

Domino effect enables dynamic electronic structure evolution for stable and efficient water purification

Corresponding Author: Professor Shuangshi Dong

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript transcends conventional static catalyst design, introducing a dynamic and self-evolving domino catalytic platform that breaks the activity-stability trade-off, thereby paving a novel path toward highly effective and sustainable water purification technologies. The domino effect enables the electronic states of active sites to undergo in-situ dynamic progressive modulation throughout the reaction sequence, adapting to each fundamental step in the advanced oxidation process. The authors demonstrated through comprehensive experiments and in-depth characterizations that this seamless and spatially ordered cascade avoids competitive adsorption and maximizes efficiency. In general, this manuscript is well organized and convincing. Therefore, I recommend this manuscript to be published after addressing the following minor questions:

1. The authors should explain how OHsurf adsorbed at Mg sites yet modulated the d orbital distribution of Co.
2. Horizontal axis in Fig. 1e-g should be fully displayed. The numbers in Fig. 3k should be described to clearly illustrate OHsurf's greater contribution to the reduction of Co³⁺ to Co²⁺ in the 4MgCo/CN DSACs/PMS/vis system compared to that in 4Co/CN SACs/PMS/vis system.
3. The authors should explain how the OHsurf generated in-situ from H₂O₂ in Fig. 3f demonstrate that CBZ degradation is primarily associated with OHsurf. Additionally, the authors should label the EDCBA markers in the figure legend for clearer presentation.
4. The authors should ensure the number of decimal places for m/z values in Fig. 3g and the names of catalysts in Fig. S12 matched with those in the main text of manuscript, respectively.
5. The total organic carbon removal by DSACs and SACs should be provided to elucidate their mineralization performance.
6. The isotope liquid mass spectrometry detection method for OHsurf and mass spectrometry detection method for degradation product should be clearly described in the Supporting Materials.
7. In the theoretical calculations, the models of MgCo/CN DSACs adsorption of H₂O₂ at the magnesium site in top and side view were inconsistent. The oxidant adsorbed on the magnesium site in top view was not H₂O₂ in Fig. S17. Please check and correct it.
8. Increased Co²⁺ ratio as reaction proceed from 0 to 12 min but unobvious Co²⁺ ratio from 12 min and 24 min in 4MgCo/CN DSACs/PMS/vis system in in-situ XPS. How did this result support the conclusion that Co with reconstructed electronic structure enable PMS activation and *SO₄ desorption?
9. The experimental method for bean sprouts cultured with aqueous solutions of CBZ and its degradation products and evaluation method for mean length should be described in the Supporting Materials.
10. To better understand the advantage of domino catalysis in overcoming the activity-stability trade-off during water purification, the role of the domino-effect-driven dynamic electronic structures evolution in peroxymonosulfate activation and radical desorption should be elaborated in detail in lines 280-284.
11. Detailed information on the light source used in the reaction should be provided, as only visible light is currently mentioned.
12. Some uncorrected descriptions be checked and corrected in this manuscript. For example, "The 3.5%, 33.6%, 52.5%, 67.7%, 14.7%, 10.4% and 85.4% of CBZ were degraded by methanol (MeOH), Isopropyl alcohol (IPA), Methyl phenyl sulfoxide (PMSO), -carotene (-caro), sodium fluoride (NaF), catalase (CAT) and sodium oxalate (Na₂C₂O₄), respectively in line 134-138".

Reviewer #2

(Remarks to the Author)

The authors propose a domino effect that enables dynamic electronic structure evolution to resolve intrinsic trade-off between high catalytic activity and long-term stability in advanced oxidation processes. Mimicking a falling domino chain where an event automatically triggers the next, our system orchestrates a seamless, spatially ordered cascade of reactions. Experiments and theoretical calculations elucidate this seamless and spatially ordered cascade avoids competitive adsorption and maximizes efficiency. Overall, this manuscript is novel and convincing. Hence, I recommend it to be published after following minor revision.

1. Domino effect enables dynamic electronic structure evolution according to reaction requirements, thereby enhancing catalytic activity. However, how can catalytic stability be regulated? Provide a detailed description.
2. What is the cobalt concentration in emission standard? Is the cobalt concentration (0.43 mg/L) leached in the MgCo/CN/PMS/vis system higher or lower compared to this standard? Provide relevant information.
3. Provide the dosage of scavengers for different active species. Additionally, add references to support the additional dosage of scavengers, as the dosage of scavengers affect the capture performance.
4. What are the experimental steps for assessing the toxicity of degradation products using bean sprouts? How can the length of the sprouts be used to determine whether degradation products inhibit growth?
5. The range of mass spectrum in the characterizations section should be revised. Revise 100–250 into 50–750.
6. The sentence “Under light irradiation, the inert magnesium site initiates the cascade by selectively photoreducing O_2 to H_2O_2 ” appears in lines 76-77. Revise the term “inert”. Magnesium can reduce oxygen to hydrogen peroxide and is not inert.
7. What are the respective roles of NaF and CAT? After their addition, the ratio of Co^{2+} to Co^{3+} also changed. How do these results relate to the OHsurf promoting Co reduction?
8. Some descriptions might require revision. For example, in the sentence “Single-atom catalysis (SAC), with its maximized atomic efficiency”, the term “atomic efficiency” should be revised to atomic utilization efficiency. Check and correct them throughout manuscript.
9. Fig. 1 was not be displayed fully might due to formatting issue. Check and correct it.
10. How can the toxicity of degradation products in the MgCo/CN DSACs/PMS/vis system and Co/CN SACs/PMS/vis system be determined based on the results of the four evaluation criteria: *Daphnia magna*, oral rat, developmental toxicity, and mutagenicity?
11. Provide more detailed information on how OHsurf modulates the d orbital distribution of cobalt. Additionally, supplement the references to support it.
12. The sentence “The correlation plot of CBZ degradation rate constant within 4 min (k_1) and CBZ degradation rate constant from 4 min to 24 min (k_2) with various possible influencing factors, including mass of Co (A), photoadsorption (B), crystallinity (C) and Co spin state (D). This result illustrated that degradation of CBZ was mainly related to OHsurf from in-situ generated H_2O_2 ($p < 0.05$) (Fig. 3f)” was described in line 201-206. How does it prove that the degradation of CBZ was primarily related to OHsurf from in situ generated H_2O_2 ($p \leq 0.05$)? Describe it in detail.

Reviewer #3

(Remarks to the Author)

This manuscript proposes a domino-catalytic strategy based on a Mg–Co dual single-atom catalyst to overcome the activity–stability trade-off in advanced oxidation processes. While the concept is potentially interesting, the current study suffers from substantial experimental and mechanistic deficiencies that undermine the central claims. Most critically, the proposed mechanism concerning in situ H_2O_2 generation, enhanced OH formation, and dynamic Co d-orbital reconstruction, remains speculative and lacks compelling direct experimental validation. Several spectral features are too weak or ambiguous to be reliably assigned. Thorough analysis and appropriate control experiments are necessary for solid assignment. Given these significant structural and mechanistic uncertainties, the conclusions appear overstated. Therefore, in its present form, the manuscript is not suitable for publication in Nature Communications.

1. The HAADF-STEM images mainly display isolated bright spots, which do not clearly distinguish between single atoms and closely spaced dual-atom pairs. Moreover, the EXAFS fitting lacks a clearly resolved Co–Mg scattering path with convincing fitting parameters, and the possibility of Co–Co bonding or small cluster formation has not been rigorously excluded. Therefore, the present data are not adequate to unambiguously confirm the existence and precise structural characteristics of the proposed dual-atom configuration.
2. Figures 1e and f are particularly confusing and require substantial clarification. In Figure 1e, the magnified inset does not appear to correspond clearly to the highlighted region in the original spectrum, making it difficult to understand what specific feature is being emphasized. More importantly, based on the presented XANES data, the oxidation state of Co in 4MgCo/CN does not seem to fall between 0 and +2 as implied by comparison with Co foil and CoO. A more rigorous quantitative analysis (e.g., linear combination fitting or edge position calibration) is necessary to support the claimed valence state. In Figure 1f, the assignment of scattering pathways is also questionable. It is unclear why a Co–N coordination path appears in Co_3O_4 , while a Co–O pathway is assigned to 4MgCo/CN. These assignments appear inconsistent with the expected local coordination environments and raise concerns about the reliability of the EXAFS fitting.
3. The fitting results in Tables S1 and S2 are insufficient. The authors are encouraged to re-examine the fitting models, clearly justify the chosen scattering paths, and provide detailed fitting parameters and model comparisons to ensure structural consistency.
4. It is unclear why a Mg signal is detected in the 4Co/CN sample in Fig. S2. The authors should clarify the origin of the Mg

signal, provide supporting compositional analysis (e.g., ICP, EDS quantification, or XPS survey spectra).

5. The authors attribute the enhanced OH formation to visible-light-induced in situ H₂O₂ generation; however, this claim lacks direct H₂O₂ quantification, appropriate dark-light control experiments, and mechanistic verification of the H₂O₂ formation pathway (e.g., 2e⁻ ORR), and therefore requires direct experimental evidence to be substantiated.

6. The authors attribute the enhanced PMS activation to the interaction between Mg–Co diatomic sites based on the appearance of a new Raman peak at 815.7 cm⁻¹. However, this peak appears to be extremely weak and close to the noise level. More solid evidence is required.

7. The manuscript concludes that the dynamically tailored Co d orbitals break the activity-stability trade-off, but lacks sufficient evidence to support this conclusion. In situ XPS evidence is limited to Co²⁺ ratio variations.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

All my concerns have been well addressed. I also reviewed the authors' responses to the issues raised by the other reviewers, and I find that all of those concerns have been thoroughly addressed as well. In my view, this revised manuscript is suitable for publication in Nature Communications.

Reviewer #2

(Remarks to the Author)

The manuscript has been improved substantially with proper responses and modifications by the authors; thus the paper can be acceptable now.

Reviewer #3

(Remarks to the Author)

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)

The manuscript has been substantially revised with more rigorous data analysis, and the paper can now be accepted for publication.

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Response Letter

Here below is our description on revision according to the reviewers' comments.

Responses to the reviewers

We appreciate the reviewers' positive and constructive comments. In this file, we respond to each comment point-by-point in detail. We copy and paste the original comments in black italic type, each comment is followed by our response in indent and blue normal font. In addition, revised portions are also marked blue in our revised manuscript. We show all changes we made in the manuscript by quoting and shading the revised words. We also highlight the added words with highlighted line numbers in the marked manuscript file.

To reviewer 1

The reviewer's comment:

Reviewer #1: This manuscript transcends conventional static catalyst design, introducing a dynamic and self-evolving domino catalytic platform that breaks the activity-stability trade-off, thereby paving a novel path toward highly effective and sustainable water purification technologies. The domino effect enables the electronic states of active sites to undergo in-situ dynamic progressive modulation throughout the reaction sequence, adapting to each fundamental step in the advanced oxidation process. The authors demonstrated through comprehensive experiments and in-depth characterizations that this seamless and spatially ordered cascade avoids competitive adsorption and maximizes efficiency. In general, this manuscript is well organized and convincing. Therefore, I recommend this manuscript to be published after addressing the following minor questions:

1. The authors should explain how OH_{surf} adsorbed at Mg sites yet modulated the d orbital distribution of Co.

Response:

We are very sorry that we haven't described clearly in the previous manuscript. The OH_{surf} adsorbed at the Mg site could leverage the π -conjugated delocalized network of carbon nitride to modulate the d-orbital distribution of non-adjacent Co atom through long-range interaction. The similar interaction has also been reported in previous work¹⁻³. To more clearly demonstrate the modulation reason for the d orbital distribution of Co by OH_{surf}, we have added corresponding descriptions in our revised

manuscript (line 387-391, page 20; line 392-398, page 21):

In summary, the dynamic domino catalysis process in overcoming the activity-stability trade-off during water purification was as follows: Under visible light irradiation, photogenerated electrons drove a two-electron oxygen reduction reaction at the Mg site, enabling the *in-situ* generation of H₂O₂. The as-formed H₂O₂ was subsequently converted to OH_{surf} via the Mg site. These OH_{surf} leveraged the π -conjugated delocalized network of carbon nitride to modulate the d-orbital configuration of non-adjacent Co atom through long-range interaction, enabling the shift of energy levels for d_{xy}, d_{x²-y²}, d_{xz}, d_{z²} and d_{yz} orbitals to lower energy levels⁵⁵⁻⁵⁷. On the one hand, this promoted the reduction of Co³⁺ to Co²⁺, thereby accelerating •SO₄⁻ generation during PMS activation for enhanced activity. On the other hand, it reduced the adsorption energy of *SO₄, optimizing its desorption process and preventing Co atom detachment to maintain stability.

References in this first response to reviewer 1:

1. Wu, Z. et al. Long-range interactions driving neighboring Fe–N₄ sites in Fenton-like reactions for sustainable water decontamination. *Nat Commun.* **15**, 7775 (2024).
2. Jin, S. et al. Remote tuning of single-atom Fe–N₅ sites via high-coordination defects for enhanced Fenton-like water decontamination. *Nat Commun.* **16**, 10455 (2025).
3. Deng, Y. C. et al. Long-range electronically polarized Fe–N₅ catalysts redirect polymerization-driven phenolic pollutant removal toward sustainable carbon

sequestration, *Angew. Chem. Int. Ed.* **64**, e202509493 (2025).

2. Horizontal axis in Fig. 1e-g should be fully displayed. The numbers in Fig. 3k should be described to clearly illustrate OH_{surf}'s greater contribution to the reduction of Co³⁺ to Co²⁺ in the 4MgCo/CN DSACs/PMS/vis system compared to that in 4Co/CN SACs/PMS/vis system.

Response:

We are very sorry for our mistake. We have corrected the horizontal axis in Fig. 1e-g to ensure that horizontal axis was fully displayed. In Fig. 3k, the numbers represented the double-layer capacitance values. To more clearly illustrate that OH_{surf}'s greater contribution to the reduction of Co³⁺ to Co²⁺ in the 4MgCo/CN DSACs/PMS/vis system compared to the 4Co/CN SACs/PMS/vis system, the unit “mF cm⁻²” has been added after the numbers in Fig. 3k in our revised manuscript.

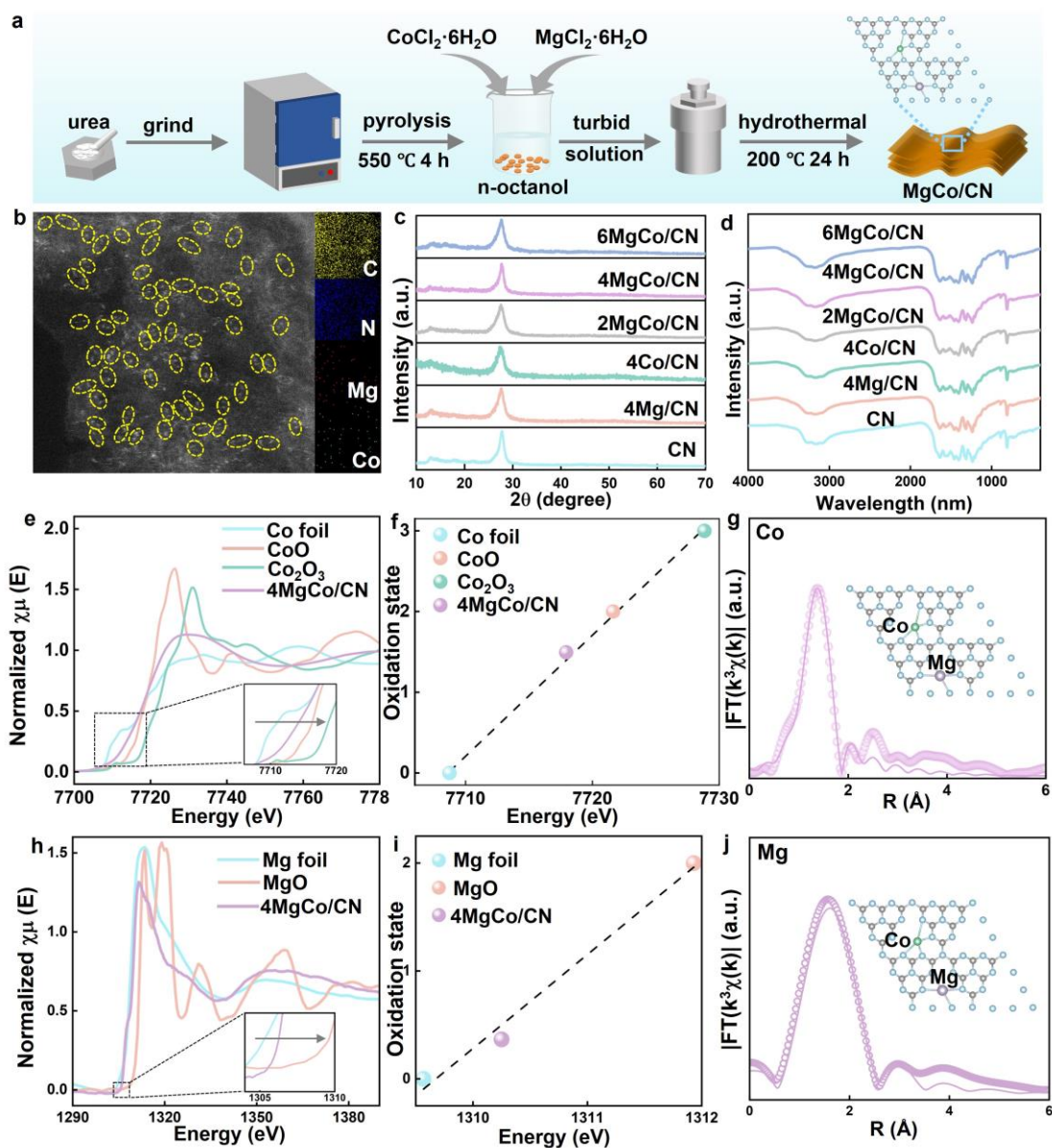


Fig. 1. (a) Synthesis of MgCo/CN DSACs. (b) Aberration-corrected HAADF-STEM image and EDS mapping of 4MgCo/CN DSACs. (c) XRD and (d) FT-IR spectra of catalysts, respectively. (e) Normalized Co K-edge XANES spectra, (f) corresponding oxidation state of Co species and (g) the fitting curves of Co K-edge EXAFS spectra in 4MgCo/CN DSACs. (h) Normalized Mg K-edge XANES spectra, (i) corresponding oxidation state of Mg species and (j) the fitting curves of Mg K-edge EXAFS spectra in 4MgCo/CN DSACs.

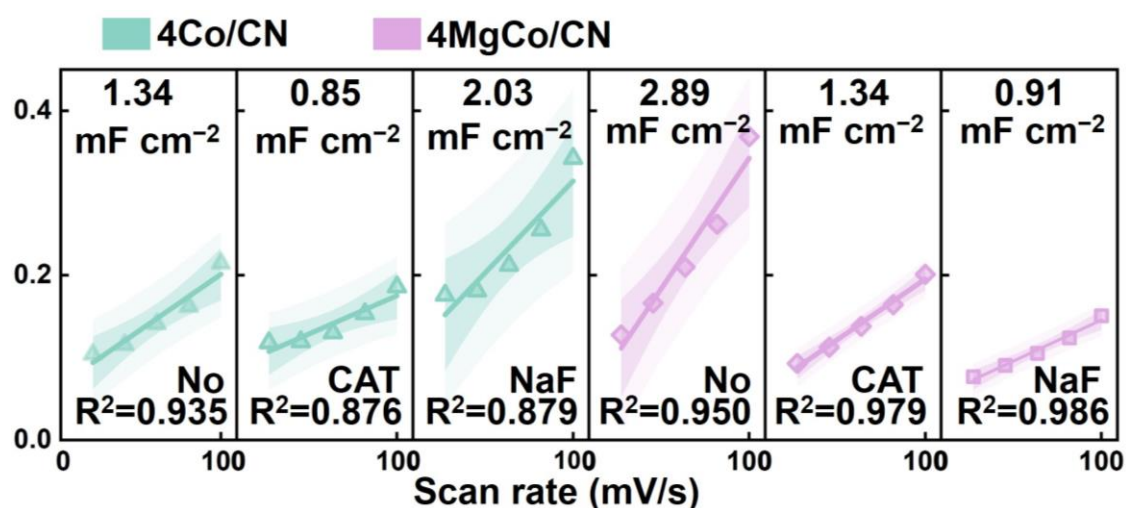


Fig. 3. (k) ECSA of 4MgCo/CN DSACs and 4Co/CN SACs under different conditions, respectively.

3. The authors should explain how the OH_{surf} generated *in-situ* from H_2O_2 in Fig. 3f demonstrate that CBZ degradation is primarily associated with OH_{surf} . Additionally, the authors should label the EDCBA markers in the figure legend for clearer presentation.

Response:

i) We are very sorry that we haven't described clearly in the previous manuscript.

Fig. 3f exhibited the correlation plot of CBZ degradation rate constant within 4 min (k_1) and CBZ degradation rate constant from 4 min to 24 min (k_2) with various possible influencing factors, including mass of Co (A), photoadsorption (B), crystallinity (C), OH_{surf} contribution ratio (D) and Co spin state (E). It was illustrated that the photoadsorption and OH_{surf} contribution ratio were crucial factors for k_1 and k_2 , respectively. In fact, the H_2O_2 was generated *in-situ* by two-electron oxygen reduction under light irradiation, which could be activated into OH_{surf} . The details were exhibited as follows:

The Gibbs free energy for two-electron oxygen reduction of H_2O_2 in the presence of PMS by MgCo/CN DSACs was negative, indicating that H_2O_2 generation was thermodynamically spontaneous (Fig. S24). Fig. S25 exhibited the time-resolved *in-situ* DRIFTS profiles of 4MgCo/CN DSACs. In the 4MgCo/CN DSACs/PMS/vis system, the characteristic O–O stretching vibrations were detected for surface-adsorbed species, including O_2^* (965 cm^{-1}), $\bullet\text{O}_2^-*$ (1151 cm^{-1}), $\bullet\text{OOH}^*$ (1205 cm^{-1}) and HOOH^* (1369 cm^{-1}). The intensities of these peaks increased progressively with reaction time from 0 to 24 min. Additionally, the ESR spectra under light irradiation (Fig. S26) also exhibited the characteristic signal of $\bullet\text{O}_2^-$. These results collectively demonstrated that the dominant route for H_2O_2 generation was the two-electron oxygen reduction under light irradiation. The OH_{surf} could be obtained by cleaving the O–O bond of H_2O_2 , which was the crucial intermediate for OH_{surf} . Hence, it was concluded that CBZ degradation was primarily associated with OH_{surf} generated *in-situ* from H_2O_2 . To more clearly demonstrate that CBZ degradation was primarily associated with OH_{surf} generated *in-situ* from H_2O_2 , we have added corresponding descriptions in our revised manuscript (line 243-255, page 13; line 256-269, 272-276, page 14):

As shown in Figs. S22 and S23, the H_2O_2 concentration decreased rapidly after introducing nitrogen (N_2), indicating that O_2 was essential for H_2O_2 generation. Upon addition of the electron-trapping agent potassium bromate (KBrO_3), the H_2O_2 concentration dropped sharply, demonstrating that the two-electron oxygen reduction reaction was the primary pathway for photocatalytic H_2O_2 production. The H_2O_2

concentration decreased by 94.1% after adding p-benzoquinone (p-BQ), suggesting that $\bullet\text{O}_2^-$ was a key intermediate in the photoreaction. The negligible H_2O_2 concentration observed upon addition of tert-butyl alcohol (TBA) indicated that $\bullet\text{OH}$ was not an intermediate in H_2O_2 production. In contrast, adding ethanol (EtOH) and benzyl alcohol (BnOH) significantly increased H_2O_2 production, mainly because these alcohols capture photogenerated holes and supply sufficient protons, thereby facilitating oxygen reduction for H_2O_2 generation. These results indicated that CBZ did not affect the types of key intermediates in the *in-situ* photocatalytic generation of H_2O_2 . The Gibbs free energy for the two-electron oxygen reduction to H_2O_2 in the presence of PMS by 4MgCo/CN DSACs was negative (Fig. S24), indicating that H_2O_2 generation was thermodynamically spontaneous. Fig. S25 exhibited the time-resolved *in-situ* DRIFTS profiles of 4MgCo/CN DSACs. In the 4MgCo/CN DSACs/PMS/vis system, the characteristic O–O stretching vibrations were detected for surface-adsorbed species, including O_2^* (965 cm^{-1}), $\bullet\text{O}_2^*$ (1151 cm^{-1}), $\bullet\text{OOH}^*$ (1205 cm^{-1}), and HOOH^* (1369 cm^{-1})⁵¹. The intensities of these peaks progressively increased with reaction time from 0 to 24 min. In the ESR spectra (Fig. S26), a distinct characteristic signal of $\bullet\text{O}_2^-$ was observed under light irradiation, whereas the signal was barely detectable in the dark. Collectively, these results demonstrated that the dominant route for H_2O_2 generation was the two-electron oxygen reduction. A correlation plot of the CBZ degradation rate constant within the first 4 min (k_1) and that from 4 min to 24 min (k_2) was generated against various possible influencing factors, including Co mass (A), photoadsorption (B), crystallinity (C), OH_{surf}

contribution ratio (D) and Co spin state (E). This result illustrated that the degradation of CBZ was mainly related to OH_{surf} from *in-situ* generated H_2O_2 ($p < 0.05$) (Fig. 3f), indicating that the photoadsorption and OH_{surf} contribution ratio were crucial factors for k_1 and k_2 , respectively. Given that visible light was used to drive photoreduction of oxygen to H_2O_2 , which served as a crucial intermediate for OH_{surf} , it could be deduced that CBZ degradation was primarily related to OH_{surf} from *in-situ* generated H_2O_2 .

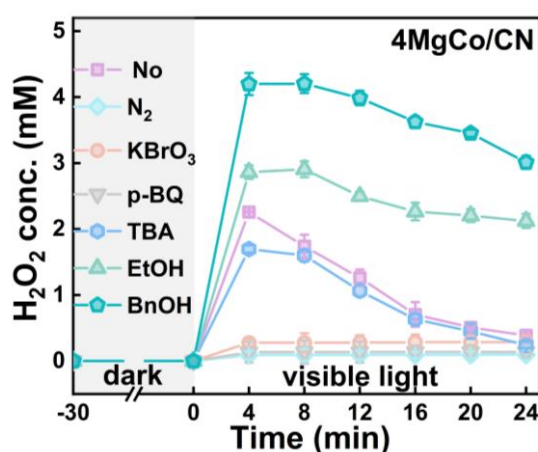


Fig. S22. H_2O_2 generation by 4MgCo/CN DSACs in the PMS/vis/CBZ system with different scavengers.

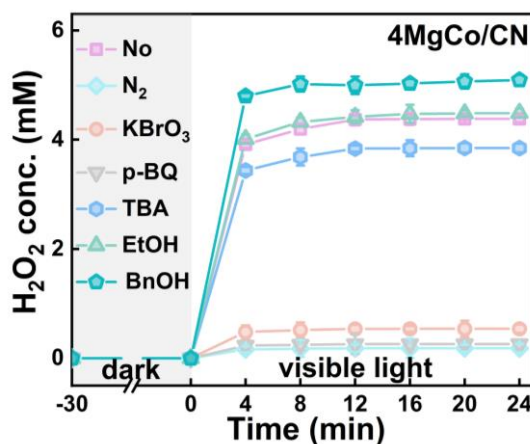


Fig. S23. H_2O_2 generation by 4MgCo/CN DSACs in the PMS/vis system with different scavengers.

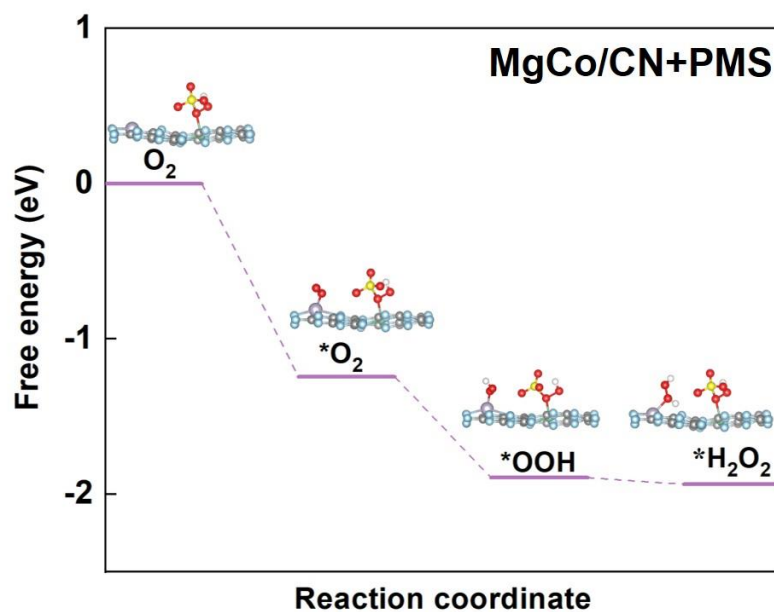


Fig. S24. Free energy curve of oxygen reduction for H_2O_2 generation by MgCo/CN DSACs in the presence of PMS.

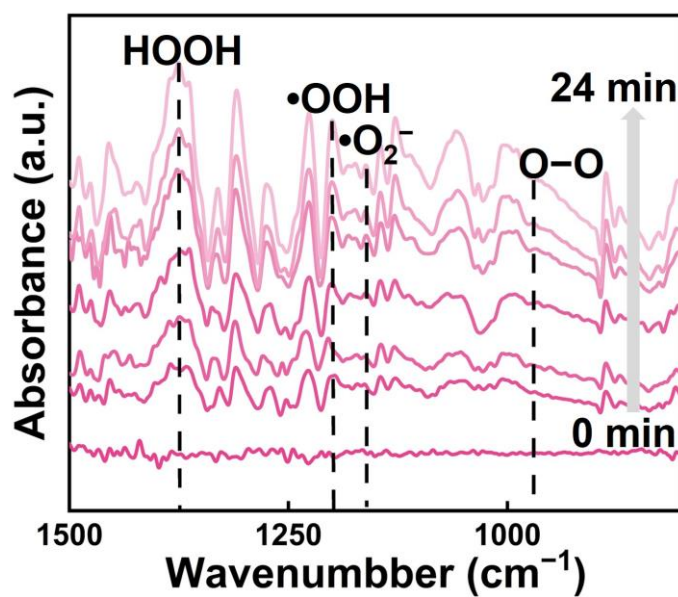


Fig. S25. The *in-situ* DRIFTS spectra of 4MgCo/CN DSACs in the PMS/vis system.

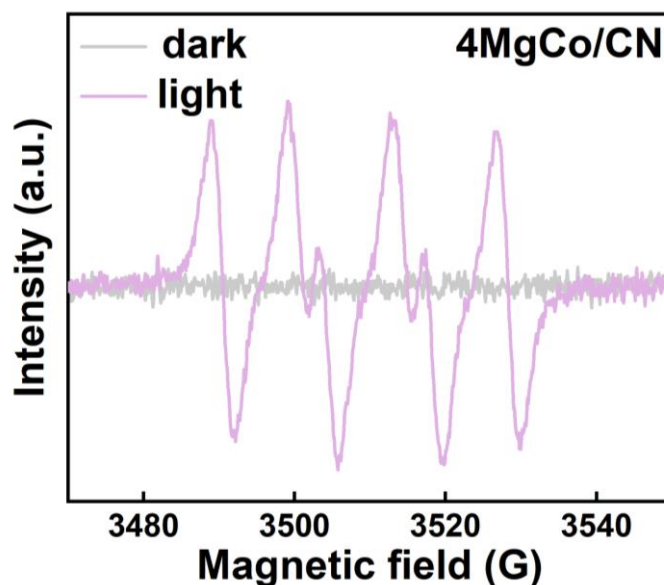


Fig. S26. The ESR spectra of $\bullet\text{O}_2^-$ by 4MgCo/CN DSACs with/without light irradiation.

ii) Thanks for your suggestion. We have labeled the EDCBA markers in the figure legend in our revised manuscript for clearer presentation (line 305-306, page 17):

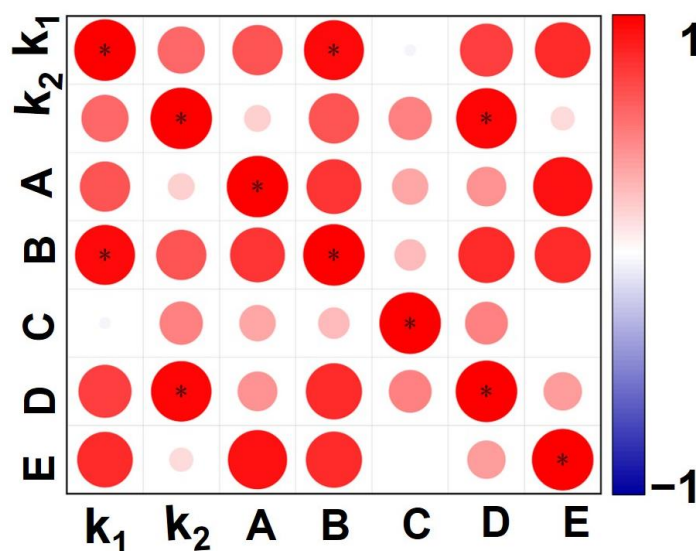


Fig. 3. (f) The correlation plot of CBZ degradation rate constant with various possible influencing factors. A, B, C, D and E represented mass of Co, photoadsorption, crystallinity, OH_{surf} contribution ratio and Co spin state.

4. The authors should ensure the number of decimal places for m/z values in Fig. 3g and the names of catalysts in Fig. S12 matched with those in the main text of manuscript, respectively.

Response:

We are very sorry for our mistake. We have corrected the number of decimal places for m/z values in Fig. 3g and the names of catalysts in Fig. S12, which has been renamed to Fig. S18, have also been matched with those in the main text of our revised manuscript.

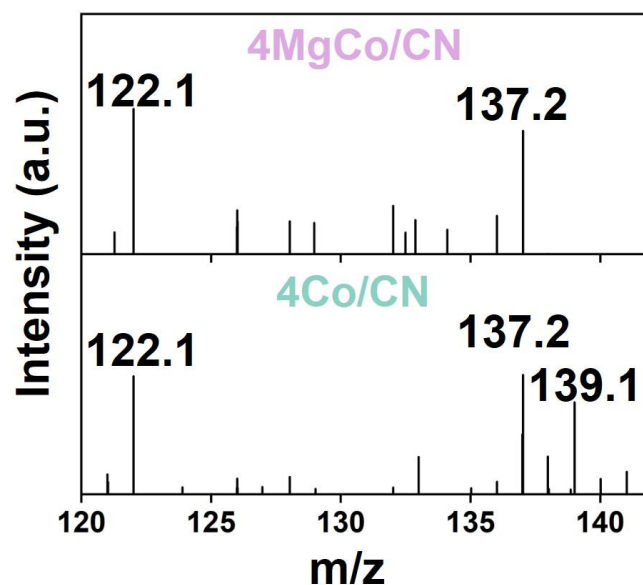


Fig. 3. (g) Isotopic mass spectra of OH_{surf} produced by 4MgCo/CN DSACs and 4Co/CN SACs in PMS/vis system with the ratio of H_2O^{16} to H_2O^{18} (1:1).

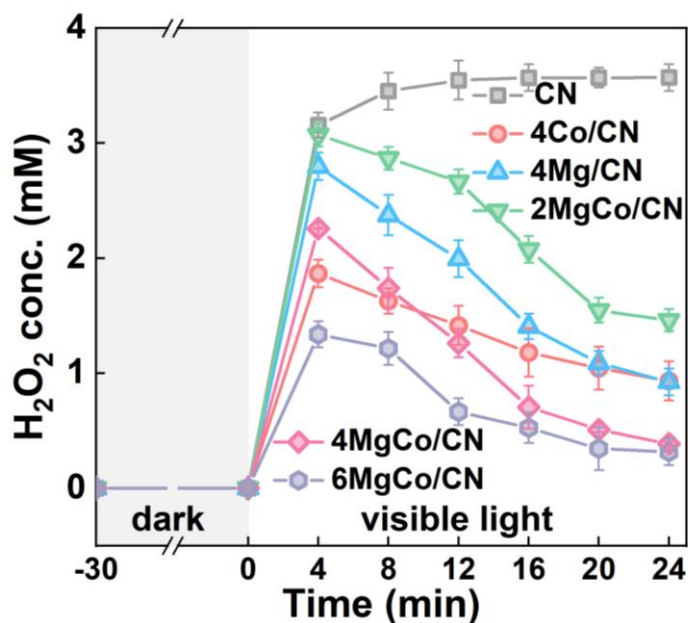


Fig. S18. *In-situ* H₂O₂ production by different catalysts.

5. The total organic carbon removal by DSACs and SACs should be provided to elucidate their mineralization performance.

Response:

Thanks for your suggestion. The total organic carbon removal efficiency by DSACs and SACs have been evaluated and shown in Fig. S11. To clearly illustrate the mineralization performance of DSACs and SACs, we have added some descriptions in our revised manuscript (line 149-151, page 8):

4MgCo/CN DSACs had 53.2% of total organic carbon (TOC) removal efficiency, which was much higher than those of CN (18.6%), 4Mg/CN (33.5%) and 4Co/CN (34.1%), respectively (Fig. S11).

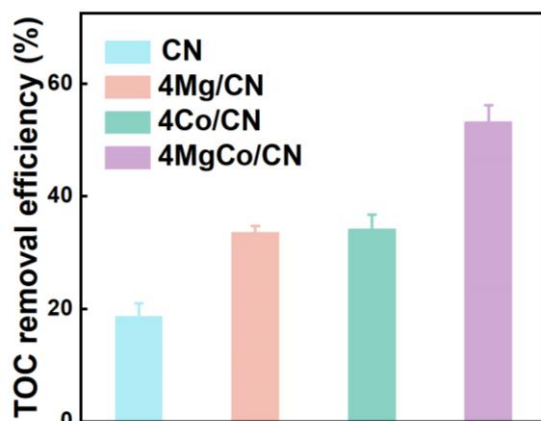


Fig. S11. TOC removal of CBZ by different catalysts in the PMS/vis system.

6.The isotope liquid mass spectrometry detection method for OH_{surf} and mass spectrometry detection method for degradation product should be clearly described in the Supporting Materials.

Response:

Thanks for your suggestion. We have added the isotope liquid mass spectrometry detection method for OH_{surf} and mass spectrometry detection method for degradation product in the Supporting Materials of our revised manuscript:

Supplementary Method 2. Isotope liquid mass spectrometry testing method

The preparation of a solution containing 5 mM benzoic acid (BA) was to be undertaken, for which 1 mL of H_2^{16}O and 1 mL of H_2^{18}O are to be utilized. Subsequently, 1 mg 4Co/CN or 4MgCo/CN should be added, and the mixture thoroughly agitated. PMS should then be added for the reaction with visible light irradiation. The reaction solution must then be filtered through a 0.22 μm membrane. The mass-to-charge (m/z) value of *p*-hydroxybenzoic acid (*p*-HBA) was determined by means of mass spectrometry. In the control experiment, 2 mL of water was utilized to prepare a 5 mM benzoic acid solution, followed by the addition of 1 mg 4Co/CN or

4MgCo/CN. Following a thorough mixing process, PMS was added to initiate the reaction. The quantification of BA degradation and *p*-HBA formation was conducted through the utilization of high-performance liquid chromatography (HPLC), utilizing an apparatus equipped with a UV detector and a C18 column (4.6 × 250 mm, 5 μm diameter). For the analysis of BA, the mobile phase comprised a mixture of acetonitrile and 0.1% trifluoroacetic acid solution (volume ratio 35:65), with a flow rate of 1 mL/min, and the detector wavelength was set at 271 nm. The mobile phase employed for the determination of *p*-HBA consisted of a mixture of acetonitrile and 0.1% trifluoroacetic acid solution (35:65 v/v), with a flow rate of 1 mL/min and a detector wavelength set at 255 nm.

Supplementary Method 6. Mass spectrometry detection method for degradation product

The degradation products were identified by the liquid chromatograph mass spectrometer (LC-MS). The mass spectrometer analysis was performed in a positive ion mode over the range of *m/z* 50-750 with an electrospray ionization (ESI) source under the following conditions: capillary voltage 3500 V, cone voltage 30 V, source temperature 110 °C, desolvation temperature 380 °C, cone gas flow 80 L/h and desolvation gas flow 600 L/h.

7. In the theoretical calculations, the models of MgCo/CN DSACs adsorption of H₂O₂ at the magnesium site in top and side view were inconsistent. The oxidant adsorbed on the magnesium site in top view was not H₂O₂ in Fig. S17. Please check and correct it.

Response:

We are very sorry for our mistake. We have checked and corrected the models of MgCo/CN DSACs adsorption of H₂O₂ at the magnesium site in top view.

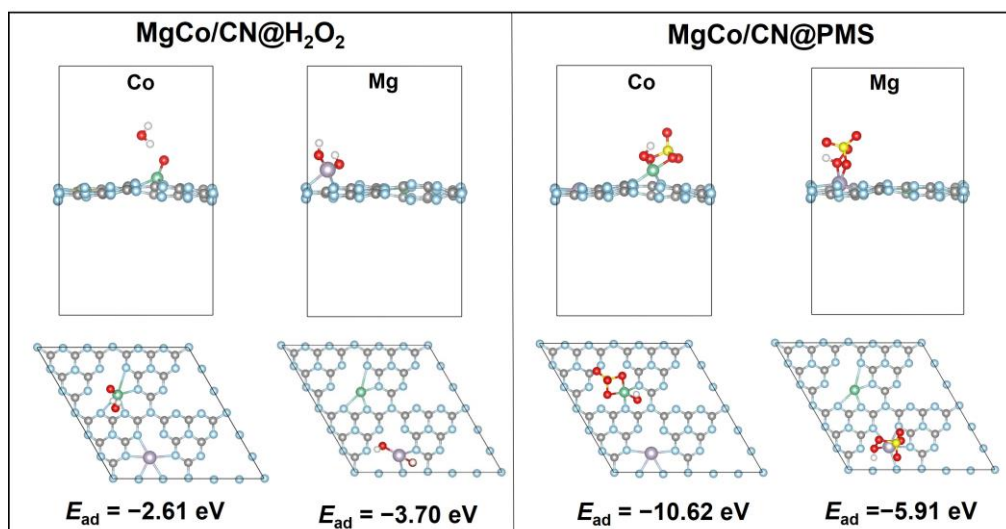


Fig. S30. Models for H₂O₂ and PMS adsorbed on MgCo/CN DSACs with different sites, respectively.

8. Increased Co²⁺ ratio as reaction proceed from 0 to 12 min but unobvious Co²⁺ ratio from 12 min and 24 min in 4MgCo/CN DSACs/PMS/vis system in *in-situ* XPS. How did this result support the conclusion that Co with reconstructed electronic structure enable PMS activation and *SO₄ desorption?

Response:

We are very sorry that we haven't described clearly in the previous manuscript. Figs. 3a and S10 showed that PMS and CBZ were primarily activated and degraded within the first 12 min and the corresponding change in performance between 12 and 24 min was relatively minor. Hence, it could be deduced that PMS activation and *SO₄ desorption were mainly facilitated within the first 12 min. That is, the reduction from Co³⁺ to Co²⁺ by OH_{surf} mainly occurred within the first 12 min. Therefore,

increased Co^{2+} ratio as reaction proceed from 0 to 12 min but unobvious Co^{2+} ratio from 12 min and 24 min in the 4MgCo/CN DSACs/PMS/vis system was observed in *in-situ* Co 2p XPS spectra (Fig. 4i). To more clearly exhibit the variation in Co^{2+} ratio, we have added the Co *K*-edge spectra of 4MgCo/CN DSACs after reaction and compared the proportion of Co^{2+} species and the Co oxidation state before and after reaction, with corresponding descriptions included in our revised manuscript (line 372-380, page 20). Additionally, to more clearly demonstrate the PMS activation and SO_4 desorption process by Co with a reconstructed electronic structure, we have revised the corresponding descriptions in our revised manuscript (line 387-391, page 20; line 392-398, page 21):

As shown in Fig. S41, the Co *K*-edge shifted negatively after the reaction compared to that before the reaction, indicating a reduction in the oxidation state of Co in the 4MgCo/CN DSACs after reaction. Based on the LCF results, the proportion of Co^{2+} species in the 4MgCo/CN DSACs increased from 28.7% before reaction to 63.4% after reaction (Figs. S2 and S42, Tables S1 and S8), while the average Co oxidation state decreased from 1.50 to 1.27 (Figs. 1f and S43). This observation was supported by the increased Co^{2+} ratio as the reaction proceeded from 0 to 24 min in the 4MgCo/CN DSACs/PMS/vis system, as shown by *in-situ* XPS spectra (Fig. 4i).

