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Tin-mediated carbon-confined Pt₃Co ordered intermetallic nanoparticles as highly efficient and durable oxygen reduction electrocatalysts for rechargeable zinc-air batteries

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ABSTRACT

The development of electrocatalysts for the oxygen reduction reaction (ORR) that bears high selectivity, exceptional activity, and long-term stability is crucial for advancing various green energy technologies. Intermetallics composed of platinum and transition metals are considered to be promising candidates for this purpose. However, they typically face challenges such as unfavorable intrinsic activity and a propensity for particle aggregation, diminishing their ORR performance. Against this backdrop, we present our findings on a N-doped carbon confined Pt₃Co intermetallic doped with *p*-block metal tin (Pt₃Co_xSn_{1-x}/NC). The introduction of Sn induces lattice strain due to its larger atomic size, which leads to the distortion of the Pt₃Co lattice structure, while the coupling of carbon polyhedra inhibits the particle aggregation. The optimized Pt₃Co_{0.8}Sn_{0.2}/NC catalyst demonstrates an impressive half-wave potential of 0.86 V versus RHE, surpassing both Pt₃Co/NC and Pt₃Sn/NC catalysts. Moreover, the Pt₃Co_{0.8}Sn_{0.2}/NC exhibits a mass-specific activity as high as 1.4 A mg_{Pt}⁻¹, ranking it in the top level among the intermetallics-based ORR electrocatalysts. When further employed as a cathode material in a self-assembled zinc-air battery, it shows stable operation for over 80 h. These results underscore the significant impact of lattice strain engineering through the strategic doping of *p*-block metal in the carbon-confined Pt₃Co intermetallic, thereby enhancing the catalytic efficiency for the ORR.

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1. Introduction

An electrochemical energy conversion system emerges as a promising contender to supplant the dominance of fossil fuel-based energy systems. Within this framework, the oxygen reduction reaction (ORR) plays an indispensable role in generating electrochemical energy, serving as the cathodic reaction in metal-air batteries and proton-exchange membrane fuel cells [1–3]. In pursuit of meeting practical application requirements, diverse initiatives have been pursued, including compositional modulation [4,5], structural engineering [6,7], and morphological design [8,9],

all of which aimed at enhancing performance metrics. At present, Pt-based catalysts are regarded as prime candidates for the electrochemical ORR due to their unparalleled activity. However, their scarcity and exorbitant cost pose limitations on widespread commercial deployment. Consequently, strategic methodologies have been devised to simultaneously reduce the reliance on Pt loading and maximize the efficiency of Pt utilization, charting a course towards a sustainable electrochemical energy conversion system [10–12].

Currently, the combination of Pt with first-row transition metals (M) is widely recognized as an effective approach to reducing the amount of Pt used. In this regard, Stamenkovic et al. claimed that Pt-M alloy exhibits improved activity over pure Pt polycrystalline surfaces [13]. Consequently, various Pt-M catalysts have been developed to enhance the electrocatalytic ORR activity. Among these, Fe [14,15], Co [16,17], and Ni [18,19] have been

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extensively studied for their superior catalytic activities. However, the stability of these binary systems remains a challenge due to the potential for dissolution of the transition metals [20]. Recent investigations suggest that introducing a third metal to form ternary Pt-based alloys can decrease the surface energy and stabilize the system [21,22]. For instance, Jia et al. synthesized Mo-doped PtNi nanoparticles (NPs) for enhanced stability for ORR with a negligible activity decay after 15,000 cyclic voltammetry (CV) cycles [21]. Following this observation, Li et al. discovered that the Co-doped PtNi alloy demonstrated superior stability compared to the undoped PtNi alloy; that is, after potential cycling from 0.6 to 1.0 V for 5000 cycles, the PtNi_{0.8}Co_{0.2} catalyst displayed an almost unchanged polarization curve [22]. Despite significant advancements, the majority of prior research primarily concentrated on the investigation of transition metal-doped Pt-M alloy catalysts, and there remains a compelling interest in exploring alternative non-transition metal-doped Pt-M alloys for application as ORR electrocatalysts.

On the other hand, the electrocatalytic activity is intimately correlated with the structure and electronic configuration of the catalysts. Three primary structural elements significantly influence electrocatalytic performance: the ensemble, ligand, and strain effects [23]. The strain effect, in particular, garners special attention as it can modulate the atomic arrangement of the material, thereby adjusting the Pt–Pt bond distance, which represents a critical determinant of ORR activity. Various strategies, such as gaseous hydrogen treatment, fabrication of core-shell structures, and heteroatom doping, have been employed to induce the desired strain in intermetallic-based electrocatalysts [24–27]. Among these, introducing a third element into the alloy lattice is a straightforward and controllable method for inducing lattice strain. This strategy allows fine-tuning of the coordination sphere around the Pt atom, which in turn modifies the electronic configuration at the Pt site. For example, Wang et al. reported the doping of Cu into Pt lattice, which causes the compressive lattice strain [28]. Owing to the lattice strain, the optimized Pt–Cu alloy delivered a mass-specific activity of 4.4 times (0.48 A mg_{Pt}^{−1}) of Pt/C (0.11 A mg^{−1}). Tsiakaras et al. reported a series of ternary PtFeM (M = Mo, V, and W) nanoalloy electrocatalysts with different levels of strain on Pt species, in which the optimized Pt₂₅Fe₇₀Mo₅ showed a mass-specific activity of 2.770 A mg_{Pt}^{−1} [29]. Compared to the commonly mentioned *d*-block transition metals (Fe, Co, Ni, Cu, and Cr), *p*-block metals such as Sn, In, and Bi bear the larger atomic size and unique physiochemical properties, so it is expected to generate an apparent lattice strain by adjusting the atomic size of the heteroatom and the concentration of doping. However, the relevant investigation is rarely reported. Furthermore, although nanosizing the Pt–M alloys is beneficial for the exposure of active sites and mass transfer, the nanosized Pt–M alloy nanoparticles are prone to aggregate during synthesis and prolonged operation, thus causing an activity degradation [14,30–32]. Therefore, it is imperative to build a unique structure to homogeneously confine the Pt–M alloy nanoparticles to address the above dilemma [33,34].

Tin (Sn), a *p*-block element with a closed-shell *d*-orbital, is generally less active than transition metals with partially filled *d*-orbitals. However, recent studies have shown that Sn can be activated by altering its coordination environment, enabling it to function as a single-atom catalyst [35,36]. Additionally, alloying *d*-block elements with Sn to form M_xSn_y alloys or intermetallic compounds has been proven effective for ORR [37–39]. Sn doping can also lower the phase transition temperature of alloys, facilitating the formation of highly ordered single-phase intermetallics at lower temperatures and preventing particle sintering, which preserves the high active surface area [40–42]. Furthermore, Sn has a larger atomic radius than Fe, Co, and Ni, thus allowing the adjustment of lattice parameters in these Pt₃M and creating tailorable

lattice strain. Meanwhile, Sn can couple with the *d*-orbitals of transition metals (M), enabling *p*–*d* hybridization between Sn, M, and Pt, which lowers the *d*-band center and reduces the adsorption energy of oxygenated intermediates on the catalyst surface, thus leading to the improvement of ORR activity [43–45].

Motivated by the above concerns, herein, we report a metal-organic framework (MOF)-driven strategy to build an N-doped carbon-confined Sn-doped Pt₃Co nanoparticles (Pt₃Co_xSn_{1−x}/NC), which were derived from zinc zeolitic imidazole frameworks (ZIF-8) for electrochemical ORR. The ZIF precursors were synthesized via the coordination method by mixing Zn(NO₃)₂·6H₂O and 2-methyl-1H-imidazole in an aqueous solution. The as-obtained precursors were treated with pyrolysis, and the N-doped carbon polyhedra supporter was obtained. Afterwards, the metals were introduced to the supporter via the impregnation method. The doping percentage of Sn was optimized subsequently. The as-obtained catalysts were utilized in electrocatalytic ORR under alkaline conditions. The Pt₃Co_{0.8}Sn_{0.2}/NC demonstrated the highest half-wave potential, which reached 0.86 V versus reversible hydrogen electrode (RHE), together with an impressive mass-specific activity as high as 1.4 mA mg_{Pt}^{−1}. Moreover, Pt₃Co_{0.8}Sn_{0.2}/NC has excellent stability and can operate for more than 24 h under alkaline conditions for ORR and more than 80 h under charge-discharge conditions for the zinc-air battery (ZAB) with neglectable decrease.

