



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

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

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†Electronic supplementary information (ESI) available: Experimental methods, FTIR spectra.

A novel method for the *in situ* precipitation of calcium sulphates within spin coated cellulose thin films is described. A key feature of the approach is the use of N-methylmorpholine N-oxide (NMMO) not only to dissolve fibrous cellulose but also to stabilize nanoparticles of amorphous calcium sulphate prior to regeneration of the polysaccharide matrix and formation of a thin composite film. Integration of the biopolymer film with amorphous or crystalline (bassanite, gypsum) calcium sulphate phases is influenced by the rate of NMMO hydration, providing a route to composite materials with stable or reactive inorganic materials that might find uses in diverse applications.

Calcium sulphate hemihydrate (bassanite, $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$) and calcium sulphate dihydrate (gypsum, $\text{CaSO}_4 \cdot 2.0 \text{H}_2\text{O}$) are of widespread use in building and construction materials, often as components or precursors of plasters, binders and plasterboards.¹ The precipitation of gypsum is also a major concern in desalination processes, and in the oil and gas industries where it is a ubiquitous contaminant in filters and piping.^{2,3} Recent studies have shown that the crystallization of gypsum from aqueous solutions of calcium chloride and sodium sulphate proceeds through an amorphous precursor and bassanite intermediate,^{4,5} suggesting that non-classical mechanisms of inorganic crystallization^{6,7} may play an important role in the nucleation and growth pathways of calcium sulphate. Moreover, numerous polymeric and molecular additives are known to influence the crystal morphologies and precipitation kinetics of calcium sulphate phases.⁸⁻¹¹

Recently, we reported a procedure for controlling under industrially relevant conditions the crystallization of gypsum on the surface of cellulose thin films.¹² The films were prepared by dissolution of fibrous cellulose in a N-methylmorpholine N-oxide (NMMO)/dimethyl sulfoxide solvent at 85°C, followed by spin coating of the viscous liquid and *in situ* regeneration of an insoluble cellulose matrix by immersion in de-ionized water. Addition of water disrupts solvation of the polysaccharide macromolecules by hydration of

NMMO,¹³⁻¹⁵ thereby inducing the formation of an entangled matrix of cellulose fibres in the form of a self-supporting thin film. Incubation of the regenerated films in bassanite dispersions or supersaturated solutions of calcium sulphate promoted gypsum nucleation and growth specifically at the polysaccharide surface.¹² Although the gypsum crystals penetrated into the near-surface layers of the cellulose matrix, the interior of the films remained essentially free of the inorganic mineral. Surface-decorated cellulose/mineral materials have also been prepared with calcium carbonates^{16,17} and calcium phosphates.¹⁸

Recently, studies have shown that infiltration of inorganic nanoparticles into cellulose films can be accomplished by regeneration of the NMMO/cellulose solutions in aqueous dispersions of gold nanoparticles.¹⁹ This approach is not generally viable for calcium salts such as calcium sulphate because nanoparticles of these materials are unstable in water and readily transform into micro-crystals. In this paper, we circumvent this problem by developing an alternative approach based on pre-loading the NMMO solutions with aqueous solutions of calcium chloride and sodium sulphate that precipitate *in situ* as NMMO-stabilized nanoparticles prior to dissolving cellulose in the organic solvent. Significantly, the amount of added water is such that it does not compromise the ability of NMMO to dissolve fibrous cellulose,¹³ and as a consequence the homogeneous dispersion can be spin coated and regenerated as thin composite films by immersion in distilled water or an ethanol/water mixture. The latter results in *in situ* crystallization of the amorphous nanoparticles to a mixture of gypsum and bassanite, whilst rapid regeneration of the cellulose matrix in water retains the amorphous phase to produce a reactive composite.

Cellulose/calcium sulphate thin films were prepared using a multi-step process (see ESI† Methods). Aqueous solutions of CaCl_2 and Na_2SO_4 (170-500 mM) were added at equimolar concentrations to liquid NMMO at 80°C to produce turbid mixtures. Fibrous cellulose (3 wt%) was dissolved in the mixture over a period of 2 hrs, after which aliquots of the viscous solution were spin coated at room temperature. Transparent, self-supporting cellulose/calcium sulphate films were then produced by immersing the spin coated samples in water or in a 70 : 30 ethanol/water solution for 24 hrs to regenerate the insoluble cellulose (Fig. 1a-c). Increasing the concentration of the inorganic components increased the opacity, as well as the surface roughness (Fig. 1d-f) of the films. For films prepared using equimolar 170, 250 or 500 mM solutions of CaCl_2 and Na_2SO_4 , the corresponding theoretical loadings of CaSO_4 were 0.5, 0.75 and 1.5 wt%, respectively, corresponding to

