Composite cellulose-polymer paper for large-scale water detoxification
(svensk titel: **Papperskompositmaterial för storskalig rening av vatten från toxiska ämnen)**
Prof. Igor Zozoulenko
Laboratory for Organic Electronics, Linköping University and
Wallenberg Wood Science Center, Linköping University

I. The first aim of the present project was to perform multi-scale theoretical modelling of a composite paper made of cellulose and conducting polymer PEDOT to answer fundamental questions concerning its morphology and ion diffusion. To address this aim we started with the investigation of the morphology of the conductive polymer PEDOT. One of the main features of PEDOT:PSS morphology is its two-phase granular structure with PEDOT-rich and PSS-rich regions. Current experimental literature provides rather vague, and in many cases conflicting conclusions concerning precise nature of PEDOT- and PSS-rich domains, as well as their chemical composition and structure. Another question of the great interest, which has never been addressed theoretically is PEDOT:PSS water intake, swelling, and ion intake in cyclic voltammetry conditions. In the present study we perform the MD simulations in the MARTINI coarse grained model to answer the above questions.
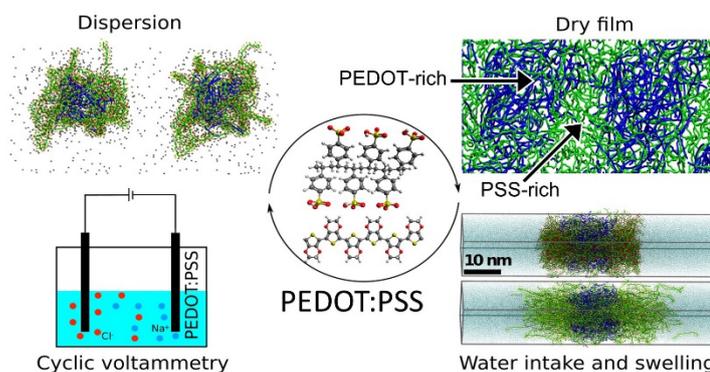
Our main findings and conclusions can be summarized as follows,

• Our MD simulations unravel the structure of PEDOT-rich and PSS-rich regions, and we show how PEDOT-rich and PSS-rich regions are formed from the solution phase during drying process. We demonstrate that PEDOT:PSS is an essentially a three component system, consisting of positively charged PEDOT chains, PSS chains with mostly deprotonated sulfonate groups, and protonated PSS chains. PEDOT-rich regions are predominantly composed of PEDOT and deprotonated PSS chains, whereas PSS-rich regions are composed of protonated PSS chains.

• When immersed in water, PEDOT:PSS film swells of about ≈ 60% and absorbs water. Our calculations unambiguously relate the swelling of PEDOT:PSS film to deprotonation of the sulfonate groups in the PSS-rich regions. It is mostly PSS-rich region that expands during swelling, while the PEDOT-rich region remains rather unchanged. Also, the water density is significantly higher in PSS-rich regions than in PEDOT-rich regions.

• We study water and ion intake during cyclic voltammetry conditions, and we demonstrate that swelling of the film is rather insignificant. We show that during CV experiment, each counterions brings on overage ≈ 4 water molecules into the polymer region. The PEDOT-rich regions exhibit a "breathing" behavior when PSS and PEDOT chains are repeatedly repealed apart and then brought closer together during each CV cycle.

• We unravel the evolution of the morphology of PEDOT:PSS film during water evaporation, focusing, in particular, on π-π stacking formation in PEDOT and PSS. .

Our simulations of swelling, CV experiments and π-π stacking formation in PEDOT and PSS match well the experimental results. We believe that our theoretical studies provide the essential insight into

one of the most important morphological aspects of one of the most important polymers for organic electronics, that have not been available before.

The result of this study was published in one of the leading journal of the American Chemical Society, Macromolecules.[1]