2. Experimental

2.1. Synthesis of N-doped porous carbon (NC)

Zn(NO₃)₂·6H₂O (960 mg) and 2-methylimidazole (2.34 g) were dissolved in 25 mL MeOH separately. Solutions were mixed and stirred at room temperature. After the reaction, the as-obtained white powder was isolated via centrifugation, washed with MeOH repeatedly, and dried in an oven at 60 °C for 24 h. The as-obtained dry product was calcinated under argon protection at 960 °C for 4 h. After thermal treatment, the product was washed with 0.5 M H₂SO₄ to remove any Zn residues and pure NC material was obtained as a white powder.

2.2. Synthesis of Pt₃Co_xSn_{1−x}/NC electrocatalysts

H₂PtCl₆·6H₂O (0.256 mol), Co(NO₃)₂·6H₂O (*x* mol, with *x* < 0.85), and 0.85−*x* mol SnCl₂·2H₂O were dissolved in 500 μL deionized water as precursor solution. 40 mg NC was added into 200 μL precursor solution and suspended in ultrasonic for 1 h. Afterwards, the suspension was freeze-dried and the as-obtained material was placed in a tube furnace with flowing nitrogen for a calcination of 2 h at 750 °C. The product was collected as a black powder.

2.3. Preparation of Pt₃Co_xSn_{1−x}/NC electrode

The catalyst ink was prepared by mixing 5 mg of Pt₃Co_xSn_{1−x}/NC with a mix solution of 970 μL EtOH and 30 μL Nafion, followed by sonication for 30 min. Subsequently, 12 μL of the prepared ink was applied onto a ring disk glassy carbon electrode, dried, and utilized for the electrochemical tests.

2.4. Physical characterization

Phase analysis of the samples was conducted using powder X-ray diffraction (PXRD) on a Bruker D8 ADVANCE X-ray diffractometer with Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). The lattice parameters and phase components were refined by the program RIETAN-2000 based on the Rietveld method [33]. The morphology and structure of the samples were examined via field-emission scanning electron

microscopy (FESEM) using an SU800 electron microscope from Hitachi, Tokyo, Japan, operated at an acceleration voltage of 20 kV. For more detailed microstructural, phase, and compositional analysis, transmission electron microscopy (TEM) was performed using an FEI Talos F200X instrument. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250Xi spectrometer from Thermo Scientific, USA, equipped with a pass energy of 30 eV and a power of 100 W (10 kV and 10 mA), using a monochromatized α X-ray source ($h\nu = 1486.65$ eV). Spectra were acquired using advantage software with a resolution of 0.05 eV.

2.5. Electrochemical measurements

The electrochemical measurements were performed on a potentiostat (BioLogic) controlled by BioLogic EC-Lab software. During the oxygen reduction test, a graphite rod served as the counter electrode, a saturated calomel electrode was used as the reference electrode, and 0.1 M KOH was employed as the electrolyte. Linear sweep voltammetry (LSV) tests were conducted in the voltage range of -1.0 to 0.1 V at a scanning rate of 5 mV s^{-1} . The current-time (I - t) curves were recorded at the potential corresponding to the limiting diffusion current.

The CV for hydrogen underpotential deposition (HUPD) was conducted in an H_2 -saturated 0.1 M HClO_4 electrolyte with a potential scan rate of 50 mV s^{-1} with a saturated calomel electrode as a reference electrode. The mass activity was calculated via Eq. (1).

$$\text{MA} = \frac{r_f \times j_k}{m} \quad (1)$$

where r_f was the surface roughness factor, j_k was the kinetic current density, and m was the mass loading of Pt. The r_f and j_k were calculated via Eqs. (2) and (3), respectively.

$$r_f = \frac{A_{\text{real}}}{A_{\text{geo}}} = \frac{Q_{\text{H}}}{0.21 \text{ mC cm}^{-2}} \quad (2)$$

Q_{H} was the integration of CV obtained from HUPD, A_{geo} was the geometric area of the electrode, and 0.21 mC cm^{-2} was an empirical value for a hydrogen monolayer.

$$j_k = \frac{j_d \times j}{j_d - j} \quad (3)$$

j_d was the limitation current density and j is the current density at selected potential, which was 0.9 V vs. RHE in this research.

2.6. Zinc-air battery test

7 mg of $\text{Pt}_3\text{Co}_x\text{Sn}_{1-x}/\text{NC}$ was taken with 1 mg of conductive carbon black in a mortar and pestled. EtOH and Nafion were added dropwise and ground until a homogenous ink was formed. The ink was uniformly coated on the carbon paper, which was washed with a mixed solution of deionized water and EtOH (water: ethanol = 1:1), ultrasonicated for $5\text{--}10 \text{ min}$, and dried in oven at 60°C , with a loading of 1 mg cm^{-2} . Zinc-air batteries were assembled by the used carbon paper loaded with $\text{Pt}_3\text{Co}_x\text{Sn}_{1-x}/\text{NC}$ as the cathode, zinc plates as anode, and a solution containing 0.2 M Zn (OAc)_2 and 6 M KOH as the electrolyte. For the charge-discharge recoverability measurements, the cathode was prepared by using equivalent $\text{Pt}_3\text{Co}_x\text{Sn}_{1-x}/\text{NC}$ (ORR) and commercial RuO_2 (i.e., oxygen evolution reaction, OER). Open circuit voltage, charge and discharge polarisation curves, and corresponding power density curves, discharge curves, and specific capacity were tested on a CHI760E electrochemical workstation. Charge-discharge recoverability measurements were recorded for a 10-minute cycle at con-

stant current densities ($10, 25, 50$, and 100 mA cm^{-2}). Long cycle tests were performed on a LANHE battery tester. The polarisation curves were tested at a scan rate of 10 mV s^{-1} . The specific capacity was calculated as follows.

$$\text{Specific capacity} = \frac{I(\text{discharge current}) \times t(\text{discharge time})}{\Delta m_{(\text{Zn})}} \quad (4)$$

2.7. Computational method

All density functional theory (DFT) calculations were performed using the Vienna Ab initio simulation package (VASP5.4) code [46] with spin polarized Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [47]. The projected augmented wave method was used to describe the core-electron interactions and the Kohn-Sham wave functions were expanded in the plane wave basis with a kinetic energy cutoff of 450 eV [48]. The Brillouin zone was sampled with a $1 \times 1 \times 1$ k -points mesh for the $2 \times 2 \times 2$ supercell, generated by the Monkhorst-Pack algorithm. The Hellmann-Feynman forces for all relaxed atoms were converged to $0.02 \text{ eV \AA}^{-1}$.

3. Results and discussion

Fig. 1 schematically illustrates the synthetic pathway adopted for preparing the catalyst. The initial step involved the synthesis of ZIF-8 precursor, which was achieved through a co-precipitation reaction involving zinc nitrate hexahydrate and 2-methylimidazole in an aqueous medium. The ZIF-8 thus obtained was subjected to a thermal treatment, where it underwent calcination at a temperature of 960°C for a duration of 3 h under a nitrogen atmosphere, during which the organic groups were liberated and in situ converted to the N-doped carbon while the Zn species were evaporated and pores were left. Therefore, this crucial step resulted in the formation of a three-dimensional (3D) porous nitrogen-doped graphene-like carbon (NC) framework, serving as a robust scaffold for subsequent stages. The thermally treated NC was then dispersed into anhydrous ethanol and sonicated to ensure a homogeneous suspension. In a subsequent step, dimethylformamide (DMF) solutions containing H_2PtCl_6 , Co^{2+} , and Sn^{2+} were introduced into the mixture, with the concentrations being carefully modulated according to the desired molar ratios. Following the introduction of these metallic precursors, the resulting powder was once again subjected to annealing under a protective nitrogen atmosphere, culminating in the production of the NC-supported $\text{Pt}_3\text{Co}_x\text{Sn}_{1-x}$ catalyst ($x = 0, 0.2, 0.5, 0.8$, and 1). This meticulously crafted synthetic route ensures the precise engineering of the catalyst, with a focus on achieving optimal structural integrity and compositional purity, essential for its performance in various catalytic applications.

