

Article

“Pharaoh’s Snakes” Reaction-Derived Carbon with Favorable Structure and Composition as Metal-Free Oxygen Reduction Reaction Electrocatalyst

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Abstract: Metal-air batteries rely on the oxygen reduction reaction (ORR) for their operation. However, the ORR is kinetically slow, necessitating the use of Pt-based catalysts, which is hindered by their high cost and limited availability. Consequently, considerable efforts have been dedicated to developing metal-free catalysts for the ORR. Among these, heteroatom-doped carbons have emerged as promising candidates by manipulating their composition and microstructure. Inspired by the ancient “Pharaoh’s snakes” reaction, this study utilized sugar, melamine, and a polymerizable ionic liquid as precursors to prepare heteroatom-doped carbons with the desired composition and structure. The resulting carbon catalyst exhibited an onset potential and half-wave potential in a 0.1 M KOH electrolyte that was comparable to those of a commercial Pt/C 20 wt.% catalyst, with values of 0.97 and 0.83 V_{RHE}, respectively. Furthermore, the catalyst demonstrated excellent stability, retaining 93% of its initial current after a 10,800-s test. To evaluate its practical application, the synthesized carbon was employed as the cathode catalyst in a Zn-air battery, which achieved a maximum power density of 90 mW cm^{−2}. This study, therefore, presents a simple yet effective method for producing metal-free heteroatom-doped carbon ORR catalysts used in various energy conversion and storage devices.

Keywords: oxygen reduction reaction; “Pharaoh’s snakes” reaction; metal-free electrocatalyst; carbon material; heteroatom doping



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1. Introduction

The continuously increasing energy consumption has resulted in an energy crisis and significant environmental problems [1]. These challenges have prompted extensive research into sustainable, efficient, and clean power sources. Metal-air batteries have garnered considerable attention as promising power sources for the future due to their excellent efficiency and environmentally friendly nature [2]. In these power sources, the oxygen reduction reaction (ORR) plays a vital role as an electrode reaction. However, due to its sluggish kinetics, high-performance electrocatalysts are necessary to facilitate the ORR [3]. Until now, platinum-group metals (PGMs) have remained the optimal catalysts for the ORR. However, the scarcity, high cost, and instability of Pt-based catalysts have significantly hindered their widespread use. The heavy reliance on Pt-based electrocatalysts

has become a major concern for the advancement of metal-air batteries [4]. Therefore, it is crucial to explore efficient and cost-effective electrocatalysts that can replace PGM-based ORR electrocatalysts [5–8].

Heteroatom-doped carbons have received significant attention as promising low-cost catalysts due to their profound electrocatalytic activity, high chemical stabilities, and excellent conductivity. Various heteroatoms such as S [9], N [10,11], P [12], and B [13] have been explored for doping into carbons as high-performance metal-free ORR electrocatalysts since these heteroatom dopants can alter the electronic properties of carbon [14]. In particular, multi-heteroatom-doped carbon shows great promise for the ORR due to the synergistic effects of the dopants [15,16]. The microstructure of the carbon also plays an essential role as it impacts electrolyte transport within the catalyst and the availability of active sites. To this end, developing a fabrication process that combines the advantages of dopants and desired structures is of utmost importance [17]. Several related studies have been conducted to explore desired synthesis processes. For instance, a metal-organic framework (MOF) templated method was investigated for preparing N- and S-doped carbon [18]. Zeolite templates were utilized to prepare Co-supported N-doped porous carbon [19]. Poly(phenylene sulfide sulfone) (PPSS) was explored as a template for synthesizing honeycomb-like N, S co-doped carbon [20]. Additionally, ZIF-8 templated porous Fe-N_x-doped carbon was prepared [21]. All these studies have demonstrated the significance of developing processes to prepare carbon materials with the desired structures and compositions for efficient ORR catalysis.

The “Pharaoh’s snakes” reaction (FSR) is a renowned ancient reaction that produces foam-like materials with diverse compositions. This reaction utilizes precursor chemicals, known as pore fabricators, that contain the desired elements to prepare ORR catalysts with high catalytic performance, such as those containing Fe [22] or Co [23]. Inspired by these studies, we propose that a precursor like that of the FSR may enable the preparation of carbon with both favorable composition and structure as an ORR catalyst.

In this study, we developed a simple one-pot method based on the FSR to synthesize a nitrogen (N), sulfur (S), and oxygen (O) co-doped carbon material with a three-dimensional (3D) interconnected porous structure. The precursor mixture consisted of sugar, melamine, NH₄HCO₃, and a polymerizable [Etvim]EtSO₄ ionic liquid (PIL). Their electrochemical tests revealed a half-wave potential of 0.83 V_{RHE} (reversible hydrogen electrode voltage) and an onset potential of 0.97 V_{RHE} for the ORR. Additionally, the catalyst demonstrated excellent durability during ORR testing. Furthermore, when employed as the ORR catalyst in a zinc-air battery, a peak power density of 90 mW cm^{−2} can be achieved.

2. Results

Sugar was chosen as the carbon precursor for several reasons. Firstly, sugar has the ability to melt at high temperatures, allowing it to effectively wrap around the melamine and NH₄HCO₃. This wrapping action facilitates the formation of pores in the carbon since the decomposition of melamine and NH₄HCO₃ releases gases. Additionally, the oxygen present in the sugar molecules serves as a source of O dopants in the carbon material. The [Etvim]EtSO₄ IL undergoes polymerization during the pyrolysis process, resulting in the formation of a carbon matrix that is doped with N and S. The difference in precursors used for the catalyst synthesis results in variations in the composition of the catalysts. For clarity, Table 1 presents the precursors and compositions used for each catalyst.

Table 1. Summary of the precursors and compositions for the three catalysts.

Sample	Precursor	Composition
C ₁	Sugar, NH ₄ HCO ₃ , melamine, [Etvim]EtSO ₄	C, N, S, O
C ₂	sugar + melamine + NH ₄ HCO ₃	C, N, O
C ₃	[Etvim]EtSO ₄ + NH ₄ HCO ₃	C, N, S

The ORR catalytic activity of the prepared carbon material was evaluated using cyclic voltammetry (CV) measurements, and the results are presented in Figure 1. The CV curves provide initial evidence of the catalytic performance of the carbon material, showing its ability to facilitate the reduction of oxygen in the electrolyte. In Figure 1a, the CV curves obtained in both N_2 - and O_2 -saturated electrolytes are compared. In the N_2 -saturated electrolyte, no significant features or peaks related to the ORR were observed. However, in the O_2 -saturated electrolyte, a distinct reduction peak appeared at 0.85 V_{RHE}. This observation suggests that the carbon material obtained here exhibits effective electrocatalytic activity for the ORR.

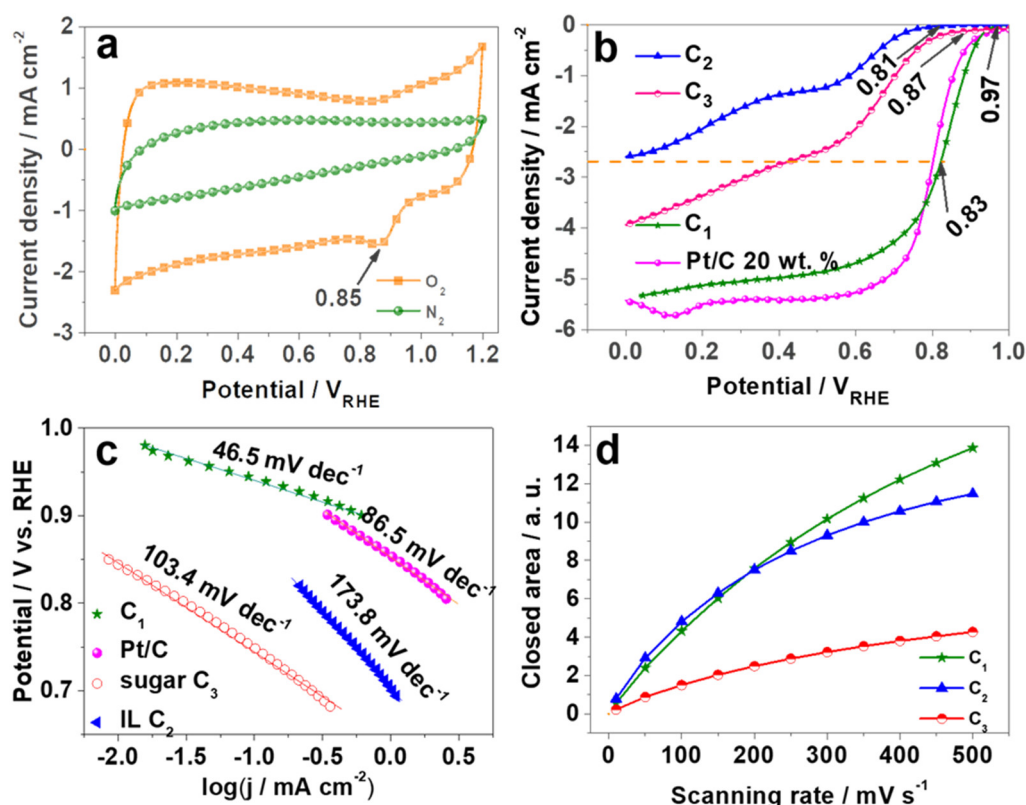


Figure 1. (a) CV curves for the C₁ in N_2 and O_2 saturated electrolyte (0.1 M KOH), (b) LSV curves at 1600 rpm for C₁, C₂ (precursor of sugar), C₃ (precursor of [Etvim]EtSO₄) and commercial Pt/C (20 wt.%), (c) corresponding Tafel plots, and (d) CV area as a function of scanning rate.

