26-May-2026

Journal: ACS Catalysis
Manuscript ID: cs-2025-02926c
Title: "The Evidence for Single-Atom Ru Catalysts Supported on N-Doped Graphdiyne/γ-Graphyne Quantum Dots is Questionable"
Author(s): Rodionov, Valentin; Richardson, Reese

Dear Dr. Rodionov:

Thank you for submitting your Correspondence with respect to Huang et al.'s article and for alerting us to the issues with this publication. Both the Correspondence and Rebuttal have been reviewed side-by-side by trusted experts.

Based on my opinion as EIC and the opinions of reviewers, I have no confidence that the paper by Huang et al. contains realistic representations of compounds that, even if they were initially present, would survive the treatments they were exposed to. Even if such compounds were present, which is highly unlikely, treatment of the apparently complex organic material at elevated temperatures would have led to the production of amorphous carbon, with catalytic activity then associated with Ru supported on amorphous carbon or graphitized carbon. Because the catalytic activity cannot be attributed to the structure drawn, a Correction in which the chemically unlikely structures are corrected would not be appropriate and the best course of action in this case is to have the paper retracted rather than publish the Correspondence and Rebuttal. While this means your Correspondence will not be published, please understand that it was a critical part of the process to allow us to assess the Huang publication and decide on next steps.

Thank you again for your assistance with this issue.

Sincerely,

Professor Cathleen Crudden
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Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Publish as is; no revisions needed.

Comments:
The authors raise questions regarding various aspects of the paper reported by Huang et al. (ACS Catal. 2023, 13, 12425-12435) The main points of concern are: (1) the synthesis of graphdiyne and γ-graphyne, (2) the syntheses of graphdiyne and γ-graphyne quantum dots and their nitrogen atom doping, (3) the synthesis of Ru single-atom catalysts, and (4) their identification by microscopy and spectroscopy. I think that each point of concern raised in the manuscript is chemically valid. Providing appropriate responses to these questions from the authors of the original work would significantly contribute to the advancement of graphdiyne and

γ-graphyne synthesis, the creation of new materials through their chemical modification, and their application as catalytic materials. In particular, as also noted in this manuscript, the chemical structures proposed in the original paper (linearly arranged two or four sp¹-N atoms) are considered highly chemically unstable. Therefore, it is essential to determine whether materials possessing these structures were actually obtained.
By accepting this paper and engaging in further discussions with the original authors, we expect continued progress in the chemistry of new carbon materials, including graphdiyne and graphyne.

Additional Questions:
Is this manuscript among the top 10% of manuscripts in catalysis?: Yes

If the manuscript is not among the top 10% of manuscripts in catalysis, could it be improved to that level with further work?:

Does the manuscript give a complete and clearly presented description of the procedures that could be reproduced by others in the field?: Yes

Are the literature references appropriate and up to date?: Yes

Please rate the manuscript with regard to its new fundamental catalytic insights and potential for significant scientific impact in catalysis and/or novelty: Excellent (appropriate for ACS Catalysis)

Reviewer: 2

Recommendation: Publish after minor revisions noted.

Comments:
The following is my combined review of the Rodionov manuscript that notes many potential problems with work published by Huang and co-workers in ACS Catalysis in 2023 (DOI: 10.1021/acscatal.3c01390), as well as my consideration of the rebuttal document by the Huang group. I have followed the graphyne/graphdiyne story for many, many years. Simply put, this is a complex, problematic area of research given the fanciful interpretations of molecular structure by people that seemingly do not understand basic chemistry.

Rodionov published a cross-coupling synthesis of gamma-graphyne in JACS in 2022, about the same time that Zhang published a different synthesis via alkyne metathesis in Nature Synth. Since that time, Rodionov has apparently been on a mission to prove that all other reports on the synthesis of gamma-graphyne are not correct. To date, I know that has resulted in (1) the retraction of the Zhang Nature Synth. paper in 2024, (2) two “notes of concern” in Matter in 2024 about the irreproducible synthesis of “holey-graphyne” using the same starting material as Rodionov, and (3) a paper in Carbon earlier this year on the irreproducible synthesis of gamma-graphyne by the mechanochemical reaction of hexabromobenzene with calcium carbide, which is the route that Huang used to prepare the graphyne used in the 2023 study. This current contribution by Rodionov makes this at least the fourth example of calling into question previously published graphyne works.

