

Supporting Information

Additive Manufacturing of Polyaniline Blends for Lightweight Structures with Tunable Conductivity

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EXPERIMENTAL SECTION

MATERIALS AND METHODS

The fumed silica is an amorphous, nonporous, and hydrophilic with a specific surface area of approximately 200 m²/g and was prepared by a flame hydrolysis process. PANI-DNNSA samples were prepared for elemental analysis by precipitating the polymer from the toluene mixture by adding excess acetone. The dispersion was then filtered and washed repeatedly with water and acetone. UV-vis absorption was used in conjunction with gravimetric analysis to determine PANI-DNNSA concentrations.

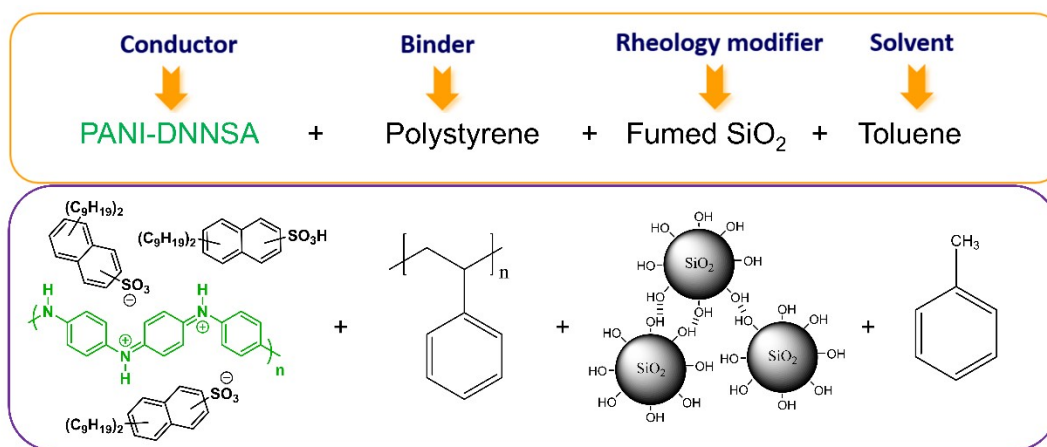
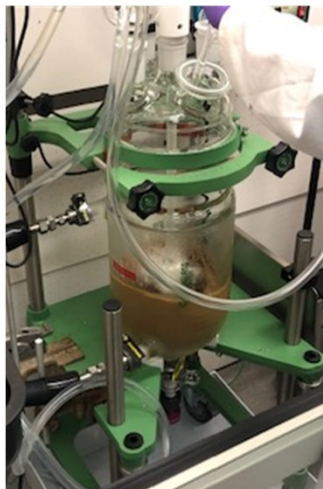


Figure S1. Chemical structures of additives used in ink formulations.

(a) Addition of aniline, water, and DNNSA mixture forms milky white emulsion



(b) Oxidant added dropwise and forms an amber mixture after an hour



(c) Bulk-scale azeotropic distillation in toluene yields 400g PANI-DNNSA

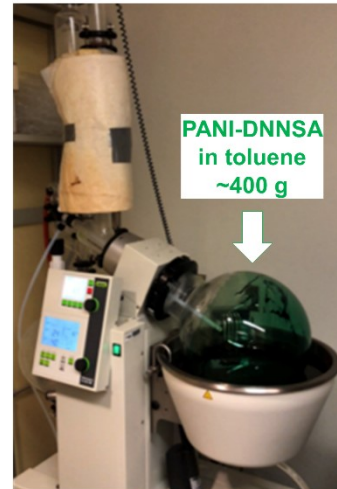


Figure S2. Main steps in bulk-scale PANI-DNNSA synthesis.

Size exclusion chromatography and viscometry were performed in N-Methyl-2-pyrrolidone (NMP, 0.02M ammonium formate) using both refractive index and viscometric detectors, respectively. Concentration determination for PANI-DNNSA/NMP solutions was performed using UV-Vis spectroscopy. For GPC sample preparation, approximately 200 mL of 50 wt% PANI-DNNSA (in toluene) was precipitated from solution by steadily metering ~ 800 mL of acetone with stirring. This powder was then redissolved in the NMP and filtered using a 0.45 μ m filter. Given that the elemental analyses indicate that the molar ratio of DNNSA/PANI in the powder is 0.5 ± 0.01 , the GPC assumes a ratio of 0.5 for the concentration calculation using the Mavern software. The intrinsic viscometry (IV) and molecular weight (MW) analyses were performed in three steps including a polystyrene calibration, a universal calibration with viscometry, and IV/MW plots were generated to determine Mark-Houwink behavior. The alpha and logK values of PANI-DNNSA were compared against VersiconTM to verify the IV/MW relationship. The alpha/logK values for PANI-DNNSA and VersiconTM were determined to be 0.667/-3.05 and 0.667/-2.997, respectively.