In summary, the dynamic domino catalysis process in overcoming the activity-stability trade-off during water purification was as follows: Under visible light irradiation, photogenerated electrons drove a two-electron oxygen reduction reaction at the Mg site, enabling the *in-situ* generation of H_2O_2 . The as-formed H_2O_2

was subsequently converted to OH_{surf} via the Mg site. These OH_{surf} leveraged the π -conjugated delocalized network of carbon nitride to modulate the d-orbital configuration of non-adjacent Co atom through long-range interaction, enabling the shift of energy levels for d_{xy} , $d_{x^2-y^2}$, d_{xz} , d_z^2 and d_{yz} orbitals to lower energy levels⁵⁵⁻⁵⁷. On the one hand, this promoted the reduction of Co^{3+} to Co^{2+} , thereby accelerating $\bullet\text{SO}_4^-$ generation during PMS activation for enhanced activity. On the other hand, it reduced the adsorption energy of *SO_4 , optimizing its desorption process and preventing Co atom detachment to maintain stability.

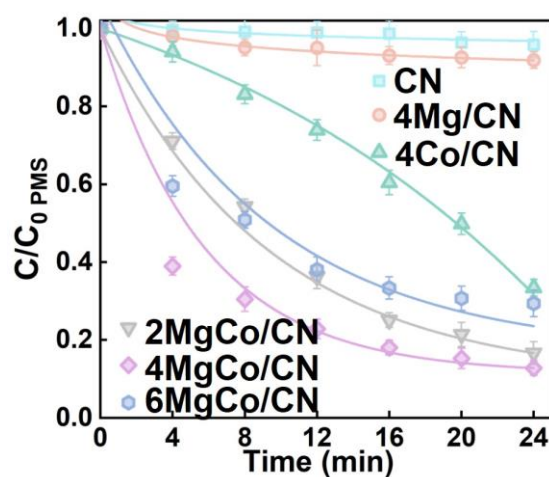


Fig. 3. (a) PMS activation by different catalysts.

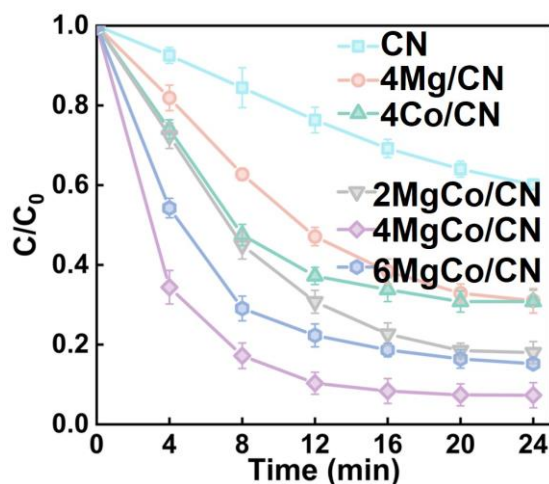


Fig. S10. Degradation of CBZ by different catalysts in photo-Fenton-like system

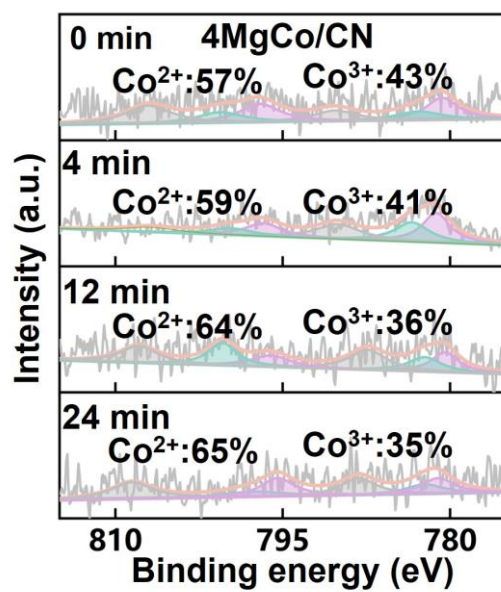


Fig. 4. (i) *in-situ* Co 2p XPS spectra of 4MgCo/CN as reaction proceed.

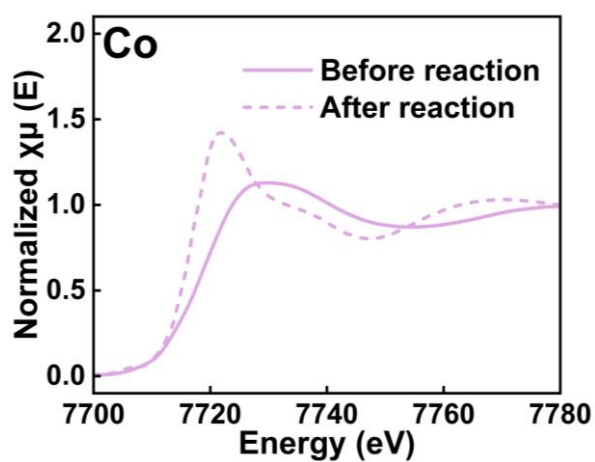


Fig. S41. The Co K-edge spectra of 4MgCo/CN DSACs before and after reaction.

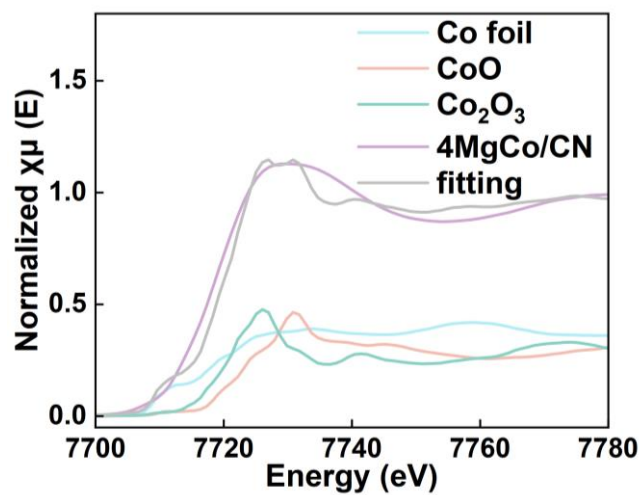


Fig. S2. The linear combination fitting result for 4MgCo/CN DSACs.

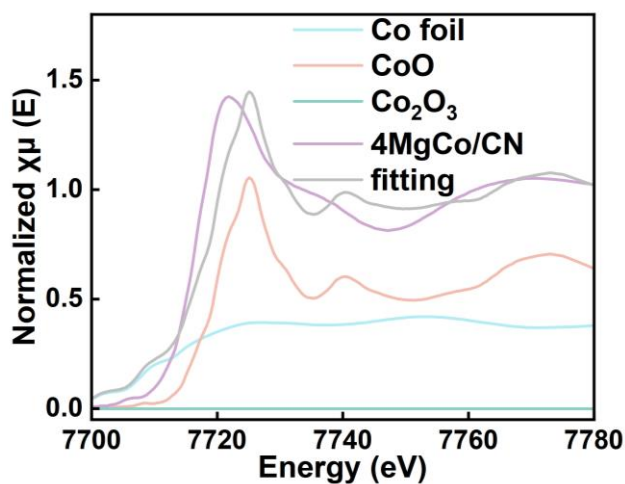


Fig. S42. The linear combination fitting result for 4MgCo/CN DSACs after reaction.

Table S1. Linear combination fitting for Co in 4MgCo/CN.

Standard	Weight	E ₀
Co foil	0.406 (0.000)	0.000 (0.000)
CoO	0.287 (0.000)	0.000 (0.000)
Co ₂ O ₃	0.307 (0.000)	0.000 (0.000)

R-factor = 0.0208785

Chi-square = 0.26227

Reduced chi-square = 0.0025463

Table S8. Linear combination fitting for Co in 4MgCo/CN after reaction.

Standard	Weight	E ₀
Co foil	0.366 (0.000)	0.000 (0.000)
CoO	0.634 (0.000)	0.000 (0.000)
Co ₂ O ₃	0.000 (0.000)	0.000 (0.000)

R-factor = 0.0769077

Chi-square = 2.41810

Reduced chi-square = 0.0144797

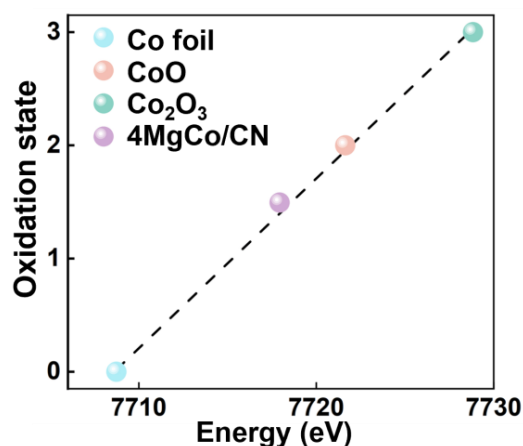


Fig. 1. (f) corresponding oxidation state of Co species in 4MgCo/CN DSACs.

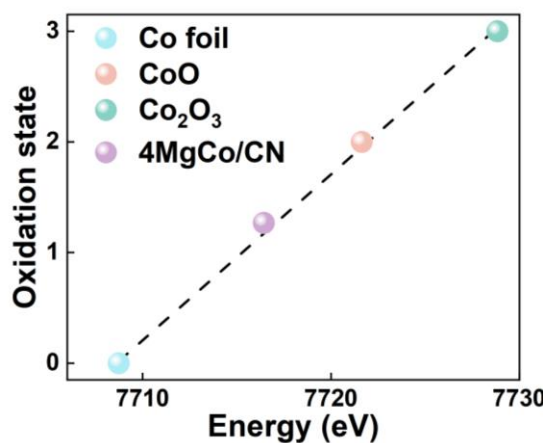


Fig. S43. The oxidation state of Co species in 4MgCo/CN DSACs after reaction.

9. The experimental method for bean sprouts cultured with aqueous solutions of CBZ and its degradation products and evaluation method for mean length should be described in the Supporting Materials.

Response:

Thanks for your suggestion. We have added the descriptions about the experimental method for bean sprouts cultured with aqueous solutions of CBZ and its degradation products and evaluation method for mean length in the Supporting Materials of our revised manuscript:

Supplementary Method 8. The experimental method for bean sprouts and evaluation method for mean length

Mung bean seeds were purchased from a local market in Changchun, China. Seeds were surface-disinfected by soaking in a 0.5% sodium hypochlorite solution for 10 min, rinsed five times with deionized water, and then dried on filter paper for germination testing. 5 mL sample obtained from the 4Co/CN SACs/PMS/vis system and 4MgCo/CN DSACs/PMS/vis system, reacted for 4, 12, and 24 min respectively, were poured into 90 mm diameter Petri dishes. Ten selected seeds were evenly distributed on each dish. Place in an artificial climate incubator for dark cultivation at 25 °C and 70% relative humidity. Germination was determined when the root tip extended beyond half the seed length. After 5 days of cultivation, record the stem and mean length of all germinated seeds.

10. To better understand the advantage of domino catalysis in overcoming the activity-stability trade-off during water purification, the role of the domino-effect-driven dynamic electronic structures evolution in peroxymonosulfate activation and radical desorption should be elaborated in detail in lines 280-284.

Response:

Thanks for your suggestion. To better understand the advantage of domino catalysis in overcoming the activity-stability trade-off during water purification, we have added detailed descriptions about the role of the domino-effect-driven dynamic electronic structures evolution in peroxymonosulfate activation and radical desorption in our revised manuscript (line 387-391, page 20; line 392-398, page 21):

In summary, the dynamic domino catalysis process in overcoming the activity-stability trade-off during water purification was as follows: Under visible light irradiation, photogenerated electrons drove a two-electron oxygen reduction reaction at the Mg site, enabling the *in-situ* generation of H₂O₂. The as-formed H₂O₂ was subsequently converted to OH_{surf} via the Mg site. These OH_{surf} leveraged the π -conjugated delocalized network of carbon nitride to modulate the d-orbital configuration of non-adjacent Co atom through long-range interaction, enabling the shift of energy levels for d_{xy}, d_{x²-y²}, d_{xz}, d_{z²} and d_{yz} orbitals to lower energy levels⁵⁵⁻⁵⁷. On the one hand, this promoted the reduction of Co³⁺ to Co²⁺, thereby accelerating •SO₄⁻ generation during PMS activation for enhanced activity. On the other hand, it reduced the adsorption energy of *SO₄, optimizing its desorption process and preventing Co atom detachment to maintain stability.

11. Detailed information on the light source used in the reaction should be provided, as only visible light is currently mentioned.

Response:

Thanks for your suggestion. We have provided detailed information on the light source used in the reaction in Methods section of our revised manuscript (line 537-538, page 28; line 539, page 29):

The light source was a 150 W Xenon lamp (CEL-HXF 300, Beijing Education Au-light Co., Ltd.) with a filter to cut off the ultraviolet light ($\lambda < 420$ nm). The light intensity was 122.4 mW/cm² (illumination area = 3.24 cm²).

12. Some incorreced descriptions be checked and corrected in this manuscript. For

example, “ The 3.5%, 33.6%, 52.5%, 67.7%, 14.7%, 10.4% and 85.4% of CBZ were degraded by methanol (MeOH), Isopropyl alcohol (IPA), Methyl phenyl sulfoxide (PMSO), β -carotene (β -caro), sodium fluoride (NaF), catalase (CAT) and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$), respectively in line 134-138”.

Response:

Thanks for your suggestion. We have checked and corrected the descriptions throughout the manuscript (line 27-28, 30, 36, 38-39, page 2; line 51, 53-55, 59, page 3; line 77, 79, page 4; line 95-96, 99-100, 103-109, page 5; line 110-131, page 6; line 132-134, 138-140, page 7; line 141, 144-145, 147-151, 154-155, 159-160, 162, page 8; line 163-170, 172, 175-178, 181-184, page 9; line 186-187, 191-197, 199, page 10; line 216-226, 228-233, page 12; line 234-255, page 13; line 256-269, 272-277, page 14; line 278-281, 283-286, 290-293, 295, page 15; line 305-306, 315, 317-320, 322-324, page 17; line 327-334, 336, 338, 341, 343, 346-347, page 18; line 352-369, page 19; line 370-391, page 20; line 392-398, page 21; line 418, 424, page 22; line 425-426, 428, 430, 440, 445-446, page 23; line 480, 483, 488, page 26; line 498, 505-511, 515, page 27; line 524, 526, 530, 535-538, page 28; line 539, page 29):

Here, we break the limitation of this static design by reporting a novel domino catalysis within a heteronuclear MgCo dual-single-atom catalyst. In this system, the Mg site selectively photoreduces O_2 to H_2O_2 under light irradiation. This *in-situ* generated H_2O_2 and its derived surface hydroxyl groups act as dynamic modulators, progressively tailoring the electronic structure of the adjacent Co site.

Experiments and theoretical calculations elucidate that this seamless and spatially ordered cascade avoids competitive adsorption and maximizes efficiency.

The system exhibits the highest normalized rate constant of $595.3 \text{ min}^{-1} \text{ M}^{-1}$ among various refractory contaminants over thirty regeneration cycles, outperforming the most state-of-the-art catalytic systems.

Among various intensification strategies, coupling these reactions with inexhaustible solar energy presents a highly sustainable avenue³. However, the widespread implementation of such photo-enhanced Fenton-like systems is critically hampered by the fundamental and persistent trade-off between simultaneously achieving high catalytic activity and long-term stability⁴. High activity demands rapid redox cycling of the metal centre, a process often accelerated by photo-generated charge carriers⁵.

Recent advances in single-atom catalysis (SACs), with its maximized atomic utilization efficiency and tailorable electronic structures, offer new hope for optimizing this activity-stability nexus⁷.

Under light irradiation, the magnesium site initiates the cascade by selectively photoreducing O_2 to H_2O_2 ¹⁷. This *in-situ* generated H_2O_2 then acts not merely as a precursor, but as the dynamic modulator whose derived surface hydroxyl groups progressively tailor the electronic structure of the adjacent cobalt site.

The heteronuclear magnesium cobalt dual single atom catalysts (MgCo/CN DSACs) were synthesized by a simple hydrothermal method (Fig. 1a). The MgCo/CN

DSACs had a sparse and three-dimensional nanosheet structure in scanning electron microscope (SEM) (Fig. S1).

The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) (Fig. 1b) exhibited the bright dual-atom pairs in yellow dashed ellipses, indicating that the dual single atom structure was successfully synthesized.

The Co and Mg K-edge X-ray absorption near-edge structure (XANES) spectra (Figs. 1e and 1h) showed that the absorption edge of Co lay between those of Co foil and CoO, while that of Mg lay between those of Mg foil and MgO, but closer to Mg foil. This indicated that the oxidation states of both Co and Mg in the 4MgCo/CN DSACs ranged between 0 and +2, yet they differed from each other. The linear combination fitting (LCF) analysis (Figs. S2, S3 and Tables S1, S2) was performed to quantify the proportions of different Co and Mg species. The proportions of Co⁰, Co²⁺ and Co³⁺ were 40.6%, 28.7%, and 30.7%, respectively, while those of Mg⁰ and Mg²⁺ were 81.7% and 18.3%, respectively. Based on the LCF results, the average oxidation states of Co and Mg in the 4MgCo/CN DSACs were estimated to be 1.50 and 0.37, respectively (Figs. 1f and 1i). Fourier transformed (FT) k³-weighted X-ray absorption fine structure (EXAFS) spectra of 4MgCo/CN DSACs (Figs. S4 and S5), the peaks corresponding to Co–N at 1.48 Å and Mg–N at 1.68 Å were observed^{19,20}. No peaks attributable to Co–Co, Co–O, Mg–Mg and Mg–O bonds were detected, suggesting the absence of metallic or oxide clusters. Additionally, no Mg–Co bond was observed in the EXAFS spectra of 4MgCo/CN DSACs, demonstrating that no direct bonding

between Mg and Co atom. The more negative formation energy of 4MgCo/CN without the Mg–Co bond (-0.75 eV), compared to that of its counterpart containing the Mg–Co bond (1.15 eV), further indicated that the former was more favorable to form (Fig. S6). Based on the FT-EXAFS fitting results in R-space (Figs. 1g and 1j, Tables S3 and S4), it was deduced that the coordination configurations of 4MgCo/CN DSACs were identified as Mg–N₄ and Co–N₄. Quantitative intensity profile analysis (Fig. S7) confirmed that the predominant configuration featured MgCo paired sites with the highest prevalence of interatomic distance of 6.48 Å, which matched well with the distance between Mg and Co in simulated MgCo/CN model featuring Mg–N₄ and Co–N₄ coordination without Mg–Co bond. The same estimation method has been reported in previous work²¹. The spin states of the catalysts were characterized by electron paramagnetic resonance (EPR) spectra (Fig. S8) and temperature-dependent inverse magnetic susceptibility measurements (Fig. S9). These results collectively confirmed the successful synthesis of MgCo/CN DSACs featuring Mg–N₄ and Co–N₄ configurations without Mg–Co bond.

Fig. 1. (a) Synthesis of MgCo/CN DSACs. (b) Aberration-corrected HAADF-STEM image and EDS mapping of 4MgCo/CN DSACs. (c) XRD and (d) FT-IR spectra of catalysts, respectively. (e) Normalized Co K-edge XANES spectra, (f) corresponding oxidation state of Co species and (g) the fitting curves of Co K-edge EXAFS spectra in 4MgCo/CN DSACs. (h) Normalized Mg K-edge XANES spectra, (i) corresponding oxidation state of Mg species and (j) the fitting curves of Mg K-edge EXAFS spectra in 4MgCo/CN DSACs.

The 2MgCo/CN DSACs degraded 82.0% of carbamazepine (CBZ) in the PMS/vis system, which was much higher than those achieved by CN (39.8%), 4Mg/CN SACs (69.0%) and 4Co/CN SACs (69.2%), respectively. The CBZ degradation efficiency first increased and then decreased with increasing Mg and Co ratio from 20% to 60% and the optimal degradation efficiency (92.7%) was obtained by 4MgCo/CN DSACs (Fig. S10). 4MgCo/CN DSACs had 53.2% of total organic carbon (TOC) removal efficiency, which was much higher than those of CN (18.6%), 4Mg/CN (33.5%) and 4Co/CN (34.1%), respectively (Fig. S11).

The degradation rate constant towards various contaminants, including sulfamethoxazole (SMX), CBZ, tetracycline hydrochloride (TCH), 4-chlorophenol (4-CP) and bisphenol A (BPA) in the 4MgCo/CN DSACs/PMS/vis system with 0.1 mM PMS was superior to most of those in previous reports (Fig. 2a, Table S5)²²⁻⁴³.

The Co dissolution concentration in the 4MgCo/CN DSACs/PMS/vis system (0.43 mg/L) was below the emission standard of GB 25467-2010 (1.0 mg/L) in China, which was also much lower than that in the 4Co/CN SACs/PMS/vis system (1.39 mg/L) after 30-time cycles^{44,45}. These results illustrated that both CBZ degradation activity and stability were superior in the 4MgCo/CN DSACs/PMS/vis system. The methanol (MeOH, 100.0 mM), isopropyl alcohol (IPA, 100.0 mM), methyl phenyl sulfoxide (PMSO, 0.2 mM), β -carotene (β -caro, 0.2 mM), sodium fluoride (NaF, 2.0 mM), catalase (CAT, 200.0 units/mL) and sodium oxalate (Na₂C₂O₄, 1.0 mM) were selected as scavengers for $\bullet\text{SO}_4^-$, $\bullet\text{OH}$, high-valent metal-oxo, $^1\text{O}_2$, OH_{surf} , H_2O_2 and h^+ , respectively⁴⁶⁻⁴⁹.

The 3.5%, 33.6%, 52.5%, 67.7%, 14.7%, 10.4% and 85.4% of CBZ were degraded after the addition of MeOH, IPA, PMSO, β -caro, NaF, CAT and $\text{Na}_2\text{C}_2\text{O}_4$, respectively, indicating that $\bullet\text{SO}_4^-$ and OH_{surf} derived from H_2O_2 were major active species in the 4MgCo/CN DSACs/PMS/vis system (Fig. 2d). This was different from the reaction dominated by only $\bullet\text{SO}_4^-$ in the 4Co/CN SACs/PMS/vis system (Fig. S12).

In the Fenton-like system, 50.6%, 70.5% and 70.2% of CBZ were degraded by β -caro, NaF and CAT, respectively, while in the photocatalytic system, 13.7%, 8.9% and 9.6% of CBZ were degraded by β -caro, NaF and CAT, respectively. The excellent photoadsorption of catalysts was observed in UV-Vis diffuse reflectance spectroscopy (DRS) (Fig. S14). These results further demonstrated that visible light contributed to the *in-situ* generation of H_2O_2 for the dominance of OH_{surf} in the contaminant removal.

The relationship among degradation efficiencies with the dosages of CAT, NaF and MeOH was further estimated. The correlation constant R^2 of 0.991 between degradation efficiency and MeOH dosage was far higher than the others, meaning that OH_{surf} secondary from H_2O_2 might be the indirect active species and $\bullet\text{SO}_4^-$ might be the direct active species in the 4MgCo/CN DSACs/PMS/vis system (Fig. 2e). In contrast, the correlation constants of R^2 for the relationship among degradation efficiencies of CAT dosage, NaF dosage and MeOH dosage in the 4Co/CN SACs/PMS/vis system were all no more than 0.732. This indicated that $\bullet\text{SO}_4^-$, H_2O_2 and OH_{surf} were indirect active species in the 4Co/CN SACs/PMS/vis system (Fig. 2f).

The ratio of Co^{2+} in 4Co/CN SACs increased from 41% to 42% and the ratio of Co^{2+} in 4MgCo/CN DSACs increased from 57% to 59% after visible light irradiation, which could be attributed to the fact that Co^{3+} was reduced into Co^{2+} by photogenerated electrons. The ratio of Co^{2+} for 4Co/CN SACs decreased from 41% to 39% after the reaction in the PMS/vis system due to the redox from PMS to $\bullet\text{SO}_4^-$, whereas the ratio of Co^{2+} increased from 57% to 69% in the 4MgCo/CN DSACs/PMS/vis system (Fig. 2c). The major contributions of $\bullet\text{SO}_4^-$ and OH_{surf} were also observed in the MgMn/CN DSACs/PMS/vis and MgFe/CN DSACs/PMS/vis systems, which differed from those in photo-Fenton-like system mediated by SACs and Fenton-like system mediated by DSACs and SACs, respectively (Fig. 2g, Table S6).

The 4MgCo/CN DSACs activated 87.2% of PMS, which was higher than that by 4Co/CN SACs (66.6%) (Fig. 3a). Furthermore, in the *in-situ* Raman spectra of 4MgCo/CN DSACs, a new peak appeared at 815.7 cm^{-1} after a 3-min reaction, and its intensity became more pronounced after 5 min, whereas this peak was absent in the *in-situ* Raman spectra of 4Co/CN SACs (Figs. S15 and S16)⁵⁰. This indicated that the interaction between MgCo dual atoms contributed to PMS activation. The PMS activation efficiency by 4MgCo/CN DSACs increased from 45.2% to 77.3% when exogenous H_2O_2 was raised from 0.0 mM to 3.97 mM (Fig. S17). The larger ring current of 4MgCo/CN DSACs compared to that of 4Co/CN SACs mainly originated from the higher amount of H_2O_2 generated by the former (Fig. 3b). Both 4MgCo/CN DSACs and 4Co/CN SACs had an n value closer to 2 (Fig. 3c). The selectivity of

4MgCo/CN DSACs (86.1%) was higher than that of 4Co/CN SACs (46.1%), indicating that dual single atom sites could increase the $2e^-$ selectivity for *in-situ* H_2O_2 generation (Fig. 3d). No H_2O_2 was generated under the dark condition, despite oxygen aeration. However, 2.26 mM and 1.87 mM of H_2O_2 were generated within the first 4 min by both catalysts, and then activated to 0.39 mM and 0.93 mM, respectively, by 4MgCo/CN DSACs and 4Co/CN SACs in the PMS/vis/CBZ system (Figs. 3e and S18). The H_2O_2 generation for these two catalysts was attributed to their conduction band potentials being higher than that of O_2/H_2O_2 (Fig. S19). The photogenerated electrons could reduce oxygen into H_2O_2 under light irradiation. The H_2O_2 production increased from 1.14 mM to 3.97 mM as the dosage of 4MgCo/CN DSACs increased from 0.005 to 0.05 g/L in the PMS/vis/CBZ system (Fig. S20). Fig. S21 showed that H_2O_2 was gradually generated up to 4.38 mM in the PMS/vis/ H_2O system within 24 min, which was higher than those in the PMS/vis/CBZ system (0.39 mM), the vis/CBZ system (0.03 mM), and the vis/ H_2O system (0.23 mM), respectively. These results indicated that visible light was essential for H_2O_2 generation, that CBZ could consume part of the *in-situ* generated H_2O_2 , and that PMS facilitated the photoreduction of H_2O_2 . As shown in Figs. S22 and S23, the H_2O_2 concentration decreased rapidly after introducing nitrogen (N_2), indicating that O_2 was essential for H_2O_2 generation. Upon addition of the electron-trapping agent potassium bromate ($KBrO_3$), the H_2O_2 concentration dropped sharply, demonstrating that the two-electron oxygen reduction reaction was the primary pathway for photocatalytic H_2O_2 production. The H_2O_2 concentration decreased by 94.1% after adding p-benzoquinone

(p-BQ), suggesting that $\bullet\text{O}_2^-$ was a key intermediate in the photoreaction. The negligible H_2O_2 concentration observed upon addition of tert-butyl alcohol (TBA) indicated that $\bullet\text{OH}$ was not an intermediate in H_2O_2 production. In contrast, adding ethanol (EtOH) and benzyl alcohol (BnOH) significantly increased H_2O_2 production, mainly because these alcohols capture photogenerated holes and supply sufficient protons, thereby facilitating oxygen reduction for H_2O_2 generation. These results indicated that CBZ did not affect the types of key intermediates in the *in-situ* photocatalytic generation of H_2O_2 . The Gibbs free energy for the two-electron oxygen reduction to H_2O_2 in the presence of PMS by 4MgCo/CN DSACs was negative (Fig. S24), indicating that H_2O_2 generation was thermodynamically spontaneous. Fig. S25 exhibited the time-resolved *in-situ* DRIFTS profiles of 4MgCo/CN DSACs. In the 4MgCo/CN DSACs/PMS/vis system, the characteristic O–O stretching vibrations were detected for surface-adsorbed species, including O_2^* (965 cm^{-1}), $\bullet\text{O}_2^-*$ (1151 cm^{-1}), $\bullet\text{OOH}^*$ (1205 cm^{-1}), and HOOH^* (1369 cm^{-1})⁵¹. The intensities of these peaks progressively increased with reaction time from 0 to 24 min. In the ESR spectra (Fig. S26), a distinct characteristic signal of $\bullet\text{O}_2^-$ was observed under light irradiation, whereas the signal was barely detectable in the dark. Collectively, these results demonstrated that the dominant route for H_2O_2 generation was the two-electron oxygen reduction. A correlation plot of the CBZ degradation rate constant within the first 4 min (k_1) and that from 4 min to 24 min (k_2) was generated against various possible influencing factors, including Co mass (A), photoadsorption (B), crystallinity (C), OH_{surf} contribution ratio (D) and Co spin state (E). This result illustrated that the

degradation of CBZ was mainly related to OH_{surf} from *in-situ* generated H_2O_2 ($p < 0.05$) (Fig. 3f), indicating that the photoadsorption and OH_{surf} contribution ratio were crucial factors for k_1 and k_2 , respectively. Given that visible light was used to drive photoreduction of oxygen to H_2O_2 , which served as a crucial intermediate for OH_{surf} , it could be deduced that CBZ degradation was primarily related to OH_{surf} from *in-situ* generated H_2O_2 .

Almost no H_2^{18}O -labeled *p*-HBA peak ($m/z=137.1$) was observed in the 4MgCo/CN DSACs/PMS/vis system, indicating that OH_{surf} originated from *in-situ* H_2O_2 generated from oxygen in the air rather than from oxygen in PMS or H_2O . However, the H_2^{18}O -labeled *p*-HBA peak ($m/z = 139.1$) was found in the 4Co/CN SACs/PMS/vis system⁵². This indicated that $\bullet\text{OH}$ mainly came from the reaction between $\bullet\text{SO}_4^-$ and H_2O in the 4Co/CN SACs/PMS/vis system (Figs. 3g and S27). The degradation efficiency of BA decreased with increasing NaF concentration, and it was remarkably reduced from 64.2% to 15.7% after the addition of 9.0 mM NaF (Fig. 3h). The activation efficiency of PMS was also reduced from 87.2% to 27.9% with increasing NaF concentration from 0 to 9 mM (Fig. S28).

These results illustrated that OH_{surf} from H_2O_2 contributed to the reduction of Co^{3+} to Co^{2+} in the 4MgCo/CN DSACs/PMS/vis system, which differed from that in the 4Co/CN SACs/PMS/vis system (Fig. 3i). This was supported by the increased radius in electrochemical impedance spectroscopy (EIS) (Fig. 3j) and the reduced Cdl (5.26 mF cm^{-2}) in electrochemical active surface area (ECSA) from cyclic voltammetry (CV) profiles⁵³ (Figs. 3k and Fig. S29) observed for 4MgCo/CN DSACs

after the addition of NaF and CAT.

(f) The correlation plot of CBZ degradation rate constant with various possible influencing factors. A, B, C, D and E represented mass of Co, photoadsorption, crystallinity, OH_{surf} contribution ratio and Co spin state.

The inclined adsorption of H₂O₂ and PMS on the Mg and Co sites with the adsorption energies of -3.70 and -10.62 eV was confirmed, respectively (Fig. S30). The activation from PMS to $\bullet\text{SO}_4^-$ by MgCo/CN DSACs@OH_{surf} was spontaneous, while it needed to overcome an energy barrier for MgCo/CN DSACs@H₂O₂ and MgCo/CN DSACs, respectively. The adsorption of $\bullet\text{SO}_4$ on MgCo/CN DSACs@OH_{surf}-PMS (-7.24 eV) was much weaker than that by MgCo/CN DSACs (-10.62 eV), indicating that OH_{surf} contributed to $\bullet\text{SO}_4$ desorption. The activation energy barrier of PMS by MgCo/CN DSACs@H₂O₂ (0.80 eV) was smaller than that by MgCo/CN DSACs (1.95 eV). The spontaneous generation of OH_{surf} from H₂O₂ confirmed that OH_{surf} was more easily generated from H₂O₂. This contributed to PMS activation rather than from PMS (Fig. 4b).

The d-band center of MgCo/CN DSACs@OH_{surf} (-0.93 eV) was much farther from the Fermi energy level compared to those of MgCo/CN DSACs@H₂O₂ (-0.12 eV) and MgCo/CN DSACs (-0.067 eV) (Fig. S31). However, the longer O–O bond in PMS was observed after adsorption on MgCo/CN DSACs@OH_{surf} (1.87 Å) than MgCo/CN DSACs@H₂O₂ (1.50 Å) and MgCo/CN DSACs (1.23 Å) was observed. These results meant that the superior PMS activation by MgCo/CN DSACs@OH_{surf} was induced not only by the high electron density of Co. This was completely

different from the traditional Fenton-like processes⁵⁴.

The orbital hybridization between the Co of different catalysts and Op of PMS and $\bullet\text{SO}_4$ was illustrated in Figs. 4d and S32. The overlap between Co d_{xy} and $d_{x^2-y^2}$ in MgCo/CN DSACs@OH_{surf}-PMS with Op of PMS and $\bullet\text{SO}_4$ was larger than that of Co 3d orbital with PMS and $\bullet\text{SO}_4$. This demonstrated that OH_{surf} contributed to PMS activation and $\bullet\text{SO}_4$ desorption. To further understand the interaction of OH_{surf} and Co site, the relationship among E_{ads} , E_{d} , Δq and $I_{\text{O-O}}$ with the amount of OH_{surf} was correlated (Figs. 4e and 4f). It was found that an optimal amount of OH_{surf} contributed to the adsorption of PMS, the extension of the O–O bond of PMS, the reduction of d-band center and increase of transferred electrons between the catalyst and PMS. Figs. 4h, 4g, S33 and Table S7 showed that OH_{surf} induced the reconstruction of Co 3d orbital, leading to the shift of the energy level for d_{xy} , $d_{x^2-y^2}$, d_{xz} , d_z^2 and d_{yz} orbitals to lower energy levels in MgCo/CN DSACs@OH_{surf}-PMS.

Fig. S34 exhibited that the Co d-band center obviously shifted as the amount of OH_{surf} varied. Figs. S35 and S36 showed the strong correlations among the d-band center with PMS adsorption energy ($R^2 = 0.9992$), electron transfer charge ($R^2 = 0.9326$), and O–O bond length ($R^2 = 0.9948$), but a weak correlation with O–H bond length ($R^2 = 0.5162$). These results indicated that OH_{surf}-modulated d-band center facilitated PMS adsorption and activation into $\bullet\text{SO}_4^-$. Moreover, the valence electron densities of Co sites were 5.09 e, 5.53 e, 6.05 e, and 5.65 e as the amount of OH_{surf} increased (Fig. S37), indicating that appropriate OH_{surf} adsorption on the Mg site modulated the electron density of the Co site via long-range interaction.

To track electronic change following the modulation of the d-band center, we performed electron paramagnetic resonance (EPR) spectroscopy, electrochemical impedance spectroscopy (EIS), ECSA measurement and Co *K*-edge XANES spectra by the 4MgCo/CN DSACs after reaction, respectively. The EPR spectra (Fig. S38) showed that the EPR signal at $g = 2.30$ for 4MgCo/CN DSACs intensified with increasing reaction time, indicating a gradual increase in unpaired electrons. The EIS results (Fig. S39) exhibited that the radius decreased markedly as the reaction proceeded, suggesting a remarkable enhancement in electron transfer performance. Furthermore, the increased C_{dl} value in the ECSA of 4MgCo/CN DSACs over reaction time (Fig. S40) demonstrated a rise in active site density, which facilitated the electron participation in the reaction. As shown in Fig. S41, the Co *K*-edge shifted negatively after the reaction compared to that before the reaction, indicating a reduction in the oxidation state of Co in the 4MgCo/CN DSACs after reaction. Based on the LCF results, the proportion of Co^{2+} species in the 4MgCo/CN DSACs increased from 28.7% before reaction to 63.4% after reaction (Figs. S2 and S42, Tables S1 and S8), while the average Co oxidation state decreased from 1.50 to 1.27 (Figs. 1f and S43). This observation was supported by the increased Co^{2+} ratio as the reaction proceeded from 0 to 24 min in the 4MgCo/CN DSACs/PMS/vis system, as shown by *in-situ* XPS spectra (Fig. 4i).

The degradation efficiencies of CBZ by 4MgCo/CN DSACs after the addition of NaF and CAT were reduced by 5.35% and 3.8%, respectively, over 30 cycles. The Co dissolution concentration in the 4MgCo/CN DSACs/PMS/vis system with NaF and

CAT exceeded 0.85 mg/L and 0.83 mg/L, which was much higher than that in the system without scavengers (0.43 mg/L) (Figs. S44 and S45). These results indicated that OH_{surf} from H_2O_2 contributed to enhancing stability in the 4MgCo/CN DSACs/PMS/vis system. In summary, the dynamic domino catalysis process in overcoming the activity-stability trade-off during water purification was as follows: Under visible light irradiation, photogenerated electrons drove a two-electron oxygen reduction reaction at the Mg site, enabling the *in-situ* generation of H_2O_2 . The as-formed H_2O_2 was subsequently converted to OH_{surf} via the Mg site. These OH_{surf} leveraged the π -conjugated delocalized network of carbon nitride to modulate the d-orbital configuration of non-adjacent Co atom through long-range interaction, enabling the shift of energy levels for d_{xy} , $d_{x^2-y^2}$, d_{xz} , d_z^2 and d_{yz} orbitals to lower energy levels⁵⁵⁻⁵⁷. On the one hand, this promoted the reduction of Co^{3+} to Co^{2+} , thereby accelerating $\bullet\text{SO}_4^-$ generation during PMS activation for enhanced activity. On the other hand, it reduced the adsorption energy of $\ast\text{SO}_4$, optimizing its desorption process and preventing Co atom detachment to maintain stability.

To evaluate the practical application potential of the 4MgCo/CN DSACs/PMS/vis system, simulated CBZ wastewater and secondary effluent from the Jilin Petrochemical Company wastewater treatment plant were removed in continuous flow reactors (Figs. 5c and 5d).

The *in-situ* OH_{surf} -induced dynamic-catalytic system has the potential to be applied in the decontamination sterilization unit (Fig. 5e). The CBZ could be rapidly transformed into small-molecular products in the 4MgCo/CN DSACs/PMS/vis

system, which was different from that in the 4Co/CN SACs/PMS/vis system (Figs. S46-49). Compared to the toxicity of pristine CBZ, the toxicity of degradation products in the 4MgCo/CN DSACs/PMS/vis system was reduced more obviously than that in the 4Co/CN DSACs/PMS/vis system (Fig. 5f, Tables S10 and S11) based on the QSAR-based toxicity prediction using T.E.S.T. software⁵⁸.

Given that the equipment could be operated at full capacity and resources could be maximized when industrial scale production was achieved in the future, the environmental impact of 4MgCo/CN DSACs would be substantially minimized during the preparation stage (Table S13).

This reconstruction was facilitated by surface hydroxyl radicals generated from *in-situ* generated H₂O₂ using green O₂ and H₂O via a domino-catalytic strategy. Using magnesium-cobalt dual single-atom catalysts as an example, it demonstrated that cobalt d-orbital configuration was dynamically changed with the *in-situ* generation of surface hydroxyl radical. Different from the conventional approach that depended on rapid photoelectron injection to reduce M³⁺ to M²⁺ at the catalyst surface under light irradiation, the domino-catalytic system leveraged cobalt d-orbital reconfiguration to enable the gradual generation of surface hydroxyl radical for dual single atomic electron internal circulation. This mechanism involved the dynamic electron transfer between the d_{xy} and d_{x²-y²} orbitals of cobalt and Op orbital of PMS, resulting in efficient and stable PMS activation.

Chemicals and materials

Certain amounts of CoCl₂·6H₂O, MgCl₂·6H₂O and 100 mg of CN were added

into 60 mL n-octanol solution. The mass ratio of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to CN were $x = 2, 4$ and 6% . The mixture was stirred for 1 h to obtain a turbid solution. Then, the turbid solution was added into a Teflon-lined autoclave and heated at 200°C for 24 h. The sample was washed with ultrapure water and ethanol several times, followed by drying under the vacuum at 60°C for 10 h. The resulting samples were named as $x\text{MgCoCN}$ ($x=2, 4$ and 6 wt%).

XRD pattern was recorded using a Rigaku D/Max-2550 diffractometer via $\text{Cu K}\alpha$ radiation at 50 kV and 200 mA in the 2θ range between 10 - 70° at a scanning rate of $5^\circ/\text{min}$.

The EPR measurements were performed on a Bruker 300 system. The ESR spectra of reactive oxygen species trapped in water and methanol by DMPO or TEMP were analyzed by a Brooke A300 system. The *in-situ* Raman spectra were recorded with a Renishaw confocal micro-Raman spectroscopy system with a 532 nm excitation laser.

The *in-situ* EPR spectra were detected a Bruker 300 system.

0.02 g catalyst was first added into 2.0 L simulated wastewater, consisted of 1.64 mM NaCl, 11.5 mM NaHCO_3 , 0.7 mM NaNO_3 , 0.016 mM $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and 10.0 mg/L a single contaminant with CBZ, BPA, SMX, ATZ or 4-CP and stirred in the dark for 30 min. Then, the reaction was activated by the visible light irradiation and the addition of 0.1 mM PMS. The light source was a 150 W Xenon lamp (CEL-HXF 300, Beijing Education Au-light Co., Ltd.) with a filter to cut off the ultraviolet light ($\lambda < 420$ nm). The light intensity was $122.4 \text{ mW}/\text{cm}^2$ (illumination area = 3.24 cm^2).

To reviewer 2

The reviewer's comment:

Reviewer #2: The authors propose a domino effect that enables dynamic electronic structure evolution to resolve intrinsic trade-off between high catalytic activity and long-term stability in advanced oxidation processes. Mimicking a falling domino chain where an event automatically triggers the next, our system orchestrates a seamless, spatially ordered cascade of reactions. Experiments and theoretical calculations elucidate this seamless and spatially ordered cascade avoids competitive adsorption and maximizes efficiency. Overall, this manuscript is novel and convincing. Hence, I recommend it to be published after following minor revision.

1. Domino effect enables dynamic electronic structure evolution according to reaction requirements, thereby enhancing catalytic activity. However, how can catalytic stability be regulated? Provide a detailed description.

Response:

We are very sorry that we haven't described clearly in the previous manuscript. The dissolution of metal active site was one of the most primary reason for catalyst deactivation, particularly in highly oxidative PMS-based oxidation system. If $^*\text{SO}_4$ adsorption onto Co was excessively strong, it would lead to overpolarization of the Co–O bond, ultimately causing Co detachment from the catalyst. The Co d orbital modulation by OH_{surf} could optimize the adsorption of $^*\text{SO}_4$, thereby preventing Co atom detachment for catalytic stability. This was supported by the 5.35% and 3.8% of reduction in the degradation efficiencies of CBZ by 4MgCo/CN DSACs after the

addition of NaF and CAT over 30 cycles as well as 0.42 mg/L and 0.40 mg/L enhancement of the Co dissolution concentration in the 4MgCo/CN DSACs/PMS/vis system with the addition of NaF and CAT, respectively (Figs. S44 and S45). To clearly demonstrate the mechanism for enhanced catalytic stability by domino effect, we have added corresponding descriptions in our revised manuscript (line 381-391, page 20; line 392-398, page 21):

The degradation efficiencies of CBZ by 4MgCo/CN DSACs after the addition of NaF and CAT were reduced by 5.35% and 3.8%, respectively, over 30 cycles. The Co dissolution concentration in the 4MgCo/CN DSACs/PMS/vis system with NaF and CAT exceeded 0.85 mg/L and 0.83 mg/L, which was much higher than that in the system without scavengers (0.43 mg/L) (Figs. S44 and S45). These results indicated that OH_{surf} from H_2O_2 contributed to enhancing stability in the 4MgCo/CN DSACs/PMS/vis system.

