Adsorption of conducting polymer to high-surface-area nanoengineered cellulose fibers to facilitate rapid fabrication of highly conductive papers

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Supporting Information

By increasing the accessibility of the fiber wall, the available surface area for adsorption is dramatically enhanced. Instead of adsorption being limited to the outer fiber surface, which has a surface area of less than 1 $m^2\ g^{-1}$, access to nanofibril aggregates or even individual nanofibrils within the fiber wall enables considerably higher loadings. Based on earlier studies, nanofibril aggregates and individual nanofibrils are expected to have cross-sectional dimensions of approximately 30 nm and 4 nm, respectively.[1,2] Assuming a cellulose density of 1.5 g cm^{-3}, these dimensions correspond to approximate specific surface areas of 89 $m^2\ g^{-1}$ for nanofibril aggregates and 667 $m^2\ g^{-1}$ for individual nanofibrils.

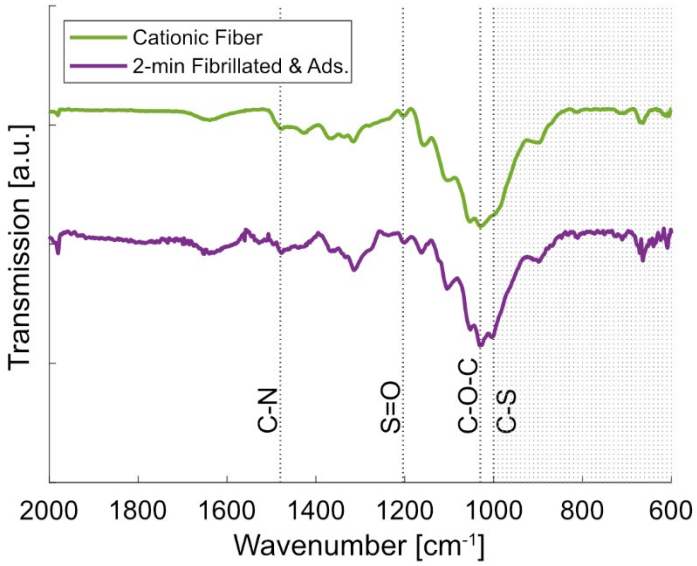

Figure S1. FT-IR spectra of cationized fibers and pre-fibrillated, PEDOT:PSS-adsorbed cationic fibers.

Fourier-transform infrared (FT-IR) spectroscopy shows indicative bands of both fiber cationization and PEDOT:PSS adsorption (Figure S2). Cationized fibers exhibited a band at 1478 cm-1, assigned to C–N stretching vibrations, confirming the successful introduction of quaternary ammonium groups and consistent with the measured charge density.[3] Fibers subjected to PEDOT:PSS adsorption showed several characteristic bands, including a band near 1000 cm-1 attributed to C–S stretching and a band at 1204 cm-1 corresponding to asymmetric sulfonyl (S=O) stretching, both characteristic of PEDOT:PSS.[4,5] The region between 600 and 1000 cm-1 further displayed multiple C–S vibrational bands, providing additional confirmation of the presence of PEDOT:PSS.[4]

Table S1. Polyelectrolyte titration values from the collected filtrate of the PEDOT:PSS-adsorbed samples.

Sample	Fiber dry mass [g]	Fiber Charge [µeq]	Added Charge [µeq]	Adsorbed Charge [µeq]	Adsorption of Added Amount [%]	Total Charge Adsorbed [%]
10 wt% Adsorption	0.5	505	404	200	49.6	39.7
20 wt% Adsorption	0.5	505	404	404	100.0	80.0
30 wt% Adsorption	0.5	525	840	830	98.8	158

Table S2. Calculated adsorbed PEDOT:PSS amounts relative to the total mass of the papers, dry mass of fibers used correspond to 2 g.

