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- **Electronic supplementary information** -

**Synthesis of textured polysaccharide-silica nanocomposites: comparison between cellulose and chitin nanorods' precursors**

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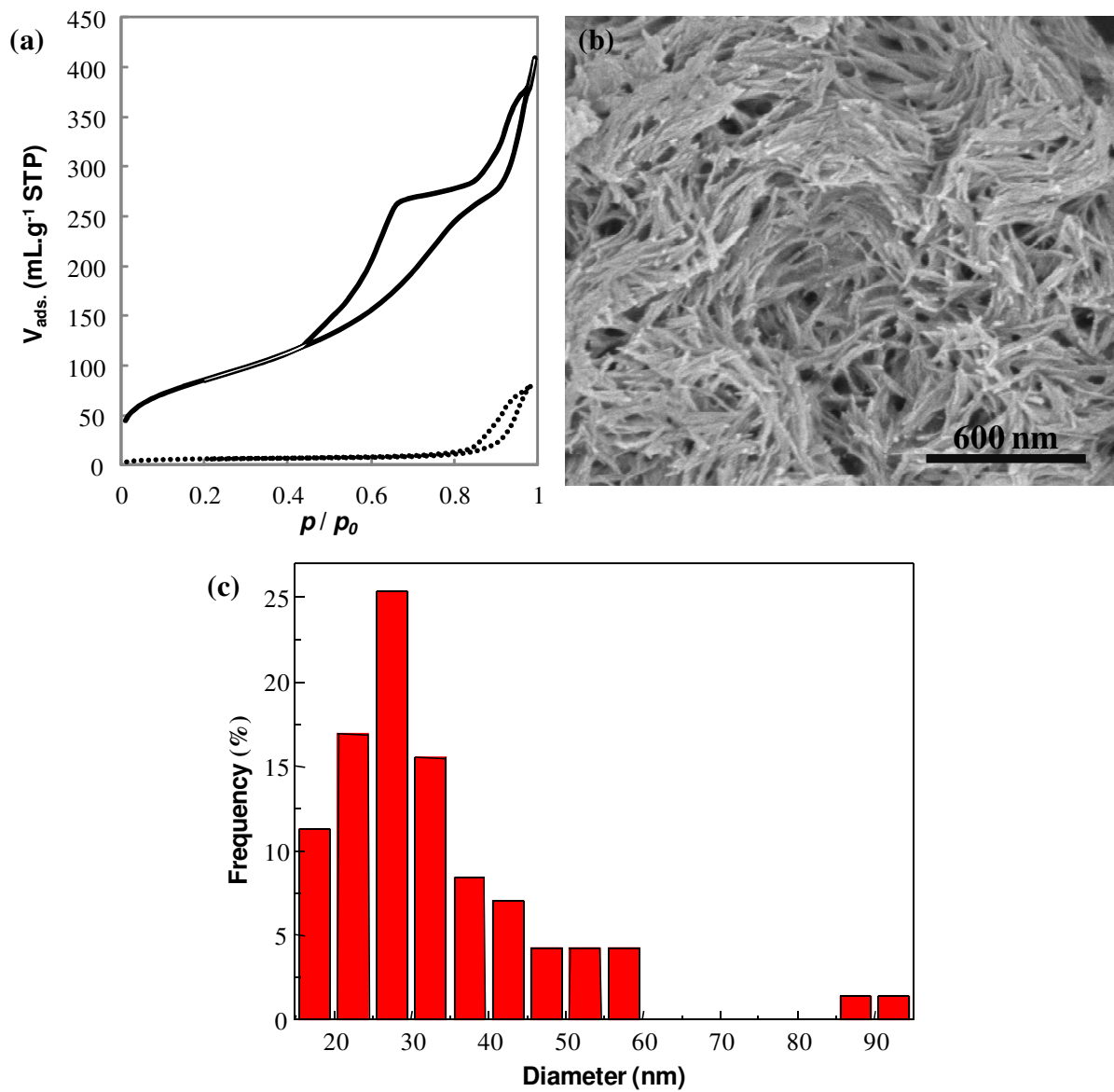
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**Fig. ESI 1.**

