Calcium sulfate hemihydrate-mediated crystallization of gypsum on Ca\(^{2+}\)-activated cellulose thin films

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Supplementary Information

**Fig. S1.** (a) X-ray diffraction profiles of (A) untreated and (B) Ca-treated cellulose thin films. Peaks at 17, 30.5, 40.5 and 42° in profile B are associated with the evaporation-induced *in situ* crystallization of CaCl\(_2\)(H\(_2\)O)\(_4\) during sample preparation. (b) XPS spectrum showing Ca 2p\(_{3/2}\) binding energies (Demri, B. *J. Mater. Processing Techn.*** **55**, 311-314 (1995)). The peak at 351.3 eV corresponds to Ca 2p\(_{1/2}\)-Ca2p\(_{3/2}\) spin-orbit splitting, while the peak at 347.8 eV is attributed to the binding energy in the CaCl\(_2\) evaporite.
Fig. S2. XRD powder patterns for sample prepared from calcium sulfate hemihydrate (bassanite)-mediated crystallization on vertically oriented spin-coated thin films of Ca-modified cellulose. Reflections observed at 2θ values of 11.8, 21.0, 23.5, 29.3, 31.3, 33.5, 34.5, 41.0, 43.5, 48.0, 51.0 and 56.7° indicated that gypsum (CaSO₄·2H₂O) was produced on the films at room temperature under stirred reaction conditions. Peaks at 10.0, 15.5 and 25.7° correspond to residual undissolved bassanite. Peaks at 16.5, 21.7 and 27.0° are related to Na₂SO₄(H₂O)₂ contamination.
Fig. S3. AFM z-height images of the surface roughness of (a) Ca-activated and (b) untreated cellulose films. Corresponding roughness profiles are shown in the right hand side panels.
Fig. S4. ATR-FTIR spectra across a range of (a) 4000-600 cm\(^{-1}\) and (b) 3800-3000 cm\(^{-1}\) for untreated cellulose film (A/A*) and Ca-activated cellulose films (B/B*). Arrows in (b) show peak shift in the presence of calcium.