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Strategies for synthesis of Prussian blue analogues

Solveig Kjeldgaard, Iulian Dugulan, Aref Mamakhel, Marnix Wagemaker, Bo Brummerstedt Iversen and Anders Bentien

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Review timeline
Original submission: 7 October 2020
Revised submission: 12 November 2020
Final acceptance: 20 November 2020

Note: Reports are unedited and appear as submitted by the referee. The review history appears in chronological order.

Review History

RSOS-201779.R0 (Original submission)

Review form: Reviewer 1

Is the manuscript scientifically sound in its present form?
Yes

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Do you have any ethical concerns with this paper?
No

Have you any concerns about statistical analyses in this paper?
No

Recommendation?
Accept with minor revision (please list in comments)

Comments to the Author(s)
The paper entitled "Strategies for Synthesis of Prussian Blue Analogues" describes different syntheses and compares the structure of the obtained PBA materials. The PBAs are well characterized by PXRD, Mössbauer spectroscopy, and TEM studies. The manuscript is well organized and uncovered the properties of different PBAs. Therefore, the manuscript can be accepted for publication after minor revision.
The critical comments are as follow:
1. Grammatical errors should be checked again.
2. IR/Raman spectroscopy could be an important tool to understand the bridging of –CN group.
3. The PBAs prepared with potassium tetracyanonickelate should be discussed in the introduction.
4. Recent references for the application of PBAs (Mater. Today Energy 2020, 16, 100404, Chem. Asian J. 2020, 15, 607-623) should be included in the introduction part.
5. Author should describe how the tuneable structure of PBAs affects their electrochemical performance.
6. Author should explain the effect of the insertion of various metal ions at P and R sites in different PBAs.

Review form: Reviewer 2

Is the manuscript scientifically sound in its present form?
No

Are the interpretations and conclusions justified by the results?
Yes

Is the language acceptable?
Yes

Do you have any ethical concerns with this paper?
No

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Recommendation?
Accept with minor revision (please list in comments)

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(1) In addition to battery, PBAs have also been widely studied as electrocatalysts for water splitting and oxygen reduction reactions. This should be briefly discussed in the introduction part

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(3) JCPDS file number of CIF number of the standard reference PBAs added in Fig. S1 should be provide, which could be helpful for readers.

(4) In Fig. S2: (a) N is not shown; (e) and (f) Cu is not shown. Similarly, in Fig. S3: (g) N is not shown; (h) Cu is not shown. Please clarify, why distribution of those elements have not be shown.

Decision letter (RSOS-201779.R0)

We hope you are keeping well at this difficult and unusual time. We continue to value your support of the journal in these challenging circumstances. If Royal Society Open Science can assist you at all, please don't hesitate to let us know at the email address below.

Dear Professor Bentien:

Title: Strategies for Synthesis of Prussian Blue Analogues
Manuscript ID: RSOS-201779

Thank you for submitting the above manuscript to Royal Society Open Science. On behalf of the Editors and the Royal Society of Chemistry, I am pleased to inform you that your manuscript will be accepted for publication in Royal Society Open Science subject to minor revision in accordance with the referee suggestions. Please find the reviewers' comments at the end of this email.

The reviewers and handling editors have recommended publication, but also suggest some minor revisions to your manuscript. Therefore, I invite you to respond to the comments and revise your manuscript.

Because the schedule for publication is very tight, it is a condition of publication that you submit the revised version of your manuscript before 15-Nov-2020. Please note that the revision deadline will expire at 00.00am on this date. If you do not think you will be able to meet this date please let me know immediately.

To revise your manuscript, log into https://mc.manuscriptcentral.com/rsos and enter your Author Centre, where you will find your manuscript title listed under "Manuscripts with Decisions". Under "Actions," click on "Create a Revision." You will be unable to make your revisions on the originally submitted version of the manuscript. Instead, revise your manuscript and upload a new version through your Author Centre.

When submitting your revised manuscript, you will be able to respond to the comments made by the referees and upload a file "Response to Referees" in "Section 6 - File Upload". You can use this to document any changes you make to the original manuscript. In order to expedite the

processing of the revised manuscript, please be as specific as possible in your response to the referees.

When uploading your revised files please make sure that you have:

1) A text file of the manuscript (tex, txt, rtf, docx or doc), references, tables (including captions) and figure captions. Do not upload a PDF as your "Main Document".
2) A separate electronic file of each figure (EPS or print-quality PDF preferred (either format should be produced directly from original creation package), or original software format)
3) Included a 100 word media summary of your paper when requested at submission. Please ensure you have entered correct contact details (email, institution and telephone) in your user account
4) Included the raw data to support the claims made in your paper. You can either include your data as electronic supplementary material or upload to a repository and include the relevant doi within your manuscript
5) All supplementary materials accompanying an accepted article will be treated as in their final form. Note that the Royal Society will neither edit nor typeset supplementary material and it will be hosted as provided. Please ensure that the supplementary material includes the paper details where possible (authors, article title, journal name).

Supplementary files will be published alongside the paper on the journal website and posted on the online figshare repository (https://figshare.com). The heading and legend provided for each supplementary file during the submission process will be used to create the figshare page, so please ensure these are accurate and informative so that your files can be found in searches. Files on figshare will be made available approximately one week before the accompanying article so that the supplementary material can be attributed a unique DOI.

Once again, thank you for submitting your manuscript to Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry. I look forward to receiving your revision. If you have any questions at all, please do not hesitate to get in touch.

Kind regards,
Dr Laura Smith
Publishing Editor, Journals

Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Dr Dattatray Late.

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RSC Associate Editor:
Comments to the Author:
Accept with minor revisions

RSC Subject Editor:
Comments to the Author:

(There are no comments.)

