

Advancing Sulfide Solid Electrolytes via Green Li₂S Synthesis

Corresponding Author: Professor Guowei Zhao

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

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This paper presents the synthesis of Li₂S via a solvent-free metathesis reaction using thiourea and lithium hydroxide. The authors effectively integrate DFT calculations with the experimental synthesis procedure, providing a well-justified rationale for the choice of precursors. The methodology is clearly described and supported by appropriate references. Additionally, the authors explore possible reaction pathways and validate them with experimental evidence. Finally, the conditions for the synthesis of Li₂S are established.

The synthesized Li₂S was subsequently employed in the preparation of two types of solid electrolytes—NASICON and argyrodite—which were further evaluated in battery assemblies.

I recommend this paper for publication after minor revision. In particular, the claims regarding eco-friendly or green synthesis, as stated in the title and abstract, should be further clarified. A discussion on the environmental impact, especially related to CO₂ generation, would strengthen these claims and enhance the manuscript's overall contribution.

Reviewer #2

(Remarks to the Author)

This paper presents an eco-friendly and low-cost synthesis method of highly pure Li₂S for sulfide solid electrolytes via solvent-free metathesis reaction between thiourea and LiOH. The reaction route proposed in this paper leads to a complete conversion to Li₂S because no Gmix would be generated during the reaction. This novel synthesis method of Li₂S allows us to decrease the cost of total manufacturing of sulfide solid electrolyte. The solid electrolytes generated from the Li₂S synthesized by this metathesis reaction show high ionic conductivity with negligible electron conductivity, demonstrating performance as a pure ionic conductor. The manuscript is well-written, with clear and visually appealing figures. The Elucidation of the reaction mechanism is thorough and accurate. However, physical and chemical characterization require improvement, and thus the comments below must be fully addressed before this paper can be considered for publication.

1. Why does the metathesis method use more thiourea than stoichiometric ratio when the authors explain that the metathesis reaction leads to complete conversion to Li₂S main product? The final composition of the materials is not verified through chemical characterization. This should be addressed by means of ICP or other related techniques.
2. What is the yield rate of Li₂S in the metathesis reaction route provided in this study.
3. Safety concerns regarding CS₂, a deleterious substance produced by the thermal decomposition of thiourea, should be explained if the authors emphasize environmental friendliness for the metathesis method proposed in this work. Does CS₂ production from excessive thiourea use pose a safety concern?
4. The Rietveld refinement lacks structural parameters. The lack raises doubts about the reliability of the results. The authors should present the structural parameters of the refined XRD patterns (Figure 3d and Figure 4b).
5. morphology properties depend on the synthesis method and are important properties that characterize the material's physical properties. It is necessary to evaluate morphologies characterization such as particle size distribution statistics.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The authors have thoroughly addressed all the comments. I believe that this work represents a valuable advance, and will make a significant contribution to battery development. I recommend that this paper be published in Nature Communications without additional revisions.

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Response to the Reviewers' Comments/Questions to NCOMMS-25-12375A-Z

Manuscript title: Advancing Sulfide Solid Electrolytes via Green Li₂S Synthesis

We thank both reviewers for their valuable comments and constructive suggestions. We have carefully considered each point and revised the manuscript accordingly to improve its clarity and scientific rigor. Below, we provide a detailed point-by-point response. All changes made in the manuscript are highlighted for clarity.

Reviewer #1:

Comment:

This paper presents the synthesis of Li₂S via a solvent-free metathesis reaction using thiourea and lithium hydroxide. The authors effectively integrate DFT calculations with the experimental synthesis procedure, providing a well-justified rationale for the choice of precursors. The methodology is clearly described and supported by appropriate references. Additionally, the authors explore possible reaction pathways and validate them with experimental evidence. Finally, the conditions for the synthesis of Li₂S are established. The synthesized Li₂S was subsequently employed in the preparation of two types of solid electrolytes-NASICON and argyrodite-which were further evaluated in battery assemblies.

I recommend this paper for publication after minor revision. In particular, the claims regarding eco-friendly or green synthesis, as stated in the title and abstract, should be further clarified. A discussion on the environmental impact, especially related to CO₂ generation, would strengthen these claims and enhance the manuscript's overall contribution.

Responses:

We sincerely appreciate the reviewer for recognizing the scientific merit of our study. Your kind suggestions help us improve our manuscript.