The linear sweep voltammetry (LSV) curves presented in Figure 1b provide further evidence of the high ORR activity of C₁ material prepared with sugar, NH_4HCO_3 , melamine, and [Etvim]EtSO₄ in this study. C₁ exhibits an onset potential of 0.97 V_{RHE}, which is comparable to the reported values in previous works (0.94 V_{RHE} [24], 0.92 V_{RHE} [16], 0.97 V_{RHE} [25], and 0.9 V_{RHE} [26]). This value is also comparable with those of other carbon-based materials, such as graphitic C₃N₄ (~0.973 V_{RHE}) [27], N-doped graphene (0.87 V_{RHE}) [28], carbon nanotube (0.92~0.97 V_{RHE}) [29], and graphene nanosheets stabilized by P3HT (~0.87 V_{RHE}) [30]. It indicates that the catalysts prepared using the facile method in this study demonstrate comparable or even higher catalytic activity compared to the carbons, which require a complex preparation process. It is worth noting that the LSV curve of the state-of-the-art commercial Pt/C is also included in Figure 1b for comparison. The LSV curve of the C₁ catalyst closely resembles that of the Pt/C, supporting its high ORR activity.

From the LSV curves, it is evident that the onset potential of C₁ is higher than that of C₂ and C₃. Additionally, the current density for C₁ increases at a much faster rate compared to C₂ and C₃. The Tafel plots constructed based on the LSV curves (see Figure 1c) further

elucidate the ORR kinetics of the corresponding catalysts. C_1 exhibits a Tafel slope of 46.5 mV dec^{-1} , which is lower than that of C_2 ($103.4 \text{ mV dec}^{-1}$) and C_3 ($173.8 \text{ mV dec}^{-1}$). A lower Tafel slope indicates a slower loss of voltage per increase in the current density, demonstrating the improved activity of C_1 . These observations suggest that the addition of both [Etvim]EtSO₄ and sugar is crucial for achieving the enhanced catalytic performance of C_1 . The absence of O when sugar is not added or the lack of S and N when [Etvim]EtSO₄ is not added leads to a significant decrease in catalytic performance. The combination of [Etvim]EtSO₄ and sugar plays a critical role in preparing the C_1 catalyst with superior ORR activity. The electrochemical surface areas (ECSA) of C_1 , C_2 , and C_3 were evaluated based on the slope of the CV closed area-scanning rate line [31] (Figure 1d). The corresponding CV curves for C_1 , C_2 , and C_3 are presented in Figure S1. Our results reveal that C_1 exhibits the highest slope, indicating the highest electrochemical surface area (ECSA) since ECSA is directly proportional to the slope of the line. [31].

Figure 2 presents the microstructure of the prepared C_1 catalyst. Two different areas are shown in Figure 2a,b, both of which exhibit a porous structure with interconnected channels and pores. This porous structure is formed by the gas generated from the decomposition of melamine and NH₄HCO₃, which can increase the exposure of the active sites of the catalyst. Additionally, the presence of pores and channels can facilitate mass transportation throughout the catalyst, contributing to enhanced catalytic performance. Figure 2c displays a transmission electron microscope (TEM) image of the catalyst, further confirming the presence of porous sheets. Figure 2d shows a high-resolution TEM (HRTEM) image, indicating that the carbon material is amorphous as no long-distance ordering is observed. The amorphous nature of the carbon suggests that it lacks a well-defined crystalline structure.

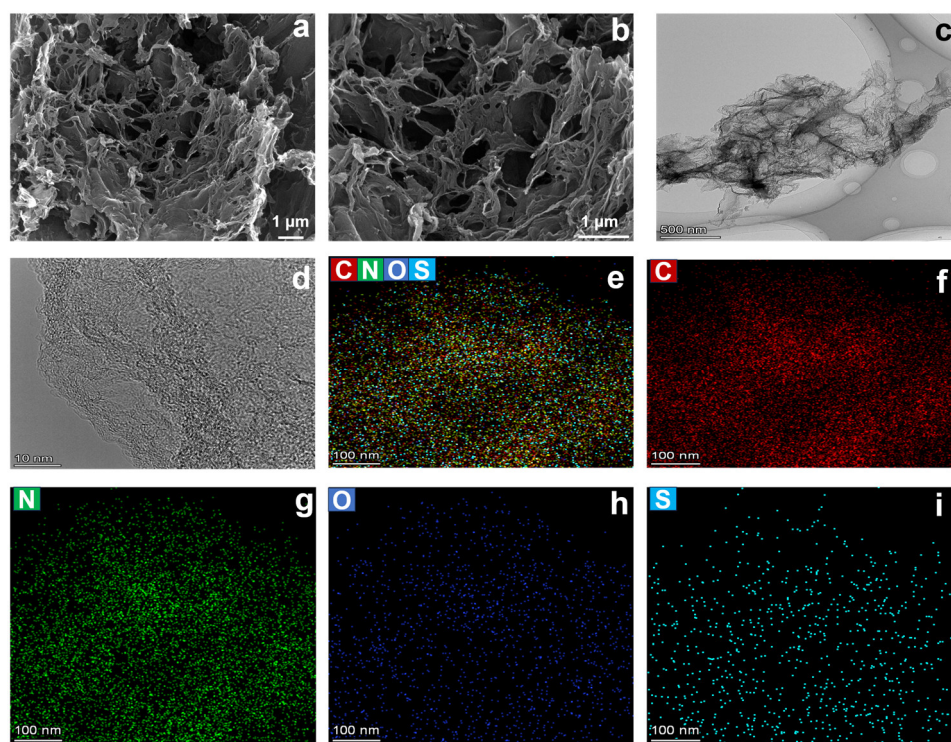


Figure 2. (a,b) SEM images of different areas; (c) TEM image; (d) HRTEM image; (e) merged EDS mapping image of C, N, O, and S; (f–i) EDS mapping images of C, N, O, and S.

To analyze the elemental distribution within the C_1 catalyst, energy-dispersive spectroscopy (EDS) characterization was conducted. The scanning transmission electron microscopy (STEM) images shown in Figure 2e–i demonstrate the uniform distribution of N, O, and S on the carbon material. This indicates the efficient incorporation of these elements (O, N, and S) into the carbon matrix, which is important for achieving the desired catalytic

properties. This further supports the role of these heteroatoms in enhancing the catalytic activity of the C_1 catalyst.

The surface area and pore size of C_1 were measured using N_2 adsorption measurements. The N_2 adsorption-desorption isotherm shown in Figure 3a exhibits a type I curve, demonstrating a significant adsorption capacity at a low relative pressure (P/P_0) and reaching equilibrium. This suggests the presence of typical micropores [32]. The inset in Figure 3a shows the pore size distribution, with a dominant pore size of approximately 1.25 nm. This confirms the micro-porous structure of the C_1 material. These micropores, particularly those with sizes below 2 nm, can serve as hosting sites for the active species involved in the ORR, thereby enhancing the catalytic activity of the material. The Brunauer-Emmett-Teller (BET) surface area of C_1 is determined to be $261 \text{ m}^2 \text{ g}^{-1}$. This value is higher than that of some ORR catalysts prepared using other methods, such as $150 \text{ m}^2 \text{ g}^{-1}$ [33] and $180 \text{ m}^2 \text{ g}^{-1}$ [34]. The higher surface area of C_1 allows for increased accessibility of the active sites, thereby contributing to improved catalytic activity.

