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Vacancy-engineered CeO₂/Co heterostructure anchored on the nitrogen-doped porous carbon nanosheet arrays vertically grown on carbon cloth as an integrated cathode for the oxygen reduction reaction of rechargeable Zn–air battery†

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A rechargeable zinc–air battery (ZAB) is regarded as a promising energy storage device owing to its high energy density, good safety, and environmental friendliness. However, the development of non-precious metal catalysts for improving the sluggish oxygen reaction kinetics of the air cathode of ZAB still presents a challenge. Herein, nitrogen-doped porous carbon nanosheet arrays vertically grown on carbon cloth decorated with CeO₂/Co heterostructure (Co/CeO₂-NCNA@CC) as an integrated cathode have been successfully constructed using a facile carbonization–hydrolysis procedure using a metal–organic framework (MOF) as a precursor. The size of CeO₂ nanoparticles can be controlled with an average diameter of about 6.0 nm through unique hydrolysis to form the heterostructure with Co species, which are uniformly dispersed on the surface of nitrogen-doped porous carbon nanosheet arrays (NCNA). NCNA vertically grown on carbon cloth (CC) has improved wettability and allows for the CeO₂/Co heterostructure to be easily accessible. The abundant intrinsic oxygen vacancies in CeO₂ bring the catalyst an excellent ability to tune the oxygen concentration during the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) processes. The integrity of the electrode accelerates the transfer of electrons from the active sites to the CC current collector. Therefore, ZAB using Co/CeO₂-NCNA@CC as the integrated cathode exhibits an impressive electrocatalytic performance toward both ORR and OER. The ZAB with Co/CeO₂-NCNA@CC cathode has an open-circuit voltage of 1.47 V and supply capacity of 784.4 mA h g_{Zn}⁻¹ even after 380 h operation at 5.0 mA cm⁻², which surpasses the catalysts of commercial Pt/C + RuO₂ and the most reported catalysts.

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1 Introduction

Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are the key processes in the energy storage and transfer systems highly related to the oxygen reactions including fuel cells, metal–air rechargeable batteries and water electrolyzers.^{1–6} However, the sluggish nature of ORR and OER in kinetics becomes one of the bottleneck problems to develop these systems.^{7–9} Therefore, catalysts with high activity and good stability are required to accelerate the oxygen reaction for the applicable energy supply. The noble metals group-based

catalysts such as Pt, Ru, and Ir are still the most used in oxygen reactions due to their high activity,^{10–12} but commercial applications are seriously limited by their scarcity, high cost, and poor durability. Although, non-precious metal-based catalysts are given great expectations to substitute the precious metals catalysts due to the advantages of low cost,^{13–16} the challenge of how to explore the non-precious catalysts with comparable activity to the precious metal catalyst and possess good durability still remains to be solved.

As a renewable energy conversion system, rechargeable zinc–air battery (ZAB) has high theoretical energy density, environmental friendliness, cost-effectiveness and intrinsic safety, and is thus receiving tremendous interest.^{17–20} Since the air cathode of ZAB must afford both ORR and OER and must have the ability to make these two reactions work cooperatively during charge and discharge, it brings the catalysts more challenges. To put ZAB forward in practical technology, air cathode with high-efficient ORR/OER and good durability are highly expected. In addition to the essence of bi-functional properties,^{21–23} whether they are

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noble metal or non-precious metal/oxide, the intrinsic activity of catalysts, is derived from their electronic and crystal structure,^{24,25} which are highly related to dynamics of ORR/OER including adsorption, electron transfer, and intermediates formation.²⁶⁻²⁸ To fully utilize the intrinsic activity of catalysts, there are several critically important factors. Firstly, active sites are uniformly distributed on the supports and are easier to access, facilitating greater transport of ions and molecules. Secondly, it is needed to keep the strong interaction of the catalyst particles with the support to avoid agglomeration and maintain good conductivity of the support for fast electrons transfer kinetics. More importantly, for practical applications, is the able ability to integrate the electrocatalytic materials' microstructure with the macroscopic features of the electrode to make the oxygen reaction cathode work cooperatively and synergistically.