In summary, the dynamic domino catalysis process in overcoming the activity-stability trade-off during water purification was as follows: Under visible light irradiation, photogenerated electrons drove a two-electron oxygen reduction reaction at the Mg site, enabling the *in-situ* generation of H_2O_2 . The as-formed H_2O_2 was subsequently converted to OH_{surf} via the Mg site. These OH_{surf} leveraged the π -conjugated delocalized network of carbon nitride to modulate the d-orbital configuration of non-adjacent Co atom through long-range interaction, enabling the shift of energy levels for d_{xy} , $d_{x^2-y^2}$, d_{xz} , d_z^2 and d_{yz} orbitals to lower energy levels⁵⁵⁻⁵⁷. On the one hand, this promoted the reduction of Co^{3+} to Co^{2+} , thereby accelerating $\bullet\text{SO}_4^-$ generation during PMS activation for enhanced activity.

On the other hand, it reduced the adsorption energy of SO_4^{2-} , optimizing its desorption process and preventing Co atom detachment to maintain stability.

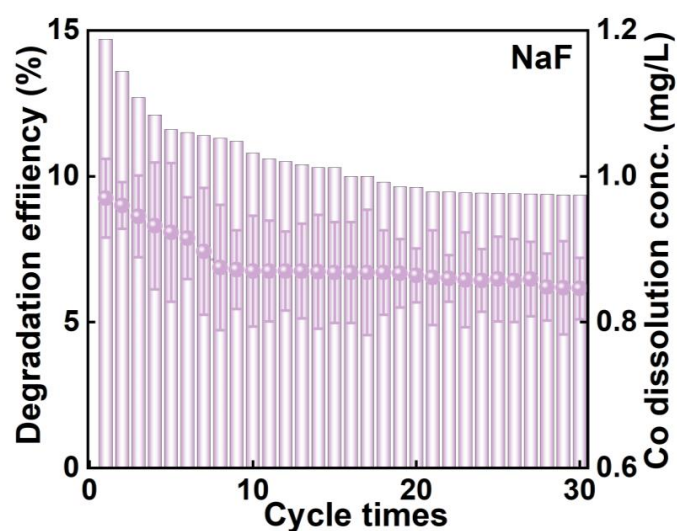


Fig. S44. Degradation of CBZ by 4MgCo/CN DSACs after the addition of NaF over 30-time cycles in the PMS/vis system.

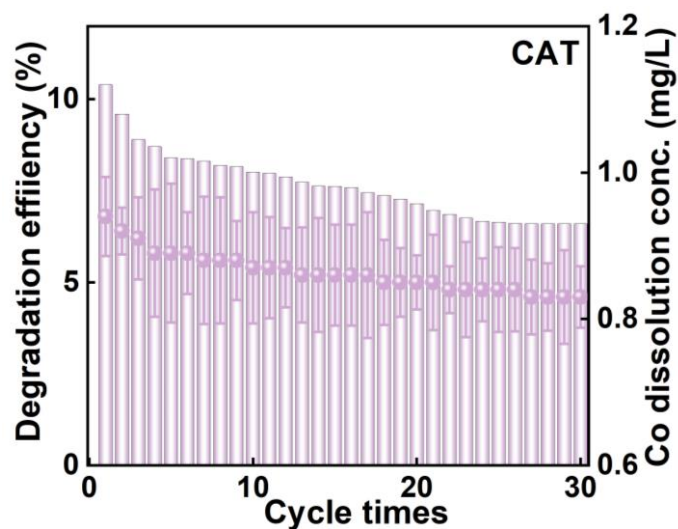


Fig. S45. Degradation of CBZ by 4MgCo/CN DSACs after the addition of CAT over 30-time cycles in the PMS/vis system.

References in this first response to reviewer 2:

55. Wu, Z. et al. Long-range interactions driving neighboring Fe-N₄ sites in Fenton-like reactions for sustainable water decontamination. *Nat Commun.* **15**, 7775

(2024).

56. Jin, S. et al. Remote tuning of single-atom Fe–N₅ sites via high-coordination defects for enhanced Fenton-like water decontamination. *Nat Commun.* **16**, 10455 (2025).

57. Deng, Y. C. et al. Long-range electronically polarized Fe–N₅ catalysts redirect polymerization-driven phenolic pollutant removal toward sustainable carbon sequestration, *Angew. Chem. Int. Ed.* **64**, e202509493 (2025).

2. What is the cobalt concentration in emission standard? Is the cobalt concentration (0.43 mg/L) leached in the MgCo/CN/PMS/vis system higher or lower compared to this standard? Provide relevant information.

Response:

Thanks for your suggestion. According to the emission standard of GB 25467-2010 in China, the Co concentration should below 1.0 mg/L^{1,2}. The 0.43 mg/L of Co dissolution concentration in the MgCo/CN/PMS/vis system was lower compared to that in standard. To clearly demonstrate that Co dissolution concentration complied with discharge standard, we have added corresponding descriptions in our revised manuscript (line 159-160, 162, page 8):

The Co dissolution concentration in the 4MgCo/CN DSACs/PMS/vis system (0.43 mg/L) was below the emission standard of GB 25467-2010 (1.0 mg/L) in China, which was also much lower than that in the 4Co/CN SACs/PMS/vis system (1.39 mg/L) after 30-time cycles.

References in this second response to reviewer 2:

1. Wang, S. Z. et al. Peroxymonosulfate activation by Fe–Co–O-codoped graphite carbon nitride for degradation of sulfamethoxazole. *Environ. Sci. Technol.* **54**, 10361–10369 (2020).
2. Zhou, L. et al. Degradation of organic pollutants in wastewater by bicarbonate-activated hydrogen peroxide with a supported cobalt catalyst. *Environ. Sci. Technol.* **47**, 3833–3839 (2013).
3. Provide the dosage of scavengers for different active species. Additionally, add references to support the additional dosage of scavengers, as the dosage of scavengers affect the capture performance.

Response:

Thanks for your suggestion. The methanol, isopropyl alcohol, methyl phenyl sulfoxide, β -carotene, sodium fluoride, catalase and sodium oxalate were the scavengers for $\bullet\text{SO}_4^-$, $\bullet\text{OH}$, high-valent metal-oxo, $^1\text{O}_2$, OH_{surf} , H_2O_2 and h^+ , respectively. The dosage of scavengers were 100.0 mM, 100.0 mM, 0.2 mM, 0.2 mM, 2.0 mM, 200.0 units/mL and 1.0 mM, respectively¹⁻⁴. We have added corresponding descriptions in our revised manuscript (line 163-167, page 9):

The methanol (MeOH, 100.0 mM), isopropyl alcohol (IPA, 100.0 mM), methyl phenyl sulfoxide (PMSO, 0.2 mM), β -carotene (β -caro, 0.2 mM), sodium fluoride (NaF, 2.0 mM), catalase (CAT, 200.0 units/mL) and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$, 1.0 mM) were selected as scavengers for $\bullet\text{SO}_4^-$, $\bullet\text{OH}$, high-valent metal-oxo, $^1\text{O}_2$, OH_{surf} , H_2O_2 and h^+ , respectively.

References in this third response to reviewer 2:

1. Wang, Z. P. et al. Non-radical activation of peracetic acid by powdered activated carbon for the degradation of sulfamethoxazole. *Environ. Sci. Technol.* **57**, 10478–10488 (2023).
2. Wang, Z. K. et al. ZIF-derived catalyst with Co–Co/Co–N dual active sites for boosting mixed pathway decontamination in Fenton-like catalysis. *Environ. Sci. Technol.* **59**, 7389–7398 (2025).
3. Zhan, H. Y. et al. Photocatalytic O₂ activation and reactive oxygen species evolution by surface B–N bond for organic pollutants degradation. *Appl. Catal. B: Environ.* **310**, 121329 (2022).
4. Li, H. et al. Oxygen vacancy associated surface Fenton chemistry: Surface structure dependent hydroxyl radicals generation and substrate dependent reactivity *Environ. Sci. Technol.* **51**, 5685–5694 (2017).
4. What are the experimental steps for assessing the toxicity of degradation products using bean sprouts? How can the length of the sprouts be used to determine whether degradation products inhibit growth?

Response:

We are very sorry that we haven't described clearly in the previous manuscript. The experimental steps for assessing the toxicity of degradation products using bean sprouts and evaluation method for mean length of the sprouts to determine whether degradation products inhibit growth was as followed. Mung bean seeds were purchased from a local market in Changchun, China. Seeds were surface-disinfected by soaking in a 0.5% sodium hypochlorite solution for 10 min, rinsed five times with

deionized water, and then dried on filter paper for germination testing. 5 mL sample obtained from the 4Co/CN SACs/PMS/vis system and 4MgCo/CN DSACs/PMS/vis system, reacted for 4, 12, and 24 min respectively, were poured into 90 mm diameter Petri dishes. Ten selected seeds were evenly distributed on each dish. Place in an artificial climate incubator for dark cultivation at 25 °C and 70% relative humidity. Germination was determined when the root tip extended beyond half the seed length. After 5 days of cultivation, record the stem and mean length of all germinated seeds to assess the toxicity of degradation products. To clearly exhibit the experimental steps, we have added corresponding descriptions in Supplementary Material of our revised manuscript:

Supplementary Method 8. The experimental method for bean sprouts and evaluation method for mean length

Mung bean seeds were purchased from a local market in Changchun, China. Seeds were surface-disinfected by soaking in a 0.5% sodium hypochlorite solution for 10 min, rinsed five times with deionized water, and then dried on filter paper for germination testing. 5 mL sample obtained from the 4Co/CN SACs/PMS/vis system and 4MgCo/CN DSACs/PMS/vis system, reacted for 4, 12, and 24 min respectively, were poured into 90 mm diameter Petri dishes. Ten selected seeds were evenly distributed on each dish. Place in an artificial climate incubator for dark cultivation at 25 °C and 70% relative humidity. Germination was determined when the root tip extended beyond half the seed length. After 5 days of cultivation, record the stem and mean length of all germinated seeds.

5. The range of mass spectrum in the characterizations section should be revised.

Revise 100–250 into 50–750.

Response:

We are very sorry for our mistake. We have revised the range of mass spectrum from 100–250 into 50–750 in Supplementary Material of our revised manuscript:

Supplementary Method 6. Mass spectrometry detection method for degradation product

The degradation products were identified by the liquid chromatograph mass spectrometer (LC-MS). The mass spectrometer analysis was performed in a positive ion mode over the range of m/z 50-750 with an electrospray ionization (ESI) source under the following conditions: capillary voltage 3500 V, cone voltage 30 V, source temperature 110 °C, desolvation temperature 380 °C, cone gas flow 80 L/h and desolvation gas flow 600 L/h.

6. The sentence “Under light irradiation, the inert magnesium site initiates the cascade by selectively photoreducing O_2 to H_2O_2 ” appears in lines 76-77. Revise the term “inert”. Magnesium can reduce oxygen to hydrogen peroxide and is not inert.

Response:

Thanks for your suggestion. We have corrected the sentence as “Under light irradiation, the magnesium site initiates the cascade by selectively photoreducing O_2 to H_2O_2 ” in our revised manuscript (line 77, page 4):

Under light irradiation, the magnesium site initiates the cascade by selectively photoreducing O_2 to H_2O_2 .

7. What are the respective roles of NaF and CAT? After their addition, the ratio of Co^{2+} to Co^{3+} also changed. How do these results relate to the OH_{surf} promoting Co reduction?

Response:

We are very sorry that we haven't described clearly in the previous manuscript. Strongly electronegative F^- ion could rapidly adsorb onto the catalyst surface, thereby occupying the adsorption sites for OH_{surf} ¹. As shown in Fig. 3i, the Co^{2+} ratio decreased from 57% to 40% after the addition of NaF in the 4MgCo/CN/PMS/vis system, suggesting that OH_{surf} facilitated the reduction of Co species. Catalase (CAT), a typical antioxidant enzyme, efficiently decomposed H_2O_2 into H_2O and O_2 via a disproportionation reaction². Given that H_2O_2 served as the precursor for OH_{surf} , the introduction of CAT led to a decrease in H_2O_2 concentration, consequently reducing the concentration of OH_{surf} . Fig. 3i further revealed that the Co^{2+} ratio decreased from 57% to 42% after the addition of CAT in the 4MgCo/CN/PMS/vis system, providing an additional evidence that OH_{surf} promoted the Co reduction. To more clearly demonstrate the role of NaF and CAT, we have added and revised some descriptions in our revised manuscript (line 163-167, page 9; line 290-293, 295, page 15):

The methanol (MeOH, 100.0 mM), isopropyl alcohol (IPA, 100.0 mM), methyl phenyl sulfoxide (PMSO, 0.2 mM), β -carotene (β -caro, 0.2 mM), sodium fluoride (NaF, 2.0 mM), catalase (CAT, 200.0 units/mL) and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$, 1.0 mM) were selected as scavengers for $\bullet\text{SO}_4^-$, $\bullet\text{OH}$, high-valent metal-oxo, $^1\text{O}_2$, OH_{surf} ,

H_2O_2 and h^+ , respectively.

The Co^{2+} ratio in 4Co/CN SACs was enhanced from 33% to 54% and 37% by CAT and NaF, respectively. However, the Co^{2+} ratio in 4MgCo/CN DSACs was reduced from 57% to 42% and 40% by CAT and NaF, respectively. These results illustrated that OH_{surf} from H_2O_2 contributed to the reduction of Co^{3+} to Co^{2+} in the 4MgCo/CN DSACs/PMS/vis system, which differed from that in the 4Co/CN SACs/PMS/vis system (Fig. 3i). This was supported by the increased radius in electrochemical impedance spectroscopy (EIS) (Fig. 3j) and the reduced Cdl (5.26 mF cm^{-2}) in electrochemical active surface area (ECSA) from cyclic voltammetry (CV) profiles⁵³ (Figs. 3k and S29) observed for 4MgCo/CN DSACs after the addition of NaF and CAT.

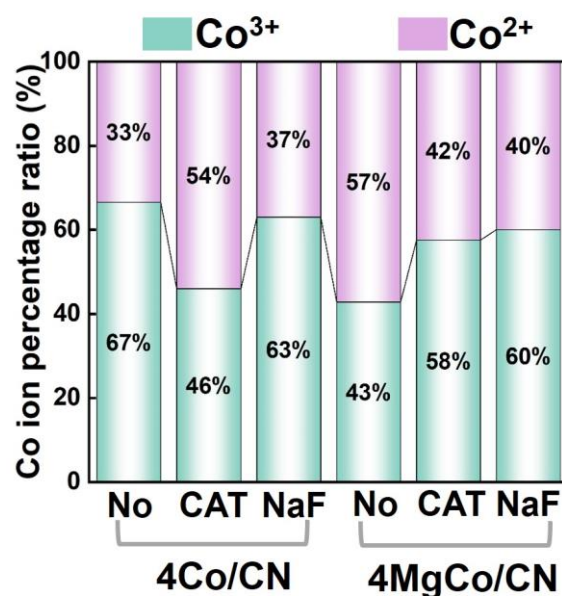


Fig. 3. (i) Co ion percentage ratio of 4MgCo/CN DSACs and 4Co/CN SACs under different conditions, respectively.

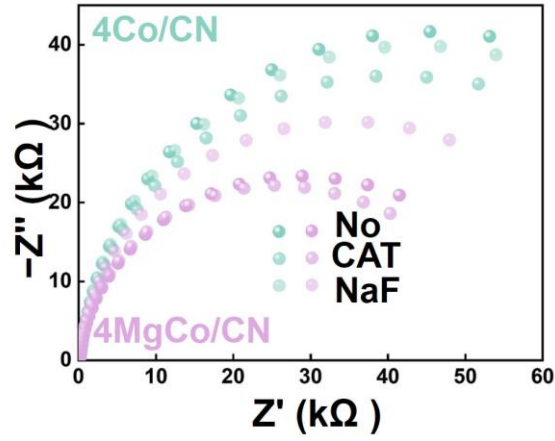


Fig. 3. (j) EIS of 4MgCo/CN DSACs and 4Co/CN SACs under different conditions, respectively.

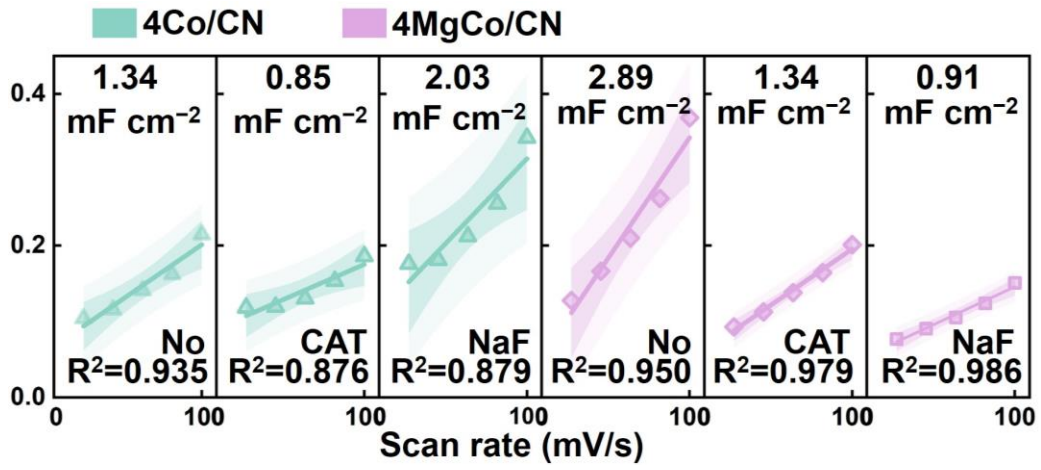


Fig. 3. (k) ECSA of 4MgCo/CN DSACs and 4Co/CN SACs under different conditions, respectively.

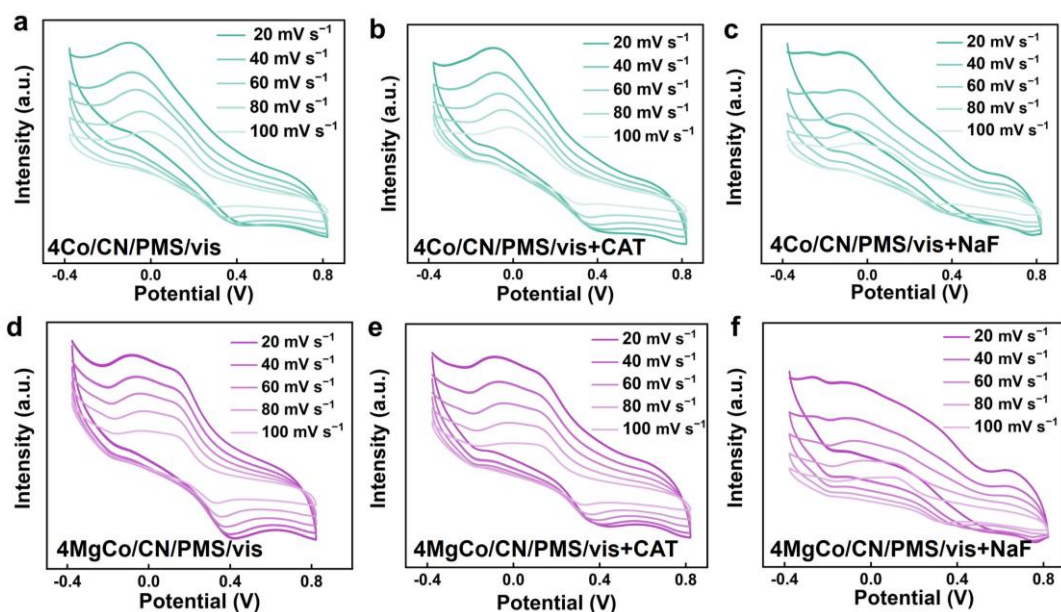


Fig. S29. CV curve of 4Co/CN SACs and 4MgCo/CN DSACs under different conditions with different scan rates, respectively.

References in this seventh response to reviewer 2:

1. Li, H. et al. Oxygen vacancy associated surface Fenton chemistry: Surface structure dependent hydroxyl radicals generation and substrate dependent reactivity *Environ. Sci. Technol.* **51**, 5685–5694 (2017).

2. Zhan, H. Y. et al. Photocatalytic O₂ activation and reactive oxygen species evolution by surface B-N bond for organic pollutants degradation. *Appl. Catal. B: Environ.* **310**, 121329 (2022).

8. Some descriptions might require revision. For example, in the sentence “Single-atom catalysis (SAC), with its maximized atomic efficiency”, the term “atomic efficiency” should be revised to atomic utilization efficiency. Check and correct them throughout manuscript.

[Response:](#)

We are very sorry for our mistake. We have checked and corrected the descriptions throughout manuscript (line 27-28, 30, 36, 38-39, page 2; line 51, 53-55, 59, page 3; line 77, 79, page 4; line 95-96, 99-100, 103-109, page 5; line 110-131, page 6; line 132-134, 138-140, page 7; line 141, 144-145, 147-151, 154-155, 159-160, 162, page 8; line 163-170, 172, 175-178, 181-184, page 9; line 186-187, 191-197, 199, page 10; line 216-226, 228-233, page 12; line 234-255, page 13; line 256-269, 272-277, page 14; line 278-281, 283-286, 290-293, 295, page 15; line 305-306, 315, 317-320, 322-324, page 17; line 327-334, 336, 338, 341, 343, 346-347, page 18; line 352-369, page 19; line 370-391, page 20; line 392-398, page 21; line 418, 424, page 22; line 425-426, 428, 430, 440, 445-446, page 23; line 480, 483, 488, page 26; line 498, 505-511, 515, page 27; line 524, 526, 530, 535-538, page 28; line 539, page 29):

Here, we break the limitation of this static design by reporting a novel domino catalysis within a heteronuclear MgCo dual-single-atom catalyst. In this system, the Mg site selectively photoreduces O_2 to H_2O_2 under light irradiation. This *in-situ* generated H_2O_2 and its derived surface hydroxyl groups act as dynamic modulators, progressively tailoring the electronic structure of the adjacent Co site.

Experiments and theoretical calculations elucidate that this seamless and spatially ordered cascade avoids competitive adsorption and maximizes efficiency.

The system exhibits the highest normalized rate constant of $595.3 \text{ min}^{-1} \text{ M}^{-1}$ among various refractory contaminants over thirty regeneration cycles, outperforming the most state-of-the-art catalytic systems.

Among various intensification strategies, coupling these reactions with inexhaustible solar energy presents a highly sustainable avenue³. However, the widespread implementation of such photo-enhanced Fenton-like systems is critically hampered by the fundamental and persistent trade-off between simultaneously achieving high catalytic activity and long-term stability⁴. High activity demands rapid redox cycling of the metal centre, a process often accelerated by photo-generated charge carriers⁵.

Recent advances in single-atom catalysis (SACs), with its maximized atomic utilization efficiency and tailorable electronic structures, offer new hope for optimizing this activity-stability nexus⁷.

Under light irradiation, the magnesium site initiates the cascade by selectively photoreducing O₂ to H₂O₂¹⁷. This *in-situ* generated H₂O₂ then acts not merely as a precursor, but as the dynamic modulator whose derived surface hydroxyl groups progressively tailor the electronic structure of the adjacent cobalt site.

The heteronuclear magnesium cobalt dual single atom catalysts (MgCo/CN DSACs) were synthesized by a simple hydrothermal method (Fig. 1a). The MgCo/CN DSACs had a sparse and three-dimensional nanosheet structure in scanning electron microscope (SEM) (Fig. S1).

The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) (Fig. 1b) exhibited the bright dual-atom pairs in yellow dashed ellipses, indicating that the dual single atom structure was successfully synthesized.

The Co and Mg K-edge X-ray absorption near-edge structure (XANES) spectra (Figs. 1e and 1h) showed that the absorption edge of Co lay between those of Co foil and CoO, while that of Mg lay between those of Mg foil and MgO, but closer to Mg foil. This indicated that the oxidation states of both Co and Mg in the 4MgCo/CN DSACs ranged between 0 and +2, yet they differed from each other. The linear combination fitting (LCF) analysis (Figs. S2, S3 and Tables S1, S2) was performed to quantify the proportions of different Co and Mg species. The proportions of Co⁰, Co²⁺ and Co³⁺ were 40.6%, 28.7%, and 30.7%, respectively, while those of Mg⁰ and Mg²⁺ were 81.7% and 18.3%, respectively. Based on the LCF results, the average oxidation states of Co and Mg in the 4MgCo/CN DSACs were estimated to be 1.50 and 0.37, respectively (Figs. 1f and 1i). Fourier transformed (FT) k³-weighted X-ray absorption fine structure (EXAFS) spectra of 4MgCo/CN DSACs (Figs. S4 and S5), the peaks corresponding to Co–N at 1.48 Å and Mg–N at 1.68 Å were observed^{19,20}. No peaks attributable to Co–Co, Co–O, Mg–Mg and Mg–O bonds were detected, suggesting the absence of metallic or oxide clusters. Additionally, no Mg–Co bond was observed in the EXAFS spectra of 4MgCo/CN DSACs, demonstrating that no direct bonding between Mg and Co atom. The more negative formation energy of 4MgCo/CN without the Mg–Co bond (–0.75 eV), compared to that of its counterpart containing the Mg–Co bond (1.15 eV), further indicated that the former was more favorable to form (Fig. S6). Based on the FT-EXAFS fitting results in R-space (Figs. 1g and 1j, Tables S3 and S4), it was deduced that the coordination configurations of 4MgCo/CN DSACs were identified as Mg–N₄ and Co–N₄. Quantitative intensity profile analysis

(Fig. S7) confirmed that the predominant configuration featured MgCo paired sites with the highest prevalence of interatomic distance of 6.48 Å, which matched well with the distance between Mg and Co in simulated MgCo/CN model featuring Mg–N₄ and Co–N₄ coordination without Mg–Co bond. The same estimation method has been reported in previous work²¹. The spin states of the catalysts were characterized by electron paramagnetic resonance (EPR) spectra (Fig. S8) and temperature-dependent inverse magnetic susceptibility measurements (Fig. S9). These results collectively confirmed the successful synthesis of MgCo/CN DSACs featuring Mg–N₄ and Co–N₄ configurations without Mg–Co bond.

Fig. 1. (a) Synthesis of MgCo/CN DSACs. (b) Aberration-corrected HAADF-STEM image and EDS mapping of 4MgCo/CN DSACs. (c) XRD and (d) FT-IR spectra of catalysts, respectively. (e) Normalized Co K-edge XANES spectra, (f) corresponding oxidation state of Co species and (g) the fitting curves of Co K-edge EXAFS spectra in 4MgCo/CN DSACs. (h) Normalized Mg K-edge XANES spectra, (i) corresponding oxidation state of Mg species and (j) the fitting curves of Mg K-edge EXAFS spectra in 4MgCo/CN DSACs.

The 2MgCo/CN DSACs degraded 82.0% of carbamazepine (CBZ) in the PMS/vis system, which was much higher than those achieved by CN (39.8%), 4Mg/CN SACs (69.0%) and 4Co/CN SACs (69.2%), respectively. The CBZ degradation efficiency first increased and then decreased with increasing Mg and Co ratio from 20% to 60% and the optimal degradation efficiency (92.7%) was obtained by 4MgCo/CN DSACs (Fig. S10). 4MgCo/CN DSACs had 53.2% of total organic

carbon (TOC) removal efficiency, which was much higher than those of CN (18.6%), 4Mg/CN (33.5%) and 4Co/CN (34.1%), respectively (Fig. S11).

The degradation rate constant towards various contaminants, including sulfamethoxazole (SMX), CBZ, tetracycline hydrochloride (TCH), 4-chlorophenol (4-CP) and bisphenol A (BPA) in the 4MgCo/CN DSACs/PMS/vis system with 0.1 mM PMS was superior to most of those in previous reports (Fig. 2a, Table S5)²²⁻⁴³.

The Co dissolution concentration in the 4MgCo/CN DSACs/PMS/vis system (0.43 mg/L) was below the emission standard of GB 25467-2010 (1.0 mg/L) in China, which was also much lower than that in the 4Co/CN SACs/PMS/vis system (1.39 mg/L) after 30-time cycles^{44,45}. These results illustrated that both CBZ degradation activity and stability were superior in the 4MgCo/CN DSACs/PMS/vis system. The methanol (MeOH, 100.0 mM), isopropyl alcohol (IPA, 100.0 mM), methyl phenyl sulfoxide (PMSO, 0.2 mM), β -carotene (β -caro, 0.2 mM), sodium fluoride (NaF, 2.0 mM), catalase (CAT, 200.0 units/mL) and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$, 1.0 mM) were selected as scavengers for $\bullet\text{SO}_4^-$, $\bullet\text{OH}$, high-valent metal-oxo, $^1\text{O}_2$, OH_{surf} , H_2O_2 and h^+ , respectively⁴⁶⁻⁴⁹.

The 3.5%, 33.6%, 52.5%, 67.7%, 14.7%, 10.4% and 85.4% of CBZ were degraded after the addition of MeOH, IPA, PMSO, β -caro, NaF, CAT and $\text{Na}_2\text{C}_2\text{O}_4$, respectively, indicating that $\bullet\text{SO}_4^-$ and OH_{surf} derived from H_2O_2 were major active species in the 4MgCo/CN DSACs/PMS/vis system (Fig. 2d). This was different from the reaction dominated by only $\bullet\text{SO}_4^-$ in the 4Co/CN SACs/PMS/vis system (Fig. S12).

In the Fenton-like system, 50.6%, 70.5% and 70.2% of CBZ were degraded by β -caro, NaF and CAT, respectively, while in the photocatalytic system, 13.7%, 8.9% and 9.6% of CBZ were degraded by β -caro, NaF and CAT, respectively. The excellent photoadsorption of catalysts was observed in UV-Vis diffuse reflectance spectroscopy (DRS) (Fig. S14). These results further demonstrated that visible light contributed to the *in-situ* generation of H_2O_2 for the dominance of OH_{surf} in the contaminant removal.

The relationship among degradation efficiencies with the dosages of CAT, NaF and MeOH was further estimated. The correlation constant R^2 of 0.991 between degradation efficiency and MeOH dosage was far higher than the others, meaning that OH_{surf} secondary from H_2O_2 might be the indirect active species and $\bullet SO_4^-$ might be the direct active species in the 4MgCo/CN DSACs/PMS/vis system (Fig. 2e). In contrast, the correlation constants of R^2 for the relationship among degradation efficiencies of CAT dosage, NaF dosage and MeOH dosage in the 4Co/CN SACs/PMS/vis system were all no more than 0.732. This indicated that $\bullet SO_4^-$, H_2O_2 and OH_{surf} were indirect active species in the 4Co/CN SACs/PMS/vis system (Fig. 2f). The ratio of Co^{2+} in 4Co/CN SACs increased from 41% to 42% and the ratio of Co^{2+} in 4MgCo/CN DSACs increased from 57% to 59% after visible light irradiation, which could be attributed to the fact that Co^{3+} was reduced into Co^{2+} by photogenerated electrons. The ratio of Co^{2+} for 4Co/CN SACs decreased from 41% to 39% after the reaction in the PMS/vis system due to the redox from PMS to $\bullet SO_4^-$, whereas the ratio of Co^{2+} increased from 57% to 69% in the 4MgCo/CN

DSACs/PMS/vis system (Fig. 2c). The major contributions of $\bullet\text{SO}_4^-$ and OH_{surf} were also observed in the MgMn/CN DSACs/PMS/vis and MgFe/CN DSACs/PMS/vis systems, which differed from those in photo-Fenton-like system mediated by SACs and Fenton-like system mediated by DSACs and SACs, respectively (Fig. 2g, Table S6).

The 4MgCo/CN DSACs activated 87.2% of PMS, which was higher than that by 4Co/CN SACs (66.6%) (Fig. 3a). Furthermore, in the *in-situ* Raman spectra of 4MgCo/CN DSACs, a new peak appeared at 815.7 cm^{-1} after a 3-min reaction, and its intensity became more pronounced after 5 min, whereas this peak was absent in the *in-situ* Raman spectra of 4Co/CN SACs (Figs. S15 and S16)⁵⁰. This indicated that the interaction between MgCo dual atoms contributed to PMS activation. The PMS activation efficiency by 4MgCo/CN DSACs increased from 45.2% to 77.3% when exogenous H_2O_2 was raised from 0.0 mM to 3.97 mM (Fig. S17). The larger ring current of 4MgCo/CN DSACs compared to that of 4Co/CN SACs mainly originated from the higher amount of H_2O_2 generated by the former (Fig. 3b). Both 4MgCo/CN DSACs and 4Co/CN SACs had an n value closer to 2 (Fig. 3c). The selectivity of 4MgCo/CN DSACs (86.1%) was higher than that of 4Co/CN SACs (46.1%), indicating that dual single atom sites could increase the $2e^-$ selectivity for *in-situ* H_2O_2 generation (Fig. 3d). No H_2O_2 was generated under the dark condition, despite oxygen aeration. However, 2.26 mM and 1.87 mM of H_2O_2 were generated within the first 4 min by both catalysts, and then activated to 0.39 mM and 0.93 mM, respectively, by 4MgCo/CN DSACs and 4Co/CN SACs in the PMS/vis/CBZ system (Fig. 3e and S18).

The H_2O_2 generation for these two catalysts was attributed to their conduction band potentials being higher than that of $\text{O}_2/\text{H}_2\text{O}_2$ (Fig. S19). The photogenerated electrons could reduce oxygen into H_2O_2 under light irradiation. The H_2O_2 production increased from 1.14 mM to 3.97 mM as the dosage of 4MgCo/CN DSACs increased from 0.005 to 0.05 g/L in the PMS/vis/CBZ system (Fig. S20). Fig. S21 showed that H_2O_2 was gradually generated up to 4.38 mM in the PMS/vis/ H_2O system within 24 min, which was higher than those in the PMS/vis/CBZ system (0.39 mM), the vis/CBZ system (0.03 mM), and the vis/ H_2O system (0.23 mM), respectively. These results indicated that visible light was essential for H_2O_2 generation, that CBZ could consume part of the *in-situ* generated H_2O_2 , and that PMS facilitated the photoreduction of H_2O_2 . As shown in Figs. S22 and S23, the H_2O_2 concentration decreased rapidly after introducing nitrogen (N_2), indicating that O_2 was essential for H_2O_2 generation. Upon addition of the electron-trapping agent potassium bromate (KBrO_3), the H_2O_2 concentration dropped sharply, demonstrating that the two-electron oxygen reduction reaction was the primary pathway for photocatalytic H_2O_2 production. The H_2O_2 concentration decreased by 94.1% after adding p-benzoquinone (p-BQ), suggesting that $\cdot\text{O}_2^-$ was a key intermediate in the photoreaction. The negligible H_2O_2 concentration observed upon addition of tert-butyl alcohol (TBA) indicated that $\cdot\text{OH}$ was not an intermediate in H_2O_2 production. In contrast, adding ethanol (EtOH) and benzyl alcohol (BnOH) significantly increased H_2O_2 production, mainly because these alcohols capture photogenerated holes and supply sufficient protons, thereby facilitating oxygen reduction for H_2O_2 generation. These results indicated that CBZ

did not affect the types of key intermediates in the *in-situ* photocatalytic generation of H_2O_2 . The Gibbs free energy for the two-electron oxygen reduction to H_2O_2 in the presence of PMS by 4MgCo/CN DSACs was negative (Fig. S24), indicating that H_2O_2 generation was thermodynamically spontaneous. Fig. S25 exhibited the time-resolved *in-situ* DRIFTS profiles of 4MgCo/CN DSACs. In the 4MgCo/CN DSACs/PMS/vis system, the characteristic O–O stretching vibrations were detected for surface-adsorbed species, including O_2^* (965 cm^{-1}), $\bullet\text{O}_2^*$ (1151 cm^{-1}), $\bullet\text{OOH}^*$ (1205 cm^{-1}), and HOOH^* (1369 cm^{-1})⁵¹. The intensities of these peaks progressively increased with reaction time from 0 to 24 min. In the ESR spectra (Fig. S26), a distinct characteristic signal of $\bullet\text{O}_2^-$ was observed under light irradiation, whereas the signal was barely detectable in the dark. Collectively, these results demonstrated that the dominant route for H_2O_2 generation was the two-electron oxygen reduction. A correlation plot of the CBZ degradation rate constant within the first 4 min (k_1) and that from 4 min to 24 min (k_2) was generated against various possible influencing factors, including Co mass (A), photoadsorption (B), crystallinity (C), OH_{surf} contribution ratio (D) and Co spin state (E). This result illustrated that the degradation of CBZ was mainly related to OH_{surf} from *in-situ* generated H_2O_2 ($p \leq 0.05$) (Fig. 3f), indicating that the photoadsorption and OH_{surf} contribution ratio were crucial factors for k_1 and k_2 , respectively. Given that visible light was used to drive photoreduction of oxygen to H_2O_2 , which served as a crucial intermediate for OH_{surf} , it could be deduced that CBZ degradation was primarily related to OH_{surf} from *in-situ* generated H_2O_2 .

Almost no H_2^{18}O -labeled *p*-HBA peak ($m/z=137.1$) was observed in the 4MgCo/CN DSACs/PMS/vis system, indicating that OH_{surf} originated from *in-situ* H_2O_2 generated from oxygen in the air rather than from oxygen in PMS or H_2O . However, the H_2^{18}O -labeled *p*-HBA peak ($m/z = 139.1$) was found in the 4Co/CN SACs/PMS/vis system⁵². This indicated that $\bullet\text{OH}$ mainly came from the reaction between $\bullet\text{SO}_4^-$ and H_2O in the 4Co/CN SACs/PMS/vis system (Figs. 3g and S27). The degradation efficiency of BA decreased with increasing NaF concentration, and it was remarkably reduced from 64.2% to 15.7% after the addition of 9.0 mM NaF (Fig. 3h). The activation efficiency of PMS was also reduced from 87.2% to 27.9% with increasing NaF concentration from 0 to 9 mM (Fig. S28).

These results illustrated that OH_{surf} from H_2O_2 contributed to the reduction of Co^{3+} to Co^{2+} in the 4MgCo/CN DSACs/PMS/vis system, which differed from that in the 4Co/CN SACs/PMS/vis system (Fig. 3i). This was supported by the increased radius in electrochemical impedance spectroscopy (EIS) (Fig. 3j) and the reduced Cdl (5.26 mF cm^{-2}) in electrochemical active surface area (ECSA) from cyclic voltammetry (CV) profiles⁵³ (Figs. 3k and S29) observed for 4MgCo/CN DSACs after the addition of NaF and CAT.

(f) The correlation plot of CBZ degradation rate constant with various possible influencing factors. A, B, C, D and E represented mass of Co, photoadsorption, crystallinity, OH_{surf} contribution ratio and Co spin state.

The inclined adsorption of H_2O_2 and PMS on the Mg and Co sites with the adsorption energies of -3.70 and -10.62 eV was confirmed, respectively (Fig. S30).

The activation from PMS to $\bullet\text{SO}_4^-$ by MgCo/CN DSACs@OH_{surf} was spontaneous, while it needed to overcome an energy barrier for MgCo/CN DSACs@H₂O₂ and MgCo/CN DSACs, respectively. The adsorption of $\bullet\text{SO}_4$ on MgCo/CN DSACs@OH_{surf}-PMS (−7.24 eV) was much weaker than that by MgCo/CN DSACs (−10.62 eV), indicating that OH_{surf} contributed to $\bullet\text{SO}_4$ desorption. The activation energy barrier of PMS by MgCo/CN DSACs@H₂O₂ (0.80 eV) was smaller than that by MgCo/CN DSACs (1.95 eV). The spontaneous generation of OH_{surf} from H₂O₂ confirmed that OH_{surf} was more easily generated from H₂O₂. This contributed to PMS activation rather than from PMS (Fig. 4b).

The d-band center of MgCo/CN DSACs@OH_{surf} (−0.93 eV) was much farther from the Fermi energy level compared to those of MgCo/CN DSACs@H₂O₂ (−0.12 eV) and MgCo/CN DSACs (−0.067 eV) (Fig. S31). However, the longer O–O bond in PMS was observed after adsorption on MgCo/CN DSACs@OH_{surf} (1.87 Å) than MgCo/CN DSACs@H₂O₂ (1.50 Å) and MgCo/CN DSACs (1.23 Å) was observed. These results meant that the superior PMS activation by MgCo/CN DSACs@OH_{surf} was induced not only by the high electron density of Co. This was completely different from the traditional Fenton-like processes⁵⁴.

The orbital hybridization between the Co of different catalysts and Op of PMS and $\bullet\text{SO}_4$ was illustrated in Figs. 4d and S32. The overlap between Co d_{xy} and d_{x²-y²} in MgCo/CN DSACs@OH_{surf}-PMS with Op of PMS and $\bullet\text{SO}_4$ was larger than that of Co 3d orbital with PMS and $\bullet\text{SO}_4$. This demonstrated that OH_{surf} contributed to PMS activation and $\bullet\text{SO}_4$ desorption. To further understand the interaction of OH_{surf} and Co

site, the relationship among E_{ads} , E_{d} , Δq and $I_{\text{O-O}}$ with the amount of OH_{surf} was correlated (Figs. 4e and 4f). It was found that an optimal amount of OH_{surf} contributed to the adsorption of PMS, the extension of the O–O bond of PMS, the reduction of d-band center and increase of transferred electrons between the catalyst and PMS. Figs. 4h, 4g, S33 and Table S7 showed that OH_{surf} induced the reconstruction of Co 3d orbital, leading to the shift of the energy level for d_{xy} , $d_{x^2-y^2}$, d_{xz} , d_z^2 and d_{yz} orbitals to lower energy levels in MgCo/CN DSACs@ OH_{surf} -PMS.

Fig. S34 exhibited that the Co d-band center obviously shifted as the amount of OH_{surf} varied. Figs. S35 and S36 showed the strong correlations among the d-band center with PMS adsorption energy ($R^2 = 0.9992$), electron transfer charge ($R^2 = 0.9326$), and O–O bond length ($R^2 = 0.9948$), but a weak correlation with O–H bond length ($R^2 = 0.5162$). These results indicated that OH_{surf} -modulated d-band center facilitated PMS adsorption and activation into $\bullet\text{SO}_4^-$. Moreover, the valence electron densities of Co sites were 5.09 e, 5.53 e, 6.05 e, and 5.65 e as the amount of OH_{surf} increased (Fig. S37), indicating that appropriate OH_{surf} adsorption on the Mg site modulated the electron density of the Co site via long-range interaction.

To track electronic change following the modulation of the d-band center, we performed electron paramagnetic resonance (EPR) spectroscopy, electrochemical impedance spectroscopy (EIS), ECSA measurement and Co *K*-edge XANES spectra by the 4MgCo/CN DSACs after reaction, respectively. The EPR spectra (Fig. S38) showed that the EPR signal at $g = 2.30$ for 4MgCo/CN DSACs intensified with increasing reaction time, indicating a gradual increase in unpaired electrons. The EIS

results (Fig. S39) exhibited that the radius decreased markedly as the reaction proceeded, suggesting a remarkable enhancement in electron transfer performance. Furthermore, the increased C_{dl} value in the ECSA of 4MgCo/CN DSACs over reaction time (Fig. S40) demonstrated a rise in active site density, which facilitated the electron participation in the reaction. As shown in Fig. S41, the Co K-edge shifted negatively after the reaction compared to that before the reaction, indicating a reduction in the oxidation state of Co in the 4MgCo/CN DSACs after reaction. Based on the LCF results, the proportion of Co^{2+} species in the 4MgCo/CN DSACs increased from 28.7% before reaction to 63.4% after reaction (Figs. S2 and S42, Tables S1 and S8), while the average Co oxidation state decreased from 1.50 to 1.27 (Figs. 1f and S43). This observation was supported by the increased Co^{2+} ratio as the reaction proceeded from 0 to 24 min in the 4MgCo/CN DSACs/PMS/vis system, as shown by *in-situ* XPS spectra (Fig. 4i).

