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Molecular coordination inheritance of single Co atom catalysts for two-electron oxygen reduction reaction†

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Electrosynthesis of hydrogen peroxide (H₂O₂) through the two-electron oxygen reduction reaction (2e-ORR) is environmentally friendly and sustainable. Transition-metal single-atom catalysts (SACs) have gained attention for this application due to their low cost, high atom utilization, adjustable coordination, and geometric isolation of active metal sites. Although various synthetic methods of SACs have been reported, the specific mechanism of the formation of active sites is still less studied. Herein, we presented the molecular coordination inheritance strategy for synthesizing 2e-ORR SACs with well-defined coordination environments and investigated the formation mechanism of the active sites. We select precursors including [Co(II)Salen], CoPc, Co(acac)₂ to achieve specific configurations (Co–N₂O₂, Co–N₄, Co–O₄). Our results indicate that the precursors undergo decomposition and are partially embedded in the carbon substrate at lower temperatures, facilitating the inheritance of the desired configurations. As the temperature increases, the inherited configurations will rearrange, forming dual-atom structures and metal particles gradually. Among the Co–N₂O₂, Co–N₄, and Co–O₄ catalysts, the Co–N₂O₂ catalyst demonstrates the highest 2e-ORR selectivity. This work reveals the mechanism of regulating SAC's active site structure by the molecular coordination inheritance strategy, which may provide new insights for further research on the precise regulation and formation mechanism of SAC's active site.

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Introduction

Hydrogen peroxide (H₂O₂) is an essential chemical with wide applications in textile bleaching, wastewater treatment, chemical synthesis, and semiconductor cleaning. Currently, its industrial production relies on the anthraquinone method, which requires large-scale equipment and generates large amounts of organic waste.^{1,2} The electrochemical production of H₂O₂ via a two-electron oxygen reduction reaction (2e-ORR) has emerged as a promising alternative. This method enables on-site production of H₂O₂, thereby simplifying the process and reducing costs while minimizing environmental impact.^{3,4} Effective 2e-ORR catalysts are critical for the electrochemical production of H₂O₂. In recent years, carbon-based transition-metal single-atom catalysts (SACs) garnered considerable atten-

tion for this application.^{5–8} The advantage of transition-metal SACs lies in their low cost, high atom utilization, adjustable coordination, and geometric isolation of active metal sites. The lack of contiguous metal ensemble sites in SACs could prevent the decomposition or further electrochemical reduction of generated H₂O₂.^{9–12}

During ORR on SACs, the selectivity towards H₂O₂ or H₂O depends on the tendency of the intermediate *OOH dissociate step.^{12–15} To tailor the performance of SACs, changing the metal center atom is a direct method to modulate the adsorption energy of the intermediate on the active site. It has been demonstrated that the cobalt-based SACs own the most promising potential for 2e-ORR.^{16–19} Meanwhile, the coordination environment of the metal center atom will affect the electron cloud center and thus change the adsorption of the intermediate. Therefore, tuning the coordination microenvironment can also effectively regulate the performance of the catalyst, such as changing the adjacent coordinative dopants^{20–23} and coordination numbers.^{24–26}

Currently, various synthesis methods exist to obtain the designed transition-metal SAC for 2e-ORR. Among them, the more common method is to mix metal salts and nitrogen sources with carbon substrates, followed by pyrolysis.^{5,26–29} For

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instance, a catalyst with the Co-N₅ sites can be obtained by pyrolysis of mixed cobalt acetate tetrahydrate, triquinoxalinyne, and carbon black.²⁶ Similarly, the pyrrole-type Co-N₄ catalyst can be obtained by mixing 4-dimethylaminopyridine, cobaltous nitrate hexahydrate, and carbon black after high-temperature heat treatment.⁵ Additionally, the method of using carbon substrate and metal complexes with target structures as pyrolysis precursors has also been reported.^{21,24} It has also been proved that it is feasible to change the coordination structure of the catalyst by adjusting the pyrolysis atmosphere.⁶ However, despite the existence of many methods, achieving precise regulation of the coordination environment of the active site remains a challenge.

Herein, we present the molecular coordination inheritance strategy for synthesizing SACs with well-defined structures and investigate the formation mechanism of the active sites. We studied various precursors, including *N,N'*-bis(salicylidene) ethylenediaminocobalt(II) ([Co(II)Salen]), cobalt phthalocyanine (CoPc), and cobalt(II) acetylacetonate (Co(acac)₂), to obtain specific configurations: Co-N₂O₂, Co-N₄, and Co-O₄ with Co as the active metal center in each case. Taking the Co-N₂O₂ catalyst as the representative catalyst, we studied the formation mechanism of the catalyst's active site during pyrolysis. We also test the electrochemical performance of Co-N₂O₂, Co-N₄, and Co-O₄ catalysts for 2e-ORR. The result shows the Co-N₂O₂ configuration demonstrates the highest 2e-ORR selectivity, followed by Co-O₄ and then Co-N₄. This work reveals the mechanism of regulating SAC's active site structure by the molecular coordination inheritance strategy, which may provide new insights for further research on the precise regulation and formation mechanism of SAC's active site.

