

α -Ag₂S nanoparticles: low-temperature syntheses, crystallisation pathway, and first operando luminescence measurements for sodium-ion battery applications

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Table of contents

1. Experimental part	3
1.1. Materials and synthesis procedures.....	3
1.1.1. Synthesis of the single-source precursor (SSP) [AgS ₂ CNH ₂]	3
1.1.2. Single-source precursor synthesis of Ag ₂ S NPs by decomposition of the solid [AgS ₂ CNH ₂]	3
1.1.3. Synthesis of the SSP [Ag(CH ₄ N ₂ S) ₂]NO ₃	3
1.1.4. Single-source precursor synthesis of Ag ₂ S NPs by decomposition of the solved [Ag(CH ₄ N ₂ S) ₂]NO ₃ via hot injection	4
1.1.5. Polyol-assisted double-source hot injection synthesis of α -Ag ₂ S NPs	4

2.1.6	Double-source synthesis of α -Ag ₂ S NPs in water	5
1.2.	In situ measurement assemblies	6
2.	Supplementary results.....	12
2.1.	Synthesis of [AgS ₂ CNH ₂] single-source precursor	12
2.2.	Synthesis of [Ag(CH ₄ N ₂ S) ₂]NO ₃ single-source precursor	13
2.3.	Hot injection synthesis of Ag ₂ S from [Ag(CH ₄ N ₂ S) ₂]NO ₃ single-source precursor	14
2.3.	Polyol-assisted double-source synthesis of α -Ag ₂ S NPs	15
2.3.1.	Reaction without capping agent	15
2.3.2.	Polyvinylpyrrolidone (PVP) as capping agent	15
2.3.3.	Sodium dodecyl sulphate (SDS) as capping agent	16
2.3.4.	Trisodium citrate (TSC) as capping agent.....	17
2.4.	Double-source synthesis of α -Ag ₂ S NPs in water.....	19
2.4.1.	Hollow Ag ₂ S spheres.....	19
2.4.2.	<i>In situ</i> infrared spectroscopy.....	20
2.5.	Ag ₂ S-based electrodes for sodium-ion batteries	20
	References.....	21

1. Experimental part

1.1. Materials and synthesis procedures

1.1.1. Synthesis of the single-source precursor (SSP) [AgS₂CNH₂]

NH₄S₂CNH₂ was synthesised according to the method previously reported by Teske *et al.* [1] CS₂ (44 mL; 0.7340 mol, 99.5%, AppliChem) was added to 400 mL ethanol (99%, Walter-CMP) under stirring and 50 mL NH₃ solution (0.7340 mol, 25%, VWR Chemicals) was slowly added. The solution was diluted to 1 L with ethanol (99%, Walter-CMP) and stirred overnight at room temperature. The reaction solution was then stored for one day at T = -18 °C and the white precipitate was dried under vacuum. The product was washed with ice-cold ethanol and stored in an argon atmosphere at T = -18 °C. The SSP mono(dithiocarbamato)silver(I) [AgS₂CNH₂] was synthesised according to the method of Teske *et al.* [2] by mixing 20 mL AgNO₃ (5 mmol, 99.8%, VWR Chemicals) in a water-ethanol (1:1) solution with 40 mL KCN (12.5 mmol, > 96%, Merck) in the same solvent mixture. After 5 min, the synthesised NH₄S₂CNH₂ (10 mmol) was dissolved in 25 mL distilled H₂O, added dropwise, stirred for 20 min and allowed to stand for 30 min. The precipitate was dried under vacuum and washed twice with distilled H₂O and ethanol.

1.1.2. Single-source precursor synthesis of Ag₂S NPs by decomposition of the solid [AgS₂CNH₂]

For this Ag₂S synthesis, 30 mL of ethylene glycol (EG, 99%, Eydam) was added to the reactor and heated to 120 °C. The synthesised [AgS₂CNH₂] (0.3 mmol) in powder form was then manually added to the reactor and stirred for a further 180 min. The product was washed twice with ethanol, centrifuged and dried at 80 °C for 12 h.

1.1.3. Synthesis of the SSP [Ag(CH₄N₂S)₂]NO₃

The precursor bis(thiourea)silver(I)nitrate [Ag(CH₄N₂S)₂]NO₃ was synthesised according to the method of Sivakumar *et al.* [3] Thiourea (CS(NH₂)₂, 10 mmol, 99%, Merck) was dissolved in 15 mL distilled H₂O and filtered. AgNO₃ (5 mmol) was

dissolved in 5 mL distilled H₂O. The aqueous thiourea was then added dropwise to the AgNO₃ solution and stirred at 60 °C for 2 h. The solution obtained was filtered and the product dried at room temperature.

1.1.4. Single-source precursor synthesis of Ag₂S NPs by decomposition of the solved [Ag(CH₄N₂S)₂]NO₃ via hot injection

For this Ag₂S synthesis, 30 mL of EG was added to the reactor and heated to 100 °C. Then, 5 mL of a solution containing the synthesised [Ag(CH₄N₂S)₂]NO₃ (0.3 mmol) in ethylene glycol was injected into the preheated reactor and stirred for 180 min. The product was washed twice with ethanol, centrifuged and dried at 80 °C for 12 h. It is important to note that the [Ag(CH₄N₂S)₂]NO₃ precursor used for the polyol hot injection approach was previously filtered to remove partially formed impurities during the SSP synthesis, as explained in detail in Section 2.2.

1.1.5. Polyol-assisted double-source hot injection synthesis of α -Ag₂S NPs

In general, for this Ag₂S synthesis, EG was introduced into the reactor and kept at 25-100 °C. Detailed information on volumes, concentrations and temperatures of these

Table S1. Experimental conditions for the polyol-assisted double-source hot injection synthesis of α -Ag₂S NPs.

Temperature / °C	Reaction time / min	Reactor Volume / mL	Added (AgNO ₃) / mmol	Added (Thiourea) / mmol	Capping agent / mmol	Figures
RT	120	40 (EG)	0.1	0.05	-	Figs. 2, S5
RT	120	40 (EG)	0.1	0.05	0.001 (PVP)	2, S6
RT	90	40 (EG)	0.1	0.05	0.001 (SDS)	2, S7
RT	120	40 (EG)	0.1	0.05	0.002 (TSC)	2, S9
40	150	40 (EG)	0.1	0.05	-	3
70	100	40 (EG)	0.1	0.05	-	3
100	90	25 (EG)	0.1	0.05	-	3

experiments can be found in Table S1. Thiourea was first added to EG as a solid. After thiourea dilution, at $t = 20$ min, a 5 mL solution of AgNO_3 (0.1 mmol) was injected into the reactor and further stirred for 90-150 min. The product was washed twice with ethanol, centrifuged and dried at $30\text{ }^\circ\text{C}$ for one day.

For experiments investigating the influence of capping agents, polyvinylpyrrolidone (PVP, Sigma-Aldrich), sodium dodecyl sulphate (SDS, >90%, Grüssing) or trisodium citrate (TSC, pure, Merck) was dissolved together with thiourea at room temperature 20 minutes before the addition of the AgNO_3 EG solution.

Samples for synchrotron-based in situ XRD measurements

In these experiments, thiourea (0.5 mmol) was first dissolved in 35 mL of EG at room temperature and $100\text{ }^\circ\text{C}$. Then 5 mmol of a solution containing AgNO_3 (1 mmol) in EG, 5 mL, was added to the reactor and stirred for several minutes. The product was washed twice with ethanol and water, centrifuged and dried at $30\text{ }^\circ\text{C}$ for one day.

