

Supplementary Information

Advancing Sulfide Solid Electrolytes via Green Li₂S Synthesis

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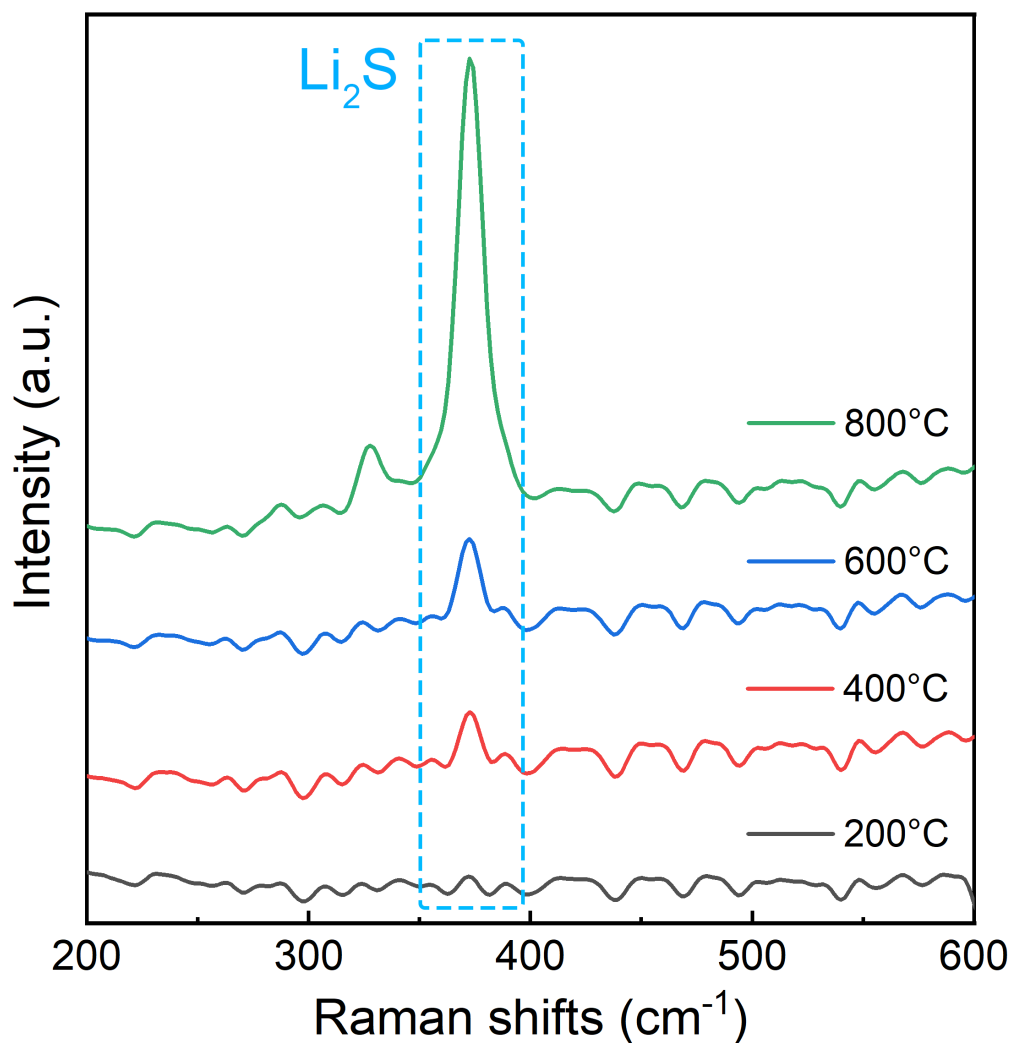
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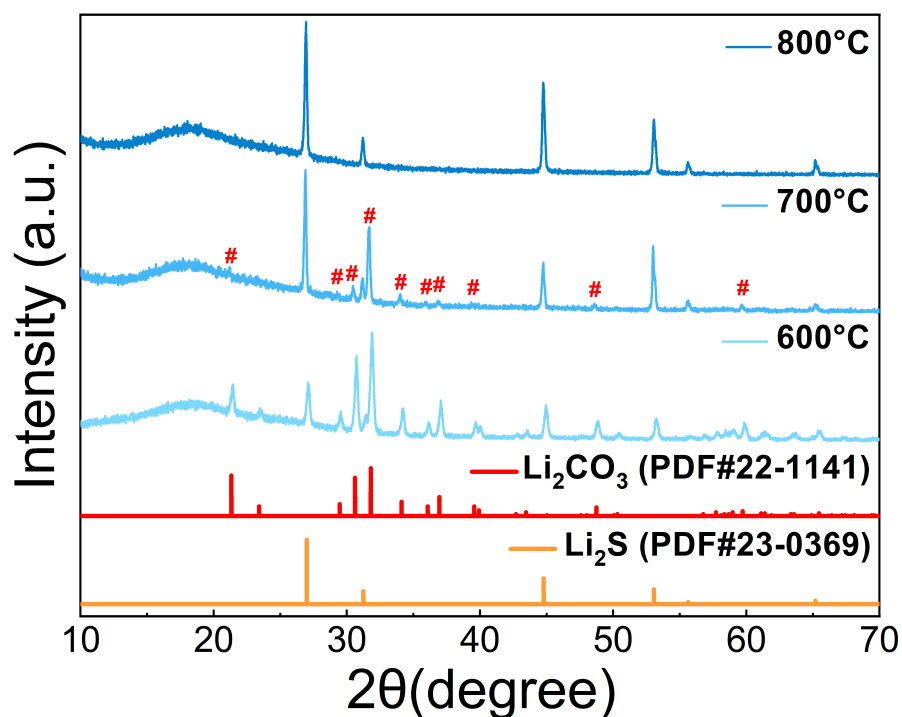
Inventory of Supplementary items