To clarify the phase evolution during synthesis, Fig. S1 firstly presented the PXRD pattern of ZIF-8, from which it could be known that the pure ZIF-8 phase with high crystallinity was successfully obtained. With further calcination, the diffraction peak belonging to carbon positioned at around 26° could be identified and no any other diffraction peaks for precursors and impurities were found, corroborating the successful transformation from ZIF-8 precursor to carbon (Fig. S2). Fig. 2(a) displays the PXRD patterns of $\text{Pt}_3\text{Co}_x\text{Sn}_{1-x}/\text{NC}$. It can be seen that the XRD patterns of all the samples showed the similar diffraction peaks without the appearance of additional new peaks. Specifically, all samples showed three major peaks at 40.5° , 47.1° , and 68.8° , which respectively correspond to (111), (200), and (220) planes of Pt_3Co ordered inter-metallic with space group of $Pm\bar{3}m$ [33]. With a magnified local pattern (Fig. 2b), it could be seen that the dominant diffraction

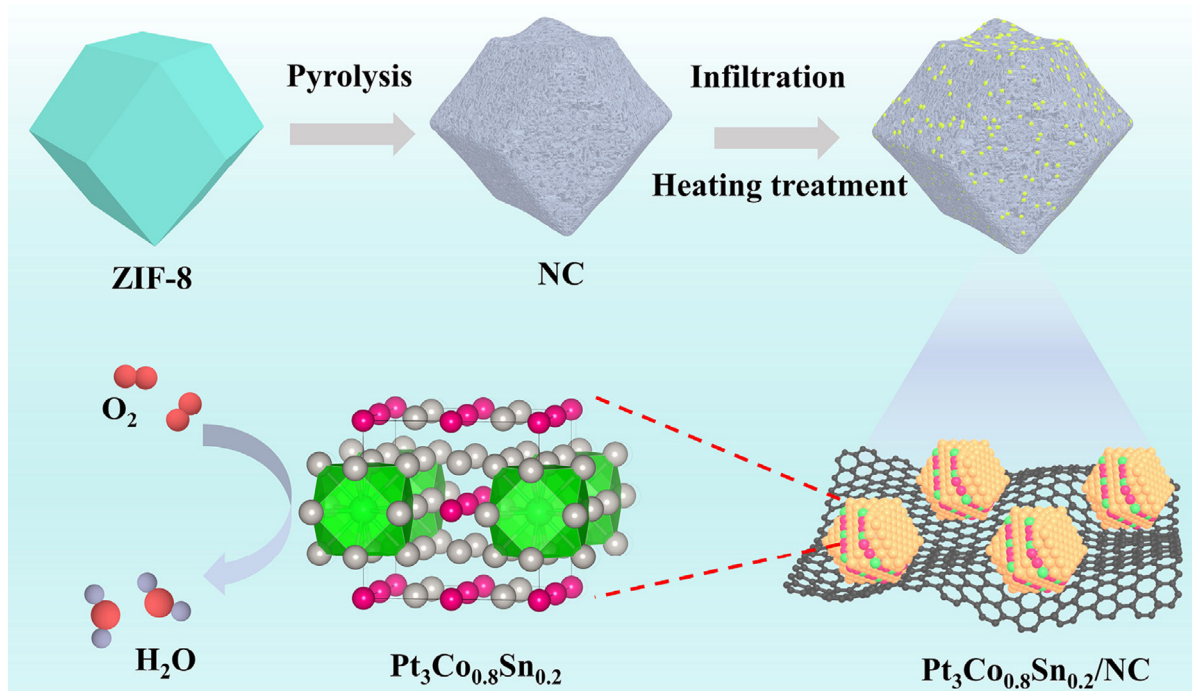
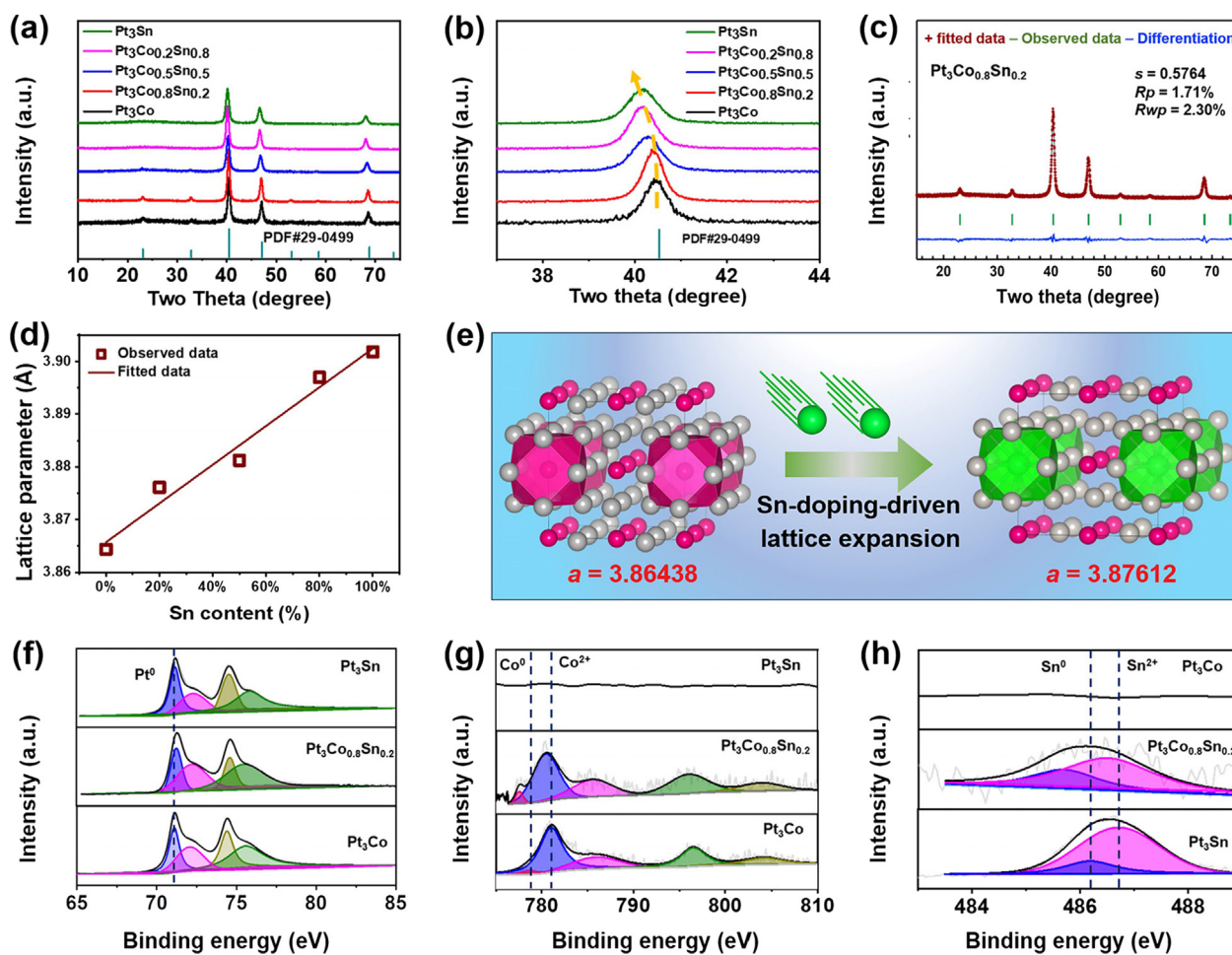
Fig. 1. Schematic illustration for the synthetic routes of Pt₃Co_{0.8}Sn_{0.2}/NC.

