# Experimental report

16/01/2024

**Proposal:** **9-11-2126** **Council:** 4/2023

**Title:** QENS study on the water and polymer side chain dynamics in PEDOT:PSS/cellulose nanofibril films

**Research area:** Soft condensed matter

**This proposal is a new proposal**


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**Local contacts:** Jacques OLLIVIER


**Samples:** PEDOT:PSS/CNF film on Si substrate

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN5 | 5 | 3 | 15/09/2023 | 18/09/2023 |


**Abstract:**

PEDOT:PSS/CNF films is a conductive and mechanical stable polymer composite system, which can be used in organic electronic devices such as solar cells and batteries. For a fundamental understanding of long-term effects such as the degradation based on humidity, the structural and dynamical properties have to be investigated. While we already analyzed the nanostructure of PEDOT:PSS/CNF films, we now want to observe the dynamics properties upon overall two humidity-induced swelling and drying processes. One cycle consists of a swelling (5, 50, and 90% relative humidity) and drying process (90, 50, and 5% relative humidity). In detail, we want to understand the role of water, its motion through the PEDOT:PSS/CNF film, and if there are different types of water, i.e., hydration and `bulk¿ water as this is highly important for film stability. In addition, we plan to investigate fast side chain polymer dynamics and how they affect the structure formation during the swelling and drying processes. To decouple polymer from water dynamics, the swelling will be induced with H2O and D2O, respectively, in two individual cyclic swelling/drying experiments.

**Scientific report for proposal 9-11-2126: QENS study on the water and polymer side chain dynamics in PEDOT:PSS/cellulose nanofibril films**

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PEDOT:PSS/CNF is a conductive and mechanical stable polymer composite system, which can be used in organic electronic devices for example in solar cells and batteries. For a fundamental understanding of long-term effects such as the degradation based on humidity, the structural and dynamical properties have to be investigated. While we already analyzed the nanostructure of PEDOT:PSS/CNF films, we now want to focus on the dynamics properties. During the performed experiment at IN5, we carried out QENS measurements upon overall three humidity-induced swelling and drying processes. One cycle consists of a swelling (final relative humidity of roughly 90%) and drying process (roughly 5% relative humidity). In detail, we wanted to understand the role of water, its motion through the PEDOT:PSS/CNF film, and if there are different types of water, i.e., hydration and 'bulk' water as this is highly important for film stability. In addition, we plan to investigate fast side chain polymer dynamics and how they affect the structure formation during the swelling and drying processes. To decouple polymer from water dynamics, two individual cyclic swelling/drying experiments have been performed, in which the swelling was induced with $H_2O$ and $D_2O$, respectively.

For this experiment, the PEDOT:PSS/CNF nanocomposite films were spray-coated onto Si wafers. The spray-coating deposition technique allowed for precise control over the film thickness. For our measurements, we chose a film thickness of 15 µm, which is a compromise between still observing thin-film effects and having sufficient scattering volume. After spray-deposition, the films can be removed from the Si substrate. The free-standing and flexible films can be rolled and mounted in a standard powder cell (provided by IN5). Thereby, the scattering volume can be increased significantly. In addition, the design of the powder cell minimizes the neutron pathway through the saturated vapor, and thus, scattering intensity from atmospheric $H_2O$ molecules is minimized. Aluminum foil was used to immobilize the PEDOT:PSS/CNF films at a fixed position within the cell. Figure 1a shows the free-standing films after separating them from the Si substrate, while Figure 1b schematically displays the mounting of the films within the sample cell. For drying, the films within the cell were exposed for approximately 15 min to a nitrogen flow. One learning from this beamtime was that drying should better be done in an oven, which is set to slightly above 100 °C to improve reproducibility of the drying (unfortunately, for this beamtime, no oven was available). Swelling was induced by adding 20 µL of water ($H_2O$ or $D_2O$) into the powder cell. The dry films were measured directly after drying, while the humidified films were measured after an equilibration time of 3 h.

