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Peer Review File

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

In this study, the authors presented an interfacial-fixing strategy for constructing high-density neighboring M-Nx sites on hollow carbon nanotubes. The unique and intriguing pre-design and anchoring mechanism of Fe2N6 sites were explored. The authors also employed various characterization methods to demonstrate the successfully maintained neighboring metal sites at a pre-designed distance. Interestingly, this strategy was extendable to a library of metal oxide matrices, resulting in corresponding high-density neighboring sites. Overall, I find this work well-organized with a compelling idea and recommend the publication of this work on Nature Communications after addressing the following minor comments.

-The authors should clarify how they ensured a fair comparison of electrochemical performances based on the same metal content in Fe1N4 and Fe2N6?

-Given that Fe2N6 was formed at the interface between Fe3O4 and carbon, the authors are suggested to investigate whether the coating thickness affects the distribution of Fe2N6 sites in the as-synthesized sample?

-When using urea for anchoring metal single atoms, the pyrolysis process typically results in the removal of a significant number of nitrogen atoms, leading to the aggregation of metal atoms. The authors are suggested to discuss how they addressed and overcame this particular challenge.

-Please review the text for grammar and ensure a smooth flow of the content.

-The reported synthetic methodology is impressive. The reviewer is not sure whether the ZAB application is best suitable for such catalysts. Are they stable in rechargeable ZAB? The authors could evaluate their application in the alkaline fuel cells or CO2 reduction in the future work.

Reviewer #2 (Remarks to the Author):

Review Comments

The manuscript outlines a new approach for synthesizing neighboring M2-Nx moieties (where M includes Fe, Cu, Co, Ni, Zn, and Mn) through an interfacial-fixing strategy from transition metal oxides to its final -N-C structures. Initially, a metal oxide template was synthesized using a hydrothermal method, followed by the coating of polydopamine (PDA) as a carbon and nitrogen source and subsequently pyrolyzing to form a carbon shell and facilitate the formation of M-Nx moieties, where the extra ligand feed of urea, NH3, or none governs the atomicity of the M. The resultant sample was tested for oxygen reduction reaction (ORR) under alkaline conditions and was further evaluated for its potential application in zinc-air battery (ZAB) systems. The central hypothesis of the work in designing and synthesizing dual-

atom M2 sites, against the conventional practice of increasing single-atom M1 population density to passively mimic the M2 effect by luck is well articulated. A recent perspective (doi.org/10.1016/j.checat.2023.100735) will help the authors to strengthen the point. However, more work is needed to resolve the following concerns before the work can be considered for publication.

1. The manuscript stated that the presence of bidentate ligand urea resulted in the successful synthesis of dual-atom Fe2-Nx catalytic sites with a lot of neighboring atoms compared to the situation where the urea was replaced by the monodentate ligand ammonia to make single-atom Fe1-Nx catalytic sites. While the single-atom catalysts with dilute Fe loading apparently have isolated atoms, the interatomic distances in the high-loading Fe dual-atom catalysts make readers wonder why the catalysts cannot be triple- or quatro-atom catalysts. The authors have shown the nearest atom from any targeted atom has an average distance of c.a. 0.3 nm, signaling the dual-atom structure derived from the two nearby Fe in Fe2O3 coordinated by the two amine terminals in urea. However, looking at the displayed STEM images for the claimed dual-atom catalysts, many of the second or third nearest atoms are often near that 0.3 nm threshold as well. Hence, the high loading of Fe makes it very hard to distinguish between high-density Fe1, Fe2, and possibly Fe3 or even Fe4. For a fair comparison and indisputable observation, authors shall develop Fe2-Nx sites with much lower loading, similar to that of the single-atom catalyst, and then gradually increase the Fe loading for at least one more stop before the current dual-site catalyst to show that the Fe2 is truly the case.

2. Considering the synthesis protocol and the low decomposition temperature of urea, at what temperatures will the bidentate urea still coordinate with two Fe atoms? How much N from urea will be present at the pyrolyzed temperature to increase the nitrogen (N) content besides the contribution of N from the PDA?

3. From the XRD peaks in Fig. S1, the Fe3O4@C sample has no carbon peak (usually around 26o), which does not confirm the presence of a carbon shell as they claim.

4. The authors mentioned that both Fe2N6 and Fe1N4 have similar specific surface area as well as pore diameter values. However, there wasn't any value stated for the BET surface area or the pore diameter. Also, from the plot (Fig. S33) the pore diameter distribution does not look the same for both samples.

5. From Fig. S34, the peaks in the CV curves do not correlate with the peak potentials recorded for Fe2N6 (0.78 V) and Fe1N4 (0.72 V) in the main manuscript (under the ORR performance section).

6. For clarity purposes, I suggest they add the LSV curve for both Pt/C and Fe2N6 to the plot in Fig. S38

7. The Accelerated Durability Test for Pt/C should also be shown or included as done for Fe2N6 and Fe1N4 in Fig. S45.

8. Under the Zinc-Air Battery (ZAB) section, I suggest they include the open circuit voltage (OCV) for the cell operating on the Pt/C cathode electrode. Moreover, for them to add 0.2 M Zinc acetate to the ZAB electrolyte means that they were operating a rechargeable ZAB, not a primary one. Hence, I suggest they include cycling performance for both their designed electrode and Pt/C.

9. The authors did not state the loading amount of the catalyst for the ZAB analysis. This factor helps in evaluating the performance of ZABs.

10. Post-reaction characterizations are necessary to prove the robustness of the critical samples.

11. In considering the findings, it appears that the synthesized Fe-catalyst demonstrates commendable performance, albeit not truly surpassing what might be considered typical for Fe in the context of ORR.

12. Fe2N6 and Fe1N4 look too much like iron nitrides. Authors may want to reconsider the naming strategy here.

Reviewer #3 (Remarks to the Author):

review attached.

In this manuscript, the authors present a study titled "General synthesis of neighboring metal-Nx moieties with a specific pre-designed distance via an interfacial-fixing strategy." The authors introduce interesting synthetic methods for fabricating single-atom catalysts. They utilize polydopamine to coat nanotemplates made of metal oxides, followed by pyrolysis to form a metal-oxide skeleton coated by rich nitrogen-doped carbon shells. After chemically etching the skeleton, only interfacial metal atoms strongly bond with the support. Various techniques are applied to analyze the atomic structure of the final catalyst materials, such as HADDF-STEM, XANES, EXAFS, and 3D atom-overlapping Gaussian-function fitting maps. During this procedure, the authors find that urea plays an important role in providing N-doped sites for Fe atom fixing and in creating pre-designed neighboring metal-Nx moieties.

The results and discussions presented are interesting to read, but there are several critical issues that hinder the publication of this manuscript in Nature Communications. Further detailed comments are provided below.

1. First and foremost, the reviewer cannot help but consider that the main results (the high concentration of neighboring metal-Nx moieties) in this manuscript might be influenced by the probability of metal loading, as mentioned by the authors in the conclusion section. Given the presence of numerous atomic metal species, the distance between each individual atom is expected to decrease. This concern also applies to another recently published paper by the authors in Nature Communications titled "Distance effect of single atoms on stability of cobalt oxide catalysts for acidic oxygen evolution". Therefore, it is crucial to exercise caution when using terms such as "specific pre-designed distance" and "tune the distance between the neighboring atoms" throughout the manuscript.

2. This is probably because that there are only one control sample to prove the validity of the interfacial fixing methods; one used urea (metal loading 2.36 wt%) and the other does not used urea (metal loading 0.32 wt%). If authors can provide more evidence to show the possibility for still making certain neighboring moieties at much lower metal loading or concentration, their argument can be much stronger.

3. The reviewer cannot find any evidence that the authors have successfully tune the distance between neighboring metal atoms. The distance between neighboring metal

atoms in this manuscript was ca. 0.29~0.30 nm. The one experiment using ethanediamine, which has a larger distance between N atom, only produce isolated sites without the formation of adjacent units, as authors claim. The resolution of Fig. S19 for this sample needs to be improved and applying same analysis for their main sample (Fe_2N_6), such as measuring distance between adjacent atoms and analyze the distribution, may give new insight.

4. Interfacial fixing strategy was interesting to make a single atom catalyst with high metal loading and high electrochemical activity. And the use of urea, which provide N-doped site, have an important role in metal atom fixing. However, if one urea held two Fe atoms to make an adjacent unit, where all the other N-sources come to form Fe_2N_6? And if high concentration of urea is considered to provide sufficient N source, the fixing effect may not from the single urea molecules, but from the abundant N-doped site.

5. The results of EXAFS fitting should be performed correctly, since the results with an R factor of 0.28 suggests that there is a discrepancy between the experimental data and the theoretical fit.

