

## Supporting Information

**High specific capacitance supercapacitors from hierarchically organized all-cellulose composites**

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## 1. Experimental Section

### *Materials*

All solvents and chemicals were purchased from VWR chemicals, except acetonitrile (AN, 99.9%, Sigma-Aldrich), tetraethylammonium tetrafluoroborate salt (TEABF<sub>4</sub>, 99.0%, Alfa Aesar), Kynar 761, Super P carbon black (Timcal) and the glass microfiber filters (separator, from Whatman). Primary and secondary paper fines were separated from bleached, sulfite pulp (mixture of spruce and beech) using a purpose-built pressure screen with a mesh size of 100  $\mu\text{m}$ . More details on the used method for fines separation can be found in the literature.<sup>[4a, 10]</sup>

Cellulose nanocrystals (CNCs) were synthesized from cotton by acidic hydrolysis according to a literature procedure.<sup>[17]</sup> The average length of the CNCs was 150 nm as determined by atomic force microscopy (Figure S1, †ESI). For all-carbon composites, primary fines (4.1 wt.%) were mixed with CNCs (6.7 wt.%, ultrasonication), diluted to 1 wt.% and stirred overnight before freeze-drying. YP-80F was used as an industrial reference to benchmark the fines-based samples

### *Pre-carbonization and activation*

The same pre-carbonization step was performed for all samples. Samples are identified by P<sub>n</sub> when made from primary fines, S<sub>n</sub> when made from secondary fines, and M<sub>n</sub> when made from a mix of primary fines with CNCs. In a typical procedure, lyophilized primary (prepared from 100 g of a 4.1 wt.% suspension) and secondary (400 g of a 1 wt.% suspension) fines were heated in a tube furnace (TZF 15/610 from Carbolite) to 400 °C with a heating ramp of 6 °C·min<sup>-1</sup> under a steady stream of argon to prevent oxidation. After one hour at 400 °C, the furnace was cooled down to ambient temperature and pre-carbonized fines (PCF; P1) were obtained. Afterwards, the samples were subjected to activated carbonization procedures. Prior to heating to 800 °C, the PCF were mixed with NaHCO<sub>3</sub> (sample P2, 75 wt.% NaHCO<sub>3</sub> and 25 wt.% PCF), or KOH (P3, P4. S1 and S2, 75 wt.% KOH and 25 wt.% PCF). Samples P2 and P3 were homogenized using a grinder while sample P4 was prepared by placing KOH and the pre-

carbonized fines in the ceramic crucible used for carbonization. The mixed primary fines/CNC samples have been made by adding 50 (sample M1) and 90 wt.% CNCs (sample M2), respectively, to primary fines suspensions followed by lyophilization, precarbonization (400°C, one hour) and activation using KOH at 800°C as described above. For this, 50 and 90 wt.% CNCs, respectively, were added to primary fines suspensions followed by lyophilization, precarbonization (400°C, one hour) and activation using KOH at 800°C as described above.

All carbonization steps were done under inert argon atmosphere at 800 °C for two hours. After cooling to room temperature, the black powders were ground and neutralized using aqueous HCl, rinsed with copious amounts of water, and dried under vacuum at 40 °C.

#### *Specific surface area*

The obtained carbon samples were analyzed by N<sub>2</sub> isothermal adsorption (77 K) for its surface area and structures using an Autosorb-iQ, Anton Paar QuantaTec Inc, USA. Prior to the analysis, samples were degassed for 2 h at 350 °C. The Brunauer-Emmett-Teller (BET) method and non-local density functional theory (NLDFT) were used to calculate the specific surface area SBET and derive PSD, respectively.

