

Cite this: *Energy Adv.*, 2024,
3, 2648

Multi-metal (Fe, Cu, and Zn) coordinated hollow porous dodecahedron nanocage catalyst for oxygen reduction in Zn–air batteries†

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The coupling of multiple low-cost metals and porous nanocarbon materials aimed at replacing precious metals to enhance electrocatalytic oxygen reduction is a critical challenge in some crucial research areas. In the present study, a hollow dodecahedron nanocage catalyst (Fe₃O₄/CuNCs/ZnN_x-PHNC) was constructed by supporting copper nanoclusters, Fe₃O₄ nanoparticles, and Zn–N_x after sintering and annealing through the coordination of ZIF-8 and by doping copper and iron ions. We observed that the synergy of the multi-metals in the magnetically separable heterojunction catalyst induced electron transfer and inhibited hydrogen peroxide formation, thus improving its catalytic performance for the oxygen-reduction reaction. The catalyst demonstrated a half-wave potential as high as 0.832 V and a Tafel slope of 54 mV decade^{−1}, superior to many non-precious metal catalysts reported in the literature. The assembled Zn–air battery (ZAB) exhibited a maximum power density of 162 mW cm^{−2} and ultrahigh stability of >500 h at 5 mA cm^{−2} current density. The ZAB's excellent performance indicates its high development and practical application prospects.

Received 8th May 2024,
Accepted 5th September 2024

DOI: 10.1039/d4ya00295d

rsc.li/energy-advances

1. Introduction

The current global energy shortage has arisen because of the ever-increasing human demand for energy and the associated depletion of available energy resources.^{1,2} Human survival, economic status, and sustenance are highly dependent on energy availability, while the exploitation and use of other resources are also energy dependent.³

Currently, the rapid development of the electronics industry requires a safe and stable energy supply system.⁴ Zn–air batteries (ZABs) are one of the most promising battery candidates because of their high theoretical energy density (1086 W h kg^{−1}), low cost, high safety, and environmental friendliness.⁵ However, ZABs face some severe setbacks,⁶ with the lack of reliable and efficient bifunctional air electrodes as the biggest obstacle to their practical applications.⁷ Generally, ZABs' efficiency depends on the catalytic performance of oxygen electrocatalysts on air electrodes, where the discharge process occurs in a kinetically retarded oxygen-reduction reaction (ORR). Therefore, ORR-efficient

electrocatalysts are crucial for improving the performance of rechargeable ZABs. Moreover, platinum-based catalysts are typical commercial electrocatalysts for the ORR with excellent activity. However, their high cost, the natural scarcity of platinum, and their unsatisfactory durability limit their large-scale industrial applications.^{8,9} Therefore, there is an urgent need to develop highly active, durable, and cost-effective ORR catalysts.

Transition metals and their derivatives (bearing aluminum, oxygen, nitrogen, sulfur, selenium, carbides and hydroxides and their corresponding oxides, nitrides, sulfides, *etc.*) have attracted huge interest owing to their earth-abundance and high catalytic properties.^{10–13} Among them, Fe- and Cu-based nanoparticles are of immense interest because of their high electrical conductivity, excellent mechanical strength, and flexible electronic structure.^{14–16} However, finding a suitable catalyst substrate to load active nanoparticles is essential to expose the active sites more entirely for improved activity.

Zeolitic imidazolate frameworks (ZIFs) constructed from coordination networks between specific metal nodes and organic ligands are attractive substrates considering their unique properties of a high specific surface area, large pore volume, and multiple organometallic nature.¹⁷ Given these properties, ZIF-based materials have been widely applied in adsorption and purification.¹⁸ Introducing metallic species into ZIF precursors can inhibit the aggregation of nanoparticles

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4ya00295d>

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using a strong anchoring effect, thereby leading to highly dispersed active sites. Additionally, calcination at high temperatures ensures a high graphitization of carbon precursors, which can improve the corrosion resistance and electrical conductivity.¹⁹ Due to their relatively high activity, Fe-doped ZIF materials are considered among the most promising oxygen-reduction electrocatalysts to replace the noble metal Pt.^{20–22} However, the H₂O₂ produced by the Fe–N–C catalyst formed by single-metal Fe doping in the ORR severely hinders the four-electron-transfer process in the ORR. As a result, the Fe active sites easily undergo the Fenton reaction with H₂O₂, potentially affecting the ORR activity.^{23,24}

To overcome this drawback, other metals can be doped to induce electron transfer and inhibit H₂O₂ production. The significant synergistic effect between Fe₃O₄ nanoparticles and Cu nanoclusters' catalytic active sites and carbon carriers effectively improves the electrocatalytic activity.^{25,26} In addition, Zn has less electronegativity ($\chi = 1.65$), making it easier to contribute its most valent electrons to Cu ($\chi = 1.90$) and Fe ($\chi = 1.83$). Therefore, Zn is compatible with Cu and Fe, and can optimize the electronic structure to produce synergy, promote the adsorption of reaction molecules and desorption of reaction intermediate, and improve the catalytic performance.²⁷ Therefore, in the present study we employed ZIF-8 with a Zn atom as the substrate and introduced Fe and Cu atoms to construct composite catalysts.

