Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Intrinsically flexible electronic materials for smart device applications

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EXPERIMENTAL

Materials

Pyrrole (98%), ammonium persulfate (98%), fibrous cellulose, benzenesulfonic acid (97%) and potassium chloride (99.9%) were supplied by Sigma Aldrich and used without further purification. Ionic liquids (ILs), 1-butyl-3-methylimidazole chloride ($[C_4mim]Cl$) and trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulpfonyl)imide $[P_{66614}][NTf_2]$, were synthesised at QUILL. Both ILs were chemically pure by NMR and had <10 ppm of water.

$[C_4mim]Cl$

^{1}H NMR ($CDCl_3$): δ 10.83 (s, 1H), 7.30 (s, 1H), 7.22 (s, 1H), 4.26 (t, *J*=7.3 Hz, 2H), 4.06 (s, 3H), 1.88-1.76 (m, 2H), 1.42-1.22 (m, 2H), 0.90 (t, *J*=7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$): δ 137.82, 124.11, 122.44, 49.89, 36.70, 32.37, 19.63, 13.64.

$[P_{66614}][NTf_2]$

^{1}H NMR ($CDCl_3$): δ 2.31-1.83 (m, 8H), 1.42 (s, 19H), 1.23-1.19 (m, 29H), 0.89 (q, *J*=6.7 Hz, 12H).

^{13}C NMR ($CDCl_3$): δ 120.32 (q, *J*=321.8 Hz, 12H), 32.31, 31.63-30.41 (m), 30.41-29.44 (m), 29.17, 23.07, 22.65, 21.84 (d, *J*=4.4 Hz), 19.34, 18.71, 14.48, 14.19.

Instrumentation

To cast the films a coating machine was used (K control coater model 101 from RK Printcoat Instruments), the components necessary for casting the films were: proofing paper (gloss/matt) using the gloss part to cast the films and bar No. 8 (wet film thickness 100 µM).

ASTM D3359 test method with slight modification was used. A piece of Scotch brand transparent tape was placed firmly on the casted polymer film and pressed gently to achieve even contact between tape and film, then gently peeled off. Any visible quantity of the composite material on the tape from the surface of the cellulose-polypyrrole material was used to determine the adhesive nature of the material.

Solid-state characterisation was carried out with a Fourier transform infrared (FTIR) spectrometer (Spectrum 100 from PerkinElmer) equipped with an attenuated total reflectance (ATR) accessory in the range of 4000- 550 cm^{-1} by accumulating 16 scans at a resolution of 4 cm$^{-1.}$

Thermogravimetric analysis (TGA) was used to determine the thermal stability of the pure compounds and the films using a thermogravimetric analyser Q5000 V3.17 build 265 from TA instruments. Experiments were carried out with a heating rate of 10ºC min^{-1} ranging from 30 to 500 ºC under dinitrogen flow at 25 mL min^{-1}. A platinum pan was used as the sample holder.

Topography and morphology characteristics were studied using a FEI Quanta FEG Scanning Electron Microscopy (SEM) attached with Energy Dispersive X-ray (EDX) spectrometer and Everhart Thornley Detector (ETD). The films were sputtered with gold prior to the examination except for film 4.

Potentiostat/Galvanostat Autolab PGSTAT302N from Eco Chemie with GPES software was used to conduct the cyclic voltammetry (CV) and chronoamperometry experiments. CV studies (potentiostat mode) were performed using a three electrodes cell, using platinum wires as counter and reference electrodes and the composite films as working electrode. The potential range chosen was −1.0 to +0.5 V versus platinum wire at scan rate of 20 mV s^{-1} in 0.1 M KCl aqueous solution. Chronoamperometry experiments were carried out in a 0.1 M KCl aqueous solution using the same cell set-up as used for the CV experiment. The potential selected for the chronoamperometry was 0.5 V for 2 and 5 minutes.

UV-Visible spectroscopy studies were carried out with a Lambda 950 UV/Vis spectrometer equipped with a STD detector module. UV/Vis Spectroscopy cells were made of quartz from PerkinElmer.

Tensile strength test of dried films (Film 2-4) with thickness between 0.3 and 0.4 mm were performed using a tensile analyser (Instron 5564). The analysis was performed at room temperature at a speed of 5 mm min^{-1} using a sample with a rectangular shape and size of 10x15 mm. The Young's modulus, tensile stress and elongation break were determined.

Resistivity measurements were carried out using Universal Probe four probe conductivity meter. The average electrical resistivity was calculated from 10 measurements from both front and back side, and the conductivity was computed using $\sigma = 1/\rho$.

