGA curve of Co-MOFs from room temperature to 700 °C in N₂ atmosphere. As shown, the evolution of Co-MOFs in N₂ atmosphere under the given conditions includes three weight loss stages: in the first stage between 120 and 200 °C, 25% of weight loss can be obtained mainly due to the release of water and partial TEA molecules in Co-MOFs [22]; The second stage from 200 to 350 °C displays a slow weight loss process, attributing to the decomposition of H₃BTC in Co-MOFs [23]. The solvent-free Co-MOFs structure is stable up to almost 350 °C and collapses at higher temperatures; The main weight loss of *ca.* 45% in the third stage between 350 and 480 °C can be observed, corresponding to the carbonization process of Co-MOFs to form Co/C composite [24]. When the pyrolysis temperature is beyond 480 °C, the product weight essentially maintains a stable status. Our experimental results demonstrate that graphitic carbon-encapsulated metallic Co (Co@C) can be obtained at 900 °C in N₂ atmosphere. Fig. 2b shows the SEM image of the pyrolysis product derived from Co-MOFs at 900 °C in N₂ atmosphere. After the pyrolysis treatment, microrod structure can be partially maintained with porous

structure of the pyrolysis product. After acid/alkali rinsing, followed by thermal treatment at 900 °C in N₂ atmosphere, the product displays layer-like structures with coarse surface morphology (Fig. 2c), obviously different with the morphology of pyrolysis product derived from Co-MOFs before acid/alkali rinsing treatment. Fig. 2d show the XRD patterns of the carbon products of Co-MOFs pyrolysis and after acid/alkali rinsing, followed by thermal treatment at 900 °C in N₂ atmosphere. As shown, all carbon products exhibit the diffraction peak at *ca.* 26°, corresponding to the (002) plane of graphitic carbon [25]. For the pyrolysis product (Co@C) from Co-MOFs, the diffraction peaks at 44.2°, 51.5° and 71.5° can be observed, ascribed to the (111), (200), and (220) crystalline planes of face centered Co⁰ (JCPDS no. 15-0806) [26]. Interestingly, no cobalt oxide related diffraction peaks were detected, suggesting the primary existent form of metallic Co in Co-MOFs derived carbon product (Co@C). However, after acid/alkali rinsing and thermal treatment, several new diffraction peaks at 36.9°, 43.2°, and 62.1° can be detected besides of metallic Co diffraction peaks, indexed to the (111), (200) and (220) crystalline planes of CoO (JCPDS no. 43-1004) [27]. The above results indicate that after acid/alkali rinsing and thermal treatment, the existent Co species in carbon product is metallic Co and CoO (Co/CoO-C) that are all active components for electrocatalysis [28]. Additionally, the carbon product (Co/CoO-C) exhibits much stronger diffraction peak of graphitic carbon compared to Co-MOFs derived Co@C sample, indicating its higher degree of graphitization favourable for improving the electrical conductivity of electrocatalyst [16].

Fig. 2

The detailed structure and morphology of Co-MOFs derived carbon products were further investigated by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). As shown in Fig. 3a, Co-related nanoparticles with primary particle sizes of <12 nm (partial particle sizes of >20 nm) can be observed to be uniformly distributed over the entire carbon for Co-MOFs derived carbon product (Co@C). Except for larger nanoparticles with sizes of >20 nm, smaller nanoparticles show an average particle size of *ca.* 7.7 ± 0.2 nm in Co@C (Fig. 3b). The HRTEM image shows that the Co-related particles are encapsulated into the graphitic carbon structure (Fig. 3c and Fig. S1). Moreover, the carbon-encapsulated Co-related particles exhibit the lattice spacing of 0.20 nm, corresponding to the (111) plane of metallic Co (Fig. 3c and Fig. S1), indicating the formation of graphitic carbon-encapsulated metallic Co (Co@C) derived from the pyrolysis of Co-MOFs precursor at 900 °C in N₂ atmosphere. The formation of metallic Co can be due to the formed graphitic carbon as reductant to in situ reduce Co²⁺ into metallic Co during Co-MOFs pyrolysis [29]. This carbon-encapsulated metallic Co structure can be further confirmed by the formation of hollow graphitic carbon structure after acid/alkali rinsing and thermal treatment of Co@C, as shown in Fig. 3d. Obviously, hollow graphitic carbon structure can be observed owing to the complete removal of carbon-encapsulated metallic Co particles after acid/alkali rinsing and thermal treatment of Co@C, favourable for improving mass transport for electrocatalysis [28]. Moreover, the surrounding carbon layers show an interplanar distance of 0.33 nm,

