## Electronic supplementary information (ESI)

# *In-situ* precipitation of amorphous and crystalline calcium sulphates in cellulose thin films

Tomi Nissinen, Mei Li, Sean Davis and Stephen Mann*

[a]Centre for Organized Matter Chemistry, School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK. Email: s.mann@bristol.ac.uk

## Experimental methods.

### Preparation of cellulose/calcium sulphate hybrid thin films

12.5 wt% of 170-500 mM $CaCl_2$ solution was added into 2.5-20 g of N-methylmorpholine-N-oxide (NMMO, Sigma-Aldrich, UK) followed by addition of an equimolar amount of aqueous $Na_2SO_4$ at 80 °C to produce a turbid solution. 3 wt% of fibrous cellulose (Sigma-Aldrich, UK) was then dissolved into the NMMO/$CaCl_2$/$Na_2SO_4$ dispersion over 2 h with vigorous stirring. 2 mL of the viscous dispersion was pipetted onto a 5 cm-diameter glass disk, and spin-coated for 30 s at 500 rpm. Self-supporting cellulose/calcium sulphate thin films were prepared by immersing the spin coated samples in de-ionized water or a 70:30 volume mixture of ethanol/de-ionized water for 24 h at room temperature. For samples prepared using equimolar 170, 250 or 500 mM solutions of $CaCl_2$ and $Na_2SO_4$, the corresponding theoretical loadings of $CaSO_4$ in the films were 0.5, 0.75 and 1.5 wt%, respectively. The corresponding cellulose/inorganic weight ratios for 170, 250 and 500 mM were 6:1, 4:1 and 2:1, respectively.

Stacked arrangements of the regenerated cellulose films were prepared by spin-coating a layer of viscous NMMO solution with 3 wt% of dissolved cellulose and 25 wt% of 0.5 M $CaCl_2$ onto a glass disk, followed by spin-coating a second layer of a NMMO solution containing 3 wt% of dissolved cellulose and 25 wt% of 0.5 M $Na_2SO_4$. The two layers were fused together by regenerating the cellulose matrix by immersion into water or an ethanol/water solution.

### Characterization

Identification of the crystal phases of calcium sulphate was undertaken using a Bruker D8 Advance powder diffractometer with Cu-Kα emission over 2θ range of 5-60° and a step size of 0.002°. AFM investigations were performed on dried samples with a Multimode V Nanoscope (Digital Instruments) atomic force microscope with a J-scanner unit working in tapping mode. Analysis of the AFM data was conducted with WSxM 4.0 beta 6.3 software.[22] Attenuated total reflectance Fourier-transform infrared (ATR FT-IR) spectroscopic characterization of the samples was conducted with a PerkinElmer Spectrum One™ spectrometer with an ATR sampling module in the range of 4000-550 $cm^{-1}$ at 2 $cm^{-1}$ resolution. Samples for TEM studies were prepared as above but without spin coating. Droplets of the NMMO/calcium sulphate liquid were added to a water or ethanol/water solution to produce macroscopic cellulose/calcium sulphate precipitates that were lyophilized, crushed and then dispersed in ethanol. 10-20 µL samples of the dispersion were air dried onto carbon coated copper grids and examined using a JEOL JEM 1200 EX Mk 2 or JEOL JEM 2011 TEM operating at 120 kV and 200 kV acceleration voltages, respectively. Energy dispersive X-ray elemental analysis was undertaken during TEM imaging using an Oxford Instruments ISIS 310 detector. SEM studies were carried out on a JEOL JSM-6330F field emission scanning electron microscope with 10 keV acceleration voltage. Samples were coated with a 15 nm silver layer before imaging.

## Supplementary data

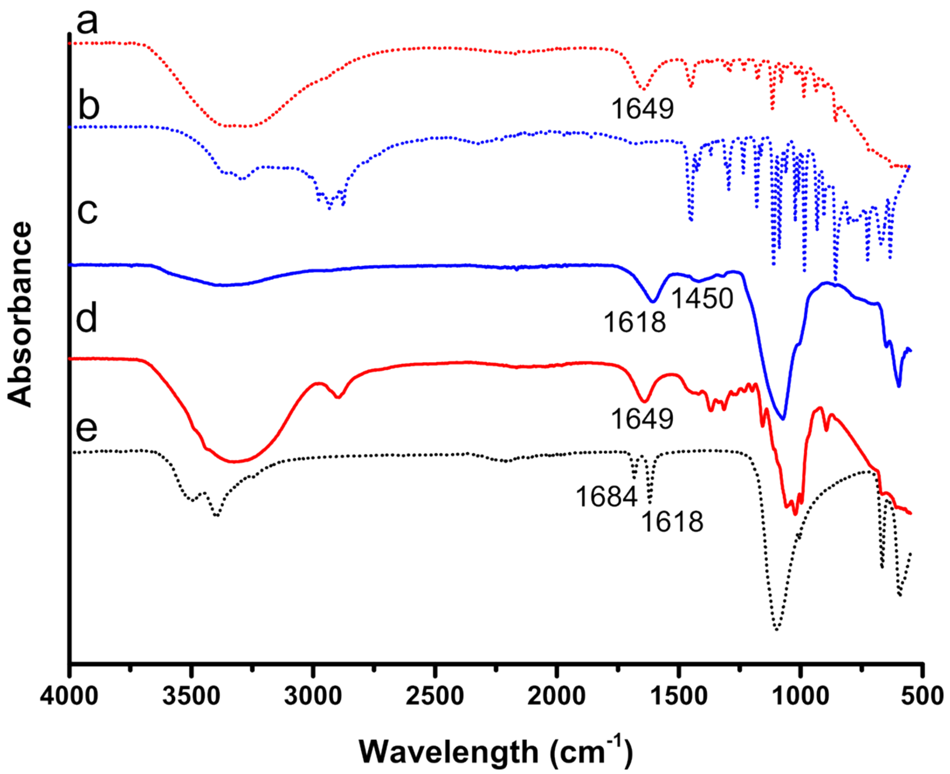

**Fig. S1**. FTIR spectra of (a) hydrated NMMO, (b) unhydrated NMMO, (c,d) cellulose/calcium sulphate thin films (500 mM $CaSO_4$; cellulose : $CaSO_4$ = 2:1) after regenerated in a 70 : 30 ethanol/water mixture for 24 h (c), or in distilled water only (d), and (e) gypsum. See text for details.