

Pt₁Co alloy nanoparticles confined in N-doped carbon nanotubes: An efficient oxygen reduction catalyst for long-lasting rechargeable Zn–air battery

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ABSTRACT: Pt-based catalysts are the most active materials for the oxygen reduction reaction in Zn–air batteries; however, most Pt-based catalysts are unfavorable for the adsorption of OOH* intermediates, which hampers battery efficiency. To address this, a strategy for precisely constructing Pt–Co alloy atomic configurations enables the immobilization and controlled release of OOH* intermediates during the four-electron O₂ reduction reaction. Using the synthetic Pt₁Co alloy nanoparticles encapsulated in N-doped carbon nanotubes (Pt₁Co-NP@NCNTs) as an example, characterization via synchrotron-radiation X-ray absorption fine structure and high-angle annular dark-field scanning transmission electron microscopy confirms that Pt single atoms are uniformly dispersed on Co nanoparticles. *In-situ* attenuated total reflectance-surface enhanced infrared absorption spectroscopy further verifies that these Pt₁Co alloy nanoparticles facilitate the immobilization of OOH* intermediates and the release of OH* intermediates, ensuring efficient H₂O production through the four-electron pathway. As a result, the Pt₁Co-NP@NCNTs exhibit outstanding oxygen reduction reaction activity with a high half-wave potential of 0.90 V vs. reversible hydrogen electrode (RHE), and when integrated into Zn–air batteries, they deliver a high power density of 141 mW·cm⁻² and an ultralong lifespan exceeding 300 h at 10 mA·cm⁻², outperforming most Pt-based electrocatalysts in rechargeable Zn–air batteries.

KEYWORDS: Pt₁Co alloy nanoparticles, oxygen reduction reaction, dual-metal sites, Zn–air battery

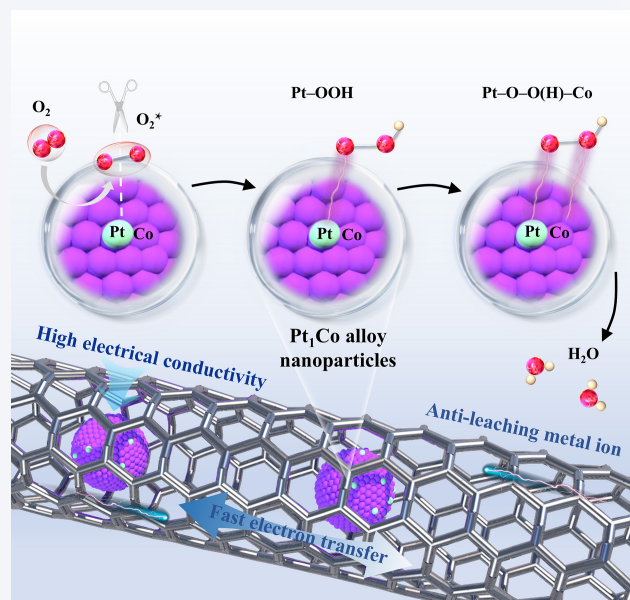
1 Introduction

Zn–air batteries (ZABs) boast an ultrahigh theoretical energy

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density of 1086 Wh·Kg⁻¹, high areal capacity, and long-lifespan performance, positioning them as ideal candidates for green energy storage [1–4]. However, the cathodic oxygen reduction reaction (ORR) in these batteries is a crucial electrochemical process involving complex multi-electron transfers. The ORR proceeds through the crucial OOH* intermediate via either a direct four-electron (4e⁻) pathway to water or a serial two-electron (2e⁻) pathway forming hydrogen peroxide as an intermediate. During the 2e⁻ process, suppression of O–O bond cleavage in OOH* leads to hydrogen peroxide accumulation. The resultant HOOH*

intermediate causes catalyst deactivation, device corrosion, and severely inhibits further reduction or dissociation to O^* and OH^* for water formation, thereby compromising energy conversion efficiency. Consequently, the $4e^-$ pathway with its higher energy conversion rate is considered favorable for Zn–air batteries. Nevertheless, this pathway faces challenges, including high overpotential and sluggish reaction kinetics, hindering practical implementation [5–7]. Platinum-based materials demonstrate significantly improved ORR activity and represent promising catalysts, but their exorbitant cost impedes widespread adoption [8, 9]. The Pt single-atom strategy aims to enhance atom utilization and intrinsic activity by minimizing Pt nanostructure size. However, studies indicate Pt single-atom catalysts (SACs) exhibit weak adsorption of the crucial OOH^* intermediate, favoring HOOH^* formation and subsequent H_2O_2 production [10–12]. Research has shown that alloying Pt with 3d transition metals (M) like PtNi or PtFe can alter local charge distribution, enhancing adsorption strength for OOH^* intermediates [13]. Unfortunately, leaching of these transition metals during prolonged ORR operation leads to phase segregation and Pt clustering, degrading catalytic activity and shortening catalyst lifespan. Accordingly, the rational development of Pt single-atom-based alloy electrocatalysts is essential to promote efficient $4e^-$ ORR energy conversion and advance the practical application of Zn–air batteries in green energy storage.