We agree with the reviewer that the terms on “eco-friendly” and “green synthesis” should be further clarified. These terms were used to compare the environmental benefits with other Li₂S synthesis routes reported in the references. As summarized in **Table 1**, conventional methods often employ explosive precursors (highlighted in red) or toxic H₂S (highlighted in blue) as raw materials. In contrast, our approach utilizes LiOH and thiourea as starting materials, both of which are stable under ambient air conditions and non-explosive. Furthermore, the gaseous emissions from our process are non-toxic and non-explosive. Therefore, this comparative analysis substantiates the relatively greener and more eco-friendly of our synthesis route.

We also highly appreciate the suggestions of discussion on CO₂ emission proposed by the reviewer, which we overlooked in original manuscript. On one hand, the CO₂ emission by Li₂S synthesis is relatively negligible compared with global CO₂ emission. According to statistics from EV Tank, a prominent data consulting firm in the new energy vehicle industry, the global demand for solid-state electrolytes is projected to reach 210 kton by 2030 (**Figure 1**). Assuming this entire 210 kton

electrolyte demand is met by $\text{Li}_6\text{PS}_5\text{Cl}$ electrolyte, the overall Li_2S requirement would be 72.4 kton/yr for energy-related applications. Therefore, the theoretical CO_2 emission would be 69 kton/yr, which is only 0.002% of the global CO_2 emission (35.8 Gton/yr).¹ On the other hand, exhaust gas treatment facilities could effectively reduce the CO_2 emission. As a proof of concept, we integrated an aluminum water tank at the reactor exhaust outlet. During the reaction, the emitted CO_2 and NH_3 are directed into this treatment system and generate non-toxic NH_4HCO_3 :



We once again thank the reviewer for your valuable feedback on the greenhouse effect. Based on your kind suggestions and the analysis above, we added corresponding discussion in the revised manuscript. “In addition, considering the potential impact of CO_2 on the greenhouse effect, a simple aluminum water tank was integrated at the reactor exhaust outlet. The exhausted CO_2 was fixed by rapid reaction with NH_3 byproducts in aqueous phase and generated non-toxic/non-volatile NH_4HCO_3 final product. Consequently, the actual CO_2 emissions from this reaction exert a negligible impact on the greenhouse effect.”

Table 1. Comparison of Li_2S synthesis methods

Starting raw materials		Reaction Method	Final Products	Safety Concern	Ref.
$\text{Li}(\text{CH}_2\text{CH}_3)_3\text{BH}$	S powder	Solution synthesis	Li_2S	explosive	2
Lithium tert-butoxide	S powder	Solution synthesis	Li_2S	explosive	3
LiH	S powder	Solid synthesis	Li_2S	explosive	4
Lithium tert-butoxide	H_2S gas	ALD synthesis	$\text{Li}_2\text{S} + \text{H}_2\text{S}$	explosive, toxic	5
Li-naphthalene	H_2S gas	Solution synthesis	$\text{Li}_2\text{S} + \text{H}_2\text{S}$	explosive, toxic	6
Li foil	H_2S gas	Solution synthesis	$\text{Li}_2\text{S} + \text{H}_2\text{S}$	toxic	7
Li foil	H_2S gas	Solution synthesis	$\text{Li}_2\text{S} + \text{H}_2\text{S}$	toxic	8
LiOH	Thiourea	Solid meta-synthesis	$\text{Li}_2\text{S} + \text{NH}_3 + \text{CO}_2$	None	This work