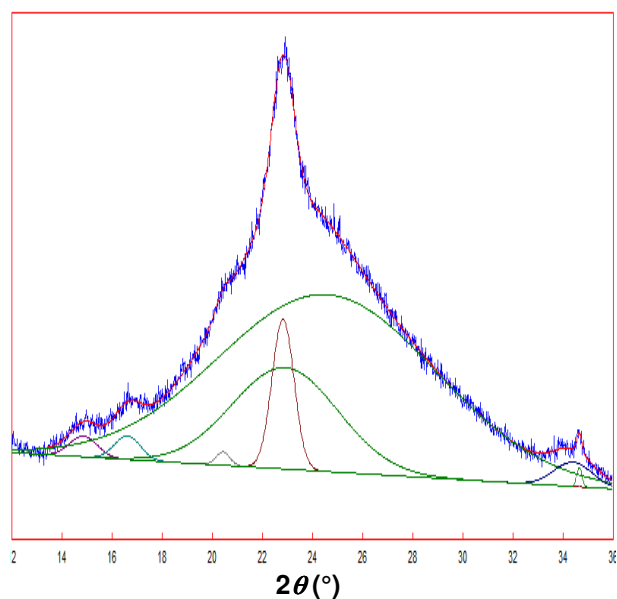
Formation of large pores at high  $\Phi_{CEL}$ . (a)  $N_2$  sorption isotherms (77 K) of spray-dried cellulose-silica nanocomposites ( $\phi_{CEL} = 0.64$ ), before (dashed lines) and after (continuous lines) calcination. (b) External surface of a spray-dried cellulose-silica microparticle ( $\phi_{CEL} = 0.64$ ) observed by SEM. (c) Size distribution of voids measured on the image in (b).



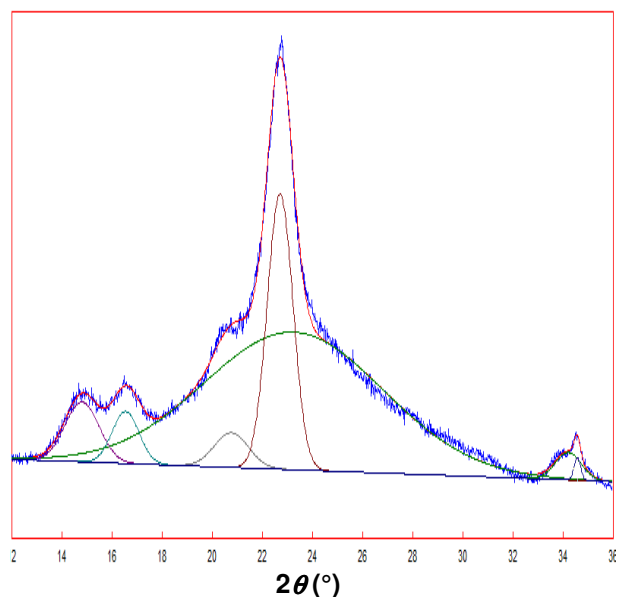
**Fig. ESI 2.**

Examples of X-Rays diffractogram deconvolutions for spray-dried cellulose-silica nanocomposites. The silica scattering and cellulose diffracting peaks are fitted using Gaussian functions. Slight variations in the width and position considered for the silica scattering peak do not affect the trends observed for the cellulose diffracting peaks.