cellulose/inorganic weight ratios of 6:1, 4:1 and 2:1. High magnification optical microscopy images of the water-regenerated films showed the presence of well-defined, optically translucent features that were around 50 μm in size and often gel-like in morphology (Fig. 1g). In contrast, the ethanol/water-regenerated films showed a homogeneous distribution of optically dense aggregates that were approximately 50 μm in size and diffuse in morphology (Fig. 1h). *In situ* growth of the aggregates was followed by recording optical microscopy images at various times after addition of the ethanol/water mixture (Fig. 1 i-l). The aggregates were visible within the incipient cellulose matrix *ca.* 70 seconds after initiation of the regeneration step, and exhibited a growth rate of approximately $0.46 \mu\text{m s}^{-1}$.

X-ray diffraction profiles for freeze-dried samples of the ethanol/water regenerated materials prepared at 500 mM $\text{CaCl}_2/\text{Na}_2\text{SO}_4$ showed a series of sharp reflections corresponding to a mixture of gypsum ($\text{CaSO}_4 \cdot 2.0 \text{H}_2\text{O}$) and bassanite (calcium sulphate hemihydrate, $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$) (Fig. 2a). The corresponding XRD profiles for the as-prepared composite films showed broadened bassanite reflections, a marked reduction in the gypsum content, and the presence of a broad peak at $2\theta = 22^\circ$ corresponding to amorphous calcium sulphate (Fig. 2b). In contrast, composite films prepared by regeneration in distilled water showed only weak intensity reflections (Fig. 2c), indicating the presence of large amounts of amorphous calcium sulphate within the non-crystalline cellulose matrix.

The XRD results were consistent with TEM and selected area electron diffraction studies of aqueous dispersed fragments of the ethanol/water regenerated materials, which revealed the presence of electron dense polycrystalline bassanite particles, along with amorphous calcium sulphate nanoparticles (Fig. 3a,b). As bassanite often adopts a needle-like crystal morphology, we attributed the formation of the irregularly shaped polycrystalline aggregates to spatial confinement and chemical inhibition imposed by the cellulose matrix on the growth of the inorganic crystals.^{20,21} On the other hand, the origin of the amorphous particles was attributed to precipitation of calcium sulphate in the $\text{CaCl}_2/\text{Na}_2\text{SO}_4/\text{NMMO}$ mixture at 80°C prior to addition of cellulose. This was confirmed by TEM investigations of a $\text{CaCl}_2/\text{Na}_2\text{SO}_4/\text{NMMO}$ mixture that was prepared as a freeze-dried powder after quenching with ethanol/water, and which consisted of beam-sensitive amorphous calcium sulphate nanoparticles embedded in a diffuse cellulose-free NMMO matrix (Fig. 3c). Thus, the results suggested that NMMO was an effective stabilizer of

amorphous calcium sulphate, and inhibited transformation into crystalline phases, similar to known retarding agents for the crystallization of gypsum.⁸⁻¹⁰

Given the stabilizing effect of NMMO, the low level of calcium sulphate crystallinity observed for films regenerated in water was attributed to a rapid rate of NMMO hydration under these conditions compared with ethanol/water-induced regeneration. This was consistent with ATR-FTIR spectra of the cellulose/calcium sulphate films, which showed a distinct –OH band for hydrated NMMO at 1649 cm^{-1} and no gypsum –OH vibration at 1618 cm^{-1} for the water-regenerated samples. In contrast, the ethanol/water-regenerated films showed a gypsum band at 1618 cm^{-1} , an absence of the hydrated NMMO 1618 cm^{-1} band, and NMMO C-H vibrations (non-overlapping with cellulose) at 1450 , 940 , 860 and 725 cm^{-1} (Fig. S1 ESI†). As a consequence, regeneration of the cellulose film by addition of water was more effective, which in turn arrested crystallization of the NMMO-stabilized calcium sulphate nanoparticles possibly by binding of cellulose fibres to the surface of the preformed particles after NMMO hydration. In contrast, the reduced rate of NMMO hydration in the presence of ethanol/water was less effective at generating a stabilizing cellulose matrix, such that partial crystallization of the preformed amorphous particles into bassanite and gypsum occurred.