Herein, atomically dispersed Pt SACs anchored to transition metals on carbon-based supports are designed to stabilize the crucial OOH^* intermediates using dual metal sites formed through Pt–M interactions, aiming to enhance the efficiency of the desired $4e^-$ ORR pathway (Scheme 1). Among Pt–M bimetallic alloys, Pt–Co alloys may exhibit exceptional ORR activity and stability, thanks to their position at the summit of the catalytic activity volcano plot as a function of d-band center. Recognizing the instability of isolated Pt SACs, which leads to weak adsorption of OOH^* , favoring H_2O_2 formation, alloying Pt SACs with Co may facilitate electron transfer from Co d orbitals to Pt d orbitals. This can alter the electronic structure of Pt, effectively immobilizing the otherwise weakly adsorbed OOH^* intermediates. Furthermore, the empty d_{z^2} orbitals of Co within the Pt–Co dual-metal sites can acquire electrons from OOH^* to establish a stabilizing d– π bond (Pt–O–O(H)–Co), further securing the OOH^* intermediate [14]. This Pt–O–O(H)–Co structure accelerates cleavage of the O–O bond, facilitating dissociation of OOH^* and enabling its participation in the subsequent $4e^-$ pathway, thereby avoiding the problematic $2e^-$ pathway observed with weakly adsorbing Pt SACs that forms HOOH^* . Additionally, encapsulation within N-doped carbon nanotubes (NCNTs) can prevent direct contact between the reaction medium and the metal active sites, effectively inhibiting metal leaching while simultaneously accelerating electron transport and enhancing overall electrical conductivity [15, 16]. Accordingly, the rational design of Pt_iCo alloys encapsulated within NCNTs is pursued to elucidate the critical role of Pt–Co dual sites in stabilizing key intermediate species through controlled alteration of local charge distribution and electronic structures.

Inspired by the preceding analysis, we first designed and synthesized Pt_iCo alloy nanoparticles encapsulated within NCNTs (Pt_iCo-NP@NCNTs), where X-ray photoelectron spectroscopy (XPS) confirmed electron transfer from Co to Pt, while synchrotron-radiation X-ray absorption fine structure (XAFS) analysis verified

the formation of the Pt_iCo alloy; furthermore, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) directly visualized atomically dispersed Pt single atoms on the Co nanoparticles. *In-situ* attenuated total reflectance-surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) further verified that the Pt–Co dual sites facilitated the stabilization of OOH^* intermediates and the dissociation of OH^* , a phenomenon attributed to the formation of a highly active Pt–O–O(H)–Co structure, which significantly enhanced the efficiency of the $4e^-$ ORR. Consequently, the Pt_iCo-NP@NCNTs catalyst exhibited exceptional ORR performance with a half-wave potential ($E_{1/2}$) of 0.90 V vs. reversible hydrogen electrode (RHE). Moreover, rechargeable Zn–air batteries employing Pt_iCo-NP@NCNTs delivered a high specific capacity of 785.8 mAh·g_{Zn}^{−1}, a power density of 141 mW·cm^{−2}, and superior stability enduring 300 h at 10 mA·cm^{−2}, surpassing the performance of commercial Pt/C-based ZABs. In summary, this study deciphers the interplay of atomic configuration and tailored electronic properties driving a unique ORR mechanism, establishing fundamental principles for next-generation electrocatalysts and air electrodes in sustainable energy devices

2 Experimental

2.1 Synthesis of CoZn-zeolitic imidazolate framework (ZIF) nanosheets

Typically, 2 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were simultaneously dissolved in 50 mL deionized (DI) water under ultrasound and then stirring, and the solution was denoted as Solution A. 20 mmol of 2-methylimidazole (2-MIM) was dissolved in another 50 mL DI water, and the solution was denoted as Solution B. Then, Solution A was rapidly injected into Solution B. After vigorous stirring for 3 h at room temperature, the mixture was aged for 24 h to enable the formation of CoZn-ZIF nanosheets. The samples were then washed several times with water and ethanol, separately, and dried in a vacuum at 60 °C overnight.

2.2 Synthesis of Pt_iCo-NP@NCNTs and Co-NP@NCNTs

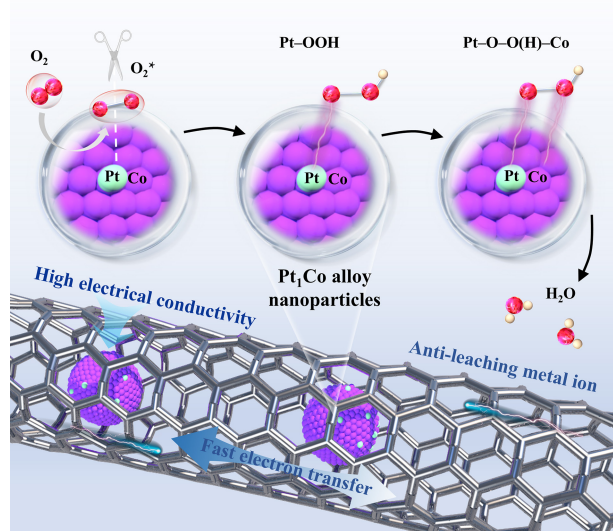
200 mg CoZn-ZIF nanosheets and 10 μmol $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mL ethanol, and the mixture was continuously stirred for 3 h. Afterward, 7 mL of 0.5 M $\text{C}_6\text{H}_8\text{O}_6$ and 0.4 mL of 0.4 M KOH solution were mixed and added dropwise into the aforementioned reaction solution, and then the solution was kept at 60 °C for 10 h under reflux conditions. The resulting Pt/CoZn-ZIF catalyst was washed with DI water, and the final product was dried at 65 °C for 24 h. As-prepared Pt/CoZn-ZIF was dispersed into a dicyandiamide (DCDA) aqueous solution, followed by stirring for 3 h. Then, freeze-drying was performed for 24 h at a temperature of −50 °C under a vacuum of 20 Pa. The synthesized Pt/CoZn-ZIF/dicyandiamide mixtures were placed in a ceramic tube and annealed at 700 °C for 2 h under a flowing N_2 atmosphere with a heating ramp rate of 5 °C·min^{−1}.

After the pyrolysis process, the Pt/CoZn-ZIF was turned into NCNT-supported Pt_iCo alloy nanoparticles with a Pt–Co dual site, marked as Pt_iCo-NP@NCNTs. Co-NP@NCNTs were synthesized via the same procedure as the Pt_iCo-NP@NCNTs, except for the addition of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$.

