Electronic Supplementary Information

For *Electroactive nanofibrillated cellulose aerogel composites with tunable structural and electrochemical properties*

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S1. Cellulose degradation and viscosity measurements

Two different experiments were performed to determine if i) 0.5 M HCl or ii) a combination of 0.5 M HCl and 0.23 M FeCl$_3$ degrades the cellulose nanofibers. In these experiments, 100 mg of nanocellulose in the form of 0.05 wt% cellulose hydrogel was allowed to react with the acid (i) for 15 minutes and 30 minutes, and the acid plus oxidant (ii) for 15 minutes, 30 minutes and 16 hours. Both the acid and oxidant concentrations used as well as the time scale of the experiments were chosen based on the experimental conditions employed in the composite synthesis.

In the first experiment, in which two samples were immersed for 15 and 30 minutes, respectively, in 0.5 M HCl, the samples were subsequently neutralized with NaOH to pH 7. The samples were then washed with water, using a Büchner funnel, until the filtrate conductivity was equal to that of deionized water. Immersed, neutralized and washed gels were then freeze dried along with a control sample treated with 0.5 M NaCl. The treated cellulose fibers were thereafter dissolved in cupriethylenediamine (CED) and the limiting viscosity number of the CED cellulose solution was determined according to ISO standard 5351.[S1] No significant change in the limiting viscosity was found between the two acid treated samples, and only a minor decrease in the limiting viscosity was found for these samples compared to the control sample treated with equimolar amounts of NaCl, see Experiment I in Table S1.

In the second experiment, three samples were immersed for 15 minutes, 30 minutes and 16 hours, respectively, in 0.5 M of HCl together with 0.23 M FeCl$_3$. The samples were thereafter washed with 0.1 M HCl to remove the iron salt. It should be noted that this mild acid wash was completed within 10 minutes. The samples were subsequently further washed with deionized water, freeze dried and analyzed in the same way as the samples in Experiment I. For comparison, two control samples, taken before and after the ultrasonication treatment used to prepare the hydrogel, were added to the study. As seen in Experiment II in Table S1, the two control experiments with non-treated and ultrasonicated cellulose fibers showed that the ultrasonication treatment, as expected, had a degrading effect on the fibers. A statistically significant decrease in the limiting viscosity was likewise observed after the acid and oxidant treatments, as compared to the two control experiments, indicating that the cellulose fibers are degraded due to the addition of the oxidant, FeCl$_3$. However, a similar decrease in the limiting viscosity was seen irrespective of the duration of the treatment, suggesting a rather fast degradation process. This further suggests that the accessible sites (the amorphous regions on the cellulose nanofibers) are degraded quickly while the remaining crystalline regions are more resistant to degradation. This is in agreement with a rapid degradation to the 'leveling off' degree of polymerization and slow subsequent degradation generally found for cellulose subjected to acid hydrolysis.[S2] On the time scale of the composite polymerization, i.e. 30 minutes, a small degradation of the fibers, based on the figures in Table S1, could therefore occur. The extent of the degradation is however likely to be even lower in the composite synthesis since the polymerization of pyrrole onto the fibers is rapid and should give rise to a protecting polypyrrole (PPy) layer as PPy is known to be insoluble in most solvents.[S3] This indicates that the conditions chosen for the polymerization of PPy cellulose composites should not be critically detrimental to the cellulose nanofibers.

Table S1. Summary of cellulose degradation experiments, the limiting viscosity numbers are expressed as mean values with standard deviations.

Experiment	Sample	Limiting viscosity number (ml/g)	Number of measurements, n
I	Control (NaCl)	169 ± 1	3
I	0.5 M HCl 15 min	164 ± 1	3
I	0.5 M HCl 30 min	163 ± 0	3
II	Control (direct from batch)	198 ± 1	5
II	Control (ultrasonicated)	176 ± 4	6
II	HCl + FeCl3 15 minutes	155 ± 1	4
II	HCl + FeCl3 30 minutes	150 ± 2	5
II	HCl + FeCl3 16 hours	153 ± 1	4

S2. CHN-analysis and determination of PPy content and theoretical charge capacities

Elemental (CHN) analyses were performed (by Eurofins Mikrokemi, Uppsala, Sweden) to determine the amount of nitrogen, and consequently the amount of polypyrrole, in the composites. Prior to the analysis the samples were vacuum oven dried over night at 70 °C. The results from the nitrogen determinations, N_{raw}, are shown in Table S2. Also shown in the table are the calculated PPy contents in mol/g and weight percentages, as well as theoretical charge capacities estimated by assuming a PPy doping level of 25% [S4] after the synthesis for all samples. The values are expressed as the mean ± the pooled standard deviation.

