EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

# Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF**.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

*https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

## Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

## Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| | | |
|---|---|---|
| ESRF | **Experiment title:**<br>Do cellulose nanocrystals show a preferred reactivity of different crystal planes? | **Experiment number**: |
| **Beamline**: | **Date of experiment**:<br>from: 21-11-2017 to: 24-11-2017 | **Date of report**: |
| **Shifts:** | **Local contact(s)**:<br>Daniel Hermida Merino | *Received at ESRF:* |


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**Report:**

We have performed several SAXS & WAXS measurements of suspensions of surface modified cellulose nanoparticles (CNCs) with different degrees of subtitution (DS) at their surface. The intent was to verify whether or not there is a preferred face of the CNCs that is more reactive as initial lab data seemed to suggest. The model for fitting the form factor used was based on a parallelepiped with rectangular cross section (or rectangular prism)[1] (see Figure 1), as used in recent works.[2,3] The aim was to identify the variation of the shape of the cross section as a function of degree of subtitution, by calculating the variation of the cross-section sides *a* and *b*. A change in the crystal structure and the form factor of CNCs as a function of the degree of surface modification would indicate a preferred reaction side on the surface of the rectangular-shaped cellulose nanocrystals, which could have relevance for the design of novel multifunctional nanocellulose materials.

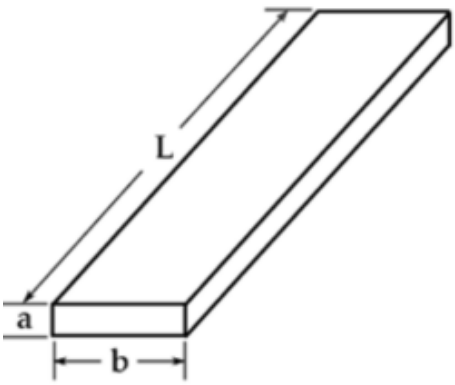


***Figure 1.*** *Parallelepiped model with rectangular cross section used in this report, as previously described.*[2]

In this report we present the results obtained for pyridinium-grafted CNCs at four different degrees of subtitution, which we have characterized in our recent work.[4] An example of the fits performed is given in Figure 2, for CNCs with a DS of 0.9 and concentration of 0.1%. The values determined from the cross section were $a$ = 6.7 ± 0.2 nm and $b$ = 10 ± 1 nm. A direct comparison with literature values for unmodified nanocrystals prepared from the same source gave a smaller cross-section.[3]
Results obtained for CNCs grafted with the same group at different degree of subtitution are shown in Figure 3. These results show a clear trend with the size $b/a$ decreasing as function of the degree of subtitution. If we compare these results to the literature value of unmodified CNCs from cotton[3] we obtain a ratio $b/a$ of around 5, which correlate well with a linear decrease of the ratio.
Considering the values of size $a$ and $b$ it can be observed that this change depends mostly on a decrease of the size $b$ as function of the degree of substitution (see Figure 3B). This behaviour could be explained considering that during the chemical reaction delamination on the $1\bar{1}0$ plane occurs, and this is in line with recent work, where delamination on the same plane was observed during surface oxidation.[5] Similarly, this hypothesis is also in line with work of Mao *et al.* which reported a reduction of the $b$ size of ~ 4 times after TEMPO-mediated oxidation, a very common way to obtain colloidally stable cellulose nanofibers.[2]