Experimental

Materials

N,N'-Bis(salicylidene)ethylenediaminocobalt(II) ([Co(II)Salen], ≥95.0%, Sigma-Aldrich), cobalt phthalocyanine (CoPc, ≥95.0%, Sigma-Aldrich), cobalt(II) acetylacetonate (Co(acac)₂, ≥99.0%, Sigma-Aldrich), nitric acid (HNO₃, 65–68 wt%, analytical reagent grade, SCR), methanol (MeOH, >99.7%, analytical reagent grade, Kermel), isopropanol (IPA, >99.7%, analytical reagent grade, Kermel), hydrogen peroxide solution (H₂O₂, 30 wt%, analytical reagent grade, Alfa Aesar), perchloric acid (HClO₄, analytical reagent grade, Alfa Aesar), deionized water (DI water, Milli-Q, 18.2 MΩ cm at 25 °C), ultrapure nitrogen (N₂, 99.999%), ultrapure oxygen (O₂, 99.999%), carbon black (BlackPearl 2000, Cabot Co.), and a Nafion D521 dispersion (5 wt%, EW = 1100, Alfa Aesar) were used as received.

Synthesis of the [Co(II)Salen]-OCB-*T* °C catalyst

Oxidized carbon black (OCB) was first prepared by oxidizing 10.0 g of carbon black in 500 mL of 70% HNO₃ for 8 h at 80 °C, rinsed with DI water, vacuum dried at 80 °C, and used as the carbon source in the synthesis. 240 mg of OCB was dispersed in 180 mL of methanol and subjected to ultra-

sonication at 25 °C for 1 h. [Co(II)Salen] (63 mg, 193.7 μmol) was dissolved into 60 mL methanol and stirred constantly at 60 °C for 1 h. Subsequently, OCB dispersion was mixed with the [Co(II)Salen] solution and underwent ultrasonication for 1 h, followed by stirring at 500 rpm at 25 °C for 24 h. The dispersion was filtered, and the resulting solid was dried under vacuum at 60 °C. The dried powder was loaded into an alumina combustion boat and heat-treated at *T* °C in a tube furnace in N₂ at 1 L min⁻¹ (*T* = 300, 500, 700, and 900, respectively). The ramping rate was 30 °C min⁻¹, and the holding time at *T* °C was one hour. The obtained product was the [Co(II)Salen]-OCB-*T* °C catalyst. When *T* = 300, the obtained catalyst ([Co(II)Salen]-OCB-300 °C) was the Co-N₂O₂ catalyst.

Synthesis of the [Co(II)Salen]-OCB catalyst

The [Co(II)Salen]-OCB catalyst was prepared by using the same synthesis method as the Co-N₂O₂ catalysts but without the pyrolysis step.

Synthesis of the Co-N₄ catalyst

The Co-N₄ catalyst was prepared by using the same synthesis method as the Co-N₂O₂ catalyst, except that the precursor molecule was CoPc (94.8 mg, 165.9 μmol) with the pyrolysis temperatures of 700 °C.

Synthesis of the Co-O₄ catalyst

The Co-O₄ catalyst was prepared by using the same synthesis method as the Co-N₂O₂ catalyst, except that the precursor molecule was Co(acac)₂ (42.7 mg, 166.1 μmol) with the pyrolysis temperatures of 300 °C.

Characterization

Powder X-ray diffraction (XRD) was performed on a Bruker D8 ADVANCE A25 using Cu Kα radiation over a 2θ range from 10° to 80°. The morphological information was examined with transmission electron microscopy (TEM, JEOL JEM-2100F). X-ray absorption fine structure measurements were carried out on the soft X-ray spectroscopy beamline at the Beijing Synchrotron Radiation Facility and Shanghai Synchrotron Radiation Facility. The end station was equipped with a hemispherical electron analyzer and a microchannel plate detector that enabled simultaneous recording of total electron yield and partial electron yield data. X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD X-ray photoelectron spectrometer, Kratos Analytical Ltd, UK) was performed using a monochromatic Al Kα source at 150 W without charge compensation. Raman spectra were recorded on a Horiba LabRAM HR Evolution Raman spectrometer using 514 nm laser as the excitation source. Fourier transform infrared (FTIR) was performed on a Thermo Fisher Scientific Nicolet iS20.

Electrochemical measurements

Electrochemical measurements were conducted using a three-electrode system controlled by a Pine Research MSR rotator (Pine Research Instrumentation Co. Ltd) and a bipotentiostat (CHI 760E, CH Instruments, Inc.). A five-necked electro-



chemical cell filled with 0.1 M HClO₄ solution was used in the experiment. A rotating-ring disk electrode (RRDE, Pine Research Instrumentation) with a glassy carbon electrode (GCE, area = 0.2475 cm²) and a Pt-ring electrode (area = 0.1866 cm²) was used as the working electrode. An Ag/AgCl (sat. KCl) electrode and graphite rod were used as the reference and counter electrode, respectively. The Ag/AgCl electrode was calibrated to a reversible hydrogen electrode (RHE), which was constructed by bubbling pure H₂ gas continuously onto a Pt coil electrode placed in a glass tube filled with 0.1 M HClO₄.