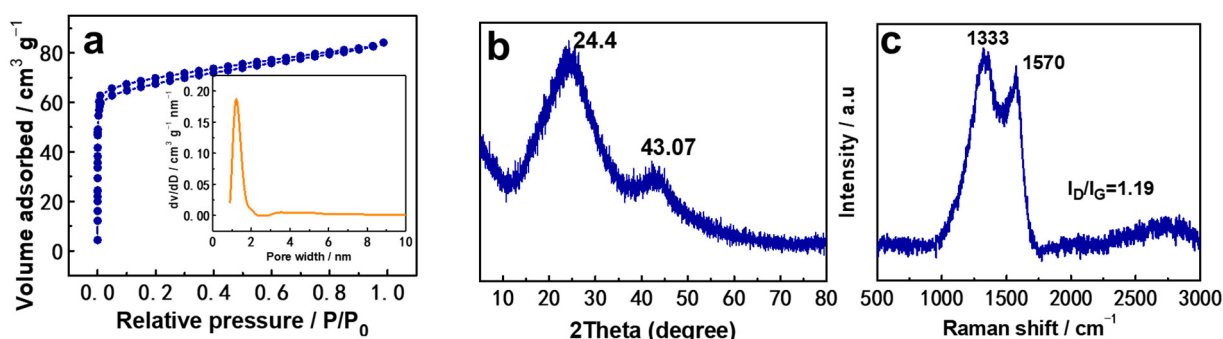


Figure 3. (a) N_2 adsorption/desorption isotherm of C_1 . Inset is the pore size distribution curve. (b) XRD pattern and (c) Raman spectra of C_1 .

The crystallography of C_1 was investigated using X-ray diffraction (XRD), as shown in Figure 3b. The XRD pattern exhibits two broad peaks at around 24.4° for C (002) and 43.07° for C (100). These broad peaks indicate the amorphous nature of C_1 [35]. This is further supported by the HRTEM image in Figure 2d, where no long-range order can be observed. The amorphous carbon structure doped with heteroatoms has been reported to exhibit higher ORR catalytic activity compared to graphitized carbon [36].

The Raman spectra of C_1 , displayed in Figure 3c, exhibit two prominent peaks corresponding to the D and G bands at approximately 1333 and 1570 cm^{-1} , respectively. The D band is typically associated with the breathing mode in graphitic materials and is indicative of certain degrees of disorder within the carbon structure [37]. Therefore, the presence of the D band suggests a disordered structure and the presence of defects in C_1 . Furthermore, the D band can also be influenced by heteroatom doping, which disrupts the local symmetry of the carbon structure. The G band, on the other hand, is related to the vibration of all hybridized sp^2 carbon atoms in the carbon layers [38]. It represents the ordered and graphitic carbon domains within the material. The ratio of the D band intensity (I_D) to the G band intensity (I_G), known as the I_D/I_G ratio, is commonly used as a measure of structural disorder in carbon materials. For C_1 , the I_D/I_G ratio is determined to be 1.19. This value is higher than that of several other carbon materials at 0.8 [39], 1.1 [40], and 1 [41]. A higher I_D/I_G ratio indicates the presence of more defective domains in the carbon structure [42,43]. These defects provide additional active sites and can enhance the electrochemical reactivity of the material. Therefore, the N_2 adsorption measurements, surface area analysis, XRD pattern, HRTEM image, and Raman spectra demonstrate the micro-porous structure, high surface area and amorphous nature of C_1 , all of which contribute to its enhanced ORR catalytic activity.

The XPS survey spectra (see Figure S2) provide an overall analysis of the elemental composition of C_1 . The presence of peaks for C (78.99 at.%), N (1.23 at.%), S (0.19 at.%),

and O (0.19 at.%) confirms the successful doping of N, O, and S into the carbon material. The C 1s spectra, presented in Figure 4a, exhibit five distinct peaks. The peaks at 284.5 eV (27.6 at.%) and 284.9 eV (28.8 at.%) can be attributed to graphitic carbon [44]. The peak at 285.4 eV (21.0 at.%) corresponds to C–N bonds [45]. The peak at 286.5 eV (11.9 at.%) is assigned to C–O–C or C–S bonds [46,47]. The peak at 288.8 eV (10.6 at.%) represents C–N bonds [48]. Figure 4b shows the N 1s spectra, which reveal three peaks. The peaks at 399.6 eV and 398.1 eV are associated with pyrrolic (9.8 at.%) and pyridinic nitrogen (26.1 at.%), respectively [49]. The peak at 401.0 eV corresponds to graphitic nitrogen (64.0 at.%) [50,51]. In the S 2p spectra (see Figure 4c), two main peaks are observed. The peaks at 163.8 eV and 164.9 eV are assigned to C–S–C bonds (58.6 at.%) [52,53]. These bonds contribute to the presence of S in the carbon material. The peaks at 168.2 eV and 169.5 eV correspond to oxidized sulfur species (41.4 at.%) [54,55]. Figure 4d presents the fine spectra of O 1s. The peak at 531.7 eV corresponds to C=O bonds (47.1 at.%) [56], indicating the presence of carbonyl groups. The peak at 532.2 eV can be assigned to singly bonded oxygen (29.6 at.%) [57]. The peak at 533.2 eV is related to O–C bonds (47.1 at.%) [58].

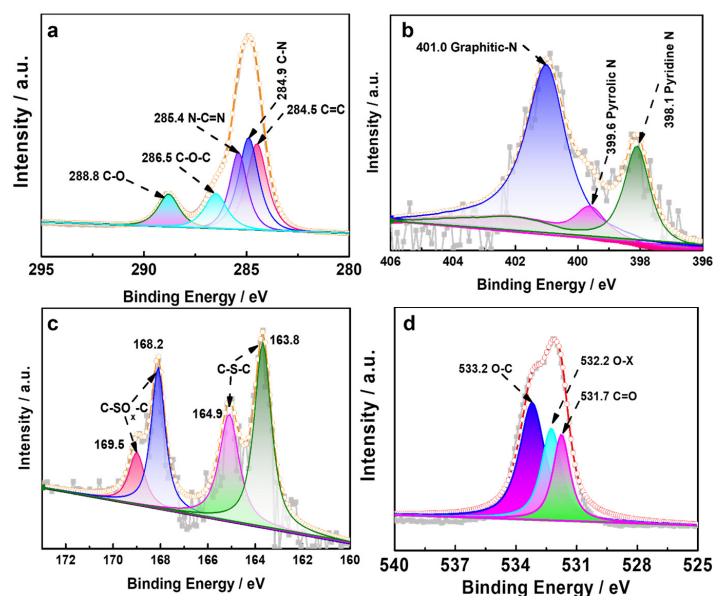


Figure 4. XPS spectra of the C₁: (a) C 1s, (b) N 1s, (c) S 2p, and (d) O 1s.

The XPS analysis of C₁ confirms the successful doping of N, S, and O into the carbon matrix. The C 1s spectra reveal the presence of graphitic carbon, C–N, and C–O–C/C–S bonds, indicating the incorporation of N, S, and O into the carbon structure. The N 1s spectra demonstrate the presence of pyrrolic, pyridinic, and graphitic N. The N-doping enhances the conductivity and wettability of the carbon material, making it easier for active species to reach the active sites. Additionally, the electronegativity of N charges adjacent to C atoms positively facilitates the adsorption of oxygen molecules [25]. N doping introduces spin density asymmetry, contributing to the ORR catalytic activity [59–61]. The S 2p spectra indicate the presence of C–S–C and oxidized sulfur species. Sulfur doping induces high strains at the edges of the carbon lattice and increases spin densities [9], which can facilitate O₂ transfer, adsorption, and reduction. The presence of S can form thiophene sulfur sites, which act as ORR active sites by positively charging neighboring carbon atoms and facilitating the adsorption of *OO, *OH, and H intermediates in the ORR process [62]. O doping introduces Lewis basicity to the carbon material, enhancing the interaction between the Lewis acidic oxygen on the active surface and the reactants [63]. This leads to improved ORR catalytic activity [64]. Therefore, when N, S, and O are doped simultaneously, these three factors work synergistically to enhance the catalytic performance of the carbon material. The combined effects of N, S, and O doping contribute to improved conductivity, increased spin density, favorable adsorption of oxygen species,

and enhanced interaction with reactants, ultimately resulting in enhanced ORR catalytic activity. Considering that the S content is significantly lower than that of N and O, it is likely that the active sites are the C atoms associated with N and O.