I have found a LOT of the claims made by various research groups over the years to be dubious, such as “tubular” graphdiyne and “holey” graphyne. The amount of strain in many of these unlikely systems would likely result in a drastic reorganization to a much lower energy material, akin to graphitization which occurs at high temperatures, a process that Baughman specifically pointed out in the original graphyne computational paper in 1987. Are these various research teams making carbon-rich materials? Absolutely. Are these materials the nicely ordered structures comprised solely of sp and sp2 carbon atoms as people like to draw them? Very likely not.

To the matter at hand – Rodionov focuses on both the chemistry behind the preparation of the graphyne/graphdiyne quantum dots and their materials characterization. Examining their points in order:

1. Chemical structures. First, and one of the most critical points, are the implausible chemical structures claimed in Figure 3 and TOC graphic in the 2023 ACS Catalysis paper as pointed out by Rodionov in Schemes 1 and 2 of their submitted manuscript. Surprisingly, and to their detriment, Huang and co-workers fail to specifically address this issue in their rebuttal, which is a major oversight. Sp1 nitrogen atoms are a rarity in organic chemistry. Aside from neutral, uncharged dinitrogen, i.e., N2 gas, any N that has four bonds to it and thus is sp1 MUST have a positive charge on the N atom—period.

(a) In the Nat. Chem. article of 2018, of which the N-doped graphyne and graphdiyne syntheses in these current manuscripts are based, Wang and co-workers specifically noted in their Figure 1 that the sp1 N-atom was indeed positively charged. Also worth noting is that these authors only considered predominantly one, and in a single case, two N atoms in the diyne linkage (Figure S5), but considered "these doping modes barely occur under the given conditions". Given that, it is essentially impossible logic to go from what is shown in Figure 1 of the 2018 Nat Chem article to Figure 3 in the 2023 ACS Catalysis paper which shows four uncharged sp1 N atoms in a row, much like a butadiyne. Simply put, this is chemically impossible, as each of the four N atoms should be positively charged.If that is the case, why would 4 N atoms with a total charge of +4 want to bind a Ru metal center? Such a structure is unknown in the chemical literature as this is chemical nonsense. Also disappointing is the fact that the referees and the associate editor handling the 2023 manuscript failed to notice these glaring chemical impossibilities, as such preposterous structures should have never been published.

(b) In the 2018 Nat. Chem. article, the authors show only five or six possible locations of the N atoms in Figure 3a and Figure S5 – two different nitriliums, a nitrile, a pyridine/pyridinium, and an aniline as possibilities. In most of these, they are single isolated N atoms. Again, this suggests the oligo-N atom structures (e.g., GDQD-Ru, GNQD-Ru, GDQD-NHs, GNQD-NHs) suggested by Huang are not realistic, especially the Ru-based ones. The combinations of amines, diazenes, triazenes, and tetrazenes in the Ru structures are simply fanciful and have no basis in known chemical molecules. In fact, I would expect such structures to be extremely unstable, even possibly explosive, as such structures should lose N2 easily. Why I bring this last point up is that all the systems are heated/annealed at very high temperatures (700-1000 °C), temperatures that would readily expel N2 gas from the purported structures, especially something like in Figure 3f in the 2023 paper. Also, at these temperatures, the alkyne groups would readily reorganize/undergo graphitization. It is worth noting that the 2018 Nat. Chem. article does not go into much, if any, detail of the chemical structure of their materials AFTER the prolonged heating, and I suspect that is because of reorganization/graphitization. To expect these new materials to have the simple phenylacetylene/diacetylene structures after heating at such high temperatures for prolonged periods is unrealistic.

