

Regulating the spin state of triple-atom catalysts for improved oxygen electrocatalysis in zinc-air batteries at subzero temperature

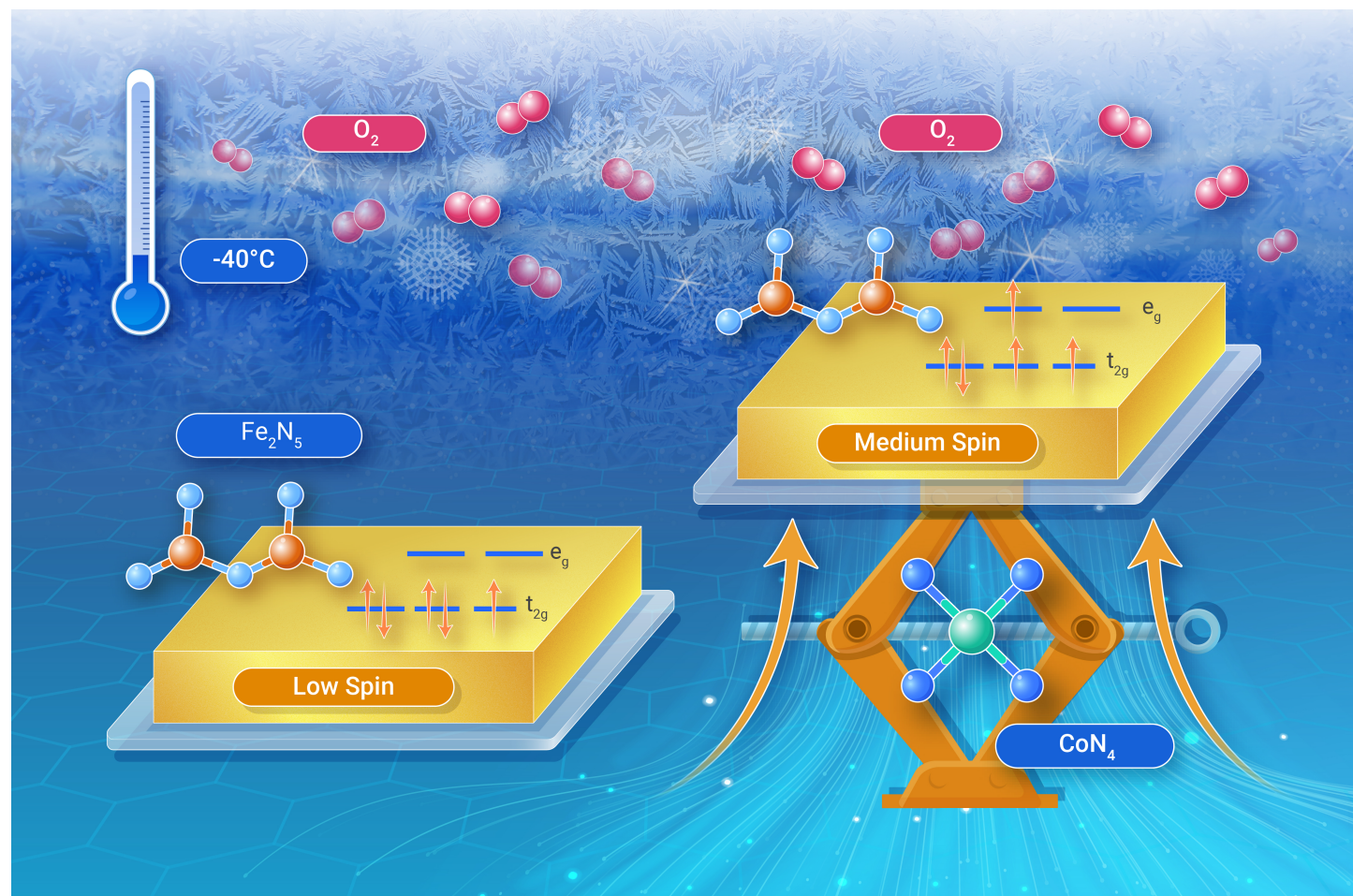
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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- Single CoN₄ site was introduced to modulate the spin state of dual-atom Fe₂N₅.
- The Fe₂/Co-NHCS with medium spin state demonstrates excellent oxygen reduction reaction performance.
- Zinc-air batteries powered by Fe₂/Co-NHCS demonstrate superior performance at normal and low temperature.

Regulating the spin state of triple-atom catalysts for improved oxygen electrocatalysis in zinc-air batteries at subzero temperature

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Triple-atom catalysts (TACs), building upon dual-atom catalysts, have demonstrated exceptional catalytic activity toward oxygen reduction reaction (ORR). Nevertheless, advancing the catalytic activity of TACs for application in low-temperature (Low-T) energy conversion devices remains a formidable challenge, primarily limited by the slow capture efficiency of oxygen reactants at catalytic sites. In this work, utilizing Fe-Fe double atomic pairs as a foundational research model, we plant the CoN₄ site adjacent to activate them to construct efficient ORR electrocatalysts (named as Fe₂/Co-NHCS) featuring the Fe₂N₅+CoN₄ tri-atomic structure. The adjacent CoN₄ site can optimize the spin state of the Fe-Fe double atomic pairs from low to medium spin with $t_{2g}^4 e_g^1$ 3d-electron configuration, which makes the catalysts bind with oxygen reactants more readily to complete ORR process. As anticipated, the Fe₂/Co-NHCS achieved a high half-wave potential of 0.92 V. Moreover, the flexible Zn-air batteries powered by Fe₂/Co-NHCS deliver a large peak power density of 57.3 mW cm⁻² and brilliant charge-discharge stability over 150 stable cycles at -40°C. This research advances ORR electrocatalysts by modulating the electron spin states at diatomic Fe sites, paving a viable route for expanding the application range of ZABs in low-temperature environment.

INTRODUCTION

Zn-air batteries (ZABs) have broad application prospects in renewable energy storage solutions due to their high energy density and the abundant zinc resources.¹⁻⁶ However, applying ZABs in low-temperature (Low-T) environments inevitably results in a loss of catalyst kinetics and a decrease in oxygen reduction reaction (ORR) activity due to enhanced polarization. Therefore, enhancing the ORR performance is crucial in improving ZABs performance.⁷⁻¹² Although traditional precious metal catalysts are effective, their scarcity and high costs constrain their widespread application. Dual atom catalysts (DACs), as an extension of the single atom catalyst (SACs), have emerged as a viable alternative with increased activity and selectivity.¹³⁻¹⁶ In particular, notable advancements have been made in the iron (Fe)-based DACs in catalysis ORR.¹⁷⁻²¹ However, the complex adsorption-desorption dynamics with reaction-related intermediates, especially in Low-T, pose a significant barrier to the further refinement of catalytic activity.²²⁻²⁴

Low-T application results in a decrease in the kinetic energy of oxygen reactants, thereby reducing the collision frequency between the oxygen reactants and catalyst surface, thereby further limiting the performance of Low-T ZABs.²⁵⁻²⁷ Inspired by the electron spin effect, transition metal Fe possesses unfilled 3d-orbitals that enable it to accommodate foreign electrons, thereby optimizing the bonding strength of OOH*/O*/OH* intermediates and enhancing their potential to catalyze the ORR process.²⁸⁻³¹ Generally, Fe³⁺ exhibits multiple states owing to the coordination environment, which can be categorized to display different forms of spin: low spin ($t_{2g}^6 e_g^0$), medium spin ($t_{2g}^4 e_g^2$), and high spin ($t_{2g}^3 e_g^3$). At low spin, the lack of eg orbitals electron filling makes it difficult for oxygen-related intermediates to bind to the active sites. The intermediate spin state's single d_{z^2} electron can readily penetrate the anti-bonding π -orbital of oxygen reactants, and such achieve the optimal adsorption behavior. The excessive eg orbitals electron filling in high spin results in the strong binding of oxygen reactive species at active sites.³²⁻³⁴ To

date, extensive research has been devoted to optimizing the coordinated environment of the active Fe site to tailor the binding strength with oxygen reactants. For instance, Guo group reported a FeCo/DA@NC catalyst characterized by a FeCoN₆ moiety, in which the spin state of the FeCo/DA@NC changed from low to medium spin relative to the Fe/SA@NC. The FeCo/DA@NC exhibiting a medium spin state of the FeCoN₆ moiety demonstrated ORR performance with a half-wave potential of 0.84 V.³⁵ Despite some progress, enhancing the spin state of metal sites to improve the capture efficiency of oxygen reactants and further enhance the intrinsic catalytic activity for applications in low-temperature environments remains a highly sought-after but challenging endeavor.

In this work, we devised a straightforward strategy by incorporating CoN₄ to activate the electronic structure of the adjacent Fe-Fe double atomic pairs and further modulate the electron spin state, thereby constructing a tri-atomic site on the N-doped hollow carbon sphere (Fe₂/Co-NHCS). Experimental results demonstrate that Fe₂/Co-NHCS displays a high onset potential of 1.06 V and a half-wave potential of 0.92 V in alkaline solution. In practical applications, the rechargeable ZABs equipped with Fe₂/Co-NHCS demonstrated a high peak power density (P_{max}) of 165.1 mW cm⁻² and robust stability beyond 900 h, respectively. At the same time, the Fe₂/Co-NHCS-based flexible ZABs (F-ZABs) both exhibit excellent P_{max} under room temperature and Low-T conditions (P_{max} (25°C)=147.7 mW cm⁻² and P_{max} (-40°C)=57.3 mW cm⁻², respectively). Notably, the F-ZABs powered by Fe₂/Co-NHCS exhibited long-term stability over 150 stable cycles at Low-T of -40°C with almost no performance loss. The collective results of the theoretical calculations and magnetic measurements elucidate that the introduction of the CoN₄ site can induce the spin state transition of the Fe-Fe double atomic pairs from low to medium spin with the electronic structure of $t_{2g}^4 e_g^1$. This spin-enhanced state, which can be maintained at both room temperature and low temperature, accompanied by the single electron occupancy of the d_{z^2} , effectively penetrates the antibonding π -orbital of oxygen, thereby achieving strong d - p interactions between metal atoms and oxygen reactants. These interactions underpin the exceptional catalytic activity and application performance in Fe₂/Co-NHCS even at Low-T. This work presents a viable method to further improve the catalytic activity and stability of Fe-based tri-atomic catalysts, potentially sparking a surge in the investigation of highly efficient and robust non-precious catalysts for use in renewable energy conversion technologies under extreme application environment.

MATERIALS AND METHODS

Materials

Hexamethylenetetramine (HMT), melamine, 2, 4-dihydroxybenzoic acid (DA), sodium oleate (SO), iron (III) chloride hexahydrate (FeCl₃·6H₂O), cobalt chloride hexahydrate (CoCl₂·6H₂O) and n-Pentane were purchased from Aladdin Chemical Co (Shanghai, China). Pluronic P123 (EO₂₀PO₇₀EO₂₀) was obtained from Sigma-Aldrich Corporation (Shanghai, China). Commercial Pt/C catalyst (20 wt%) was obtained from Johnson Matthey Company (Shanghai, China). 5% Nafion solution and ruthenium oxide (RuO₂) were obtained from Sigma-Aldrich. All chemicals were purchased and used directly without any processing.

Preparations of catalyst

Typically, 50 mg HPS powder was homogeneously dispersed in 10 mL of pentane by ultrasonicated for 30 min. Then, a certain amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was introduced into the HPS suspension under stirring. After continuously stirring for 1 h, the powder was collected and labeled as Fe/Co-HPS. The obtained Fe/Ni-HPS was grounded with melamine and then carbonized to obtain $\text{Fe}_2/\text{Co-NHCS}$ at 900°C for 180 min under a nitrogen atmosphere. The control $\text{Fe}_2\text{-NHCS}$ and Co-NHCS samples were also prepared by the similar synthetic procedure of $\text{Fe}_2/\text{Co-NHCS}$ except that only a certain amount $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was added, respectively.