II. Having understood the morphology of PEDOT, we proceed to understanding of the structure of cellulose and interaction between the cellulose nanocrystallites (CNC) and their formation in bundles. We studied the inter-CNC interaction and self-assembly of native and modified CNCs in bundle using molecular dynamics simulation. We considered two types of surface modifications, sulfated CNCs (SCNCs) and TEMPO-oxidized CNCs (TCNCs) in the presence of two types of counterions, Na^+ and Ca^{2+} in the solution. The inter-CNC interaction was analyzed by calculating the potential of mean force (PMF) using the umbrella sampling method. We found that the strength of interaction for sulfated and TEMPO oxidized surfaces are reduced as compared to the native CNC. The type of counterion also affects the PMF: The interaction between CNC with Ca^{2+} counterion is stronger as compared to Na^+, which is corroborated with the experimental rheological measurements. We found a significant difference in the PMF between the two CNCs for different surface combinations. Also, the pushing and pulling umbrella simulations give different PMF profiles, where the first minina in the PMF curve is absent in pushing process as compared to the pulling. This implies that the water in between the CNCs acts as an energy barrier.
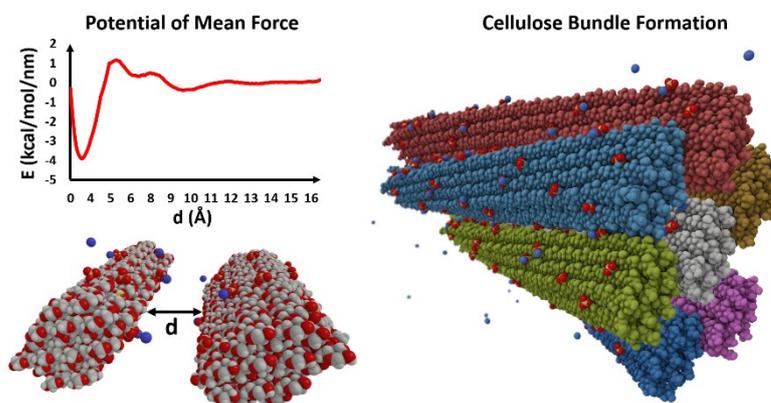
Next, we studied the self-assembly of the CNCs in the bundle and analyzed various properties such as degree of twist, inter-CNC distance, content of the bound water and the strength of inter-CNC interaction. The twist of the individual CNCs increases with surface modification. The twist of SCNC-Na^+ is higher compared to SCNC-Ca^{2+} followed by NCNC, which is in agreement with previous experimental measurements. The inter-CNC gap between the CNCs increases as we modify the surface of CNC which is further complemented by the PMF results. The amount of the bound water inside the CNCs also increases as we modify the surface of the CNCs. This is in close agreement with the experimental measurements of swelling of CNCs in the presence of surface charge and counterions. We calculated the van der Waals and Coulombic interaction between different CNCs, which proves a further understanding of the interaction between CNCs. For NCNC the hydrophobic surface, i.e. (100)/(100), the van der Waals interaction is dominant as compared to the Coulomb interaction. This is in contrast to the hydrophilic surfaces (110)/(110) or (1-10)/(1-10) where the Coulombic interaction is dominant. For the modified CNC surfaces van der Waals interaction vanishes whereas the Coulombic interaction remains the major driving force in CNCs aggregation.

The calculations performed in the present study help to shed a light on the key factors at play in the aggregation and self-assembly processes of native and modified cellulose nanocrystals. Also, calculations of the PMF for different surface modifications and different counterions will be instrumental for the development of a supra coarse-grained molecular dynamics models for modified cellulose, spanning into the micrometer and microsecond scales.

The result of this study was published in one of the leading journal of the American Chemical Society, Biomacromolecules.[2]