Preparation of cellulose and polypyrrole composite films

Preparation of cellulose film (Film 1)

In a 100 mL round bottom flask equipped with a mechanical stirrer, ~3g of [C_4mim]Cl was added and heated under nitrogen at 100 ºC until the IL was melted and mobile. Fibrous cellulose (10% of the IL weight) was added, stirred and heated at 100 ºC for 3 hours as was described by Swatloski *et al*. in 2002 (Ref 13 in the manuscript). After all the cellulose was dissolved in the ionic liquid to form a clear solution, the mixture was cast between two proofing papers using a coating machine. Afterwards, the wet film cast was immersed into a water bath (antisolvent) to regenerate the cellulose and obtain the free-standing Film 1. After being washed several times with water, the cellulose film formed was dried at room temperature for 24 hours.

Preparation of cellulose + polypyrrole undoped film (Film 2)

Firstly, the dissolution of the fibrous cellulose in [C_4mim]Cl was achieved as in the case of Film 1. To this cellulose-[C_4mim]Cl mixture, at room temperature, 10 wt% of pyrrole to IL was added. A little amount of oxidant, ammonium persulfate (0.09 mmol), was added slowly and the mixture was stirred for 10 minutes. When the mixture was homogeneously black, film 2 was cast using the coating machine, regenerated and dried as described in case of Film 1.

Preparation of cellulose + [P_{66614}][NTf_2] IL plasticiser film (Film 3)

After dissolving the fibrous cellulose in the ionic liquid, as described for Film 1, 10 wt% of [P_{66614}][NTf_2] IL plasticiser was added into the mixture. The mixture was stirred for 10 minutes until was homogeneous. After that, Film 3 was cast using the coating machine, regenerated and dried as described for Film 1.

Preparation of cellulose + polypyrrole + [P_{66614}][NTf_2] IL plasticiser + benzenesulfonic acid doped film (Film 4)

To prepare Film 4, firstly, the dissolution of fibrous cellulose in [C_4mim]Cl and the addition of [P_{66614}][NTf_2] IL plasticiser was carried out as was described for Film 3. After this mixture turned homogeneous, at room temperature, ammonium persulfate (0.09 mmol) and dopant, benzenesulfonic acid (0.05 mmol) were added. The dopant quantity was 0.1 mol relative to pyrrole. The mixture was stirred until homogeneity and then, 10 wt% of pyrrole to IL was added and stirred further. The mixture was cast as described in Film 1. Regenerated film was washed several times with water and dried at room temperature for 24 hours.

Preparation of polypyrrole powder (PPy powder)

In a 50 mL round bottom flask immersed in an ice bath, 0.1065 g (0.047 mmol) of ammonium persulfate and 0.2280 g (1.44 mmol) of benzenesulfonic acid were added over 5 mL of methanol and was stirred for 30 minutes. 1 mL of H_2O was added to help the oxidant dissolution. After the oxidant and dopant were completely dissolved to form a homogenous solution, 1 mL of pyrrole was added. The solution was stirred slowly for 1 hour in the ice bath and for an hour at room temperature. When pyrrole was added, the solution turned from colourless to green and finally to black obtaining a black powder that was filtered and washed with methanol (2x10 mL) and then followed by water (2x10 mL). Finally, the polypyrrole powder obtained was dried in air and then stored in the vacuum desiccator with phosphorous pentoxide as the desiccant.

