Engineering unsymmetrically coordinated Cu-S$_1$N$_3$ single atom sites with enhanced oxygen reduction activity

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Atomic interface regulation is thought to be an efficient method to adjust the performance of single atom catalysts. Herein, a practical strategy was reported to rationally design single copper atoms coordinated with both sulfur and nitrogen atoms in metal-organic framework derived hierarchically porous carbon (S-Cu-ISA/SNC). The atomic interface configuration of the copper site in S-Cu-ISA/SNC is detected to be an unsymmetrically arranged Cu-S$_1$N$_3$ moiety. The catalyst exhibits excellent oxygen reduction reaction activity with a half-wave potential of 0.918 V vs. RHE. Additionally, through in situ X-ray absorption fine structure tests, we discover that the low-valent Cuprous-S$_1$N$_3$ moiety acts as an active center during the oxygen reduction process. Our discovery provides a universal scheme for the controllable synthesis and performance regulation of single metal atom catalysts toward energy applications.

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The developing of advanced fuel cells and metal-air batteries equipped with oxygen electrodes provides new opportunities for the applications of future sustainable energy\(^1\)-\(^3\). To realize energy conversion with highly efficiency, it’s crucial to improve the oxygen reduction reaction (ORR) procedure, among these electrochemical devices\(^4\)-\(^6\). Currently platinum-based materials have been widely used for ORR, but are unfortunately precluded by their rarity and high price\(^6\). Although the newly developed catalysts with earth-abundant elements exhibit some fancy properties, the overall performance including activity and durability is still far from satisfactory\(^7\)-\(^10\). Hence, the rational design of ideal oxygen electrode materials with low-cost but high activity and good stability under applied conditions remains a formidable challenge.

Due to the high atomic utilization, single atom catalysts have gained great attention in heterogeneous catalysis, and significantly, they provide new horizons for the discovery of innovative materials to energy applications\(^11\)-\(^20\). Especially both the theoretical and experimental explorations have suggested that isolated single metal-N\(_x\) (M-N\(_x\)) modified carbon-based materials can serve as desirable oxygen electrocatalysts with promising performance\(^21\)-\(^29\). Particularly, density functional theory (DFT) calculations demonstrate the standard symmetrical planar four-coordinated structure (denoted as M-N\(_x\)) might serve as the most favorable catalytic site for M-N\(_x\) catalysts, seemingly supported by plenty of experimental results\(^30\)-\(^33\). But some recent researches also point out that for the M-N\(_x\) moiety, the large electronegativity of the symmetrical neighboring nitrogen atoms around the metal site would result in unsuitable free energy for adsorption the intermediate products\(^34\),\(^35\). Obviously, the non-adsorption of the ORR intermediates badly decreases the kinetic activity and hampers the performance. As a solution to overcome the obstacles, the adsorption strength of ORR intermediates in the active sites could be modified by adjusting the interface configuration of the central metal atoms to reduce the potential barriers, which results in boosted catalytic activity\(^26\),\(^36\),\(^37\). Due to the comparative weak electronegativity, sulfur-permeating species worked as active sites for ORR. Furthermore, this strategy of atomic interface engineering could be used to other metals (Mn, Fe, Co, Ni, etc.).

**Results**

**Synthesis and morphology characterizations of S-Cu-ISA/SNC.** The sample was prepared through a three-step process (Supplementary Fig. 1). In step one, zeolitic imidazolate frameworks (ZIF-8) were adopted as molecular-scale cages to absorb and encapsulate the copper precursor. Typically, Cu(acac)\(_2\) was mixed with the precursors of ZIF-8 (Zn\(_2\)\(^{2+}\) and 2-methylimidazole), and through a self-assembly process, Cu(acac)\(_2\) were committed to the ZIF-8 cages (Cu-ZIF-8). In the second step, Cu-ZIF-8 and sulfur powder were jointly dispersed in carbon tetrachloride (CCl\(_4\)) and then dried by stirring, ensuring the sulfur was absorbed on the surface of Cu-ZIF-8 powder (labeled as S-Cu-ZIF-8, Supplementary Figs. 2 and 3). In the final step, S-Cu-ISA/SNC was obtained after the pyrolyzation of the S-Cu-ZIF-8 at 950 °C under Ar atmosphere. It was necessary to noted that the formed metallic zinc was evaporated (>907 °C) and meanwhile sulfur permeated in the ZIF-8 frameworks during pyrolysis\(^47\),\(^48\). Cu-ISA/SNC (S was separated from Cu), Cu-ISA/NC (S free), SNC (S, N co-modified carbon) and NC (N-modified carbon) were also prepared as comparison.

