Experimental report

08/11/2024

Proposal: **9-11-2132**

Council: 4/2023

Title: Unusual thickness triggered doubling of the volume of LbL-films composed of rigid and soft components

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Si wafers
multilayered films composed of tunicate cellulose nanocrystals and poly(vinyl amine)

Instrument	Requested days	Allocated days	From	To
D17	2	2	20/11/2023	22/11/2023
FIGARO	2	0		

Abstract:

The remarkable properties of natural composite materials (e.g. plant cell wall, animal exoskeleton) have attracted a wealth of research to understand their structure-property relationships at all length scales and to design novel materials with superior mechanical and optical performance. As such complex bio-inspired materials can presently not be made synthetically with a nanoscale precision, ICS and CERMAV propose to combine layer-by-layer assembly and grazing incidence spraying to design hierarchical helical architectures of nanocelluloses and (bio-)polymers with tunable structural features. Preliminary results indicate that this approach is well adapted for designing complex multilayer films. But during this study, films made of tunicate cellulose nanocrystal and poly(vinyl amine) showed a highly unusual film-growth behavior by dipping and grazing incidence spraying methods that is in strong contrast with the literature. In the proposed experiment, neutron reflectivity will be used to provide quantitative data on the multilayered assemblies' dimensions, composition and geometry that will bring valuable insight into the origin of these intriguing physico-chemical phenomena.

Here we report on the analysis of neutron reflectometry experiments which we carried out on a series of 11 samples composed of deuterated tunicate cellulose nanocrystals ($tCNC_d$) and protonated poly(vinylamine) (PVAm). As suggested in the proposal multilayers films corresponding to different situations, namely before the jump, during the jump and after the jump, were prepared on silicon wafers pre-coated either by a poly(ethylene imine) (PEI) layer or a $PEI(PSS/PAH)_{10}$ film, by dipping, spin-assisted assembly and grazing incidence spraying. All films were assembled from a $tCNC_d$ suspension and a PVAm solution (unmodified pH) at respective concentrations of 0.4 g/L and 1 g/L.

Reflectometry measurements were performed at the solid/air interface using rectangular (4 cm x 4 cm) Si-wafers at 298K, ambient pressure and controlled relative humidity on the D17 instrument. The data were collected in the wavelength range from 2-30 Å with a wavelength resolution $\delta\lambda/\lambda$ of 1-7%. We used collimation slits of 0.8 and 3.8 mm for the two used reflection angles of 0.8° and 3.8°, respectively. Our datasets were analyzed using the Refnx software package which uses the Abeles matrix formalism. More specifically, we have used a classic box model in which each layer i (slab) is characterised by three variables: a scattering length density (SLD_i), a thickness (D_i) and a surface roughness (σ_i).

Surprisingly, none of the measured reflectivity curves showed any internal layered structure for the $(tCNC_d/PVAm)_n$ films, independently of the deposition method, the pre-coating and the relative humidity (Figure 1a). We were only able to observe clear Kiessig fringes corresponding to the $PEI/(PSS/PAH)_{10}$ film on top of which the tCNC-based films were deposited (Figure 1b).

