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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Patrick Aggrey

PhD Program: Materials Science and Engineering

Title of Thesis: Nanoscale phase separation and transformations in the silicon-oxygen and related systems

Supervisor: Professor Alexander Korsunsky
Co-supervisor: Alexey Salimon, Senior Research Engineer

Name of the Reviewer: Aksyonov Dmitry

I confirm the absence of any conflict of interest	**Date: 30-05-2023**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

The thesis is well written though the structure should improved. In particular the introduction section should highlight the motivation, formulate the problem as well as its novelty, and clearly state the goal and tasks of the study. The section methods contains numerous excursions to motivation and literature. Normally this should be given either in introduction or literature review. Some of the figures should be improved. The conclusions should highlight the novelty of the obtained results. I suggest to highlight 3-4 most important outcomes of the study.

The content of the thesis is relevant to its topic and the used methods are adequate. The results comply with the international level and relevant for applications related to optics and energy storage. The results are well published in international journals.

The summary of issues to be addressed before/during the thesis defense

In Abstract:

- “drew on a wide range of characterization techniques” what do you mean here? Please be more specific

- “opened the possibilities for producing nanostructured silicon materials with a vast range of functionalities in a facile, eco-friendly and cost-effective way … a vast range of functionalities”. What possibilities do you mean? What is the vast range of functionalities? Please be more specific.

In introduction

- it is mentioned that “certain shortcomings and challenges are encountered in the nanostructuring of materials …”. Do you mean the challenges with the process of nanostructuring or problems with nanostructured materials? Should be clarified.

In methods:

- What was the partial pressure of oxygen during calcination and roasting?

- Why the temperature of 1100 C and time of 4 hours were used for calcination and roasting?

- First and second paragraphs of Section “2.4.2 In situ formed Silicon nanoflakes” should be moved to introduction or results

- It should be clarified what silica powders (pristine of after roasted) were used to create coatings

- In section 2.8 Electrode Preparation and Electrochemical Measurement it is stated “All measurements were carried out at a constant temperature of 20 °C.” How did you control the temperature?

In results

- “When tested as anode materials, the calcined diatom-derived silica powder showed the best discharge capacity of 550mAhg -1 amongst the three silica types (380mAhg -1 for roasted and 175mAhg -1 for the pristine powders).” Why did the calcined samples show the highest capacity? How does it compare to other silica materials obtained in literature?

In Section 3.1.1 Modifications in Color, Particle and Crystallite Sizes

- you present analysis of chemical composition. Please mention this in the title.

- “It is evident from this study that particle size reduction is an effective tool to improve electrochemical performance in devices” Here this statement was not proved yet or do you mean literature data?. Reformulate.

- “In this work, the calcined and roasted diatom-derived silica powders had crystallite sizes of 8.58 nm and 11.44 nm respectively for the main cristobalite phase as shown in Table 4.” Clarify how the size of crystallites was determined? The fact that cristobalite is the main phase is shown only in the next section. Please correct.

- “The limited flow of oxygen (argon environment) appears to not only limit coloration but is equally suitable for obtaining small cristobalite crystallites.” Why are you interested in a limited air flow? The size of crystallites during roasting is only slightly larger.

- Figure 12. What is the space group of cristobalite phase? Is it alpha-phase or beta phase? Please clarify in the text and in the caption.

- Figure 17. The capacity of heat treated sample is increasing each cycle. Why? The currently given explanation should be expanded and requires clarification about the mechanism of electrochemical milling.

- What is the coulombic efficiency? It should be provided.

- Figure 17. What is the electrochemical reaction taking place here? What are the discharge products? Is there any O2 gas formation upon discharge? Do you consider insulating SiO2 as a viable anode material?

- A summary for Section 3.1 is required. What are the advantages and disadvantages of each heat treatrement? What are the main differences between them in terms of microstructure, composition and properties?

- Why XRD in Fig 12a and Fig19a are strongly different?

- Figure 22. Why only five cycles are provided?

In section 3.3.5 Optical Properties of Silicon nanoflakes

- “The silicon nanoflakes suppressed light reflection to less than 15% in the infrared region compared to the 45% light reflection from the c-Si wafer surface.” Is it for pristine or roasted SiO2 powder? How does it compare to black silicon?

- A summary for Section 3.2 is required.

Conclusions:

- “results could help provide guidelines for selecting the most ideal precursor diatom derived silica for the synthesis of silicon based materials for energy related applications.” Can you formulate these guidelines here?

- “possessed very intricate details of the precursor diatomite powder to some extent” Can you be more specific?

- “A preliminary adhesion scratch test also confirmed a good bonding of the silicon nanoflakes

to the surface of the substrate silicon wafer.”

Figures:

- Improve the quality of Fig. 9 and 10. The y axis label is hardly visible.

- Improve Fig 14. The figures are compressed along the horizontal line. Looks strange.

- Improve Fig 16 and Fig 17. figures have different size. Looks inaccurate

- improve Figure 31, b and c are blurred

The mentioned issues do not reduce the overall quality of the thesis work. Therefore I recommend that the candidate should defend the thesis by means of a formal thesis defense after the appropriate changes to the thesis.

Provisional Recommendation

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*

Assistant Professor of Skolkovo Institute of Science and Technology, Dr. Aksyonov D.A.		30.05.2023