corresponding to the (002) plane of graphitic carbon (Fig. 3d). Interestingly, after acid/alkali rinsing and thermal treatment of Co@C, the resulting carbon product surface exhibits smaller nanoparticle morphology with an average particle size of 1.8 ± 0.2 nm (Fig. 3e, f). Furthermore, the HRTEM analysis reveals that the surface small Co-related particles display the lattice spacings of 0.24 nm and 0.20 nm, consistent with the (111) planes of CoO and Co respectively (Fig. 3g, h) [25]. This can be further verified by the selected area electron diffraction patterns of sample (Fig. 3i). The above results demonstrate that after acid/alkali rinsing and thermal treatment of Co@C, the resulting sample is consisted of CoO, metallic Co and graphitic carbon (Co/CoO-C). The spatial distribution of different elements in Co/CoO-C was analyzed by STEM-EDS (Fig. 3j-n). The elemental mapping results clearly indicate that the elements of C, N, O and Co are homogeneously distributed over the porous carbon, possibly suggesting the presence of ultrafine Co/CoO nanoparticles on the surface of porous graphitic carbon, beneficial for high-performance electrocatalysis [28]. This can be further verified by the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Co/CoO-C, in where ultrafine Co-related nanoparticles can be observed on the porous graphitic carbon (Fig. S2). The N element in Co/CoO-C is mainly from precursor Co-MOFs pores adsorbed triethylamine (TEA) as N source, possibly meaning the formation of N and Co-N_x doping in Co/CoO-C that are active components for electrocatalysis, which need to be further confirmed by other characterization techniques [30].

Fig. 3

The above results demonstrate that the Co-related species in Co-MOFs derived

carbon product changes from carbon-encapsulated metallic Co into highly exposed Co/CoO nanoparticles on graphitic carbon by different treatment processes. The formation process of Co/CoO nanoparticles on graphitic carbon can be speculated as follows: carbon-encapsulated metallic Co first dissolves to form Co^{2+} in 1.0 M HNO_3 (at 40 °C) (eq. (5)); partial Co^{2+} adsorbed on graphitic carbon subsequently reacts with 6.0 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ (at 40 °C) to form $\text{Co}(\text{OH})_2$ (eq. (6)), at the same time, N doping content in resulting carbon product may be enhanced owing to the utilization of $\text{NH}_3 \cdot \text{H}_2\text{O}$, which would be further confirmed in following characterizations; finally, $\text{Co}^{2+}/\text{Co}(\text{OH})_2$ adsorbed on graphitic carbon transform into highly exposed Co/CoO nanoparticles at 900 °C in N_2 atmosphere (eq. (7)).

Fig. 4a shows the N_2 adsorption-desorption isotherm of Co@C and Co/CoO-C samples. The calculated Brunauer-Emmett-Teller (BET) surface areas of Co@C and Co/CoO-C are $184 \text{ m}^2 \text{ g}^{-1}$ and $247 \text{ m}^2 \text{ g}^{-1}$, respectively. Comparatively, Co/CoO-C shows higher surface area due to the formation of porous carbon, favourable for the exposure of catalytic active sites for high-performance electrocatalysis. Fig. 4b shows the pore size distribution curves of Co@C and Co/CoO-C. As shown, Co@C exhibits dominant microporous structure with pore sizes centered at $\sim 1.4 \text{ nm}$, while Co/CoO-C displays primary mesoporous structure with pore sizes concentrated at $\sim 3.9 \text{ nm}$ and $\sim 18.0 \text{ nm}$. The presence of mesoporous structure in Co/CoO-C is not only favourable for improving its surface area for more catalytic active sites exposure, but also enhancing mass transport for electrocatalysis. The elemental composition and surface

chemical state of Co@C and Co/CoO-C samples were analyzed by XPS technique. Fig. S3 shows the surface survey XPS spectra of Co@C and Co/CoO-C, exhibiting C, N, O and Co elements for these two samples. Comparatively, Co/CoO-C shows a decreased Co content and obviously enhanced N/O content (Table S1). The decrease of Co content in Co/CoO-C compared to Co@C is possibly attributed to the loss of Co-related species during acid/alkali rinsing, while the increase of N and O contents in Co/CoO-C compared to Co@C may be due to graphitic carbon adsorbed $\text{NH}_3 \cdot \text{H}_2\text{O}$ providing additional N source and the formation of CoO, respectively. The enhancement of N doping content in Co/CoO-C is favourable for improving its ORR performance [31]. Fig. 4c shows the high-resolution N 1s XPS spectra of Co@C and Co/CoO-C. As shown, the N 1s XPS spectra of Co@C and Co/CoO-C can be fitted into four peaks at around 398.8, 399.9, 400.8, 401.9 eV, corresponding to pyridinic-N, Co-N_x, pyrrolic-N and graphitic-N [26]. For Co/CoO-C sample, pyridinic-N and graphitic-N are dominant components (Table S2), favourable for enhancing the electrical conductivity and electrocatalytic activity [32]. This has been further verified by the electrochemical impedance spectroscopy (EIS) measurements of Co@C and Co/CoO-C samples. As shown in Fig. S4, the Co/CoO-C sample exhibits obviously smaller radius of semicircle in EIS than that of Co@C, indicating its higher charge transfer capability [27]. Interestingly, Co-N_x species can be clearly found in both Co@C and Co/CoO-C samples, which has been proven to be catalytic active species of ORR [28]. The high-resolution Co 2p XPS spectra (Fig. 4d) indicate that Co⁰ can be detected at binding energy of 777.8 eV for both Co@C and Co/CoO-C, while the presence of CoO species in Co/CoO-C can be evidenced by the characteristic peaks of the Co(II) oxidation states located at 780.1 eV (Co 2p_{3/2}) and 795.2 eV (Co 2p_{1/2}) [33]. For Co@C sample, low content Co(II/III) oxidation states (Co 2p_{3/2} and Co 2p_{1/2}) can

