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Core-shell carbon materials derived from metal-organic frameworks as an efficient oxygen bifunctional electrocatalyst

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Abstract

Noble-metal free and durable electrocatalysts with high catalytic activity toward oxygen reduction and evolution reactions are crucial to high-performance primary or rechargeable Zn-air batteries (ZnABs) and fuel cells. Herein, we report an efficient bifunctional electrocatalyst with core-shell structure obtained from ZIF-8@ZIF-67 through hydrothermal and carbonization treatment. The resulted material, i.e. highly graphitic carbon (GC, carbonized from ZIF-67) on nitrogen-doped carbon (NC, carbonized from ZIF-8) (NC@GC), combines the distinguished advantages of NC, including high surface area, presence of Co doping and high nitrogen content, and those of GC including high crystallinity, good conductivity and stability of GC. This unique core-shell structure with potential synergistic interaction leads to high activities towards oxygen reduction and oxygen evolution reactions. As a proof-of-concept, the as-prepared NC@GC catalyst exhibits excellent performance in the primary and

rechargeable ZnABs. This study might inspire new thought on the development of carbon-based electrocatalytic materials derived from MOF materials.

1. Introduction

Rechargeable metal-air batteries are regarded as a promising technology for electrochemical energy conversion.^[1] Zinc-air batteries (ZnABs) are particularly attractive as they utilize earth-abundant zinc with easy recycling feature, aqueous alkaline electrolyte and cost-effective air-cathode of well-defined electrochemistry. Furthermore, ZnABs have additional advantages of flat discharge voltage and long shelf-life.^[2] Durable electrocatalysts with high catalytic activity toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are crucial to practical applications of ZnABs. Towards that end, noble metals such as platinum, ruthenium, iridium and their respective compounds are commonly used as such electrocatalysts. However, their scarcity and high costs greatly hamper the commercialization of this technology.^[3] Faced with these challenges, much effort has been expanded in the search of efficient, low-cost and robust oxygen electrocatalysts for both ORR and OER to enable the operation of ZnAB at high current density. This has led to the discovery of a number of new catalysts and many interesting findings.^[3-4]

Recently, metal-organic frameworks (MOFs) have attracted a lot of attention as electrocatalyst precursors due to the existence of abundant cobalt, carbon and nitrogen species.^[5] However, MOF-derived nanocomposites possess poor graphitic degree, which is unfavorable for electron transport. As such, although many MOF-derived nanocomposites have been investigated, their electrocatalytic performance has not been very satisfactory.^[5a] In particular, there are very few reports on bifunctional electrocatalysts applied in the ZnAB with good performance.

Herein, we designed a bifunctional electrocatalyst with core-shell structure which utilizes two different types of MOFs as the core and shell, respectively. This enables us to combine

their unique individual properties. As shown in **Scheme 1**, ZIF-8 and ZIF-67 have similar structures. After carbonization, they form nitrogen-doped carbon (NC) and highly graphitic carbon (GC), respectively. The resultant NC and GC carbon materials each have their own distinguished properties. Nanoporous NC prepared from ZIF-8 has a relatively high N content and large surface area.^[6] However, the carbon present in NC is amorphous, which has poor conductivity and stability. This problem is circumvented by including GC derived from ZIF-67 in the structure. GC consists of highly graphitic carbon, which has good conductivity and stability.^[6] The presence of Co, high conductivity and good stability will also be beneficial to the ORR and OER. Therefore the core-shell structure of NC@GC reasonably integrates the advantages of these two carbon materials. As expected, this material demonstrated good electrocatalytic activity toward ORR and OER.

2. Results and Discussion

The NC@GC core-shell carbon material was converted thermally from a ZIF-8@ZIF-67 MOF (**Scheme 1**). The core-shell ZIF-8@ZIF-67 MOF was prepared by a seed-mediated growth technique through a hydrothermal method (See details in the Experimental part). The formation of ZIF-8@ZIF-67 core-shell structure is due to their isorecticular structures as $[M(\text{MeIm})_2]_n$ ($M=\text{Zn}$ for ZIF-8 and Co for ZIF-67, $\text{MeIm}=2\text{-methylimidazole}$) and their similar unit cell parameters between ZIF-8 ($a=b=c=16.9910\text{ \AA}$)^[7] and ZIF-67 ($a=b=c=16.9598\text{ \AA}$)^[8] which has been determined by single crystal X-ray diffraction studies. In brief, the ZIF-8 seeds were first synthesized by the coordination of Zn^{2+} with MeIm (**Scheme 1c**). Then the ZIF-8 seeds were dispersed in methanol by sonication. Here, the ZIF-8 with a diameter of 500 nm was chosen because it can be dispersed well in methanol, which is important for the uniform coating with ZIF-67.^[6] After adding CoCl_2 , Co^{2+} ions were easily immobilized on the surface of ZIF-8 due to the coordination between Co^{2+} and MeIm on the surface of ZIF-8. After that, ZIF-67 shell grew through the interaction with additive MeIm linkers. It should be