The synthetic samples were characterized by Powder X-ray diffraction (PXRD) patterns and Raman spectra (Supplementary Fig. 4). The results indicated that the ZIF-8 derived carbon frameworks were poorly crystallized after pyrolysis and also implied that plenty of defects existed in the carbon substrate, which was favorable for the anchoring of isolated metal atoms\(^49\). The morphology of S-Cu-ISA/SNC was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 1a showed that S-Cu-ISA/SNC roughly remained the polyhedral shape, but the surfaces became extremely bumpy. The TEM images (Fig. 1b and Supplementary Fig. 5a) indicated that the obtained sample possessed a highly open porous structure, meanwhile small Cu particles were not detected. The high-resolution transmission electron microscopy image (HRTEM) in Supplementary Fig. 5b told us that graphite carbon layers existed in the porous frameworks, which were beneficial for promoting the conductivity\(^50\). N\(_2\) adsorption-desorption isotherms (Supplementary Fig. 6) demonstrated the fairly high specific surface area and the hierarchically porous characteristics of S-Cu-ISA/SNC. Our further in-situ environmental microscopic studies (Supplementary Figs. 7, 8, Supplementary Note 1 and Supplementary Movies 1-2) suggested that the permutation of sulfur played an important role for etching the carbon frameworks. The hierarchically porous architecture could facilitate the charge and mass transportation for electrochemical reactions\(^51\). Energy-dispersive X-ray spectroscopy (EDS) (Fig. 1c and Supplementary Fig. 9) in the scanning transmission electron microscope (STEM) indicated Cu, S and N on the support were distributed uniformly. The Cu content in S-Cu-ISA/SNC was 0.73 at%, according to the ICP-OES results. The monodispersion of Cu could be directly monitored by spherical aberration STEM (Fig. 1d, e and Supplementary Fig. 10). The Cu atoms were confirmed by isolated bright dots in the high-magnification HAADF-STEM image. The sizes of dots were below 2.0 Å as shown in Supplementary Fig. 11. As elucidated in Fig. 1f, the distance between Cu atoms was more than 0.38 nm, which
confirmed that Cu existed in isolated feature in S-Cu-ISA/SNC. Furthermore, the SEM, TEM and HAADF-STEM characterizations of NC, SNC, Cu-ISA/NC and Cu-ISA/SNC were also exhibited, respectively (Supplementary Figs. 12-15). We found that all the S-added samples (S-Cu-ISA/SNC, Cu-ISA/SNC and SNC) displayed etched porous feature, compared to those without sulfur participation (Cu-ISA/NC and NC). Additionally, the Zn content in S-Cu-ISA/SNC was as low as 0.028 at% according to the ICP-OES analysis, which excluded the possible influence to catalytic performance by the residue Zn species52.

Chemical state and atomic structure analysis of S-Cu-ISA/SNC. To probe the electronic and atomic interplay of Cu, S, N and C in S-Cu-ISA/SNC, synchrotron-radiation-based soft XANES was carried out (Supplementary Note 2)53. The L3 edge and L2 edge of Cu XANES in S-Cu-ISA/SNC located at 931.2 eV and 950.9 eV (Fig. 2a). The L-edge position of S-Cu-ISA/SNC was between those of CuPc and CuS, implying the possible formation of Cu-S coordination. Furthermore, there was no related peak (Supplementary Figs. 21 and 22), which indicated the formation of Cu-S bonding. Additionally, the sulfur in S-Cu-ISA/SNC was slightly positive charge, which might be attributed to the existence of S-N coordination, since N had higher electronegativity than S, as well as the existence of C-SOx species in the sample. The S K-edge EXAFS for S-Cu-ISA/SNC demonstrated the presence of S/C/N and S-Cu bonding, with FT peaks located at 1.3 Å and 2.1 Å, respectively (Supplementary Fig. 19).

