Selective and Facile Synthesis of Sodium Sulfide and Sodium Disulfide Polymorphs

Hany El-Shinawi,[‡] Edmund J. Cussen,[†] and Serena A. Corr*,[‡]

[‡]School of Chemistry, WestCHEM, University of Glasgow, Glasgow G12 8QQ, U.K.

[†]Department of Pure and Applied Chemistry, WestCHEM, The University of Strathclyde, Glasgow G1 1XL, U.K.

S Supporting Information

ABSTRACT: Na_2S and Na_2S_2 were selectively synthesized using a microwave-assisted thermal treatment of a Na^+/S solution in tetraglyme between 100 and 200 °C, considerably lower than that of current routes. This novel synthetic pathway yields the Na_2S phase in high purity and allows for good selectivity between the polymorphs of Na_2S_2 (α and β phases). These materials show promising electrochemical properties and are particularly interesting for the continued development of Na−S batteries.

High-purity sodium sulfide and polysulfides are key reactants in a range of organic and inorganic processes, with applications across industries including dye manufacturing, textiles, and the synthesis of organic intermediates. Industrially, Na_2S is prepared by the carbon reduction of Na_2SO_4. On a laboratory scale, a reaction between elemental Na and S is typically carried out. The former synthesis requires temperatures between 600 and 1100 °C and produces CO_2 as a byproduct, according to the reaction $Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$.[1] The reaction between Na and S ($2Na + S \rightarrow Na_2S$), on the other hand, is performed in liquid ammonia and requires extreme precautions because of the hazardous nature of some of these reactants.[2] Na_2S and sodium polysulfides may also be accessed by the reaction between Na and S, either by a direct molten reaction or in dimethoxyethane in the presence of catalytic aromatic hydrocarbons.[3−5] These techniques offer a good degree of selectivity; however, they do not avoid the use of elemental Na, which again presents a considerable hazard. Beyond the carboreduction of Na_2SO_4, Na-metal-free syntheses are limited to the drying of hydrous sodium sulfide, which is both time- and energy-consuming because of the requirements of several heat treatments under controlled pressure. With the considerable use of these materials in industrial processes and their potential for applications in energy storage, there is a pressing need to develop new chemistries to access these compounds through more benign routes. Here, we report a novel and facile synthesis that avoids the use of elemental Na and produces high-purity materials at low cost and at temperatures not exceeding 200 °C. Additionally, this approach not only is very selective toward producing either Na_2S or Na_2S_2 but also provides good separation of the α and β phases of Na_2S_2.

High-purity anhydrous Na_2S was successfully prepared using a simple microwave-assisted heat treatment of a Na^+/S solution in tetraglyme (see the Supporting Information). Elemental S and sodium *tert*-butoxide were dissolved in a 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 min. A 5 mL aliquot of this solution was heated to 200 °C in a sealed 10 mL microwave tube for 30 min using a CEM Discover SP microwave synthesizer (2.45 GHz). The resulting product was washed thoroughly with tetrahydrofuran (3 × 3 mL) and finally dried at 100 °C for 2 h. The washing and drying steps were performed under an argon atmosphere. Powder X-ray diffraction (XRD) showed that the as-prepared material is phase-pure, crystalline Na_2S. No significant change in the XRD pattern was observed when the as-prepared material was calcined at 700 °C under argon for 1 h. The XRD patterns of the synthesized material, compared to commercial Na_2S (anhydrous; Alfa Aesar), are shown in Figure 1. It should be noted that sulfur readily dissolves in tetraglyme in the presence of sodium *tert*-butoxide. This suggests that S likely combines with a sodium tetraglyme complex[6] to form a soluble, green precursor complex, which subsequently decomposes by microwave-assisted heating to Na_2S. A microwave heat treatment is essential here because the reaction could not be achieved by conventional heating in a Teflon-lined autoclave.

