Ni$_3$Fe-N Doped Carbon Sheets as a Bifunctional Electro catalyst for Air Cathodes

Gengtao Fu, Zhiming Cui,* Yifan Chen, Yutao Li, Yawen Tang,* and John B. Goodenough*

A promising bifunctional electrocatalyst is reported for air cathodes consisting of Ni$_3$Fe nanoparticles embedded in porous nitrogen-doped carbon sheets (Ni$_3$Fe/N-C sheets) by a facile and effective pyrolysis-based route with sodium chloride (NaCl) crystals as a template. The Ni$_3$Fe/N-C sheets show excellent catalytic activity, selectivity, and durability toward both the oxygen-reduction and oxygen-evolution reactions (ORR and OER). They are shown to provide a superior, low-cost cathode for a rechargeable Zn-air battery. At a discharge–charge current density of 10 mA cm$^{-2}$, the Ni$_3$Fe/N-C sheets enable a Zn–air battery to cycle steadily up to 420 h with only a small increase in the round-trip overpotential, outperforming the more costly Pt/C + IrO$_2$ mixture catalyst (160 h). With the simplicity and scalability of the synthetic approach and its remarkable bifunctional electrocatalytic performance, the Ni$_3$Fe/N-C sheets offer a promising rechargeable air cathode operating at room temperature in an alkaline electrolyte.

1. Introduction

Rechargeable Zn–air batteries have been targeted for electrical-energy storage because of their high theoretical energy density (1086 Wh kg$^{-1}$), low cost, and safety.$^{[1–13]}$ The rechargeable reactions at an air cathode are $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^-$ on discharge, the oxygen reduction reaction (ORR) moves to the right and on charge, the oxygen evolution reaction (OER) moves to the left.$^{[1,2]}$ Catalysts for these two reactions are critical components for a rechargeable air cathode. The best solution would be a single cathode on which both reactions are activated independently of one another by a bifunctional catalyst that is stable over a long cycle life. To date, the best catalytic performance is obtained with Pt-based catalytic particles for the ORR and either IrO$_2$ or RuO$_2$ for the OER. However, the high cost and limited cycle life of these electrocatalysts have made these materials increasingly unattractive.$^{[1,2,4–6]}$ Therefore, it is critical to develop highly active, stable, and low cost alternatives for use in a single cathode.

Emerging as a class of outstanding alternatives, the transition-metals (Mn, Co, Ni, Fe, etc) and their derivatives have attracted great attention recently as the oxygen electrocatalysts.$^{[14–22]}$ In 1952, Edison and Jungner first discovered the poisoning effect of Fe impurities on Ni-based alkaline batteries,$^{[22]}$ and Ni–Fe alloys have since been studied and shown to be active for the OER but not for the ORR.$^{[17–20,23–28]}$ Moreover, recent studies have demonstrated that heteroatoms (N, P, or S) doped-carbon materials can be efficient, low-cost, metal-free alternatives to Pt-based catalysts for the ORR.$^{[29–35]}$ Therefore, attaching a Ni-Fe alloy as a nanoparticle on heteroatoms doped carbon is a logical strategy for a bifunctional electrocatalyst of a single rechargeable air cathode. However, conventional methods that disperse alloy nanoparticles on a carbon-based material have failed to give well-anchored nanoparticles; loss of the nanoparticles from the surface degrade the performance.$^{[36,37]}$

Herein, we report the design and synthesis of Ni$_3$Fe nanoparticles embedded in N-doped 2D porous graphitic carbon sheets (Ni$_3$Fe/N-C sheets) and demonstrate the Ni$_3$Fe/N-C sheets are a highly active and stable bifunctional electrocatalyst for the ORR and OER. Embedding the Ni$_3$Fe nanoparticles within the 2D graphitic carbon sheets stabilizes the composite to give a superior long-term cycling stability. We demonstrate a Zn-air battery with Ni$_3$Fe/N-C sheets as the air cathode shows much better rechargeable performance and a greater cycle life than that with a Pt/C + IrO$_2$ mixture as the cathode catalyst.