2.1.6 Double-source synthesis of α - Ag_2S NPs in water

Hollow α - Ag_2S spheres

This synthesis is based on the work of Lv et al. [4], where silver dodecanoate ($\text{C}_{12}\text{H}_{23}\text{AgO}_2$) was first prepared and then used as silver for the Ag_2S NPs. For this procedure, AgNO_3 (2 mmol) and sodium dodecanoate ($\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$, 2 mmol, 98%, Acros Organics) were added to 50 mL of a mixture of deionised water and ethanol (1:1) and stirred at $30\text{ }^\circ\text{C}$ for 30 min. The product was then washed with water and ethanol and dried at $T = 30\text{ }^\circ\text{C}$ for 20 hours.

The synthesised silver dodecanoate (0.5 mmol) was then dispersed in a mixture of 27 mL of distilled water and 3 mL of n-butylamine (99+%, Acros Organics). Then 15 mL of a solution of PVP (1.33 mmol) and thiourea (0.9 mmol) in distilled water was added to the reactor and stirred for a further 30 min. The product was washed once with water and ethanol, centrifuged and dried at $30\text{ }^\circ\text{C}$ for one day.

Samples for in situ infrared spectroscopy measurements

Exploring an additional method for α -Ag₂S synthesis, SDS (0.02 mmol) and ethylenediaminetetraacetic acid (0.08 mmol, EDTA, p.a., Grüssing) were dissolved in 38.5 mL of distilled water at room temperature. The pH was then adjusted to 10 with NH₃ (25%, VWR Chemicals). After 3 minutes, 4 mL of an aqueous solution of AgNO₃ (0.08 mmol) was added. After a further minute, 4 mL of aqueous thiourea (0.04 mmol) solution was added and stirred for a further 90 minutes. The product was washed twice with ethanol and water, centrifuged and dried at 30 °C for one day.

1.2. In situ measurement assemblies

Setup A

Experimental setup A [5] was used for the synthesis of Ag₂S NPs from single source precursors. This setup consisted of an EasyMax® 102 stationary workstation (Mettler Toledo, Giessen, Germany), which allowed automatic and precise control of stirring conditions, temperature and solution dosing into the glass reactor. The cover of the glass reactor has several openings through which all the in situ sensors were attached to the reactor. To monitor changes in solution turbidity, the reactor was illuminated from the outside by a UV light source (Sahlmann Photochemical Solutions, Bad Segeberg, Germany). A portable EPP2000 spectrometer (StellarNet Inc., Tampa, FL, United States) equipped with a CCD-based detector was used to record optical spectra every 30 s. The spectrometer was connected to an optical fibre immersed in the reactant mixture. During the experiments, product formation was identified by the increase in turbidity and the decrease in intensity of the detected light source through the reaction solution.

Setup B

Experimental setup B [6] was used for the synthesis of Ag₂S NPs from double source precursors. It consisted of a Titrand 902 dosing unit (Metrohm AG, Filderstadt, Germany) and an 856 conductivity module (Metrohm AG), which allowed automatic and precise control of temperature and solution dosing in the glass reactor. In situ UV-Vis transmission spectroscopy was measured with a fibre-coupled miniature spectrometer RPS-Mini from Laser 2000 GmbH.

For the synchrotron-based experiments, a modified glass reactor with an inserted glass tube was used to achieve the shortest possible path for the X-ray beam through the reaction mixture, as described in one of our previous papers. [7] Here, the reactor contents were analysed at the P23 beamline of the PETRA III storage ring at the German Electron Synchrotron (DESY). The reactor holder consisted of an integrated stirring and heating system. In addition, the reactor holder was provided with X-ray ingress and egress apertures and a perpendicular aperture to allow illumination with a light source. X-ray diffraction (XRD) patterns were recorded every 10 s (23 keV, $\lambda = 0.53906 \text{ \AA}$). The beamline was equipped with a 2D detector (model Rad-ikon 2329, Teledyne DALSA, Canada). Data were analysed using DawnDiamond software. For the sake of clarity in the assignment of the Bragg peaks measured in situ to the corresponding simulated diffraction patterns, the XRD data were treated in the manner suggested by Platero-Prats et al. [8] for the in situ pair-distribution function analysis. Thus, our in situ XRD data were normalised to overcome the oscillation of the intensity of the synchrotron X-ray beam. We used the first measurement, before mixing the precursor solutions, as a baseline to subtract the background caused by the reactor walls and the solvent.

1.3. *Ex situ* measurements

A STOE Stadi-p powder diffractometer (Cu-K α 1 radiation, $\lambda = 1.540598 \text{ \AA}$, equipped with a Ge monochromator and a Mythen 1k detector) was used for the ex situ XRD measurements. Absorption and reflection spectra were recorded at room temperature using a Varian Techtron Pty two channel UV/Vis/NIR Cary 5000 spectrometer, with BaSO₄ as reference material. Dynamic light scattering measurements were performed using a Beckman Coulter Delsa Nano C Particle Analyzer. A JEOL Ltd. transmission electron microscope (JEM-2100 (200 kV, LaB₆)) was used for the TEM images. Simultaneous DTA/TG analysis was performed using a Netzsch STA 409 CD with a heating rate of 4 K/min.

1.4. Sodium-ion battery (SIB) applications

The α -Ag₂S samples used for the SIB cycling stability tests were prepared heating 20 mL EG in an oil bath. Upon reaching the target temperature of 120 °C, 10 mL of a 0.1 mol/L solution of thiourea and 10 mL of a 0.2 mol/L AgNO₃ solution in EG were added to the reactor and

further stirred for one hour. The product was centrifuged, washed twice with ethanol and dried at 60 °C under vacuum for two days. For producing additional materials for the operando luminescence measurements, the volume of solvents and mass of reagents were doubled, keeping the concentration constant.

For setting up film cells for the SIB cycling stability tests, electrode films must be prepared. These films were composed by the active material (α -Ag₂S), carbon Super C65 (99.9 + %, Timcal) and polyvinylidene fluoride (PVDF, [CH₂CF₂]_n, Solvay) as binder. These compounds were mixed in a ratio of 60:30:10. The additive Super C65 is used to enhance the electronic conductivity of the electrode slurry. The binder PVDF ensures cohesion of all components. The solvent N-Methyl-2-pyrrolidone (NMP, 99.8 %, Fisher Bioreagents) allows a good mixing of the used substances.

In a grinding vessel, 60 wt% active material, 30 wt% Super C65 and 10 wt% PVDF were weighed with 300 mg of NMP and mixed in a ball mill (Retsch MM400) at 15 Hz for 20 min. The suspended electrode material was applied to a carbon coated copper foil using a notch bar via doctor blade casting method. The height of the notch bar was set to 300 μ m. The electrode film was dried for 24 h at room temperature and then dried for 24 h at 60°C in a vacuum oven.

From the dried electrode films, circle-shaped electrodes with a diameter of 10 mm were punched out for use in SwagelokTM-type cells (Fig. S1). This type of cells consists of contact cylinders (1 + 6), to which the current is applied. Seals (2) are applied to the lower cylinder. The cylinder is then placed in the lower part of the cell casing (3) and the center piece (4) is screwed on. The punched electrode foil is placed in this assembly and covered with a SeparionTM Separator (d = 21 μ m, porosity =48 %, Litarion) and a glass microfibre filter (WhatmanTM, Grüssing). Then the back contact stamp (5) is placed and the upper contact cylinder (6) with integrated spring is attached. This is in turn sealed with additional sealings (7). Finally, the cell is screwed tightly to the upper part of the cell casing.