X-ray absorption fine structure (XAFS) was carried out to gain insight into the interface structure at atomic scale. The position of the Cu K-edge absorption threshold was the reflection of average oxidation state of Cu species37,58. As illustrated in Fig. 2d, the edge position of S-Cu-ISA/SNC was between CuS and CuPc, demonstrating the average oxidation state of Cu was between the two references. In supplementary Fig. 20, the fitted oxidation state of Cu in S-Cu-ISA/SNC from K-edge XANES spectra was 1.97, agreeing well with XPS and soft L-edge XANES analysis. The Fourier transform (FT) EXAFS spectra of S-Cu-ISA/SNC and the references (Cu foil, CuS and CuPc) were illustrated in Fig. 2e. We found that the sample exhibited one obvious FT peak located at 1.55 Å, which was mainly attributed to the scattering of Cu-N coordination. Surprisingly, a shoulder peak located at 1.81 Å was also detected. By contrast with other FT-EXAFS spectra, this signal in S-Cu-ISA/SNC was considered owing to Cu-S scattering (Supplementary Figs. 21 and 22), which indicated the formation of Cu-S scattering. Furthermore, there was no related peak corresponding to Cu-Cu coordination, compared with Cu foil. Due to the powerful resolution in both k and R spaces, the Cu K-edge wavelet transform (WT)-EXAFS was applied to investigated the atomic configuration of S-Cu-ISA/SNC (Fig. 2f)59. By comprehensive consideration of the Cu-N and Cu-S contributions, the WT contour plots in S-Cu-ISA/SNC exhibited the
maximum peak at 3.9 Å⁻¹. In addition, compared with the WT signals of Cu foil, no Cu-Cu coordination was observed in S-Cu-ISA/SNC (Supplementary Fig. 23). These further identified the isolated feature of Cu species in S-Cu-ISA/SNC.60

Quantitatively, the structural parameters at Cu K-edge was extracted by least-square EXAFS fitting. The results were exhibited in Fig. 2g, Supplementary Fig. 24 and Supplementary Table 1. It was observed that the fitting curves matched quite well with the experiment spectra. Depend on the results, the first shell of the central atom Cu displayed a coordination number of four, directly connected by one S atom and three N atoms, with the mean bond lengths of 2.32 Å and 1.98 Å, respectively (Fig. 2h).

Furthermore, we investigated the simulated EXAFS spectra based on the models of Cu-S1N3, Cu-S2N2, Cu-S3N1 and Cu-N4, given in Supplementary Fig. 25a. We could find that when the atom number of sulfur increased from one to three, the FT peak intensity of Cu-S increased understandably, compared to that of Cu-N.61 The relative intensity of Cu-S and Cu-N in the Cu-S1N3 curve accorded quite well with the experimental spectrum. The theoretical XANES spectrum was also calculated based on the Cu-S1N3 model (Supplementary Fig. 25b) as well as Cu-N6, Cu-S2N2 and Cu-S3N1 (Supplementary Fig. 26). We could see that the calculation result for Cu-S1N3 could best reproduce the main features of the experimental curve of S-Cu-ISA/SNC. Moreover, we also tried linear combination fitting (LCF) of the experimental spectrum with the calculated spectrum for Cu-N6 and experimental spectra for CuS and/or Cu2S, as shown in Supplementary Figs. 27–29. We found that although the fitted curves near the edge seemed coincide with the experimental spectrum in some way, the curves after the white line were quite different, suggesting the absence of copper sulfide species. Based on the EXAFS fittings and simulations together with XANES calculations, the unsymmetrical Cu-S1N3 moiety in S-Cu-ISA/SNC was appropriately confirmed. The EXAFS results of Cu foil, CuS and CuPc were also exhibited in Supplementary Fig. 30 and Supplementary Table 1. By contrast, the EXAFS analysis of Cu-ISA/NC and Cu-ISA/SNC were showed in Supplementary Figs. 31, 32 and Supplementary Table 1, respectively. Both the Cu species in Cu-ISA/NC and Cu-ISA/SNC existed in the form of symmetrical Cu-N6 different from that of S-Cu-ISA/SNC.