6. Author applied acetylene TPD analysis to validate the quantitative and qualitative analysis for single and dual site. A. Fe2N6 sample has ca. 8 times larger amount of active sites than Fe1N4, but the intensity of TPD signal is almost similar to each other. How can it be explained? B. The distance for the C-C bonding in acetylene is only 0.12 nm. How does author think it can be adsorbed to dual Fe site via a bidentate mode? If the binding energy can be simulated from theoretical calculations, it is recommended to be provided for the reader to understand. C. how is the value for the purity of dual site changed from 91.4% to 95.5%? please explains the details of the process.

7. The result of Pt/C catalyst (E1/2= 0.8V) significantly lower performance compared to the results of other report literatures. How does the performance of commercial catalyst show much lower results than usual? Please provide a justification for the observed inconsistency.

Point-by-point response to reviewers' comments
Manuscript ID: NCOMMS-24-02257
Title: General synthesis of neighboring metal-N$_x$ moieties with a specific pre-designed distance via an interfacial-fixing strategy

Reviewer #1

"In this study, the authors presented an interfacial-fixing strategy for constructing high-density neighboring M-Nx sites on hollow carbon nanotubes. The unique and intriguing pre-design and anchoring mechanism of Fe2N6 sites were explored. The authors also employed various characterization methods to demonstrate the successfully maintained neighboring metal sites at a pre-designed distance. Interestingly, this strategy was extendable to a library of metal oxide matrices, resulting in corresponding high-density neighboring sites. Overall, I find this work well-organized with a compelling idea and recommend the publication of this work on Nature Communications after addressing the following minor comments."

We sincerely thank the reviewer for the constructive suggestions, which have helped us to improve the quality of our work. We have addressed the reviewer's comments as follows.

"-The authors should clarify how they ensured a fair comparison of electrochemical performances based on the same metal content in Fe1N4 and Fe2N6?"

We genuinely thank this reviewer for his/her valuable comments. In order to make a comparison between the catalytic activities of Fe$_1$-N$_4$ and Fe$_2$-N$_6$ samples, we have mixed Fe$_2$-N$_6$ with the C-N matrix in an electrode to ensure the same content of Fe atoms in the prepared electrode as that in Fe$_1$-N$_4$. Specifically, For Fe$_1$-N$_4$, 2 mg of the sample (0.32 wt% Fe) and 5 μL of Nafion solution (5 wt%) were dispersed in 400 μL of ethanol solution by sonication for 1 h to form a homogeneous ink. Next, 10 μL of the catalyst dispersion was pipetted onto a glassy carbon electrode with a diameter of 5 mm. The Fe content in this electrode was 1.6×10^{-4} mg. For Fe$_2$N$_6$, 0.678 mg of the sample (2.36 wt%) and 4.32 mg of C-N sample were mixed with 12 μL of Nafion solution in 1000 μL of ethanol solution by sonication for 1 h to form homogeneous ink. Next, 10 μL of the catalyst dispersion was pipetted onto a glassy carbon electrode with a diameter of 5 mm, and the mixed catalyst was denoted as Fe$_2$-N$_6$/C-N. As such, the Fe content in this electrode was also 1.6×10^{-4} mg, equal to that of the electrode containing Fe$_1$-N$_4$. The resulted electrochemical analysis was shown in Figure S39. Fe$_2$-N$_6$/C-N sample shows a more positive $E_{1/2}$ than that of Fe$_1$-N$_4$ catalyst.

We have added the relevant discussion in the revised manuscript (p. 11, lines 20-26, p. 20, lines 16-26, p. 21, lines 1-2, Supplementary Fig. 39, highlighted in yellow color).

"-Given that Fe2N6 was formed at the interface between Fe3O4 and carbon, the authors are suggested to investigate whether the coating thickness affects the distribution of Fe2N6 sites in the as-synthesized sample?"

Thanks for raising this issue. In the revised work, we have increased the thickness of the nanotubes by applying double usage of PDA. Adjacently anchored Fe sites were also obtained,

as confirmed in Supplementary Figures 12 and 13. We have added the relevant discussion in the revised manuscript (p. 7, lines 2-3, Supplementary Figs. 12 and 13, highlighted in yellow color).

"-When using urea for anchoring metal single atoms, the pyrolysis process typically results in the removal of a significant number of nitrogen atoms, leading to the aggregation of metal atoms. The authors are suggested to discuss how they addressed and overcame this particular challenge."

Thanks for raising this point. This question is just the difference between our "top-down" strategy and other "bottom-up" strategies for the synthesis of single-atom catalysts. General "bottom-up" strategies directly loaded metal precursors on the supports *via* electrostatic adsorption, chemical reduction, electrochemical deposition, and others [*Nature* 2022, 611, 284; *Science* 2016, 352, 797-800; *Nature Commun.* 2020, 11, 1215]. For these strategies, the use of urea to anchor metal single atoms on the supports is likely to encounter the reviewer's problem where most of the N atoms of urea are removed as N_2, resulting in the aggregation of neighboring metal atoms. In stark contrast, our work offers a "top-down" strategy. The urea was used as a coating layer between Fe_2O_3 interface and polydopamine (PDA) layer. After pyrolysis, urea molecules were decomposed into two parts. One part is merged in the outer carbon layer, along with the pyrolysis of PDA. The other part becomes N atoms to link Fe atoms in the inner Fe_3O_4 core and C atoms in the outer carbon layer. Fe singe atoms come from the etching of Fe_3O_4. Since Fe atoms on the surface of Fe_3O_4 are already separated by lattice O atoms, we do not need to worry about the aggregation of Fe atoms induced by the removal of N atoms in urea. The loss of N atoms can only induce fewer anchoring sites between Fe_3O_4 and carbon layers and result in more isolated sites, instead of leading to aggregation. This is why we added excessive urea molecules for the preparation of Fe dual sites. The pyrolysis temperature possibly influences the loss of N atoms and thus the purity of Fe dual sites. In principle, our "top-down" strategy never meets the problem of aggregation.

"-Please review the text for grammar and ensure a smooth flow of the content."

Thanks for constructive suggestions. We have carefully checked the language and corrected the typos in the revised manuscript.

"-The reported synthetic methodology is impressive. The reviewer is not sure whether the ZAB application is best suitable for such catalysts. Are they stable in rechargeable ZAB? The authors could evaluate their application in the alkaline fuel cells or CO_2 reduction in the future work."

Thanks very much for your suggestions. We have assembled rechargeable ZAB with synthesized Fe_1-N_4 and Fe_2-N_6 in the revised manuscript. Supplementary Figure S50 shows the corresponding cycling performance. According to the reviewer's comments, we have tested the CO_2 reduction capability of these two catalysts (Figure R1). In alkaline (1 M KOH, pH=14.0) electrolyte, both catalysts enabled the production of CO. Specifically, Fe_1-N_4 showed the faradaic efficiency for CO (FE_{CO}) of 12.8% at -1.0 V versus relative hydrogen electrode. In contrast, Fe_2-N_6 achieved a higher FE_{CO} of 33.2% at -1.0 V versus relative hydrogen electrode. Thus, Fe_1-N_4 and Fe_2-N_6 were not suitable for CO_2 reduction reactions. We have added the relevant discussion in the revised manuscript (p. 13, lines 13-15, Supplementary Fig. 50,
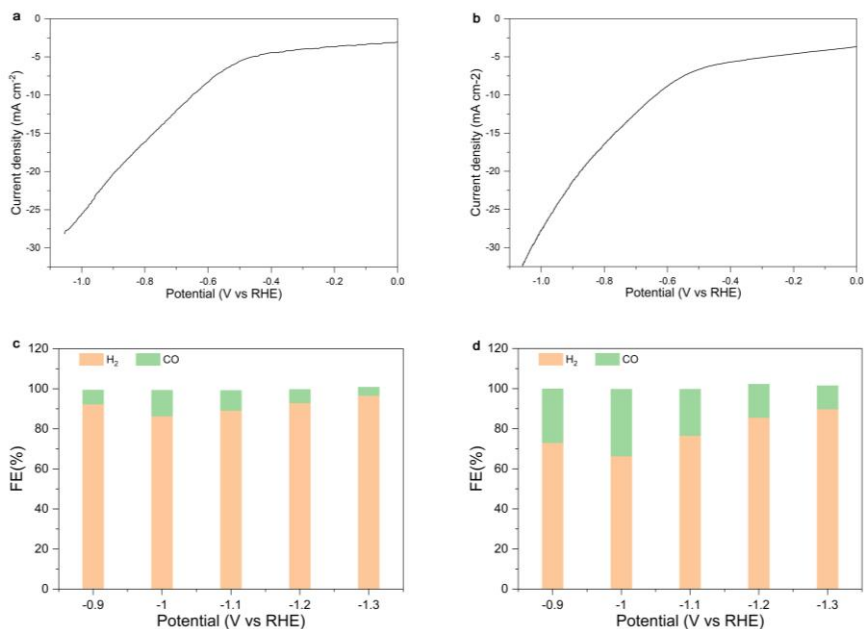
highlighted in yellow color).