noted that ZIF-8 is white while ZIF-67 is purple. However, the final ZIF-8@ZIF-67 is bright purple (**Figure S1**), which indicates successful growth of the ZIF-67 shell onto the ZIF-8 core to form a core-shell structure. In contrast, a control experiment has been done in an attempt to synthesize ZIF-67@ZIF-8 core-shell structure using the same protocol. However, only a mixture of ZIF-8 and ZIF 67 crystals was obtained, and no core-shell ZIF-67@ZIF-8 structure was observed (**Figure S2**). This might be due to the fast nucleation reaction of ZIF-8 crystals,^[6] which is not favorable for the heterogeneous seed-induced nucleation on the surface of ZIF-67 seeds. This control experiment result further reflects the formation of ZIF-8@ZIF-67 core-shell structure. In addition, the wide-angle powder X-ray diffraction (PXRD) pattern of ZIF-8@ZIF-67 crystal (**Figure S3**) simulated from single crystal structure of ZIF-8^[7] and ZIF-67,^[8] which indicated that the ZIF-8@ZIF-67 core-shell structure has been successfully formed via epitaxial growth.^[6] The obtained ZIF-8@ZIF-67 core-shell structure was further carbonized at 800 °C under Ar flow. During the heat treatment process, the organic linkers, i.e. MeIm, are thermally carbonized into carbon network of NC@GC.

The scanning electron microscope (SEM) image showed that the obtained NC@GC retained the original rhombic dodecahedron shape with a distorted, bumpy surface (**Figure 1a**) and hollow structure (indicated by the arrow in **Figure 1a**). The shape of NC@GC was similar to NC obtained from ZIF-8 (**Figure S4a**). But NC showed a smooth surface without any large pores or cracks. In contrast, GC particles prepared from ZIF-67 exhibited distorted, bumpy surface (**Figure S4b**). Therefore, the bumpy surface of NC@GC comes from GC, which confirmed that ZIF-67 has been successfully grown on the surface of ZIF-8 to form a core-shell structure. Energy Dispersive Spectroscopy (EDS) mapping was also performed (**Figure 1b**). A typical EDS spectrum indicated that the Co, Zn, C, N and O are uniformly distributed in the NC@GC. This observation was also verified by our XPS results which will be discussed in detail later (**Figure 4**).

A more detailed structure of NC@GC was observed via images obtained from TEM and high-resolution TEM (HRTEM). The NC@GC showed a hollow structure with nanotubes extruded out from the amorphous carbon layer (**Figure 2a**), which is consistent with the SEM result (**Figure 1a**). The distance between the lattice fringes in certain region of the shell is measured to be 0.348 nm (**Figure 2b**), corresponding to the (002) layers of graphitic carbon.^[9] The graphitic carbon and nanotubes likely formed during the carbonization process in the presence of Co nanoparticles.^[10] Graphitization of amorphous carbon supposedly induced the formation of a bumpy surface, as mentioned above (**Figure 1a**). Inside the graphitic carbon shell, metal particles which are smaller than 10 nm are fully covered with the carbon layers. Such graphitic coating on metal/metal oxide can improve the electric conductivity and enhance catalytic activity of the metal/metal oxides.^[4c, 5b, 11]

The NC@GC was also characterized by X-ray diffraction (XRD) (**Figure 3a**). The presence of crystalline carbon (JCPDS No.46-0943) is consistent with the HRTEM results (**Figure 2b**).^[12] Moreover, the peaks at 44.2° 51.4° and 75.5° correspond to crystalline facets of Co (111), Co (200) and Co (220) (JCPDS No.15-0806),^[13] demonstrating the successful reduction of Co ions to a metallic state after carbonization. The size of Co particles was about 10 nm as determined by the Scherrer equation.^[14] It should be noted that the absence of Zn peak indicated that NC has been covered with GC due to the limited depth of XRD, which is an indirect evidence for the formation of a core-shell structure.

The structure of NC@GC was further confirmed by Raman spectroscopy (**Figure 3b**). The peaks at 1346 and 1580 cm⁻¹ correspond to the D (disordered carbon) and G (graphitic carbon) bands, respectively. The peaks at 509 and 674 cm⁻¹ can be attributed to the Co nanoparticles,^[15] which is consistent with the XRD (**Figure 3a**) and TEM results (**Figure 2b**).

