

Supplementary Information

Spontaneous formation of barium sulfate crystals at liquid-liquid interfaces

Nazanin Ghaheri¹, Benjamin J. J. Austen¹, Grégoire Herzog², Mark I. Ogden¹, Franca Jones^{1*}, Damien W. M. Arrigan^{1*}

¹School of Molecular and Life Sciences, Curtin University, Perth, Western Australia 6845, Australia

²Université de Lorraine, CNRS, LCPME, F-54000 Nancy, France

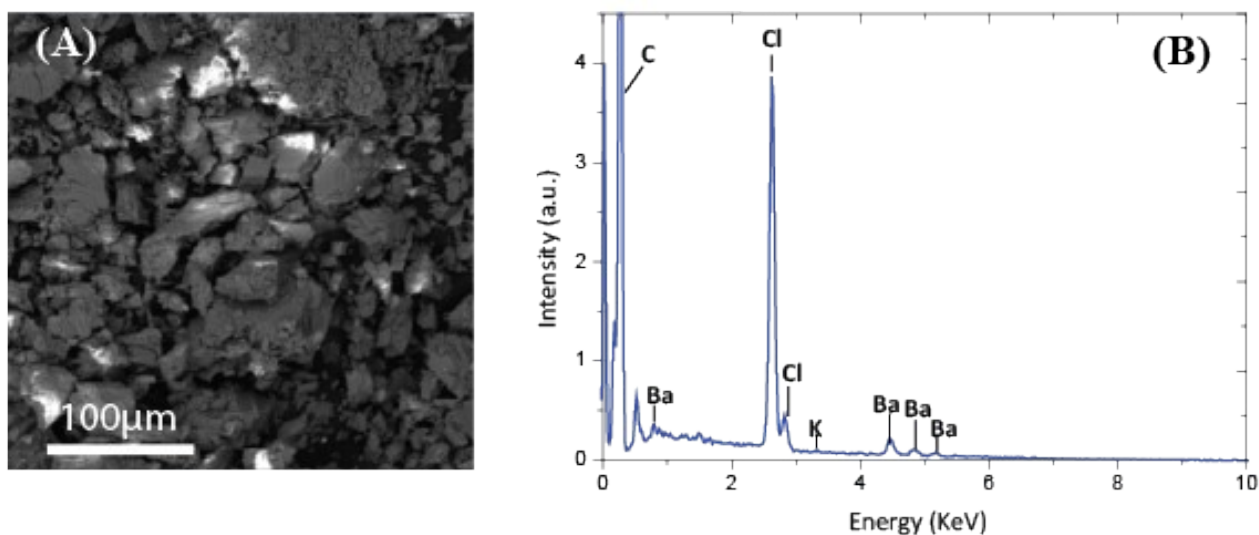
* D.Arrigan@curtin.edu.au; F.Jones@curtin.edu.au

Contents of Supplementary Information

- Characterisation of Ba(TPBCl)₂ – Fig. S1 – p. 2
- Characterisation of tetrabutylammonium hydrogen sulfate transfer – Figs. S2, S3 – p. 3
- Scanning electron microscopy and Energy dispersive X-ray spectroscopy – Fig. S4 – p. 4
- Transmission Electron Microscopy – Figs S5, S6 – p. 5, 6.

Characterisation of Ba(TPBCl)₂

EDS was used for analysis of the synthesised barium organic salt (Ba(TPBCl)₂). As determined by SEM-EDS (Figure S1), the predominant elements in the synthesised Ba(TPBCl)₂ salt were carbon, chlorine, potassium and barium. The quantification results (Figure S1c) indicate that 12.8 % of Ba was found in the sample against 0.6% of K. CHN combustion analysis (Figure S1c) confirmed the carbon and hydrogen components of the salt. The elemental composition is consistent with the formation of Ba(TPBCl)₂.



(C)

Element	Energy (KeV)	Mass %	Counts	Atomic%	Theoretical Atomic%	C-H-N Analysis%
C	0.277	27.90	9425	56	54.8	49.2
Cl	2.547	41.72	2.561	30	27.0	-
K	3.312	0.55	94	0.6	0.0	-
Ba	4.457	29.83	214	13	13.1	-
H	-	-	-	-	3.0	3.5
N	-	-	-	-	-	0.0

Figure S1. SEM-EDS analysis of Ba(TPBCl)₂. (A), SEM micrograph of synthesised barium organic salt (Ba(TPBCl)₂). (B), EDS spectrum and (C) corresponding wt% results are listed in the table.

