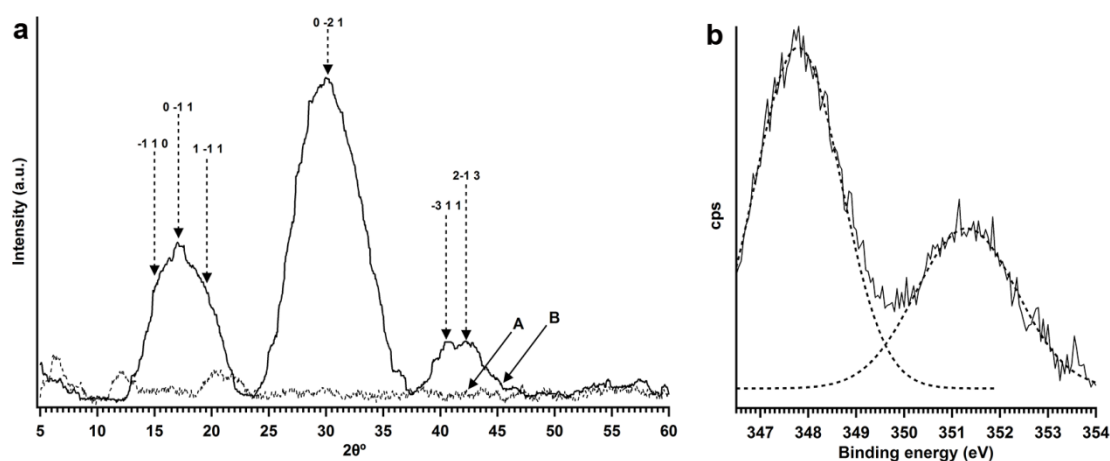


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## Calcium sulfate hemihydrate-mediated crystallization of gypsum on $\text{Ca}^{2+}$ -activated cellulose thin films

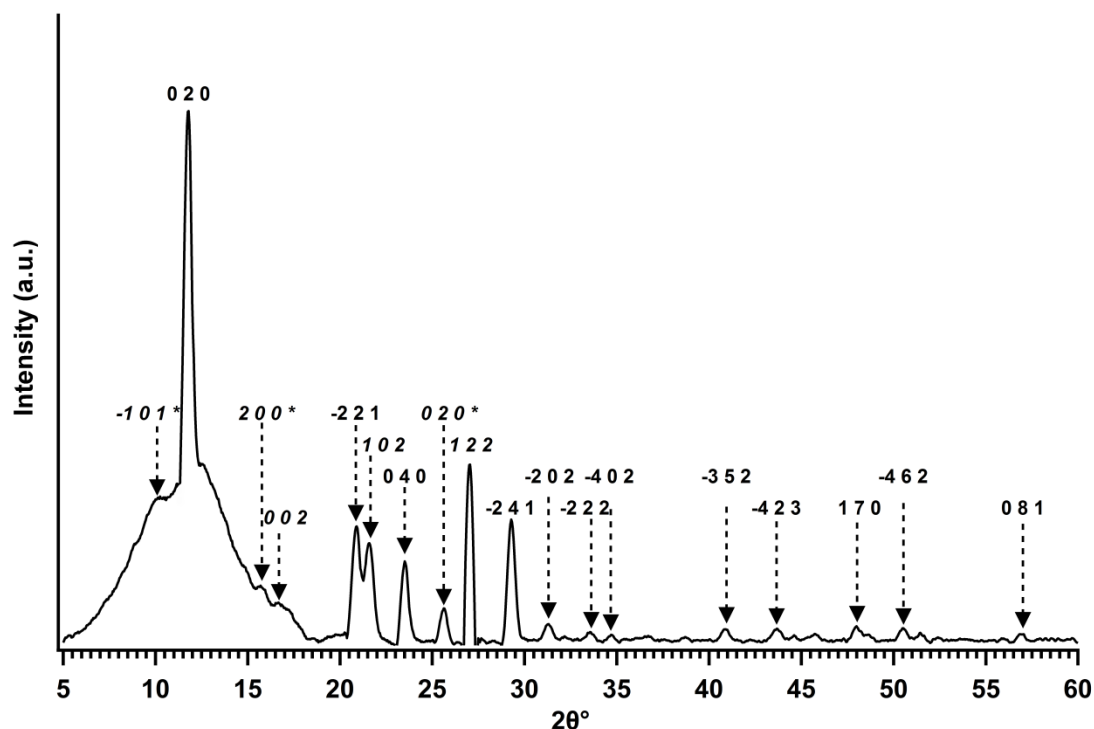
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### Supplementary Information

