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Nanocellulose Coupled Flexible Polypyrrole@Graphene Oxide Composite Paper Electrodes with High Volumetric Capacitance

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Experimental Section

Materials Synthesis

Cladophora green algae were collected from the Baltic Sea and the nanocellulose was extracted using grinding and acid hydrolysis as previously described.[1] Iron (III) nitrate nonahydrate ($FeNO_3 \cdot 9H_2O$), concentrated nitric acid (HNO_3), hydrochloric acid (HCl), sodium nitrate ($NaNO_3$), pyrrole (Py) and graphene oxide (GO) were purchased from Sigma-Aldrich and used as received. Deionised water was used throughout the synthesis. Filter papers (Munktell, Sweden, General purpose filter papers, 0.15 mm thickness) were used as obtained from Sigma-Aldrich. The carbon filaments (C005715/1, Grade XAS, Number of filaments: 6000, Filament diameter 0.007 mm) were obtained from Goodfellow, UK. Graphite foils (SIGRAFLEX, SGL Carbon, Germany, grade Z, 0.12 mm thickness) were obtained from VTT, Finland.

Preparation of free-standing PPy@nanocellulose@graphene oxide (PNG) paper: *Cladophora* cellulose (100 mg) was dispersed in water (20 mL) by sonication for a total pulse time of 10 min with water cooling. The sonication was carried out using high-energy ultrasonic equipment (Sonics and Materials Inc., USA, Vibra-Cell 750) at an amplitude of 30% with a pulse length of 30 s and pulse-off duration of 30 s. Pyrrole (0.335 mL) and 0.5 M nitric acid (15 mL) were mixed with the cellulose dispersion employing magnetic stirring for 5 min. 10 mL of GO solution (2 mg mL^{-1}) was subsequently added to the above dispersion followed by stirring for 10 min. The polymerisation of PPy was then started by employing iron (III) nitrate (4.3 g) dissolved in pre-cooled 0.5 M nitric acid (20 mL) as the oxidant. The polymerisation was allowed to proceed for 30 min with stirring of the solution, after which the composite was collected in an Büchner funnel connected to a suction flask and washed with 0.5 M nitric acid (3 L) followed by 0.1 M $NaNO_3$ (0.5 L). The composite was then drained on a filter paper by vacuum filtration to form a filter cake and then subsequently dried to form a paper sheet. The final weight of the material was about 340 mg. The mass fractions of nanocellulose, PPy and GO in the composites were estimated at 29 %, 65% and 6 %. The PNG composites with different GO contents (i.e., nanocellulose : GO ratios of 10:1 and 20:1) were also synthesized analogously. The bulk density, i.e., the ratio between the mass of the sample and its volume, was estimated from the dimensions of a piece of composite paper, using a high precision digital calliper (Mitutoyo, Japan).

Preparation of polypyrrole/graphene oxide PPy@GO: The PG composite powder used for comparisons was prepared without any nanocellulose by employing the experimental procedure described above.

Preparation of chopped carbon fibre reinforced PNG (CCF-PNG) paper: Chopped carbon fibres (CCF) was first prepared from carbon filaments as previously described.[1] The PNG composites were then prepared using the experimental conditions described above, after which the composites were mixed with 100 mg CCFs using a mechanical homogeniser (IKA T25 Ultra-Turrax, Germany) operated at 6800 rpm for 10 minutes. The mixture was then drained on a filter paper to form a filter cake which subsequently was dried to form a paper sheet. The final weight of the material was about 438 mg. The mass fractions of nanocellulose, CCF, PPy and GO in the CCF-PNG composites were estimated at 23 %, 23%, 50 % and 4 %.

Fabrication of the paper-based charge storage devices: The as-obtained free-standing PNG paper could be directly used as working electrodes without any additions of polymeric binders or conductive additives. A symmetrical device, hermetically heat-sealed in a coffee-bag arrangement was made as previously described.[2] A piece of ordinary filter paper, used as the separator, was thus sandwiched between two pieces of the composite paper material (with a 1 cm^2 size and weighing ~7 mg each). A 2 M NaCl solution was used as the electrolyte while graphite foils was used as current collectors. The PG electrodes used for comparison, were prepared by mixing 80 wt.% electroactive material with 10 wt.% acetylene black and 10 wt.% polytetrafluoroethylene (PTFE) dissolved in N-methyl-2-pyrrolidone to form a slurry. The resulting mixture was coated onto a nickel foam substrate with a 1 cm^2 geometric area, followed by pressing and drying under vacuum at 100 °C for 12 h. The as-obtained electrodes contained ~2.5 mg cm^{-2} of PG.