Characterisation of tetrabutylammonium hydrogen sulfate transfer

TBuAHSO₄ in water (0.1 M) was analysed by Raman spectroscopy. The Raman spectrum was collected at 295 K on a WITec alpha 300SAR confocal spectrometer, equipped by a 532 nm wavelength laser, of with 20 spectra collected and a collection time of 0.05 seconds. Figure S2 shows the spectrum in water.

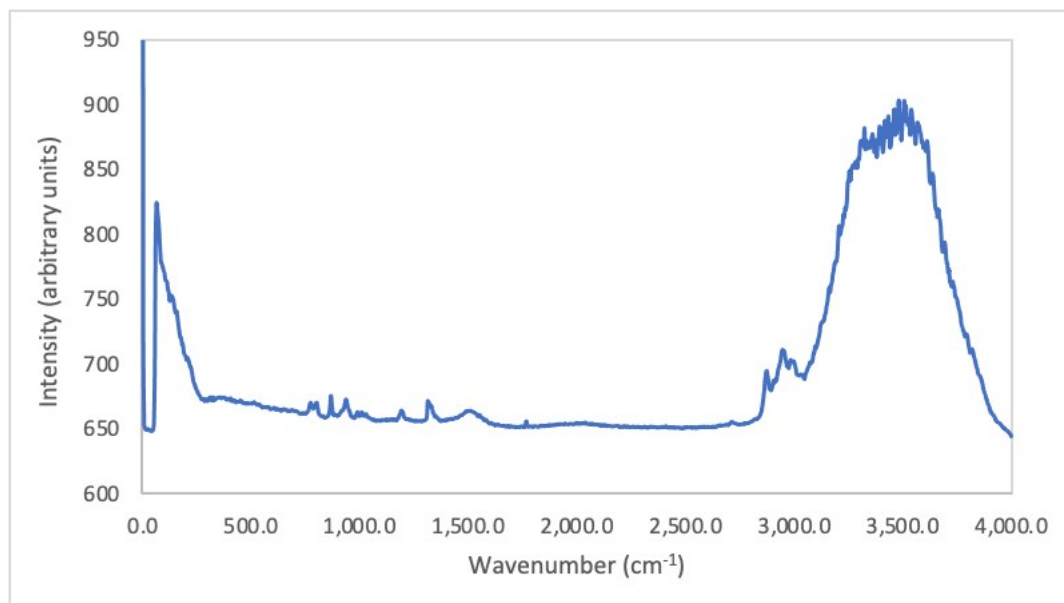


Figure S2. Raman spectrum of TBuAHSO₄ in water.

A drop of TBuAHSO₄ in DCE (0.2 M) was brought into contact with a drop of water on a glass slide. The drop of water was monitored using Raman spectroscopy over 10 minutes. The Raman spectrum was collected at 295 K on a WITec alpha 300SAR confocal spectrometer, equipped by a laser wavelength of 532 nm with 20 spectra collected and a collection time of 0.05 seconds. The spectrum indicated the transfer of TBuAHSO₄ from DCE to water in that 10 minute period (Figure S3).

