Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2011

Supplementary Information

# A New Precipitation Pathway for Calcium Sulfate Dihydrate (Gypsum) via Amorphous and Hemihydrate Intermediates

**Yun-Wei Wang, Yi-Yeoun Kim, Hugo K. Christenson and Fiona C. Meldrum**

***Precipitation and Analysis of Calcium Sulfate***

Calcium sulfate was precipitated by combining equal volumes of equimolar solutions of calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$, Sigma-Aldrich) and sodium sulfate ($Na_2SO_4$, Sigma-Aldrich) in Milli-Q water, to give final $Ca^{2+}$ and $SO_4^{2-}$ concentrations of 15 mM – 100 mM. Samples were taken from the reaction solutions for TEM analysis at times between 10 s and 7 days and were prepared by dipping a carbon-coated Cu TEM grid into the reaction solution for 2 s, rinsing with a 4:1 ethanol to water mixture, and finally drying at room temperature. TEM analysis and electron diffraction were performed using a Phillips Tecnai FEG-TEM operating at 200 kV, with associated Energy-Dispersive X-ray Analysis (EDXA). Further confirmation of polymorph was carried out using Raman microscopy, powder XRD and Thermogravimetric Analysis (TGA). Samples were isolated by filtration, and the Raman analysis was performed using a Renishaw 2000 inVia-Raman microscope, operating with a 785 nm laser. PXRD was performed using a Bruker D8 Advanced diffractometer with X-ray source emitting Cu $K\alpha_1$ radiation. Samples were gently ground and placed on a piece of silicon wafer, and XRD data were collected between $10^o$ and $60^o$ in intervals of $0.02^o$ and a scan rate of $1^o$/ minute. The composition of the precipitates was determined using a TA-Instruments Q600 Simultaneous TGA/DSC, with analysis being performed under air in the temperature range ambient to 850 °C with a heating rate of 5 °C/min.

***Preparation of Reference Samples***

Calcium sulfate dihydrate was precipitated by mixing equal volumes of 100 mM $CaCl_2$ solution and 100 mM $Na_2SO_4$ solution. Calcium sulfate hemihydrate was formed by heating calcium sulfate dihydrate to 120 $^oC$ for 4 h.

# Supplementary Information

**Table S1**. Measured d-spacings of electron diffraction patterns obtained from calcium sulfate particles (a) precipitated from a 50 mM solution after 2 h, showing calcium sulfate dihydrate and (b) 1 min, corresponding to calcium sulfate hemihydrate. (c) Gypsum particles produced by heating amorphous calcium sulfate (ACS) particles, precipitated from 15 mM reaction solutions after 30 s, with prolonged exposure to the electron beam in TEM. Powder XRD data of calcium sulfate hemihydrate, calcium sulfate dihydrate and anhydrite are shown for the sake of comparison. The numbers in brackets represent the expected relative intensities of randomly oriented powder samples.

| **(a) d (Å) 50 mM after 2 h** | **(b) d (Å) 50 mM after 1 min** | **(c) d (Å) ACS after heating in TEM** | **d (Å) $CaSO_4$** | **d (Å) $CaSO_4 \cdot 0.5H_2O$** | **d (Å) $CaSO_4 \cdot 2H_2O$** |
|---|---|---|---|---|---|
| | 5.9898 | | 6.0384 (99.90) | 6.0051 (99.74) | |
| 4.2614 | | | 4.3607 (1.70) | 4.285 (2.35) | 4.2669 (100.00) |
| | 3.4560 | | 3.4850 (15.10) | 3.4647 (30.80) | 3.5427 (4.09) |
| | | 3.0157 | 3.0192 (40.3) | 3.0394 (7.36) | 3.0497 (73.30) |
| | 2.9833 | | | 3.0026 (100.00) | |
| 2.8692 | 2.8043 | 2.8555 | | 2.8044 (83.69) | 2.8621 (52.99) |
| | | 2.7226 | 2.7230 (50.0) | 2.7157 (8.31) | 2.7168 (1.57) |
| 2.6631 | | 2.6734 | | 2.6942 (1.05) | 2.6679 (36.27) |
| 2.4826 | | 2.5006 | | | 2.4929 (12.46) |