Material and Electrochemical Characterizations

Scanning Electron Microscopy (SEM) images of all samples were obtained by employing a Leo Gemini 1550 FEG SEM instrument (UK) whereas the specific surface areas of the composites were determined with a ASAP 2020 instrument (Micromeritics, USA) using a multipoint Brunauer-Emmett-Teller (BET) approach involving N_2 gas adsorption isotherm analysis. The Fourier transform infrared spectrometry (FTIR) experiments were performed with a Spectrum One FTIR spectrometer equipped with a Diamond/ZnSe crystal (PerkinElmer, U.S.). The mechanical properties of the composite paper were tested on a Shimadzu Autograph AGS-X tensile machine.

The electrochemical performance of the composite electrodes was studied with cyclic voltammetry and galvanostatic charge-discharge measurements at room temperature employing an Autolab/GPES instrument (ECO Chemie, The Netherlands).

***Cyclic voltammetry*:** The cyclic voltammetry (CV) measurements were performed with the composite electrode as the working electrode in a three-electrode electrochemical cell in which a platinum wire served as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The composite pieces used as the working electrode were cut out pieces weighing about 3 mg, which were contacted by a platinum wire coiled around the composite. A solution of 2 M NaCl, purged with nitrogen for 15 min prior to the measurements, was used as the electrolyte. In the specific capacity calculations all values were normalised with respect to the total mass of the composite. To investigate the electrochemical performance of the PNG paper electrodes under bending condition, CV experiments were performed on ~ 4 mg of the PNG paper electrode employing two different bending angles, i.e. 0° and 180°, at a scan rate of 20 mV s^{-1}.

Electrochemical Impedance Spectroscopy (EIS): The EIS measurements were performed with a CH Instruments 660D potentiostat (CH Instruments, Inc., USA) at a cell potential of 0 V, using an *ac* amplitude of 10 mV. The frequency was varied between 100 kHz and 0.01 Hz.

***Galvanostatic Charge/Discharge Measurements*:** During the galvanostatic measurements on the symmetric charge storage devices these were pressed with a clip applying a force of about 25 N to enable a good contact between the graphite paper current collector and the composite paper electrodes. Different current densities between 0.1 A g^{-1} and 10 A g^{-1} were then applied while a current density of 5 A g^{-1} was used in the cycling stability tests, as the cell was charged to a cell voltage of 0.8 V. The cell capacitances of the symmetric devices were derived from the galvanostatic discharge curves according to $C = I\Delta t/\Delta V$, where C denotes the device capacitance, I the discharge current and ΔV represents the potential change within the discharge time Δt. The electrode specific capacitances reported for the symmetric devices were obtained by multiplying the cell capacitance by a factor of 4. The mass-specific cell capacitances were calculated as C_m=4C/M, where M refers to the active mass of the two paper composite electrodes. The volumetric capacitance of single-electrode was calculated as $C_v = \rho C_m$, where C_v and ρ denote the volumetric capacitance and the bulk density of the active material in the electrode, respectively. The device energy density was calculated using $E = 1/2\ C_m\ (\Delta V)^2$ while the power density was derived as $P = E/\Delta t$.

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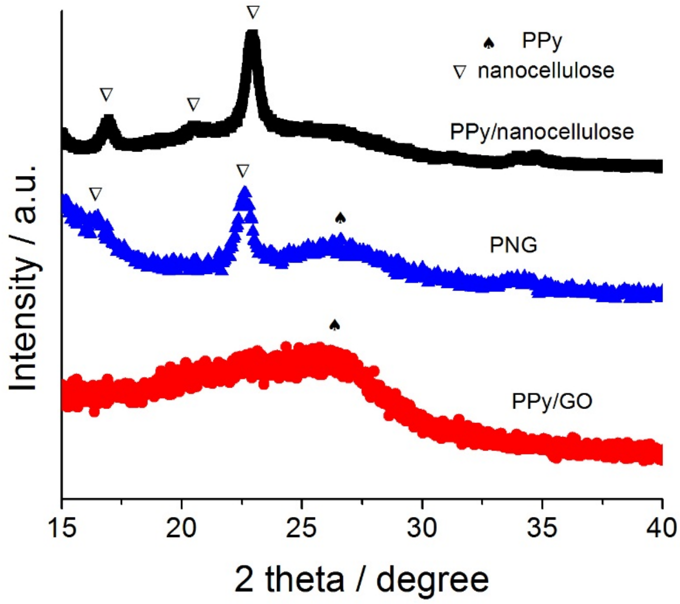

Figure S1. XRD patterns for different PPy-based composites.