Figure R1. (a) LSV curve and (c) CO$_2$RR properties of Fe$_1$-N$_4$. (b) LSV curve and (d) CO$_2$RR properties of Fe$_2$-N$_6$ catalyst.

Reviewer #2

"The manuscript outlines a new approach for synthesizing neighboring M2-Nx moieties (where M includes Fe, Cu, Co, Ni, Zn, and Mn) through an interfacial-fixing strategy from transition metal oxides to its final -N-C structures. Initially, a metal oxide template was synthesized using a hydrothermal method, followed by the coating of polydopamine (PDA) as a carbon and nitrogen source and subsequently pyrolyzing to form a carbon shell and facilitate the formation of M-Nx moieties, where the extra ligand feed of urea, NH3, or none governs the atomicity of the M. The resultant sample was tested for oxygen reduction reaction (ORR) under alkaline conditions and was further evaluated for its potential application in zinc-air battery (ZAB) systems. The central hypothesis of the work in designing and synthesizing dual-atom M2 sites, against the conventional practice of increasing single-atom M1 population density to passively mimic the M2 effect by luck is well articulated. A recent perspective (doi.org/10.1016/j.checat.2023.100735) will help the authors to strengthen the point. However, more work is needed to resolve the following concerns before the work can be considered for publication."

We sincerely thank the reviewer for his/her valuable comments, which have helped us to enhance the reliability and quality of our work. The perspective raised by the reviewer (doi.org/10.1016/j.checat.2023.100735) is particularly insightful, especially in the section on "Interatomic interactions control supported metal reactivity in ADSMCs." We have cited this work in the revised manuscript (Ref. 13). We believe our work supports this perspective, as we propose a novel strategy to fabricate dual atom pairs systematically rather than relying on chance

by increasing metal loading. Detailed responses to the reviewer's concerns are listed below.

"1. The manuscript stated that the presence of bidentate ligand urea resulted in the successful synthesis of dual-atom Fe2-Nx catalytic sites with a lot of neighboring atoms compared to the situation where the urea was replaced by the monodentate ligand ammonia to make single-atom Fe1-Nx catalytic sites. While the single-atom catalysts with dilute Fe loading apparently have isolated atoms, the interatomic distances in the high-loading Fe dual-atom catalysts make readers wonder why the catalysts cannot be triple- or quatro-atom catalysts. The authors have shown the nearest atom from any targeted atom has an average distance of c.a. 0.3 nm, signaling the dual-atom structure derived from the two nearby Fe in Fe2O3 coordinated by the two amine terminals in urea. However, looking at the displayed STEM images for the claimed dual-atom catalysts, many of the second or third nearest atoms are often near that 0.3 nm threshold as well. Hence, the high loading of Fe makes it very hard to distinguish between high-density Fe1, Fe2, and possibly Fe3 or even Fe4. For a fair comparison and indisputable observation, authors shall develop Fe2-Nx sites with much lower loading, similar to that of the single-atom catalyst, and then gradually increase the Fe loading for at least one more stop before the current dual-site catalyst to show that the Fe2 is truly the case."

As this reviewer mentioned, the key to synthesizing isolated or neighboring Fe atoms is whether a monodentate ligand, such as ammonia, or a bidentate ligand, such as urea, is used. However, in our initial manuscript, we found that the purity of dual Fe pairs was influenced by the amount of urea added, even though excess amount of urea is used as the ligand. This discrepancy arises because we used a pyrolysis temperature of 700 °C, while urea is decomposed at 200-250 °C. When the amount of urea was low, many urea molecules decomposed, preventing each urea molecule from fixing two Fe atoms, which resulted in a predominance of Fe monoatoms. Conversely, when an excess of urea molecules was used, they were replenished even after decomposition, maintaining a high Fe diatomic purity. Therefore, the more urea present in the ligand molecule, the higher the Fe content and purity of the Fe diatoms. In other words, we have yet to decouple diatomic purity from Fe content. Thus, achieving a sample with low Fe loading and high Fe diatomic purity is crucial to proving the validity of our synthesis method.

Following the reviewer's suggestion, we have adjusted the amount of urea added during the synthesis process and measured the Fe loading and the distance between Fe atoms. We found that as the amount of urea increased from 10 to 100 mg, the Fe loading increased from 0.55 to 2.36 wt%, while the distance between iron atoms decreased from 0.54 to 0.29 nm, with the distribution of distances between Fe atoms becoming more concentrated (Fig. R2). When the amount of urea exceeded 100 mg (e.g. 120 mg), the Fe loading and the distance between iron atoms remained largely unchanged at 2.37 wt% and 0.29 nm, respectively, due to saturation (Fig. R3). This demonstrates that this distance is the intrinsic distance between Fe atoms under our synthesis method.

Table R1. Comparison of synthesis conditions.

Sample	Coordination molecules	Usage of coordination molecules (mg)	Pyrolysis temperature (°C)	Fe contents (wt%)
Fe$_1$N$_4$	No urea	/	700	0.32

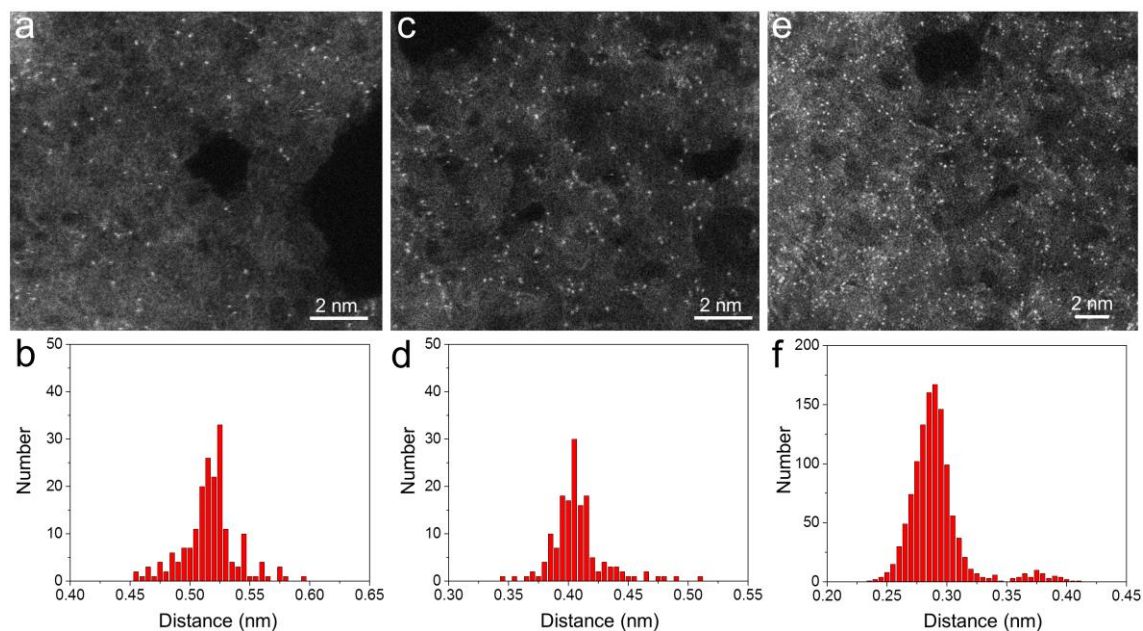| Fe₂N₆	Urea	10	700	0.55
Fe_2N_6	Urea	10	700	0.55
Fe_2N_6	Urea	30	700	0.96
Fe_2N_6	Urea	50	700	1.32
Fe_2N_6	Urea	100	700	2.36
Fe_2N_6	Urea	120	700	2.37
Fe_2N_6	Urea	50	500	1.62

Figure R2. HAADF-STEM images of dual-atom Fe_2-N_x catalyst by using (a) 10, (c) 50, and (e) 100 mg of urea. (b, d, f) Distance distribution between neighboring Fe atoms.
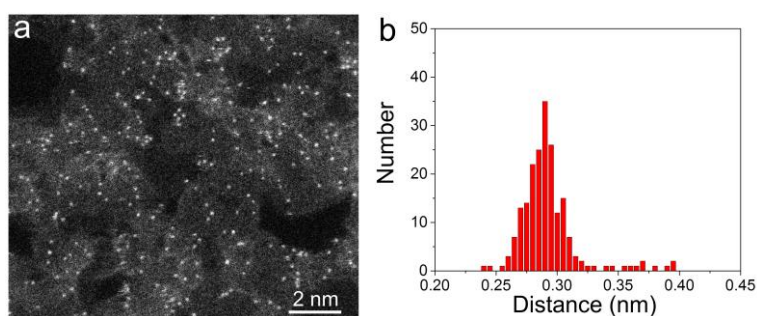

Figure R3. HAADF-STEM images of dual-atom Fe_2-N_x catalyst by using 120 mg of urea and the corresponding distance distribution between neighboring Fe atoms.