Table S2. Nitrogen content and the derived PPy content and theoretical charge capacity.

Sample	Number of CHN analyses, n	N_{raw} (wt%)	PPy (mmol/g)	PPy (wt%)	Theoretical charge capacity (C/g)
Comp_Air	2	13.5 ± 0.2	9.6 ± 0.2	62.5 ± 1.1	232 ± 4
Comp_Water	3	12.6 ± 0.2	9.0 ± 0.2	58.4 ± 1.1	216 ± 4
Comp_t-But	3	14.3 ± 0.2	10.2 ± 0.2	66.4 ± 1.1	246 ± 4
Comp_CO_2	2	14.6 ± 0.2	10.4 ± 0.2	67.8 ± 1.1	251 ± 4

There are statistically significant differences between all samples except for between Comp_t-But and Comp_CO_2. However, although the samples were dried prior to CHN-analysis, varying amounts of solvent can be expected to remain in the samples. To allow a proper comparison of the nitrogen contents, and thus the PPy content and the theoretical charge capacities, the weight contributed by the remaining solvents should be compensated for. This was done as described below in sections S4 and S5.

S3. Cellulose content estimation

The cellulose content was estimated by drying a complete synthesis batch for 11 days in the ambient and thereafter three days in a desiccator with P_2O_5 followed by weighing. Since 100 mg of cellulose raw material was added in the synthesis and the composite weight after drying was found to be 1233 mg, a cellulose content of 8.1 wt% was obtained. However, since it was suspected that this drying did not result in complete removal of the water from the sample, the weight contribution of the remaining water was compensated for as described below sections S4 and S5.

S4. Determination of remaining solvents and impurities in the samples after drying

To determine the remaining amount of solvent in the samples after their respective additional drying procedures, Thermo Gravimetric Analysis (TGA) was employed, which could also indicate the weight contribution of possible impurities. The TGA analyses were performed with a Mettler Toledo TGA/SDTA851 instrument. After the additional drying at 70 °C in a vacuum oven overnight (for nitrogen content determination) or in a desiccator with P_2O_5 for three days (for cellulose content estimation), the samples (weighing ~3 mg) were placed in an inert ceramic crucible and heated from 25 to 800 °C at a heating rate of 5 °C/min. As a control, a Comp_Water sample from another batch was analyzed in the same way without the additional drying. Comp_Water from this batch contained clearly visible (by eye) impurities and is henceforth denoted Comp_Water_Impure. The resulting wt% vs. temperature curves for the composites are shown in Fig. S1a and the corresponding weight change vs. temperature curves are seen in Fig. S1b, in which Comp_Air_P_2O_5 refers to the Comp_Air sample dried during three days in a desiccator.
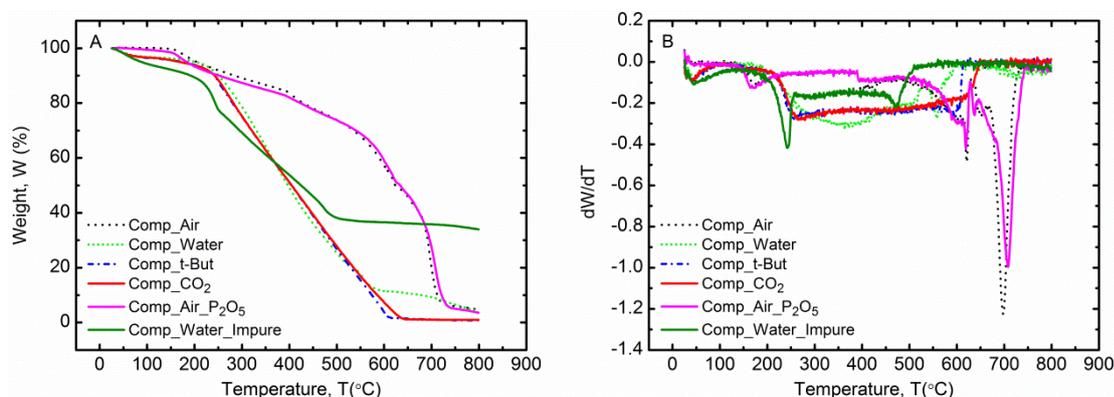

Figure S1. Weight (a) and weight change (b) as a function of temperature.