The catalytic activity and kinetics of C₁ towards ORR were further analyzed using rotating disk electrode (RDE) technology. Figure 5a shows the LSV curves at various rotational speeds. It can be observed that the current density increases with higher rotational speed. This increase is attributed to the reduction in the thickness of the diffusion layer at higher rotational rates, which enhances the transport of oxygen to the catalyst surface. The development of a diffusion-limited current platform is evident at all rotational speeds. Furthermore, the LSV curves are nearly parallel to each other, indicating first-order reaction kinetics with respect to the oxygen concentration. The number of electrons (n) involved in the ORR process was then determined using Koutecky-Levich (K-L) analysis. The K-L lines (see Figure 5b) were obtained by plotting J^{-1} (where J is the current density) against $\omega^{-1/2}$ (where ω is the rotation speed) based on the LSV curves shown in Figure 5a. The slope of the K-L line was then used to calculate n according to Equations (1) and (2):

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

$$B = 0.2nFC_0D_0^{2/3}\gamma^{-1/6} \quad (2)$$

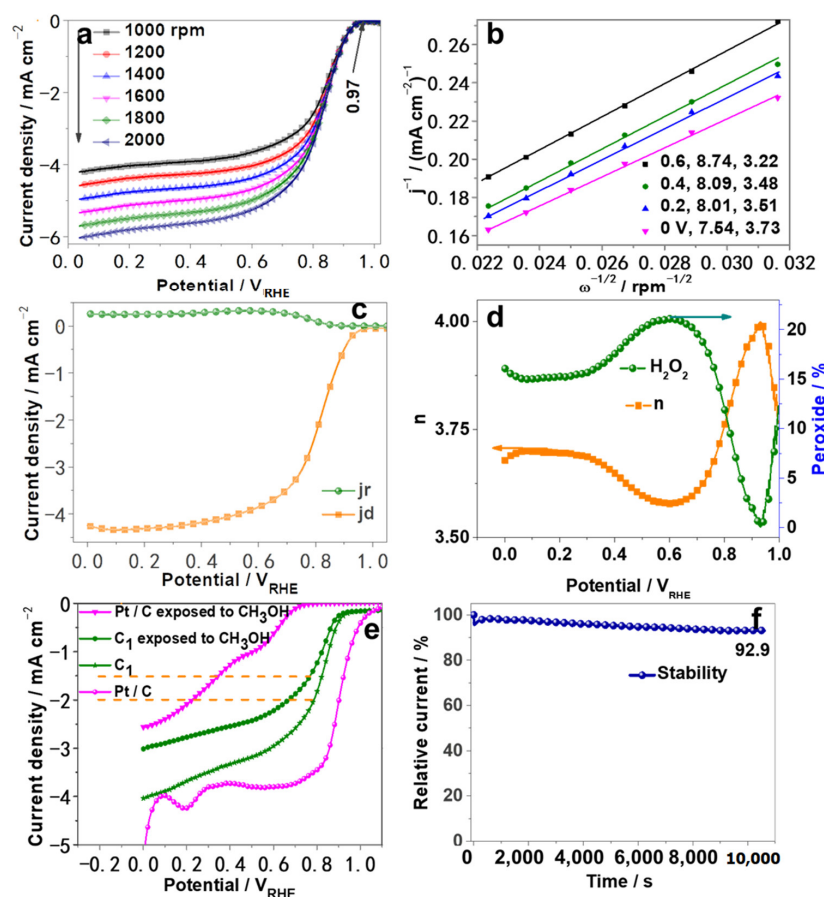


Figure 5. (a) LSV curves for the C₁ at different rotational speeds; (b) the Koutecky-Levich plots; (c) the LSV of the RRDE (1600 rpm) of C₁; (d) the H₂O₂% and n at different potentials; (e) LSV curves for the C₁, Pt/C, C₁ exposed to CH₃OH (20,000 ppm) and Pt/C exposed to CH₃OH (20,000 ppm); and (f) current-time curve 0.73 V_{RHE} of C₁ for ORR.

In these equations, j_k represents the density of the kinetic current, j is the measured current, F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), C_0 is the bulk concentration of oxygen ($1.1 \times 10^{-3} \text{ mol L}^{-3}$), γ is the electrolyte kinetic viscosity ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and D_0 is the diffusion coefficient for oxygen in the electrolyte of 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$). The constant 0.2 is used when expressing the rotation rate in rpm [65]. The calculated values of n range from 3.22 to 3.73, which confirm the 4-electron ORR process [66].

Figure 5c reveals that the C_1 catalyst exhibits a high disc current density and a low ring current density during the RRDE tests conducted at 1600 rpm. The high disc current density indicates a strong catalytic activity of the C_1 catalyst towards the ORR. This suggests that the catalyst effectively promotes the reduction of oxygen molecules, leading to a high current density at the working electrode (disc). On the other hand, the low ring current density indicates a low production of hydrogen peroxide (H_2O_2), which is a common byproduct of the ORR. Based on Equations (3) and (4), the number of electron transfers (n) and % H_2O_2 can be calculated using the ring and disc current values obtained from the RRDE tests at 1600 rpm.

$$n = \frac{4 \times i_d}{i_d + i_r/N} \quad (3)$$

$$\text{HO}_2^- \% = 200 \frac{i_r/N}{i_d + i_r/N} \quad (4)$$

where i_d represents the disc current and i_r represents the ring current. N is the collection efficiency, which is given as 0.39 in this case. These values are presented in Figure 5d. Based on the results, it is indicated that the value of n is higher than 3.5, suggesting a largely 4-electron process for the ORR on the C_1 catalyst. Additionally, the % H_2O_2 is below 20%, indicating low production of hydrogen peroxide, which is desirable for efficient ORR in metal-air batteries.

A major advantage of metal-free electrocatalysts is their high tolerance to methanol. To evaluate the CH_3OH tolerance of the C_1 , the LSVs of C_1 and Pt/C before and after exposure to CH_3OH of 20,000 ppm were measured. The results are presented in Figure 5e. The catalytic performance of the Pt/C decreased dramatically after being exposed to CH_3OH , with the onset potential shift from 1.1 to $\sim 0.7 \text{ V}_{\text{RHE}}$. For the C_1 , the limit current and half-wave potential only decreased by 10 mA cm^{-2} and 14 mV, respectively. More importantly, the onset potential remained nearly unchanged after the CH_3OH . The methanol-tolerance tests confirmed the superiority of the C_1 metal-free catalyst compared to the metal-based catalysts in terms of methanol tolerance.

Furthermore, the stability of the C_1 catalyst was evaluated through chronoamperometry at $0.73 \text{ V}_{\text{RHE}}$ in an O_2 -purged electrolyte. The current-time curve (Figure 5f) shows that approximately 93% of the initial current remains after the stability test of 10,800 s, demonstrating the profound stability of the C_1 catalyst. Comparing this stability performance with other reported catalysts, the C_1 catalyst outperforms or shows comparable stability to some reported catalysts with 86% [67], 81.4% [68], and 72.3% [69] current retention after a stability test. The stability of the present work is $\sim 95\%$ at 2000 s, which is similar to that observed for functionalized graphene [70]. This high stability is of significant importance for practical applications, as it ensures the long-term durability and reliability of the catalyst, making it a promising candidate for use in various electrochemical devices and systems.

To assess the practical application of the prepared carbon catalyst, zinc-air batteries (ZABs) were assembled and tested. The structure of ZABs is illustrated in Figure 6a. Figure 6b shows the performance comparison between the ZAB with three doped carbon catalysts and the ZAB without the catalyst. It can be observed that the ZAB with the C_1 catalyst exhibits a smooth discharge process, while the ZAB without the catalyst is unable to function properly, resulting in a significantly lower peak power density. The ZAB with the C_1 catalyst achieves a peak power density of 90 mW cm^{-2} , which is even higher than that of batteries utilizing Pt/C+ RuO_2 catalysts with peak power densities of 80 mW cm^{-2} [71] or 50 mW cm^{-2} [72]. It demonstrates the excellent catalytic activity of the C_1 catalyst for

the oxygen reduction reaction (ORR) in the ZAB system. Furthermore, Figure 6c shows that the ZAB with the C_1 catalyst is capable of lighting LEDs to provide practical power output. Overall, the electrochemical results from the ZAB tests confirm that the N, S, and O co-doped C_1 catalyst possesses profound ORR catalytic activity, enabling its effective utilization in the ZAB system.

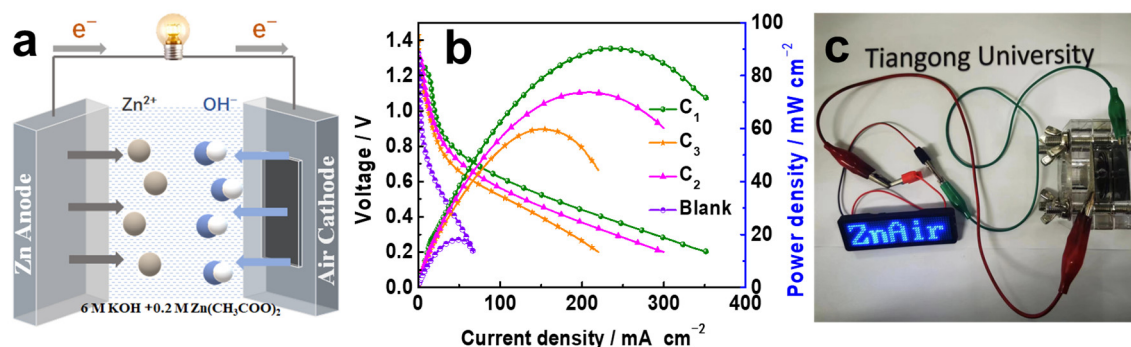


Figure 6. (a) Diagram of the ZABs; (b) polarization and power density curves of ZABs with (C_1 , C_2 , C_3) and without (Blank) catalysts prepared in this work; and (c) photo images of a panel being lit by a Zn-air battery with C_1 .