****

Reviewer comments to Author:
Reviewer: 1

Comments to the Author(s)
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Reviewer: 2

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Author's Response to Decision Letter for (RSOS-201779.R0)

See Appendix A.

Decision letter (RSOS-201779.R1)

We hope you are keeping well at this difficult and unusual time. We continue to value your support of the journal in these challenging circumstances. If Royal Society Open Science can assist you at all, please don't hesitate to let us know at the email address below.

Dear Professor Bentien:

Title: Strategies for Synthesis of Prussian Blue Analogues
Manuscript ID: RSOS-201779.R1

It is a pleasure to accept your manuscript in its current form for publication in Royal Society Open Science. The chemistry content of Royal Society Open Science is published in collaboration with the Royal Society of Chemistry.

The comments of the reviewer(s) who reviewed your manuscript are included at the end of this email.

Thank you for your fine contribution. On behalf of the Editors of Royal Society Open Science and the Royal Society of Chemistry, I look forward to your continued contributions to the Journal.

Yours sincerely,
Dr Laura Smith
Publishing Editor, Journals

Royal Society of Chemistry
Thomas Graham House
Science Park, Milton Road
Cambridge, CB4 0WF
Royal Society Open Science - Chemistry Editorial Office

On behalf of the Subject Editor Professor Anthony Stace and the Associate Editor Dr Dattatray Late.

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RSC Associate Editor
Comments to the Author:
Accept as is

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Reviewer(s)' Comments to Author:

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Appendix A

Response to referees

Reviewer: 1

Comments to the Author(s)
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The critical comments are as follow:

1) Grammatical errors should be checked again.

2) IR/Raman spectroscopy could be an important tool to understand the bridging of –CN group.

   Answer: We agree, however, there is already substantial number of different experimental techniques involved (X-ray diffraction, Mössbauer spectroscopy, TEM and STEM-EDS) and we have in the present case decided to not to include more. Still, our conclusions hold and our work provide new information.

3) The PBAs prepared with potassium tetracyanonickelate should be discussed in the introduction.

   Answer: PBA prepared from tetracyanonickelate yields a four-fold coordinated PBA, and is therefore structurally significantly different than PBA prepared from hexacyanoferrates. PBA offer such a wide range of structural tuning, and in the current study we focus on PBA prepared from hexacyanoferrate, stated on page 3, line 24.

4) Recent references for the application of PBAs (Mater. Today Energy 2020, 16, 100404, Chem. Asian J. 2020, 15, 607-623) should be included in the introduction part.

   Answer: The references have now been included.

5) Author should describe how the tuneable structure of PBAs affects their electrochemical performance.

   Answer: A section has been added to the introduction (end of page one to page two) on the relationship between structural variation and electrochemistry.

6) Author should explain the effect of the insertion of various metal ions at P and R sites in different PBAs.

   Answer: We have now included this in the introduction (same section as indicated above).

Reviewer: 2

Comments to the Author(s)
This manuscript reports different common synthetic strategies for preparation of Prussian Blue Analogues (PBAs), particularly taking examples of Cu-Fe PBAs. Altogether 11 different Cu-Fe PBAs and one Mn-Fe based PBA have synthesized and characterized. The work is a comprehensive work on the synthetic strategies of PBAs and the manuscript provides various information on PBAs, which could be very helpful to material scientists working on PB structure-based materials. The manuscript is well-written and organized. In my views, the manuscript is suitable to be accepted in Royal Society Open Science after minor revision on the followings.

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   Answer: The references have now been included.

2) In Page 11, Line 30: it is stated that "It is well known that Prussian White, FeII[FeII], easily oxidizes to Prussian Blue, FeIII[FeII]. In contrast, in Page11, Line 40-4: it is stated that "Mössbauer spectroscopy reveals partial reduction of assynthesized CuII[FeIII]: In Sample C, 34 % of iron has been reduced to iron(II),…."
   Authors should explain why oxidation takes place selectively from FeII[FeII] to FeIII[FeII], but not to FeII [FeIII], while reduction take place from CuII[FeIII] to CuII[FeII], but not to CuIII[FeII].

   Answer: Copper(III) is not a common oxidation state for copper, and oxidation therefore takes place from $Cu^{II}[Fe^{II}]$ to $Cu^{II}[Fe^{III}]$.
   In the case of iron hexacyanoferrate, Prussian Blue and Turnbull's blue were for a long time believed to be different compounds. Prussian Blue was prepared from an iron(III) salt and potassium ferricyanide, whereas Turnbull's Blue was prepared from an iron(II) salt and potassium ferrocyanide. The resulting compounds were believed to be $Fe^{III}[Fe^{II}]$ and $Fe^{II}[Fe^{III}]$, respectively. In 1968, Mössbauer studies proved that both compounds were identical, namely $Fe^{III}[Fe^{II}]$.[1]

3) JCPDS file number of CIF number of the standard reference PBAs added in Fig. S1 should be provide, which could be helpful for readers.

   Answer: The initial structural model was ICSD-89338. This is included in the experimental section under Materials characterization, Powder X-ray Diffraction.

4) In Fig. S2: (a) N is not shown; (e) and (f) Cu is not shown. Similarly, in Fig. S3: (g) N is not shown; (h) Cu is not shown. Please clarify, why distribution of those elements have not be shown.

   Answer: Samples E, F and G are iron hexacyanoferrate (see table 1) and copper is therefore not present in the sample and is not included in STEM-EDS. For copper hexacyanoferrate samples the nitrogen distribution corresponds with the iron distribution (from $[Fe(CN)_6]$ units, and for some copper hexacyanoferrate samples nitrogen is therefore not shown.

References

1 A. Ito, M. Suenaga and K. Ôno, *J. Chem. Phys.*, 1968, **48**, 3597–3599.