Additionally, we have tuned the pyrolysis temperature to minimize the decomposition loss of urea molecules while ensuring the occurrence of the pyrolysis reaction. In the revised manuscript, we lowered the pyrolysis temperature to 500 °C and reduced the urea content to 50 mg (see Table R1 for synthesis condition comparison). The Fe content in the synthesized sample was reduced to 1.62%, while maintaining high Fe diatomic purity (Fig. R4). Notably, the Fe content of 1.62% at a pyrolysis temperature of 500 °C was higher than that (1.32%) at 700 ºC, implying

R5

that lowering the pyrolysis temperature indeed decreased the loss of urea molecules and thereby increased the amount of anchored Fe atoms.
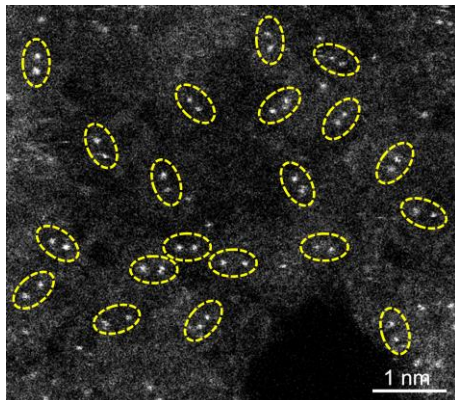

Figure R4. HAADF-STEM image of dual-atom Fe_2-N_x catalyst by using 50 mg of bidentate ligand of urea at a pyrolysis temperature of 500 °C.

With the reviewer's suggestion, we shifted the focus of our synthesis method from adjusting the amount of urea to changing the type of ligand. Specifically, the monodentate ligand ammonia yields isolated Fe single atoms, while the bidentate ligand urea yields Fe atom pairs. This was confirmed experimentally. Thus, we can decouple the relationship between metal loading and metal diatomic purity, thoroughly explaining that our synthesis method is unaffected by loading probability. We are very grateful to the reviewers for their suggestions, which greatly enhance the novelty and credibility of the article.

We have added the relevant discussion in the revised manuscript (p. 9, lines 27-31; p. 10, lines 1-10, p. 15, lines 8-10, Supplementary Figs. 27-29, Supplementary Table 3, highlighted in yellow color).

"2. Considering the synthesis protocol and the low decomposition temperature of urea, at what temperatures will the bidentate urea still coordinate with two Fe atoms? How much N from urea will be present at the pyrolyzed temperature to increase the nitrogen (N) content besides the contribution of N from the PDA?"

We genuinely thank this reviewer for his/her valuable comments. We think the bidentate urea still coordinate with the two Fe atoms before they were decomposition (250 °C). As shown in Table R2, pure N-C obtained from carbonized PDA contained the same amount of nitrogen as that of Fe_1-N_4 (5.1 wt%), which was lower than that (9.2 wt%) of Fe_2-N_6. As such, additional urea molecules contribute 4.1 wt% of nitrogen containing to the resulted F_2-N_6 sample given the 5.1 wt % of nitrogen from PDA. We have added the relevant discussion in the revised manuscript (p. 5, lines 8-12; Supplementary Table 1, highlighted in yellow color).

Table R2. Nitrogen containing in samples of pure N-C, Fe_1-N_4 and Fe_2-N_6.

Samples	Before etching

Pure N-C from PDA	5.1 wt%
Fe_1-N_4	5.1 wt%
Fe_2-N_6	9.2 wt%

"3. From the XRD peaks in Fig. S1, the Fe_3O_4@C sample has no carbon peak (usually around 26°), which does not confirm the presence of a carbon shell as they claim."

Thanks for raising this issue. The absence of carbon peak, typically observed at around 26°, can be attributed to the strong diffraction peak of Fe_3O_4. The walls of the formed carbon tubes were too thin to produce noticeable diffraction peaks. This phenomenon has also been documented in other literature (Fig. R5) [Carbon 2021, 179, 327-336]. We have added the relevant explanation in the note of Supplementary Figure 1.
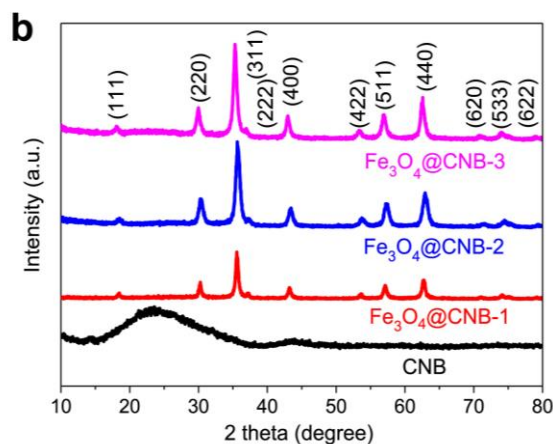

Figure R5. XRD patterns of prepared Fe_3O_4@CNBs and other samples. (Ref. Carbon 2021, 179, 327-336.)

"4. The authors mentioned that both Fe2N6 and Fe1N4 have similar specific surface area as well as pore diameter values. However, there wasn't any value stated for the BET surface area or the pore diameter. Also, from the plot (Fig. S33) the pore diameter distribution does not look the same for both samples."

Thanks for the reviewer's reminding. We have included the BET surface area and pore diameters in the original manuscript (Table R3). Specifically, Fe_1-N_4 exhibited a specific surface area of 521 $m^2\,g^{-1}$ with a main pore size of approximately 15.0 nm, while Fe_2-N_6 had a specific surface area of 507 $m^2\,g^{-1}$ with a main pore size of 13.6 nm. These results indicate that the two samples have similar specific surface areas and porosities.

To ensure the accuracy and reliability of our data, we have conducted the BET measurements two additional times and provided the average values with the standard deviation in Table R3. This reinforces our confidence that both samples have similar specific surface areas and porosities, effectively excluding the influence of pore structures.

Table R3. Average specific surface area and pore size for Fe_1-N_4 and Fe_2-N_6 samples.

Samples	Items	No. 1	No. 2	No. 3	Average value	Standard deviation
Fe_1-N_4	Surface area ($m^2\ g^{-1}$)	521	509	514	515	5
Fe_2-N_6	Surface area ($m^2\ g^{-1}$)	507	518	515	513	5
Fe_1-N_4	Pore size (nm)	15.0	13.2	14.1	14.1	0.7
Fe_2-N_6	Pore size (nm)	13.6	14.5	14.9	14.3	0.5

We have added the relevant discussion in the revised manuscript (p. 10, line 31; p. 11, lines 1-2; Supplementary Fig. 36, Supplementary Table 4, highlighted in yellow color).

"5. From Fig. S34, the peaks in the CV curves do not correlate with the peak potentials recorded for Fe2N6 (0.78 V) and Fe1N4 (0.72 V) in the main manuscript (under the ORR performance section)."

Thanks for your reminder. Now we have checked the curves and the values. The peak potentials should be 0.92 V vs RHE for Fe_2-N_6 and 0.87 V vs RHE for Fe_1-N_4, respectively. We have added these values in the revised manuscript (p. 11, lines 4-6, Supplementary Fig. 37, highlighted in yellow color).

"6. For clarity purposes, I suggest they add the LSV curve for both Pt/C and Fe2N6 to the plot in Fig. S38"

As suggested, we have added the LSV curves of both Pt/C and Fe_2-N_6 (Fig. R6) in the revised manuscript (Supplementary Fig. 41).
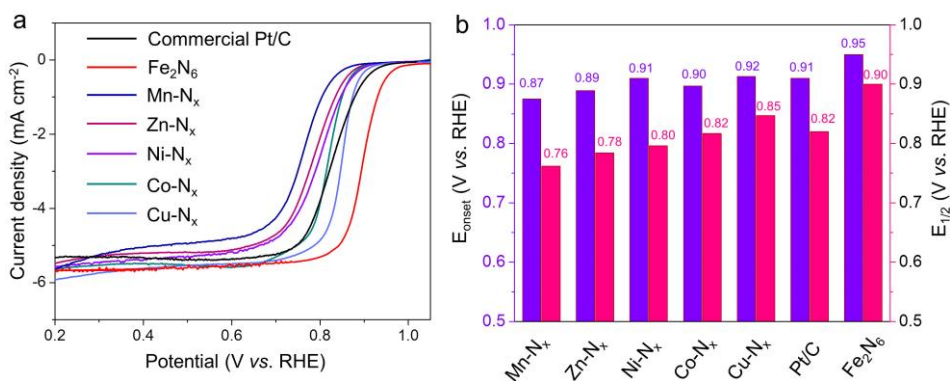

Figure R6. Comparison in ORR activities of different neighboring $M-N_x$ (M = Cu, Co, Ni, Zn, and Mn) moieties. (a) LSV curves and (b) corresponding electrochemical values of $M-N_x$ (M = Cu, Co, Ni, Zn, and Mn), Fe_2-N_6, and commercial Pt/C.