Metal-organic frameworks (MOF) are promising precursors and templates to prepare the metal (compounds) loading carbon-supported catalysts since their emerging advantages of highly porous and containing uniformly distributed coordination metal sites.²⁹⁻³² A variety of metals and their oxides containing the intrinsic catalysis on ORR/OER such as Fe, Co, Ni has been used to prepare the MOF-derived carbon supported catalysts.³³⁻³⁷ Owing to the porous carbon structure and the well-distributed active sites, MOF-derived catalysts exhibited good electrocatalytic performance on oxygen reactions.³⁸⁻⁴⁰ However, because the mechanical and thermal stabilities of MOF are not strong enough, it is not easy to convert MOF into porous carbon with the completely same structure as MOF using simple carbonization processes. In addition, carbon particles prepared by the carbonization of MOF may agglomerate. These problems will hinder the widespread utilization of MOF. Therefore, the critical factors to obtaining metal-loaded porous carbon-derived MOF with good quality boils down to how well the morphology and structure of MOF-derived carbons are maintained, and the agglomeration of carbon particles is avoided.

Co and its compounds have been widely studied as catalysts in the oxygen reduction reaction because of their activity derived the unpaired electrons of 3d orbit and adjustable surface electronic structure.⁹ Coincidentally, Co is commonly

2.4 Preparation of Pt/C or RuO₂ electrode

Commercial Pt/C (20 wt%, Alfa Aesar) or RuO₂ was well-dispersed in diluted Nafion alcohol solution (500 μL of ethanol and 50 μL of Nafion) to form a homogeneous suspension. Then, the suspension was dropwise added onto CC with the same mass loading as that of the Co/CeO₂-NCNA and dried at room temperature before the test.

2.5 Material characterization

The structure, morphology, and compositions of the samples were characterized by scanning electron microscopy (SEM, Thermo Fisher Scientific Apreos), transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN), X-ray photoelectron spectroscopy (XPS, Kratos AXIS-SUPRA), X-ray diffraction (XRD, D8 ADVANCE), elemental analysis (GENESIS XM), temperature-programmed desorption of O₂ (O₂-TPD, Auto Chem II 2920), and contact angle tester (Dataphysics OCA50).

2.6 Electrochemical measurement

All of the electrochemical measurements were conducted on a rotating disk electrode (RDE) controller connected to an electrochemical workstation. To investigate the ORR activity, the catalytic activities of the air cathodes were tested at room temperature using a standard three-electrode system in 0.1 M potassium hydroxide (KOH) electrolyte (pH = 13) in an O₂-saturated environment, with Ag/AgCl electrode as the reference electrode, a platinum wire as the counter electrode, and a catalyst-modified glassy carbon electrode (GCE) as the working electrode. Acrylic tape (3M VHB tape) was used to secure the samples (such as Co/CeO₂-NCNA@CC and Pt/C on carbon cloth, 5 × 5 mm²) on the glassy carbon rotating disc electrode tip (5 mm diameter). The electrochemical activity of the catalyst was investigated by linear sweeping voltammetry (LSV) in an O₂-saturated 0.1 M KOH solution with sweeping rates of 5 mV s⁻¹ at different rotating speeds (400–2500 rpm). Cyclic voltammetry (CV) was carried out in N₂/O₂-saturated 0.1 M KOH solution at a scan rate of 20 mV s⁻¹. All potentials in this study were converted to the reversible hydrogen electrode (RHE). The RHE was determined by calibrating the Ag/AgCl reference electrode in hydrogen-saturated electrolyte and thermodynamic potential was determined by the cyclic voltammetry scan. $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.209 \text{ V} + 0.059 \text{ V} \times \text{pH}$. Tafel plots were constructed using the Tafel equation, $\eta = \log \eta + \dots$, where i is the current density, b is the Tafel slope, and a is the intercept relative to the exchange current density.

To study the ORR kinetic properties, the Koutecky–Levich equation can be used for determining the electron transfer number (n) for each O₂ molecule at different rotation rates:

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

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6} \quad (2)$$

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

where J , J_k and J_L are the measured current density, kinetic and diffusion-limiting current densities, respectively. ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the rotation speed), n is the electron transfer number, F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$). In 0.1 M KOH electrolyte, the values of diffusion coefficient and saturation concentration of O₂ are $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (D_0) and $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ (C_0), respectively. The kinematic viscosity (ν) of the electrolyte was $0.01 \text{ cm}^2 \text{ s}^{-1}$ and k is the electron transfer rate constant. The number of electrons (n) was obtained by calculating the slope of $J^{-1} \propto \omega^{-1/2}$ in the plot. Rotating ring electrode (RDE) tests were conducted at a rotation speed of 1600 rpm with a scan rate of 10 mV s⁻¹ in O₂-saturated 0.1 M KOH solution.

