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Ionic Exchange of Metal–Organic Frameworks for Constructing Unsaturated Copper Single Atom Catalysts for Boosting Oxygen Reduction Reaction

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Keywords: single atom, copper, unsaturated coordination, oxygen reduction reaction

Regulating the coordination environment of atomically dispersed catalysts is vital for catalytic reaction but still remains challenge. Herein, an ionic exchange strategy has been developed to fabricate atomically dispersed copper catalysts with controllable coordination structure. In this process, the adsorbed Cu ions exchange with Zn nodes in ZIF-8 under high temperature, resulting in the trapping of Cu atoms within the cavities of the MOF and thus forming Cu single atom catalysts. More importantly, altering pyrolysis temperature can effectively control the structure of active metal center at atomic level. Specifically, higher treatment temperature (900 °C) leads to unsaturated copper-nitrogen architecture (Cu-N₃ moieties) in atomically dispersed Cu catalysts. Electrochemical test indicates atomically dispersed Cu catalysts with Cu-N₃ moieties possess superior ORR performance than that with higher copper-nitrogen coordination number (Cu-N₄ moieties), with a higher half-wave potential of 180 mV and the 10 times turnover frequency than that of CuN₄. DFT calculation analysis further shows that the low N coordination number of Cu single atom catalysts (Cu-N₃) is favorable to the formation of O₂* intermediate and thus boosts the oxygen reduction reaction.

Searching for platinum free catalysts to overcome the sluggish kinetics of oxygen reduction reaction (ORR) at the cathode was the key to realize large-scale application of metal-air batteries and proton-exchange membrane fuel cells.^[1-6] Owing to their cost-effective and high-performance, transition metals single atom with N-doped carbon materials (M SAs/NC) were recognized as one of the most promising candidates.^[7-15] The local coordination environment of M SAs/NC generally played a significant role for the catalytic activity and selectivity.^[4, 16-19] However, precisely regulating the coordination environment of active center in M SAs/NC still **remains challenges** due to the high mobility and instability of highly dispersed single metal atoms.

Copper metalloenzymes with unsaturated Cu-N centers **have** been demonstrated to efficiently active oxygen molecular at low overpotentials.^[20, 21] Recently, CuN₃ moieties supported on carbon matrix was also reported as efficient ORR catalysts, further corroborating the high ORR activity for unsaturated Cu-N centers with charge density asymmetry.^[22] **And, copper single atom ORR catalysts have attracted much attention.**^[22-27] However, the rational design and efficient construction of atomically dispersed Cu catalysts with unsaturated centers remained imperative and challenging. In this work, we adopt an ionic exchange method to construct unsaturated copper single atom catalysts. Under high temperature, the adsorbed copper ion was trapped in the defective sites derived from the volatile Zn nodes in ZIF-8, thus forming Cu single atom catalysts.^[28] Altering the treatment temperature could effectively regulate the coordination structure of Cu sites in atomic level. For example, the CuN₃ and CuN₄ coordination structures were prepared at 900 and 800 °C, respectively. The corresponding material was labelled as Cu SAs/NC-900 and Cu SAs/NC-800, respectively. Moreover, Cu SAs/NC-900 with unsaturated Cu-N₃ moieties exhibited exceptional ORR activity and superior Zn-air battery performance.

As shown in Figure S1, ZIF-8 exhibited a rhombododecahedral shape with a smooth surface. Most of the particle size was about 200 nm. Cu SAs/NC-800 and Cu SAs/NC-900 maintained the rhombododecahedral shape with a smaller particle size of about 100 nm (Figure S2), probably due to the thermal shrinkage of ZIF-8, which could be also observed in pyrolyzed ZIF-8 (NC-900) (Figure S3). Notably, more pores architecture could be observed in Cu SAs/NC-900 than in Cu SAs/NC-800. This might be attributed to the higher pyrolysis temperature, which induced the volatilization of more proposed CN_x fragment.^[29] Figure S4 showed the N_2 -sorption isotherms, and the detailed sorption data were collected in Table S1. ZIF-8 showed a BET surface area of $1184 \text{ m}^2 \text{ g}^{-1}$. After pyrolysis, the BET surface area was decreased to $673 \text{ m}^2 \text{ g}^{-1}$ for Cu SAs/NC-800 and $733 \text{ m}^2 \text{ g}^{-1}$ for Cu SAs/NC-900.