Sample	Mn	Mw	IV	Mp	Mw/Mn	Rh(w)
Standard PANI	18,794	36,146	0.0918	45,670	1.923	3.46
Scale-up PANI-DNNSA	27,988	49,499	0.0651	60,236	1.769	3.43

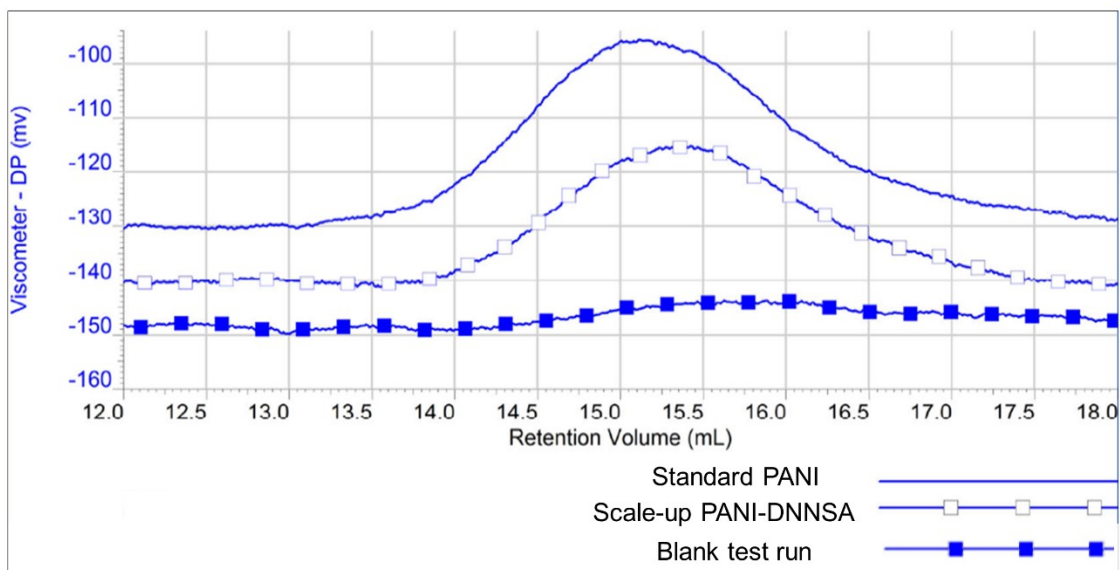


Figure S3. GPC of PANI-DNNSA referenced to polystyrene with a viscometric detector.

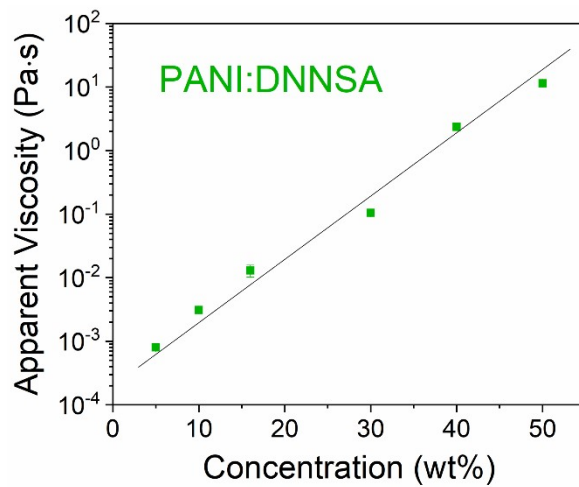


Figure S4. Apparent viscosity measured as a function of PANI-DNNSA concentration in toluene.

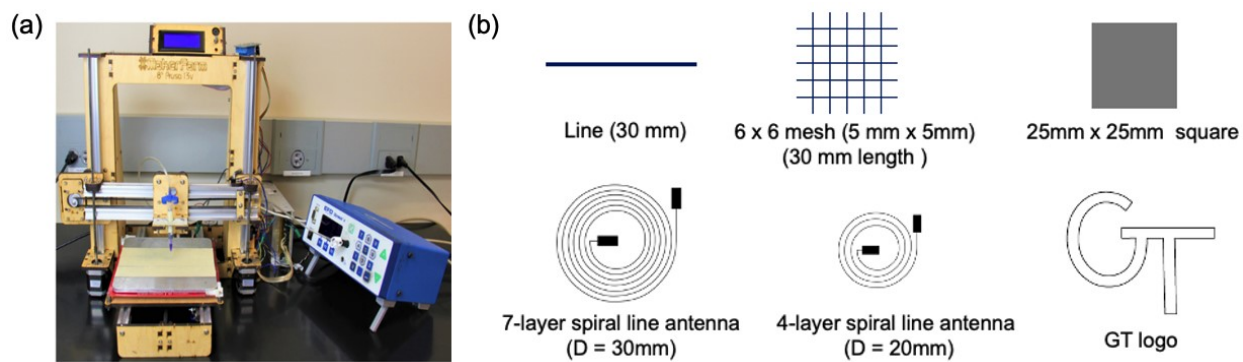


Figure S5. (a) A photograph of the custom-built DIW 3D printer setup and (b) the digital patterns used to print all structures in this work are shown to provide shape comparison and details of printed objects.