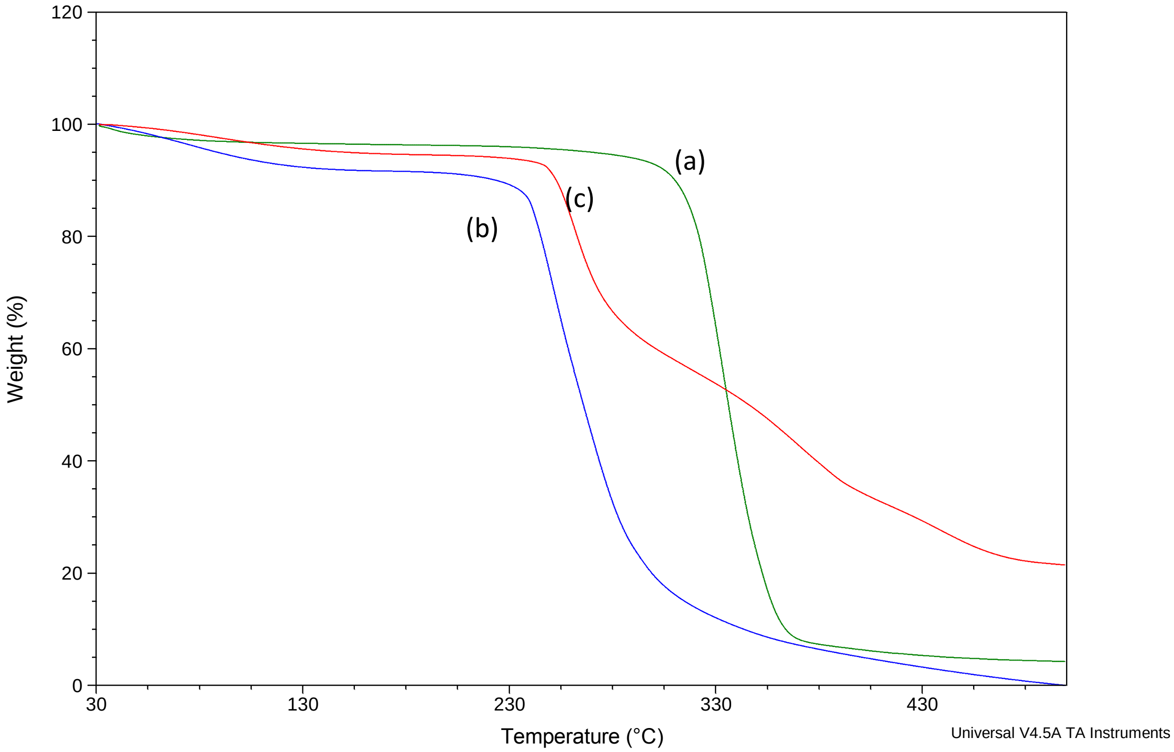


Figure S1: Thermal decompositions (TGA thermogram) of (a) cellulose powder, (b) Film 1, (c) Film 3

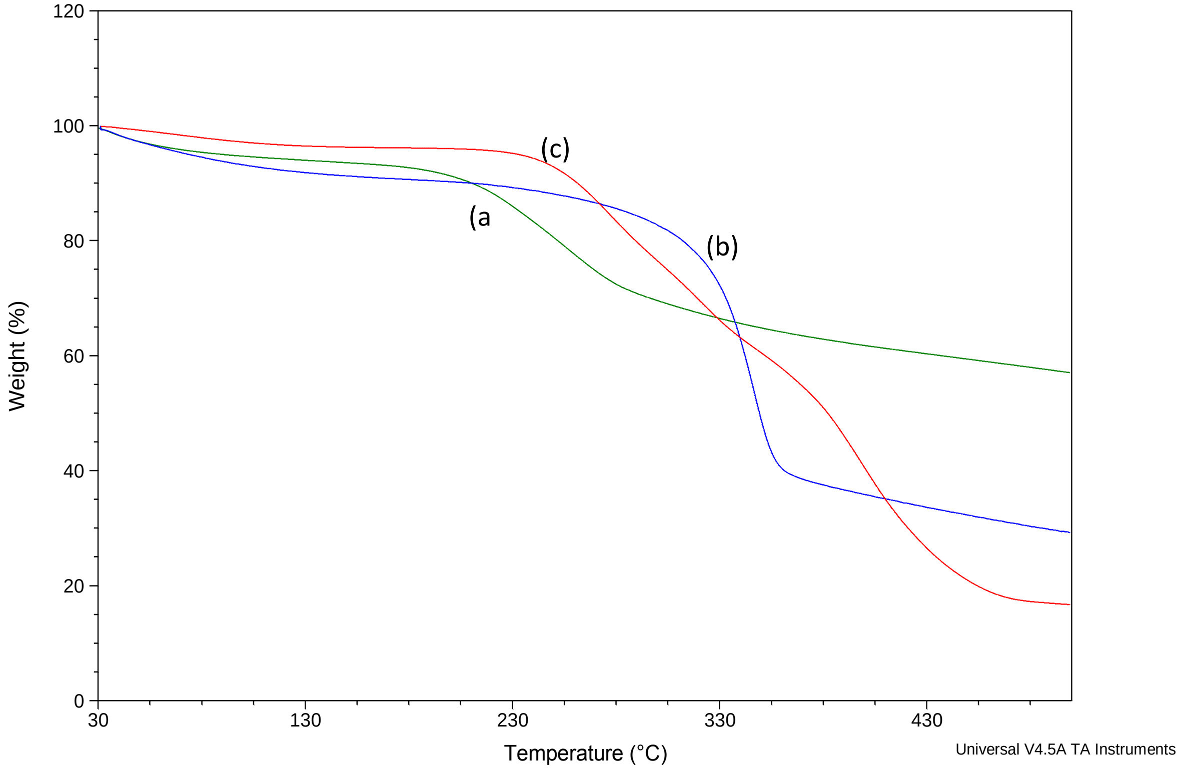


Figure S2: Thermal decompositions (TGA thermogram) of (a) polypyrrole powder, (b) Film 2, (c) Film 4