$$\phi_{CEL} = 0.30$$

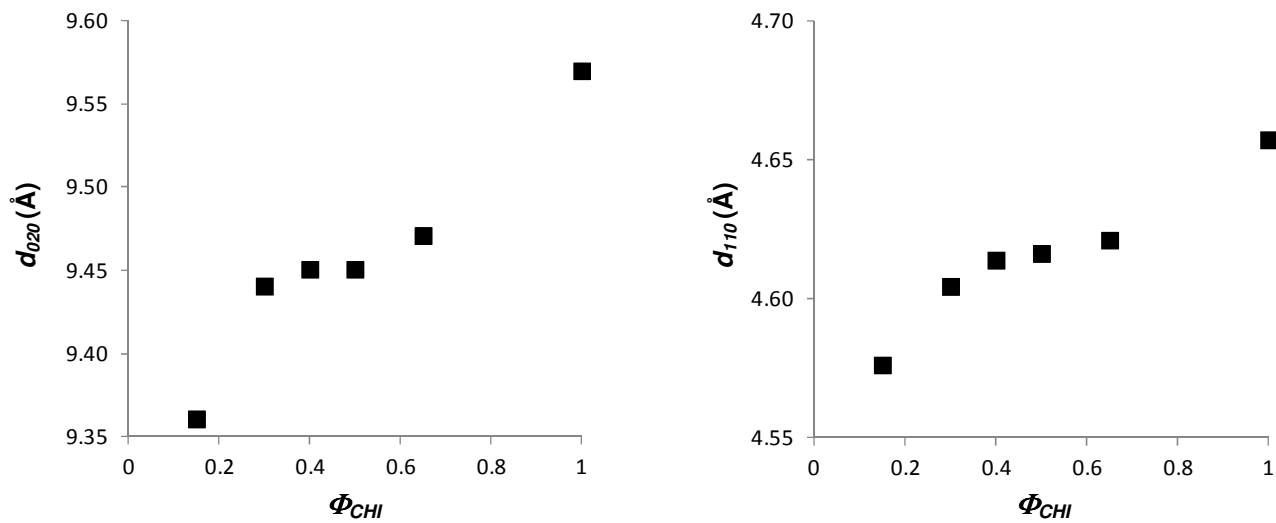


$$\phi_{CEL} = 0.55$$



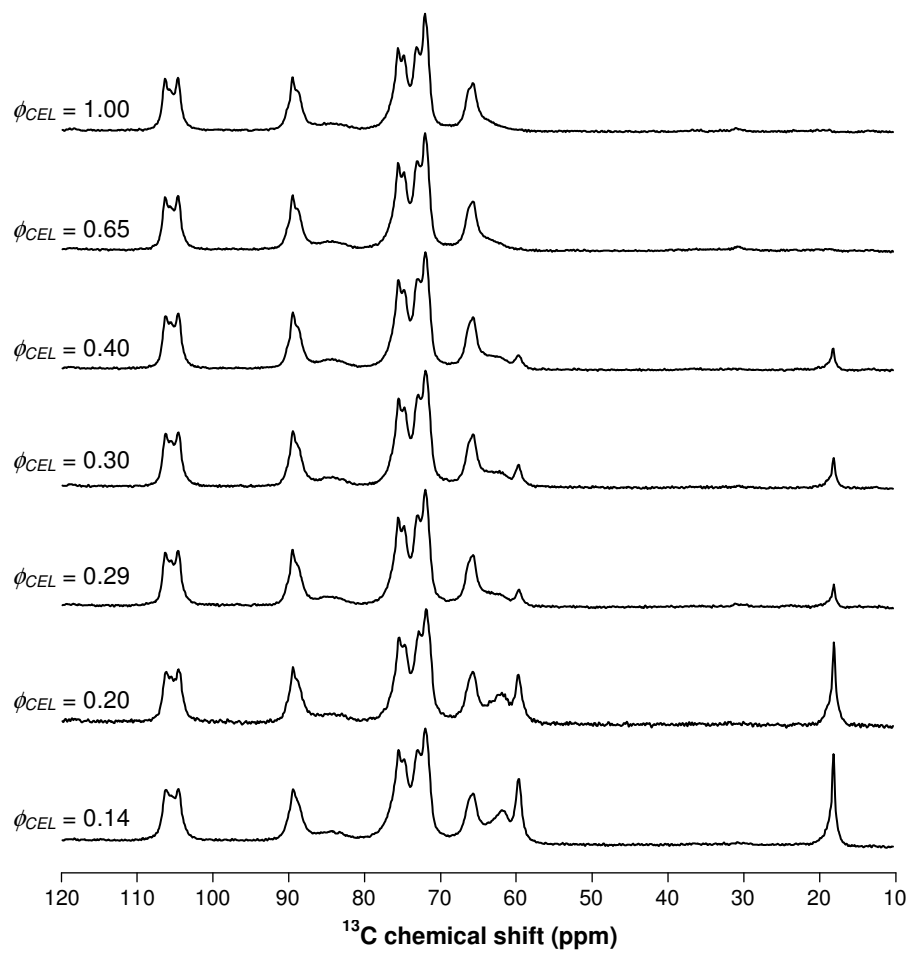
**Fig. ESI 3.**

Variation of  $d_{020}$  and  $d_{110}$  inter-reticular distances of  $\alpha$ -chitin monocrystals as a function of the chitin volume fraction  $\phi_{CHI}$  for spray-dried chitin-silica nanocomposites.