3. Materials and Methods

The polymerizable [Etvim]EtSO₄ ionic liquid was prepared using a method similar to the one previously described [17], as illustrated in Figure 7. Diethyl sulfate (0.1 mol) was first added dropwise to vinyl imidazole while stirring the mixture in an ice-water bath. After the complete addition of diethyl sulfate, the system was further stirred in a water bath at 50 °C for 3 h. Following the reaction, a viscous, slightly yellow liquid was obtained. A Bruker DRX500 instrument was used to conduct proton nuclear magnetic resonance (¹H NMR) spectroscopy analysis on the obtained liquid. In addition, deuterium oxide (D₂O) was used as the solvent. The ¹H NMR spectrum of the product is presented in Figure S3, indicating the successful synthesis of the expected product.

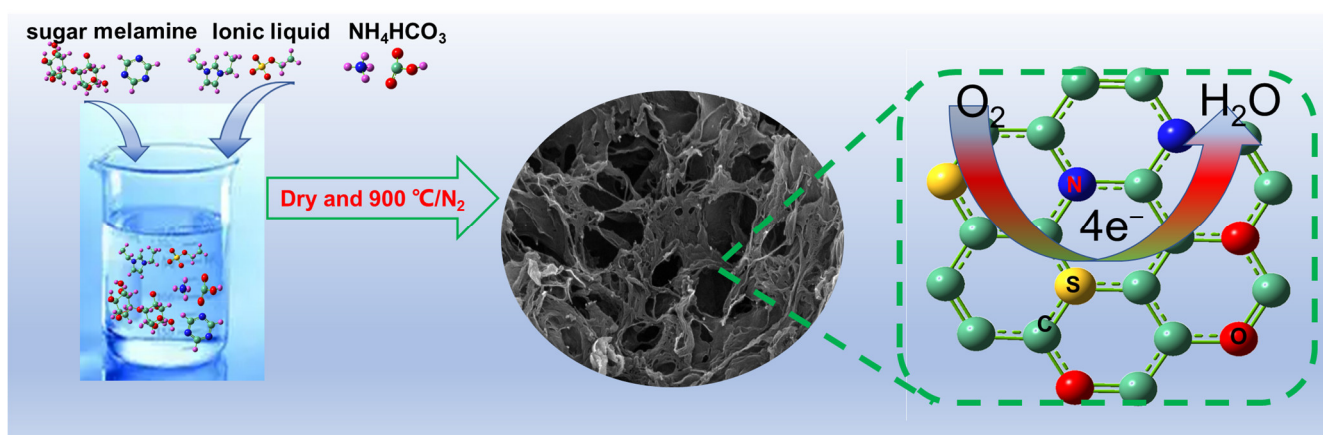


Figure 7. Illustration of the catalyst preparation process.

The catalyst was prepared using the obtained IL. In a typical procedure, sugar (1.5 g), NH₄HCO₃ (0.4 g), melamine (1.2 g), and [Etvim]EtSO₄ (1.2 g) were dissolved in water to form a turbid solution. The turbid solution was then dried. The resulting solid material was subjected to pyrolysis in a tubular furnace under an N₂ atmosphere. The pyrolysis process was conducted at 900 °C for 1 h with a temperature ramp rate of 5 °C/min. After the furnace was allowed to cool down to room temperature, a foam-like black sample (C_1 , Figure S4) was obtained. For comparison, two other carbon materials doped with N and O (C_2) and N and S (C_3) were also prepared using similar procedures but with

different precursor compositions. C₂ was prepared using a mixture of sugar, melamine, and NH₄HCO₃, while C₃ was prepared using a mixture of the polymerizable ionic liquid [Etvim]EtSO₄ and NH₄HCO₃ (see Table 1).

The electrochemical measurements were conducted using a CHI 760E electrochemical workstation (Chenhua, Shanghai, China). A three-electrode cell configuration was employed, with a mercury/mercuric oxide (Hg/HgO) electrode and a platinum wire serving as the reference and counter electrodes, respectively. To make the working electrode, a homogeneous catalyst ink was prepared by mixing 2.5 mg of the catalyst sample, 50 μ L of a 5 wt.% Nafion solution, and 450 μ L of ethanol. A glass carbon electrode was utilized as the substrate for the working electrode. After that, 10 μ L of the prepared catalyst ink was drop-casted onto the glass carbon electrode. The catalyst loading on the working electrode was set at 0.25 mg cm^{−2}. For comparison, the commercial Pt/C (20 wt.% Pt) catalyst was also measured with a loading equal to that of the catalyst obtained in this study.

During the electrochemical measurements, all potentials were referenced to a reversible hydrogen electrode (RHE) by $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.93$. The detail for the conversion is presented in Figure S5. The potential of Hg/HgO was calibrated with the method described elsewhere [73]. The ORR activity was investigated using CV and LSV techniques in N₂- or O₂-purged 0.1 M KOH electrolyte. To further investigate the ORR mechanism, the RRDE experiments were conducted at a scan rate of 10 mV s^{−1}. The ring potential was set at 1.5 V_{RHE} in the O₂-saturated electrolyte [74]. The stability of the catalyst was assessed by recording chronoamperometric current-time (i-t) curves at −0.2 V vs. Hg/HgO (0.73 V_{RHE}) in the O₂-saturated electrolyte, with a rotation speed of 400 rpm.

The carbon morphologies were examined using the SEM with the JEOL JSM-7500F model. The TEM was performed using the JEOL JEM-2100F model. The XRD patterns were obtained using Cu K α radiation ($\lambda = 1.5406$ Å) with a Panalytical Empyrean instrument. The XPS spectra were collected using a monochromatic Al K α X-ray source on a V.G. Escalab220i-XL instrument. The pore size distribution and specific surface area measurements were conducted using an N₂ adsorption/desorption isotherm with the Micromeritics ASAP 2020 V3.00 H instrument. The BET and Barrett-Joyner-Halenda (BJH) methods were applied to analyze the data. Raman spectra were collected using an XploRA PLUS spectrometer equipped with a laser operating at a wavelength of 526 nm.

To prepare the catalyst ink for preparing ZABs, a mixture of 350 μ L of ethanol, 5 mg of the prepared catalyst, and 50 μ L of Nafion solution (5 wt.%) was sonicated for 45 min. Next, 80 μ L of the catalyst ink was pipetted and coated onto a hydrophilic carbon paper, serving as the cathode, with a catalyst loading of 1 mg cm^{−2}. A polished zinc plane was used as the negative electrode. For the electrolyte, a mixture solution of 0.2 M Zn(CH₃COO)₂ and 6 M KOH was used. A battery with a working area of 1 cm² was assembled. The prepared ZABs were allowed to stabilize at room temperature for 1 h before testing. The discharge behavior of the batteries was recorded using a CHI 760E instrument. For comparison, batteries with C₁, C₂, and C₃ catalysts as well as a battery without any catalyst were assembled and tested under similar conditions.

4. Conclusions

In this study, a facile method has been developed to prepare a porous N, S, and O co-doped carbon catalyst with favorable composition and structure for the electrocatalytic ORR. The carbon catalyst was synthesized using a precursor similar to that of the “Pharaoh’s snakes” reaction. The presence of multiple dopants and the unique structure of the carbon catalyst contribute to its significantly improved catalytic performance compared to control samples doped with only one or two heteroatoms. Based on the electrochemical measurement results, this catalyst exhibits profound electrocatalytic activity for the ORR through a 4-electron pathway. It displayed an onset potential of 0.97 V_{RHE} and a half-wave potential of approximately 0.83 V_{RHE}. These performance parameters are comparable to those of commercially available Pt/C (20 wt.% Pt) catalysts. Furthermore, the stability of the N, S, and O co-doped carbon catalyst was assessed. It demonstrated excellent stability,

with 93% of the initial current remaining after a stability test of 10,800 s. These findings highlight the great potential of N, S, and O co-doped carbon catalysts as metal-free alternatives for ORR catalysis, which is a critical cathode reaction in various emerging power sources. The study, therefore, contributes to the development of alternative processes in a facile approach for preparing high-performance metal-free ORR catalysts.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal13071059/s1>: Figure S1: CV curves of C₁, C₂, and C₃; Figure S2: XPS spectra of C₁; Figure S3: ¹H NMR with D₂O as the solvent; Figure S4: Picture of the prepared carbon from sugar powder, NH₄HCO₃, melamine and ionic liquid of [Etmim]EtSO₄; Figure S5: CV curves for the calibration of Hg/HgO reference electrode.

