Co@CoO Core-shell Nanoparticles Immobilized on Co-N-doped Carbon as a Trifunctional Electrocatalyst for Oxygen Reduction, Oxygen Evolution and Hydrogen Evolution Reactions

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Co@CoO core-shell nanoparticles immobilized on Co-N-doped carbon was successfully developed using shrimp-shell derived N-doped carbon nanodots as precursor by a combined approach of polymerization and pyrolysis, as an electrocatalyst exhibiting trifunctional catalytic activity toward oxygen reduction, oxygen evolution and hydrogen evolution reactions and high performance in rechargeable zinc-air battery.

Electrocatalysts for oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are of particular significance for some promising clean energy technologies such as metal-air batteries, fuel cells and water splitting to generate hydrogen and oxygen.^{1,2} Moreover, effective rechargeable metal-air batteries and fuel cells require bifunctional catalysts with low overpotentials for both the OER and ORR.^{1,2} Bifunctional electrocatalysts for the OER and HER together in the same electrolyte is of practical values to accomplish overall water splitting.³ However, current precious metal Pt-based electrocatalysts and iridium/ruthenium oxide-based electrocatalysts cannot meet the practical requirements of these energy devices owing to their non-bifunctional ORR/OER or OER/HER activity and high cost/source scarcity.⁴ Therefore, development of multifunctional electrocatalysts with high activity at low cost remains a great challenge for the practical applications of related energy devices.

Up to now, various transition metal cobalt-based materials have been reported for HER, such as metal Co,⁵ CoS₂,⁶ CoP,⁷ and CoSe,⁸ showing high electrocatalytic HER activity. Recently, cobalt oxides/(oxy)hydroxides have demonstrated better catalytic activity toward OER—the other half reaction of water splitting.^{9,10} This means that cobalt-based materials with

different cobalt active species are capable of accomplishing overall water splitting to produce hydrogen and oxygen.^{3,10,11} However, the pure metal Co or Co_xO_y material possesses many disadvantage features, such as the easy accumulation and low conductivity, which would decrease the catalytic active sites and hamper the transport of electrons or protons during the electrocatalysis process.^{12,13} Recently, it is noteworthy that the cobalt-carbon based electrocatalysts have demonstrated bifunctional electrocatalytic activities, such as N-CG-CoO¹⁴ and Co1-xFexS@N-MC¹⁵ for ORR/OER; CoOx@CN¹⁶ and CoMnO@CN¹⁷ for OER/HER. The introduction of graphitic carbon not only improves electron transfer and electrocatalysis-related mass transport during the electrocatalysis, also the formed Co-N_x moieties in graphitic carbon structure provide catalytic active sites for high performance ORR.^{8,18,19} Based on the above discussion, design and development of carbon-based electrocatalysts with cobalt-related active species including metal Co, cobalt oxides and Co-N doping may realize the multifunctionality of ORR, OER and HER.

Herein, we report the synthesis of Co@CoO core-shell nanoparticles immobilized on Co-N-doped carbon (Co@CoO/Co-N-C) using shrimp-shell derived N-doped carbon nanodots (N-CNs) as carbon and nitrogen sources by a combined approach of polymerization and pyrolysis. Fig. 1 shows a schematic illustration of the synthesis of Co@CoO/Co-N-C catalysts (see experimental section for detailed information, ESI†). The experimental results demonstrate that Co@CoO/Co-N-C obtained at a pyrolysis of 800 °C (Co@CoO/Co-N-C-800) exhibits a microporous structure and high surface area of 647.7 m² g⁻¹. As electrocatalyst, Co@CoO/Co-N-C-800 displays superior trifunctional ORR, OER

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Fig. 1 Schematic illustration of the synthesis of Co@CoO/Co-N-C.

and HER catalytic activity in alkaline media. Further, Co@CoO/Co-N-C-800 was evaluated as air cathode material for rechargeable Zn-air battery measurements, exhibiting high performance and recycling stability. Simultaneously, Co@CoO/Co-N-C-800 was also used as anode and cathode material, demonstrating high capability of water splitting to generate hydrogen and oxygen.