Supplementary Figures and Tables.....	3
Supplementary Figure 1 Raman spectra of the products from Eq. 1 at different temperature.....	3
Supplementary Figure 2 XRD patterns of CA-Li ₂ S-600, CA-Li ₂ S-700, CA-Li ₂ S-800 samples.	4
Supplementary Figure 3 SEM images of the obtained samples.....	5
Supplementary Figure 4 Digital picture of HY-Li ₂ S-800 and CA-Li ₂ S-800 after dissolved in absolute alcohol.	5
Supplementary Figure 5 The morphology and corresponding particle size of Li ₂ S-Smeta sample.....	6
Supplementary Figure 6 The ball-milled LGPS-SmetaLi ₂ S precursors.....	7
Supplementary Figure 7 XRD Refinement Patterns.	7
Supplementary Figure 8 The morphology and corresponding particle size of the obtained typical sample of LGPS-SmetaLi ₂ S.....	8
Supplementary Figure 9 The ball-milled LPSC _{1.5} -SmetaLi ₂ S precursors.....	9
Supplementary Figure 10 XRD Refinement Patterns.	9
Supplementary Figure 11 The morphology and corresponding particle size of LPSC _{1.5} -SmetaLi ₂ S sample. 10	
Experimental reproducibility	11
EIS data analysis and reproducibility.....	11
Supplementary Table 1 Diagram for the comparison of Li ₂ S synthesis methods.....	12
Supplementary Table 2 Crystallographic parameters refined by Rietveld method of the obtained samples..	13
Supplementary Table 3 Elemental composition.....	13
Calculation of Theoretical Minimum Costs for Li₂S Production.....	14
Supplementary Table 4 The price of raw materials with large-scale base on internet sources.....	15
Supplementary Table 5 The cost of the strategy for 1 Kg Li ₂ S based on Ref 6.....	16
Supplementary Table 6 The cost of the strategy for 1 Kg Li ₂ S based on Ref 7.....	17
Supplementary Table 7 The cost of the strategy for 1 Kg Li ₂ S based on Ref 12.....	18
Supplementary Table 8 The cost of the strategy for 1 Kg Li ₂ S based on Ref 8.....	19
Supplementary Table 9 The cost of the strategy for 1 Kg Li ₂ S based on Ref 1.....	20
Supplementary Table 10 The cost of the strategy for 1 Kg Li ₂ S based on Ref 14.....	21
Supplementary Table 11 The cost of the strategy for 1 Kg Li ₂ S based on this work	22
Supplementary Table 12 Raw materials costs of LGPS-SmetaLi ₂ S and LGPS-CommLi ₂ S for 1 Kg scale based on this work.....	23
Supplementary Table 13 Raw materials costs of LPSC _{1.5} -SmetaLi ₂ S and LPSC _{1.5} -CommLi ₂ S for 1 Kg scale based on this work.....	23
References.....	24

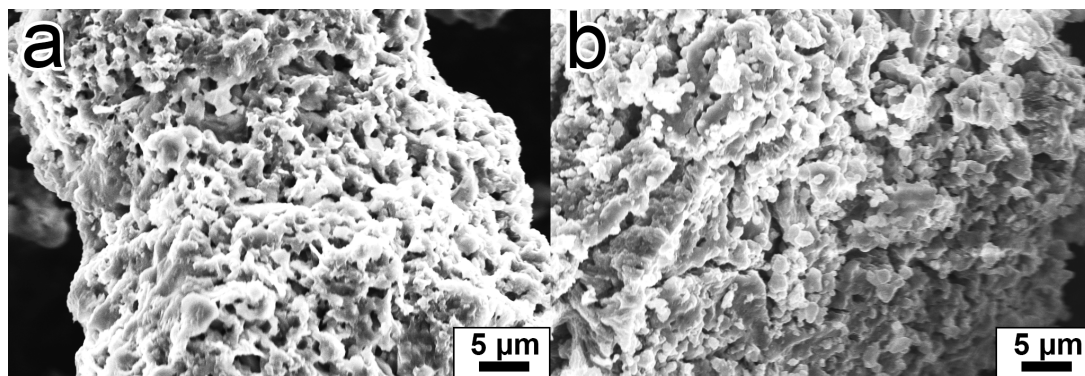
Supplementary Figures and Tables



Supplementary Figure 1 | Raman spectra of the products from Eq. 1 at different temperature. When the reaction temperature is set at 200 °C, no Raman signal of Li₂S can be observed. As the reaction temperature gradually increases, the characteristic peak of lithium sulfide at 375 cm⁻¹ becomes more intense, indicating that high temperatures facilitate the formation of Li₂S products.



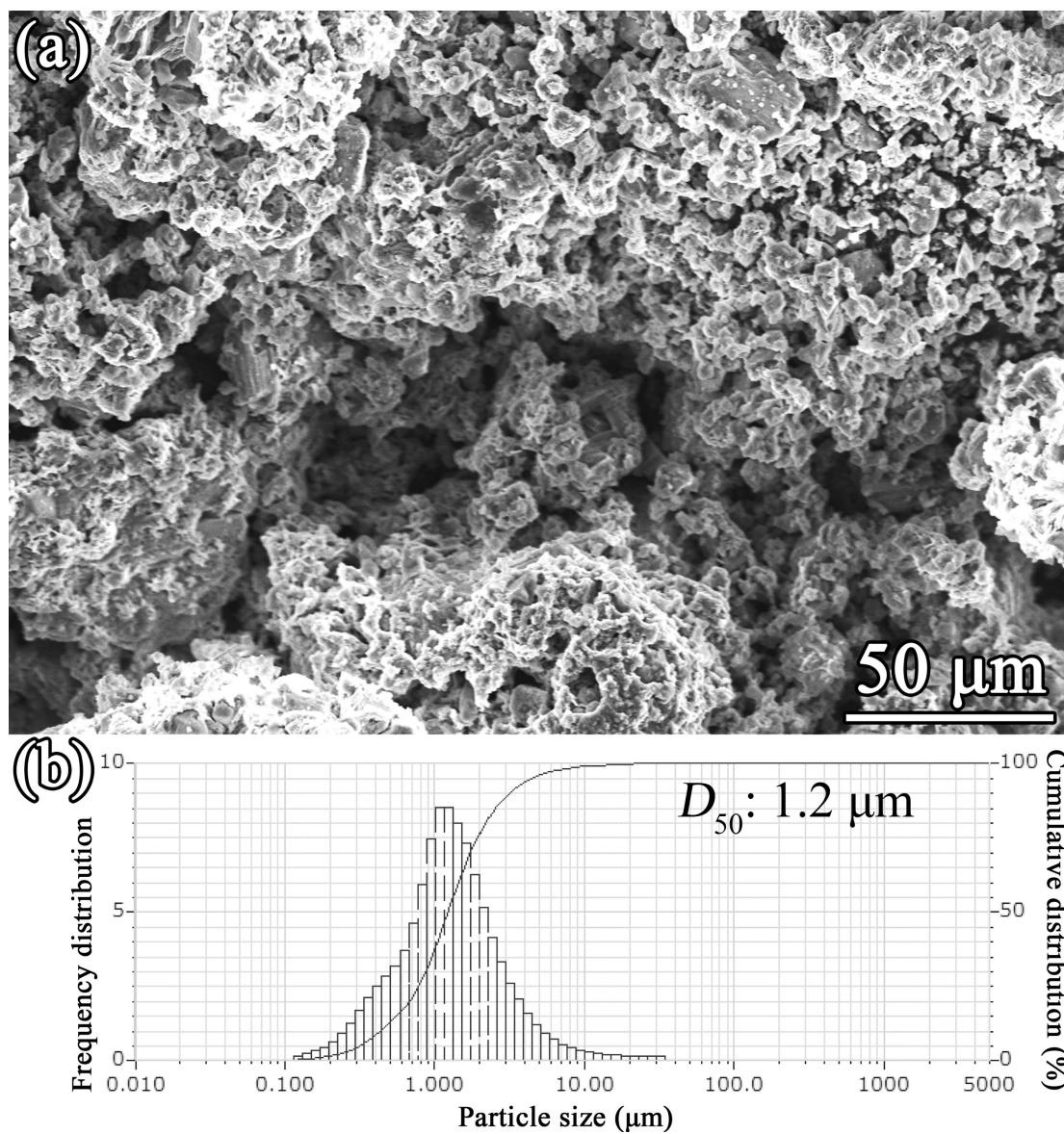
Supplementary Figure 2 | XRD patterns of CA-Li₂S-600, CA-Li₂S-700, CA-Li₂S-800 samples. When the reaction temperature reaches 800 °C, only the characteristic peaks of Li₂S appear in the product. In contrast, no peaks of lithium carbonate can be observed, indicating that using Li₂CO₃ instead of LiOH as a raw material to react with thiourea under the same conditions can also produce Li₂S.