Here, the obtained values of onset points and half-wave potentials over $M-N_x$ (M = Cu, Co, Ni, Zn, and Mn) moieties were lower than those over $Fe-N_x$ species.

We have added the relevant discussion in the revised manuscript (p. 11, lines 27-30; Supplementary Fig. 41, highlighted in yellow color).

"7. The Accelerated Durability Test for Pt/C should also be shown or included as done for Fe2N6 and Fe1N4 in Fig. S45."

As requested, we have added the durability test of commercial Pt/C in the revised manuscript. Pt/C exhibited an $E_{1/2}$ decay of 55 mV after 50,000 cycles, which was significantly larger than those of Fe_2-N_6 (10 mV) and Fe_1-N_4 (36 mV) (Fig. R7). As seen in Supplementary Figure 48. We have added the relevant discussion in the revised manuscript (p. 13, line 1; highlighted in yellow color).
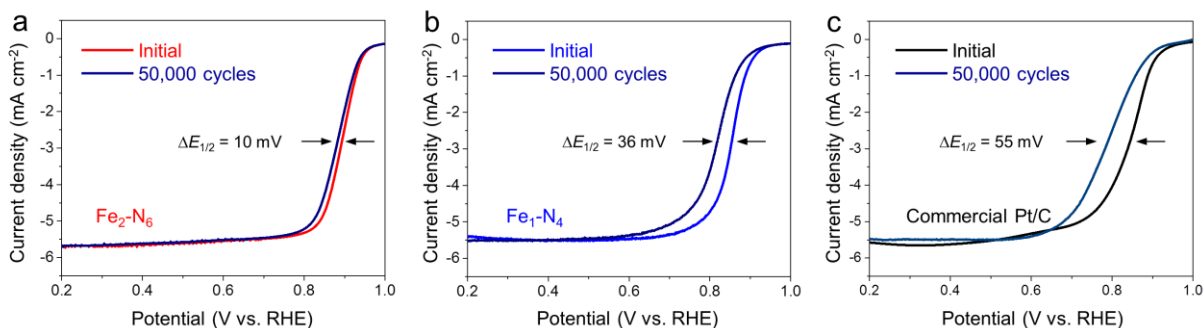

Figure R7. ORR polarization curves before and after 50,000 cycles. (a) Fe_2-N_6, (b) Fe_1-N_4 and (c) commercial Pt/C.

"8. Under the Zinc-Air Battery (ZAB) section, I suggest they include the open circuit voltage (OCV) for the cell operating on the Pt/C cathode electrode. Moreover, for them to add 0.2 M Zinc acetate to the ZAB electrolyte means that they were operating a rechargeable ZAB, not a primary one. Hence, I suggest they include cycling performance for both their designed electrode and Pt/C."

As requested, we have provided the open circuit voltage for the cell operating on the Pt/C cathode electrode. As seen in Figure R8, Zn-air batteries with Fe_2-N_6, Fe_1-N_4, and commercial Pt/C cathode electrode showed open circuit voltages of 1.425, 1.380 and 1.410 V, respectively. We have added the relevant discussion in the revised manuscript (p. 13, lines 5-7; Supplementary Fig. 49, highlighted in yellow color).
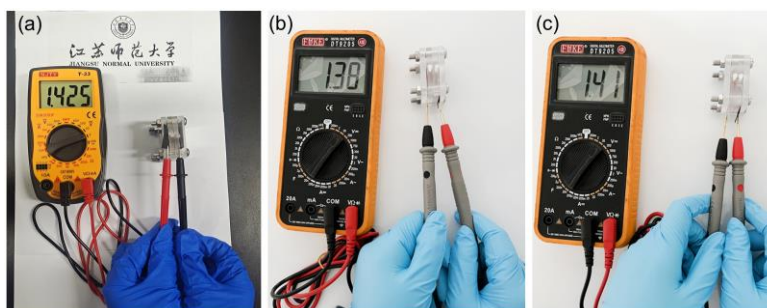
Figure R8. Photo showing the voltage of a single Zn-air battery with (a) Fe_2-N_6 , (b) Fe_1-N_4, and (c) commercial Pt/C as the cathodic catalyst.

Additionally, we have also provided the cycling performance of Fe_2-N_6, Fe_1-N_4, and commercial Pt/C. As seen in Figure R9, Fe_2-N_6 were stably cycled up to 70 h, much more stable than Fe_1-N_4 and commercial Pt/C. We have added the relevant discussion in the revised manuscript (p. 13, lines 13-15; Supplementary Fig. 50, highlighted in yellow color).
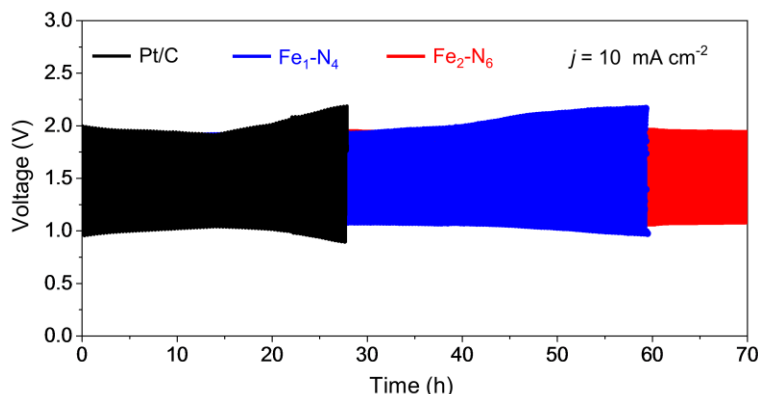

Figure R9. Long-term cycling performance of commercial Pt/C, Fe_1-N_4 and Fe_2-N_6 samples.

"9. The authors did not state the loading amount of the catalyst for the ZAB analysis. This factor helps in evaluating the performance of ZABs."

The amount of catalysts used in the cathode was 0.25 mg cm^{-2} for Fe_2-N_6, Fe_1-N_4, and commercial Pt/C. We have added this value in the revised experimental section. We have added this information in the revised manuscript (p. 22, lines 14-15; highlighted in yellow color).

"10. Post-reaction characterizations are necessary to prove the robustness of the critical samples."

As suggested, we have characterized Fe_2-N_6 catalysts after 50,000 times cycling in the revised manuscript. The HAADF-STEM image of the spent Fe_2-N_6 showed the preservation of Fe atom pairs, suggesting the robustness of this catalyst (Fig. R10). We have added the relevant discussion in the revised manuscript (p. 13, lines 24-25; Supplementary Fig. 52, highlighted in yellow color).
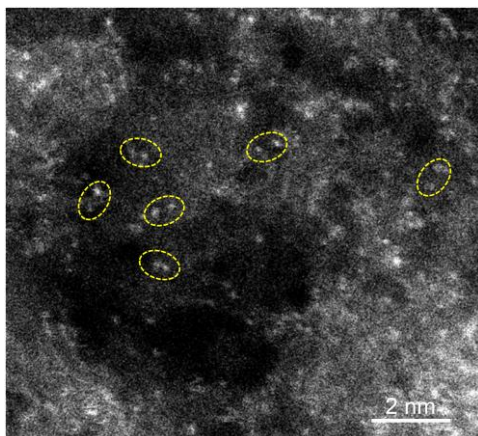
Figure R10. HAADF-STEM image of prepared Fe_2-N_6 catalyst after long-term cycling of 50,000 times.

"11. In considering the findings, it appears that the synthesized Fe-catalyst demonstrates commendable performance, albeit not truly surpassing what might be considered typical for Fe in the context of ORR."

The primary focus of this work is to introduce a novel methodology for fabricating metal atom pairs, rather than to report a record-high ORR catalyst. We used ORR merely as a model reaction to compare the differences between isolated and neighboring Fe atoms. While we acknowledge that our developed catalysts did not surpass the state-of-the-art ORR catalysts, we believe that our methodology has become more solid after incorporating the reviewer's suggestions.

"12. Fe2N6 and Fe1N4 look too much like iron nitrides. Authors may want to reconsider the naming strategy here."

Thanks for the reviewer's comment. To avoid any confusion with iron nitrides, we have renamed the samples as "Fe_2-N_6" and "Fe_1-N_4" in both the revised text and figures.