The degradation efficiencies of CBZ by 4MgCo/CN DSACs after the addition of NaF and CAT were reduced by 5.35% and 3.8%, respectively, over 30 cycles. The Co dissolution concentration in the 4MgCo/CN DSACs/PMS/vis system with NaF and CAT exceeded 0.85 mg/L and 0.83 mg/L, which was much higher than that in the system without scavengers (0.43 mg/L) (Figs. S44 and S45). These results indicated that OH_{surf} from H_2O_2 contributed to enhancing stability in the 4MgCo/CN DSACs/PMS/vis system. In summary, the dynamic domino catalysis process in overcoming the activity-stability trade-off during water purification was as follows: Under visible light irradiation, photogenerated electrons drove a two-electron oxygen

reduction reaction at the Mg site, enabling the *in-situ* generation of H₂O₂. The as-formed H₂O₂ was subsequently converted to OH_{surf} via the Mg site. These OH_{surf} leveraged the π -conjugated delocalized network of carbon nitride to modulate the d-orbital configuration of non-adjacent Co atom through long-range interaction, enabling the shift of energy levels for d_{xy}, d_{x²-y²}, d_{xz}, d_{z²} and d_{yz} orbitals to lower energy levels⁵⁵⁻⁵⁷. On the one hand, this promoted the reduction of Co³⁺ to Co²⁺, thereby accelerating •SO₄⁻ generation during PMS activation for enhanced activity. On the other hand, it reduced the adsorption energy of *SO₄, optimizing its desorption process and preventing Co atom detachment to maintain stability.

To evaluate the practical application potential of the 4MgCo/CN DSACs/PMS/vis system, simulated CBZ wastewater and secondary effluent from the Jilin Petrochemical Company wastewater treatment plant were removed in continuous flow reactors (Figs. 5c and 5d).

The *in-situ* OH_{surf}-induced dynamic-catalytic system has the potential to be applied in the decontamination sterilization unit (Fig. 5e). The CBZ could be rapidly transformed into small-molecular products in the 4MgCo/CN DSACs/PMS/vis system, which was different from that in the 4Co/CN SACs/PMS/vis system (Figs. S46-49). Compared to the toxicity of pristine CBZ, the toxicity of degradation products in the 4MgCo/CN DSACs/PMS/vis system was reduced more obviously than that in the 4Co/CN DSACs/PMS/vis system (Fig. 5f, Tables S10 and S11) based on the QSAR-based toxicity prediction using T.E.S.T. software⁵⁸.

Given that the equipment could be operated at full capacity and resources could be maximized when industrial scale production was achieved in the future, the environmental impact of 4MgCo/CN DSACs would be substantially minimized during the preparation stage (Table S13).

This reconstruction was facilitated by surface hydroxyl radicals generated from *in-situ* generated H₂O₂ using green O₂ and H₂O via a domino-catalytic strategy. Using magnesium-cobalt dual single-atom catalysts as an example, it demonstrated that cobalt d-orbital configuration was dynamically changed with the *in-situ* generation of surface hydroxyl radical. Different from the conventional approach that depended on rapid photoelectron injection to reduce M³⁺ to M²⁺ at the catalyst surface under light irradiation, the domino-catalytic system leveraged cobalt d-orbital reconfiguration to enable the gradual generation of surface hydroxyl radical for dual single atomic electron internal circulation. This mechanism involved the dynamic electron transfer between the d_{xy} and d_{x²-y²} orbitals of cobalt and Op orbital of PMS, resulting in efficient and stable PMS activation.

Chemicals and materials

Certain amounts of CoCl₂·6H₂O, MgCl₂·6H₂O and 100 mg of CN were added into 60 mL n-octanol solution. The mass ratio of CoCl₂·6H₂O or MgCl₂·6H₂O to CN were x = 2, 4 and 6%. The mixture was stirred for 1 h to obtain a turbid solution. Then, the turbid solution was added into a Teflon-lined autoclave and heated at 200°C for 24 h. The sample was washed with ultrapure water and ethanol several times, followed by drying under the vacuum at 60°C for 10 h. The resulting samples were named as

xMgCoCN (x=2, 4 and 6 wt%).

XRD pattern was recorded using a Rigaku D/Max-2550 diffractometer via Cu K α radiation at 50 kV and 200 mA in the 2 θ range between 10-70° at a scanning rate of 5°/min.

The EPR measurements were performed on a Bruker 300 system. The ESR spectra of reactive oxygen species trapped in water and methanol by DMPO or TEMP were analyzed by a Brooke A300 system. The *in-situ* Raman spectra were recorded with a Renishaw confocal micro-Raman spectroscopy system with a 532 nm excitation laser.

The *in-situ* EPR spectra were detected a Bruker 300 system.

0.02 g catalyst was first added into 2.0 L simulated wastewater, consisted of 1.64 mM NaCl, 11.5 mM NaHCO₃, 0.7 mM NaNO₃, 0.016 mM Na₃PO₄·12H₂O and 10.0 mg/L a single contaminant with CBZ, BPA, SMX, ATZ or 4-CP and stirred in the dark for 30 min. Then, the reaction was activated by the visible light irradiation and the addition of 0.1 mM PMS. The light source was a 150 W Xenon lamp (CEL-HXF 300, Beijing Education Au-light Co., Ltd.) with a filter to cut off the ultraviolet light ($\lambda < 420$ nm). The light intensity was 122.4 mW/cm² (illumination area = 3.24 cm²).

9. Fig. 1 was not be displayed fully might due to formatting issue. Check and correct it.

Response:

We are very sorry for our mistake. We have checked and corrected the Fig. 1 of our revised manuscript.

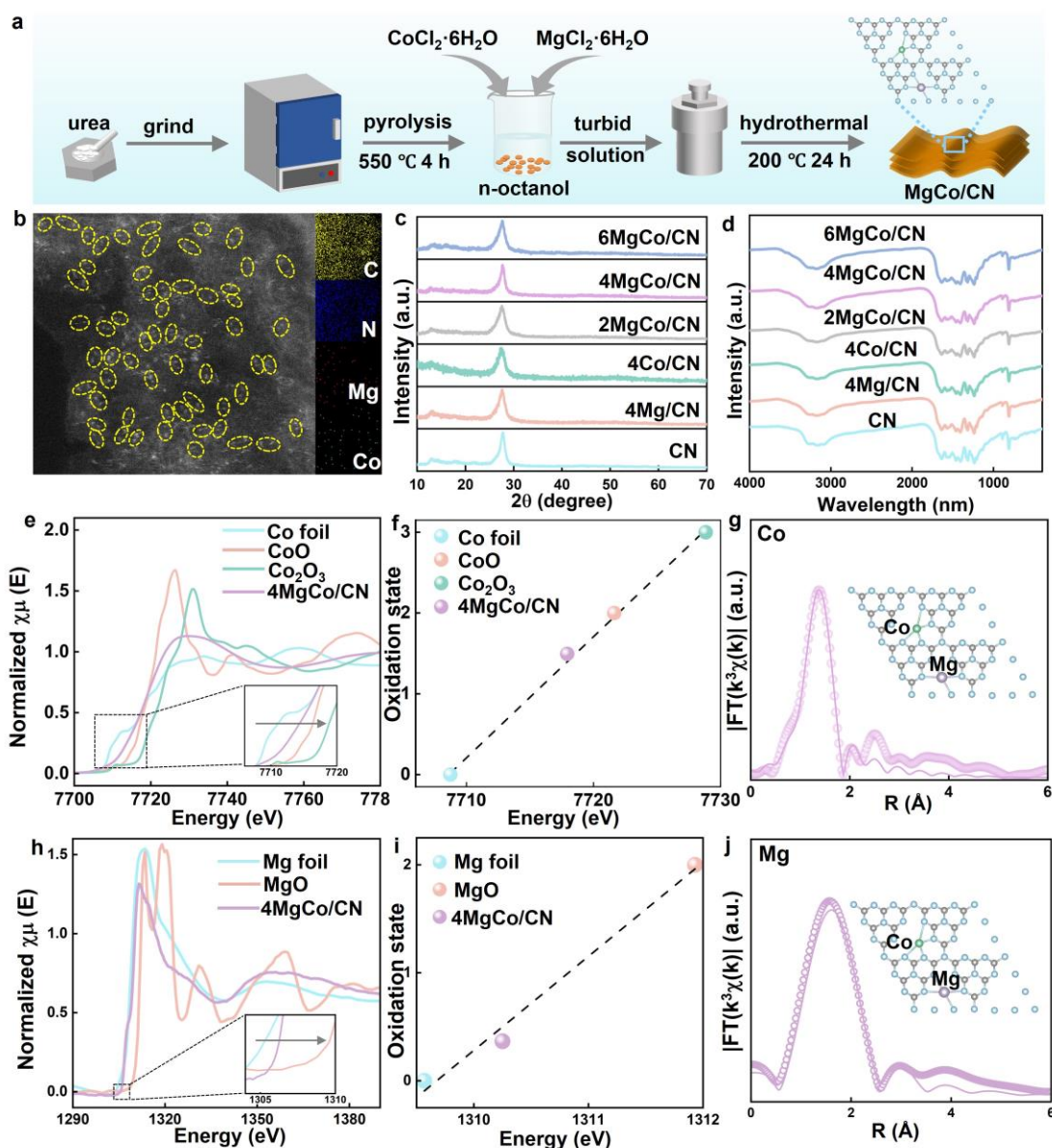


Fig. 1. (a) Synthesis of MgCo/CN DSACs. (b) Aberration-corrected HAADF-STEM image and EDS mapping of 4MgCo/CN DSACs. (c) XRD and (d) FT-IR spectra of catalysts, respectively. (e) Normalized Co K-edge XANES spectra, (f) corresponding oxidation state of Co species and (g) the fitting curves of Co K-edge EXAFS spectra in 4MgCo/CN DSACs. (h) Normalized Mg K-edge XANES spectra, (i) corresponding oxidation state of Mg species and (j) the fitting curves of Mg K-edge EXAFS spectra in 4MgCo/CN DSACs.

10. How can the toxicity of degradation products in the MgCo/CN DSACs/PMS/vis system and Co/CN SACs/PMS/vis system be determined based on the results of the four evaluation criteria: *Daphnia magna*, oral rat, developmental toxicity, and mutagenicity?

Response:

We are very sorry that we haven't described clearly in the previous manuscript. To assess the toxicity of the degradation products in the MgCo/CN DSACs/PMS/vis system and Co/CN SACs/PMS/vis system, we conducted quantitative structure activity relationship (QSAR) predication using Toxicity Estimation Software Tool (T.E.S.T.) in the consensus method with four evaluation criteria for acute toxicity of *daphnia magna* and oral rat toxicity, developmental toxicity and mutagenicity. The details were as follows:

(1) Acute toxicity to the *daphnia magna* was evaluated using the 48-h LC_{50} , defined as the concentration of a chemical that caused 50% of *daphnia magna* to die after 48 h. An increase in the LC_{50} value of the degradation products compared to the parent contaminant indicated a reduction in toxicity, whereas a decrease suggested the formation of more toxic intermediates.

(2) Oral rat acute toxicity was assessed based on the LD_{50} , which was the dosage of chemical that caused the death of 50% rat after oral ingestion. Predicted LD_{50} values were categorized into four toxicity classes: very toxic, toxic, harmful, and non-toxic. An ideal result for degradation products relative to the parent contaminant was a shift in toxicity classification toward the non-toxic one.

(3) Developmental toxicity was assessed to evaluate the potential for causing developmental abnormalities. The parent contaminant and its degradation products were classified as either a developmental toxicant or a non-developmental toxicant. The ideal result was a non-toxicant, indicating a reduction in toxicity of degradation product compared to the parent contaminant.

(4) Mutagenicity was used to evaluate the potential for causing genetic mutations. According to the T.E.S.T. classification standard, a predicted value greater than 0.5 indicated a positive result, while a value below 0.5 indicated a negative result. Therefore, the ideal result of the degradation process was to achieve the negative mutagenicity.

To clearly demonstrate the toxicity evaluation of degradation products using Toxicity Estimation Software Tool (T.E.S.T.) in the consensus method based on the results of the four evaluation criteria for daphnia magna, oral rat, developmental toxicity and mutagenicity, we have added corresponding descriptions in the Supplementary Method 7 of our revised manuscript.

Supplementary Method 7. Toxicity theoretical and experimental evaluation of CBZ and its degradation products

The acute toxicity of LC₅₀, LD₅₀, developmental toxicity and mutagenicity for CBZ and its products were assessed by quantitative structure activity relationship (QSAR) predication using Toxicity Estimation Software Tool (T.E.S.T.) in the consensus method with four evaluation criteria for acute toxicity of daphnia magna and oral rat toxicity, developmental toxicity and mutagenicity. The details were as

follows:

(1) Acute toxicity to daphnia magna was evaluated using the 48-h LC_{50} , defined as the concentration of a chemical that caused 50% of daphnia magna to die after 48 h. An increase in the LC_{50} value of the degradation products compared to the parent contaminant indicated a reduction in toxicity, whereas a decrease suggested the formation of more toxic intermediates.

(2) Oral rat acute toxicity was assessed based on the LD_{50} , which was the dosage of chemical that caused the death of 50% rat after oral ingestion. Predicted LD_{50} values were categorized into four toxicity classes: very toxic, toxic, harmful, and non-toxic. An ideal result for degradation products relative to the parent contaminant was a shift in toxicity classification toward the non-toxic one.

(3) Developmental toxicity was assessed to evaluate the potential for causing developmental abnormalities. The parent contaminant and its degradation products were classified as either a developmental toxicant or a non-developmental toxicant. The ideal result was a non-toxicant, indicating a reduction in toxicity of degradation product compared to the parent contaminant.

(4) Mutagenicity was used to evaluate the potential for causing genetic mutations. According to the T.E.S.T. classification standard, a predicted value greater than 0.5 indicated a positive result, while a value below 0.5 indicated a negative result. Therefore, the ideal result of the degradation process was to achieve the negative mutagenicity.

11. Provide more detailed information on how OH_{surf} modulates the d orbital distribution of cobalt. Additionally, supplement the references to support it.

Response:

We are very sorry that we haven't described clearly in the previous manuscript. The OH_{surf} adsorbed at Mg site could modulate the d orbital distribution of Co by leveraging the π -conjugated delocalized network of carbon nitride with long-range interaction. The similar long-range electronic modulation has also been reported in previous work¹⁻³. The energy levels for d_{xy} , $d_{x^2-y^2}$, d_{xz} , d_z^2 and d_{yz} orbitals were shifted to lower energy levels after d orbital distribution of Co, enabling continuous electron transfer between Co d_{xy} or $d_{x^2-y^2}$ orbitals and Op orbital of PMS as well as appropriate desorption of *SO₄. We have added more detailed information on how OH_{surf} modulates the d orbital distribution of cobalt and supplemented the references to support it in our revised manuscript (line 387-391, page 20; line 392-398, page 21):

In summary, the dynamic domino catalysis process in overcoming the activity-stability trade-off during water purification was as follows: Under visible light irradiation, photogenerated electrons drove a two-electron oxygen reduction reaction at the Mg site, enabling the *in-situ* generation of H₂O₂. The as-formed H₂O₂ was subsequently converted to OH_{surf} via the Mg site. These OH_{surf} leveraged the π -conjugated delocalized network of carbon nitride to modulate the d-orbital configuration of non-adjacent Co atom through long-range interaction, enabling the shift of energy levels for d_{xy} , $d_{x^2-y^2}$, d_{xz} , d_z^2 and d_{yz} orbitals to lower energy levels⁵⁵⁻⁵⁷. On the one hand, this promoted the reduction of Co³⁺ to Co²⁺, thereby accelerating

•SO₄⁻ generation during PMS activation for enhanced activity. On the other hand, it reduced the adsorption energy of *SO₄, optimizing its desorption process and preventing Co atom detachment to maintain stability.

References in this eleventh response to reviewer 2:

1. Wu, Z. et al. Long-range interactions driving neighboring Fe–N₄ sites in Fenton-like reactions for sustainable water decontamination. *Nat Commun.* **15**, 7775 (2024).
2. Jin, S. et al. Remote tuning of single-atom Fe–N₅ sites via high-coordination defects for enhanced Fenton-like water decontamination. *Nat Commun.* **16**, 10455 (2025).
3. Deng, Y. C. et al. Long-range electronically polarized Fe–N₅ catalysts redirect polymerization-driven phenolic pollutant removal toward sustainable carbon sequestration, *Angew. Chem. Int. Ed.* **64**, e202509493 (2025).

12. The sentence “The correlation plot of CBZ degradation rate constant within 4 min (k_1) and CBZ degradation rate constant from 4 min to 24 min (k_2) with various possible influencing factors, including mass of Co (A), photoadsorption (B), crystallinity (C) and Co spin state (D). This result illustrated that degradation of CBZ was mainly related to OH_{surf} from *in-situ* generated H₂O₂ ($p \leq 0.05$) (Fig. 3f)” was described in line 201-206. How does it prove that the degradation of CBZ was primarily related to OH_{surf} from *in-situ* generated H₂O₂ ($p \leq 0.05$)? Describe it in detail.

[Response:](#)

We are very sorry that we haven't described clearly in the previous manuscript.

Fig. 3f exhibited the correlation plot of CBZ degradation rate constant within 4 min (k_1) and CBZ degradation rate constant from 4 min to 24 min (k_2) with various possible influencing factors, including mass of Co (A), photoadsorption (B), crystallinity (C), OH_{surf} contribution ratio (D) and Co spin state (E). It was illustrated that the photoadsorption and OH_{surf} contribution ratio were crucial factors for k_1 and k_2 , respectively. The Gibbs free energy for two-electron oxygen reduction of H_2O_2 in the presence of PMS by MgCo/CN DSACs was negative, indicating that H_2O_2 generation was thermodynamically spontaneous (Fig. S24). Fig. S25 exhibited the time-resolved *in-situ* DRIFTS profiles of 4MgCo/CN DSACs. In the 4MgCo/CN DSACs/PMS/vis system, characteristic O–O stretching vibrations were detected for surface-adsorbed species, including O_2^* (965 cm^{-1}), $\bullet\text{O}_2^-*$ (1151 cm^{-1}), $\bullet\text{OOH}^*$ (1205 cm^{-1}) and HOOH^* (1369 cm^{-1}). The intensities of these peaks increased progressively with reaction time from 0 to 24 min. Additionally, the ESR spectra under light irradiation (Fig. S26) also revealed the characteristic signal of $\bullet\text{O}_2^-$. These results collectively demonstrated that the dominant route for H_2O_2 generation was the two-electron oxygen reduction under light irradiation. The H_2O_2 was the crucial intermediate for OH_{surf} . Hence, it was concluded that CBZ degradation was primarily associated with OH_{surf} generated *in-situ* from H_2O_2 . To more clearly prove that the degradation of CBZ was primarily related to OH_{surf} from in situ generated H_2O_2 , we have added some descriptions in our revised manuscript (line 243-255, page 13; line 256-269, 272-276, page 14):

As shown in Figs. S22 and S23, the H_2O_2 concentration decreased rapidly after introducing nitrogen (N_2), indicating that O_2 was essential for H_2O_2 generation. Upon addition of the electron-trapping agent potassium bromate (KBrO_3), the H_2O_2 concentration dropped sharply, demonstrating that the two-electron oxygen reduction reaction was the primary pathway for photocatalytic H_2O_2 production. The H_2O_2 concentration decreased by 94.1% after adding p-benzoquinone (p-BQ), suggesting that $\bullet\text{O}_2^-$ was a key intermediate in the photoreaction. The negligible H_2O_2 concentration observed upon addition of tert-butyl alcohol (TBA) indicated that $\bullet\text{OH}$ was not an intermediate in H_2O_2 production. In contrast, adding ethanol (EtOH) and benzyl alcohol (BnOH) significantly increased H_2O_2 production, mainly because these alcohols capture photogenerated holes and supply sufficient protons, thereby facilitating oxygen reduction for H_2O_2 generation. These results indicated that CBZ did not affect the types of key intermediates in the *in-situ* photocatalytic generation of H_2O_2 . The Gibbs free energy for the two-electron oxygen reduction to H_2O_2 in the presence of PMS by 4MgCo/CN DSACs was negative (Fig. S24), indicating that H_2O_2 generation was thermodynamically spontaneous. Fig. S25 exhibited the time-resolved *in-situ* DRIFTS profiles of 4MgCo/CN DSACs. In the 4MgCo/CN DSACs/PMS/vis system, the characteristic O–O stretching vibrations were detected for surface-adsorbed species, including O_2^* (965 cm^{-1}), $\bullet\text{O}_2^-*$ (1151 cm^{-1}), $\bullet\text{OOH}^*$ (1205 cm^{-1}), and HOOH^* (1369 cm^{-1})⁵¹. The intensities of these peaks progressively increased with reaction time from 0 to 24 min. In the ESR spectra (Fig. S26), a distinct characteristic signal of $\bullet\text{O}_2^-$ was observed under light irradiation, whereas the

signal was barely detectable in the dark. Collectively, these results demonstrated that the dominant route for H_2O_2 generation was the two-electron oxygen reduction. A correlation plot of the CBZ degradation rate constant within the first 4 min (k_1) and that from 4 min to 24 min (k_2) was generated against various possible influencing factors, including Co mass (A), photoadsorption (B), crystallinity (C), OH_{surf} contribution ratio (D) and Co spin state (E). This result illustrated that the degradation of CBZ was mainly related to OH_{surf} from *in-situ* generated H_2O_2 ($p < = 0.05$) (Fig. 3f), indicating that the photoadsorption and OH_{surf} contribution ratio were crucial factors for k_1 and k_2 , respectively. Given that visible light was used to drive photoreduction of oxygen to H_2O_2 , which served as a crucial intermediate for OH_{surf} , it could be deduced that CBZ degradation was primarily related to OH_{surf} from *in-situ* generated H_2O_2 .

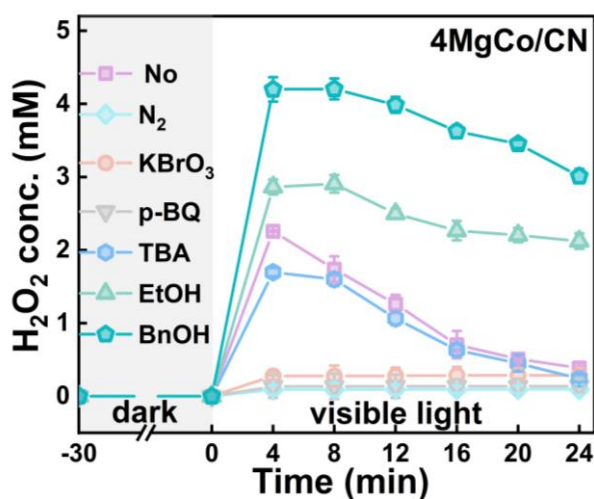


Fig. S22. H_2O_2 generation by 4MgCo/CN DSACs in the PMS/vis/CBZ system with different scavengers.

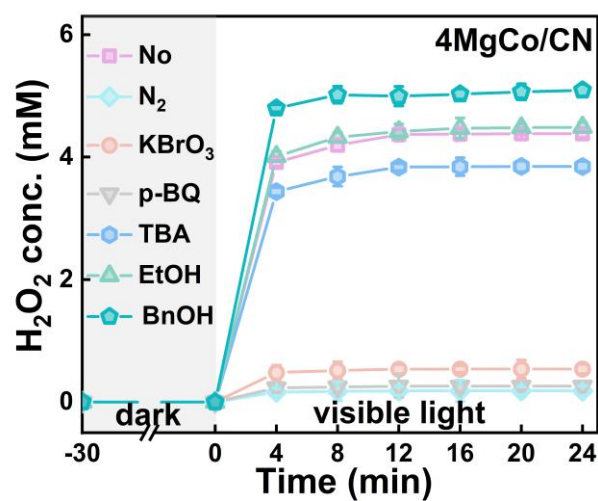


Fig. S23. H_2O_2 generation by 4MgCo/CN DSACs in the PMS/vis system with different scavengers.

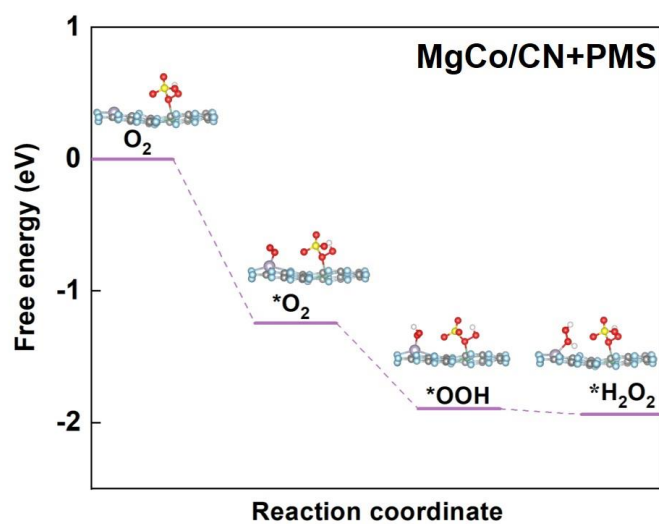


Fig. S24. Free energy curve of oxygen reduction for H_2O_2 generation by MgCo/CN DSACs in the presence of PMS.

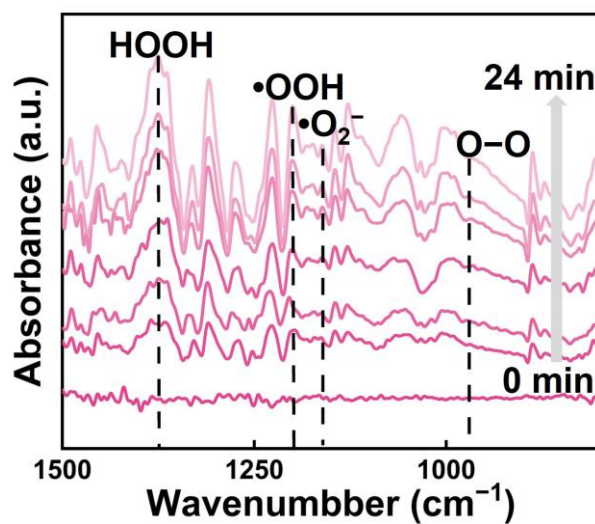


Fig. S25. The *in-situ* DRIFTS spectra of 4MgCo/CN DSACs in the PMS/vis system.

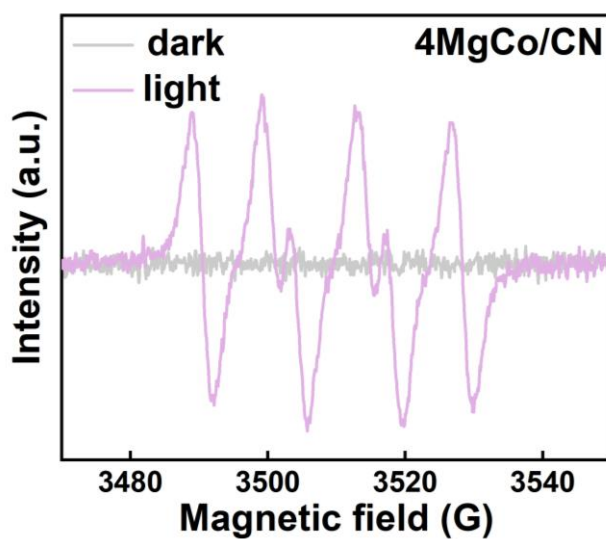


Fig. S26. The ESR spectra of $\bullet\text{O}_2^-$ by 4MgCo/CN DSACs with/without light irradiation.

To reviewer 3

The reviewer's comment:

Reviewer #3: This manuscript proposes a domino-catalytic strategy based on a Mg–Co dual single-atom catalyst to overcome the activity–stability trade-off in advanced oxidation processes. While the concept is potentially interesting, the current study suffers from substantial experimental and mechanistic deficiencies that undermine the central claims. Most critically, the proposed mechanism concerning in situ H_2O_2 generation, enhanced OH formation, and dynamic Co d-orbital reconstruction, remains speculative and lacks compelling direct experimental validation. Several spectral features are too weak or ambiguous to be reliably assigned. Thorough analysis and appropriate control experiments are necessary for solid assignment. Given these significant structural and mechanistic uncertainties, the conclusions appear overstated. Therefore, in its present form, the manuscript is not suitable for publication in Nature Communications.

1. The HAADF-STEM images mainly display isolated bright spots, which do not clearly distinguish between single atoms and closely spaced dual-atom pairs. Moreover, the EXAFS fitting lacks a clearly resolved Co–Mg scattering path with convincing fitting parameters, and the possibility of Co–Co bonding or small cluster formation has not been rigorously excluded. Therefore, the present data are not adequate to unambiguously confirm the existence and precise structural characteristics of the proposed dual-atom configuration.

[Response:](#)

i) We are very sorry for our mistake. During previous HAADF-STEM measurement, improper instrument operation made it difficult to clearly distinguish between single atoms and closely spaced dual-atom pairs in the image. To achieve a clear differentiation, we have remeasured the HAADF-STEM of 4MgCo/CN DSACs. Fig. 1b exhibited a series of closely spaced dual-atom pairs in the 4MgCo/CN DSACs. The EDS mapping showed the coexistence of C, N, Mg and Co elements in the 4MgCo/CN DSACs. To more clearly illustrate the dual-atom pairs in the 4MgCo/CN DSACs, we have added corresponding descriptions in our revised manuscript (line 99-100, page 5):

The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) (Fig. 1b) exhibited the bright dual-atom pairs in yellow dashed ellipses, indicating that the dual single atom structure was successfully synthesized.

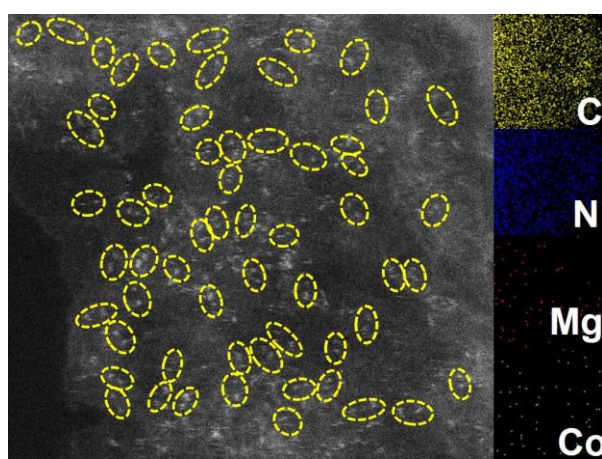


Fig. 1. (b) Aberration-corrected HAADF-STEM image and EDS mapping of 4MgCo/CN DSACs.

ii) We are very sorry for our mistake. Co_3O_4 and 4MgCo/CN were labeled inversely in the Co *K*-edge EXAFS spectra of the previous manuscript. The Mg–N₄ and Co–N₄ were the coordination configurations in the 4MgCo/CN DSACs with no Mg–Co bond involved. Similar coordination configurations in dual single atom catalysts have also been reported in other dual single atom catalysts of previous reports¹⁻³. The detailed evidences were as follow:

Fourier transformed (FT) k^3 -weighted X-ray absorption fine structure (EXAFS) spectra of 4MgCo/CN DSACs (Figs. S4 and S5), the peaks corresponding to Co–N at 1.48 Å and Mg–N at 1.68 Å were observed^{4,5}. No peaks attributable to Co–Co, Co–O, Mg–Mg and Mg–O bonds were detected, suggesting the absence of metallic or oxide clusters. Additionally, no Mg–Co bond was observed in the EXAFS spectra of 4MgCo/CN DSACs, demonstrating no direct bonding between Mg and Co atom. The more negative formation energy of 4MgCo/CN without the Mg–Co bond (–0.75 eV), compared to that of its counterpart containing the Mg–Co bond (1.15 eV), further indicating that the former was more favorable to form (Fig. S6). Based on the FT-EXAFS fitting results in R-space (Figs. 1g and 1j, Tables S3 and S4), it was deduced that the coordination configurations of 4MgCo/CN DSACs were identified as Mg–N₄ and Co–N₄. Quantitative intensity profile analysis (Fig. S7) confirmed that the predominant configuration featured MgCo paired sites with the highest prevalence of interatomic distance of 6.48 Å, which matched well with the distance between Mg and Co in simulated MgCo/CN model featuring Mg–N₄ and Co–N₄ coordination without Mg–Co bond. The same estimation method has been reported in previous

work⁶. These results collectively confirmed the successful synthesis of MgCo/CN DSACs featuring Mg–N₄ and Co–N₄ configurations without Mg–Co bond. To more clearly demonstrate the existence and structural characteristics of dual single atom configuration, as well as the Co species proportion and the average oxidation state of Co in the 4MgCo/CN DSACs, we selected Co foil, CoO, and Co₂O₃ as the standard samples and revised the corresponding descriptions in our revised manuscript (line 103-109, page 5; line 110-131, page 6; line 132-134, page 7):

The Co and Mg K-edge X-ray absorption near-edge structure (XANES) spectra (Figs. 1e and 1h) showed that the absorption edge of Co lay between those of Co foil and CoO, while that of Mg lay between those of Mg foil and MgO, but closer to Mg foil. This indicated that the oxidation states of both Co and Mg in the 4MgCo/CN DSACs ranged between 0 and +2, yet they differed from each other. The linear combination fitting (LCF) analysis (Figs. S2, S3 and Tables S1, S2) was performed to quantify the proportions of different Co and Mg species. The proportions of Co⁰, Co²⁺ and Co³⁺ were 40.6%, 28.7%, and 30.7%, respectively, while those of Mg⁰ and Mg²⁺ were 81.7% and 18.3%, respectively. Based on the LCF results, the average oxidation states of Co and Mg in the 4MgCo/CN DSACs were estimated to be 1.50 and 0.37, respectively (Figs. 1f and 1i). Fourier transformed (FT) k³-weighted X-ray absorption fine structure (EXAFS) spectra of 4MgCo/CN DSACs (Figs. S4 and S5), the peaks corresponding to Co–N at 1.48 Å and Mg–N at 1.68 Å were observed^{19,20}. No peaks attributable to Co–Co, Co–O, Mg–Mg and Mg–O bonds were detected, suggesting the absence of metallic or oxide clusters. Additionally, no Mg–Co bond was observed in

the EXAFS spectra of 4MgCo/CN DSACs, demonstrating that no direct bonding between Mg and Co atom. The more negative formation energy of 4MgCo/CN without the Mg–Co bond (−0.75 eV), compared to that of its counterpart containing the Mg–Co bond (1.15 eV), further indicated that the former was more favorable to form (Fig. S6). Based on the FT-EXAFS fitting results in R-space (Figs. 1g and 1j, Tables S3 and S4), it was deduced that the coordination configurations of 4MgCo/CN DSACs were identified as Mg–N₄ and Co–N₄. Quantitative intensity profile analysis (Fig. S7) confirmed that the predominant configuration featured MgCo paired sites with the highest prevalence of interatomic distance of 6.48 Å, which matched well with the distance between Mg and Co in simulated MgCo/CN model featuring Mg–N₄ and Co–N₄ coordination without Mg–Co bond. The same estimation method has been reported in previous work²¹. These results collectively confirmed the successful synthesis of MgCo/CN DSACs featuring Mg–N₄ and Co–N₄ configurations without Mg–Co bond.

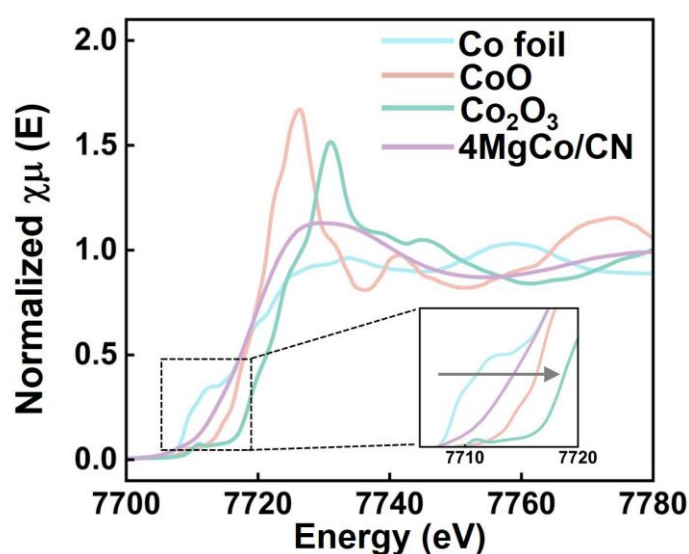


Fig. 1. (e) Normalized Co *K*-edge XANES spectra of 4MgCo/CN DSACs.

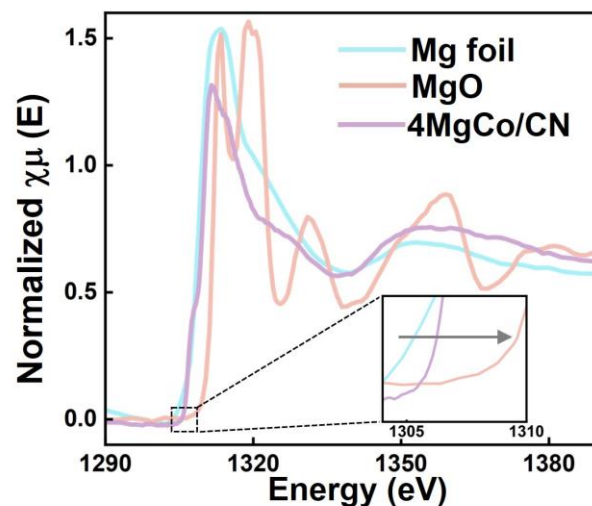


Fig. 1. (h) Normalized Mg K-edge XANES spectra of 4MgCo/CN DSACs.

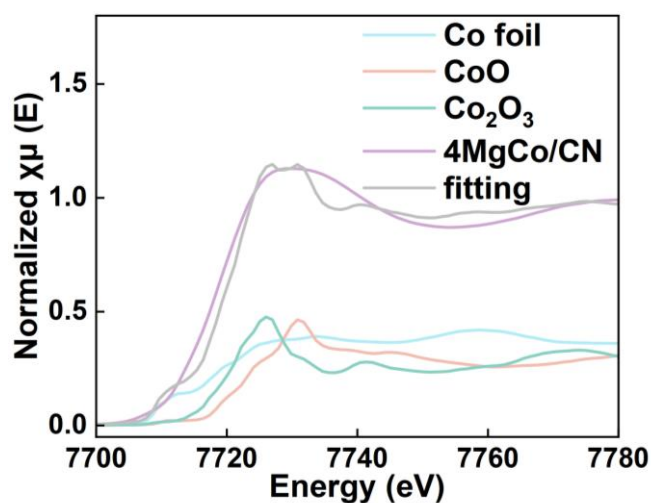


Fig. S2. The linear combination fitting result for 4MgCo/CN DSACs.

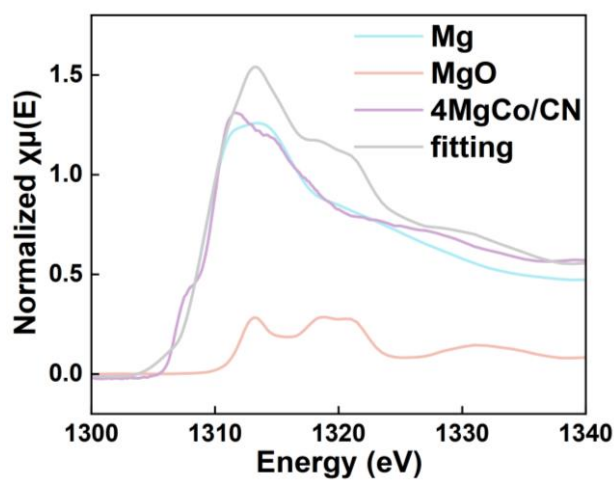


Fig. S3. The linear combination fitting result for 4MgCo/CN DSACs.

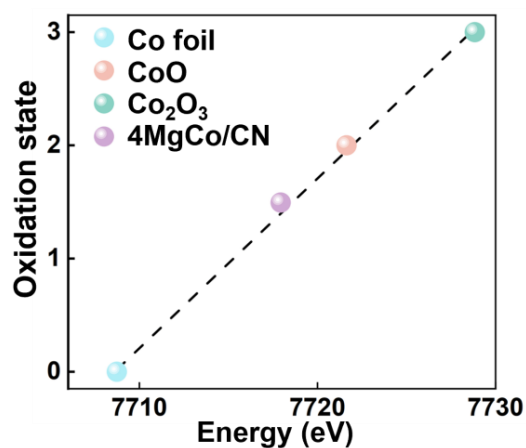


Fig. 1. (f) corresponding oxidation state of Co species in 4MgCo/CN DSACs.

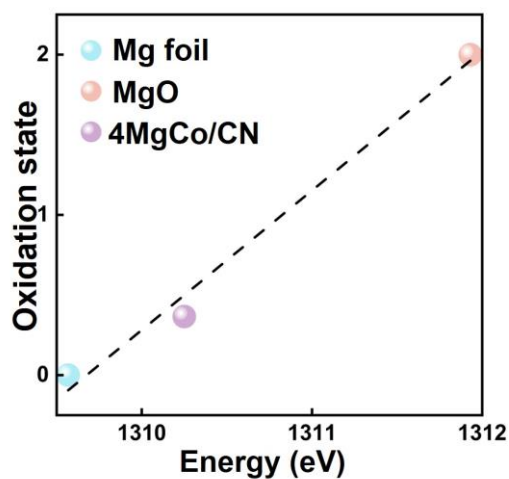


Fig. 1. (i) corresponding oxidation state of Mg species in 4MgCo/CN DSACs.

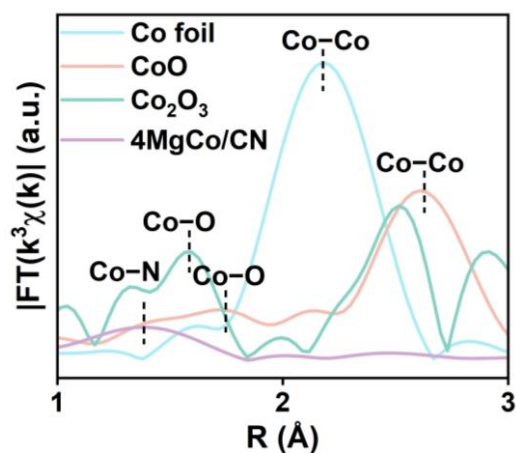


Fig. S4. FT k^3 -weighted Co K -edge EXAFS spectra of 4MgCo/CN DSACs.

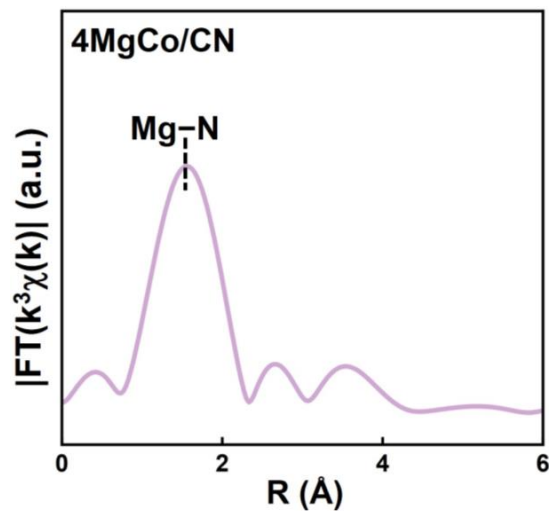


Fig. S5. FT k^3 -weighted Mg K -edge EXAFS spectra of 4MgCo/CN DSACs

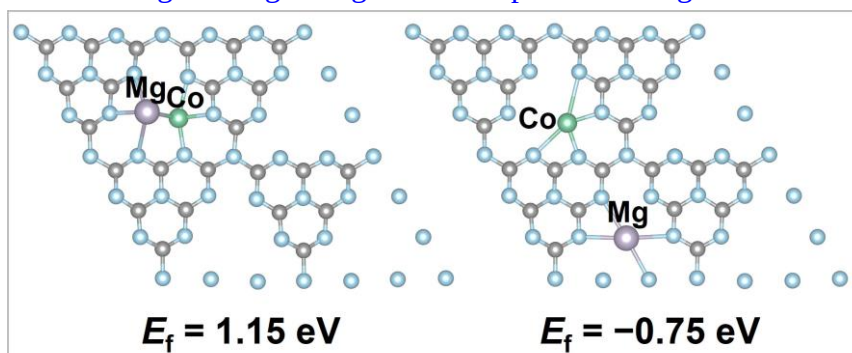


Fig. S6. The formation energy for MgCo/CN DSACs with different coordination configurations.