3 Results and discussion

3.1 Synthesis and characterizations

Herein, we synthesized Pt₁Co alloy nanoparticles encapsulated in NCNTs, designated as Pt₁Co-NP@NCNTs, using a chemical reflux reduction followed by thermal treatment as detailed in Scheme S1 in the Electronic Supplementary Material (ESM). Scanning electron microscopy (SEM) images in Figs. S1(a) and S1(b) in the ESM alongside TEM images in Fig. 1(a) and Fig. S1(c) in the ESM reveal bamboo-shaped NCNTs averaging 50 to 200 nm in diameter, which fully encapsulate Co nanoparticles measuring 10 to 20 nm. Elemental mapping results from Figs. S1(d) and S2 in the ESM confirmed the presence of Pt, Co, C, N, and O; inductively coupled plasma optical emission spectrometry (ICP-OES) quantified the Pt loading at 0.23 wt.%, shown in Table S1 in the ESM. Aberration-corrected (AC)-HAADF-STEM imaging in Fig. 1(b) identifies a 0.21 nm interplanar spacing corresponding to Co (111) lattice planes. Figure 1(c) displays isolated brighter spots within yellow circles, illustrating atomically dispersed Pt atoms on individual Co NPs. X-ray diffraction (XRD) patterns in Fig. S4 in the ESM show peaks matching metallic Co according to JCPDS card No. 15-0806, with a peak at 26.4° assignable to the carbon (002) plane, while the absence of Pt-related peaks confirmed high Pt dispersion [17]. XPS survey spectra for Pt₁Co-NP@NCNTs appeared in Figs. S5(a) and S5(b) in the ESM. High-resolution Pt 4f XPS spectra in Fig. S5(c) in the ESM present peaks at 71.3 eV for Pt 4f_{7/2} and 74.8 eV for Pt 4f_{5/2}, signifying metallic Pt⁰ as supported by Refs. [18, 19]. Co 2p XPS spectra in Fig. S5(d) in the ESM reveal the dominant Co⁰ at 778.2 eV as well as Co²⁺ at 780.7 and 794.3 eV, and Co³⁺ at 785.4 eV [20, 21]. The presence of oxidized states Co²⁺ and Co³⁺ confirmed metal–N bonding within Pt₁Co-NP@NCNTs. Notably, depth-



Scheme 1 This scheme illustrates the ORR mechanism on Pt₁Co alloy nanoparticles encapsulated within NCNTs. Alloying Pt single atoms with Co induces electron transfer from Co to Pt d orbitals, facilitating O₂ adsorption and activation. Simultaneously, the empty d_{z²} orbitals of Co within the Pt–Co dual-metal sites acquire electrons from the OOH* intermediate to form a stabilizing Pt–O–O(H)–Co structure, thereby driving the efficient 4e[−] pathway. Critically, the NCNT encapsulation prevents metal ion leaching while enhancing electrical conductivity and facilitating rapid interfacial electron transfer, ultimately promoting the overall catalytic performance.

dependent XPS analysis (Table S2 in the ESM) revealed a significant decrease in the Pt/Co atomic ratio after 40 s of Ar ion sputtering compared to the surface composition, indicating that Pt is enriched on the surface of the Co nanoparticles. Furthermore, the Co 2p peak in Pt₁Co-NP@NCNTs exhibited a positive binding energy shift compared to Co-NP@NCNTs, synthesized for comparison via a similar method without Pt atoms and characterized in Figs. S3–S9 in the ESM. This shift indicated electronic interaction between Pt single atoms and Co nanoparticles [22]. Charge balance within the Pt₁Co alloy facilitated electron transfer from Co to Pt, resulting in negatively charged isolated Pt atoms denoted Pt^{δ−}.

To investigate the local chemical environment of Pt within the Co nanoparticles, synchrotron-radiation X-ray absorption near-edge structure (XANES) and extended XAFS (EXAFS) measurements were conducted. Pt L₃-edge XANES spectra in Fig. 1(d) and Fig. S6 in the ESM reveal a slightly lower white line (WL) intensity for Pt₁Co-NP@NCNTs compared to Pt foil, signaling modifications in the electronic structure. Furthermore, k²-weighted Pt L₃-edge EXAFS spectra in Fig. 1(e) display a prominent peak at 2.10 Å attributed specifically to Pt–Co contribution rather than Pt–Pt or Pt–O contributions, confirming atomically dispersed Pt single atoms on the Co nanoparticles [8]. Supporting this, Co K-edge XANES spectra in Fig. S7(a) in the ESM show decreased peak intensity for Pt₁Co-NP@NCNTs relative to Co-NP@NCNTs, consistent with charge transfer from Co to Pt and indicative of Pt₁Co alloy nanoparticle formation as visualized in Fig. S8 in the ESM [23]. Co K-edge EXAFS spectra in Fig. S7(b) in the ESM further corroborate alloy formation, revealing a slight shift of the Co–Co bond peak toward a shorter radial distance due to hybridization between the Co nanoparticles and Pt 5d orbitals, which altered electron density and the Pt coordination environment [24]. Wavelet transform (WT) contour plots in Fig. 1(f) and quantitative analysis in Table S3 in the ESM identify the Pt species within Pt₁Co-NP@NCNTs, showing an intensity maximum near 8 Å^{−1} corresponding to Pt–Co coordination. Crucially, these plots detected no Pt–Pt or Pt–O signals observed in Pt foil or PtO₂ references, unequivocally demonstrating exclusive Co coordination of isolated Pt atoms. Collectively, these analyses indicate that partial charge transfer from Co 3d to Pt 5d orbitals drives Pt–Co coordination, resulting in the formation of Pt₁Co alloy nanoparticles.