The high surface area and short diffusion path of hollow nanocages provide more active sites, a larger liquid–solid contact area, and a relatively large functional surface for the adsorption–desorption of the substrate molecules themselves to promote the adsorption–desorption rate.^{28,29} Meanwhile, the hollow interior can prevent the encapsulated transition metal oxide nanoparticles from aggregating. The high dispersion of metal nanoparticles on the carbon skeleton can expose more active sites, providing excellent electrical conductivity and allowing for fast mass transfer. In addition, anisotropic nanocages have the characteristics of a uniform size, low density, large void space, and strong shell permeability, *etc.*, which have strong utilization value for electrocatalysis.³⁰ The synergetic enhancement of the interface structure and active sites on the catalyst utilizes the inherent advantages of the interface structure.³¹ Therefore, distributing the various nanoparticles entirely on the graded porous carbon and leveraging their synergistic advantages to promote catalytic performance has become a major challenge. Therefore, it is imperative to develop a transition metal-regulated skeletonization gold nanocage structure with a controllable microstructure to reveal changes in the electronic and environmental properties at the coupling interface, clarify the structural performance of the synergistic effect, and improve the ORR performance.³²

The current research prepared a hollow-graded, porous carbon-based, cage-like catalyst co-regulated by multiple metals, and successfully applied it to ORR reactions and zinc–air batteries. We used ZIF-8 containing zinc, nitrogen, carbon, and oxygen as the precursor, which was transformable into a material with porous carbon-containing Zn–N_x active

sites after high-temperature pyrolysis. Fe and Cu ions were introduced through coordination during ZIF-8 synthesis, and high-temperature sintering synchronously generated a hollow carbon-based catalyst controlled by the multiple metals. Further, salt melting and high-temperature annealing resulted in pore formation, and a hollow-graded porous carbon-based catalyst (named Fe₃O₄/CuNCs/ZnN_x-PHNC) was obtained. The magnetically separable catalyst had a high specific surface area and high metal loading capacity. Moreover, Fe₃O₄, composed of Fe species with various valence states, could provide active sites for electron acquisition and loss, ensuring a high ORR activity. Second, the Cu nanoclusters have excellent stability, conductivity, and abundant oxygen defects, which can accelerate the conductivity of O-containing intermediates, thereby extending the lifespan of the Fe₃O₄/CuNCs/ZnN_x-PHNC catalysts.

This study provides an effective strategy for synthesizing non-noble metal catalysts for use in ZABs. The assembled ZABs and flexible zinc–air batteries (FZABs) exhibited excellent discharge performances and strong stability, reflecting their optimistic commercial prospects and application value as air cathode catalysts.

2. Experimental section

2.1 Synthesis of ZIF-8

The production method for ZIF-8 refers followed the literature with some improvements.^{33,34} First, zinc nitrate hexahydrate (1.16 g) and dimethylimidazole (2.46 g) were dissolved in 40 ml of methanol, sonicated for 10 min, mixed and stirred for 12 h, and then rested at room temperature for 12 h. The supernatant after resting was poured out, then washed three times each with ultrapure water and ethanol, and dried in a vacuum oven at 60 °C to obtain ZIF-8 white crystals.

2.2 Synthesis of Fe-ZIF-8 and Cu-ZIF-8

Following the same procedure used for the synthesis of ZIF-8, zinc nitrate hexahydrate (1.16 g) and iron acetylacetonate (0.35 g) were dissolved in 40 ml of methanol, and dimethylimidazole (2.46 g) was dissolved in 40 ml of methanol, sonicated for 10 min, mixed and stirred for 12 h, and then rested at room temperature for 12 h. The supernatant after resting was poured out, then washed three times each with ultrapure water and ethanol, and dried in a vacuum oven at 60 °C and the final product was named Fe-ZIF-8. The synthesis process was the same as for Fe-ZIF-8 except that iron acetylacetonate was replaced by copper nitrate (0.1 g), and the resulting product was named Cu-ZIF-8.

2.3 Synthesis of Fe/Cu-ZIF-8

Iron acetylacetonate (0.35 g), copper nitrate (0.1 g), and zinc nitrate hexahydrate (1.16 g) were dissolved simultaneously in 40 ml of methanol, and the subsequent treatment was the same as that for the synthesis of ZIF-8.

2.4 Synthesis of Fe₃O₄/CuNCs/ZnN_x-PHNC

The dried product was mixed with NaCl and KCl (1 : 4 : 1). After sintering at 925 °C for 2 h, the calcined products of ZIF-8,



Cu-ZIF-8, Fe-ZIF-8, and Fe/Cu-ZIF-8 were extracted and filtered. The final catalysts were named $\text{ZnN}_x\text{-PNC}$, $\text{CuNCs/ZnN}_x\text{-PNC}$, $\text{Fe}_3\text{O}_4/\text{ZnN}_x\text{-PHNC}$, and $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$. For the convenience of readers, we list the raw materials and the corresponding obtained materials in Table S1 (ESI†).