Finally, we used the above methodology to prepare cellulose films with reactive interfaces. For this, we prepared a bi-layered stack of the regenerated cellulose films by spin-coating a layer of viscous NMMO/cellulose/ CaCl_2 solution onto a glass disk, followed by spin-coating a second layer of a NMMO/cellulose/ Na_2SO_4 mixture. The two layers were then fused together by regenerating the cellulose matrix by immersion into water or an ethanol/water solution. As a consequence, precipitation of crystals of calcium sulphate in the form of gypsum (water regeneration) or bassanite (ethanol/water regeneration) occurred predominately at the interface of the fused films to produce composites with the central region of the interior highly enriched in the inorganic phase (Fig. 4).

In summary, a novel method for the *in situ* precipitation of calcium sulphates within cellulose thin films has been described. A key feature of the approach is the use of NMMO not only to dissolve fibrous cellulose but also to stabilize nanoparticles of amorphous calcium sulphate prior to regeneration of the polysaccharide matrix and formation of a thin composite film. Integration of the biopolymer film with amorphous or crystalline calcium sulphate phases is influenced by the rate of NMMO hydration, providing a route to

composite materials with stable or reactive inorganic components. Such materials could find uses in different applications, for example in the accelerated, delayed or triggered onset of composite hardening, or for the adsorption and release of internally trapped additives in biocompatible stem cell scaffolds with differentiation capability.^{22,23} In general, the concept of incorporating water-soluble ionic precursors into solutions of dissolved cellulose provides diverse opportunities in the field of nanoparticle synthesis, preparation of functional hybrid materials and cellulosic composites. Moreover the possibility of controlled precipitation of the inorganic component on the boundaries of multicomponent spin coated precursors could provide a step towards compartmentalized composites or thin film cellulose materials with active boundaries and interfaces.

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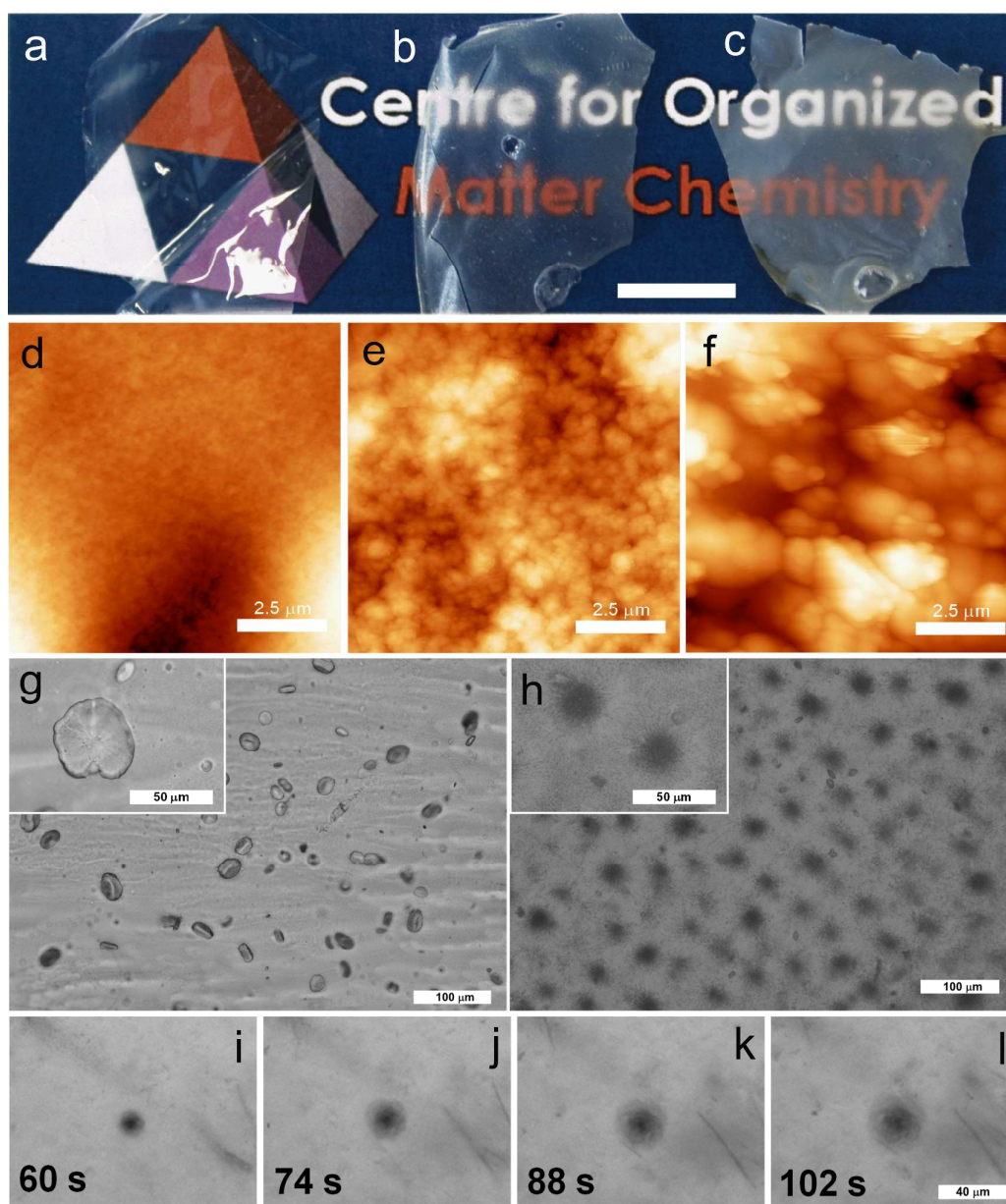