#### *Low Voltage – Scanning Electron Microscopy*

The surface of the activated carbon was visualized by Low Voltage – Scanning Electron Microscopy (LV-SEM) using the Inlens detector (detection of secondary electrons) of the high resolution scanning electron microscope Zeiss Ultra 55 (Zeiss, Oberkochen, Germany). Lower beam energies (0.5-5 keV) offer the advantage of surface sensitive imaging due to a reduced interaction volume of the electrons in the sample compared to conventional electron beam energies. Additionally, it enables imaging bare surfaces of non-conducting samples, which may avoid potential artefacts coming from a coating (e.g., by C, Au, Pt, etc.) or from heating during preparation. In previous measurements, a beam energy of 0.650 keV had proved to be most successful for the investigation of cellulose specimens.<sup>[8]</sup>

*X-ray photoelectron spectroscopy*

XPS spectra were recorded on a Kratos Axis Supra photoelectron spectrometer employing a monochromated Al  $K_{\alpha}$  ( $h\nu = 1486.7$  eV, 10 mA emission) X-ray source, hybrid (magnetic/electrostatic) optics with a slot aperture and hemispherical analyzer. The analyzer was operated in fixed analyzer transmission (FAT) mode with survey scans taken with an energy of 160 eV. Samples were electrically isolated from the instrument. All scans were acquired under charge neutralization conditions using a low energy electron gun within the field of the magnetic lens. The resulting spectra were processed using CasaXPS software. Binding energy was referenced to  $sp^2$  carbon at 284.4 eV. Empirical relative sensitivity factors supplied by Kratos Analytical (Manchester, UK) were used for quantification. A uniform distribution of elements within the information depth was assumed during quantification and no correction for matrix effects was performed.

*Raman Spectroscopy*

Room temperature Raman spectra were collected using a Renishaw inVia microscope-coupled Raman spectrometer (with a 50x objective) which was calibrated using a silicon standard. Samples were excited with a Crystalaser CL-2000 diode laser (wavelength = 532 nm, incident power at the sample = 0.5 mW), and as-obtained spectra were deconvoluted into two Lorentzians.

*Cell preparation*

10.0 mg PTFE (from 60 wt.% suspension in  $H_2O$ ) were suspended in isopropanol, mixed with 10.0 mg SuperP, and 100 mg activated carbon and stirred for 3 hours at 60°C. The slurry was rolled into a free-standing film by a cylinder (diameter 2 cm) and dried overnight at 60°. Afterwards, round electrodes with 6 mm diameter were punched. The electrochemical double layer supercapacitor (EDLC) was assembled in a Swagelok-type 3-electrode test cell by using two symmetrical activated carbon electrodes and a partially delithiated  $Li_{1-x}FePO_4$  reference electrode in an argon filled glove box. Two separators soaked with electrolyte prevented contact

between the electrodes. 1 M TEABF<sub>4</sub> solution (150  $\mu$ l) in acetonitrile was used as the electrolyte. Long term cycling was performed in coin cells with the same assembly as described above using 80  $\mu$ l electrolyte.

### *Electrochemical tests*

Electrochemical measurements were carried out using a Biologic MPG-2 potentiostat (BioLogic, France). Electrochemical impedance spectroscopy was measured by applying an AC voltage with an amplitude of 5 mV and a frequency ranging from 10 mHz to 100 kHz.

Cyclic voltammetry and galvanostatic cycling experiments were conducted at ambient temperature. For cyclic voltammetry (CV) studies voltage limits of 0 to 2.3 V between working and counter electrode and scan rates from 2 to 100 mV·s<sup>-1</sup> were used. Galvanostatic charging-discharging (GCD) cycling was measured in the voltage range of 0 to 2.3 V and charge-discharge currents between ~0.1 and 8 A·g<sup>-1</sup>. Long-term GCD cycling was performed in the coin cell with 0.6 A·g<sup>-1</sup> over 4,000 cycles between 0 to 1.4 V.

## 2. Figures and Tables

**Table S1.** Single electrode mass for cyclovoltammetry and cyclopotentiometry. Deviations in the targeted value of active material (3.5 mg cm<sup>-2</sup>) are due to differences in processability of the materials, with M2 forming much denser layers.