Our synthetic approach also proved to be successful in synthesizing phase-pure Na_2S_2 (in the form of a mixture of α and β polymorphs) simply by varying the reaction temperature. At temperatures below 150 °C, the same sulfur/sodium *tert*-butoxide solution yields phase-pure Na_2S_2 in the form of a mixture of α (low-temperature) and β (high-temperature) phases, with no evidence for the formation of Na_2S (see the Supporting Information). By careful control of the reaction conditions, we could prepare α and β phases with good separation. Figure 2 shows the XRD patterns of Na_2S_2 obtained after the heat treatment of 10 mL of a Na^+/S solution at 110 and 120 °C. These α and β polymorphs are the only phases present, i.e., there are no traces of Na_2S, demonstrating the high selectivity of our synthesis method. Additionally, we clearly observe that α-Na_2S_2 predominates in the material prepared at 110 °C, while β-Na_2S_2 predominates in the material prepared at 120 °C, indicating good separation of the two polymorphs. At higher treatment temperatures (>150 °C), we begin to see the emergence of Na_2S together with α-Na_2S_2 (see Figure S1). A mixture of Na_2S and Na_2S_2 is also obtained when the S/Na ratio in the initial S/Na^+ solution is changed from 1:2 (e.g., to 1:1), indicating that a 1:2 ratio is crucial for obtaining the precursor

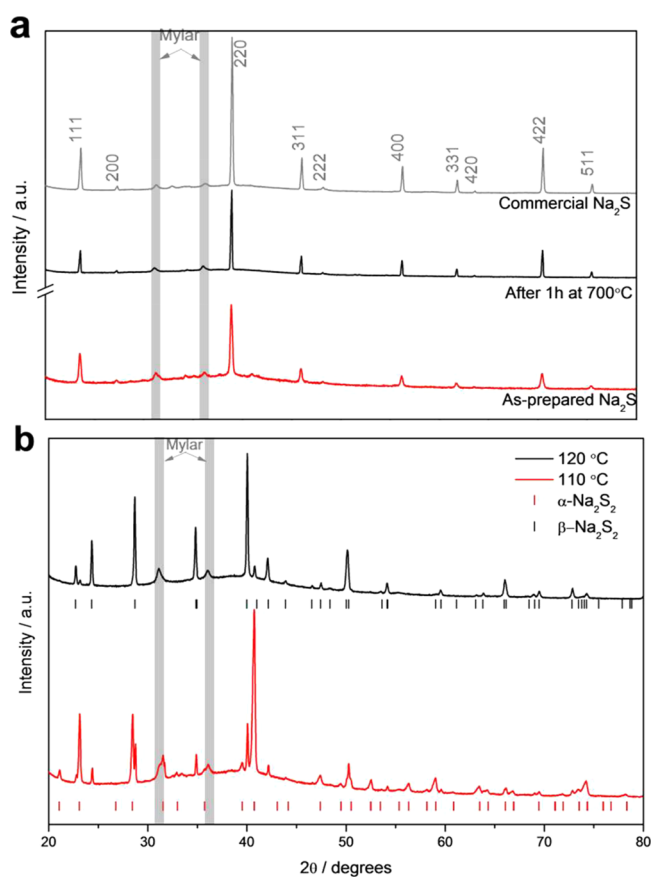**Figure 1.** (a) XRD patterns of as-prepared Na_2S and Na_2S after calcination at 700 °C for 1 h under argon compared with commercial Na_2S (Alfa Aesar). (b) XRD patterns of Na_2S_2 prepared at 110 and 120 °C, showing a predominance of the α phase (PDF 01-089-275181-1771) at 110 °C, while the β phase (PDF 01-089-275329-793) predominates at 120 °C. The powder materials were sealed in an airtight XRD sample holder (with a Mylar window) in an argon-filled glovebox to prevent reaction with moisture.
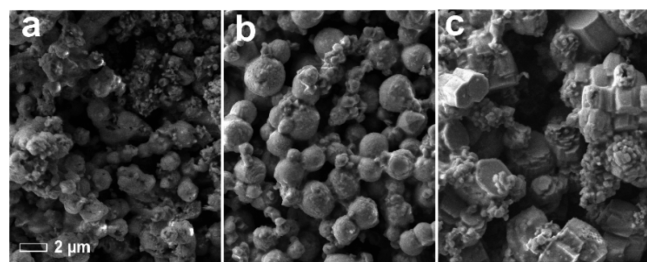

Figure 2. Morphologies of as-prepared Na_2S (a), Na_2S_2 prepared at 110 °C (b), and Na_2S_2 prepared at 120 °C (c). The scale bar of 2 μm is for all figures.

complex that decomposes to either Na_2S or Na_2S_2 depending on the temperature.

