Supplementary Material (ESI) for Green Chemistry

Supplementary material for Manuscript:
"Development of micro- and nano-porous composite materials by processing cellulose with ionic liquids and supercritical CO_2"

Experimental

Thermogravimetric analysis (TGA) of the cellulose-composite samples was carried out in air atmosphere with a 10 ^{o}C/min heating rate and for the temperature range from 25 ^{o}C to 600 ^{o}C. The mass at 150 ^{o}C was set as 100% mass. Thermogravimetric analysis (TGA) of AmimCl was carried out in nitrogen atmosphere with a 10 ^{o}C/min heating rate and for the temperature range from 25 ^{o}C to 600 ^{o}C. The mass at 150 ^{o}C was set as 100% mass. The TGA analyzer was from Shimadzu, model TGA-50. Differential scanning calorimetry was carried out in nitrogen atmosphere from 22 ^{o}C to 100 ^{o}C with a 10 ^{o}C/min heating rate. The DSC unit was from Shimadzu, model DSC-50Q. XRD measurements were carried out with a Rigaku Miniflex X–ray diffractometer (Cu, λ=1.5405 Å) in the range of 2θ between 5 and 60 ^{o} with a scan rate of 2^{o}/min.The microscopic image of the aerogel was recorded with an AFM (Multimode IIId, Veeco Inc.) operating in tapping mode.

Results

The composite cellulose-hydroxyapatite material exhibits better thermal stability compared to cellulose. 5% mass loss occurs at 277 ^{o}C for cellulose and at 300 ^{o}C for the composite (figure S1). However the SiO_2-cellulose composite is thermally less stable than cellulose due, probably, to the incompatibility of the materials. In figure S2 the XRD patterns of the composite materials are presented. The broad peak around 20^{o} is of cellulose. The other peaks are of hydroxyapatite, while the amorphous SiO_2 has no contribution to the diffraction. In figures S3a and S3b, SEM pictures of the composites are presented. Surface roughness is visible due to the dispersion of the inorganic particles. In figure S3c the porous structure of a cellulose-SiO_2 composite is shown. In figure S4 the TGA curve of the synthesized AmimCl is shown. The onset degradation temperature is estimated to be 247 ^{o}C. In the DSC curve of AmimCl (figure S5) no change is observed in the temperature range 22-100 ^{o}C. Thus, it can be concluded that the melting point of this ionic liquid is lower than 22 ^{o}C. AFM image of the aerogel is shown in figure S6.

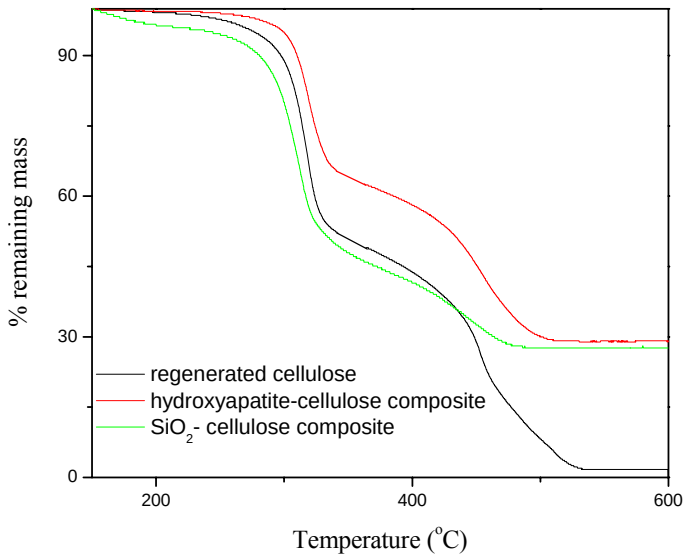


Figure S1. TGA curves of regenerated cellulose and cellulose-hydroxyapatite composite