Supplementary Figure 3 | SEM images of the obtained samples. HY-Li₂S-800 (a) and CA-Li₂S-800 (b). It can be observed that the Li₂S products synthesized using either LiOH or Li₂CO₃ as raw materials exhibit very similar morphologies.



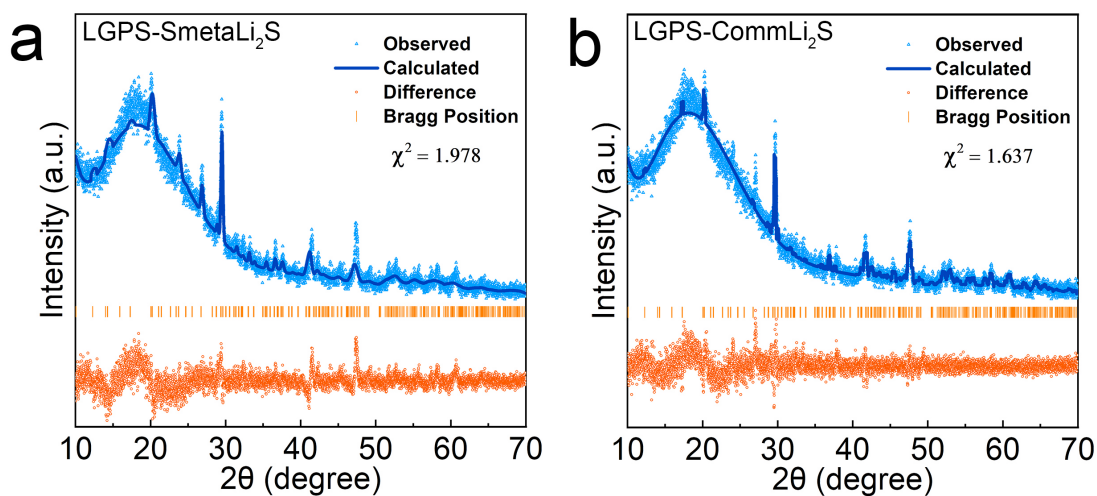
Supplementary Figure 4 | Digital picture of HY-Li₂S-800 and CA-Li₂S-800 after dissolved in absolute alcohol. The CA-Li₂S-800 synthesized from Li₂CO₃ exhibits a pale yellow color in ethanol, while the HY-Li₂S-800 synthesized from LiOH appears greyish white indicating that these two Li₂S products differ in properties, confirming that Li₂CO₃ cannot be used as a substitute for LiOH in the production of Li₂S.



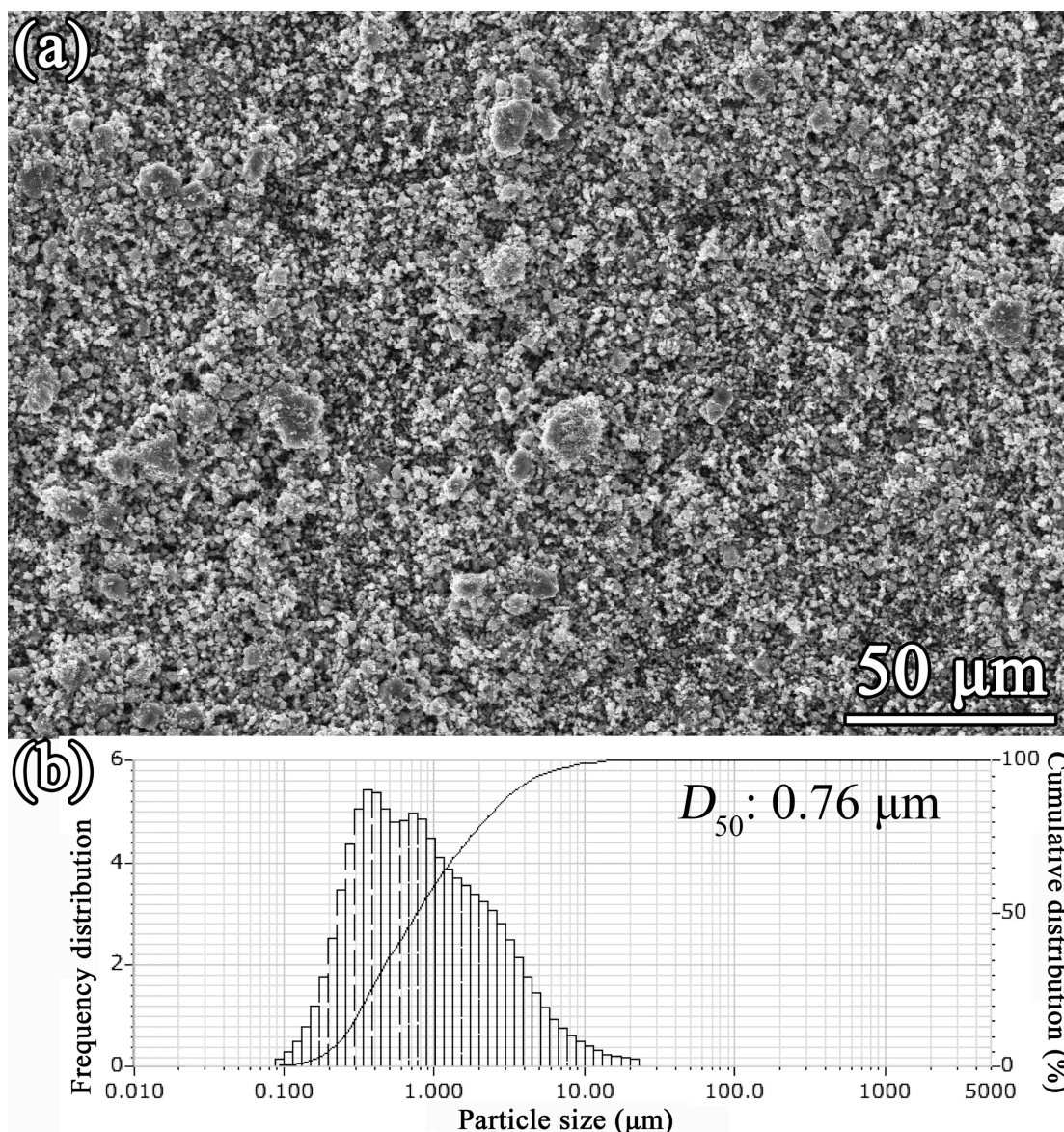
Supplementary Figure 5 | The morphology and corresponding particle size of Li_2S -Smeta sample. The average particle size (D_{50}) of the Li_2S -Smeta products is 1.2 μm . (a) The morphology of Li_2S -Smeta sample. (b) Particle size distribution of Li_2S -Smeta sample.