Our previous report has demonstrated that shrimp-shell derived carbon nanodots possess small nanodot sizes (1.5~5.5 nm) and surface rich N- and O-containing functional groups, favorable for further assembling and transforming into N-doped graphitic carbon for ORR.²⁰ In this work, shrimp-shell derived N-CNs can be used as carbon and nitrogen sources to fabricate cobalt-based N-doped carbon material for multifunctional electrocatalysis applications. After polymerization, Co²⁺ contained composite exhibits particle-like aggregates (Fig. S1, ESI[†]), and similar morphology can be obtained for further pyrolytic sample (Fig. S2, ESI[†], take Co@CoO/Co-N-C-800 as an example). Fig. 2a shows the XRD patterns of Co@CoO/Co-N-C composites obtained at different pyrolysis temperatures. As shown, all pyrolytic samples exhibit an inter-plane (002) diffraction peak at around 24.7°, ascribed to graphitic carbon.²¹ Additionally, some new diffraction peaks due to CoO and zero valent Co can be observed for Co@CoO/Co-N-C-700 and Co@CoO/Co-N-C-800, while only zero valent Co can be found for Co@CoO/Co-N-C-900 and Co@CoO/Co-N-C-1000, indicating high pyrolysis temperature unfavourable for the formation of CoO owing to the oxygen removal at such temperatures. The XRD results reveal that pyrolysis temperature plays an important role in determining the composition of resulting pyrolytic product, thus leading to different electrocatalytic activities. A detailed structure information on pyrolytic sample (take Co@CoO/Co-N-C-800 as an example) was obtained by TEM characterization. As shown, a stacked carbon structure with deposited cobalt-based nanoparticles can be observed for Co@CoO/Co-N-C-800 (Fig. S3, ESI[†]). A high magnification TEM image further confirms this

(Fig. 2b). The corresponding energy-filtered TEM (EFTEM) spectrum analysis (Fig. 2c) verifies that the Co@CoO/Co-N-C-800 is composed of O, Co, N and C elements, indicating possible presence of zero valent Co, cobalt oxide and doped N in composite. From the elemental mapping signals of graphitic carbon without cobalt-based nanoparticle (Fig. S4, ESI[†]), it can be seen that Co and N elements are uniformly distributed in graphitic carbon structure, implying that the Co atoms are possibly bonded with the doped N in carbon structure to form Co-N_x moieties, which have been verified to be responsible for electrocatalytic activity.^{18,22} Interestingly, it is found that the deposited cobalt-based nanoparticle onto graphitic carbon exhibits two sets of crystalline lattices of 0.246 nm and 0.207 nm, corresponding to the (111) plane of CoO phase and (111) plane of Co phase respectively, consistent with the XRD results of Co@CoO/Co-N-C-800 (Fig. 2d). The above TEM analysis confirms that the deposited cobalt-based nanoparticle onto graphitic carbon is a Co@CoO core-shell structure.

Fig. S5a (ESI[†]) shows a surface survey XPS spectra of Co@CoO/Co-N-C-800, indicating the presence of C (83.41%), O (7.94%), N (7.44%) and Co (1.21%) elements. The high resolution N 1s spectrum (Fig. S5b, ESI[†]) can be divided into four peaks at 398.5, 400.2, 401.1, and 404.6 eV, corresponding to pyridinic-N (28.1%), pyrrolic-N (26.4%) graphitic-N (33.6%), and quaternary N⁺-O⁻ (11.9%).^{23,24} It has been generally accepted that pyridinic-N and pyrrolic-N can serve as metal-coordination sites owing to their lone-pair electrons, whereas pyridinic-N and graphitic-N are responsible for ORR.^{23,24} The high resolution Co 2p spectrum (Fig. S5c, ESI[†]) shows five peaks at 778.5, 780.5, 786.1, 796.4 and 803.6 eV. Among them, the intense peaks at 786.1 and 803.6 eV were satellite peaks can be ascribed to the shakeup excitation of the high-spin Co²⁺ ions.³ The peaks at 778.5 and 780.5 eV can be ascribed to the binding energies of the 2p_{3/2} orbits of Co species and the peaks at 796.4 eV corresponding to 2p_{1/2} orbits of Co species.¹⁸ After deconvolution, the peaks around 780.5 eV are assigned to CoO_x phase, while those around 778.5 eV corresponding to Co⁰.¹⁸ The above XPS analysis is consistent with the XRD results. As shown in Fig. S6 (ESI[†]) the Brunauer-Emmett-Teller surface area and total pore volume of Co@CoO/Co-N-C-800 are 647.7 m² g⁻¹ and 0.342 cm³ g⁻¹, respectively. The Co@CoO/Co-N-C-800 exhibits a microporous structure with high surface area and large pore volume, favorable for the exposure of catalytic active sites and electrocatalysis-related mass transport.