Reviewer #3

"In this manuscript, the authors present a study titled "General synthesis of neighboring metalNx moieties with a specific pre-designed distance via an interfacial-fixing strategy." The authors introduce interesting synthetic methods for fabricating single-atom catalysts. They utilize polydopamine to coat nanotemplates made of metal oxides, followed by pyrolysis to form a metal-oxide skeleton coated by rich nitrogen-doped carbon shells. After chemically etching the skeleton, only interfacial metal atoms strongly bond with the support. Various techniques are applied to analyze the atomic structure of the final catalyst materials, such as HADDF-STEM, XANES, EXAFS, and 3D atom-overlapping Gaussian-function fitting maps. During this procedure, the authors find that urea plays an important role in providing N doped sites for Fe atom fixing and in creating pre-designed neighboring metal-Nx moieties.
The results and discussions presented are interesting to read, but there are several critical issues that hinder the publication of this manuscript in Nature Communications. Further detailed

comments are provided below."

We sincerely thank this reviewer for his/her valuable comments which help us improve the quality of our work.

"1. First and foremost, the reviewer cannot help but consider that the main results (the high concentration of neighboring metal-Nx moieties) in this manuscript might be influenced by the probability of metal loading, as mentioned by the authors in the conclusion section. Given the presence of numerous atomic metal species, the distance between each individual atom is expected to decrease. This concern also applies to another recently published paper by the authors in Nature Communications titled "Distance effect of single atoms on stability of cobalt oxide catalysts for acidic oxygen evolution". Therefore, it is crucial to exercise caution when using terms such as "specific pre-designed distance" and "tune the distance between the neighboring atoms" throughout the manuscript."

Thanks for raising this point. In the original manuscript, we indeed did not clearly explain the issue of distance regulation. This made it appear that as the addition amount of urea increased, the Fe loading also increased, while Fe atoms became closer to each other. This gave the impression that higher Fe loading led to closer Fe atoms. However, this is not the fact we want to emphasize. In our work, due to the limitations of the lattice spacing of Fe-based templates and the distance between the two N atoms in the urea ligand, the closest two Fe atoms cannot approach infinitely and have a minimum value, which is the current distance of 0.29 nm. Our synthesis method ensured the absence of clusters because we etched away any potential clusters during the acid etching stage.

To verify this point, we have adjusted the amount of urea added during the synthesis process and also measured the Fe loading and the distance between Fe atoms. We found that as the addition amount of urea increased from 10 to 100 mg, the Fe loading increased from 0.55 to 2.36 wt%, while the distance between iron atoms decreased from 0.54 to 0.29 nm, with the distribution of distances between Fe atoms becoming more concentrated (Fig. R2). When the amount of urea exceeded 100 mg (e.g. 120 mg), the Fe loading and the distance between iron atoms remained largely unchanged at 2.37 wt% and 0.29 nm, respectively, due to saturation (Fig. R3). This demonstrates that this distance is the intrinsic distance between Fe atoms under our synthesis method.
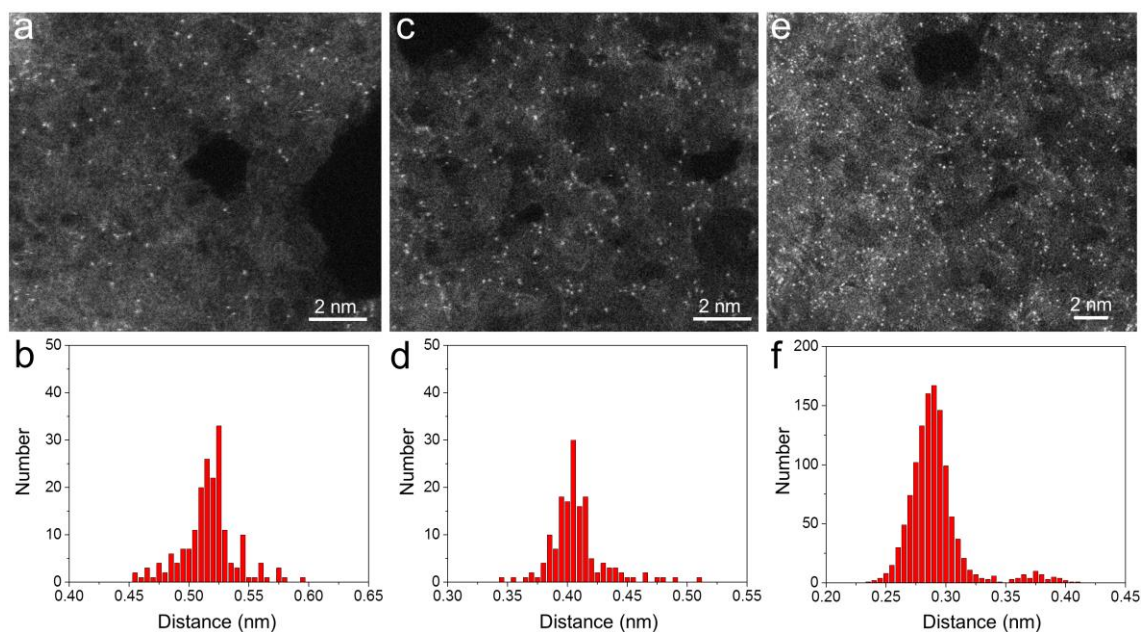
Figure R2. HAADF-STEM images of dual-atom Fe_2-N_x catalyst by using (a) 10, (c) 50, and (e) 100 mg of urea. (b, d, f) Distance distribution between neighboring Fe atoms.
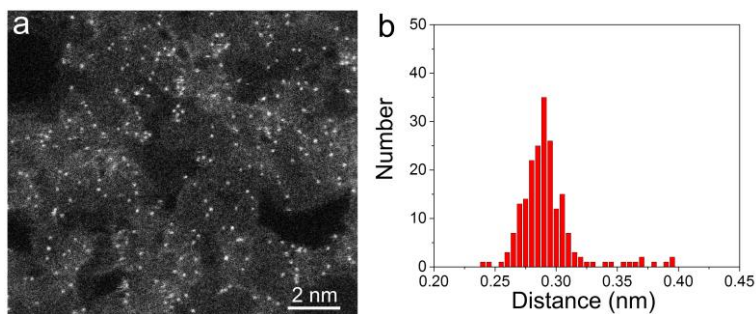

Figure R3. HAADF-STEM images of dual-atom Fe_2-N_x catalyst by using 120 mg of urea and the corresponding distance distribution between neighboring Fe atoms.

Table R1. Comparison of synthesis conditions.

Sample	Coordination molecules	Usage of coordination molecules	Pyrolysis temperature	Fe contents (wt%)
Fe_1-N_4	No urea	/	700	0.32
Fe_2-N_6	Urea	10	700	0.55
Fe_2-N_6	Urea	30	700	0.96
Fe_2-N_6	Urea	50	700	1.32
Fe_2-N_6	Urea	100	700	2.36
Fe_2-N_6	Urea	120	700	2.37
Fe_2-N_6	Urea	50	500	1.62

The above results occurred because the pyrolysis temperature we used was 700 ºC, while the

decomposition temperature of urea was 250 ºC. When the urea content was low, a large number of urea molecules could decompose, preventing each urea molecule from fixing two Fe atoms, leading to a random distribution of Fe single atoms. When we used an excess of urea molecules, even if some decomposed, there would still be a supplement, maintaining a high purity of Fe atom pairs. Using this method, the more urea molecules, the higher the Fe content and the higher the purity of Fe atom pairs. In other words, we still cannot decouple the purity of diatomic species from the Fe content. Therefore, achieving a sample with low Fe loading and high Fe diatomic purity is the key to proving the rationality of our synthesis method. To this end, we need to adjust the pyrolysis temperature to minimize the decomposition loss of urea molecules while ensuring the occurrence of the pyrolysis reaction. In the revised manuscript, we have lowered the pyrolysis temperature to 500 ºC and decreased the urea content to 50 mg (see Table 1 for synthesis condition comparison). The Fe content in the synthesized sample was reduced to 1.62 wt%, while maintaining high Fe diatomic purity (Fig. R4). Notably, the Fe content of 1.62% at a pyrolysis temperature of 500 °C was higher than that (1.32%) at 700 ºC, implying that lowering the pyrolysis temperature indeed decreased the loss of urea molecules and thereby increased the amount of anchored Fe atoms.
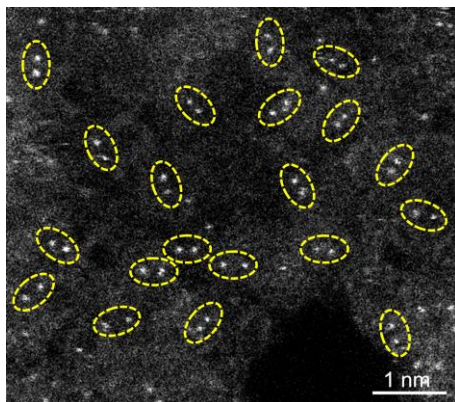

Figure R4. HAADF-STEM image of dual-atom Fe_2-N_x catalyst by using 50 mg of bidentate ligand of urea at a pyrolysis temperature of 500 °C.