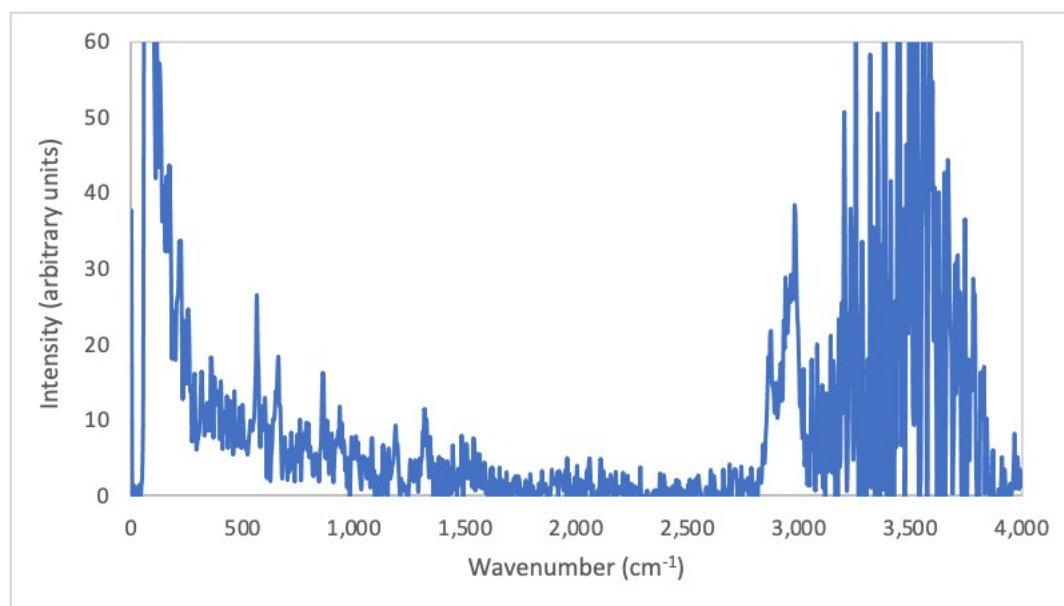


Figure S3. Raman spectrum of TBuAHSO₄ in water after 10 minutes contact of DCE solution with water

Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDS)

SEM and EDS line scans across the crystalline materials that were deposited onto the glass microporous membrane were performed to study elemental distribution. These distributions were taken along the yellow lines shown in Figure S5a, for the electrochemical cell composition in Scheme 1, and in Figure S5c, for the equivalent Scheme 2 set-up. Figure S5 (b), (d) show the co-location of Ba, S and O in the crystals of BaSO₄ formed on the glass membrane.