Sample	Total Charge Adsorbed [%] *	Adsorbed Charge Correspondence [µeq]	Adsorbed PEDOT:PSS Relative to Total Mass [%]
10 wt% Adsorption	39.7	801	10.29
20 wt% Adsorption	80.0	1616	18.79
30 wt% Adsorption	158.0	3192	30.32

The amount of adsorbed PEDOT:PSS relative to the total mass was calculated for a single paper sheet with a total fiber weight of 2 grams. The charge density of PEDOT:PSS was determined to be 3490 μeq g^{-1} by polyelectrolyte titration. The total charge density of the cationic fibers was estimated to be approximately 1010 μeq g^{-1} using conductometric titration. The PEDOT:PSS concentration in the batch was reported to be between 1.0 and 1.3 wt%, and a value of 1.15 wt% was assumed for the calculations.

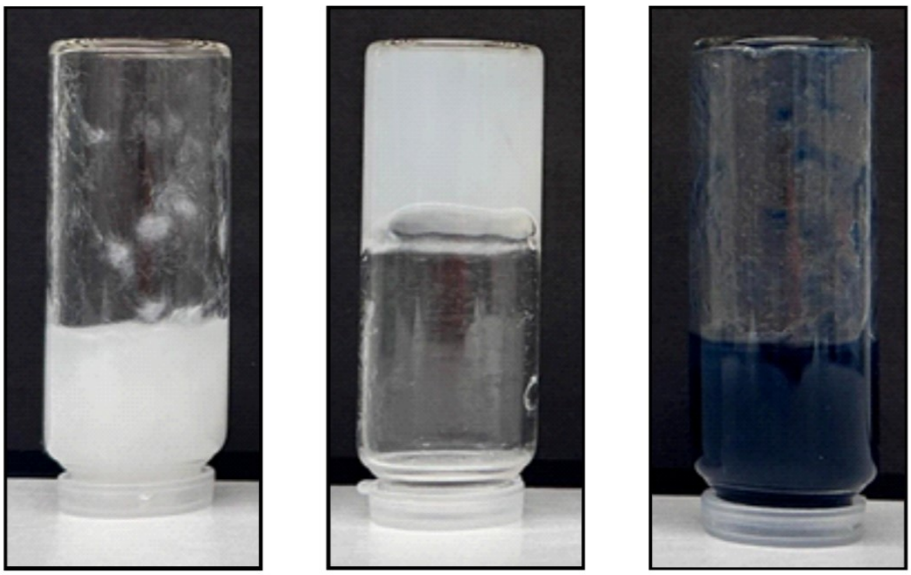

Figure S2. From left to right: cationized fibers; cationized fibers mixed under mild agitation for 7 days, showing visual gelation where the material does not fall off; PEDOT:PSS-adsorbed 7-day sample.

Table S3. Duration of paper-making steps before and after adsorption.

Steps	**Cationized Fibers**	**20 wt% ads.**	**1min-Fibrillated 20 wt% ads.**	**2min-Fibrillated 20 wt% ads.**	**2min-Fibrillated 30 wt% ads.**
Filling Time [s]	10	10	10	10	10
Agitation Time [s]	7	7	7	7	7
Calming Time [s]	5	5	5	5	5
De-watering Time [s]	9	19	32	118	~2000
Draining Time [s]	12	12	12	12	12
Total Time [s]	43	53	66	152	~2000