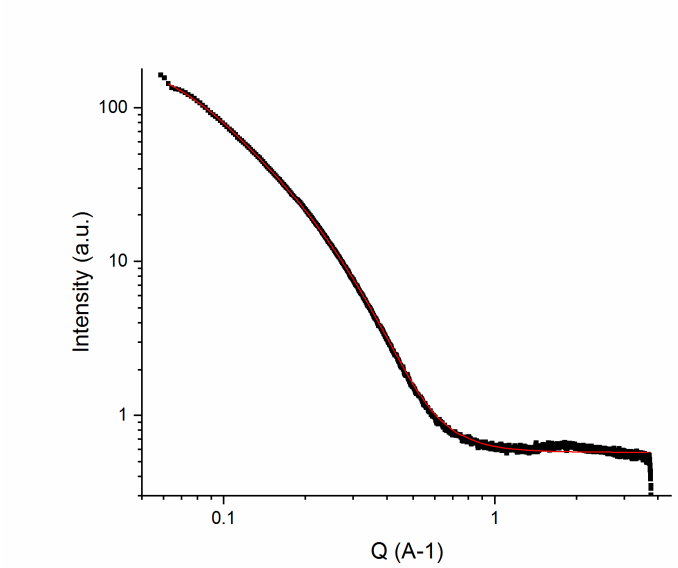


***Figure 2.*** *An example of a SAXS curve of pyridinium grafted CNCs (DS 0,9; concentration 0,1 wt%)*

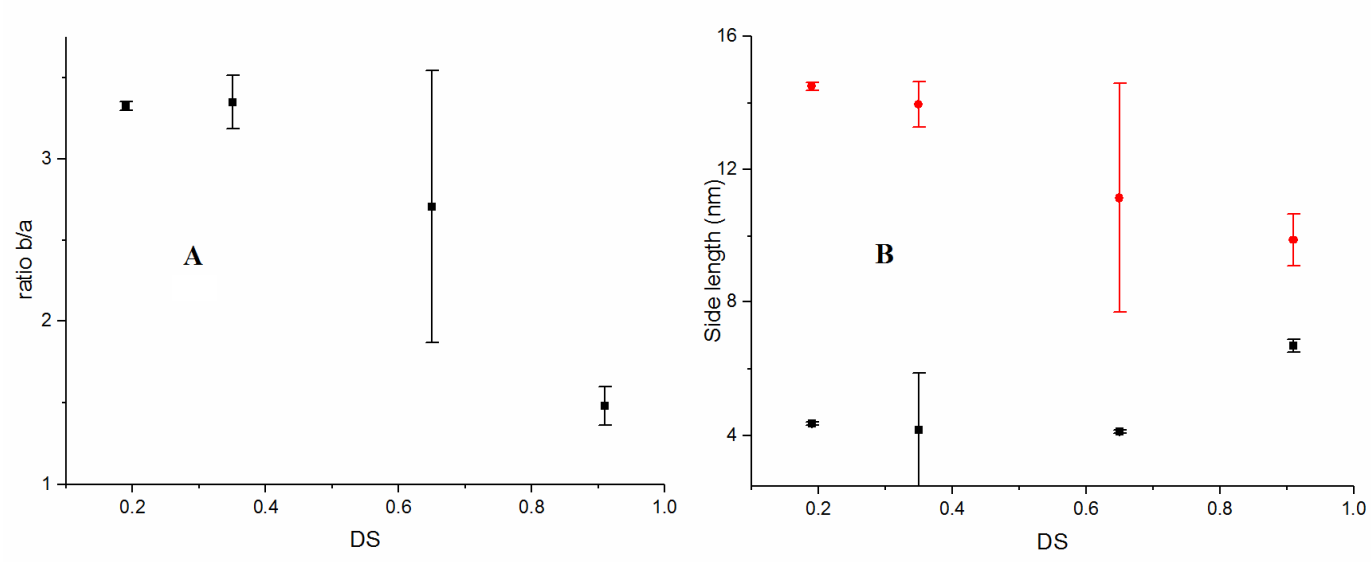


***Figure 3.*** *(A) Values determined for the ratio of size* b/a *as function of the degree of substitution. (B) Values of side length a (black squares) and b (red circles) as function of the degree of substitution.*

**Future work**

We continue working on fitting of other modified nanocrystals with different modification and various degrees of subtitution, which we measured during this beamtime. Our hypothesis is that we find a similar trend for other modified cellulose nanoparticles and we aim to publish these results in a highly ranked journal.

**References**


(1) Nayuk, R.; Huber, K. Formfactors of Hollow and Massive Rectangular Parallelepipeds at Variable Degree of Anisometry. *Z. Phys. Chem.* **2012**, *226*, 837–854.

(2) Mao, Y.; Liu, K.; Zhan, C.; Geng, L.; Chu, B.; Hsiao, B. S. Characterization of Nanocellulose Using Small-Angle Neutron, X-Ray, and Dynamic Light Scattering Techniques. *J. Phys. Chem. B* **2017**, *121* (6), 1340–1351.

(3) Schütz, C.; Van Rie, J.; Eyley, S.; Gençer, A.; van Gorp, H.; Rosenfeldt, S.; Kang, K.; Thielemans, W. Effect of Source on the Properties and Behavior of Cellulose Nanocrystal Suspensions. *ACS Sustain. Chem. Eng.* **2018**, acssuschemeng.8b00334.

(4) Jasmani, L.; Eyley, S.; Wallbridge, R.; Thielemans, W. A Facile One-Pot Route to Cationic Cellulose Nanocrystals. *Nanoscale* **2013**, *5* (21), 10207–10211.

(5) Su, Y.; Burger, C.; Ma, H.; Chu, B.; Hsiao, B. S. Exploring the Nature of Cellulose Microfibrils. *Biomacromolecules* **2015**, *16* (4), 1201–1209.