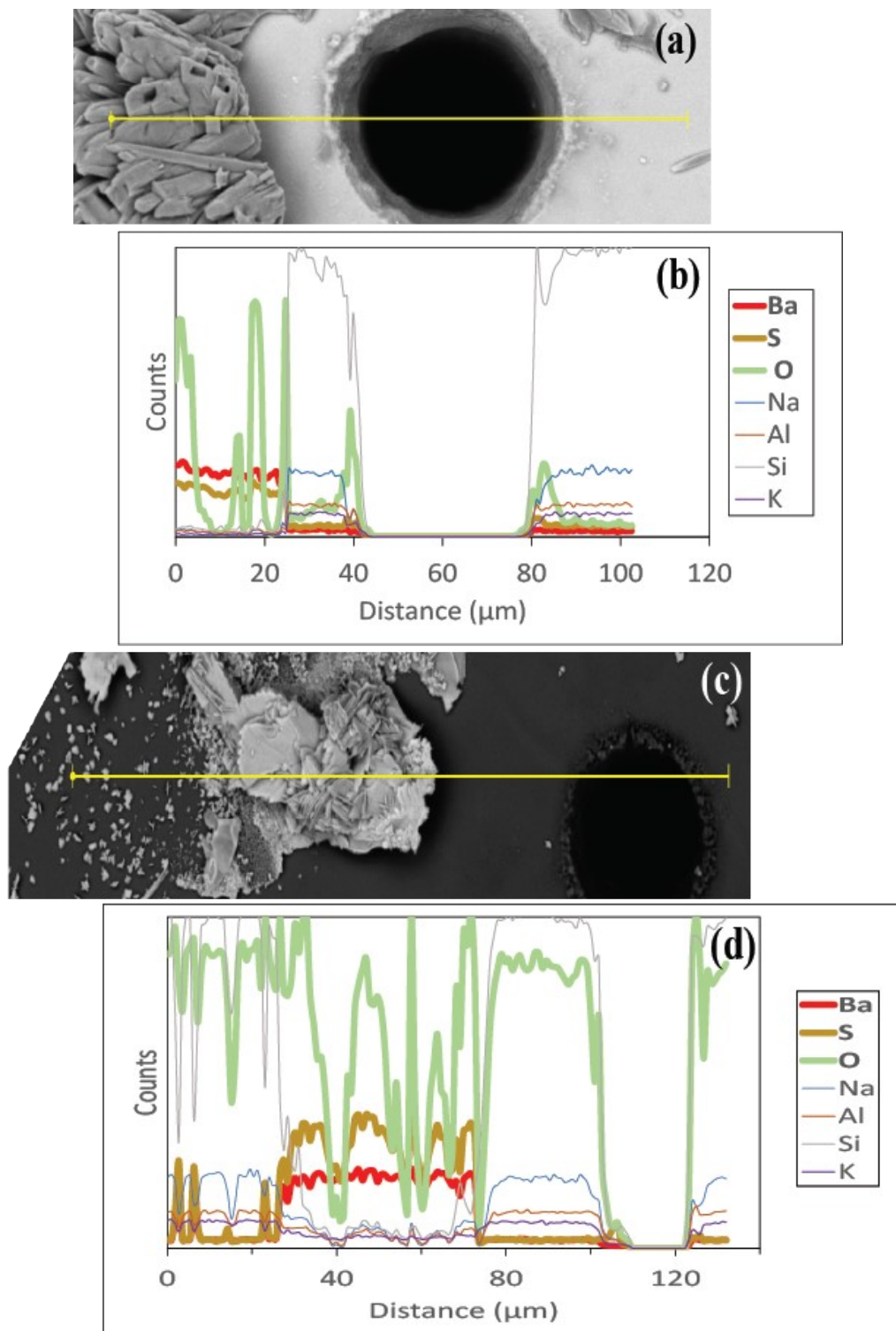


Figure S4. SEM images and corresponding EDS elemental line scan results (yellow lines in the images) for crystallized barium sulfate. (a), (c) SEM images of crystals formed around the membrane pores for organic and aqueous phases containing barium ions, respectively. (b), (d) elemental distribution from EDS line scans along the yellow lines in the SEM images.

Transmission Electron Microscopy (TEM)

Figures S5 and S6 present the high angle annular dark field-transmission electron microscopy (HAADF-TEM) images with their corresponding elemental maps of particles. These maps confirmed that barium sulfate has been crystallized by spontaneous Ba^{+2} transfer from aqueous to organic phase (Figure S6) or spontaneous transfer of hydrogen sulfate from organic phase to aqueous phase (Figure S7). The homogeneous distribution of Ba and S suggests their uniform incorporation into ionic crystal materials rather than forming any localized domains.