Name	Single electrode mass [mg]	Active material [mg·cm <sup>-2</sup> ]	Current density at 3 mA [mA·g <sup>-1</sup> ]
P3	4.3	3.3	0.91
M1	4	3	0.98
M2	2.6	1.9	1.57
Reference (YP-80F)	3.78	2.9	1.03

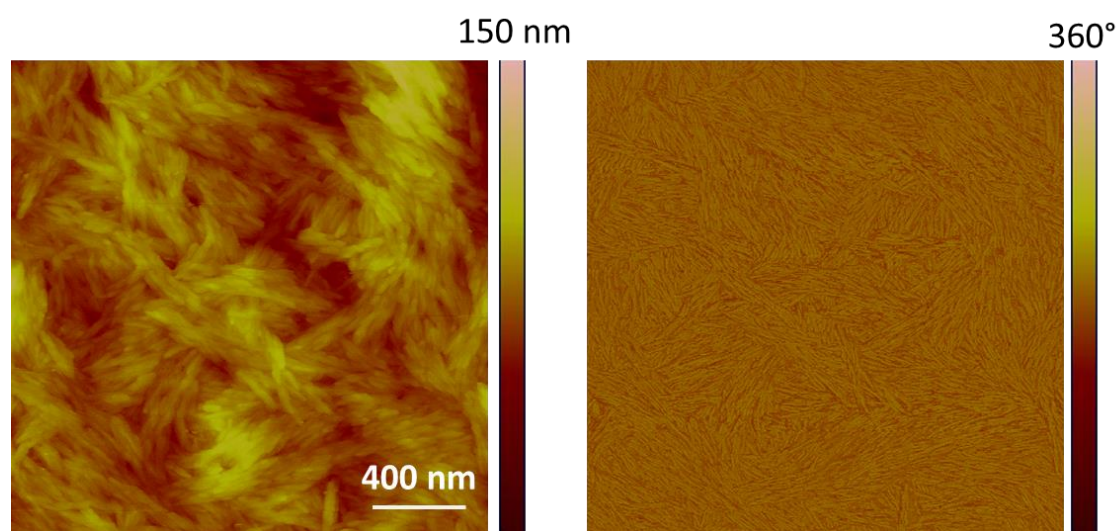
**Table S2.** Electrode mass and active material in coin cells for long term cycling (target value for single electrode mass: 3.5 mg cm<sup>-2</sup>), corresponding electrochemical data can be found in Figure 3c.

Name	Single electrode mass [mg]	Active material [mg·cm <sup>-2</sup> ]	Current density [mA·g <sup>-1</sup> ]
P3	3.2	2.2	0.63
M1	3.6	2.5	0.64
M2	3.1	2.3	0.67
Reference (YP-80F)	3.5	2.62	0.69

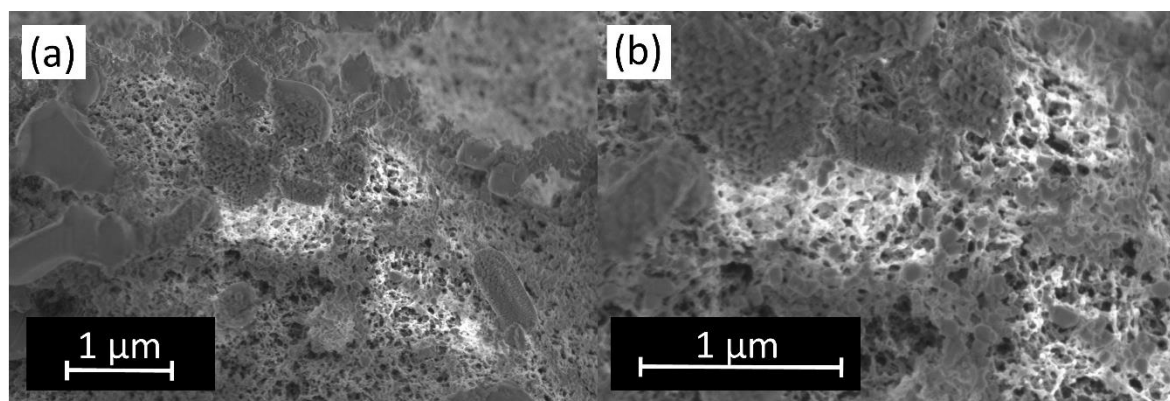
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Summary of the analysis of the bleached paper pulps towards impurities by ICPMS.