Supplementary Figure 6 | The ball-milled LGPS-SmetaLi₂S precursors. 39.02 g as-synthesized Li₂S, 23.23 g GeS₂ and 37.75 g P₂S₅ are mixed into 1 L ZrO₂ pot with 80 ZrO₂ balls of 10 mm diameter and 180 ZrO₂ balls of 5 mm diameter. The LGPS-SmetaLi₂S yellow precursors can be obtained after 8 h ball-milling with a rotational speed of 400 rpm.



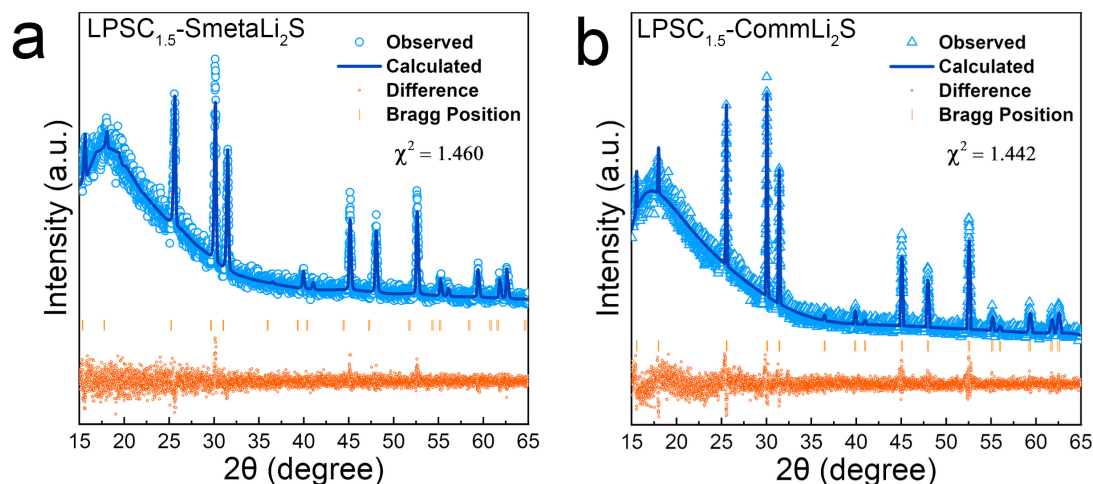
Supplementary Figure 7 | XRD Refinement Patterns. Detailed Rietveld refinements are performed to calculate the lattice parameters of LGPS-SmetaLi₂S (a) and LGPS-CommLi₂S samples (b). The refined crystallographic data of LGPS-SmetaLi₂S and LGPS-CommLi₂S are listed in Supplementary Table 2.



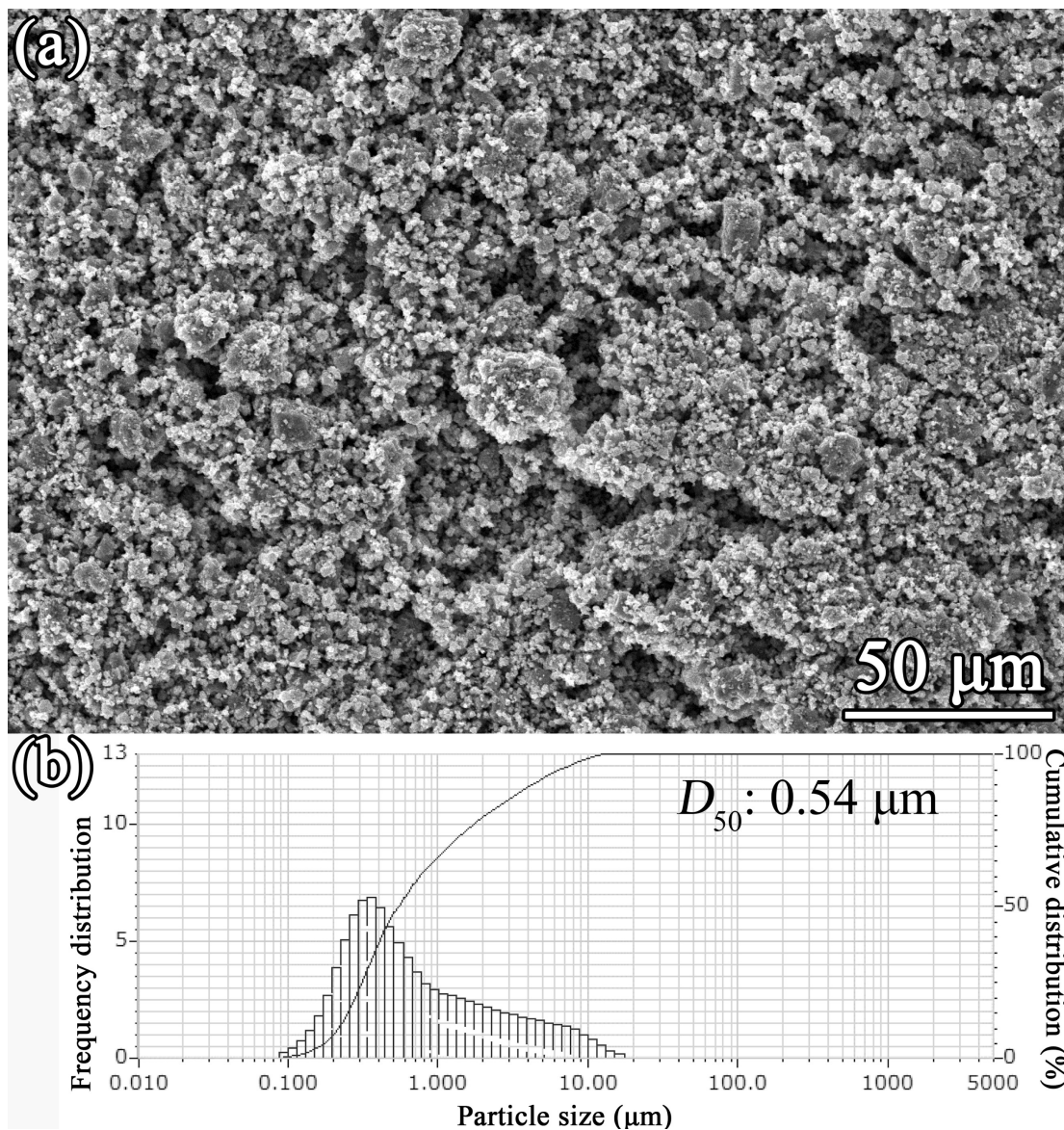
Supplementary Figure 8 | The morphology and corresponding particle size of the obtained typical sample of LGPS-SmetaLi₂S. The average particle size (D_{50}) of the LGPS-SmetaLi₂S products is 0.76 μm. (a) The morphology of LGPS-SmetaLi₂S sample. (b) Particle size distribution of LGPS-SmetaLi₂S sample.