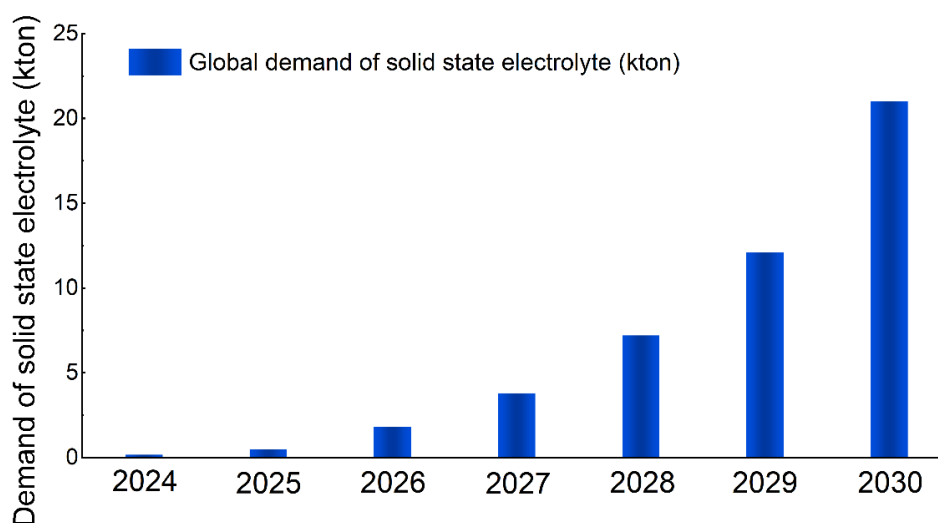


Figure 1. The global demand of solid-state electrolyte.

- [1] Liu Z, Deng Z, Davis S J, et al. Global carbon emissions in 2023[J]. *Nature Reviews Earth & Environment*, 2024, 5 (4): 253-254.
- [2] Lin Z, Liu Z, Dudney N J, et al. Lithium Superionic Sulfide Cathode for All-Solid Lithium–Sulfur Batteries[J]. *ACS Nano*, 2013, 7 (3): 2829-2833.
- [3] El-Shinawi H, Cussen E J and Corr S A. A facile synthetic approach to nanostructured Li_2S cathodes for rechargeable solid-state Li–S batteries[J]. *Nanoscale*, 2019, 11 (41): 19297-19300.
- [4] Li X, Gao M, Du W, et al. A mechanochemical synthesis of submicron-sized Li_2S and a mesoporous $\text{Li}_2\text{S}/\text{C}$ hybrid for high performance lithium/sulfur battery cathodes[J]. *Journal of Materials Chemistry A*, 2017, 5 (14): 6471-6482.
- [5] Meng X, Comstock D J, Fister T T, et al. Vapor-phase atomic-controllable growth of amorphous Li_2S for high-performance lithium-sulfur batteries[J]. *ACS Nano*, 2014, 8 (10): 10963-72.
- [6] Li X, Wolden C A, Ban C, et al. Facile Synthesis of Lithium Sulfide Nanocrystals for Use in Advanced Rechargeable Batteries[J]. *ACS Applied Materials & Interfaces*, 2015, 7 (51): 28444-51.
- [7] Zhao Y, Smith W and Wolden C A. Scalable Synthesis of Li_2S Nanocrystals for Solid-State Electrolyte Applications[J]. *Journal of The Electrochemical Society*, 2020, 167 (7): 070520.
- [8] Zhao Y, Yang Y and Wolden C A. Scalable Synthesis of Size-Controlled Li_2S Nanocrystals for Next-Generation Battery Technologies[J]. *ACS Applied Energy Materials*, 2019, 2 (3): 2246-2254.

Reviewer #2:**Comments:**

This paper presents an eco-friendly and low-cost synthesis method of highly pure Li_2S for sulfide solid electrolytes via solvent-free metathesis reaction between thiourea and LiOH . The reaction route proposed in this paper leads to a complete conversion to Li_2S because no G_{mix} would be generated during the reaction. This novel synthesis method of Li_2S allows us to decrease the cost of total manufacturing of sulfide solid electrolyte. The solid electrolytes generated from the Li_2S synthesized by this metathesis reaction show high ionic conductivity with negligible electron conductivity, demonstrating performance as a pure ionic conductor. The manuscript is well-written, with clear and visually appealing figures. The Elucidation of the reaction mechanism is thorough and accurate. However, physical and chemical characterization require improvement, and thus the comments below must be fully addressed before this paper can be considered for publication.

- 1. Why does the metathesis method use more thiourea than stoichiometric ratio when the authors explain that the metathesis reaction leads to complete conversion to Li_2S main product? The final composition of the materials is not verified through chemical characterization. This should be addressed by means of ICP or other related techniques.*
- 2. What is the yield rate of Li_2S in the metathesis reaction route provided in this study?*
- 3. Safety concerns regarding CS_2 , a deleterious substance produced by the thermal decomposition of thiourea, should be explained if the authors emphasize environmental friendliness for the metathesis method proposed in this work. Does CS_2 production from excessive thiourea use pose a safety concern?*
- 4. The Rietveld refinement lacks structural parameters. The lack raises doubts about the reliability of the results. The authors should present the structural parameters of the refined XRD patterns (Figure 3d and Figure 4b).*
- 5. Morphology properties depend on the synthesis method and are important properties that characterize the material's physical properties. It is necessary to evaluate morphologies characterization such as particle size distribution statistics.*

General Responses:

We highly appreciate the positive evaluation of the reviewer to our manuscript. We also thank the reviewer for the valuable comments and suggestions, which help us to improve our paper. We have made a point-to-point response to your questions and concerns. Thank you again for your kind effort.