The chemical composition of the NC@GC was confirmed by X-ray photoelectron spectroscopy (XPS) in **Figure 4**. The full spectrum of NC@GC suggests the co-existence of C, Co, N and O in the sample, which is similar to that of GC (**Figure 4a**). However, the Zn

peak which is present in NC cannot be observed in the NC@GC compared with the EDS results (**Figure 1b**). It is known that both EDS and XPS can analyze the surface element of the materials. However, their depth of penetration is different. In the EDS analysis, the depth of penetration is about 2 μm , which is much deeper than that of XPS (10 nm). From the SEM image (**Figure 1a**), it can be seen that the thickness of the GC shell is around 20 nm. Therefore, the XPS element analysis result is only from the GC shell while the EDS analysis includes both GC and NC. Therefore, Zn element present in NC core can not be observed in the XPS analysis result due to the limited detection depth of XPS. In addition, the different EDS and XPS elemental analysis results confirmed that NC has been fully covered with GC to form a core-shell structure, which is consistent with the TEM (**Figure 2**), XRD (**Figure 3a**) and Raman results (**Figure 3b**).

The C 1s, N 1s and Co 2p peaks in the NC@GC XPS spectrum were analyzed in detail (**Figure 4b, c and d**). The high-resolution C 1s spectrum can be deconvoluted into two bonds, corresponding to C-C (284.5 eV) and C=N (285.7 eV), respectively (**Figure 4b**).^[4c] The resolved N 1s in **Figure 4c** reveals the co-existence of pyridinic N (397.5 eV) and Co-N (399.1 eV),^[14] with the former being the dominant species. It was recently reported that pyridinic N is the active site for oxygen reduction reaction (ORR).^[16] In addition, the Co-N bond also plays an important role in the ORR.^[14] Therefore, the enriched pyridinic N-doped carbon as well as Co-N bond present might have a positive effect on the electrocatalytic activity of NC@GC.

In the cobalt region (**Figure 4d**), characteristic peaks at 780.3 eV and 793.5 eV can be attributed to Co 2p_{3/2} and Co 2p_{1/2}, respectively. The deconvoluted Co 2p profile accounts for Co⁰, Co²⁺ and the shake-up (satellites) peaks (**Figure 4d**).^[4c] The first peak at 778.4 eV is consistent with the Co 2p_{3/2} binding energy of Co in a zero valent state.^[4c] The second peak maximum is found at 780.7 eV, which is attributed to Co in a 2+ valence state.^[17] The existence of Co²⁺ in the XPS analysis indicates that the Co nanoparticles on the surface of

NC@GC is sensitive to the aerobic atmosphere and can be oxidized slowly upon long storage in ambient air.^[5b, 18]

The control experiment indicates that NC@GC obtained at 800 °C showed the best ORR activity (**Figure S5**). Therefore, the following discussion including electrochemical activity and the application in Zn-air battery will only focus on the NC@GC obtained at 800 °C. The ORR activity of NC@GC was tested by cyclic voltammetry (CV) in 0.1 M KOH solution and the results are shown in **Figure 5a**. As anticipated, no noticeable reduction peak is seen in N₂-saturated aqueous KOH electrolyte. Switch of electrolyte to O₂-saturated KOH solution leads to the rising of a well-defined cathodic peak at 0.81 V, accounting for a pronounced ORR activity. To understand the electrocatalytic behaviors of NC@GC, rotating disk electrode (RDE) voltammograms were recorded from electrodes with NC, GC, NC+GC (physical mixture), NC@GC and benchmark Pt/C catalyst (20 wt% platinum on Vulcan XC-72 carbon) under the same experimental conditions (**Figure 5b**). In a typical test, one of such catalysts was loaded onto a glassy carbon RDE, and voltammetric curves were obtained in O₂-saturated 0.1 M KOH aqueous solution at a rotation rate of 1,600 rpm. The geometrical area of the electrode was used to calculate the current density.^[19] The ORR onset potentials for NC, GC, NC+GC, NC@GC and Pt/C were found to be 0.90, 0.99, 0.98 V, 1.0 V and 0.99 V, respectively. It is rather clear that in contrast to NC and GC, notable improvement is seen for NC@GC. As compared to Pt/C, NC@GC also shows a slightly more positive ORR onset potential (1.0 V *vs.* 0.99 V) but a steeper polarization curve with higher half-wave potential (0.93 V *vs.* 0.89 V), suggesting an even higher ORR activity. This extraordinary ORR activity can be attributed to the unique structure of NC@GC, which combines the advantages of both NC and GC. First, the good graphitization from GC (**Figure 2b and 3a**) improves electron transfer and results in high conductivity for the entire electrode. Moreover, N-doping into carbon contributed by NC also plays an important role in this unusual ORR activity.^[9] The presence of doped N with its electron rich nature, i.e. pyridinic N (**Figure 4c**), likely creates

partial positive charges on their adjacent carbon atoms. This facilitates the adsorption and activation of O_2 and thus accelerates ORR.^[16] The metallic Co cores in GC are ORR “boosters” as they improve the electron transport behavior to the carbon layer. It should be noted that Co nanoparticles are located on the shell of the NC@GC, which may contribute directly to the improved performance. A similar phenomenon was observed previously when iron was encapsulated within carbon nanotubes.^[11a] A further comparison on the onset and half-wave potentials of NC@GC and NC+GC (physical mixture) suggests a synergistic effect between these two types of carbons.^[13]

