nature portfolio

Peer Review File

Synthesis of adaptive 15N-nitrosyl-Co7 nanocluster for electrocatalytic C-H functionalization

Corresponding Author: Professor Man-Bo Li

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This manuscript by Wu et al. describes the synthesis and activity of Co7-based nanoclusters that feature NO ligands capping several of the cobalt centers. The authors describe the in situ formation of the NO ligands from the NO3- salt of the Co(II) precursor, confirmed by isotopic labeling studies, which is a very clever approach to integrating this ligand that would otherwise present significant safety concerns or low yielding syntheses. The authors are able to isolate two variations of the cluster that have slightly different NO geometries (linear vs. bent) and show they are electrochemically distinguishable. The clusters are active for electrocatalytic HER, and impressively, are also active catalysts for C-H functionalization of allene compounds. Overall, I think this is an outstanding paper! The new synthesis for incorporating NO ligands into clusters will likely be adopted by many groups interested in similar architectures. Furthermore, the electrocatalytic activity presented nicely demonstrates the interplay between stability and activity. The paper is clear and well-written, I am happy to recommend publication.

Reviewer #2

(Remarks to the Author)
The manuscript by Li and coworkers reports a nitrosyl-Co_7 nanocluster in which the nitrosyl (NO) ligand acts adaptively to balance stability and catalytic activity. This novel structure is unambiguously characterized using a 15N-labelling strategy with 15N-cobalt nitrate serving a dual role as both the nitrosyl and metal source. Leveraging the synergy between the NO ligand and the cobalt core, the nanocluster demonstrates high catalytic efficiency for the hydrogen evolution reaction (HER), which is further applied to drive electrochemical allene C-H functionalization under high-current-density conditions. The protocol shows excellent functional group tolerance, high efficiency, and scalability. A significant mechanistic insight is the identification of a critical nitroxyl anion (NO-)-Co7 nanocluster intermediate. Given the significance and innovation of this work, I recommend its publication in Nature Communications after the authors address the following minor points.
1.The manuscript highlights the essential role of the cobalt core in forming the active nitrosyl nanoclusters. To strengthen this claim, control experiments using iron or nickel salts instead of cobalt could be included to demonstrate the unique capability of cobalt in this context.
2.Could the authors comment on the feasibility of using a combination of CoCl2 and NaNO3 to replace cobalt nitrate for the nanocluster synthesis? If feasible, this alternative route might facilitate the synthesis of the 15N-labelled nitrosyl-Co7 nanocluster.
3.In the investigation of substrate generality, 1-phenylallene is exclusively converted to product 3am, demonstrating the catalyst's superiority. A brief explanation for this high selectivity should be added to the manuscript.
4.While the manuscript focuses on the cathodic HER, a brief discussion of the anodic half-reaction (e.g., oxidation of the solvent or electrolyte) would provide a more complete electrochemical context for the overall process.

Reviewer #3

(Remarks to the Author)
This manuscript describes a novel adaptive nitrosyl-Co_7 nanocluster for electrocatalytic C–H functionalization and presents a comprehensive combination of synthesis, structural characterization, mechanistic studies, and catalytic applications. The work is scientifically sound, the conclusions are well supported by the experimental data, and the findings will be of broad

interest to the catalysis and nanocluster communities. I recommend publication after minor revision. My only comment concerns the presentation of the cyclic voltammograms in Fig. 3. The current and potential axes appear to combine elements of both the US and IUPAC plotting conventions, with cathodic currents plotted in the negative direction while more negative potentials are displayed toward the right. For clarity and consistency with established electrochemical practice, the authors should adopt a single convention throughout the manuscript and explicitly state the convention used.

Version 1:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
The author has provided a very satisfactory response to the questions I raised. The revised version can now be accepted for publication.

Response to the reviewer's comments

Manuscript number: NCOMMS-26-008827-T

Title: "Synthesis of adaptive ^{15}N-nitrosyl-Co_7 nanocluster for electrocatalytic C-H functionalization"

Response: We sincerely appreciate the time and effort of the three reviewers who evaluated our manuscript. Their thoughtful comments and constructive suggestions have significantly enhanced the quality of this work.