The cells were transferred into an argon glovebox and the separators were moistened with 120 μ L of the electrolyte solution. In this case, the electrolyte solution (Solvionic) was composed by 1 mol/L NaPF₆ in a 1:1 mixture of propylene carbonate (PC) and fluoroethylene carbonate (FEC). A sodium electrode (99.7 %, abcr, diameter = 10 mm) was then added and the cells were sealed airtight.

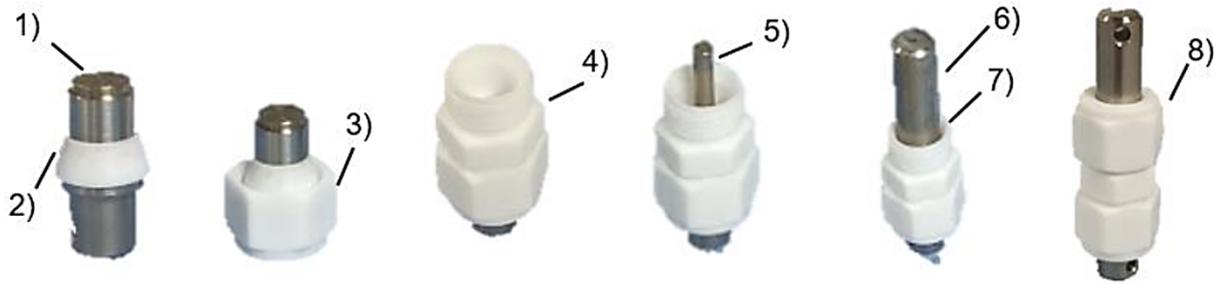


Figure S1: Stepwise assembly of the Swagelok™ type cells.

Cycling stability and rate capability tests

All materials were tested in a potential window of 3.0 V to 0.1 V during the galvanostatic measurements. This is a typical potential window for testing anode materials of SIBs. [9, 10] The mode of operation was the constant current mode, where the current density stayed the same for the entire measurement. For the cycling stability test a current density of 0.1 A/g was applied to all cells. The currents used were determined by the mass of active material used in the cell. For the powder cells and the operando cells, the current intensity was given in C rates. A rate of 1C represents the current at which a cell discharges or charges to its theoretical capacity within one hour. Since a relatively large amount of active material is used in the powder pellets, it makes sense to select a low rate in order to achieve as complete a rate as possible. The current strength of the C rates as well as the current strengths per gram of active material can be derived from Faradays laws (eq. 1).

$$I = \frac{x(\text{Na}) \cdot m \cdot F}{t \cdot M} \quad (1)$$

with I = current, $x(\text{Na})$ = Electrons transferred per unit, m = mass of the active material, F = Faraday constant, t = charge/discharge time and M = molar mass of the active material.

Operando luminescence measurements

Swagelok test cells have also been used for powder cells to test the possibility of using operando luminescence measurements to monitor galvanostatic cycling. For this reason, a new operando cell was designed. The main objective was to provide a uniformly adjustable pressure on the active material with the spring deflection. This was to prevent any loss of electrical contact during the measurement and to ensure that

the working electrode maintained a constant connection to the separator and the electrolyte. At the same time, the cell must remain airtight over a long period of time and be chemically stable with respect to the electrodes and the electrolyte. The operando cell is described in detail in Figure S2.

In detail, the operando luminescence cell consists of the two housing parts (**1**, **2**) with the adjustable rotary lock (**5**) at the rear and an observation window (**10**, $\varnothing \approx 10$ mm) at the front, as well as the front and rear contacts (**18**, **3**). The housing is made of polyether ether ketone (PEEK). PEEK has an exceptional heat resistance and stability to organic solvents, and is a proven material in other electrochemical applications. Airtightness is ensured by several O-rings, between the housing halves (**9**), between the rear contact and the twist lock (**7**) and between the twist lock and the rear of the housing. The contacts for connection to the external circuit are made of brass, which offers a good compromise between electrical conductivity, corrosion resistance and cost.

The stamp-shaped back contact provides even pressure distribution, and a spring washer (**4**) with 5 mm of spring deflection placed on top counteracts volume expansion of the active material. The spring effect is enhanced by the Whatman™ glass microfibre filter (**11**) and can be further enhanced by the use of a second spring washer. A thin copper mesh (**15**) is used to connect the analysable electrode to the electrical contact (**18**), which is permeable to the liquid electrolyte while providing maximum contact area with the electrode.

The powder pellets for operando measurements were prepared using 20.8 mg of active material, produced as an 8 mm diameter pressed pellet at a pressure of 5 t for 5 min. Celgard punches with a diameter of 18 mm were used as separators. The cells were also assembled in the argon-filled glove box with 150 μ L of electrolyte solution consisting of 1 mol/L sodium trifluoromethanesulphonate (NaOTf, 98%, Sigma-Aldrich) in bis(2-methoxyethyl)ether (diglyme, 99+%, Acros).

NaOTf in diglyme has been previously tested as an electrolyte for similar transition metal sulfides. [9] In addition, ether-based solvents facilitate the formation of a stable SEI at transition metal sulfide anodes. [11]

Operando luminescence measurements were performed applying a FL3-22 Fluorolog-3 fluorescence spectrometer (HORIBA Jobin Yvon GmbH, Unterhaching, Germany), containing a Synchrony charge-coupled device (CCD) detector, a 450 W xenon lamp

and an iHR-320-FA triple grating imaging spectrograph. The spectrometer was connected to the battery cell by means of a Y-shaped optical fibre ($\varnothing_{window} \approx 1$ mm), which transported the excitation light from the spectrometer to the sample and the emitted light from the sample to the detector.