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References

- Li, G.; Wang, X.L.; Fu, J.; Li, J.D.; Park, M.G.; Zhang, Y.N.; Lui, G.; Chen, Z.W. Pomegranate-inspired design of highly active and durable bifunctional electrocatalysts for rechargeable metal-air batteries. *Angew. Chem. Int. Ed.* **2016**, *55*, 4977–4982. [\[CrossRef\]](#) [\[PubMed\]](#)
- Borghei, M.; Laocharoen, N.; Kibena-Pöldsepp, E.; Johansson, L.-S.; Campbell, J.; Kauppinen, E.; Tammeveski, K.; Rojas, O.J. Porous N, P-doped carbon from coconut shells with high electrocatalytic activity for oxygen reduction: Alternative to Pt-C for alkaline fuel cells. *Appl. Catal. B-Environ.* **2017**, *204*, 394–402. [\[CrossRef\]](#)
- Adith, R.V.; Madasamy, K.; Ebenezer, J.; Mohanapriya, N.; Kosame, S.; Ramesh, B.K.; Kathiresan, M.; Kumar, S.S.; Chandrasekaran, N. Molecularly engineered oxygen deficient magnetite decorated carbon as electrocatalysts for oxygen reduction reaction. *Mol. Catal.* **2021**, *514*, 11837–11847. [\[CrossRef\]](#)
- Yin, Z.; Lin, L.; Ma, D. Construction of Pd-based nanocatalysts for fuel cells: Opportunities and challenges. *Catal. Sci. Technol.* **2014**, *4*, 4116–4128. [\[CrossRef\]](#)
- Gao, J.; Ma, N.; Zhai, J.; Li, T.; Qin, W.; Zhang, T.; Yin, Z. Polymerizable ionic liquid as nitrogen-doping precursor for Co-N-C catalyst with enhanced oxygen reduction activity. *Ind. Eng. Chem. Res.* **2015**, *54*, 7984–7989. [\[CrossRef\]](#)
- Gao, J.; Ma, N.; Zheng, Y.; Zhang, J.; Gui, J.; Guo, C.; An, H.; Tan, X.; Yin, Z.; Ma, D. Cobalt/nitrogen-doped porous carbon nanosheets derived from polymerizable ionic liquids as bifunctional electrocatalyst for oxygen evolution and oxygen reduction reaction. *ChemCatChem* **2017**, *9*, 1601–1609. [\[CrossRef\]](#)
- Zhuang, Q.; Ma, N.; Yin, Z.; Yang, X.; Yin, Z.; Gao, J.; Xu, Y.; Gao, Z.; Wang, H.; Kang, J. Rich surface oxygen vacancies of MnO₂ for enhancing electrocatalytic oxygen reduction and oxygen evolution reactions. *Adv. Energy Sustain. Res.* **2021**, *2*, 2100030. [\[CrossRef\]](#)
- Yin, Z.; Chi, M.; Zhu, Q.; Ma, D.; Sun, J.; Bao, X. Supported bimetallic PdAu nanoparticles with superior electrocatalytic activity towards methanol oxidation. *J. Mater. Chem. A* **2013**, *1*, 9157–9163. [\[CrossRef\]](#)
- Yang, Z.; Yao, Z.; Li, G.; Fang, G.; Nie, H.; Liu, Z.; Zhou, X.; Chen, X.; Huang, S. Sulfur-doped graphene as an efficient metal-free cathode catalyst for oxygen reduction. *ACS Nano* **2012**, *6*, 205–211. [\[CrossRef\]](#)
- Yang, W.G.; Gong, Z.W.; Chen, Y.N.; Chen, R.R.; Meng, D.L.; Cao, M.N. Nitrogen Doped Carbon as Efficient Catalyst toward Oxygen Reduction Reaction. *Chin. J. Struct. Chem.* **2020**, *39*, 287–293.
- Gao, J.; Wang, Y.; Wu, H.; Liu, X.; Wang, L.; Yu, Q.; Li, A.; Wang, H.; Song, C.; Gao, Z.; et al. Construction of a sp³/sp² carbon interface in 3D N-doped nanocarbons for the oxygen reduction reaction. *Angew. Chem. Int. Ed.* **2019**, *58*, 15089–15097. [\[CrossRef\]](#) [\[PubMed\]](#)
- Wu, J.; Jin, C.; Yang, Z.; Tian, J.; Yang, R. Synthesis of phosphorus-doped carbon hollow spheres as efficient metal-free electrocatalysts for oxygen reduction. *Carbon* **2015**, *82*, 562–571. [\[CrossRef\]](#)