Table S4. Summary of the mechanical test results

Sample	Density [kg m^{-3}]	Strain [%]	Stress [MPa]	Modulus [GPa]
Cationic Fiber	710	6.8 ± 0.4	56.6 ± 1.5	3.6 ± 0.3
Cationic Fibers – 7 day (stirred)	790	6.3 ± 0.9	84.4 ± 9.0	4.8 ± 0.8
1-day Ads. (10 wt% PEDOT:PSS)	750	6.1 ± 0.3	62.5 ±4.8	3.7 ± 0.9
7-day Ads. (20 wt% PEDOT:PSS)	980	3.7 ± 0.8	87.2 ± 9.5	6.0 ± 0.5
1min-Fibrillated & Ads. (20 wt% PEDOT:PSS)	1040	4.6 ± 0.5	95.8 ± 6.3	5.5 ± 0.8
2min-Fibrillated & Ads. (20 wt% PEDOT:PSS)	1050	4.5 ± 0.5	110 ± 11	6.1 ± 1.1
2min-Fibrillated & Ads. (20 wt% PEDOT:PSS) DMSO:IPA Treatment	1350	1.7 ± 0.3	5.8 ± 1.2	0.77 ± 0.14
2min-Fibrillated & Ads. (20 wt% PEDOT:PSS) IPA Treatment	1530	1.8 ± 0.9	1.3 ± 0.5	0.18 ± 0.05
2min-Fibrillated & Ads. (30 wt% PEDOT:PSS) DMSO:IPA Treatment	1530	2.6 ± 0.3	7.4 ± 0.9	0.92 ± 0.08
2min-Fibrillated & Ads. (30 wt% PEDOT:PSS) IPA Treatment	1600	4.4 ± 0.8	2.6 ± 0.2	0.31 ± 0.02

Table S5. Comparison of electrical performance of PEDOT:PSS-based conductive paper systems reported in the literature and in this work.

Material	Adsorption/ Coating Amount [wt%]	Electrical Conductivity [S cm^{-1}]	Sheet Resistance [ohm sq^{-1}]/ Resistance [ohm]	Reference
PEDOT:PSS/ Cationic Cellulose Fibers	1.00	0.028	NA	[6]
PEDOT:PSS/ Paper	NA	78	Sheet Resistance: 30	[7]
PEDOT:PSS/ Cationic Cellulose Fibers/ Carbon Black/ Activated Carbon/ Cellulose Nanofibers	Cationic Fibers with PEDOT: PSS : 53.2 Activated Carbon: 45.9 Carbon Black with Cellulose Nanofibers: 0.7 Retention Aid: 0.2	~4	NA	[8]
PEDOT:PSS/ Cellulose Nanofibers	38.6 ± 2.12 62.5 ± 3.6	3.57 126.21	NA NA	[9]
PEDOT:PSS/ Paper	NA	NA	Resistance: 19.64	[10]
PEDOT:PSS/ Cationic Cellulose Fibers	20 30	7.0 ± 0.4 13.0 ± 0.7	Sheet Resistance: 23 ± 1 Sheet Resistance: 14 ± 1	This Work