Characterization

Transmission electron microscopy (TEM, H-7650, Tokyo, Japan), high-resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDS, JEM-2100F) and atomic resolution aberration-corrected high-angle annular dark field scanning transmission electron microscopy (AC HAADF-STEM, FEI Titan Cube Themis G2 300, Netherlands) were employed to characterize the morphology and structure of synthesized samples. Ultraviolet photoelectron spectroscopy (UPS) measurements were conducted with a HeI discharge lamp on the Thermo ESCALAB XI+ (California, USA). X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA utilizing CuK α radiation ($\lambda = 1.54178 \text{ \AA}$). Raman spectroscopy was performed with a Thermo Fisher spectrometer equipped with helium-neon (633 nm) and argon lasers (532 nm; Horiba LabRAM HR Evolution, Palaiseau, France). X-ray photoelectron spectroscopy (XPS) analyses were carried out using the Thermo ESCALAB 250XI system in Waltham, USA. X-ray absorption near-edge structures (XANES) and extended X-ray absorption fine structures (EXAFS) at Fe and Co K edges were investigated through fluorescence models on beamline BL14W1 of the Shanghai Synchrotron Radiation Facility. Finally, room temperature X-band electron paramagnetic resonance spectra at 300 K were recorded on the Bruker EMX PLUS instrument located in Saarbrücken, Germany.

Electrochemical tests

Electrochemical measurements are performed on the CHI-842 electrochemical workstation using a traditional three-electrode system in which a rotating disk electrode (RDE) or a rotating ring disk electrode (RRDE) serves as the working electrode; Ag/AgCl (saturated KCl) was used as the reference electrode, and Pt filament was used as the reverse electrode. The 2 mg catalyst was dispersed into 1 mL of mixed solution (deionized water, isopropyl alcohol and 5% Nafion = 4:1:0.1), and ultrasonic action was performed for 1 h

to form a homogeneous catalyst ink. The 42 μL catalyst ink was moved to a working electrode with a diameter of 5 mm and a mass load of 0.43 mg cm^{-2} . Linear sweep voltammetry (LSV) was used to track the performance of ORR at a scanning rate of 10 mV s^{-1} at 0.1 mol L^{-1} KOH saturated O_2 . The LSV was used to measure the OER performance at the scan rate of 5 mV s^{-1} in 1 mol L^{-1} KOH solution with IR correction.

Assembly of zinc-air batteries

The catalyst ink is prepared by dispersing 10.0 mg of catalyst in a 1 mL mixture comprising DMF, isopropyl alcohol, and Nafion (v/v/v = 4:1:0.1). A self-assembled zinc-air batteries (ZABs) was constructed to evaluate the performance of the sample. A polished zinc plate serves as the anode, while a hydrophilic carbon paper coated with 1 mg cm^{-2} of catalyst functions as the air cathode. The electrolyte consists of a mixed solution containing 6.0 M KOH and 0.2 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The discharge polarization curve was recorded using a CHI-660E electrochemical workstation at a scan rate of 10 mV s^{-1} . The specific discharge capacity is normalized based on the mass of zinc consumed during prolonged discharge tests. Constant current charge-discharge measurements were conducted at room temperature utilizing the LAND test system with a current density of 5 mA cm^{-2} , involving cycles of 5 minutes for both discharge and charge phases. For comparative analysis, we assembled basic Pt/C + RuO_2 -based ZABs employing a blend of Pt/C and RuO_2 catalysts for the air cathode.

Calculation methods

Within the framework of Density Functional Theory (DFT), we employ the Vienna Ab Initio Simulation Package (VASP 5.4.4) to conduct all calculations. We adopt the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation along with the Projected Augmented Wave (PAW) method to address the interactions between valence electrons and ionic nuclei. To ensure computational accuracy, we set the plane wave cutoff energy to 450 eV. Additionally, a Monkhorst-Pack special K-point mesh of $3 \times 3 \times 1$ is utilized for geometric optimization and electronic structure calculations. During the geometric optimization process, all atoms are permitted to relax freely until convergence criteria for maximum force and energy— $0.01 \text{ eV/\AA}$ and $1.0 \times 10^{-5} \text{ eV/atom}$, respectively—are achieved. To mitigate interactions between periodic images, a vacuum layer of 15 $\text{\AA}$ is incorporated into the model.

RESULTS AND DISCUSSION

Catalyst synthesis and characterization

Figure 1 depicts the fabrication process of the target electrocatalysts with tri-atomic sites on N-doped hollow carbon spheres (named as $\text{Fe}_2/\text{Co-}$

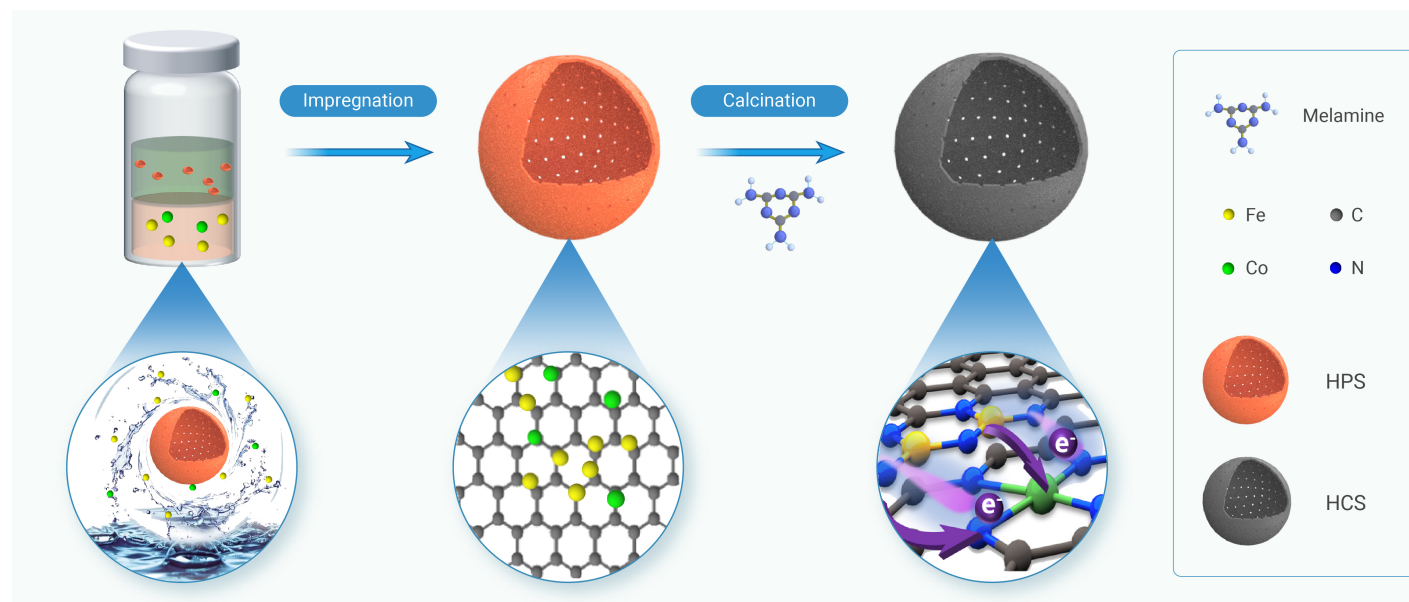


Figure 1. Preparation method and process of $\text{Fe}_2/\text{Co-NHCS}$.

NHCS). First, hollow polymer spheres (HPS) were synthesized using hexamethylenetetramine, 2,4-dihydroxybenzoic acid, and sodium oleate as raw materials, following previously reported method.³⁶ Next, the double-solvents (water-pentane) impregnation method was employed to introduce the Fe^{3+} and Co^{2+} into the prepared HPS. After subsequent pyrolysis, mixed with melamine under a nitrogen (N_2) atmosphere, the Fe and Co atoms were successfully embedded into the N-doped hollow carbon spheres (HCS), resulting in the formation of $\text{Fe}_2/\text{Co-NHCS}$. For comparison, the control catalysts of $\text{Fe}_2\text{-NHCS}$ and Co-NHCS were also prepared using similar synthetic method, with only the injection of Fe^{3+} or Co^{2+} source, respectively. The transmission electron microscope (TEM) image confirmed that all investigated catalysts exhibit complete spherical structure, with no Fe or Co-based nanoparticles observed (Figures 2A & S1). The absence of the Fe or Co-based nanoparticles was further supported by X-ray diffraction (XRD) and high-resolution TEM (HRTEM) results (Figures 2B & S2). High angle angular dark field-scanning transmission electron microscopy (HAADF-STEM) image (Figure 2C) and corresponding energy dispersive spectroscopy (EDS) mapping (Figure 2D) revealed the uniform distribution of C, N, O, Co, and Fe elements throughout the $\text{Fe}_2/\text{Co-NHCS}$. These results suggest that the Fe or Co-based species likely exist as atoms on the carbon support.

In order to deeply clarify the existence status of Fe and Co-based species in all investigated catalysts, and considering the Fe and Co metals are situ-

ated within the atomic dispersion, the aberration-corrected HAADF-STEM (AC HAADF-STEM) was further performed.^{37,38} As shown in Figure S3, a large number of bright spots can be observed on carbon support of the $\text{Fe}_2\text{-NHCS}$ and many of which can be attributed to Fe-Fe metal pairs (marked with red circles). Interestingly, in contrast to the $\text{Fe}_2\text{-NHCS}$, additional single bright spots (marked with yellow circles) are consistently observed around the Fe-Fe metal pairs in $\text{Fe}_2/\text{Co-NHCS}$ (Figures 2E-F), which suggesting that the Fe-Fe metal pairs and single Co atom may coexist in a tri-atomic structure. Furthermore, single bright spots corresponding to the Co atoms are also observed in Co-NHCS (Figure S4). Upon selecting 50 pairs of Fe-Fe metal pairs for statistical measurement in Figure 2G, the analysis revealed that the Fe-Fe metal pairs' spatial spacing was around 0.25 nm, indicating the formation of Fe-Fe double atomic pairs. Moreover, the spatial distance between one of the Fe atoms in the Fe-Fe double atomic pairs and the neighboring single Co atom can also be calculated to be 0.45 nm (Figure 2H). To more intuitively visualize the distances within the tri-atomic structure, region A was selected for further analysis, and a 3D atom-overlapping Gaussian-function fitting map was generated (Figures 2I-J). The distances between Fe-Fe and Fe-Co in region A were found to be 2.62 Å and 4.25 Å, respectively, consistent with the results of the intensity profiles in Figure S5 and the electron energy-loss spectroscopy in Figure 2K. These results collectively confirm the presence of a tri-atomic structure composed of Fe-Fe double atomic pairs