be also detected possibly owing to the surface oxidation of residual Co on graphitic carbon under ambient air, while Co^0 species is obviously dominant. For Co/CoO-C sample, Co(II) oxidation states ($\text{Co } 2p_{3/2}$ and $\text{Co } 2p_{1/2}$) are apparently predominant compared to Co^0 species, consistent with the XRD results. Also, Co-N_x species can be found in both Co@C and Co/CoO-C samples, possibly contributing their ORR catalytic activities [28]. The above XPS results further confirm the presence of metallic Co, CoO, Co-N_x and N doping in Co/CoO-C, which may contribute the ORR and OER activities [28-32]. This would be further validated by following electrochemical measurements.

Fig. 4

Some studies have demonstrated that transition metal active species incorporated into N-doped graphitic carbon is ideal electrocatalyst for ORR and OER [34-36]. In this work, we also measured the ORR and OER activities of Co@C and Co/CoO-C in 0.1 M KOH solution. Fig. 5a shows the cyclic voltammetry (CV) curves of Co/CoO-C with a rotation disk electrode (RDE) setup in N_2 - and O_2 -saturated 0.1 M KOH solution. As shown, no obvious reduction peak can be observed in N_2 -saturated 0.1 M KOH, while a prominent cathodic peak appeared at 0.69 V (vs. RHE) can be observed in O_2 -saturated electrolyte, suggesting its excellent ORR activity. Fig. 5b displays the polarization plots of Co@C and Co/CoO-C measured by linear sweep voltammetry (LSV). For comparison, the commercial Pt/C (20 wt.% Pt on Vulcan carbon black) was also measured in this work. As shown, the commercial Pt/C displays an onset potential of $E_{\text{onset}}=0.95$ V (vs. RHE) and a half-wave potential of $E_{1/2}=0.85$ V (vs. RHE), along with a diffusion-limited current density of $J_L=5.07$ mA cm^{-2} at 0.75 V (vs.

RHE). Comparatively, Co/CoO-C shows larger diffusion-limited current densities at the potentials of <0.64 V (*vs.* RHE), indicating its superior ORR activity. Also, Co/CoO-C exhibits $E_{onset}=0.90$ V and $E_{1/2}=0.82$ V (*vs.* RHE), very close to the Pt/C catalyst. Notably, the ORR activity of Co/CoO-C is superior to that of Co@C. Higher N doping content and more Co-N_x active species in Co/CoO-C may contribute its superior ORR activity compared to Co@C [37, 38]. The corresponding Tafel plots are shown in Fig. 5c, where the slope was determined to be 133 mV dec^{-1} for Co@C, 70 mV dec^{-1} for Co/CoO-C and 61 mV dec^{-1} for Pt/C, indicating Co/CoO-C with good reaction kinetics for ORR. Fig. 5d shows the LSV curves of Co/CoO-C at various rotation speeds in O₂-saturated 0.1 M KOH, indicating mass transport controlled ORR process [37]. The corresponding Koutecky-Levich (K-L) plots (inset in Fig. 5e) reveal the inverse of current density (j^{-1}) as a function of the inverse of square root of rotating speed ($\omega^{-1/2}$) at different potentials from 0.2 to 0.7 V. The number (*n*) of electron transfer involved per O₂ in the ORR for Co/CoO-C was determined by the K-L equation (Fig. 5e). The *n* value was calculated to be 3.97, suggesting a four-electron transfer ORR process. This is very important for its practical application in fuel cells. Long term stability and fuel crossover effects are also major concerns for cathodic catalysts in fuel cells. Fig. 5f shows the chronoamperometric response recorded at a constant voltage of 0.35 V (*vs.* RHE). As shown, Co/CoO-C displays high stability with only ~5% loss of the original ORR current density over 30,000 s of continuous operation, whereas Pt/C shows 32% loss of its original current density.

Fig. 5

The Co/CoO-C and commercial Pt/C catalysts are further compared by measuring the methanol crossover effect *via* chronoamperometric responses at the potential of 0.5 V (*vs.* RHE) in O₂-saturated 0.1 M KOH electrolyte at a rotation speed of 1600 rpm (Fig. S5). When 3.0 M methanol is introduced into the electrolyte, there is an instant drop in the current of Pt/C catalyst, while the current of Co/CoO-C remains almost unchanged, suggesting its excellent tolerance for methanol. The above results demonstrate that Co/CoO-C possesses superior ORR activity and high applicable stability, promising as air cathode catalyst for fuel cells.