Fig. 2. (a) XRD patterns of a series of as-prepared Pt₃Co_xSn_{1-x}/NC composites and (b) corresponding local magnified XRD patterns in the two-theta region ranging from 37° to 44°; (c) Rietveld refinement for the XRD pattern of Pt₃Co_{0.8}Sn_{0.2}/NC; (d) dependence of lattice parameter on the doping percentage of Sn into Pt₃Co; (e) schematic illustration of the lattice expansion after Sn doping; (f–h) high-resolution XPS spectra of Pt 4f, Co 2p, and Sn 3d in Pt₃Co_{0.8}Sn_{0.2}/NC, Pt₃Co, and Pt₃Sn, respectively. Herein, we define the term 'Pt₃Co_xSn_{1-x}/NC' as 'Pt₃Co_xSn_{1-x}' in figures for convenience.

peaks belonging to (1 1 1) facet gradually shifted to the lower angle with the increase of the amount of Sn-dopant, implying the gradual lattice expansion due to the augmented doping of Sn into Pt_3Co lattice. To further confirm this point, the Rietveld refinement was performed to these PXRD patterns (Fig. 2c and Figs. S3–S6), from which the lattice parameters for Pt_3Co indeed increase with the increase of the amount of Sn-dopant (Fig. 2d). Typically, the lattice parameters for $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}$ were measured to be 3.876 Å, representing a 3% expansion compared to those of Pt_3Co and a 6% contraction relative to those of Pt_3Sn , resulting in a 0.91% increase in lattice volume compared to the pristine Pt_3Co (Fig. 2d and Table S1). Such a lattice variation can well be consistent with that fact that with an atomic radius of 0.151 nm, Sn is 17% larger than Co, which has a radius of 0.125 nm. Consequently, the lattice parameter increases with the higher percentage of Sn doping (Fig. 2e). Note that because of the high crystallinity of intermetallic phase, the diffraction peaks assigned to carbon were hardly to be clearly observed in the XRD patterns.

Nevertheless, the presence of C and N could be demonstrated by XPS results. As shown in Fig. S7, for the high-resolution XPS spectra of N 1s in the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ composite, peaks at 398.6 and 400.5 eV represent the pyridinic N and pyrrolic N, respectively [49]. The peak at 404.6 eV of N 1s is believed to be NO_x species caused by surface oxidation, aligning with the previous report [50,51]. The C 1s high-resolution XPS was split into three peaks

at 284.8, 285.8, and 288.7 eV, corresponding to C–C/C–N, C=N, and C=O bonding, respectively (Fig. S8) [52,53]. Furthermore, the pronounced peaks at binding energies of 71.1 and 74.3 eV correspond to Pt^0 4f_{7/2} and Pt^0 4f_{5/2} (Fig. 2f), respectively, which are indicative of elemental platinum (Pt^0) being the predominant species present in the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}$ catalyst [54]. The characteristic peak for metallic cobalt (Co^0) was observed at 777.5 eV, exhibiting a slightly negative shift compared to the standard peak for metallic cobalt in as-prepared Pt_3Co sample, which is typically situated at 778.1 eV [55]. This suggests a subtle alteration in the electronic environment surrounding the cobalt atoms (Fig. 2g). An intense peak detected at 780.5 eV, along with another one at 796.2 eV, can be attributed to the 2p_{1/2} and 2p_{3/2} orbitals of Co^{2+} , respectively. This divalent state of cobalt is commonly associated with surface oxidation processes [56]. The investigation into the Sn 3d orbitals revealed two distinct peaks at 485.4 and 486.5 eV, corresponding to metallic tin (Sn^0) and Sn in the +2 oxidation state (Sn^{2+}), respectively. This dual presence of Sn^0 and Sn^{2+} is consistent with the behavior of tin in other reported intermetallic compounds (Fig. 2h) [57]. The presence of Sn^{2+} is potentially caused by surface oxidation due to the exposure to the air, which can be commonly observed in previous findings [58]. It is noteworthy that the Pt peaks in $\text{Pt}_3\text{Co}/\text{NC}$ and $\text{Pt}_3\text{Sn}/\text{NC}$ have similar binding energies, whereas the Pt peak in $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ has a positive shift of approximately 0.3 eV compared to that in $\text{Pt}_3\text{Co}/\text{NC}$ and $\text{Pt}_3\text{Sn}/$

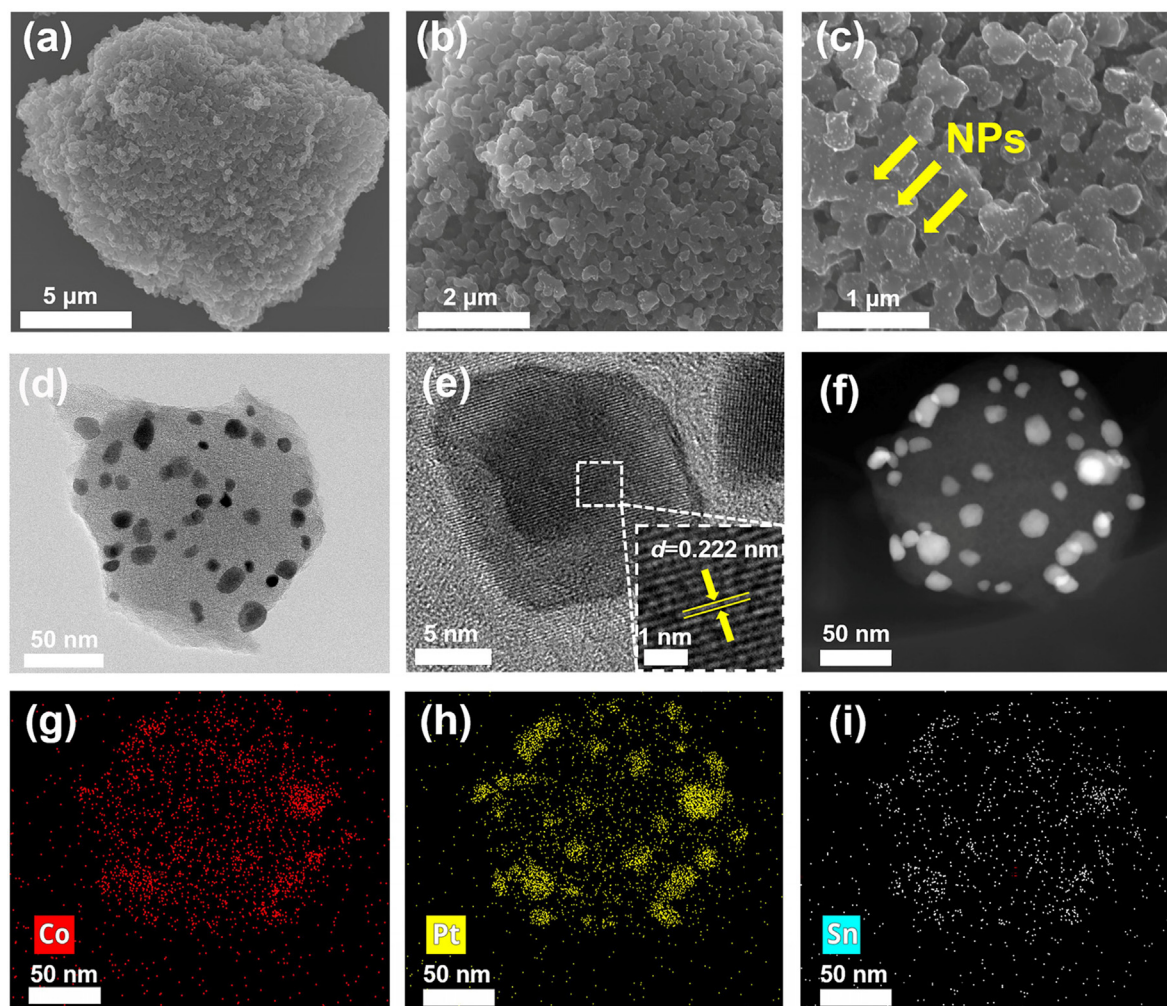


Fig. 3. (a–c) FESEM images of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$; (d) TEM image and (e) HRTEM image of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$; (f–i) HAADF image of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ with corresponding EDS mapping of Co, Pt, and Sn, respectively.