2. Results and Discussion

2.1. Characterization of the Samples

The 2D porous Ni$_3$Fe/N-C sheets were fabricated by a facile and effective dissolution–recrystallization–pyrolysis process under NH$_3$ atmosphere with Ni(Ac)$_2$, Fe(Ac)$_2$, chitosan (CS), and NaCl as raw materials, as illustrated in Figure 1a. Here, CS was chosen as the carbon source because it not only has abundant carbon atoms but also is a powerful chelating agent.
which makes it easy to form complexes with transition-metal ions like Ni(II) and Fe(II) (Figure S1, Supporting Information), as confirmed by the Fourier transform infrared (FT-IR) spectra (Figure S2, Supporting Information). As a result, Ni(II)/Fe(II) can be homogenously distributed in the CS framework at molecular dimension. After the pyrolysis, CS is transformed to a porous carbon while the metal cations are reduced to Ni$_3$Fe alloy nanoparticles. Remarkably, CS molecules possess outstanding film-forming ability on the surface of the selected template, which provides an excellent platform for the construction of sheet-like structures (Figure S3, Supporting Information). In this work, we selected NaCl as the solid synthetic template because it is more easily precipitated than CS and metal precursors during recrystallization. It is noteworthy that the excessive NaCl involved in the synthesis could effectively avoid the agglomeration of the obtained products. During the pyrolysis, CS is turned into molten syrup and carboxyl groups depart from the CS and metal precursors in the form of CO$_2$. The molten syrup of CS could be easily blown to form bubbles in the presence of gas, endowing the products with porosity. Moreover, NH$_3$ as a nitrogen source ensured that N was continuously doped into carbon with increasing pyrolysis time, thus generating the Ni$_3$Fe/N-C composite. Finally, the Ni$_3$Fe/N-C@NaCl was treated with water/ethonal to dissolve the NaCl for obtaining pure Ni$_3$Fe/N-C sheets. Embedding the Ni$_3$Fe nanoparticles within the 2D carbon sheets can effectively avoid the separation of the alloy particles from the carbon sheet during the washing process, thus maintaining the structural integrity of the sheet-like Ni$_3$Fe/N-C composite materials. The experimental details are presented in the Experimental section. The synthetic strategy outlined here can be adapted easily for large-scale manufacturing due to its process simplicity, the accessibility of precursors, and the recycling of NaCl. Figure 1b shows the X-ray powder diffraction (XRD) pattern of the Ni$_3$Fe/N-C sheets. The XRD spectrum shows a good crystalline structure of Ni$_3$Fe as evidenced by sharp diffraction peaks corresponding to (111), (200), and (220) crystal facets from the face-centered-cubic Ni$_3$Fe phase (space group: Pm-3m (221), JCPDS (Joint Committee on Powder Diffraction Standards) No. 65-3244). A broad diffraction peak at $23.1^\circ$ was also observed, corresponding to the (002) reflection of the graphitic carbon. The XRD results, Figure S4 (Supporting Information), prove that the Ni$_3$Fe alloy phase was successfully introduced into the carbon matrix. The XRD patterns of the samples annealed under air atmosphere at different temperatures for 6 h indicate that the Ni$_3$Fe phase is stable in air. The Ni$_3$Fe content of the Ni$_3$Fe/N-C composite was determined by thermogravimetric analysis (TGA, Figure 1c) during which the Ni$_3$Fe was oxidized to NiO and Fe$_3$O$_4$ completely, and carbon was oxidized to CO$_2$ (Figure S5, Supporting Information). According to the final content of metal oxide, the original content of Ni$_3$Fe was calculated to be 34.92 wt%.

