

**Supporting Information for:**

**Conductive recycled PETG additive manufacturing filament with  
Graphene/MWCNT/Carbon Black for electrochemical  
applications**

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## **Experimental Section**

### **Chemicals**

All chemicals used of analytical grade and were used as received without any further purification. All solutions were prepared with deionised water of resistivity not less than 18.2 M $\Omega$  cm from a Milli-Q Integral 3 system from Millipore UK (Watford, UK). Hexaamineruthenium (III) chloride (RuHex, 98%), potassium ferricyanide (III) (99%), potassium hexacyanoferrate (II) trihydrate (98.5-102.0%), sodium hydroxide (>98%), potassium chloride (99.0-100.5%), and graphene nanoplatelets were purchased from Merck (Gillingham, UK). Carbon black (Super P®, >99+%) and pure ethanol were purchased from Fisher Scientific (Loughborough, UK). Long (10 – 30  $\mu$ m) multi-walled carbon nanotubes (MWCNT, 10-20 nm outer diameter) were purchased from Cheap Tubes (VT, United States). Natural PETg filament and commercial conductive PLA/carbon black filament (1.75 mm, ProtoPasta, Vancouver, Canada) were purchased from Farnell (Leeds, UK).

### **Recycled filament production**

Prior to any mixing or filament production all rPETg was dried in an oven at 60 °C for a minimum of 2.5 h, which removed any residual water in the polymer. The polymer composition was prepared using 70 wt% rPETg and 30 wt% conductive filler. Four variations of conductive filler were produced: variation 1 utilised 30 wt% carbon black, variation 2 utilised 25 wt% carbon black and 5 wt% multi-walled carbon nanotubes, variation 3 utilised 25 wt% carbon black and 5 wt% graphene nanoplatelets, and variation 4 utilised 25 wt% carbon black, 2.5 wt% multi-walled carbon nanotubes and 2.5 wt% graphene nanoplatelets. The components in each case were added into a chamber of 63 cm<sup>3</sup> and mixed at 230 °C with Banbury rotors at 70 rpm for 5 min using a Thermo Haake Poydrive dynamometer fitted with a Thermo Haake Rheomix 600 (Thermo-Haake, Germany). Each resulting polymer composite was allowed to cool to room temperature before being granulated to create a finer granule size using a Rapid Granulator 1528 (Rapid, Sweden). The granulated sample was collected and processed through the hopper of a EX6 extrusion line (Filabot, VA, United States). The EX6 was set up with a single screw and had four set heat zones of 60, 230, 230 and 235 °C respectively. The molten polymer was extruded from a 1.75 mm die head, pulled along an Airpath cooling line (Filabot, VA, United States, through an inline measure (Mitutoyo, Japan)

and collected on a Filabot spooler (Filabot, VA, United States). The filament was then ready to use for Additive Manufacturing.

### **Additive Manufacturing**

All computer designs and .3MF files seen throughout this manuscript were produced using Fusion 360® (Autodesk®, CA, United States). These files were sliced and converted to .GCODE files ready for printing by the open source software, PrusaSlicer (Prusa Research, Prague, Czech Republic). The additive manufacturing electrodes were 3D-printed using fused filament fabrication (FFF) technology on a Prusa i3 MK3S+ (Prusa Research, Prague, Czech Republic). All additive manufacturing electrodes were printed using a 0.6 mm nozzle with a nozzle temperature of 250 °C, 100% rectilinear infill, 0.15 mm layer height, and print speed of 35 mm s<sup>-1</sup>. All additive manufactured electrodes used throughout this work were “lollipop” designs with a 5 mm disc, 8 x 2 mm connection stem and 1 mm thick <sup>[19]</sup>. In all cases, polyimide tape was placed on top of the print bed as PETg can cause damage upon removal due to the strength of adhesion.

### **Physicochemical Characterisation**

Thermogravimetric analysis (TGA) was performed using a Discovery Series SDT 650 controlled by Trios Software (TA Instruments, DA, USA). Samples were mounted in alumina pans (90 µL) and tested using a ramp profile (10 °C min<sup>-1</sup>) from 0 – 800 °C under N<sub>2</sub> (100 mL min<sup>-1</sup>).

