Experimental report

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Proposal: **9-11-1885** **Council:** 4/2018

Title: GISANS study on conducting polymerinfiltration in porous cellulose thin films.

Research area: Materials

This proposal is a new proposal

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Samples: silicon wafer
Cellulose
pedot:dpss

Instrument	Requested days	Allocated days	From	To
D22	6	3	09/10/2018	12/10/2018

Abstract:

We intend to follow a novel route for fabricating cellulose-functional polymer nanocomposites ("functional nanopaper") by spray coating. Cellulose nanofibrils (CNF) serve as high strength building blocks for porous thin film templates. poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as a functional polymer is commonly used as active layer material in organic solar cells. We aim to investigate the filling and penetration of deuterated PEDOT:PSS using spray coating into porous CNF films, also prepared by spray coating. Depending of the surface charge of the CNFs, a change in CNF nanostructure and porosity of such thin films is expected, which in turn will strongly influence the filling by the functional polymer. We plan to employ GISANS, as it offers the unique possibility of elucidating the porosity, nanostructure and three-dimensional morphology of the thin film, yet at the same time to retrieve the filling by the deuterated PEDOT:PSS due to contrast variation in the nanocomposite. Ultimately the goal is to establish a fully sprayed organic solar cells based on resource saving and renewable materials, making use of their flexibility and mechanical stability.

GISANS study on conducting polymer infiltration in porous cellulose thin films.

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Nanocellulose as renewable and sustainable material is used as building block for high-strength materials. Especially cellulose nanofibrils (CNF) have proven their strengths in barrier coatings, as well as in conductive and transparent films. Fabrication of thin films in large-industrial scale can be performed with spray deposition using water-based technologies. The resulting porous CNF matrices are excellent candidates to infiltrate nanoparticles or polymers for functionalization. A conductive polymer, namely poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), widely used in organic photovoltaics and electronics, was used to study the infiltration and resulting structural rearrangement within the thin CNF film having a thickness of 400 nm. Grazing incidence small-angle neutron scattering (GISANS) was performed at D22-ILL facilitating a humidity chamber to cycle different pre-treated CNF/PEDOT:PSS composite thin films.