Figure 1 showed the high-angle annular dark-field transmission electron microscope (HAADF-TEM) images of Cu SAs/NC materials coupled with electron energy loss spectroscopy (EELS). It could be observed that Cu and N were homogeneously dispersed over Cu SAs/NC-800 (Figure 1A) and Cu SAs/NC-900 (Figure 1C). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Cu SAs/NC-800 (Figure 1B) and Cu SAs/NC-900 (Figure 1D) further revealed that copper was atomically dispersed. The size of bright spots in both Cu SAs/NC-800 and Cu SAs/NC-900 were about $1.24 \text{ \AA}$, according to the corresponding intensity profiles (Figure 1, Figure S5 and Figure S6), in line with the reported size of single copper sites.^[23]

In the powder X-ray diffraction (XRD) patterns, only one broad peak in the ranges of $20\text{--}30^\circ$ could be observed (Figure S7), corresponding to the (002) planes of carbon.^[18] No Cu characteristic peaks could be observed in Cu SAs/NC materials, indicating the poor crystallinity of copper. Figure S8 showed the survey scan X-ray photoelectron spectroscopy (XPS) spectra of Cu SAs/NC materials. The proportion of copper was nearly identical for Cu SAs/NC-800 and Cu SAs/NC-900, in agreement with the result of ICP-OES (Table S1). **Figure 2** showed the corresponding C 1s, N 1s and Cu 2p XPS spectra of Cu SAs/NC

materials. The peaks at 284.4, 285.6 and 287.8 eV in the C 1s spectrum (Figure 2A) could be assigned to C-C, C=N and C-N, respectively.^[22, 23] Four peaks at 398.3, 399.8, 400.9, and 402.3 eV were corresponding to pyridinic-N, pyrrolic-N, graphitic-N, and oxide-N, respectively (Figure 2B).^[15] The Cu 2p_{3/2} peak for both Cu SAs/NC-800 and Cu SAs/NC-900 was situated at around 933 eV (Figure 2C), which located between Cu⁰ and Cu²⁺, and was similar to the reported value for atomically dispersed Cu-N-C material.^[23] It should be noticed that the Cu 2p_{3/2} peak for Cu SAs/NC-900 seemed slightly more negative compared with Cu SAs/NC-800.

X-ray absorption fine structure (XAFS) spectroscopy was used to clarify the detailed structural information of copper atoms. Cu k-edge XANES spectra of Cu foil, CuO and Cu SAs/NC materials (Figure 2D) revealed that the adsorption edge of Cu SAs/NC materials was between copper foil and CuO, revealing the partial positive charge of copper atoms in Cu SAs/NC materials. Moreover, the white-line intensity of Cu SAs/NC-900 was lower than that of Cu SAs/NC-800, revealing the lower valence state of copper atoms for Cu SAs/NC-900, which confirmed the XPS results. The EXAFS spectrum (Figure 2E) revealed that copper atoms in Cu SAs/NC-800 and Cu SAs/NC-900 formed isolated Cu-N coordination structure. This was because that the main peak was situated at about 1.48 Å, corresponding to the Cu-N coordination.^[23, 24] Furthermore, no peak at 2.2 Å was detected, which was corresponding to the Cu-Cu coordination. In comparison, the interatomic distance of Cu-N and the intensity of the main peak in Cu SAs/NC-900 were reduced compared with that of Cu SAs/NC-800, suggesting the lower coordination number for Cu SAs/NC-900. The EXAFS spectrum of Cu SAs/NC-800 and Cu SAs/NC-900 was further fitted by possible Cu-N coordination structures. As a result, the spectrum of Cu SAs/NC-800 and Cu SAs/NC-900 was well fitted by CuN₄ and CuN₃ coordination structure, respectively (Figure 2F). Table S2 showed the phase corrected interatomic distance of Cu-N for Cu SAs/NC-800 (1.98 Å) and Cu SAs/NC-900 (1.96 Å), which was consistent with the reported value for CuN₄ (1.98 Å)^[23] and CuN₃ (1.95