Supplementary Figure 9 | The ball-milled LPSC_{1.5}-SmetaLi₂S precursors. 34.47 g as-synthesized Li₂S, 23.85 g LiCl and 41.68 g P₂S₅ were mixed into 1 L ZrO₂ pot with 80 ZrO₂ balls of 10 mm diameter and 180 ZrO₂ balls of 5 mm diameter. The LPSC_{1.5}-SmetaLi₂S yellow precursors can be obtained after 8 h ball-milling with a rotational speed of 400 rpm.



Supplementary Figure 10 | XRD Refinement Patterns. Refined XRD patterns of LPSC_{1.5}-SmetaLi₂S (a) and LPSC_{1.5}-CommLi₂S (b). Detailed Rietveld refinements are performed to calculate the lattice parameters of LPSC_{1.5}-SmetaLi₂S and LPSC_{1.5}-CommLi₂S. samples. The refined crystallographic data of LPSC_{1.5}-SmetaLi₂S and LPSC_{1.5}-CommLi₂S are listed in Supplementary Table 2.



Supplementary Figure 11 | The morphology and corresponding particle size of LPSC_{1.5}-SmetaLi₂S sample. The average particle size (D_{50}) of the LPSC_{1.5}-SmetaLi₂S products is 0.54 μm. (a) The morphology of LPSC_{1.5}-SmetaLi₂S sample. (b) Particle size distribution of LPSC_{1.5}-SmetaLi₂S sample.

Experimental reproducibility

All electrochemical measurements reported in this study were conducted on multiple independent cells to ensure reproducibility. The figures in the main text present typical experimental results, not selectively chosen data. Additional experiments were performed under varied pressures, charge/discharge rates, and areal capacities. All results consistently support the trends and conclusions reported in the main text. These additional measurements are not shown, as they extend beyond the standard experimental conditions and do not materially affect the key findings regarding the green synthesis of Li_2S and its application in sulfide solid electrolytes. This approach ensures that the presented data are both representative and reliable.

EIS data analysis and reproducibility

The EIS spectra consistently display a well-defined semicircle followed by a tail, typical for these sulfide solid electrolytes. The ohmic resistance at the high-frequency intercept of the semicircle ($\sim 30\ \Omega$) was used to calculate the ionic conductivity. We verified that fitting the spectra with equivalent circuit elements produces the same ionic conductivity values (mS/cm) to within two decimal places. Therefore, reporting additional equivalent-circuit fits and fitting errors was deemed unnecessary, as it does not provide additional insight into the material performance. This approach ensures clarity while accurately representing the ionic transport properties.

Supplementary Table 1 | Diagram for the comparison of Li₂S synthesis methods.

Li Source	S Source or Reductant	Reaction Condition	Byproduct	Further purifying process	Safety	Batch scale	Ref.
Li ₂ SO ₄	C ₁₂ H ₂₂ O ₁₁	mixing, sintered (820 °C)	Carbon	ethanol filtering, evaporating with Ar	yes	unknown	1
Li ₂ SO ₄	Mg	mixing, sintered (700 °C)	MgO	ethanol filtering, centrifuging, evaporating with Ar	yes	unknown	2
Li ₂ SO ₄	Al	milling, sintered (525 °C)	Al ₂ O ₃ , LiAlO ₂	ethanol filtering, centrifuging, evaporating with Ar	yes	unknown	3
Li(CH ₂ CH ₃) ₃ BH	S powder	stirring in THF	(CH ₂ CH ₃) ₃ B	filtering with Ar	explosive	unknown	4
Lithium tert-butoxide	S powder	tetraglyme, microwave	none	THF washing with Ar	explosive	< 1 g	5
LiH	S powder	milling	none	not need	explosive	unknown	6
LiOH	S powder	sintered (200–220 °C)	Li ₂ SO ₃ , Li ₂ S ₂ O ₃ , H ₂ O	n-propanol washing, filtering	yes	unknown	7
Lithium tert-butoxide	H ₂ S gas	Atomic layer deposition	none	not need	explosive, toxic	unknown	8
Li-naphthalene	H ₂ S gas	DME	none	evaporating with Ar	explosive, toxic	< 1 g	9
Li foil	H ₂ S gas	ethanol	none	evaporating with Ar	toxic	< 1 g	10
Li foil	H ₂ S gas	ethanol/DMF	none	evaporating with Ar	toxic	unknown	11
Li ₂ SO ₄	H ₂ gas	Sintered (700–800 °C)	none	not need	explosive	< 1 g	12
LiCl	anhydrous Na ₂ S	stirring in Ethanol or 1-propanol	NaCl	centrifuging, filtering, evaporating with Ar	yes	< 1 g	13
LiCl	anhydrous Na ₂ S	stirring in Ethanol	NaCl	centrifuging, filtering, evaporating with Ar	yes	unknown	14
LiCl	anhydrous Na ₂ S	stirring in Ethanol	NaCl	centrifuging, filtering, evaporating with Ar	yes	unknown	15
LiNO ₃	anhydrous Na ₂ S	stirring in NMP	NaNO ₃	centrifuging, filtering, DME washing, evaporating with Ar	yes	10g	16
LiOH	Thiourea	milling, sintered (800–900 °C)	none	not need	yes	> 100 g	This work

Supplementary Table 2 | Crystallographic parameters refined by Rietveld method of the obtained samples. HY-Li₂S-800, CA-Li₂S-800, L₂S-Smeta, LGPS-SmetaLi₂S, LGPS-CommLi₂S, LPSC_{1.5}-SmetaLi₂S and LPSC_{1.5}-CommLi₂S.

Refine Result	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>	<i>R</i> _{wp}
HY-Li ₂ S-800	5.67034 Å	5.67034 Å	5.67034 Å	182.31706 Å ³	4.29%
CA-Li ₂ S-800	5.66298 Å	5.66298 Å	5.66298 Å	181.60804 Å ³	4.95%
L ₂ S-Smeta	5.68145 Å	5.68145 Å	5.68145 Å	183.39081 Å ³	5.69%
LGPS-SmetaLi ₂ S	8.79218 Å	8.79218 Å	12.66212 Å	978.81263 Å ³	4.69%
LGPS-CommLi ₂ S	8.78765 Å	8.78765 Å	12.65755 Å	977.45137 Å ³	5.18%
LPSC _{1.5} -SmetaLi ₂ S	9.89502 Å	9.89502 Å	9.89502 Å	968.83546 Å ³	4.87%
LPSC _{1.5} -CommLi ₂ S	9.88634 Å	9.88634 Å	9.88634 Å	966.28809 Å ³	5.02%

Supplementary Table 3 | Elemental composition of the Li₂S-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

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.

Calculation of Theoretical Minimum Costs for Li₂S Production

In this part, the prices of the raw materials were obtained by comparing the information between different chemical reagent platforms or companys. We have listed the most economical prices and the corresponding source of information in Supplementary Table 3.