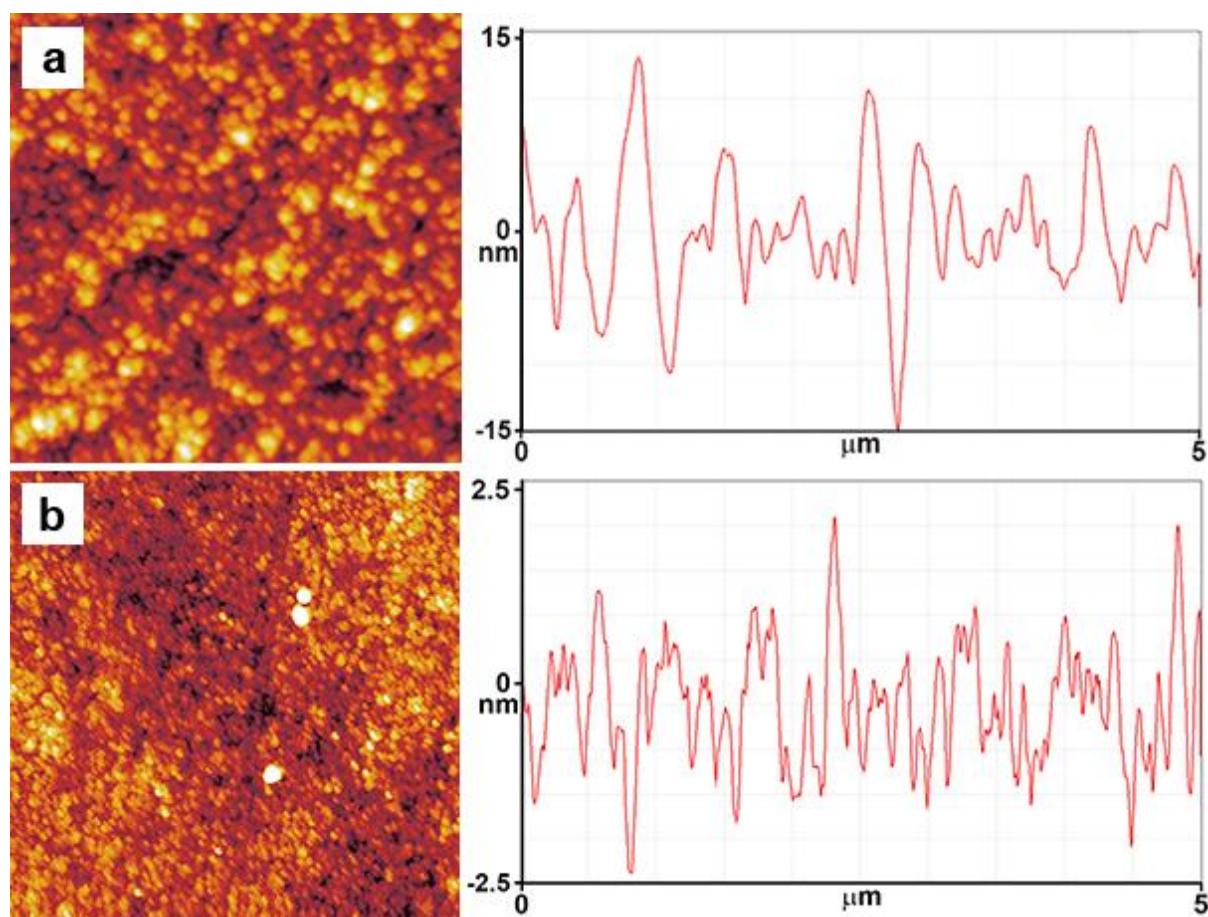


**Fig. S1.** (a) X-ray diffraction profiles of (A) untreated and (B) Ca-treated cellulose thin films. Peaks at 17, 30.5, 40.5 and 42° in profile **B** are associated with the evaporation-induced *in situ* crystallization of  $\text{CaCl}_2(\text{H}_2\text{O})_4$  during sample preparation. (b) XPS spectrum 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  $2p_{1/2}$ -Ca $2p_{3/2}$  spin-orbit splitting, while the peak at 347.8 eV is attributed to the binding energy in the  $\text{CaCl}_2$  evaporite.