# Supplementary Information

**Figure S1**: Raman spectra of reference samples (a) calcium sulfate hemihydrate and (b) calcium sulfate dihydrate. The peaks correspond to the $\nu_1$ symmetric stretch of sulfate (1019 $cm^{-1}$ in hemihydrate and 1012 $cm^{-1}$ in gypsum), the $\nu_2$ symmetric bending of sulfate (435 $cm^{-1}$ and 495 $cm^{-1}$ in hemihydrate, and 419 $cm^{-1}$ and 497 $cm^{-1}$ in gypsum), the $\nu_3$ antisymmetric stretching of sulfate (1139 $cm^{-1}$ in gypsum and less well-defined in hemihydrate) and the $\nu_4$ antsymmetric bending of sulfate (632 and 671 $cm^{-1}$ in hemihydrate, and 624 $cm^{-1}$ and 675 $cm^{-1}$ in gypsum).[1]

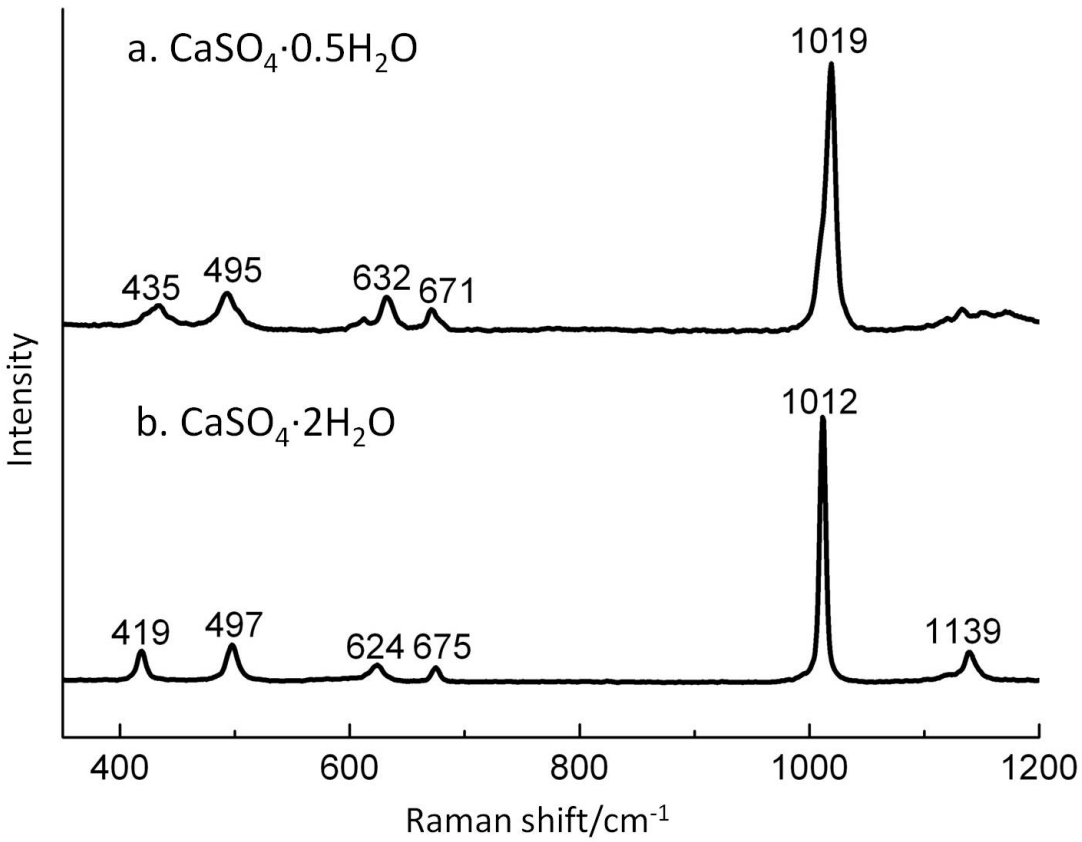


**Figure S2**: XRD spectra of the reference samples shown in Figure SI1, where (a) is calcium sulfate hemihydrate and (b) is calcium sulfate dihydrate.