3. Results and discussion

3.1. Structure and characterization of the catalysts

The preparation procedure of $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$ is shown in Fig. 1a. To synthesize Fe-Cu-ZIF-8, the precursors were first synthesized by dissolving a mixture of iron acetylacetonate, copper nitrate, and zinc nitrate hexahydrate in methanol before introducing imidazole dialdehyde dissolved in methanol with stirring at room temperature. Calcining $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$ in the presence of NaCl and KCl under an Ar atmosphere formed the hollow-structured $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$.

Metal doping was determined from the X-ray diffraction (XRD) images of all the materials before sintering. As shown in Fig. S1 (ESI†), all the synthesized precursors conformed with the theoretical ZIF-8 peak structure. However, spurious peaks

appeared at individual locations, attributable to the metal doping. Fig. 2a shows the XRD diffraction images of the four materials after sintering. The graphitic structure formed after calcination evinced the (002) diffraction peak centered at 25.4° and the (101) diffraction peak at 43.2° as the major crystallographic planes of C. For $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$, the 19.7° and 43.1° spikes corresponded to the crystallographic planes (212) and (440) of Fe_3O_4 (PDF#76-0956), respectively. Combined with the standard PDF card for Cu (PDF#04-0836), peaks for the Cu nanoclusters were also evident in the XRD pattern of $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$. The uniform embedding of Cu nanoclusters in the carbon layer as active sites is crucial for promoting the ORR performance. The XRD pattern of $\text{Fe}_3\text{O}_4/\text{ZnN}_x\text{-PHNC}$ only showed a weak Fe_3O_4 characteristic peak at 15.3° , likely due to the lack of Cu regulation and the minute Fe_3O_4 produced, mainly responsible for the lack of expected catalytic effect. Also, the XRD pattern of $\text{CuNCs/ZnN}_x\text{-PNC}$ did not show any Cu peak, indicating that single-metal doping could not stably form metal nanoclusters. In addition, only carbon peaks were observed in $\text{ZnN}_x\text{-PNC}$.

The hysteresis curve (VSM) represents the magnetization of a ferromagnetic substance under alternating external magnetic

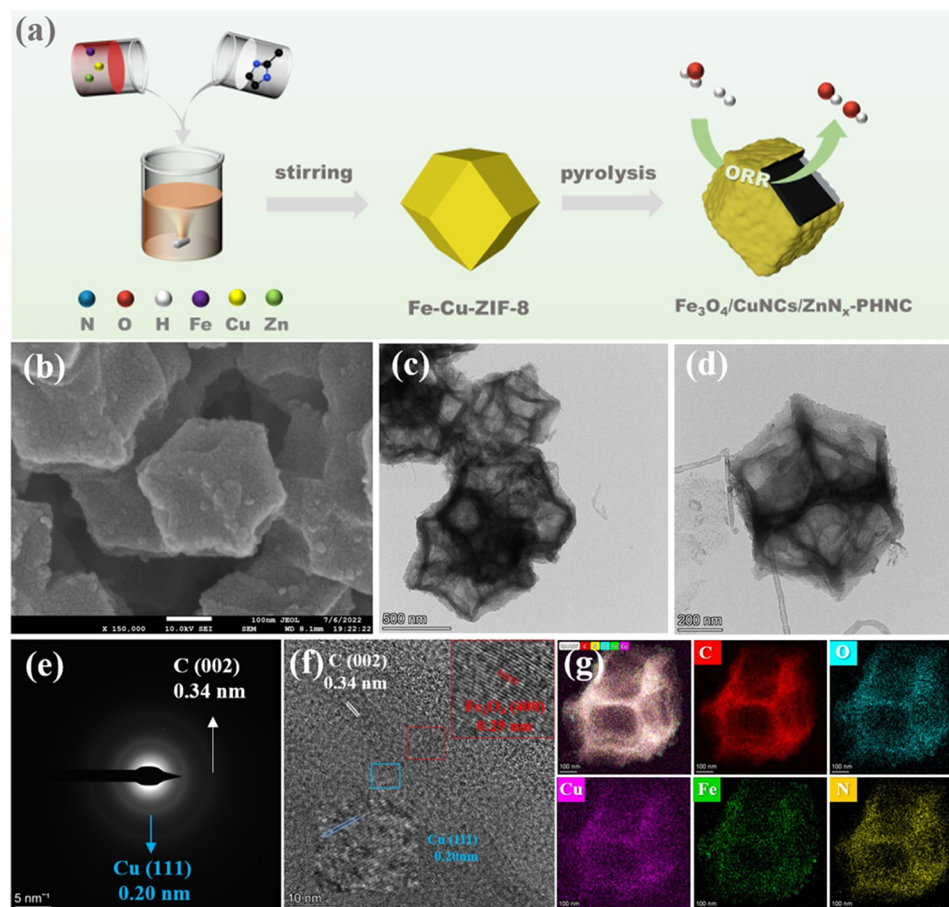


Fig. 1 (a) Flow chart for the preparation of $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$; (b) SEM images of $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$ at different resolutions; (c) and (d) TEM images of $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$ at different resolutions; (e) selected area electron diffraction images of $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$; (f) high-resolution TEM images of $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$; (g) HAADF-STEM images of $\text{Fe}_3\text{O}_4/\text{CuNCs/ZnN}_x\text{-PHNC}$ and its elemental distribution images.