Å) ^[22]. Such a phenomenon was also observed in the study of atomically dispersed Ni-N-C materials, in which the interatomic distance of Ni-N for NiN₃ was slightly decreased compared with NiN₄. ^[18] Under higher temperature, we supposed that partial of nitrogen was removed, resulting in the formation of Cu SAs/NC with CuN₃ moieties (Figure 2G). In this case, the valence state of copper atoms was slightly decreased, due to the loss of one nitrogen coordination.

The ORR performance of Cu SAs/NC-800, Cu SAs/NC-900 and references was firstly evaluated through linear sweep voltammetry (LSV) technology in 0.1 M KOH at O₂ saturated condition (**Figure 3**). The NC reference catalysts exhibited extremely poor activity compared with Cu SAs/NC materials (Figure 3A and Figure S9), which showed the ORR activity **mainly** stemmed from Cu metal sites rather than NC supports **and other elements**. Moreover, Cu SAs/NC-900 exhibited much better activity than Cu SAs/NC-800, the half-wave potential ($E_{1/2}$) and the onset potential of Cu SAs/NC-900 was much higher than that of Cu SAs/NC-800. The detailed data were collected in Figure 3B. The half-wave potential of Cu SAs/NC-900 was measured at 0.87 V, 180 mV higher than that of Cu SAs/NC-800. At 0.9 V, Cu SAs/NC-900 displayed a kinetic current density (J_k) at 2.74 mA cm⁻², which was significantly higher than Cu SAs/NC-800 (0.21 mA cm⁻²). As shown in Figure 3C, Cu SAs/NC-900 exhibited a lower Tafel slope (79 mV dec⁻¹) than Cu SAs/NC-800 (122 mV dec⁻¹), further demonstrated the much higher activity of Cu SAs/NC-900 than Cu SAs/NC-800. Figure S10 showed the polarization curves of Cu SAs/NC-900 at various rotation rates and the Koutecky–Levich (K-L) plots, in which the electron transfer number (n) was calculated at 3.91. The rotating ring-disk electrode (RRDE) test confirmed the near 4-electron ORR pathway for Cu SAs/NC materials (Figure 3D). The turnover frequency (TOF) of SAs/NC-900 at 0.9 V was calculated at 0.16 Hz, which was more than 10 times as that of Cu SAs/NC-800 (0.015 Hz). These results above provided strong evidence that unsaturated copper single atom catalysts possessed better oxygen reduction reaction activity than Cu SACs with CuN₄ moieties.

Importantly, the ORR activity of Cu SAs/NC-900 also outperformed the commercial Pt/C (Figure 3A-C) and most of the reported high-performance noble metal-free ORR catalysts (Table S3).

The electrochemical stability of Cu SAs/NC-900 was tested based on the electrochemical accelerated durability test (EADT) and chronoamperometry. After the 5000 cycles of EADT (Figure S11), no significant activity decay could be observed in $E_{1/2}$. In the long-term stability test at 0.65 V (Figure S12), Cu SAs/NC-900 lost 7 % of the original current after 10000 s, while around 40 % attenuation of the original current could be observed for Pt/C. These results revealed the strong electrochemical stability of Cu SAs/NC-900 in alkaline media, which could be attributed to the stable Cu-N₃ coordination structure. The HAAD-STEM confirmed that copper atoms in Cu SAs/NC-900 could remain atomically dispersed after the durability test (Figure S13). The EXAFS results further revealed that the Cu-N coordination structure was not modified after test (Figure S14). Furthermore, a zinc-air (Zn-air) battery test was carried out using the zinc foil as the anode and Cu SAs/NC-900 coated carbon paper as the air cathode. The specific capacity of Cu SAs/NC-900 based Zn-air battery was 712 mAh g⁻¹ at the discharge of 50 mA cm⁻² (Figure 3E), which was superior to the Pt/C based Zn-air battery (608 mAh g⁻¹). In addition, Figure 3F shows the discharge polarization and the corresponding power density plots of Cu SAs/NC-900 and Pt/C based Zn-air battery. The maximum power density of Cu SAs/NC-900 based Zn-air battery was 242 mW cm⁻², higher than that of the Pt/C-based Zn-air battery (192 mW cm⁻²) and most of the reported catalysts (Table S4), again verifying the excellent activity of Cu SAs/NC-900 in ORR.