3.2 Electrocatalytic performance

To evaluate the electrochemical ORR performance of Pt₁Co-NP@NCNTs, measurements were conducted in oxygen-saturated 0.1 M KOH using a three-electrode system. Koutecky–Levich (K–L) plots yielded an electron transfer number (n) of approximately 4, confirming a dominant four-electron ORR pathway as shown in Fig. S9 in the ESM [25]. This mechanism was further corroborated by rotating ring disk electrode (RRDE) tests (Fig. S10 in the ESM). From 0.3 to 0.7 V vs. RHE, the electron transfer number of Pt₁Co-NP@NCNTs was in the range of 3.89–3.97, and the corresponding H₂O₂ production ratio remained below 5.8%, further evidencing a direct four-electron reduction pathway. Cyclic voltammograms (CVs) in Fig. S12 in the ESM revealed distinct oxygen reduction peaks for Pt₁Co-NP@NCNTs in O₂-saturated electrolyte, demonstrating intrinsic catalytic activity. Notably, its cathodic peak potential was more positive than that of Co-NP@NCNTs, indicating that alloying Co nanoparticles with Pt single atoms significantly enhanced the ORR activity [26]. Linear

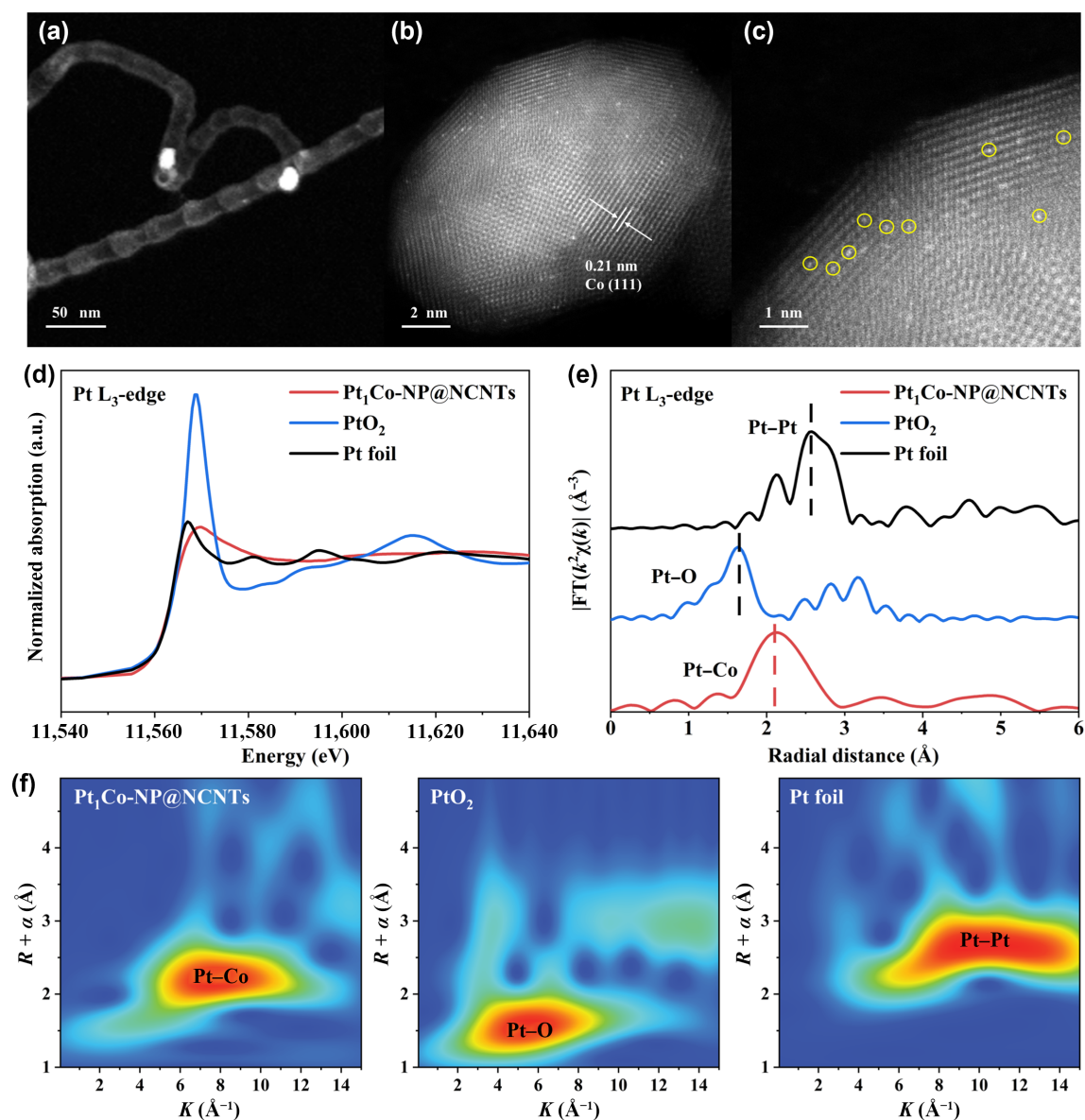


Figure 1 (a) TEM image of the Pt₁Co-NP@NCNTs. ((b) and (c)) AC-HAADF-STEM images of the Pt₁Co-NP@NCNTs, where the brighter spots in the yellow circle represent the isolated Pt atoms. (d) Pt L₃-edge XANES and (e) EXAFS spectra of the Pt₁Co-NP@NCNTs, the PtO₂, and the Pt foil. (f) The wavelet transform of EXAFS spectra at the Pt L₃-edge of the Pt₁Co-NP@NCNTs, the PtO₂, and the Pt foil.