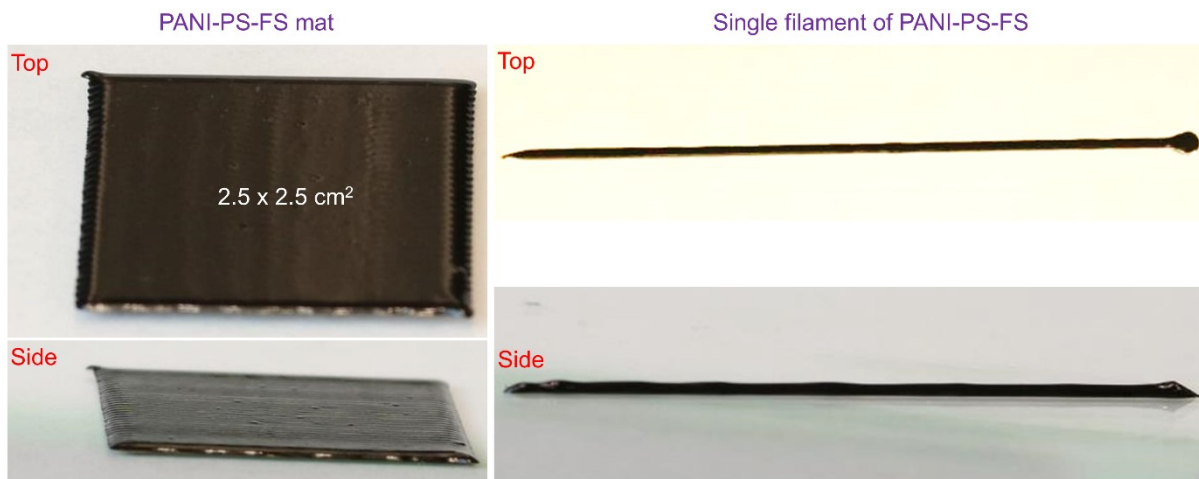


Figure S6. A photograph of a 3D printed mat (4 layers, 2.5 x 2.5 cm) of PANI-PS-FS (77, 1.5, and 4.7 wt%, respectively) is shown on the left and a microscope image of a single filament is on the right, demonstrating the printed filament is continuous and homogeneous in size.

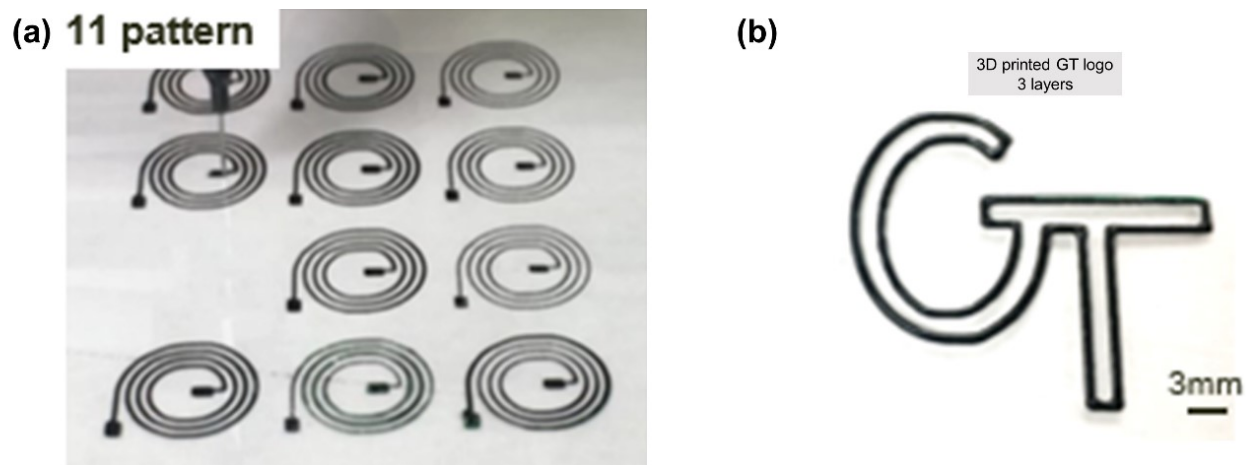


Figure S7. (a) DIW 3D printing of conducting PANI-PS-FS antennae onto PET. (b) Photograph of 3D printed GT logo (3 layers, height = 1.2 mm).

PANI-PS-FS (50, 1, 3 wt%, respectively)