Question 1. *Why does the metathesis method use more thiourea than stoichiometric ratio when the authors explain that the metathesis reaction leads to complete conversion to Li_2S main product? The final composition of the materials is not verified through chemical characterization. This should be addressed by means of ICP or other related techniques.*

Response :

We sincerely appreciate the reviewer's insightful question concerning the excess thiourea employed in our synthesis process. This is a critical step in this work. Our investigation revealed that the decomposition of thiourea begins above 200 °C with the generation of CS₂, whereas the reaction between LiOH and carbon disulfide CS₂ to yield lithium sulfide Li₂S starts at 400 °C. Therefore, during the crucial temperature window between 200 °C and 400 °C, the unreacted CS₂ would flow away from the reaction system via the N₂ gas stream. To compensate for the loss of CS₂ occurring during this temperature window and ensure the final product achieves the target stoichiometry, we introduced an excess of thiourea into the initial reactants.

We acknowledge and sincerely regret that the manuscript did not explicitly clarify this fundamental reason (CS₂ volatilization loss between 200 °C and 400 °C) for the thiourea excess. Following your valuable suggestion, we have comprehensively addressed this mechanism in the revised manuscript. This clarification will significantly enhance the readers' understanding and enable the successful replication of our synthesis protocol.

Based on the information above, we added the describe “The decomposition of thiourea begins above 200 °C with the generation of CS₂, whereas the reaction between LiOH and carbon disulfide CS₂ to yield lithium sulfide Li₂S starts at 400 °C. Therefore, during the crucial temperature window between 200 °C and 400 °C, the lack of reaction between CS₂ and LiOH results in the loss of CS₂ from the reaction system via the flowing N₂ purge gas stream. To compensate for the loss of CS₂ occurring during this temperature window and ensure the final product achieves the target stoichiometry, we introduced an excess of thiourea into the initial reactant.” in the Supplementary Materials with red color.

We have also made the material composition analysis regarding your kind suggestion. According to the ICP and High-frequency infrared carbon-sulfur analysis results, the total impurity content in the Li₂S-Smeta products was below 0.2wt.%. The impurity final composition of the product contained trace amount of Al, Zr, Na, Si and C elements. We attribute the presence of impurity elements to the following sources: Zr (0.0153%) was originated from the yttria-stabilized zirconia grinding media used during ball milling; Al (0.0117%) was derived from the alumina (Al₂O₃) crucible employed in the calcination process; Na (0.0075%) and Si (0.0066%) were introduced by the fused quartz tube utilized in the calcination furnace. C (0.092%) was introduced by the excess of thiourea. The percentage compositions of each component were summarized in **Table 2**.

Based on the information above, we added the describe “Based on ICP and high-frequency infrared carbon-sulfur analysis, the total impurity content in the Li₂S-Smeta products is less than 0.2 wt.%. The constituent impurities and their respective concentrations are listed in **Table S3**.” in the revised manuscript.

In addition, “According to the ICP and High-frequency infrared carbon-sulfur analysis results, the total impurity content in the Li₂S-Smeta products was below 0.2wt.%. The impurity final composition of the product contained trace amount of Al,

Zr, Na, Si and C elements. We attribute the presence of impurity elements to the following sources: Zr (0.0153%) was originated from the yttria-stabilized zirconia grinding media used during ball milling; Al (0.0117%) was derived from the alumina (Al_2O_3) crucible employed in the calcination process; Na (0.0075%) and Si (0.0066%) were introduced by the fused quartz tube utilized in the calcination furnace. C (0.092%) was introduced by the excess of thiourea.”, “**ICP testing:** The elemental composition of the Li_2S -Smeta sample was conducted by using ICP-OES measurements (Agilent 5110, America). The Pump Rate was 60 r/min; Plasma gas was 12.0 L/min; Nebulizer Flow was 0.70 L/min, Auxiliary Gas was 1.0L/min, RF Power was 1250 w.” and “**High-frequency infrared carbon–sulfur analyzer testing:** The carbon content of the Li_2S -Smeta sample was conducted by using High-frequency infrared carbon–sulfur analyzer (HCS-140, China). The Oxygen flow rate was 1.5 L/min, Purge time was 20 s, Integration Delay was 10 s, O_2 Supply Pressure was 0.25 MPa.” were added in the Supplementary Materials with red color. Table 2 was added in Supplementary Materials as Table S3.