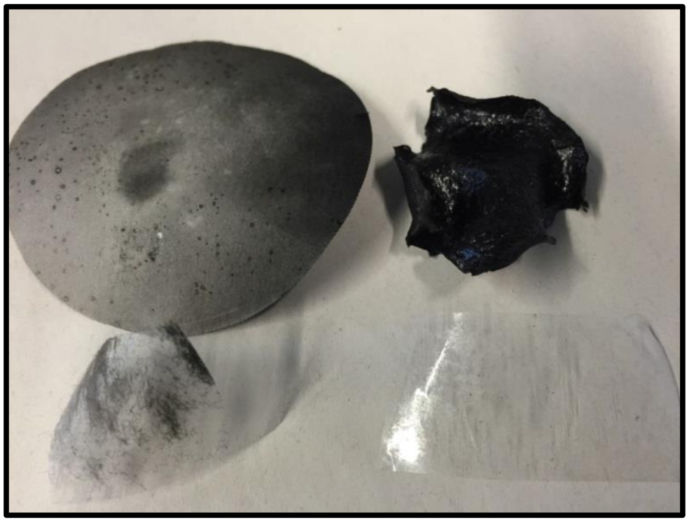


Figure S3: Adhesion by Tape Test (a) Polypyrrole grafted on laboratory filter paper, (b) Film 4

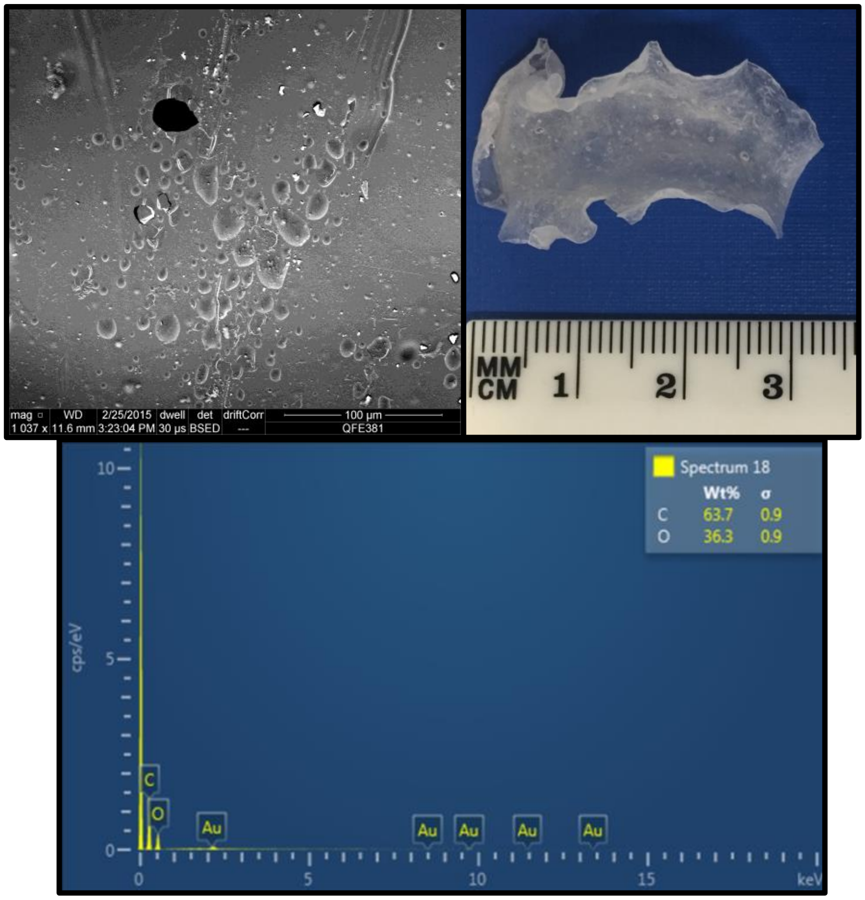


Figure S4: Photograph, SEM image and EDX spectra of Film 1 (presence of gold from sputtering)