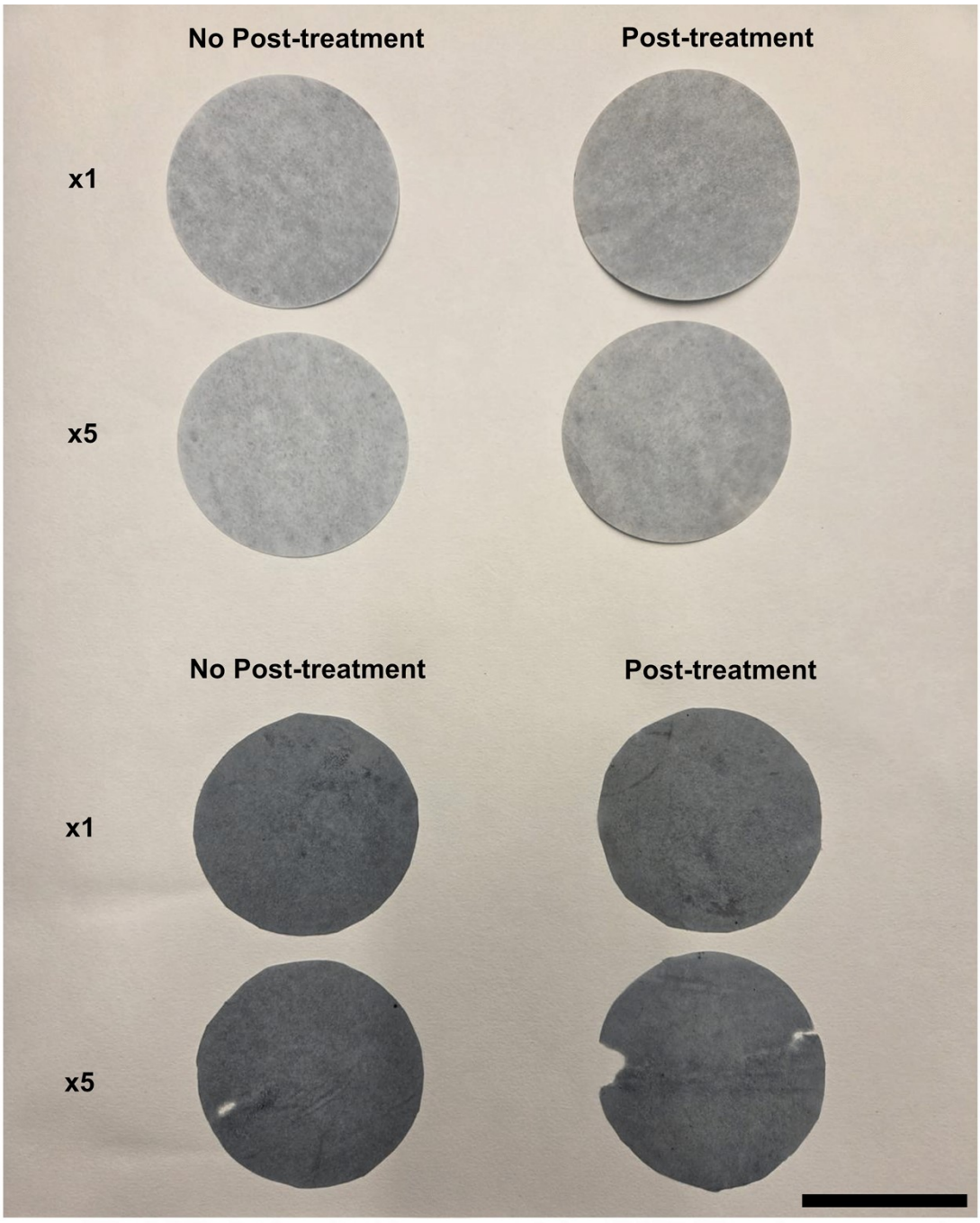

Figure S3. Images of commercial Whatman cellulose paper and paper fabricated from cationic cellulose fibers, each dip-coated either once or five times with PEDOT:PSS, followed by post-treatment with sulfuric acid and a DMSO:IPA mixture. Scale bar: 5cm.