The morphology and structure of the Ni$_3$Fe/N-C sheets were characterized with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A full-view panoramic SEM image (Figure 2a) reveals a predominantly 2D sheet-like structure with high density. Figure 2b shows a magnified SEM image of the Ni$_3$Fe/N-C sheets. The Ni$_3$Fe nanoparticles with uniform particle size are homogenously embedded on the surface of the carbon sheets (white arrows), and many pores are also observed on the surface (red arrows). The Ni$_3$Fe particles are rarely aggregated, indicating a good dispersion in the carbon sheets. The thickness of the Ni$_3$Fe/N-C sheets was estimated to be about 41 nm taken from a cross-section of a single Ni$_3$Fe/N-C sheet (Figure S6, Supporting Information). TEM images display a similar result to the SEM images, as shown in Figure 2c and Figure S7a (Supporting Information). The histogram of Ni$_3$Fe particle diameters was obtained from a sampling size of 100 particles in random regions (Figure S7b, Supporting Information). It shows a relatively narrow particle-size distribution with an average size of $\approx 39.7$ nm. Figure 2d shows the high-resolution TEM (HRTEM) image taken from a
single Ni$_3$Fe particle marked by red square in Figure 2c. The interplanar spacing of the adjacent fringes was measured to be $\approx 0.206$ nm, which matches well with the (111) facet of Ni$_3$Fe (JCPDS No. 65-3244).

The energy dispersive X-ray analysis (EDX) mappings (Figure 3a) and line scanning profiles recorded through an individual Ni$_3$Fe particle (Figure S8, Supporting Information) reveal that a homogeneous distribution of both Ni and Fe in the Ni$_3$Fe phase, which is further indicative of Ni$_3$Fe alloy formation. The molar ratio of Ni and Fe is around 73.8:26.2 as confirmed by the EDX spectrum (Figure 3b), in agreement with the stoichiometric ratio of Ni/Fe. Moreover, the N element is clearly evidenced in the EDX mappings and the N signals well match the C signals, indicating that the doped N is uniformly distributed in the carbon sheets. A X-ray photoelectron spectroscopy (XPS) survey-scan spectrum further confirmed the existence of N atoms in the Ni$_3$Fe/N-C sheets (Figure 3c). The atomic percentages of C, N, Ni, and Fe are estimated to be 81.8%, 6.2%, 8.8%, and 3.2%, respectively. The corresponding weight percentages of C, N, Ni, and Fe are calculated to be 55.6%, 4.9%, 29.4%, and 10.1%, respectively. The high-resolution N1s spectrum (the inset in Figure 3c) can be deconvoluted into three peaks located at 398.3, 399.5, and 400.6 eV which can be assigned to pyridinic-N, pyrrolic-N, and graphitic-N, respectively.[29,41,42] Considering the high content of pyridinic-N and graphitic-N in the Ni$_3$Fe/N-C sheets, an excellent catalytic performance toward oxygen redox catalysis is anticipated owing to the fact that the pyridinic-N species improves the onset potential for the ORR and the graphitic-N greatly increases the limiting current density.[30,31]

For a comparison, the Ni$_3$Fe/C sheets were synthesized through similar steps to the Ni$_3$Fe/N-C sheets, except for the use of Ar atmosphere instead of NH$_3$. The characterization of Ni$_3$Fe/C sheets is presented in Figure S9 (Supporting Information). Although CS molecules contain a small amount of N atoms, the N signals were hardly detected in the Ni$_3$Fe/C sheets, as evidenced by the XPS spectrum (Figure S10, Supporting Information). The presence of NaCl in the synthesis was found to play an important role in the formation of the 2D sheet-like structure. When observing the SEM images (Figure S11, Supporting Information) and EDX mappings (Figure S12, Supporting Information) of the Ni$_3$Fe/N-C@NaCl, we found that the Ni$_3$Fe/N-C sheets were actually formed on the NaCl surface. In the absence of NaCl, only micrometer sized carbon blocks with Ni$_3$Fe nanoparticles embedded were obtained (bulk Ni$_3$Fe/C), as shown in Figure S13 (Supporting Information). The results indicate that the NaCl surface functions as the template to direct the formation of the 2D sheet-like structure.[43,44]