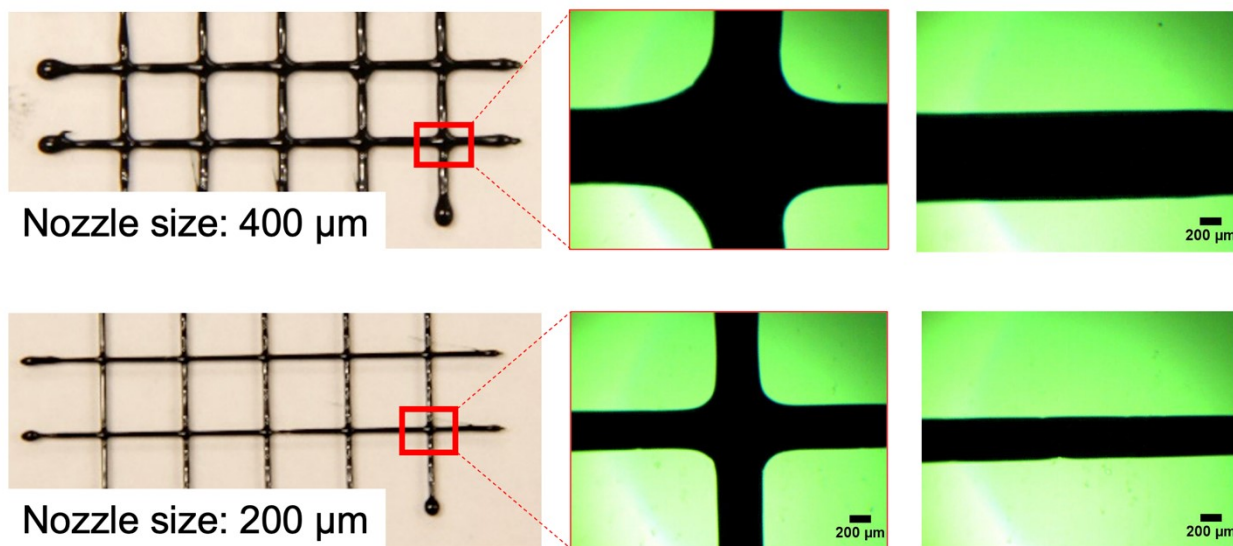


Figure S8. Photographs and optical microscope images of PANI-PS-FS (50, 1, 3 wt% with respect to the total solution, respectively) at 54 wt% total solids in 46 wt% toluene. The grid lines in the top and bottom images were printed using nozzle sizes of 400 and 200 μm , respectively. Scale bars for optical micrographs represent 200 μm .

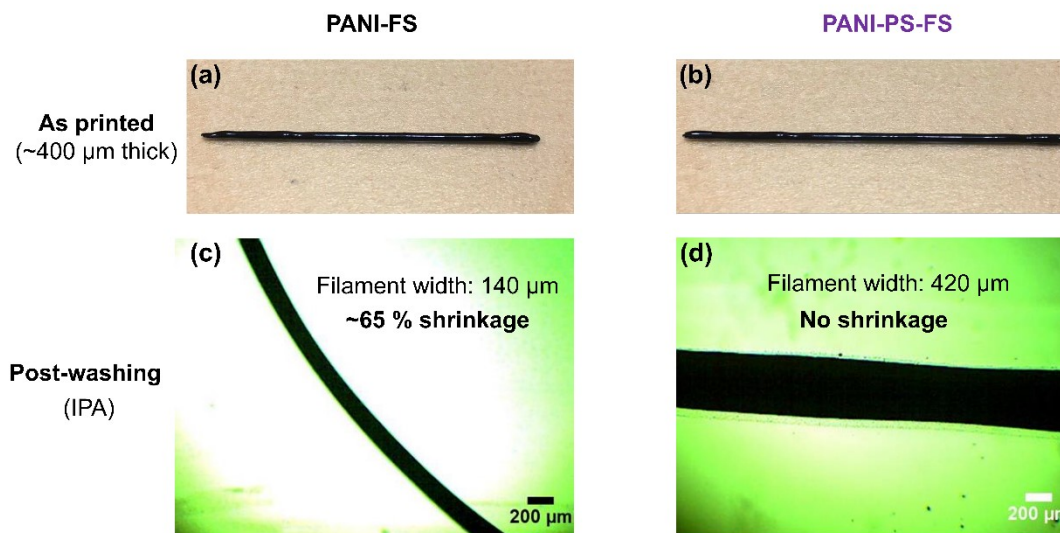


Figure S9. Photographs of printed filaments (approximately 400 micrometers wide) for both (a) PANI-FS and (b) PANI-PS-FS. Optical microscopy images of (c) PANI-FS and (d) PANI-PS-FS illustrate the effect of 30 second IPA washing has on the size of the filament.

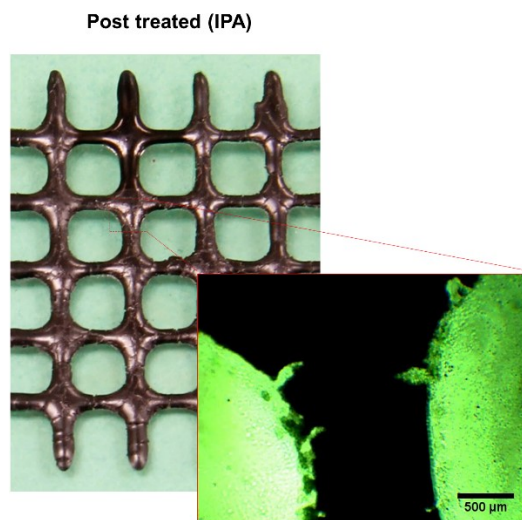


Figure S10. Photograph and optical microscopy (inset) of PANI-PS-FS post-treated with IPA for 5 minutes.