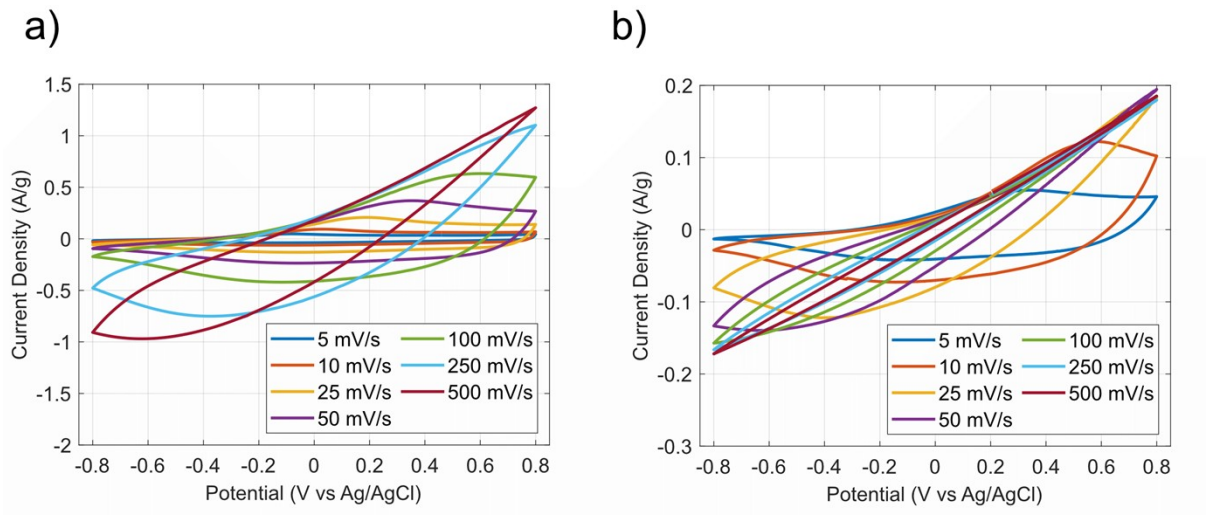

Figure S4. CV profiles recorded at scan rates from 5 to 500 mV s^{-1} in 0.1 M NaCl solution for a) DMSO:IPA post-treated paper and b) untreated paper.