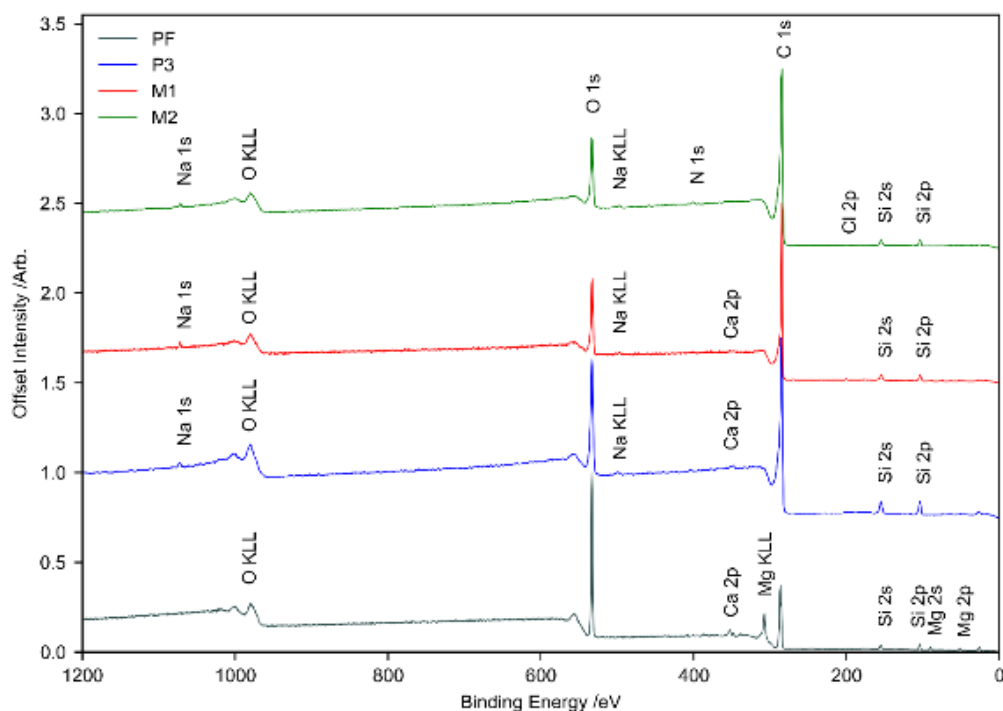
	S [g·kg <sup>-1</sup> ]	Na [g·kg <sup>-1</sup> ]	Ni [g·kg <sup>-1</sup> ]	Fe [g·kg <sup>-1</sup> ]	Zn [g·kg <sup>-1</sup> ]	Cu [g·kg <sup>-1</sup> ]
<b>Bleached sulfite pulp</b>	1.4 ± 0.1	0.42 ± 0.04	< 0.01	< 0.01	0.10 ± 0.01	< 0.01

**Figure S1.**

AFM topography ( $2 \times 2 \mu\text{m}^2$ ) and phase images of the cellulose nanocrystals (deposited on a silicon wafer) used for the preparation of samples M1 and M2.

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LVSEM images of pre-activated fines (P1) at different magnification.