CONDUCTIVITY MEASUREMENTS

Glass substrates ($75 \times 50 \times 1 \text{ mm}^3$) used to cast thin films and print square mats were rinsed and sonicated in sodium dodecyl sulfate-water, deionized water, acetone, and finally isopropanol. As previously mentioned in the main text, the gap height and blade speed were kept constant to allow control over film thickness using the concentration of the polymer solution as the only variable. Various PANI-DNNSA mixtures were prepared in toluene with a concentration of 5-20

mg/mL. After coating, the polymer films were treated with two low molecular weight alcohols: isopropanol (IPA, 99.5 %, Fisher Chemical) and n-butanol (BuOH). Tosylic acid (pTSA) was also added to n-butanol at 5 wt% to be used as a dopant exchange treatment. Initially, post-treatment was performed by dipping the polymer film into a beaker filled with IPA or BuOH:pTSA to allow it to be submerged for ~ 2 seconds. This was repeated three times. However, it was found that continuous dipping was detrimental to maintaining consistent, smooth films. Therefore, the IPA or BuOH:pTSA were drop-cast onto polymer films and allowed to soak for ~ 20 seconds. The films treated with BuOH:pTSA were subsequently gently rinsed with IPA to remove excess pTSA from the surface. Extruded filaments required longer treatment times to fully remove the DNNSA. These were dipped in the treatment solutions for 30 s -10 mins. The thicker films required longer dip times to achieve the elevated conductivity values. These polymer films and filaments were dried for at least 72 hours under vacuum at room temperature.

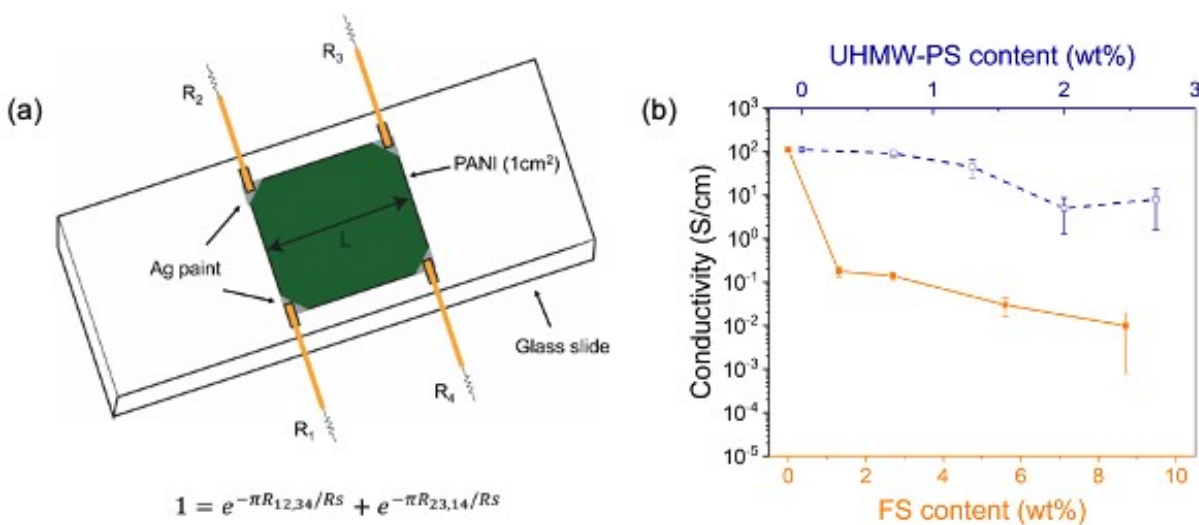


Figure S11. (a) General measurement configuration for the solid-state electrical conductivity of PANI-DNNSA and PANI-PS-FS thin films and printed mats. (b) Solid-state conductivity data measured as a function of FS and UHMW-PS content, whereby the effect of each additive on the electrical conductivity of PANI-DNNSA was evaluated by testing extruded structures prepared with inks of varying content of UHMW-PS (blue curve) and FS (orange curve) after 30 s treatment with BuOH/pTSA.

X-RAY PHOTOELECTRON SPECTROSCOPY

XPS spectra were recorded on a Thermo K-Alpha instrument under ultra-high vacuum ($< 10^{-7}$ mbar) using a charge-neutralizing flood gun. High-resolution spectra were recorded at a 0.1 eV energy resolution and a pass energy of 50 eV. XPS peak deconvolution was performed using CasaXPS analysis software. Each of analyses was performed with a Shirley background and the binding energy was calibrated according to the principal C(1s) peak attributed to alkyl carbon atoms (284.8 eV) present in all of the samples. The FWHM of the deconvoluted peaks were set to be equal for all peaks associated with each element. For the S(2p) spectra, the 3/2 and 1/2 peaks

were set to a 1.16 eV energy offset and the area ratios were constrained to 2:1 respectively. The line shapes used were a combination of Gaussian and Lorentzian line shapes with the relative proportion being 60 % Lorentzian (ex. (GL(60)). An asymmetric line shape with damping were used to fit the sulfur peaks arising from DNNSA. For these peaks, the built-in LF (a, b, w, g) peak shape was used with parameters for spread of the Lorentzian shape above and below the peak binding energy (a and b , respectively), a width parameter constraining the area of the peak (w), and a factor for the Gaussian contribution (g). An example line shape used was LF (1, 2, 20, 80). Peak ratios for the deconvoluted species were calculated using the following formula:

$$Atomic\ ratio = \frac{A_{rel}}{KE^{0.6}(RSF)}$$

Where the relative area (A_{rel}) for each element was integrated on CasaXPS, KE is the kinetic energy of the peak (1486- Binding energy) and RSF is the relative sensitivity factor.