Reviewer 1

This manuscript by Wu et al. describes the synthesis and activity of Co_7-based nanoclusters that feature NO ligands capping several of the cobalt centers. The authors describe the in situ formation of the NO ligands from the NO_3^- salt of the Co(II) precursor, confirmed by isotopic labeling studies, which is a very clever approach to integrating this ligand that would otherwise present significant safety concerns or low yielding syntheses. The authors are able to isolate two variations of the cluster that have slightly different NO geometries (linear vs. bent) and show they are electrochemically distinguishable. The clusters are active for electrocatalytic HER, and impressively, are also active catalysts for C-H functionalization of allene compounds. Overall, I think this is an outstanding paper! The new synthesis for incorporating NO ligands into clusters will likely be adopted by many groups interested in similar architectures. Furthermore, the electrocatalytic activity presented nicely demonstrates the interplay between stability and activity. The paper is clear and well-written, I am happy to recommend publication.

Response: We thank the reviewer for the positive assessment on our manuscript.

Reviewer 2

The manuscript by Li and coworkers reports a nitrosyl-Co_7 nanocluster in which the nitrosyl (NO) ligand acts adaptively to balance stability and catalytic activity. This novel structure is unambiguously characterized using a ^{15}N-labelling strategy with ^{15}N-cobalt nitrate serving a dual role as both the nitrosyl and metal source. Leveraging the synergy between the NO ligand and the cobalt core, the nanocluster demonstrates high catalytic efficiency for the hydrogen evolution reaction (HER), which is further applied to drive electrochemical allene C-H functionalization under high-current-density conditions. The protocol shows excellent functional group tolerance, high efficiency, and scalability. A significant mechanistic insight is the identification of a critical nitroxyl anion (NO-)-Co_7 nanocluster intermediate. Given the significance and innovation of this work, I recommend its publication in Nature Communications after the authors address the following minor points.

Response: We thank the reviewer for the positive comment and insightful suggestions on our work.

1. The manuscript highlights the essential role of the cobalt core in forming the active nitrosyl nanoclusters. To strengthen this claim, control experiments using iron or nickel salts instead of cobalt could be included to demonstrate the unique capability of cobalt in this context.

Response: The control experiments using iron and nickel salts have been conducted based on the suggestion of the reviewer. The results show that neither iron(III) nitrate nor nickel(II) nitrate afford the corresponding iron or nickel nanoclusters. The revisions are also shown below:

"Initial examination employing alternative metal salts showed that neither iron(III) nitrate nor nickel(II) nitrate afforded the corresponding nitrosyl iron or nickel nanoclusters (Fig S8-S9)."

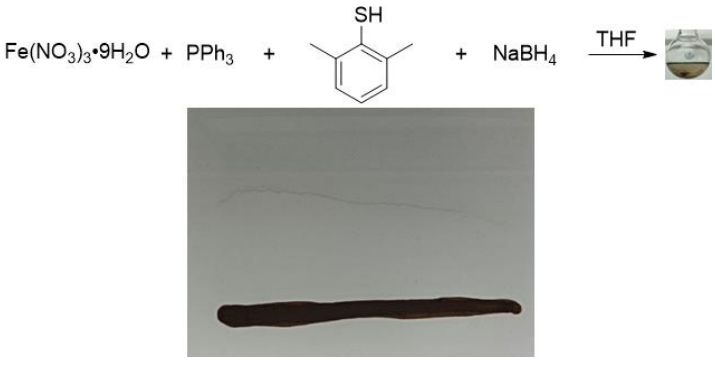


Fig S8. TLC picture of the reaction mixture.