The electron transfer kinetics of NC@GC was investigated using rotating disk electrode setup at varied rotating rates, and the results are shown in **Figure 5c**. The current density (J) increases steadily as the rotation rate (ω) was elevated from 625 to 2,500 rpm. The relationship between J^{-1} and $\omega^{-1/2}$, i.e. the Koutecky-Levich (K-L) curves, were plotted and given as the inset of **Figure 5c**. The good linearity and parallelism of these plots at electrode potentials between 0.3 to 0.7 V suggest typical first-order reaction kinetics with respect to the dissolved O_2 concentration. The number of electrons (n) transferred per oxygen molecule (O_2) are calculated from the slopes using K-L equation (see details in the Experimental Section), and the obtained values in the range of 3.98 to 4.08 (**Figure S6**) suggest a desirable four-electron transfer dominated ORR process.

The ORR activity of NC@GC was further evaluated in rotating ring-disk electrode (RRDE) experiments conducted in alkaline solution. A typical sweeping voltammogram at a rotating rate of 1,600 rpm is shown in **Figure 5d**. The yield of HO_2^- was found below 10% (**Figure S7**) over the potential range of 0.1 V to 1.0 V, giving an n value of 3.69 to 4.0 (inset of **Figure 5d**). This is consistent with the results derived from the K-L plots of RDE measurements (inset of **Figure 5c**), confirming the efficient ORR with a pseudo 4-electron transfer reaction pathway for NC@GC.

The durability of NC@GC was evaluated by recording its current-time chronoamperometric responses in ORR, with benchmark Pt/C taken as control sample. As shown in **Figure 5e**, Pt/C suffers a rapid current loss at the initial stage of discharge and the total current loss was about 28% over the similar length of period. The rapid current loss for Pt/C at its initial stage is understandable, considering some of the Pt nanoparticles are prone to be detached from the carbon support or aggregate in alkaline medium.^[20] This degradation has been investigated by combining electrochemical measurements and identical location transmission electron microscopy.^[20] However, this sudden drop did not happen to our developed NC@GC (Figure 5e) as such problem of nanoparticle aggregation does not exist in the current catalyst system. This good stability also resulted from the unique structure of NC@GC. GC consists of highly graphitic carbon, which ensures good stability.^[6] The Co nanoparticles are fully covered with carbon layers. Such graphitic coating on metal can improve the stability of the metal. Therefore, our NC@GC core-shell catalyst exhibits good stability.

Methanol tolerance of ORR catalyst is also of great importance to direct methanol fuel cell application. The tolerance of NC@GC to the crossover effect of methanol was tested, together with the benchmark catalyst Pt/C as a control sample (**Figure 5f**). In general, the permeation of CH₃OH through polymer membrane from anode to cathode side adversely impacts the performance of catalyst on cathode. With the addition of CH₃OH, the current of Pt/C electrode underwent an immediate and sharp increase. In contrast, the NC@GC electrode shows negligible change. The outstanding performance of the latter as compared to Pt/C suggests the specificity of carbon based catalyst for ORR.^[11a]

The catalytic activity of the as-synthesized catalyst towards oxygen evolution has been investigated in alkaline solution (1 M KOH) in a standard three-electrode setup. During the measurement, the rotating rate was maintained at 1,600 rpm to remove the generated oxygen bubbles. Linear sweep voltammetry (LSV) curves of all the catalysts are shown in **Figure 6a**.

The NC@GC exhibits better OER activity than the pure NC, GC, the physical mixture of NC+GC and commercial Pt/C (**Figure 6a**). Even compared to the commercial Ir/C, the NC@GC showed slightly better OER activity. To achieve a current density of $j=10 \text{ mA cm}^{-2}$, it requires a lower potential (1.57 V vs. 1.59 V). Other than the large specific surface area and good conductivity from the NC@GC structure, it is believed that the synergetic effect between NC and GC in NC@GC is the main reason for its good performance.^[4c, 13] The strong interaction between NC and GC in NC@GC can significantly improve the electron transport and reaction kinetics during the OER.^[4c, 21]

Furthermore, the stability of NC@GC towards OER is assessed by repeated potential cycling for 1000 cycles and the results are shown in **Figure 6b**. It is clear that this catalyst exhibits negligible performance loss during the durability test.