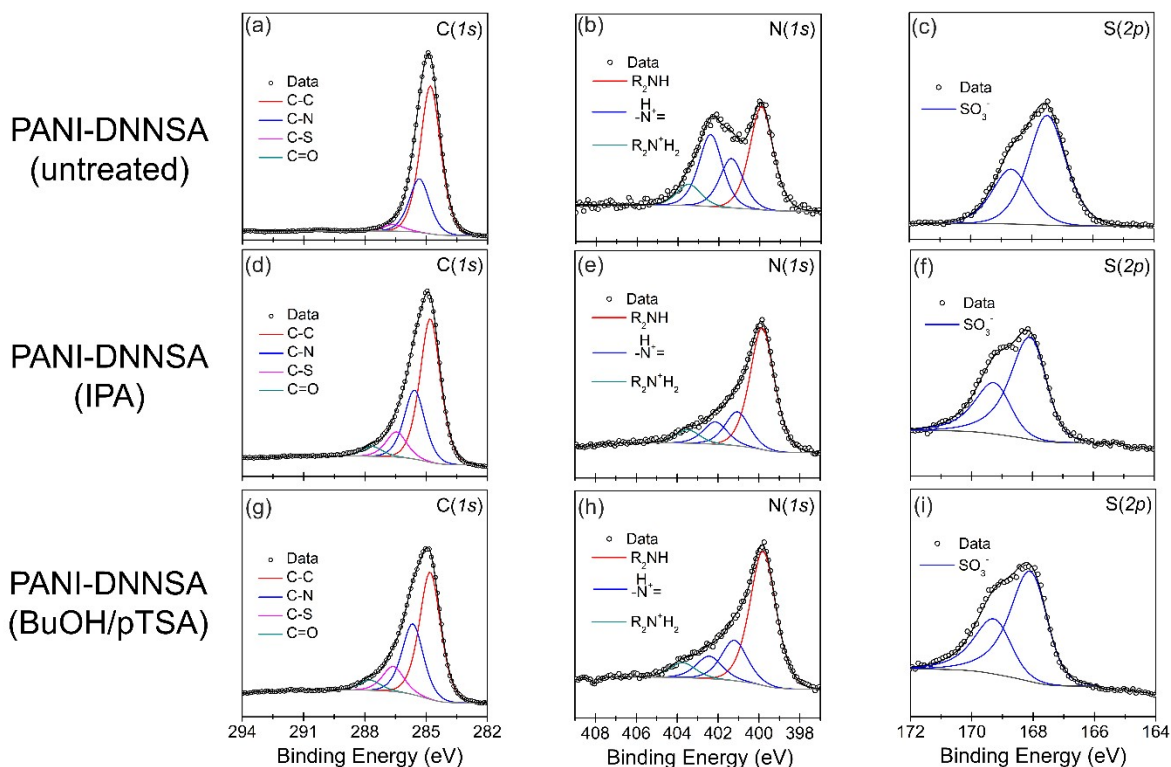


Figure S12. High-resolution XPS spectra for Pristine PANI C(1s) (a), N(1s) (b), and S(2p) (c), IPA-rinsed PANI C(1s) (d), N(1s) (e), and S(2p) (f), and pTSA / nBuOH-rinsed PANI C(1s) (g), N(1s) (h), and S(2p) (i). Peak assignments for deconvolutions appear in each legend.

ELECTROCHEMICAL MEASUREMENTS

The redox response of the films was characterized using cyclic voltammetry and were performed in a three-electrode cell using a Princeton Applied Research 273A potentiostat/galvanostat under CorrWare control. 0.5 M tetrabutylammonium hexafluorophosphate (TBAPF₆, Acros Organics, 98%, recrystallized from hot ethanol) in propylene carbonate was the selected electrolyte. A glassy carbon electrode (3 mm diameter) served as the working electrode. A Ag/Ag⁺ electrode (inner solution: 10 mM AgNO₃ and 0.5 M TBAPF₆ in acetonitrile, 0.065 V vs. Fc/Fc⁺) was used as the reference electrode. A platinum flag was selected as the counter electrode.