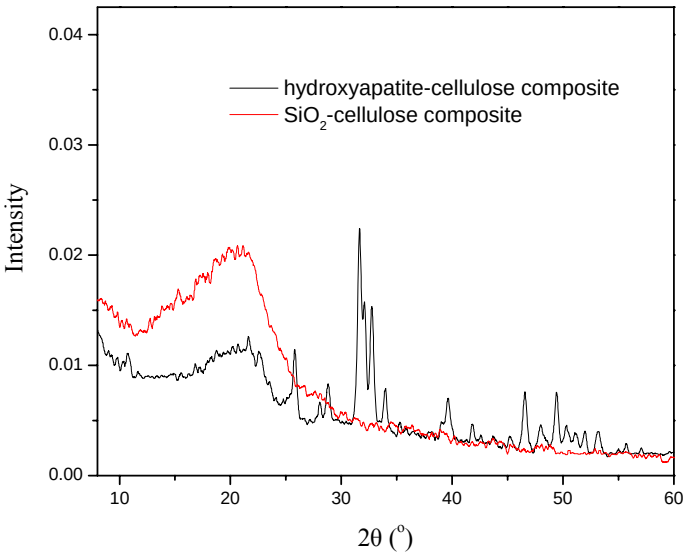
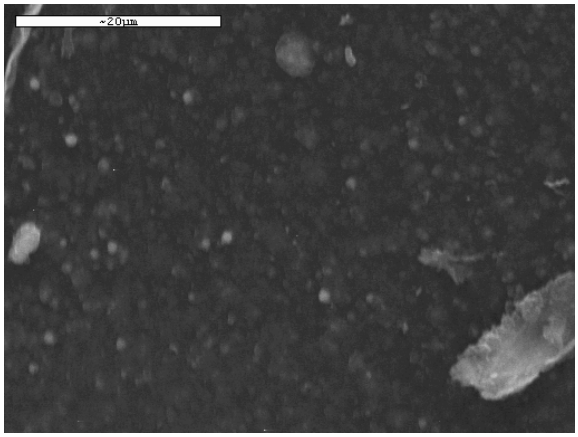
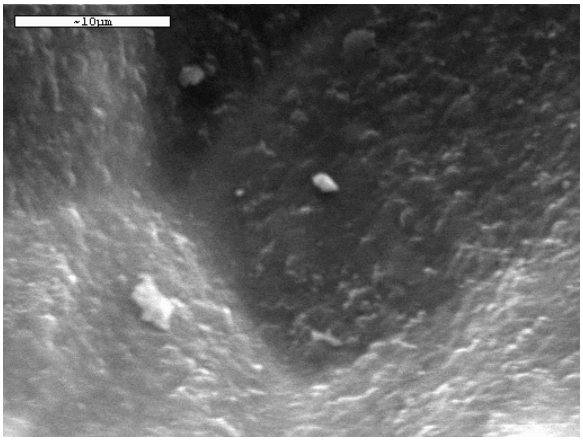


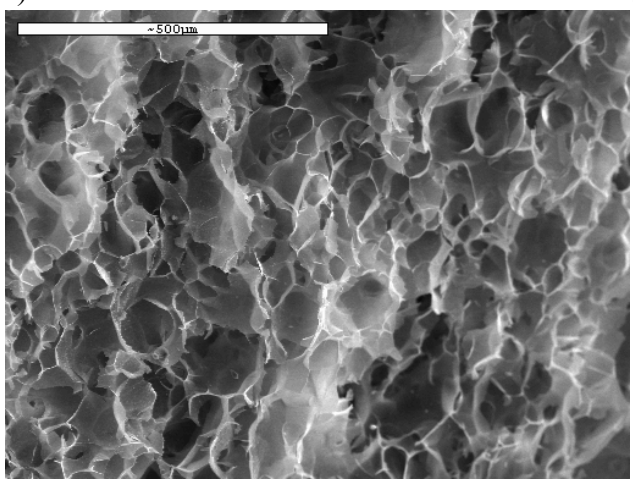
Figure S2. XRD patterns of cellulose-hydroxyapatite and cellulose-SiO_2 composites



a)



b)



c)

Figure S3. SEM figures of the composite materials a) Hydroxyapatite aggregates on the surface of a pore, scale bar 20 µm, b) SiO_2 aggregates on the surface of a pore, scale bar 10 µm, c) porous structure of cellulose-SiO_2 composite foamed at 125 bar and 80 ^{o}C , scale bar 500 µm.

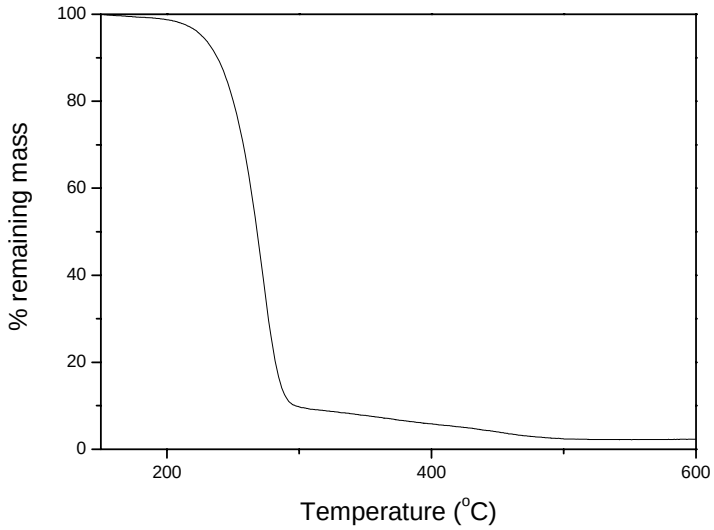


Figure S4. TGA curve of the synthesized AmimCl.