From Fig. S1, it can be concluded that the main decomposition of both Comp_Air and Comp_Air_P_2O_5 is slower and requires higher temperatures compared to the decomposition of the Comp_Water, Comp_t-But and Comp_CO_2 samples due to their more compact structure. For the latter samples, the initial process of solvent evaporation takes place from room temperature up to around 200 °C. The combustion of the composite material itself follows at temperatures greater than 200 °C. In contrast, at ~200 °C a transient combustion process is ongoing in both Comp_Air samples, which levels off at around 250 °C, as can be seen in Fig. S1b. Given that the main combustion process of Comp_Air is slower compared to the other samples and that the combustion process in Comp_Air up to 250 °C is transient, it is reasonable to consider the weight loss up to 250 °C in these samples to be solvent evaporation. Further, a closed (low porosity) structure is expected to trap solvents more effectively and thus inhibit the solvent evaporation. The corresponding temperature for the three porous samples is taken to be 180 °C (slightly below the temperature at which the main decomposition starts, to not overestimate the solvent content).

Additionally, at around 600 °C the combustion of Comp_Water deviates from the two other porous samples, indicating impurities corresponding to 11.2 wt%. This is supported by the TGA analysis of Comp_Water_Impure which contained clearly visible impurities on its surface (in contrast to Comp_Water) and thus contained a higher amount of impurities compared to Comp_Water. The combustion of Comp_Water_Impure deviates greatly from the other porous samples, starting at around 500 °C which corresponds to approximately 35-40 wt%. The impurity is undoubtedly a result of a reaction between the sample (containing an acidic aqueous solution) and the aluminum cup used as container during the freeze drying,

resulting in aluminum chloride precipitated on the sample. In Comp_Water_Impure the sample was in direct contact with the freeze drying cup prior to and during the freeze drying, while the bottom of the aluminum cup was covered with a piece of parafilm to avoid a direct contact between the cup and the sample Comp_Water. Clearly, in future freeze drying experiments employing acidic aqueous solvents, further measures will have to be taken to prevent the sample of coming in contact with the freeze drying cup.

The change in decomposition behavior starting around 700 °C in both Comp_Air samples could also indicate impurities. However, since the decomposition process differs greatly from the other samples and as there is no reason as to why impurities would be present in these samples, this behavior cannot be ascribed to impurities. Comp_t-But and Comp_CO_2 samples did not appear to contain significant amounts of impurities. Table S3 summarizes, in weight percentage, the amount of solvent and impurities in the samples also analyzed with CHN-analysis.

Table S3. Solvent and impurity content in composites after drying in 70 °C and vacuum overnight as determined from TGA.

Sample	Solvent wt%	Impurity wt%
Comp_Air	8.0	0
Comp_Water	4.2	11.2
Comp_t-But	5.3	0
Comp_CO_2	5.4	0

The amount of solvent remaining in the Comp_Air sample after drying in a desiccator with P_2O_5 for three days (Comp_Air_P_2O_5 in Fig. S1) was found to be 9.9 wt%.

S5. Determination of PPy content, theoretical charge capacities and cellulose content after compensation for solvents and impurities

To compensate for the varying solvent and impurity contents in the samples, the compensated nitrogen contents, N_{comp}, were calculated from N_{raw} as shown in equation S1.

$$N_{comp} = \frac{N_{raw}}{(100\ wt\% - Solvent\ wt\% - Impurity\ wt\%)} * 100\ wt\% \qquad \text{(eq. S1)}$$

Based on N_{comp}, the PPy contents in mol/g composite and in weight percentages were calculated and the theoretical charge capacities were again estimated by assuming a PPy doping level of 25 %. The results of the calculations are summarized in Table S4 as the mean ± the pooled standard deviation and these are the values that are reported in the article.

Table S4. Nitrogen and PPy contents in the composites and the corresponding theoretical charge capacities.

Sample	Number of CHN analyses, n	N_{raw} (wt%)	N_{comp} (wt%)	PPy (mmol/g)	PPy (wt%)	Theoretical charge capacity (C/g)
Comp_Air	2	13.5 ± 0.2	14.6 ± 0.3	10.4 ± 0.2	67.9 ± 1.3	252 ± 5
Comp_Water	3	12.6 ± 0.2	14.9 ± 0.3	10.6 ± 0.2	69.0 ± 1.3	256 ± 5
Comp_t-But	3	14.3 ± 0.2	15.1 ± 0.3	10.8 ± 0.2	70.1 ± 1.3	260 ± 5
Comp_CO_2	2	14.6 ± 0.2	15.4 ± 0.3	11.0 ± 0.2	71.7 ± 1.3	266 ± 5

After correction for remaining solvent and impurities it can be concluded that there is no significant difference between the samples in terms of PPy content and, thus, the theoretical charge capacities.