On the whole, performance of the NC@GC catalyst benefits from good synergistic interaction and its unique structure. Additionally, the presence of doped nitrogen in the electrocatalyst as well as interaction between the Co nanoparticles and highly graphitized carbon layer could also contribute to the improved bifunctional catalytic activity of NC@GC. As such, NC@GC is a promising candidate for Zn-air battery and fuel cell applications.

As a proof-of-concept application, NC@GC was employed as an ORR catalyst in a primary Zn-air battery. The cell consisted of a NC@GC loaded carbon fiber paper as the air cathode, a thin Zn plate as anode and 6 M aqueous solution of KOH as the electrolyte, respectively (**Figure 7a**). Pt/C was also tested under the same conditions to provide a benchmark value. With an open circuit voltage of $\sim 1.30 \text{ V}$, the NC@GC-based battery delivers an almost constant voltage of 1.29 V when it was galvanostatically discharged at 5 mA cm^{-2} over 140 h (**Figure 7b**). The performance of NC@GC thus benefitted from its high stability toward ORR.^[4a] In contrast, the discharge voltage at this current density for Pt/C based Zn-air battery decreases from 1.31 V to 1.24 V over 140 h, which is 50 mV lower than that derived from the NC@GC-based battery (**Figure 7b**). As the discharge current density was increased to 10 mA

cm^{-2} and 30 mA cm^{-2} , it can be seen that the discharge voltages dropped to about 1.22 V and 1.15 V, respectively. In particular, sudden drop of the voltage occurs at ~65 h when discharged at 30 mA cm^{-2} , due to the gradually thinned Zn foil and the accumulated soluble zinc salts.^[4a]

Next, we evaluated the performance of NC@GC and Pt/C as air catalysts when used in rechargeable Zn-air batteries. The catalyst was loaded on a single cathode for the charge and discharge cycling experiments (**Figure 8a**). Zn plate and a solution of zinc chloride (0.2 M) in 6 M KOH were used as anode and electrolyte, respectively. Compared to the primary Zn-air battery, zinc chloride was introduced to the electrolyte, which ensures reversible Zn electrochemical reaction at the anode. Such a battery exhibited cycling stability when charged and discharged at 5 mA cm^{-2} (**Figure 8b**) with 1 h as one cycle time (**Figure S8**). The battery containing NC@GC exhibits lower charge and discharge voltage compared to Pt/C. This might be due to the effect of concentrated KOH solution on Pt/C^[13] and the better OER performance of NC@GC compared to Pt/C (**Figure 6a**). This observation is in agreement with the conclusions made from the primary Zn-air (**Figure 7**) and electrochemical (**Figure 5 and 6**) studies. Impressively, the battery with NC@GC can be operated at even higher current rate with high stability, as demonstrated in **Figure 8c**. At a current density of 20 mA cm^{-2} at 1 h per cycle, the voltage gap increased only about 0.07 V after 30 cycles.

3. Conclusion

In conclusion, we have successfully fabricated NC@GC core-shell materials which combine the unique advantages of NC and GC, respectively. For example, NC exhibits high surface area and high nitrogen content. On the other hand, GC contains Co nanoparticles which function as a catalyst booster as it possesses high crystallinity, good conductivity and stability. These properties resulted in good ORR and OER performances. NC@GC was also employed in primary and rechargeable Zn-air batteries that we constructed. NC@GC catalysts showed

stable and robust discharge performance in the primary Zn-air battery. Furthermore, NC@GC recorded lower charge and discharge voltages in the rechargeable Zn-air battery compared to Pt/C when tested under the same conditions. Impressively, the rechargeable Zn-air battery with NC@GC can be operated at even higher current density (20 mA cm^{-2}) with high stability. These excellent performances originate from its porous structure, high specific surface area, small charge transfer resistance, the N/Co-doping effect and synergistic interaction between NC and GC. The strategy reported herein can be further expanded to other MOF materials to develop new electrocatalysts with high activity.

4. Experimental Section

Chemicals and Materials: Experimental Details. Cobalt chloride (CoCl_2 , 97%, Sigma), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Sigma), 2-methylimidazole (MeIm, 99%, Sigma), methanol (99.8%, Sigma), Nafion 117 solution (5 wt%, Sigma), potassium hydroxide (99.9%, Sigma), 20 wt% platinum supported on Vulcan XC-72 carbon (Pt/C, E-Tek) and 20 wt% iridium on Vulcan XC-72 carbon (Ir/C, Premetek) were used as received. The aqueous solutions in this work were prepared from ultrapure water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$, obtained from a Milli Q Plus water purification system (Millipore, USA).