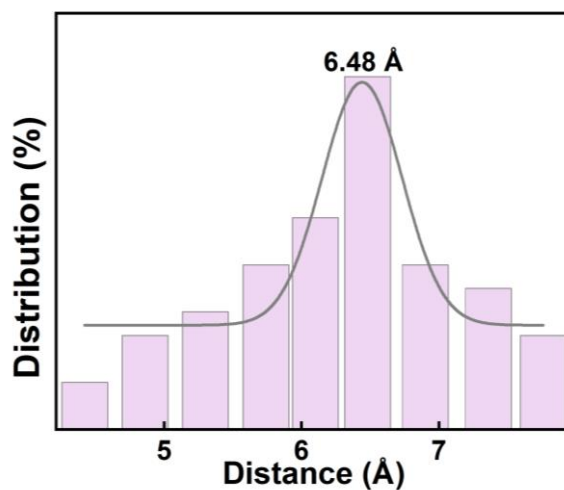


Fig. S7. Histogram of the observed atomic distance of 4MgCo/CN DSACs obtained by the kernel method of frequency statistic and Gauss fitting of diatomic distances.

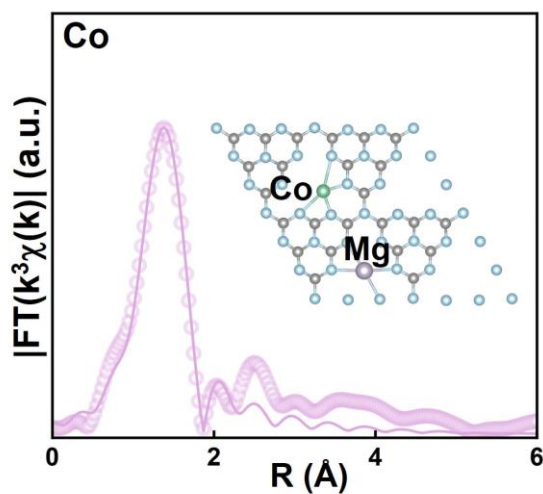


Fig. 1. (g) the fitting curves of Co K-edge EXAFS spectra in 4MgCo/CN DSACs.

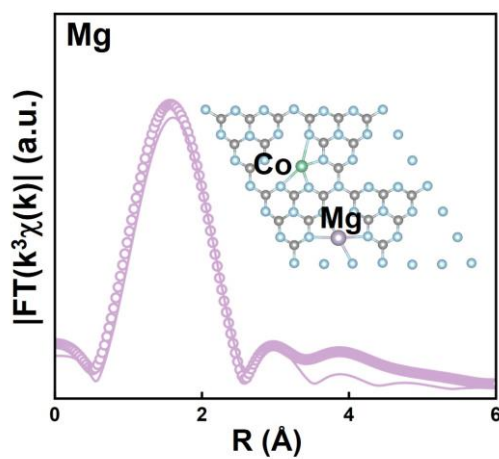


Fig. 1. (j) the fitting curves of Mg K-edge EXAFS spectra in 4MgCo/CN DSACs.

Table S1. Linear combination fitting for Co in 4MgCo/CN.

Standard	Weight	E ₀
Co foil	0.406 (0.000)	0.000 (0.000)
CoO	0.287 (0.000)	0.000 (0.000)
Co ₂ O ₃	0.307 (0.000)	0.000 (0.000)

R-factor = 0.0208785

Chi-square = 0.26227

Reduced chi-square = 0.0025463

Table S2. Linear combination fitting for Mg in 4MgCo/CN.

Standard	Weight	E ₀
Mg foil	0.817 (0.000)	0.000 (0.000)
MgO	0.183 (0.000)	0.000 (0.000)

R-factor = 0.0989203

Chi-square = 3.78914

Reduced chi-square = 0.0225544

Table S3. EXAFS fitting parameters at the Co *K*-edge for various samples.

sample	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Co foil	Co	1.62	3.70	0.0057	6.781	0.012
CoO	Co–O	6.51	3.26	0.0149	7.523	0.013
Co ₂ O ₃	Co–O	3.40	1.90	0.0015	−9.260	0.014
4MgCo/CN	Co–N	3.53	1.89	0.0089	−5.675	0.015

Supplementary Note: CN: Coordination Number; R: Bond Distance; σ^2 :

Debye-Waller Factor; ΔE_0 : Inner Potential Correction; R Factors: Goodness of Fitting.

Table S4. EXAFS fitting parameters at the Mg *K*-edge for various samples.

sample	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Mg foil	Mg	0.50	3.34	0.0442	−14.612	0.019
MgO	Mg–O	6.00	3.07	0.0115	9.062	0.020
4MgCo/CN	Mg–N	3.59	2.12	0.0030	6.364	0.013

Supplementary Note: CN: Coordination Number; R: Bond Distance; σ^2 :

Debye-Waller Factor; ΔE_0 : Inner Potential Correction; R Factors: Goodness of Fitting.

References in this first response to reviewer 3:

1. Lian, Z. C. et al. Spatial decoupling of adsorption and transformation sites on Ag-Cu dual-single-atom catalysts for highly selective photocatalytic nitrate-to-ammonia reduction. *Angew. Chem. Int. Ed.* **65**, e202516964 (2026).
 2. Guo, J. R. et al. Synergistic dual-single-atom catalysis driving auto-catalytic process toward oxidant-free Fenton-like chemistry for water purification. *Angew. Chem. Int. Ed.* **65**, e23480 (2026).
 3. Ma, Y. F. et al. Ligand-restricted synthesis of highly paired dual-atom catalysts. *Nature Mater.* **25**, 80–90 (2026).
 4. Zhao, P. et al. Cu–Mg dual single-atom catalysts with CO spillover for efficient CO₂ electroreduction to CH₄. *Angew. Chem. Int. Ed.* **64**, e202516184 (2025).
 5. Luo, Q. L. et al. Tailoring single-atom coordination environments in carbon nanofibers via flash heating for highly efficient bifunctional oxygen electrocatalysis. *Angew. Chem. Int. Ed.* **64**, e202413369 (2025).
 6. Liu, C. H. et al. Cascade hydrogen peroxide reduction reaction endows Cu-Fe dual-atom catalyst with durable oxygen reduction performance. *Adv. Funct. Mater.* **35**, 2503079 (2025).
2. Figures 1e and f are particularly confusing and require substantial clarification. In Figure 1e, the magnified inset does not appear to correspond clearly to the highlighted region in the original spectrum, making it difficult to understand what specific feature is being emphasized. More importantly, based on the presented XANES data, the oxidation state of Co in 4MgCo/CN does not seem to fall between 0 and +2 as

implied by comparison with Co foil and CoO. A more rigorous quantitative analysis (e.g., linear combination fitting or edge position calibration) is necessary to support the claimed valence state. In Figure 1f, the assignment of scattering pathways is also questionable. It is unclear why a Co–N coordination path appears in Co₃O₄, while a Co–O pathway is assigned to 4MgCo/CN. These assignments appear inconsistent with the expected local coordination environments and raise concerns about the reliability of the EXAFS fitting.

Response:

i) We are very sorry for our mistake. The magnified inset did not appear to correspond clearly to the highlighted region in the original spectrum due to our carelessness in the previous manuscript. To clearly exhibit the specific feature, we have checked and corrected it in Fig. 1e of our revised manuscript.

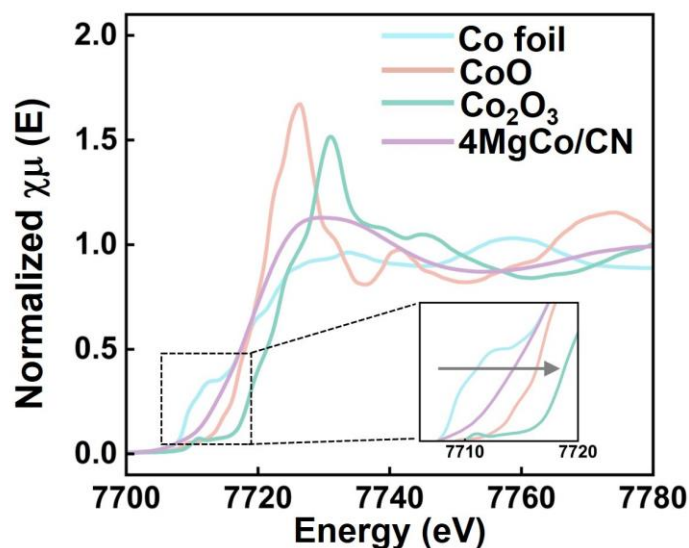


Fig. 1. (e) Normalized Co K-edge XANES spectra of 4MgCo/CN DSACs.

ii) We are very sorry for our mistake. In the magnified inset of the normalized Co K-edge XANES spectra (Fig. 1e), the color labels for CoO and 4MgCo/CN were

reversed. To clearly exhibit the Co oxidation state between 0 and +2, we have checked and corrected this to ensure consistency between the magnified inset and the original spectrum in Fig. 1e of our revised manuscript. To obtain the accurate valence states of Co and Mg, a more rigorous quantitative analysis by linear combination fitting (LCF) was performed (Figs. S2, S3 and Tables S1, S2). The proportions of Co^0 , Co^{2+} and Co^{3+} were 40.6%, 28.7%, and 30.7%, respectively, while those of Mg^0 and Mg^{2+} were 81.7% and 18.3%, respectively. Based on the LCF results, the average oxidation states of Co and Mg in the 4MgCo/CN DSACs were estimated to be 1.50 and 0.37, respectively (Figs. 1f and 1i). To more clearly exhibit the oxidation states of Co and Mg in the 4MgCo/CN DSACs, we have added corresponding descriptions in our revised manuscript (line 103-109, page 5; line 110-114, page 6):

The Co and Mg K-edge X-ray absorption near-edge structure (XANES) spectra (Figs. 1e and 1h) showed that the absorption edge of Co lay between those of Co foil and CoO, while that of Mg lay between those of Mg foil and MgO, but closer to Mg foil. This indicated that the oxidation states of both Co and Mg in the 4MgCo/CN DSACs ranged between 0 and +2, yet they differed from each other. The linear combination fitting (LCF) analysis (Figs. S2, S3 and Tables S1, S2) was performed to quantify the proportions of different Co and Mg species. The proportions of Co^0 , Co^{2+} and Co^{3+} were 40.6%, 28.7%, and 30.7%, respectively, while those of Mg^0 and Mg^{2+} were 81.7% and 18.3%, respectively. Based on the LCF results, the average oxidation states of Co and Mg in the 4MgCo/CN DSACs were estimated to be 1.50 and 0.37, respectively (Figs. 1f and 1i).

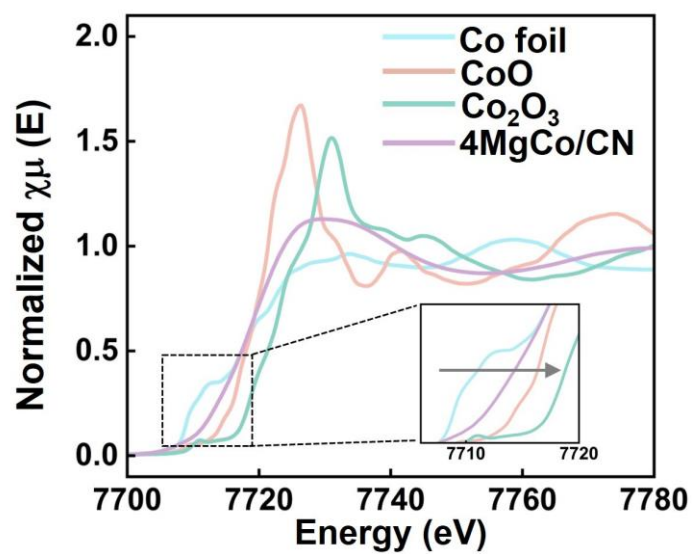


Fig. 1. (e) Normalized Co K-edge XANES spectra of 4MgCo/CN DSACs.

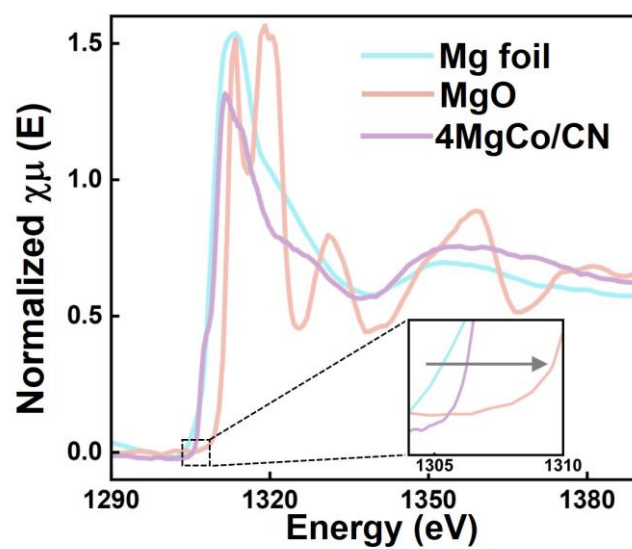


Fig. 1. (h) Normalized Mg K-edge XANES spectra of 4MgCo/CN DSACs.

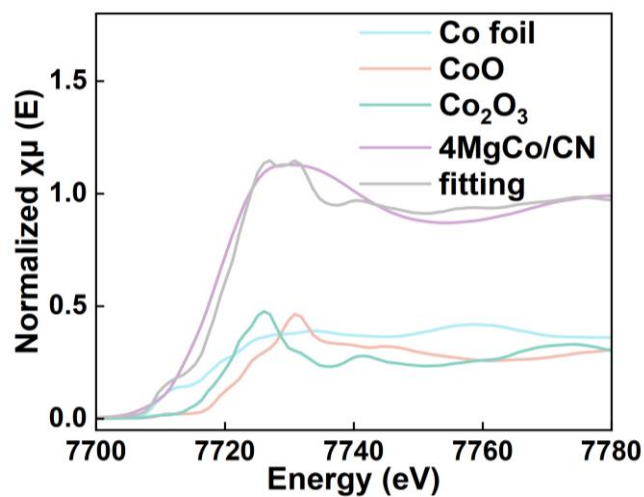


Fig. S2. The linear combination fitting result for 4MgCo/CN DSACs.

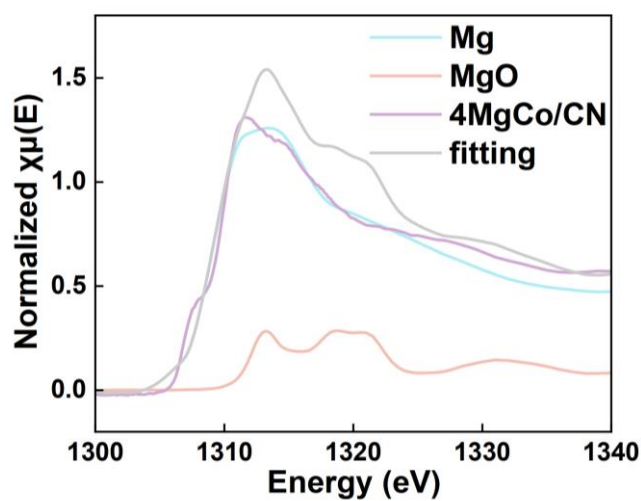


Fig. S3. The linear combination fitting result for 4MgCo/CN DSACs.

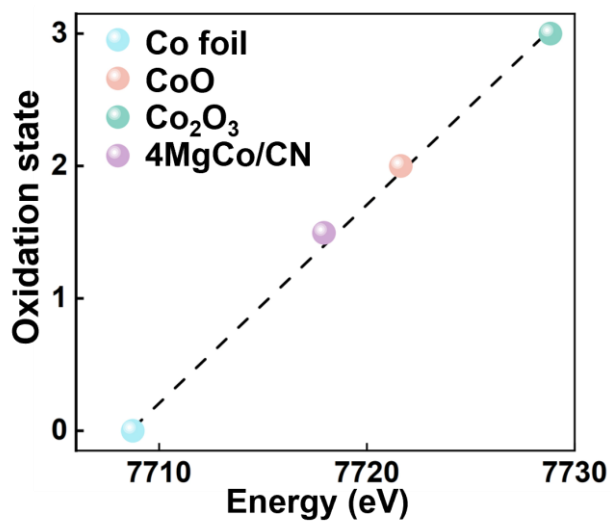


Fig. 1. (f) corresponding oxidation state of Co species in 4MgCo/CN DSACs.

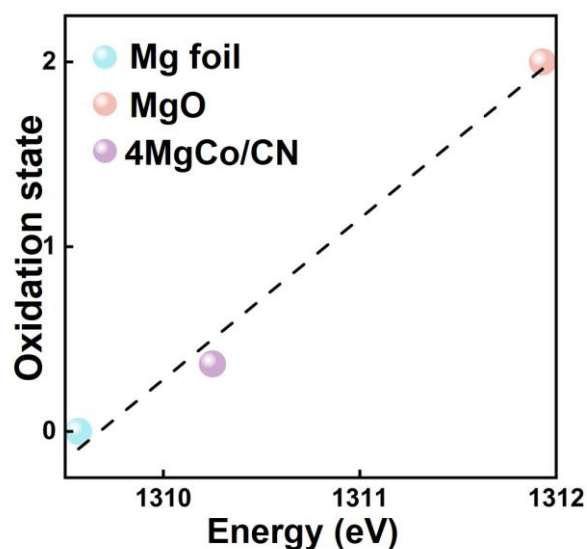


Fig. 1. (i) corresponding oxidation state of Mg species in 4MgCo/CN DSACs.

Table S1. Linear combination fitting for Co in 4MgCo/CN.

Standard	Weight	E_0
Co foil	0.406 (0.000)	0.000 (0.000)
CoO	0.287 (0.000)	0.000 (0.000)
Co ₂ O ₃	0.307 (0.000)	0.000 (0.000)

R-factor = 0.0208785

Chi-square = 0.26227

Reduced chi-square = 0.0025463

Table S2. Linear combination fitting for Mg in 4MgCo/CN.

Standard	Weight	E_0
Mg foil	0.817 (0.000)	0.000 (0.000)
MgO	0.183 (0.000)	0.000 (0.000)

R-factor = 0.0989203

Chi-square = 3.78914

Reduced chi-square = 0.0225544

iii) We are very sorry for our mistake. The Co_3O_4 and 4MgCo/CN were labeled inversely in the FT k^3 -weighted Co K -edge EXAFS spectra of previous manuscript (Fig. S4). In fact, the Co–N coordination path should appear in 4MgCo/CN , while the Co–O coordination path should be assigned to Co_3O_4 . This result was consistent with previous reports¹⁻³. To more clearly illustrate the oxidation state of Co in 4MgCo/CN , we replaced Co_3O_4 with Co_2O_3 . In Co_2O_3 , the peak corresponding to Co–O at 1.59 Å was also clearly found⁴. However, it was absent in 4MgCo/CN , where only the Co–N peak at 1.48 Å was present⁵. To further confirm the local coordination environment in the 4MgCo/CN DSACs, we also supplemented the FT k^3 -weighted Mg K -edge EXAFS spectra. Fig. S5 showed a Mg–N peak at 1.68 Å without Mg–Mg or Mg–O bonds⁶. Combined with the FT-EXAFS fitting results (Figs. 1g and 1j, Tables S3 and S4), it was deduced that the coordination configurations of the MgCo/CN DSACs were Mg–N_4 and Co–N_4 .

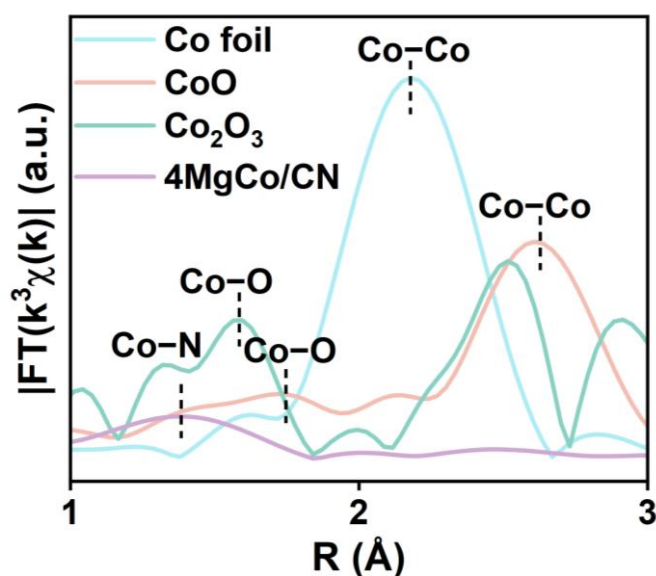


Fig. S4. FT k^3 -weighted Co K -edge EXAFS spectra of 4MgCo/CN DSACs.

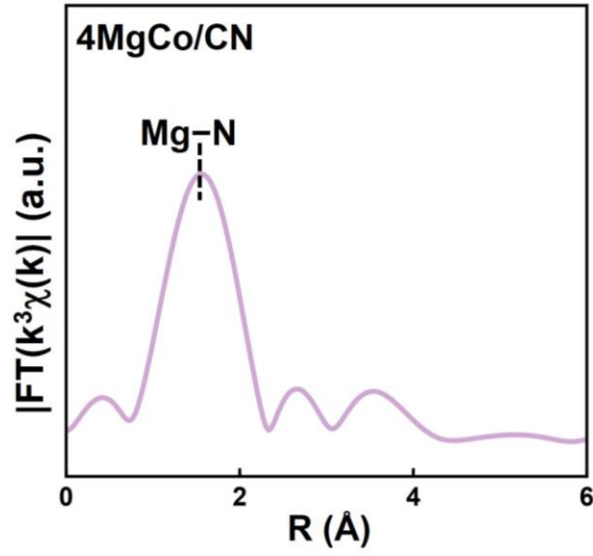


Fig. S5. FT k^3 -weighted Mg K -edge EXAFS spectra of 4MgCo/CN DSACs.

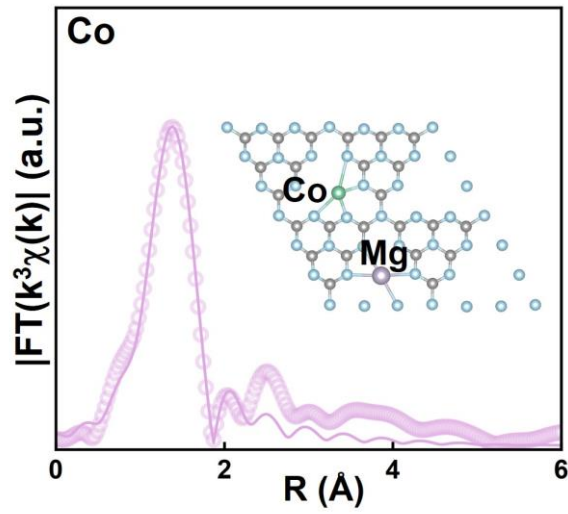


Fig. 1. (g) the fitting curves of Co K -edge EXAFS spectra in 4MgCo/CN DSACs.

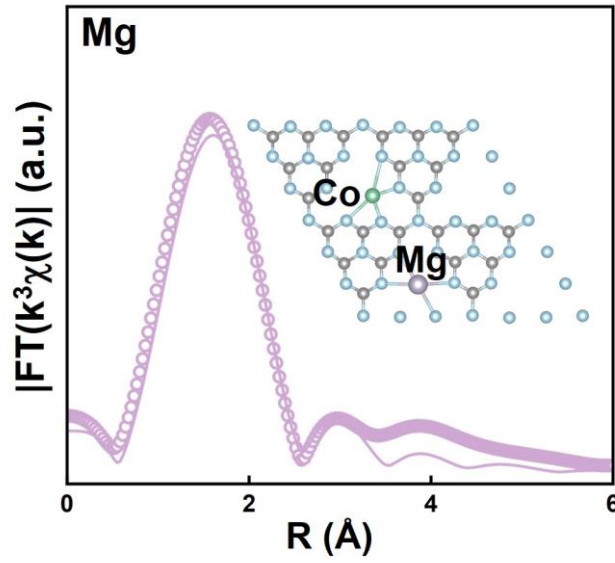


Fig. 1. (j) the fitting curves of Mg K-edge EXAFS spectra in 4MgCo/CN DSACs.

Table S3. EXAFS fitting parameters at the Co K-edge for various samples.

sample	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Co foil	Co	1.62	3.70	0.0057	6.781	0.012
CoO	Co–O	6.51	3.26	0.0149	7.523	0.013
Co ₂ O ₃	Co–O	3.40	1.90	0.0015	−9.260	0.014
4MgCo/CN	Co–N	3.53	1.89	0.0089	−5.675	0.015

Supplementary Note: CN: Coordination Number; R: Bond Distance; σ^2 : Debye-Waller Factor; ΔE_0 : Inner Potential Correction; R Factors: Goodness of Fitting.

Table S4. EXAFS fitting parameters at the Mg K-edge for various samples.

sample	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Mg foil	Mg	0.50	3.34	0.0442	−14.612	0.019
MgO	Mg–O	6.00	3.07	0.0115	9.062	0.020
4MgCo/CN	Mg–N	3.59	2.12	0.0030	6.364	0.013

Supplementary Note: CN: Coordination Number; R: Bond Distance; σ^2 :

Debye-Waller Factor; ΔE_0 : Inner Potential Correction; R Factors: Goodness of Fitting.

References in this second response to reviewer 3:

1. Xu, S. H. et al. Iron/cobalt dual-atom catalyst orchestrate photothermal-chemodynamic immunotherapy against MRSA: Multi-omics dissection in murine and porcine models. *Adv. Sci.* **13**, 2198–3844 (2026).
2. Tang, T. M. et al. Diatomic Fe-Co catalysts synergistically catalyze oxygen evolution reaction. *Nano Res.* **17**, 3794–3800 (2024).
3. Li, T. T. et al. A pH-dependent microkinetic modeling guided synthesis of porous dual-atom catalysts for efficient oxygen reduction in Zn-air batteries. *Energy & Environ. Sci.* **18**, 4949–4961 (2025).
4. Zhao, Z. Y. et al. Regulating nonradicals generation through peroxymonosulfate activation via localized dipole to enhance wastewater biodegradability, *Nature Commun.* **16**, 5861 (2025).
5. Luo, Q. L. et al. Tailoring single-atom coordination environments in carbon nanofibers via flash heating for highly efficient bifunctional oxygen electrocatalysis. *Angew. Chem. Int. Ed.* **64**, e202413369 (2025).
6. Zhao, P. et al. Cu–Mg dual single-atom catalysts with CO spillover for efficient CO₂ electroreduction to CH₄. *Angew. Chem. Int. Ed.* **64**, e202516184 (2025).
3. The fitting results in Tables S1 and S2 are insufficient. The authors are encouraged to re-examine the fitting models, clearly justify the chosen scattering paths, and provide detailed fitting parameters and model comparisons to ensure structural consistency.

Response:

Thanks for your suggestion. To ensure structural consistency, we have re-examined the fitting models, clearly justified the chosen scattering paths and provided detailed fitting parameters and model comparisons in our revised manuscript.

Table S3. EXAFS fitting parameters at the Co K-edge for various samples.

sample	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Co foil	Co	1.62	3.70	0.0057	6.781	0.012
CoO	Co–O	6.51	3.26	0.0149	7.523	0.013
Co ₂ O ₃	Co–O	3.40	1.90	0.0015	–9.260	0.014
4MgCo/CN	Co–N	3.53	1.89	0.0089	–5.675	0.015

Supplementary Note: CN: Coordination Number; R: Bond Distance; σ^2 : Debye-Waller Factor; ΔE_0 : Inner Potential Correction; R Factors: Goodness of Fitting.

Table S4. EXAFS fitting parameters at the Mg K-edge for various samples.

sample	shell	CN	R(Å)	σ^2	ΔE_0	R factor
Mg foil	Mg	0.50	3.34	0.0442	–14.612	0.019
MgO	Mg–O	6.00	3.07	0.0115	9.062	0.020
4MgCo/CN	Mg–N	3.59	2.12	0.0030	6.364	0.013

Supplementary Note: CN: Coordination Number; R: Bond Distance; σ^2 : Debye-Waller Factor; ΔE_0 : Inner Potential Correction; R Factors: Goodness of Fitting.

4. It is unclear why a Mg signal is detected in the 4Co/CN sample in Fig. S2. The authors should clarify the origin of the Mg signal, provide supporting compositional analysis (e.g., ICP, EDS quantification, or XPS survey spectra).

Response:

We are very sorry for our mistake. In the previous manuscript, MgO was mistakenly written as 4Co/CN due to our carelessness. The 4Co/CN sample was only composed of the Co, C, and N three elements, and contained no Mg element. To clearly demonstrate the elements in 4Co/CN SACs, the inductively coupled plasma (ICP), energy-dispersive X-ray elemental spectra (EDS) quantification and X-ray photoelectron spectroscopy (XPS) were detected, respectively. The mass ratio of Co in Co/CN SACs was 1.03% from the result of ICP, respectively. The EDS (Fig. 1) exhibited the coexistence of Co, C and N elements in the Co/CN SACs. In the XPS survey spectra (Fig. 2) of Co/CN SACs, the peaks with the binding energies of 780.98 eV, 397.95 eV and 284.94 eV were attributed to Co 2p, N 1s and C 1s, respectively¹⁻³. The above results demonstrated that Co/CN SACs was composed of Co, C and N elements without Mg element.

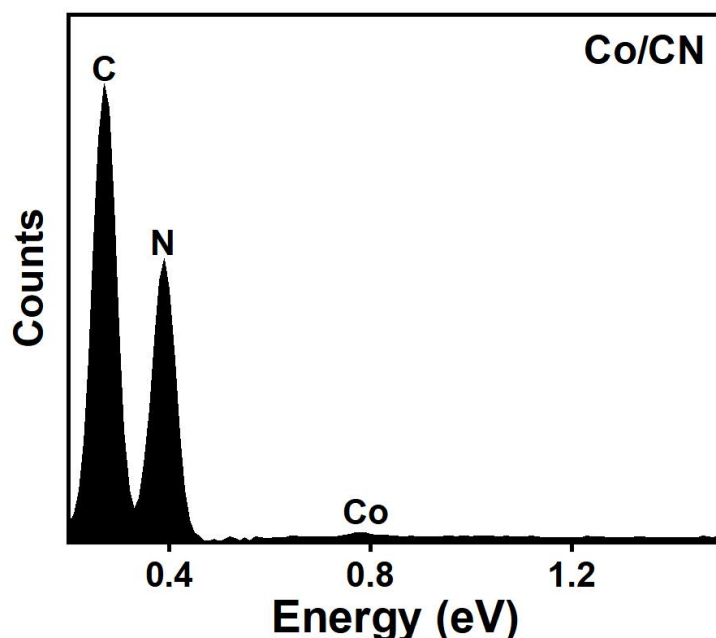


Fig. 1. EDS of Co/CN.

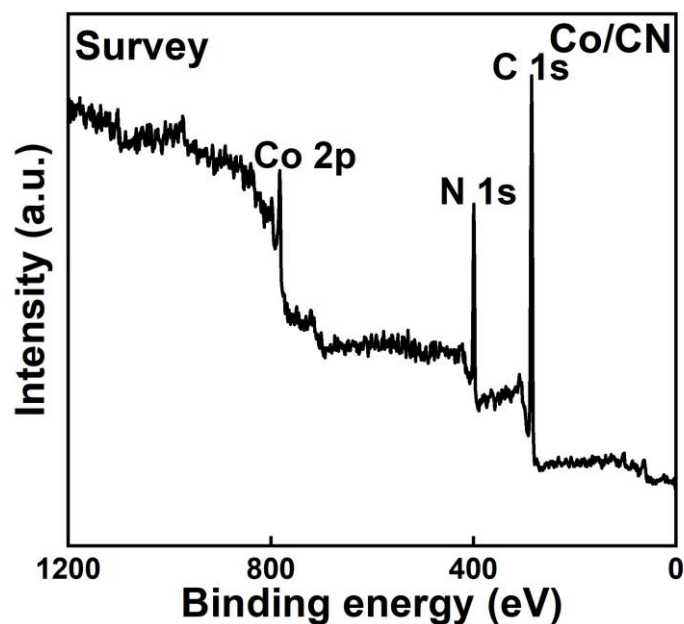


Fig. 2. XPS survey spectra of Co/CN SACs.

In the previous manuscript, the normalized Mg *K*-edge XANES spectra, FT k^3 -weighted Mg *K*-edge EXAFS spectra and the fitting curves of Mg *K*-edge EXAFS spectra in 4MgCo/CN DSACs were measured to reveal the oxidation state, coordination environment, and coordination number of Mg. To clearly exhibit the relevant information, we have replotted normalized Mg *K*-edge XANES spectra, FT k^3 -weighted Mg *K*-edge EXAFS spectra and the fitting curves of Mg *K*-edge EXAFS spectra of the 4MgCo/CN DSACs using Mg foil and MgO as reference standards. Furthermore, linear combination fitting (LCF) analysis was performed (Fig. S3 and Table S2) to quantify the proportions of different Mg species. Based on the LCF results, we calculated the average oxidation state of Mg in the 4MgCo/CN DSACs. The details were as follows:

The normalized Mg *K*-edge X-ray absorption near-edge structure (XANES) spectra (Fig. 1h) showed that the absorption edge of Mg lay between those of Mg foil

and MgO, but closer to Mg foil. The linear combination fitting (LCF) analysis (Fig. S3 and Table S2) exhibited that the proportions of Mg^0 and Mg^{2+} were 81.7% and 18.3%, respectively. Based on the LCF results, the average oxidation state of Mg in the 4MgCo/CN DSACs was estimated to be 0.37. In the FT k^3 -weighted Mg *K*-edge X-ray absorption fine structure (EXAFS) spectra of MgCo/CN DSACs (Fig. S5), the peak corresponding to Mg–N at 1.68 Å was observed⁴. No peaks attributable to Mg–Mg, and Mg–O bonds were detected, suggesting the absence of metallic or oxide clusters. Based on the FT-EXAFS fitting results in R-space (Fig. 1j, Table S4), it was deduced that the Mg coordination configuration in MgCo/CN DSACs was identified as Mg–N₄.

To more clearly exhibit the oxidation state, coordination environment, and coordination number of Mg in the MgCo/CN DSACs, we have added some descriptions in our revised manuscript (line 103-109, page 5; line 110-131, page 6; line 132-134, page 7):

The Co and Mg *K*-edge X-ray absorption near-edge structure (XANES) spectra (Figs. 1e and 1h) showed that the absorption edge of Co lay between those of Co foil and CoO, while that of Mg lay between those of Mg foil and MgO, but closer to Mg foil. This indicated that the oxidation states of both Co and Mg in the 4MgCo/CN DSACs ranged between 0 and +2, yet they differed from each other. The linear combination fitting (LCF) analysis (Figs. S2, S3 and Tables S1, S2) was performed to quantify the proportions of different Co and Mg species. The proportions of Co^0 , Co^{2+} and Co^{3+} were 40.6%, 28.7%, and 30.7%, respectively, while those of Mg^0 and Mg^{2+}

were 81.7% and 18.3%, respectively. Based on the LCF results, the average oxidation states of Co and Mg in the 4MgCo/CN DSACs were estimated to be 1.50 and 0.37, respectively (Figs. 1f and 1i). Fourier transformed (FT) k^3 -weighted X-ray absorption fine structure (EXAFS) spectra of 4MgCo/CN DSACs (Figs. S4 and S5), the peaks corresponding to Co–N at 1.48 Å and Mg–N at 1.68 Å were observed^{19,20}. No peaks attributable to Co–Co, Co–O, Mg–Mg and Mg–O bonds were detected, suggesting the absence of metallic or oxide clusters. Additionally, no Mg–Co bond was observed in the EXAFS spectra of 4MgCo/CN DSACs, demonstrating that no direct bonding between Mg and Co atom. The more negative formation energy of 4MgCo/CN without the Mg–Co bond (–0.75 eV), compared to that of its counterpart containing the Mg–Co bond (1.15 eV), further indicated that the former was more favorable to form (Fig. S6). Based on the FT-EXAFS fitting results in R-space (Figs. 1g and 1j, Tables S3 and S4), it was deduced that the coordination configurations of 4MgCo/CN DSACs were identified as Mg–N₄ and Co–N₄. Quantitative intensity profile analysis (Fig. S7) confirmed that the predominant configuration featured MgCo paired sites with the highest prevalence of interatomic distance of 6.48 Å, which matched well with the distance between Mg and Co in simulated MgCo/CN model featuring Mg–N₄ and Co–N₄ coordination without Mg–Co bond. The same estimation method has been reported in previous work²¹. The spin states of the catalysts were characterized by electron paramagnetic resonance (EPR) spectra (Fig. S8) and temperature-dependent inverse magnetic susceptibility measurements (Fig. S9). These

results collectively confirmed the successful synthesis of MgCo/CN DSACs featuring Mg–N₄ and Co–N₄ configurations without Mg–Co bond.

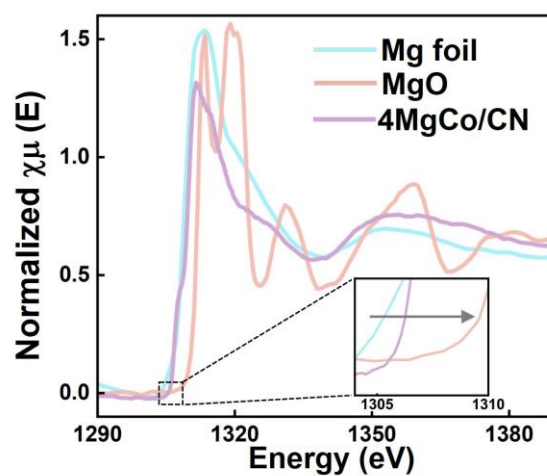


Fig. 1. (h) Normalized Mg K-edge XANES spectra of 4MgCo/CN DSACs.

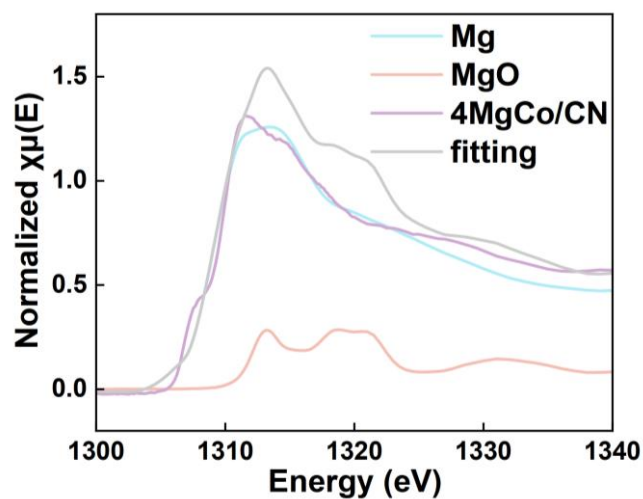


Fig. S3. The linear combination fitting result for 4MgCo/CN DSACs.

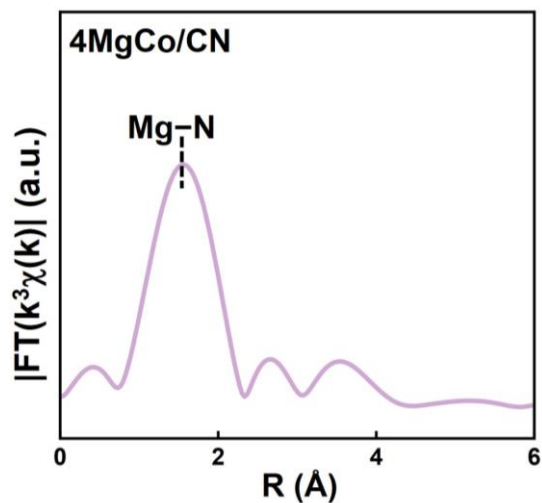


Fig. S5. FT k^3 -weighted Mg *K*-edge EXAFS spectra of 4MgCo/CN DSACs

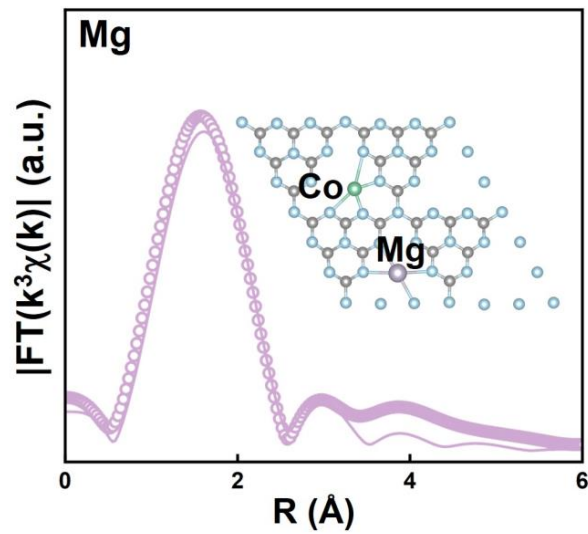


Fig. 1. (j) the fitting curves of Mg *K*-edge EXAFS spectra in 4MgCo/CN DSACs.

Table S2. Linear combination fitting for Mg in 4MgCo/CN.

Standard	Weight	E_0
Mg foil	0.817 (0.000)	0.000 (0.000)
MgO	0.183 (0.000)	0.000 (0.000)

R-factor = 0.0989203

Chi-square = 3.78914

Reduced chi-square = 0.0225544

Table S4. EXAFS fitting parameters at the Mg *K*-edge for various samples.

sample	shell	CN	$R(\text{Å})$	σ^2	ΔE_0	R factor
Mg foil	Mg	0.50	3.34	0.0442	-14.612	0.019
MgO	Mg–O	6.00	3.07	0.0115	9.062	0.020
4MgCo/CN	Mg–N	3.59	2.12	0.0030	6.364	0.013

Supplementary Note: CN: Coordination Number; R: Bond Distance; σ^2 : Debye-Waller Factor; ΔE_0 : Inner Potential Correction; R Factors: Goodness of Fitting.

References in this fourth response to reviewer 3:

1. Yao, X. Y. et al. A novel magnetically induced Co@NC-modified electrochemical membrane for continuous peroxymonosulfate activation: achieving ultrafast and cost-effective purification with elucidation of mechanism and application potential. *Water Res.* **287**, 124436 (2025).
2. Liu, L. et al. Coordination reconstruction enhanced synergistic nonradical oxidation pathways in cobalt single-atom catalysts for sustained pollutant destruction. *Angew. Chem. Int. Ed.* **64**, e202508330 (2025).
3. Xu, Y. et al. Boosting CO₂ photoreduction via ligand-engineered single-atom cobalt sites in covalent organic frameworks. *Angew. Chem. Int. Ed.* **65**, e17289 (2026).
4. Zhao, P. et al. Cu–Mg dual single-atom catalysts with CO spillover for efficient CO₂ electroreduction to CH₄. *Angew. Chem. Int. Ed.* **64**, e202516184 (2025).
5. The authors attribute the enhanced OH formation to visible-light-induced in situ H₂O₂ generation; however, this claim lacks direct H₂O₂ quantification, appropriate dark-light control experiments, and mechanistic verification of the H₂O₂ formation pathway (e.g., 2e⁻ ORR), and therefore requires direct experimental evidence to be substantiated.