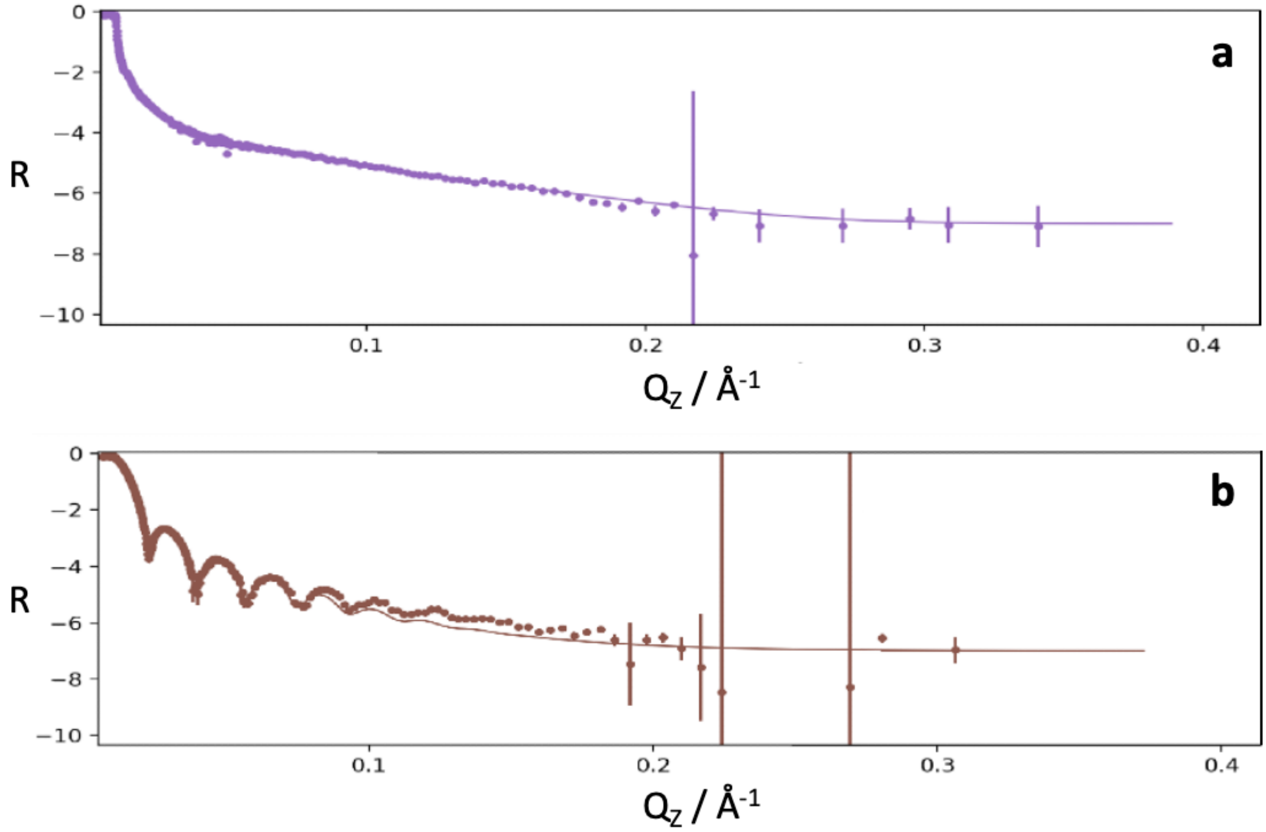

Figure 1. Reflectivity curves for the $(tCNC/PVAm)_n$ prepared by dipping on silicon wafers pre-coated either by a PEI layer (a) or a $PEI(PSS/PAH)_{10}$ film (b). Points represent the experimental data and the lines represent the fit.

Films built on a pre-coated PEI layer showed very rough layers as can be appreciated in Figure 2.