Synthesis of ZIF-8 and nitrogen-doped carbon (NC). In the synthesis of ZIF-8, a methanolic solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (810 mg, 40 mL) and a methanolic solution of MeIm (526 mg, 40 mL) were mixed under stirring for 12 h at room temperature. Then the mixture was transferred to autoclave and kept at 100°C for 12 h. The white precipitate was collected by centrifugation and washed with methanol several times. After dry at 80°C overnight, white powder was obtained (**Figure S1**). The obtained white powder was calcined by heating it up to 800°C at a temperature ramp of 5°C min^{-1} under Ar atmosphere and maintained at 800°C for 3 h to get NC.

Synthesis of ZIF-67 and graphitic carbon (GC). In a typical synthesis procedure, CoCl_2 (519 mg), polyvinylpyrrolidone (PVP, 600 mg) and MeIm (2,630 mg) were added into methanolic solution (80 mL) under stirring in sequence. Then the mixture was kept at room temperature for 12 h. The precipitates were collected via centrifugation and washed thoroughly with methanol. After dry at 80 °C, the bright purple powder of ZIF-67 was obtained (**Figure S1**).^[6] After cooling down to room temperature, the resultant powder was calcined by heating it up to 800 °C at a temperature ramp of 5 °C min⁻¹ under Ar atmosphere and maintained at 800 °C for 3 h to get GC.

Synthesis of ZIF-8@ZIF-67 and NC@GC. In a typical synthesis, ZIF-8 (80 mg) was dispersed in methanol (10 mL) by sonication for 30 min. After stirring for 20 min, a methanolic solution of CoCl_2 (177 mg, 3 mL) and a methanolic solution of MeIm (895 mg, 3 mL) were injected into the above solution, respectively. After stirring for another 5 min, the solution was transferred to autoclave and kept at 100 °C for 12 h. After cooling down to room temperature, the purple precipitate (**Figure S1**) was obtained by centrifugation, washing with methanol and dried at 80 °C. ZIF-8@ZIF-67 powder was calcined by heating it up to 800 °C at a temperature ramp of 5 °C min⁻¹ under Ar atmosphere and maintained at 800 °C for 3 h to get NC@GC.

Synthesis of ZIF-67@ZIF-8. The core-shell structure of ZIF-67@ZIF-8 has been tried to be synthesized using the same protocol of ZIF-8@ZIF-67.

Physical mixture of NC+GC. The obtained NC (100 mg) and GC (100 mg) powder were mixed physically.

Characterization. Crystal phase structure of NC@GC was studied using a Bruker D8 advanced diffractometer with Cu K α radiation source ($\lambda=1.5406$ Å). The surface morphology was characterized using a field emission scanning electron microscope (FESEM, JEOL JSM7600F) operating at an accelerating voltage of 5 kV. The fine nanostructure was characterized by a transmission electron microscope (TEM, JEOL, JSM-2100F) operating at

an accelerating voltage of 200 kV. The elements and their valence status in the sample were analyzed by X-ray photoelectron spectroscopy (XPS) with a monochromatic Al K α radiation (VGESCALAB 200i-XL). The graphitic structure was evidenced by Raman spectra collected under a RenishawinVia confocal Raman microscope with a 532 nm laser.

Electrochemical measurements. The electrochemical measurements were carried out on an Autolab PGSTAT302N (Metrohm) using a three-electrode cell configuration. Glassy carbon electrode (GCE, 5 mm in diameter), platinum foil (Pt) and saturated calomel electrode (SCE) were used as working electrode, counter electrode and reference electrode, respectively. All electrode potentials in this study refer to RHE by $E_{\text{RHE}} = E_{\text{SCE}} + 0.990 \text{ V}$ (0.1 M KOH) or $E_{\text{RHE}} = E_{\text{SCE}} + 1.051 \text{ V}$ (1 M KOH). To form a catalyst ink, 13 mg of catalyst and 65 μL of 5 wt% Nafion aqueous solution were dispersed in 2.4 mL of water/isopropanol (v/v, 2.5:1) mixed solvent by sonication for 2 h. 10 μL of the catalyst ink was applied to a glassy carbon rotating disk electrode (RDE) and allowed to dry in air, giving a catalyst loading of 0.25 mg cm^{-2} . The benchmark catalyst inks of commercial Pt/C or Ir/C were prepared in the following way. 4 mg of a catalyst and 13 μL 5 wt% Nafion aqueous solution into 1 mL of water/isopropanol (v/v, 2.5:1) mixed solvent by sonication for 30 min. 5 μL of such ink was pipetted onto a GCE, resulting in a catalyst loading of 0.1 mg cm^{-2} . The cyclic voltammogram (CV) profiles were obtained in N_2 - or O_2 -saturated 0.1 M KOH with a scan rate of 50 mV s^{-1} . Before the scanning, high-purity N_2 or O_2 was used to purge 0.1 M KOH for 30 min to achieve O_2 -free or O_2 -saturated electrolyte solution, respectively.