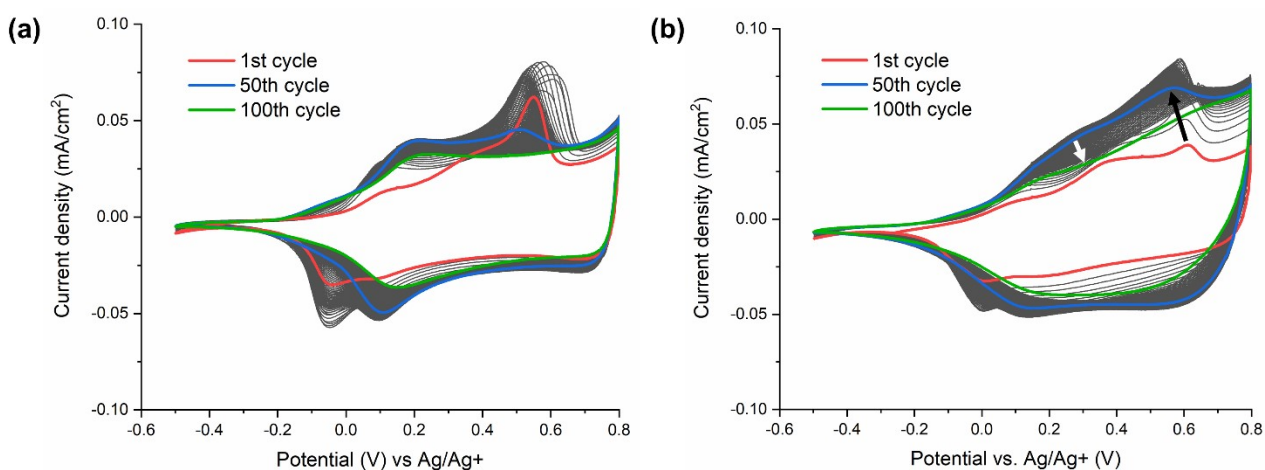


Figure S13. Cyclic voltammograms of (a) PANI-DNNSA and (b) PANI-PS-FS up to 100 cycles in 0.5 M TBAPF₆/PC, scan rate 50 mV/s.

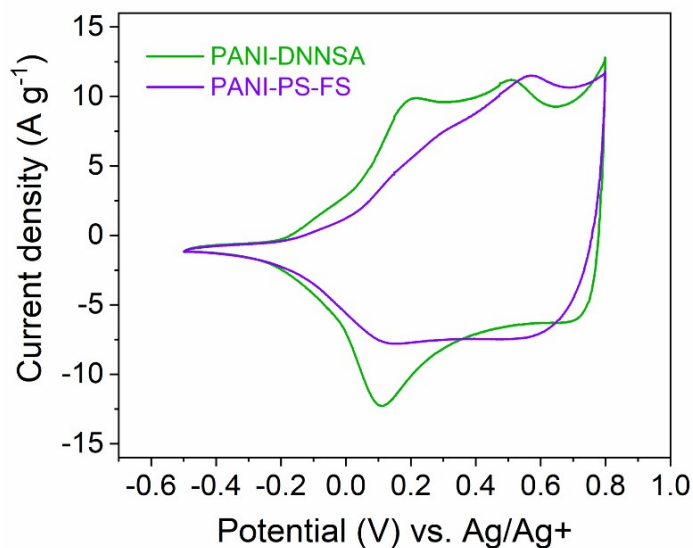


Figure S14. Overlaid cyclic voltammograms of PANI-DNNSA and PANI-PS-FS (after break-in and post treatment, 50th cycle).

MECHANICAL AND THERMAL CHARACTERIZATION

The tensile test was conducted on a DMA tester at room temperature. Samples were prepared by solution casting via extrusion with varying polymer concentrations into filaments. The filaments were made by extrusion from dilute inks and were trimmed to $\sim 20.0\text{mm} \times 4.0\text{mm} \times 1.5\text{mm}$ dimensions. A small value of loading rate, 0.5mm per min, was chosen to minimize viscoelastic effects. PANI-DNNSA, PANI-FS, and PANI-PS-FS were all prepared at 80, 50-6, 77-1.5-4.7, respectively. PANI-DNNSA and PANI-FS were unable to be measured due to brittle fracture prior to measurements.

Differential scanning calorimetry was performed using a Mettler Toledo DSC1 instrument with a Huber TC100 cooler for temperature control. Thermogravimetric analysis was conducted using a Mettler Toledo TGA2 STAR System. All measurements were made in inert atmospheres through nitrogen purging. Samples were prepared for DSC and TGA via blade coating, drying under reduced pressure for 72 hours, and subsequently by scraping (viscoelastic) solid polymer/dried ink into the pans. TGA was performed using a scan rate of 10 °C/minute. DSC was conducted with a scan rate of 20 °C/minute. According to TGA, the onset of degradation for the materials is approximately 225 °C.