The polarization curves for OER were measured at the scan rate of 5 mV s⁻¹ in 1.0 M KOH. The electrochemical surface area (ECSA) was calculated from the electrical double layer capacitance (C_{dl}) measurements, which were cycled at scan rates of 5, 10, 15, 20, 25 and 30 mV s⁻¹ with a potential range from 0.95 to 1.02 V . RHE.

2.7 Zn–air battery test

The air electrode was prepared by rolling the catalyst, which was loaded on carbon cloth onto a gas diffusion layer and nickel foam to form an air electrode. Nickel foam was used as the current collector for the air cathode. In order to ensure reversible zinc electrochemical reactions at the Zn anode, a rechargeable zinc–air battery was assembled using the as-prepared air-cathode, polished zinc plate as the anode, and 6 M KOH aqueous solution with 0.2 M Zn(CH₃COO)₂ as the electrolyte. The air cathode had an effective contact area of 1 cm² to the electrolyte and air. Measurements were carried out at 25 °C with an electrochemical workstation (CHI 660E). The polarization curve measurements were performed using LSV at 5 mV s⁻¹ and power density plots were obtained using a galvanodynamic method. The galvanodynamic charge and discharge profiles of the battery were obtained by scaling the current density from 2 to 50 mA cm⁻². A cycling test was performed using the recurrent galvanostatic pulse method with 15 min discharges with a constant current density of 5 mA cm⁻². Both the current density and power density were normalized to the effective surface area of the air electrode. The specific capacity was calculated from the galvanostatic discharge curve, normalized to the mass of consumed Zn anode.

3 Results and discussion

3.1 Structural and surface chemistry of catalyst

The fabrication process of the integrated cathode of Co/CeO₂-NCNA@CC and the corresponding morphology and structure of samples are shown in Fig. 1. Firstly, carbon cloth was simply treated in an HNO₃ solution by a hydrothermal method to improve the surface activity of CC for MOF growth, which did not alter the pristine morphology of CC as shown in Fig. 1b. Then, CC was immersed in a certain amount of 2-methylimidazole (2-MeIm) solution containing Co²⁺ at room temperature for 4.0 h to obtain the material of Co-MOF nanosheet