X-ray Photoelectron Spectroscopy (XPS) data were acquired using an AXIS Supra (Kratos, UK), equipped with a monochromated Al X-ray source (1486.6 eV) operating at 225 W and a hemispherical sector analyser. It was operated in fixed transmission mode with a pass energy of 160 eV for survey scans and 20 eV for region scans with the collimator operating in slot mode for an analysis area of approximately 700 x 300 µm, the FWHM of the Ag 3d<sub>5/2</sub> peak using a pass energy of 20 eV was 0.613 eV. Before analysis, each sample was ultrasonicated for 15 min in propan-2-ol and then dried for 2.5 hours at 60 °C as this has been shown in our unpublished data to remove excess contamination and therefore minimise the risk of

misleading data. The binding energy scale was calibrated by setting the graphitic  $sp^2$  C 1s peak to 284.5 eV; this calibration is acknowledged to be flawed [20], but was nonetheless used in the absence of reasonable alternatives, and because only limited information was to be inferred from absolute peak positions.

Scanning Electron Microscopy (SEM) micrographs were obtained using a Crossbeam 350 Focussed Ion Beam – Scanning Electron Microscope (FIB-SEM) (Carl Zeiss Ltd., Cambridge, UK) fitted with a field emission electron gun. Imaging was completed using a Secondary Electron Secondary Ion (SESI) detector. Samples were mounted on the aluminium SEM pin stubs (12 mm diameter, Agar Scientific, Essex, UK) using adhesive carbon tabs (12 mm diameter, Agar Scientific, Essex, UK) and coated with a 3nm layer of Au/Pd metal using a Leica EM ACE200 coating system prior to imaging.

Raman spectroscopy was performed on a Renishaw PLC in Via Raman Microscope controlled by WiRE 2 software at a laser wavelength of 514 nm.

Changes in the mechanical performance of the recycled filament was performed through tensile testing of 3D-printed parts using a Hounsfield H10KS. Tensile testing was carried out in accordance with ASTM D638, specifically using Type IV specimen dimensions and a testing rate of 5 mm  $\text{min}^{-1}$ . Cross-sectional areas used to determine ultimate tensile strength were calculated using the average width and thickness measurements taken from three points along the gauge length of each test coupon.