In ORR experiments, 0.1 M aqueous solution of KOH was universally used as the electrolyte. High-purity O_2 was used to purge the solution for 30 min to achieve O_2 -saturated electrolyte solution prior to the start of experiment, respectively. During the measurement, the flow of high-purity O_2 was maintained over the electrolyte in order to ensure the O_2 saturation. The rotating rate increased from 400 to 2,500 rpm in an O_2 -saturated electrolyte at a scan rate of 5 mV s^{-1} .

The number of transferred electrons (n) per O_2 molecule in the ORR and kinetic current density was calculated from the Koutecky-Levich equations:^[5b, 13, 19]

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

$$J_K = nFkC_0 \quad (3)$$

where J is the measured current density, J_K and J_L are the kinetic- and diffusion-limiting current densities, respectively; ω is the angular velocity of the disk ($\omega=2\pi N$, N is the linear rotation speed), n is the number of electrons transferred in ORR, F is the Faraday constant ($F=96,485 \text{ C mol}^{-1}$), C_0 is the bulk concentration of O_2 ($C_0=1.2\times 10^{-6} \text{ mol cm}^{-3}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($D_0=1.9\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), and ν is the kinematic viscosity of the electrolyte ($\nu=0.01 \text{ cm}^2 \text{ s}^{-1}$). The constant of 0.2 is adopted when the rotation rate is expressed in rpm.

The generated peroxide ion content during ORR was determined by a rotating ring-disk electrode (RRDE) setup with an E7R9 AFE7R9GCPT tip (Pine Instruments). RRDE electrode experiment was carried out at a rotating rate of 1,600 rpm. The formation of peroxide ions (HO_2^-) and n during the ORR can be calculated according to following equations:^[3, 13, 22]

$$X_{peroxide} = \frac{2I_R}{NI_D + I_R} \quad (4)$$

$$n = 4I_D / (I_D + I_R/N) \quad (5)$$

where $X_{peroxide}$, I_D , I_R and N are the percentage of HO_2^- formed, the disk current, ring current, and current collection efficiency of RRDE, respectively. N was calibrated using degassed 0.1 M NaOH with 0.01 M $K_3Fe(CN)_6$ at an electrode rotating speed of 1,600 rpm and a potential

scanning rate of 5 mV s⁻¹ (**Figure S9**). The calculated N is 38.8±0.2%, which is close to the manufacturer's data 37%.

Liner sweep voltammograms for OER are obtained in 1 M KOH at a scan rate of 5 mV s⁻¹ with a rotating speed of 1,600 rpm. The resulted curve was calibrated by *iR*-compensation. The solution resistance is determined by the electrochemical impedance spectroscopy (EIS) technique.

For the crossover effect of methanol (CH₃OH) test, the chronoamperometric response at 0.7 V was recorded in 0.1 M KOH with a rotation rate of 1,600 rpm. After obtaining the stable chronoamperometric response curve, 27.3 mL methanol was added to the above solution and the final concentration of methanol in KOH solution was 3 M.

Primary and rechargeable Zn-air battery (ZnAB) assembly and tests. The performance of primary Zn-air battery (ZnAB) was tested in a home-built electrochemical cell (**Figure 7a**). A two-electrode configuration was used by pairing NC@GC loaded carbon paper electrode (1.26 cm² loaded with 1.26 mg catalyst for the cell discharged at 5 mA cm⁻², and 0.785 cm² loaded with 0.785 mg catalyst for the cell discharged at 30 mA cm⁻²) with a Zn plate in 6 M KOH. Using Pt/C-based electrodes with similar catalyst loading to replace NC@GC loaded carbon paper electrode, the benchmarking Zn-air cells were also constructed and tested under the same experimental conditions.

The difference between the primary and rechargeable Zn-air cell is the electrolyte. In the rechargeable Zn-air cell (**Figure 8a**), zinc chloride (0.2 M) in 6 M KOH is used as the electrolyte. Others are the same as the primary ZnAB.

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Scheme 1. Illustrative expression of the procedures in the synthesis of (a) ZIF-8 and NC, (b) ZIF-67 and GC, and (c) ZIF-8@ZIF-67 and NC@GC.

Figure 1. (a) SEM image of NC@GC, (b) the corresponding EDS spectrum and EDS elemental mapping images of C, Co, N, Zn and O.

Figure 2. (a)TEM and (b) high-resolution TEM images of NC@GC.

Figure 3. (a) Wide-angle powder X-ray diffraction pattern and (b) Raman spectrum of NC@GC.

Figure 4. X-ray photoelectron spectroscopy (XPS) (a) full spectra of NC, GC and NC@GC, high-resolution and the corresponding deconvoluted spectra of (b) C 1s, (c) N 1s and (d) Co 2p in the NC@GC spectrum.