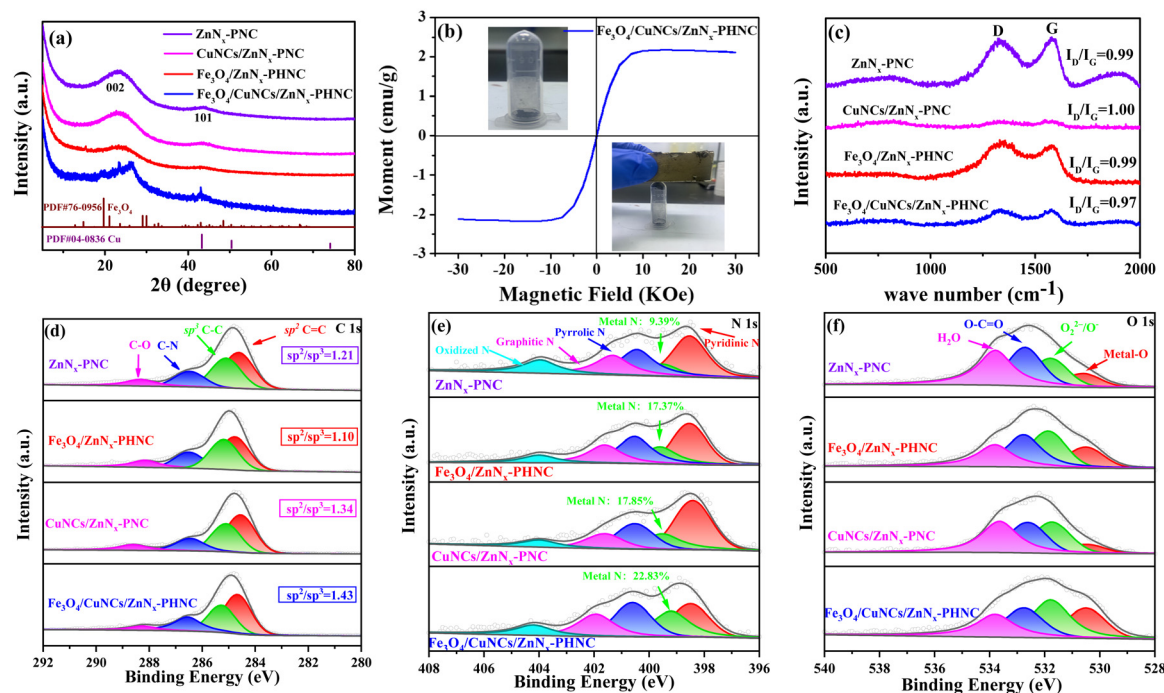


Fig. 2 (a) XRD spectra of Fe₃O₄/CuNCs/ZnN_x-PHNC, Fe₃O₄/ZnN_x-PHNC, CuNCs/ZnN_x-PNC and ZnN_x-PNC; (b) VSM curves of Fe₃O₄/CuNCs/ZnN_x-PHNC; (c) Raman spectra of Fe₃O₄/CuNCs/ZnN_x-PHNC, Fe₃O₄/ZnN_x-PHNC, CuNCs/ZnN_x-PNC and ZnN_x-PNC; (d) C 1s, (e) N 1s and (f) O 1s XPS spectra of Fe₃O₄/CuNCs/ZnN_x-PHNC, Fe₃O₄/ZnN_x-PHNC, CuNCs/ZnN_x-PNC and ZnN_x-PNC.

field strengths. When the magnetization starts (Fig. 2b), the magnetic induction strength of the ferromagnet increases with the external magnetic field strength and the unit moment. At a certain magnetic field strength, the magnetic induction strength of the ferromagnet is optimized, and the unit moment plateaus. The inset shows the Fe₃O₄/CuNCs/ZnN_x-PHNC catalyst powder, which was suspended when magnetized, indicating its strong magnetic property. This observation was consistent with the peak structure of Fe₃O₄ nanoparticles from the XRD spectra.

To investigate the structural defects and the degree of graphitization in the carbon materials, the Raman spectra of Fe₃O₄/CuNCs/ZnN_x-PHNC, Fe₃O₄/ZnN_x-PHNC, CuNCs/ZnN_x-PNC, and ZnN_x-PNC were examined (Fig. 2c). The D-band (1350 cm⁻¹) was the vibration caused by lattice defects in the carbon matrix, corresponding to the defect position of sp³, while the G-band (1580 cm⁻¹) was caused by vibrations belonging to the sp² bonded graphitic carbon. The samples' intensity ratios (I_D/I_G) of the D-band to G-band were 0.97, 0.99, 1.00, and 0.99, respectively. The intensity ratio for Fe₃O₄/CuNCs/ZnN_x-PHNC was 0.97, indicating the presence of many defects in the carbon matrix. These defects in the lattice are essential sites for enhancing the electrocatalytic performance of the catalyst.³⁵ Comparing the other three materials, we observed that the materials showed a large number of carbon defects and increased graphitization when calcined with added protective and stripping agents. This result shows that sintering and activators are crucial for preparing nanocarbon materials.^{36,37}