Hence, our approach provides a facile, selective, and fast approach to preparing phase-pure Na_2S and Na_2S_2. This approach is cost-effective and provides a safer alternative by avoiding the use of Na metal or liquid ammonia. The material morphology was examined by scanning electron microscopy (SEM; also see Figure S2). Figure 2 shows that Na_2S and α-Na_2S_2 prepared at 110 °C are formed as solid spheres with typical diameters between 1 and 2 μm. Interestingly, the morphology of β-Na_2S_2 (prepared at 120 °C) is significantly different, showing

agglomerated, large hexagonal-shaped crystals as the main morphological feature.

Recent research on Na-based batteries as a low-cost alternative to Li batteries has seen a considerable focus on the development of room temperature Na−S batteries,[7−16] which can employ sodium sulfide/polysulfides as positive electrodes.[13−16] The use of a sodiated cathode, such as Na_2S or Na_2S_2, allows the application of sodium-free anodes, such as hard C, Si, and Sn. This improves the safety features of the battery and may also reduce capacity fade, which can result from the reaction between Na-metal anodes and the polysulfide ions migrating from the cathode. This shuttling effect of polysulfide ions in Li/Na−S batteries, in addition to the insulating nature of the S electrode itself and severe volume changes associated with Na^+ or Li^+ (de)insertion process, is a persistent issue that results in deleterious capacity fading upon cycling and precludes the more widespread development of these battery chemistries.[7−16] Room temperature Na−S batteries face even more serious challenges associated with the S active material, the inherent capacity fade during cycling, and their short lifespan.[7,8] This is due to more sluggish electrochemical activity, rapid polysulfide migration, potential vigorous reactions between the Na anode and Na_2S_n species, and even greater volume changes in the S electrode. Batteries employing Na-free anodes and sodiated cathodes (e.g., Na_2S and Na_2S_2) are expected to exhibit better performances. For example, employing Na_2S_2 as a cathode and a Na-free anode would eliminate the potential solid−solid Na_2S_2/ Na_2S conversion step, which, because of the nonconductive nature of Na_2S_2 and Na_2S, is kinetically slow and suffers from high polarization.[12,13]

To assess the electrochemical activity of our materials, we have applied them as positive electrodes in Na−S batteries using Na metal as the negative electrode and 1.5 M $NaClO_4$/0.3 M $NaNO_3$ in tetraglyme as the electrolyte. The active material was simply mixed with conductive C and a poly(tetrafluoroethylene) binder (in a 6:2.5:1.5 weight ratio) and pressed into a thin pellet (~3 mg). Our procedure is not suitable to evaluate the cycling performance of these batteries because no precautions are undertaken to avoid deleterious shuttle activity, and this is beyond the scope of our current paper.[15,16] Our aim here is to evaluate the electrochemical activity and initial utilization of the active species for each of the materials we have synthesized. The electrochemical activity of Na_2S_2 has not been previously reported independently, most likely because of the difficulties in obtaining a sufficiently pure material. Figure 3a shows representative cyclic voltammograms (CVs) for the three materials: Na_2S, β-Na_2S_2, and α-Na_2S_2. The large oxidation peak in the first cycle corresponds to the removal of Na^+ from the cathode, and this peak appears at a slightly higher potential for Na_2S_2. After this oxidation process, the CVs for each material displays the typical I−V behavior of a conventional Na−S cell, with two major reduction peaks at ~2.2 and ~1.6 V and two oxidation peaks at ~1.8 and ~2.4 V, indicating the reversible nature of these redox processes.[7,8,12−16]