**Electrocatalytic performance of S-Cu-ISA/SNC on ORR.**

The ORR activity of S-Cu-ISA/SNC was then evaluated in a typical three-electrode system (Supplementary Figs. 33 and 34).
As illustrated in Fig. 3a, b and Supplementary Fig. 35 (the CV curves of S-Cu-ISA/SNC and Pt/C were exhibited in Supplementary Fig. 36), all the three single copper atom samples (S-Cu-ISA/SNC, Cu-ISA/SNC and Cu-ISA/NC) showed an optimistic performance. Especially, the S-Cu-ISA/SNC displayed an optimal activity with the highest kinetic current density \( J_k \) at 0.918 V among the studied catalysts, which was the same as the theoretical value for Pt/C. As shown in the Supplementary Fig. 37, from 0.2 to 0.9 V, the electron transfer number for S-Cu-ISA/SNC was in the range of 3.92-3.99 and the \( E_{1/2} \) yield remained below 4\%, indicating that the catalytic process on the S-Cu-ISA/SNC electrode underwent a high efficiency four-electron ORR process. The Tafel slope for S-Cu-ISA/SNC was 90 mV decade\(^{-1}\), further conforming the excellent ORR activity for S-Cu-ISA/SNC (50 mV decade\(^{-1}\)) was much lower than that of Pt/C (90 mV decade\(^{-1}\)), further conforms the excellent ORR activity for S-Cu-ISA/SNC (Supplementary Fig. 38). Supplementary Figs. 39, 40 demonstrated that S-Cu-ISA/SNC exhibited excellent methanol tolerance. In Fig. 3f, after 5000 cycles, little change in \( E_{1/2} \) was observed for S-Cu-ISA/SNC. The chronoamperometry at 0.90 V vs. RHE of S-Cu-ISA/SNC catalyst showed that the ORR current remained 98% after 100 h test (Supplementary Fig. 41). The HAADF images and EXAFS spectra (Supplementary Figs. 42, 43) also proved that S-Cu-ISA/SNC had excellent stability for ORR. When tested in acidic media (0.5 M H\(_2\)SO\(_4\) solution), the S-Cu-ISA/SNC catalyst also exhibited improved activity (Supplementary Fig. 44). The catalyst displayed \( E_{1/2} \) of 0.74 V. The Tafel slope was 106.9 mV decade\(^{-1}\). Furthermore, it showed comparable activity compared with other catalyst shown in
Supplementary Table 3. In addition, S-Cu-ISA/SNC in acid possessed good stability as well (Supplementary Fig. 44f).

Additionally, we tested the potential application of S-Cu-ISA/SNC in a home-made Zn-air battery (Fig. 3g and Supplementary Fig. 45a). As exhibited in Fig. 3h, the Zn-air battery using S-Cu-ISA/SNC catalyst as the air cathode displayed good activity. The maximum power density was 225 mW cm⁻², outperformed Pt/C (155 mW cm⁻²) as well as the listed catalysts in Supplementary Table 4. In Supplementary Fig. 45b, the specific capacity of the battery employing S-Cu-ISA/SNC as air-cathode was estimated to be 735 mAh g⁻¹ at the discharge of 10 mA cm⁻². Moreover, the S-Cu-ISA/SNC-based battery could robustly serve up to 50 h with little discharge voltage decrease (Supplementary Fig. 45c), which indicated the outstanding durability for S-Cu-ISA/SNC based device.

In situ XAS measurements of S-Cu-ISA/SNC. In order to monitor the structural evolution of the isolated copper sites during ORR, potential-dependent Cu K-edge XAS of S-Cu-ISA/SNC was carried out. The in situ XAS tests were carried out using a home-made cell (Fig. 4a and Supplementary Fig. 46), and all the spectra were collected in fluorescence model by a common-used Lytle detector. The S-Cu-ISA/SNC sample was uniformly dropped on a carbon paper, ensuring that all the Cu species took part in the ORR reaction (Supplementary Fig. 47). Furthermore, the possible X-ray radiation damage on S-Cu-ISA/SNC was examined (Supplementary Fig. 48a), and it was found that the XANES region at Cu K-edge was with no obvious change after a longtime irradiation (2 h), suggesting that the radiation damage was negligible. Then the sample-loaded carbon paper was immersed in 0.1 M KOH solution, without electricity and oxygen inpouring. The collected XANES spectra (Supplementary Fig. 48b) implied that the solution has little influence on the structure before ORR test. The Cu K-edge in situ XANES spectra for S-Cu-ISA/SNC was examined at different potentials (Supplementary Fig. 49). The results were displayed in Fig. 4b and Supplementary Fig. 50, respectively. From 1.05 V to 0.75 V, the edge position was gradually moved to the lower energy, together with reduce of the white line intensity, which suggested a decrease of the valence of Cu in S-Cu-ISA/SNC during ORR. The trend could be reflected more clearly from the XANES difference curves (Fig. 4c). The average oxidation states (Fig. 4d and Supplementary Figs. 51 and 52) indicated that the valence of Cu species decreased from approximately +2 to +1, implying that Cu (+1) sites might work as the active centers for ORR. When the applied potential returned from 0.75 V to 1.05 V, Cu XANES edge shifted back to higher energy along with increase of the white line peak (Supplementary Figs. 53 and 54). This provided unequivocal evidence that the XANES spectra as a function of applied potential were reversible, which might be due to the strong anchor effect of N and S atom to the Cu sites. The reversible change of Cu valence state was a reflection of its significant contribution to the outstanding catalytic activity for ORR.