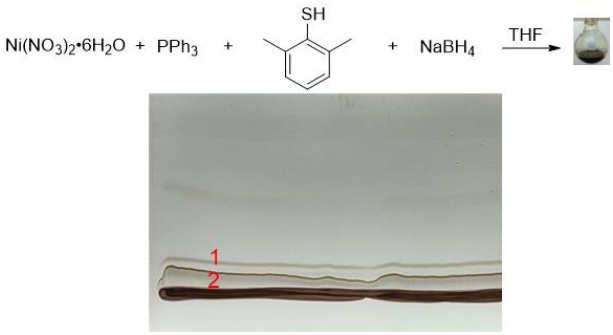
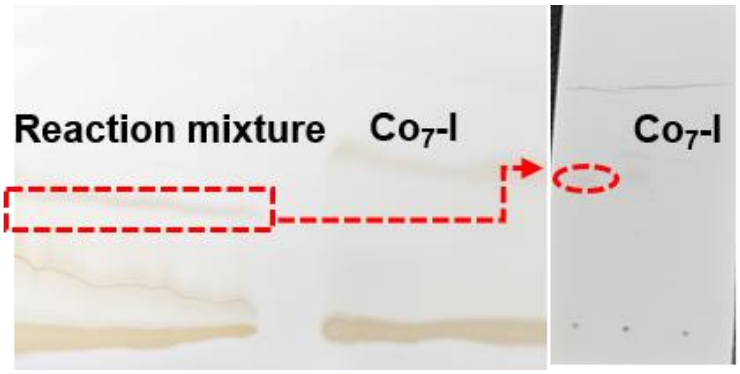


Fig S9. TLC picture of the reaction mixture.

2. Could the authors comment on the feasibility of using a combination of $CoCl_2$ and $NaNO_3$ to replace cobalt nitrate for the nanocluster synthesis? If feasible, this alternative route might facilitate the synthesis of the ^{15}N-labelled nitrosyl-Co_7 nanocluster.

Response: We thank the reviewer for this suggestion, and we fully agree with this point. When we tried to synthesize ^{15}N-labelled nitrosyl-Co_7 nanocluster, this method had been studied and it failed to give the desired nanocluster. This result might be attributed to the poor solubility of $NaNO_3$ in the reaction solvent THF, which would lead to inefficient ion exchange. The revisions are also shown below:

"Additionally, the combination of $NaNO_3$ and $CoCl_2$ also failed to give the desired nanocluster, presumably due to inefficient ion exchange in THF solvent (entry 7, Fig S10d)."



3. In the investigation of substrate generality, 1-phenylallene is exclusively converted to product **3am**, demonstrating the catalyst's superiority. A brief explanation for this high selectivity should be added to the manuscript.

Response: We thank the reviewer for pointing out this. The brief explanation for this high selectivity has been included in the manuscript. The revisions are also shown below:

"This high regioselectivity may be attributed to the efficient carbanion interception enabled by the nanocluster catalyst, which suppresses the competing isomerization pathway."

4. While the manuscript focuses on the cathodic HER, a brief discussion of the anodic half-reaction (e.g., oxidation of the solvent or electrolyte) would provide a more complete electrochemical context for the overall process.

Response: We thank the reviewer for this comment, which significantly improved the quality of our work. The brief description for anodic reaction has been included in the manuscript. The revisions are also shown below:

"Noteworthy, the oxidation of DMF is proposed to be the predominant reaction at the anode, owing to its reported lower oxidation potential.[27]"

Reviewer 3

This manuscript describes a novel adaptive nitrosyl-Co_7 nanocluster for electrocatalytic C–H functionalization and presents a comprehensive combination of synthesis, structural characterization, mechanistic studies, and catalytic applications. The work is scientifically sound, the conclusions are well supported by the experimental data, and the findings will be of broad interest to the catalysis and nanocluster communities. I recommend publication after minor revision. My only comment concerns the presentation of the cyclic voltammograms in Fig. 3. The current and potential axes appear to combine elements of both the US and IUPAC plotting conventions, with cathodic currents plotted in the negative direction while more negative potentials are displayed toward the right. For clarity and consistency with established electrochemical practice, the authors should adopt a single convention throughout the manuscript and explicitly state the convention used.