NC, indicating a synergistic effect of Co and Sn (Fig. 2f and Fig. S9). The Co^0 peaks in $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ exhibited a negative shift, suggesting the electron transfer from platinum to cobalt compared to that in $\text{Pt}_3\text{Co}/\text{NC}$ (Fig. 2g and Fig. S10). This electron redistribution further corroborates the adjustment in the electronic states within the catalyst system. Interestingly, a peak splitting was observed in the XPS spectrum of Sn 3d in $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ composite, whereas only a broad peak was detected in $\text{Pt}_3\text{Sn}/\text{NC}$ (Fig. 2h and Fig. S11). A 0.7 eV negative shift of the Sn^0 peak was observed in $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ compared to Pt_3Sn , while only a 0.3 eV negative shift of Sn^{2+} was detected. This suggests that the electron-donating character of Sn in the metallic phase is stronger than in the oxidized phase [59]. Additionally, there was no notable shift for both C and N in $\text{Pt}_3\text{Co}/\text{NC}$, $\text{Pt}_3\text{Sn}/\text{NC}$, and $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ system (Figs. S12 and S13).

To further check the morphology evolution during synthesis, FESEM images and TEM images are firstly provided for the precursors and resultant products. Fig. S14 firstly gave the FESEM images of ZIF-8, from which the polyhedral shape with smooth surface could be clearly observed. After the calcination of ZIF-8, the surface became very rough, accompanied by porous features due to the thermal-induced liberation and stress (Fig. S15). With further impregnation and pyrolysis, more nanoparticles could be identified on the surface, implying the generation of nanoparticles (Fig. 3a–c and Figs. S16–S19). Note that the morphologies for $\text{Pt}_3\text{Co}_x\text{Sn}_{1-x}/\text{NC}$ with different Sn-doping amounts were quite similar. The coral-

like architecture was composed of abundant nanoparticles (NPs) which were homogeneously confined by 3D porous carbon with rich channels, which is anticipated to facilitate enhancing mass transport and accessibility of active sites. TEM further substantiated the strong coupling of NPs with the NC supporter, with a narrow particle size distribution ranging from 10 to 20 nm in $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ (Fig. 3d). The high-resolution TEM (HRTEM) image confirmed the crystalline nature of the catalyst particles, aligning with the XRD results. The clear lattice fringes with a spacing of 0.222 nm were consistent with the space group of Pt_3Co , specifically the (111) plane (Fig. 3e) [14]. Additionally, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) combined with elemental mapping provided a vivid illustration of the elemental distribution within the catalyst. The homogeneous distribution of C and N species signified the robust skeletal structure of the NC supporter (Fig. S20), while the presence of Pt, Co, and Sn on the NPs indicated successful doping and uniform distribution of these elements (Fig. 3f–i). The energy dispersive X-ray spectroscopy (EDS) analysis further reinforced the successful incorporation of Sn into the Pt_3Co lattice, as indicated by the data presented in Fig. S20 and Table S2. The absence of any unaccounted elements or phases validated the purity and intended composition of the synthesized material. Therefore, the confinement effect exerted by the porous NC supporter is postulated to be instrumental in achieving such a restricted particle size distribution, contributing to the high dispersion and stability of the NPs.

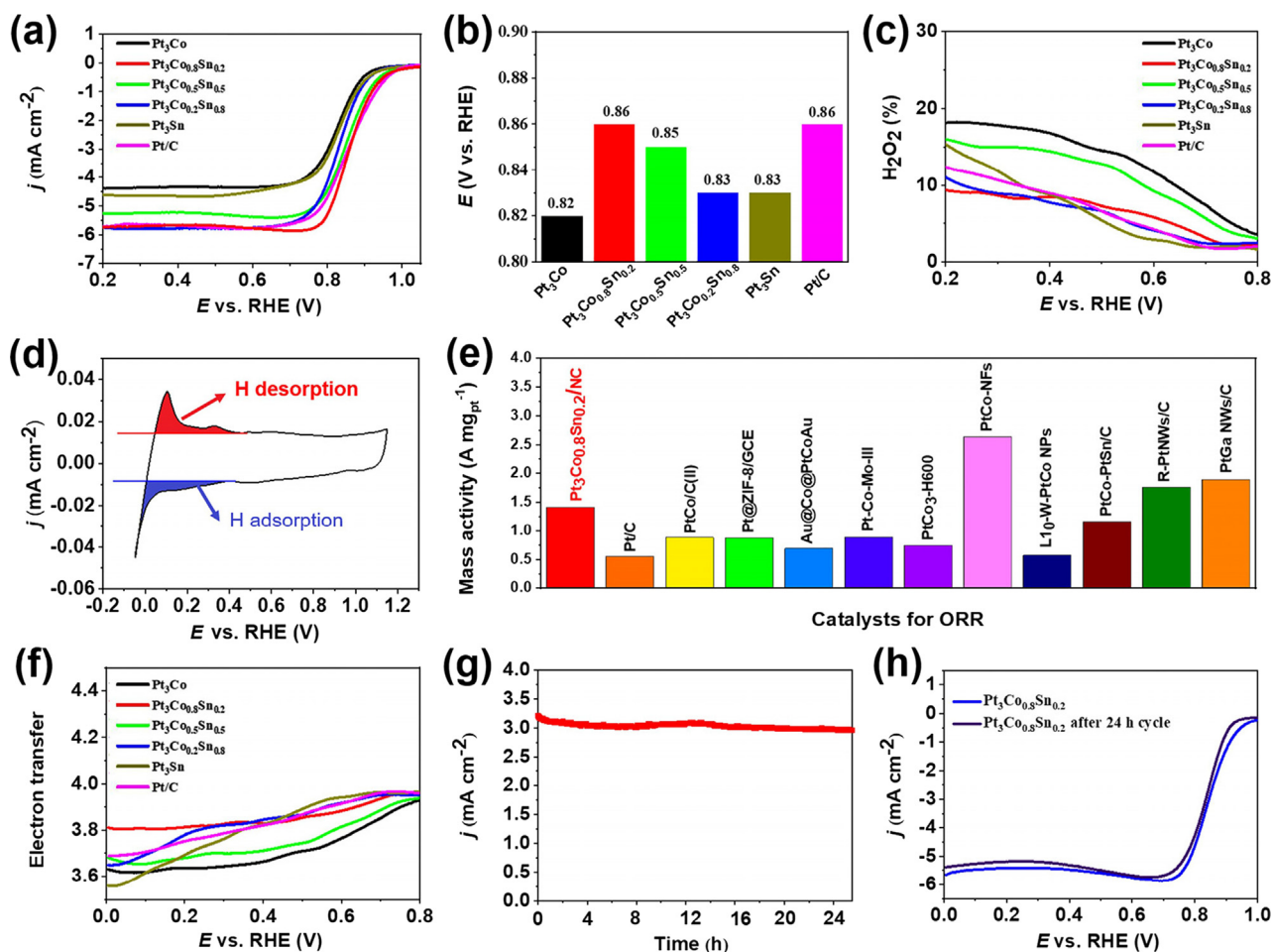


Fig. 4. Electrochemical measurements. (a) Polarized LSV; (b) the half-wave potential from LSV of $\text{Pt}_3\text{Co}_x\text{Sn}_{1-x}/\text{NC}$ composites and Pt/C ; (c) H_2O_2 production in relationship with an applied potential; (d) CV curve for HUPD in H_2 -saturated electrolyte; (e) comparison of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ catalyst with other reported ORR electrocatalysts in mass-specific activity; (f) electron transfer in relationship with applied potential; (g) CA of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$; (h) LSV of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ before and after 24 h CA.