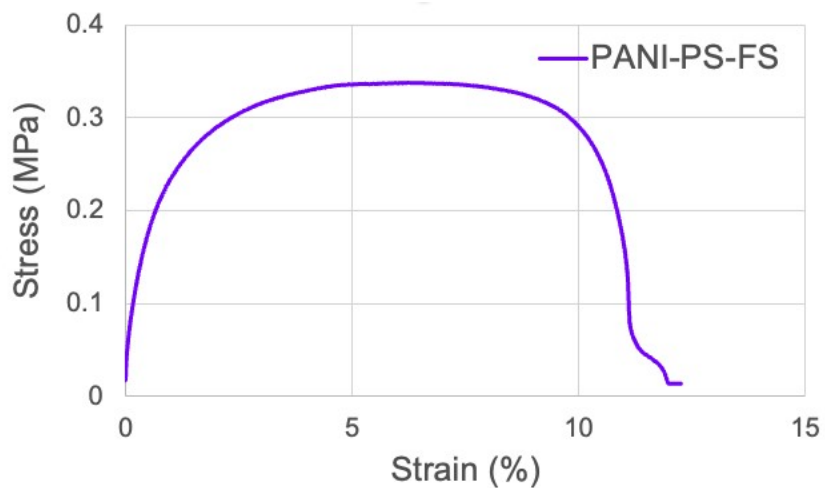


Figure S15. Stress-strain curve for the failure test of a PANI-PS-FS filament ($\sim 20.0\text{mm} \times 4.0\text{mm} \times 1.5\text{mm}$ dimensions) performed at room temperature.

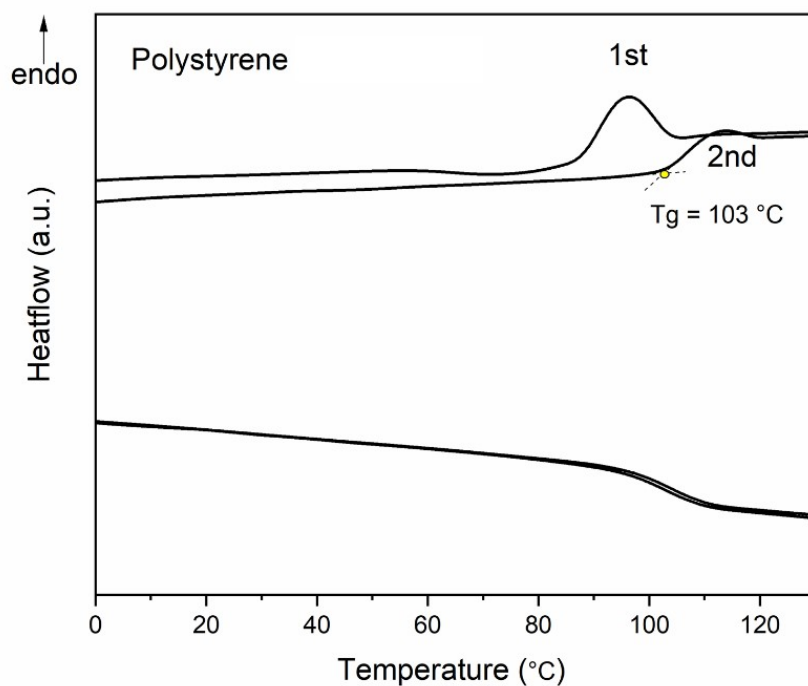


Figure S16. DSC thermograms of 30,000 kg/mol polystyrene received from Polysciences. DSC was conducted with a scan rate of 20 °C/minute. Sample was transferred directly as a powder from commercial container to the DSC pan.

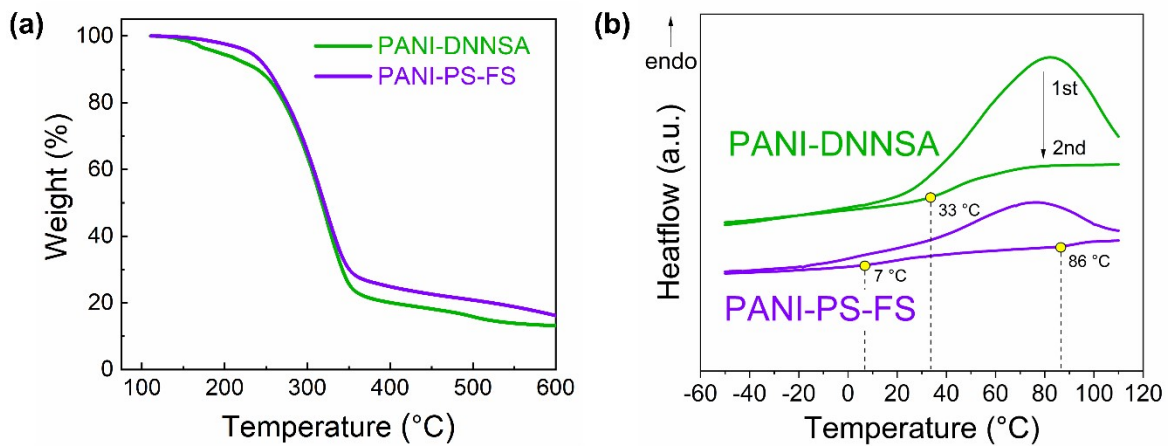


Figure S17. (a) TGA and (b) DSC of both PANI-DNNSA (green) and PANI-PS-FS (purple). DSCs show first and second scans and were conducted with a scan rate of 20 °C/minute.