Table 2. Elemental composition of the Li_2S -Smeta sample by ICP and High-frequency infrared carbon–sulfur analyzer testing.

Testing elements	Percentage compositions of each component	Testing Method
Al	0.0117%	ICP
Zr	0.0153%	ICP
Na	0.0075%	ICP
Si	0.0066%	ICP
C	0.092%	High-frequency infrared carbon–sulfur analyzer

Question 2. *What is the yield rate of Li_2S in the metathesis reaction route provided in this study?*

Response :

We appreciate the reviewer for this kind question.

The yield rate of Li_2S -Smeta products is approximately 95.4% of theoretical yield. We speculated that the mass loss arises from ball-milling and calcination-driven volatilization.

Based on the information above, we added the describe “The yield rate of Li_2S -Smeta products is approximately 95.4%.” in the manuscript with red color.

Question 3. Safety concerns regarding CS_2 , a deleterious substance produced by the thermal decomposition of thiourea, should be explained if the authors emphasize environmental friendliness for the metathesis method proposed in this work. Does CS_2 production from excessive thiourea use pose a safety concern?

Response :

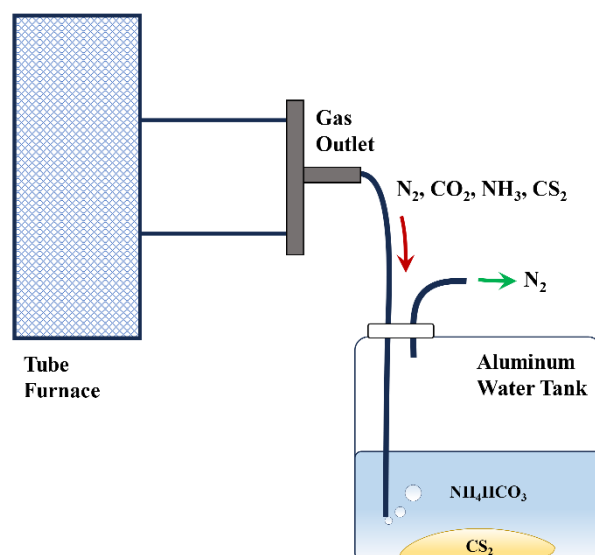


Figure 2. The schematic diagram of aluminum water tank for Carbon Disulfide Recovery and Storage.

We appreciate the reviewer for this kind question.

Industrial processes commonly employ condensation to recover and preserve CS_2 . In the present work, we adapted this principle by installing an aluminum water tank at the reactor outlet. Taking the low boiling point of CS_2 (46.3°C) into consideration, this setup facilitates the liquefaction and recovery of the evolved CS_2 vapor via controlled cooling (Figure 2). We anticipate that upon scale-up, process enhancements will provide a more comprehensive solution to this matter.

Question 4. The Rietveld refinement lacks structural parameters. The lack raises doubts about the reliability of the results. The authors should present the structural parameters of the refined XRD patterns (Figure 3d and Figure 4b).

Response :

We appreciate the reviewer for this kind suggestion. The relevant structural parameters of the refined XRD patterns (HY- Li_2S -800, CA- Li_2S -800 and L_2S -Smeta) have been added into Table S2 with red color in Supplementary Materials.

Question 5. Morphology properties depend on the synthesis method and are

important properties that characterize the material's physical properties. It is necessary to evaluate morphologies characterization such as particle size distribution statistics.

Response :

We appreciate the reviewer for this kind suggestion. The morphologies characterization and the corresponding particle size (D_{50}) of Li_2S -Smeta, LGPS-Smeta Li_2S , and $\text{LPSC}_{1.5}$ -Smeta Li_2S are exhibited in Figure 3, Figure 4 and Figure 5.