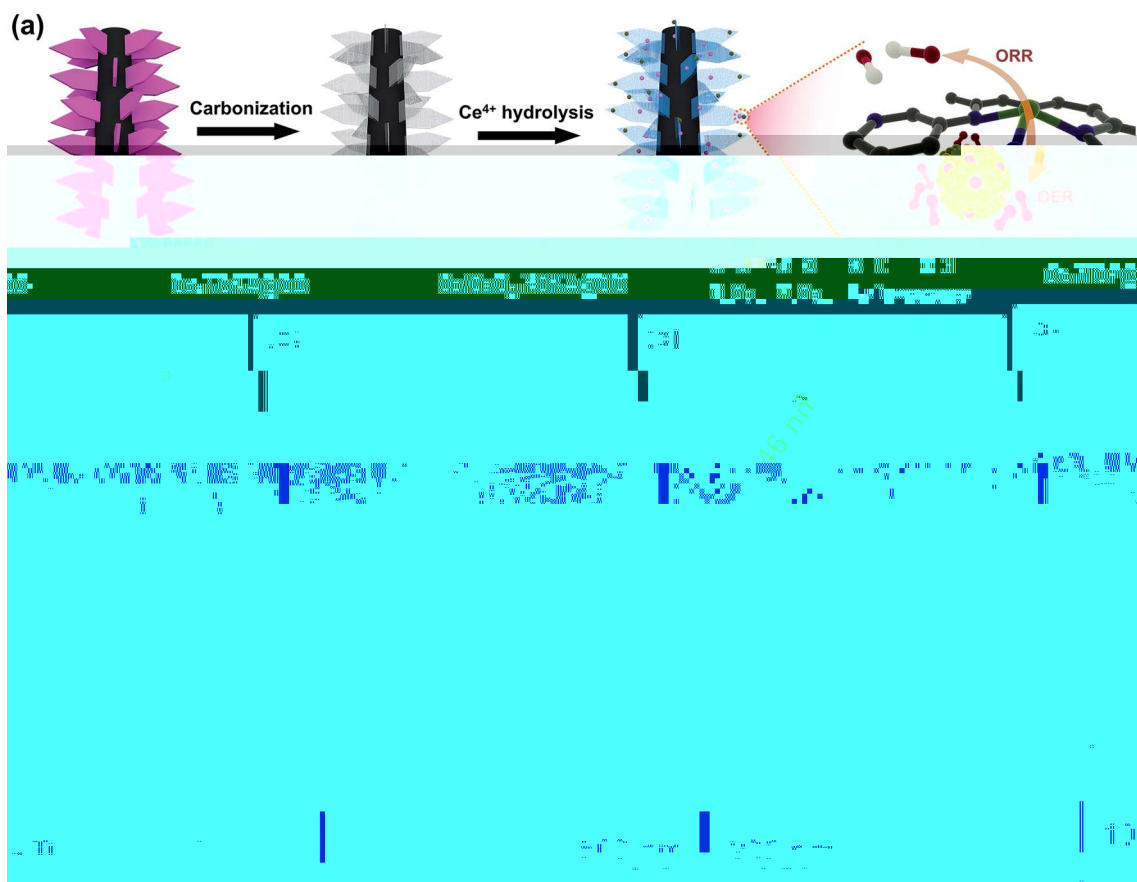


Fig. 1 (a) Schematic illustration of the fabrication of the integrated cathode of Co/CeO₂-NCNA@CC. SEM images of (b) HNO₃-treated carbon cloth, (c) and (d) Co-MOF@CC, (e) and (f) Co-NCNA@CC. TEM images of (g) Co-NCNA@CC.

arrays vertically grown to CC, which formed Co-MOF@CC. The scanning electron microscopy (SEM) images (Fig. 1c, d and S1a†) demonstrate that the Co-MOF nanosheet has an average thickness of about 346 nm and width of about 1.2 μm and is uniformly and vertically grown on CC. It can be noted that almost every MOF nanosheet is isolated when grown on CC to form the arrays, which could avoid the agglomeration of nanosheets in the next step of heat treatment. The structure of a single nanosheet was further examined using a transmission electron microscope (TEM) as shown in Fig. S1b;† one can see that the Co-MOF@CC nanosheets have solid features with a smooth surface. As shown in Fig. 1e and S1c,† the morphology of Co-MOF nanosheet arrays was well maintained after the carbonization and the acidic etching to remove the inactive Co species (Fig. S2†). During annealing in the N₂ atmosphere, the organic ligands from MOF were transformed into nitrogen-doped porous carbon and a part of the Co ions were reduced to Co nanoparticles. As a result, Co nanoparticles embedded to nitrogen-doped carbon nanosheet arrays grown on carbon cloth (Co-NCNA@CC) can be successfully obtained. The average thickness of Co-NCNA@CC shrinks to about 284 nm (Fig. 1d and f) from the original Co-MOF nanosheets (346 nm). As shown in Fig. 1g and S3,† the porous structure, and plenty of tiny Co nanoparticles with average diameters of 13 nm uniformly distributed in the carbon matrix can be observed.

Such a porous structure can not only improve the accessibility of active sites but also facilitate the fast dissipation of gaseous products during electrocatalysis. The content of Co in the Co-NCNA@CC is 0.81 wt% (Table S1†) measured using inductively coupled plasma (ICP). The integrated cathode can be illustrated by the macroscopic appearance as shown in Fig. S4,† the full preparation process can keep the integrity of Co-NCNA@CC.

To utilize the advantages of CeO₂ in tuning oxygen vacancies, the heterostructure of CeO₂/Co was constructed through a successive hydrolysis reaction process. It can be seen that the hydrolysis reaction does not alter the morphology of the MOF-derived NCNA (Fig. 2a–c and S5†). Moreover, it can be clearly observed from the TEM images (Fig. 2d) that the ultrafine CeO₂ nanocrystals with sizes 5 to 8 nm were successfully obtained (Fig. 2f and S6†). The high-resolution TEM (HR-TEM) image in Fig. 2e demonstrates the lattice spacing of 0.31 nm corresponding to the (111) plane of CeO₂ interfaced with Co indexing by lattice spacing of 0.20 nm of the (111) plane. The elemental mapping analysis of Co/CeO₂-NCNA@CC reveals a uniform distribution of C, N, O, Co and Ce over the profile of the nanosheet (Fig. 2g). As shown in the X-ray diffraction (XRD) pattern of Co/CeO₂-NCNA@CC (Fig. 3a), the diffraction peaks at 2θ values of 28.5°, 47.4°, 56.3°, 76.6° are corresponding to the (111), (220), (311) and (420) planes of the CeO₂ (JCPDS: 34-0394), respectively. The perspective views of the unit cells of CeO₂



Fig. 2 (a–c) SEM images of Co/CeO₂-NCNA@CC. (d) TEM and (e) HRTEM images of Co/CeO₂-NCNA@CC. (f) Normal distribution plot of CeO₂ nanoparticles. (g) Elemental mapping results of mixed elements C, N, O, Co and Ce. (h) The contact angle of CC and Co/CeO₂-NCNA@CC.