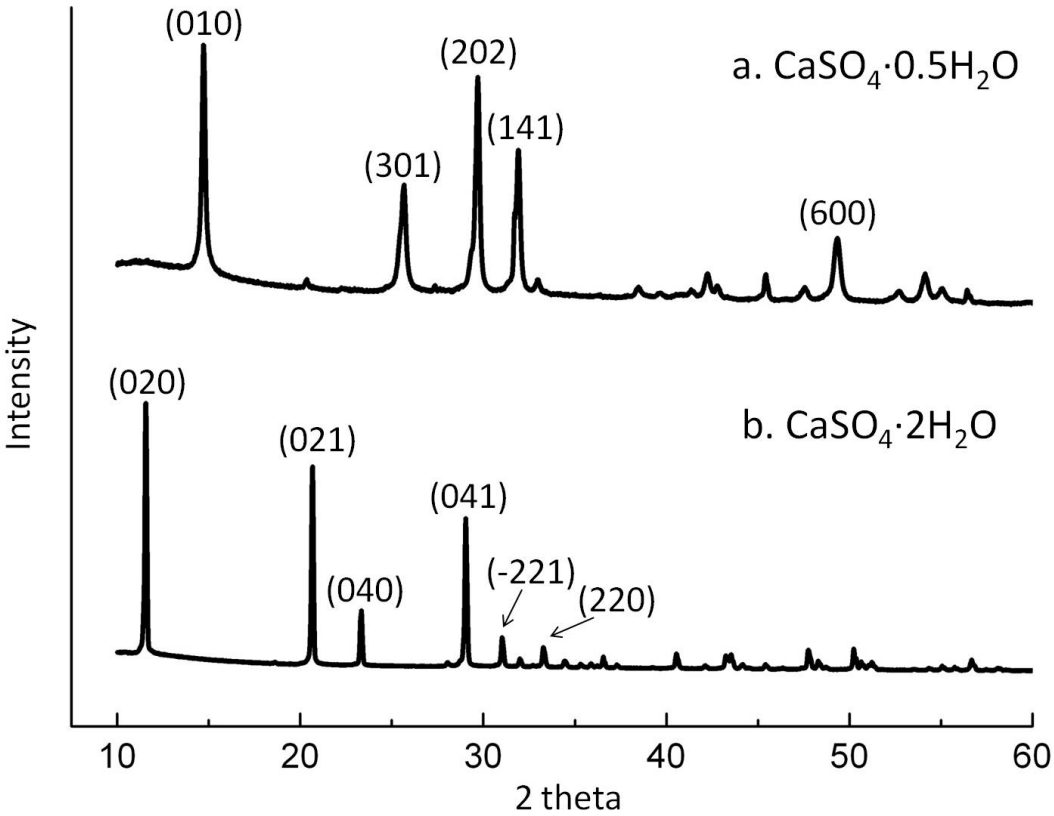
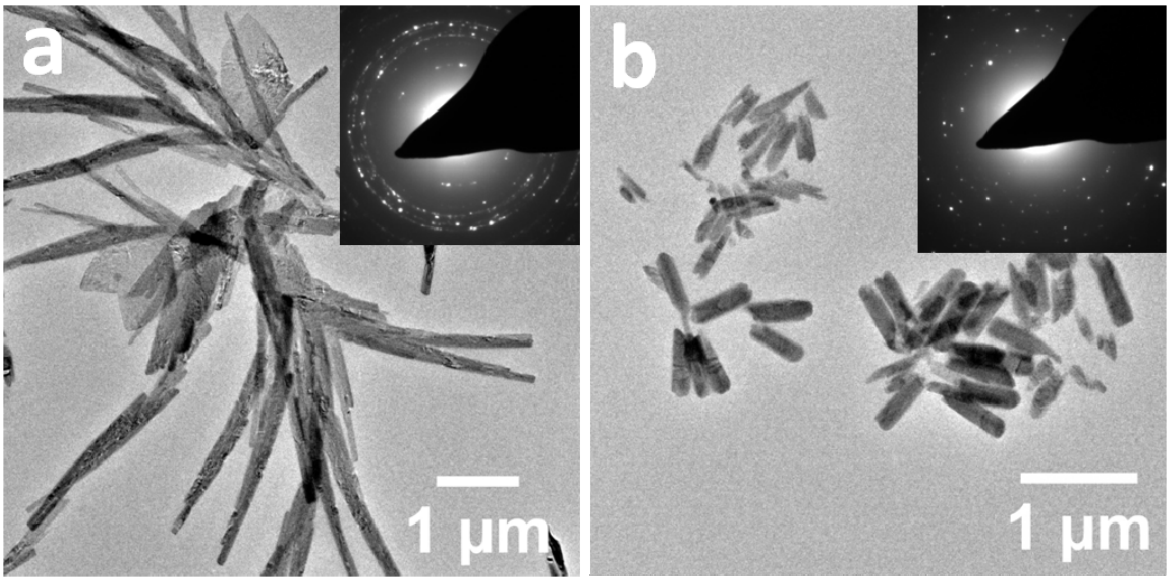