The electrocatalytic performances of Co@C and Co/CoO-C towards oxygen evolution reaction (OER) were also evaluated in 0.1 M KOH solution. For comparison, commercial RuO₂ was selected as the catalyst for OER measurement in this work. Fig. 6a shows the polarization curves with *iR* compensation of Co@C, Co/CoO-C and RuO₂. As shown, the onset potentials are 1.56, 1.46, and 1.42 V (*vs.* RHE) for Co@C, Co/CoO-C and RuO₂ respectively, indicating Co/CoO-C with higher OER activity compared to Co@C and close OER activity to commercial RuO₂. It is well known that the potential required for water oxidation is usually applied to evaluate the OER performance of an electrocatalyst at a current density of 10 mA cm⁻² [39-41]. The potential value of Co/CoO-C at 10 mA cm⁻² is 1.57 V (*vs.* RHE), close to that (1.52 V *vs.* RHE) of commercial RuO₂ and obviously superior to that (1.63 V *vs.* RHE) of Co@C, indicating its excellent OER activity. Furthermore, the Tafel slope values (Fig. 6b) are 166.2, 85.4 and 78.3 mV dec⁻¹ for Co@C, Co/CoO-C and RuO₂ respectively, implying Co/CoO-C with good reaction kinetics for OER.

The durability measurement displays that Co/Co-C can maintain almost 98% its initial current density after 10 h of run at 1.6 V (Fig. 6c), indicating its high applicable stability. After 1000 cycling measurement of Co/CoO-C, the XPS technique was applied to characterize the changes of surface composition and chemical state of Co/CoO-C to illustrate the OER active mechanism. As shown in Fig. 6d, the XPS peak of metallic Co^0 is disappeared, possibly transforming into other active Co (II/III) species such as cobalt oxides/hydroxides/oxyhydroxides in alkaline media, which are primarily responsible for the OER activities [42]. In a word, this highly exposed Co/CoO-C nanoparticles on graphitic carbon converted from core-shell structure Co@C is very beneficial for providing more Co-related catalytic active sites for high performance OER.

Fig. 6

Owing to the superior bifunctional catalytic activities toward ORR and OER, Co/CoO-C was used as air cathode material to construct primary and rechargeable zinc-air batteries for measurements. As shown in Fig. 7a, the open-circuit voltage was determined to be ~ 1.4 V for Co/CoO-C constructed primary zinc-air battery, almost identical to that of Pt/C, indicating its high performance of zinc-air battery. Fig. 7b shows the power density curves of zinc-air batteries assembled with Co/CoO-C and Pt/C. In the discharge process, the zinc-air battery made from Co/CoO-C shows a high current density of 96 mA cm^{-2} at 1.0 V, close to that of the Pt/C based zinc-air battery (113 mA cm^{-2} at 1.0 V). The peak power density of the zinc-air battery assembled with Co/CoO-C is 157 mW cm^{-2} at 0.75 V, which is approximate to that of

the Pt/C based zinc-air battery (173 mW cm^{-2} at 0.7 V). Based on its efficient ORR and OER performance, Co/CoO-C was further constructed to a rechargeable zinc-air battery, which was tested in a 6.0 M KOH electrolyte including 0.2 M zinc acetate. To obtain a meaningful comparison, a mixture of commercial Pt/C and RuO_2 with a mass ratio of 1:1 was used in this work for rechargeable battery measurements. During the charge-discharge process (Fig. 7c), the battery made from Co/CoO-C exhibits similar current densities to the rechargeable battery assembled with Pt/C- RuO_2 , indicating the superior charge-discharge performance of Co/CoO-C in the rechargeable zinc-air battery. The durability test of Co/CoO-C is shown in Fig. 7d. The initial charge and discharge potentials of the Co/CoO-C based zinc-air battery were 2.05 and 1.25 V , respectively. After 50 cycles, the charge and discharge potentials were 2.10 and 1.20 V , respectively, indicating the excellent stability of the Co/CoO-C catalyst in zinc-air batteries. As shown in Fig. 7e, the photographs of a LED pattern (CEEN, Centre for Environmental and Energy Nanomaterials, 2.4 V) powered by two Co/CoO-C assembled zinc-air batteries. The above results reveal that the as-obtained Co/CoO-C has great potential as air cathode catalyst for the rechargeable zinc-air batteries.

Fig. 7

4. Conclusions

In summary, Co/CoO-C electrocatalysts have been successfully prepared by converting Co-MOFs derived core-shell structure Co@C through a simple two-step pyrolytic treatment process. The as-fabricated Co/CoO-C exhibits

ultrafine Co/CoO nanoparticles morphology exposed on graphitic carbon with a high surface area of $247 \text{ m}^2 \text{ g}^{-1}$ and mesoporous structure. As the electrocatalyst, Co/CoO-C demonstrates superior ORR/OER bifunctional activities and impressive stability in rechargeable zinc-air batteries. Our experimental results reveal that the formed Co-N_x and N doping in graphitic carbon structure of Co/CoO-C should be responsible for its ORR activity, while its high OER activity can be ascribed to the Co-related catalytic active species resulted from highly exposed Co/CoO nanoparticles on graphitic carbon in alkaline media. Our findings in this work demonstrate the feasibility of converting low catalytic active electrocatalysts into high active ones for energy applications.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 51672277 and 51432009), the CAS Pioneer Hundred Talents Program, and the CAS/SAFEA International Partnership Program for Creative Research Teams of Chinese Academy of Sciences, China.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/>