The Ni$_3$Fe loadings on the carbon support determined by TGA are 36.70 wt% for Ni$_3$Fe/C sheets and 35.44 wt% for bulk Ni$_3$Fe/C, respectively. Due to the release of gases during the pyrolysis,[45] many pores or much free space would be produced within the carbon matrix, as proved by N$_2$ adsorption–desorption isotherms (Figure S14, Supporting Information). All the samples exhibit the obvious profiles of the hysteresis loops, indicating the adsorption–desorption characteristics of porous materials. It was found that the Brunauer–Emmett–Teller (BET) surface area was 447.0 m$^2$ g$^{-1}$ for Ni$_3$Fe/N-C sheets, 361.5 m$^2$ g$^{-1}$ for Ni$_3$Fe/C sheets, which is much higher than that of the bulk Ni$_3$Fe/C (62.7 m$^2$ g$^{-1}$). In addition, the Ni$_3$Fe/N-C sheets show a relatively high BET surface area compared with that of the Ni$_3$Fe/C sheets, which can be attributed to an activation effect under NH$_3$.[46,47] This observation shows that the NH$_3$ activation not merely provides a nitrogen source but also dramatically improves the porosity of the samples. The larger
surface area is anticipated to provide more active surface sites, leading to a higher electrocatalytic activity.

2.2. Bifunctional Electrocatalytic Activities for the OER and ORR

Figure 4a shows the OER polarization curves for the Ni$_3$Fe/N-C sheets, Ni$_3$Fe/C sheets, bulk Ni$_3$Fe/C, and IrO$_2$ catalysts in O$_2$-saturated 0.1 M KOH (Potassium hydroxide) obtained with a rotating disk electrode (RDE). As observed, the Ni$_3$Fe/N-C sheets exhibit much greater current density (9.88 mA cm$^{-2}$) than those of the Ni$_3$Fe/C sheets (5.27 mA cm$^{-2}$) and bulk Ni$_3$Fe/C catalysts (2.85 mA cm$^{-2}$), they even exceed that of the commercial IrO$_2$ (8.26 mA cm$^{-2}$) at a potential of 1.60 V (vs reversible hydrogen electrode (RHE)). This performance indicates that the Ni$_3$Fe/N-C sheets are a highly active OER catalyst. The operating overpotentials to deliver a 10 mA cm$^{-2}$ current density were then compared for different catalysts. The overpotentials corresponding to the current density of 10 mA cm$^{-2}$ follow the order (Figure 4b): Ni$_3$Fe/N-C sheets (0.37 V) < IrO$_2$ (0.39 V) < Ni$_3$Fe/C sheets (0.42 V) < bulk Ni$_3$Fe/C (0.46 V). Particularly, the overpotential of the Ni$_3$Fe/N-C sheets acquired at 10 mA cm$^{-2}$ was comparable to those of other reported OER catalysts (Table S1, Supporting Information). The Tafel slope was determined by fitting polarization data to the Tafel equation ($\eta = a + b \log|J|$), where $\eta$ is the overpotential, $b$ is the Tafel slope, and $J$ is the current density. As shown in Figure 4c, the Ni$_3$Fe/N-C sheets exhibit the smallest Tafel slope (77 mV dec$^{-1}$) relative to those of the Ni$_3$Fe/C sheets (81 mV dec$^{-1}$), bulk Ni$_3$Fe/C (91 mV dec$^{-1}$), and IrO$_2$ (110 mV dec$^{-1}$) catalysts, indicating the outstanding OER kinetics of the Ni$_3$Fe nanoparticles supported N-doped carbon. In comparison with the Ni/N-C sheets (Figure S15d, Supporting Information) and Fe/N-C sheets (Figure S16b, Supporting Information), the Ni$_3$Fe/N-C catalyst reduces remarkably the OER overpotential, indicating that the Ni$_3$Fe alloy gives a significant enhancement of the OER activity. Moreover, since N-doped carbon alone shows a very poor activity for the OER (Figure S17d, Supporting Information), the remarkable OER activity measured with the Ni$_3$Fe/N-C sheets can be attributed to the Ni$_3$Fe phase. The alloy of Ni$_3$Fe possesses a stable crystal structure of ordered Fe and Ni atoms, which not only injects electrons efficiently to the hydroxide but also is more resistant to oxidization than Ni metal. N-rich doped carbon enhances the electronic interaction with nearby metal atoms and increasing electronic conductivity.$^{[47–49]}$ The stability of all the catalysts was assessed by chronoamperometry as shown in Figure 4d.
Continuous operations of the oxygen evolution for 12 000 s at 1.60 V on Ni3Fe/N-C sheets, Ni3Fe/C sheets, bulk Ni3Fe/C, and IrO2 electrodes cause ≈49.7%, 57.1%, 62.2%, and 61.5% decrease in current density, respectively. Although the Ni3Fe/N-C sheets are more stable than other catalysts, they undergo obvious performance degradation, which is mainly due to corrosion of the carbon support at relatively high potentials.[50,51]