For the PPy/GO composite, the XRD pattern exhibits a broad band at ~26°, which fits in well with previous reported PPy-GO data.[1] No peaks for GO can be seen because of the low GO weight ratio. Compared to PPy/GO, the XRD pattern of PPy@nanocellulose shows many new peaks corresponding to nanocellulose, while the broad peak for PPy was masked by the high peak intensity for the crystallized nanocellulose. [2] For the PNG sample, the peak at 22.5° (due to nanocellulose) and the peak at 26° (due to PPy) in the XRD pattern of the PPy/GO composites demonstrates the successful development of the composite, in good agreement with the FTIR and SEM data.

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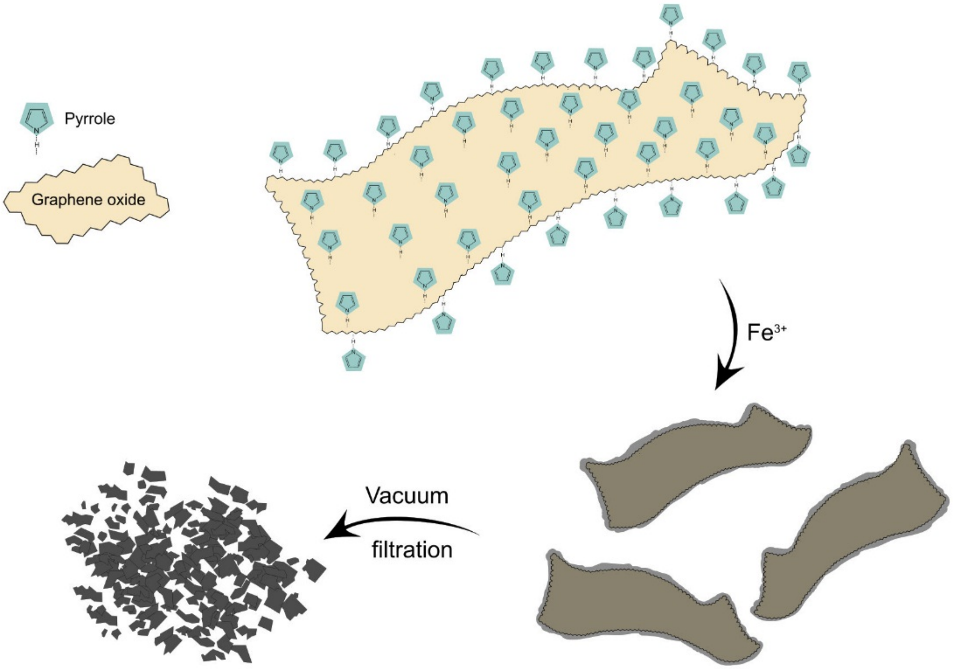

Figure S2. Schematic illustrations depicting the preparation and structure of the PPy/GO powder.