Response:

i) Thanks for your suggestion. We have quantified the concentration of *in-situ* H₂O₂ generation and performed a series of dark-light control experiments to evidence the visible-light-induced *in-situ* H₂O₂ generation. No H₂O₂ was generated under the

dark condition, despite oxygen aeration in different systems. However, 2.26 mM and 1.87 mM of H₂O₂ were generated within the first 4 min by both catalysts, and then activated to 0.39 mM and 0.93 mM by 4MgCo/CN DSACs and 4Co/CN SACs in the PMS/vis/CBZ system, respectively (Figs. 3e and S18). The H₂O₂ production increased from 1.14 mM to 3.97 mM as the mass of 4MgCo/CN DSACs increased from 0.005 to 0.05 g/L in the PMS/vis/CBZ system (Fig. S20). Fig. S21 showed that H₂O₂ was gradually generated up to 4.38 mM in the PMS/vis system after 24-min reaction, which was higher than those in the PMS/vis/CBZ system (0.39 mM), the vis/CBZ system (0.03 mM), and the vis/H₂O system (0.23 mM), respectively. These results indicated that visible light was essential for H₂O₂ generation, that CBZ could consume part of the *in-situ* generated H₂O₂, and that PMS facilitated the photoreduction of H₂O₂. We have added corresponding descriptions in our revised manuscript (line 229-233, page 12; line 234-243, page 13):

No H₂O₂ was generated under the dark condition, despite oxygen aeration. However, 2.26 mM and 1.87 mM of H₂O₂ were generated within the first 4 min by both catalysts, and then activated to 0.39 mM and 0.93 mM, respectively, by 4MgCo/CN DSACs and 4Co/CN SACs in the PMS/vis/CBZ system (Figs. 3e and S18). The H₂O₂ generation for these two catalysts was attributed to their conduction band potentials being higher than that of O₂/H₂O₂ (Fig. S19). The photogenerated electrons could reduce oxygen into H₂O₂ under light irradiation. The H₂O₂ production increased from 1.14 mM to 3.97 mM as the dosage of 4MgCo/CN DSACs increased from 0.005 to 0.05 g/L in the PMS/vis/CBZ system (Fig. S20). Fig. S21 showed that

H_2O_2 was gradually generated up to 4.38 mM in the PMS/vis/ H_2O system within 24 min, which was higher than those in the PMS/vis/CBZ system (0.39 mM), the vis/CBZ system (0.03 mM), and the vis/ H_2O system (0.23 mM), respectively. These results indicated that visible light was essential for H_2O_2 generation, that CBZ could consume part of the *in-situ* generated H_2O_2 , and that PMS facilitated the photoreduction of H_2O_2 .

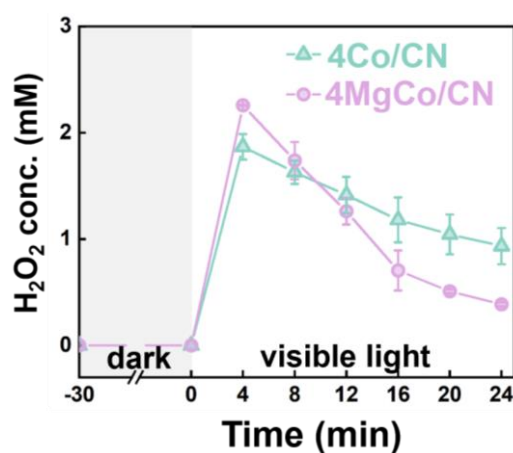


Fig. 3. (e) H_2O_2 generation concentration with different reaction time by 4MgCo/CN DSACs and 4Co/CN SACs in the PMS/vis/CBZ system, respectively.

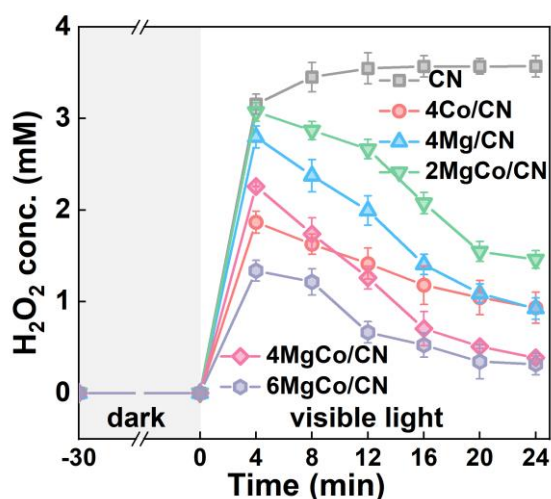


Fig. S18. *In-situ* H_2O_2 production by different catalysts.

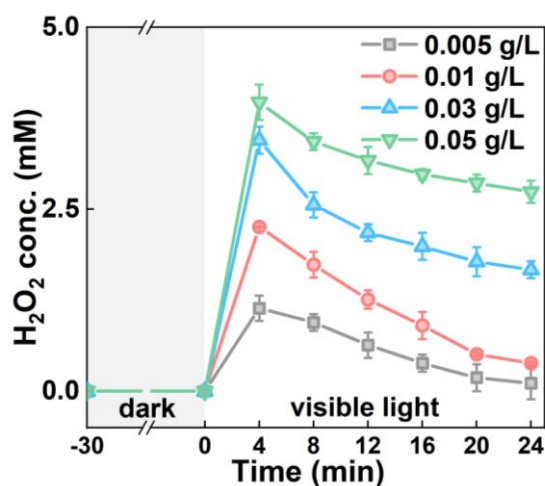


Fig. S20. *In-situ* H₂O₂ production by 4MgCo/CN DSACs with different dosages.

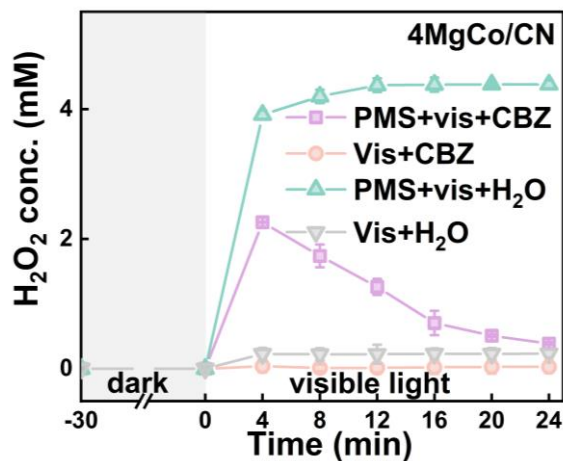


Fig. S21. H₂O₂ generation concentration by 4MgCo/CN DSACs under different conditions, respectively.

ii) We performed a series of experiments to verify the mechanism of H₂O₂ formation. These included intermediate scavenger tests during *in-situ* H₂O₂ generation under different systems, evaluation of the Gibbs free energy curve for two-electron oxygen reduction to H₂O₂ based on density functional theory (DFT) calculations, and detection of time-resolved *in-situ* DRIFTS profiles, electron spin resonance (ESR) spectra of •O₂⁻, and rotating ring-disk electrode (RRDE) polarization curves.

As shown in Figs. S22 and S23, the H₂O₂ concentration decreased rapidly after

introducing nitrogen (N₂), indicating that O₂ was essential for H₂O₂ generation¹. Upon addition of the electron-trapping agent potassium bromate (KBrO₃), the H₂O₂ concentration dropped sharply, demonstrating that the two-electron oxygen reduction reaction was the primary pathway for photocatalytic H₂O₂ production². The H₂O₂ concentration decreased by 94.1% after adding p-benzoquinone (p-BQ), suggesting that $\bullet\text{O}_2^-$ was a key intermediate in the photoreaction³. The negligible H₂O₂ concentration observed upon addition of tert-butyl alcohol (TBA) indicated that $\bullet\text{OH}$ was not an intermediate in H₂O₂ production⁴. In contrast, adding ethanol (EtOH) and benzyl alcohol (BnOH) significantly increased H₂O₂ production^{5,6}, mainly because these alcohols capture photogenerated holes and supply sufficient protons, thereby facilitating oxygen reduction for H₂O₂ generation. These results indicated that CBZ did not affect the types of key intermediates in the *in-situ* photocatalytic generation of H₂O₂. The Gibbs free energy for the two-electron oxygen reduction to H₂O₂ in the presence of PMS by MgCo/CN DSACs was negative (Fig. S24), indicating that H₂O₂ generation was thermodynamically spontaneous. Fig. S25 exhibited the time-resolved *in-situ* DRIFTS profiles of 4MgCo/CN DSACs. In the 4MgCo/CN DSACs/PMS/vis system, characteristic O–O stretching vibrations were detected for surface-adsorbed species, including O₂* (965 cm⁻¹), $\bullet\text{O}_2^-$ * (1151 cm⁻¹), $\bullet\text{OOH}^*$ (1205 cm⁻¹), and HOOH* (1369 cm⁻¹)⁷. The intensities of these peaks progressively increased with reaction time from 0 to 24 min. Additionally, ESR spectra under light irradiation (Fig. S26) exhibited the characteristic signal of $\bullet\text{O}_2^-$. RRDE measurements (Fig. 3c) showed that the electron transfer number (n) for 4MgCo/CN DSACs was

approximately 2, indicating a dominant $2e^-$ ORR pathway for H_2O_2 generation. Collectively, these results demonstrated that the dominant route for H_2O_2 generation was the two-electron oxygen reduction. We have added corresponding descriptions in our revised manuscript to verify the H_2O_2 formation pathway (line 243-255, page 13; line 256-267, page 14):

As shown in Figs. S22 and S23, the H_2O_2 concentration decreased rapidly after introducing nitrogen (N_2), indicating that O_2 was essential for H_2O_2 generation. Upon addition of the electron-trapping agent potassium bromate ($KBrO_3$), the H_2O_2 concentration dropped sharply, demonstrating that the two-electron oxygen reduction reaction was the primary pathway for photocatalytic H_2O_2 production. The H_2O_2 concentration decreased by 94.1% after adding p-benzoquinone (p-BQ), suggesting that $\bullet O_2^-$ was a key intermediate in the photoreaction. The negligible H_2O_2 concentration observed upon addition of tert-butyl alcohol (TBA) indicated that $\bullet OH$ was not an intermediate in H_2O_2 production. In contrast, adding ethanol (EtOH) and benzyl alcohol (BnOH) significantly increased H_2O_2 production, mainly because these alcohols capture photogenerated holes and supply sufficient protons, thereby facilitating oxygen reduction for H_2O_2 generation. These results indicated that CBZ did not affect the types of key intermediates in the *in-situ* photocatalytic generation of H_2O_2 . The Gibbs free energy for the two-electron oxygen reduction to H_2O_2 in the presence of PMS by 4MgCo/CN DSACs was negative (Fig. S24), indicating that H_2O_2 generation was thermodynamically spontaneous. Fig. S25 exhibited the time-resolved *in-situ* DRIFTS profiles of 4MgCo/CN DSACs. In the 4MgCo/CN

DSACs/PMS/vis system, the characteristic O–O stretching vibrations were detected for surface-adsorbed species, including O_2^* (965 cm^{-1}), $\bullet\text{O}_2^-$ (1151 cm^{-1}), $\bullet\text{OOH}^*$ (1205 cm^{-1}), and HOOH^* (1369 cm^{-1})⁵¹. The intensities of these peaks progressively increased with reaction time from 0 to 24 min. In the ESR spectra (Fig. S26), a distinct characteristic signal of $\bullet\text{O}_2^-$ was observed under light irradiation, whereas the signal was barely detectable in the dark. Collectively, these results demonstrated that the dominant route for H_2O_2 generation was the two-electron oxygen reduction.

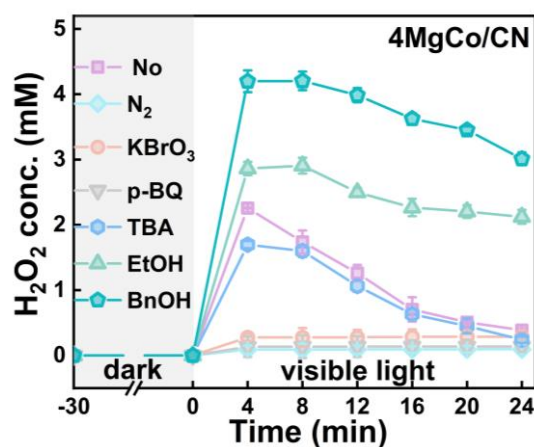


Fig. S22. H_2O_2 generation by 4MgCo/CN DSACs in the PMS/vis/CBZ system with different scavengers.

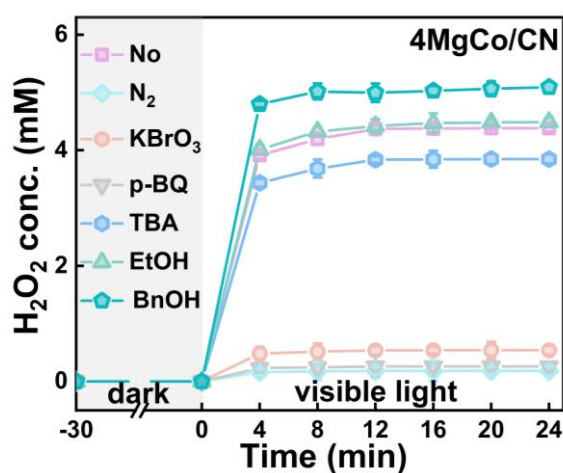


Fig. S23. H_2O_2 generation by 4MgCo/CN DSACs in the PMS/vis system with different scavengers.

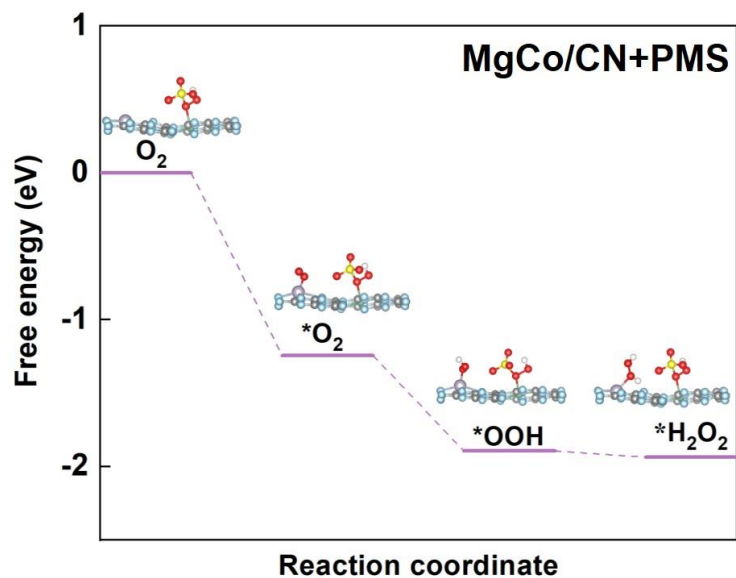


Fig. S24. Free energy curve of oxygen reduction for H_2O_2 generation by MgCo/CN DSACs in the presence of PMS.

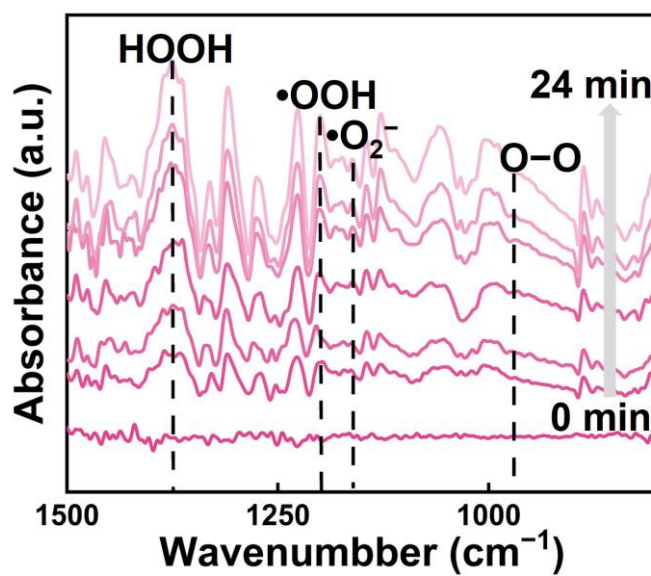


Fig. S25. The *in-situ* DRIFTS spectra of 4MgCo/CN DSACs in the PMS/vis system.

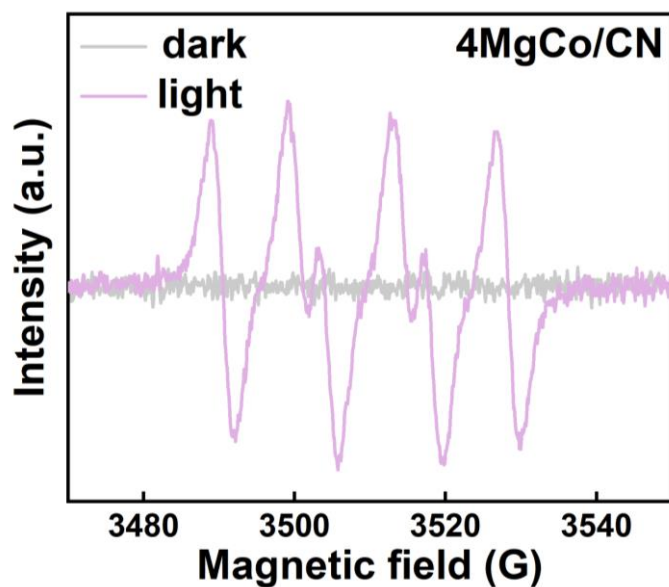


Fig. S26. The ESR spectra of $\bullet\text{O}_2^-$ by 4MgCo/CN DSACs with/without light irradiation.

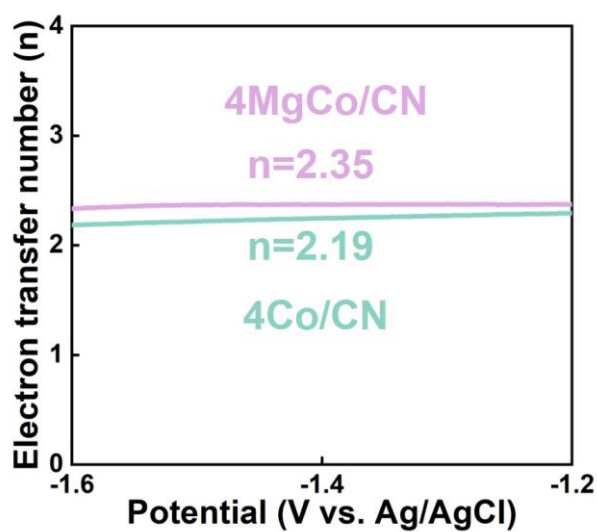


Fig. 3. (c) The average electron transfer number (n) varied systematically with applied potential.

References in this fifth response to reviewer 3:

1. Peng, X. et al. Synergy of triphase interface engineering and electronic modulation of carbon nitride networks for continuous-flow photosynthesis of H_2O_2 . *Adv. Funct. Mater.* **36**, e22655 (2025).

2. Deng, Y. et al. Reduction of superoxide radical intermediate by polydopamine for efficient hydrogen peroxide photosynthesis. *Angew. Chem. Int. Ed.* **63**, e202319216 (2024).

3. Wang, L. et al. Overlooked formation of H₂O₂ during the hydroxyl radical scavenging process when using alcohols as scavengers. *Environ. Sci. Technol.* **56**, 3386–3396 (2022).

4. Yang, J. et al. Homologous heteropolyaromatic covalent organic frameworks for enhancing photocatalytic hydrogen peroxide production and aerobic oxidation. *Nat. Commun.* **16**, 7654 (2025).

5. Xue, Z. et al. Sacrificial-agent-triggered mass transfer gating in covalent organic framework for hydrogen peroxide photocatalysis. *Adv. Mater.* **37**, e10201 (2025).

6. Wang, Y. et al. Facile construction of fully conjugated benzotriazole-based covalent organic frameworks for efficient photocatalytic H₂O₂ production. *Adv. Funct. Mater.* **35**, 2508550 (2025).

7. Bai, X. G. et al. Halogen engineering in supramolecular halogen-bonded organic frameworks enables efficient photocatalytic hydrogen peroxide production. *Adv. Funct. Mater.* **36**, e27110 (2026).

6. The authors attribute the enhanced PMS activation to the interaction between Mg–Co diatomic sites based on the appearance of a new Raman peak at 815.7 cm⁻¹. However, this peak appears to be extremely weak and close to the noise level. More solid evidence is required.

Response:

We are very sorry for our mistake. Previously, improper operation of the instrument resulted in an extremely weak signal for the new Raman peak at 815.7 cm^{-1} . To more clearly exhibit the appearance of the new Raman peak, we re-measured the Raman spectra. Fig. S15 showed that a new Raman peak at 815.7 cm^{-1} emerged after a 3-min reaction between 4MgCo/CN and PMS. After 5-min reaction, the intensity of this new Raman peak obviously increased. To more clearly exhibit the new Raman peak, we have added some descriptions in our revised manuscript (line 217-221, page 12):

Furthermore, in the *in-situ* Raman spectra of 4MgCo/CN DSACs, a new peak appeared at 815.7 cm^{-1} after a 3-min reaction, and its intensity became more pronounced after 5 min, whereas this peak was absent in the *in-situ* Raman spectra of 4Co/CN SACs (Figs. S15 and S16)⁵⁰. This indicated that the interaction between MgCo dual atoms contributed to PMS activation.

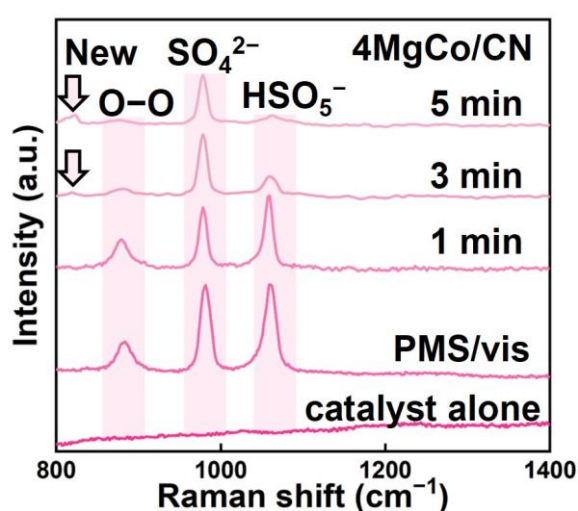


Fig. S15. *In-situ* Raman of 4MgCo/CN DSACs with PMS at different reaction time.

7. The manuscript concludes that the dynamically tailored Co d orbitals to break the activity-stability trade-off, but lacks sufficient evidence to support this conclusion. In situ XPS evidence is limited to Co²⁺ ratio variations.

Response:

We are very sorry for our mistake. We did not provide sufficient evidences to support the conclusion that dynamically tailored Co d orbitals to break the activity-stability trade-off, and the in-situ XPS data alone for Co²⁺ ratio variation was indeed limited in previous manuscript. To rigorously address this concern, we have added substantial theoretical and experimental evidences linking OH_{surf}-mediated dynamic tailoring of Co d orbitals to both enhanced activity and stability. The details were as follows:

(i) Theoretical evidences for the dynamic tailoring of Co d orbitals by OH_{surf}

First, we evaluated the d-band center of MgCo/CN DSACs with varying amounts of OH_{surf} (Fig. S34). The d-band center first shifted toward the Fermi energy level (from -0.88 to -0.69 eV) as the amount of OH_{surf} increased from one to three, and then shifted away from the Fermi level when the amount of OH_{surf} further increased from three to four.

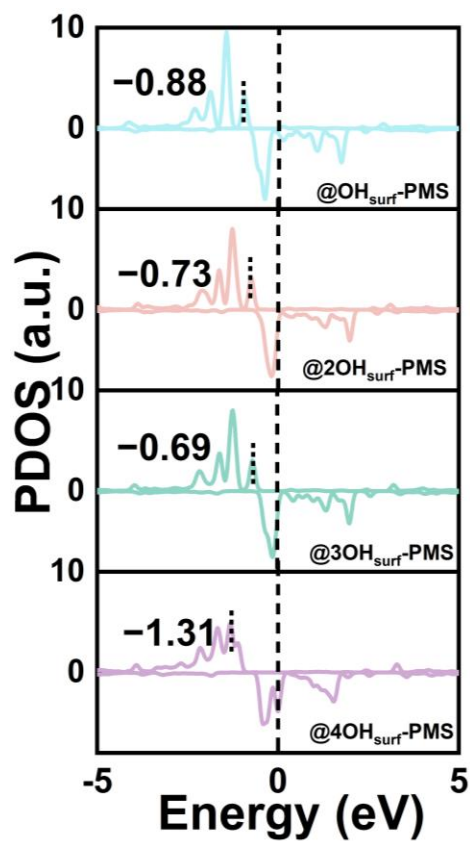


Fig. S34. The d-band center of Co site in MgCo/CN DSACs with different amounts of OH_{surf} .

Second, we examined the valence electron density of the Co site in MgCo/CN DSACs with different OH_{surf} amounts (Fig. S37). The valence electron densities were 5.09 e, 5.53 e, 6.05 e, and 5.65 e as OH_{surf} increased, indicating that appropriate OH_{surf} adsorption on the Mg site modulated the electron density of Co site via long-range interaction.

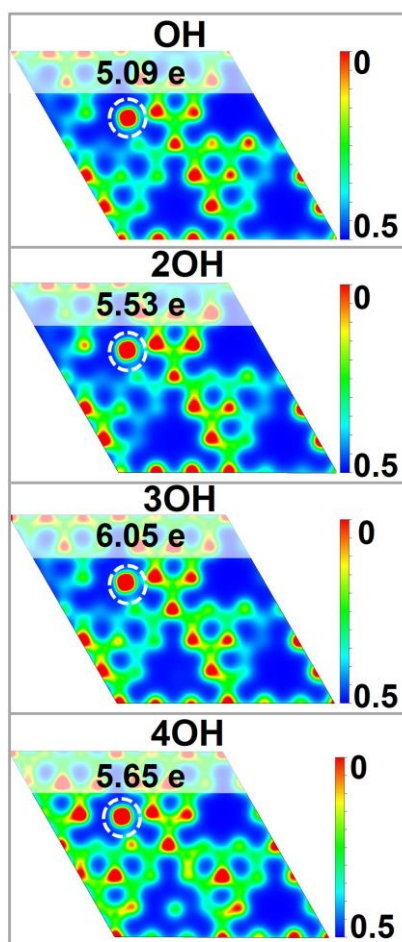


Fig. S37. Valence electron densities of Co sites in MgCo/CN DSACs with different amounts of OH_{surf}.

Finally, we correlated the d-band center with PMS adsorption energy, electron transfer between catalyst and PMS, and the O–O and O–H bond lengths of PMS. Fig. S36 showed the strong linear correlations between the d-band center and PMS adsorption ($R^2 = 0.9992$), electron transfer ($R^2 = 0.9326$), and O–O bond length ($R^2 = 0.9948$), but a weak correlation with O–H bond length ($R^2 = 0.5162$). These results indicated that OH_{surf}-modulated d-band center facilitated PMS adsorption and activation.

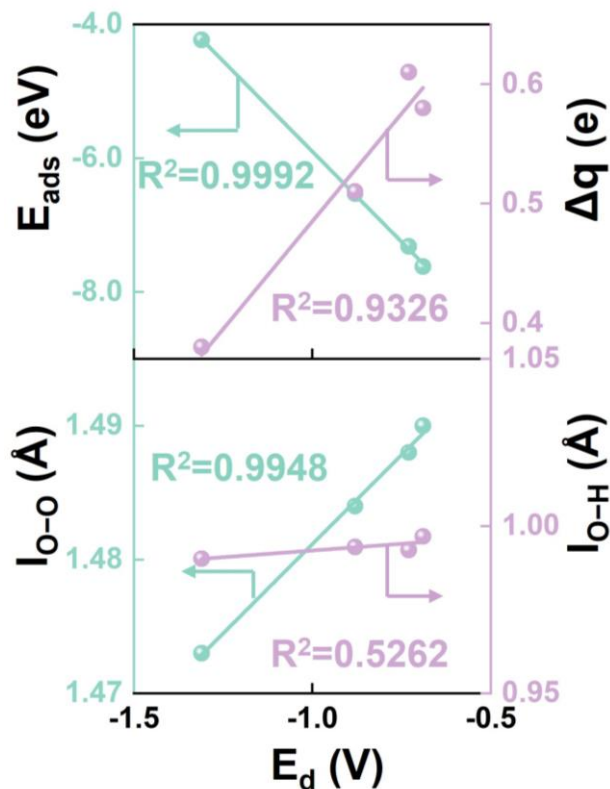


Fig. S36. Relationship among E_{ads} , Δq , E_d , $I_{\text{O-O}}$ and $I_{\text{O-H}}$ with Co d-band center of MgCo/CN DSACs with different amounts of OH_{surf} .

(ii) Experimental evidences for breaking the activity-stability trade-off via d-orbital tailoring

First, we characterized the 4MgCo/CN DSACs after different reaction time using electron paramagnetic resonance (EPR) spectroscopy, electrochemical impedance spectroscopy (EIS), and electrochemical active surface area (ECSA) measurements to track electronic change following the modulation of the d-band center. The EPR spectra (Fig. S38) showed that the EPR signal at $g=2.30$ for 4MgCo/CN DSACs intensified with increasing reaction time, indicating a gradual increase in unpaired electrons. The EIS results (Fig. S39) revealed that the radius decreased markedly as the reaction proceeded, suggesting a remarkable enhancement in electron transfer

performance. Furthermore, the increased C_{dl} value in the ECSA of 4MgCo/CN DSACs over reaction time (Fig. S40) demonstrated a rise in active site density, which facilitated the electron participation in the reaction.

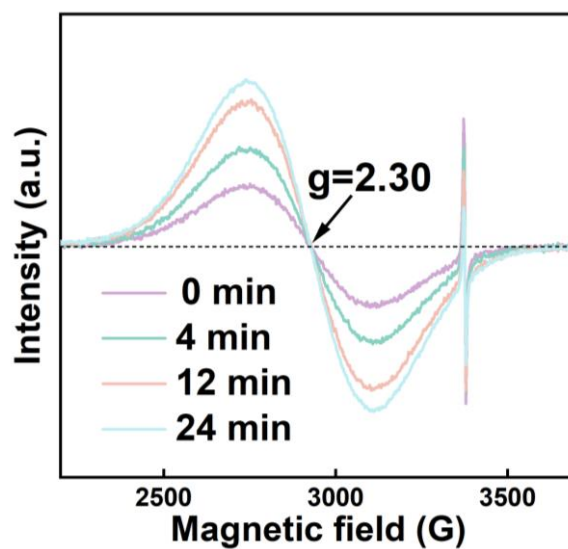


Fig. S38. EPR spectroscopy of MgCo/CN DSACs after different reaction time.

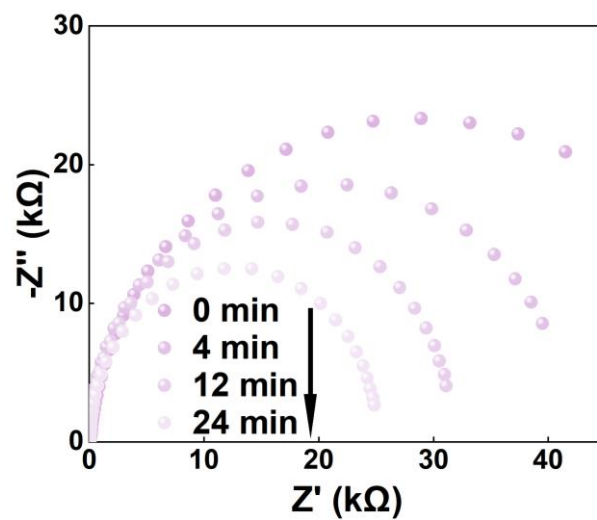


Fig. S39. EIS of MgCo/CN DSACs after different reaction time.

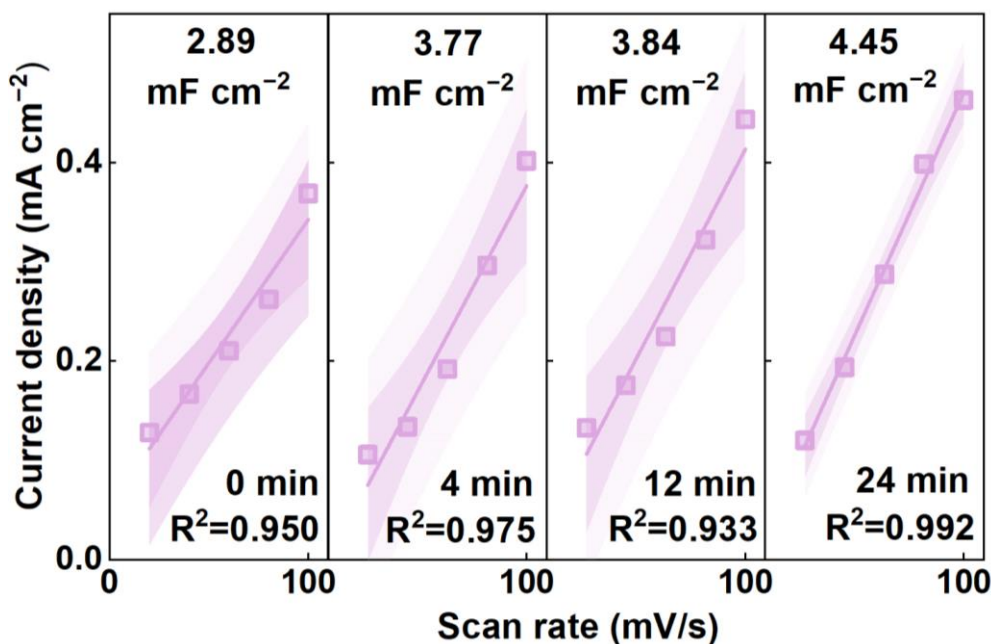


Fig. S40. ECSA of 4MgCo/CN DSACs after different reaction time.

Second, we compared the Co *K*-edge XANES spectra of 4MgCo/CN DSACs before and after the reaction. As shown in Fig. S41, the Co *K*-edge shifted negatively after the reaction compared to that before the reaction, indicating a reduction in the Co oxidation state of 4MgCo/CN DSACs after reaction. The LCF was performed to further evaluate the variation of Co species and valence state in the 4MgCo/CN DSACs before and after the reaction (Figs. S2 and S42, Tables S1 and S8). The proportions of Co⁰, Co²⁺ and Co³⁺ in the 4MgCo/CN DSACs before the reaction were 40.6%, 28.7%, and 30.7%, respectively, while the proportions of Co⁰, Co²⁺ and Co³⁺ in the 4MgCo/CN DSACs after the reaction were 36.6%, 63.4% and 0%, respectively. Based on the results of LCF, the Co valence state in the 4MgCo/CN DSACs after the reaction was 1.27, which was lower than that in the 4MgCo/CN DSACs before the reaction (1.50) (Figs. 1f and S43). This observation was consistent with the increased Co²⁺ ratio as the reaction proceeded from 0 to 24 min (Fig. 4i).

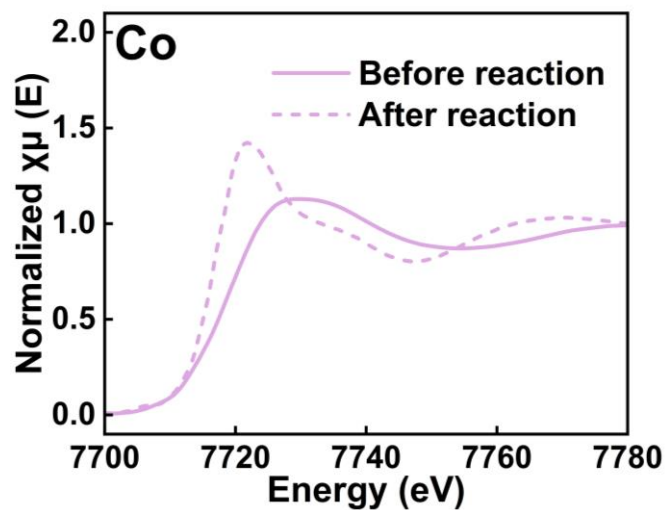


Fig. S41. The Co K-edge spectra of 4MgCo/CN DSACs before and after reaction.

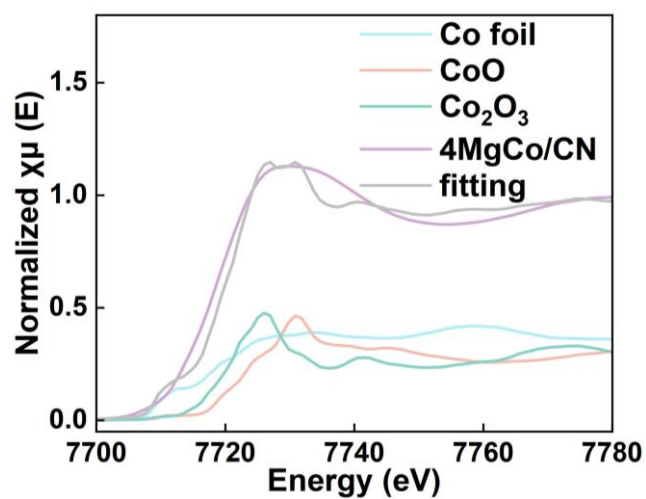


Fig. S2. The linear combination fitting result for 4MgCo/CN DSACs.

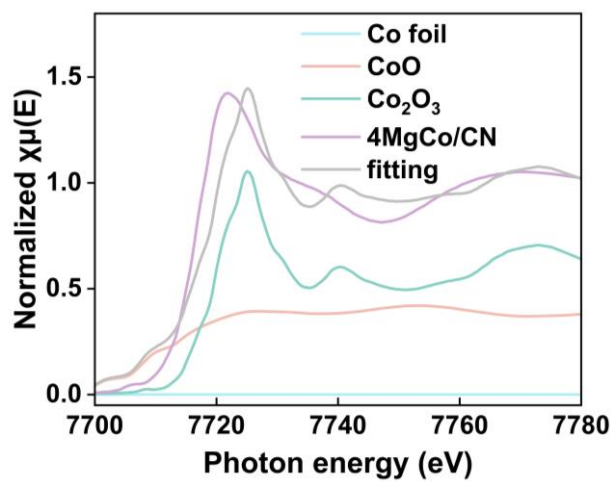


Fig. S42. The linear combination fitting result for 4MgCo/CN DSACs after reaction.

Table S1. Linear combination fitting for Co in 4MgCo/CN.

Standard	Weight	E ₀
Co foil	0.406 (0.000)	0.000 (0.000)
CoO	0.287 (0.000)	0.000 (0.000)
Co ₂ O ₃	0.307 (0.000)	0.000 (0.000)

R-factor = 0.0208785

Chi-square = 0.26227

Reduced chi-square = 0.0025463

Table S8. Linear combination fitting for Co in 4MgCo/CN after reaction.

Standard	Weight	E ₀
Co foil	0.366 (0.000)	0.000 (0.000)
CoO	0.634 (0.000)	0.000 (0.000)
Co ₂ O ₃	0.000 (0.000)	0.000 (0.000)

R-factor = 0.0769077

Chi-square = 2.41810

Reduced chi-square = 0.0144797

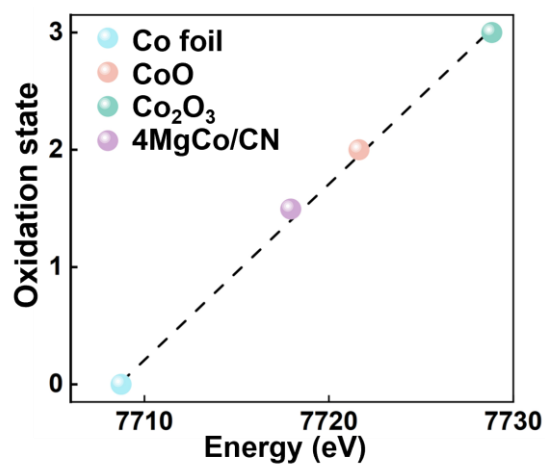


Fig. 1. (f) corresponding oxidation state of Co species in 4MgCo/CN DSACs.

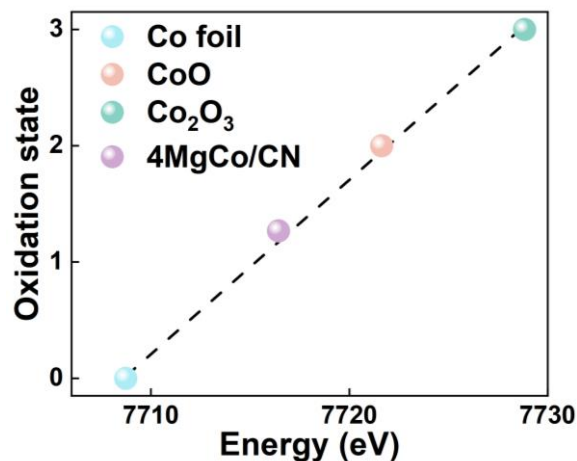


Fig. S43. The oxidation state of Co species in 4MgCo/CN DSACs after reaction.

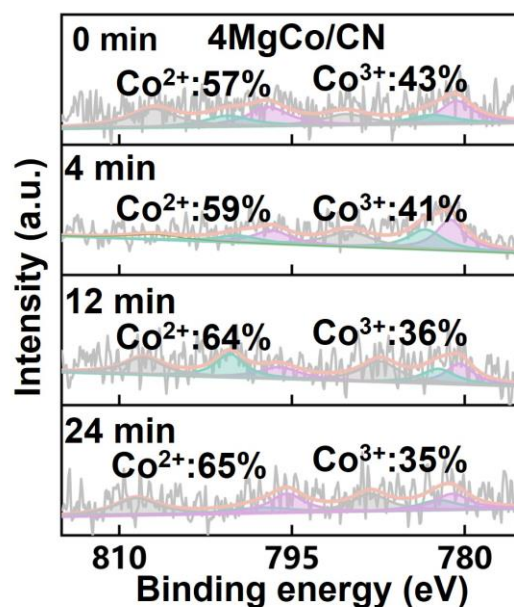


Fig. 4. (i) *in-situ* Co 2p XPS spectra of 4MgCo/CN as reaction proceed.

Finally, we evaluated the degradation efficiency of BA and the activation efficiency of PMS after the addition of varying dosages of NaF to analyze the effect of NaF on PMS activation and $\bullet\text{SO}_4^-$ generation. Figs. 3h and S28 showed that the degradation efficiency of BA and the activation efficiency of PMS were reduced by 48.5% and 59.3% after the addition of 9.0 mM NaF, respectively. The degradation efficiencies of CBZ by 4MgCo/CN DSACs after the addition of 9.0 mM NaF and 9.0

mM CAT were reduced by 5.35% and 3.8%, respectively, over 30 cycles. The Co dissolution concentration in the 4MgCo/CN DSACs/PMS/vis system with NaF and CAT exceeded 0.85 mg/L and 0.83 mg/L, which was much higher than that in the system without scavengers (0.43 mg/L) (Figs. S44 and S45).

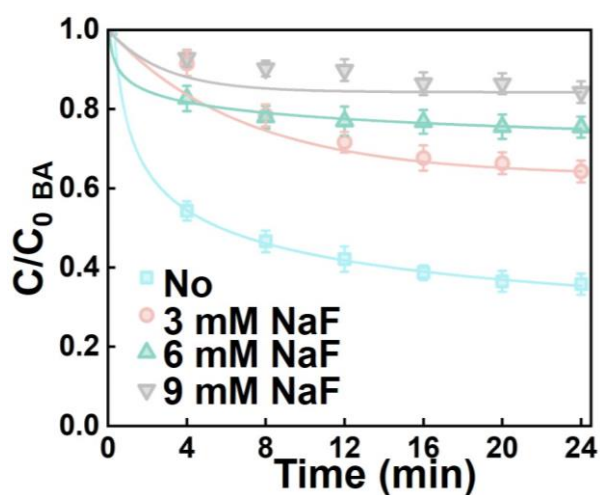


Fig. 3. (h) Degradation of BA by 4MgCo/CN DSACs with different NaF dosages.

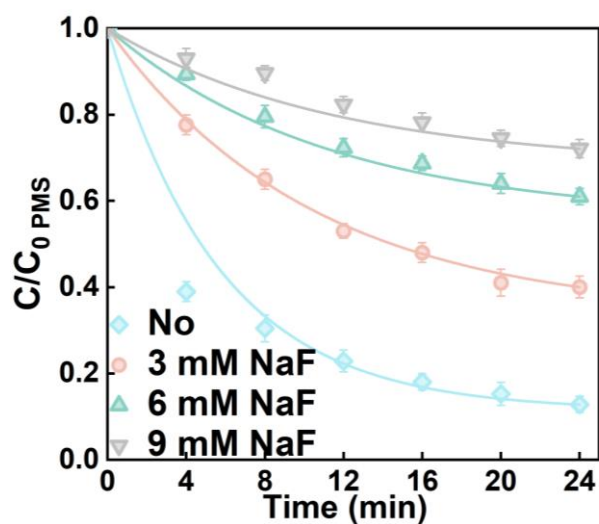


Fig. S28. PMS activation by 4MgCo/CN DSACs with different dosages of NaF.