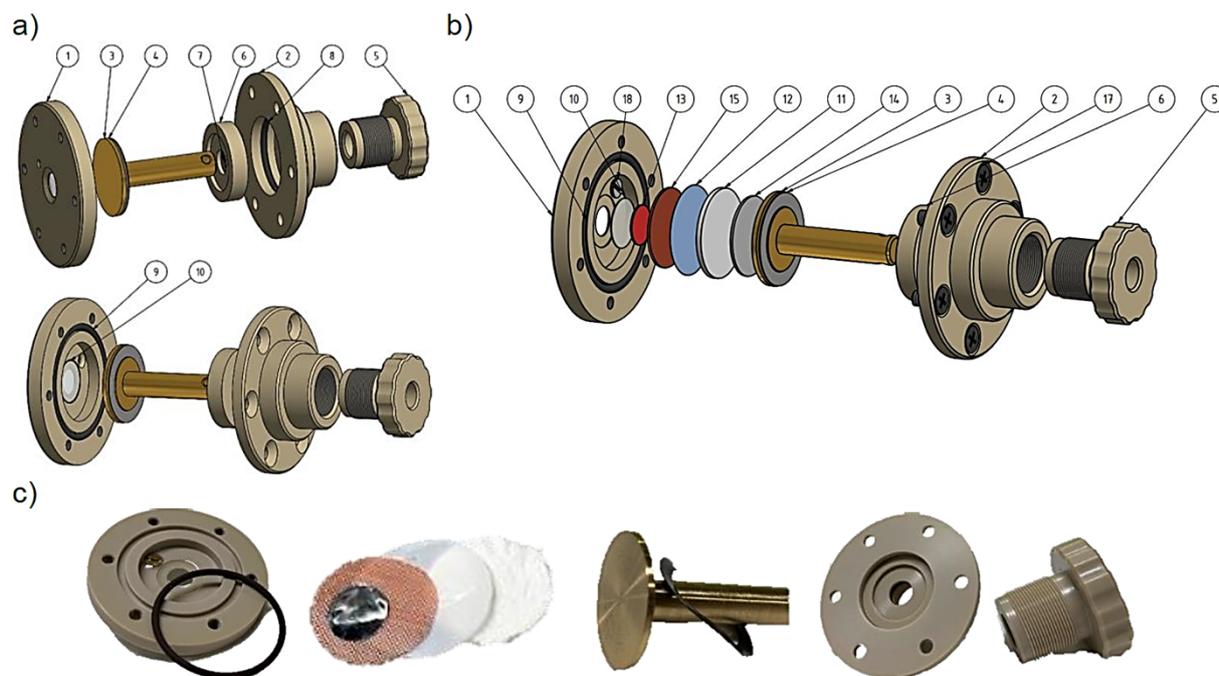


Figure S2: a) and b) Technical drawings and construction parts. c) Pictures of the disassembled operando luminescence cell.

2. Supplementary results

2.1. Synthesis of $[\text{AgS}_2\text{CNH}_2]$ single-source precursor

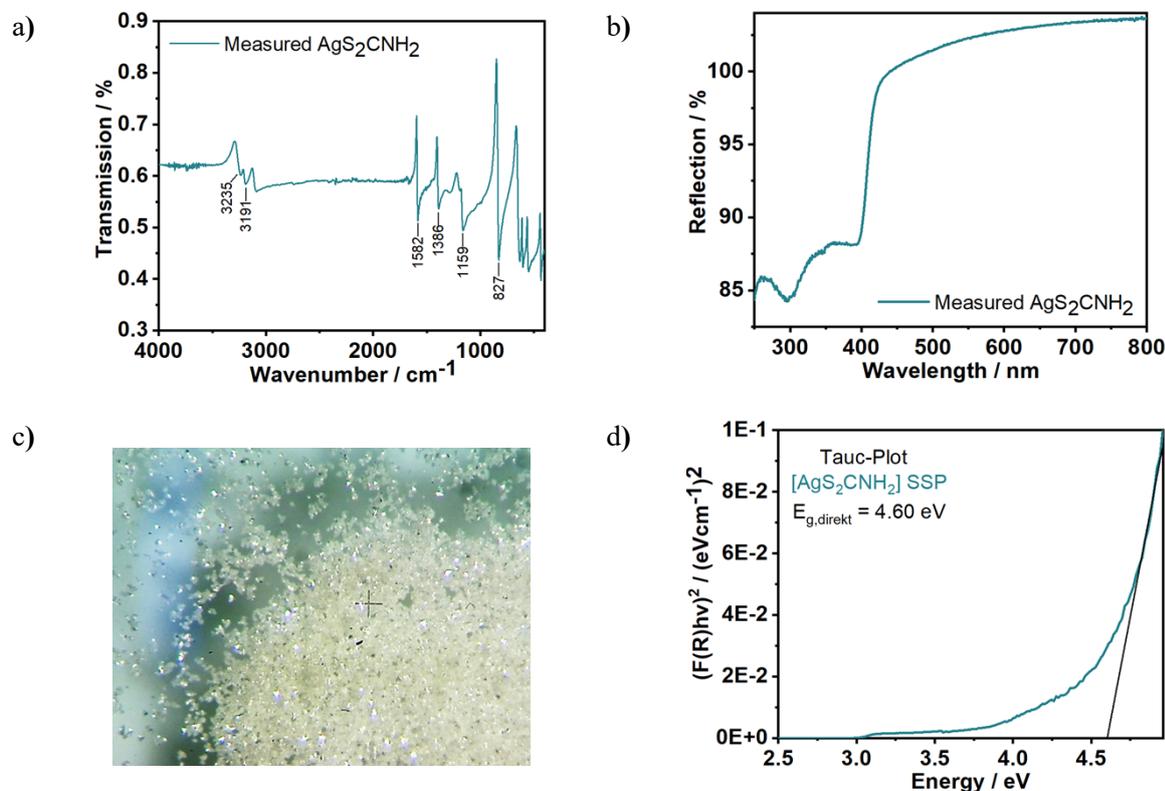


Figure S3: a) *Ex situ* infrared and UV/Vis reflectance spectra of the single source precursor $[\text{AgS}_2\text{CNH}_2]$ and b) corresponding optical microscope image. c) Tauc plot to determine the band gap of $[\text{AgS}_2\text{CNH}_2]$.

Table S2: Assignment of IR bands of the single source precursor $[\text{AgS}_2\text{CNH}_2]$, corresponding to Fig. S3a†. [12]

Wavenumber / cm^{-1}	Intensity	Type
3235	w	prim NH_2 -Val.
3191	w	prim NH_2 -Val.
1582	m	prim NH_2 , deformation
1386	m	C-N-Val.
1159	m	C-S-Val.
827	s	N-C-S-Val.