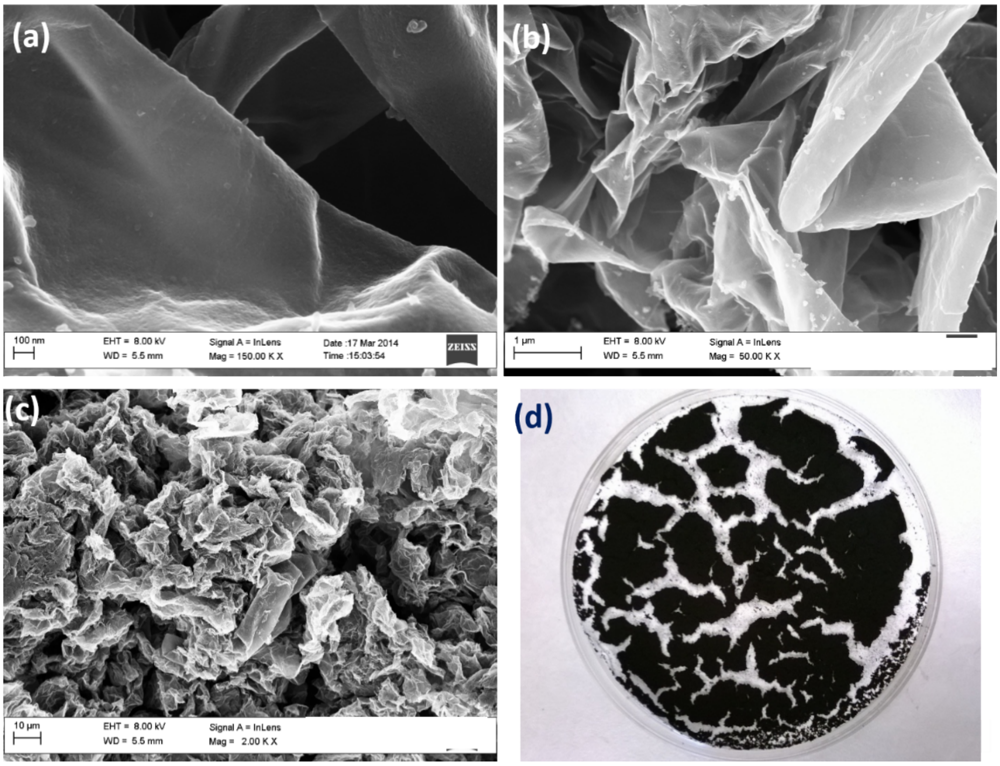

Figure S3. (a-c) SEM images for the PG composite at different magnifications. (d) Digital image of the PG composite prepared in the absence of nanocellulose. Note that the PG composite only could be obtained as a dried powder.

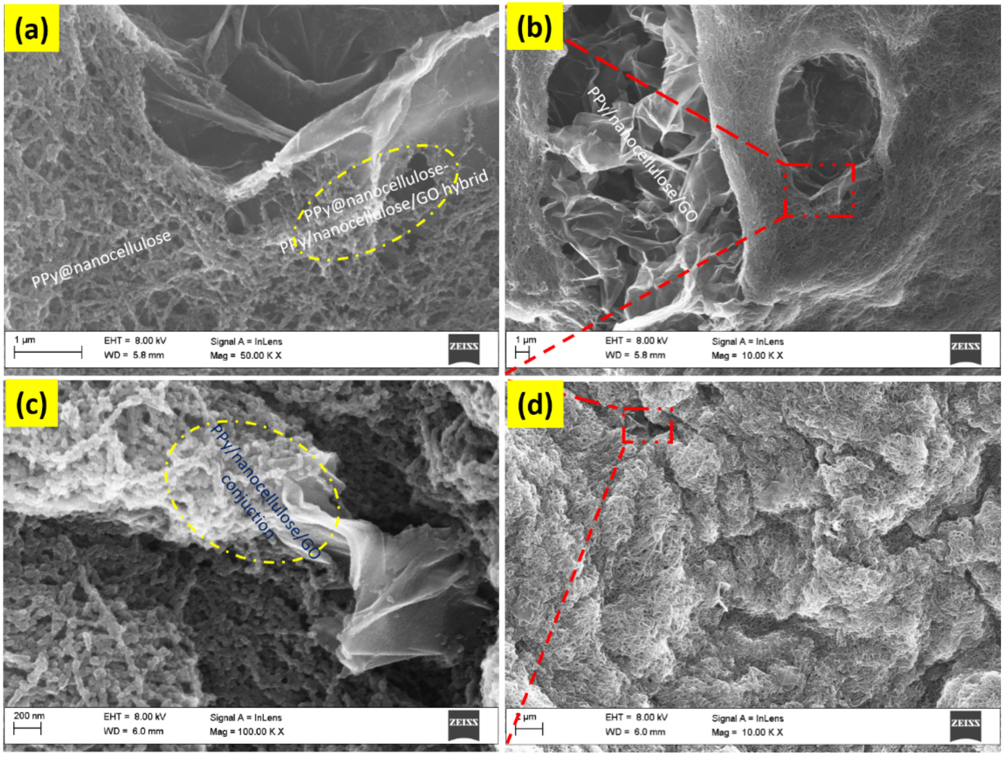

Figure S4. SEM images of PNG composites prepared with different nanocellulose to graphene oxide ratios: (a) and (b) nanocellulose : GO = 10:1; (c) and (d) nanocellulose : GO = 20:1.