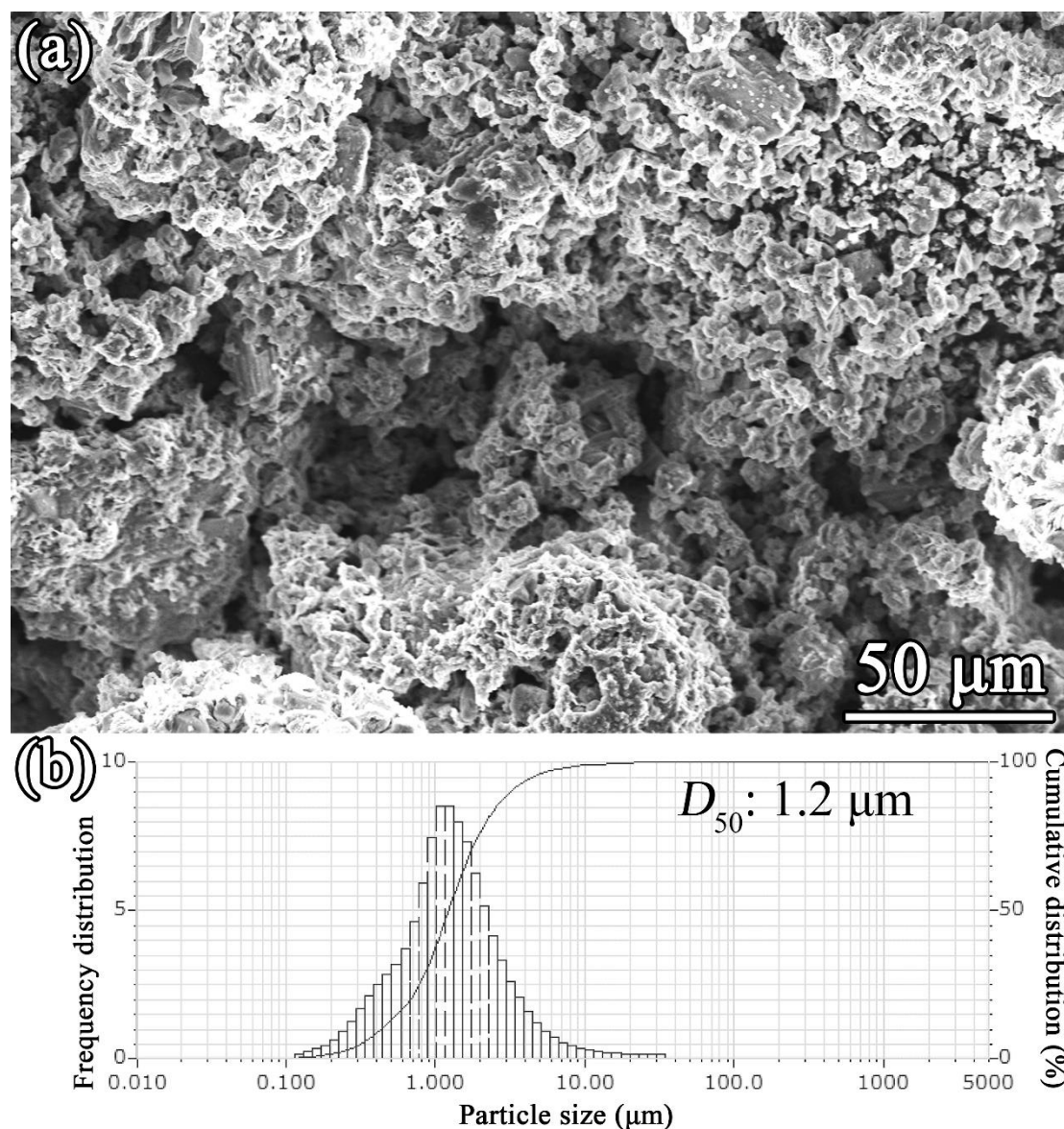


Figure 3. (a) The morphology of Li_2S -Smeta sample. (b) Particle size distribution of Li_2S -Smeta sample.