With the reviewer's suggestion, we have shifted the core of our synthesis method from adjusting the amount of urea to changing the type of ligand. That is, the monodentate ligand ammonia can yield Fe single atoms, while the bidentate ligand urea can yield Fe atom pairs. This was confirmed experimentally. In this way, we can decouple the relationship between metal loading and metal diatomic purity, thoroughly explaining that our synthesis method is not affected by the probability of loading.

To regulate the distance between two atoms, we replaced urea with ethylenediamine ligand. The distance between the two N atoms in urea is 0.29 nm, while in ethylenediamine it is 0.27 and 0.38 nm. Using a similar synthesis method, we found that the distance between Fe atoms became 0.27-0.39 nm (Figure R11), but this distance distribution was wider. This is because ethylenediamine is a flexible molecule, and the distance between the two N atoms on the carbon chain can easily change, making it difficult to fix the distance between two Fe atoms. As seen in Supplementary Figure S19.
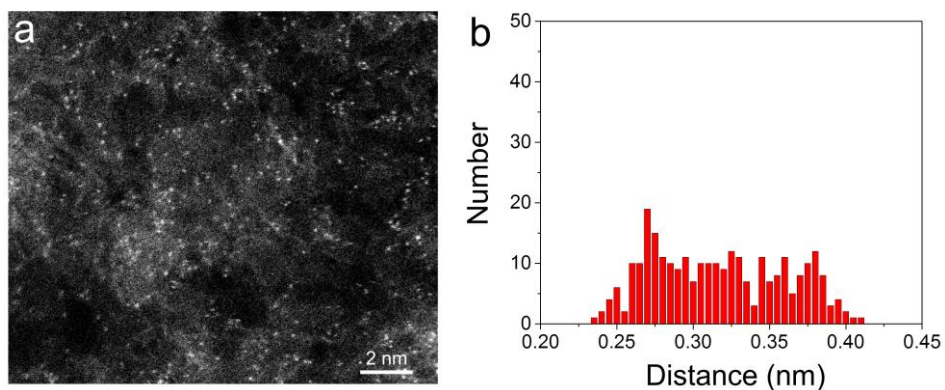
Figure R11. (a) HAADF-STEM image of prepared Fe moiety with ligand of ethanediamine. (b) Distance distribution between adjacent atoms.

In summary, we acknowledge that our current synthesis method cannot achieve 100% precise control of the distance between two metal atoms. However, the reviewer's suggestion helped us improve and refine our synthesis methodology, greatly enhancing the novelty and credibility of our paper.

We have added the relevant discussion in the revised manuscript (p. 9, lines 27-31; p. 10, lines 1-10; p. 7, lines 23-27; p. 17, lines 23-28, Supplementary Figs. 27-29, Supplementary Table 3, highlighted in yellow color).

"2. This is probably because that there are only one control sample to prove the validity of the interfacial fixing methods; one used urea (metal loading 2.36 wt%) and the other does not used urea (metal loading 0.32 wt%). If authors can provide more evidence to show the possibility for still making certain neighboring moieties at much lower metal loading or concentration, their argument can be much stronger."

We appreciate the reviewer's insightful suggestions. In our original manuscript, we observed that the purity of Fe atom pairs was strongly influenced by the amount of urea added during synthesis. In the revised manuscript, we have adjusted the amount of urea added during the synthesis process and also measured the Fe loading and the distance between Fe atoms. We found that as the addition amount of urea increased from zero to 10 mg, the Fe loading increased from 0.32 to 0.55 wt%, while the distance between iron atoms decreased from 0.6 to 0.54 nm, with the distribution of distances between Fe atoms becoming more concentrated (Fig. R2). When the amount of urea exceeded 100, the Fe loading and the distance between iron atoms remained largely unchanged at 2.36 wt% and 0.29 nm, respectively, due to the saturation (Fig. R3). This is due to the pyrolysis temperature we used being 700 °C, while the decomposition temperature of urea is 250 °C. With lower urea contents, a significant number of urea molecules decomposed before they could effectively coordinate with Fe atoms, leading to a random distribution of Fe single atoms. In contrast, when an excess of urea was added, there were sufficient urea molecules remaining, even after partial decomposition, to maintain a high purity of Fe atom pairs. This relationship implies that increasing the number of urea molecules leads to higher Fe content and higher purity of Fe atom pairs. Consequently, it becomes challenging to decouple the purity of diatomic species from the overall Fe content.

To validate our synthesis method, it is crucial to achieve a sample with both low Fe loading and high Fe diatomic purity. To this end, we need to optimize the pyrolysis temperature to minimize the decomposition of urea while ensuring the occurrence of the pyrolysis reaction.

In the revised manuscript, we have addressed this by lowering the pyrolysis temperature to 500 °C and reducing the urea content to 50 mg (refer to Table R1 for a detailed comparison of synthesis conditions). As a result, we synthesized a sample with an Fe content reduced to 1.62 wt%, while successfully maintaining high Fe diatomic purity (Fig. R4). This adjustment demonstrates the effectiveness and rationality of our synthesis approach in the revised manuscript.

We have added these experimental details in the revised manuscript (p. 10, lines 3-10; p. 17, lines 23-28, Supplementary Fig. 29, Supplementary Table 3, highlighted in yellow color).

"3. The reviewer cannot find any evidence that the authors have successfully tune the distance between neighboring metal atoms. The distance between neighboring metal atoms in this manuscript was ca. 0.29~0.30 nm. The one experiment using ethanediamine, which has a larger distance between N atom, only produce isolated sites without the formation of adjacent units, as authors claim. The resolution of Fig. S19 for this sample needs to be improved and applying same analysis for their main sample (Fe₂N₆), such as measuring distance between adjacent atoms and analyze the distribution, may give new insight."

Thanks for your constructive suggestion. As suggested, we have provided a high-resolution HAADF-STEM image of Fe moieties prepared using ethanediamine as the ligand. The average distance between Fe atoms was measured to be 0.27-0.38 nm, which was shorter than the distance (0.38 nm) between the two N atoms in ethylenediamine (Fig. R12). However, the distance between adjacent atoms varied widely because ethylenediamine is a flexible molecule (Fig. R11). The distance between the two N atoms on the carbon chain can easily change, making it challenging to maintain a fixed distance between the two Fe atoms.
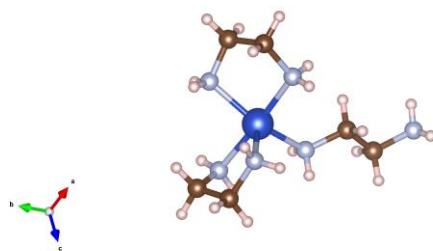

Figure R12. Crystal structure of ethanediamine.

"4. Interfacial fixing strategy was interesting to make a single atom catalyst with high metal loading and high electrochemical activity. And the use of urea, which provide N-doped site, have an important role in metal atom fixing. However, if one urea held two Fe atoms to make an adjacent unit, where all the other N-sources come to form Fe₂N₆? And if high concentration of

urea is considered to provide sufficient N source, the fixing effect may not from the single urea molecules, but from the abundant N-doped site."

Thanks for raising this issue. Urea was used as a coating layer between the Fe_2O_3 template and the polydopamine (PDA) layer. During pyrolysis, urea decomposed into two parts: one part merged with the outer carbon layer along with the pyrolysis of PDA, while the other part provided N atoms to link Fe atoms in the inner Fe_3O_4 core and C atoms in the outer carbon layer.

We believe that urea plays a crucial role in anchoring Fe atoms. This is evident when comparing samples with and without urea. Without urea, only 0.32 wt% of Fe species were retained after etching, resulting in isolated Fe atoms. In contrast, an excess of urea led to a high Fe loading of 2.36 wt%, forming neighboring Fe atoms. This occurs because the pyrolysis temperature we used was 700 °C, while the decomposition temperature of urea was 250 °C. When the urea content was low, many urea molecules decomposed, preventing each molecule from fixing two Fe atoms and leading to a random distribution of Fe single atoms. With an excess of urea molecules, even if some decomposed, there was still a sufficient amount to maintain a high purity of Fe atom pairs. Therefore, the more urea molecules used, the higher the Fe content and the higher the purity of Fe atom pairs.

To demonstrate the validity of our synthesis method, it is essential to achieve a sample with low Fe loading and high Fe diatomic purity. This requires adjusting the pyrolysis temperature to minimize the decomposition loss of urea molecules while ensuring the pyrolysis reaction occurs. In the revised manuscript, we have lowered the pyrolysis temperature to 500 °C and decreased the urea content to 50 mg (see Table R1 for synthesis condition comparison). The Fe content in the synthesized sample was reduced to 1.62 wt%, while maintaining high Fe diatomic purity (Fig. R4).