The catalyst ink was prepared by dispersing 5 mg of catalyst in a mixture of DI-water (500 μL), IPA (500 μL), and D521 Nafion dispersion (10 μL, 5 wt%) in a sonication bath for one hour. Then, electrodes with a catalyst loading of 0.12 mg cm⁻² were prepared by depositing 10 μL of the ink onto the GCE on the RRDE.

Cyclic voltammograms (CV) were recorded from 0.0 to 1.0 V vs. RHE at a scan rate of 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄ solution. Linear sweep voltammetry (LSV) measurements were conducted in O₂-saturated conditions between 0.0 and 1.0 V at a scan rate of 5.0 mV s⁻¹ at 1600 rpm. To detect the produced H₂O₂, a fixed potential of 1.3 V vs. RHE was applied to the Pt-ring electrode. All the polarization curves were corrected with 90% iR-compensation.

The collection efficiency (*N*) of the Pt-ring electrode was measured to be 37%. The H₂O₂ selectivity (H₂O₂%) and the stoichiometric number of transferred electrons (*n*) in the ORR were calculated from the disk current (*I_d*) and ring current (*I_r*) results based on the following equations:

$$\text{H}_2\text{O}_2(\%) = 200 \frac{\left(\frac{I_r}{N}\right)}{\left(I_d + \frac{I_r}{N}\right)} \quad (1)$$

$$n = \frac{\left(\frac{I_r}{N}\right)}{\left(I_d + \frac{I_r}{N}\right)} \quad (2)$$

The kinetically limited current density (*j_k*) was determined using the Koutecký-Levich equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} \quad (3)$$

where *j* is the measured current density and *j_L* is the diffusion-limited current density. The *j_L* is obtained by the equation:

$$j_L = 0.62nFC_{\text{O}_2}D_{\text{O}_2}^{\frac{2}{3}}\nu^{-\frac{1}{6}}\omega^{\frac{1}{2}} \quad (4)$$

where *n* is the stoichiometric number of electrons transferred in the ORR, *F* is the Faraday constant (96 485 C mol⁻¹), *A* is the electrode area, *C_{O₂}* is the concentration of dissolved O₂ (1.26 × 10⁻³ mol L⁻¹ in 0.1 M HClO₄), *D_{O₂}* is the diffusion coefficient (1.93 × 10⁻⁵ cm² s⁻¹ in 0.1 M HClO₄), *ν* is the kinetic viscosity of the solution (1.009 × 10⁻² cm² s⁻¹ in 0.1 M HClO₄), and *ω* is the rotation rate of the disc electrode.

Results and discussion

Molecular coordination inheritance strategy for the synthesis of the well-defined Co–N₂O₂, Co–N₄, and Co–O₄ sites

We present the molecular coordination inheritance strategy, especially for the precise synthesis of well-defined Co–N₂O₂, Co–N₄, and Co–O₄ sites with detailed characterization analysis. Fig. 1 illustrates this molecular coordination inheritance strategy. [Co(II)Salen], CoPc, and Co(acac)₂ were selected as the precursor molecules due to their well-defined coordination structure, which provides the necessary ligands that form a precise coordination environment with the Co atom center. After the precursor molecules are uniformly distributed across the substrate, pyrolysis is taken to break down part of the organic structure while inheriting or preserving the Co–N₂O₂, Co–N₄, and Co–O₄ configurations. Combined with the thermogravimetric analysis results of the three precursor molecules (Fig. S1†), the pyrolysis temperatures of 300 °C, 300 °C, and 700 °C were selected to achieve this effect.

Fig. 2 presents the results of the structural and elemental analysis for the Co–N₂O₂, Co–N₄, and Co–O₄ catalysts. The TEM image (Fig. 2a) reveals only carbon nanoparticles without noticeable metal particles. The XRD patterns (Fig. 2b) show only broad peaks associated with the (002) and (100) reflections of graphitized carbon.

Notably, there are no diffraction peaks indicative of metal, metal nitride, or metal oxide. This observation suggests that any cobalt present in three samples is highly dispersed or in an amorphous state, consistent with the TEM results.^{5,30} The XPS analysis (Table S1†) suggests that three catalysts own similar Co doping content of approximately 0.5 atom%. The content of O in Co–N₂O₂, Co–N₄, and Co–O₄ catalysts is 7.58%, 2.75%, and 8.36%, and the content of N in Co–N₂O₂ and Co–N₄ catalysts is 1.97% and 3.87%, respectively. No significant signal of the N element is present in the Co–O₄ catalyst (Fig. S2†).