To calculate the theoretical minimum costs of different Li₂S synthesis methods, we have set some rules since most of references did not offer the detailed synthesis conditions:

1. we assume all the synthesis methods can achieve 1 kg Li₂S in one batch, though many methods can achieve only 1 g in one batch;
2. The flow rate of the inert-gas (such as N₂ or Ar) during the high-temperature calculation is 1 SCCM (Standard Cubic Centimeters per Minute);
3. The consumption of the gaseous reactants (such as H₂ or H₂S) are calculated by the stoichiometric ratio of the reaction instead of flow rate;
4. During the purification steps, the solvents (such as anhydrous ethanol, N-propanol Tetrahydrofuran or dimethyl ether) can be recycled 85% for repeated use, which means 15% of the solvents have been depleted.
5. According to our experimental result, dissolving 1 g Li₂S requires at least 30 mL anhydrous ethanol, 36 mL N-propanol.
6. The stirring and evaporating time for purification are 2 h.
7. Under standard conditions (25°C, 15 MPa), a 40 L industrial cylinder holds about 4.5 kg of gas (hydrogen 5% and Ar 95%).
8. The synthesis methods by using organic lithium salts (such as Li(CH₂CH₃)₃BH, Lithium tert-butoxide or Li-naphthalene) or lithium metal as raw materials will not be considered for costs calculation since the price of these organic lithium salts and Li metal are very expensive.
9. The Average industrial electricity price is 0.083 \$/kWh.
10. Labor costs are not counted into the total costs.

Supplementary Table 4 | The price of raw materials with large-scale base on internet sources.

Materials	Price	Source of Information
Thiourea	890 \$/ton	https://www.rawmex.cn/
Anhydrous LiOH	9500 \$/ton	https://li.mysteel.com/m/24123112/F9F942B2FFF8AEA.B.html
Li ₂ S	958.9 \$/kg	https://www.hptect.com/index.html
GeS ₂	4110 \$/kg	https://www.hptect.com/index.html
P ₂ S ₅	27.4 \$/kg	https://www.energy-chemical.com/front/index.htm
Anhydrous LiCl	11065 \$/ton	https://www.chemicalbook.com/PriceInfo_577076.htm
C ₁₂ H ₂₂ O ₁₁	1637.9 \$/ton	https://www.aladdin-e.com/zh_cn/catalogsearch/result/?q=S639498
Anhydrous Li ₂ SO ₄	11728.9 \$/ton	https://www.chemicalbook.com/priceindex_cb3408669.htm#changjiabaojia
Al	2856.8 \$/ton	https://jiage.cngold.org/metall/aluminium.html
S	328.8 \$/ton	https://m.cngold.org/price/lm3561/
Li(CH ₂ CH ₃) ₃ BH	2978.8 \$/kg	https://china.guidechem.com/trade/pdetail1179752.html
Li	1521 \$/kg	https://www.aladdin-e.com/zh_cn/1106891.html
LiH	942.7 \$/kg	https://www.macklin.cn/search/7580-67-8
Lithium tert-butoxide	1506.3 \$/kg	https://www.tansoole.com/upload/detail/01/135G_PP65_012042816.html
Anhydrous LiNO ₃	13831 \$/ton	https://www.chemicalbook.com/PriceInfo_550315.htm
Na ₂ S·9H ₂ O	4.15 \$/ton	https://www.rawmex.cn/
N-propanol	25175.7 \$/kL	https://www.aladdin-e.com/zh_cn/catalogsearch/result/?q=P433373
THF (Tetrahydrofuran)	28553.5 \$/kL	https://www.sigmaaldrich.cn/CN/zh/product/mm/108114?lang=zh&region=CN&utm_medium=brandpromo&utm_source=chemicalbook&utm_campaign=chemicalbook+product+china&utm_term=1.08114
Anhydrous Ethanol	4979.2 \$/kL	https://www.aladdin-e.com/zh_cn/catalogsearch/result/?q=Ethanol
DME (dimethyl ether)	5437.6 \$/kg	https://www.sigmaaldrich.cn/CN/zh/product/aldrich/743925?utm_medium=brandpromo&utm_source=chemicalbook&utm_campaign=chemicalbook+product+china&utm_term=743925
Hydrogen	1037.3 \$/kL or 9.2 \$/kg (5%H ₂ S/95%Ar)	https://gas-buy.cn/
Hydrogen Sulfide	17116.2 \$/kL (2%H ₂ S/98%N ₂)	https://gas-buy.cn/
Argon	795.3 \$/kL	https://gas-buy.cn/
Nitrogen	570.5 \$/kL	https://gas-buy.cn/

Supplementary Table 5 | The cost of the strategy for 1 Kg Li₂S based on Ref 6.

Strategy	S + LiH → Ball-milling →No Purification required					
	Item		Unit Price	Amount	Price	
Raw Materials Costs	S		328.8 \$/ton	695.65 g	0.229 \$	328.129 \$
	LiH		942.7 \$/kg	347.82 g	327.9 \$	
Synthesis Condition Costs	Gas Costs	Hydrogen	1037.3 \$/kL or 9.2 \$/kg (5%H ₂ S/95%Ar)	—	—	1.494 \$
		Hydrogen Sulfide	17116.2 \$/kL (2%H ₂ S/98%N ₂)	—	—	
		Argon	795.3 \$/kL	—	—	
		Helium	570.5 \$/kL	—	—	
	Electricity Costs	Ball-milling (750 W)	0.083 \$/kWh	24 h	1.494 \$	
		Calcination (2500 W)		—	—	
		Stirring (800 W)		—	—	
		Evaporating (250 W)		—	—	
Purification Costs	Ethanol		4979.2 \$/kL	—	—	— — — —
	N-propanol		25175.7 \$/kL	—	—	
	THF (Tetrahydrofuran)		28553.5 \$/kL	—	—	
	DME (dimethyl ether)		5437.6 \$/kg	—	—	
Total costs						330.07 \$

Supplementary Table 6 | The cost of the strategy for 1 Kg Li₂S based on Ref 7.

Supplementary Table 3 The cost of the strategy for Fig. 2-25 based on Ref. 9						
Strategy	S + LiOH → Ball-milling → 200°C Calcination → N-propanol Purification					
	Item		Unit Price	Amount	Price	
Raw Materials Costs	S		328.8 \$/ton	1043.48 g	0.343 \$	15.212 \$
	Anhydrous LiOH		9500 \$/ton	1565.21 g	14.869 \$	
Synthesis Condition Costs	Gas Costs	Hydrogen	1037.3 \$/kL or 9.2 \$/kg (5%H ₂ S/95%Ar)	—	—	1.494 \$
		Hydrogen Sulfide	17116.2 \$/kL (2%H ₂ S/98%N ₂)	—	—	
		Argon	795.3 \$/kL	0.48 L	0.382 \$	
		Helium	570.5 \$/kL	—	—	
	Electricity Costs	Ball-milling (750 W)	0.083 \$/kWh	—	—	
		Calcination (2500 W)		8 h	1.66 \$	
		Stirring (800 W)		2 h	0.133 \$	
		Evaporating (250 W)		2 h	0.042 \$	
Purification Costs	Ethanol		4979.2 \$/kL	—	—	135.95 \$
	N-propanol		25175.7 \$/kL	36 L*15%	135.95 \$	
	THF (Tetrahydrofuran)		28553.5 \$/kL	—	—	
	DME (dimethyl ether)		5437.6 \$/kg	—	—	
Total costs						152.66 \$

Supplementary Table 7 | The cost of the strategy for 1 Kg Li₂S based on Ref 12.