Fig. 1. (a-c) Transparent cellulose-based thin films prepared by matrix regeneration of spin coated NMMO/cellulose solutions using a 70 : 30 ethanol/water mixture. (a) Native (unmineralized) cellulose film. (b,c) Cellulose/calcium sulphate composite thin films prepared from NMMO solutions containing dissolved cellulose and equimolar concentrations of CaCl_2 and Na_2SO_4 ; 170 mM (cellulose : CaSO_4 weight ratio = 6:1) (b) and 500 mM (2:1) (c); scale bar = 20 mm. (d-f) AFM images of native cellulose film (d), cellulose/calcium sulphate film (6:1) (e) and cellulose/calcium sulphate film (2:1) (f). Note the increased in surface roughness with increased mineral content; corresponding height profiles over $5 \mu\text{m}^2$ areas gave values for the root mean square roughness of 38, 50 and 145 nm for (d-f), respectively; scale bars = 2.5 μm . (g,h) Optical microscopy images of cellulose/calcium sulphate films (500 mM CaSO_4 ; 2:1) regenerated in distilled water (g) or a 70:30 volume mixture of ethanol and water (h); scale bars = 100 μm (inset, 50 μm). (i-l) Time-dependent optical microscopy image showing growth of a calcium sulphate aggregate within the cellulose matrix after

regeneration in a 70 : 30 ethanol/water mixture ($\text{CaSO}_4 = 250 \text{ mM}$, cellulose : $\text{CaSO}_4 = 4:1$). The aggregate approximately doubles in size (from 17 to 37 μm) over 42 s; scale bar = 40 μm .