N₂ adsorption-desorption experiments were performed to further investigate the pore structures and specific surface areas of Fe₃O₄/CuNCs/ZnN_x-PHNC, Fe₃O₄/ZnN_x-PHNC,

CuNCs/ZnN_x-PNC, and ZnN_x-PNC. The adsorption isotherms (Fig. S2a, ESI†) illustrated that the materials were characterized by hysteresis-return type IV profiles. Also, the samples had high specific surface areas and extensive porosity. From Fig. S2b (ESI†), the specific surface areas of Fe₃O₄/CuNCs/ZnN_x-PHNC, Fe₃O₄/ZnN_x-PHNC, CuNCs/ZnN_x-PNC, and ZnN_x-PNC were derived as 702, 773, 853, and 894 m² g⁻¹, respectively. Their pore size distribution (Fig. S2c, ESI†) was mainly dominated by micropores and mesopores, in which the hierarchical porous structure can shorten the distance for O₂, thus accelerating the electron transport and mass transfer.³⁸ Table S2 (ESI†) suggests that introducing Fe and Cu decreased the microporosity of Fe₃O₄/CuNCs/ZnN_x-PHNC, whereas the average pore size (calculated by BJH) was the largest. This was related to the fact that the total BET, micropore area, and pore capacity ratio were reduced correspondingly with the magnitude of metal doping. CuNCs/ZnN_x-PNC and ZnN_x-PNC showed some folds spreading and may also exfoliate some graphitized lamellae, thus significantly altering their pore structure.

Furthermore, X-ray photoelectron spectroscopy (XPS) was used to assess the elemental composition of the catalysts. The samples' surface elemental contents are listed in Table S3 (ESI†). Fig. S3a (ESI†) illustrates the full spectra of Fe₃O₄/CuNCs/ZnN_x-PHNC, Fe₃O₄/ZnN_x-PHNC, CuNCs/ZnN_x-PNC, and ZnN_x-PNC, showing the peaks of the elements in the various speciations. From the high-resolution spectrum of C 1s (Fig. 2d), the C peaks could be divided into four peaks: 284.7 ± 0.1, 285.2 ± 0.1, 286.5 ± 0.1, and 288.4 ± 0.2 eV, corresponding to C=C, C-C, C-N, and C-O bonds, respectively. Among these, the C-N bond indicated the successful doping of N atoms into the carbon nanostructures.

Furthermore, the XPS high-resolution spectra of Cu 2p were dominated by Cu at peak positions of 934.1 ± 0.4 and 955.0 ± 0.6 eV, with Cu 2p_{3/2} and Cu 2p_{1/2} present (Fig. S3c, ESI[†]). These were consistent with the XPS images of Cu 2p in copper nanoclusters documented in other literature.⁴⁵ In the XPS spectra of Zn 2p (Fig. S3d, ESI[†]), peaks were observed at 1021.9 ± 0.1 and 1045.2 ± 0.2 eV, corresponding to Zn²⁺.⁴⁶

Further morphological observations were done using transmission electron microscopy (TEM). Fig. 1c depicts the TEM images of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ at 500 nm resolution, showing that the sintered ZIF-8 did not agglomerate, retaining the dodecahedral structure.⁴⁸ Fig. 1d shows that the $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ dodecahedra had a laminar wrinkled nanosheet structure in the outer layer and distinct skeletonization in the inner layer, showing several dispersed skeletonized nanocage structures overall. The large number of defects formed in the outer and inner layers after calcination provided abundant electron-transport channels that enhanced O_2 adsorption and shortened the mass-transfer distance, which were primarily responsible for the enhanced activity of