The significant different ORR activity of Cu SAs/NC-900 and Cu SAs/NC-800 should be mainly attributed to the different nature of CuN₃ and CuN₄. Therefore, the free energy diagrams of CuN₃ and CuN₄ in ORR processes were calculated at different overpotentials (Figure 4). Figure 4A and Figure 4C showed the optimized structure of the models, adsorbed OOH, O and OH, over the proposed CuN₄ and CuN₃, respectively. For CuN₄, all reaction

procedures were thermodynamically downslope, except the O₂ adsorption step (Figure 4B), suggesting that the O₂ adsorption was the rate-determining step for the oxygen reduction on CuN₄, in agreement with previous reports [24]. Despite similar tendency was observed over CuN₃, the O₂ adsorption upslope for CuN₃ (0.17 eV, Figure 4D) was much weaker than that of CuN₄ (0.87 eV), demonstrating the origin of the high ORR activity for Cu SAs/NC-900. In addition, the O₂ adsorption upslope for NC materials and the OH* formation upslope for Pt (111) surface in alkaline solution was about 2.1 and 0.65 eV, respectively. [24, 30] These results well fitted our experimental findings.

In summary, an ionic exchange strategy was developed to fabricate atomically dispersed Cu-N-C material with unsaturated Cu-N centers (Cu-N₃ moieties). Electrochemical test indicated that atomically dispersed Cu-N-C material with Cu-N₃ moieties possess superior ORR performance than atomically dispersed Cu-N-C material with Cu-N₄ moieties, with a higher half-wave potential of 180 mV and the 10 times turnover frequency than that with CuN₄ moieties. It was well known that the addition of one N coordinated to the axial direction of MN₄ would result in a higher activity. Our result revealed that decreasing the N coordination number of active center could also lead to a greatly enhanced activity, which provides significant inspiration on design and preparing high-performance single atom catalysts.

Experimental Section

Preparation of Cu SAs/NC materials. 100 mg ZIF-8 was dispersed in 10 ml n-hexane under ultrasound at room temperature until homogeneous solution was formed. Then, 50 μ l of 100 mg ml⁻¹ Cu (NO₃)₂ aqueous solution was added into the mixed solution slowly under ultrasound at room temperature. Next, the mixed solution was under stirring for 6 h at room temperature, centrifuged and dried in vacuum at 80 °C. Then, the obtained powder was ground and calcined at 800 °C and 900 °C for 1 h in argon atmosphere, labelled as Cu

SAs/NC-800 and Cu SAs/NC-900, respectively. The commercial Pt/C catalyst and the pyrolyzed ZIF-8 (calcined at 800 °C and 900 °C for 1 h in argon atmosphere, labelled as NC-800 and NC-900, respectively) were used as references.

Details for Characterizations, Electrochemical tests and DFT calculation are presented in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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Figure 1. Characterization of Cu SAs/NC. HAADF-TEM imaging of Cu SAs/NC-800 (A) and Cu SAs/NC-900 (C) coupled with electron energy loss spectroscopy; HAADF-STEM image of Cu SAs/NC-800 (B) and Cu SAs/NC-900 (D), the inset showed corresponding intensity profiles.

Figure 2. Chemical state, coordination information and preparation mechanism of Cu SAs/NC. C 1s (A), N 1s (B) and Cu 2p (C) XPS spectra of Cu SAs/NC-800 and Cu SAs/NC-900; (D) Cu K edge XANES spectra of Cu SAs/NC and the reference samples; (E) K³-weighted $\chi(k)$ function of EXAFS spectra for Cu SAs/NC and the reference samples. the Cu foil and CuO data were transformed by 0.3 and 0.7, respectively; (F) EXAFS fitting curve for Cu SAs/NC-800 and Cu SAs/NC-900, respectively. Inset showed the proposed CuN₃ and CuN₄ coordination environment, respectively; (G) Supposed formation mechanism of CuN₃ and CuN₄.