References

- [1] Y. Li, F. Cheng, J. Zhang, Z. Chen, Q. Xu, S. Guo, Cobalt-carbon core-shell nanoparticles aligned on wrinkle of N-doped carbon nanosheets with Pt-like activity for oxygen reduction, *Small*, 12 (2016) 2839-2845.
- [2] B. Wang, C. Hu, L. Dai, Functionalized carbon nanotubes and graphene-based materials for energy storage, *Chem Commun*, 52 (2016) 14350-14360.
- [3] S. Guo, S. Zhang, S. Sun, Tuning nanoparticle catalysis for the oxygen reduction reaction, *Angew Chem Int Ed*, 52 (2013) 8526-8544.
- [4] T.Y. Ma, S. Dai, M. Jaroniec, S.Z. Qiao, Metal-organic framework derived hybrid Co_3O_4 -carbon porous nanowire arrays as reversible oxygen evolution electrodes, *J Am Chem Soc*, 136 (2014) 13925-13931.
- [5] Y. Li, H. Dai, Recent advances in zinc-air batteries, *Chem Soc Rev*, 43 (2014) 5257-5275.
- [6] A. Aijaz, J. Masa, C. Rosler, W. Xia, P. Weide, A. J. Botz, R. A. Fischer, W. Schuhmann and M. Muhler, $\text{Co}@\text{Co}_3\text{O}_4$ encapsulated in carbon nanotube-grafted nitrogen-doped carbon polyhedra as an advanced bifunctional oxygen electrode, *Angew Chem Int Ed*, 55 (2016) 4087-4091.
- [7] J. Liu, M. Jiao, L. Lu, H. M. Barkholtz, Y. Li, Y. Wang, L. Jiang, Z. Wu, D. J. Liu, L. Zhuang, C. Ma, J. Zeng, B. Zhang, D. Su, P. Song, W. Xing, W. Xu, Y. Wang, Z. Jiang and G. Sun, High performance platinum single atom electrocatalyst for oxygen reduction reaction, *Nat Commun*, 8 (2017) 15938.
- [8] X. Zhang, R. Liu, Y. Zang, G. Liu, G. Wang, Y. Zhang, H. Zhang and H. Zhao,

Co/CoO nanoparticles immobilized on Co-N-doped carbon as trifunctional electrocatalysts for oxygen reduction, oxygen evolution and hydrogen evolution reactions, *Chem Commun*, 52 (2016) 5946-5949.

[9] X. Wang, J. Zhou, H. Fu, W. Li, X. Fan, G. Xin, J. Zheng and X. Li, MOF derived catalysts for electrochemical oxygen reduction, *J Mater Chem A*, 2 (2014) 14064-14070.

[10] S. Zhao, H. Yin, L. Du, L. He, K. Zhao, L. Chang, G. Yin, H. Zhao, S. Liu, Z. Tang, Carbonized nanoscale metal-organic frameworks as high performance electrocatalyst for oxygen reduction reaction, *ACS nano*, 8 (2014) 12660-12668.

[11] L. Ai, T. Tian, J. Jiang, Ultrathin graphene layers encapsulating nickel nanoparticles derived metal-organic frameworks for highly efficient electrocatalytic hydrogen and oxygen evolution reactions, *ACS Sustainable Chem Eng*, 5 (2017) 4771-4777.

[12] Y. Qian, Z. Hu, X. Ge, S. Yang, Y. Peng, Z. Kang, Z. Liu, J. Y. Lee and D. Zhao, A metal-free ORR/OER bifunctional electrocatalyst derived from metal-organic frameworks for rechargeable Zn-Air batteries, *Carbon*, 111 (2017) 641-650.

[13] C. Tang, H. F. Wang, X. Chen, B. Q. Li, T. Z. Hou, B. Zhang, Q. Zhang, M. M. Titirici and F. Wei, Topological defects in metal-free nanocarbon for oxygen electrocatalysis, *Adv Mater*, 28 (2016) 6845-6851.

[14] Y. Zang, H. Zhang, X. Zhang, R. Liu, S. Liu, G. Wang, Y. Zhang and H. Zhao, Fe/Fe₂O₃ nanoparticles anchored on Fe-N-doped carbon nanosheets as bifunctional

oxygen electrocatalysts for rechargeable zinc-air batteries, *Nano Research*, 9 (2016) 2123-2137.

[15] X. Zhang, S. Liu, Y. Zang, R. Liu, G. Liu, G. Wang, Y. Zhang, H. Zhang and H. Zhao, Co/Co₉S₈@S, N-doped porous graphene sheets derived from S, N dual organic ligands assembled Co-MOFs as superior electrocatalysts for full water splitting in alkaline media, *Nano Energy* 30 (2016) 93-102.