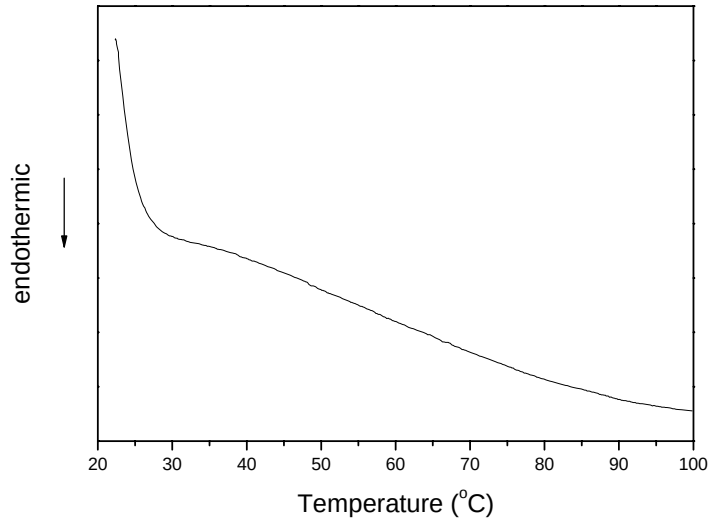


Figure S5. DSC curve of the synthesized AmimCl

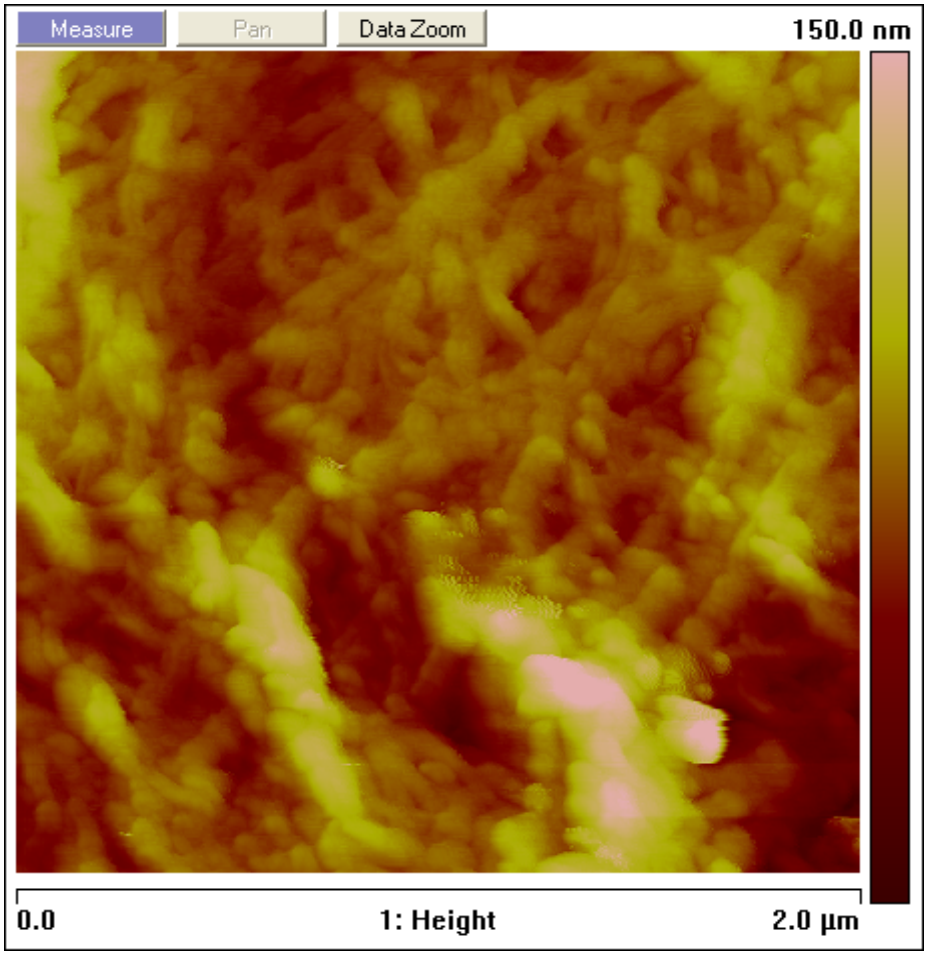


Figure S6. AFM image of cellulose aerogel

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