2.2. Synthesis of $[\text{Ag}(\text{CH}_4\text{N}_2\text{S})_2]\text{NO}_3$ single-source precursor

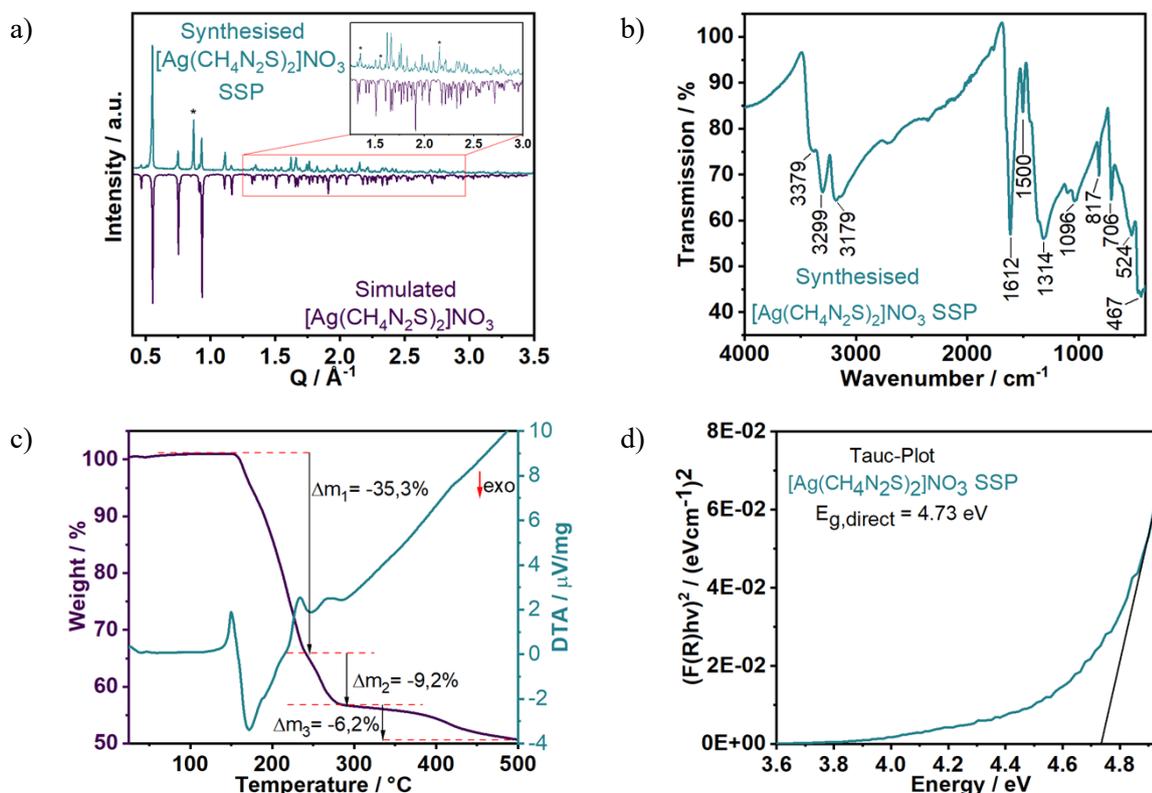


Figure S4: a) XRD measurement of the single source precursor $[\text{Ag}(\text{CH}_4\text{N}_2\text{S})_2]\text{NO}_3$ compared to the corresponding simulated diffraction pattern [3]. The asterisks (*) mark the main reflection that do not match the simulated pattern. b) IR measurement, c) DTA / TG curve and d) Tauc plot to determine the band gap of $[\text{Ag}(\text{CH}_4\text{N}_2\text{S})_2]\text{NO}_3$.

Table S3: Assignment of IR bands of the single source precursor $[\text{Ag}(\text{CH}_4\text{N}_2\text{S})_2]\text{NO}_3$, corresponding to Fig. S4b†. [12]

Wavenumber / cm^{-1}	Intensity	Type
3379	w	prim NH_2 -Val.
3299	m	prim NH_2 -Val.
3179	m	prim NH_2 -Val.
1612	s	prim NH_2 , deformation
1500	w	N-O-Val.
1314	s	C-N-Val.
1096	w	C-S-Val.
817	m	C-S-Val.
706	m	C-S-Val.
516	w	N-C-S-Val.
472	w	N-C-N-Val.

2.3. Hot injection synthesis of Ag_2S from $[\text{Ag}(\text{CH}_4\text{N}_2\text{S})_2]\text{NO}_3$ single-source precursor

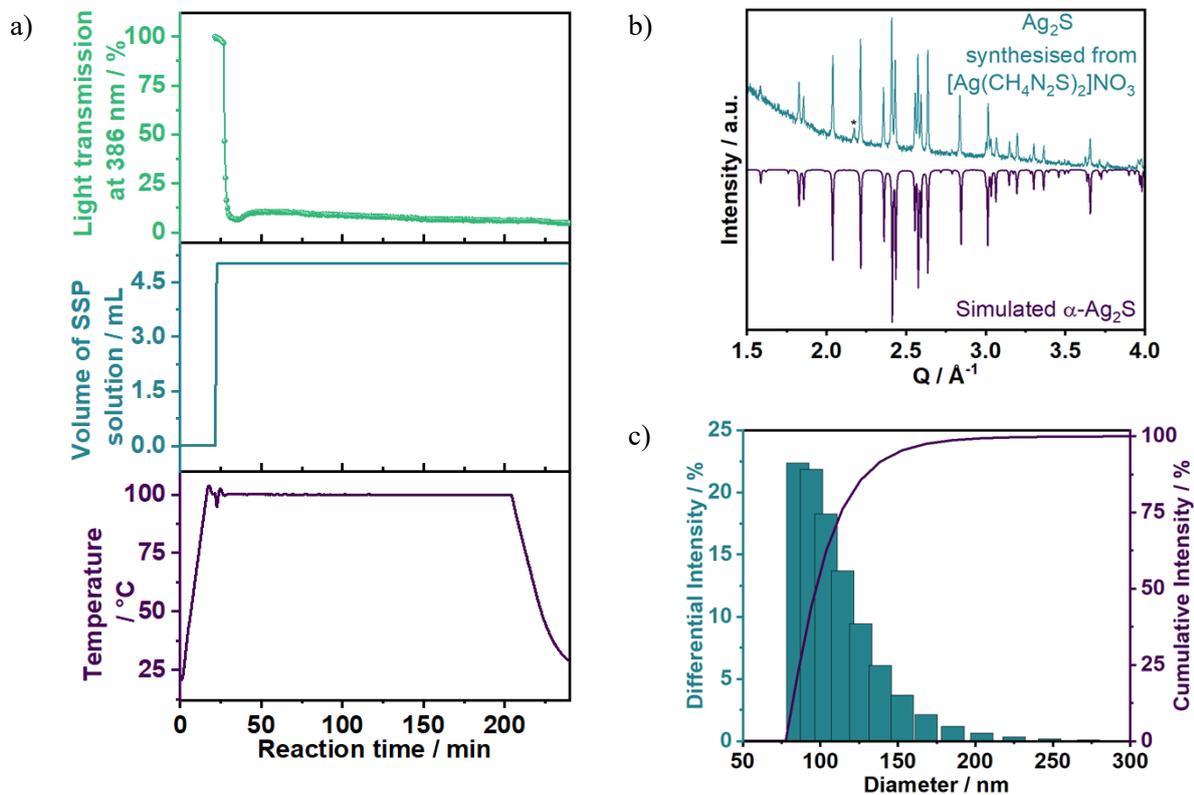


Figure S5: a) Time dependence of the temperature, the volume of $[\text{Ag}(\text{CH}_4\text{N}_2\text{S})_2]\text{NO}_3$ SSP solution added in the preheated EG and the intensity of the light source through the solution at 386 nm. b) XRD measurement of the resulting Ag_2S NPs compared to the simulated patterns of its α -phase [13]. c) Size distribution of synthesised Ag_2S NPs recorded by dynamic light scattering.

2.3. Polyol-assisted double-source synthesis of α -Ag₂S NPs

2.3.1. Reaction without capping agent

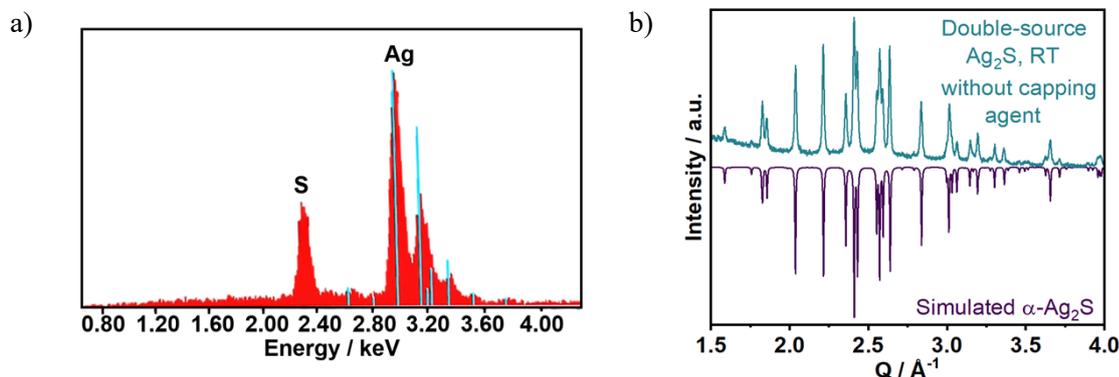


Figure S6: a) Energy dispersive X-ray spectroscopy results for α -Ag₂S synthesised via the mixture of thiourea and AgNO₃ without capping agent as well as b) the corresponding measured and simulated [13] X-ray diffraction patterns.