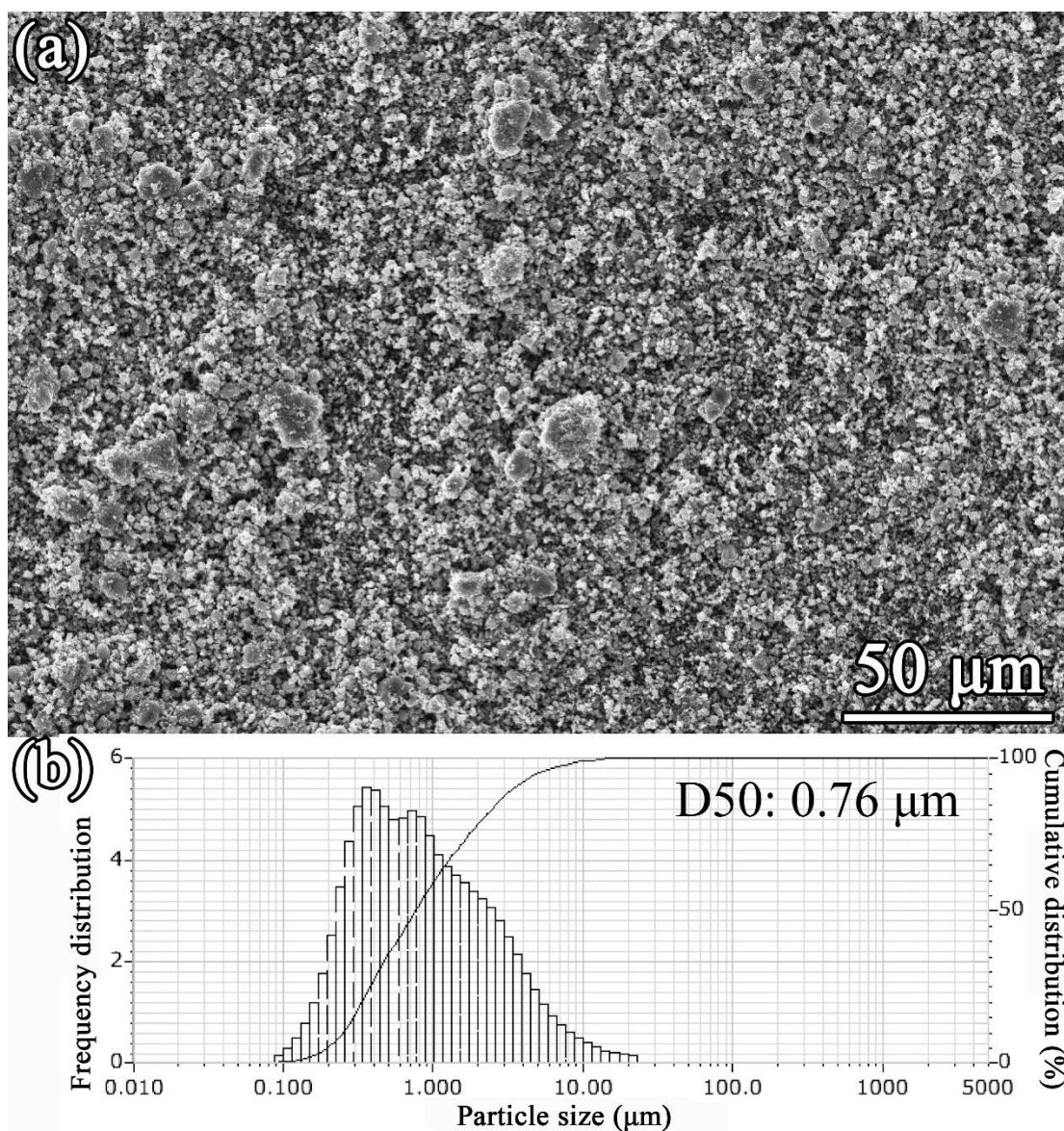


Figure 4. (a) The morphology of LGPS-SmetaLi₂S sample. (b) Particle size distribution of LGPS-SmetaLi₂S sample.