The N 1s XPS spectra (Fig. 2c and Table S2†) for Co–N₂O₂ and Co–N₄ catalysts can be fitted with five main types of N species: pyridinic-N, Co–N_x, pyrrolic-N, graphitic N, and oxidized N.^{29,31,32} Compared to the Co–N₄ catalyst, the binding energy peak centers of pyridinic-N and Co–N_x in the Co–N₂O₂

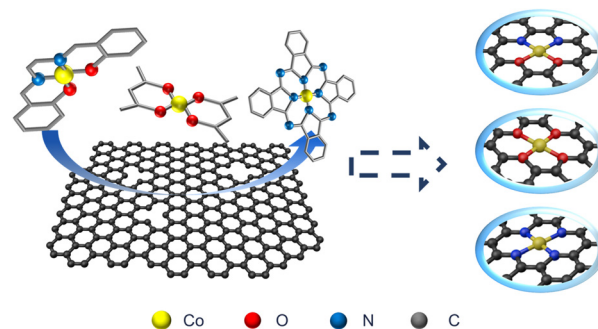


Fig. 1 Schematic illustration of the molecular coordination inheritance strategy design.



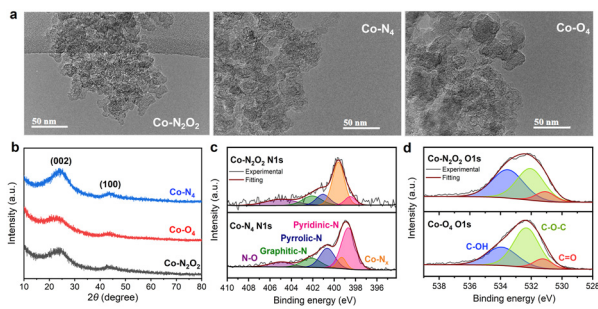


Fig. 2 (a) TEM micrographs and (b) XRD patterns of Co-N₂O₂, Co-N₄, Co-O₄ catalysts. (c) N 1s XPS spectra of Co-N₂O₂ and Co-N₄ catalyst. (d) O 1s XPS spectra of Co-N₂O₂ and Co-O₄ catalyst.

catalyst exhibit a noticeable shift to higher binding energies obviously (>0.2 eV). This difference is attributed to the distinct chemical environments of the N species in the two catalysts. In the Co-N₂O₂ configuration, the O atom possesses a stronger electron-accepting ability, leading to fewer electrons being received by the N atoms. The O atoms reduce the electron density on the neighboring N atoms in the Co-N₂O₂, whereas in the Co-N₄ catalyst, the N atoms fully retain electrons donated by the Co atom. In addition, the proportions of N species (Fig. S3[†]) in the Co-N₂O₂ and Co-N₄ catalysts are very different. The relative content of pyrrolic-N in the Co-N₂O₂ catalyst is greater than that of pyridinic-N, while the relative content of pyridinic-N in the Co-N₄ catalyst is higher.

The O 1s XPS spectra (Fig. 2d) of Co-N₂O₂ and Co-O₄ catalyst can be deconvoluted into three peaks: hydroxyl groups (C-OH), etheric groups (C-O-C), and carbonyl groups (C=O).^{27,33} Compared with Co-N₂O₂ catalyst, the binding energy peak centers of C-OH and C-O-C of Co-O₄ catalyst are shifted to higher binding energy obviously (>0.2 eV) (Table S3[†]). Similarly, the reason is that the O atom in the Co-N₂O₂ catalyst gained more electrons than the N atom due to the larger electronegativity of O, which increases the electron density on the O atom in the Co-N₂O₂ catalyst. The relative content of C-O-C in Co-O₄ is higher than that of Co-N₂O₂ catalyst (Fig. S4[†]), since the C-O-C bond results from the bonding between the O atom at the active site and the carbon substrate. The above structural and elemental analysis results indicate that three catalysts are primarily carbon matrices doped with atomically dispersed Co and N/O elements. The electron distribution state and coordination environment of the Co center between the three catalysts are completely different.

X-ray absorption spectroscopy (XAS) was further used to determine the chemical states and local coordination environment of the Co atom in three SACs. In the Co K-edge X-ray absorption near-edge structure (XANES) spectra (Fig. 3a), the pre-edge absorption energy of the Co-N₂O₂ catalyst is higher than the Co foil, indicating the positive valency of Co. The absorption edge of the Co-N₂O₂ catalyst is lower than the Co-O₄ catalyst but higher than the Co-N₄ catalyst since N is less electronegative than O. The Fourier-transformed extended

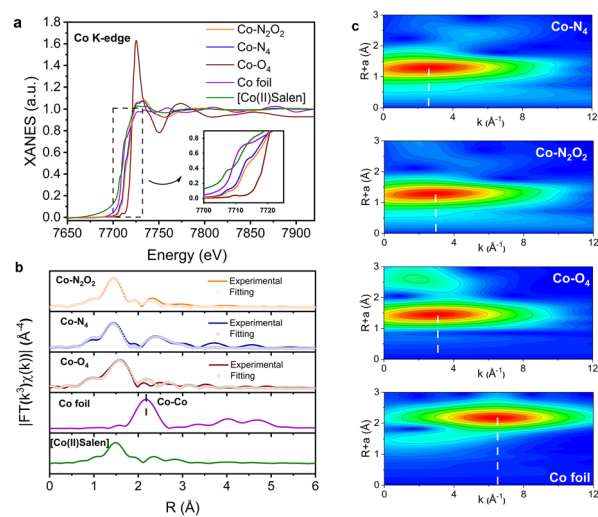


Fig. 3 (a) Co K-edge XANES spectra and (b) FT k^2 -weighted and fitting EXAFS spectra of the Co-N₂O₂, Co-N₄, Co-O₄ catalysts, and Co foil, [Co(II)Salen] as reference. (c) Wavelet transform (WT) k^2 -weighted EXAFS contour plots of the Co-N₄, Co-N₂O₂, Co-O₄ catalysts, and Co foil as reference.