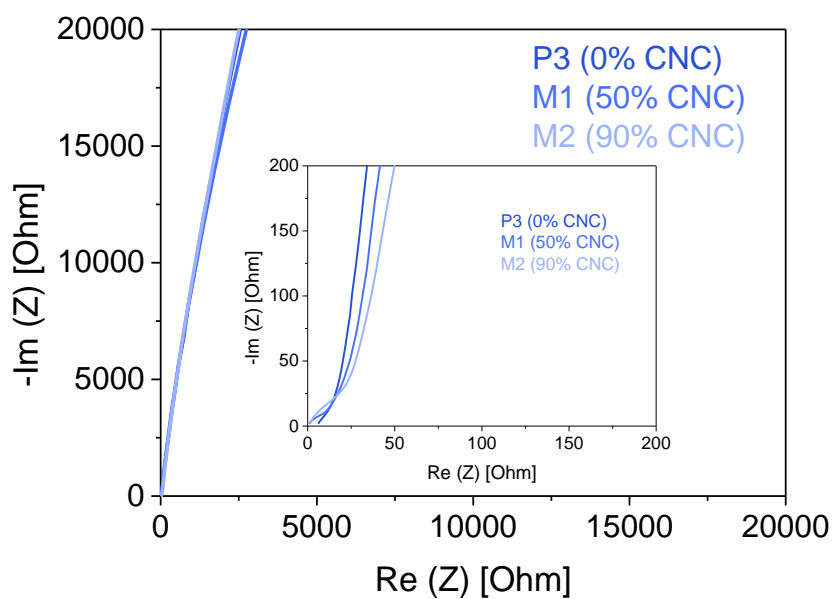


**Figure S3.**  
Comparison of the XPS survey scans of PF, P3, M1 and M2.

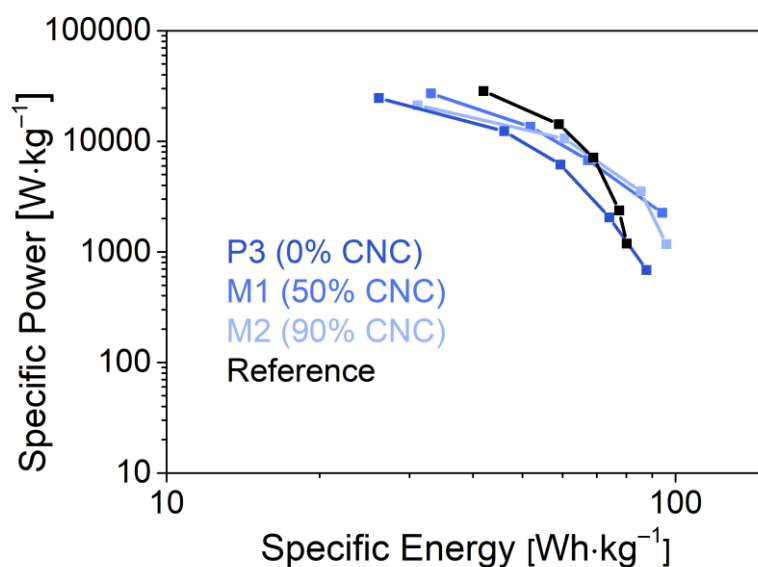
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XPS quantification data for primary fines and carbonized samples. Errors represent uncertainty associated with integration only.

	Na 1s /%	O 1s /%	N 1s /%	K 2s /%	Ca 2p /%	C 1s /%	Cl 2p /%	Si 2p /%	Mg 2s /%
PF	-	35.05 ± 0.33	-	0.46 ± 0.30	1.40 ± 0.09	56.91 ± 0.39	-	3.63 ±0.16	2.58 ± 0.16
P3	0.32 ± 0.06	15.47 ± 0.14	-	-	0.20 ± 0.04	79.98 ± 0.18	0.09 ± 0.02	3.94 ± 0.10	-
M1	0.24 ± 0.10	13.88 ± 0.16	-	-	0.11 ± 0.06	82.97 ± 0.21	0.11 ± 0.05	2.70 ± 0.11	-
M2	0.21 ± 0.05	9.85 ± 0.13	0.59 ± 0.11	-	-	87.65 ± 0.17	0.06 ± 0.02	1.63 ± 0.05	-



**Figure S4.**

Impedance spectroscopies of supercapacitor electrodes based on fines containing 0% (P3), 50% (M1) and 90% (M2) CNCs. All the curves displayed here were measured in the frequency range of 7 MHz to 0.05 Hz.