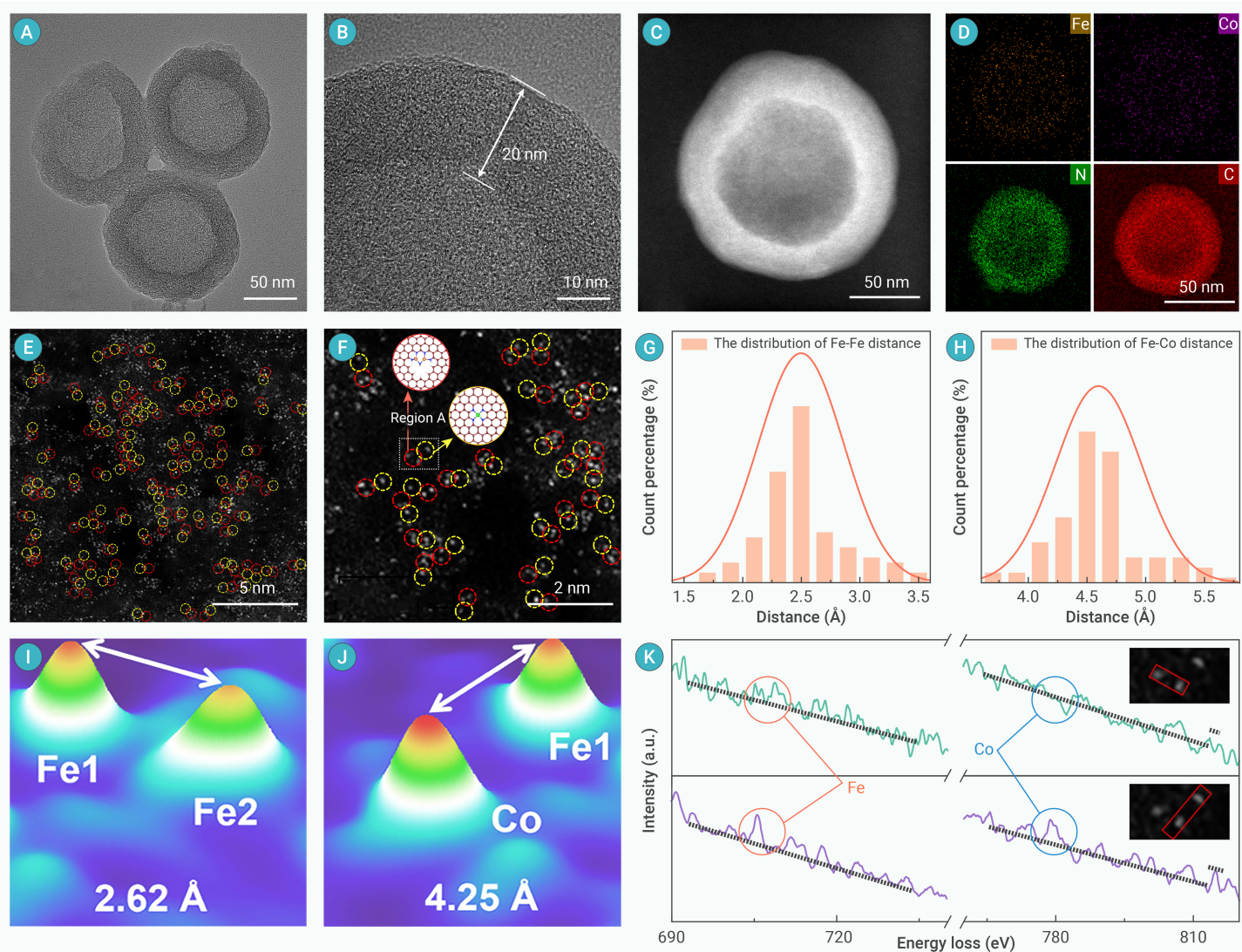


Figure 2. Morphology and structural characterization of $\text{Fe}_2/\text{Co-NHCS}$ (A-B) TEM images of $\text{Fe}_2/\text{Co-NHCS}$, (C) the HAADF-STEM image of $\text{Fe}_2/\text{Co-NHCS}$, (D) EDS mapping of Fe, Co, N and C elements in the $\text{Fe}_2/\text{Co-NHCS}$, (E-F) AC HAADF-STEM images of $\text{Fe}_2/\text{Co-NHCS}$, (G) the distance distribution of Fe atoms in the Fe-Fe double atomic pair, (H) the distance distribution of Fe atoms and Co atoms in Figure 2E, (I-J) 3D atom-overlapping Gaussian-function fitting image of Fe-Fe and Fe-Co atomic position circled from Region A in Figure 2F, (K) Atomic-resolution EELS spectrum extracted of the Fe-Fe and Fe-Co marked with red and blue case from Region A.

coupled with single Co atoms in the synthesized $\text{Fe}_2/\text{Co-NHCS}$. As shown in Figure S6 and Table S1, the two peaks, corresponding to the A_{1g} vibration mode of disordered carbon (D-band, located at 1350 cm^{-1}) and the E_{2g} vibration mode of ordered graphitic carbon (G-band, located at 1590 cm^{-1}), were observed in the Raman spectra. The ratio of these two peaks reflects the defect level of the investigated catalysts. Figure S7 shows that $\text{Fe}_2/\text{Co-NHCS}$ exhibits a higher I_D/I_G ratio (1.64) than $\text{Fe}_2\text{-NHCS}$ (1.48) and Co-NHCS (1.20), suggesting that $\text{Fe}_2/\text{Co-NHCS}$ may possess more defect sites. The higher degree of the defect is primarily attributed to the removal of some carbon atoms during the formation of the M-N_x species, which could facilitate the rapid mass transfer process. The contents of Fe and Co in $\text{Fe}_2/\text{Co-NHCS}$ were determined to be 1.08 wt% and 0.40 wt%, respectively, by inductively coupled plasma-optical emission spectrometer (ICP-OES). In comparison, the Fe content in $\text{Fe}_2\text{-NHCS}$ was measured to be 1.01 wt%, while the Co content in Co-NHCS was found to be 0.58 wt% (Table S2). We also recorded the N_2 adsorption-desorption curves to analysis the pore structure of all investigated catalysts. These curves, shown in Figures S8 and S9 exhibit a type IV isotherm, confirming that the catalysts possess a mesoporous structure. The Brunauer-Emmett-Teller (BET) surface areas of $\text{Fe}_2/\text{Co-NHCS}$, $\text{Fe}_2\text{-NHCS}$, and Co-NHCS can be calculated to be $578.2\text{ m}^2/\text{g}$, $537.2\text{ m}^2/\text{g}$, and $477.3\text{ m}^2/\text{g}$, respectively. The large specific surface area of $\text{Fe}_2/\text{Co-NHCS}$ is expected to enhance the exposure of catalytic active sites and promote the efficient transfer of reaction-related species during ORR process.

Atomic structure analysis

The valence state information and coordination structure of Fe or Co atoms of the $\text{Fe}_2/\text{Co-NHCS}$ were investigated using X-ray photoelectron spectroscopy (XPS) and synchrotron X-ray absorption spectroscopy (XAS) tests.³⁹⁻⁴¹ Firstly, the XPS survey demonstrated the existence of The Fe $2p$ high-resolution spectra (shown in Figure 3A) of both $\text{Fe}_2/\text{Co-NHCS}$ and $\text{Fe}_2\text{-NHCS}$ deconvoluted into four peaks, corresponding to Fe-N_x (712.1 eV and 726.2 eV, 710.7 eV and 723.6 eV) and satellite peaks (717.3 eV and 730.7 eV, 714.5 eV and 728.2 eV), respectively. Compared to the $\text{Fe}_2\text{-NHCS}$, the binding energy of the Fe-N_x in $\text{Fe}_2/\text{Co-NHCS}$ exhibits a significant positive shift of 1.4 eV, which can be attributed to the electronic interaction induced by the introduction of Co atoms. Similarly, the Co $2p$ spectrum of $\text{Fe}_2/\text{Co-NHCS}$ and Co-NHCS displays four peaks (780.6 eV and 795.3 eV, 784.4 eV and 803.4 eV for $\text{Fe}_2/\text{Co-NHCS}$, 780.7 eV and 795.7 eV, 785.0 eV and 802.3 eV for Co-NHCS), which correspond to Co-N_x and satellite peaks, respectively. Also, the Co-N_x of $\text{Fe}_2/\text{Co-NHCS}$ demonstrated a negative shift of 0.1 eV relative to Co-NHCS in Figure 3B, again indicating an electronic interaction between Fe-N_x and Co-N_x .^{42,43} The high-resolution N $1s$ spectra of all investigated catalysts in Figure 3C were fitted to four peaks, attributed to pyridine-N (398.1 eV), M-N (399.4 eV), graphite-N (400.8 eV), and oxidized-N (402.3 eV), respectively.⁴⁴ Additionally, the C $1s$ XPS spectra in Figure 3D of the investigated catalysts all displayed three similar distinct peaks corresponding to O-C=O , C-O-C , and C-O , respectively.

To further investigate the atomic structure and coordination environment of Fe-Fe double atomic pairs and single Co atoms in the $\text{Fe}_2/\text{Co-NHCS}$, the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were recorded.⁴⁵⁻⁴⁷ As shown in Figure 3E, the Fe K -edge XANES for $\text{Fe}_2/\text{Co-NHCS}$ revealed an absorption position close to that of FePc , indicating a similar electronic environment. The calculated valence state of the Fe site in $\text{Fe}_2/\text{Co-NHCS}$ was determined to be 2.1 (Figure S10), suggesting a high oxidation state. Furthermore, the Fe K -edge k^3 -weighted Fourier transform EXAFS (FT-EXAFS) exhibited a strong peak at $1.45\text{ \AA}$, which can be attributed to the presence of a Fe-N bond, consistent with the reference to the FePc (Figure 3G). Additionally, an extra peak similar to that of Fe foil at $2.2\text{ \AA}$ confirmed the existence of a Fe-Fe bond within $\text{Fe}_2/\text{Co-NHCS}$. The wavelet transform (WT)-EXAFS also demonstrate the presence of Fe-Fe and Fe-N bond (Figure 3I). To further elucidate the coordination number (CN) of the dual Fe-Fe sites, quantitative EXAFS fitting was employed. The fitting results depicted that the coordination number (CN) of Fe-N(O) and Fe-Fe are around 4 and 1, respectively (Figure 3K & Table S3), which suggesting the formation of Fe_2 diatomic pairs in $\text{Fe}_2/\text{Co-NHCS}$. AC HAADF-STEM image of $\text{Fe}_2/\text{Co-NHCS}$ in Figure S11 reveals numerous

carbon defects (marked by yellow lines) surrounding the paired Fe-Fe sites, implying that the Fe_2 diatomic pairs are likely positioned at the edge of the carbon support. To further investigate, We conducted the DFT calculation to determine the formation energy of a series of Fe_2 diatomic pairs. The result show that the model 15 (edge-adjacent married Fe_2N_5 structure) exhibits the lowest formation energy of -2.90 eV (Figure S12). Additionally, we simulated the experimental EXAFS spectra to validate the existence of the proposed Fe_2N_5 structure. In simulated R-space FT-EXAFS results (Figure S13), the blue and green lines correspond to the coordination contributions of the Fe-N(O) and Fe-Fe bonds, respectively. The peak positions corresponding to $1.50\text{ \AA}$ and $2.2\text{ \AA}$, respectively, further confirm the presence of Fe-N and Fe-Fe coordination in $\text{Fe}_2/\text{Co-NHCS}$. Through the Co K -edge XANES spectrum (Figure 3F), the absorption edge of Co atom in the $\text{Fe}_2/\text{Co-NHCS}$ is observed to be located between Co foil and CoPc , which confirms that the valence of Co atoms ranges between 0 and +2. The k^3 -weighted FT-EXAFS spectrum of Co K -edge (Figure 3H) exhibited a main peak at approximately $1.50\text{ \AA}$, corresponding to the reference CoPc , thereby confirming the existence of Co-N coordination in $\text{Fe}_2/\text{Co-NHCS}$. The WT-EXAFS at Co K edge also shows a maximum signal corresponding to Co-N, which provides evidence for the formation of CoN_4 configuration (Figure 3J). Further quantitative EXAFS fitting analysis of the Co atomic coordination environment indicated that Co atoms are coordinated with four N atoms, suggesting the formation of CoN_4 atomic configuration (Figure 3L & Table S4). Notably, the absence of Co-Co signal, as observed in the reference Co foil, confirms the presence of Co metal as a single atom in the $\text{Fe}_2/\text{Co-NHCS}$. These results collectively demonstrate that the Fe-Fe double atomic pairs and Co single atoms in the $\text{Fe}_2/\text{Co-NHCS}$ featuring the Fe_2N_5 and CoN_4 atomic structures, respectively.