X-ray absorption fine structure (FT-EXAFS) spectra (Fig. 3b) indicate the absence of Co-Co bonds (~ 2.17 Å) in the three catalysts, further confirming the single-atom dispersion of Co. The prominent peaks of Co-O₄ (1.60 Å), Co-N₄ (1.44 Å), and Co-N₂O₂ (1.44 Å) catalysts are attributed to Co-O, Co-N, Co-N/Co-O bonds, respectively. The prominent peaks in Co-N₂O₂ and Co-N₄ catalysts are close because the length of the Co-N and Co-O bonds in the precursor molecule [Co(II)Salen] are similar to the Co-N bonds in the CoPc molecule (Fig. S5 and Table S4[†]).

The local coordination configuration was further studied by quantitative least squares EXAFS curve fitting analysis, and the detailed fitting parameters are shown in Table S5.[†] According to the fitted parameters, the best-fitting result of Co-N₂O₂ for the first coordination sphere of Co includes two backscattering paths: Co-O and Co-N. The coordination numbers for Co-N and Co-O are both approximately 2, and the fitted bond lengths of Co-N and Co-O are 1.86 and 1.87 Å, respectively. For Co-N₄ and Co-O₄ catalysts, the coordination numbers of N and O are both approximately 4, and the fitted bond lengths of Co-N and Co-O are 1.89 and 1.88 Å, respectively. The wavelet-transform (WT) EXAFS analysis (Fig. 3c) further elucidates the differences in the coordination environments across the samples. In WT-EXAFS analysis, lighter atoms show the strongest oscillations at low k positions, while heavier atoms peak at high k . The Co-N₄, Co-N₂O₂, and Co-O₄ catalysts exhibit intensity maximum of 2.6, 2.9, and 3.1 Å⁻¹ respectively, which can be assigned to the backscattering of Co-N, Co-N/Co-O, and Co-O bonds. Since the atomic number of O is greater than N, the intensity maximum of the Co-N₂O₂ catalyst is between the Co-N₄ and Co-O₄ catalyst, consistent with the fitted coordination numbers. Meanwhile, the XPS analysis result showed that the contents of N and O elements in the two catalysts



were very different, which also confirmed our conclusion. Summarizing the above results, we have experimentally obtained the catalysts featuring well-defined Co-N₂O₂, Co-N₄, and Co-O₄ sites, confirming the effectiveness of the molecular coordination inheritance strategy.

Pyrolysis mechanism in molecular coordination inheritance strategy

We investigate the pyrolysis process within the molecular coordination inheritance strategy represented by [Co(II)Salen]-OCB precursor. Fig. 4a presents the cyclic voltammograms (CV) of the OCB substrate, [Co(II)Salen]-OCB precursor, and Co-N₂O₂ ([Co(II)Salen]-OCB-300 °C) catalyst. After heat treatment at 300 °C, the peak in *area 3* is retained, which corresponds to the redox reaction of the quinone functional groups in OCB substrates. In contrast, the redox peaks in *areas 1* and *2*, attributed to the [Co(II)Salen]-OCB precursor, only preserve peaks in *area 2*. We speculated that the missing redox peaks in *area 1* came from a part of the hydrocarbon organic functional group of the precursor [Co(II)Salen], and the decomposition of which after pyrolysis led to the disappearance of the peak. The retained redox peaks in *area 2* are likely derived from the -N₂O₂ coordination structure around the Co atom, suggesting that the Co-N₂O₂ structure was probably directly inherited from the precursor.

Fig. 4b presents FTIR spectra of OCB, [Co(II)Salen]-OCB, and Co-N₂O₂ catalysts. The peak (yellow region) ranging from

1760 cm⁻¹ to 1650 cm⁻¹ corresponds to carboxylic acid (-COOH), while the peaks (pink region) around 1500 cm⁻¹ are attributed to the skeleton vibration of sp²-hybridized C=C bond. The peak (purple region) at 1100 to 1030 cm⁻¹ represents the asymmetric stretching vibration of the C-O-C group, and the peaks (blue region) at 770 cm⁻¹ to 730 cm⁻¹ arise from the out-of-plane bending or twisting of the hydrocarbons group (-CH).³⁴⁻³⁷ A careful analysis of the peaks across the three spectra reveals that after heat treatment, the broad peak (purple region, 1100 cm⁻¹-1030 cm⁻¹) corresponding to the asymmetric stretching vibration of the C-O-C group appears exclusively in the Co-N₂O₂ catalyst. This result indicates that the Co-N₂O₂ site is chemically bonded to the carbon framework after pyrolysis, as depicted in Fig. 4c, rather than the precursor molecule simply adsorbed onto the carbon substrate. Furthermore, the -COOH, -C=C, and -CH groups in the precursor remain after heat treatment, indicating that the catalyst retains part of the precursor structure.