2.3.2. Polyvinylpyrrolidone (PVP) as capping agent

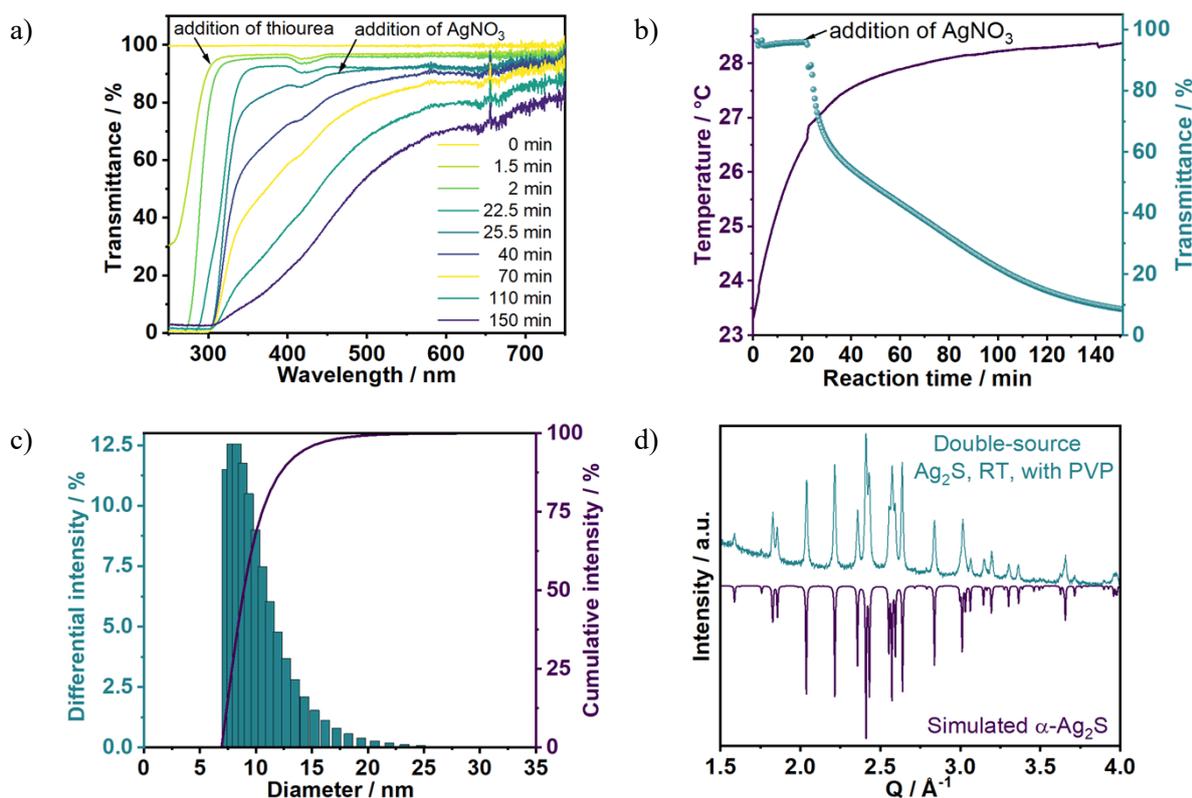


Figure S7: a) In situ UV/Vis transmittance spectra recorded during the double source synthesis of Ag₂S at RT with PVP and b) time dependence of temperature and transmittance at 340 nm. c) Size distribution and d) XRD pattern of the product compared to the corresponding simulated diffraction pattern [13].

2.3.3. Sodium dodecyl sulphate (SDS) as capping agent

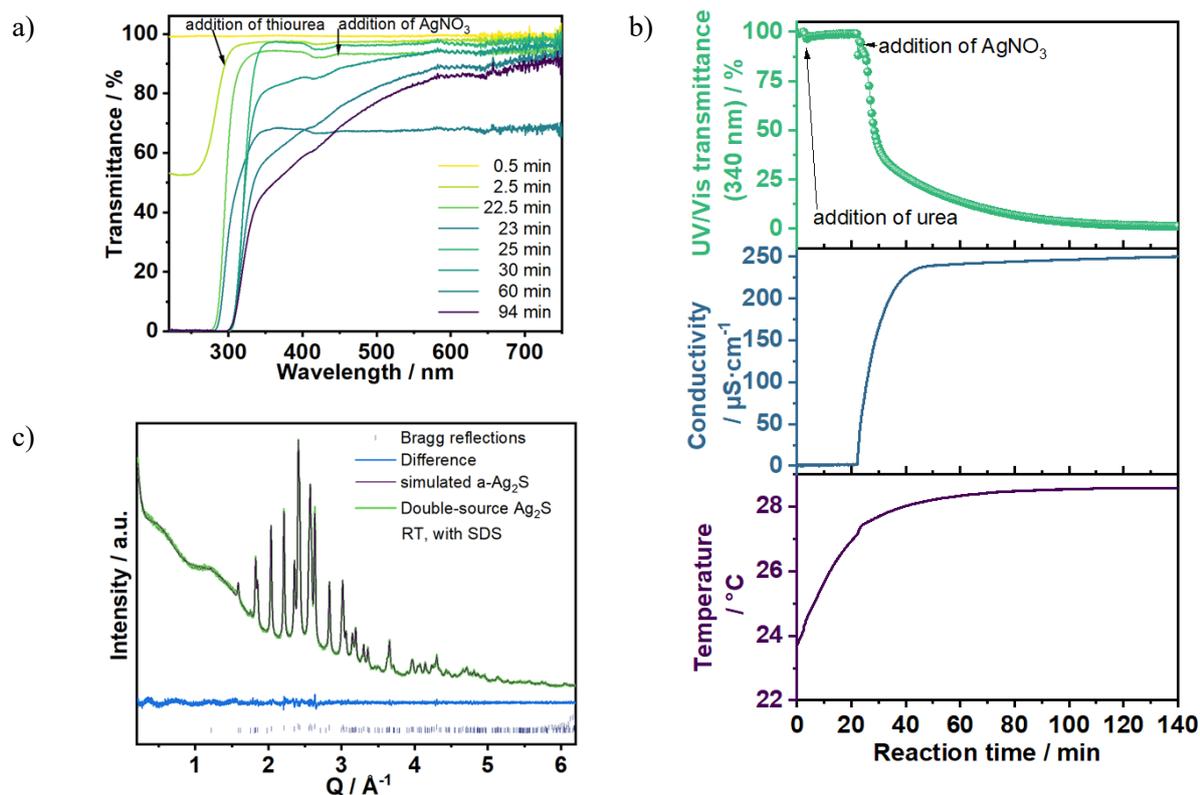


Figure S8: a) In situ UV/Vis transmittance spectra recorded during the synthesis of Ag_2S at RT with SDS and b) time dependence of temperature, ion conductivity and transmittance at 340 nm. c) final plot of the Pawley refinement of the measured Ag_2S sample (black), the simulated pattern [13] (green), the difference (light blue), beside the positions of the respective Bragg reflections (dark blue bars).

Table S4: Results of the Pawley refinement for Ag_2S .