sweep voltammetry (LSV) curves in Fig. 2(a) further show that Pt₁Co-NP@NCNTs achieved an $E_{1/2}$ of 0.90 V vs. RHE and a limiting current density of 5.77 mA·cm⁻². This $E_{1/2}$ value surpassed Co-NP@NCNTs and commercial 20 wt.% Pt/C by 20 and 30 mV, respectively, while outperforming most reported catalysts under comparable conditions as benchmarked in Fig. 2(c) and Table S4 in the ESM [27–32]. Kinetic analysis via Tafel slopes in Fig. 2(b) yields a value of 67.21 mV·dec⁻¹ for Pt₁Co-NP@NCNTs, lower than both reference catalysts, indicating faster electron transfer kinetics. To further investigate the charge transfer kinetics, electrochemical impedance spectroscopy (EIS) measurement was performed. As shown in Fig. S11 in the ESM, the Pt₁Co-NP@NCNTs exhibited a significantly smaller charge transfer resistance (R_{ct}) compared to Co-NP@NCNTs, confirming significantly accelerated electron transfer kinetics. Additionally, Pt₁Co-NP@NCNTs delivered a kinetic current density (j_k) of 10.8 mA·cm⁻² at 0.85 V vs. RHE (Fig. 2(d)), exceeding values for Co-NP@NCNTs and Pt/C. The catalyst also

demonstrated exceptional stability, retaining 91% of its initial current density after 50,000 s of continuous operation (Fig. 2(e)), significantly outperforming both counterparts. Meanwhile, the accelerated durability test (ADT) of the Pt₁Co-NP@NCNTs was further performed, where only an insignificant $E_{1/2}$ drop was observed after 5000 cycles, indicating their high durability (Fig. S13 in the ESM). These results collectively established that Pt single atoms on Co nanoparticles substantially enhanced ORR activity through a four-electron transfer mechanism while improving durability.

3.3 Mechanism investigations

To characterize the intrinsic catalytic activity of Pt₁Co-NP@NCNTs, electrochemically active surface areas (ECSA) were determined via electrochemical double-layer capacitance (C_{dl}) measurements using Eqs. (S10) and (S11) in the ESM. Notably, Pt₁Co-NP@NCNTs exhibited higher capacitance than Co-NP@NCNTs as shown in Fig.

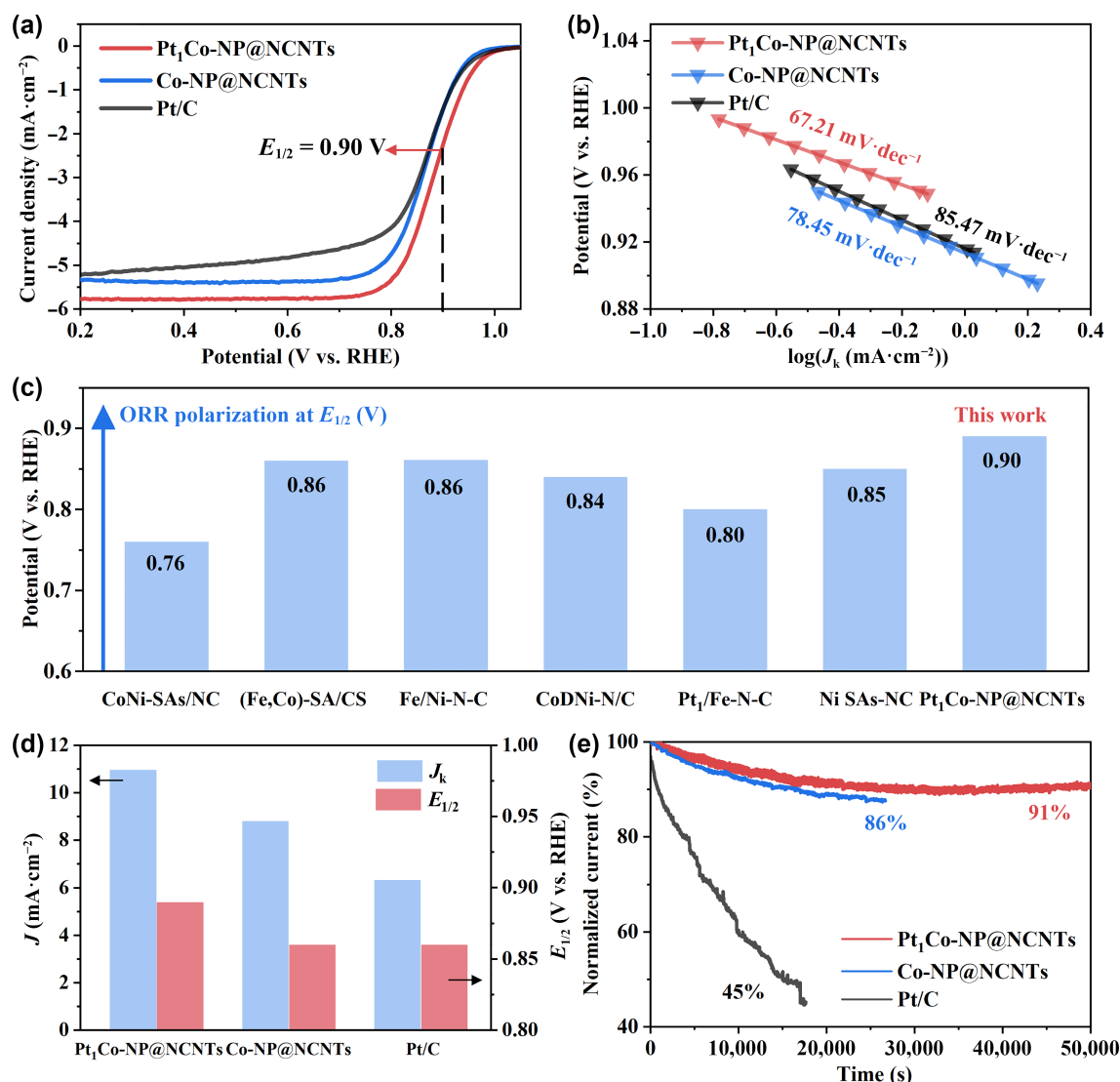


Figure 2 (a) LSV polarization curves for ORR of the Pt₁Co-NP@NCNTs, the Co-NP@NCNTs, and the Pt/C at a rotating speed of 1600 rpm in 0.1 M KOH, and (b) corresponding Tafel plots of ORR derived from the LSV curves. (c) Comparison of previously reported similar catalysts with our catalyst in terms of their $E_{1/2}$. (d) Comparison of J_k at 0.85 V vs. RHE and half-wave potential for the Pt₁Co-NP@NCNTs and other reference catalysts. (e) ORR current-time chronoamperometric response of the Pt₁Co-NP@NCNTs, the Co-NP@NCNTs, and the Pt/C for ORR at 1600 rpm in 0.1 M KOH.