[16] H.-S. Lu, H. Zhang, R. Liu, X. Zhang, H. Zhao, G. Wang, Macroscale cobalt-MOFs derived metallic Co nanoparticles embedded in N-doped porous carbon layers as efficient oxygen electrocatalysts, *Applied Surface Science*, 392 (2017) 402-409.

[17] X. Zhao, F. Li, R. Wang, J.-M. Seo, H.-J. Choi, S.-M. Jung, J. Mahmood, I.-Y. Jeon, J.-B. Baek, Controlled fabrication of hierarchically structured nitrogen-doped carbon nanotubes as a highly active bifunctional oxygen electrocatalyst, *Advanced Functional Materials*, 27 (2017) 1605717.

[18] D. Deng, L. Yu, X. Chen, G. Wang, L. Jin, X. Pan, J. Deng, G. Sun, X. Bao, Iron encapsulated within pod-like carbon nanotubes for oxygen reduction reaction, *Angew Chem Int Ed*, 52 (2013) 371-375.

[19] X. Zhao, H. Zhao, T. Zhang, X. Yan, Y. Yuan, H. Zhang, H. Zhao, D. Zhang, G. Zhu, X. Yao, One-step synthesis of nitrogen-doped microporous carbon materials as metal-free electrocatalysts for oxygen reduction reaction, *J Mater Chem A*, 2 (2014) 11666-11671.

- [20] M. Al-Mamun, Y. Wang, P. Liu, Y.L. Zhong, H. Yin, X. Su, H. Zhang, H. Yang, D. Wang, Z. Tang, H. Zhao, One-step solid phase synthesis of a highly efficient and robust cobalt pentlandite electrocatalyst for the oxygen evolution reaction, *J Mater Chem A*, 4 (2016) 18314-18321.
- [21] Y.W. Fu, X. Y.; Li, G. B.; Liao, F. H.; Xiong, M.; Lin, J. H., synthesis, structure, and magnetic property of $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$, *Chin. J. Inorg. Chem.*, 24 (2008) 1224.
- [22] H.S. Lu, L. Bai, W.W. Xiong, P. Li, J. Ding, G. Zhang, T. Wu, Y. Zhao, J.M. Lee, Y. Yang, B. Geng, Q. Zhang, Surfactant media to grow new crystalline cobalt 1,3,5-benzenetricarboxylate metal-organic frameworks, *Inorg Chem*, 53 (2014) 8529-8537.
- [23] J. Gao, K. Ye, L. Yang, W.W. Xiong, L. Ye, Y. Wang, Q. Zhang, Growing crystalline zinc-1,3,5-benzenetricarboxylate metal-organic frameworks in different surfactants, *Inorg Chem*, 53 (2014) 691-693.
- [24] X. Yu, Y.S. Toh, J. Zhao, L. Nie, K. Ye, Y. Wang, D. Li, Q. Zhang, Surfactant-thermal method to prepare two new cobalt metal-organic frameworks, *Journal of Solid State Chemistry*, 232 (2015) 14-18.
- [25] E. Zhang, Y. Xie, S. Ci, J. Jia, P. Cai, L. Yi, Z. Wen, Multifunctional high-activity and robust electrocatalyst derived from metal-organic frameworks, *J Mater Chem A*, 4 (2016) 17288-17298.
- [26] C. Lin, S.S. Shinde, Z. Jiang, X. Song, Y. Sun, L. Guo, H. Zhang, J.-Y. Jung, X. Li, J.-H. Lee, In situ directional formation of Co@CoOx -embedded 1D carbon

nanotubes as an efficient oxygen electrocatalyst for ultra-high rate Zn-air batteries, *J Mater Chem A*, 5 (2017) 13994-14002.

[27] S. Zhang, X. Yu, F. Yan, C. Li, X. Zhang, Y. Chen, N-Doped graphene-supported Co@CoO core-shell nanoparticles as high-performance bifunctional electrocatalysts for overall water splitting, *J Mater Chem A*, 4 (2016) 12046-12053.

[28] Y. Niu, X. Huang, X. Wu, L. Zhao, W. Hu, C. Ming Li, One-pot synthesis of Co/N-doped mesoporous graphene with embedded Co/CoO_x nanoparticles for efficient oxygen reduction reaction, *Nanoscale*, 9 (2017) 10233-10239.

[29] W. Xia, R. Zou, L. An, D. Xia, S. Guo, A metal-organic framework route to in situ encapsulation of Co@Co₃O₄@C core-shell nanoparticles into a highly ordered porous carbon matrix for oxygen reduction, *Energy Environ Sci*, 8 (2015) 568-576.

[30] H. Tang, S. Cai, S. Xie, Z. Wang, Y. Tong, M. Pan, X. Lu, Metal-organic-framework-derived dual metal- and nitrogen-doped carbon as efficient and robust oxygen reduction reaction catalysts for microbial fuel cells, *Adv Sci*, 3 (2016) 1500265.

[31] X.X. Liu, J.B. Zang, L. Chen, L.B. Chen, X. Chen, P. Wu, S.Y. Zhou, Y.H. Wang, A microwave-assisted synthesis of CoO@Co core-shell structures coupled with N-doped reduced graphene oxide used as a superior multi-functional electrocatalyst for hydrogen evolution, oxygen reduction and oxygen evolution reactions, *J Mater Chem A*, 5 (2017) 5865-5872.