13. He, B.; Shen, J.; Ma, D.; Lu, Z.; Yang, Z. Boron-Doped C₃N Monolayer as a Promising Metal-Free Oxygen Reduction Reaction Catalyst: A Theoretical Insight. *J. Phys. Chem. C* **2018**, *122*, 20312–20322. [[CrossRef](#)]
14. Lin, Y.; Hu, Z.; Shao, Y.; Chen, Z.; Wei, X.; Wu, Z. Single-precursor design and solvent-free nanocasting synthesis of N/S/O-doped ordered mesoporous carbons with trimodal pores for excellent oxygen reduction. *Carbon* **2021**, *183*, 390–403. [[CrossRef](#)]
15. Shah, S.S.A.; Najam, T.; Nazir, M.A.; Wu, Y.Y.; Ali, H.; Rehman, A.U.; Rahman, M.M.; Imran, M.; Javed, M.S. Salt-assisted gas-liquid interfacial fluorine doping: Metal-free defect-induced electrocatalyst for oxygen reduction reaction. *Mol. Catal.* **2021**, *514*, 11878–11888. [[CrossRef](#)]
16. Gao, J.; He, C.; Liu, J.; Ren, P.; Lu, H.; Feng, J.; Zou, Z.; Yin, Z.; Wen, X.; Tan, X. Polymerizable ionic liquid as a precursor for N, P co-doped carbon toward the oxygen reduction reaction. *Catal. Sci. Technol.* **2018**, *8*, 1142–1150. [[CrossRef](#)]
17. Cao, S.; Shang, W.; Li, G.-L.; Lu, Z.-F.; Wang, X.; Yan, Y.; Hao, C.; Wang, S.; Sun, G. Defect-rich and metal-free N, S co-doped 3D interconnected mesoporous carbon material as an advanced electrocatalyst towards oxygen reduction reaction. *Carbon* **2021**, *184*, 127–135. [[CrossRef](#)]
18. Li, J.; Chen, Y.; Tang, Y.; Li, S.; Dong, H.; Li, K.; Han, M.; Lan, Y.-Q.; Bao, J.; Dai, Z. Metal–organic framework templated nitrogen and sulfur co-doped porous carbons as highly efficient metal-free electrocatalysts for oxygen reduction reactions. *J. Mater. Chem. A* **2014**, *2*, 6316–6319. [[CrossRef](#)]
19. Bera, R.K.; Park, H.; Ryoo, R. Co₃O₄ nanosheets on zeolite-templated carbon as an efficient oxygen electrocatalyst for a zinc–air battery. *J. Mater. Chem. A* **2019**, *7*, 9988–9996. [[CrossRef](#)]
20. Yang, J.; Xiang, F.; Guo, H.; Wang, L.; Niu, X. Honeycomb-like porous carbon with N and S dual-doping as metal-free catalyst for the oxygen reduction reaction. *Carbon* **2020**, *156*, 514–522. [[CrossRef](#)]
21. Zhu, Q.; Lian, J.; Chen, X.; Zhao, J.; Gao, Y.; Wang, X. Dual optimization strategy to construct hierarchical reticulated porous framework with enriched Fe-NX active species for the highly efficient oxygen reduction reaction. *Int. J. Hydrogen Energy* **2022**, *47*, 16840–16851. [[CrossRef](#)]
22. Jalili, A.H.; Shokouhi, M.; Maurer, G.; Hosseini-Jenab, M. Solubility of CO₂ and H₂S in the ionic liquid 1-ethyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate. *J. Chem. Thermodyn.* **2014**, *74*, 286. [[CrossRef](#)]
23. Gao, J.; Zhou, M.; Wang, X.; Wang, H.; Yin, Z.; Tan, X.; Li, Y. Preparing Co/N-Doped Carbon as Electrocatalyst toward Oxygen Reduction Reaction via the Ancient “Pharaoh’s Snakes” Reaction. *Batteries* **2022**, *8*, 150. [[CrossRef](#)]
24. Zhang, J.; Zhao, Z.; Xia, Z.; Dai, L. A metal-free bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions. *Nat. Nanotechnol.* **2015**, *10*, 444–452. [[CrossRef](#)]
25. Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction. *Science* **2009**, *323*, 760–764. [[CrossRef](#)]
26. Zhang, J.; Dai, L. Nitrogen, phosphorus, and fluorine tri-doped graphene as a multifunctional catalyst for self-powered electrochemical water splitting. *Angew. Chem. Int. Ed.* **2016**, *55*, 13296–13300. [[CrossRef](#)]
27. Zhu, Y.P.; Guo, C.X.; Zheng, Y.; Qiao, S.Z. Surface and interface engineering of noble-metal-free electrocatalysts for efficient energy conversion processes. *Acc. Chem. Res.* **2017**, *50*, 915–923. [[CrossRef](#)] [[PubMed](#)]
28. Ito, Y.; Qiu, H.J.; Fujita, T.; Tanabe, Y.; Tanigaki, K.; Chen, M.W. Bicontinuous Nanoporous N-doped Graphene for the Oxygen Reduction Reaction. *Adv. Mater.* **2014**, *26*, 4145–4150. [[CrossRef](#)]
29. Dai, L.; Xue, Y.; Qu, L.; Choi, H.J.; Baek, J.B. Metal-free catalysts for oxygen reduction reaction. *Chem. Rev.* **2015**, *115*, 4823–4892. [[CrossRef](#)]
30. Tran, T.S.; Balu, R.; Nguyen, C.K.; Mata, J.; Truong, V.K.; Dutta, N.K.; Choudhury, N.R. Graphene Nanosheets Stabilized by P3HT Nanoparticles for Printable Metal-Free Electrocatalysts for Oxygen Reduction. *ACS Appl. Nano Mater.* **2023**, *6*, 908–917. [[CrossRef](#)]
31. McCrory, C.C.L.; Jung, S.; Peters, J.C.; Jaramillo, T.F. Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction. *J. Am. Chem. Soc.* **2013**, *135*, 16977–16987. [[CrossRef](#)] [[PubMed](#)]
32. Tan, L.; Wang, P.; Lu, R.; Feng, S.; Yuan, G.; Wang, C. Design and synthesis of hollow Ce/Zr-UiO-66 nanoreactors for synergistic and efficient catalysis. *J. Solid State Chem.* **2022**, *312*, 123306. [[CrossRef](#)]
33. Patel, P.P.; Datta, M.K.; Velikokhatnyi, O.I.; Kuruba, R.; Damodaran, K.; Jampani, P.; Gattu, B.; Shanthi, P.M.; Damle, S.S.; Kumta, P.N. Noble metal-free bifunctional oxygen evolution and oxygen reduction acidic media electro-catalysts. *Sci. Rep.* **2016**, *6*, 28367. [[CrossRef](#)] [[PubMed](#)]
34. Pavel, C.C.; Cecconi, F.; Emiliani, C.; Santiccioli, S.; Scaffidi, A.; Catanorchi, S.; Comotti, M. Highly efficient platinum group metal free based membrane-electrode assembly for anion exchange membrane water electrolysis. *Angew. Chem. Int. Ed.* **2014**, *53*, 1378–1381. [[CrossRef](#)]
35. Chen, J.; Wang, X.; Cui, X.; Yang, G.; Zheng, W. Amorphous carbon enriched with pyridinic nitrogen as an efficient metal-free electrocatalyst for oxygen reduction reaction. *Chem. Commun.* **2014**, *50*, 557–559. [[CrossRef](#)]
36. Cao, L.; Lin, Z.; Huang, J.; Yu, X.; Wu, X.; Zhang, B.; Zhan, Y.; Xie, F.; Zhang, W.; Chen, J. Nitrogen doped amorphous carbon as metal free electrocatalyst for oxygen reduction reaction. *Int. J. Hydrogen Energy* **2017**, *42*, 876–885. [[CrossRef](#)]
37. Wei, D.; Liu, Y.; Wang, Y.; Zhang, H.; Huang, L.; Yu, G. Synthesis of N-Doped Graphene by Chemical Vapor Deposition and Its Electrical Properties. *Nano Lett.* **2009**, *9*, 1752–1758.
38. Wang, J.; Gao, D.; Wang, G.; Miao, S.; Wu, H.; Li, J.; Bao, X. Cobalt nanoparticles encapsulated in nitrogen-doped carbon as a bifunctional catalyst for water electrolysis. *J. Mater. Chem. A* **2014**, *2*, 20067–20074.