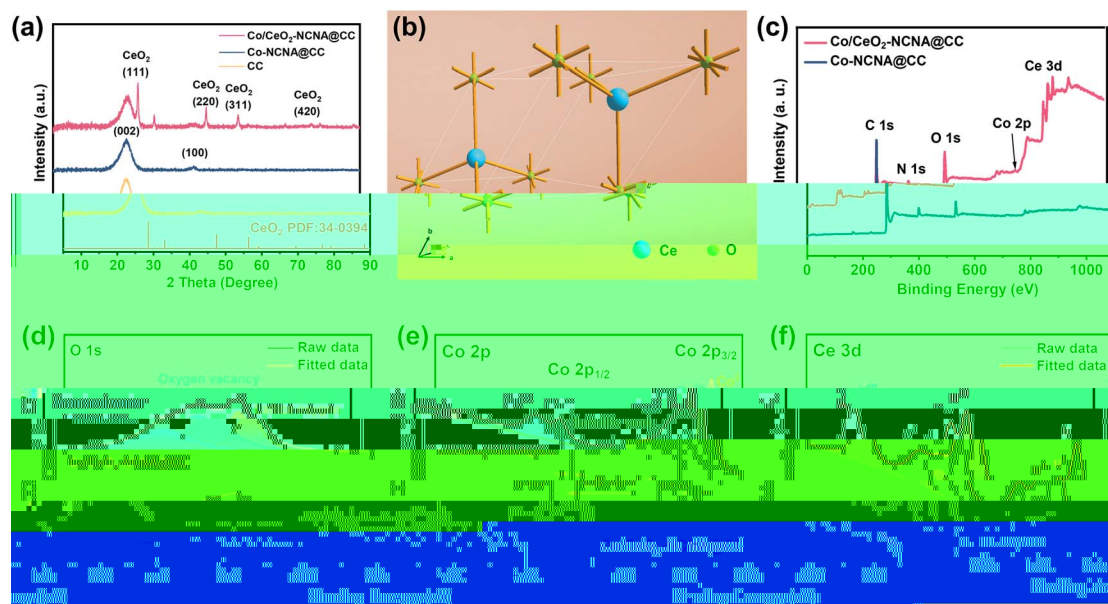


Fig. 3 (a) XRD patterns of CC, Co-NCNA@CC and Co/CeO₂-NCNA@CC. (b) The unit cell of CeO₂ structures. XPS spectra of (c) survey, (d) O 1s, (e) Co 2p, and (f) Ce 3d for Co/CeO₂-NCNA@CC and Co-NCNA@CC.

(space group $P6_3/$ (194)) are shown in Fig. 3b, confirming that the CeO_2 nanocrystals have been successfully introduced into the composites, which could be promising to support a synergistic effect on oxygen reaction catalysis. The feature of porous structure and uniform multiphase distribution of $\text{Co}/\text{CeO}_2\text{-NCNA@CC}$ bring improved surface hydrophilicity. As shown in Fig. 2h, carbon cloth has an obvious hydrophobicity with a contact angle of 151° , as a current collector, which may adversely impact the adsorption of reagents onto the cathode in the subsequent reaction. However, $\text{Co}/\text{CeO}_2\text{-NCNA}$ grown on CC results in a sharp decrease of the contact angle to 12° . The improved wettability of the $\text{Co}/\text{CeO}_2\text{-NCNA@CC}$ electrode not only enhances the interaction of reagents with the active sites but also promotes mass transport for electrocatalytic reaction kinetics.⁴⁹ Therefore, it will contribute to the electrocatalysis performance of the integrated cathode of the Zn-air battery.