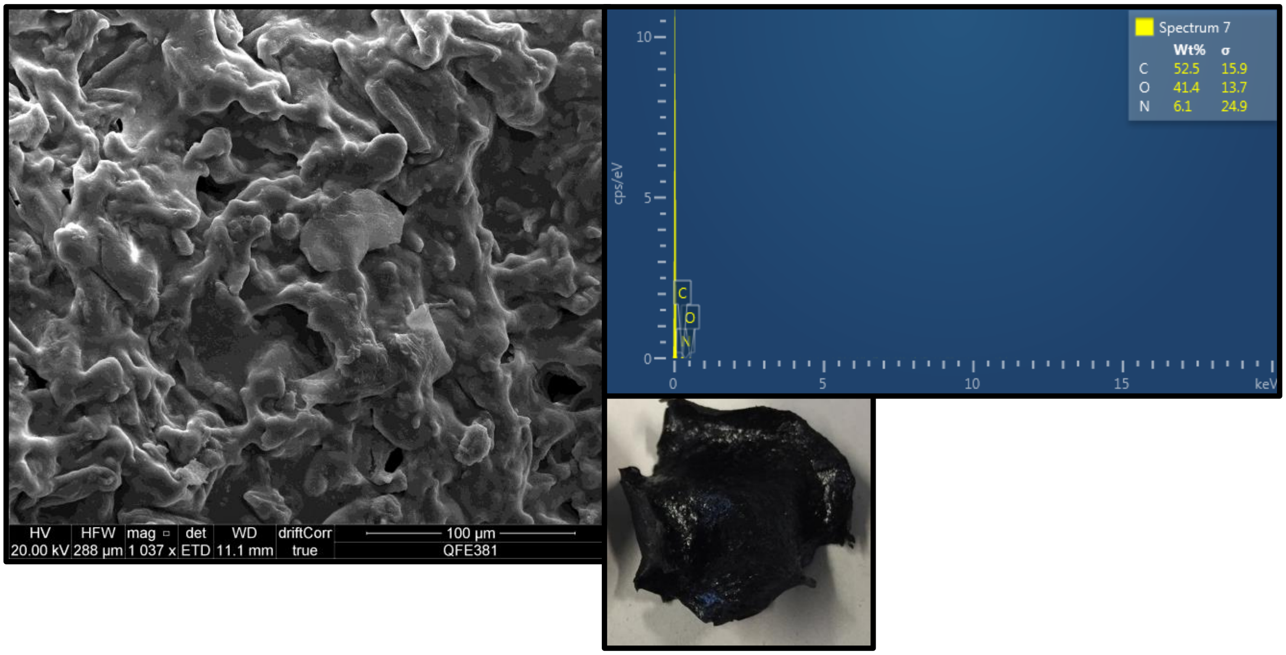


Figure S5: Photograph, SEM image and EDX spectra of Film 2

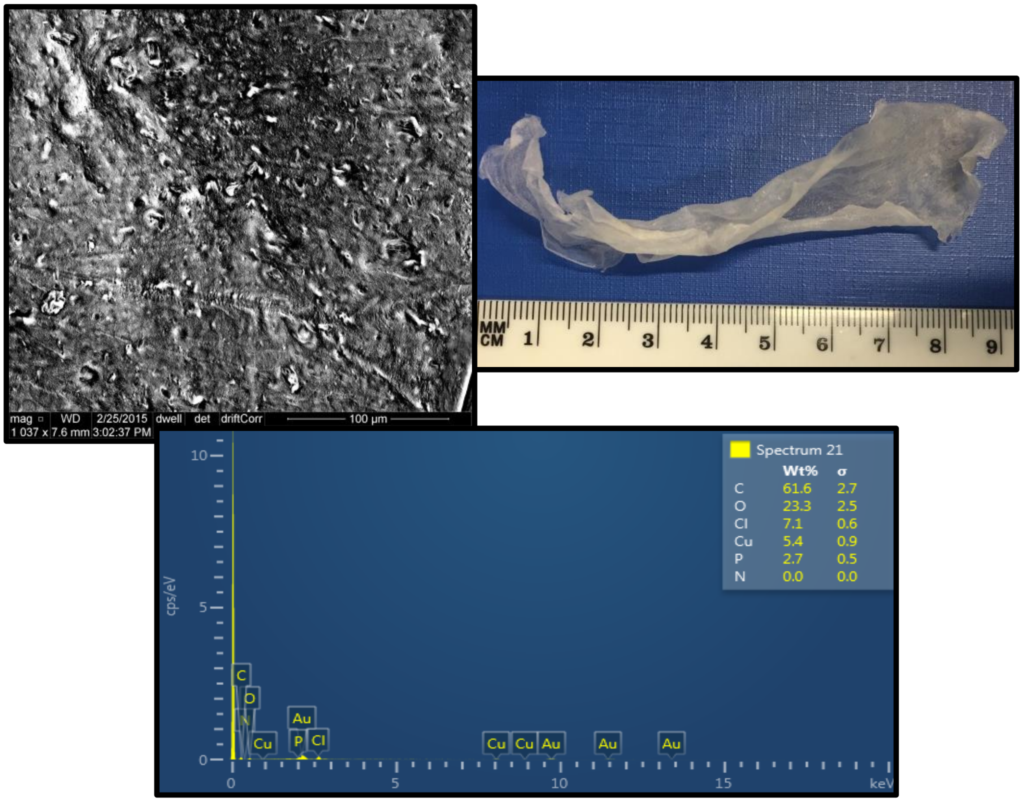
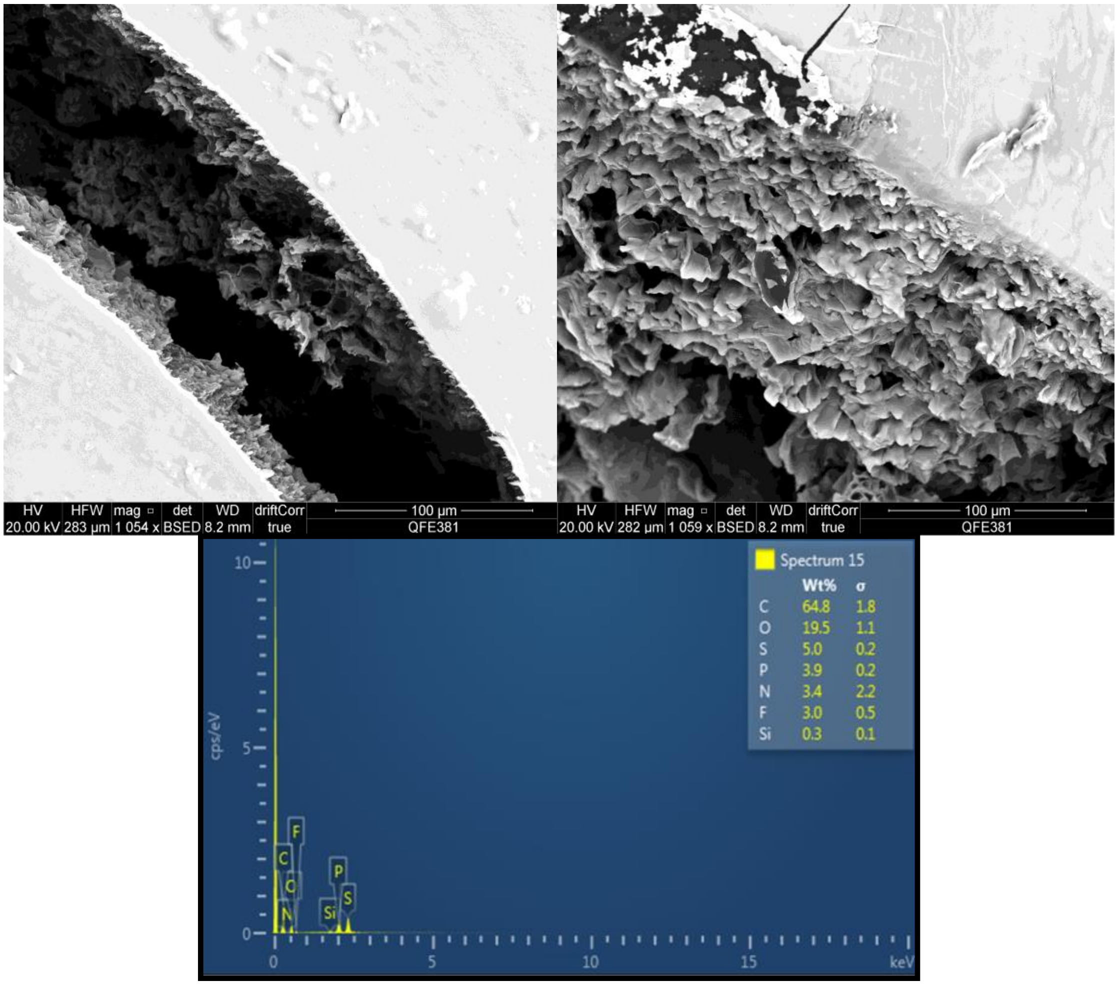