Meanwhile, the unique structure may offer a larger surface area for catalytic reactions, thereby potentially increasing the overall activity of the catalyst system.

Inspired by the favorable composition and morphology, the electrochemical ORR performance of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ was evaluated, together with other $\text{Pt}_3\text{Co}_x\text{Sn}_{1-x}/\text{NC}$ references and Pt/C. The electrochemical performance was conducted in an O_2 -saturated 1 M KOH aqueous solution with a three-electrode system on a rotation ring-disk electrode (RRDE) at 1600 r min^{-1} . The polarization curves are shown in Fig. 4(a), and the corresponding half-wave potentials are listed in Fig. 4(b). As expected, the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ presented the highest half-wave potential of 0.86 V vs. RHE, which was the same as that of Pt/C, followed by $\text{Pt}_3\text{Co}_{0.5}\text{Sn}_{0.5}/\text{NC}$ and $\text{Pt}_3\text{Co}_{0.2}\text{Sn}_{0.8}/\text{NC}$, which have a half-wave potential of 0.85 and 0.83 V vs. RHE, respectively. In addition, $\text{Pt}_3\text{Sn}/\text{NC}$ exhibited a similar half-wave potential to $\text{Pt}_3\text{Co}_{0.2}\text{Sn}_{0.8}/\text{NC}$, while $\text{Pt}_3\text{Co}/\text{NC}$ has the lowest half-wave potential of 0.82 V vs. RHE. These further confirmed the synergistic effect among Pt, Co, and Sn.

The Pt–Pt distance in the surface layer is considered a crucial determinant of ORR activity. A shorter Pt–Pt distance weakens the adsorption of intermediates whereas a longer Pt–Pt distance enhances the binding of Pt atoms with the adsorbed intermediates [60]. During the ORR, a Pt-skin is formed, while the intermetallic

phase is submerged into the bottom layer. Surface strain occurs when there is a lattice mismatch between the surface layer and the bulk structure [34]. Given that the surface lattice tends to align with the lattice parameter in the bulk phase, it is reasonable to assume that the bulk structure can influence the adsorption by adjusting the surface lattice and the Pt–Pt distance. Therefore, we hypothesize that the lattice parameter of Pt_3Co was too short, leading to weak adsorption of intermediates, whereas the Pt–Pt distance in Pt_3Sn was excessively long, causing strong adsorption of intermediates. The $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}$ alloy achieved an optimal lattice parameter, facilitating a preferred Pt–Pt distance by generating surface strain compared to the pure bulk lattice.

Furthermore, we analyzed the production of hydrogen peroxide (H_2O_2) (Fig. 4c) and the number of electron transfer (Fig. 4f). At a potential of 0.8 V vs. RHE, all samples showed low H_2O_2 production, with an electron transfer count of approximately 3.95, indicating a high selectivity towards a four-electron reaction, where oxygen (O_2) is reduced to water (H_2O). However, at a lower potential of 0.2 V vs. RHE, H_2O_2 production increased, with Pt_3Co exhibiting nearly 20% H_2O_2 production, while $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ displayed the lowest H_2O_2 production of 9%, showcasing superior selectivity compared to pure Pt_3Co . The mass activity, an important criterion for measuring catalyst activity, reached $1.4 \text{ A mg}_{\text{Pt}}^{-1}$ for $\text{Pt}_3\text{Co}_{0.8}$ -

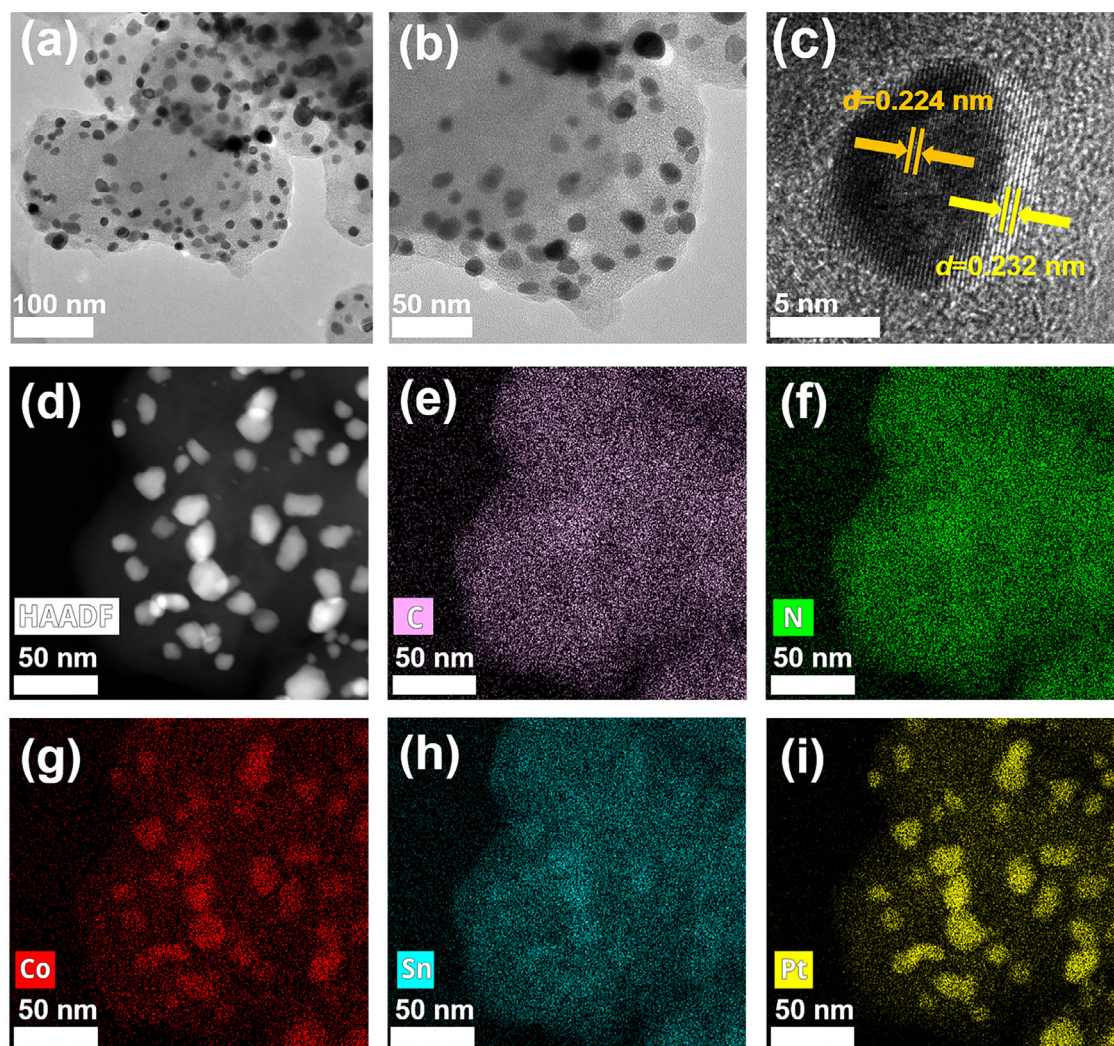


Fig. 5. (a, b) TEM images of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ after 24 h of CA at different magnifications; (c) HRTEM image with interplanar distance of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}$ NPs after 24 h of CA; (d) HAADF image and (e–i) EDS mapping image of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ after 24 h of CA for C, N, Co, Sn, and Pt, respectively.

Sn_{0.2}/NC, surpassing most of other previously reported Pt-based catalysts (Table S3) and the commercial Pt/C benchmark (Fig. 4d and e).