The chemical state of samples is highly related to the intrinsic electrocatalysis activity. X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemical state and bonding configuration of Co-NCNA@CC and $\text{Co}/\text{CeO}_2\text{-NCNA@CC}$. XPS survey spectra of Fig. 3c confirm the surface elemental composition of C, N, O, Co in Co-NCNA@CC and the additional element of Ce in $\text{Co}/\text{CeO}_2\text{-NCNA@CC}$. The peaks corresponding to C 1s (284.6 eV), N 1s (398.0 eV), O 1s (531.5 eV) and Co 2p (780.7 eV) can be detected for both the samples. The peaks at around 886.0 eV are assigned to Ce 3d suggesting the successful introduction of Ce element in $\text{Co}/\text{CeO}_2\text{-NCNA@CC}$. These elemental contents in both samples are shown in Tables S1 and S2.†

The high-resolution spectrum of N 1s, O 1s, Co 2p and Ce 3d are shown in Fig. S7† and 3d-f. The N 1s spectra indicate four types of N containing species of pyridinic N (398.5 eV), Co-N (399.3 eV), pyrrolic N (400.4 eV) and graphitic N (401.2 eV) in both samples, which should be produced during the conversion of Co-MOF nanosheet arrays into Co-NCNA. Apart from improving the wettability, N-containing functional groups such as pyridinic-N and graphitic-N can enhance oxygen adsorption, weak O-O band and thus have electrocatalytic activity in the basic electrolyte.⁵⁰ Furthermore, it has been identified that Co-N sites show significant activity in the reversible oxygen reactions.⁵¹ As shown in Fig. 3d, the high-resolution spectra of O 1s can be decoupled into three characteristic peaks located at 533.1, 531.4 and 529.9 eV, respectively, derived from the adsorbed molecular water, the surface oxygen vacancies, and the lattice oxygen arising from metal oxides.^{52,53} Compared to Co-NCNA@CC , the larger peaks area percentage for the oxygen vacancies fraction in $\text{Co}/\text{CeO}_2\text{-NCNA@CC}$ implies that the introduction of CeO_2 significantly enlarges the tuning spaces for oxygen species and the existence of more oxygen vacancies. In the Co 2p spectrum (Fig. 3e), the peaks of the binding energy at 779.9 eV and 793.9 eV correspond to the characteristics of Co^{3+} , while the peaks at 781.6 eV and 796.4 eV are assigned to Co^{2+} . Both Co^{2+} and Co^{3+} are attributed to Co-N species.^{54,55} Moreover, a sharp peak at 778.3 eV assigned to Co^0 can be clearly observed in $\text{Co}/\text{CeO}_2\text{-NCNA@CC}$, which should be produced by carbothermal reduction of Co ions during the carbonization of Co-MOF nanosheet arrays. It is especially noted that the introduction of CeO_2 results in the peaks $\text{Co } 2p_{3/2}$ and $\text{Co } 2p_{1/2}$ positively shifting to 0.6 and

0.4 eV, respectively. This phenomenon suggests a strong chemical binding of CeO_2/Co heterostructure, which makes Co centers more positively charged and thus facilitates the electrostatic attraction of more anionic intermediates for a fast redox process in the alkaline medium.⁵⁶ When OH^- is oxidized and oxygen is released from the active site of Co species, the oxygen vacancy on CeO_2 can enhance OH^- adsorption due to the ability to fast store oxygen in O_2 -rich conditions.⁵⁷ Thus, the charge transfer effect may accelerate the redox process and enhance the OER performance of the catalyst. Fig. 3f depicts the Ce 3d-level spectrum that was fitted into Ce $3d_{3/2}$ (marked as V) and Ce $3d_{5/2}$ (marked as U) spin-orbit states. The peaks represented as V, V', V'', U, U' and U'' are ascribed to the characteristic peaks of Ce^{4+} , while the deconvoluted V' and U' peaks around 905.9 and 885.5 eV can be assigned to Ce^{3+}

decreases from 0.92 V to 0.86 V, indicating that Co-N sites play a key role in the highly electrocatalytic activity of ORR. It can be also noted that after the introduction of CeO₂, the half-wave potential is 20 mV higher than that of Pt/C (Fig. 4a), which is attributed to CeO₂ playing an essential role as an effective catalyst for “oxygen buffer”

TOF provide the evidence that Co/CeO₂-NCNA@CC presents the highest OER activity on a per-site basis, which is consistent with the Tafel and impedance spectroscopy results.