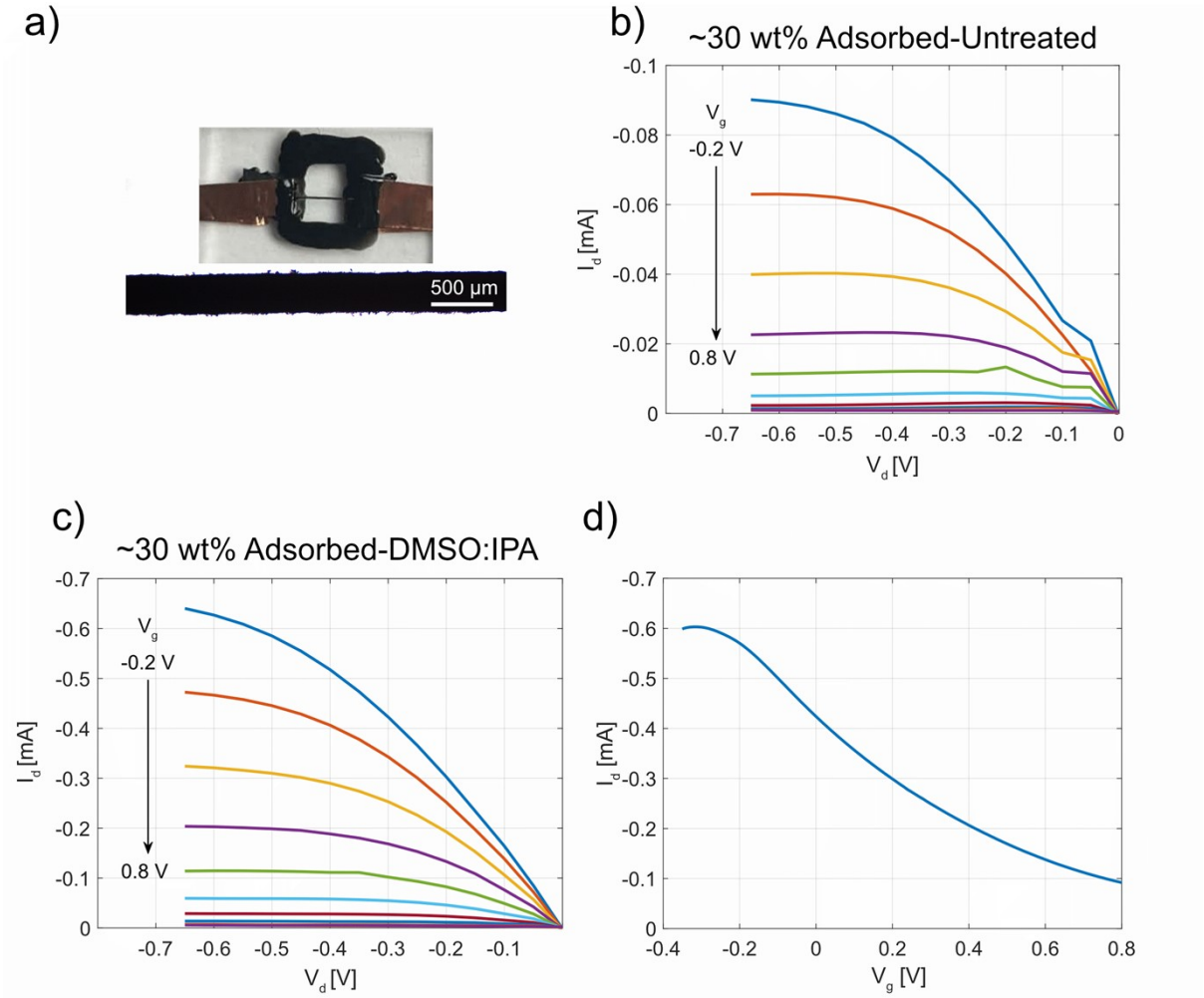

Figure S5. a) Image of the fabricated device (top), together with an optical microscopy image of the paper channel (bottom). Output characteristics of devices based on 30 wt% PEDOT:PSS-adsorbed paper b) without post-treatment and c) with DMSO:IPA post-treatment. d) transfer curve of the same device remeasured after 6 months.

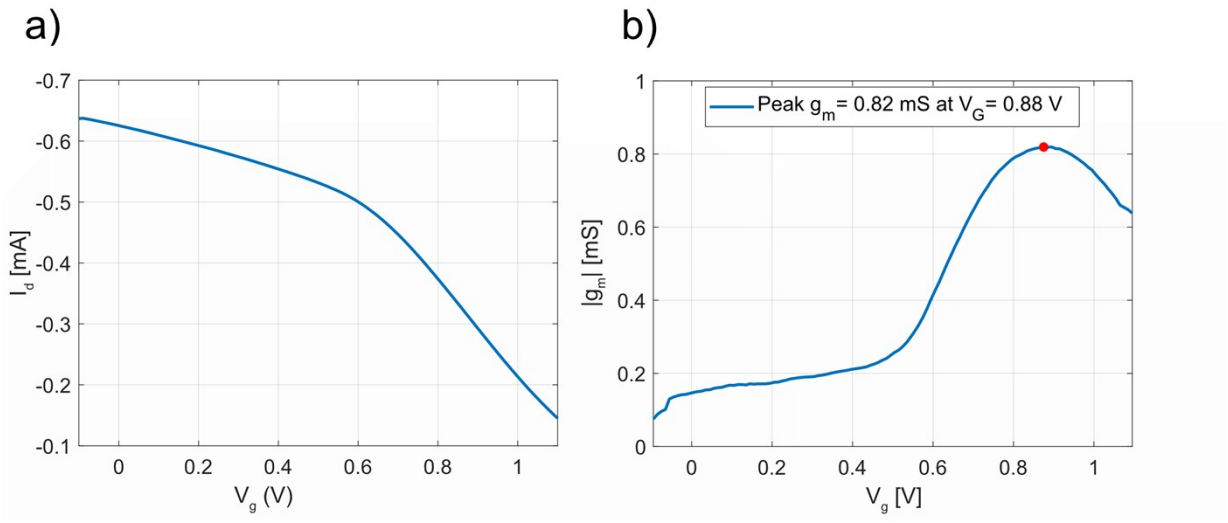

Figure S6. a) Transfer characteristics and b) transconductance of 20 wt% PEDOT:PSS-adsorbed paper channels after DMSO:IPA post-treatment, measured in PBS with an Au/PEDOT:PSS/Pt disk electrode gate.

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