

Supplementary material to Soft Matter manuscript B615224D

## “Anisotropic nano-papier mache microcapsules”

by Benjamin Holt,<sup>a</sup> Rey Lam,<sup>b</sup> Fiona C. Meldrum,<sup>b</sup> Simeon D. Stoyanov<sup>c</sup> and  
Vesselin N. Paunov<sup>\*a</sup>

<sup>a</sup> Department of Chemistry, University of Hull, Hull, HU6 7RX, UK,

<sup>b</sup> School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK,

<sup>c</sup> Food Structural Design/UFHRI, Unilever Research, Vlaardingen, Olivier van Noortlaan 120, 3133 AT Vlaardingen, The Netherlands

**1) Dimensions and structure of the nano-cotton fibres.** Nanocotton structure is defined as long, slender monocrystalline microfibrils (chains) of glucose units that are arranged in parallel with a two fold screw symmetry along their length (which means the true repeating unit is cellobiose, comprising of two glucose units) to form larger fibrillar structures.<sup>1</sup>

Table 1. Effect of hydrolysis time at 45°C on the properties of cellulose crystallites.<sup>2</sup>

<sup>a</sup>Elemental analysis, <sup>b</sup>conductometric titration, <sup>c</sup>PCS

Sample	Hydrolysis time (min)	Total sulfur content (%) <sup>a</sup>	Surface charge (OSO <sub>3</sub> <sup>-</sup> )(S%) <sup>b</sup>	Particle length (nm) <sup>c</sup>	Ordered phase
6	10	0.53	0.30	390	–
7	20	0.50	0.33	332	+
8	30	0.58	0.50	276	+
9	45	0.62	0.64	226	+
10	60	0.69	0.68	197	+
11	120	0.74	0.68	179	+
12	240	0.75	0.62	177	+

The table above is from Dong *et al.*<sup>2</sup> we used hydrolysis time of 75 mins at 45°C and so estimating around 200nm for crystallite length is appropriate. Lengths of the particles were estimated from photon correlation spectroscopy assuming a constant diameter of 7nm.<sup>2</sup>

Beyond the nanometre resolution afforded by electron microscopy, the ultra structure of individual cellulose crystallites has been investigated by Baker *et al.*<sup>3</sup> Atomic Force Microscopy (AFM) was used to image the surface of native cellulose micro crystals obtained from the sulphuric acid hydrolysis of the green alga *Valonia ventricosa*.<sup>3</sup> It was clearly resolved that the intra-chain periodicities for the glucose and cellobiose (true repeating unit) were 0.52 nm and 1.04 nm respectively, as well as the spacing between adjacent cellulose chains on the surface of 0.6nm.<sup>3</sup>

**2) Permeability of polyelectrolyte microcapsules.** As far as the latex cubosomes go, large gaps between latex particles and even were latex particles have come away after core dissolution mean that these capsules are permeable to a variety of high m.w polymers and even other particles. The permeability of similar polyelectrolyte capsules (spherical) has already been addressed by other authors, e.g. the work done by Caruso *et al.*<sup>4</sup> describing osmotic pressure build up as one of the causes of morphology change when solubilising previously crystalline catalase enzyme. Hence solubilised catalase enzyme cannot permeate through the polyelectrolyte (PE) layer however, while water molecules can. Our anisotropic capsules consist of relatively few PAH layers (2 at most) and so it is difficult to compare permeability a lot of the work done with traditional PE layer no.s of 8 or more. Also our crystalline PE of nano cotton fibres is sure to affect permeability as oppose to the normal flexible polystyrene-sulfonate alternative. It is certain that the anisotropic capsules are freely permeable with respect to low-molecular species (e.g. Ca<sup>2+</sup> and other ions). However, the release profile of the capsules is non-uniform in 3D and we are currently developing the methodology to study the permeability of the anisotropic capsules which a non-trivial problem and will be addressed in a follow up paper.

#### References

1. K. Fleming, D.G.Gray, S. Matthews, *Chem. Eur. J.* **2001**, 7, 1831.
2. X. M. Dong, J. F. Revol, D. G. Gray, *Cellulose*, **1998**, 5, 19.
3. A. A. Baker, W. Helbert, J. Sugiyama, M. J. Miles, *Appl. Phys. A* **1998**, 66, S559.

4. F. Caruso, D. Trau, H. Möhwald, R. Renneburg, *Langmuir*, **2000**, *16*, 1485.