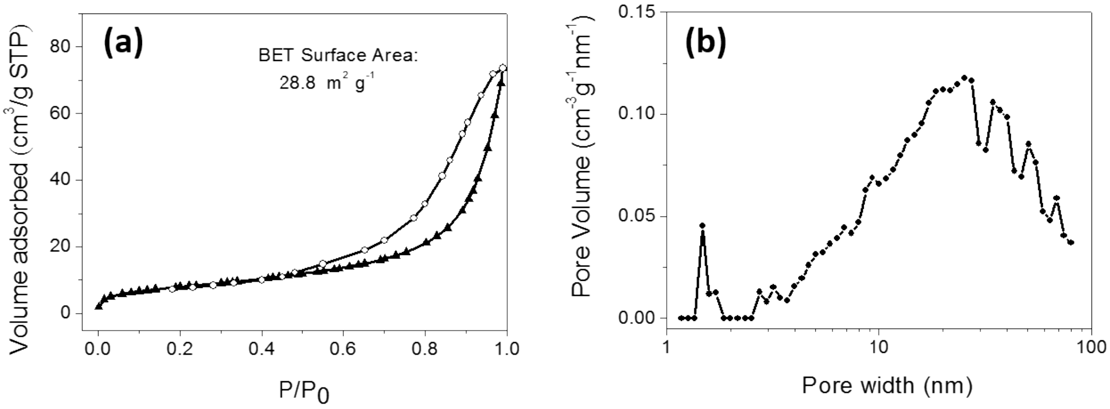

Figure S5. (a) N_2 adsorption/desorption isotherms and (b) pore size distribution curve calculated from the adsorption isotherms for a PNG paper electrode using the non-local density functional theory method.

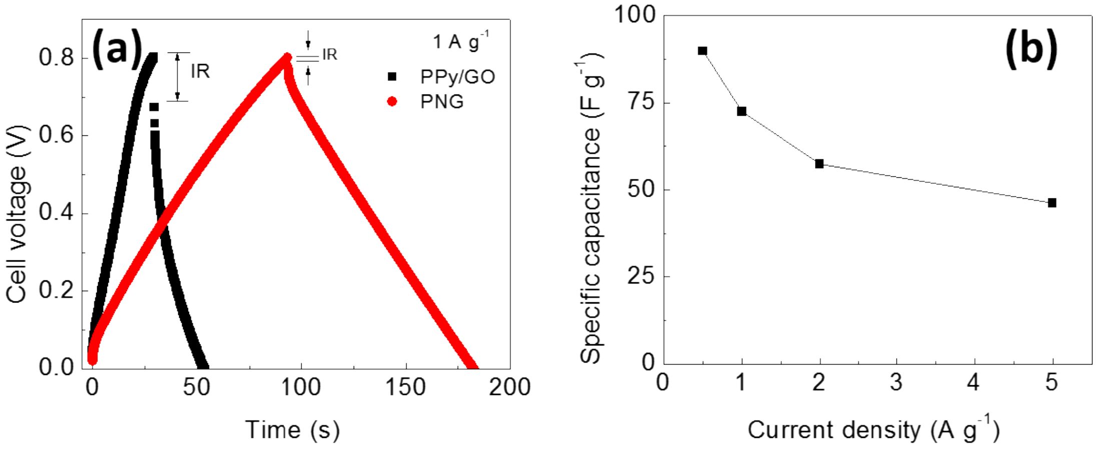

Figure S6. (a) Galvanostatic charge/discharge curves for a PNG paper and a PG electrode based symmetric device, respectively, using a current density of 1 A g^{-1}. (b) Specific capacitance as a function of the current density for a PG electrode.