Strategy		H ₂ + Li ₂ SO ₄ → 800°C Calcination → No Purification					
		Item	Unit Price	Amount	Price		
Raw Materials Costs		Anhydrous Li ₂ SO ₄		11728.9 \$/ton	2391.3 g	28.047 \$	28.047 \$
		—		—	—	—	
Synthesis Condition Costs		Gas Costs	Hydrogen	1037.3 \$/kL or 9.2 \$/kg (5%H ₂ S/95%Ar)	174/0.05 g	32.016 \$	35.336 \$
			Hydrogen Sulfide	17116.2 \$/kL (2%H ₂ S/98%N ₂)	—	—	
			Argon	795.3 \$/kL	—	—	
			Helium	570.5 \$/kL	—	—	
		Electricity Costs	Ball-milling (750 W)	0.083 \$/kWh	—	—	
			Calcination (2500 W)		16 h	3.32 \$	
			Stirring (800 W)		—	—	
			Evaporating (250 W)		—	—	
Purification Costs		Ethanol		4979.2 \$/kL	—	—	0 \$
		N-propanol		25175.7 \$/kL	—	—	
		THF (Tetrahydrofuran)		28553.5 \$/kL	—	—	
		DME (dimethyl ether)		5437.6 \$/kg	—	—	
Total costs							63.38 \$

Supplementary Table 8 | The cost of the strategy for 1 Kg Li₂S based on Ref 8.

Supplementary Table 6 The cost of the strategy for Fig. 2125 based on Ref. 6.						
Strategy	Al + Li ₂ SO ₄ → Ball-milling → 800°C Calcination → Ethanol Purification					
	Item		Unit Price	Amount	Price	
Raw Materials Costs	Al		2856.8 \$/ton	1565.2 g	4.471 \$	32.518 \$
	Anhydrous Li ₂ SO ₄		11728.9 \$/ton	2391.3 g	28.047 \$	
Synthesis Condition Costs	Gas Costs	Hydrogen	1037.3 \$/kL or 9.2 \$/kg (5%H ₂ S/95%Ar)	—	—	3.422 \$
		Hydrogen Sulfide	17116.2 \$/kL (2%H ₂ S/98%N ₂)	—	—	
		Argon	795.3 \$/kL	0.36 L	0.286	
		Helium	570.5 \$/kL	—	—	
	Electricity Costs	Ball-milling (750 W)	0.083 \$/kWh	0.33 h	0.498 \$	
		Calcination (2500 W)		6 h	2.49 \$	
		Stirring (800 W)		2 h	0.133 \$	
		Evaporating (250 W)		2 h	0.042 \$	
Purification Costs	Ethanol		4979.2 \$/kL	30 L*15%	22.41	22.41 \$
	N-propanol		25175.7 \$/kL	—	—	
	THF (Tetrahydrofuran)		28553.5 \$/kL	—	—	
	DME (dimethyl ether)		5437.6 \$/kg	—	—	
Total costs						58.35 \$

Supplementary Table 9 | The cost of the strategy for 1 Kg Li₂S based on Ref 1.

Strategy	C ₁₂ H ₂₂ O ₁₁ + Li ₂ SO ₄ → Ball-milling → 820°C Calcination → Ethanol Purification					
	Item		Unit Price	Amount	Price	
Raw Materials Costs	C ₁₂ H ₂₂ O ₁₁		1637.9 \$/ton	1240.22 g	2.031 \$	30.078 \$
	Anhydrous Li ₂ SO ₄		11728.9 \$/ton	2391.3 g	28.047 \$	
Synthesis Condition Costs	Gas Costs	Hydrogen	1037.3 \$/kL or 9.2 \$/kg (5%H ₂ S/95%Ar)	—	—	1.88 \$
		Hydrogen Sulfide	17116.2 \$/kL (2%H ₂ S/98%N ₂)	—	—	
		Argon	795.3 \$/kL	—	—	
		Helium	570.5 \$/kL	0.3 L	0.17 \$	
	Electricity Costs	Ball-milling (750 W)	0.083 \$/kWh	8 h	0.498 \$	
		Calcination (2500 W)		5 h	1.037 \$	
		Stirring (800 W)		2 h	0.133 \$	
		Evaporating (250 W)		2 h	0.042 \$	
Purification Costs	Ethanol		4979.2 \$/kL	30 L*15%	22.41	22.41 \$
	N-propanol		25175.7 \$/kL	—	—	
	THF (Tetrahydrofuran)		28553.5 \$/kL	—	—	
	DME (dimethyl ether)		5437.6 \$/kg	—	—	
Total costs						54.37 \$

Supplementary Table 10 | The cost of the strategy for 1 Kg Li₂S based on Ref 14.

Strategy	Na ₂ S·9H ₂ O → 220°C Calcination → Na ₂ S					
	Na ₂ S + LiCl → Stirring in Ethanol (Li ₂ S = 0.5 mol/L) → Evaporating					
	Item		Unit Price	Amount	Price	
Raw Materials Costs	Na ₂ S·9H ₂ O		4.15 \$/ton	5217.4 g	0.022 \$	20.422 \$
	Anhydrous LiCl		11065 \$/ton	1843.5 g	20.4 \$	
Synthesis Condition Costs	Gas Costs	Hydrogen	1037.3 \$/kL or 9.2 \$/kg (5%H ₂ S/95%Ar)	—	—	1.005 \$
		Hydrogen Sulfide	17116.2 \$/kL (2%H ₂ S/98%N ₂)	—	—	
		Argon	795.3 \$/kL	—	—	
		Helium	570.5 \$/kL	—	—	
	Electricity Costs	Ball-milling (750 W)	0.083 \$/kWh	—	—	
		Calcination (2500 W)		4 h	0.83 \$	
		Stirring (800 W)		2 h	0.133 \$	
		Evaporating (250 W)		2 h	0.042 \$	
Purification Costs	Ethanol		4979.2 \$/kL	43.48L*15%	32.47 \$	32.47 \$
	N-propanol		25175.7 \$/kL	—	—	
	THF (Tetrahydrofuran)		28553.5 \$/kL	—	—	
	DME (dimethyl ether)		5437.6 \$/kg	—	—	
Total costs						53.897 \$

Supplementary Table 11 | The cost of the strategy for 1 Kg Li₂S based on this work.

Supplementary Table 11 The cost of the strategy for THF-L2S based on this work						
Strategy	Thiourea + LiOH → Ball-milling → 800°C Calcination → No Purification required					
	Item		Unit Price	Amount	Price	
Raw Materials Costs	Thiourea		890 \$/ton	1654.35 g	1.742 \$	11.655 \$
	Anhydrous LiOH		9500 \$/ton	1043.48 g	9.913 \$	
Synthesis Condition Costs	Gas Costs	Hydrogen	1037.3 \$/kL or 9.2 \$/kg (5%H ₂ S/95%Ar)	—	—	2.54 \$
		Hydrogen Sulfide	17116.2 \$/kL (2%H ₂ S/98%N ₂)	—	—	
		Argon	795.3 \$/kL	0.48 L	0.382 \$	
		Helium	570.5 \$/kL	—	—	
	Electricity Costs	Ball-milling (750 W)	0.083 \$/kWh	8 h	0.498 \$	
		Calcination (2500 W)		8 h	1.66 \$	
		Stirring (800 W)		—	—	
		Evaporating (250 W)		—	—	
Purification Costs	Ethanol		4979.2 \$/kL	—	—	0 \$
	N-propanol		25175.7 \$/kL	—	—	
	THF (Tetrahydrofuran)		28553.5 \$/kL	—	—	
	DME (dimethyl ether)		5437.6 \$/kg	—	—	
Total costs						14.2 \$

Supplementary Table 12 | Raw materials costs of LGPS-SmetaLi₂S and LGPS-CommLi₂S for 1 Kg scale based on this work.