Recommendations – at a bare minimum the Guangzhou team must address the chemical improbability of their posited structures and take steps to correct the potential structures of products upon N enrichment, but with chemically sound molecular structures. The explanations offered in their rebuttal document border at times as to not understanding the myriad problems. For example, Wiley Youngs showed in the 1990s that tribenzohexadehydro[12]annulene, the simplest macrocyclic subunit of gamma-graphyne, could form metal complexes with Ni(0) and a few other low valent metals; however, the corresponding molecules replacing C2 with N2 are not capable of analogous chemistry given their orthogonal pi-orbitals of the sp2 N-atoms, rendering the sp1 N-atoms in "GNQD-Ru" as fictitious.

2. Synthesis. The Guangzhou team prepared the graphyne sample via the hexabromobenzene/calcium carbide ball-milling route, a route that Rodionov very likely debunked earlier this year in Carbon. The graphdiyne synthetic route is via Cu-mediated polymerization of hexaethynylbenzene, an established method, though this is the first instance I have encountered using "Cu-foam" as the catalyst. Given that the graphdiyne synthetic route has been claimed/accomplished by multiple groups, I have less inclination than Rodionov to dispute its

authenticity and that the authors made what they said. Nonetheless, I do return to the point of the extended heating of the graphyne/graphdiyne materials. Rodionov correctly points out that prolonged heating of the acetylenic materials above 300 °C results in destruction/graphitization of the materials. Given that they heated their samples to 700+ °C, the likelihood that the resultant carbonaceous materials had acetylenic units, while not zero, is indeed extremely low. I suspect any alkynes would be randomly located, which could explain the multiple alkyne Raman bands. As noted before, any random N2 units would have also likely be extruded as N2 gas at these high temperatures.

Recommendations – I do not think Huang and co-workers need to go out on a limb here other than to say that the pristine graphyne/graphdiyne structures as drawn are likely implausible after heating/annealing at such high temperatures. They allude to this partially in their rebuttal, but this point should be made crystal clear. It is worth noting, unless I am mistaken, Wang and co-workers do not continue to emphasize the graphdiyne structure in the 2018 Nat Chem paper after the treatment with melamine at elevated temperatures, knowing full well the probability that the scaffold is no longer highly rich in sp-hybridized carbons.

3. Synthesis of Ru-single atom catalysts. As noted above, the chemical structures shown for the graphyne- and graphdiyne-based single-atom Ru catalysts have no basis in chemical reality. Six sp1 N-atoms in a graphyne material binding Ru (Scheme 2 in Rodionov manuscript)? No. Eight to twelve sp2 N-atoms in a complex with Ru(II) as in Scheme 1 of the Rodionov manuscript? Also, an emphatic no – how do these go from being sp1 N all the sudden to sp2 hybridization? All that said, have the authors made a (likely) amorphous carbon-rich material that behaves like a single-Ru catalyst? Possibly, but the chemical characterization of the carbon-rich support material is dubious at best currently. In their rebuttal the original authors state that these structures are “merely proposed structures based on characterization results, and also implies that there may be room for speculation regarding the actual structure”. While I do not disagree that one can speculate, one needs to speculate chemically plausible structures, which did not happen in the 2023 paper. Also, one should speculate based on what the 2018 Nat Chem paper suggested as plausible structures.

Recommendations – aside from revising/deleting the improbable chemical structures incorporating Ru metal atoms with unknown/impossible/improbable oligonitrogen motifs, other potential structures based on known binding of Ni(0) and Co(0) could emerge from research into this problem.

4. Raman spectroscopy. As noted earlier, given that they heated their samples to 700+ °C, the likelihood that the resultant carbonaceous materials had acetylenic units, while not zero, is indeed extremely low. I suspect any alkynes would be randomly located, which could explain the multiple alkyne Raman bands. Still, Rodionov’s arguments make chemical sense.

Recommendations – Huang and co-authors need a better explanation as they do not satisfactorily address the issue.

5. Electron microscopy. Rodionov’s explanation supports my hypothesis of material graphitization at these very high temperatures. These are no longer graphyne/ graphdiyne but carbonaceous material predominantly comprised of sp2 carbon atoms.