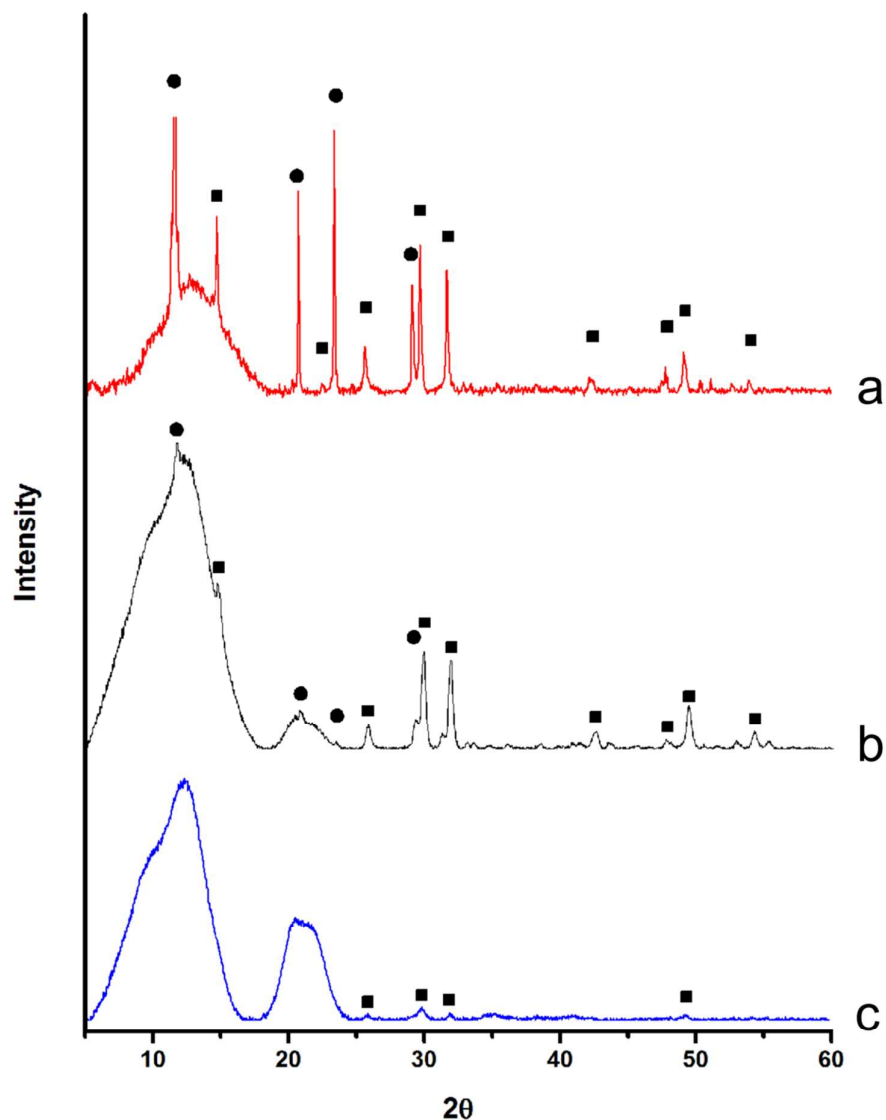


Fig. 2. X-ray diffraction patterns of (a) freeze-dried sample of cellulose/calcium sulphate prepared by immersing a NMMO solution containing 500 mM CaSO_4 into a 70 : 30 ethanol/water mixture; and (b,c) cellulose/calcium sulphate thin films (cellulose : $\text{CaSO}_4 = 2:1$) after regeneration in a 70 : 30 ethanol/water mixture for 24 h (b) or in distilled water only (c). Reflections corresponding to gypsum (●) ((020), (-221), (-131), (-241)) or bassanite (■) ((200), (-103), (020), (400), (204), (422), (602), (-424), (-141) planes) were observed. The broad peak at $2\theta = 13^\circ$ is from the silicon wafer.