Figure 3. Electrochemical evaluation of Cu SAs/NC. (A) Polarization curve for Cu SAs/NC-800, Cu SAs/NC-900 and the reference samples; (B) Half-wave potentials ($E_{1/2}$) and kinetic currents (J_k , at 0.9 V) of Cu SAs/NC and Pt/C; (C) Corresponding Tafel plots of various samples; (D) Electron transfer number (n , bottom) and H_2O_2 yield (top) versus potential; (E) Specific capacities of Cu SAs/NC-900 and Pt/C based Zn-air battery; (F) Discharge polarization and corresponding power density plots of Cu SAs/NC-900 and Pt/C based Zn-air battery.

Figure 4. Theoretical study. View of the model, adsorbed OOH, O and OH, respectively, over the CuN₄ model (A) and CuN₃ model (C). Gray, blue, orange, red and white represent C, N, Cu, O and H atoms, respectively. Free energy diagrams for ORR process on CuN₄ (B) and CuN₃ (D) at different overpotentials.

An ionic exchange strategy is developed to fabricate atomically dispersed Cu-N-C material with unsaturated Cu-N centers (Cu-N₃ moieties), which possess a higher half-wave potential of 180 mV and the 10 times turnover frequency than that with Cu-N₄ moieties in the ORR test. Furthermore, the optimum Cu-N₃ catalyst demonstrates a better performance in ORR and zinc-air batteries compared with commercial Pt/C.

Keyword: single atom, copper, unsaturated coordination, oxygen reduction reaction

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Supporting Information

Ionic Exchange of Metal–Organic Frameworks for Constructing Unsaturated Copper Single Atom Catalysts for Boosting Oxygen Reduction Reaction

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Material characterizations. X-ray diffraction patterns were performed on Bruker D8 ADVANCE diffractometer with Cu K α radiation ($\lambda=0.15418$ nm). High-resolution TEM testing was carried out using a FEI Tecnai G2 F20 S-TWIN. HAADF-STEM images and corresponding EELS were obtained on a JEOL JEMARM200F TEM/STEM system. XPS measurements were performed on a PHI-5400 photoelectron spectrometer. N₂ isotherms was obtained on Micrometrics ASAP 2020. Elemental analysis of copper in the solid samples was detected by ICP-OES (Optima 7300 DV). XAFS spectra at the copper K edge were collected at the Beijing Synchrotron Radiation Facility in China.

Electrochemical tests. Electrochemical measurements were carried out on an electrochemical workstation (CHI 760E) with 5 mm diameter glassy carbon rotating-disk electrode (RDE), Ag/AgCl reference electrode and graphite rod counter electrode.

The catalyst ink was prepared by mixing 1 mg catalyst with 480 μ l ethanol, 480 μ l H₂O and 40 μ l 5% Nafion solution under ultrasonic. And, the working electrode was prepared by coating 5 μ l catalyst ink on glassy carbon RDE for 4 times.

The TOF values were obtained based on the equation:

$$\text{TOF} = \frac{J \times a}{4 \times m \times F}$$

where J represents the current density measured at 0.9 V, a is the surface area of the glassy carbon disk electrode (0.196 cm²), 4 is the number of electrons transferred during O₂

reduction, m is the mole number of copper single sites on the electrode, and F is the Faraday constant (96485 C mol^{-1}).

The RDE measurement was performed at a sweep rate of 10 mV s^{-1} with different rotating speeds (900 to 2500 r.p.m.). The electron transfer number (n) and kinetic current density (J_K) were obtained according to the Koutecky–Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{J_K}$$

$$B = 0.62nFC_0D_0^{\frac{2}{3}}V^{-\frac{1}{6}}$$

where J is the current density measured from the ORR, J_K is the kinetic current density, J_L is the limiting current density, ω represents the angular velocity of the disk, C_0 is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_0 is the diffusion coefficient of O_2 in 0.1 M KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and V is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$). The accelerated durability test of Cu SAs/NC-900 were performed by applying potential cycling between 1.0 and 0.6 V versus RHE for 5000 cycles (O_2 saturated 0.1 M KOH, 50 mV s^{-1} , room temperature).