In addition, in situ EXAFS was conducted to monitor the atomic interface structure of the Cu sites during ORR (Fig. 4e and Supplementary Fig. 55). Figure 4e showed the corresponding k³-weighted FT-EXAFS spectra for S-Cu-ISA/SNC at 0.90 V and 0.75 V vs. RHE. Just like the ex situ data, the in situ FT-EXAFS curves still exhibited one main peak (Cu-N) along with a shoulder peak (Cu-S). However, under the realistic condition, the Cu-N peaks appeared an obvious low-R move from 1.55 Å to 1.49 Å. This implied that the local structure of the active site was changed, which was monitored through the shrinking of Cu-N bond length. The EXAFS curve-fitting results were exhibited in Supplementary Figs. 56, 57 and Supplementary Table 5, where...

Fig. 4 In situ XAFS characterization of S-Cu-ISA/SNC. a Schematic of the in situ electrochemical cell set-up. CE, counter electrode; WE, working electrode; RE, reference electrode. b Cu K-edge XANES spectra of S-Cu-ISA/SNC at various potentials during ORR catalysis in O₂-saturated 0.1 M KOH. c Current density as a function of potential for S-Cu-ISA/SNC (left) and the average oxidation number of Cu species in S-Cu-ISA/SNC as a function of potential (right). d k³-weighted FT-EXAFS at ex-situ, 0.90 V and 0.75 V vs. RHE. The shaded region highlighted the variations in the peak position of the first coordination shell. e The proposed ORR mechanism for the S-Cu-ISA/SNC.
three backscattering paths including Cu-N, Cu-O and Cu-S were considered. The ex situ spectrum indicated the Cu-N bond lengths of 1.98 Å, while the bond lengths were shortened to 1.94 Å (0.90 V vs. RHE) and 1.93 Å (0.75 V vs. RHE), respectively, at real-time working conditions. The most possible geometric configuration was considered as an isolated unsymmetrical Cu-S$_2$N$_3$ moiety linked with the OOH*, O* and OH* intermediates as shown in Fig. 4f, which was also detected by our in situ Fourier Transform infrared spectroscopy (FTIR) test (Supplementary type plot and locates at the right side, suggesting that the Cu atom unsymmetrical Cu-ortho-S$_2$N$_2$) was much less stable than the moieties (Fig. 5a, b, Supplementary Figs. 61 and 62 and Supplementary Tables 7 and 8). According to the Savatier principle, the best catalysts which located at the vertex of volcano-type plot should bind reaction intermediates neither too strongly nor too weakly. In ORR reaction, for catalysts (such as Fe-N$_4$ and Mn-N$_4$) that strongly bound intermediates, locating at the left side of volcano-type plot, the potential-limiting step was the desorption of OH* intermediate. While for catalysts (such as Co-N$_4$ and Ni-N$_4$) that weakly bound intermediates, locating at the right side of volcano-type plot, the potential-limiting step was the adsorption of OOH* intermediate. Fig. 5a showed that the ORR activity of Cu-N$_4$ was far away from the vertex of the volcano-type plot and locates at the right side, suggesting that the Cu atom in Cu-N$_4$ moiety bound ORR intermediates too weakly. With the introduction of sulfur atoms, the ORR activities were improved greatly. Particularly, the Cu atom in unsymmetrical Cu-S$_2$N$_3$ moiety had the best ORR activity among all Cu-centered moieties (Fig. 5a, b), with the overpotential of 0.39 V, which was even better than that of Fe-N$_4$ moiety. Thus, we demonstrated that the formation of the unsymmetrical Cu-S$_2$N$_3$ atomic interface in the carbon matrix benefited the improved ORR activity of the catalyst, which was consistent with the experimental results.