S14 in the ESM, indicating superior intrinsic ORR activity. To further highlight the atom-utilization efficiency of the Pt₁Co-NP@NCNTs, the mass activity (MA) and specific activity (SA) were evaluated. At 0.85 V vs. RHE, the Pt₁Co-NP@NCNTs delivered an ultrahigh MA that markedly exceeded that of commercial Pt/C. Moreover, its competitive SA highlighted the superior intrinsic activity of the isolated Pt sites. Further mechanistic insight was gained through time-dependent *in-situ* ATR-SEIRAS spectra recorded at constant potential in Fig. 3. Analysis of spectra acquired at varying electrolysis times revealed structural and electronic changes during catalysis. Figures 3(a)–3(d) demonstrate that both catalysts exhibited downward shifts in O–O stretching frequencies for adsorbed O₂^{*} species due to O–O bond cleavage (Step I, Fig. 3(f)) [33], with Pt₁Co-NP@NCNTs showing significantly lower frequencies than Co-NP@NCNTs. This shift indicated enhanced O₂^{*} adsorption at Pt–Co dual-sites, facilitating electron transfer from Pt 5d_{z²} orbitals to unfilled O 2p orbitals and accelerating O–O cleavage as illustrated in Fig. 3(e) [34, 35]. Critically, while OOH^{*} adsorption intensity strengthened progressively over time on Pt₁Co-

NP@NCNTs, no significant OOH^{*} signal appeared on Co-NP@NCNTs. This contrast highlighted Pt's role as a collaborative catalytic site where strong Pt–OOH bonding enabled rapid OOH^{*} intermediate adsorption (Step II) [36]. During Pt–OOH formation, electron transfer occurred from Co 3d_{z²} to Pt 5d_{z²}, orienting the O–O bond parallel to the Pt–Co axis (Step III). This alignment promoted π -orbital overlap between Co and OH^{*}, generating a highly active Pt–O–O(H)–Co transition structure [37–40]. In contrast, Co-NP@NCNTs showed progressive HOOH^{*} signal intensification in Figs. 3(b) and 3(d), reflecting sluggish OOH^{*} desorption kinetics that favored two-electron pathway HOOH^{*} intermediates [41]. Summarized in the proposed ORR pathway in Fig. 3(f), the proposed ORR process was as follows



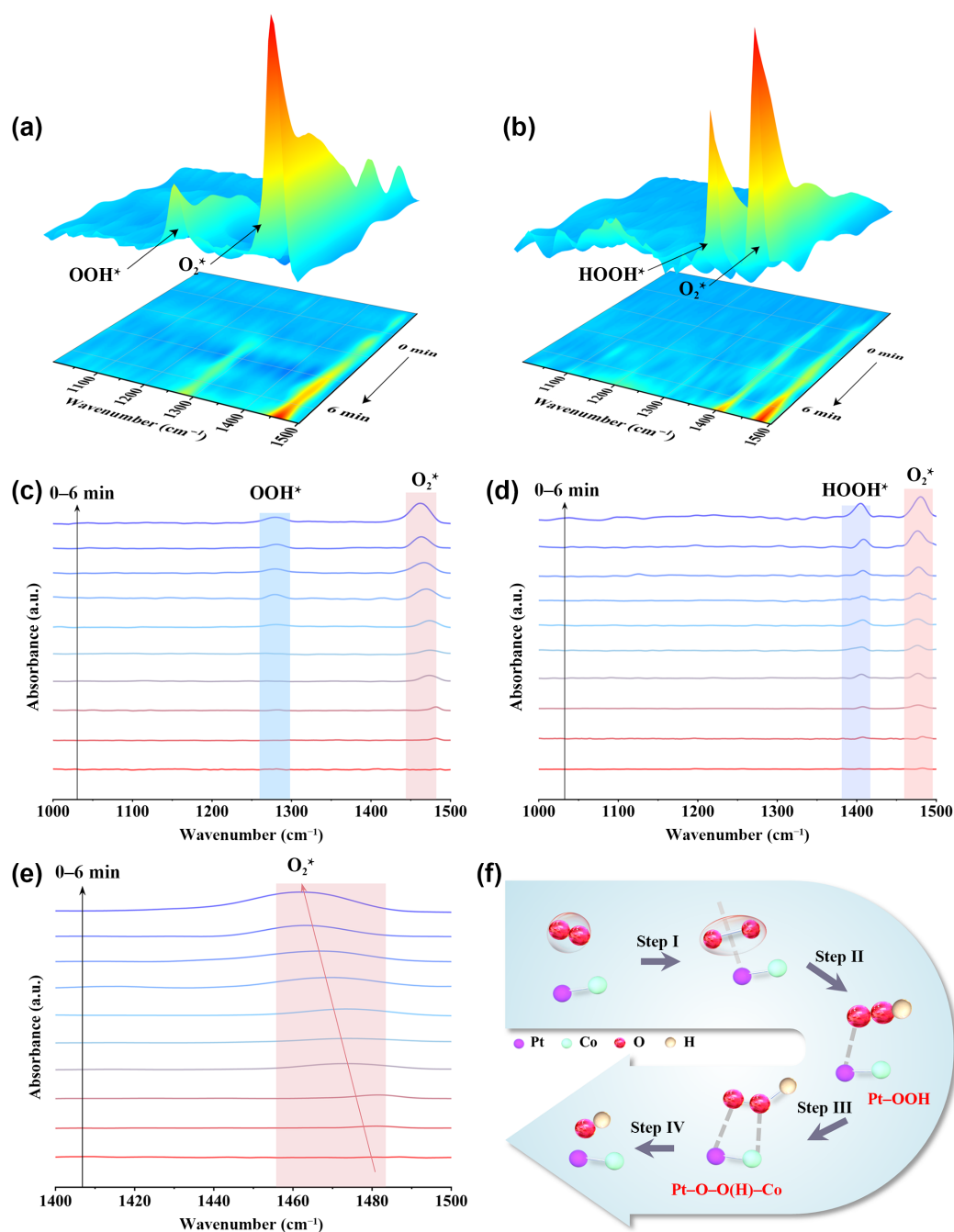
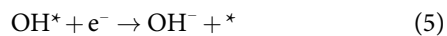
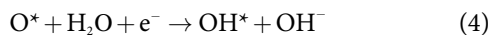