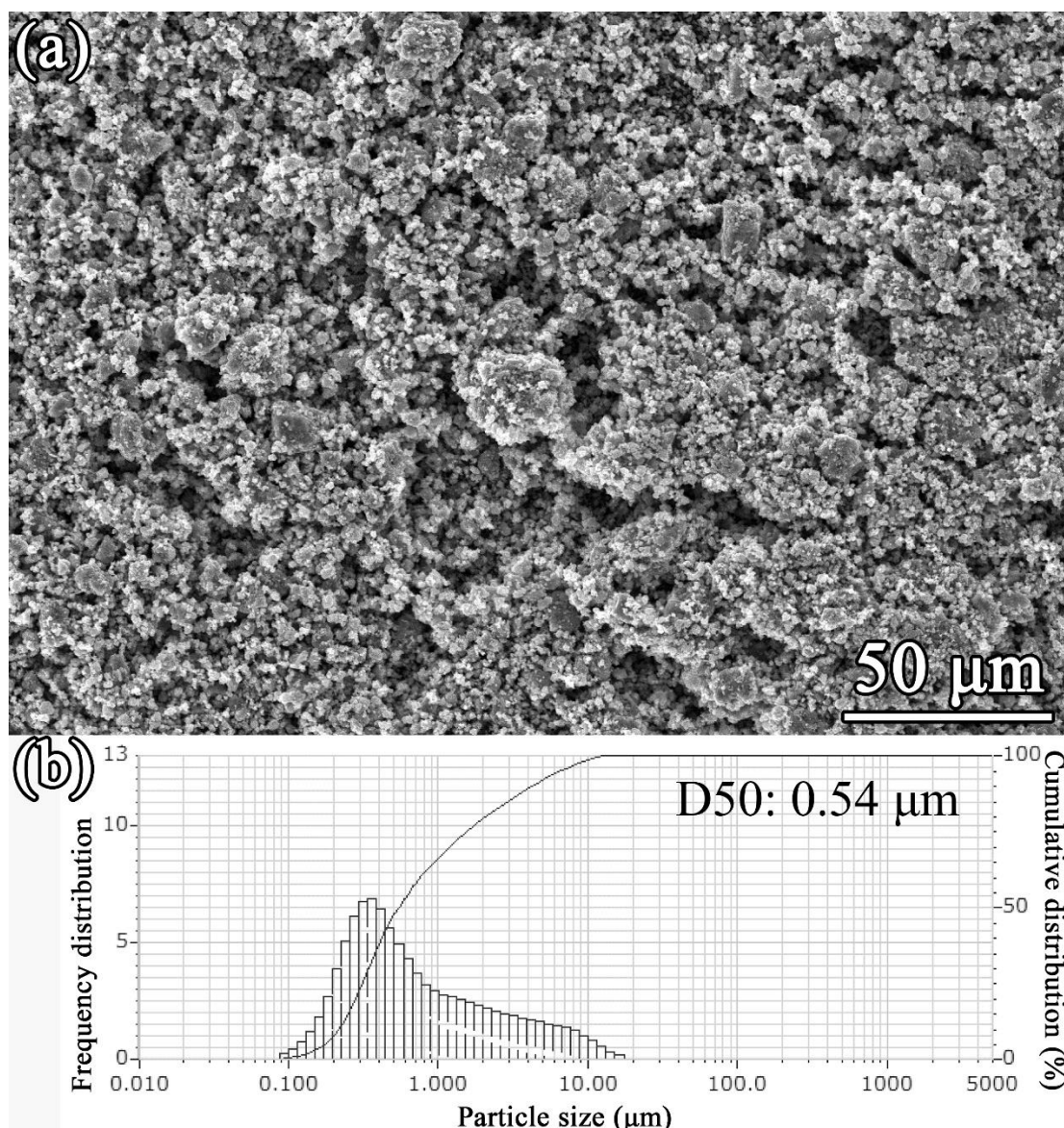


Figure 5. (a) The morphology of LPSC_{1.5}-SmetaLi₂S sample. (b) Particle size distribution of LPSC_{1.5}-SmetaLi₂S sample.

Based on the information above, we added the describe “Numerous pores could be seen from the SEM image of Li₂S-Smeta products (**Figure S5a**), which could be attributed to the formation of gas byproducts during the metathesis reaction. The average particle size (D_{50}) for Li₂S-Smeta products were 1.2 μm (**Figure S5b**).”, “The SEM image of LGPS-SmetaLi₂S was displayed in **Figure S8a** and the corresponding D_{50} value for LGPS-SmetaLi₂S products were 0.76 μm (**Figure S8b**).” and “The SEM image of LPSC_{1.5}-CommLi₂S was shown in **Figure S11a** and the corresponding D_{50} value for LPSC_{1.5}-CommLi₂S products was 0.54 μm (**Figure S11b**).”in the manuscript with red color. The Figure 3, Figure 4 and Figure 5 were added into Supplementary Materials as **Figure S5**, **Figure S8** and **FigureS11**.

Closing Statement:

We once again thank both reviewers for their thoughtful comments, which have helped us significantly improve the clarity and impact of the manuscript. We believe the revised version satisfactorily addresses the concerns raised and better conveys the novelty and practical significance of our proposed synthesis approach. Please do not hesitate to contact us for any further clarifications or suggestions.