We have added these experimental details in the revised manuscript (p. 9, lines 27-31; p. 10, lines 1-10, Supplementary Figs. 27-29, Supplementary Table 3, highlighted in yellow color).

"5. The results of EXAFS fitting should be performed correctly, since the results with an R factor of 0.28 suggests that there is a discrepancy between the experimental data and the theoretical fit."

As requested, we have re-conducted the EXAFS fitting of Fe_1-N_4 and Fe_2-N_6 in the revised manuscript. The *R* factors of Fe_1-N_4 and Fe_2-N_6 are 0.0002 and 0.0005, respectively, suggesting the consistency with the experimental data. We have added relevant revisions in the revised manuscript (p. 8, lines 8-13, Supplementary Table 2, highlighted in yellow color).

"6. Author applied acetylene TPD analysis to validate the quantitative and qualitative analysis for single and dual site. A. Fe2N6 sample has ca. 8 times larger amount of active sites than Fe1N4, but the intensity of TPD signal is almost similar to each other. How can it be explained?"

Thanks for your valuable questions. The intensity of the TPD signals appears similar because we initially normalized these two peaks to the same intensity. We have now replaced the normalized

R17

data with the original data. As shown in Figure R13, the characteristic peak of Fe_2-N_6 was evidently stronger than that of Fe_1-N_4.
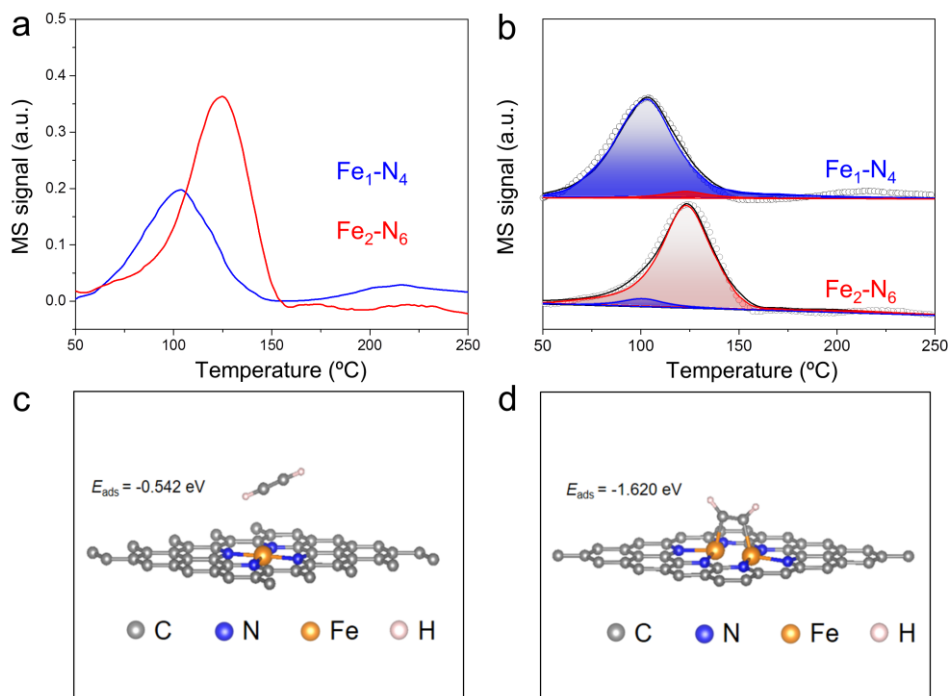

Figure R13. C_2H_2-TPD-MS profiles of Fe_1-N_4 and Fe_2-N_6. (a) Original C_2H_2-TPD-MS profiles of Fe_1-N_4 and Fe_2-N_6. (b) Peak fitting results. The adsorption configurations of acetylene on (c) Fe_1-N_4 and (d) Fe_2-N_6.

We have added these experimental details in the revised manuscript (p. 9, lines 10-13, Supplementary Fig. 26, highlighted in yellow color).

"B. The distance for the C-C bonding in acetylene is only 0.12 nm. How does author think it can be adsorbed to dual Fe site via a bidentate mode? If the binding energy can be simulated from theoretical calculations, it is recommended to be provided for the reader to understand."

As suggested, we have conducted DFT calculations for acetylene adsorption in the revised manuscript. As shown in Figure R7, the acetylene molecule is physically adsorbed on Fe_1-N_4 with an adsorption energy (E_{ads}) of -0.542 eV. As for Fe_2-N_6, the acetylene molecule is adsorbed *via* a flat-lying bidentate configuration, with an E_{ads} of -1.620 eV, where the C-C bond was stretched to 1.306 Å. As such, the adsorption of acetylene on dual Fe sites is stronger than that on isolated sites, corresponding to our assumption in C_2H_2-TPD-MS experiments (Figure R13c-d). We have added the relevant discussion in the revised manuscript (p. 9, lines 10-13, Supplementary Fig. 26, highlighted in yellow color).

"C. how is the value for the purity of dual site changed from 91.4% to 95.5%? please explains the details of the process."

As requested, we have provided the calculation details. The C_2H_2-TPD-MS profile of Fe_1-N_4 shows a symmetric peak at 103.2 $^\circ$C which we assigned to the adsorption on isolated Fe sites. As for C_2H_2-TPD-MS profile of Fe_2-N_6, the peak was obviously shifted to higher temperature. This phenomenon is rational since the adsorption on dual Fe sites should be stronger than that on isolated site. Moreover, the shape of this peak was asymmetric, indicating the existence of more than one peaks. In this work, we attributed the other peak to that for isolated Fe sites. As such, we adopted the temperature of 103.2 $^\circ$C for isolated Fe sites and the peak temperature of 123.6 $^\circ$C to fit the profile of Fe_2-N_6. The latter we assigned to the adsorption on dual Fe sites. As shown in the fitting profile of Fe_2-N_6, the peak area ratio of dual Fe sites to isolated Fe sites was 10.6:1 (Figure R13). When we assume that one Fe site adsorbs one acetylene molecule, the purity of dual sites in the Fe_2N_6 sample was 91.4% based on the following equation.

Purity of dual sites = $S_{dual\ sites}$ / ($S_{dual\ sites}$ + $S_{isolated\ sites}$) = 10.6 / (10.6 + 1) = 91.4%

Actually, it is more rational that one isolated Fe site adsorb one acetylene molecule *via* an end-on mode, while a pair of dual Fe sites adsorb one acetylene molecule *via* a bidentate mode. In other words, for dual sites, one acetylene molecule corresponds to two Fe atoms. Thus, the purity of dual sites in the Fe_2-N_6 sample should be 95.5%, based on the following equation.

Purity of dual sites = $2 \times S_{dual\ sites}$ / ($2 \times S_{dual\ sites}$ + $S_{isolated\ sites}$) = 2×10.6 / (2×10.6 + 1) = 95.5%

We have added these experimental details in the revised manuscript (p. 9, lines 19-24, Note of Supplementary Fig. 26, highlighted in yellow color).

"7. The result of Pt/C catalyst (E1/2= 0.8V) significantly lower performance compared to the results of other report literatures. How does the performance of commercial catalyst show much lower results than usual? Please provide a justification for the observed inconsistency."

Thanks for your reminding. We have purchased new commercial Pt/C and used them as reference sample. The commercial Pt/C exhibited a half-wave potential of 0.85 V vs RHE. This value was comparable to the result in previously reported literatures, approaching that (0.84 V) of Fe_1-N_4 and lower than that (0.894 V) of Fe_2-N_6 (Table R4). We have added the relevant discussion in the revised manuscript (p. 11, lines 7-11, Fig. 3a, highlighted in yellow color).

Table R4. Half-wave potentials of various catalysts towards ORR.

Catalysts	Half-wave potential	References
Fe_2-N_6	0.894 V	
Fe_1-N_4	0.84 V	This work
Pt/C	0.85 V	
Pt/C	0.85 V	*Nat. Commun.* 2020, *11*, 5892.
Pt/C	0.85 V	*ACS Nano* 2022, *16*, 7890-7903.
Pt/C	0.86 V	*ACS Nano* 2024, *18*, 750-760.
Pt/C	0.84 V	*Nat. Commun.* 2018, *9*, 5422.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have addressed the concerns from this reviewer.

Reviewer #2 (Remarks to the Author):

The authors put excellent efforts in improving the manuscript. I recommend the manuscript for publication.

Reviewer #3 (Remarks to the Author):

In this revision, the authors clearly understood the reviewers' concerns and effectively addressed the critical issues both experimentally and computationally. They acknowledged the challenges associated with achieving high purity diatomic active sites at low metal concentrations and have transparently updated this information in the revised manuscript. Additionally, by conducting pyrolysis at a lower temperature (500 °C), they demonstrated the potential to achieve high diatomic purity even at lower metal concentrations. These efforts have convincingly supported their hypothesis and findings, making the manuscript suitable for publication in Nature Communications.