Figure 3 Three-dimensional time-resolved *in-situ* ATR-SEIRAS spectra of (a) the Pt₁Co-NP@NCNTs and (b) the Co-NP@NCNTs at 0.8 V vs. RHE in O₂-saturated 0.1 M KOH. Two-dimensional time-resolved *in-situ* ATR-SEIRAS spectra of (c) the Pt₁Co-NP@NCNTs and (d) the Co-NP@NCNTs at 0.8 V vs. RHE in O₂-saturated 0.1 M KOH. (e) Enlarged view of the wavelength range 1400–1500 cm⁻¹ in (c). (f) Schematic representation of the ORR path over the Pt₁Co-NP@NCNTs.



This *in-situ* spectroscopic evidence demonstrated that Pt-Co dual-sites dynamically optimized through Pt's electronic structure efficiently adsorb O₂* and activate OOH*, thereby significantly enhancing four-electron pathway selectivity for water production (Step IV).

3.4 Performance in ZABs

To further investigate the practical applicability, a rechargeable ZAB was assembled employing synthesized Pt₁Co-NP@NCNTs as ORR sites, as shown in Fig. 4(a). The open-circuit voltage (OCV) of the Pt₁Co-NP@NCNTs-based ZAB was 1.41 V, which was higher than the OCV of 1.38 V for the Pt/C-based ZAB as seen in Fig. S15 in the ESM. Furthermore, the power density of the Pt₁Co-NP@NCNTs-based ZAB reached 141 mW·cm⁻², exceeding the 97 mW·cm⁻² of the Pt/C-based ZAB as demonstrated in Fig. 4(b). The discharge process of the Pt₁Co-NP@NCNTs-based ZAB remained stable across current densities from 1 to 30 mA·cm⁻²,

