

Supplementary information for:

A selective and facile synthesis of sodium sulfide and sodium disulfide polymorphs

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Experimental details:

Synthesis of Na₂S

Elemental S and sodium tert-butoxide were dissolved in 1:2 molar ratio in tetraglyme at room temperature (the S concentration was approximately 0.1 M). A clear green solution was obtained after stirring in a glovebox for 30 minutes. A 5 ml aliquot of this solution was heated to 200 °C in a sealed 10 mL microwave tube for 30 minutes using a CEM Discover SP microwave synthesizer (2.45 GHz). After the reaction is complete, a yellow-brown solid in a colourless mother liquor is obtained. The resulting solid product was washed thoroughly with THF (3 × 3 ml) and finally dried at 100 °C for 2h. The washing and drying steps were performed under an argon atmosphere.

Synthesis of α- and β-Na₂S₂

α- and β-Na₂S₂ were prepared by heating 10 ml aliquots of the same S/sodium tert-butoxide solution in 50 mL microwave tubes for 30 minutes at 110 and 120 °C, respectively.

XRD

XRD analysis was performed using a PANalytical X'Pert PRO diffractometer in reflection mode using Cu-K α radiation. The powder materials were sealed in an airtight XRD sample holder in an argon filled glovebox to prevent reaction with moisture and oxygen. All presented patterns are overnight runs with data collection times exceeding 12h.

SEM

SEM images were collected using Zeiss Sigma field emission scanning electron microscope. Samples for SEM analysis were prepared in an argon filled glovebox, with air exposure time not exceeding 10 s during the introduction of the samples into the microscope.

Electrochemical characterization

For electrochemical characterization of the synthesized materials, laboratory-scale batteries were fabricated using Na metal as the negative electrode and 1.5 M NaClO₄/0.3 M NaNO₃ in tetraglyme as the electrolyte. The active material was simply mixed with conductive carbon and a PTFE binder (in 6:2.5:1.5 weight ratio) and pressed in a thin pellet (~3 mg), to prepare the positive electrode. The electrochemical performance of the assembled cells was evaluated in Swagelok cells using a BioLogic VSP potentiostat. The cells were tested between 1.2 and 3 V vs Na/Na⁺.

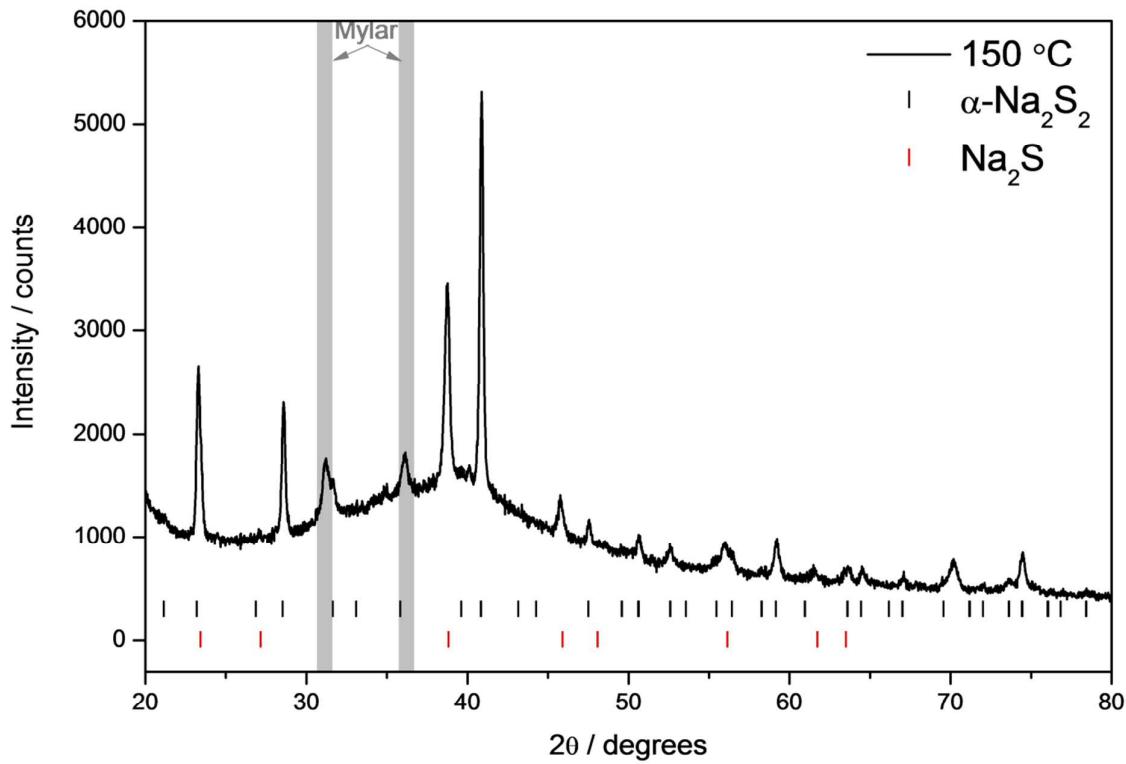


Figure S1. XRD pattern of the material prepared at 150 °C, showing a mixture of Na₂S₂ (α -phase) and Na₂S.

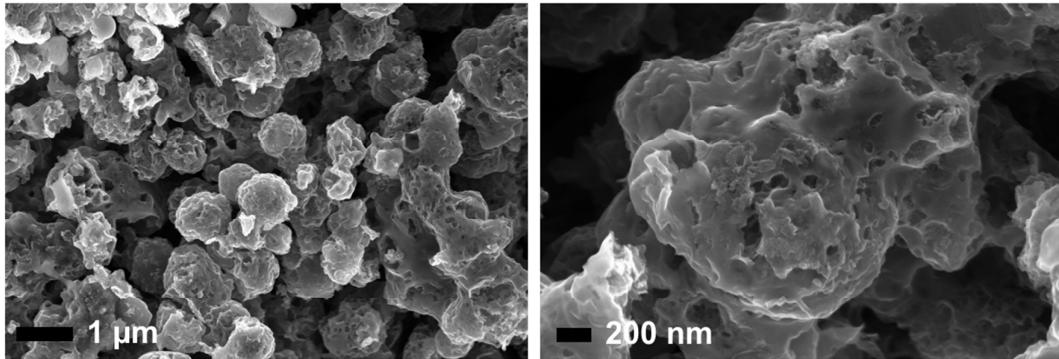


Figure S2. Morphology of Na₂S calcined at 700 °C for 1h under argon, showing that the material gains some porosity on calcination.