The Raman spectrum of the OCB substrate, [Co(II)Salen]-OCB precursor, and Co-N₂O₂ catalyst (Fig. S6†) includes two peaks of D-band (1350 cm⁻¹) and G-band (1580 cm⁻¹), which were assigned to the sp³ and sp²-hybridized carbon. The ratio of the relative intensity of D and G bands (*I_D/I_G*) in carbon-based nanocomposites indicates the disorder content in the graphitic structure and structural defects, which are likely to influence the performance of the catalysts.⁸ The *I_D/I_G* ratio of the OCB substrate, [Co(II)Salen]-OCB precursor, and Co-N₂O₂

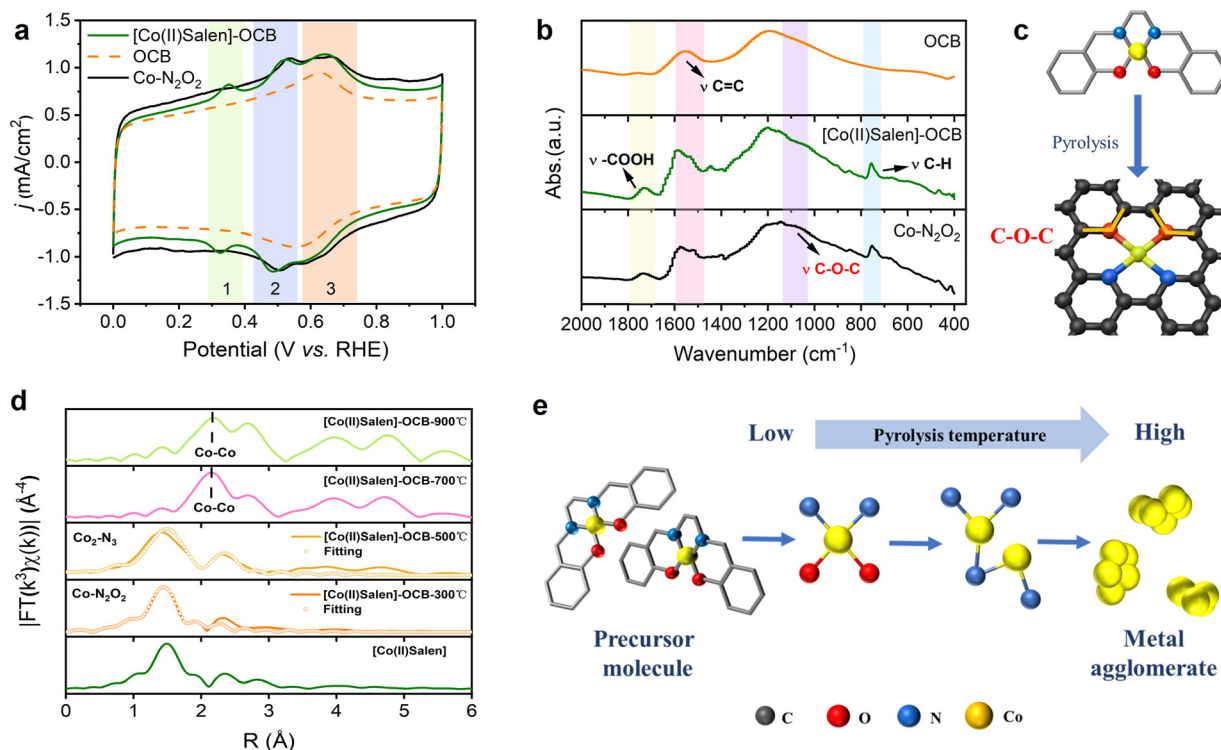


Fig. 4 (a) The cyclic voltammetry curves and (b) FTIR spectra of OCB, [Co(II)Salen]-OCB, and Co-N₂O₂ catalysts. (c) Schematic illustration of the mechanism of the Co-N₂O₂ site bonding to the carbon substrate after pyrolysis. (d) FT *k*₂-weighted and fitting EXAFS spectra of the [Co(II)Salen]-OCB-*T* °C catalysts (*T* = 300, 500, 700, 900). (e) Schematic illustration of the pyrolysis process of [Co(II)Salen] molecules on carbon substrate.



catalyst were similar, suggesting that precursor loading and pyrolysis won't significantly change the carbon substrate's graphitic structure and structural defects. The polarization curve of the OCB substrate, [Co(II)Salen]-OCB precursor, and Co-N₂O₂ catalyst showed apparent differences (Fig. S7†), suggesting that the chemical bond formed by low pyrolysis temperature plays a vital role in the activity.