To further investigate the physical origin of the superior ORR performance for S-Cu-ISA/SNC, we also analyzed the electronic structures feature of different Cu-center moieties. As the electronegativity of S was smaller than that of N (Supplementary Table 6), Cu in S-Cu-ISA/SNC was likely to lose less valence electron since one coordinated N was substituted by S than Cu in Cu-ISA/NC (Fig. 5c and Supplementary Table 8). However, as shown in Fig. 5c, there was no clear linear correlation between the number of Bader charge of Cu and the adsorption free energy of O* for different moieties, suggesting that the superior ORR performance of S-Cu-ISA/SNC was not directly determined by the number of valance electron of Cu atom. Figure 5d, e showed the projected density of states (PDOS) for d orbitals of Cu before and after O* adsorption on the Cu-S$_2$N$_3$ atomic interface of S-Cu-ISA/SNC, respectively. Clearly, due to the introduction of the coordinated S, the Cu atom in the Cu-S$_2$N$_3$ moiety had more electrons which occupied the $d_{x^2-y^2}$ orbital than that in the Cu-N$_4$ moiety (Supplementary Fig. 63). After the O* adsorption, for the Cu-N$_4$ moiety, the $p$ orbital of O and the $d_{x^2-y^2}$ orbital of Cu formed $\sigma$ bond. Meanwhile, the $p$ orbital of O and only $d_{yz}$ and $d_{xz}$ orbitals of Cu could form $\pi$ bonds. For Cu-S$_2$N$_3$ moiety, the $\sigma$ bond was also derived from the O $p$ orbital and the Cu $d_{xy}$ orbital, while the $\pi$ bonds originated from the O $p$ orbital and the Cu $d_{y^2}$, $d_{xz}$, and as well as $d_{x^2-y^2}$ orbitals, which was quite different from that of Cu-N$_4$ (Fig. 5f, Supplementary Fig. 63). Dramatically, the additional $\pi$ bonds contributed from the Cu $d_{x^2-y^2}$ orbitals strengthened the weak bonding of ORR intermediates, resulting in the boosted ORR performance of Cu centers. Furthermore, it was clearly shown in Supplementary Fig. 61, for the unsymmetrical Cu-S$_2$N$_3$ atomic interface, the O$^*$ intermediates of ORR were not located exactly at the top site of Cu atom, so the O $p$ orbital could interact with the Cu $d_{x^2-y^2}$ orbitals. While for the symmetrical Cu-N$_4$ moiety, the O$^*$ intermediates of ORR were located at the top site of Cu due to the symmetry confinement, without the interaction of O $p$ orbital and Cu $d_{x^2-y^2}$ orbitals. Based on the experimental and theoretical results, the activity trend of ORR was well-confirmed.

**Synthesis and ORR performance of S-M-ISA/SNC (M = Mn, Fe, Co, Ni).** The synthetic method could expand to other 3d metal (Mn, Fe, Co and Ni, etc.) (Supplementary Table 9). HAADF-STEM images identified the isolated feature of Mn, Fe, Co and Ni in the obtained catalysts, which was further revealed by FT-EXAFS curves (Fig. 6 and Supplementary Figs. 64–71). Quantitative EXAFS fittings were also carried out (Supplementary Table 10), which suggested the center metal coordinated directly with N and S atom to form M-S$_2$N$_3$ moiety at the atomic surface. The extended study identified the universal of the synthetic strategy. The ORR catalytic activities of S-M-ISA/SNC (Mn, Fe, Co, Ni) was then evaluated by electrochemical measurements in 0.1 M KOH. Supplementary Fig. 72 exhibited the LSV curves for S-Mn-ISA/SNC, S-Fe-ISA/SNC, S-Co-ISA/SNC and S-Ni-ISA/SNC. As we could see, the samples of S-M-ISA/SNC (M = Mn, Fe, Co, Ni) showed optimistic performance. The half-wave potential ($E_{1/2}$) of 14.5, 40.0, 27.0 and 5.1 mA cm$^{-2}$ (Supplementary Fig. 73). The Tafel slope of S-Mn-ISA/SNC, S-Fe-ISA/SNC, S-Co-ISA/SNC and S-Ni-ISA/SNC was calculated to be 83.8, 62.6, 72.5 and 91.7 mV dec$^{-1}$ (Supplementary Fig. 74). These results further demonstrated the desirable ORR kinetics for S-M-ISA/SNC.
Fig. 5 Theoretical ORR activity of S-Cu-ISA/SNC. a ORR overpotential ($\eta_{ORR}$) as a function of O* adsorption free energy ($\Delta G_{O^*}$) on different Cu-centered moieties. Gray, blue, orange and yellow balls represent C, N, Cu and S atoms, respectively. b Free-energy diagram for different Cu-centered moieties. c Relationship between the number of Bader charge of Cu and $\Delta G_{O^*}$ for different Cu-centered moieties. Projected density of states of Cu and O* d before and e after O* adsorption for Cu-S1N3 in S-Cu-ISA/SNC. f Molecular orbitals of O* adsorbed on Cu-S1N3 in S-Cu-ISA/SNC. $\sigma$ and $\sigma^*$ represent the bonding and antibonding between $dz^2$ orbital of Cu and $p$ orbital of O, $\pi_1$ and $\pi_1^*$ represent the bonding and antibonding between $dyz/ dxz$ orbital of Cu and $p$ orbital of O, $\pi_2$ represents the bonding between $dx^2–y^2$ orbital of Cu and $p$ orbital of O.

Fig. 6 HAADF-STEM and FT-EXAFS characterization of S-M-ISA/SNC (M=Mn, Fe, Co, Ni). HAADF-STEM images of a S-Mn-ISA/SNC, c S-Fe-ISA/SNC, e S-Co-ISA/SNC and g S-Ni-ISA/SNC. FT-EXAFS spectra of b S-Mn-ISA/SNC, d S-Fe-ISA/SNC, f S-Co-ISA/SNC and h S-Ni-ISA/SNC.
originating from the unsymmetrical M-Si-N₃ atomic interface structure.

**Discussion**

In summary, we developed an single Cu atom ORR electrocatalyst consisting of unsymmetrical Cu-Si-N₃ complexes anchored in MOF-derived hierarchically porous carbon frameworks through an atomic interface engineering strategy. Benefiting from the rational construction of the active sites, the S-Cu-ISA/SNC sample exhibited outstanding ORR activity in alkaline media. Our experimental explorations and theoretical analysis revealed the enhanced ORR performance owed to the optimized atomic arrangement and density-of-states distribution of the Cu-Si-N₃ centers. The proposed strategy of local structure regulation may promote the research of advanced oxygen-involved reactions, as well as other electrochemical process.

**Methods**

**Chemicals.** Cupric Acetate Monohydrate (Cu(acac)₂, 99%, Alfa Aesar), 2-methylimidazole (Acros), sulfur powder (325 mesh, 99.5%, Alfa), commercial Pt/C (20 wt% metal, Alfa Aesar), zinc nitrate hexahydrate (98%, Alfa Aesar), KOH (analytical grade), Sodium acetate trihydrate (inhomogeneous technical grade methanol (Sinopharm Chemical), Nafion D-521 dispersion (Alfa Aesar), N, N-dimethyformamide (DMF) (Sinopharm Chemical) were used without any further purification. The distilled water with a resistivity of 18.2 MΩ cm⁻¹ was used in all experiments.

**Preparation of S-Cu-ISA/SNC and the comparison samples.** In a typical synthesis of S-Cu-ISA/SNC catalyst, firstly the precursors were prepared by mixing sulfur powder and Cu-ZIF-8 (Supplementary Note. 4) in 20 ml of mixture solution (carbon tetrachloride: ethanol = 4:1) under sonication. The mass ration of sulfur powder and Cu-ZIF-8 is 1: 10. Subsequently, the solution was heated at 60 °C under vigorous stirring until drying. Afterwards, the samples were pyrolyzed in quartz tube. The pyrolysis process was in the Ar atmosphere, maintaining 450 °C (2 h) and then 950 °C (4 h). The ramping rate during the heating process was 5 °C/min. For the comparison samples, SNC (without the addition of Cu(acac)₂) was prepared as the same process. Cu-ISA/NC (single-atom Cu-N₄ supported on N doped carbon polyhedral, without the addition of S and Cu) were obtained by pyrolysis of Cu-ZIF-8 and pure ZIF-8, respectively. The preparation of Cu-ISA/SNC (single-atom Cu-N₄ supported on N and S co-doped carbon polyhedral) was described in Supplementary Note. 5.

**Characterizations.** We used the SEM (JSM-6700F), TEM (JEOL-JEM-1200EX) and TEM (JEOL-2100F) to characterize the morphology. The in situ ETEM was carried out in Titan G2 60-300 microscope (FEI) equipped with a probe C corrector, with voltage of 300 KV. Using JEOL JEM-ARM200F to gain the HAADF-STEM images, the accelerating voltage was 300 KV. The Bruker D8 ADVANCE X-ray Diffractometer was performed to characterize XRD patterns. HORIBA Jobin Yvon (LabRAM HR Evolution) was used to perform the Raman measurements with the laser of 532 nm. NOVA 4206e was used to obtain the BET surface area and the pore size distribution of the materials.

**Electrochemical measurements for ORR.** We used the three-electrode cell to perform the electrochemical tests. The working electrode was rotating disk electrode (glassy carbon), with a diameter of 5 mm. The counter electrode was graphite rod. The reference electrode was Ag/AgCl (in 3.0 M KCl solution). Dispersing 1 mg catalyst to the mixture solution (0.75 ml isopropyl alcohol, 0.25 ml deionized water, 0.02 ml 5% Na₂SO₄), the edges of the materials were filled with saturated KCl solution. The electrochemical cell was used for in situ XAFS measurements (Fig. 4a and Supplementary Fig. 4). The experiments were performed at BL14W1 station in SSRF. The detail of in situ XAFS measurements was exhibited in Supplementary Note. 8. The in situ FTIR tests were performed at the BL18B at NSRL through a home-made set-up with a ZnSe crystal as the infrared transmission window. The detail for the in situ FTIR measurements is described in Supplementary Note. 9.

**The detail of DFT calculations.** Spin polarized DFT calculations were performed within the Vienna ab initio Simulation Package (VASP) with the projector augmented wave (PAW) scheme. The exchange correlation energy was described by using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. The k-point sampling of the Brillouin zone was used by the 3 × 3 × 1 grid for structural relaxation and the 5 × 5 × 1 grid for electronic structure calculations. The empirical DFT-D3 correction was used to describe van der Waals (vdW) interactions. Atomic charges were calculated by using the atom-in-molecule (AIM) scheme proposed by Bader. Following the RHE model developed by Norskov et al, the voltage-dependent ORR free energy pathway during electrocatalysis reaction were obtained. The free energies of ORR intermediates are defined as 

\[ G = E_{RHE} + E_{PE} \]

TS, where \( E_{RHE} \), \( E_{PE} \), \( T \) and \( S \) represent the calculated ground state energy, zero-point energy, temperature (298 K) and the entropy, respectively.

**Data availability**

The data supporting the findings of this study are available within the article and its Supplementary Information files. All other relevant data are available from the corresponding authors upon reasonable request.

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Author contributions

W.C., D.W. and J.T.Z. conceived the idea, designed the study and wrote the paper. W.C. and H.S. carried out the sample synthesis, characterization and ORR measurement. W. C. carried out the XAFS characterizations and data analysis. J.D., Y.W., L.Z., R.C. and R.S. helped with the hard XAFS measurements and discussion. X.S.Z. helped with the XPS test. J.Z. and W.Y. helped with soft XAS test. A.L. performed the in-situ environmental microscopic measurements and analysis. Y.L. helped with the spherical aberration electron microscopy test and discussion. Z.Y. carried out the Zn-air battery measurements. Q.L. and X.Z. performed the in-situ IR test and analysis. X.Y.Z., X.Y. and J.L. performed the DFT calculations. J.P. and Z.Z. helped with the electrochemical tests and data analysis. Z.J., D.Z. T.S. and Z.L. helped with the modification of the paper. Y.D.L. gave very useful suggestions.

Competing interests

The authors declare no competing interests.

Additional information

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