Electrochemical oxygen reduction performance

To evaluate the oxygen reduction reaction (ORR) performance of $\text{Fe}_2/\text{Co-NHCS}$, a series of electrochemical tests were conducted in O_2 -saturated $0.1\text{ mol L}^{-1}\text{ KOH}$ at 1600 rpm .⁴⁸ First, the linear scan voltammetry (LSV) curves in Figures 4A-B were measured to apprise the ORR performance for all investigated catalysts. The LSV curves showed that the $\text{Fe}_2/\text{Co-NHCS}$ had the most positive ORR performance with an onset potential of 1.01 V and the half-wave potential of 0.92 V , which is higher than that of the $\text{Fe}_2\text{-NHCS}$ ($E_{\text{onset}}=0.96\text{ V}$, $E_{1/2}=0.88\text{ V}$), Co-NHCS ($E_{\text{onset}}=0.89\text{ V}$, $E_{1/2}=0.82\text{ V}$), NHCS ($E_{\text{onset}}=0.86\text{ V}$, $E_{1/2}=0.78\text{ V}$), and commercial Pt/C ($E_{\text{onset}}=0.97\text{ V}$, $E_{1/2}=0.86\text{ V}$). The superior ORR performance for $\text{Fe}_2/\text{Co-NHCS}$ compared to that of the $\text{Fe}_2\text{-NHCS}$ may be attributed to the modulation of the electronic structure of the single Co atom an introduced adjacent to Fe_2N_5 diatomic pairs. Next, the Tafel plots derived from the LSV data were used to further estimate the kinetics toward ORR (Figure 4C). As expected, the $\text{Fe}_2/\text{Co-NHCS}$ demonstrated a Tafel slope of 74.4 mV dec^{-1} , which is lower than those of $\text{Fe}_2\text{-NHCS}$ (77.6 mV dec^{-1}), Co-NHCS (74.7 mV dec^{-1}), NHCS (76.9 mV dec^{-1}), and commercial Pt/C (84.0 mV dec^{-1}), demonstrating its faster reaction kinetics. The kinetic current density can also manifest the fast ORR kinetics of $\text{Fe}_2/\text{Co-NHCS}$. As displayed in Figure S14, compared with $\text{Fe}_2\text{-NHCS}$ (2.92 mA cm^{-2}), Co-NHCS (0.15 mA cm^{-2}), NHCS (0.09 mA cm^{-2}), and commercial Pt/C (2.34 mA cm^{-2}), the $\text{Fe}_2/\text{Co-NHCS}$ delivered the highest value of the kinetic current density at 0.9 V (9.45 mA cm^{-2}). This result is four times higher than that of the commercial Pt/C , which further support the superior ORR kinetics. We also calculated the turnover frequency (TOF) for the oxygen reduction reaction (ORR) to evaluate the intrinsic electrochemical activity of the active metal sites. As illustrated in Figure S15, $\text{Fe}_2/\text{Co-NHCS}$ exhibited the highest TOF value of $0.34\text{ e}^- \text{ site}^{-1} \text{ s}^{-1}$ at 0.9 V , which is 3.4 times greater than that of $\text{Fe}_2\text{-NHCS}$ ($0.10\text{ e}^- \text{ site}^{-1} \text{ s}^{-1}$) and 4.3 times higher than that of commercial Pt/C ($0.08\text{ e}^- \text{ site}^{-1} \text{ s}^{-1}$). The LSV curves at different rotation speeds, ranging from $225\text{--}2500\text{ rpm}$, were recorded to calculate the average number of transferred elections (Figure 4D). As shown in Figure S16, the K-L plots are derived from the LSV curves. We calculated that the electron transfer number is near 4 through the K-L plots, indicating the ideal 4e^- ORR reaction process. Rotating ring-disk electrode (RRDE) measurements also demonstrated the number of transfer electrons and the yield of the by-product H_2O_2 is 4 and

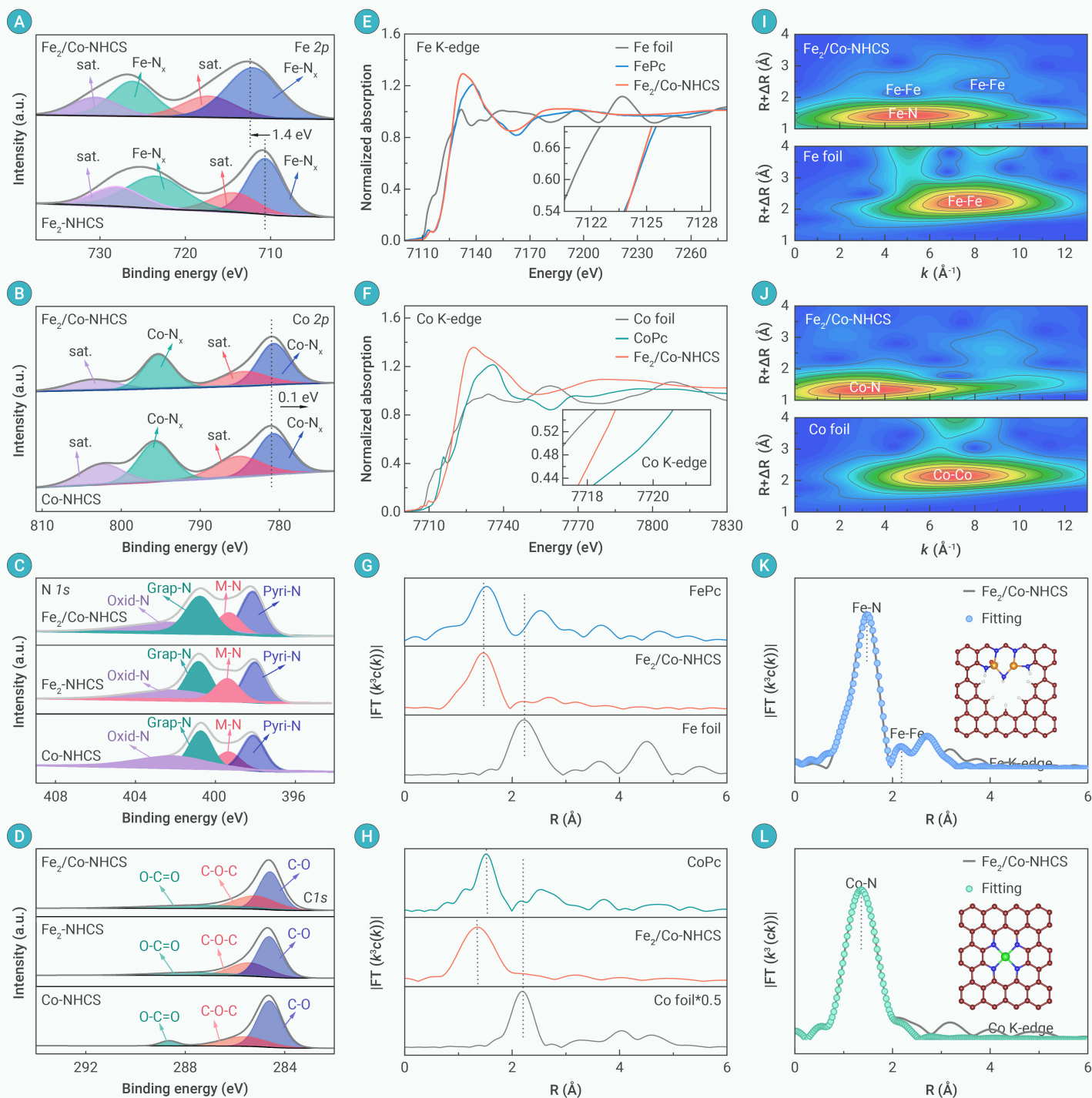


Figure 3. Atomic configurations of $\text{Fe}_2/\text{Co-NHCS}$ catalysts of $\text{Fe}_2/\text{Co-NHCS}$ (A) The Fe 2p XPS spectra of $\text{Fe}_2/\text{Co-NHCS}$ and $\text{Fe}_2\text{-NHCS}$, (B) the Co 2p XPS spectra of $\text{Fe}_2/\text{Co-NHCS}$ and Co-NHCS , (C and D) the N 1s and C 1s XPS spectra of $\text{Fe}_2/\text{Co-NHCS}$, $\text{Fe}_2\text{-NHCS}$ and Co-NHCS . (E) Fe K-edge XANES spectra of $\text{Fe}_2/\text{Co-NHCS}$, FePc , and Fe foil. (F) Co K-edge XANES spectra of $\text{Fe}_2/\text{Co-NHCS}$, CoPc , and Co foil. (G and H) k^3 -weighted FT-EXAFS spectra of $\text{Fe}_2/\text{Co-NHCS}$, FePc , Fe foil, CoPc , and Co foil. (I and J) WT-EXAFS fitting curves of $\text{Fe}_2/\text{Co-NHCS}$ at Fe and Co K-edge. (K and L) FT-EXAFS fitting curves of $\text{Fe}_2/\text{Co-NHCS}$ at Fe and Co K-edge.

0.56% (Figure 4E), respectively, which provides further evidence for the desirable $4e^-$ reaction pathway. Additionally, we performed the chronoamperometric test to investigate the ORR durability of the $\text{Fe}_2/\text{Co-NHCS}$. After 24 hrs of continued work, the current density of $\text{Fe}_2/\text{Co-NHCS}$ still retained 90.36% as indicated in Figure 4F. In comparison, the commercial Pt/C retained only 64.96%, indicating the excellent long-term stability and potential applicability of $\text{Fe}_2/\text{Co-NHCS}$. In order to confirm the structural stability of the $\text{Fe}_2/\text{Co-NHCS}$, we conducted the X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses. As shown in Figure S17, no obvious Fe-based and Co-based nanoparticles were found in the TEM image of $\text{Fe}_2/\text{Co-NHCS}$.

NHCS, indicating the atomic dispersion of Fe-based and Co-based species after the ORR test. The XRD pattern in Figure S18 also shows that no peak indexing Fe/Co-based species was captured for $\text{Fe}_2/\text{Co-NHCS}$ after the long-term durability test. These results indicate the structural robustness of $\text{Fe}_2/\text{Co-NHCS}$.

To assess the suitability of the $\text{Fe}_2/\text{Co-NHCS}$ for rechargeable Zn-air batteries (ZABs), we also evaluated its oxygen evolution reaction (OER) catalytic activity in 1 M KOH.^{49–52} As illustrated in Figure 4G, the $\text{Fe}_2/\text{Co-NHCS}$ requires only 0.264 V to achieve a current density of 10 mA cm^{-2} , which is significantly lower than that of the $\text{Fe}_2\text{-NHCS}$ (0.387 V), Co-NHCS (0.407 V),