39. Zhimin, L.; Dongliang, Y.; Guangqin, Q.; Jingzhi, S.; Huanping, Y.; Yanlong, W.; Lihui, Y.; Ting, Y.; Wei, H.; Lianhui, W. Microwave-assisted solvothermal preparation of nitrogen and sulfur co-doped reduced graphene oxide and graphene quantum dots hybrids for highly efficient oxygen reduction. *J. Mater. Chem. A* **2014**, *2*, 20605–20611.
40. Wu, H.; Shi, L.; Lei, J.; Liu, D.; Qu, D.; Xie, Z.; Du, X.; Yang, P.; Hu, X.; Li, J. Nitrogen and sulfur co-doped carbon with three-dimensional ordered macroporosity: An efficient metal-free oxygen reduction catalyst derived from ionic liquid. *J. Power Sources* **2016**, *323*, 90–96. [\[CrossRef\]](#)
41. Chen, X.; Xu, X.; Yang, Z.; Liu, Z.; Zhang, L.; Xu, X.; Chen, Y.; Huang, S. Sulfur-doped porous reduced graphene oxide hollow nanosphere frameworks as metal-free electrocatalysts for oxygen reduction reaction and as supercapacitor electrode materials. *Nanoscale* **2014**, *6*, 13740–13747. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Yan, X.; Jia, Y.; Chen, F.; Zhu, Z.; Yao, X. Defective-activated-carbon-supported Mn-Co nanoparticles as a highly efficient electrocatalyst for oxygen reduction. *Adv. Mater.* **2016**, *28*, 8771–8778. [\[CrossRef\]](#)
43. Yan, X.; Jia, Y.; Odedairo, T.; Zhao, X.; Jin, Z.; Zhu, Z.; Yao, X. Activated carbon becomes active for oxygen reduction and hydrogen evolution reactions. *Chem. Commun.* **2016**, *52*, 8156–8159. [\[CrossRef\]](#)
44. Barik, R.; Raulo, A.; Jha, S.; Nandan, B.; Ingole, P.P. Polymer-derived electrospun Co_3O_4 @C porous nanofiber network for flexible, high-performance, and stable supercapacitors. *ACS Appl. Energy Mater.* **2020**, *3*, 11002–11014. [\[CrossRef\]](#)
45. Zhang, X.; Hu, X.; Lv, S.; Li, Y.; Ren, J.; Huang, Y. Hollow NH_2 -MIL-101@TA derived electrocatalyst for enhanced oxygen reduction reaction and oxygen evolution reaction. *Int. J. Hydrogen Energy* **2021**, *46*, 38692–38700. [\[CrossRef\]](#)
46. Wang, S.; Dong, S.; Wang, J.; Zhang, L.; Han, P.; Zhang, C.; Wang, X.; Zhang, K.; Lan, Z.; Cui, G. Oxygen-enriched carbon material for catalyzing oxygen reduction towards hybrid electrolyte Li-air battery. *J. Mater. Chem.* **2012**, *22*, 21051–21056. [\[CrossRef\]](#)
47. Sevilla, M.; Fuertes, A.B. Highly porous S-doped carbons. *Micropo. Mesopor. Mat.* **2012**, *158*, 318–323. [\[CrossRef\]](#)
48. Shen, M.; Ruan, C.; Chen, Y.; Jiang, C.; Ai, K.; Lu, L. Covalent entrapment of cobalt–iron sulfides in N-doped mesoporous carbon: Extraordinary bifunctional electrocatalysts for oxygen reduction and evolution reactions. *ACS Appl. Mater. Interfaces* **2015**, *7*, 1207–1218. [\[CrossRef\]](#) [\[PubMed\]](#)
49. Kurak, K.A.; Anderson, A.B. Nitrogen-treated graphite and oxygen electroreduction on pyridinic edge sites. *J. Phys. Chem. C* **2009**, *113*, 6730–6734. [\[CrossRef\]](#)
50. Zhu, J.; He, C.; Li, Y.; Kang, S.; Shen, P.K. One-step synthesis of boron and nitrogen-dual-self-doped graphene sheets as non-metal catalysts for oxygen reduction reaction. *J. Mater. Chem. A* **2013**, *1*, 14700–14705. [\[CrossRef\]](#)
51. Wang, P.; Wang, Z.; Jia, L.; Xiao, Z. Origin of the catalytic activity of graphite nitride for the electrochemical reduction of oxygen: Geometric factors vs. electronic factors. *Phys. Chem. Chem. Phys.* **2009**, *11*, 2730–2740. [\[CrossRef\]](#) [\[PubMed\]](#)
52. Wu, Z.; Wu, H.; Niu, T.; Wang, S.; Fu, G.; Jin, W.; Ma, T. Sulfurated metal–organic framework-derived nanocomposites for efficient bifunctional oxygen electrocatalysis and rechargeable Zn–air battery. *ACS Sustain. Chem. Eng.* **2020**, *8*, 9226–9234. [\[CrossRef\]](#)
53. Zhou, H.; Hu, J. Facile synthesis of multi-walled carbon nanotubes/Co₉S₈ composites with enhanced performances for sodium-ion battery. *Mater. Lett.* **2017**, *195*, 26–30. [\[CrossRef\]](#)
54. Wang, A.; Liang, H.; Chen, F.; Tian, X.; Yin, S.; Jing, S.; Tsiakaras, P. Facile synthesis of C_3N_4 /NiIn₂S₄ heterostructure with novel solar steam evaporation efficiency and photocatalytic H_2O_2 production performance. *Appl. Catal. B-Environ.* **2022**, *310*, 121336. [\[CrossRef\]](#)
55. Ingavale, S.B.; Patil, I.M.; Parse, H.B.; Ramgir, N.; Kakade, B.; Swami, A. B, N, S tri-doped reduced graphite oxide–cobalt oxide composite: A bifunctional electrocatalyst for enhanced oxygen reduction and oxygen evolution reactions. *New J. Chem.* **2018**, *42*, 12908–12917. [\[CrossRef\]](#)
56. Mahmood, J.; Li, F.; Kim, C.; Choi, H.-J.; Gwon, O.; Jung, S.-M.; Seo, J.-M.; Cho, S.-J.; Ju, Y.-W.; Jeong, H.Y. Fe@C₂N: A highly-efficient indirect-contact oxygen reduction catalyst. *Nano Energy* **2018**, *44*, 304–310. [\[CrossRef\]](#)
57. Zhang, D.; Han, M.; Li, Y.; Lei, L.; Shang, Y.; Wang, K.; Wang, Y.; Zhang, Z.; Zhang, X.; Feng, H. Phosphorus and sulfur dual doped hierarchic porous carbons with superior supercapacitance performance. *Electrochim. Acta* **2016**, *222*, 141–148. [\[CrossRef\]](#)
58. Li, Y.; Li, W.; Liu, D.; Chen, T.; Jia, S.; Yang, F.; Zhang, X. Carboxyl functionalized double-walled carbon nanotubes for oxygen evolution reaction. *Electrochim. Acta* **2022**, *419*, 140395. [\[CrossRef\]](#)
59. Zhang, L.; Xia, Z. Mechanisms of Oxygen Reduction Reaction on Nitrogen-Doped Graphene for Fuel Cells. *J. Phys. Chem. C* **2011**, *115*, 11170–11176. [\[CrossRef\]](#)
60. Sun, J.; Lowe, S.E.; Zhang, L.; Wang, Y.; Pang, K.; Wang, Y.; Zhong, Y.; Liu, P.; Zhao, K.; Tang, Z. Ultrathin nitrogen-doped holey carbon@graphene bifunctional electrocatalyst for oxygen reduction and evolution reactions in alkaline and acidic media. *Angew. Chem. Int. Ed.* **2018**, *57*, 16511–16515. [\[CrossRef\]](#)
61. Liu, X.; Jiang, L.; Zhu, Z.; Chen, S.; Dou, Y.; Liu, P.; Wang, Y.; Yin, H.; Tang, Z.; Zhao, H. Wet-chemistry grafted active pyridinic nitrogen sites on holey graphene edges as high performance ORR electrocatalyst for Zn–Air batteries. *Mater. Today Energy* **2019**, *11*, 24–29. [\[CrossRef\]](#)
62. Fan, H.; Wang, Y.; Gao, F.; Yang, L.; Liu, M.; Du, X.; Wang, P.; Yang, L.; Wu, Q.; Wang, X. Hierarchical sulfur and nitrogen co-doped carbon nanocages as efficient bifunctional oxygen electrocatalysts for rechargeable Zn–air battery. *J. Energy Chem.* **2019**, *34*, 64–71. [\[CrossRef\]](#)
63. Paraknowitsch, J.P.; Thomas, A.; Antonietti, M. A detailed view on the polycondensation of ionic liquid monomers towards nitrogen doped carbon materials. *J. Mater. Chem.* **2010**, *20*, 6746–6758. [\[CrossRef\]](#)

64. Flyagina, I.; Hughes, K.; Pourkashanian, M.; Ingham, D. A theoretical study of molecular oxygen chemisorption on N, B, or O doped carbon edge sites. *Fuel Cells* **2014**, *14*, 709–719. [[CrossRef](#)]
65. Wang, S.; Yu, D.; Dai, L. Polyelectrolyte functionalized carbon nanotubes as efficient metal-free electrocatalysts for oxygen reduction. *J. Am. Chem. Soc.* **2011**, *133*, 5182–5185. [[CrossRef](#)]
66. Subramanian, P.; Schechter, A. Electrochemical oxygen reduction activity of cobalt-nitrogen-carbon composite catalyst prepared by single precursor pyrolysis under autogenic pressure. *J. Electrochem. Soc.* **2016**, *163*, F428–F436. [[CrossRef](#)]
67. Wang, J.; Pan, J.; Zeng, X.; Tang, G.; Cai, J.; Khan, A.; Sun, Y.; Liu, X. A facile preparation of nano-Ag₄Bi₂O₅/MnOx on wrinkled rGO as greatly enhanced ternary catalyst for oxygen reduction reaction in alkaline electrolyte. *J. Solid State Electrochem.* **2019**, *23*, 2737–2746. [[CrossRef](#)]
68. Karimi-Maleh, H.; Karaman, C.; Karaman, O.; Karimi, F.; Vasseghian, Y.; Fu, L.; Baghayeri, M.; Rouhi, J.; Senthil Kumar, P.; Show, P.-L. Nanochemistry approach for the fabrication of Fe and N co-decorated biomass-derived activated carbon frameworks: A promising oxygen reduction reaction electrocatalyst in neutral media. *J. Nanostructure Chem.* **2022**, *12*, 429–439. [[CrossRef](#)]
69. Goswami, C.; Saikia, H.; Tada, K.; Tanaka, S.; Sudarsanam, P.; Bhargava, S.K.; Bharali, P. Bimetallic palladium–nickel nanoparticles anchored on carbon as high-performance electrocatalysts for oxygen reduction and formic acid oxidation reactions. *ACS Appl. Energy Mater.* **2020**, *3*, 9285–9295. [[CrossRef](#)]
70. Tran, T.S.; Balu, R.; de Campo, L.; Dutta, N.K.; Choudhury, N.R. Sulfonated polythiophene-interfaced graphene for water-redispersible graphene powder with high conductivity and electrocatalytic activity. *Energy Adv.* **2023**, *2*, 365–374. [[CrossRef](#)]
71. Gan, R.; Song, Y.; Ma, C.; Shi, J. In situ growth of N-doped carbon nanotubes in Fe-Nx/Fe₂O₃/Fe₃O₄-encapsulated carbon sheets for efficient bifunctional oxygen catalysis. *Appl. Catal. B-Environ.* **2023**, *327*, 122443–122452. [[CrossRef](#)]
72. Tang, C.; Wang, B.; Wang, H.F.; Zhang, Q. Defect engineering toward atomic Co–Nx–C in hierarchical graphene for rechargeable flexible solid Zn-air batteries. *Adv. Mater.* **2017**, *29*, 1703185–1703194. [[CrossRef](#)] [[PubMed](#)]
73. Li, Y.G.; Zhou, W.; Wang, H.L.; Xie, L.M.; Liang, Y.Y.; Wei, F.; Idrobo, J.C.; Pennycook, S.J.; Dai, H.J. An oxygen reduction electrocatalyst based on carbon nanotube-graphene complexes. *Nat. Nanotechnol.* **2012**, *7*, 394–400. [[CrossRef](#)] [[PubMed](#)]
74. Yang, L.; Yu, J.; Wei, Z.; Li, G.; Cao, L.; Zhou, W.; Chen, S. Co-N-doped MoO₂ nanowires as efficient electrocatalysts for the oxygen reduction reaction and hydrogen evolution reaction. *Nano Energy* **2017**, *41*, 772–779. [[CrossRef](#)]

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