The amount of solvent remaining in the Comp_Air sample after drying in a desiccator (Comp_Air_P_2O_5 in Fig. S1) was found to be 9.9 wt% in the TG-analysis. The weight of the entire sample was found to be 1233 mg after drying in the desiccator and the dry weight of the sample can thus be calculated to be 1111 mg. Given that 100 mg of cellulose raw material was added in the synthesis, the cellulose content corresponds to 9.0 wt%.

S6. Tensile tests

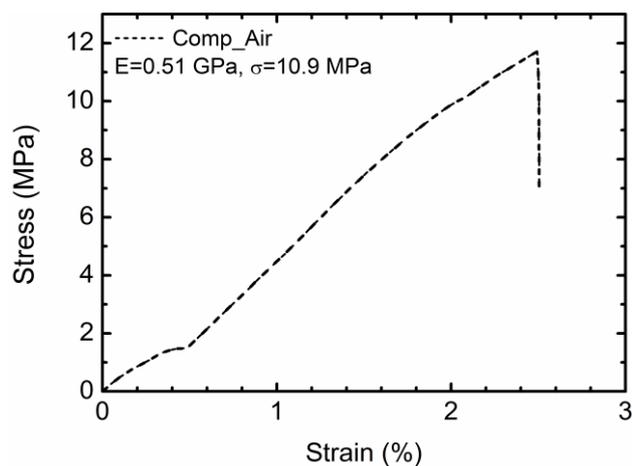A representative tensile stress strain curve for the Comp_Air sample is shown in Fig. S2.

Figure S2. Tensile stress strain curve for the Comp_Air sample.

S7. Cyclic Voltammograms

Cyclic voltammograms for the Comp_Air and Comp_CO_2 samples at scan rates of 10 and 25 mV/s are shown in Fig. S3a and b, respectively.
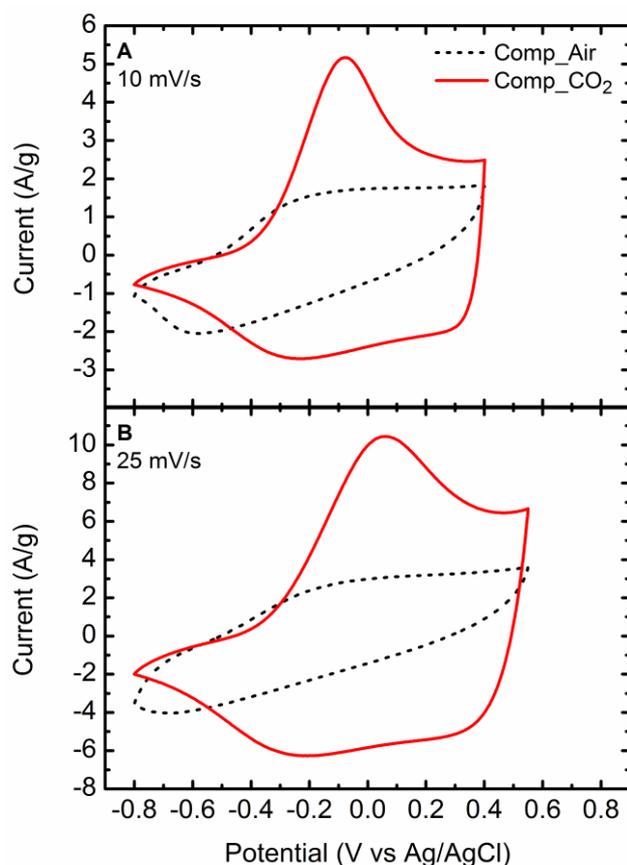

Figure S3. Cyclic voltammograms for the Comp_Air and Comp_CO_2 samples recorded at scan rates of 10 mV/s (a) and 25 mV/s (b).

Supporting References

(S1) Pulps - Determination of Limiting Viscosity Number in Cupri-Ethylenediamine (CED) Solution, International Organization for Standardization, ISO 5351:2010.

(S2) Habibi, Y.; Lucia, L. A.; Rojas, O. J., Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications. *Chem. Rev.* **2010,** 110, (6), 3479.

(S3) Skotheim, T. A.; Reynolds, J. R., *Conjugated Polymers - Theory, Synthesis, Properties and Characterization*. 3rd ed.; CRC Press: Boca Raton, 2007.

(S4) Katz, H. E.; Searson, P. C.; Poehler, T. O., Batteries and Charge Storage Devices Based on Electronically Conducting Polymers. *J. Mater. Res.* **2010,** 25, (8), 1561.