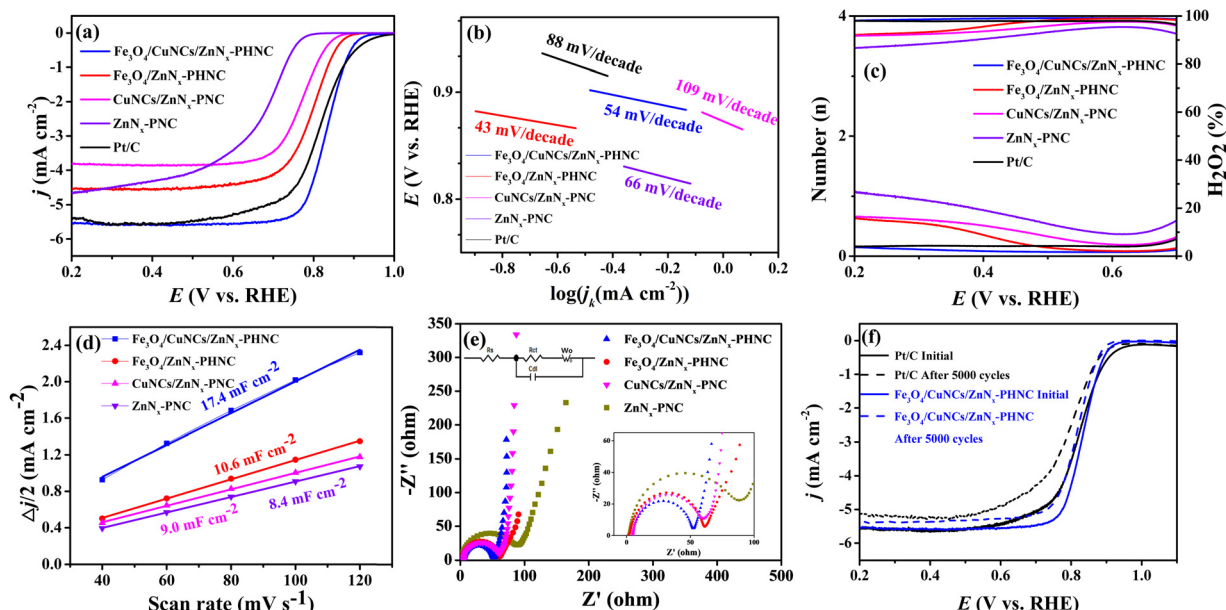


Fig. 3 (a) LSV curves for $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$, $\text{Fe}_3\text{O}_4/\text{ZnN}_x\text{-PHNC}$, $\text{CuNCs}/\text{ZnN}_x\text{-PNC}$, $\text{ZnN}_x\text{-PNC}$ and Pt/C ; (b) Tafel curves; (c) hydrogen peroxide yield and average number of electrons transferred; (d) double-layer capacitance (C_{dl}); (e) impedance diagrams of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$, $\text{Fe}_3\text{O}_4/\text{ZnN}_x\text{-PHNC}$, $\text{CuNCs}/\text{ZnN}_x\text{-PNC}$ and $\text{ZnN}_x\text{-PNC}$ (insets show partial enlargements); (f) stability experiments of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C .

to calculate the respective electron-transfer number (n) and the corresponding hydrogen peroxide yield ($\text{H}_2\text{O}_2\%$) according to the measured ring and disk currents. Fig. 3c illustrates that the electron-transfer numbers of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C were close to four, indicating that they were mainly involved in a four-electron transfer in the ORR reaction. Therefore, H_2O_2 , as a product in the path of a two-electron reaction, was meager. At the same time, the electron-transfer numbers of $\text{Fe}_3\text{O}_4/\text{ZnN}_x\text{-PHNC}$, $\text{CuNCs}/\text{ZnN}_x\text{-PNC}$, and $\text{ZnN}_x\text{-PNC}$ were between three and four, suggesting a large number of two-electron-transfer pathways in their ORR reactions, generating a large amount of H_2O_2 , thereby resulting in a relatively poor ORR activity. Also, it indicates that the synergistic effect of bimetals reduced the H_2O_2 production rate and accelerated the four-electron-transfer process during the reaction.

The magnitude of the electrochemical double-layer capacitance (C_{dl}) of an electrode is related linearly to the active specific surface area of the catalyst, with a larger C_{dl} resulting in a larger active specific surface area of the catalyst. The CV curves of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ were tested under various scan rates at 1.106–1.175 V (vs. RHE) (Fig. S9, ESI†). At different scan rates, half of the sum of the absolute values of the current densities of the cathode and anode at 1.15 V were taken, and the slopes obtained were plotted and fitted to the C_{dl} of the electrodes of 17.4, 10.6, 9.0, and 8.4 mF cm^{-2} (Fig. 3d). We noticed that the catalytic active sites significantly affected the double-layer capacitance of the catalyst. As the material underwent catalysis, PHNC increased the active specific surface area and the exposure of active sites, thus exhibiting higher catalysis.

Electrochemical impedance spectroscopy (EIS) was next performed focused on the electrical conductivity and charge-transfer kinetics of the electrodes. For the collection of the EIS

spectrum, it was obtained at a potential of -0.15 V, amplitude of 0.005 V, and frequency of 0.005 Hz to 1000 Hz. Fig. 3e shows the EIS measurements of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$, $\text{Fe}_3\text{O}_4/\text{ZnN}_x\text{-PHNC}$, $\text{CuNCs}/\text{ZnN}_x\text{-PNC}$, and $\text{ZnN}_x\text{-PNC}$ fitted to the simulated equivalent circuit diagram based on the shape of the curve. The curves had semicircular and linear parts, so the simulation yielded the main components of the circuit consisting of R_s , R_{ct} , C_{dl} , and W_o , where R_s is the electrolyte internal resistance, which is the sum of the material's internal resistance and the contact resistance between the material and the electrolyte surface, while R_{ct} is the charge-transfer resistance, expressed by the radius of the fitted semicircle. According to the fitted impedance values of the circuit diagram (Table S8, ESI†), $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ had the least resistance and the fastest charge transfer during the charge and material transfers. The accelerated charge transfer could be attributed to the following: (1) the doping of Fe_3O_4 and Cu nanoparticles increased the material's conductivity; (2) the skeletonized nanocage structure accelerated O_2 diffusion, thereby shortening the electron-transport distance; (3) the graphitized carbon and abundant carbon defects after sintering further accelerated the electron transport.⁵⁷