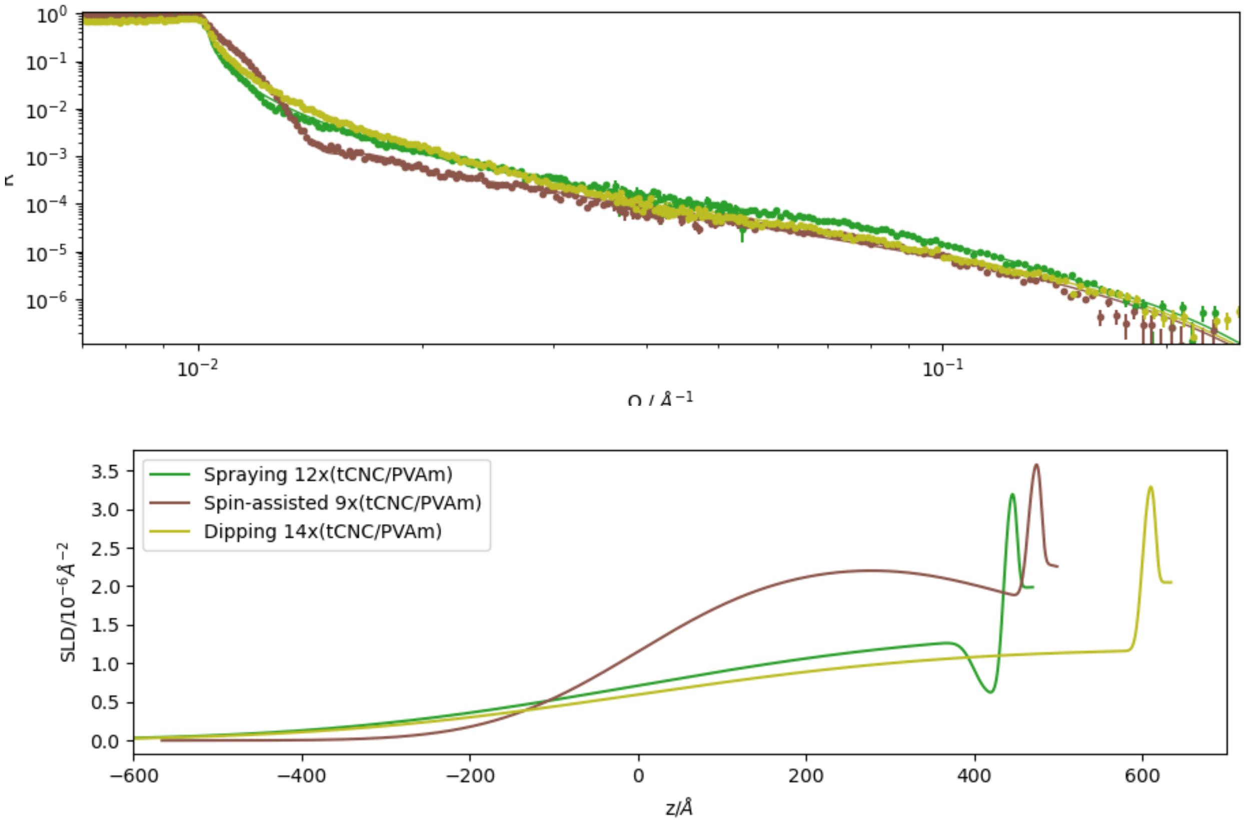

Figure 2. Reflectivity curves (top) and fitted SLD profiles (bottom) for the (tCNC/PVAm)$_n$ systems on silicon wafers pre-coated by a PEI layer during the jump prepared as noted in the legend. Points represent the experimental data and the lines represent the fit.

The diffuse nature of the layers is corroborated by the strong off-specular reflectometry signal of the various samples shown in Figure 3. The significant difference in thickness between tCNC and PVAm leads indeed to the piling up of "Mikado" like layers creating macroporous structures. Such porous/rough architectures are responsible for the scattering of the neutron beam in different directions. We expected less beam scattering for oriented t-CNC films prepared by spin-assisted and grazing incidence spraying (GIS) as the in-plane alignment of tCNC would lead to more compact and organized films. Unfortunately, none of these samples showed internal layered structure, meaning that architectures created during the film build-up are not stratified as in polyelectrolyte films but are very diffuse (we don't see Kiessig fringes and Bragg-peaks).

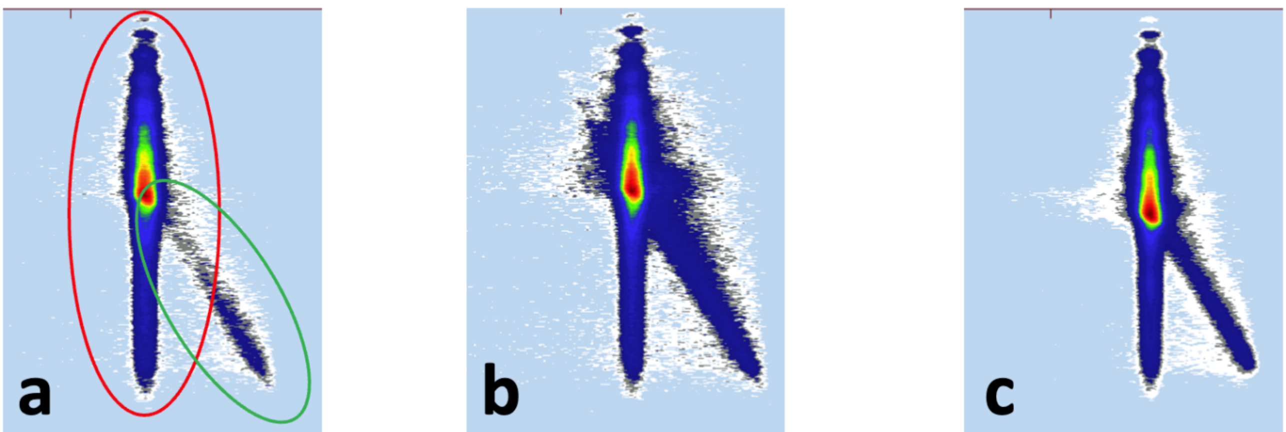

Figure 3. 2D pictures of the specular (red ellipse) and off-specular (green ellipse) reflection for (tCNC/PVAm)$_n$ films prepared by dipping before the jump (a), during the jump (b) and after the jump (c) with a relative humidity of 50%.

However, among these very porous/rough layers still differences can be observed as can be appreciated in Figure 2. The sprayed and dipped samples show a low density very rough layer, whereas the sample prepared by spin-assisted assembly shows a significantly more compact structure (although still not layered). In addition the cellulose distribution in these films is not homogeneous, but denser in the middle of the layer and less dense at the air/solid interfaces (the SLD profile is not flat, but shows a 'hump'). The density of the cellulose is twice as high for the spin-coated sample than for the other two (the 'hump' in the SLD profile is much more visible in this case). We suspect that deposition conditions used for spin-assisted assembly allow a better alignment of the nano-cellulose "sticks" leading to more compact layers limiting the film porosity upon addition of subsequent layers leading to the jump in thickness.