Figure 5. (a) Cyclic voltammograms of oxygen reduction reaction on NC@GC in O_2 -saturated and N_2 -saturated 0.1 M KOH aqueous solution at a scan rate of 50 mV s^{-1} ; (b) Rotating disk electrode (RDE) voltammograms of NC, GC, NC+GC (physical mixture), NC@GC and Pt/C at a rotation rate of 1,600 rpm; (c) RDE linear sweep voltammograms of NC@GC in O_2 -saturated 0.1 M KOH at various rotation rates and a scan rate of 5 mV s^{-1} . Inset: Koutecky-Levich plots of NC@GC at different electrode potentials; (d) Voltammograms of NC@GC measured with rotating ring-disk electrode (RRDE) in O_2 -saturated 0.1 M KOH at a rotating rate of 1,600 rpm and a potential scanning rate of 5 mV s^{-1} . The inset shows the corresponding electron transfer number at various potentials; (e) Chronoamperometric response of NC@GC and Pt/C at 0.7 V; (f) Chronoamperometric response of NC@GC and Pt/C upon addition of CH_3OH into O_2 -saturated 0.1 M KOH at 0.7 V. The final concentration of CH_3OH is 3 M.

Figure 6. (a) Polarization curves of Pt/C, NC, NC+GC (physical mixture), GC, NC@GC and Ir/C in 1 M KOH at a rotation rate of 1,600 rpm; (b) OER stability test of NC@GC, the initial and 1000th polarization curve in 1 M KOH.

Figure 7. (a) A schematic of the primary Zn-air battery; (b) Long-time discharge curve of a primary batteries using NC@GC cathode catalyst at three different current densities compared with the battery using Pt/C as the cathode catalyst.

Figure 8. (a) A schematic of the rechargeable Zn-air battery; (b) Cycling performance of the Zn-air battery using NC@GC and Pt/C at 5 mA cm^{-2} ; (c) Cycling performance of the Zn-air battery using NC@GC at 20 mA cm^{-2} .

Table of contents (TOC)

Keyword

metal-organic frameworks, electrocatalyst, oxygen reduction reaction, oxygen evolution reaction, Zn-air battery

Zhijuan Wang, Yizhong Lu, Ya Yan, Thia Yi Ping Larissa, Xiao Zhang, Delvin Wu, Hua Zhang, Yanghui Yang,^{*} Xin Wang^{*}

Core-shell carbon materials derived from metal-organic frameworks as an efficient oxygen bifunctional electrocatalyst

An efficient bifunctional electrocatalyst with core-shell structure, i.e. highly graphitic carbon (GC, carbonized from ZIF-8) on nitrogen-doped carbon (NC, carbonized from ZIF-67) (NC@GC), derived from ZIF-8@ZIF-67 has been obtained through hydrothermal and carbonization treatment. The resulted NC@GC combines their individual distinguished advantages, leading to high activities towards oxygen reduction and oxygen evolution reactions. As a proof-of-concept, the as-prepared NC@GC catalyst exhibits excellent performance in the primary and rechargeable Zn-air batteries.

Supporting Information

Core-shell carbon materials derived from metal-organic frameworks as an efficient oxygen bifunctional electrocatalyst

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Figure S1. Digital picture of white ZIF-8 solution, white ZIF-8 powder, purple ZIF-8@ZIF-67 solution, purple ZIF-8@ZIF-67 powder, and black NC@GC powder.

Figure S2. SEM image of the product used to try to synthesize core-shell ZIF-67@ZIF-8.

Figure S3. Wide-angle powder X-ray diffraction (XRD) pattern of ZIF-8@ZIF-67.

Figure S4. SEM images of (a) NC and (b) GC.

Figure S5. Rotating disk electrode (RDE) voltammograms of NC@GC carbonized with different temperature at a rotation rate of 1,600 rpm in O₂-saturated 0.1 M KOH.

Figure S6. The number (n) of electrons transferred per oxygen molecule (O₂) in ORR for NC@GC obtained from its Koutecky-Levich plots shown in **Figure 5c**.

Figure S7. Calculation results of measured yield of HO_2^- using equation 4 (see experimental section in detail) based on RRDE result (**Figure 5d**).

Figure S8. Cycling performance of Zn-air battery at 5 mA cm^{-2} in long cycle period (1 h per cycle).

Figure S9. Ring ($\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$) and disk ($\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$) currents for the determination of collection efficiency of RRDE loaded with NC@GC catalyst. The electrolyte is degassed 0.1 M NaOH with 0.01 M $\text{K}_3\text{Fe}(\text{CN})_6$. The rotating rate of RRDE is 1,600 rpm. The collection efficiency is calculated to be $(36.2 \pm 0.2)\%$, close to the manufactures data 37%.