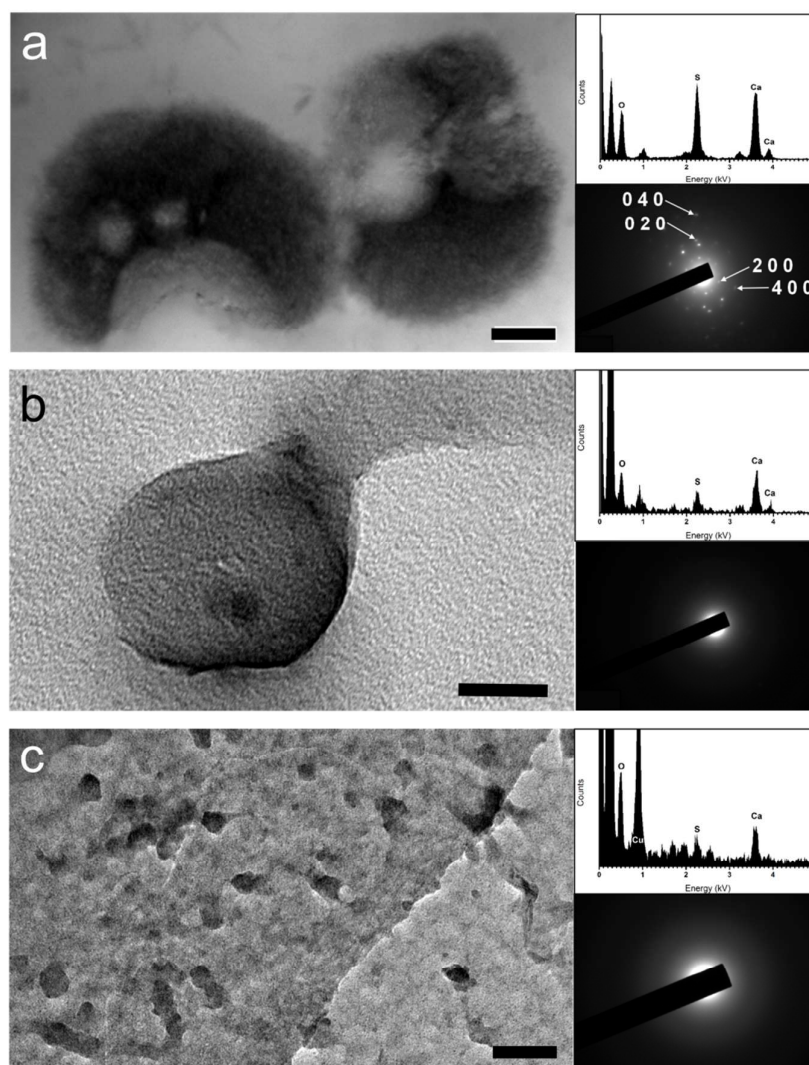


Fig. 3. TEM, EDX and electron diffraction analysis. (a,b) Cellulose/calcium sulphate composite prepared by regeneration in ethanol/water ($\text{CaSO}_4 = 250 \text{ mM}$; cellulose : $\text{CaSO}_4 = 4:1$) showing polycrystalline particles of bassanite (a), and nanoparticles of amorphous calcium sulphate (b) with corresponding EDX analyses and selected areas electron diffraction (SAED) patterns; scale bars, 200 nm (a) and 20 nm (b). The SAED pattern in (a) was recorded from the particle shown on the left of the TEM image; the SAED pattern shows diffuse polycrystalline rings and occasional high intensity spots that are assigned with bassanite Miller indices. (c) Sample prepared by adding a $\text{CaCl}_2/\text{Na}_2\text{SO}_4/\text{NMMO}$ mixture ($\text{CaSO}_4 = 170 \text{ mM}$; 0.5 wt%) to ethanol/water followed by freeze drying, showing amorphous calcium sulphate nanoparticles embedded in a cellulose-free NMMO matrix; scale bar = 100 nm. The EDX analyses show the presence of Ca, S associated with the inorganic mineral, and Cl as a background electrolyte. No evidence of crystallinity was observed in the electron diffraction patterns shown in (b) and (c).

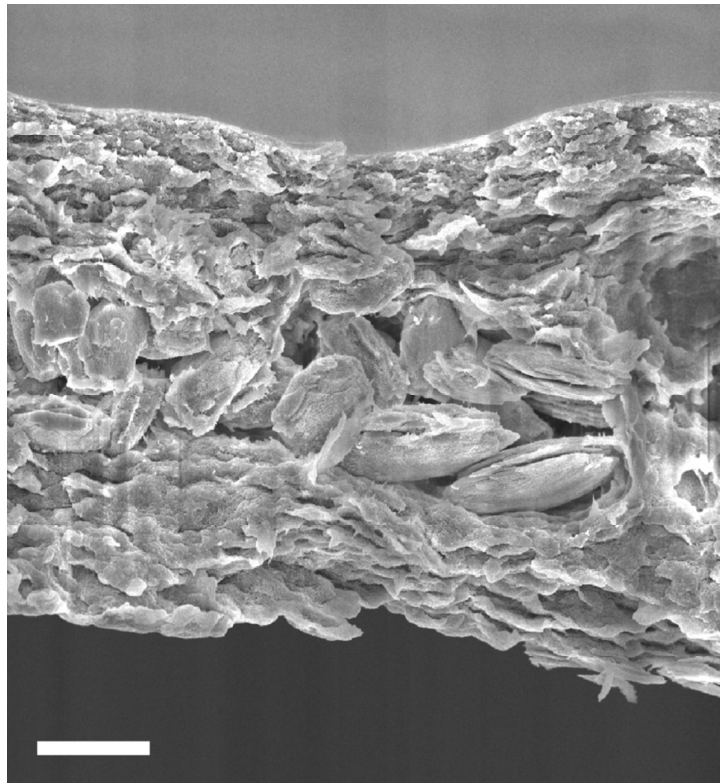


Fig. 4. SEM micrograph showing the cross section of a cellulose/calcium sulphate composite prepared from the layering and in situ regeneration of NMMO/cellulose solutions containing CaCl_2 or Na_2SO_4 (500 mM; cellulose : $\text{CaSO}_4 = 2:1$). Disk-like bassanite crystals are produced specifically at the interface of the two films to produce a highly mineralized central region; scale bar = 5 μm .

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†Electronic supplementary information (ESI) available: Experimental methods, FTIR spectra.

ToC graphic



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Cellulose films regenerated with calcium sulphate are fabricated using N-methylmorpholine N-oxide as a solvent and capping agent for polysaccharide dissolution and nanoparticle stabilization, respectively.