- [32] J. Liu, A. Shen, X. Wei, K. Zhou, W. Chen, F. Chen, J. Xu, S. Wang, L. Dai, Ultrathin wrinkled N-doped carbon nanotubes for noble-metal loading and oxygen reduction reaction, *ACS Appl Mater Interfaces*, 7 (2015) 20507-20512.
- [33] T. Meng, J. Qin, S. Wang, D. Zhao, B. Mao, M. Cao, In situ coupling of $\text{Co}_{0.85}\text{Se}$ and N-doped carbon via one-step selenization of metal-organic frameworks as a trifunctional catalyst for overall water splitting and Zn-air batteries, *J Mater Chem A*, 5 (2017) 7001-7014.
- [34] L. Zhang, Z. Su, F. Jiang, L. Yang, J. Qian, Y. Zhou, W. Li and M. Hong, Highly graphitized nitrogen-doped porous carbon nanopolyhedra derived from ZIF-8 nanocrystals as efficient electrocatalysts for oxygen reduction reactions, *Nanoscale*, 6 (2014) 6590-6602.
- [35] W. Wan, Q. Wang, L. Zhang, H.-W. Liang, P. Chen and S.-H. Yu, N-, P-and Fe-tridoped nanoporous carbon derived from plant biomass: an excellent oxygen reduction electrocatalyst for zinc-air batteries, *J Mater Chem A*, 4 (2016) 8602-8609.
- [36] T. Zhang, J. Du, P. Xi and C. Xu, Hybrids of cobalt/iron phosphides derived from bimetal-organic frameworks as highly efficient electrocatalysts for oxygen evolution reaction, *ACS Appl Mater Interfaces*, 9 (2017) 362-370.
- [37] H. Li, Y. Huang, H. Zhou, W. Yang, M. Li, Z. Huang, C. Fu and Y. Kuang, One step in-situ synthesis of Co@N , S co-doped CNTs composite with excellent HER and ORR bi-functional electrocatalytic performances, *Electrochimica Acta*, 247 (2017) 736-744.

- [38] H. Tabassum, R. Zou, A. Mahmood, Z. Liang, S. Guo, A catalyst-free synthesis of B, N co-doped graphene nanostructures with tunable dimensions as highly efficient metal free dual electrocatalysts, *J Mater Chem A*, 4(2016), 16469-16475.
- [39] S. Dou, X. Li, L. Tao, J. Huo and S. Wang, Cobalt nanoparticle-embedded carbon nanotube/porous carbon hybrid derived from MOF-encapsulated Co_3O_4 for oxygen electrocatalysis, *Chem Commun*, 52 (2016) 9727-9730.
- [40] C. Si, Y. Zhang, C. Zhang, H. Gao, W. Ma, L. Lv, Z. Zhang, Mesoporous nanostructured spinel-type MFe_2O_4 (M= Co, Mn, Ni) oxides as efficient bi-functional electrocatalysts towards oxygen reduction and oxygen evolution. *Electrochimica Acta*, 245 (2017) 829-838.
- [41] B. Chen, R. Li, G. Ma, X. Gou, Y. Zhu and Y. Xia, Cobalt sulfide/N, S codoped porous carbon core-shell nanocomposites as superior bifunctional electrocatalysts for oxygen reduction and evolution reactions, *Nanoscale*, 7 (2015) 20674-20684.
- [42] C. W. Tung, Y. Y. Hsu, Y. P. Shen, Y. Zheng, T. S. Chan, H. S. Sheu, Y. C. Cheng and H. M. Chen, Reversible adapting layer produces robust single-crystal electrocatalyst for oxygen evolution, *Nat Commun*, 6 (2015) 8106.

Figure Captions:

Fig. 1 (a) SEM image of the as-prepared Co-MOFs, inset of Co-MOFs optical photograph. (b) XRD patterns of the as-prepared Co-MOFs. (c) Secondary building unit of Co-MOFs structure. (d) B-axis projections of the crystal structure of Co-MOFs (Light blue, red, grey and light grey represent the cobalt, oxygen, carbon and hydrogen atoms, respectively).

Fig. 2 (a) Thermogravimetric analysis (TGA) curve of Co-MOFs under N₂ atmosphere. SEM images of (b) Co-MOFs derived Co@C and (c) Co/CoO-C after acid/alkali rinsing and thermal treatment of Co@C. (d) XRD patterns of Co@C and Co/CoO-C.

Fig. 3 (a) TEM image of Co-MOFs derived Co@C. (b) Corresponding Co particle size distribution. (c) HRTEM image of Co@C. (d) TEM image, (e) HAADF image and (f) Corresponding Co/CoO particle size distribution. (g) and (h) HRTEM images, (i) SAED patterns of Co/CoO, and corresponding elemental mapping images (j-n).