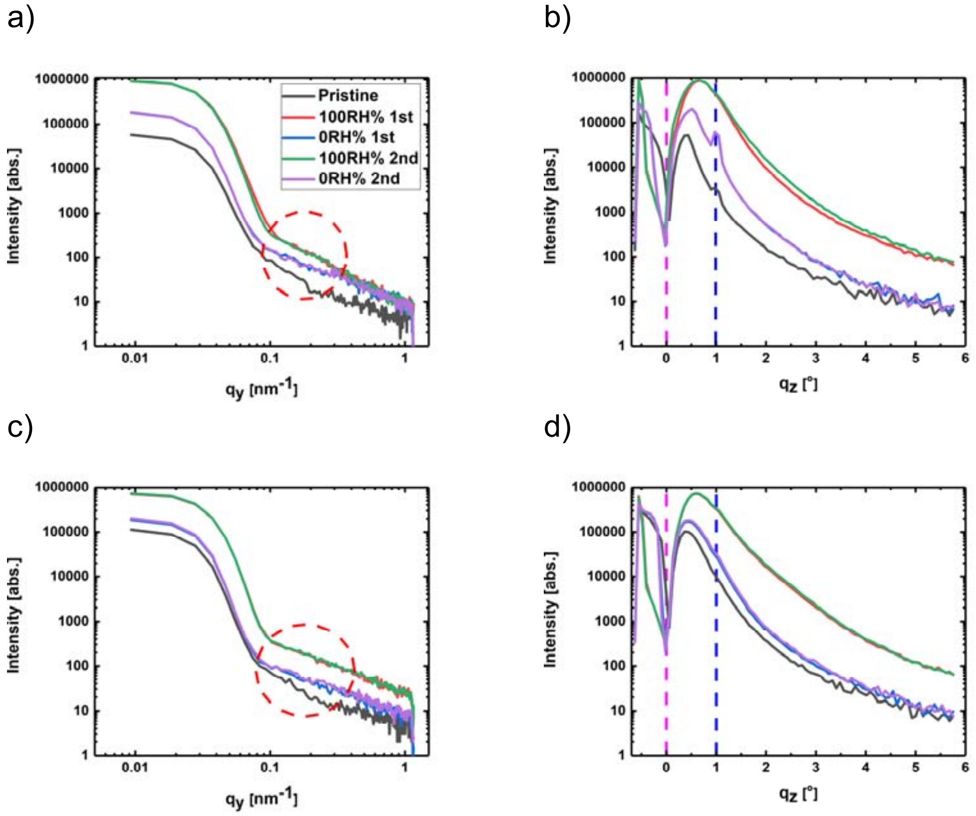

Figure 1 *Reduced one-dimensional scattering data for thin films humidification cycled from 0% RH to approximately 100% RH. a) Intensity distribution along q_y at the Yoneda region of CNF from a pure CNF thin film. The red-dashed circle marks the change from cylindrical to spherical form factor. b) Intensity distribution along q_z at q_y = 0 nm^{-1} for the CNF thin film. The purple dashed line marks the horizon, the blue dashed line marks the specular reflection. c) Intensity distribution along q_y at the Yoneda region of PEDOT:PSS from a CNF/PEDOT:PSS thin film composite. The red-dashed line marks the region where a*

change from cylindrical to spherical appearance of the scattering centers is expected. d) Intensity distribution along q_z at $q_y = 0\ nm^{-1}$ for the CNF/PEDOT:PSS thin film composite.*

In total, 9 *ex situ* samples and 2 *in situ* humidity cycled samples were measured. Figure 1 a,c) shows the one-dimensional integration along the Yoneda region of CNF in a) and PEDOT:PSS in c). It is clearly visible that the cyclic humidification is reversible changing the nanoscale structure within the film. From previous GISANS measurements we know that CNF thin films as shown in Figure 1 a,b) change their scattering features from cylindrical structures to spherical structures, from the dry to the wet state respectively, which might be attributed to voids or coiling. This feature is present around $q_y = 0.2\ nm^{-1}$ in the wet state. The measurements here prove that this behavior is also present when cycled two times. After drying, we observe that the scattered intensity is slightly increased in comparison to the pristine samples. This is attributed to the deuteration of the CNF, where *H* atoms are replaced by *D* atoms. Figure 1 c,d) shows the scattering for a CNF/PEDOT:PSS thin film composite and its change under humidification. It seems that we do not have here any coiling, which should be visible around $q_y = 0.2\ nm^{-1}$; hence, morphological changes within the film are inhibited, which might be due to the fact that the polymer completely filled any porous structure within the thin film. The slope in q_z-direction is changing when humidified, which could be due to a selective swelling of the PEDOT:PSS component within the film, as the pure CNF thin film in Figure 1 a) does not show this behavior. The humidification cycles are presented in Figure 2.

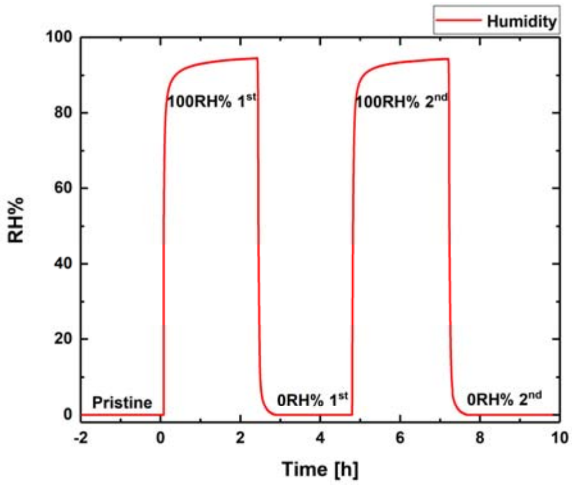

***Figure 2** Humidification curve. The red line shows the humidification along the cycle. The samples above were measured at the desired humidity for 2h and during humification and during drying the samples were additionally measured in 1 min steps.*

To conclude, we could resolve morphological rearrangement within the CNF thin film from cylindrical to spherical structures. We showed that this behavior is reversible over at least two cycles. The CNF/PEDOT:PSS composite does show not any structural rearrangement, but rather a swelling process. To foster these statements further neutron reflectometry (NR) data would be highly beneficial as they would allow us to state if the polymer may be only assembled at the substrate/sample or sample/air interface rather than blended in the full film. Additionally, using NR we could confirm if the polymer or the CNF parts begin to swell. In our labs we will correlate this data with conductive measurements to understand the nanoscale impact to the meso- or macroscale in a device application.