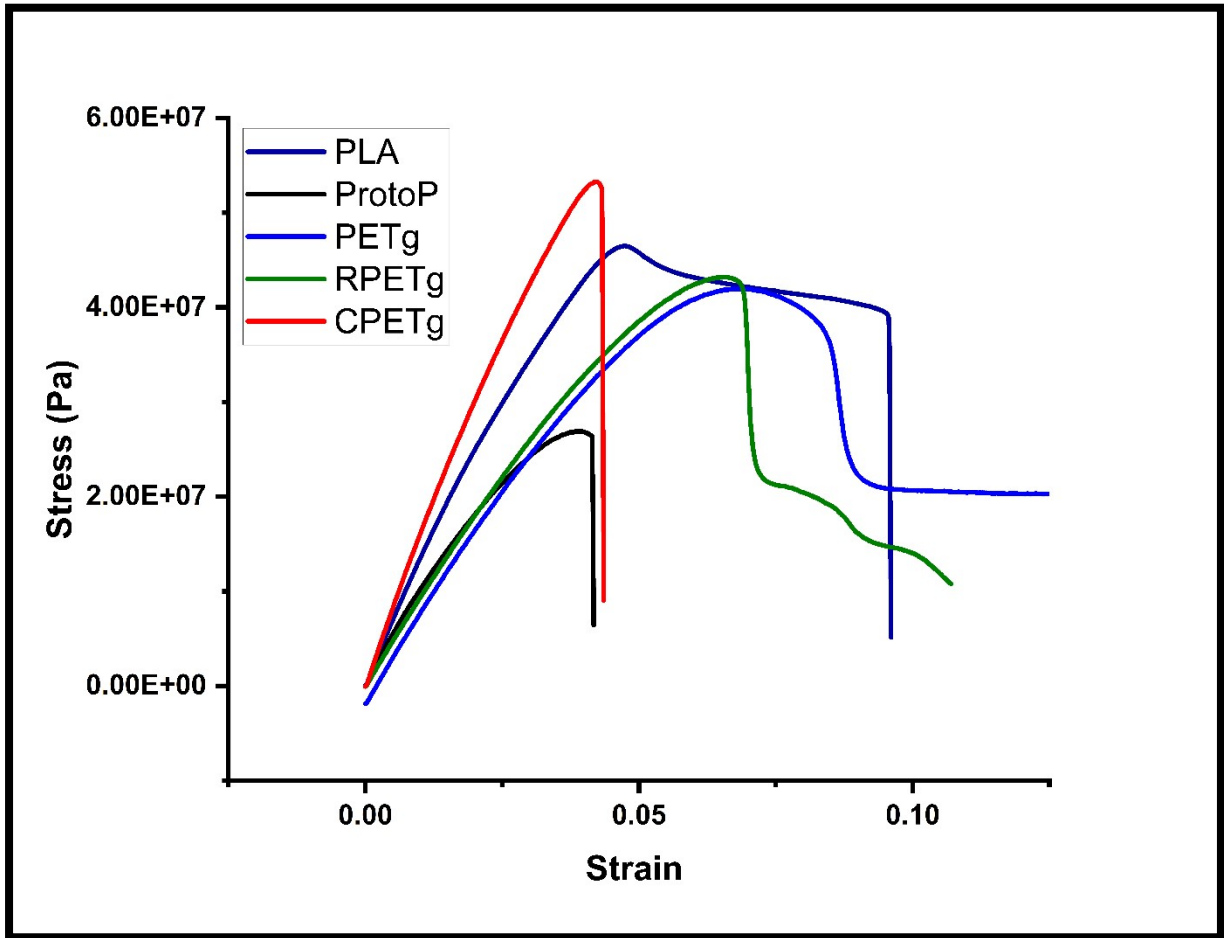
### **Electrochemical Experiments**

All electrochemical measurements were performed on an Autolab 100N potentiostat controlled by NOVA 2.1.6 (Utrecht, the Netherlands). The electrochemical characterisation of the bespoke filaments and comparison to the benchmark were performed using a lollipop design ( $\varnothing$  5 mm, 10 x 2 mm connection length, 1 mm thickness) electrodes alongside an external commercial Ag|AgCl (3 M KCl) reference electrode and a nichrome wire counter electrode. All solutions were prepared using deionised water of resistivity not less than 18.2

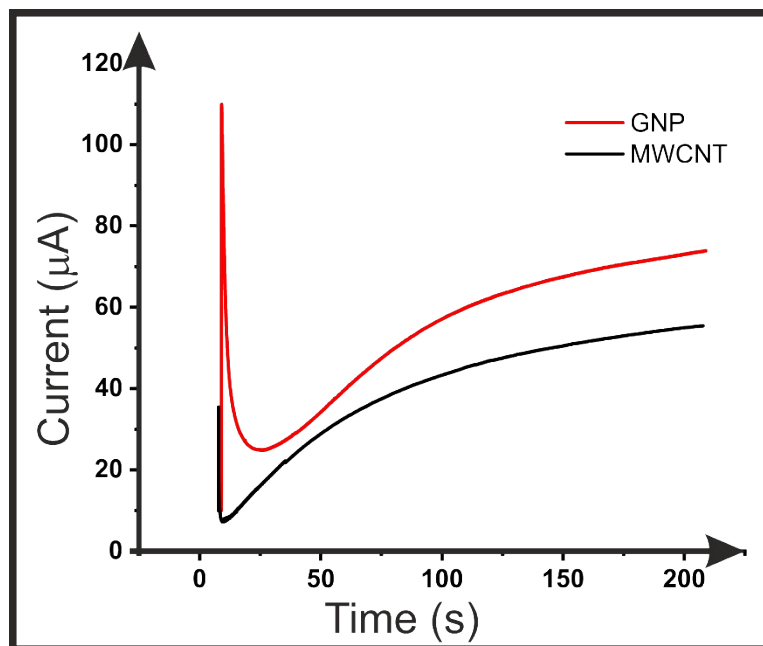
M $\Omega$  cm from a Milli-Q system (Merck, Gillingham, UK). All solutions were purged of O<sub>2</sub> thoroughly using N<sub>2</sub> prior to any electrochemical experiments.

Activation of the additive manufactured electrodes, when applicable, was achieved through the use of chronoamperometry as seen previously in the literature <sup>[5a]</sup>. Briefly, the additive manufactured electrode was submerged in sodium hydroxide (0.5 M) and a voltage of +1.4 V was applied for 200 s, followed by -1.0 V for 200 s. Following this, the additive manufactured electrode was thoroughly rinsed with deionised water and dried with compressed air.