III. Water and moisture uptake in cellulose nanofibers were investigated. We show that anisotropic foams based on aligned cellulose nanofibrils are superinsulating also at high relative humidity (RH). Thermal conductivity measurements and non-equilibrium molecular dynamic simulations show that the moisture induced swelling and increase of the inter-fibrillar distance results in a reduction of the thermal boundary conductance that exceeds the thermal conductivity increase due to water uptake up to 75% RH. Phonon engineering by moisture could be used to tailor the heat transfer properties of hygroscopic nanofibrillar materials.[3] We also performed a combination of hybrid Grand Canonical Monte Carlo and Molecular Dynamics simulations and experimental measurements to investigate the moisture uptake within nanocellulose foams. To explore the effect of surface modification on moisture uptake we used two types of celluloses, namely TEMPO-oxidized cellulose nanofibrils and carboxymethylated cellulose nanofibrils. We find that the moisture uptake in both the cellulose nanomaterials increases with increasing relative humidity (RH) and decreases with increasing temperature, which is explained using the basic thermodynamic principles. The measured and calculated moisture uptake in amorphous cellulose (for a given RH or temperature) is higher as compared to crystalline cellulose with TEMPO- and CM-modified surfaces. The high water uptake of amorphous cellulose films is related to the formation of water-filled pores with increasing RH. The microscopic insight of water uptake in nanocellulose provided in this study can assist the design and fabrication of high-performance cellulose materials with improved properties for thermal insulation in humid climates or packaging of water sensitive goods.[4]
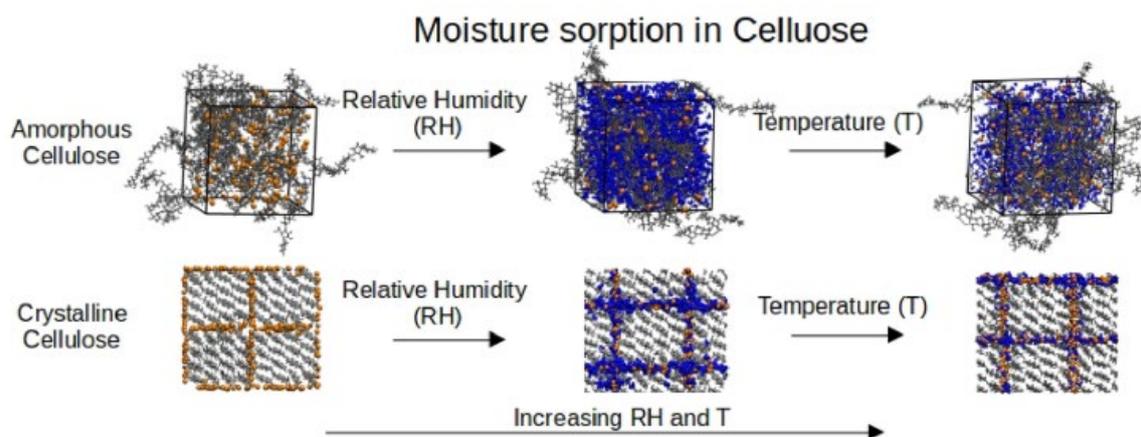
IV. Having understood the interaction between cellulose fibers, we computationally assemble the cellulose fibers into a gelated state to investigate its morphological properties. So far, because of the large sizes of such the systems, it was not possible to study them using conventional molecular dynamics simulations. Therefore, we developed a novel description of the systems at hand based on the MARTINI coarse-grained force field, which makes it possible to describe the systems of the realistic dimensions. Figure below illustrates the evolution of the morphology of the surface-modified nanocellulose fibers when electrolyte concentration is varied. Currently, we are finalizing the manuscript, which will be submitted soon.[5]

(a) Pristine cellulose **(b)** NaCl 0mM **(c)** NaCl 60mM

(d) NaCl 100mM **(e)** NaCl 200mM **(f)** NaCl 600mM
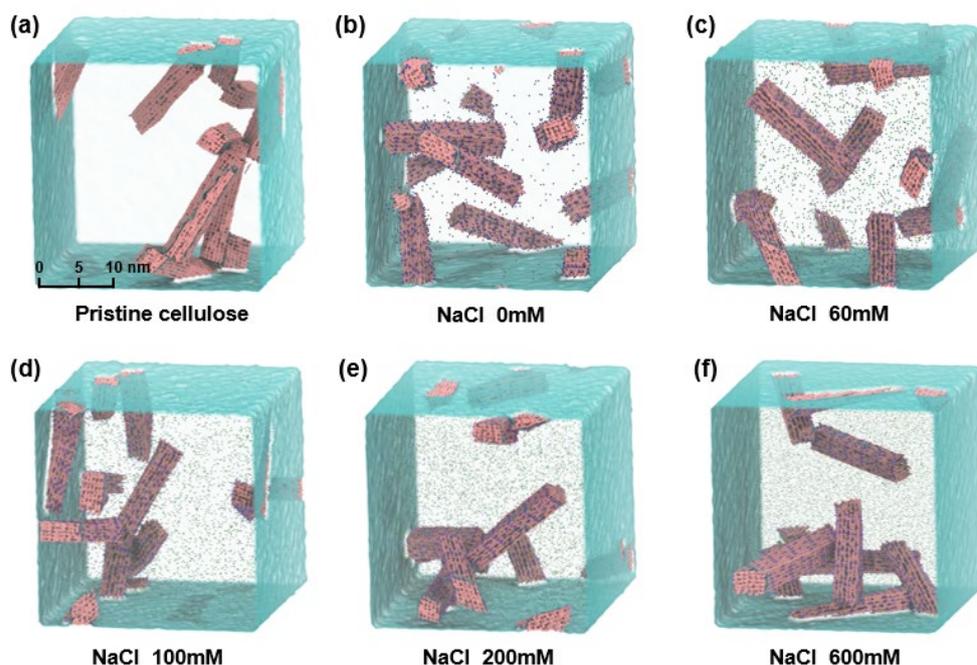
Published papers and papers in preparation.

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