We further investigate the evolution of the [Co(II)Salen]-OCB precursor at elevated temperatures, as shown in Fig. 4d. The parameters related to the best EXAFS fitting results are shown in Table S5.† Through quantitative least squares EXAFS curve fitting analysis, the optimal fitting result for the sample pyrolyzed at 500 °C reveals two backscattering paths: Co-N and Co-Co. The coordination number of Co in the first coordination sphere of Co is approximately 1. For the samples pyrolyzed at 700 °C and 900 °C, the pronounced peaks at 2.17 Å belong to the Co-Co bond, indicating the presence of Co metal agglomerates. This fitting result suggests that with pyrolysis at 500 °C, the Co-O bond is almost completely broken, and the Co-N bond is partially retained. The distribution of metal atoms begins to reorganize and gradually move closer to each other, and the coexistence of single-atom structure and dual-atom structure appears. When the pyrolysis temperature increases to 700 °C and above, the Co-N bond is further broken, and more metal atoms gather to form agglomeration.

Based on the results presented above, the pyrolysis process of [Co(II)Salen] molecules on the carbon substrate, as we speculate, is illustrated in Fig. 4e. At lower heat treatment temperatures, the Co-N₂O₂ structure of the [Co(II)Salen] molecule is partially inherited and embedded within the carbon substrate. As the pyrolysis temperature increases, the Co-N and Co-O bonds gradually break, and the distribution of metal atoms begins to reorganize. The metal atoms gradually change from the initial single atomic state to the diatomic structure and finally to the metal agglomeration. After pyrolysis at higher temperatures, more metal atoms aggregate to form Co metal clusters or particles. This result demonstrates that the Co-N₂O₂ structure in [Co(II)Salen] molecules is preserved at low pyrolysis temperature, and the active site of the Co-N₂O₂ catalyst is directly inherited from the precursor.

Electrochemical performance

Following the synthesis of well-defined Co-N₂O₂, Co-N₄, and Co-O₄ sites, we analyzed the relationship between their configurations and the corresponding 2e-ORR activity. As illustrated in Fig. 5a, the significant shift in polarization curves upon the introduction of SCN⁻ ions indicate a substantial decrease in the ORR activity of all three catalysts. This result suggested that the Co atom acts as the actual active center in these catalysts since SCN⁻ ions can strongly bind to the single metal atom, which would block that metal site for O₂ adsorption.^{38,39}

Fig. 5b and c show the polarization curves, the corresponding H₂O₂ selectivity, and electron transfer number (*n*) as a function of applied potential. The Co-N₂O₂ catalyst exhibits an onset potential of 0.684 V vs. RHE (defined as the potential

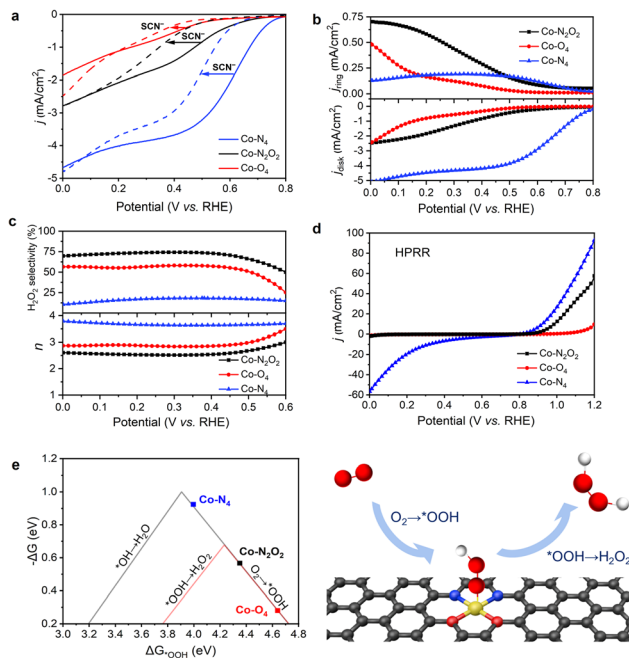


Fig. 5 (a) Polarization curves of the Co-N₂O₂, Co-N₄, and Co-O₄ catalysts in O₂-saturated 0.1 M HClO₄ (with and without 5 mM SCN⁻ ions). (b) Linear sweep voltammetry curves recorded at 1600 rpm and a scan rate of 5 mV s⁻¹ in O₂-saturated 0.1 M HClO₄, together with the detected H₂O₂ currents density on the ring electrode at a fixed potential of 1.3 V vs. RHE. (c) The calculated H₂O₂ selectivity and electron transfer number *n* during LSV scan. (d) Polarization curves of the Co-N₂O₂, Co-N₄, and Co-O₄ catalysts in N₂-saturated 0.5 M H₂SO₄ electrolyte containing 0.5 M H₂O₂. (e) Calculated catalytic volcanoes for the production of H₂O (black lines) and H₂O₂ (red lines) via ORR with the schematic illustration of the structure active site. The values of the *OOH adsorption energy (ΔG_{*OOH}) and the free energy change along each ORR step ($-\Delta G$) are obtained from the literature.⁴⁰