Response: We thank the reviewer for the positive assessment on our manuscript and the suggestion regarding the cyclic voltammogram presentations in Fig. 3. Per the reviewer's comment, we have revised all CV plots to consistently follow the IUPAC convention throughout the manuscript. The revisions are also shown below:

Fig 3.

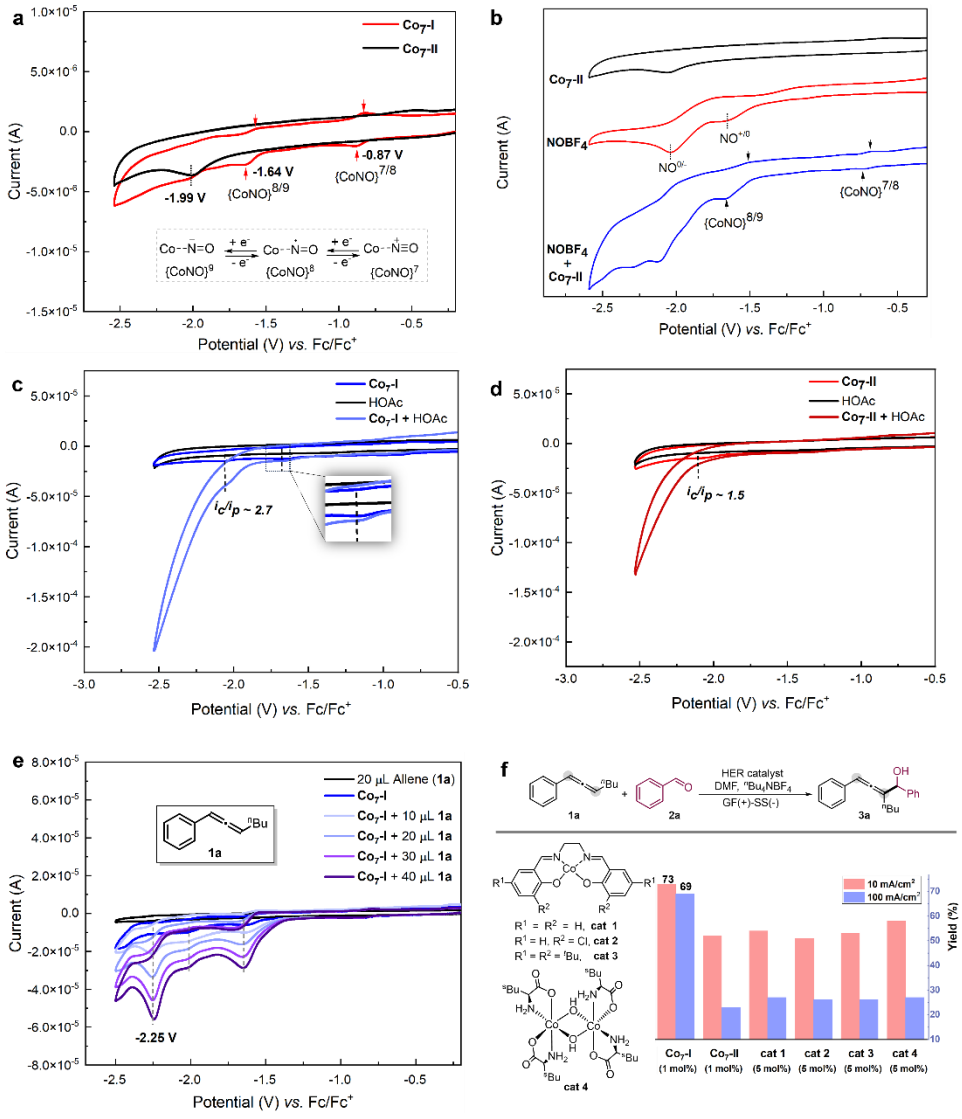


Fig S23.