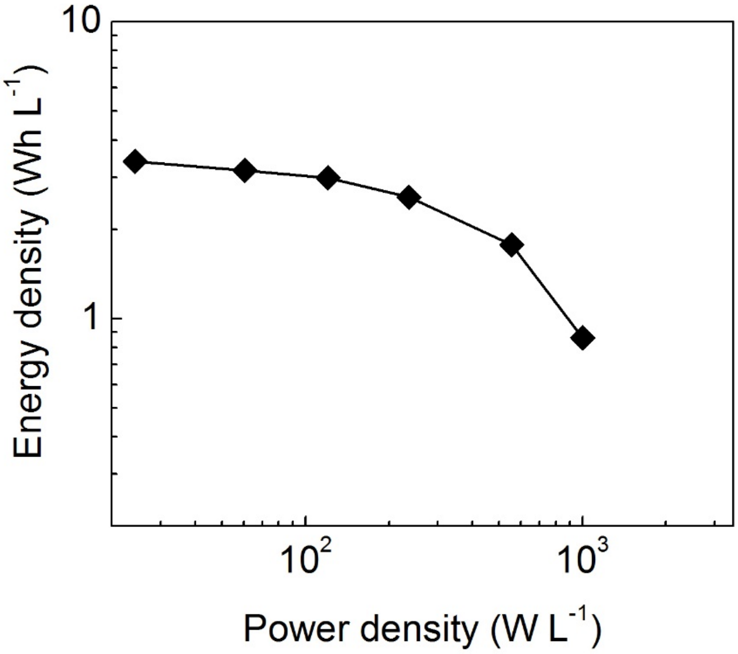

Figure S7. Ragone plot for a PNG paper electrode based device.

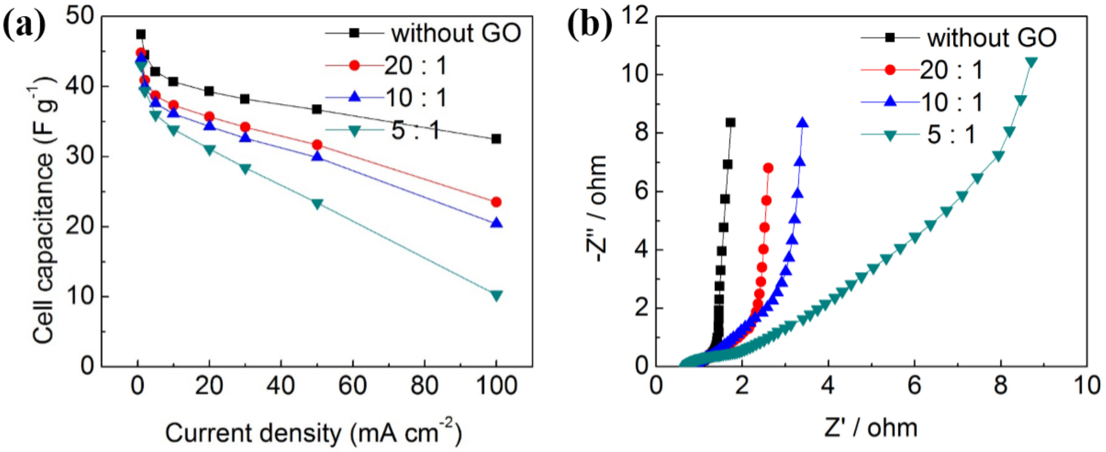

Figure S8. Rate performance (a) and Nyquist plots (b) for PNG electrodes-based supercapacitors with different nanocellulose:GO ratios.