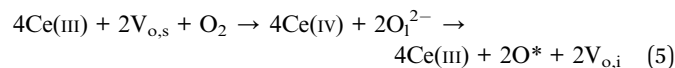
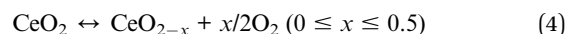
As a bifunctional electrocatalyst, the overall catalysis of oxygen reactions is generally assessed by the voltage gaps (ΔE) between the OER potential at 10 mA cm⁻² and ORR half-wave potential metrics ($\Delta E = E_{=10} - E_{1/2}$) and the results are shown in Fig. 4g. Remarkably, the ΔE value of Co/CeO₂-

voltage gap of 0.96 V after the first operation of 40 h, and only a slight increase in the voltage gap after 380 h of the operation. In contrast, ZAB with the Pt/C + RuO₂ cathode causes a large voltage gap of 1.26 V after the operation of 16 h. The excellent stability of ZAB can be attributed to the unique integrated structure of Co/CeO₂-NCNA@CC. The morphology and elemental composition of Co/CeO₂-NCNA@CC cathode after 100 cycles (Fig. S22†) proves that the nanosheet arrays are well kept to avoid the agglomeration and elements of Co, Ce, O and N are still uniformly distributed in NCNA to supply the active sites.

3.4 The proposed mechanism

To characterize the O₂ adsorption ability and the intrinsic oxygen vacancies of catalysts, temperature-programmed desorption of O₂ (O₂-TPD) was performed for the Co embedded nitrogen-doped carbon (Co-NC) and the CeO₂/Co heterostructure on the nitrogen-doped carbon (Co/CeO₂-NC) samples and the results are shown in Fig. 6a. To eliminate the influence of the carbon cloth, Co-NC and Co/CeO₂-NC were prepared by a similar synthesis method without using carbon cloth as a precursor. Usually, the oxygen desorption peaks below 500 °C can be attributed to physical absorption of oxygen (< 100 °C) and chemisorbed oxygen on the surface (250–350 °C).^{68,69} It can be concluded according to the peak area of O₂-TPD that both Co-NC and Co/CeO₂-NC can adsorb a considerable amount of oxygen, but the latter desorbs chemisorbed oxygen at a higher temperature and intensity. It indicates that Co/CeO₂-NC shows a much better capability for absorbing oxygen due to the excellent ability

of oxygen vacancy of CeO₂. Electron paramagnetic spin resonance (EPR) measurements (Fig. 6b) provide stronger evidence that CeO₂ has the ability to boost oxygen adsorption. Both samples show one EPR signal with a *g*-value of 2.003 that is caused by the trapped electrons due to the surface oxygen vacancies of the catalysts.^{70,71} Co/CeO₂-NCNA@CC exhibits a stronger peak intensity, revealing its ability to contain abundant oxygen vacancies to trap more electrons. It is consistent with the O₂-TPD analyses and the previous XPS analysis that the introduction of CeO₂ alters the surface electronic structure and enhances the adsorption energy of oxygen onto the catalyst.



On basis of the results above, a catalysis mechanism is proposed as illustrated by Fig. 6d. In the integrated cathode of Co/CeO₂-NCNA@CC, carbon cloth as the substrate and the current collector can enhance the electron transfer between each Co/CeO₂-NCNA. The porous and hydrophilic NCNA facilitate the adsorption and transport of active ions and molecules (O₂, OH⁻, OOH^{*}, O^{*}, and H₂O), and enhance the effective collision between reactants and active sites. CeO₂ has an excellent oxygen regulation ability to boost the activity of the heterostructure of CeO₂/Co due to the reversible conversion between reduced and oxidized states, which can be expressed by eqn (4).⁷² The catalytic mechanism involves three steps. Firstly,