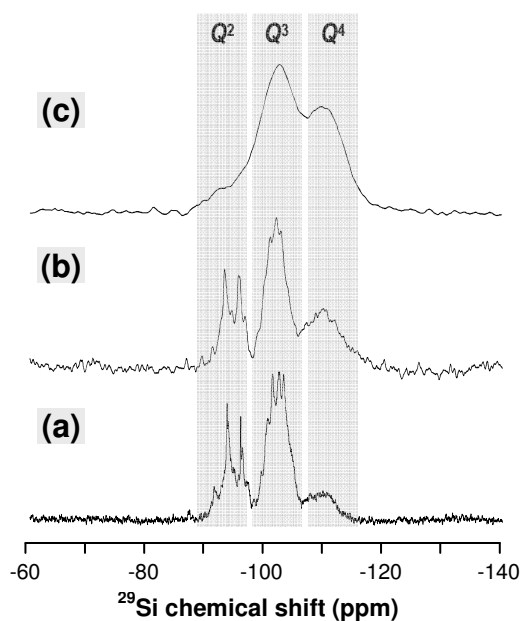
**Fig. ESI 4.**

$^{13}\text{C}\{^1\text{H}\}$  solid-state NMR CP-MAS spectra of spray-dried cellulose-silica nanocomposites for various cellulose volume fractions  $\phi_{\text{CEL}}$ .



**Fig. ESI 5.**

$^{29}\text{Si}$  NMR spectroscopy of chitin containing suspensions and solids. (a)  $^{29}\text{Si}$  liquid-state NMR spectrum of initial siloxane oligomers sols ( $[\text{Si}] \sim 2.5 \text{ mmol.g}^{-1}$ , 1615 scans). (b)  $^{29}\text{Si}$  liquid-state NMR spectrum of hybrid chitin-siloxane suspension analyzed 24 H after mixing the siloxane oligomers sol (a) and the chitin suspension ( $\phi_{\text{CHI}} = 0.3$ ,  $[\text{Si}] \sim 0.25 \text{ mmol.g}^{-1}$ , 18432 scans). (c)  $^{29}\text{Si}$  solid-state NMR spectrum of spray-dried chitin-silica nanocomposites obtained from hybrid suspensions (b) ( $\phi_{\text{CHI}} = 0.3$ ).

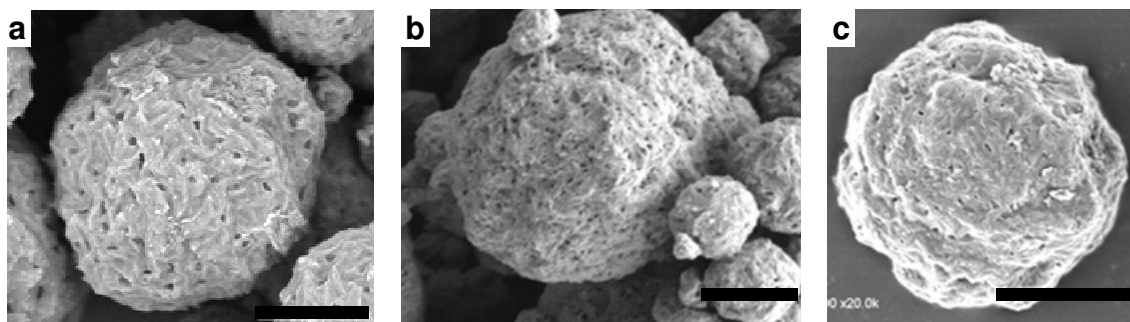


**Fig. ESI 6.**

***Spray-dried cellulose-silica nanocomposites before and after post-synthesis treatments.***

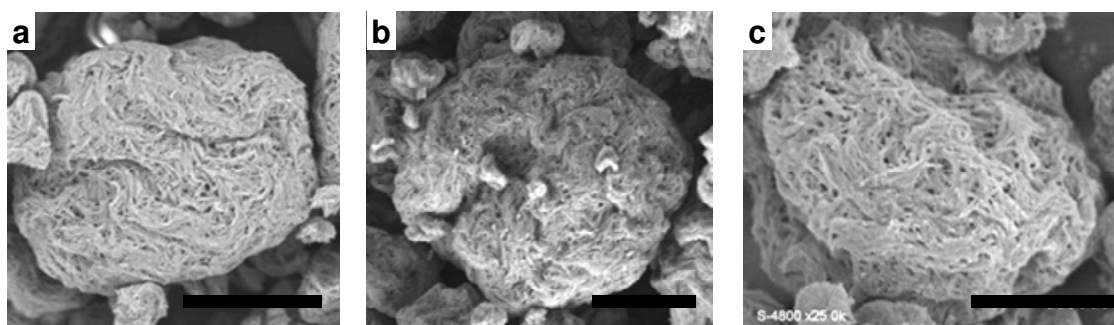
Cellulose volume fraction  $\phi_{CEL} = 0.29$

The micrographs correspond to: (a) hybrid nanocomposite; (b) calcined porous silica; (c) ammonia treated nanocomposite. The scale bars is 2  $\mu\text{m}$ .