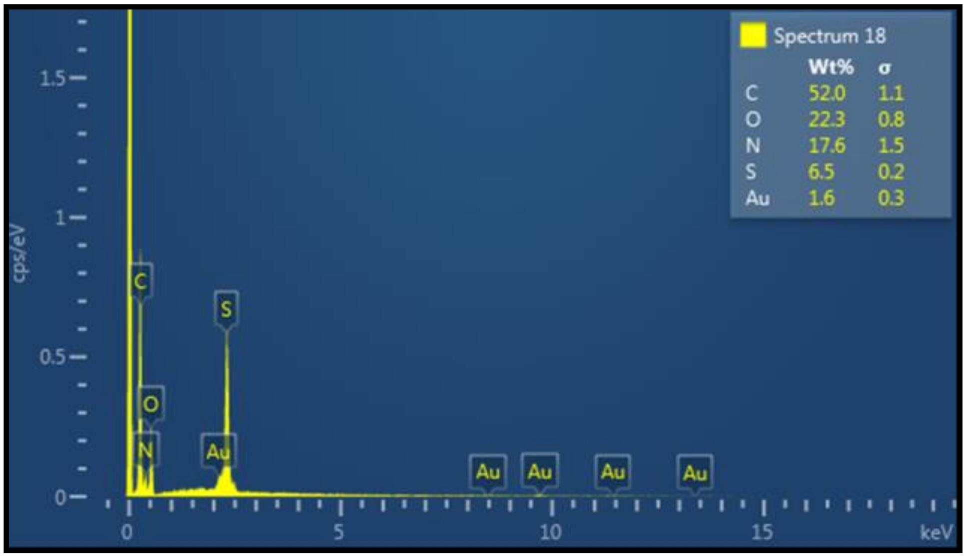
Figure S6: Photograph, SEM image and EDX spectra of Film 3 (presence of Cu from copper tape and gold from sputtering)



Spectrum 15

	Wt%	σ
C	64.8	1.8
O	19.5	1.1
S	5.0	0.2
P	3.9	0.2
N	3.4	2.2
F	3.0	0.5
Si	0.3	0.1

Figure S7: Cross-section SEM image and EDX spectra of Film 4



Spectrum 18

	Wt%	σ
C	52.0	1.1
O	22.3	0.8
N	17.6	1.5
S	6.5	0.2
Au	1.6	0.3

Figure S8: EDX spectra of polypyrrole powder (presence of O and S from dopant, N and C for polypyrrole and Au from sputtering)