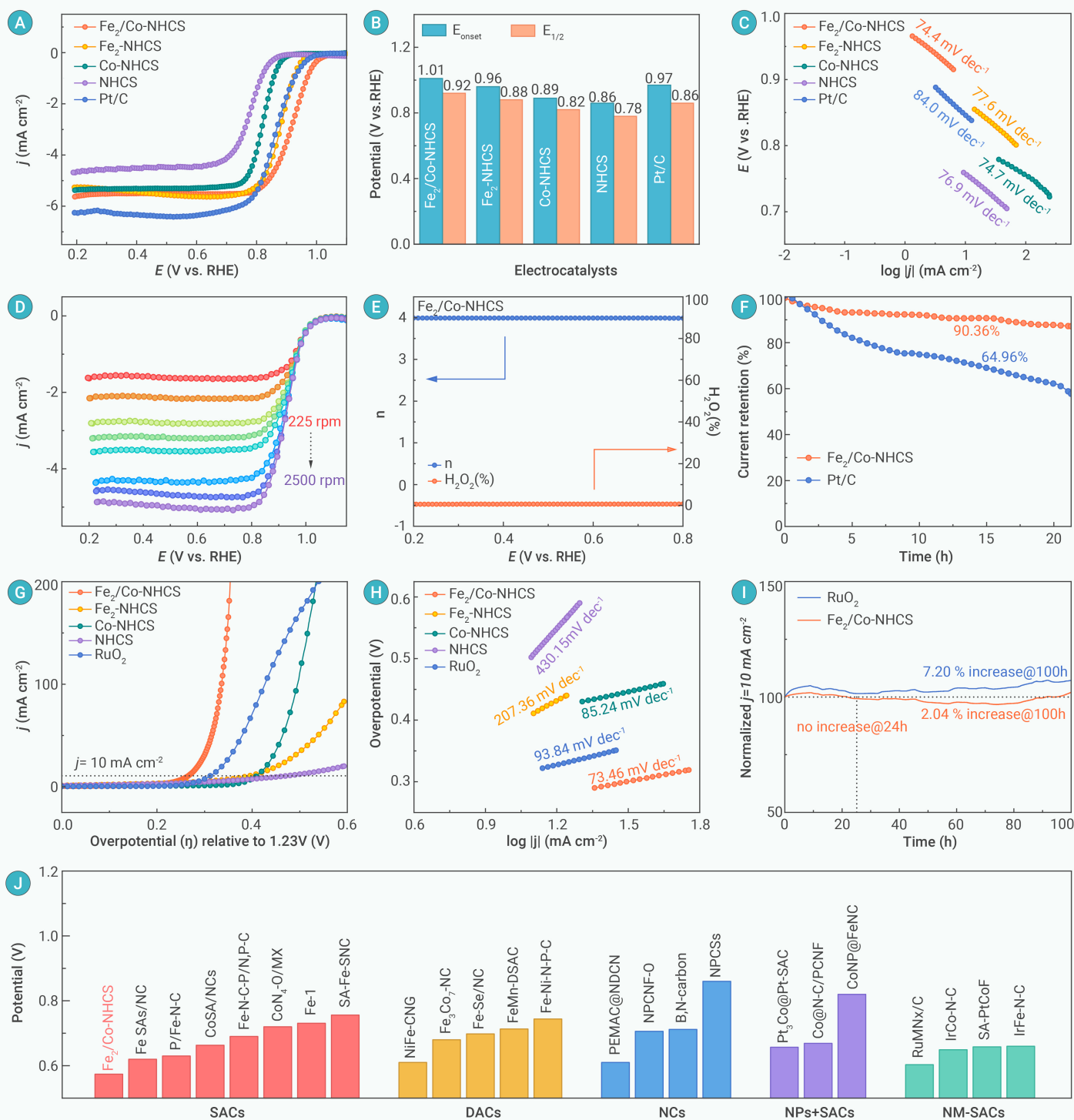


Figure 4. Electrocatalytic performance of Fe₂/Co-NHCS (A) LSV curves, (B) E_{onset} and $E_{1/2}$, and (C) corresponding Tafel plots for Fe₂/Co-NHCS, Fe₂-NHCS, Co-NHCS, NHCS, and commercial Pt/C toward ORR. (D) LSV curves of Fe₂/Co-NHCS at different rotation rates in 0.1 m KOH. (E) Electron transfer number (n) and H₂O₂ yield for the Fe₂/Co-NHCS. (F) Relative current density-time curves of Fe₂/Co-NHCS and commercial Pt/C at 0.7 V with a rotation speed of 200 rpm. (G) LSV curves, (H) Tafel plots for Fe₂/Co-NHCS, Fe₂-NHCS, Co-NHCS, NHCS, and commercial Pt/C. (I) Durability test for OER. (J) Comparison of ΔE between the Fe₂/Co-NHCS and literature data.

NHCS (0.458 V), and RuO₂ (0.310 V). The Fe₂/Co-NHCS also exhibited the lowest Tafel slope value of 73.46 mV dec⁻¹ among all investigated catalysts, indicating its outstanding reaction kinetics (Figure 4H). As shown in Figure S19, Fe₂/Co-NHCS has the minimum semicircle diameter of all catalysts, which displays its lowest charge transfer resistance. We also conducted a chrono-potentiometric measurement at 10 mA cm⁻² to explore the durability of Fe₂/Co-NHCS. After 24 hours of tests in Figure 4I, the current density of Fe₂/Co-NHCS showed almost no change. Even after 100 hours, the current

density of Fe₂/Co-NHCS increased by a mere 2.04%. This minimal increase is much lower than the 7.20% rise seen with commercial RuO₂, indicating the superior stability of Fe₂/Co-NHCS. Interestingly, the potential gap ΔE between the $E_{1/2}$ of ORR and the potential of OER at 10 mA cm⁻² ($E_{j=10}$) can be used to evaluate the bifunctional oxygen electrocatalytic performance of the Fe₂/Co-NHCS. As captured in Figure S20, the Fe₂/Co-NHCS exhibited superior bifunctional catalytic performance. The potential gap (ΔE) of 0.57 V of Fe₂/Co-NHCS outperforms that of NHCS (0.90 V), Co-NHCS (0.82 V), Fe₂-NHCS

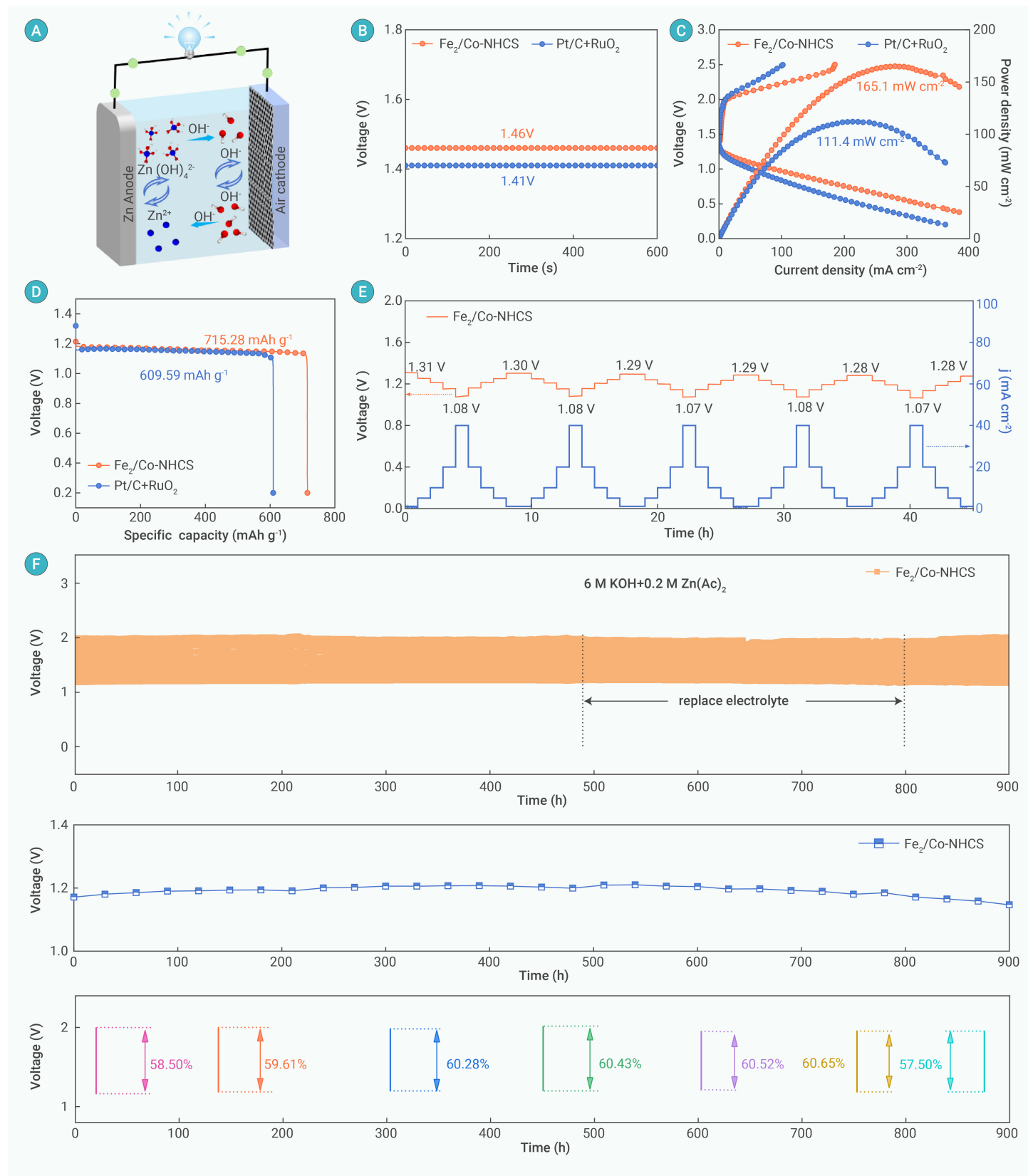


Figure 5. ZABs performance (A) Schematic diagram of ZABs, (B) open circuit potential, and (C) discharge/charge polarization curves and corresponding power densities of ZABs powered by Fe₂/Co-NHCS and Pt/C+RuO₂, respectively, (D) specific capacities. (E) Discharge curves of the ZABs equipped with Fe₂/Co-NHCS at different current densities. (F) The galvanostatic charge-discharge cycling curve of Fe₂/Co-NHCS driven ZABs was conducted at the current density of 5 mA cm⁻².

(0.73 V), the commercial Pt/C+RuO₂ couple catalyst (0.69 V) and the recently reported bifunctional oxygen electrocatalysts (Figure 4J & Table S5).

Zinc-air batteries performance

Considering its excellent ORR/OER performance, the ZABs were constructed to explore the application potential of the Fe₂/Co-NHCS (Figure

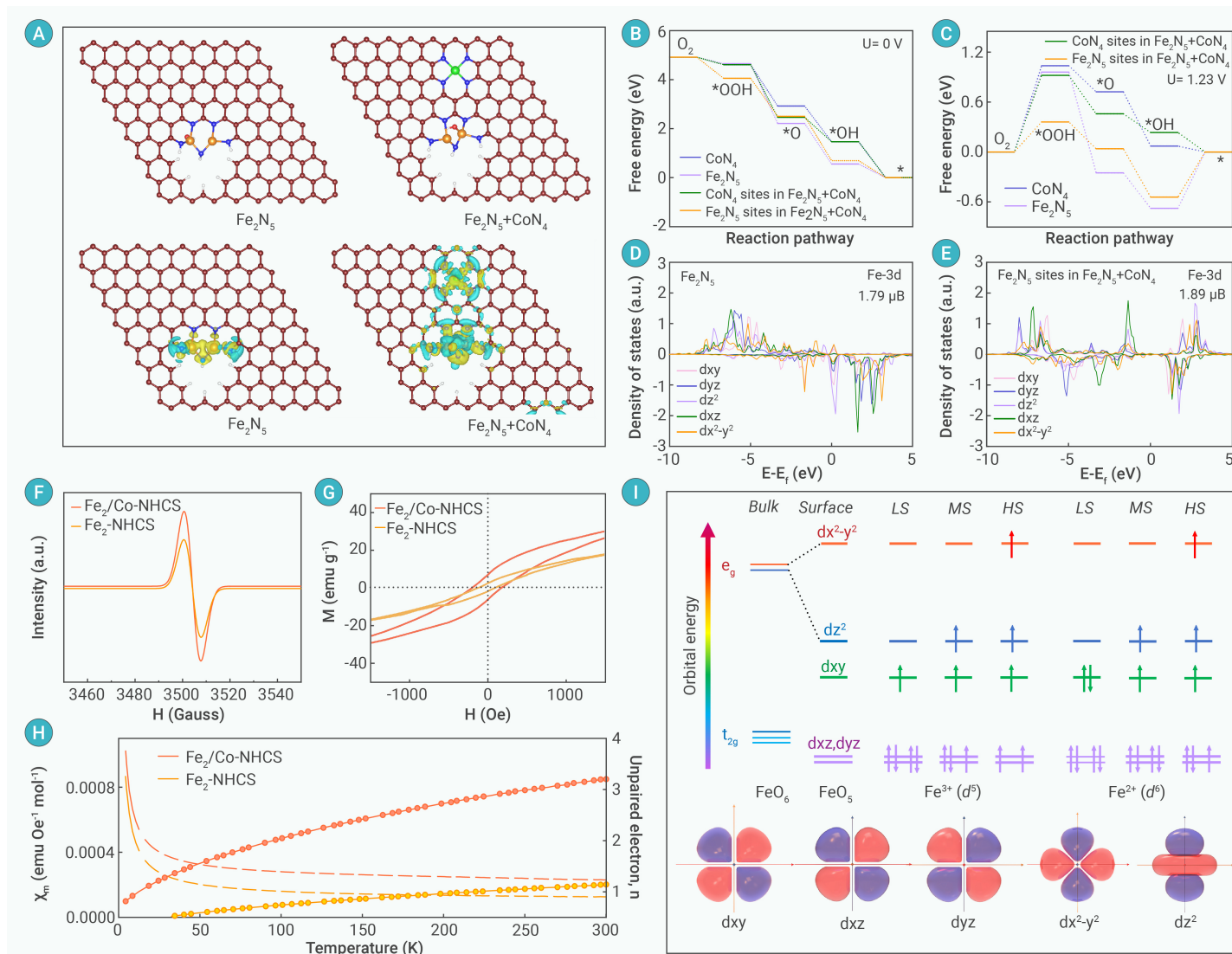


Figure 7. DFT calculations (A) The atomic configuration and differential charge density map of Fe₂N₅ and Fe₂N₅+CoN₄ model, (B and C) ORR Gibbs free energy diagram at $U=0$ and 1.23 V for the all investigated model, (D and E) PDOS image for Fe-3d orbitals in Fe₂N₅ model and Fe₂N₅ sites in Fe₂N₅+CoN₄ model, (F-H) EPR spectra, magnetic hysteresis loops, and M-T plots and the unpaired 3d-electron number of Fe₂-NHCS and Fe₂/Co-NHCS, (I) Schematic diagram of the 3d-orbital splitting manner for 5-coordinated Fe atoms.