**Figure S5.**

Ragone plot of the fines-based electrode materials (P3, dark; M1, intermediate and M2, light, 1 M TEABF<sub>4</sub>/AN as electrolyte) and comparison to the reference (YP-80F).

## Calculations

In case of two symmetrical electrodes, the series association of two supercapacitive electrodes allow the following relation.

$$\frac{1}{C_{Disp}} = \frac{1}{C_{Elec1}} + \frac{1}{C_{Elec2}} \quad (S1)$$

with  $C_{Disp}$ , the device capacity with 2, symmetrical electrodes,  $C_{Elec,1}$  and  $C_{Elec,2}$ , capacitance of electrodes 1 and 2 respectively.

However, in this case, the material being identical for the two electrodes, the masses and the potential windows thereof are the same. The relation (12) can therefore be simplified as follows:

$$\frac{1}{C_{disp}} = \frac{1}{C_{Elec1}} + \frac{1}{C_{Elec2}} = \frac{2}{C_{Electrodes}} \quad (S2)$$

with  $C_{Elec}$  the capacitance of one electrode in a symmetrical device:

$$C_{Electrodes} = 2 \cdot C_{disp} \quad (S3)$$

$$C_{Electrodes} = 2 \cdot \frac{\int_{V_i}^{V_f} i \cdot dV}{\Delta V \cdot v} \quad (S4)$$

with  $\int_{V_i}^{V_f} i \cdot dV$  the integral of the area under the curve i-V (for positive currents) obtained for mounting two symmetrical electrodes, m the mass of active material of a single electrode.

The calculation for the Ragone plots is explained in the next section. For these calculations the weight of activated carbon in both electrodes has been considered.

The values presented in the Ragone plots were calculated from the capacitance determined from cyclic voltammetry experiments at various scan rates. Stored energy in the supercapacitor is calculated according equation 1 in the manuscript:

$$E = \frac{1}{2} C \cdot \Delta E^2 \quad (S5)$$

With  $C$  being the capacity (in F) and  $\Delta E$  (in Volt).

Energy density (again capacitance is relative to the weight of active material in both electrodes) is given by equation 7 ( $E_d$ ):

$$E_d = \frac{E}{m} = \frac{1}{2} \cdot C_s \cdot \Delta E^2 = \frac{1}{2} \frac{c}{m} \Delta E^2 \quad (\text{S6})$$

$E_d$ , energy density (in  $\text{J.kg}^{-1}$ ),  $m$ , weight of activated carbon in both electrodes (in Kg),  $C_s = \frac{c}{m}$ , and  $\Delta E$  (in Volt). Energy density is converted in  $\text{Wh.kg}^{-1}$  by multiplying by

$$\frac{1}{3600}$$

Power density in  $\text{W.kg}^{-1}$  is given by equation 8:

$$P = \frac{E_d v}{\Delta E} \quad (\text{S8})$$

$v$  is the scan rate of cyclic voltammetry (in  $\text{volt s}^{-1}$ ) and  $\Delta E$  (in Volt).

Ragone plots are widely used to characterize specific energy and power of electrochemical storage devices. For the electrode materials produced here, the results are shown in **Figure S5**.

Data were obtained by galvanostatic cycling at current densities between  $\sim 0.1$  and  $8 \text{ A.g}^{-1}$  of active material in the assembled cell. Specific energy and power values were obtained using equations (S9-10). The specific energy  $E$  depends on the specific capacitance of the device  $C_s$  and the cell voltage  $\Delta V$  according to Equation (2). These calculations consider the active material mass in both electrodes.

$$E = \frac{1}{2} \cdot C_s \cdot \Delta V^2 \quad (\text{S9})$$

$$P = \frac{E_d \cdot v}{\Delta E} \cdot 3600 \quad (\text{S10})$$

$P$  is the specific power of the device in per mass of active material,  $v$  the scan rate, and  $m$  the active mass in both electrodes.