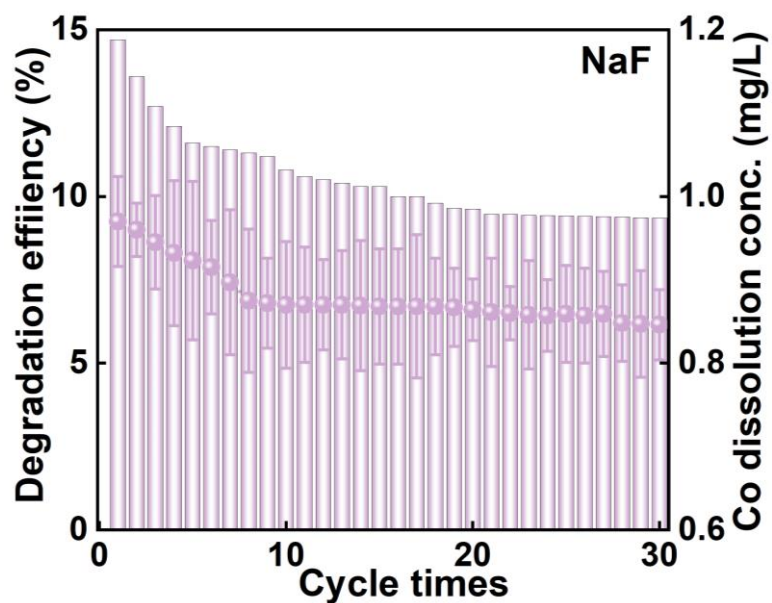


Fig. S44. Degradation of CBZ by 4MgCo/CN DSACs after the addition of NaF over 30-time cycles in the PMS/vis system.

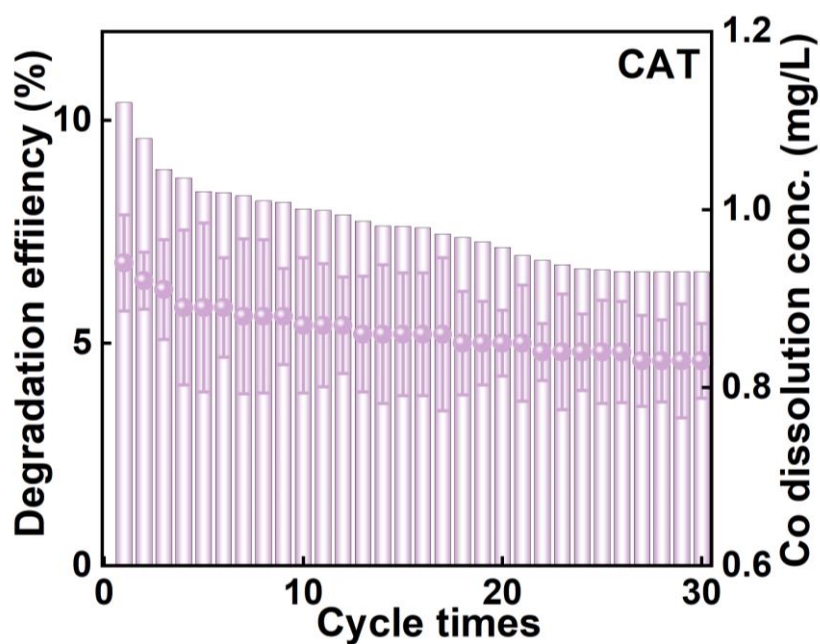


Fig. S45. Degradation of CBZ by 4MgCo/CN DSACs after the addition of CAT over 30-time cycles in the PMS/vis system.

The combined theoretical and experimental results demonstrated that OH_{surf} dynamically tailored the Co d orbitals to break the activity-stability trade-off. The corresponding descriptions have also been added into our revised manuscript (line

283-286, page 15; line 352-369, page 19; line 370-391, page 20; line 392-398, page 21):

The degradation efficiency of BA decreased with increasing NaF concentration, and it was remarkably reduced from 64.2% to 15.7% after the addition of 9.0 mM NaF (Fig. 3h). The activation efficiency of PMS was also reduced from 87.2% to 27.9% with increasing NaF concentration from 0 to 9 mM (Fig. S28).

Fig. S34 exhibited that the Co d-band center obviously shifted as the amount of OH_{surf} varied. Figs. S35 and S36 showed the strong correlations among the d-band center with PMS adsorption energy ($R^2 = 0.9992$), electron transfer charge ($R^2 = 0.9326$), and O–O bond length ($R^2 = 0.9948$), but a weak correlation with O–H bond length ($R^2 = 0.5162$). These results indicated that OH_{surf}-modulated d-band center facilitated PMS adsorption and activation into $\bullet\text{SO}_4^-$. Moreover, the valence electron densities of Co sites were 5.09 e, 5.53 e, 6.05 e, and 5.65 e as the amount of OH_{surf} increased (Fig. S37), indicating that appropriate OH_{surf} adsorption on the Mg site modulated the electron density of the Co site via long-range interaction.

To track electronic change following the modulation of the d-band center, we performed electron paramagnetic resonance (EPR) spectroscopy, electrochemical impedance spectroscopy (EIS), ECSA measurement and Co K-edge XANES spectra by the 4MgCo/CN DSACs after reaction, respectively. The EPR spectra (Fig. S38) showed that the EPR signal at $g = 2.30$ for 4MgCo/CN DSACs intensified with increasing reaction time, indicating a gradual increase in unpaired electrons. The EIS results (Fig. S39) exhibited that the radius decreased markedly as the reaction

proceeded, suggesting a remarkable enhancement in electron transfer performance. Furthermore, the increased C_{dl} value in the ECSA of 4MgCo/CN DSACs over reaction time (Fig. S40) demonstrated a rise in active site density, which facilitated the electron participation in the reaction. As shown in Fig. S41, the Co K -edge shifted negatively after the reaction compared to that before the reaction, indicating a reduction in the oxidation state of Co in the 4MgCo/CN DSACs after reaction. Based on the LCF results, the proportion of Co^{2+} species in the 4MgCo/CN DSACs increased from 28.7% before reaction to 63.4% after reaction (Figs. S2 and S42, Tables S1 and S8), while the average Co oxidation state decreased from 1.50 to 1.27 (Figs. 1f and S43). This observation was supported by the increased Co^{2+} ratio as the reaction proceeded from 0 to 24 min in the 4MgCo/CN DSACs/PMS/vis system, as shown by *in-situ* XPS spectra (Fig. 4i).

The degradation efficiencies of CBZ by 4MgCo/CN DSACs after the addition of NaF and CAT were reduced by 5.35% and 3.8%, respectively, over 30 cycles. The Co dissolution concentration in the 4MgCo/CN DSACs/PMS/vis system with NaF and CAT exceeded 0.85 mg/L and 0.83 mg/L, which was much higher than that in the system without scavengers (0.43 mg/L) (Figs. S44 and S45). These results indicated that OH_{surf} from H_2O_2 contributed to enhancing stability in the 4MgCo/CN DSACs/PMS/vis system. In summary, the dynamic domino catalysis process in overcoming the activity-stability trade-off during water purification was as follows: Under visible light irradiation, photogenerated electrons drove a two-electron oxygen reduction reaction at the Mg site, enabling the *in-situ* generation of H_2O_2 . The

as-formed H_2O_2 was subsequently converted to OH_{surf} via the Mg site. These OH_{surf} leveraged the π -conjugated delocalized network of carbon nitride to modulate the d-orbital configuration of non-adjacent Co atom through long-range interaction, enabling the shift of energy levels for d_{xy} , $d_{x^2-y^2}$, d_{xz} , d_z^2 and d_{yz} orbitals to lower energy levels⁵⁵⁻⁵⁷. On the one hand, this promoted the reduction of Co^{3+} to Co^{2+} , thereby accelerating $\bullet\text{SO}_4^-$ generation during PMS activation for enhanced activity. On the other hand, it reduced the adsorption energy of *SO_4 , optimizing its desorption process and preventing Co atom detachment to maintain stability.

Response Letter

Here below is our description on revision according to the reviewers' comments.

Responses to the reviewers

We appreciate the reviewers' positive and constructive comments. In this file, we respond to each comment point-by-point in detail. We copy and paste the original comments in black italic type, each comment is followed by our response in indent and blue normal font. In addition, revised portions are also marked blue in our revised manuscript. We show all changes we made in the manuscript by quoting and shading the revised words. We also highlight the added words with highlighted line numbers in the marked manuscript file.

To reviewer 3

The reviewer's comment:

Reviewer #3: I appreciate the authors' efforts to address most of my previous concerns. Nevertheless, upon examining the revised data, several aspects of their structural analysis remain unsatisfactory, and I cannot recommend publication in the current form. The authors are advised to perform more rigorous data analysis to ensure data reproducibility and reliability, particularly given the high standards required for publication in Nature Communications.

1. The authors claim the formation of Co–Mg dual-atom pairs in the revised manuscript. However, insufficient experimental evidence is provided to validate this conclusion. (1) Single-atom dispersion shown in the STM images appears randomly distributed, and the selected dual-atom configurations are chosen arbitrarily. Additional STEM images with both high and low magnifications should be supplemented in the SI, alongside detailed descriptions of the corresponding statistical analysis protocols. (2) No solid evidence is available to unambiguously distinguish Co and Mg sites within the proposed paired configurations, even assuming such dual sites exist. It remains unclear why Co and Mg atoms preferentially aggregate with one another. The authors must supply convincing evidence to rule out homonuclear pairing configurations including CoN₄–CoN₄ and MgN₄–MgN₄.

Response:

(1) We are very sorry that we haven't described clearly in the previous manuscript. We have supplemented the STEM images with both high and low

magnifications in the Fig. S2 of our revised manuscript and added detailed descriptions of the corresponding statistical analysis protocols in Supplementary Method 2 of our revised manuscript. In fact, the dual single atoms were defined as two atoms that exhibited mutual electronic interaction. To establish a rigorous criterion for identifying such dual single atoms, we adopted the net electron difference evaluation method via density functional theory (DFT) calculation (Fig. S8), as previously reported in the literature¹. Specifically, we embedded Mg and Co atoms into two distinct cavities of the tri-s-triazine framework in graphitic carbon nitride (CN), where they coordinated with the N atom of support. According to the position of cavity, we constructed two typical MgCo/CN dual single atom catalyst models with different interatomic distances as dMgCo-6.48 Å and dMgCo-11.91 Å, respectively (Fig. S9). The results showed that the net electron difference of Mg and Co was 0.11e and 0.25e for the dMgCo-6.48 Å exhibited a distinct electronic interaction between the Mg and Co atoms. In contrast, the net electron difference of Mg and Co was negligible for the dMgCo-11.91 Å and almost identical to those of the sMg and sCo models. These results confirmed a interatomic distance threshold of 11.91 Å for distinguishing interacting dual single atoms from non-interacting single atom. Therefore, all the dual single atomic distances we marked were smaller than this threshold in the STEM images.

For the reliable statistical analysis, we collected signals from more than 200 atoms in the STEM images with both high and low magnifications. We applied the kernel method of frequency statistics combined with Gauss fitting to analyze the

interatomic distances (Fig. S2). To ensure valid statistics, we restricted atomic distance evaluation to the thin regions, obtained by ion beam thinning, where atoms could be easily counted.

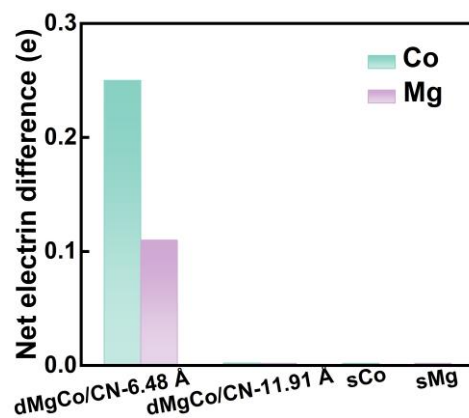


Fig. S8. Net electron difference of Mg and Co in different catalysts.

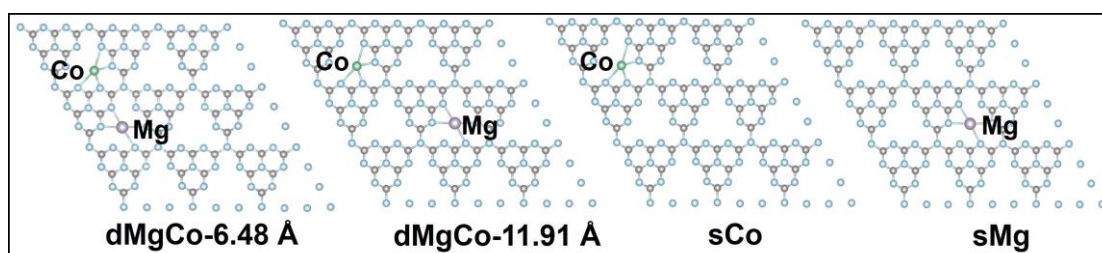


Fig. S9. Different catalyst modes for net electron difference evaluation.

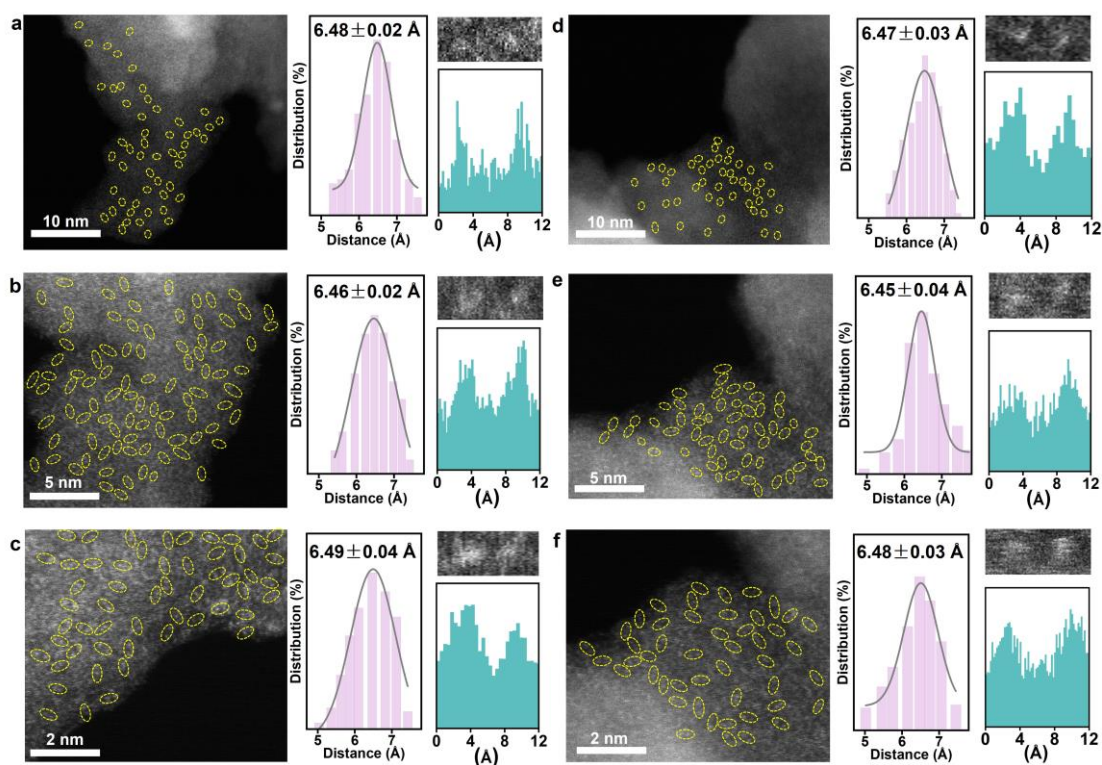


Fig. S2. The AC HAADF-STEM images of 4MgCo/CN DSACs with different magnifications at different regions and corresponding atomic distance distribution, respectively.

Supplementary Method 2. The statistical analysis protocols for dual single atoms

Histogram of the observed atomic distance of 4MgCo/CN DSACs obtained by the kernel method of frequency statistic and Gauss fitting of dual single atom distances. In an attempt to increase the reliability, we collected the interatomic distance from more than 200 atoms in STEM images with both high and low magnifications, all of which were below 11.91 Å, a threshold distance for non-interacting dual single atoms. To ensure valid statistics, we restricted our atomic distance evaluation to the thin regions, obtained by ion beam thinning, where atoms could be easily counted.

(2) We are very sorry that we haven't described clearly in the previous manuscript. To fully address your concern, we have added a series of experimental and theoretical evidences. The details were as follows.

Formation mechanism: During the synthesis, Mg^{2+} and Co^{2+} ions were first electrostatically enriched on the negatively charged CN, then embedded into the cavities of tri-s-triazine framework, where they coordinated with the lone-pair electrons of pyridinic N atom. This above process ensured the stable incorporation of Mg and Co atoms into the tri-s-triazine framework of CN.

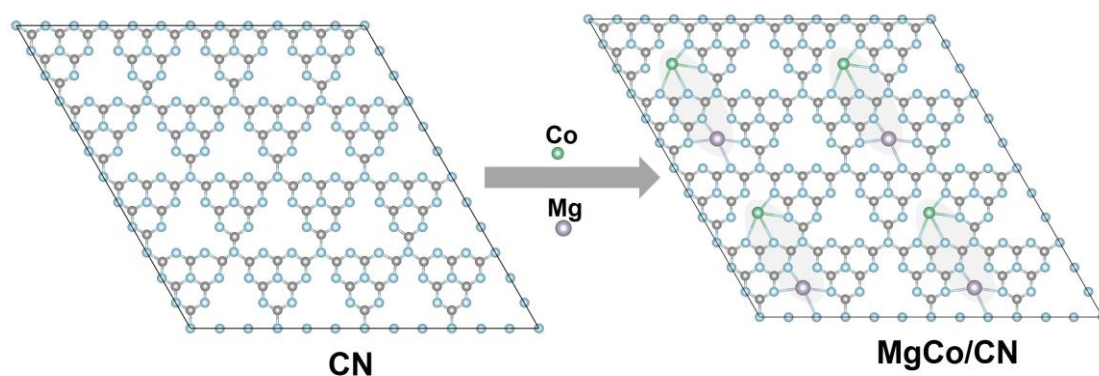


Fig. 1. The coordination process for Mg and Co into CN.

Distance determination: According to the Gauss fitting results of the dual-single-atom distance derived from the STEM images with both high and low magnifications at different regions, the dominant interatomic distance of MgCo dual single atoms ranged from 6.41 Å to 6.53 Å (Fig. S2). This distance matched well with the 6.48 Å atomic distance of MgCo in the simulated MgCo/CN model, where Mg and Co were coordinated as Mg-N_4 and Co-N_4 without any direct Mg–Co bond (Fig. 2).

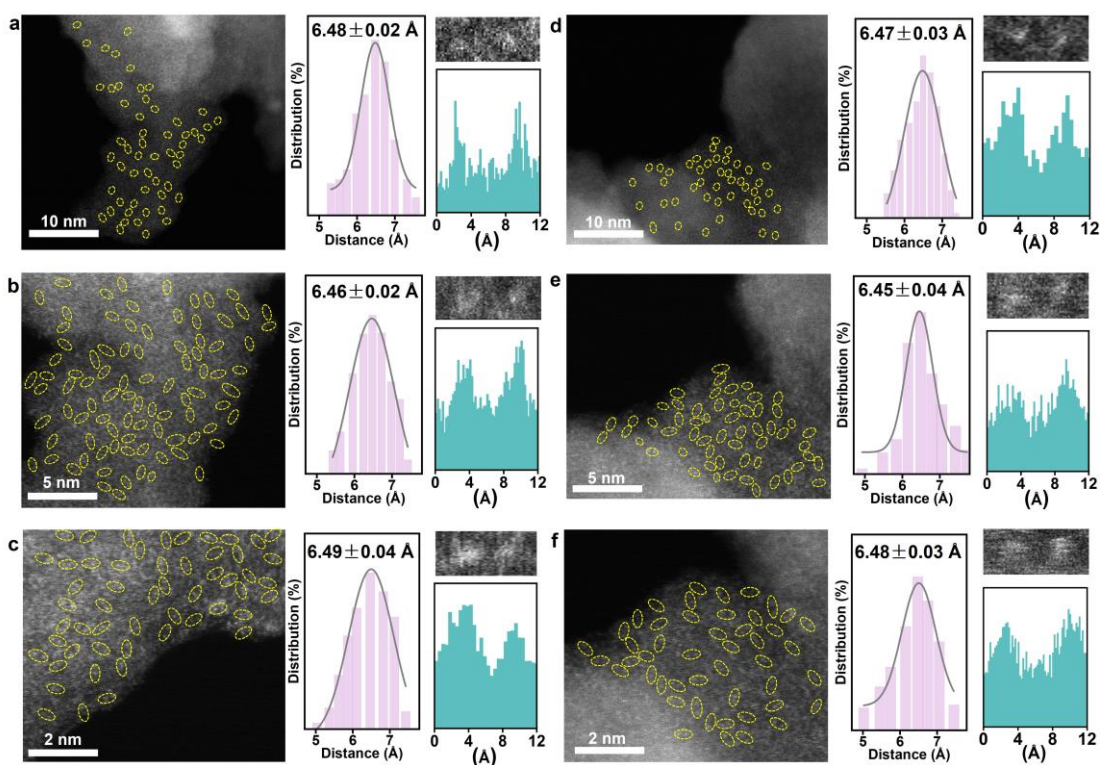


Fig. S2. The AC HAADF-STEM images of 4MgCo/CN DSACs with different magnifications at different regions and corresponding atomic distance distribution, respectively.

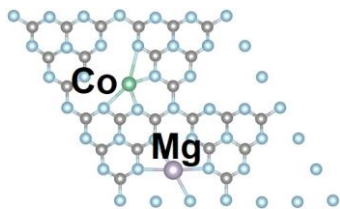


Fig. 2. The MgCo/CN dual single atom catalyst mode.

Thermodynamic preference: To rule out homonuclear pairing configurations including $\text{CoN}_4\text{--CoN}_4$ and $\text{MgN}_4\text{--MgN}_4$, we calculated the formation energies of different configurations for MgCo/CN (without Mg–Co bond and with Mg–Co bond), CoCo/CN (without Co–Co bond and with Co–Co bond), and MgMg/CN (without Mg–Mg bond and with Mg–Mg bond), respectively (Fig. S7). The results showed that the MgCo/CN (without Mg–Co bond) possessed the most negative formation energy

(−0.75 eV), significantly lower than those of other models. This demonstrated that, thermodynamically, heteronuclear Mg and Co dual single atoms strongly preferred to be embed independently into the cavities of CN without forming homonuclear ones, and they favored a separated configuration without Mg–Co bond over a bonded one.

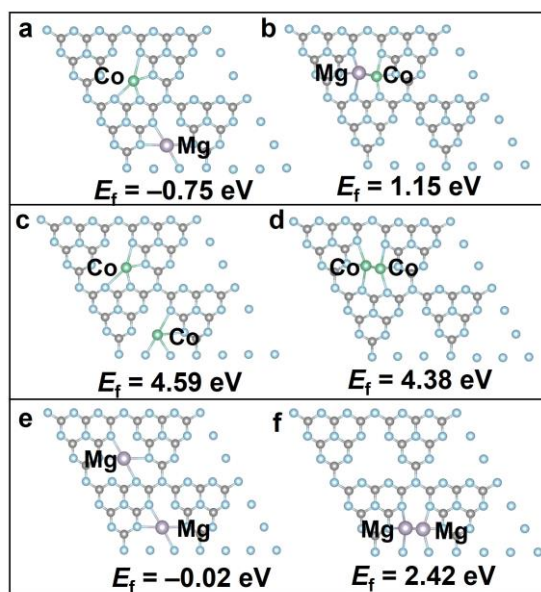


Fig. S7. The formation energies for different catalysts.

Exclusion of metal-metal bond: We further compared the FT k^3 -weighted Co and Mg *K*-edge EXAFS spectra of 4MgCo/CN DSACs with various standard samples (Figs. S5 and S6). The spectra clearly showed no Co–Co or Mg–Mg scattering paths in the 4MgCo/CN DSACs. The similar heteronuclear dual single atom configuration without M–M bond has also been reported in previous work²⁻⁴.

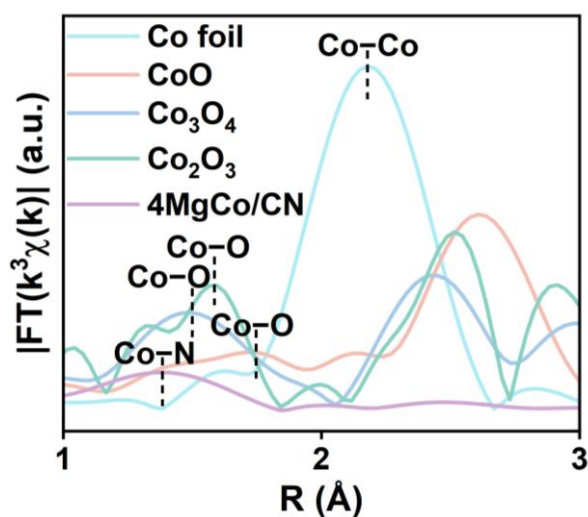


Fig. S5. FT k^3 -weighted Co K -edge EXAFS spectra of 4MgCo/CN DSACs.

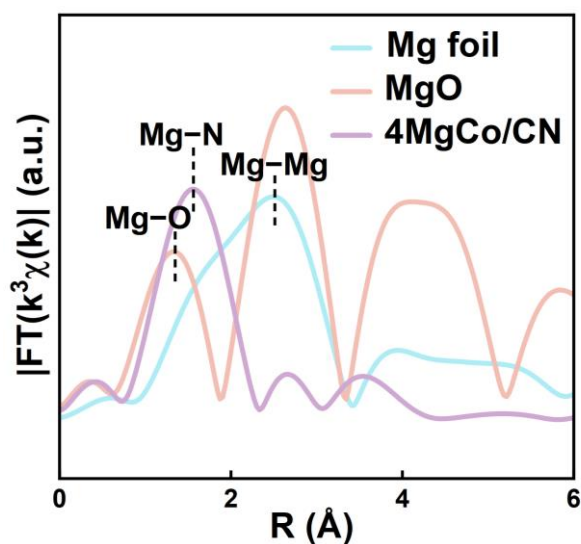


Fig. S6. FT k^3 -weighted Mg K -edge EXAFS spectra of 4MgCo/CN DSACs

References in this first response to reviewer 3:

1. Yao, D. Z. et al. Inter-metal interaction with a threshold effect in NiCu dual-atom catalysts for CO₂ electroreduction. *Adv. Mater.* **35**, 2209386 (2023).
2. Lian, Z. C. et al. Spatial decoupling of adsorption and transformation sites on Ag-Cu dual-single-atom catalysts for highly selective photocatalytic nitrate-to-ammonia reduction. *Angew. Chem. Int. Ed.* **65**, e202516964 (2026).

3. Hafijul I. et al. Pa atomic-level synergy of dual single-atom catalysts for photocatalytic hydrogen evolution reaction. *Small*, **0**, e74100 (2026).

4. Lian, Z. C. et al. Photo-self-Fenton reaction mediated by atomically dispersed Ag. *Angew. Chem. Int. Ed.* **63**, e202318927 (2024).

To more clearly demonstrate the coordination structure of 4MgCo/CN DSACs, we have added corresponding descriptions in our revised manuscript (line 98-99, 102-105, page 5; line 113-114, 116, 123-128, 130-131, page 6; line 132-139, page 7):

The heteronuclear magnesium cobalt dual single atom catalysts (MgCo/CN DSACs) were synthesized by a simple hydrothermal method (Fig. 1a). The MgCo/CN DSACs had a sparse and three-dimensional nanosheet structure in scanning electron microscope (SEM) (Fig. S1). The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) images with both high and low magnifications (Figs. 1b and S2) exhibited the bright dual single atoms in yellow dashed ellipses, indicating that the dual single atom structure was successfully synthesized. The energy-dispersive X-ray elemental spectra (EDS) mapping showed the coexistence of C, N, Mg and Co elements. The diffraction peak and functional group of CN were observed in the XRD patterns (Fig. 1c) and FT-IR spectra (Fig. 1d)¹⁸, whereas no diffraction peaks of cobalt oxides were evident in the former, nor were any signals of their functional groups detected in the latter. The Co and Mg K-edge X-ray absorption near-edge structure (XANES) spectra (Figs. 1e and 1h) showed that the absorption edge of Co lay between those of Co foil and CoO, while that of Mg lay between those of Mg foil and MgO, but closer to Mg foil. This

indicated that the oxidation states of both Co and Mg in the 4MgCo/CN DSACs ranged between 0 and +2, yet they differed from each other. The linear combination fitting (LCF) analysis (Figs. S3, S4 and Tables S1, S2) was performed to quantify the proportions of different Co and Mg species with R-factor of 0.0078 and 0.0185, respectively. The proportions of Co⁰, Co²⁺ and Co³⁺ were 25.1%, 32.4%, and 42.5%, respectively, while those of Mg⁰ and Mg²⁺ were 77.6% and 22.4%, respectively. Based on the LCF results, the average oxidation states of Co and Mg in the 4MgCo/CN DSACs were estimated to be 1.923 and 0.448, respectively (Figs. 1f and 1i). Fourier transformed (FT) k³-weighted X-ray absorption fine structure (EXAFS) spectra of 4MgCo/CN DSACs (Figs. S5 and S6), the peaks corresponding to Co–N at 1.48 Å and Mg–N at 1.68 Å were observed^{19,20}. No peaks attributable to Co–Co, Co–O, Mg–Mg and Mg–O bonds were detected, suggesting the absence of metallic or oxide clusters. Additionally, no Mg–Co bond was observed in the EXAFS spectra of 4MgCo/CN DSACs, demonstrating that no direct bonding between Mg and Co atom. The formation energy of 4MgCo/CN without the Mg–Co bond was –0.75 eV, which was more negative than those of 4MgCo/CN with the Mg–Co bond (1.15 eV), CoCo/CN without (4.59 eV) and with (4.38 eV) the Co–Co bond, and MgMg/CN without (–0.02 eV) and with (2.42 eV) the Mg–Mg bond. This indicated that the 4MgCo/CN without the Mg–Co bond configuration was thermodynamically more favorable to form (Fig. S7). Based on the FT-EXAFS fitting results in R-space (Figs. 1g and 1j, Tables S3 and S4), it was deduced that the coordination configurations of 4MgCo/CN DSACs were identified as Mg–N₄ and Co–N₄. We applied the kernel

method of frequency statistics combined with Gauss fitting to analyze the interatomic distances. We collected the interatomic distance from more than 200 atoms in STEM images, all of which were below 11.91 Å, a threshold distance for non-interacting dual single atoms, as determined by net charge difference calculation (Figs. S8 and S9). Quantitative intensity profile analysis (Figs. S2 and S10) exhibited that the predominant configuration consisted of MgCo dual single atoms, with the highest prevalence of interatomic distance ranging from 6.41 Å to 6.53 Å. This distance matched well with the 6.48 Å atomic distance of MgCo in the simulated MgCo/CN model, where Mg and Co adopt isolated N₄ coordination without Mg–Co bond. The same estimation method has been reported in previous work²¹. The spin states of the catalysts were characterized by electron paramagnetic resonance (EPR) spectra (Fig. S11) and temperature-dependent inverse magnetic susceptibility measurements (Fig. S12). These results collectively confirmed the successful synthesis of MgCo/CN DSACs featuring Mg–N₄ and Co–N₄ configurations without Mg–Co bond.

2. The 4MgCo spectrum presented in Figure 1e differs substantially from that in the previous revision, which cannot be ascribed to simple mislabeling. The authors need to clarify the underlying reason for this discrepancy. Such drastic variation raises serious concerns regarding the reproducibility of their measurements. Raw data from replicate experiments together with full details of data processing must be provided to substantiate the reliability of the reported results. Both Co₂O₃ and Co₃O₄ standard should be provided in the same plot.

Response:

(1) We sincerely thank the reviewer for raising this critical point and for the opportunity to clarify the issue. We apologize for any confusion caused by the inconsistency between the spectra in the previous and current version of Fig. 1e. We fully agree that such a discrepancy must be rigorously explained and supported with raw data and detailed processing procedures. We have carefully re-examined our data and identified three main factors that led to the observed differences:

Change in plotting range: In the previous revision, the main panel used an x-axis range of 7690–7800 eV and a y-axis range of –0.2 to 1.9 eV, while the inset had an x-axis range of 7707–7718 eV and a y-axis range of 0–0.4 eV. In the new Fig. 1e, we have adopted more appropriate ranges with x-axis of 7700–7780 eV and y-axis of –0.1 to 2.1 eV, while the inset had an x-axis range of 7706–7720 eV and a y-axis range of 0.05–0.5 eV to better display the absorption edge feature.

Sample mislabeling: In the previous submission, we inadvertently mislabeled the spectra of 4MgCo/CN and Co₃O₄. This error has been corrected in new Fig. 1e of our revised manuscript.

Energy calibration inconsistency: In the new Fig. 1e, we performed a more rigorous energy calibration using a Co foil reference. The energy axis was calibrated by setting the maximum of the first derivative of the Co *K*-edge absorption spectra of the foil to 7709 eV, which corrected any drift during data acquisition. This calibration step was not applied consistently in the previous version, leading to the difference of spectral feature.

To substantiate the reliability of the results, we have added raw data from replicate experiments into Nature Communications online manuscript submission system together with full details of data processing in our revised manuscript.

Supplementary Method 3. Process of X-ray absorption spectroscopy data

The raw X-ray absorption spectroscopy (XAS) data was processed using the Athena software package. Energy calibration was first performed using a Co foil reference, with the maximum of the first derivative of the Co *K*-edge absorption spectra (7709 eV) defined as the reference energy to correct for any energy drift during data acquisition. Subsequently, pre-edge background subtraction and post-edge normalization were carried out to remove non-structural contributions and normalize the absorption intensity, yielding normalized X-ray absorption near-edge structure (XANES) spectra for further analysis. For EXAFS analysis, the normalized $\chi(E)$ data were converted into $\chi(k)$ functions and weighted by k^3 to enhance the contribution of high-*k* oscillations. Subsequently, Fourier transformation was performed to convert the $\chi(k)$ data into *R*-space, providing information on the local coordination environment surrounding the absorbing atom. EXAFS fitting was carried out using the Artemis software package. The amplitude reduction factor (S_0^2) was determined from the corresponding reference sample and fixed during the fitting process. Structural parameters, including coordination number (CN), bond distance (*R*), Debye–Waller factor (σ^2), and energy shift (ΔE_0), were optimized by nonlinear least-squares fitting. In EXAFS fitting of metal foils and metal oxide standards, the coordination number was typically not treated as a free fitting parameter, instead, it

was fixed according to the known crystallographic structure. Only in the case of synthesized or unknown samples was the coordination number released and refined during fitting.

(2) Both Co_2O_3 and Co_3O_4 standard samples have been energy calibrated rigorously using a Co foil standard and provided in the Figs. 1e and S5 in our revised manuscript. The new Fig. 1e clearly showed that the absorption edge of Co lay between those of Co foil and CoO. This indicated that the oxidation state of Co in the 4MgCo/CN DSACs was between 0 and +2. Fig. S5 exhibited that Co–N bond existed in the 4MgCo/CN DSACs. No peaks attributable to Co–Co and Co–O bonds were detected in the 4MgCo/CN DSACs, suggesting the absence of metallic or oxide clusters.

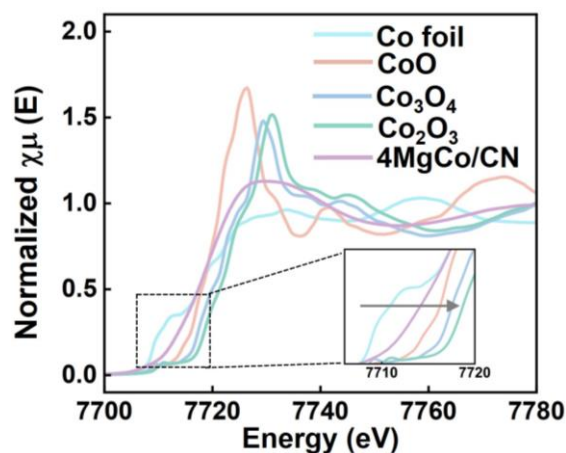


Fig. 1. (e) Normalized Co K-edge XANES spectra of Co species in 4MgCo/CN DSACs.

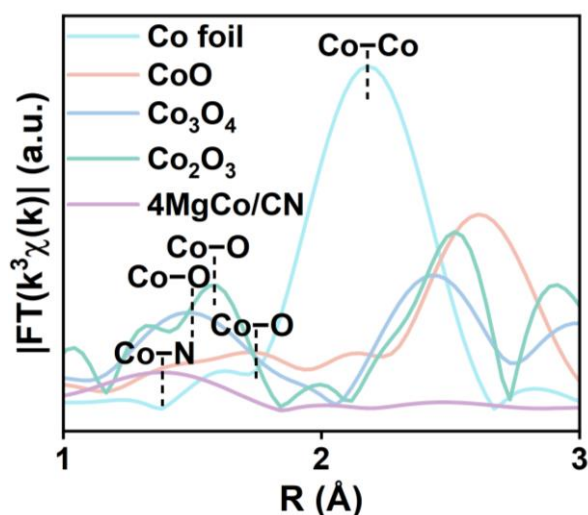


Fig. S5. FT k^3 -weighted Co K -edge EXAFS spectra of 4MgCo/CN DSACs.

3. In Table S3, Co-O and Co-N distance are very close. How could you differentiate CoN₄ rather than CoO₄ coordination. The fitting error for CN and R should be given.

Response:

(1) We are very sorry that we haven't described clearly in the previous manuscript. The Co-O bond lengths for CoO, Co₂O₃ and Co₃O₄, as well as the Co-N bond length for CoN, could be obtained from the standard crystallographic information files (CIF) files in the Materials Project database. These values were very close due to the close ionic radii of N and O. To more precisely differentiate the CoN₄ coordination rather than CoO₄ coordination, we have re-adjusted the fitting parameters according to the method reported previously¹⁻³ and re-fitted the Co foil, CoO, Co₂O₃, Co₃O₄ and 4MgCo/CN samples. The results showed that the Co-O bond lengths for CoO, Co₂O₃, Co₃O₄ were 2.10 ± 0.011 Å, 1.92 ± 0.008 Å and 1.92 ± 0.006 Å, respectively, while the Co-N bond length for 4MgCo/CN was 1.89 ± 0.012 Å. The bond lengths of Co-O and Co-N were almost identical to those in previous work^{4,5}. In addition, no diffraction peaks and functional groups of cobalt oxides were observed in

the XRD pattern (Fig. 1c) and FT-IR spectra (Fig. 1d) of 4MgCo/CN DSACs, respectively, indicating that CoO, Co₂O₃, and Co₃O₄ were absent in the 4MgCo/CN DSACs. We have added corresponding descriptions in main text (line 102-105, page 5) and revised fitting parameter into Table S3 of Supplementary Material in our revised manuscript.

The diffraction peak and functional group of CN were observed in the XRD patterns (Fig. 1c) and FT-IR spectra (Fig. 1d)¹⁸, whereas no diffraction peaks of cobalt oxides were evident in the former, nor were any signals of their functional groups detected in the latter.

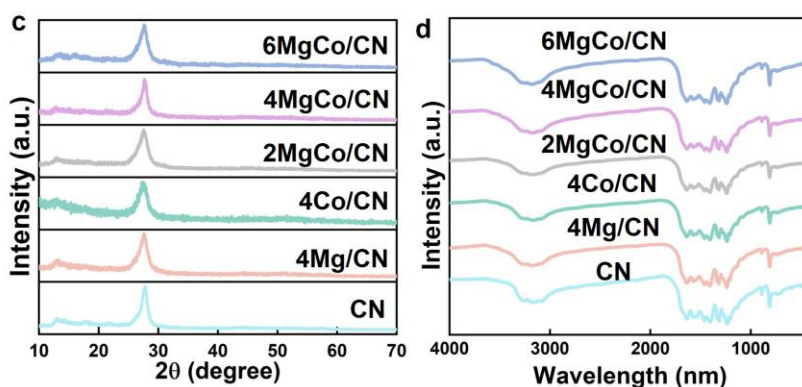


Fig. 1. (c) XRD and (d) FT-IR spectra of catalysts, respectively.

Table S3. EXAFS fitting parameters at the Co K-edge for various samples.

Sample	shell	CN	R(Å)	ΔE_0	σ^2 ($10^{-3}\text{\AA}^2$)	R factor
Co foil	Co–Co	12 (fix)	2.49±0.003	2.08±0.45	5.78±0.32	0.002
CoO	Co–O	6 (fix)	2.10±0.011	−1.27±0.85	8.59±1.33	0.019
	Co–Co	12 (fix)	3.01±0.006	−1.27±0.85	7.47±0.34	
Co ₃ O ₄	Co–O	6 (fix)	1.92±0.006	−7.52±0.89	4.72±0.61	0.015
	Co–Co	6 (fix)	2.86±0.007	−7.52±0.89	6.02±0.45	

Co ₂ O ₃	Co–Co	6 (fix)	3.37±0.008	–7.52±0.89	4.73±0.52	
	Co–O	6 (fix)	1.92±0.008	–5.83±1.69	4.22±1.57	
	Co–Co	8 (fix)	2.89±0.018	–5.83±1.69	7.95±0.69	0.005
4MgCo/CN before reaction	Co–Co	2 (fix)	3.38±0.011	–5.83±1.69	4.07±3.28	
	Co–N	3.53± 0.48	1.89±0.012	–5.68±1.92	8.90± 1.90	0.015
4MgCo/CN after reaction	Co–N	4.02±0. 84	2.09±0.015	2.12±0.13	7.24± 2.58	0.018

Supplementary Note: CN: Coordination Number; R: Bond Distance; σ^2 : Debye-Waller Factor; ΔE_0 : Inner Potential Correction; R Factors: Goodness of Fitting.

References in this third response to reviewer 3:

1. Hai, X. et al. Geminal-atom catalysis for cross-coupling. *Nature*. **622**, 754–760 (2023).
2. Cao, L. L. et al. Identification of single-atom active sites in carbon-based cobalt catalysts during electrocatalytic hydrogen evolution. *Nature Catal.* **2**, 134–141 (2019).
3. Yang, H. et al. Intramolecular hydroxyl nucleophilic attack pathway by a polymeric water oxidation catalyst with single cobalt sites. *Nature Catal.* **5**, 414–429 (2022).
4. Feng, Y. et al. Breathing mode in Nd–CoO_x for active and stable proton exchange membrane water electrolysis. *Nature Commun.* **16**, 10998 (2025).
5. Ma, Z. et al. Synthesis of aromatic amides from lignin and its derivatives. *Nature Commun.* **16**, 3476 (2025).

(2) Thanks for your suggestion. In EXAFS fitting of metal foils and metal oxide standards, the coordination number was typically not treated as a free fitting parameter, instead, it was fixed according to the known crystallographic structure.

Only in the case of synthesized or unknown samples was the coordination number released and refined during fitting. Hence, we added fitting errors for CN and R of 4MgCo/CN before and after reaction in Table S3 of our revised manuscript. The details were as follows.

Table S3. EXAFS fitting parameters at the Co K-edge for various samples.

Sample	shell	CN	R(Å)	ΔE_0	σ^2 ($10^{-3}\text{\AA}^2$)	R factor
Co foil	Co-Co	12 (fix)	2.49±0.003	2.08±0.45	5.78±0.32	0.002
CoO	Co-O	6 (fix)	2.10±0.011	-1.27±0.85	8.59±1.33	0.019
	Co-Co	12 (fix)	3.01±0.006	-1.27±0.85	7.47±0.34	
	Co-O	6 (fix)	1.92±0.006	-7.52±0.89	4.72±0.61	
	Co-O	6 (fix)	1.92±0.006	-7.52±0.89	4.72±0.61	
Co ₃ O ₄	Co-Co	6 (fix)	2.86±0.007	-7.52±0.89	6.02±0.45	0.015
	Co-Co	6 (fix)	3.37±0.008	-7.52±0.89	4.73±0.52	
Co ₂ O ₃	Co-O	6 (fix)	1.92±0.008	-5.83±1.69	4.22±1.57	0.005
	Co-Co	8 (fix)	2.89±0.018	-5.83±1.69	7.95±0.69	
	Co-Co	2 (fix)	3.38±0.011	-5.83±1.69	4.07±3.28	
	Co-Co	2 (fix)	3.38±0.011	-5.83±1.69	4.07±3.28	
4MgCo/CN before reaction	Co-N	3.53± 0.48	1.89±0.012	-5.68±1.92	8.90± 1.90	0.015
4MgCo/CN after reaction	Co-N	4.02±0. 84	2.09±0.015	2.12±0.13	7.24± 2.58	0.018

Supplementary Note: CN: Coordination Number; R: Bond Distance; σ^2 : Debye-Waller Factor; ΔE_0 : Inner Potential Correction; R Factors: Goodness of Fitting.