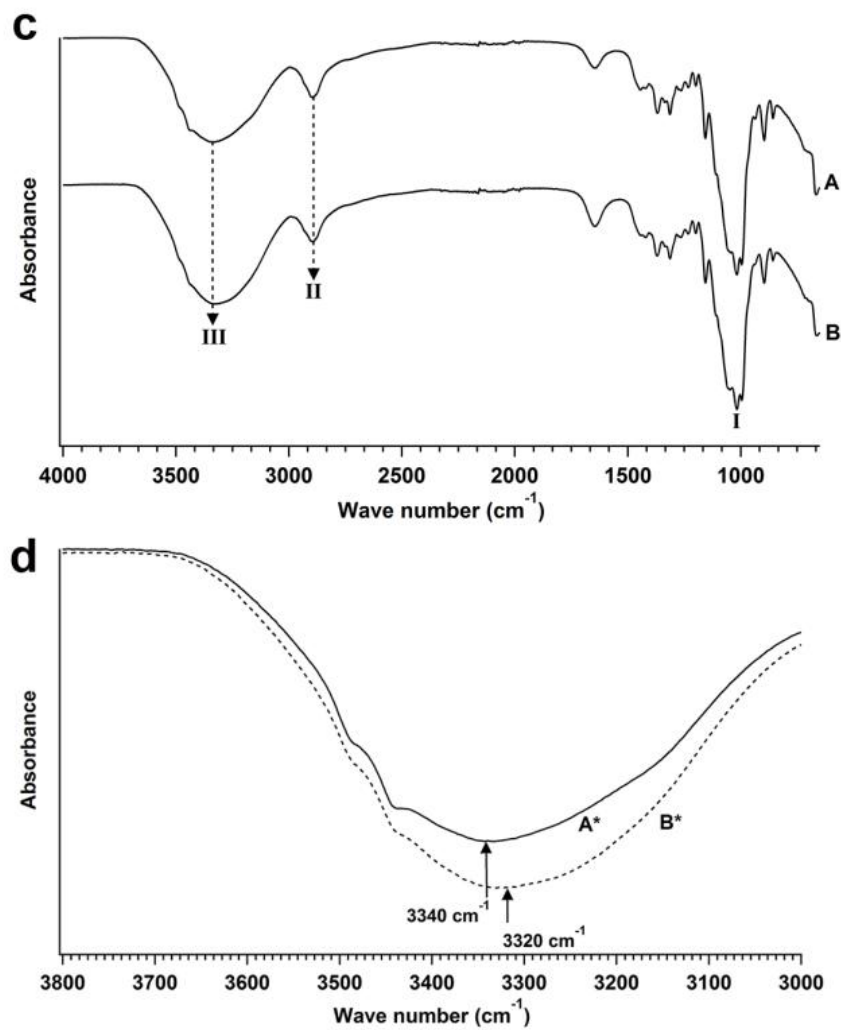
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**Fig. S2.** XRD powder patterns for sample prepared from calcium sulfate hemihydrate (bassanite)-mediated crystallization on vertically oriented spin-coated thin films of Ca-modified cellulose. Reflections observed at  $2\theta$  values of 11.8, 21.0, 23.5, 29.3, 31.3, 33.5, 34.5, 41.0, 43.5, 48.0, 51.0 and 56.7° indicated that gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) 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  $\text{Na}_2\text{SO}_4(\text{H}_2\text{O})_2$  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  $\text{cm}^{-1}$  and (b) 3800-3000  $\text{cm}^{-1}$  for untreated cellulose film (A/A\*) and Ca-activated cellulose films (B/B\*). Arrows in (b) show peak shift in the presence of calcium.