Recommendations – Huang and co-authors need a better explanation as they do not satisfactorily address the issue.

6. XPS. My knowledge of XPS is limited, so I will make only a few comments. Rodionov’s arguments about the various oxidation states make sense. More troublesome are the claims in the 2023 paper of substantial N content, when clearly this is not the case in the original 2018 Nat Chem paper.

Recommendations – Huang and co-authors need to explain satisfactorily why the 2023 study incorporates so much more N into the doped graphyne and graphdiyne than the original 2018 study.

“Room for speculation” is not a scientifically valid argument.

7. EDS. My knowledge of EDS is very limited, so I will offer no comments here.

Recommendations – none.

In the end, I feel that the myriad mistakes in the 2023 ACS Catalysis paper warrant a retraction of the original article. I do not argue that the authors made a carbon-rich material doped with Ru that does the claimed catalytic activity. Rather, the many chemically implausible structures in Figure 3 render the calculated free energy pathways in Figure 3i meaningless. Huang and co-authors’ rebuttal document dances around the myriad issues and does not properly address the serious concerns raised in Rodionov’s manuscript.

Additional Questions:
Is this manuscript among the top 10% of manuscripts in catalysis?: No

If the manuscript is not among the top 10% of manuscripts in catalysis, could it be improved to that level with further work?: Maybe (see comments)

Does the manuscript give a complete and clearly presented description of the procedures that could be reproduced by others in the field?: Not applicable

Are the literature references appropriate and up to date?: Yes

Please rate the manuscript with regard to its new fundamental catalytic insights and potential for significant scientific impact in catalysis and/or novelty: Excellent (appropriate for ACS Catalysis)

Reviewer: 3

Recommendation: Not suitable for publication in ACS Catalysis.

Comments:
I took a look to the comments from Valentin O. Rodionov, Reese A. K. Richardson
First of all, I am very sorry that I have no ability to judge the results in original article by Huang, Dionysiou, and co-workers [1] since we did no research about single-atom catalysts in my group. As for the synthesis of γ-graphyne in this paper, the mechanochemical method follows Cui’s protocol in 2018[2].

In 2018, Cui and co-workers proposed mechanochemical synthesis of γ-graphyne [2] on the base of previous reports about the mechanochemical reaction of CaC2 and hexachlorobenzene, and so on.[3, 4] I have noticed that Cui’s paper has attracted extensive attention, and subsequent studies have further advanced this field. Graphyne-related carbon materials synthesized through a mechanochemical strategy have exhibited outstanding performance in various fields, including electromagnetic absorption, energy storage, adsorbents, catalysis, and so on.

Except for the work of Huang, Dionysiou, and co-workers [1], Yun et al.[5] modified conventional mechanochemical treatment by employing Nylon tank equipped ZrO2 balls to synthesize γ-graphyne, which exhibits remarkable absorbability for organic dyes. Zhang et al. [6] also synthesized γ-graphyne by the mechanochemical route using CaC2 and hexabromobenzene, demonstrating much enhanced electromagnetic wave absorbing properties from the synergistic effect of graphene/γ-graphyne.

Following the application of mechanochemical synthesis of γ-graphyne from calcium carbide and hexabromobenzene, the development of other graphyne-related carbon scaffolds, such as naphyne (naphthyl-based)[7] , and nitrogen-rich graphyne (aromatic nitrile-based)[8], were also pursued.

In 2020, Li and co-workers reported the mechanochemical reaction between CaC2 and perchloronaphthy to obtain naphyne featured with an alkynyl-linked naphthyl skeleton[7]. Recently, S-doped graphyne was fabricated by the same group, taking CaC2 and tetrabromothiophene as precursors.[9] Both the high Hg(II) adsorption capability and supercapacitor application were demonstrated. Anyway, these as-fabricated γ-graphyne-related carbon materials exhibit good performance (e.g., energy storage, catalysis, adsorption, and other applications) compared to pure graphitic carbon or amorphous carbon, thereby demonstrating their broad potential from a materials perspective.