Table S1: Mechanical properties of cellulose composites

Sample name	Thickness (mm)	Ultimate tensile strength (MPa)	Young’s modulus (MPa)
Film 2	0.35	0.78 ± 2.1	4.8 ± 3.1
Film 3	0.3	8.0 ± 0.8	194.5 ± 98.4
Film 4	0.4	1.8 ± 0.2	57.6 ± 6.2

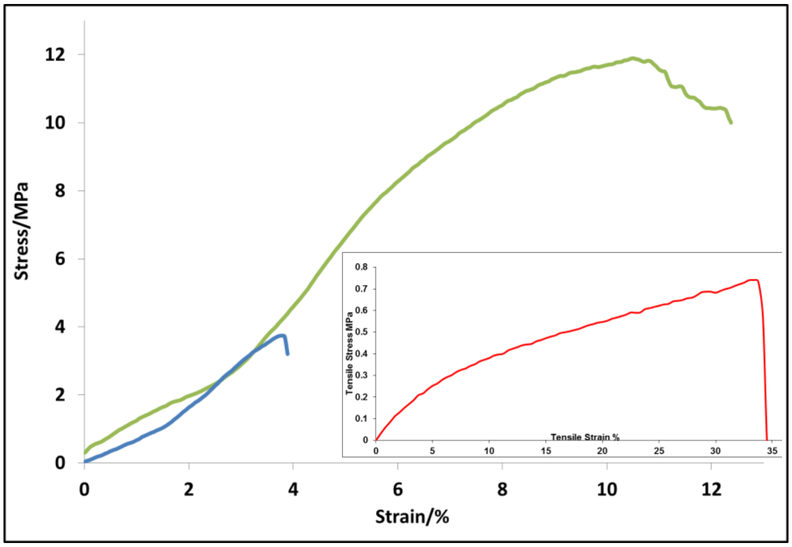


Figure S9: Representative stress-strain curves of Films 3 (green) and Film 4 (blue); inset film 2