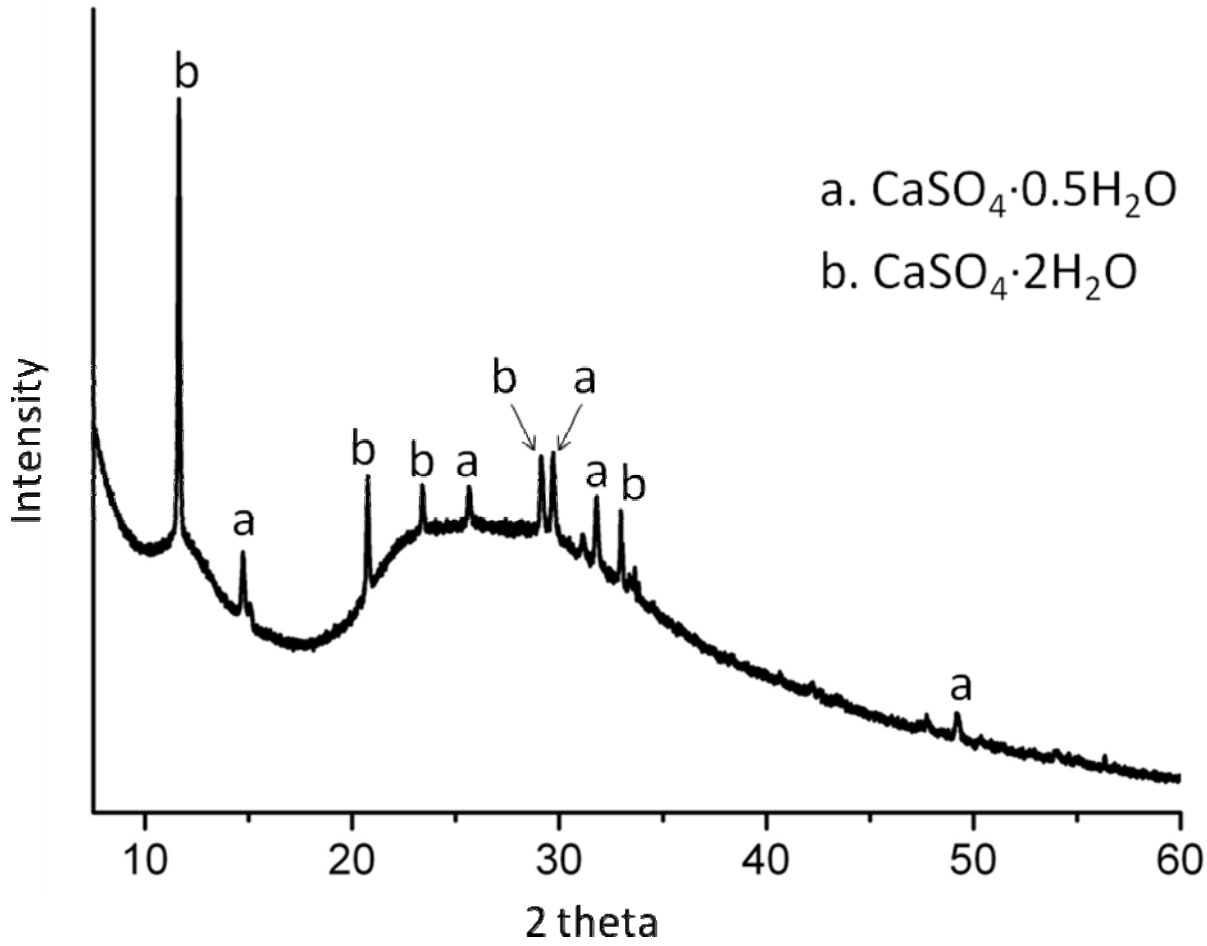