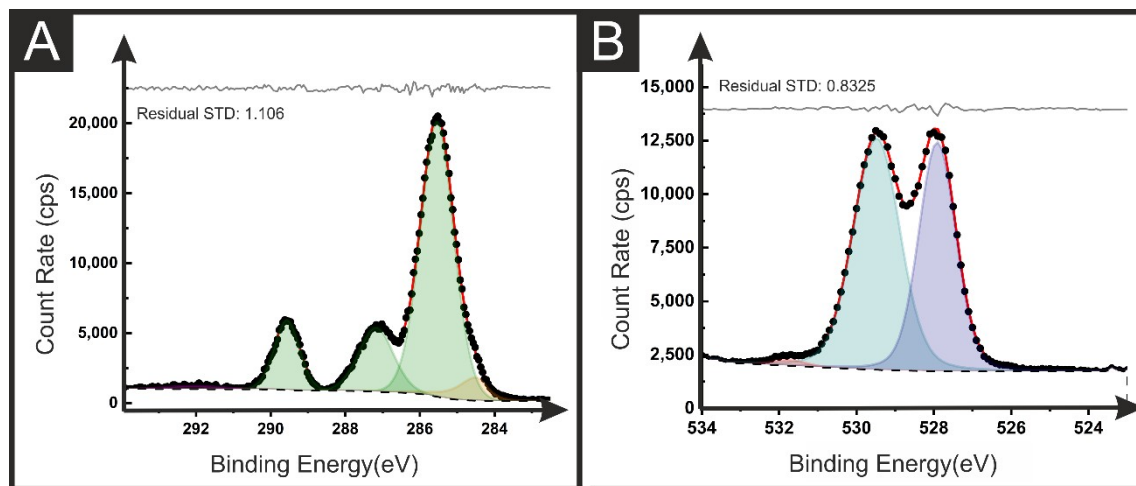
**Figures:**



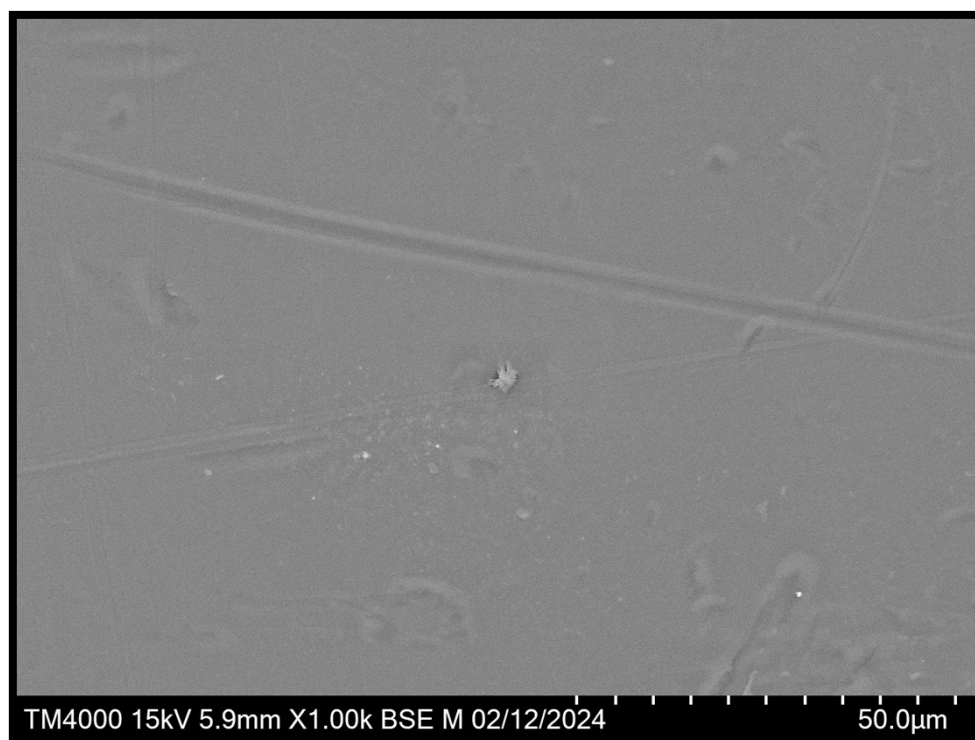
**Figure S1.** Example stress versus strain plots for the 5 different materials tested, non-conductive PLA, conductive PLA, non-conductive PETg, recycled non-conductive PETg, and conductive PETg.



**Figure S2.** Electrochemical activation profiles for additive manufactured electrodes printed from the GNP and MWCNT rPETg filaments.



**Figure S3.** XPS data corresponding to the A) C 1s and B) O 1s spectra for a non-activated additive manufactured electrode made from the CB/MWCNT/GNP (25/2.5/2.5 wt%) filament.



**Figure S4.** SEM Image of the surface of commercial PETg filament without any addition of nanofillers.