The ORR electrocatalytic activities of the Ni3Fe/N-C sheets, Ni3Fe/C sheets, and bulk Ni3Fe/C catalysts were also investigated and compared in O2-saturated 0.1 m KOH using a RDE. The onset potential of the ORR, which was defined as the potential corresponding to −10 μA cm−2,[52] was used to evaluate ORR activity. Remarkably, the Ni3Fe/N-C sheets exhibit a high ORR onset potential of 0.90 V, which is much more positive than those of the Ni3Fe/C sheets (0.84 V) and bulk Ni3Fe/C (0.73 V) catalysts (Figure 5a). An enhancement of ORR activity on Ni3Fe/N-C sheets (0.78 V) was also indicated by its reduction potential at a current density of −3 mA cm−2 relative to Ni3Fe/C sheets (0.70 V) and bulk Ni3Fe/C (0.36 V), which proves that oxygen is more easily reduced on Ni3Fe/N-C sheets. The Ni3Fe/N-C sheets sample was benchmarked with a commercial Pt/C electrocatalyst for the ORR. Although the reduction potential of the Ni3Fe/N-C sheets (0.78 V) is still more negative by 70 mV compared to the Pt/C (0.85 V), its ORR activity is comparable to many of the nonnoble metal-based catalysts that have been reported (Table S2, Supporting Information). The rotating ring-disk electrode (RRDE) measurements were further employed to quantify the catalysts’ ORR efficiency (Figure S18, Supporting Information). The hydrogen peroxide (H2O2) yield and the electron transfer number n were calculated from the corresponding disk and ring currents (Figure 5b). The ORR on Ni3Fe/N-C sheets yields about 6.3%–12.4% HO2− over the potential range from 0.2 to 0.7 V with n ranging from 3.75 to 3.87, which shows it is approximately close to that of a Pt/C catalyst (HO2−: 5.4%–8.6%; n: 3.82–3.89), which suggests that the desirable four-electron reduction is dominant in the ORR activity of Ni3Fe/N-C sheets with a lower HO2− yield and higher n than those of the Ni3Fe/C sheets and bulk Ni3Fe/C catalysts. The remarkable ORR activity measured with the Ni3Fe/N-C sheets is mainly contributed from the N-doped carbon and/or the N-metal interaction on the carbon supports,[21,22] since the Ni3Fe alone shows a very poor activity for the ORR (Figure S19b, Supporting Information). The long-term stability of all samples was investigated by chronoamperometry at 0.7 V for 12 000 s in O2-saturated 0.1 m KOH solution (Figure 5c). During the period, about 96.5% of the original current density is retained for the Ni3Fe/N-C sheets electrode, whereas the Ni3Fe/C sheets, bulk Ni3Fe/C, and Pt/C electrodes show much higher current loss of 16.0%, 27.6%, and 25.9%, respectively, indicating a superior stability of the Ni3Fe/N-C sheets. The Ni3Fe nanoparticles uniformly embedded in the carbon sheets surface can strengthen their interfacial contact and suppress the agglomeration/dissolution of the Ni3Fe nanoparticles, thus enhancing the OER and ORR electrocatalytic stabilities.