delivering 0.1 mA cm⁻² current density) and a *j*_L of -2.5 mA cm⁻². The calculated selectivity of H₂O₂ is up to 76% with an *n* value of 2.5, indicating that the ORR on the Co-N₂O₂ surface is predominantly a 2e-process. In contrast, the Co-N₄ catalyst displays an onset potential of 0.91 V vs. RHE and a *j*_L of about -5 mA cm⁻². The H₂O₂ selectivity for Co-N₄ is 16%, and its *n* is close to 3.7, suggesting a 4e-ORR pathway. This result is consistent with existing studies that the Co SAC catalyst with the pyridine-type CoN₄ active site is more inclined to facilitate 4e-path ORR, as XPS shows that the main N species in Co-N₄ catalyst is pyridinic-N.⁵ The onset potential of the Co-O₄ catalyst is 0.521 V vs. RHE, and the *j*_L is not reached. The calculated H₂O₂ selectivity and *n* for the Co-O₄ catalyst are about 58% and 2.9 respectively, showing a mixed 2e- and 4e-ORR pathway. The results show that the Co-N₂O₂ catalyst showed much better 2e-ORR performance than the Co-N₄, Co-O₄ catalysts. The electrochemical performance of the [Co(II)Salen]-OCB-*T* °C catalysts (*T* = 500, 700, 900) was also tested (Fig. S8†), revealing lower 2e-ORR selectivity compared to the Co-N₂O₂ catalyst. This performance degradation arises from the fact that high-temperature-induced coordination recon-



struction at metal centers generates heterogeneous active sites, thereby driving a transition from dominant 2e-ORR to mixed 2e-/4e-ORR pathways.

The catalytic activity of these catalysts toward the H₂O₂ reduction reaction (HPRR) was also evaluated.^{41,42} As shown in Fig. 5d, the negligible current density of Co-N₂O₂ and Co-O₄ catalysts indicate the poor HPRR activity of these two catalysts. Meanwhile, the Co-N₄ catalyst exhibits much better HPRR activity with significant current density. This result suggests that H₂O₂ generated by Co-N₂O₂ and Co-O₄ catalysts will hardly be reduced, while the Co-N₄ catalyst is likely to further reduce H₂O₂ to H₂O. The difference in HPRR activity also explains why Co-N₂O₂ is more inclined to 2e-ORR and Co-N₄ is more inclined to 4e-ORR. The Co-N₂O₂ catalyst was also evaluated in an H-cell configuration (Fig. S9[†]), demonstrating significant initial current density that highlights its practical potential for applications. Further investigations will systematically explore the optimization of the triple-phase boundary and mass transfer efficiency to enhance its performance under operational conditions.

In short, the electrochemical performance shows that the Co-N₂O₂ configuration demonstrates the highest 2e-ORR selectivity, followed by Co-O₄ and then Co-N₄. According to the recent study, the superior 2e-ORR performance of the Co-N₂O₂ catalyst can be attributed to the synergistic interplay between the electronic state of the Co center and its coordination environment.⁴⁰ As shown in Fig. 5e, the density functional theory (DFT) calculations reveal that the Co-N₂O₂ configuration is positioned closer to the top of the volcano plot compared to the Co-N₄ and Co-O₄ structures, which accounts for its enhanced 2e-ORR activity.

Conclusions

In summary, we presented the molecular coordination inheritance strategy for synthesizing SACs with well-defined coordination environments and investigated the formation mechanism of the active sites. We selected precursors including [Co(II) Salen], CoPc, and Co(acac)₂ to achieve specific configurations (Co-N₂O₂, Co-N₄, Co-O₄). Taking the Co-N₂O₂ catalyst as the representative catalyst, our investigations into the pyrolysis mechanism reveal that the precursors undergo decomposition and are partially embedded in the carbon substrate at lower temperatures, facilitating the inheritance of the desired configurations. As the temperature increases, the inherited configurations will rearrange, forming dual-atom structures and metal particles. Following the successful synthesis of these well-defined sites, we analyzed the relationship between their configurations and their 2e-ORR activity. Our findings indicate that the Co-N₂O₂ configuration demonstrates the highest 2e-ORR selectivity, followed by Co-O₄ and then Co-N₄. This work reveals the mechanism of regulating SAC's active site structure by the molecular coordination inheritance strategy, which may provide new insights for further research on the precise regulation and formation mechanism of SAC's active site.

Author contributions

Qianqian Qin: writing – original draft, methodology, investigation, visualization. Mengxue Huang: investigation. Chaoqi Han: investigation. Xue Jing: investigation. Wenwen Shi: writing – original draft, methodology. Ruimin Ding: writing – review & editing, supervision, funding acquisition. Xi Yin: writing – review & editing, conceptualization, methodology, supervision, funding acquisition.

Data availability

The data supporting this article have been included as part of the ESI.[†]

Conflicts of interest

There are no conflicts to declare.

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