4. The poor-quality fitting curves displayed in Figures S2 and S3 render the assigned oxidation states of Co and Mg questionable. The authors are required to repeat the LCF fitting with rigorous procedures and report the corresponding R-factor values for all fits.

Response:

We are very sorry for our mistake. We have refitted and corrected the LCF fitting curves with rigorous procedures and the detailed procedures have been added to the Supplementary Material of our revised manuscript. The R-factor values for LCF fitting of Co and Mg in 4MgCo/CN before reaction were 0.0078 and 0.0185 and R-factor value for LCF fitting of Co in 4MgCo/CN after reaction was 0.0142 respectively. We have updated corresponding LCF fitting curves in new Figs. S3, S4 and S46 and added the corresponding R-factor values for all fitting curves in Supplementary Material of our revised manuscript.

Supplementary Method 4. Linear combination fitting of Co and Mg K-edge XANES spectra

Linear combination fitting (LCF) of the normalized Co and Mg K-edge XANES spectra was performed to estimate the apparent average oxidation states of Co and Mg in 4MgCo/CN. For Co K-edge LCF, Co foil, CoO, and Co₂O₃ were selected as reference compounds for Co⁰, Co²⁺, and Co³⁺, respectively. For Mg K-edge LCF, Mg foil and MgO were selected as reference compounds for Mg⁰ and Mg²⁺, respectively.

All XANES spectra were first energy calibrated and normalized using the same procedure. The LCF analysis was conducted in the XANES region based on the normalized $\mu(E)$ spectra. During fitting, the sum of all weighting factors was constrained to unity, all weighting factors were constrained between 0 and 1, and the energy shift, E₀, of each reference spectrum was fixed at 0 eV. The fitting quality was evaluated using the R-factor, chi-square, and reduced chi-square values.

For Co *K*-edge LCF, the fitted spectrum was expressed as:

$$\mu_{\text{fit}}(E) = w_{\text{Co foil}} \mu_{\text{Co foil}}(E) + w_{\text{CoO}} \mu_{\text{CoO}}(E) + w_{\text{Co}_2\text{O}_3} \mu_{\text{Co}_2\text{O}_3}(E)$$

where $w_{\text{Co foil}}$, w_{CoO} , and $w_{\text{Co}_2\text{O}_3}$ are the fitted weighting factors of Co foil, CoO, and Co₂O₃, respectively. The weighting factors were constrained as:

$$w_{\text{Co foil}} + w_{\text{CoO}} + w_{\text{Co}_2\text{O}_3} = 1$$

The apparent average Co valence was calculated according to the assigned valence states of the reference compounds:

$$\text{Co valence} = 0 \times w_{\text{Co foil}} + 2 \times w_{\text{CoO}} + 3 \times w_{\text{Co}_2\text{O}_3}$$

For Mg *K*-edge LCF, the fitted spectrum was expressed as:

$$\mu_{\text{fit}}(E) = w_{\text{Mg foil}} \mu_{\text{Mg foil}}(E) + w_{\text{MgO}} \mu_{\text{MgO}}(E)$$

where $w_{\text{Mg foil}}$ and w_{MgO} are the fitted weighting factors of Mg foil and MgO, respectively. The weighting factors were constrained as:

$$w_{\text{Mg foil}} + w_{\text{MgO}} = 1$$

The apparent average Mg valence was calculated according to the assigned valence states of the reference compounds:

$$\text{Mg valence} = 0 \times w_{\text{Mg foil}} + 2 \times w_{\text{MgO}}$$

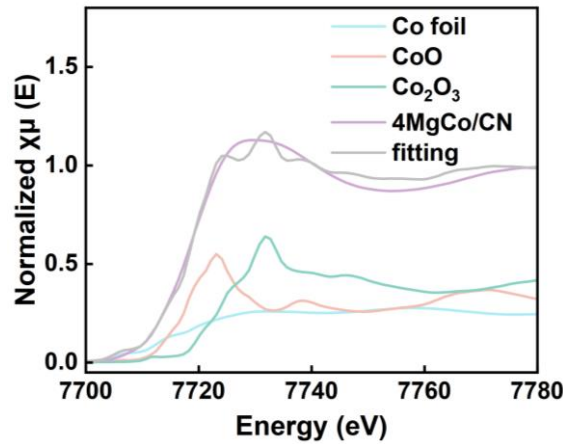


Fig. S3. The linear combination fitting result for 4MgCo/CN DSACs.

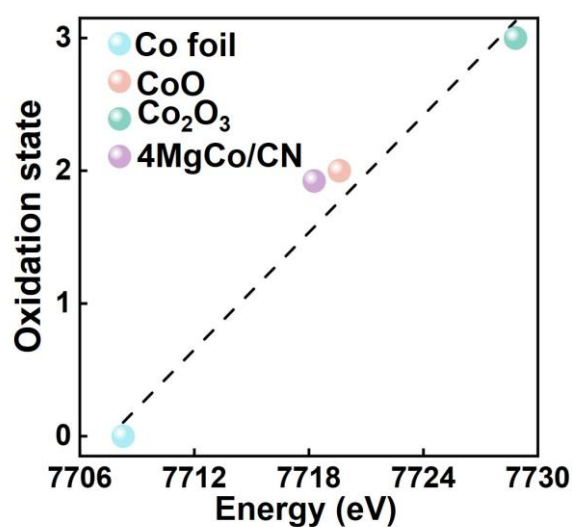


Fig. 1. (f) corresponding oxidation state of Co species.

Table S1. Linear combination fitting for Co in 4MgCo/CN

Standard	Weight	E ₀
Co foil	0.251 (0.039)	0.000 (0.000)
CoO	0.324 (0.024)	0.000 (0.000)
Co ₂ O ₃	0.425 (0.046)	0.000 (0.000)

R-factor = 0.0078

Chi-square = 0.0818

Reduced chi-square = 0.0015

Co in 4MgCo/CN = $0 \times 0.251 + 2 \times 0.324 + 3 \times 0.425 = 1.923$

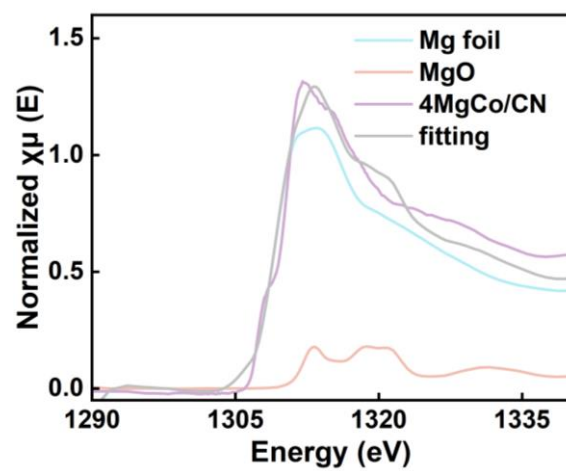


Fig. S4. The linear combination fitting result for 4MgCo/CN DSACs.

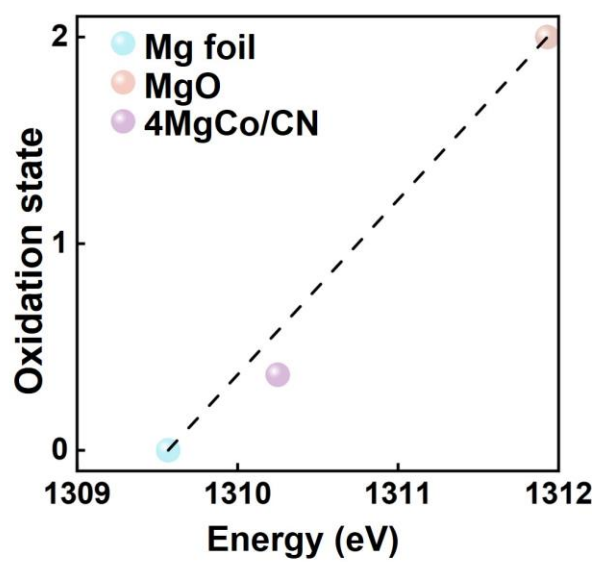


Fig. 1. (i) corresponding oxidation state of Mg species.

Table S2. Linear combination fitting for Mg in 4MgCo/CN

Standard	Weight	E ₀
Mg foil	0.776 (0.012)	0.000 (0.000)
MgO	0.224 (0.054)	0.000 (0.000)

R-factor = 0.0185

Chi-square = 0.7127

Reduced chi-square = 0.0043

Mg in 4MgCo/CN = $0 \times 0.776 + 2 \times 0.224 = 0.448$

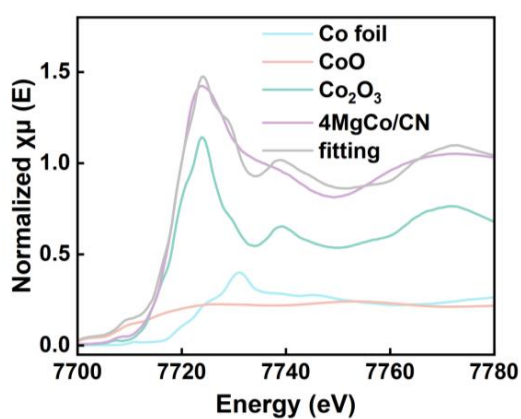


Fig. S46. The linear combination fitting result for 4MgCo/CN DSACs after reaction.

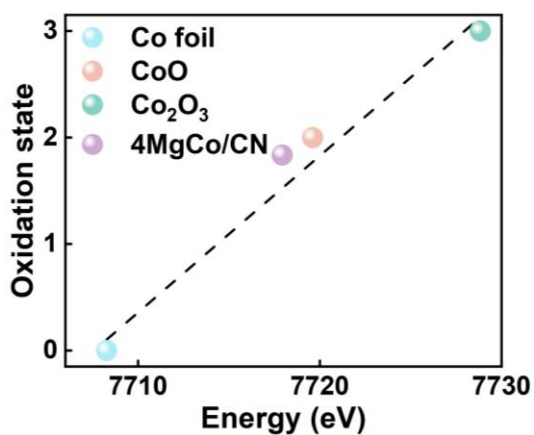


Fig. S47. The oxidation state of Co species in 4MgCo/CN DSACs after reaction.

Table S8. Linear combination fitting for Co in 4MgCo/CN after reaction

Standard	Weight	E ₀
Co foil	0.172 (0.023)	0.000 (0.000)
CoO	0.648 (0.021)	0.000 (0.000)
Co ₂ O ₃	0.180 (0.041)	0.000 (0.000)

R-factor = 0.0142

Chi-square = 0.4662

Reduced chi-square = 0.0025

Co in 4MgCo/CN=0*0.172+2*0.648+3*0.180=1.836

5. Figure S41 suggest that Co undergoes irreversible oxidation upon catalysis rather than the proposed d-orbital modulation. The full characterization of spent catalyst including STEM, EXAFS should be provided.

Response:

(1) We are very sorry that we haven't described clearly in the previous manuscript. We realized that the previous description of the XANES data was insufficient. In fact, as shown in our revised XANES data, the Co K-edge exhibited a negative shift after the reaction compared to that before the reaction, which clearly indicated a reduction in the oxidation state of Co in the 4MgCo/CN DSACs after reaction. To make this trend unambiguous, we have now added an enlarged inset of the absorption edge in new Fig. S44, highlighting the edge position shift more clearly.

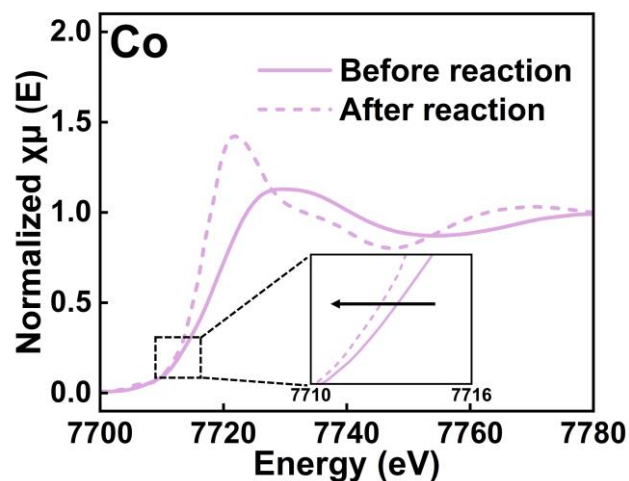


Fig. S44. The Co K-edge XANES spectra of 4MgCo/CN DSACs before and after reaction.

To provide a more precise and quantitative analysis, we have re-performed linear combination fitting (LCF) of the Co K-edge XANES spectra for 4MgCo/CN before and after reaction (Figs. S3 and S46, Tables S1 and S8). The LCF results demonstrated that the average oxidation state of Co decreased from +1.923 to +1.836 (Figs. 1f and S47). This quantitative evidences confirmed that the Co specie undergo a partial reduction during the domino reaction process. The change in the Co K-edge XANES spectra after PMS activation has also been observed in previous work^{1,2}.

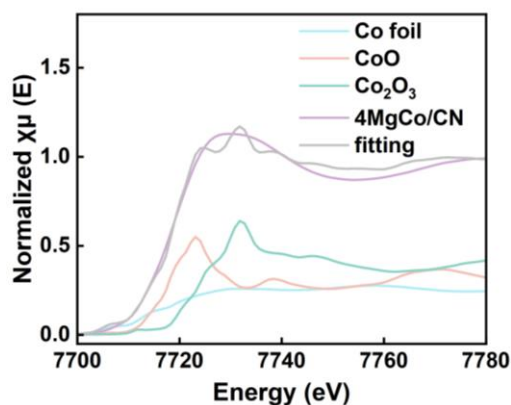


Fig. S3. The linear combination fitting result for 4MgCo/CN DSACs.

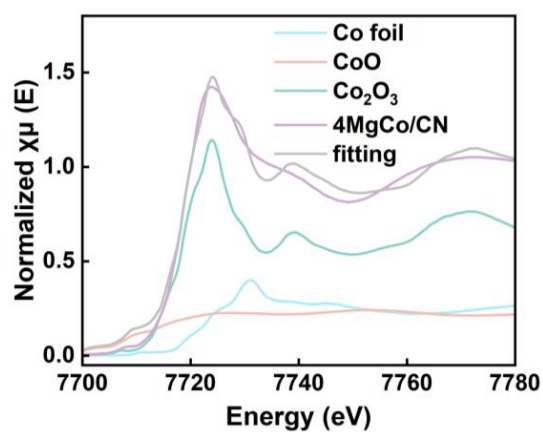


Fig. S46. The linear combination fitting result for 4MgCo/CN DSACs after reaction.

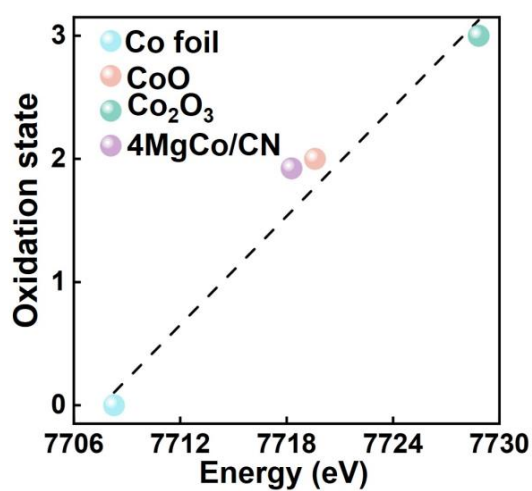


Fig. 1. (f) corresponding oxidation state of Co species.

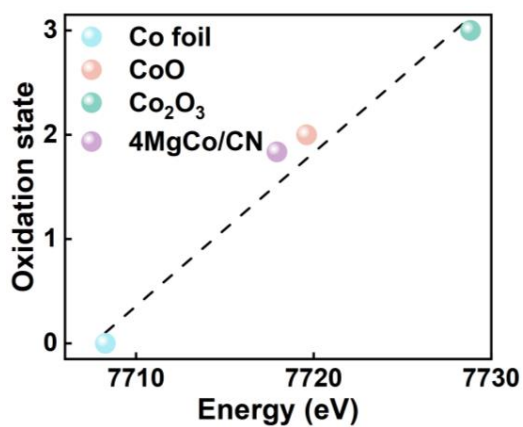


Fig. S47. The oxidation state of Co species in 4MgCo/CN DSACs after reaction.

Table S1. Linear combination fitting for Co in 4MgCo/CN

Standard	Weight	E ₀
Co foil	0.251 (0.039)	0.000 (0.000)
CoO	0.324 (0.024)	0.000 (0.000)
Co ₂ O ₃	0.425 (0.046)	0.000 (0.000)

R-factor = 0.0078

Chi-square = 0.0818

Reduced chi-square = 0.0015

Co in 4MgCo/CN=0*0.251+2*0.324+3*0.425=1.923

Table S8. Linear combination fitting for Co in 4MgCo/CN after reaction

Standard	Weight	E ₀
Co foil	0.172 (0.023)	0.000 (0.000)
CoO	0.648 (0.021)	0.000 (0.000)
Co ₂ O ₃	0.180 (0.041)	0.000 (0.000)

R-factor = 0.0142

Chi-square = 0.4662

Reduced chi-square = 0.0025

Co in 4MgCo/CN=0*0.172+2*0.648+3*0.180=1.836

References in this fifth response to reviewer 3:

1 Lan, M. Y. et al. Multi-channel electron transfer induced by polyvanadate in metal-organic framework for boosted peroxymonosulfate activation. *Nature Commun.* **15**, 7208 (2024).

2 Zhao, Z. Y. et al. Regulating nonradicals generation through peroxymonosulfate activation via localized dipole to enhance wastewater biodegradability. *Nature*

(2) Thanks for your suggestion. We have added a series of characterizations on the spent 4MgCo/CN DSACs and the results were summarized as follows:

The SEM image (Fig. S50) exhibited that the spent catalyst maintained the original sparse and three-dimensional nanosheet-like morphology. The aberration-corrected HAADF-STEM images at different magnifications in different regions (Fig. S51) showed that the dual single atoms remain atomically dispersed after the reaction, and their atomic spacing was consistent with that of the 4MgCo/CN DSACs before reaction. The fitting curve of Co *K*-edge EXAFS spectra for the spent 4MgCo/CN DSACs exhibited a coordination number of four, identical to that of the fresh catalyst (Fig. S52), but the Co–N bond length was slightly longer in FT k^3 -weighted Co *K*-edge EXAFS spectra of 4MgCo/CN DSACs (Fig. S45). This elongation might be attributed to the reduced Co oxidation state after reaction decreased the nuclear charge attraction to the lone-pair electrons of N atom, thereby slightly lengthening the bond. This was consistent with negative shift of Co *K*-edge XANES spectra of 4MgCo/CN after reaction. The XRD patterns (Fig. S53) exhibited that no new diffraction peaks corresponding to crystalline CoO, Co₃O₄, or metallic Co appeared in the spent catalyst, ruling out the variation of physical phase of 4MgCo/CN during the reaction. The FT-IR spectra (Fig. S54) showed that the characteristic peak of the 4MgCo/CN remained unchanged after reaction in comparison to that before reaction, indicating that the functional group of 4MgCo/CN was stable. The band gap and VB spectra (Fig. S55) exhibited almost no change in the

absorption edge and valence band, indicating that the energy band structure of 4MgCo/CN was well preserved after reaction.

The above results demonstrated that 4MgCo/CN DSACs exhibited structural stability during the PMS activation process. The observed decrease in Co oxidation state was mainly attributable to d-orbital modulation of non-adjacent Co atom by OH_{surf} , which promoted the reduction of Co active center and sustained the PMS activation. We have added corresponding descriptions in our revised manuscript (line 384-388, 398-400, page 21) and updated the Supplementary Material with all new figures and tables.

The slight elongation of Co–N bond in the FT k^3 -weighted Co *K*-edge EXAFS spectra of 4MgCo/CN DSACs was mainly attributed to the fact that Co with reduced oxidation state after reaction decreased the nuclear charge attraction to the lone-pair electrons of N atom (Fig. S45).

The morphology, physical phase, functional group, coordination number and energy band structure of 4MgCo/CN DSACs remained unchanged after reaction compared with those before reaction (Figs. S50-S55).

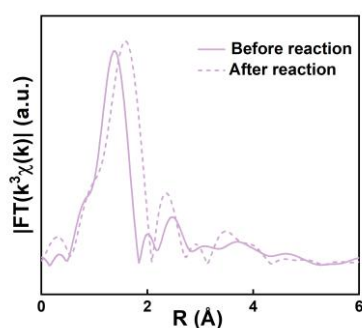


Fig. S45. FT k^3 -weighted Co *K*-edge EXAFS spectra of 4MgCo/CN DSACs before and after reaction.

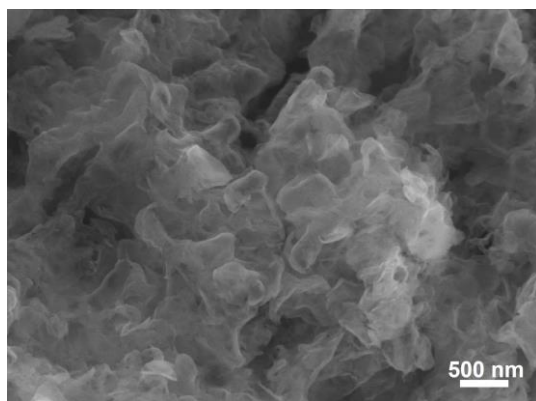


Fig. S50. SEM image of 4MgCo/CN DSACs after reaction.

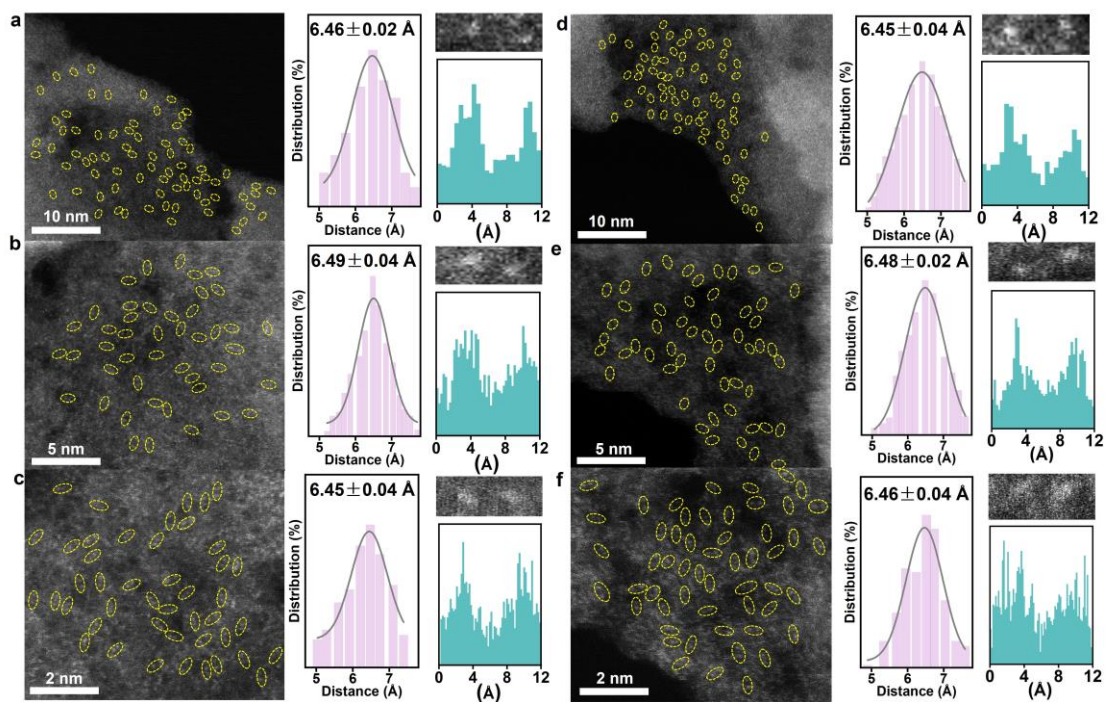


Fig. S51. The AC HAADF-STEM images of 4MgCo/CN DSACs after reaction with different magnifications at different regions and corresponding atomic distance distribution, respectively.

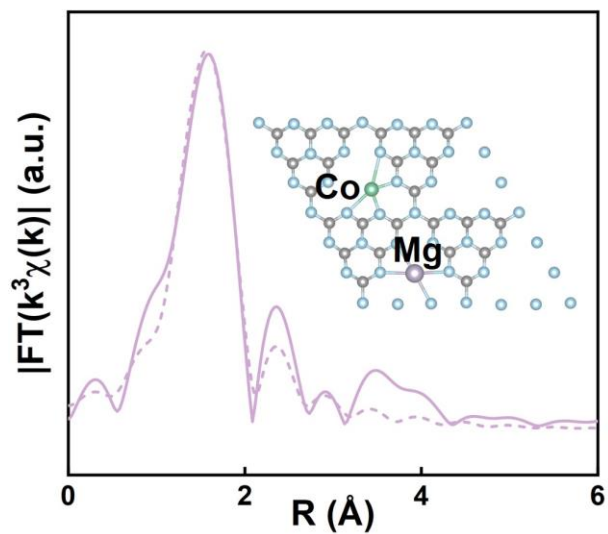


Fig. S52. FT k^3 -weighted Co K -edge EXAFS spectra of 4MgCo/CN DSACs after reaction.

Table S3. EXAFS fitting parameters at the Co K -edge for various samples.

Sample	shell	CN	$R(\text{\AA})$	ΔE_0	σ^2 ($10^{-3}\text{\AA}^2$)	R factor
Co foil	Co–Co	12 (fix)	2.49 ± 0.003	2.08 ± 0.45	5.78 ± 0.32	0.002
CoO	Co–O	6 (fix)	2.10 ± 0.011	-1.27 ± 0.85	8.59 ± 1.33	0.019
	Co–Co	12 (fix)	3.01 ± 0.006	-1.27 ± 0.85	7.47 ± 0.34	
	Co–O	6 (fix)	1.92 ± 0.006	-7.52 ± 0.89	4.72 ± 0.61	
Co ₃ O ₄	Co–Co	6 (fix)	2.86 ± 0.007	-7.52 ± 0.89	6.02 ± 0.45	0.015
	Co–Co	6 (fix)	3.37 ± 0.008	-7.52 ± 0.89	4.73 ± 0.52	
Co ₂ O ₃	Co–O	6 (fix)	1.92 ± 0.008	-5.83 ± 1.69	4.22 ± 1.57	0.005
	Co–Co	8 (fix)	2.89 ± 0.018	-5.83 ± 1.69	7.95 ± 0.69	
	Co–Co	2 (fix)	3.38 ± 0.011	-5.83 ± 1.69	4.07 ± 3.28	
4MgCo/CN before reaction	Co–N	3.53 ± 0.48	1.89 ± 0.012	-5.68 ± 1.92	8.90 ± 1.90	0.015
4MgCo/CN after reaction	Co–N	4.02 ± 0.84	2.09 ± 0.015	2.12 ± 0.13	7.24 ± 2.58	0.018

Supplementary Note: CN: Coordination Number; R: Bond Distance; σ^2 : Debye-Waller Factor; ΔE_0 : Inner Potential Correction; R Factors: Goodness of Fitting.

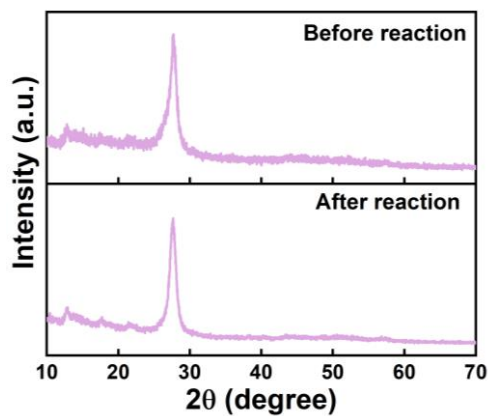


Fig. S53. XRD spectra of 4MgCo/CN DSACs before and after reaction.

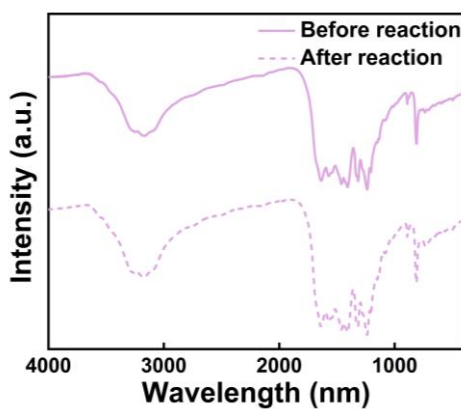


Fig. S54. FT-IR spectra of 4MgCo/CN DSACs before and after reaction.

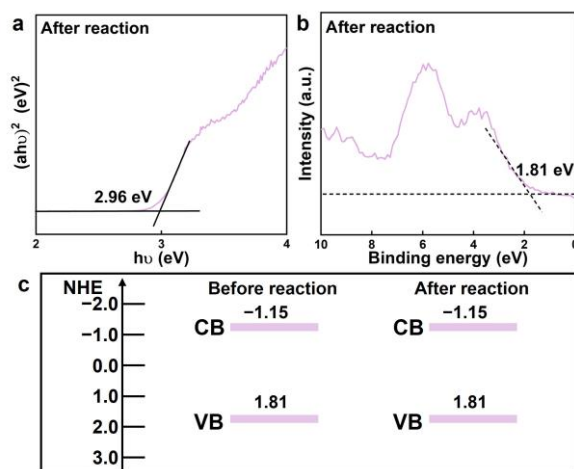


Fig. S55. (a) Band gap and (b) VB spectra of 4MgCo/CN DSACs after reaction; (c)

Energy band level structures of 4MgCo/CN DSACs before and after reaction.

6. The XPS data in Figure 4i is too noisy which cannot provide any reliable information. Owing to the severe noise interference, the corresponding peak deconvolution is arbitrarily conducted. These XPS data should be removed unless the author can provide high-quality data.

Response:

We are very sorry for our mistake. The XPS data in Fig. 4i of previous manuscript was of poor quality due to severe noise interference, and that corresponding peak deconvolution was arbitrary and unreliable. The weak signal was primarily due to the slightly low Co content in the 4MgCo/CN (0.71 wt%), which was below the detection limit of the XPS instrument. Because the data did not meet the standard for reliable analysis, we have removed the noisy XPS data and the corresponding discussion from previous Fig. 4i in our revised manuscript.

To more precisely exhibit the electronic change of Co after reaction compared to that before reaction, we have re-performed linear combination fitting (LCF) of the Co K-edge XANES spectra for 4MgCo/CN before and after reaction. The new LCF results shown in Figs. S3, 1f, S46 and S47 indicated that the oxidation state of Co decreased from 1.923 to 1.836 after reaction, confirming the reduction of Co species during reaction. We have also revised corresponding descriptions in our revised manuscript (line 389, 391, page 21)

Based on the LCF results, the proportion of Co^{2+} species in the 4MgCo/CN DSACs increased from 32.4% before reaction to 64.8% after reaction (Figs. S3 and S46, Tables S1 and S8), while the average Co oxidation state decreased from 1.923 to

1.836 (Figs. 1f and S47).

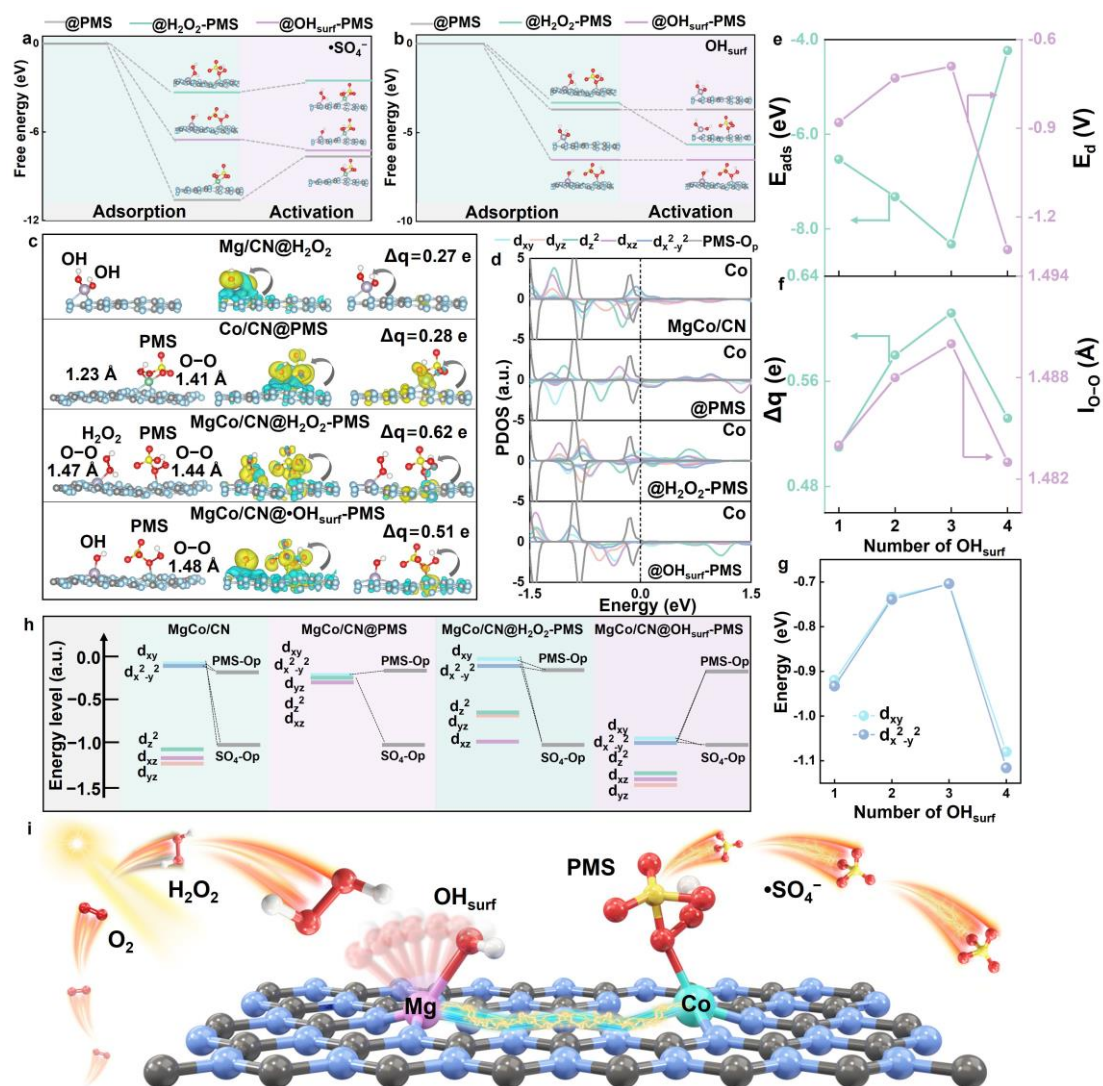


Fig. 4. Energy profiles of (a) $\bullet\text{SO}_4^-$ and (b) OH_{surf} formation for MgCo/CN DSACs and Co/CN SACs by PMS activation. (c) Differential charge density and spin electron density models of different models. (d) PDOS of Co 3d in different catalyst models. Relationship among (e) E_{ads} and E_{d} and (f) Δq and $I_{\text{O-O}}$ with number of OH_{surf}. (g) Energy variation of d_{xy} and $d_{x^2-y^2}$ as the increase in number of OH_{surf}. (h) Orbital structure between PMS and different models. (i) The dynamic-catalytic process by dynamic cobalt d-orbital reconstruction for breaking activity-stability trade-off in water decontamination.

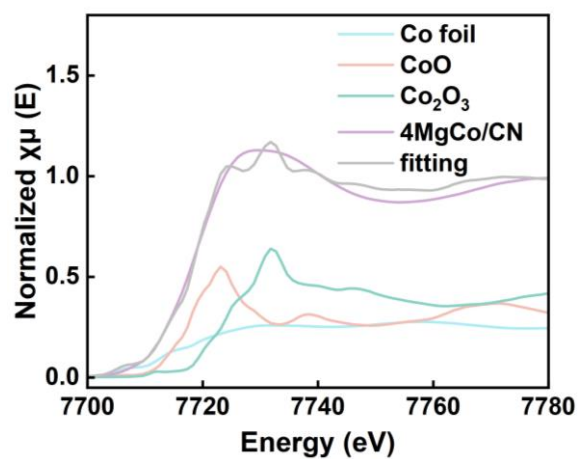


Fig. S3. The linear combination fitting result for 4MgCo/CN DSACs.

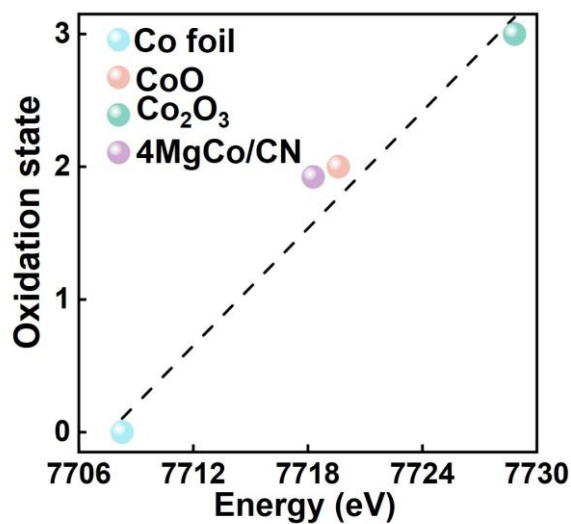


Fig. 1. (f) corresponding oxidation state of Co species.

Table S1. Linear combination fitting for Co in 4MgCo/CN

Standard	Weight	E_0
Co foil	0.251 (0.039)	0.000 (0.000)
CoO	0.324 (0.024)	0.000 (0.000)
Co ₂ O ₃	0.425 (0.046)	0.000 (0.000)

R-factor = 0.0078

Chi-square = 0.0818

Reduced chi-square = 0.0015

Co in 4MgCo/CN= $0 \times 0.251 + 2 \times 0.324 + 3 \times 0.425 = 1.923$

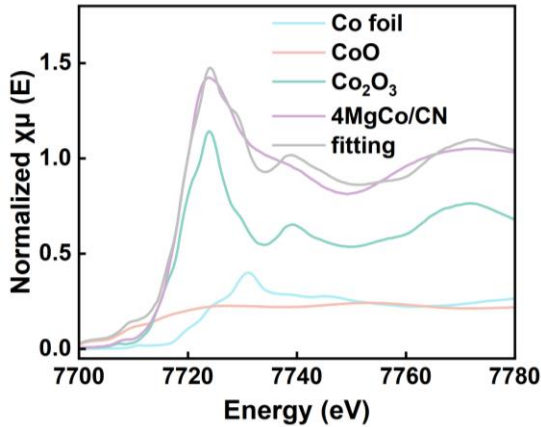


Fig. S46. The linear combination fitting result for 4MgCo/CN DSACs after reaction.

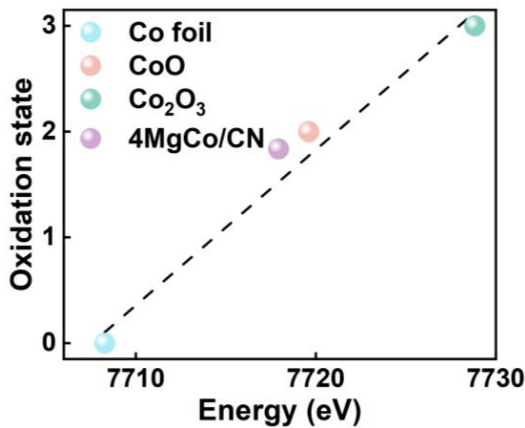


Fig. S47. The oxidation state of Co species in 4MgCo/CN DSACs after reaction.

Table S8. Linear combination fitting for Co in 4MgCo/CN after reaction

Standard	Weight	E ₀
Co foil	0.172 (0.023)	0.000 (0.000)
CoO	0.648 (0.021)	0.000 (0.000)
Co ₂ O ₃	0.180 (0.041)	0.000 (0.000)

R-factor = 0.0142

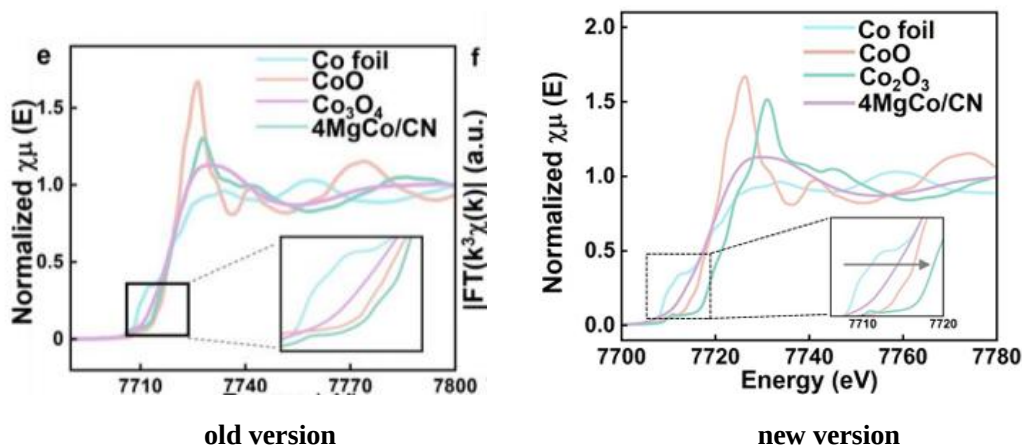
Chi-square = 0.4662

Reduced chi-square = 0.0025

Co in 4MgCo/CN=0*0.172+2*0.648+3*0.180=1.836

I appreciate the authors' efforts to address most of my previous concerns. Nevertheless, upon examining the revised data, several aspects of their structural analysis remain unsatisfactory, and I cannot recommend publication in the current form. The authors are advised to perform more rigorous data analysis to ensure data reproducibility and reliability, particularly given the high standards required for publication in Nature Communications.

1. The authors claim the formation of Co–Mg dual-atom pairs in the revised manuscript. However, insufficient experimental evidence is provided to validate this conclusion. (1) Single-atom dispersion shown in the STM images appears randomly distributed, and the selected dual-atom configurations are chosen arbitrarily. Additional STEM images with both high and low magnifications should be supplemented in the SI, alongside detailed descriptions of the corresponding statistical analysis protocols. (2) No solid evidence is available to unambiguously distinguish Co and Mg sites within the proposed paired configurations, even assuming such dual sites exist. It remains unclear why Co and Mg atoms preferentially aggregate with one another. The authors must supply convincing evidence to rule out homonuclear pairing configurations including CoN₄–CoN₄ and MgN₄–MgN₄.
2. The 4MgCo spectrum presented in Figure 1e differs substantially from that in the previous revision, which cannot be ascribed to simple mislabeling. The authors need to clarify the underlying reason for this discrepancy. Such drastic variation raises serious concerns regarding the reproducibility of their measurements. Raw data from replicate experiments together with full details of data processing must be provided to substantiate the reliability of the reported results. Both Co₂O₃ and Co₃O₄ standard should be provided in the same plot.



3. In Table S3, Co-O and Co-N distance are very close. How could you differentiate CoN₄ rather than CoO₄ coordination. The fitting error for CN and R should be given.
4. The poor-quality fitting curves displayed in Figures S2 and S3 render the assigned oxidation states of Co and Mg questionable. The authors are required to repeat the LCF fitting with rigorous procedures and report the corresponding R-factor values for all fits.
5. Figure S41 suggest that Co undergoes irreversible oxidation upon catalysis rather than the proposed d-orbital modulation. The full characterization of spent catalyst including STEM, EXAFS should be provided.
6. The XPS data in Figure 4i is too noisy which cannot provide any reliable information. Owing to the severe noise interference, the corresponding peak deconvolution is arbitrarily conducted. These XPS data should be removed unless the author can provide high-quality data.