Crystal system	Space group	a / \AA	b / \AA	c / \AA	$\alpha / ^\circ$	$\beta / ^\circ$	$\gamma / ^\circ$	GoF	$R_{wp} / \%$
Monoclinic	$P2_1/n$	4.2259(7)	6.935(1)	7.877(1)	90	99.543(2)	90	1.09	1.54

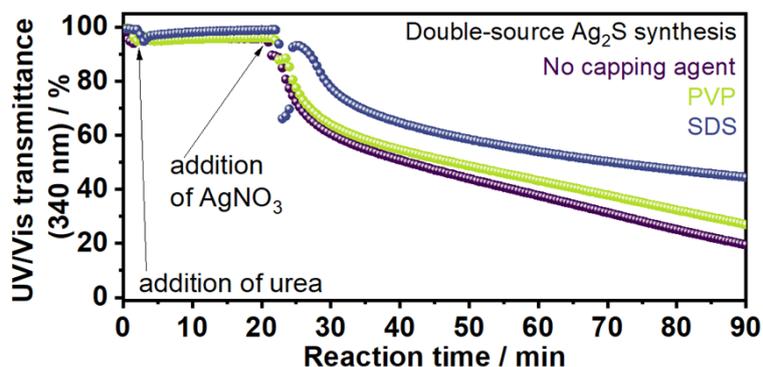


Figure S9: Comparison of the time-dependent profile of in situ UV/Vis transmittance spectroscopy during Ag_2S double-source synthesis with and without capping agents.

2.3.4. Trisodium citrate (TSC) as capping agent

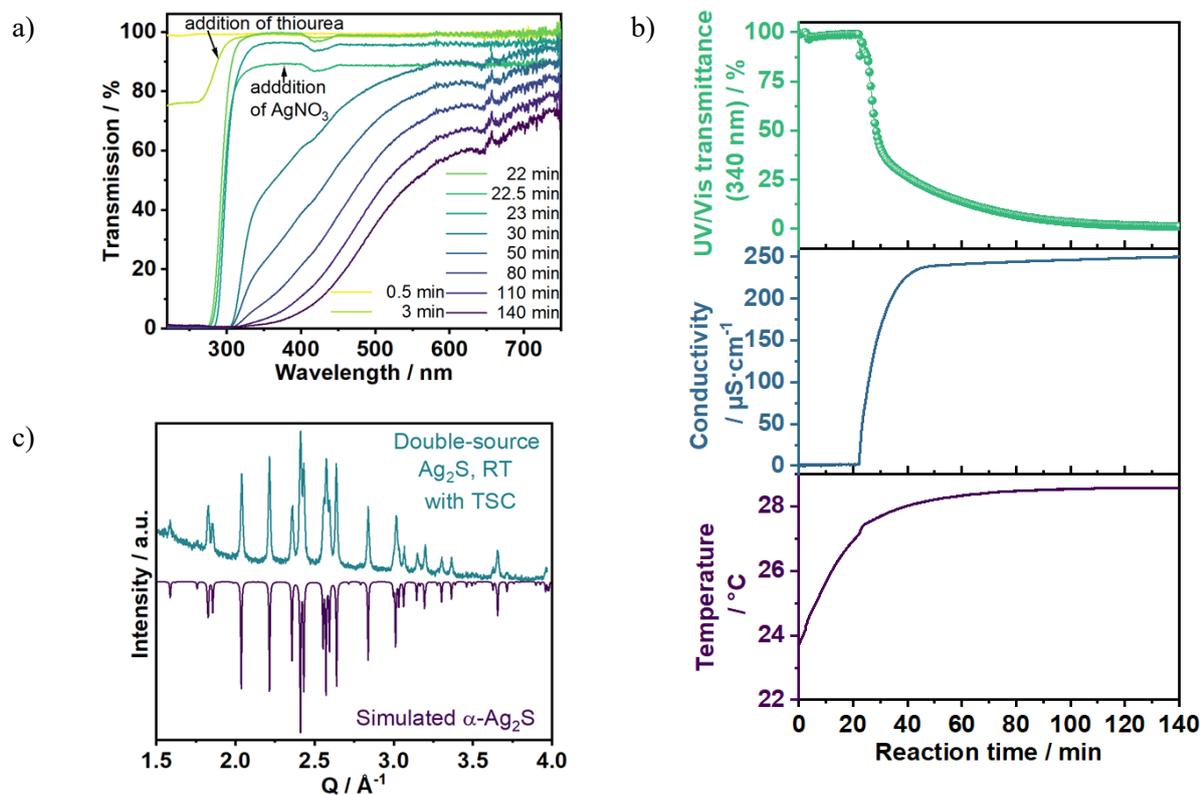


Figure S10: a) In situ UV/Vis transmittance spectra recorded during the synthesis of Ag_2S at RT with TSC and b) time dependence of temperature, ion conductivity and transmittance at $\lambda = 340$ nm. c) Measured and simulated α - Ag_2S powder patterns [13].

2.4.3. Synchrotron-based in situ X-ray diffraction analysis

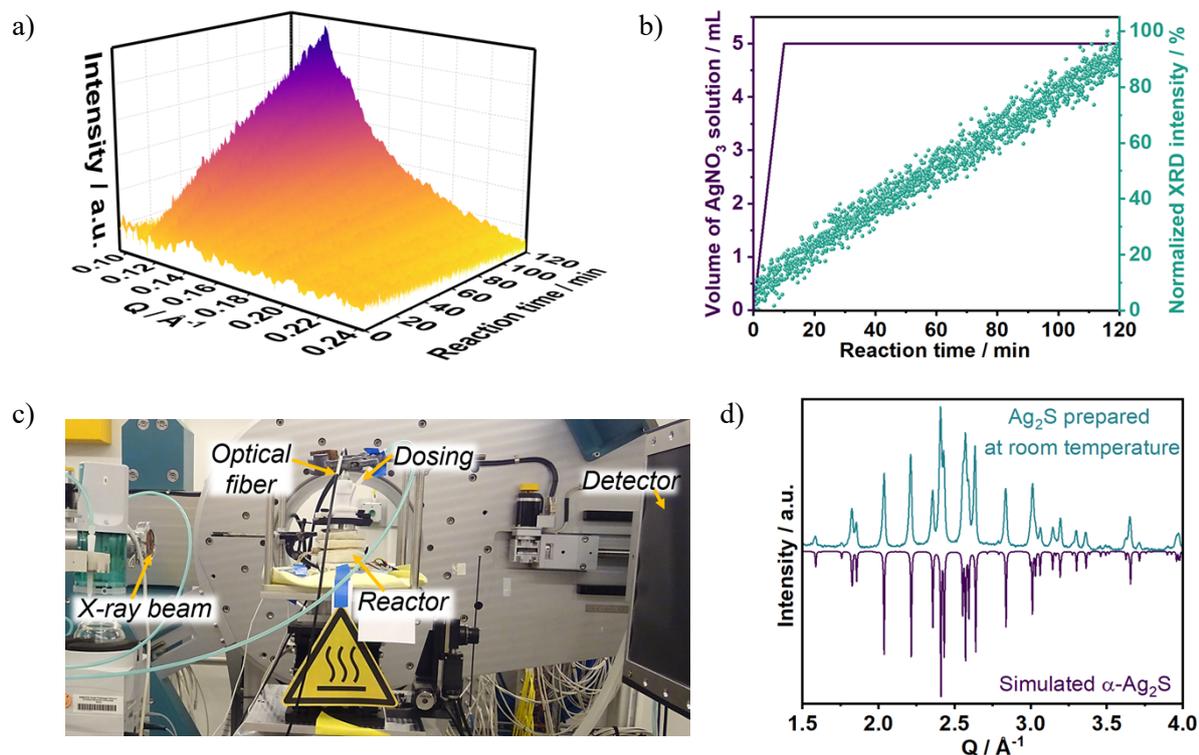


Figure S11: a) In situ XRD patterns recorded during the double-source synthesis of Ag_2S at room temperature. b) Time-dependent evolution of the small angle signal at 0.14 \AA^{-1} and the volume of the AgNO_3 solution to the reactor containing thiourea in EG. c) Experimental setup at the DESY P23 beamline. d) Respective measured and simulated α - Ag_2S powder patterns [13].