The rotating ring-disk electrode (RRDE) test was carried out using high potential (1.2 V vs RHE) on the ring electrode, and the disk electrode was scanned negative (10 mV s^{-1}). The hydrogen peroxide yield (H_2O_2 (%)) and electron transfer number (n) was calculated based on the following equations:

$$H_2O_2(\%) = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}}$$

$$n = 4 \times \frac{I_d}{I_d + \frac{I_r}{N}}$$

where I_d is the disk current, I_r is the ring current and $N = 0.4$ is the current collection efficiency of the platinum ring.

The Zn-air battery was assembled in a two-electrode configuration. The air cathode was prepared by dispersing the as-prepared catalyst ink onto teflon-coated carbon fiber paper (1.0 mg cm^{-2}), and drying at 60°C for 2 h. The polished 1 cm^2 commercial Zn foil with a thickness of 0.2 mm was used as anode. The electrolyte was composed of 6 M KOH and saturated with O_2 . The battery performance was tested on the as-constructed cell at room temperature with CHI 760E electrochemical workstation.

DFT calculation. The calculation was carried out by first-principles based on density functional theory (DFT) with the Vienna ab initio package (VASP), and the pseudopotential by the projector-augmented wave (PAW) and the Perdew-Burke-Ernzerhof (PBE) has been used. In our work, the cut-off energy has been set to 400 eV and the Brillouin zone has been used with a $3 \times 3 \times 1$ Γ -centered k-mesh for surface structure.

Figure S1. TEM images of ZIF-8.

Figure S2. TEM images of Cu SAs/NC-800 (A) and Cu SAs/NC-900 (B).

Figure S3. TEM images of NC-900.

Figure S4. The N₂ isotherms of various samples.

Figure S5. HAADF-STEM image of Cu SAs/NC-800 and the corresponding intensity profiles.

Figure S6. HAADF-STEM image of Cu SAs/NC-900 and the corresponding intensity profiles.

Figure S7. XRD patterns of various samples. Inset showed the position of face centered cubic Cu PDF#04-0836.

Figure S8. XPS spectra for the survey scan of Cu SAs/NC-900 (A) and Cu SAs/NC-800 (B).

Figure S9. Polarization curve of NC-800 and NC-900.

Figure S10. Polarization curves of Cu SAs/NC-900 at different rotation rates. Inset: Koutecky–Levich plots and the obtained electron transfer number.

Figure S11. Polarization curves of Cu SAs/NC-900 before and after 5000 cycles of accelerated durability test.

Figure S12. Chronoamperometric response of Cu SAs/NC-900 and Pt/C in 0.1 M KOH solution (oxygen saturated) at 0.65 V.

Figure S13. HAADF-STEM image of Cu SAs/NC-900 after durability test and the corresponding intensity profiles.

Figure S14. K³-weighted $\chi(k)$ function of the EXAFS spectra of Cu SAs/NC-900 before and after durability test.

Table S1. Textual properties and chemical composition.

Sample	Cu (wt%) ^{a)}	BET surface area (m ² g ⁻¹) ^{b)}
ZIF-8	-	1184
NC-800	-	697
NC-900	-	774
Cu SAs/NC-800	2.1	673
Cu SAs/NC-900	1.9	733

^{a)} ICP-OES; ^{b)} Brunauer–Emmett–Teller

Table S2. Structural parameters extracted from the Cu K-edge EXAFS fitting.

Sample	Scattering pair	CN	R [Å]	σ^2 [Å ²]	ΔE_0 [eV]	R factor
Cu SAs/NC-800	Cu-N/C	4.1	1.98	0.00419	-4.36814	0.00803
Cu SAs/NC-900	Cu-N/C	3.0	1.96	0.00308	-3.88223	0.00864

CN, coordination number; R, interatomic distance; σ^2 , Debye-Waller factor; ΔE_0 , edge-energy shift; R factor is used to value the goodness of the fitting.