I have noticed that Valentin O. Rodionov et al. questioned the mechanochemical method for the synthesis of γ-graphyne and did so-called Replication experiments[10]. In my opinion, the so-called “Replication” should be questionable, since the experimental conditions are different from the original case. [2]

Besides, I have noticed that Prof. Valentin O. Rodionov et al also questioned the synthesis of holey graphyne and related organic reaction mechanism[11,12] that reported by Do Hyun Ryu, Feng Ding, Hyoyoung Lee, and co-workers.[13] Hyoyoung Lee et al. have proposed a response letter to give explanations and clarification. [14]

As a new kind of two-dimensional artificial carbon allotrope that contains sp2 carbon, the synthesis and research about graphdiyne and γ-graphyne and their applications are still underway. Valentin O. Rodionov et al themself also synthesized so-called γ-graphyne[15], and claimed its thermal stability below 300 °C. While Duan et al. [16] synthesized this γ-graphyne sample independently, and proved its structural stability to at least 400 °C. It seems that even with the same predicted chemical structure, the actual characterizations may vary due to the variation in the synthetic procedures.
Just as Huang et al mentioned that the obtained γ-graphyne material, including the sample synthesized by Valentin O. Rodionov et al., still contains a lot of impurities and it is not purely 100% carbon element.

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Additional Questions:
Is this manuscript among the top 10% of manuscripts in catalysis?: No

If the manuscript is not among the top 10% of manuscripts in catalysis, could it be improved to that level with further work?: No

Does the manuscript give a complete and clearly presented description of the procedures that could be reproduced by others in the field?: Not applicable

Are the literature references appropriate and up to date?: Yes

Please rate the manuscript with regard to its new fundamental catalytic insights and potential for significant scientific impact in catalysis and/or novelty: Fair (not appropriate for ACS Catalysis)

Reviewer: 4

Recommendation: Publish as is; no revisions needed.

Comments:
The Comment by Rodionov and Richardson provides a technically well-founded critisism that shows fundamental flaws in the original publication.
Their analysis of the reported graphdiyne and gamma-graphyne syntheses is entirely correct: the described procedures contradict established reaction mechanisms, require implausible operating conditions, and rely on literature that have been experimentally invalidated. The issues raised regarding HEB scalability, Cu-mediated coupling under inert atmosphere, and acetone “reflux” at impossible temperatures reflect real eyperimental impossibilities rather than minor procedural ambiguities. Equally compelling is their demonstration that the gamma-graphyne pathway used by the authors is not chemically credible, given both the absence of known mechanisms for such CC-triple bond formation and the documented failure of these procedures in replication studies.
The Comment also correctly emphasizes that the harsh oxidative and ammonolysis treatments cannot produce N-doped graphdiyne or graphyne quantum dots, nor preserve sp-carbon motifs. The structural models proposed in the original paper (including multi-nitrogen chains and diazene-derived ligands) have no proof and are incompatible with the stated reaction conditions. The critique of the Raman, TEM, and HAADF-STEM data is likewise justified: the reported fringe spacings, spectral features, and image artifacts do not show and prove any graphyne allotrope but instead graphitic char (as many times in this field, it is not the first time).

Overall, the Comment convincingly demonstrates that the substrate materials were misidentified and that the conclusions regarding single-atom Ru loading and coordination environments lack a credible structural basis. The issues raised are very significant and show that the central claims of the original work are not valid. This reviewer finds the Comment is rigorous, and in my view, it should be published urgently. As a consequence, I recommend the editors retract the original paper.

Additional Questions:
Is this manuscript among the top 10% of manuscripts in catalysis?: Yes

If the manuscript is not among the top 10% of manuscripts in catalysis, could it be improved to that level with further work?:

Does the manuscript give a complete and clearly presented description of the procedures that could be reproduced by others in the field?: Yes

Are the literature references appropriate and up to date?: Yes

Please rate the manuscript with regard to its new fundamental catalytic insights and potential for significant scientific impact in catalysis and/or novelty: Excellent (appropriate for ACS Catalysis)

Thank you.