As electrocatalyst, we first evaluated the ORR performance of Co@CoO/Co-N-C-800 in 0.1 M KOH solution. The cyclic voltammetry (CV) curve indicates that Co@CoO/Co-N-C-800 possesses comparable catalytic activity of ORR to that of Pt/C (Fig. S7, ESI[†]). Fig. 3a shows the linear sweep voltammogram (LSV) responses of Co@CoO/Co-N-C composites and Pt/C. As shown, the investigated electrocatalysts exhibit the onset potentials of -0.08, -0.05, -0.09, -0.11 and -0.03 V for Co@CoO/Co-N-C-700, Co@CoO/Co-N-C-800, Co@CoO/Co-N-C-900, Co@CoO/Co-N-C-1000 and Pt/C, respectively. Very approximate onset potential value of Co@CoO/Co-N-C-800 and Pt/C indicates a superior ORR activity of Co@CoO/Co-N-C-

Fig. 2 (a) XRD patterns of the fabricated Co@CoO/Co-N-C composites obtained at different pyrolysis temperatures. (b) TEM image of Co@CoO/Co-N-C-800. (c) Energy-filtered TEM elemental mapping of Co@CoO/Co-N-C-800. (d) High resolution TEM image of an individual Co@CoO nanoparticle.

800. Additionally, Co@CoO/Co-N-C-800 also displays the highest limiting current within the investigated potential range among all catalysts, further indicating its superior ORR performance. Compared to other Co@CoO/Co-N-C composites, the high ORR catalytic activity of Co@CoO/Co-N-C-800 may be due to many attributes such as high surface area, porous structure and suitable content of ORR-related active species (e.g., Co, N doping).¹⁶ Fig. 3b shows the LSV curves of Co@CoO/Co-N-C-800 obtained from an O₂-saturated 0.1 M KOH solution under different rotation rates. Based on Fig. 3b and corresponding Koutecky-Levich (K-L) plots (inset in Fig. 3b), the average value of transferred electron number at -0.30 ~ -0.45 V was calculated to be 3.8 for Co@CoO/Co-N-C-800, approximate to the theoretical value of Pt/C catalyst ($n=4.0$), indicating a near four electron ORR process. The resistance to fuel molecule interference and durability are important parameters to evaluate an ORR catalyst for practical application. Fig. S8 (ESI[†]) shows the crossover effect and durability measurements of Co@CoO/Co-N-C-800 and Pt/C catalysts under identical experimental conditions. Apparently, Co@CoO/Co-N-C-800 exhibits high resistance to methanol crossover effect and good durability. This is very important for a practical application of Co@CoO/Co-N-C-800 catalyst.

As we know, it is critically important to develop an electrocatalyst with bifunctional ORR and OER catalytic activity for a rechargeable zinc-air battery.^{25,26} In this work, the OER activity of Co@CoO/Co-N-C and commercial RuO₂ catalysts was investigated in 0.1 M KOH electrolyte. Fig. 3c shows the polarization curves of Co@CoO/Co-N-C and commercial RuO₂ catalysts. As shown, the overpotentials at current density of 10 mA cm⁻² are 0.76, 0.64, 0.63, 0.71 and 0.55 V for Co@CoO/Co-N-C-700, Co@CoO/Co-N-C-800, Co@CoO/Co-N-C-900, Co@CoO/Co-N-C-1000 and RuO₂, respectively, indicating that the samples obtained at 800 and 900 °C possess very similar overpotentials for OER, close to the commercial RuO₂ catalyst.

However, too low or too high pyrolysis temperature (e.g., 700 or 1000 °C) is not beneficial for high OER activity of catalyst. The durability test shows that only overpotential of 0.08 V decrease in the initial activity was observed at current density of 10 mA cm⁻² for Co@CoO/Co-N-C-800 catalyst after 1000th run, indicating a high applicable stability of Co@CoO/Co-N-C-800 (Fig. S9, ESI[†]). The above results indicate that Co@CoO/Co-N-C-800 possesses bifunctional catalytic activity for both ORR and OER. Further, we also evaluated the electrocatalytic HER performance of Co@CoO/Co-N-C composites and commercial Pt/C in 0.1 M KOH solution. On the one hand, pairing the OER and HER catalysts together in the same electrolyte is of practical values to accomplish overall water splitting. On the other hand, alkaline electrolysis is an attractive alternative to proton exchange membrane (PEM)-based electrolysis because the non-noble metal electrocatalysts involved in alkaline electrolysis tend to be more stable and exhibit relatively high activities for the HER.^{6,27} As shown in polarization curves of Co@CoO/Co-N-C and Pt/C catalysts (Fig. 3d), the required overpotentials at current density of 20 mA cm⁻² are -1.61, -1.40, -1.37, -1.44 and -1.12 V for Co@CoO/Co-N-C-700, Co@CoO/Co-N-C-800, Co@CoO/Co-N-C-900, Co@CoO/Co-N-C-1000 and Pt/C, respectively, confirming that Co@CoO/Co-N-C-800 and Co@CoO/Co-N-C-900 possess good HER catalytic activity. Simultaneously, the Co@CoO/Co-N-C-800 also demonstrates high durability during HER (Fig. S10, ESI[†]). Recently, carbon-based electrocatalysts with different formed cobalt active species have demonstrated high electrocatalytic activities of ORR, OER and HER.^{3,11,28} It is believed that the trifunctionality of ORR, OER and HER of Co@CoO/Co-N-C catalyst in this work can be ascribed to a synergistic effect of Co, CoO and Co-N doping in graphitic carbon structure creating catalytic active sites.