5A). In comparison, the ZABs assembled by Pt/C+RuO₂ couple catalysts were also prepared. As shown in Figures 5B-C, the Fe₂/Co-NHCS-based-ZABs achieved an open circuit potential (OCP) of 1.46 V and the peak power density (P_{max}) of 165.1 mW cm⁻², which are higher than those of the ZABs driven by Pt/C+RuO₂ (1.41 V and 111.4 mW cm⁻²) as well as reported carbon-supported catalysts (Table S6). In contrast to the Pt/C+RuO₂-based ZABs (609.59 mAh g⁻¹, Figure 5D), the ZABs fabricated by Fe₂/Co-NHCS delivered a higher specific capacity of 715.28 mAh g⁻¹. The rate performance at various current densities is recorded to provide more evidence for the superiority of the Fe₂/Co-NHCS-based ZABs. As displayed in Figure 5E, when the current density was at 1 and 40 mA cm⁻², the Fe₂/Co-NHCS-based ZABs supplied corresponding voltages of 1.31 V and 1.08 V, respectively. After 5 cycles, the ZABs assembled with Fe₂/Co-NHCS exhibited only 0.03 V voltage attenuation, demonstrating its excellent stability with negligible voltage loss. Galvanostatic charge-discharge cycles at 5 mA cm⁻² were conducted to evaluate the long-term durability of the Fe₂/Co-NHCS-based ZABs. Figure 5F illustrates the constant current charge-discharge curve of Fe₂/Co-NHCS-based ZABs over 900 hours. At a current density of 5 mA cm⁻², the charge/discharge potentials were 2.00 V and 1.17 V, respectively. Remarkably, even after 900 hours, these potentials remain stable at 2.00 V and 1.15 V accompanied with negligible decay, showcasing the excellent stability of the Fe₂/Co-NHCS-based ZABs. We further utilized round-trip efficiency to assess the rechargeable performance of the ZABs equipped with the Fe₂/Co-NHCS.

After 900 hours of stable operation, its round-trip efficiency decreased from 58.5% to 57.5%, demonstrating brilliant charge-discharge cycling capability. To verify the application capability of ZABs under low-temperature conditions, we tested its performance at -30°C. As displayed in Figure S21, the Low-T ZABs supported by Fe₂/Co-NHCS delivered higher OCP and P_{max} (OCP=1.52 V and P_{max} =86.6 mW cm⁻²) than those of the commercial Pt/C+RuO₂ (OCP=1.47 V and P_{max} =35.2 mW cm⁻²). Additionally, the Fe₂/Co-NHCS-based low temperature ZABs, which were discharged for 5 cycles at different current densities, only experienced a voltage drop of 0.02V, demonstrating their tolerance at low temperatures (Figure S22). We also recorded the charge-discharge curve to appraise the applicability of the Low-T ZABs equipped with Fe₂/Co-NHCS. As can be seen in Figure S23, the Fe₂/Co-NHCS-based Low-T ZABs were capable of stable operation over 60 hours at a temperature of -30°C.

Furthermore, we also employed the Fe₂/Co-NHCS as the key electrocatalysts for the air-cathode to fabricate flexible ZABs (F-ZABs, Figure 6A). As shown in Figures 6B-C, the F-ZABs powered by Fe₂/Co-NHCS achieved a high open-circuit potential (OCP) of 1.47 V and a remarkable maximum power density (P_{max}) of 147.7 mW cm⁻². This performance surpasses that of the commercial Pt/C+RuO₂ (OCP=1.33 V and P_{max} = 106.5 mW cm⁻²). Taking advantage of the excellent performance of the Fe₂/Co-NHCS-based F-ZABs, a series of F-ZABs fabricated with Fe₂/Co-NHCS illuminated LEDs with a rated voltage of 3 V. In order to appraise the rate performance of the F-ZABs

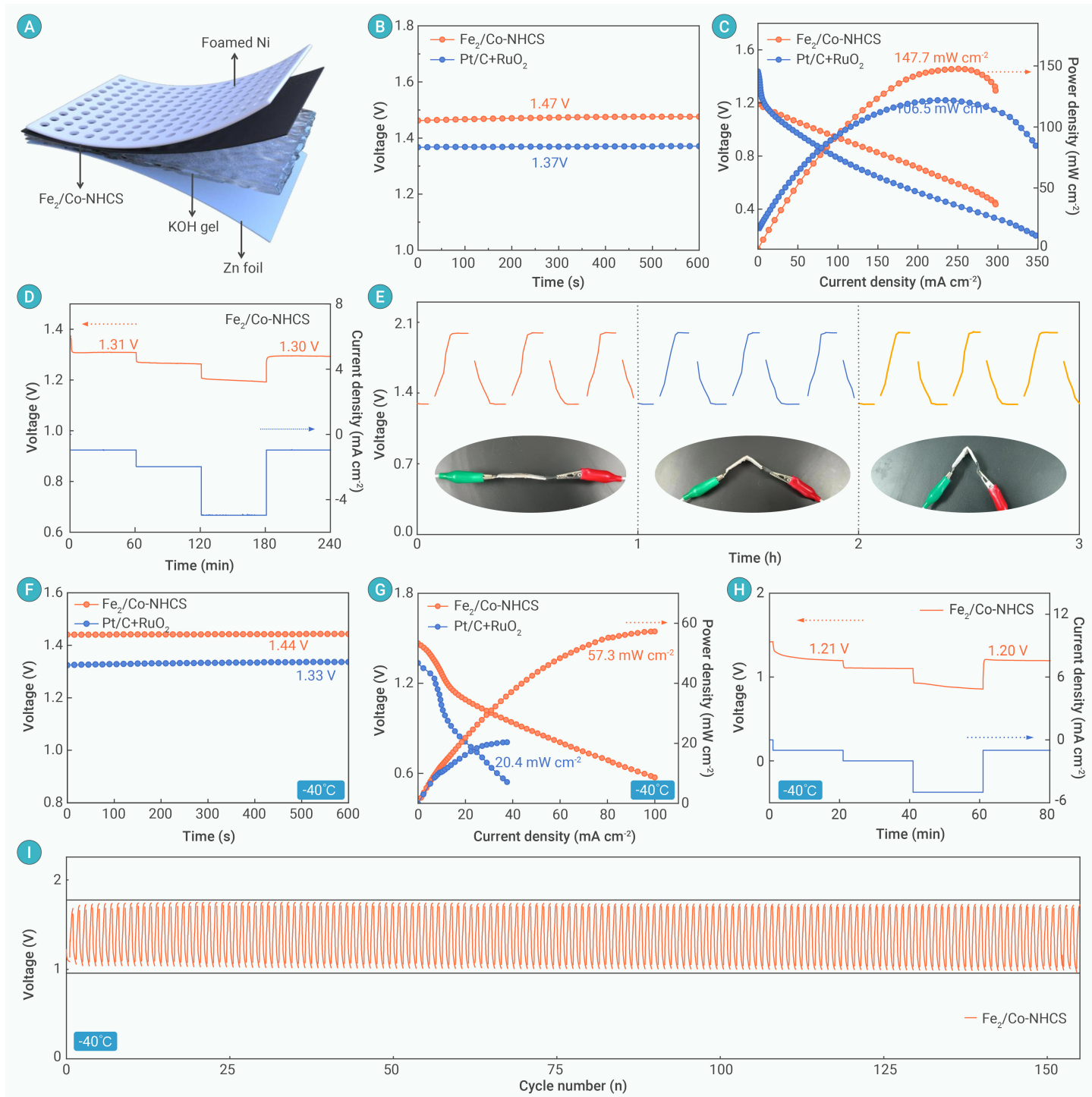


Figure 6. F-ZABs performance (A) Schematic diagram of F-ZABs. (B) OCP and (C) discharge/charge polarization curves and corresponding power densities of F-ZABs powered by $\text{Fe}_2/\text{Co-NHCS}$ and Pt/C+RuO_2 , respectively. (D) Discharge curves of the ZABs powered by the $\text{Fe}_2/\text{Co-NHCS}$ at different current densities. (E) Flexibility tests. (F) OCP and (G) discharge/charge polarization curves and corresponding power densities of F-ZABs powered by $\text{Fe}_2/\text{Co-NHCS}$ and Pt/C+RuO_2 at Low-T. (H) Discharge curves of the ZABs powered by the $\text{Fe}_2/\text{Co-NHCS}$ at different current densities at Low-T. (I) The galvanostatic charge-discharge cycling curve of $\text{Fe}_2/\text{Co-NHCS}$ -based F-ZABs at 1 mA cm^{-2} at Low-T.

equipped with $\text{Fe}_2/\text{Co-NHCS}$, we tested the voltage at different densities of 1, 2, and 5 mA cm^{-2} . After one cycle, the voltage of the F-ZABs constructed with $\text{Fe}_2/\text{Co-NHCS}$ could recover approaching the initial voltage, only with negligible voltage loss observed (Figure 6D). Additionally, the $\text{Fe}_2/\text{Co-NHCS}$ -based F-ZABs exhibited highly stable discharge-charge profiles under various bending angles (Figure 6E), demonstrating their superior flexibility. To further demonstrate its robust stability and reversibility, we conducted continuous galvanostatic discharge-charge cycling measurements at a current density of 5 mA cm^{-2} , with each cycle lasting 10 minutes. As shown in Figures S24–S25, compared to the commercial Pt/C+RuO_2 with 12 hours of durability, the F-

ZABs utilizing the $\text{Fe}_2/\text{Co-NHCS}$ demonstrated 110 hours of continuous galvanostatic discharge-charge cycling, clearly affirming its exceptional long-term rechargeability.

We also explored the low-temperature (Low-T) adaptability of the F-ZABs equipped with $\text{Fe}_2/\text{Co-NHCS}$ at -40°C . As illustrated in Figures 6F–G, the $\text{Fe}_2/\text{Co-NHCS}$ -based F-ZABs afforded the high OCP and P_{max} of 1.44 V and 57.3 mW cm^{-2} , which is higher than that of the commercial Pt/C+RuO_2 -based F-ZABs (OCP=1.33 V, $P_{\text{max}}=20.4 \text{ mW cm}^{-2}$) and comparable to recent reported works (Table S7), indicating its good Low-T tolerance. At the same time, the rate performance of the F-ZABs propelled by $\text{Fe}_2/\text{Co-NHCS}$ also

delivered a strong voltage recovery capability (Figure 6G). After one cycle, the voltage was able to recover from 1.21 V to 1.20 V, and only a 0.01 V deterioration was observed at lower temperature (Figure 6H). More importantly, we also performed the galvanostatic discharge-charge cycling measurement at 1 mA cm⁻² to appraise the F-ZABs' long-term recycling ability. As displayed in Figure 6I, the Fe₂/Co-NHCS-based F-ZABs can be continuously charged and discharged for more than 150 stable cycles with negligible voltage loss. In contrast, the Pt/C+RuO₂-based F-ZABs experienced significant performance degradation after only 120 cycles (Figure S26). These results strongly suggesting the application superiority of Fe₂/Co-NHCS in low-temperature environments.