1 kg scale	Item	Unit Price	Amount	Price	
LGPS-CommLi ₂ S	P ₂ S ₅	27.4 \$/kg	377.54 g	10.3 \$	1339.1 \$
	GeS ₂	4110 \$/kg	232.25 g	954.6 \$	
	Li ₂ S-Comm	958.9 \$/kg	390.21 g	374.2 \$	
LGPS-SmetaLi ₂ S	P ₂ S ₅	27.4 \$/kg	377.54 g	10.3 \$	970.4 \$
	GeS ₂	4110 \$/kg	232.25 g	954.6 \$	
	Li ₂ S-Smeta	14.195 \$/kg	390.21 g	5.5 \$	

Supplementary Table 13 | Raw materials costs of LPSC_{1.5}-SmetaLi₂S and LPSC_{1.5}-CommLi₂S for 1 Kg scale based on this work.

1 kg scale	Item	Unit Price	Amount	Price	
LPSC _{1.5} -CommLi ₂ S	P ₂ S ₅	27.4 \$/kg	416.8 g	11.4 \$	351.7 \$
	LiCl	41.1 \$/kg	238.5 g	9.8 \$	
	Li ₂ S-Comm	958.9 \$/kg	344.7 g	330.5 \$	
LPSC _{1.5} -SmetaLi ₂ S	P ₂ S ₅	27.4 \$/kg	416.8 g	10.3 \$	25.0 \$
	LiCl	41.1 \$/kg	238.5 g	9.8 \$	
	Li ₂ S-Smeta	14.195 \$/kg	344.7 g	4.9 \$	

References

1. Tu, F.; Zhao, Z.; Zhang, X.; Wang, Z.; Ma, Y.; Zhang, H.; Song, D.; Zhang, L.; Yang, Y.; Zhu, L. Low-Cost and Scalable Synthesis of High-Purity Li_2S for Sulfide Solid Electrolyte. *ACS Sustainable Chem. Eng.* **2022**, *10* (47), 15365-15371.
2. Zhang, X.; Yang, H.; Sun, Y.; Yang, Y. Lithium Sulfide: Magnesothermal Synthesis and Battery Applications. *ACS Appl. Mater. Interfaces* **2022**, *14* (36), 41003-41012.
3. Yang, H.; Sun, Y.; Yang, S.; Han, A.; Hu, X.; Zhang, H.; Yao, X.; Zhang, X.; Yang, Y. "One Stone Two Birds" Strategy of Synthesizing the Battery Material Lithium Sulfide: Aluminothermal Reduction of Lithium Sulfate. *Inorg. Chem.* **2023**, *62* (14), 5576-5585.
4. Lin, Z.; Liu, Z.; Dudney, N. J.; Liang, C. Lithium Superionic Sulfide Cathode for All-Solid Lithium–Sulfur Batteries. *ACS Nano* **2013**, *7* (3), 2829-2833.
5. El-Shinawi, H.; Cussen, E. J.; Corr, S. A. A facile synthetic approach to nanostructured Li_2S cathodes for rechargeable solid-state Li–S batteries. *Nanoscale* **2019**, *11* (41), 19297-19300.
6. Li, X.; Gao, M.; Du, W.; Ni, B.; Wu, Y.; Liu, Y.; Shang, C.; Guo, Z.; Pan, H. 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. Mater. Chem. A* **2017**, *5* (14), 6471-6482.
7. Yang, S.; Hu, X.; Xu, S.; Han, A.; Zhang, X.; Zhang, N.; Chen, X.; Tian, R.; Song, D.; Yang, Y. Synthesis of Deliquescent Lithium Sulfide in Air. *ACS Appl. Mater. Interfaces* **2023**, *15* (34), 40633-40647.
8. Meng, X.; Comstock, D. J.; Fister, T. T.; Elam, J. W. Vapor-phase atomic-controllable growth of amorphous Li_2S for high-performance lithium-sulfur batteries. *ACS Nano* **2014**, *8* (10), 10963-72.
9. Li, X.; Wolden, C. A.; Ban, C.; Yang, Y. Facile Synthesis of Lithium Sulfide Nanocrystals for Use in Advanced Rechargeable Batteries. *ACS Appl. Mater. Interfaces* **2015**, *7* (51), 28444-51.
10. Zhao, Y.; Smith, W.; Wolden, C. A. Scalable Synthesis of Li_2S Nanocrystals for Solid-State Electrolyte Applications. *J. Electrochem. Soc.* **2020**, *167* (7), 070520.
11. Zhao, Y.; Yang, Y.; Wolden, C. A. Scalable Synthesis of Size-Controlled Li_2S Nanocrystals for Next-Generation Battery Technologies. *ACS Appl. Energy Mater.* **2019**, *2* (3), 2246-2254.
12. Sun, Y.; Zhang, X.; Xu, S.; Yang, S.; Wang, X.; Cao, X.; Sun, X.; Zhang, Y.; Ren, D.; Hu, X.; Yang, H.; Zhang, Q.; Lu, Z.; Zhang, X.; Yang, Y. A Green Method of Synthesizing Battery-Grade Lithium Sulfide: Hydrogen Reduction of Lithium Sulfate. *ACS Sustainable Chem. Eng.* **2024**, *12* (7), 2813-2824.
13. Smith, W. H.; Vaselabadi, S. A.; Wolden, C. A. Synthesis of high-purity Li_2S nanocrystals via metathesis for solid-state electrolyte applications. *J. Mater. Chem. A* **2023**, *11* (14), 7652-7661.
14. Smith, W. H.; Vaselabadi, S. A.; Wolden, C. A. Argyrodite Superionic Conductors Fabricated from Metathesis-Derived Li_2S . *ACS Appl. Energy Mater.* **2022**, *5* (4), 4029-4035.

15. Fang, L.; Zhang, Q.; Han, A.; Zhao, Z.; Hu, X.; Wan, F.; Yang, H.; Song, D.; Zhang, X.; Yang, Y. Green synthesis of the battery material lithium sulfide via metathetic reactions. *Chem. Commun.* **2022**, 58 (36), 5498-5501.
16. Zhang, Q.; Han, A.; Zhang, X.; Tian, R.; Yang, S.; Xu, S.; Song, D.; Yang, Y. Green Synthesis for Battery Materials: A Case Study of Making Lithium Sulfide via Metathetic Precipitation. *ACS Appl. Mater. Interfaces* **2023**, 15 (1), 1358-1366.