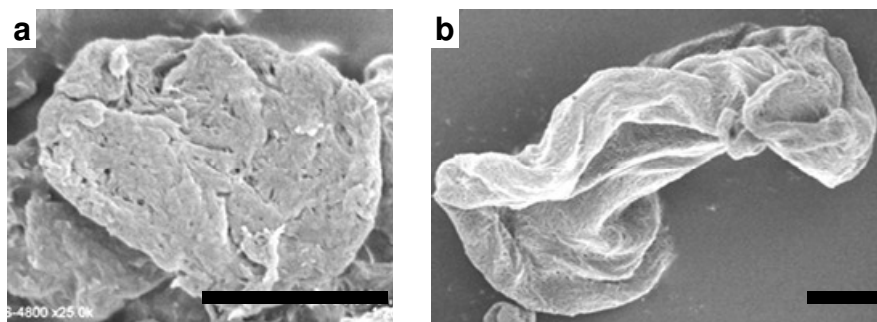
Cellulose volume fraction  $\phi_{CEL} = 0.64$

The micrographs correspond to: (a) hybrid nanocomposite; (b) calcined porous silica; (c) ammonia treated nanocomposite. The scale bars is 2  $\mu\text{m}$ .



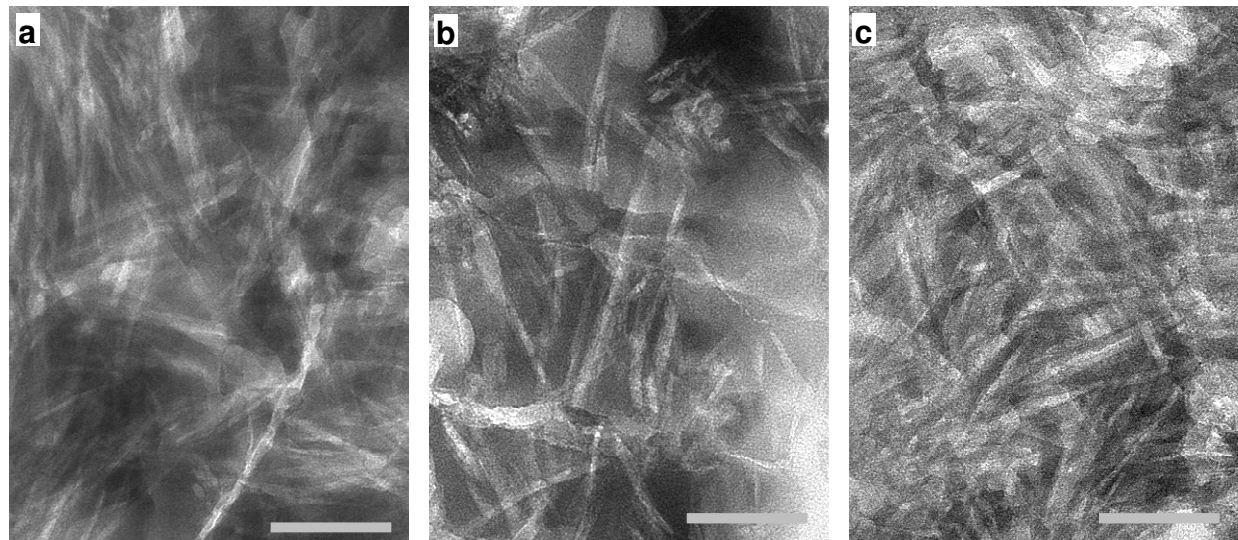
***Spray-dried polysaccharide nanorods.***

The micrographs correspond to: (a) cellulose; (b) chitin. The scale bars is 2  $\mu\text{m}$ .



**Fig. ESI 7.**

TEM micrographs of spray-dried hybrid cellulose-silica nanocomposites with increasing initial cellulose volume fraction  $\phi_{CEL} = 0.14, 0.29$  and  $0.48$  (in a, b, c resp.). The scale bars correspond to 100 nm.





**Fig. ESI 8.**

TEM micrographs of the spray-dried polysaccharide nanorods' suspensions: (a, b), chitin ( $\phi_{CHI} = 1$ ); (c, d), cellulose ( $\phi_{CEL} = 1$ ). The scale bar is 1  $\mu\text{m}$  in (a) and (c), and 100 nm in (b) and (d).