Theoretical calculations

The underlying enhanced catalytic activity mechanism of the Fe₂/Co-NHCS can be unraveled through the density functional theory (DFT) calculations and relevant magnetic measurements. As illustrated in Figures 7A & S27, the basic atomic model of Fe₂N₅ and CoN₄ model were first constructed. Furthermore, the tri-atomic structure containing Fe₂N₅ and CoN₄ site (Fe₂N₅+CoN₄ model) was built to explore the promoting effect of the incorporation of the CoN₄ model for the Fe₂N₅ site toward the oxygen reduction reaction (ORR). To visually reconnoiter the electronic interaction between the Fe₂N₅ and CoN₄ site, we calculated the charge density difference of the Fe₂N₅ and Fe₂N₅+CoN₄ model (Figure 7A). Compared to the Fe₂N₅ model, which has a symmetric electron cloud shape, the introduction of CoN₄ sites caused significant polarization in the electron cloud of the Fe₂N₅ sites within the Fe₂N₅+CoN₄ model. This observation reveals the charge modulation effect that CoN₄ sites have on Fe₂N₅ sites. Figures 7B-C depicted the pathways for ORR in four models (e.g., Fe₂N₅, CoN₄, Fe₂N₅ site in Fe₂N₅+CoN₄, and CoN₄ site in Fe₂N₅+CoN₄). It demonstrated that at U=0 V, the ORR processes in all investigated models are characterized by a gradual decrease in energy, indicating that the ORR processes can occur spontaneously in all investigated models. The reaction pathway at U=1.23 V reflected the influence of CoN₄ incorporation on the catalytic activity of Fe₂N₅. At U=1.23 V, the rate-determining step (RDS) for the ORR process on pure Fe₂N₅ model is the generation of OOH* (O₂+*+H₂O+e⁻→OOH*+OH⁻), with high energy barriers of 0.96 eV. However, with the introduction of CoN₄, the RDS for ORR process on Fe₂N₅ sites in the Fe₂N₅+CoN₄ model shifts to the desorption of OH* and delivers a lower energy barrier (0.54 eV) than that of the pure Fe₂N₅ model. In order to explore the origin of the Fe₂N₅+CoN₄ model's superiority in catalyzing OER, we also used DFT to calculate the Gibbs free energy of Fe₂N₅ and CoN₄ as OER active sites, respectively. As displayed in Figure S28, we found that when CoN₄ sites in Fe₂N₅+CoN₄ were used as the OER active site, the RDS energy barrier (0.46 eV) was lower than that of Fe₂N₅ sites in Fe₂N₅+CoN₄ (0.58 eV), the pure Fe₂N₅ model (1.21 eV), and the pure CoN₄ model (0.65 eV). Then the density of states (DOS) calculation was performed to reveal the origin of the catalytic superiority of the Fe₂N₅ site in Fe₂N₅+CoN₄ model. Observations from Figures 7D-E showed that the Fe-3d orbital electrons are asymmetrically arranged in the spin channel, indicating the presence of spin polarization for the Fe₂N₅ sites in the Fe₂N₅+CoN₄ model. In detail, the magnetic moment of Fe₂N₅ sites in Fe₂N₅+CoN₄ model is measured at 1.89 μB, exceeding that of the pure Fe₂N₅ model (1.79 μB), which suggests that the enhanced spin polarization originated from the introduction of CoN₄ sites. According to the d-band center theory, the more substantial the negative value of the d-band center energy level, the more attenuated the adsorption interaction between the active site and the reaction-related intermediates. From Figure S29, it is evident that the d-band center energy level of Fe₂N₅ sites in Fe₂N₅+CoN₄ model (-1.17 eV) is lower than that of the pure Fe₂N₅ model (-1.16 eV). Due to the lower d-band center energy level of Fe₂N₅ sites in Fe₂N₅+CoN₄ model, OH* desorption can occur more readily, with a lower barrier of 0.54 eV. These findings demonstrate that the introduction of CoN₄ refines the spin state of Fe₂N₅ site, significantly improving its catalytic activity for the ORR reaction.

X-band electron paramagnetic resonance (EPR) measurements were performed to assess the paramagnetic properties of the Fe₂N₅ diatomic pairs in both Fe₂-NHCS and Fe₂/Co-NHCS. As illustrated in Figure 7F, the Fe₂/Co-NHCS demonstrated enhanced spin polarization of the Fe₂N₅ diatomic pairs following the incorporation of CoN₄ sites, compared to Fe₂-NHCS. The ferromagnetic hysteresis loop of Fe₂-NHCS and Fe₂/Co-NHCS at 300 K showed a

saturation magnetization. Following the incorporation of the CoN₄ site, the saturation magnetization significantly increases, which can be attributed to more unpaired electrons in Fe₂/Co-NHCS (Figure 7H).

An enlarged view of the curve around H = 0 is presented in the Figure 7G, indicating that Fe₂/Co-NHCS possesses a coercive magnetic field (H_c) of 234.49 Oe and a residual magnetization (M_r) of 6.76 emu g⁻¹, which is stronger than that of Fe₂-NHCS (166.16 Oe and 2.09 emu g⁻¹). To further elucidate the electron spin state of the Fe-3d orbitals, zero-field cooling (ZFC) temperature-dependent magnetic susceptibility was conducted. The number of unpaired 3d electrons (n) at the Fe center, which is related to the effective magnetic moment (μ_{eff}), can be calculated using the equation: $2.828\sqrt{x_m T} = \mu_{\text{eff}} = \sqrt{n(n+2)}$. For Fe₂/Co-NHCS, this value is determined to be 3.3, which is higher than that of Fe₂-NHCS (~1.1). The d-orbital and electron configurations of the five-coordinated Fe^{2+/3+} (FeO₅) were illustrated in Figure 7I, which are recognized as potential reaction sites on the surface due to their unsaturated coordination. The specially engineered FeO₅ environment is expected to modify the energy levels and local symmetry of the Fe d-orbitals, potentially leading to a diversity of spin states.^{53,54}

Despite their significance, alterations in d-orbital splitting are often overlooked in contemporary literature. This highlights the need for a comprehensive analysis of these intricate variations, especially for Fe₂N₅ diatomic pairs. Figure 6I exhibited the transformation and orientation of the five d-orbitals following Hund's rule and the Pauli exclusion principle. Notably, the interaction between the p orbitals of O₂ molecules and the solitary d_{z²} electrons at medium spin Fe₂N₅ diatomic pairs within Fe₂/Co-NHCS is identified as the catalyst for the augmented ORR activity. Furthermore, the more efficient binding of O₂ by enhancing the spin state can be demonstrated through calculating the adsorption energy of O₂. Figure S30 shows that the Fe₂N₅+CoN₄ model exhibits higher adsorption ability for O₂ (E_{ads}(O₂) = -0.86 eV) compared to the pure Fe₂N₅ model (E_{ads}(O₂) = -0.84 eV), confirming that the spin state-enhanced Fe₂N₅+CoN₄ model can effectively capture O₂ to complete ORR process. Ultraviolet photoelectron spectroscopy (UPS) analysis was employed to further investigate the electronic state characteristics of the Fe₂/Co-NHCS. As illustrated in Figures S31-33, the binding energy of the secondary electron cutoff edge of the Fe₂/Co-NHCS catalyst (15.6 eV) demonstrated a slight increase compared to the Fe₂-NHCS catalyst (15.5 eV). This difference suggested that the introduction of CoN₄ sites reduces the work function of the Fe₂/Co-NHCS, promoting electron emission and accelerating electron transfer on the catalyst surface. Furthermore, compared to Fe₂-NHCS at 2.0 eV, Fe₂/Co-NHCS delivered a higher energy of the highest occupied molecular orbital (HOMO), reaching 2.2 eV. This suggests that the introduction of CoN₄ may lead to spin polarization in the 3d-orbitals, contributing to the reduced electron density of the Fe₂N₅ diatomic pairs.³³

Interestingly, we also performed the low-temperature EPR test at Low-T of 233 K, and the corresponding result delivers that the signal of Fe₂/Co-NHCS is also stronger than that of the Fe₂-NHCS (Figure S34). This indicates that Fe₂/Co-NHCS possesses an enhanced spin state with low-temperature tolerance and more unpaired electrons. As a result, it can more easily capture oxygen even at Low-T to complete ORR process. This property reveals the origin of the excellent performance of Fe₂/Co-NHCS when applied in Low-T ZABs.

CONCLUSION

In conclusion, we have constructed a tri-atomic electrocatalyst, Fe₂/Co-NHCS featuring Fe₂N₅+CoN₄ active site, which achieves a high E_{1/2} of 0.92 V and J_k of 9.45 mA cm⁻² at 0.9 V. When employing the Fe₂/Co-NHCS as the air-cathode electrocatalysts, the ZABs and F-ZABs driven by Fe₂/Co-NHCS deliver a high P_{max} (165.1 mW cm⁻² and 147.7 mW cm⁻²) and outstanding charge-discharge stability (900 and 110 h). Even at Low-T of -40°C, the Fe₂/Co-NHCS-based F-ZABs still can supply the P_{max} of 57.3 mW cm⁻² and continuous work over 150 stable cycles without activity decay. Further theoretical calculations and magnetic measurements unlock that the adjacent single Co site can induce spin polarization and thus optimize the spin state of the Fe₂N₅ diatomic pairs from the low spin state to the medium spin state. The medium spin Fe₂N₅ diatomic pairs, possessing a t_{2g}⁴ e_g¹ electron configuration, bind more readily with oxygen reactants, thereby enhancing the ORR activity and applicability in Low-T. This work offers a novel perspective on

investigating the origins of activity enhancement in tri-atomic catalysts through electron spin optimization. It suggests approaches for the rational design of efficient catalysts that ensure excellent long-term stability for use in energy conversion devices under Low-T.