Table S3. Comparison of the ORR activity between Cu SAs/NC-900 and other noble metal free catalysts under alkaline condition (0.1 M KOH) in literature.

Sample	$E_{1/2}$ (V vs RHE)	TOF (Hz)	n	Reference
Cu SAs/NC-900	0.87	0.16	3.91	This work
FeN _x /C	0.82	-	-	J. Am. Chem. Soc. 2014, 136, 10882.
W ₂ N/WC	0.83		3.92	Adv. Mater. 2019, 1905679.
Fe single atoms	0.92	0.16	3.8	Small 2018, 14, 1704282.
Fe-N/C-800	0.81		3.96	J. Am. Chem. Soc. 2014, 136, 11027.
(Fe-P) _n MOF	0.81	0.1	3.82	J. Am. Chem. Soc. 2012, 134, 6707.
Co-N/CNFs	0.82		3.4	ACS. Catal. 2017, 7, 6864.
CoZn-NC-700	0.82		3.67	ACS Appl. Mater. Interfaces. 2017, 9, 12574.
pCNT@Fe _{1.5} @GL	0.81	0.24	3.96	Adv. Mater. 2017, 29, 1606534.
Co SAs/N-C(900)	0.88	0.14	3.98	Angew. Chem. Int. Ed. 2016, 55, 10800.
NC@Co-NGC	0.82		3.9	Adv. Mater. 2017, 27, 1700874.
Fe SAs/N-C	0.9	0.1	3.9	Angew. Chem. Int. Ed. 2017, 56, 6937.
CoP-CMP	0.81		3.94	Adv. Mater. 2014, 26, 1450.
Cu-N-C	0.869		3.97	Energy Environ. Sci. 2018, 11, 2263.
Cu-N@C	0.8		3.96	Energy Environ. Sci. 2016, 9, 3736.
Cu ISAS/NC	0.92		3.99	Nat. Commun. 2019, 10, 3734.
CoO _x NPs/BNG	0.805		4.0	Angew. Chem. Int. Ed. 2017, 56, 7121.
FeN ₄ -GN	0.86		3.99	Nano Energy 2017, 32, 353.
LDH@ZIF-67-800	0.83		4.0	Adv. Mater. 2016, 28, 2337.
NCNTFs	0.87		3.97	Nature Energy 2016, 1, 15006.
Cu-SA/SNC	0.893		4.0	Energy Environ. Sci. 2019, 12, 3508

Table S4. Comparison of the peak power density of Cu SAs/NC-900 based Zn-air battery and other reported Zn-air batteries in literature.

Sample	Loading (mg cm ⁻²)	Peak power density (mW cm ⁻²)	Reference
Cu SAs/NC-900	1	242	This work
Cu-N@C	0.4	210	Energy Environ. Sci. 2016, 9, 3736.
W ₂ N/WC	0.6	172	Adv. Mater. 2019, 1905679.
Fe@N-C-700	2.2	220	Nano Energy 2015, 13, 387.
Mn ₃ O ₄ /graphene	2	120	Energy Environ. Sci. 2011, 4, 4148.
Fe SAs/N-G	1	275	Adv. Mater. 2019, 1904496.
CuPt-NC	2	251	ACS Catal. 2015, 5, 1445.
Fe-N-MC	1.2	190	Nano Energy 2016, 26, 131.
Co-doped TiO ₂	2	136	J. Mater. Chem. A 2016, 4, 7841.
Co ₃ O ₄ -SP/NGr	1	190	ACS Appl. Mater. Interfaces 2015, 7, 21138.
Cu ISAS/NC	1	280	Nat. Commun. 2019, 10, 3734.
N-CNT	0.2	70	Electrochim. Acta 2011, 56, 5080.
Co ₄ N/CNW/CC	1	174	J. Am. Chem. Soc. 2016, 138, 10226.
FeCo-N-C	1.5	232	J. Power Sources 2011, 196, 3673.
Cu-SA/SNC	1	220	Energy Environ. Sci. 2019, 12, 3508
Cu SAC	2	196	J. Mater. Chem. A 2019, 7, 16690