**Figure S3**: (a) Calcium sulfate dihydrate and (b) calcium sulfate hemihydrate crystals precipitated from the 50 mM solution after 1 hour, and the corresponding selected-area electron diffraction pattern.



Supplementary Information

**Figure S4**: XRD spectra of precipitate isolated from the 50 mM solution after approximately 1 minute showing the presence of both hemihydrate (peaks labelled a) and gypsum (peaks labelled b). A mixture of polymorphs was obtained due to the time taken to filter the volumes of solution required to give sufficient material for analysis. Subsequent TGA analysis, shown in Figure S5, demonstrates that the sample comprises 84 mol% hemihydrate and 16 mol% gypsum.



Supplementary Information

**Figure S5**: TGA spectra of (a) the precipitate isolated from the 50 mM solution after approximately 1 minute and (b) a sample of gypsum. The gypsum sample loses 21.6 wt% on heating, which is consistent with the loss of $2H_2O$ per $CaSO_4$ unit, while the precipitate loses 8.6 wt% on heating which is consistent with the sample comprising 84 mol% hemihydrate ($CaSO_4{\cdot}0.5H_2O$) and 16 mol% gypsum.

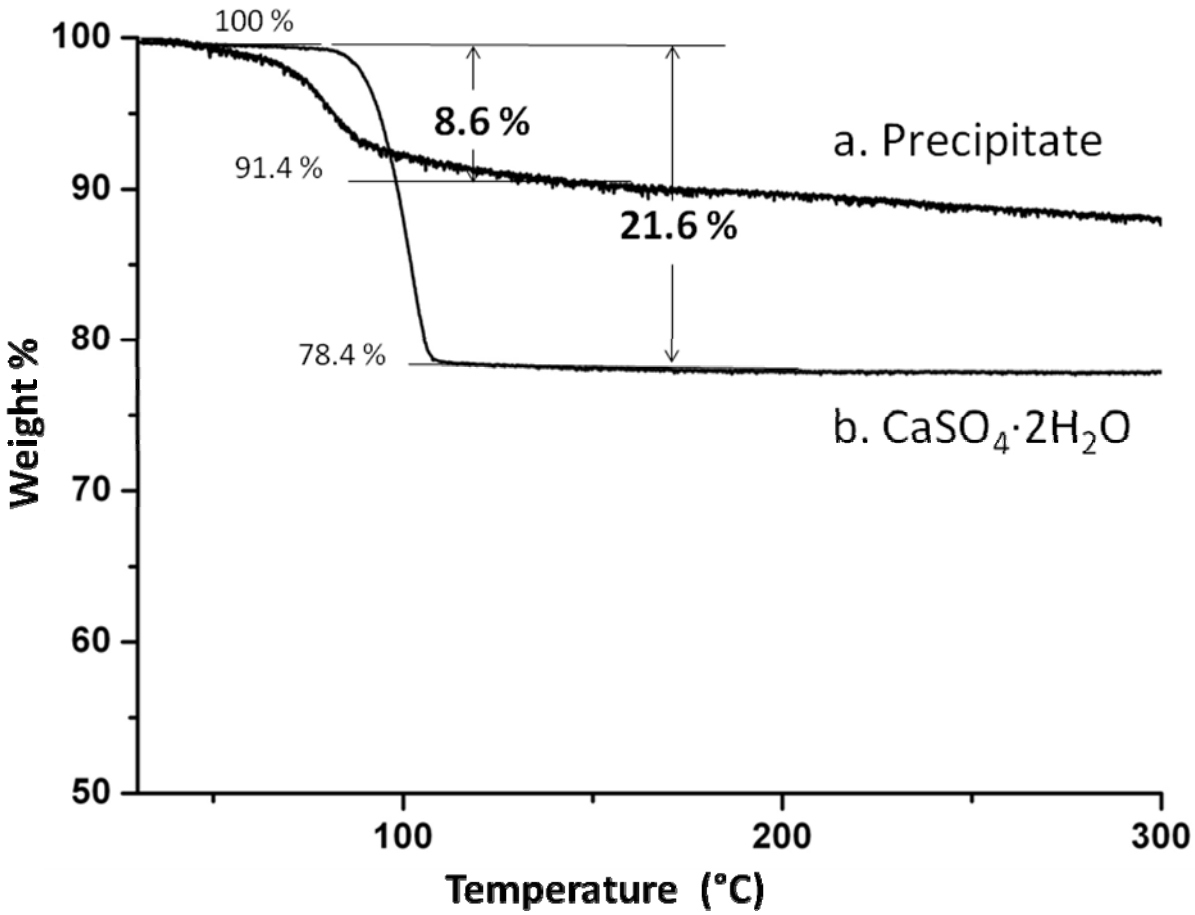
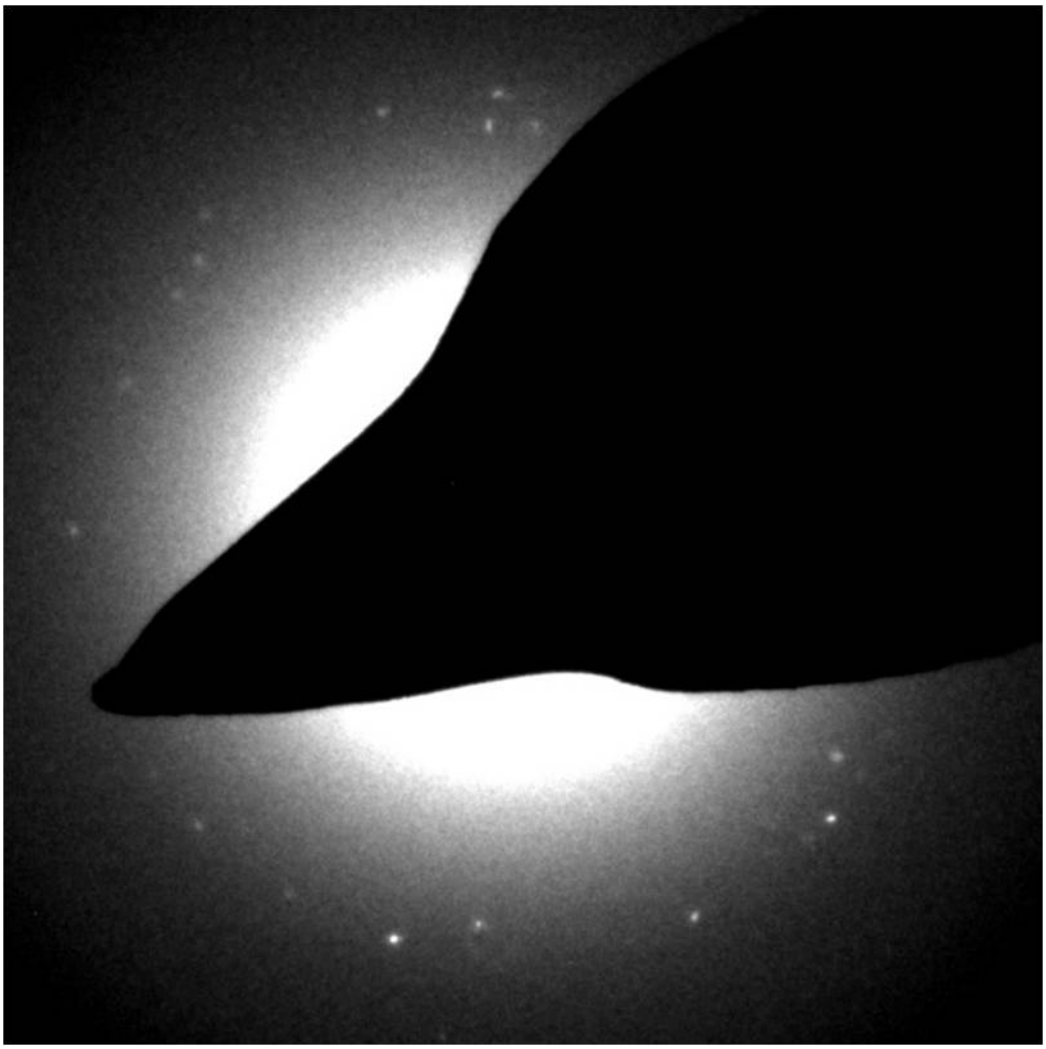


**Figure S6**: Selected area electron diffraction pattern of amorphous $CaSO_4$ particles precipitated from a 15 mM solution after irradiation with the electron beam. The diffraction spots which emerge correspond to $CaSO_4$ dihydrate (gypsum), demonstrating that crystallisation occurs. This is a large-scale view of the image shown in Figure 3c.



**References**

1. L. P. Sarma, P. S. R. Prasad and N. Ravikumar, J. Raman Spectrosc., 1998, 29, 851-856.