REFERENCES

- Zhao C. X., Liu X., Liu J. N., et al. (2023). Inductive effect on single-atom sites. *J. Am. Chem. Soc.* **145**:27531–27538. DOI:10.1021/jacs.3c09190
- Zhang C., Wang X., Ma Z., et al. (2023). Spin state modulation on dual Fe center by adjacent Ni sites enabling the boosted activities and ultra-long stability in Zn-air batteries. *Sci. Bull.* **68**:2042–2053. DOI:10.1016/j.scib.2023.07.049
- Sun J.-K., Pan Y.-W., Xu M.-Q., et al. (2023). Heteroatom doping regulates the catalytic performance of single-atom catalyst supported on graphene for ORR. *Nano Res.* **17**:1086–1093. DOI:10.1007/s12274-023-5898-1
- Zhao Y., Tian Z., Wang W., et al. (2024). Size-dependent activity of Fe-N-doped mesoporous carbon nanoparticles towards oxygen reduction reaction. *Green Carbon* **2**:221–230. DOI:10.1016/j.greenca.2024.03.002
- Kang D., Zhang C., Wang X., et al. (2024). Efficient atomically dispersed Fe catalysts with robust three-phase interface for stable seawater-based zinc-air batteries. *Green Carbon* **3**:1–10. DOI:10.1016/j.greenca.2024.09.002
- Li S., Shi L., Guo Y., et al. (2024). Selective oxygen reduction reaction: mechanism understanding, catalyst design and practical application. *Chem. Sci.* **15**:11188–11228. DOI:10.1039/d4sc02853h
- Dan M., Zhang X., Yang Y., et al. (2024). Dual-axial engineering on atomically dispersed catalysts for ultra-stable oxygen reduction in acidic and alkaline solutions. *Proc. Natl. Acad. Sci. USA* **121**:2318174121. DOI:10.1073/pnas.2318174121
- Wang Y., Zhang C., Wang X., et al. (2023). Engineering carbon-chainmail-shell coated Co₃Se₂ nanoparticles as efficient and durable catalysts in seawater-based Zn-air batteries. *Acta Phys-Chim. Sin.* **40**:2305004. DOI:10.3866/pku.Whxb202305004
- Chen J., Qiu C., Zhang L., et al. (2024). Wood-derived Fe cluster reinforced asymmetric single-atom catalysts and weather-resistant organohydrogel for wide temperature flexible Zn-air batteries. *Energy Environ. Sci.* **17**:4746–4757. DOI:10.1039/d4ee01226g
- Dong Y., Wang Y., Tian Z., et al. (2021). Enhanced catalytic performance of Pt by coupling with carbon defects. *The Innovation* **2**:100161. DOI:10.1016/j.xinn.2021.100161
- Yuan Y., Adimi S., Thomas T., et al. (2021). Co₃Mo₃N-An efficient multifunctional electrocatalyst. *The Innovation* **2**:100096. DOI:10.1016/j.xinn.2021.100096
- Xu L., Iqbal R., Wang Y., et al. (2024). Emerging two-dimensional materials: Synthesis, physical properties, and application for catalysis in energy conversion and storage. *Innov. Mater.* **2**:100060. DOI:10.59717/j.xinn-mater.2024.100060
- Wang X., Zhou X., Li C., et al. (2022). Asymmetric Co-N₃P₁ trifunctional catalyst with tailored electronic structures enabling boosted activities and corrosion resistance in an uninterrupted seawater splitting system. *Adv. Mater.* **34**:2204021. DOI:10.1002/adma.202204021
- Tong K., Xu L., Yao H., et al. (2024). Hydrogen spillover bridged dual nano-islands triggered by built-in electric field for efficient and robust alkaline hydrogen evolution at ampere-level current density. *Nano Res.* **17**:5050–5060. DOI:10.1007/s12274-024-6520-x
- Tang B., Zhou Y., Ji Q., et al. (2024). A Janus dual-atom catalyst for electrocatalytic oxygen reduction and evolution. *Nat. Synth.* **3**:878–890. DOI:10.1038/s44160-024-00545-1
- Hao L., Gao Y., Robertson A. W., et al. (2024). A universal strategy for fabrication of dual atom materials for multifunctional electrocatalysis. *Innov. Mater.* **2**:100050. DOI:10.59717/j.xinn-mater.2024.100050
- Zeng R., Gao Q., Xiao L., et al. (2024). Precise tuning of the d-band center of dual-atomic enzymes for catalytic therapy. *J. Am. Chem. Soc.* **146**:10023–10031. DOI:10.1021/jacs.4c00791
- Li R., Zhang Z., Liang X., et al. (2023). Polystyrene waste thermochemical hydrogenation to ethylbenzene by a N-bridged Co, Ni dual-atom catalyst. *J. Am. Chem. Soc.* **145**:16218–16227. DOI:10.1021/jacs.3c05184
- Zhang J., Zhao Y., Zhao W., et al. (2023). Improving electrocatalytic oxygen evolution through local field distortion in Mg/Fe dual-site catalysts. *Angew. Chem. Int. Ed.* **62**:202314303. DOI:10.1002/anie.202314303
- Li L., Zhu J., Kong F., et al. (2024). Tailoring atomic strain environment for high-performance acidic oxygen reduction by Fe-Ru dual atoms communicative effect. *Matter* **7**:1517–1532. DOI:10.1016/j.matt.2024.01.019
- Wang H., Yang T., Wang J., et al. (2024). Coordination engineering in single-site catalysts: General principles, characterizations, and recent advances. *Chem* **10**:48–85. DOI:10.1016/j.chempr.2023.08.014
- Chen S., Wang T., Ma L., et al. (2022). Aqueous rechargeable zinc air batteries operated at -110°C. *Chem* **9**:497–510. DOI:10.1016/j.chempr.2022.10.028
- Ye C., Zheng M., Li Z., et al. (2022). Electrical pulse induced one-step formation of atomically dispersed Pt on oxide clusters for ultra-low-temperature zinc-air battery. *Angew. Chem. Int. Ed.* **61**:202213366. DOI:10.1002/anie.202213366
- Wang Y., Wu J., Tang S., et al. (2023). Synergistic Fe-Se atom pairs as bifunctional oxygen electrocatalysts boost low-temperature rechargeable Zn-air battery. *Angew. Chem. Int. Ed.* **62**:202219191. DOI:10.1002/anie.202219191
- Wang Q., Tan Y., Tang S., et al. (2023). Edge-hosted Mn-N₄-C₁₂ site tunes adsorption energy for ultralow-temperature and high-capacity solid-state Zn-air battery. *ACS Nano* **17**:9565–9574. DOI:10.1021/acsnano.3c02521
- Cui T., Wang Y. P., Ye T., et al. (2022). Engineering dual single-atom sites on 2D ultrathin N-doped carbon nanosheets attaining ultra-low-temperature zinc-air battery. *Angew. Chem. Int. Ed.* **61**:202115219. DOI:10.1002/anie.202115219
- Yan Y., Wen B., Liu M., et al. (2024). Orienting electron fillings in d orbitals of cobalt single atoms for effective zinc-air battery at a subzero temperature. *Adv. Funct. Mater.* **34**:2316100. DOI:10.1002/adfm.202316100
- Yang G., Zhu J., Yuan P., et al. (2021). Regulating Fe-spin state by atomically dispersed Mn-N in Fe-N-C catalysts with high oxygen reduction activity. *Nat. Commun.* **12**:1734. DOI:10.1038/s41467-021-21919-5
- Xu S., Feng S., Yu Y., et al. (2024). Dual-site segmentally synergistic catalysis mechanism: boosting CoFeS_x nanocluster for sustainable water oxidation. *Nat. Commun.* **15**:1720. DOI:10.1038/s41467-024-45700-6
- Liu Y., Liu X., Lv Z., et al. (2022). Tuning the spin state of the iron center by bridge-bonded Fe-O-Ti ligands for enhanced oxygen reduction. *Angew. Chem. Int. Ed.* **61**:202117617. DOI:10.1002/anie.202117617
- Zhang H., Chen H. C., Feizpoor S., et al. (2024). Tailoring oxygen reduction reaction kinetics of Fe-N-C catalyst via spin manipulation for efficient zinc-air batteries. *Adv. Mater.* **36**:2400523. DOI:10.1002/adma.202400523
- Xue D., Yuan P., Jiang S., et al. (2023). Altering the spin state of Fe-N-C through ligand field modulation of single-atom sites boosts the oxygen reduction reaction. *Nano Energy* **105**:108020. DOI:10.1016/j.nanoen.2022.108020
- Li Y., Ji Y., Zhao Y., et al. (2022). Local spin-state tuning of iron single-atom electrocatalyst by S-coordinated doping for kinetics-boosted ammonia synthesis. *Adv. Mater.* **34**:2202240. DOI:10.1002/adma.202202240
- Sun Y., Sun S., Yang H., et al. (2020). Spin-related electron transfer and orbital interactions in oxygen electrocatalysis. *Adv. Mater.* **32**:2003297. DOI:10.1002/adma.202003297
- Sheng X., Mei Z., Jing Q., et al. (2024). Revealing the orbital interactions between dissimilar metal sites during oxygen reduction process. *Small* **20**:2305390. DOI:10.1002/smll.202305390
- Wang X., Xu L., Li C., et al. (2023). Developing a class of dual atom materials for multifunctional catalytic reactions. *Nat. Commun.* **14**:7210. DOI:10.1038/s41467-023-42756-8
- Ni B., Shen P., Zhang G., et al. (2024). Second-shell N dopants regulate acidic O₂ reduction pathways on isolated Pt sites. *J. Am. Chem. Soc.* **146**:11181–11192. DOI:10.1021/jacs.3c14186
- Liu Y., Li J., Lv Z., et al. (2024). Efficient proton-exchange membrane fuel cell performance of atomic Fe sites via p-d hybridization with Al dopants. *J. Am. Chem. Soc.* **146**:12636–12644. DOI:10.1021/jacs.4c01598
- Han A., Sun W., Wan X., et al. (2023). Construction of Co₄ atomic clusters to enable Fe-N₄ motifs with highly active and durable oxygen reduction performance. *Angew. Chem. Int. Ed.* **62**:202303185. DOI:10.1002/anie.202303185
- Guo P., Liu B., Tu F., et al. (2024). Breaking Sabatier's vertex via switching the oxygen adsorption configuration and reaction pathway on dual active sites for acidic oxygen reduction. *Energy Environ. Sci.* **17**:3077–3087. DOI:10.1039/d4ee00823e
- Chen Z., Fan Q., Zhou J., et al. (2023). Toward understanding the formation mechanism and OER catalytic mechanism of hydroxides by In situ and operando techniques. *Angew. Chem. Int. Ed.* **62**:202309293. DOI:10.1002/anie.202309293
- Zhou J., Ren Z., Qiao F., et al. (2024). Unraveling volcano trend in OER of metal-organic frameworks with asymmetric configuration through energy band engineering. *Appl. Catal. B: Environ. Energy* **353**:124089. DOI:10.1016/j.apcatb.2024.124089
- Wang X., Yao H., Zhang C., et al. (2023). Double-tuned RuCo dual metal single atoms and nanoalloy with synchronously expedited Volmer/Tafel kinetics for effective and ultra-stable ampere-level current density hydrogen production. *Adv. Funct. Mater.* **33**:2301804. DOI:10.1002/adfm.202301804
- Lu X. F., Chen Y., Wang S., et al. (2019). Interfacing manganese oxide and cobalt in porous graphitic carbon polyhedrons boosts oxygen electrocatalysis for Zn-air batteries. *Adv. Mater.* **31**:1902339. DOI:10.1002/adma.201902339
- Huang H., Sun M., Li S., et al. (2024). Enhancing H₂O₂ electrosynthesis at industrial-relevant current in acidic media on atomically dispersed cobalt sites. *J. Am. Chem. Soc.* **146**:9434–9443. DOI:10.1021/jacs.4c02031
- Li Y., Zuo S., Wei F., et al. (2024). Boosted hydrogen evolution kinetics of heteroatom-doped carbons with isolated Zn as an accelerant. *Proc. Natl. Acad. Sci. USA* **121**:2315362121. DOI:10.1073/pnas.2315362121
- Wang X., Zhang J., Wang P., et al. (2023). Terbium-induced cobalt valence-band narrowing boosts electrocatalytic oxygen reduction. *Energy Environ. Sci.* **16**:5500–5512. DOI:10.1039/d3ee02503a

48. Shi L., Lin X., Liu F., et al. (2022). Geometrically deformed iron-based single-atom catalysts for high-performance acidic proton exchange membrane fuel cells. *ACS Catal.* **12**:5397–5406. DOI:10.1021/acscatal.2c00915
49. Liu J.-N., Zhao C.-X., Wang J., et al. (2024). A data-driven bifunctional oxygen electrocatalyst with a record-breaking $\Delta E = 0.57$ V for ampere-hour-scale zinc-air batteries. *Joule*. **8**:1804-1819 DOI:10.1016/j.joule.2024.03.017
50. Zhang Y. L., Liu B., Dai Y. K., et al. (2024). Engineering Co-N-Cr cross-interfacial electron bridges to break activity-stability trade-off for superdurable bifunctional single atom oxygen electrocatalysts. *Angew. Chem. Int. Ed.* **63**:202400577. DOI:10.1002/anie.202400577
51. Zhao B., Luo H., Liu J., et al. (2024). S-doped carbonized wood fiber decorated with sulfide heterojunction-embedded S, N-doped carbon microleaf arrays for efficient high-current-density oxygen evolution. *Chin. Chem. Lett.* **36**:109919. DOI:10.1016/j.ccllet.2024.109919
52. Zhou S., Shi L., Li Y., et al. (2024). Metal - organic framework - based electrocatalysts for acidic water splitting. *Adv. Funct. Mater.* **34**:2400767. DOI:10.1002/adfm.202400767
53. Jing Q., Mei Z., Sheng X., et al. (2023). Tuning the bonding behavior of d - p orbitals to enhance oxygen reduction through push-pull electronic effects. *Adv. Funct. Mater.* **34**:2307002. DOI:10.1002/adfm.202307002
54. Wang L., Mei Z., An Q., et al. (2023). Modulating the electronic spin state of atomically dispersed iron sites by adjacent zinc atoms for enhanced spin-dependent oxygen electrocatalysis. *Chem. Catal.* **3**:1000758. DOI:10.1016/j.checat.2023.100758

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AUTHOR CONTRIBUTIONS

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DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

Data are available from the corresponding author upon reasonable request.

SUPPLEMENTAL INFORMATION

It can be found online at <https://doi.org/10.59717/j.xinn-mater.2025.100131>.