2.4. Double-source synthesis of α -Ag₂S NPs in water

2.4.1. Hollow Ag₂S spheres

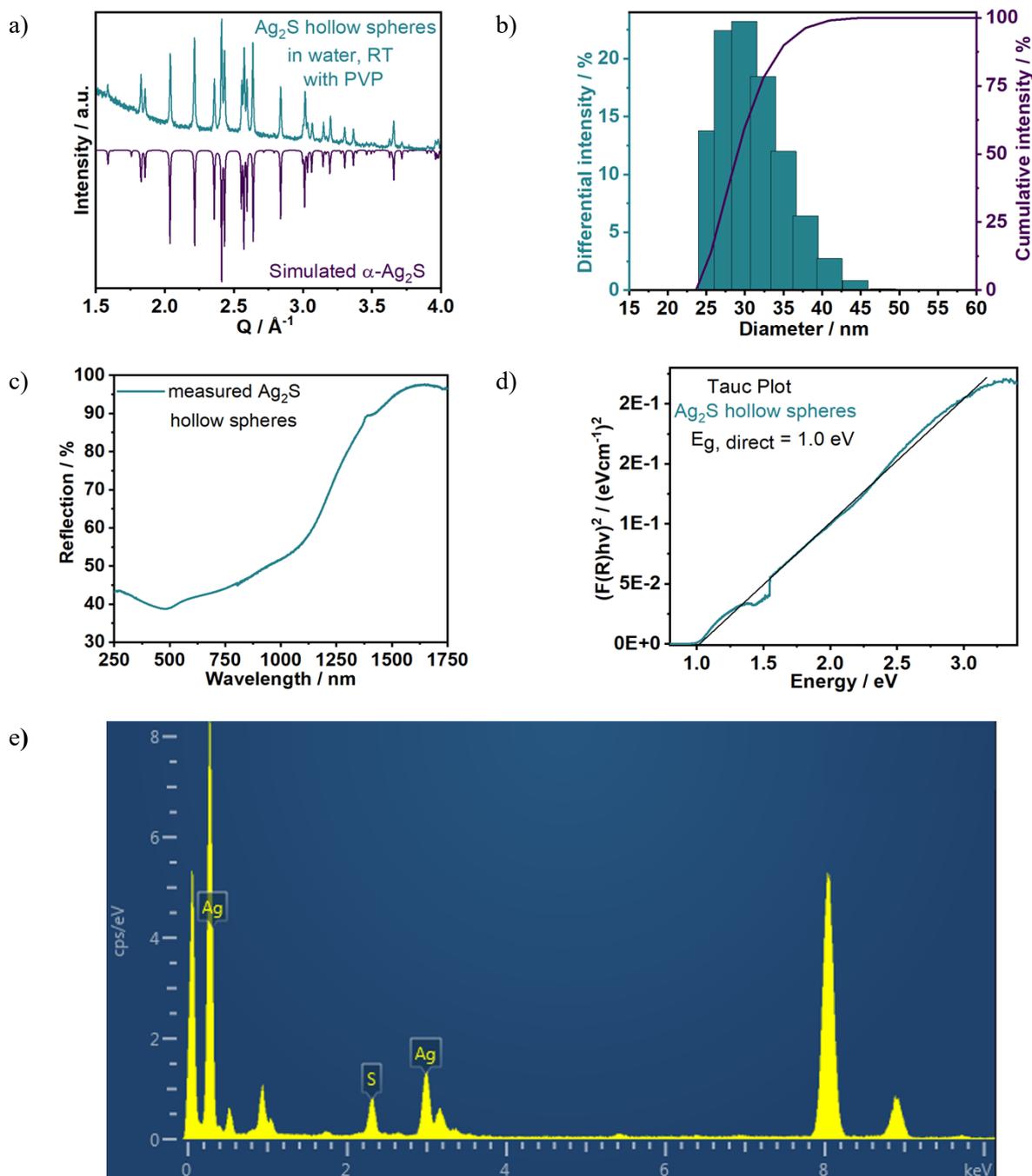


Figure S12: a) Measured and simulated [13] powder patterns of α -Ag₂S hollow spheres synthesised in H₂O at RT with PVP as stabiliser. Corresponding b) particle size distribution, c) ex situ UV/Vis reflectance spectroscopy, d) band gap calculation and e) EDX results.

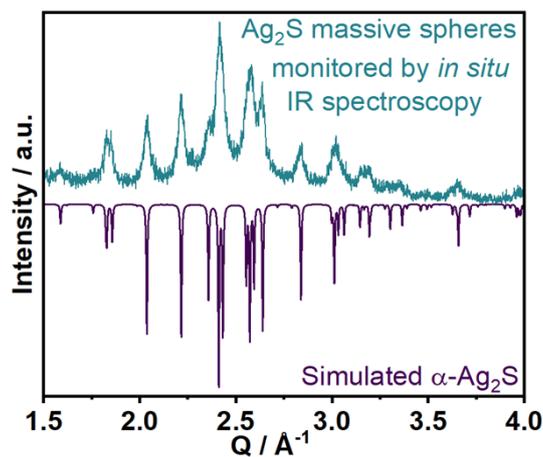
2.4.2. *In situ* infrared spectroscopy

Figure S13: a) XRD pattern of the measured sample compared to the simulated α -Ag₂S powder pattern [13].

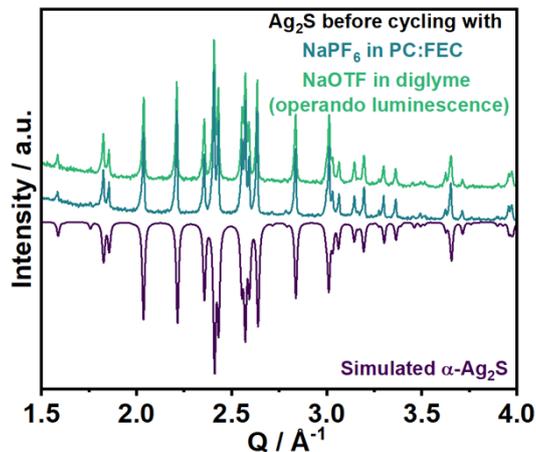
2.5. Ag₂S-based electrodes for sodium-ion batteries

Figure S14: XRD results of α -Ag₂S NPs before GDC cycling with two different electrolytes: (i) NaPF₆ in PC:FEC (41±3 nm diameter according to Scherrer equation) and (ii) NaOTF in diglyme (49±3 nm diameter according to Scherrer equation).

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