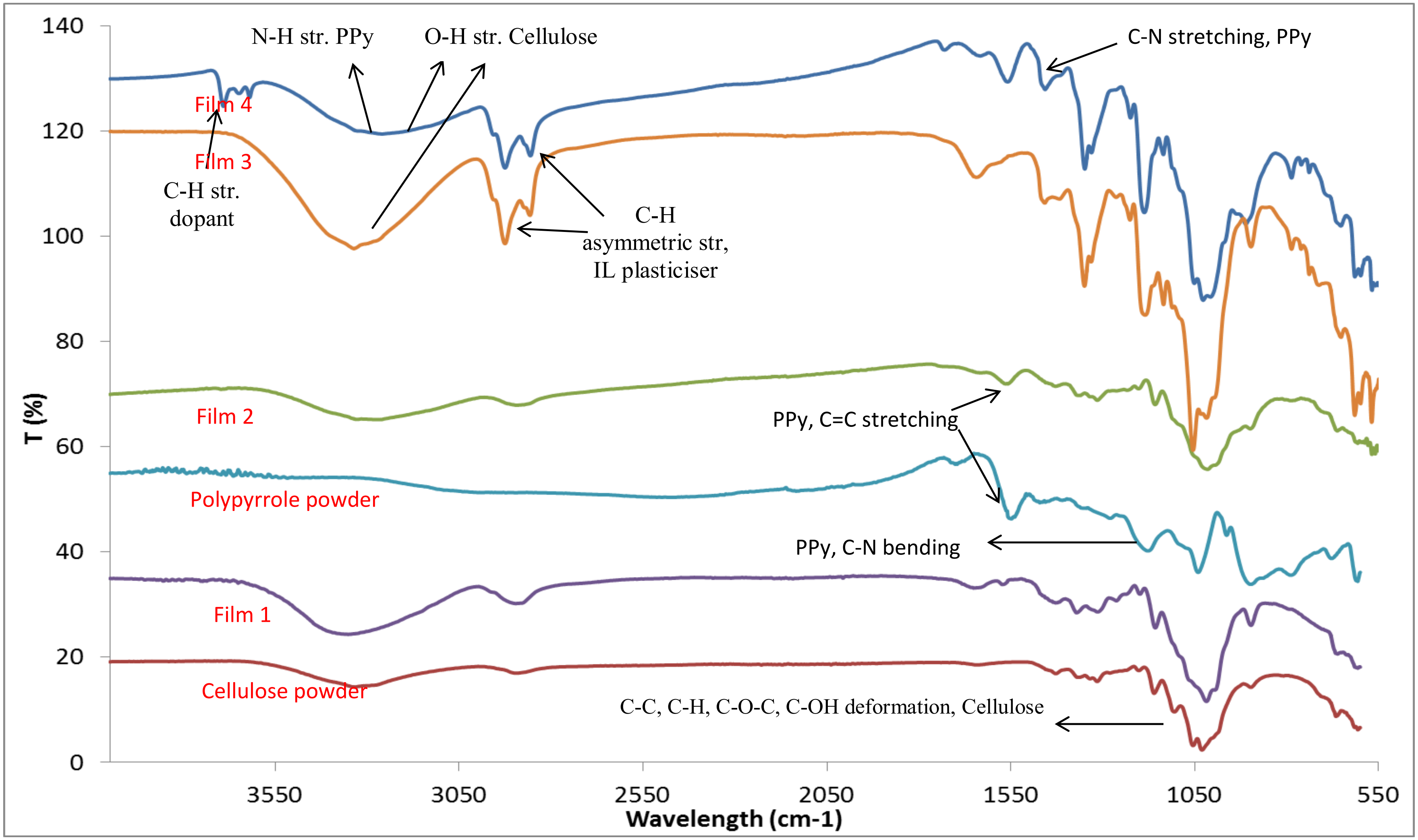


Figure S10: Infra-red spectra of various materials presented in Table 1 in the manuscript

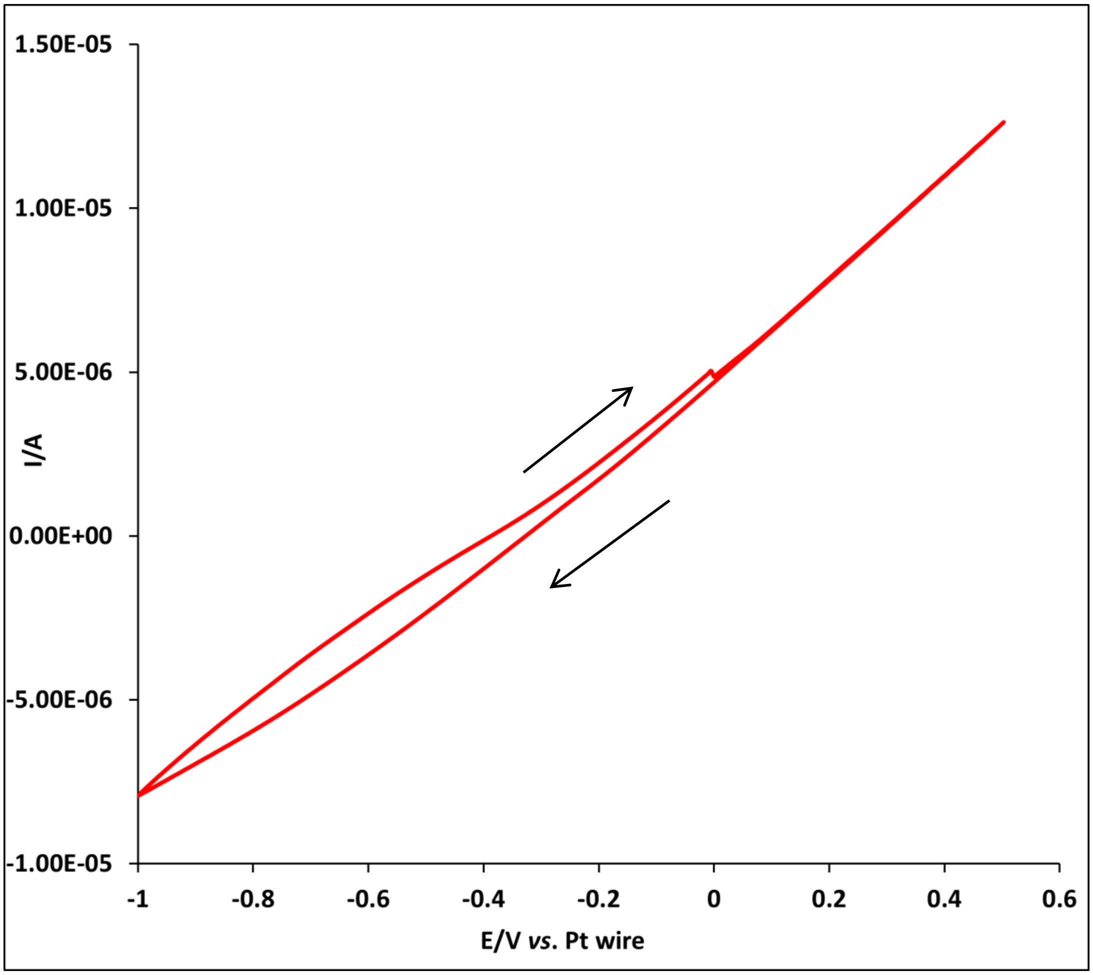


Figure S11: Cyclic voltammogram of Film 1 in 0.1 M of KCl solution in water, arrows indicate scan direction