With the synergistic effect arising from the Ni3Fe particles and N-doped carbon, the Ni3Fe/N-C sheets can be anticipated...
to be a highly active bifunctional OER and ORR electrocatalyst. The overall oxygen electrode activities were evaluated by the difference in potential between the OER current density at 10 mA cm\(^{-2}\) and the ORR current density at -3 mA cm\(^{-2}\) (\(\Delta E = E_{j10} - E_{j-3}\)). The lower the \(\Delta E\) value is, the better bifunctional activity the catalyst has. [1,5,31,42] As shown in Figure 5d, the Ni\(_3\)Fe/N-C sheets exhibit the smallest \(\Delta E\) with a value of 0.84 V among the studied catalysts. More importantly, such a \(\Delta E\) value is even smaller than state-of-the-art Ir/C, Ru/C and most of the many nonnoble metal-based bifunctional catalysts reported before (Table S3, Supporting Information), confirming the high bifunctional activity of the Ni\(_3\)Fe/N-C sheets for OER and ORR. Based on the structure−property relationship, the 2D porous architecture also contributes to its efficient OER and ORR activities. The 2D porous carbon sheets with high BET surface area can provide more catalytically active sites and facilitate the mass transport (i.e., oxygen and electrolyte)\[47,48\] and electron transport\[34\] during the reactions.

2.3. Rechargeable Zn-Air Batteries

To evaluate the utility of the Ni\(_3\)Fe/N-C sheets, a rechargeable Zn-air battery was built, in which a Zn plate was used as the anode and the Ni\(_3\)Fe/N-C sheets electrode as the air-cathode. The Zn-air battery configuration is shown in Figure S20 (Supporting Information). Figure 6a,b shows the total 105 cycles voltage profiles as well as the enlarged 1st and 105th cycle voltage profiles. Since the discharge and charge voltage profiles of Zn-air batteries are almost flat, we represent the activity of the catalysts by the cell voltage at the end of discharge and charge of each cycle. The voltaic efficiency is calculated based on the discharge end voltage divided by charge end voltage. The initial round-trip overpotential is 0.78 V, contributing to a volatile efficiency of 61.4%. After 105 cycles for 420 h, the round-trip overpotential increased to 0.98 V, leading to a residue voltaic efficiency of 51.8%. This catalyst gives among the best cycle performances reported so far for Zn-air batteries with alkaline catholyte (Table S4, Supporting Information). For comparison, a conventional Pt/C + IrO\(_2\) mixture catalyst was also tested under the same conditions. The round-trip overpotential increases from 0.74 V at the 1st cycle to 1.07 V at the 40th cycle, while the voltaic efficiency decreased dramatically from 62.9% at the 1st cycle to 47.7% at the 40th cycle. The specific capacity was measured according to the consumption of Zn. At a current density of 10 mA cm\(^{-2}\), Ni\(_3\)Fe/N-C sheets enabled a Zn-air battery with a specific capacity of 528 mA h g\(_{\text{Zn}}\)\(^{-1}\), corresponding to an energy density of \(\approx634\) Wh Kg\(_{\text{Zn}}\)\(^{-1}\). Clearly, the developed Ni\(_3\)Fe/N-C sheets catalyst not only possess high intrinsic catalytic activity and stability, but also enable Zn-air batteries with a high cell efficiency and a long cycle life.

3. Conclusion

In summary, we demonstrated a facile and effective pyrolysis route for the synthesis of Ni\(_3\)Fe nanoparticles embedded in
obtain very fine powders. Subsequently, 18.0 mL of distilled water and 2.0 mL acetic acid were added into the above mixture with stirring. After stirring for 2 h, the resultant mixture was dried in a drying oven at 80 °C (12 h) for recrystallization of the metal and carbon precursors on the surface of the NaCl. Finally, the mixture was calcined in a tube furnace at 750 °C under a flow of 5% NH₃ in an Ar atmosphere for 6 h (ramp rate: 5 °C min⁻¹). Once cooled down to room temperature, the obtained puffy product was washed with distilled water and absolute alcohol several times to remove the NaCl and subsequently dried at 60 °C.