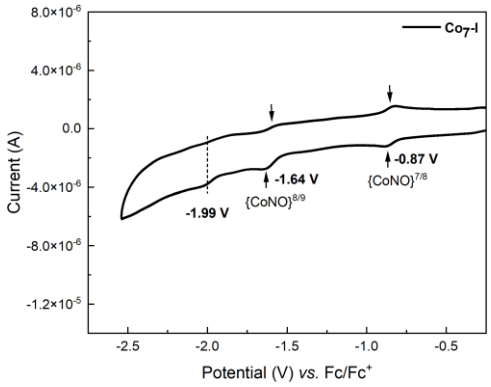


Fig S24.

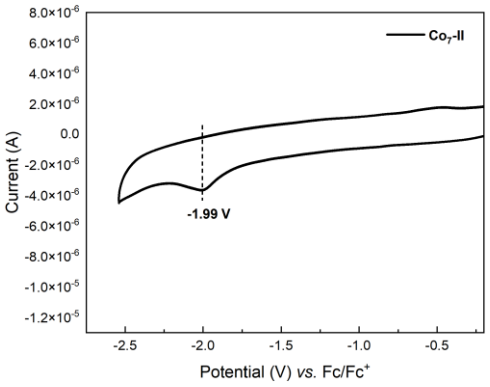


Fig S25.

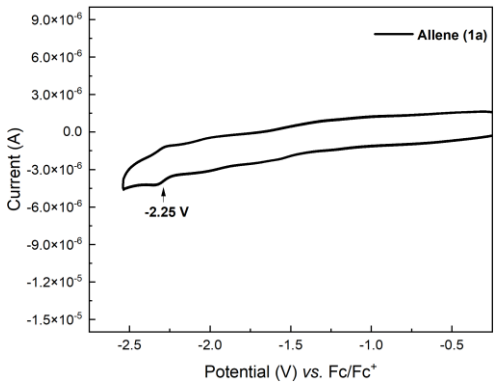


Fig S26.

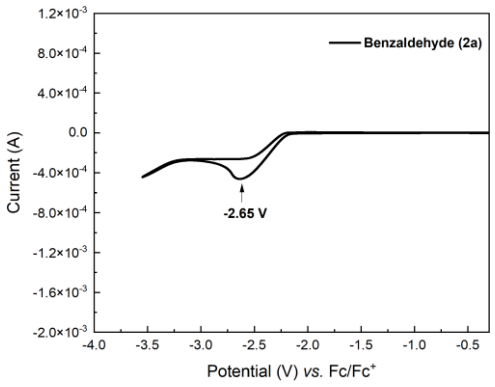


Fig S27.

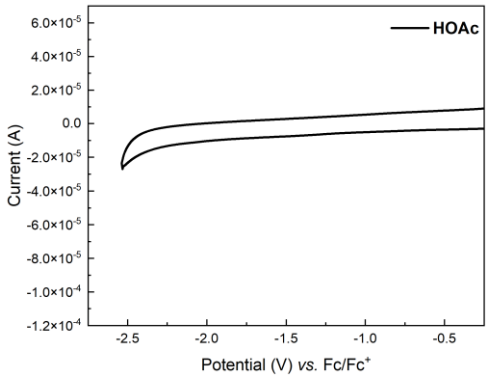


Fig S28.

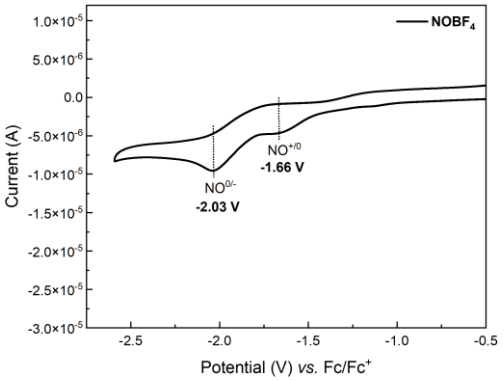


Fig S29.