Figure 3b shows voltage profiles of the first charge/discharge for each material. These profiles are consistent with the measured CVs, showing one charge plateau and two discharge plateaus for the first charge and discharge cycles, respectively. Under the applied conditions, the initial charge capacities (normalized to the masses of Na_2S and Na_2S_2) of ~450, 410, and 390 mAh g^{-1} are observed for Na_2S, β-Na_2S_2, and α-Na_2S_2, respectively. These correspond to ~65%, 84%, and 80% utilization of Na^+ in these materials, respectively. These results suggest excellent electro-
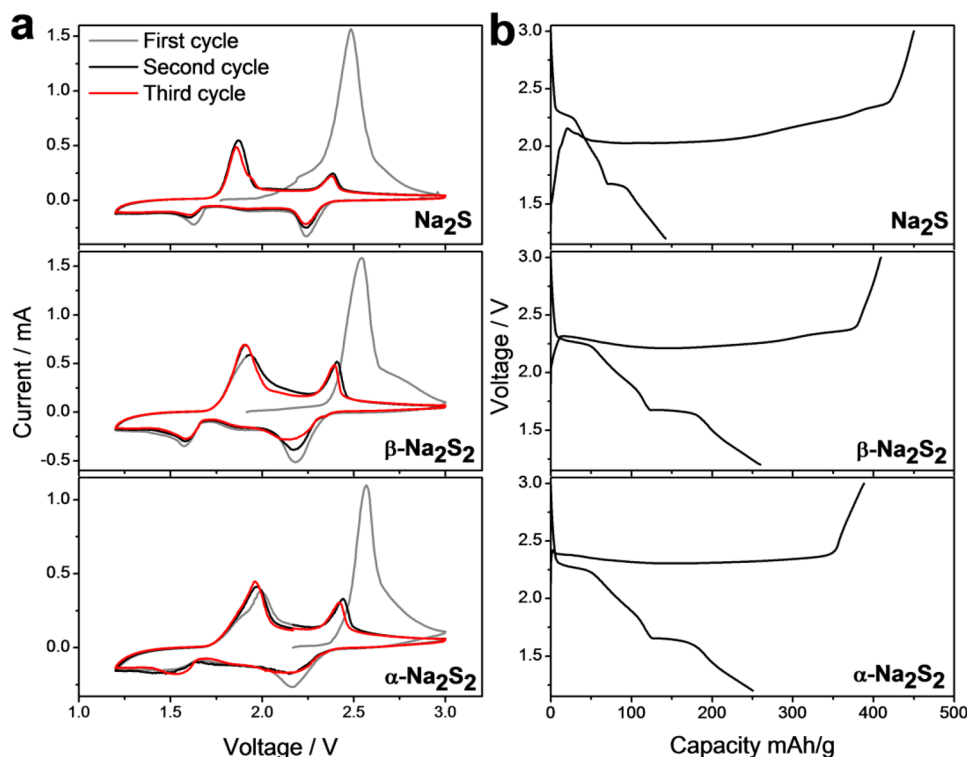
Figure 3. (a) CVs of Na_2S, β-Na_2S_2, and α-Na_2S_2 at a potential sweep rate of 0.1 mV s^{-1} between 1.2 and 3.0 V. (b) First charge/discharge profiles for each material cycled at C/10 rate. One C corresponds to 687 and 487 mA g^{-1} for Na_2S and Na_2S_2, respectively.

chemical activity of Na_2S_2. In the first discharge, Na_2S_2 also shows a higher capacity (normalized to the S content) than Na_2S (~440 mAh g^{-1} for β-Na_2S_2, compared with ~350 mAh g^{-1} for Na_2S). We could not observe a significant difference in the electro-chemical activity between α- and β-Na_2S_2. The slightly higher specific capacity observed for β-Na_2S_2 is, most likely, due to the difference in the crystal structure, as well as changes in the particle morphology.

We have demonstrated a new, facile approach for the selective synthesis of Na_2S and polymorphs of Na_2S_2. The proposed synthesis is fast and cost-effective and avoids the use of Na metal. The synthesis of such highly pure materials has enabled their demonstration as positive electrodes in room temperature Na−S batteries. Preliminary studies confirm a promising electro-chemical activity of Na_2S_2. Optimization to control the polysulfide shuttle activity and further detailed investigations of these materials are now underway.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00776.

> Experimental details, XRD pattern of the sample prepared at 150 °C, and SEM images of Na_2S calcined at 700 °C (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: serena.corr@glasgow.ac.uk.

ORCID 🟢

Hany El-Shinawi: 0000-0002-4743-5576

Serena A. Corr: 0000-0002-9303-4220

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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