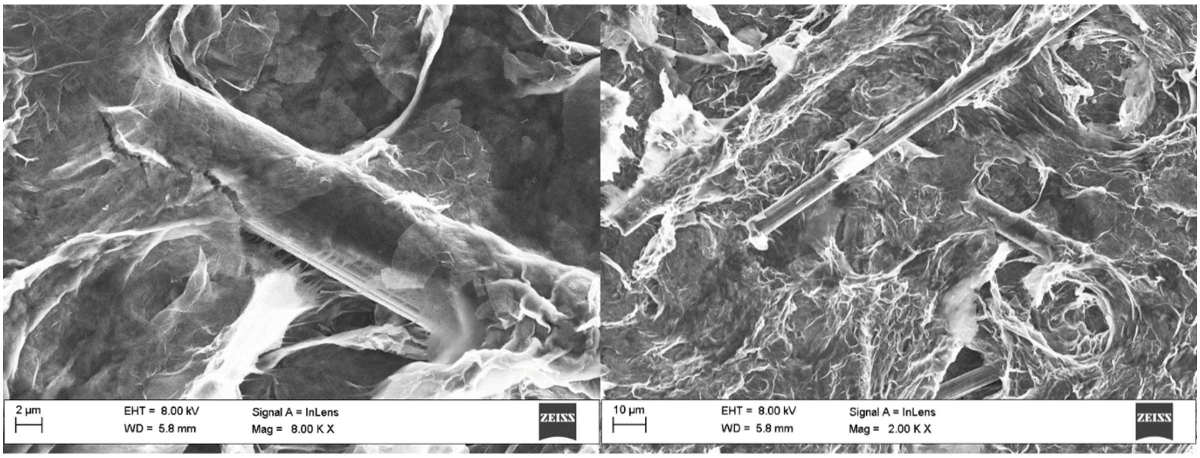

Figure S9. SEM images of a CCF-PNG paper electrode at different magnifications.

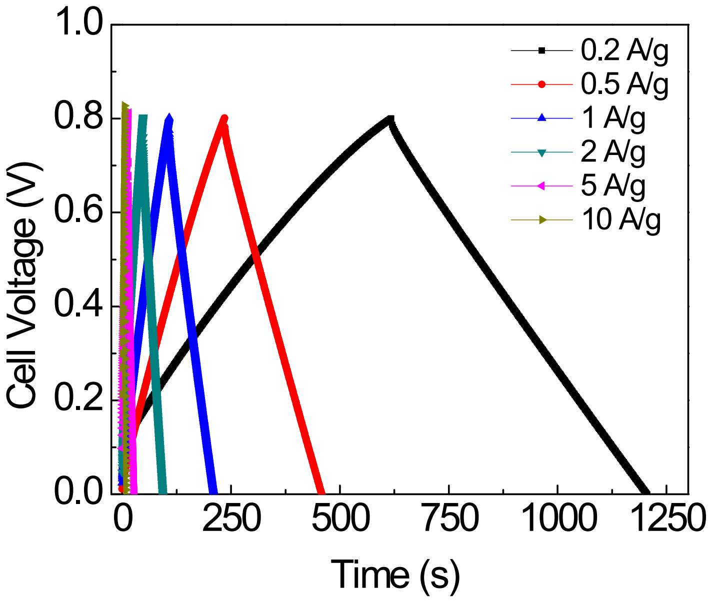

Figure S10. Galvanostatic charge/discharge curves recorded with different current densities for a symmetric CCF-PNG paper electrode based device.

Table S1. Electrochemical performance of the flexible polymer-based electrodes.

Materials	C_g (F g^{-1})	C_v (F cm^{-3})	Density (g cm^{-3})	Cycling retention	Remarks	Ref.
PNG	**244**	**301[a]** **198[b]**	**1.25**	**84.8%, 16000th**	**two electrode**	**This work**
CCF-PNG	**276**	**221[a]** **138[b]**	**0.8**	**—**	**two electrode**	
PANI-rGO/CF	224	—	—	89%, 1000th	two electrode	S1
rGO/PANI	233	135[b]	0.58	—	two electrode	S2
PANI-NF	210	160[a]	0.76	78.7%, 800th	two electrode	S3
GN-PPy/CNT	211	122[a]	0.58	95%, 5000th	three electrode	S4
PPy/CNT	164	67[a]	0.41	55%, 5000th	three electrode	S4
rGO-PANI	763	153[a]	0.2	82%, 1000th	three electrode	S5
PEDOT/MWNT	125	179[b]	1.43	92-99%, 10000th	two electrode	S6
PPy/rGO	284	—	—	93%, 5000th	three electrode	S7
PPy/MnO2/PPF	110	—	—	83%, 1600th	three electrode	S8
G/PPy	237	—	—	—	three electrode	S9
PANI/Au/PVDF	235	—	—	84%, 10000th	three electrode	S10
PANI/Au/PVDF	125	—	—	65%, 10000th	two electrode	S10
PPy-nylon fabric	125	—	—	55%, 500	two electrode	S11
PVP/rGO	180	72[b]	0.4	80%, 10000th	two electrode	S12

[a] Normalized with active mass. [b] Normalized with a weight of the electrode (active mass + conductive agent + binder).

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