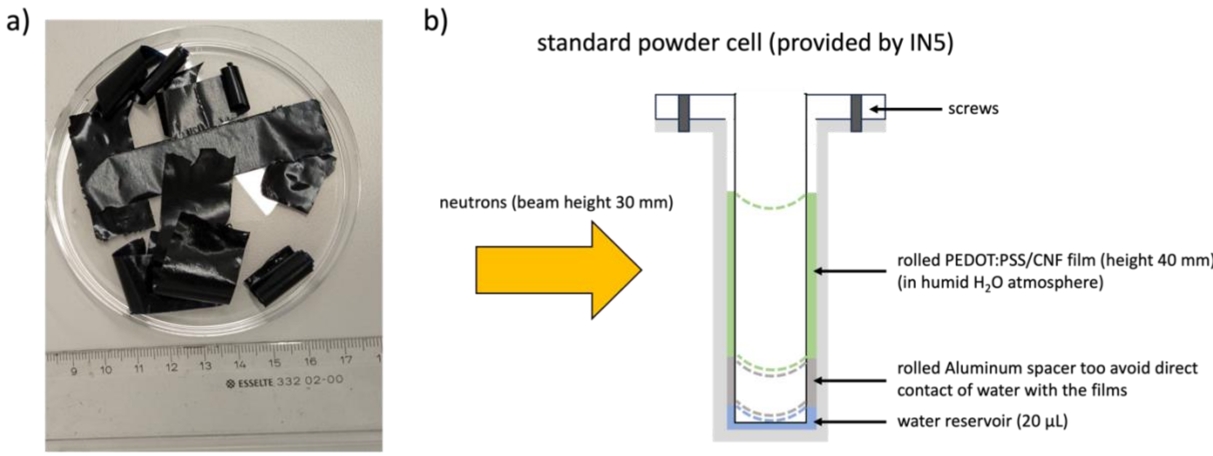


Figure 1: a) Image of freestanding spray-coated PEDOT:PSS/CNF films. b) Layout of a standard powder cell of the IN5 instrument with the loaded PEDOT:PSS/CNF films inside. Added water inside the powder cell provides a saturated water vapor atmosphere (either of $H_2O$ or $D_2O$). An aluminum spacer is used to prevent direct contact of the PEDOT:PSS/CNF films and water.

QENS experiments were performed at a wavelength of 5 Å (corresponds to an $E_i$ of 3.272 meV) with a total measurement time of 2.5 h per measurement. The temperature was set to 293 K. In total, we performed three cycles of swelling and drying with $H_2O$ and $D_2O$, respectively (overall six swelling/drying cycles), to obtain and decouple water and (fast) polymer dynamics. A vanadium standard and empty cell measurement [empty dry and humid ($H_2O$ and $D_2O$)] have been performed for calibration purposes. Figure 2 shows the resulting S(Q, ω) curves of the PEDOT:PSS/CNF films for the drying and swelling cycles in $H_2O$ (Figure 2a) and $D_2O$ (Figure 2b), measured at Q = 1.5 Å.

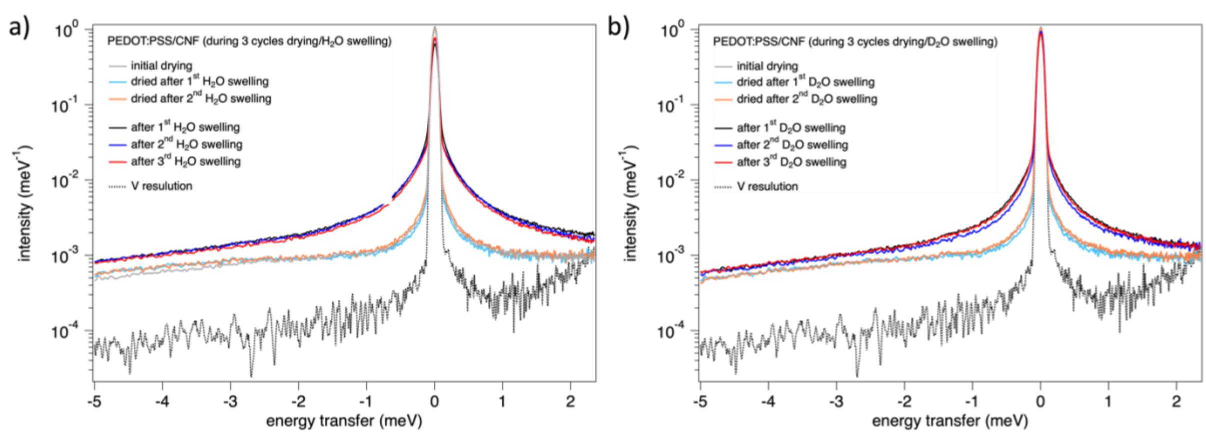


Figure 2: S(Q,w) curves (at Q = 1.5 Å) of the PEDOT:PSS/CNF films for the individual drying and swelling cycles in (a) $H_2O$ and (b) $D_2O$ vapor, respectively.

From a first, preliminary analysis of the data, one can already see that the three drying and swelling cycles in both $H_2O$ and $D_2O$ vapor are relatively reproducible. Furthermore, the S(Q,w) of the swollen PEDOT:PSS/CNF films in $H_2O$ vapor feature a higher intensity around the elastic line as compared to the swollen films in $D_2O$ vapor. This indicates, more hydrogen movement within this energy range, most probably originating from the $H_2O$ water molecules within the PEDOT:PSS/CNF films. For a more detailed data analysis, we plan to transform the dynamic structure factors $S(q, \Delta E)$ into the imaginary part of the dynamic susceptibility $\chi''(q,v)$ according to established protocols [1]. With this approach different contributions to the scattering signal, which originate from different types of water can be analyzed at different thin film states. Thus, release and adsorption of water molecules by the PEDOT:PSS/CNF films can be correlated with structural properties. Furthermore, the QENS study will provide valuable (dynamical) data that can be used as input for MD (or other) simulations.

As a final remark, we want to highlight that besides the shown measurements at 293 K, also temperature dependent QENS experiments during some of the $H_2O$ swelling processes, have been performed. Since we plan to first focus on the measurements at constant temperature (see Figure 2), these temperature-dependent measurements are not shown in this report.

## References

[1] Niebuur, B.-J.; Lohstroh, W.; Ko, C.-H.; Appavou, M.-S.; Schulte, A.; Papadakis, C. M. Pressure Dependence of Water Dynamics in Concentrated Aqueous Poly(N-Isopropylacrylamide) Solutions with a Methanol Cosolvent. *Macromolecules* **2021**, *54* (9), 4387–4400. https://doi.org/10.1021/acs.macromol.1c00111.