**Physicochemical Characterization:** The phase purity and crystallinity of the products were identified by XRD on a Rigaku MiniFlex 600 i diffractometer with Cu Kα radiation (λ = 0.15406 nm). SEM and EDX were performed with a Hitachi S5500 SEM/STEM (scanning TEM). TEM and STEM were performed with a JEOl 2010F TEM/STEM operated at 200 kV. TGA of the samples was carried out with a Perkin-Elmer thermal analysis system. Measurements were made by heating from 40 to 650 °C at a heating rate of 10 °C min⁻¹ under air atmosphere. BET specific surface area was measured at 77 K with a Micromeritics ASAP 2050 system. XPS was carried out on a Thermo VG Scientific ESCALAB 250 spectrometer with an Al Kα x-ray radiator. The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. FT-IR spectroscopy was carried out with a Nicolet 520 SXFTIR spectrometer.

**Electrochemical Measurements:** All electrochemical tests were performed on an Autolab Electrochemical Instrumentation equipped with high-speed rotators from Pine Instruments. A conventional three-electrode system was used, including a RDE or RRDE as the working electrodes (0.196 cm²), a Pt wire as the auxiliary electrode, and a Ag/AgCl (1 M NaCl) electrode as the reference electrode. All potentials are reported versus the RHE, and for conversion of the obtained potential (vs Ag/AgCl) to RHE, the following equation was used: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0592 \, \text{pH} + 0.1972 \, (\text{in } 1 \, \text{M KCl})$. $E_{\text{RHE}} = +0.235 \text{V, pH = 12.9 for } 0.3 \text{ M KOH}$.

Electrodes were prepared by drop-casting ink containing catalyst powder on a glassy carbon electrode. Typically, 5 mg of the electrocatalyst sample was sonicated in a mixture of 1.9 mL ethanol and 100 μL neutralized Nafion (5 wt%, Sigma-Aldrich) for 30 min to form a homogeneous catalyst ink. The catalyst ink was then coated onto the RDE or RRDE at a loading of 10 μg and dried at room temperature (loading density of ≈0.13 mg cm⁻²). The OER and ORR activities of catalysts were measured via the RDE voltammograms in 0.1 M KOH electrolyte at predefined rotation rates and a scan rate of 5 mV s⁻¹. Pure oxygen gas (99.9%) was purged for 30 min before each RDE experiment to make the electrolyte saturated with oxygen. For the RRDE measurements, catalyst inks and electrodes were prepared by the same method as for RDE. The disk electrode was scanned at a rate of 5 mV s⁻¹, and the ring potential was constant at 1.3 V versus RHE. The percentage of HO₂⁻ intermediate production (%HO₂⁻) and electron transfer number (n) were determined by the followed equations[33–35]

$$% \text{HO}_2^- = \frac{200I_r}{N_{\text{dis}} + I_d} \quad n = \frac{4N_{\text{dis}}}{N_{\text{dis}} + I_d}$$

where $I_d$ is the disk current, $I_r$ is the ring current, and N is the current collection efficiency of the Pt ring, which was determined to be 0.37.

The Zn-air batteries tests were performed with a homemade Zn-air full cell. The catalysts coated on a carbon paper and a polished Zn plate was used as the air cathode and anode, respectively. A 0.2 M ZnCl₂ + 6 M KOH mixed solution was used as the electrolyte (Note: containing 0.2 M ZnCl₂ to facilitate the reversible Zn electrochemical reactions). A Land CT2001A system was used to carry out the cycling test with a five-minute rest time between each discharge and charge at a current density of 10 mA cm⁻². Each discharge and charge period was set to be 2 h. The discharge and charge voltage profiles were collected by two independent Land CT2001 channels alternatively.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.
Acknowledgements

G.F. and Z.C. contributed equally to this work. Physical measurements including TEM, XPS and TGA were supported by the National Natural Science Foundation of China (Grant Nos. 21376122 and 21273116), National and Local Joint Engineering Research Center of Biomedical Functional Material and the Priority Academic Program Development of Jiangsu Higher Education Institutions. The rest of the work was supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Science Engineering under Award No. DE-SC0005397.

Received: June 2, 2016
Revised: July 6, 2016
Published online:
