Adsorption-regulated precise synthesis of atomically-dispersed bimetallic Fe-Co sites on carbon for electrocatalytic nitrogen reduction reaction

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Abstract

The intriguing features of single-atom catalysts (SACs) could bring catalysis into a new paradigm, however, controllably synthesising SACs with desired SA loadings and coordination forms are challenging. Here, we report an adsorption-regulated approach to precisely control the synthesis of bimetallic Fe-Co SAs on carbon. Bacterial cellulose (BC) is utilised as an adsorption regulator to controllably impregnate Fe3+/Co2+ on BC and through carbonisation to anchor Fe-Co SAs on BC-derived carbon via bimetallic [(O-C2)3Fe-Co(O-C2)3] coordination with desired Fe/Co contents and atomic ratios. Under electrocatalytic nitrogen reduction reaction (NRR) conditions, [(O-C2)3Fe-Co(O-C2)3] is operando transformed to [(O-C2)3Fe-Co(O-C)C2] that promotes and sustains NRR performance. A superb ammonia yield of 574.8 ± 35.3 μg h⁻¹ mgcat⁻¹ with an exceptional faradaic efficiency of 73.2 ± 4.6% are obtained from an electrocatalyst with the highest bimetallic Fe-Co site density. The exemplified synthetic approach would be of generically applicable to controllably anchor SAs on carbon that enables meaningfully investigate and rationally design SACs.

Background

Owing to their ultimate mass-catalytic activity, simple active site configuration and readily tuneable electronic structures, single-atom catalysts (SACs) have emerged as a class of catalysts with exemplified superiority over other forms of catalysts. Although still in an early stage, it has been widely assented that such intriguing features of SACs could bring the catalysis into a new paradigm, nevertheless, key challenges must be met. One of the key challenges hindering rational design and development of SACs is the lack of insight into the performance–SA loading relationship, due mainly to our inability to precisely control the synthesis of SACs with desired loading densities and active site coordination forms. For electrocatalytic N₂ reduction reaction (NRR), Au, Ag, Ru, Pd, Mo, Mn, Y, Sc, Cu, Fe, Co and Ni based single-atom electrocatalysts (SAECs) have been reported. The vast majority of such SAECs have been fabricated by anchoring SAs to carbon support almost exclusively via metal-nitrogen (M–Nₓ) or metal-carbon (M–Cₓ) coordination (Supplementary Table 1). To date, the carbon supported SAECs have been fabricated via two common approaches. One anchors SAs to carbon supports through calcination, while another employs metal ions-impregnated carbonisable precursors to anchor SAs via carbonisation. The former normally involves a simple one-pot synthetic procedure, however, through the calcination process to precisely control SAs loading on a pre-carbonised support is difficult. The late involves multiple synthetic steps (e.g., metal ion adsorption, carbonisation and acid etching), but has potentials to achieve controllable synthesis, although it has yet been realised.

Over the past few years, numerous SAECs with the atomically-dispersed Fe-Co, Ni-Fe and Zn-Co bimetallic sites on N-doped carbon supports have been constructed via M–Nₓ coordination and demonstrated to possess higher electrocatalytic activities than their mono-metallic SA counterparts towards oxygen and carbon dioxide reduction reactions. Recently, Wang et al. reported a NRR electrocatalyst with N-coordinated Fe-Cu clusters anchored on C₃N₄ modified carbon nanotubes to achieve an NH₃ yield rate of
~10 µg h⁻¹ mg⁻¹ cat. at -1.2 V (vs. Ag/AgCl) with an impressive faradaic efficiency (FE) of 34.0% at -0.8 V (vs. Ag/AgCl)³². Very recently, Xin's group reported a NRR electrocatalyst with bimetallic Pd-Cu sites on N-doped carbon support to achieve a high NH₃ yield rate of 69.2 ± 2.5 µg h⁻¹ mg⁻¹ cat. at -1.2 V (vs. Ag/AgCl)³². Both studies attributed the enhanced NRR performance to the bimetallic sites induced synergistic modulations on the electronic structures. Despite the demonstrated attractions of bimetallic SAECs, one can easily apprehend the tough challenge involved in the controllable synthesis of such bimetallic SAECs.

Here, we report an adsorption-regulated approach to precisely control the synthesis of oxygen-coordinated bimetallic Fe-Co SAs sites on carbon with the desired Fe and Co contents, and Fe/Co atomic ratios as efficient SAECs for NRR. The bacterial cellulose (BC) with rich oxygen groups is utilised as an adsorption regulator to realise controllable adsorption of Fe³⁺/Co²⁺ on BC, while the resultant Fe³⁺/Co²⁺ impregnated BC is carbonised to anchor Fe-Co SAs on BC-derived graphitic carbon via [(O-C₂)₃Fe-Co(O-C₂)₃] coordination bonds. The obtained bimetallic Fe-Co SAEC with an optimal Fe/Co atomic ratio of 1:1 possesses the highest bimetallic Fe-Co site density and exhibits a superb NH₃ yield rate of 574.8 ± 35.3 µg h⁻¹ mg⁻¹ cat. (185.4 ± 11.4 µg h⁻¹ mg⁻¹ Fe+Co⁻¹) with an exceptional FE of 73.2 ± 4.6%. The synchrotron-based X-ray absorption spectra and density functional theory (DFT) calculations confirm that under the electrocatalytic NRR conditions, [(O-C₂)₃Fe-Co(O-C₂)₃] in the as-synthesised bimetallic Fe-Co SAEC is operando transformed to a more stable coordination configuration of [(O-C₂)₃Fe-Co(O-C)C₂] to promote and sustain NRR performance.

**Results**

**Controllable synthesis and structural characterisation.** A synthetic approach combining wet-chemistry impregnation with carbonisation fixation (Supplementary Fig. 1) is developed to precisely control the fabrication of bimetallic Fe/Co SAs on the carbon support. The pre-treated BC, having rich oxygen groups and nanofiber network structures (Fig. 1a, b), was used as the adsorption regulator to controllably impregnate Fe³⁺ and Co²⁺. The adsorption experiments were performed using adsorption solutions containing 20 mmol L⁻¹ of Fe³⁺ or Co²⁺, and Fe³⁺/Co²⁺ mixture solutions having a fixed total Fe³⁺ and Co²⁺ concentration of 20 mmol L⁻¹ with different [Fe³⁺]/[Co²⁺] ratios of 15/5, 10/10, 5/15 and 1/19. The corresponding Fe³⁺/Co²⁺ impregnated BC samples are denoted as Fe³⁺-20-BC, Co²⁺-20-BC and Fe³⁺/Co²⁺-x/y-BC (x/y: [Fe³⁺]/[Co²⁺] ratios in adsorption solutions). As unveiled by Supplementary Fig. 2, for all cases investigated, the adsorption equilibriums can be reached within 4 h, nevertheless, for assurance purpose, an adsorption period of 6 h was selected for all subsequent adsorption experiments. The impregnated Fe³⁺ and Co²⁺ contents in Fe³⁺-20-BC, Co²⁺-20-BC and Fe³⁺/Co²⁺-x/y-BC are summarised in Supplementary Table 2. As shown in Fig. 1c, the impregnated Fe³⁺ and Co²⁺ contents on BC are directly proportional to [Fe³⁺] and [Co²⁺] in the adsorption solutions. In effect, the slopes of these curves are the distribution factors of Fe³⁺ ($k_{Fe}^{3+} = 0.021$ L g⁻¹) and Co²⁺ ($k_{Co}^{2+} = \ldots$
that quantitatively define the solid/solution phase distributions of Fe$^{3+}$ and Co$^{2+}$. Interestingly, a proportional relationship is also obtained from the plot of Fe$^{3+}$/Co$^{2+}$ molar ratios in Fe$^{3+}$/Co$^{2+}$-x/y-BC against [Fe$^{3+}$]/[Co$^{2+}$] ratios in the adsorption solutions (Fig. 1d). The obtained slope of $k_{Fe^{3+}/Co^{2+}} = 1.092$ confirms an almost identical ratio between the impregnated Fe$^{3+}$/Co$^{2+}$ in Fe$^{3+}$/Co$^{2+}$-x/y-BC and [Fe$^{3+}$]/[Co$^{2+}$] in adsorption solutions. That is, the quantitative relationships unveiled in Fig. 1c, d can be readily used to precisely guide the impregnation of both Fe$^{3+}$ and Co$^{2+}$ contents, and Fe$^{3+}$/Co$^{2+}$ molar ratio on BC by simply selecting an adsorption solution with suitable [Fe$^{3+}$], [Co$^{2+}$] and [Fe$^{3+}$]/[Co$^{2+}$].

Fe$^{3+}$-20-BC, Co$^{2+}$-20-BC and Fe$^{3+}$/Co$^{2+}$-x/y-BC were then used as precursors and subjected to the thermal treatments to carbothermally reduce the impregnated Fe$^{3+}$ and Co$^{2+}$ into metallic Fe and Co, and simultaneously carbonise BC into graphitic carbon. The resultant metallic Fe and Co supported on the carbonised BC (CBC) are denoted as Fe-20-CBC, Co-20-CBC and Fe/Co-x/y-CBC. The scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images, and X-ray diffraction (XRD) patterns (Supplementary Figs. 3, 4) confirm that the carbothermal reduction leads to the formation of metallic Fe, Co and Fe/Co alloy nanoparticles (NPs) on CBC$^{34-35}$. The metal contents in these samples were determined by the inductively coupled plasma atomic emission spectrometer (ICP-AES) and summarised in Supplementary Table 2. These Fe, Co and Fe/Co alloy NPs samples were then subjected to an acid-etching process to remove metal NPs and the remaining Fe, Co and Fe/Co contents in the acid etched samples are summarised in Supplementary Table 2. Fe-O-C and Co-O-C derived from Fe-20-CBC and Co-20-CBC contain 0.27 and 0.22 wt.% of Fe and Co, respectively. While for Fe/Co-O-C-r (r: Fe/Co atomic ratio) derived from Fe/Co-x/y-CBC, the Fe and Co contents are ranged from 0.10–0.22 and 0.08–0.19 wt.%, respectively, corresponding to Fe/Co atomic ratios of 2.9 (Fe/Co-O-C-2.9), 1.5 (Fe/Co-O-C-1.5), 1.0 (Fe/Co-O-C-1.0) and 0.56 (Fe/Co-O-C-0.56). The drastically reduced Fe/Co contents in the acid-etched samples indicate the efficient removal of metallic NPs, which can be further evidenced by the relevant XRD patterns (Supplementary Fig. 4) and TEM images (Supplementary Fig. 5). The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 1e and Supplementary Figs. 6, 7) disclose the existence of densely populated and atomically dispersed bright dots on all acid-etched samples, suggesting that the remaining Fe and Co contents in these samples are of SAs supported on CBC$^{28,29}$. The Raman spectra (Supplementary Fig. 8) display distinctive peaks assignable to the D and G bands of graphitic carbon$^{19,20,26}$, implying that Fe/Co SAs are supported on graphitic carbon. The pore structure measurements (Supplementary Fig. 9) confirm that Fe-O-C, Co-O-C and Fe/Co-O-C-r possess similar micro-/meso-porous structures with Brunauer-Emmett-Teller (BET) specific surface areas ranged from 368.4 to 559.2 m$^2$ g$^{-1}$ (Supplementary Table 3). The loaded Fe SAs in Fe-O-C, Co SAs in Co-O-C and Fe/Co SAs in Fe/Co-O-C-r (Supplementary Table 2) are subsequently plotted against the impregnated Fe$^{3+}$ and Co$^{2+}$ contents in Fe$^{3+}$-20-BC, Co$^{2+}$-20-BC and Fe$^{3+}$/Co$^{2+}$-x/y-BC (Fig. 1f). The unveiled linear relationships confirm that the impregnated Fe$^{3+}$ and Co$^{2+}$ on BC can be proportionally converted into Fe and Co SAs on CBC. The slopes of these curves are the conversion ratios, for which,
$k_{\text{Fe}^0/\text{Fe}^{3+}} = 0.074$ and $k_{\text{Co}^0/\text{Co}^{2+}} = 0.107$ infer that 7.4% and 10.7% of the impregnated Fe$^{3+}$ and Co$^{2+}$ on BC are converted to Fe and Co SAs on CBC. In fact, the linear relationships with slopes of $k_{\text{Fe}^0/[\text{Fe}^{3+}]} = 0.0015 \text{ L g}^{-1}$ and $k_{\text{Co}^0/[\text{Co}^{2+}]} = 0.0014 \text{ L g}^{-1}$ (Fig. 1g) can be obtained from the plot of the loaded Fe and Co SAs on CBC against [Fe$^{3+}$] and [Co$^{2+}$] in the adsorption solutions, disclosing that for a desired loading of Fe, Co and bimetallic Fe/Co SAs on CBC, the required adsorption solution composition can be precisely projected. Remarkably, plotting the bimetallic Fe/Co SAs atomic ratio in Fe/Co-O-C-r against the Fe$^{3+}$/Co$^{2+}$ molar ratio in Fe$^{3+}$/Co$^{2+}$-x/y-BC gives a linear relationship with a proportional factor of $k = 0.772$ (Fig. 1h). As expected, a linear relationship is also obtained from the plot of bimetallic Fe/Co SAs atomic ratios in Fe/Co-O-C-r against [Fe$^{3+}$]/[Co$^{2+}$] ratios in the adsorption solutions (Fig. 1i). The slope of the curve ($k^t$) is 0.809, which can be used to precisely project the required [Fe$^{3+}$]/[Co$^{2+}$] ratio in the adsorption solution for a desired bimetallic Fe/Co SAs ratio in CBC. The quantitative relationships unveiled here can therefore be used to accurately guide the synthesis of Fe, Co and bimetallic Fe/Co SAECs with desirable Fe and Co SAs contents and Fe/Co atomic ratios.

**Coordination configuration of bimetallic Fe-Co sites**. It has been well-documented that the catalytic activities of SACs are determined collectively by the nature of SA, physiochemical properties of support, importantly, the coordination bonds that anchor SAs to support$^{5,6}$. The coordination configurations of the bimetallic Fe-Co sites in Fe/Co-O-C-r were therefore thoroughly investigated using Fe/Co-O-C-1.0 as a representative. The HAADF-STEM and corresponding EDX elemental mapping images reveal the homogeneously distributed C, O, Fe and Co in Fe/Co-O-C-1.0 (Supplementary Fig. 10). The presence of Fe/Co SAs is further evidenced by the aberration-corrected HAADF-STEM image took from different locations of a Fe/Co-O-C-1.0 sample (Supplementary Fig. 11). The existence of rich O-containing groups and the formation of Fe/Co-O-C bonds are unveiled by the X-ray photoelectron spectroscopy (XPS, Supplementary Fig. 12)$^{19}$. The undetectable Fe/Co elements in Co 2p and Fe 2p XPS spectra (Supplementary Fig. 12d) are due to the low Fe/Co contents$^{31}$.

The synchrotron-based X-ray absorption near-edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) spectra were obtained to further validate the Fe/Co-O-C coordination configurations. The Fe $K$ edge XANES spectra (Fig. 2a) reveal that the valence states of Fe species in Fe/Co-O-C-1.0 situate in between Fe$^0$ and Fe$^{3+}$ (ref. $^{28,29}$). The observed shoulder peak (A) in the pre-edge region indicates the formation of Fe-O bond$^{19}$. Notably, the characteristic peak at $\sim 2.20$ Å is absented in the Fourier-transformation $k^3$-weighted Fe $K$ edge EXAFS spectrum of Fe/Co-O-C-1.0 (Fig. 2b), confirming the absence of Fe-Fe metallic bonds, while the presence of the peak at $\sim 2.41$ Å suggests the existence of the bimetallic Fe-Co bonds$^{28,29}$. The prominent EXAFS peak at $\sim 1.69$ Å observed from Fe/Co-O-C-1.0 further endorses the presence of Fe-O coordination bonds$^{19}$. According to the Co $K$ edge XANES spectra (Fig. 2c), the valence states of Co species in Fe/Co-O-C-1.0 is in between the metallic Co and the valence states of Co species in Co$_3$O$_4$. As unveiled by Fig. 2d, the absented peak at $\sim 2.20$ Å and the presented peak at $\sim 2.41$ Å in the EXAFS spectrum of Fe/Co-O-C-1.0 confirm the absence of Co-Co metallic bonds and the presence of the bimetallic Fe-Co
bonds\textsuperscript{28,29}. Additionally, the observed prominent Co K edge EXAFS peak at $\sim$1.61 Å from Fe/Co-O-C-1.0 confirms the existence of Co-O coordination bonds. The Fe and Co K edge wavelet transform (WT)-EXAFS spectra were also obtained to further depict the bonding states of the adjacent metal atoms in Fe/Co-O-C-1.0. As displayed in Fig. 2e, the WT contour peak at $\sim$8.4 Å\textsuperscript{-1} related to the metallic Fe-Fe bond is abSENT FROM Fe/Co-O-C-1.0. Also, comparing to the reference samples, the WT-EXAFS spectrum of Fe/Co-O-C-1.0 shows a sole contour peak with a maximum intensity at $\sim$6.8 Å\textsuperscript{-1}, evidencing the existence of Fe-O coordination bonds\textsuperscript{28,29}. As unveiled in Fig. 2f, the characteristic contour peak at $\sim$8.2 Å\textsuperscript{-1} corresponding to the metallic Co-Co bonds is abSENT FROM the Co K edge WT-EXAFS spectrum of Fe/Co-O-C-1.0. Importantly, the observed contour peak at $\sim$12.0 Å\textsuperscript{-1} FROM Fe/Co-O-C-1.0 signifies the formation of Fe-Co bimetallic bonds\textsuperscript{28,29}, while the observed intensity maximum at $\sim$9.8 Å\textsuperscript{-1} confirms the existence of Co-O coordination bonds\textsuperscript{36}. The above experimental results unambiguously confirm the presence of the atomically-dispersed bimetallic Fe-Co in Fe/Co-O-C-1.0 and both Fe and Co species are anchored to the graphitic carbon via oxygen-coordinated bridge bonds. The fitting of EXAFS spectra was performed to deduce the coordination number and geometric configuration. As shown in Fig. 2g, h, the fitting curves match well with the experimental spectra of Fe/Co-O-C-1.0 at both $R$- and $K$-spaces. As summarised in Supplementary Table 4, Fe species in Fe/Co-O-C-1.0 has two coordinating interactions, one at 2.00 Å with a coordination number of 2.80 and another at 2.13 Å with a coordination number of 1.00, corresponding to Fe-O and Fe-Co, respectively. Similarly, Co species in Fe/Co-O-C-1.0 also has two coordinating interactions, one at 2.05 Å with a coordination number of 2.80 corresponding to Co-O and another at 2.13 Å with a coordination number of 0.80 assignable to Fe-Co. The above results suggest that the atomically dispersed Fe and Co species in Fe/Co-O-C-1.0 are anchored to CBC via a bimetallic Fe-Co arrangement that coordinates with the graphitic carbon through six O-bridging bonds, for which, the \textit{[(O-C\textsubscript{2})\textsubscript{3}Fe-Co(O-C\textsubscript{2})\textsubscript{3}]} is the most likely bimetallic unit in Fe/Co-O-C-1.0 with a possible configuration as shown in the inset of Fig. 2g.

**Electrocatalytic N\textsubscript{2} reduction performance.** All experiments were performed strictly following the protocols recommended in the published literatures\textsuperscript{19,26,37-46}. The experimental system setup and analytical methods are illustrated in Supplementary Figs. 13-16 and detailed in Method section. The NRR performance of Fe/Co-O-C-1.0 was firstly examined. Fig. 3a shows the dependence of NH\textsubscript{3} yield rate ($R_{\text{NH}_3}$) and faradaic efficiency (FE) on applied potentials. The reported $R_{\text{NH}_3}$ and FE in Fig. 3a are derived from the recorded chronoamperometric curves (Supplementary Fig. 17a) under different potentials over a 2 h reaction period with the yielded NH\textsubscript{3} being determined by the indophenol blue method (Supplementary Fig. 17b). It should note that under the experimental conditions, NH\textsubscript{3} is the sole NRR product and N\textsubscript{2}H\textsubscript{4} is undetectable (Supplementary Fig. 18). Although the observed steady-state cathodic current densities are increased with the applied cathodic potentials (Supplementary Fig. 17a), the determined $R_{\text{NH}_3}$ and FE (Fig. 3a) are increased initially with cathodic potentials, peaked at -0.30 V (vs. RHE) and rapidly decreased with the further increased cathodic potentials due to the favoured conditions for hydrogen evolution reaction under high cathodic potentials\textsuperscript{47}. An superb $R_{\text{NH}_3}$ of $574.8 \pm 35.3 \mu g h^{-1} mg_{\text{cat.}}^{-1}$ (185.4 ± 11.4 mg h\textsuperscript{-1} mg\textsubscript{Fe+Co}\textsuperscript{-1}) with an
exceptional FE of 73.2 ± 4.6% are attained at -0.30 V (vs. RHE). To the best of our knowledge, the achieved \( R_{\text{NH}_3} \) and FE by Fe/Co-O-C-1.0 are the highest among all reported NRR SAECs (Supplementary Table 1).

To confirm whether the yielded \( \text{NH}_3 \) is exclusively resulted from Fe/Co-O-C-1.0 catalysed NRR, the isotopic labelling validation experiments were performed using \( ^{15}\text{N}_2 \) and \( ^{14}\text{N}_2 \) saturated 0.1 M \( \text{Na}_2\text{SO}_4 \) electrolyte at -0.30 V (vs. RHE) over a 2 h reaction period. The yielded \( ^{15}\text{NH}_4^+ \) and \( ^{14}\text{NH}_4^+ \) concentrations were quantified by both the indophenol blue method and \(^1\text{H} \) nuclear magnetic resonance (NMR) analysis. As shown in Fig. 3b and Supplementary Fig. 19, the yielded \( ^{14}\text{NH}_4^+ \) and \( ^{15}\text{NH}_4^+ \) concentrations determined by \(^1\text{H} \) NMR method are 39.7 ± 2.1 and 39.2 ± 2.4 µg mL\(^{-1}\), corresponding to \( \text{NH}_3 \) yield rates of 535.7 ± 28.7 and 531.4 ± 32.8 µg h\(^{-1}\) mg\(_{\text{cat.}}\)\(^{-1}\), respectively, very closely approximated to those determined by the indophenol blue method (41.2 ± 2.8 µg mL\(^{-1}\) for \( ^{14}\text{NH}_4^+ \) and 40.7 ± 2.6 µg mL\(^{-1}\) for \( ^{15}\text{NH}_4^+ \), corresponding to \( \text{NH}_3 \) yield rates of 555.9 ± 37.8 and 551.4 ± 35.2 µg h\(^{-1}\) mg\(_{\text{cat.}}\)\(^{-1}\), respectively). Such closely approximated \( \text{NH}_3 \) yield rates from \( ^{15}\text{N}_2 \) and \( ^{14}\text{N}_2 \) confirmed by the two analytical methods infer that the yielded \( \text{NH}_3 \) is indeed originated from the Fe/Co-O-C-1.0 catalysed NRR. The control experiments were subsequently conducted to eliminate potential environmental interferences. As unveiled in Supplementary Fig. 20, only ignorable \( \text{NH}_3 \) concentrations can be detected when the experiments were carried out using \( \text{N}_2 \)-saturated 0.1 M \( \text{Na}_2\text{SO}_4 \) without electrocatalyst (blank), with electrocatalyst but without applied potential (open-circuit) and with electrocatalyst in Ar-saturated 0.1 M \( \text{Na}_2\text{SO}_4 \) at -0.30 V (vs. RHE) for 2 h. These control experimental results eliminate any noticeable environmental interference and further confirm that the yielded \( \text{NH}_3 \) is resulted exclusively from the Fe/Co-O-C-1.0 catalysed NRR.

The stability of Fe/Co-O-C-1.0 was examined using \( \text{N}_2 \)-saturated 0.1 M \( \text{Na}_2\text{SO}_4 \) electrolyte at -0.30 V (vs. RHE) over a 72 h period (Fig. 3c). The recorded chronoamperometric profile exhibits no noticeable change in current density over the entire testing period, demonstrating an excellent stability. The cycling stability was examined using \( \text{N}_2 \)-saturated 0.1 M \( \text{Na}_2\text{SO}_4 \) electrolyte at -0.30 V (vs. RHE) with 1 h as a testing cycle for 10 consecutive cycles (Supplementary Fig. 21). The nearly identical chronoamperometric profiles adding to the almost unchanged \( R_{\text{NH}_3} \) and FE obtained from the cycling tests demonstrate a superior cycling stability. The superb stability of Fe/Co-O-C-1.0 can be attributed to its structural stability as evidenced by the well retained atomically-dispersed Fe/Co species (Supplementary Fig. 22) without aggregated metallic Fe/Co NPs (Supplementary Fig. 23) for Fe/Co-O-C-1.0 after 72 h stability test. Interestingly, the XANES and EXAFS spectra (Supplementary Fig. 24 and Supplementary Table 4) unveil that after 10 NRR testing cycles, the bimetallic Fe-Co in Fe/Co-O-C-1.0 could be fitted into a coordination structure of [(O-C\(_2\))\(_3\)Fe-Co(O-C)C\(_2\)], which might be the actual catalytic active sites, deserving a further investigation.

The NRR performances of Fe-O-C with Fe SAs, Co-O-C with Co SAs and Fe/Co-O-C-\( r \) with bimetallic Fe-Co SAs including Fe/Co-O-C-2.9, Fe/Co-O-C-1.5, and Fe/Co-O-C-0.56 were examined. For comparison
purpose, CBC without Fe/Co content (Supplementary Fig. 25 and Table 3) was synthesised and its NRR performance was evaluated. Supplementary Fig. 26 shows the recorded chronoamperometric profiles from all targeted electrocatalysts in N₂-saturated 0.1 M Na₂SO₄ electrolyte under -0.30 V (vs. RHE) over 1 h reaction period. The derived RᵣNH₃ and FE are summarised in Fig. 3d, e. Interestingly, both RᵣNH₃ and FE follow the same trend of CBC < Co-O-C < Fe-O-C < Fe/Co-O-C-2.9 < Fe/Co-O-C-0.56 < Fe/Co-O-C-1.5 < Fe/Co-O-C-1.0. Obviously, Fe/Co-O-C-r with bimetallic Fe-Co SAs outperforms CBC without Fe/Co, and Fe-O-C and Co-O-C with only Fe or Co SAs. This alludes to a bimetallic Fe-Co site induced synergistic effect as the total Fe and Co SAs contents in Co-O-C and Fe-O-C are similar to those in Fe/Co-O-C-r (Supplementary Table 2). Notably, the total Fe and Co SAs contents in Fe/Co-O-C-r are also closely approximated each other, therefore, for a given total Fe/Co content, the NRR performance of Fe/Co-O-C-r is likely determined by their Fe/Co atomic ratio. In fact, the NRR performance of Fe/Co-O-C-r increases as the Fe/Co atomic ratios closer to the unity, and Fe/Co-O-C-1.0 with a Fe/Co atomic ratio of 0.99 (Supplementary Table 2) exhibits the best NRR performance. This could be due to that Fe/Co-O-C-r with a Fe/Co atomic ratio approaching the unity possesses higher density of the bimetallic Fe-Co sites that dictate the NRR performance. Nonetheless, to our knowledge, no existing analytical technique is capable of quantitatively determining the density of such atomically-dispersed bimetallic Fe-Co sites. Fortunately, the controllable synthetic approach used in this work enables us to precisely control both the content and the atomic ratio of Fe and Co. As such, if we assume that for a given Fe/Co-O-C-r, the bimetallic Fe-Co sites are homogeneously distributed and the maximum possible bimetallic Fe-Co site density is determined by the lower Fe or Co content in a sample, then according to Supplementary Table 5, the maximum density of the bimetallic Fe-Co sites can be estimated as 6.72 ± 0.24, 8.87 ± 0.28, 10.93 ± 0.31 and 13.31 ± 0.51 nmol cm⁻² for Fe/Co-O-C-2.9, Fe/Co-O-C-0.56, Fe/Co-O-C-1.5 and Fe/Co-O-C-1.0, respectively. Excitingly, the plot of RᵣNH₃ against the density of bimetallic Fe-Co sites unveils a linear relationship (Fig. 3f), signifying that the trend of the bimetallic Fe-Co site density matches the trend of the experimentally determined NRR performance. This provides us with a reasonable confidence that the density of the bimetallic Fe-Co sites is a decisive factor for NRR performance of Fe/Co-O-C-r, nevertheless, further elucidation on the NRR activity origin of the bimetallic Fe-Co sites is needed.

Mechanistic studies. The experimentally identified Fe-Co sites configurations were used to construct the bimetallic Fe-Co sites structural model for the density functional theory (DFT) calculations. Fig. 4a shows the DFT optimised [(O-C)₃Fe-Co(O-C)₃] configuration on graphitic carbon. For N₂ adsorption on the bimetallic [(O-C)₃Fe-Co(O-C)₃] unit, we considered three possible adsorption sites: Fe, Co and Fe-Co sites in [(O-C)₃Fe-Co(O-C)₃]. Our DFT calculations indicate that N₂ can adsorb separately on Fe and Co sites via end-on approach (Supplementary Fig. 27) or concurrently adsorb on Fe-Co site via side-on adsorption (Fig. 4b). With side-on adsorption, the calculated charge density difference (Supplementary Fig. 28) discloses that the electrons in d orbitals of Fe and Co are transferred to the empty π* orbitals of N₂.

As a result, the adsorbed N₂ gains 0.72 e⁻ from the bimetallic site, and the N-N bond is elongated from 1.120 Å (free gaseous N₂ state) to 1.225 Å, suggesting that the adsorbed N₂ is activated. Notably, the calculated reaction free energy of the first hydrogenation step (*N₂ + H⁺ + e⁻ → *NH-N) for side-on
adsorption on Fe-Co site is 0.61 eV, which is approximately half of that for the end-on adsorption on Fe (1.16 eV) and Co (1.30 eV) sites, confirming that the side-on adsorbed N$_2$ on the bimetallic Fe-Co site is favourable for NRR.

The catalytic activity origin and NRR pathway on the bimetallic [(O-C$_2$)$_3$Fe-Co(O-C$_2$)$_3$] sites were subsequently investigated in details. Supplementary Fig. 29 shows the projected density of states (PDOS) before and after side-on adsorption on the bimetallic Fe-Co site. The broadened Fe-3$d$ and Co-3$d$ states after N$_2$ adsorption adding to the overlapped Fe, Co and N states imply the hybridized Fe/Co 3$d$ orbitals with N 2$p$ orbital. The overlapped PDOS between Fe-3$d$ and *N$_2$-2$p$, and Co-3$d$ and *N$_2$-2$p$ are distributed below and above the Fermi energy, signifying a back-bonding between the bimetallic Fe-Co site and *N$_2$.$^{48}$ These suggest that the electrocatalytic NRR activity of Fe/Co-O-C-*$r$ electrocatalysts is resulted from the effective hybridisation of N 2$p$ orbital with the synergistically configured bimetallic Fe-Co site.

We consequently calculated the Gibbs free energy diagram of side-on adsorption NRR pathway and intermediates structures on [(O-C$_2$)$_3$Fe-Co(O-C$_2$)$_3$] corresponding to each reaction step (Fig. 4c). The 1$^{st}$ hydrogenation requires an energy input of 0.614 eV to form *NH-N and its N-N bond is elongated from 1.225 to 1.286 Å. The 2$^{nd}$ hydrogenation to form *NH-NH* is more favourable than the formation of *NH$_2$-N*, as the former is exothermic and the latter requires an energy input of 0.869 eV. In this process, the N-N bond of *NH-NH* is elongated to 1.339 Å. The formation of *NH$_2$-NH* requires an energy input of 0.209 eV and the N-N bond is further elongated to 1.451 Å. During the 4$^{th}$ hydrogenation step, the N-N bond breaks to form *NH$_3$ + *NH and/or *NH$_2$ + *NH$_2$, which are thermodynamically favoured by 3.19 and 2.49 eV, respectively. For the last hydrogenation step, the formation of *NH$_3$ from *NH$_2$ is uphill by 0.631 eV, which is the likely determining step.

Surprisingly, at the end of the initial NRR cycle (Fig. 4c), [(O-C$_2$)$_3$Fe-Co(O-C)$_2$] is transformed into [(O-C$_2$)$_3$Fe-Co(O-C)C$_2$], because the latter is 2.176 eV favourable in energy, consistent with the observed structural change by the X-ray absorption analysis of Fe/Co-O-C-1.0 after 10 NRR testing cycles (Supplementary Fig. 24). The DFT calculations were then conducted to depict whether [(O-C$_2$)$_3$Fe-Co(O-C)C$_2$] is the actual bimetallic active site of Fe/Co-O-C-$r$. Fig. 4d shows the DFT optimised structure of [(O-C$_2$)$_3$Fe-Co(O-C)C$_2$] at the end of the initial NRR cycle. We found that N$_2$ can adsorb separately on Fe and Co sites via the end-on adsorption (Supplementary Fig. 30) and concurrently on Fe-Co site via the side-on adsorption (Fig. 4e), respectively. The calculated charge density difference unveils that the side-on adsorbed N$_2$ gains 0.62 e$^-$ from the Fe-Co site in [(O-C$_2$)$_3$Fe-Co(O-C)C$_2$] (Supplementary Fig. 31). Deferring from [(O-C$_2$)$_3$Fe-Co(O-C)$_2$], the PDOSs of [(O-C$_2$)$_3$Fe-Co(O-C)C$_2$] (Supplementary Fig. 32) uncover that the side-on adsorption on the Fe-Co site leads to spin-down/beta orbital of Fe-3$d$ shifting away slightly from the Fermi level, suggesting a less effective charge transfer with *N$_2$. Similar to the case of [(O-C$_2$)$_3$Fe-Co(O-C)$_2$], for the 1$^{st}$ hydrogenation step, the side-on adsorption on Fe-Co site in [(O-C$_2$)$_3$Fe-Co(O-C)C$_2$] requires a lower reaction free energy (0.767 eV) than that of end-on adsorption on Fe (0.922 eV) and
Co (0.906 eV) sites. The calculated Gibbs free energy diagram of side-on adsorption NRR pathway and intermediates structures on \([\text{O-C}_2\text{Fe-Co(O-C)}\text{C}_2]\) corresponding to each reaction step are shown in Fig. 4f. As can be seen, the unveiled NRR pathway is identical to the case of \([\text{O-C}_2\text{Fe-Co(O-C)}_3]\). However, differing from \([\text{O-C}_2\text{Fe-Co(O-C)}_3]\), where the last hydrogenation step with a uphill energy of 0.631 eV is the likely determining step, the 1\(^{st}\) hydrogenation step on \([\text{O-C}_2\text{Fe-Co(O-C)}\text{C}_2]\) requires an energy input of 0.767 eV to form \(*\text{NH-N}\), which is the highest among all the hydrogenation steps. Importantly, our calculations confirm that the \([\text{O-C}_2\text{Fe-Co(O-C)}\text{C}_2]\) configuration can be regenerated at the end of a NRR cycle upon the desorption of \(*\text{NH}_3\) (Fig. 4f) and readily available to catalyse the next NRR cycle, inferring that \([\text{O-C}_2\text{Fe-Co(O-C)}\text{C}_2]\) is likely the actual active site of Fe/Co-O-C under the operando conditions and responsible for the attained superb NRR performance.

**Discussion**

In summary, we exemplified an adsorption-regulated synthetic strategy to fabricate atomically dispersed Fe-Co SAs supported on carbon in a precisely controllable manner via metal-oxygen coordination. The quantitative relationships defining Fe\(^{3+}\)/Co\(^{2+}\) distributions between the adsorption solution and bacterial cellulose adsorbent, and the percentage of the adsorbed Fe\(^{3+}\)/Co\(^{2+}\) converting to Fe/Co SAs were unveiled and used to guide the controllable synthesis of bimetallic Fe-Co SACs with desired Fe/Co contents and atomic ratios. We demonstrated that the controllably synthesised SACs can be used to meaningfully depict the composition-performance relationship. The catalyst with a Fe/Co atomic ratio of 1:1 possesses the highest bimetallic Fe-Co site density and exhibits the best NRR performance. The exemplified approach would be of generically applicable to controllably anchor a wide spectrum of other SAs on carbon. We envisage that an ability to controllably synthesise SACs with variety of desired compositions is essential for depicting the factual composition-performance relationships that enable rationally design and development of SACs.

**Methods**

*Reagents and materials.* Bacterial cellulose (BC) pellicle was obtained from Guilin Qihong Technology Co., Ltd., China. Co\((\text{SO}_4\))\(_3\)·7H\(_2\)O, Fe\(_2\)(\text{SO}_4\))\(_3\)·10H\(_2\)O, HCl (36.0–38.0%), C\(_2\)H\(_5\)OH (75.0%) and N\(_2\)H\(_4\)·H\(_2\)O (≥85.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Na\(_2\)SO\(_4\) (95.0%), C\(_5\)FeN\(_6\)Na\(_2\)O·2H\(_2\)O (99.0%), C\(_6\)H\(_5\)Na\(_3\)O\(_7\)-2H\(_2\)O (99.0%), NaOH (96.0%), C\(_7\)H\(_6\)O\(_3\) (99.5%), NaClO (available chlorine ≥ 5.0%), NH\(_4\)Cl (99.5%), C\(_9\)H\(_{11}\)NO (99.0%) were purchased from Aladdin. \((^{15}\text{NH}_4)\)\(_2\)SO\(_4\), was provided by Shanghai Chemical Research Institute Co., Ltd.\(^{14}\text{N}_2\) (99.99%) and \(^{15}\text{N}_2\) (99.83%) feeding gases were supplied by Hefei Ninte Gas Management Co., Ltd. All solutions were prepared using deionised water (Millipore Corp., 18.2 M\(_2\)cm). Glassy carbon (GC) disk electrode (3.0 mm in diameter) was purchased from Wuhan Gaoss Union Technology Co., Ltd.
Fabrication of Fe-O-C, Co-O-C, Fe/Co-O-C-\textit{r} and CBC. BC pellicle was frozen by liquid nitrogen and freeze-dried in a bulk tray dryer at a sublimating temperature of -75 °C and a pressure of 0.01 m bar for 48 h. To remove organic contaminations, the freeze-dried BC was dispersed in 200 mL piranha solution under constant stirring at room temperature for 6 h, thoroughly washed with deionised water and freeze-dried. The pre-treated BC was used as the adsorbent to controllably impregnate Fe$^{3+}$ and Co$^{2+}$. For Fe$^{3+}$-20-BC or Co$^{2+}$-20-BC, 1.0 g pre-treated BC was dispersed in 400 mL of 20 mmol L$^{-1}$ Fe$^{3+}$ or Co$^{2+}$ solution at room temperature for 6 h to complete the adsorption. For Fe$^{3+}$/Co$^{2+}$-x/y-BC (x/y: [Fe$^{3+}$]/[Co$^{2+}$] ratio in adsorption solution), 1.0 g pre-treated BC was dispersed in 400 mL of Fe$^{3+}$/Co$^{2+}$ mixture solutions with a fixed total Fe$^{3+}$ and Co$^{2+}$ concentration of 20 mmol L$^{-1}$ and x/y of 15/5, 10/10, 5/15 and 1/19 at room temperature for 6 h to complete the adsorption. The obtained Fe$^{3+}$-20-BC, Co$^{2+}$-20-BC and Fe$^{3+}$/Co$^{2+}$-x/y-BC were adequately washed with deionised water, freeze-dried and carbonised in a tubular furnace under an Ar atmosphere. The sample was firstly heated to 360 °C with a heating rate of 2 °C min$^{-1}$ and kept for 2 h, then heated to 700 °C with a heating rate of 5 °C min$^{-1}$ and kept for 3h to carbothermally reduce the adsorbed Fe$^{3+}$ and Co$^{2+}$ on BC to metallic Fe/Co NPs and simultaneously carbonise BC into graphitic carbon (CBC). The resultant Fe-20-CBC, Co-20-CBC and Fe/Co-x/y-CBC were adequately washed with deionised water and ethanol, dried at 60 °C under vacuum for 6 h, then subjected to a refluxing acid-etching process using 4.0 M HCl at 120 °C for 4 h to remove metallic Fe/Co NPs. The acid-etched Fe-20-CBC, Co-20-CBC, Fe/Co-x/y-CBC were thoroughly washed by deionised water and ethanol, and dried at 60 °C under vacuum for 12 h to obtain Fe-O-C, Co-O-C and Fe/Co-O-C-\textit{r}.

CBC without Fe and Co was fabricated by thermally treating the pre-treated BC precursor in a tubular furnace under an Ar atmosphere. The pre-treated BC was firstly heated to 360 °C with a heating rate of 2 °C min$^{-1}$ and kept for 2 h, then heated to 700 °C with a heating rate of 5 °C min$^{-1}$ and kept for 3h.

Characterisation. XRD patterns were acquired using Philips X’pert PRO with Cu Ka radiation (\(\lambda = 1.5418 \ \text{Å}\)) at 40 kV and 40 mA. FT-IR measurements were conducted by a Nicolet Nexus FT-IR spectrometer. Raman spectra were recorded by a Renishaw Micro-Raman Spectroscopy (Renishaw in Via Reflex) with 532 nm excitation laser. SEM images were obtained using SU8020 (Hitachi, Japan). TEM images were obtained using JEMARM 200F. HAADF-STEM measurements and EDX spectroscopy were performed on a JEM-ARM200F. XPS spectra were obtained using an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America). Nitrogen adsorption-desorption isotherms were measured using Autosorb-iQ-Cx. The synchrotron-based X-ray absorption measurements were performed at the 1W1B station of Beijing Synchrotron Radiation Facility, China. Fe$^{3+}$/Co$^{2+}$ and metallic Fe/Co contents were quantitatively determined by ICP-AES (ICP-6300, Thermo Fisher Scientific).

Electrochemical measurements. All potentiostatic NRR measurements were conducted using N$_2$-saturated 0.1 M Na$_2$SO$_4$ electrolyte under ambient conditions and continuous bubbling N$_2$ through the electrolyte. Supplementary Fig. 13 shows the electrochemical experimental setup. Unless otherwise stated, all electrochemical measurements were performed on a CHI 660E electrochemical workstation (CH
Instrumental Corporation, Shanghai, China) under ambient conditions using a Nafion 117 proton exchange membrane separated two-compartment H-type electrochemical cell (ZY-CD02A, Chintek Instrument & Equipment Co., Ltd. China) that accommodated 30 mL of N\textsubscript{2}-saturated 0.1 M Na\textsubscript{2}SO\textsubscript{4} electrolyte in each compartment and a three-electrode electrochemical system with a Co-O-C, Fe-O-C, Fe/Co-O-C-r or CBC based working electrode, an Ag/AgCl (Saturated KCl) reference electrode and a Pt mesh counter electrode. Before use, the Nafion 117 membrane was treated by successive heating at 80 °C in H\textsubscript{2}O\textsubscript{2} (5.0 wt.%) aqueous solution for 1 h and in deionised water for another 1 h. The working electrode was prepared as follows: 3.5 mg of the targeted electrocatalyst was firstly dispersed in 950 µL of absolute ethanol and 50 µL of Nafion solution (5.0 wt.%) unndersonication for 30 min to form a homogeneous ink. 10 µL of ink was loaded onto a GC disk electrode (3.0 mm in diameter, equivalent to 0.5 mg cm\textsuperscript{-2}) and dried under ambient conditions for 40 min before use. For quality assurance purpose, a feeding gas purification system\textsuperscript{19,26,37-44} and a tail gas NH\textsubscript{3} recovery unit\textsuperscript{19,26,37,42,45} were incorporated in the experimental system (Supplementary Fig. 13). All experiments were performed strictly following the recommended protocols by the published literatures\textsuperscript{19,26,37-46}. A Cu-Fe-Al catalyst unit (Supplementary Fig. 14) was introduced to remove possible NO\textsubscript{x} interference from the N\textsubscript{2} feeding gas\textsuperscript{19,26,39}. To eliminate possible NO interferences, a CrO\textsubscript{3} column was also incorporated into the gas purification system to convert the NO passing through the Cu-Fe-Al catalyst unit into water soluble form of NO\textsubscript{2}, which can then be removed by the H\textsubscript{2}SO\textsubscript{4} and distilled water absorption units before reaching the electrochemical cell\textsuperscript{19,26,39}. The N\textsubscript{2} feeding gas with a flow rate of 20 mL min\textsuperscript{-1} was successively purged through the above mentioned purification system before reaching the cathodic compartment to bubble the electrolyte solution ~2.0 cm from the working electrode surface. It should be noted that the reported NH\textsubscript{3} yield in this work is the NH\textsubscript{3} product collected only from cathodic compartment because the NH\textsubscript{3} concentration in the anodic compartment and tail gas absorber units are below the detection limit of the indophenol blue method.

In this work, all measured potentials vs. Ag/AgCl were converted to the potentials vs. RHE (E\textsubscript{RHE}) according to the following equation:

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059pH + E^{0}_{\text{Ag/AgCl}}
\]

where, \(E_{\text{Ag/AgCl}}\) is the equilibrium potential under standard conditions, \(E^{0}_{\text{Ag/AgCl}} = 0.1967\) V vs. RHE at 25 °C.

\textit{Determination of ammonia and hydrazine.} The yielded ammonia was determined by the standard indophenol blue method\textsuperscript{19,26}. The standard Watt and Chrisp method was employed to determine the hydrazine\textsuperscript{19,26}. 
When quality assurance required, \(^{15}\text{N}\) isotopic labelling experiments were conducted using \(^{15}\text{N}_{2}\) as the feeding gas with identical experimental procedure as that of \(^{14}\text{N}_{2}\) experiments. The yielded \(^{15}\text{NH}_4^+\) was quantified by the \(^1\text{H}\) NMR method\(^{19,26,37-46}\) using Bruker Avance-400 MHZ.

**Calculation of \(R_{\text{NH}_3}\) and FE.** \(R_{\text{NH}_3}\) and FE are calculated by the following equations:

\[
R_{\text{NH}_3} (\mu g \ h^{-1} \ mg_{\text{cat}}^{-1}) = \frac{C_{\text{NH}_3} (\mu g \ mL^{-1}) \times V(mL)}{t (h) \times m_{\text{cat}} (mg)}
\]

\[
FE (%) = \frac{3 \times n_{\text{NH}_3} (\text{mol}) \times F (\text{C mol}^{-1})}{Q (C)} \times 100\%
\]

where, \(C_{\text{NH}_3}\) and \(V\) are the measured \(\text{NH}_3\) concentration and the electrolyte solution volume, respectively, \(t\) is the NRR period and \(m_{\text{cat}}\) is the amount of the loaded electrocatalyst, \(F\) is the Faradaic constant (96485 C mol\(^{-1}\)) and \(Q\) is the total charge transferred during NRR period.

**Theoretical calculations.** The first-principle calculations were performed within the framework of DFT as implemented in the Vienna Ab initio Simulation Package (VASP)\(^{49-51}\). The projector augmented wave (PAW) method has been used to describe the inert core electrons\(^{52}\). A cut off energy of 400 eV was used for the expansion of the wave functions. The electronic exchange-correlation effects were described with Perdew-Burke-Ernzerh of generalized gradient approximation (PBE-GGA) functional\(^{53}\). The basic bimetallic Fe-Co SAEC model was built using a periodic graphene structure containing 62 C atoms, one Fe atom and one Co atom, where Fe and Co are neighboured and each Fe and Co is coordinated with three O atoms. A vacuum of 15 Å in the z-direction is used. The gamma (Γ) cantered \(1 \times 1 \times 1\) Monkhorst-Pack k-point sampling was used throughout\(^ {54}\). The Fermi level was slightly broadened using a Fermi-Dirac smearing of 50 meV. All relaxations were done until the force of the system converges to 0.05 eV/Å. For NRR process, six coupled proton and electron (\(\text{H}^+/\text{e}^-\)) transfer steps are involved and the Gibbs free energy change of each step is calculated based on:

\[
\Delta G = \Delta E + \Delta E_{\text{ZPE}} \uparrow T \Delta S
\]

where, \(\Delta E\) is the chemisorption energy change between the reactant and product species adsorbed on catalyst surface obtained directly from DFT calculations, \(\Delta E_{\text{ZPE}}\) is the difference in zero point energy, \(T\) is the temperature \((T = 298.15 \text{ K})\) and \(\Delta S\) is the entropy difference\(^{55}\). For the adsorbed species, only the vibrational frequencies and entropy were considered for the energy correction.

**Data Availability**
The supporting data are available in supplementary information file accompanied with the submitted manuscript.

**Code Availability**

The authors declare no any code access restrictions.

**Declarations**

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**Author contribution**

H.Z., H.Z. and G.M. conceived the concept and designed the experiments. S.Z. fabricated the catalysts and performed the material characterization and electrochemical measurements. M.H. conducted DFT calculations. L.Z. carried out the XAFS measurements and T.S. analysed the XAFS results. Y.L. performed the STEM measurements. X.Z., H.Z. C.C. Y.Z., G.W. and H.Y. contributed to the experimental design. H.Z. and H.Z. supervised the research. H.Z., H.Z. G.M. and S.Z. co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

**Competing interests**

The authors declare no competing interests.

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**Figures**
Controllable synthesis of bimetallic Fe-Co SAs. a, b, FT-IR spectrum (a) and SEM image (b) of pre-treated BC. c, Plots of impregnated Fe3+ and Co2+ contents on BC under equilibrium conditions against [Fe3+] and [Co2+] in adsorption solutions. d, Plot of impregnated Fe3+/Co2+ molar ratios on Fe3+/Co2+-x/y-BC against [Fe3+]/[Co2+] ratios in adsorption solutions. e, Low- and high-magnification HAADF-STEM images of Fe/Co-O-C-1.0. f, g, Plots of loaded Fe and Co SAs on Fe-O-C, Co-O-C and Fe/Co-O-C-r against impregnated Fe3+ and Co2+ on BC (f), and [Fe3+] and [Co2+] in adsorption solutions (g). h, i, Plots of Fe/Co SAs atomic ratios in Fe/Co-O-C-r against Fe3+/Co2+ molar ratios in Fe3+/Co2+-x/y-BC (h), and [Fe3+]/[Co2+] ratios in adsorption solutions. Error bars shown in (c, d), and (f-i) represent data obtained from three-replicated experiments.

Figure 1
Figure 2

Bimetallic Fe-Co site configuration. a-d, Fe K edge XANES spectra (a) and k3-weighted FT-EXAFS spectra (b), Co K edge XANES spectra (c) and k3-weighted FT-EXAFS spectra (d) of Fe/Co-O-C-1.0 and references. 

e, f, Fe K edge WT-EXAFS (e) and Co K edge WT-EXAFS (f) of Fe/Co-O-C-1.0 and references. g, h, Fe and Co K edge EXAFS fitting curves of Fe/Co-O-C-1.0 at R space (g) and k space (h). Inset in (g) is the proposed bimetallic Fe-Co coordination configuration in Fe/Co-O-C-1.0 (Brown: C, red: O, orange: Fe, blue: Co).
Figure 3

NRR performance. a, Dependence of RNH₃ and FE on applied potentials. b, Determined RNH₃ by indophenol blue and 1H NMR methods from 14N and 15N sources. c, Stability test of Fe/Co-O-C-1.0 at -0.30 V (vs. RHE). d, e, RNH₃ and FE of CBC, Fe-O-C, Fe/Co-O-C-2.9, Fe/Co-O-C-1.5, Fe/Co-O-C-1.0, Fe/Co-O-C-0.56 and Co-O-Cat -0.30 V (vs. RHE). f, Plot of RNH₃ against the estimated bimetallic Fe-Co sites density in Fe/Co-C-O-r. Error bars in (a, b) and (d-f) represent data obtained from three-replicated experiments.
Figure 4

NRR activity origin of bimetallic Fe-Co site. a, b, DFT optimised configurations of \([\text{O-(C2)}_3\text{Fe-Co}(\text{O-C2})_3]\) (a) and side-on N2 adsorption on bimetallic Fe-Co site in \([\text{O-(C2)}_3\text{Fe-Co}(\text{O-C2})_3]\) (b). c, Gibbs free energy diagram of side-on N2 adsorption NRR pathway and DFT calculated intermediates structures on \([\text{O-(C2)}_3\text{Fe-Co}(\text{O-C2})_3]\) for initial electrocatalytic NRR cycle. d, e, DFT optimised configurations of \([\text{O-(C2)}_3\text{Fe-Co}(\text{O-C2})_3]\) after initial electrocatalytic NRR cycle (d) and side-on N2 adsorption on bimetallic Fe-Co site.
in [(O-C2)3Fe-Co(O-C)C2] (e). f, Gibbs free energy diagram of side-on N2 adsorption NRR pathway and DFT calculated intermediates structures on [(O-C2)3Fe-Co(O-C)C2]. Brown sphere: C; Red sphere: O; Orange sphere: Fe; Blue sphere: Co.

**Supplementary Files**

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