Methanol tolerance and stability are important indicators for evaluating the catalytic activity and reproducibility of materials. Fig. S10a–c (ESI†) show that the current of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ decreased by 2% after adding different molar concentrations of methanol, albeit the current normalized quickly. The curves of Pt/C further indicated that the current did not return to the original current after a 5% drop. Such a high tolerance and stability of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ was mainly attributed to the stable skeletonized nanocages and the increased graphitization. Fig. 3f shows the durability of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C . After 5000 CV cycles, the ultimate



current density decreased by 5% and 6.9% for $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C , respectively. Accordingly, the onset electricity of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C decreased by 6 and 20 mV, respectively, and the half-wave potential depreciated by 8 and 24 mV, respectively. These values proved that the skeletonized nanocage structure and the degree of graphitization in $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ were essential for enhancing the stability.⁵⁸

3.3. Liquid and solid-state Zn–air battery performances of the catalysts

To verify the practical application of the material, we constructed a ZAB with a polished zinc plate as the anode and $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ material-coated nickel foam as the cathode (Fig. 4a). The alkaline electrolyte was 6 M KOH + 0.2 M $\text{Zn}(\text{CH}_3\text{COO})_2$. The $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ assembled cell showed relatively strong stability. The inset in Fig. 4b depicts the actual test of the open-circuit voltage of the cell using a multimeter (OCV = 1.45 V). The multiplier performance of the

battery was tested in the multi-current steps mode. Fig. S11 (ESI†) shows that the voltage changed at the beginning when various current densities were applied. However, the voltage was normal at the same current density, indicating that the material had excellent stability and multiplier performance.⁵⁹

The power densities of the $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C -based ZABs were 162 and 144 mW cm^{-2} , respectively (Fig. 4c). Comparing the power densities suggests that the $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ -based assembled cells were significantly stronger than the Pt/C -based ones in terms of the discharge. The discrepancy could be ascribed to the superior ORR from the $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ catalytic activity.⁶⁰ Fig. 4d illustrates the specific capacities of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ at 5, 10, and 15 mA cm^{-2} as 818, 760, and 721 mA h g^{-1} , respectively. Comparing the specific capacities of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C at a 10 mA cm^{-2} discharge density (Fig. 4e) showed that $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ had superior ORR activity over Pt/C . Further, Fig. 4f depicts a 30 min discharge and 30 min charge cycle test for