Stability is an essential factor for catalyst performance in industrial applications. To assess stability, Pt₃Co_{0.8}Sn_{0.2}/NC underwent chronoamperometry (CA) testing, demonstrating successful operation for over 24 h at 0.86 V vs. RHE with little degradation (Fig. 4g). Moreover, the LSV curve after post-CA revealed only a slight increase in the half-wave potential by less than 10 mV, achieving a half-wave potential of 0.85 V vs. RHE (Fig. 4h).

To further elucidate the morphological changes and structural integrity of the Pt₃Co_{0.8}Sn_{0.2}/NC catalyst system under operational conditions, we employed TEM, HAADF, and EDS to gain the in-depth information of the catalyst nanoparticles and the carbonaceous supporter after 24-hour period of catalytic operation. The TEM images, as depicted in Fig. 5(a and b), provided compelling evidence of the robustness between the NPs and the NC supporter. The TEM images showcased the maintenance of the catalyst structure, indicating a high level of mechanical stability under the applied catalytic conditions. The HRTEM image showed quite bright atoms around the surface of the particle, which could be assigned to the (1 1 1) facet of Pt phase (Fig. 5c). This could be interpreted as the formation of a Pt-enriched surface layer, commonly referred to as “Pt skin”. The emergence of such a Pt skin over the Pt₃Co_{0.8}Sn_{0.2} bulk could have significant implications for the activity and durability, as it may facilitate improving reaction kinetics and resistance to degradation [61,62]. The discovery of the formation of a potential Pt skin adds an exciting dimension to the under-

standing of this catalytic behavior of intermetallic. It may guide future research directions aimed at optimizing its performance for energy conversion applications. Furthermore, the HAADF image combined with EDS mapping, shown in Fig. 5(d–i), offered a vivid illustration of the elemental distribution within the catalyst particles. This comprehensive analysis revealed that Pt was the predominant element within the NPs, which is consistent with the expected composition of the Pt₃Co_{0.8}Sn_{0.2} intermetallic compound. Notably, marginal leaching of Co or Sn was observed, as confirmed by the EDS analysis summarized in Table S4. This result is indicative of the high chemical stability of the catalyst, which is crucial for maintaining long-term performance. An intriguing observation from the surface EDS analysis was the apparent increase in Pt content after the CA measurement, which was consistent with the HRTEM result.

To further elucidate the function of Sn-doping, the DFT calculations were performed to investigate the electronic structures of Pt₃Co and Pt₃Co_{0.8}Sn_{0.2}. The charge-density distributions of Pt₃Co and Pt₃Co_{0.8}Sn_{0.2} are shown in Fig. 6(a and b), respectively. Note that the charge density in Pt₃Co_{0.8}Sn_{0.2} is polarized towards the Pt atoms in the first coordination of Sn atoms, whereas the charge density is homogeneously distributed among the Pt atoms in Pt₃Co. This change of the local chemical environment may facilitate the hybridization of the Pt 4f orbitals, Co 3d orbitals, and Sn 5p orbitals, which is believed to enhance ORR catalytic activity of the coupled Pt skin [43]. Furthermore, the density of states (DOS) indicates that Pt₃Co_{0.8}Sn_{0.2} exhibits a stronger DOS near the Fermi level compared to pristine Pt₃Co (Fig. 6c and d). The integrated area near

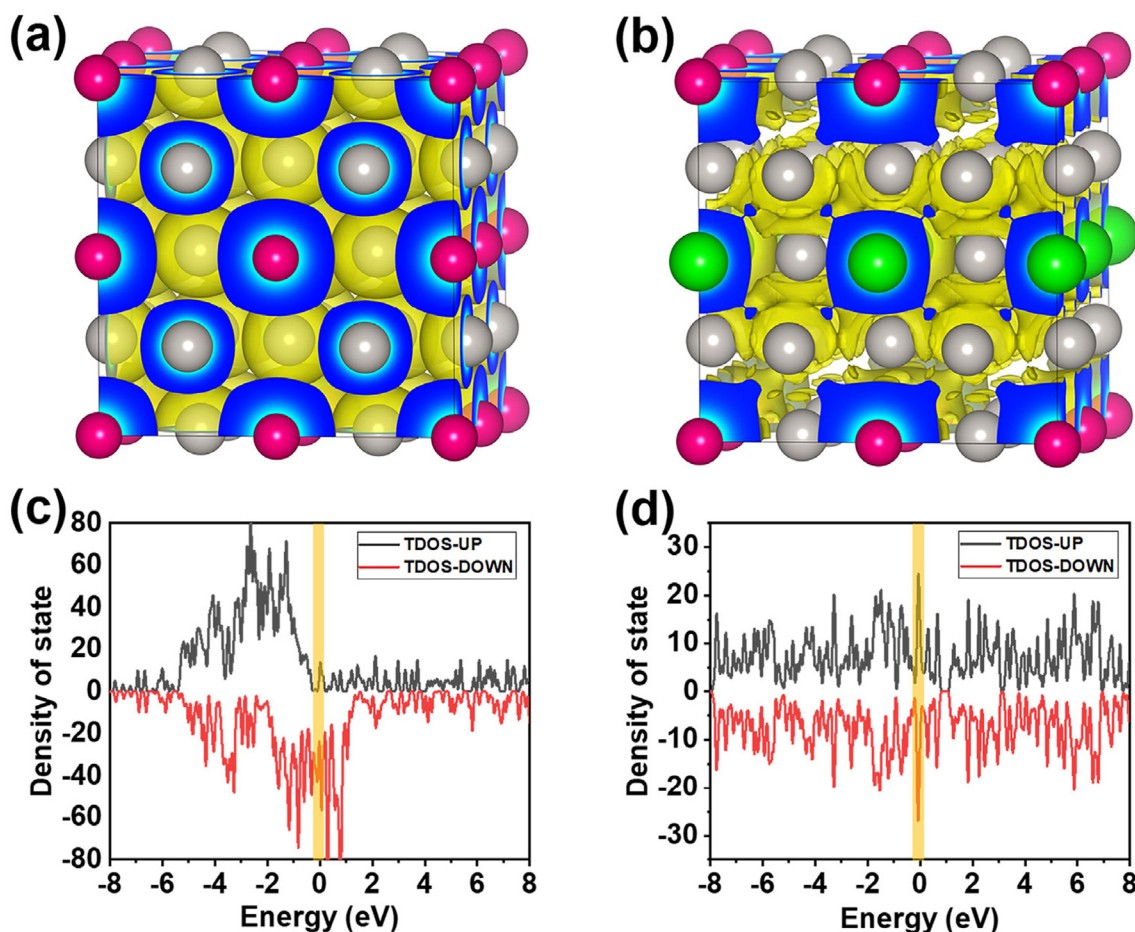


Fig. 6. (a, b) Charge density distributions of Pt₃Co and Pt₃Co_{0.8}Sn_{0.2}; (c, d) total density of states for Pt₃Co and Pt₃Co_{0.8}Sn_{0.2}. The Fermi level is normalized to zero, and the highlighted areas represent the integration area. The purple, green, and grey atoms represent the Co, Sn, and Pt atoms, respectively.

the Fermi level (within the range from -0.2 to 0.2 eV) for $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}$ is approximately 3.9, whereas it is about 2.1 for Pt_3Co . This suggests that $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}$ has more metallic behavior and higher electronic conductivity, which will effectively enhance the electron-transfer capability of the catalyst.