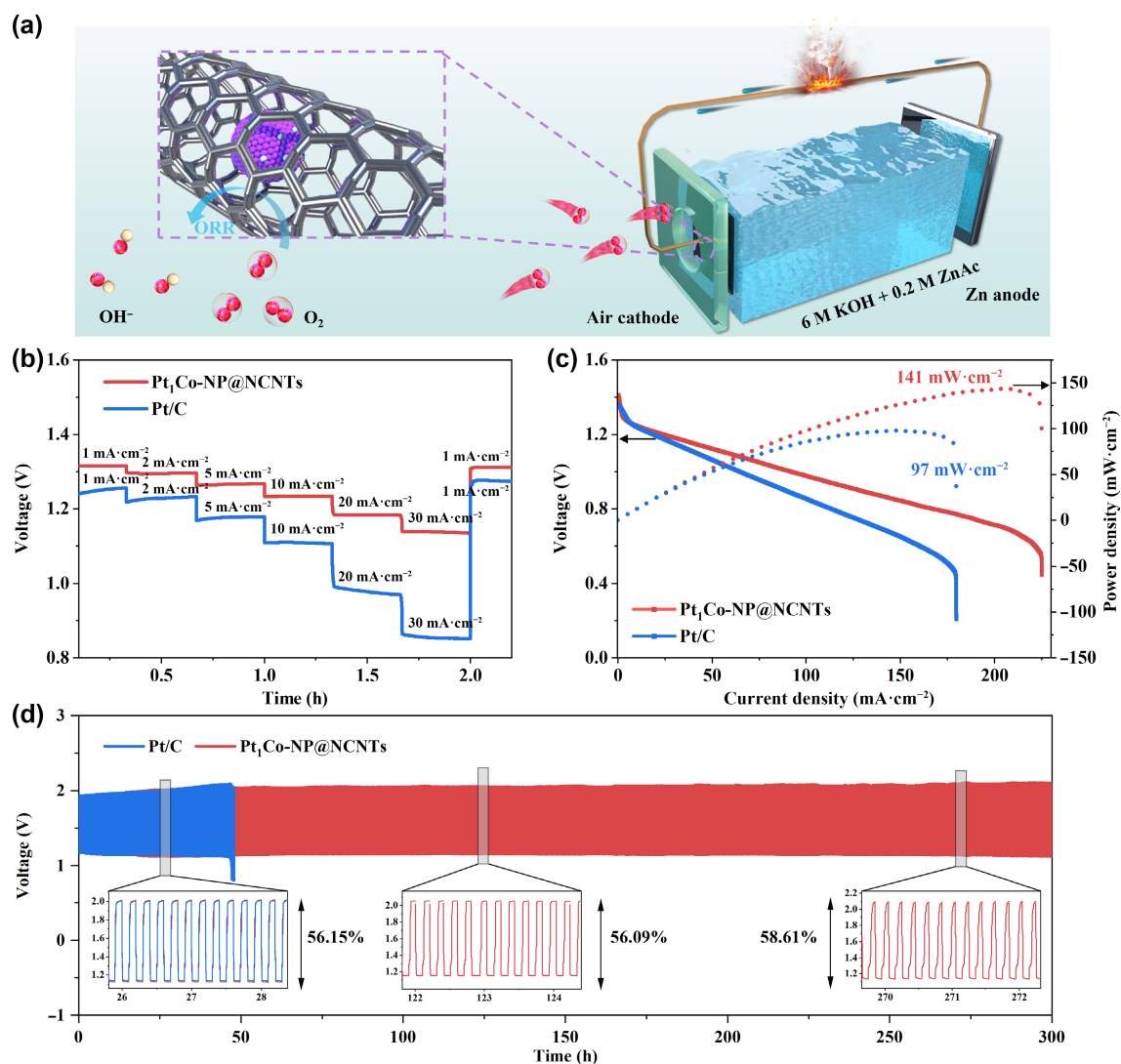


Figure 4 (a) Schematic illustration of the Zn-air battery configuration. (b) Rate performances and (c) discharge polarization curves (solid line) and the corresponding power density plots (dotted line) of the Zn-air battery. (d) Long-term discharge and charge cycling curves at $10 \text{ mA}\cdot\text{cm}^{-2}$ (inset shows the discharge and charge curves at different cycles).

consistently exhibiting a higher discharging plateau than the Pt/C-based ZAB, as illustrated in Fig. 4(c). Remarkably, after discharge at $30 \text{ mA}\cdot\text{cm}^{-2}$, the voltage remained essentially constant upon returning to $1 \text{ mA}\cdot\text{cm}^{-2}$, indicating its significant reversibility. Figure S16 in the ESM compares the galvanostatic discharge profiles of both batteries at $10 \text{ mA}\cdot\text{cm}^{-2}$, revealing that the Pt₁Co-NP@NCNTs-based ZAB achieved a specific capacity of $785.8 \text{ mAh}\cdot\text{g}_{\text{Zn}}^{-1}$ and an energy density of $981.3 \text{ Wh}\cdot\text{kg}_{\text{Zn}}^{-1}$. These values outperformed most similarly reported ZABs listed in Table S5 in the ESM and significantly exceeded the Pt/C-based ZAB's performance of $664.2 \text{ mAh}\cdot\text{g}_{\text{Zn}}^{-1}$ and $712.5 \text{ Wh}\cdot\text{kg}_{\text{Zn}}^{-1}$. The rechargeability was investigated through galvanostatic charge-discharge cycles at $10 \text{ mA}\cdot\text{cm}^{-2}$, as shown in Fig. 4(d). The round-trip efficiency initially dropped slightly from 56.15% to 56.09% before increasing to 58.61%, maintaining excellent efficiency. Crucially, the Pt₁Co-NP@NCNTs-based ZAB demonstrated stable operation for over 300 h, significantly surpassing the 49 h test period of the Pt/C-based ZAB. To confirm structural stability after 300 h of cycling, the spent catalyst was characterized (Figs. S17 and S18 in the ESM). HAADF-STEM and high-resolution TEM (HRTEM) images showed that

the Pt single atoms remained isolated, with no detectable aggregation, and the NCNT-supported Co nanoparticles retained their morphology. XPS and energy dispersive X-ray spectroscopy (EDS) mapping images further confirmed negligible Co loss and no degradation of the NCNT framework. These results demonstrated the excellent structural robustness of the Pt₁Co-NP@NCNTs, which contributes to prolonged zinc-air battery lifetime.

4 Conclusions

In summary, we first designed an alloying strategy between Pt single atoms and transition metals to precisely construct a Pt-M alloy atomic configuration, aiming to stabilize OOH* intermediates and enhance the efficiency of the $4e^-$ ORR pathway. Using Pt₁Co-NP@NCNTs as an example, AC-HAADF-STEM images of Pt₁Co-NP@NCNTs unambiguously confirmed isolated Pt atoms on Co nanoparticles, while synchrotron-radiation XAFS spectra revealed Pt₁Co alloy formation with distinct Pt-Co coordination. Critically, XPS spectra further affirmed charge transfer from Co to Pt via d-orbital hybridization. *In-situ* ATR-SEIRAS experimentally verified

that the Pt–Co dual-site facilitates accelerated O_2^* adsorption and stabilization of OOH^* , thereby destabilizing the O–O bond to release OH^* . Leveraging these advantages, the Pt₁Co-NP@NCNTs enabled efficient O_2 reduction, exhibiting an $E_{1/2}$ of 0.90 V vs. RHE and a limiting current density of 5.77 mA·cm⁻², along with a J_k of 10.8 mA·cm⁻² at 0.85 V vs. RHE. Consequently, a full-cell test in Zn–air batteries using Pt₁Co-NP@NCNTs as the cathode catalyst delivered a power density of 141 mW·cm⁻² and demonstrated good durability over 300 h at 10 mA·cm⁻². Collectively, this work establishes the pivotal influence of precisely engineered Pt–Co atomic configurations in optimizing the ORR mechanism at a fundamental level, offering transformative insights for advancing next-generation renewable energy technologies.

Electronic Supplementary Material: Supplementary material (details of other catalyst preparation processes, catalyst stability tests, catalyst characterization, and catalytic activity tests of different catalytic materials) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908833>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

J. C. L.: Methodology, investigation, formal analysis, writing – original draft. L. W. Y.: Methodology, writing – review & editing. P. Z. Q.: Software. M. Y. Z.: Software. Q. Z. Q.: Software. Z. G. H.: Software, writing – review & editing. Y. F. S.: Conceptualization, writing – review & editing. Y. X.: Writing – review & editing. All the authors have approved the final manuscript.

Use of AI statement

None.

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