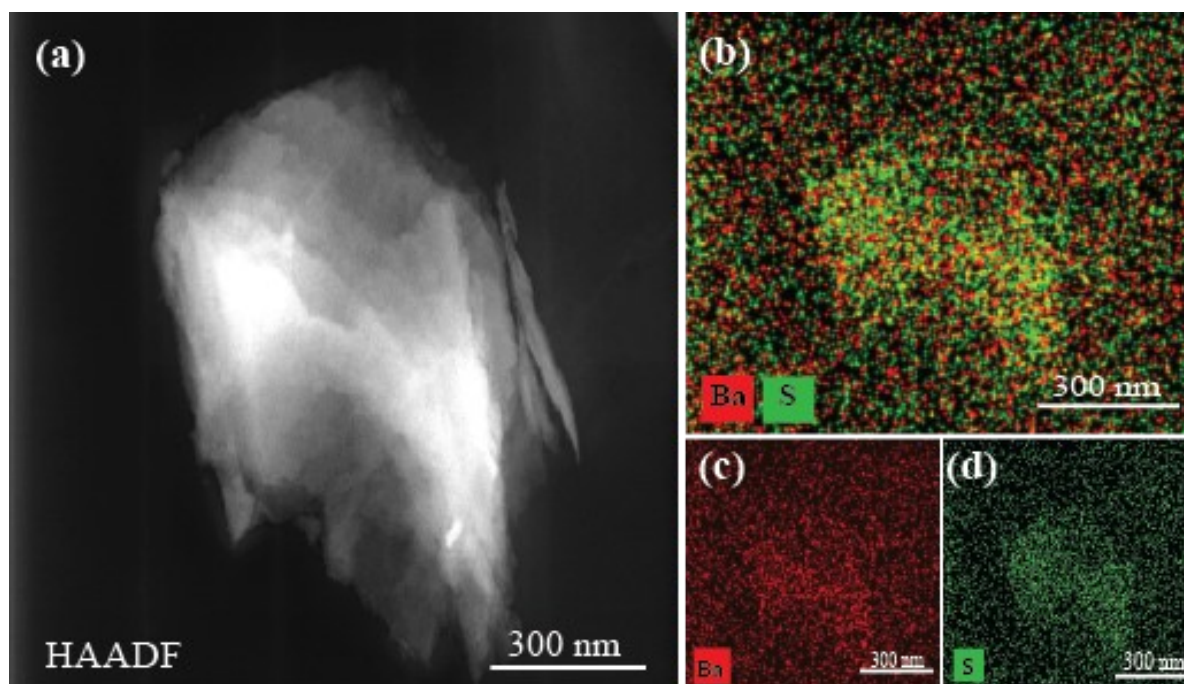


Figure S5. TEM analysis of barium sulfate precipitates formed at the interface of organic solution containing $\text{Ba}(\text{TPBCl})_2$ and aqueous solution of Na_2SO_4 . (a) HAADF TEM image showing crystals formed on the membrane. (b) EDX elemental maps of the region depicted in (a). (c) Ba distribution, (d) S distribution.

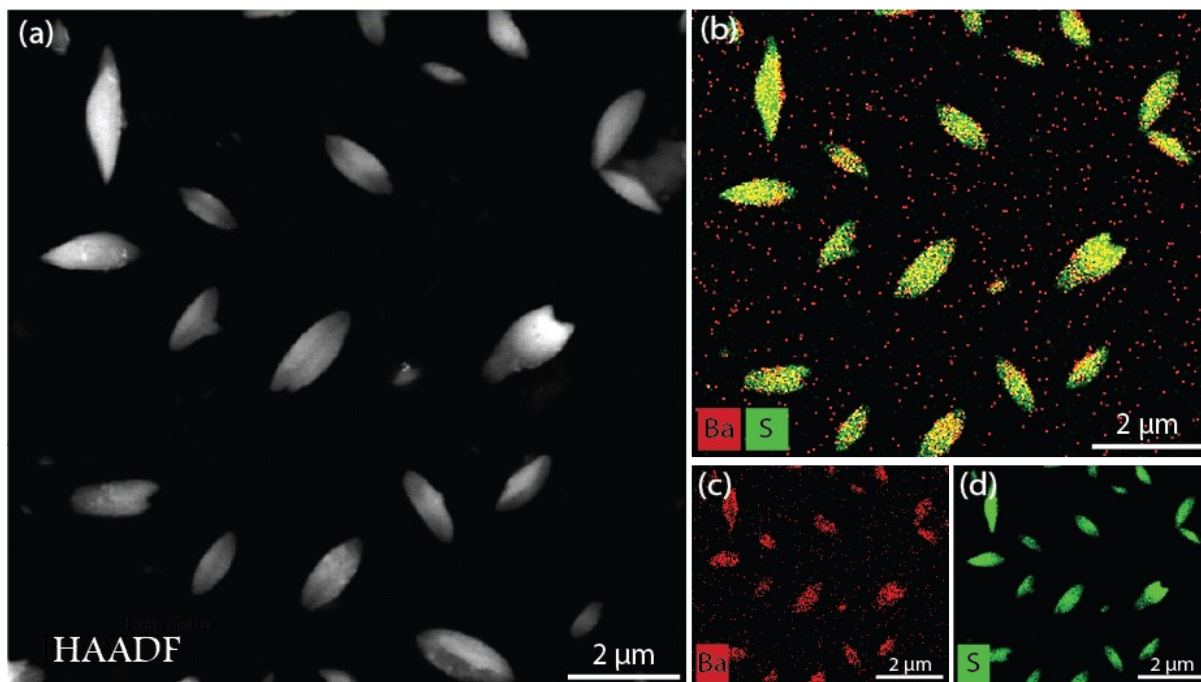


Figure S6. TEM analysis of barium sulfate precipitates formed at the interface of BaCl_2 aqueous solution and TBuAHSO_4 organic phase on the glass membrane. (a) HAADF TEM image showing crystals formed on the membrane. (b) EDX elemental maps of the region depicted in (a). (c) Ba distribution, (d) S distribution.