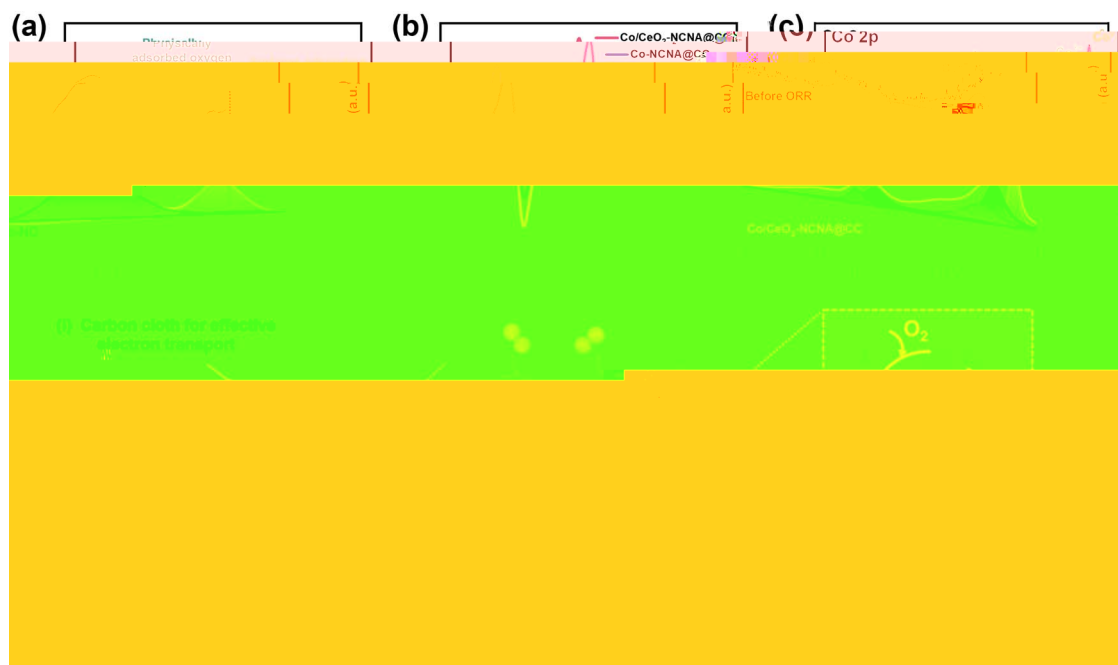


Fig. 6 (a) O₂-TPD profiles of Co-NC and Co/CeO₂-NC. (b) EPR spectra of Co-NCNA@CC and Co/CeO₂-NCNA@CC. (c) High-resolution XPS spectra of Co 2p for Co/CeO₂-NCNA@CC before and after the ORR tests. (d) Schematic diagram illustrating the structural advantages of Co/CeO₂-NCNA@CC in terms of electrochemical reactivity and synergistic effect.

the surface oxygen vacancies ($V_{o,s}$) in CeO_2 (Ce^{3+}) adsorb a large number of oxygen molecules to form the lattice oxygen (O_l^{2-}), and then Ce^{3+} undergoes the oxidation to form Ce^{4+} by eqn (5). Secondly, the lattice oxygen deviates its position to form active oxygen species (O^*) spontaneously and leaves the intrinsic oxygen vacancies ($V_{o,i}$).⁷³ The O^* can effectively migrate to the Co-containing active sites through the CeO_2/Co heterostructure and accept the electrons derived from the oxidation of Co^{2+} into Co^{3+} . The XPS of $Co/CeO_2-NCNA@CC$ before and after the ORR tests are shown in Fig. 6c. It can be noted that the percentages of Co^{3+}/Co^{2+} among the Co-N is 0.92 before the ORR test, but it increases to 1.47 after the ORR test. The significant increase in Co^{3+} after the ORR test evidently suggests the mechanism that O^* generates through CeO_2 and then traps the electrons from the oxidation of Co^{2+} . In the third step, the intrinsic oxygen vacancies ($V_{o,i}$) transfer to the surface of lattices, and the oxygen will fill the surface oxygen vacancies ($V_{o,s}$). The catalysis cycles illustrate that the mutual conversion of the three kinds of oxygen species promotes a continuous catalytic reaction process. The intrinsic oxygen vacancies of CeO_2 play as an oxygen storage station to supply oxygen species to the Co species active sites continuously, which greatly improves both half-wave potential and limiting current density.^{74,75}

4 Conclusions

A unique integrated cathode of ZAB containing a CeO_2/Co heterostructure embedded in N-doped carbon nanosheet arrays (NCNA) and vertically grown onto carbon cloth ($Co/CeO_2-NCNA@CC$) has been successfully constructed by a facile carbonization-acid etching process of Co-MOF grown on the carbon cloth and the subsequent successive hydrolysis reaction. In the integrated cathode, N-doped porous nanosheets are uniformly grown and isolated on the carbon cloth, which facilitates not only mass transport but also makes the CeO_2/Co heterostructure more accessible. The great oxygen tunability of CeO_2 enhances the catalytic activity and efficiency, and generate a synergistic effect on ORR and OER. As a result, the integrated cathode of $Co/CeO_2-NCNA@CC$ exhibits outstanding bifunctional performance with ΔE of 0.80 V. In a practical application, rechargeable zinc-air batteries with the $Co/CeO_2-NCNA@CC$ cathode deliver extraordinary performances with a high peak power density of 123 mW cm^{-2} , an ultrahigh capacity of 784.4 mA h g_{Zn}^{-1} and a spectacular energy density (1011 W h kg_{Zn}^{-1}), which are much better than those displayed by a commercial catalyst of Pt/C + RuO_2 .

Conflicts of interest

There are no conflicts of interest to declare.

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