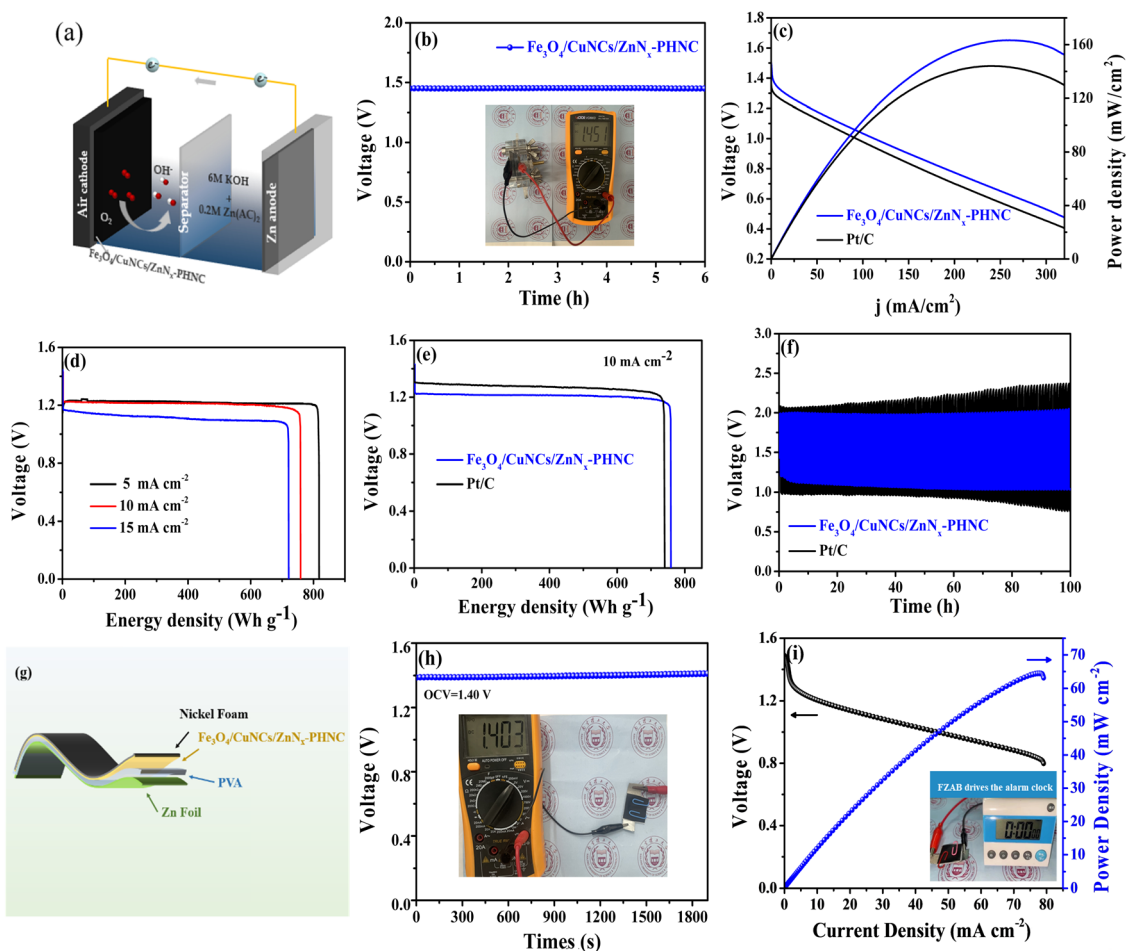


Fig. 4 (a) Schematic of the assembled ZAB; (b) open-circuit voltage of the $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ -based ZAB (inset is the actual measurement using the universal meter). (c) Polarization curves and power density curves of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C -based ZABs. (d) Specific capacity curves of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ -based ZABs at different current densities. (e) Specific capacity curves of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C -based ZABs at a current density of 10 mA cm^{-2} . (f) Charge/discharge curves of $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C -based ZABs at a current density of 10 mA cm^{-2} . (g) Schematic of a FZAB. (h) OCV plots (inset: multimeter measurement picture). (i) Polarization and power density curves (inset: FZAB powering an alarm clock).

$\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ and Pt/C-based catalyst cells at 10 mA cm^{-2} . After 100 h of cycling, the Pt/C-based ZAB showed an unstable charging and discharging voltage plateau, while $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ maintained a stable charging and discharging voltage. Fig. S12a (ESI[†]) shows a stable charge/discharge plateau of the cell for 500 h at a current density of 5 mA cm^{-2} . A stable charge/discharge was also maintained at 15 mA cm^{-2} for up to 200 h (Fig. S12b, ESI[†]). When the current density is too high, the durability of the battery will decrease, and the charging and discharging platforms will increase. Therefore, when the current density reached up to 20 mA cm^{-2} , the charge/discharge test was conducted for 10 min each, and the battery maintained an excellent plateau for 500 cycles (Fig. S12c, ESI[†]). The combined charge/discharge tests at various current densities revealed that the $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ -based battery had excellent stability, mainly due to the skeletonized nanocage structure and abundant active sites of the material.⁶¹ By comparing recent articles (Table S9, ESI[†]), the $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ -based ZABs evinced a relatively impressive performance compared to that of other reported systems.

To further research into the potential of the rechargeable ZABs and their application in the increasingly attractive wearable electronic devices, we assembled FZABs and tested their performance. Among them, a 0.1 mm zinc plate was used as the anode, a PVA gel polymer as the electrolyte, and a nickel foam-loaded $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ as the air cathode (Fig. 4g). After a long-time open-circuit voltage test, we observed that the open-circuit voltage of the assembled FZAB was stable at 1.40 V (Fig. 4h), as proven by the attached multimeter picture. Fig. 4i illustrates that it demonstrated an excellent peak power density of 64.5 mW cm^{-2} . To ascertain its practical usability, despite the adequate data support, we assembled a battery-driven LED electronic screen alarm clock. Here, we found that it could be used seamlessly, showing its future commercial prospects and practical applicability (video 1, ESI[†]).

4. Conclusions

A heterogeneous skeletonized nanocage catalyst $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ loaded with bimetals was prepared by stirring at room temperature and annealing at high temperature with NaCl and KCl as protectants and stripping agents, respectively. The rich active sites produced by the synergistic action of various metals and hollow nanostructures enabled the catalysts to show excellent ORR performance. When the prepared materials were used as liquid ZAB cathode catalysts, the ZABs exhibited excellent performance with a high OCV (1.45 V) and peak power density (162 mW cm^{-2}). In addition, the ultrahigh specific capacity (760 mA h g^{-2}) at a 10 mA cm^{-2} current density was far superior to that of the benchmark Pt/C-based catalyst. In addition, the $\text{Fe}_3\text{O}_4/\text{CuNCs}/\text{ZnN}_x\text{-PHNC}$ -based ZAB could be charged and discharged for more than 500 h at a 5 mA cm^{-2} current density, thus demonstrating high stability and high cycling performance. The excellent performance of the assembled FZABs also proved their practical application potential as wearable flexible batteries.

Overall, this study provides a feasible way to prepare efficient catalysts for ZAB cathodes to replace noble metal catalysts in practical applications.

Data availability

The data supporting this article have been included as part of the ESI[†] and in the Experimental section of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

The Jiangsu Provincial Key Research and Development Program (BE2023820, BE2021720), Qinglan Project of Jiangsu Province of China, State Key Laboratory of Pollution Control and Resource Reuse Foundation (PCRRF19032) are greatly acknowledged.

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