Fig. 4 (a) Nitrogen adsorption-desorption isotherm and (b) Corresponding pore diameter distribution of Co@C and Co/CoO-C. High-resolution deconvoluted XPS spectra of (c) N 1s and (d) Co 2p of Co@C and Co/CoO-C.

Fig. 5 (a) Cyclic voltammograms of Co/CoO-C in N₂/O₂-saturated 0.1 M KOH. (b) Linear-sweep voltammograms of Co@C, Co/CoO-C and Pt/C in O₂-saturated 0.1 M KOH with a sweep rate of 5.0 mV s⁻¹ and electrode rotation speed of 1600 rpm. (c) Tafel plots of Co@C, Co/CoO-C and Pt/C. (d) Linear-sweep voltammograms of Co/CoO-C at different rotation speeds. (e) Electron transfer number as a function of potential for Co/CoO-C (inset: the Koutecky-Levich (K-L) plots at different

potentials). (f) Current-time (i-t) responses of Co/CoO-C and Pt/C electrodes at 1600 rpm at -0.35 V in O₂-saturated 0.1 M KOH solution.

Fig. 6 (a) LSV curves of Co@C, Co/CoO-C and RuO₂/C loaded onto glassy carbon electrodes measured in 0.1 M KOH. (b) Tafel plots of Co@C, Co/CoO-C and RuO₂/C for OER. (c) Durability evaluation of Co/CoO-C catalysts for 10 h at 1.6 V vs. RHE. (d) High-resolution deconvoluted XPS Co 2p spectra of polarization curves the Co/CoO-C after 1000 cycles.

Fig. 7 (a) Open circuit voltage measurements of zinc-air batteries assembled with different catalysts. (b) Power density plots of zinc-air batteries assembled with different catalysts. (c) Charge-discharge polarization curves of rechargeable zinc-air batteries made from different catalysts. (d) Recycling durability test of a rechargeable zinc-air battery made from Co/CoO-C. (e) Photographs of a LED pattern powered by two Co-CoO-C assembled zinc-air batteries.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Supplementary Materials

Transformation of carbon-encapsulated metallic Co into ultrafine Co/CoO nanoparticles exposed on N-doped graphitic carbon for high-performance rechargeable zinc-air battery

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Table S1 XPS analysis of Co@C and Co/CoO-C.

Sample	C 1s (at.%)	N 1s (at.%)	O 1s (at.%)	Co 2p (at.%)
Co@C	90.8	1.97	5.85	1.38
Co/CoO-C	90.3	2.46	6.63	0.61

Table S2 The detailed information of high-resolution N 1s XPS of Co@C and Co/CoO-C samples.

Sample	N type	Peak position (eV)	Half-peak width (eV)	Intensity	Fitted peak area
Co@C	graphitic-N	401.9±0.2	2.4±0.2	4160±60	207±3
	pyrrolic-N	400.8±0.1	1.6±0.1	4162±40	295±5
	Co-N _x	399.9±0.2	1.2±0.1	4057±40	66±1
	Pyridinic-N	398.8±0.1	1.4±0.1	4132±50	207±3
Co/CoO-C	graphitic-N	401.9±0.2	2.4±0.2	4433±70	272±6
	pyrrolic-N	400.7±0.1	1.6±0.1	4430±60	218±5
	Co-N _x	399.9±0.2	1.2±0.1	4455±60	160±3
	Pyridinic-N	398.8±0.1	1.4±0.1	4492±40	362±4

Fig. S1 TEM (a) and HRTEM (b) images of the Co-MOFs derived Co@C sample.

Fig. S2 The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Co/CoO-C sample.

Fig. S3 Typical survey scan XPS spectrum of Co@C and Co/CoO-C samples.

Fig. S4 EIS curves of the Co@C and Co/CoO-C samples.

Fig. S5 Chronoamperometric responses of Co/CoO-C and Pt/C catalysts obtained at 0.5 V in O₂-saturated 0.1 M KOH solution (150 mL) with addition of methanol at the time of 200 s.

Highlights

- Ultrafine Co/CoO nanoparticles anchored on graphitic carbon were successfully prepared.
- Co/CoO-C exhibited bifunctional electrocatalytic activities of ORR and OER.
- Co/CoO-C assembled zinc-air battery displayed high performance and stability.

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Full Length Article

Transformation of carbon-encapsulated metallic Co into ultrafine Co/CoO nanoparticles exposed on N-doped graphitic carbon for high-performance rechargeable zinc-air battery

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PII: S0169-4332(18)31106-1
DOI: <https://doi.org/10.1016/j.apsusc.2018.04.146>
Reference: APSUSC 39145

To appear in: *Applied Surface Science*

Received Date: 19 December 2017
Revised Date: 10 April 2018
Accepted Date: 15 April 2018

Please cite this article as: H-S. Lu, H. Zhang, X. Zhang, N. Sun, X. Zhu, H. Zhao, G. Wang, Transformation of carbon-encapsulated metallic Co into ultrafine Co/CoO nanoparticles exposed on N-doped graphitic carbon for high-performance rechargeable zinc-air battery, *Applied Surface Science* (2018), doi: <https://doi.org/10.1016/j.apsusc.2018.04.146>

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