To demonstrate the enhanced electrochemical performance of the trimetallic $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ intermetallic compound, we incorporated it into a zinc-air battery (ZAB) system as a catalyst and anchored it on carbon paper ($\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC@CP}$). The efficacy of this material was benchmarked against a conventional ZAB utilizing a zinc anode in conjunction with a state-of-the-art Pt/C catalyst. The experimental setup for the ZABs involved using an alkaline electrolyte, with a zinc foil serving as the anode. The cathode material in our test was the novel $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC@CP}$ composite, whereas a conventional Pt/C catalyst was used in the

control ZAB for comparison purposes. Fig. 7(a) presents a digital photograph of the assembled ZABs, displaying an open-circuit voltage of 1.537 V, which is indicative of the suitability of the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC@CP}$ catalyst for the application in ZAB systems. Furthermore, the open-circuit voltage for the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC@CP}$ -based ZAB was stabilized at 1.525 V, which is a notable improvement over the 1.46 V recorded for the Pt/C cathode, as illustrated in Fig. 7(b). Galvanostatic discharge measurements, as depicted in Fig. 7(c), revealed that the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC@CP}$ -based ZAB had an impressive specific capacity of 804 mA h g^{-1} at a discharge current density of 10 mA cm^{-2} , outperforming the Pt/C-based ZAB with specific capacity of 754 mA h g^{-1} . Additionally, the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC@CP}$ ZAB maintained a higher discharge voltage plateau at current densities ranging from 2 to 50 mA cm^{-2} and was subsequently recharged to 2 mA cm^{-2} without any signif-

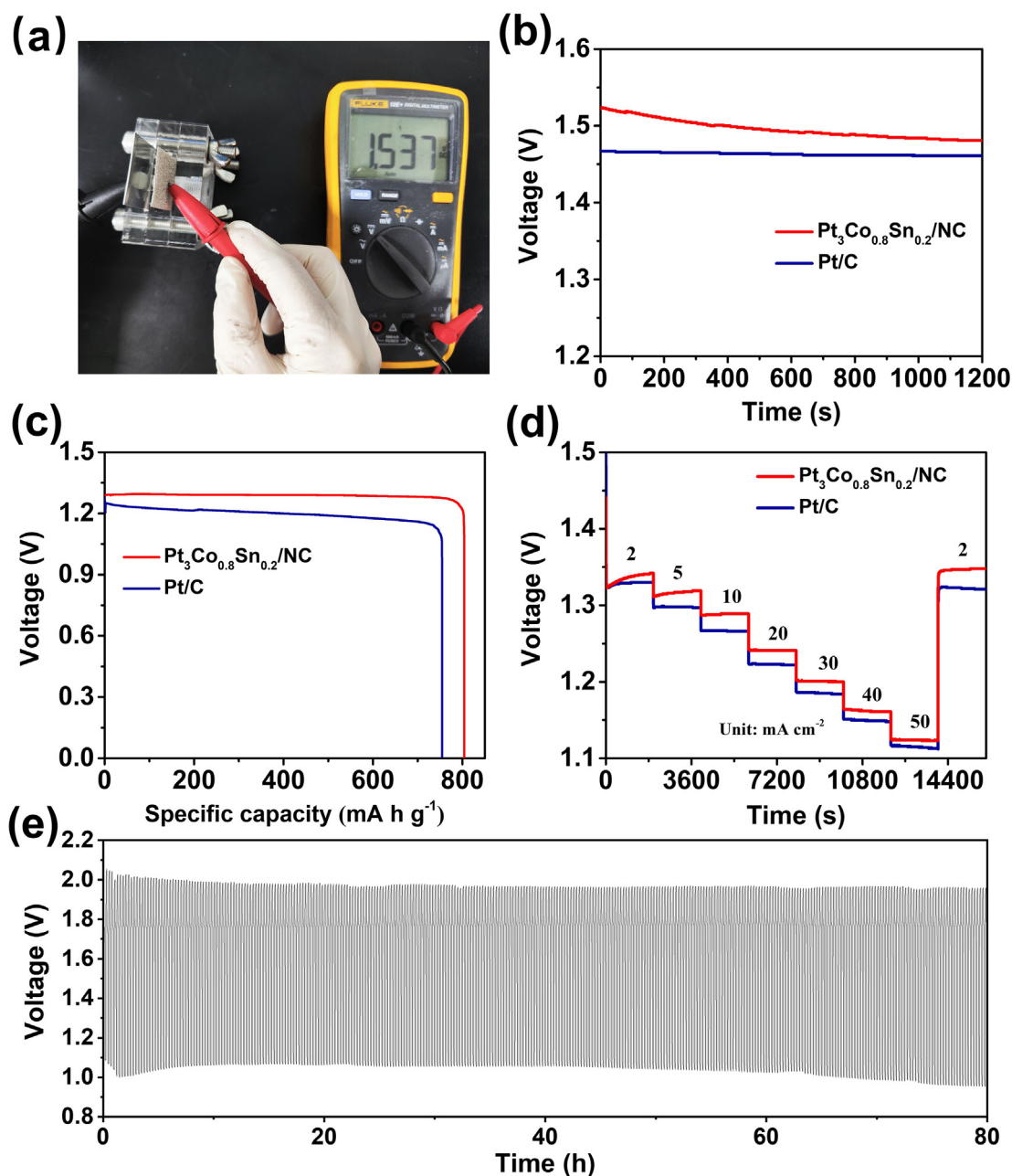


Fig. 7. (a) Digital photograph of self-assembled $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC@CP}$ ZAB with a measured open-circuit voltage shown on the amperemeter; (b) measured curves of open-circuit voltage; (c) galvanostatic discharge measurements of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC@CP}$ and Pt/C@CP; (d) discharge curves of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC@CP}$ ZAB and Pt/C@CP ZAB at current density ranging from 2 to 50 mA cm^{-2} ; (e) long-term charge-discharge cycle of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC@CP}$.

icant energy loss, highlighting its superior efficiency and stability (Fig. 7d). To further assess the practical applicability and durability of the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}@CP$ -based ZAB, it was subjected to an extended charge-discharge cycling process. The cell completed more than 80 h of cycling, as evidenced by the data in Fig. 7(e), affirming its resilience under operational conditions. Therefore, integrating the trimetallic $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}$ catalyst into the ZAB system has demonstrated markedly enhanced performance, including higher open-circuit voltage, improved specific capacity, and increased durability during prolonged cycling. These findings underscore the potential of $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}@CP$ as a cathode material for next-generation zinc-air batteries, offering a promising avenue for future research and development in the field of metal-air battery technology.

4. Conclusions

In summary, we have successfully engineered a nanocarbon-supported $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}$ intermetallic catalyst, which has shown remarkable performance for the ORR and the applications in zinc-air battery. The successful incorporation of Sn into the Pt_3Co lattice was corroborated by XRD analysis, which allowed for the precise determination of lattice distortion within the intermetallic compound. This distortion resulted in an incremental expansion of the lattice parameter by 0.31% and a concomitant increase in the unit cell volume by 0.91%. These subtle alterations in the crystal structure indicated the successful doping process and may have significant implications for the catalytic performance. Further analysis using XPS and TEM revealed that the majority of the Pt, Co, and Sn species were homogeneously confined by N-doped porous carbon, which is essential for optimal catalytic activity. When benchmarked against Pt_3Co and Pt_3Sn catalysts, the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ exhibited an enhanced half-wave potential, signifying an improvement in ORR activity. The durability of the catalyst was assessed through CA measurements, which demonstrated its resilience under prolonged electrochemical stress. Additionally, the performance of the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ catalyst was evaluated within a self-assembled zinc-air battery context, where it maintained operational stability for over 80 h under cyclic charge-discharge conditions. This endurance test suggests the catalyst holds considerable promise for practical applications in the zinc-air battery industry. The innovative design and synthesis of the $\text{Pt}_3\text{Co}_{0.8}\text{Sn}_{0.2}/\text{NC}$ catalyst and its superior performance in ORR and zinc-air battery systems underscored its potential as a next-generation cathode catalyst.

CRedit authorship contribution statement

Ruotao Yang: Writing – original draft, Methodology, Data curation. **Chuhan Dai:** Writing – original draft, Methodology, Investigation, Data curation. **Laiwei Zhang:** Data curation, Methodology. **Ruirui Wang:** Methodology, Funding acquisition, Conceptualization. **Kui Yin:** Methodology, Funding acquisition, Data curation. **Bo Liu:** Methodology, Funding acquisition. **Ziliang Chen:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jechem.2024.06.035>.

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