The primary zinc-air battery device was constructed by assembling zinc foil anode with Co@CoO/Co-N-C-800 loaded air cathode, and was tested in 6.0 M KOH electrolyte. As shown in Fig. 4a the open-circuit voltage was determined to be ~1.4 V for Co@CoO/Co-N-C-800, almost identical with commercial Pt/C. Fig. 4b shows the power density curves of zinc-air batteries assembled with Co@CoO/Co-N-C-800 and commercial Pt/C. In the discharge process, the zinc-air battery made from Co@CoO/Co-N-C-800 shows a high current density of 96 mA cm⁻² at 1.0 V, close to that of Pt/C based zinc-air battery (113 mA cm⁻² at 1.0 V) (Fig. 4b). The peak power density of zinc-air battery assembled with Co@CoO/Co-N-C-800 is 157 mW cm⁻² reached at 0.75 V, which is approximate to that of Pt/C based zinc-air battery (173 mW cm⁻² at 0.7 V). Based its efficient ORR and OER performance, the Co@CoO/Co-N-C-800 was further constructed to rechargeable zinc-air battery, which was tested in 6.0 M KOH electrolyte including 0.2 M zinc acetate. To obtain a meaningful comparison, a commercial mixture of Pt/C and RuO₂ with a mass ratio of 1:1 was used in this work for rechargeable battery measurements. During the charge-discharge process (Fig. 4c), the battery made from Co@CoO/Co-N-C-800 exhibits similar current densities as the rechargeable battery assembled with Pt/C-RuO₂, indicating superior charge-

Fig. 3 (a) LSV curves of Co@CoO/Co-N-C composites and Pt/C in O₂ saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹ and a rotation speed of 1600 rpm. (b) LSV curves of Co@CoO/Co-N-C-800 under different rotation speeds and inset of corresponding K-L plots. (c) LSV curves of Co@CoO/Co-N-C composites and RuO₂ in O₂-saturated 0.1 M KOH solution at a scan rate of 5.0 mV s⁻¹. (d) LSV curves of Co@CoO/Co-N-C composites and Pt/C in N₂-saturated 0.1 M KOH solution at a scan rate of 5.0 mV s⁻¹.

discharge performance of Co@CoO/Co-N-C-800 in rechargeable zinc-air battery. The durability test of

Fig. 4 (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 rechargeable zinc-air battery made from Co@CoO/Co-N-C-800.

Co@CoO/Co-N-C-800 in rechargeable zinc-air battery is shown in Fig. 4d. The initial charge and discharge potentials of Co@CoO/Co-N-C-800 based zinc-air battery are 1.92 and 1.25 V, respectively. After 100 cycles, the charge and discharge potentials are 2.05 and 1.19 V, respectively, indicating high recycling durability of Co@CoO/Co-N-C-800 in rechargeable zinc-air battery. Concurrently, as cathode and anode material, Co@CoO/Co-N-C-800 was also loaded onto carbon fiber paper to evaluate water splitting to generate hydrogen and oxygen performance in 0.1 M KOH solution. As shown in Fig. S11 (ESI[†]), a great deal of air bubbles can be observed due to the generation of hydrogen and oxygen on Co@CoO/Co-N-C-800 cathode and anode by water splitting, further confirming the superior OER and HER catalytic activity of Co@CoO/Co-N-C-800.

In summary, Co@CoO/Co-N-C composite was successfully fabricated using shrimp-shell derived N-doped carbon nanodots as precursor by a combined approach of polymerization and pyrolysis. As electrocatalyst, Co@CoO/Co-N-C exhibited trifunctional catalytic activity toward ORR, OER and HER and high performance of rechargeable zinc-air battery and water splitting.

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