Electronic Supporting Information

Fabrication of 3D PEDOT:PSS Composite Microstructures via Two-Photon Polymerisation

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Materials and Methods

Macroscale photopolymerisation and characterisation

Photorheology. Photorheological measurements were carried out at room temperature in an AR-G2 rheometer (TA Instruments) using a UV-light lamp (λ = 365 nm, power = 1 mW cm^{-2}), oscillation stress of 100 Pa, and 2 Hz frequency. The gel point was determined by placing the samples on a glass parallel plate of 20 mm diameter, letting them stabilise for 60 s to be subsequently irradiated for 20 s, and continuing to register the elastic modulus (G′) and loss modulus (G″) until a plateau was reached.

Infrared spectroscopy. The polymerisation was evidenced by Fourier transformed infrared spectroscopy (FTIR) using a Thermo scientific model Nicolet FTIR spectrometer. 1 drop of the photoresist 1 or 2 was placed onto the zinc selenide glass and the spectra was recorded in the attenuated total reflectance mode (ATR) before and after UV curing (λ = 365 nm) for 1 min, with a resolution of 4 cm^{-1} and 32 scans.

Tensile Test (macroscale). Type V probes of 1 mm thickness were printed with both photoresists. The tensile test was applied to probes in the dried and swollen state by the ASTM D638 criterion universal testing system using an Instron 5569 in a single uniaxial tensile mode (n = 5). The controlled tension force (load cell of 100 N) was applied at a rate of 1 mm min^{-1}, and the results were plotted as stress–strain curves. Samples were analysed in triplicate, and results were expressed as mean ± standard deviation.

Electrical conductivity (macroscale). Discs of 10 mm diameter and 0.85 mm thickness were printed and their electrical conductivity was measured. The electrical conductivity was calculated taking into account the thickness of each sample at each condition tested. Samples were analysed in triplicate and testing three different sample areas. Results were expressed as mean ± standard deviation.

Electrochemical characterisation. Cyclic voltammetry was performed using a VMP-3 potentiostat (Biologic Science Instruments) in a three-electrode setup, employing a platinum wire as the counter electrode, Ag/AgCl as the reference electrode, and glassy carbon as the working electrode. Hydrogels were fabricated by depositing 10 µL of the photoresist in the working electrode, followed by a photopolymerisation step with UV light irradiation. Finally, they were cleaned in water for 5 min. 0.1 M NaCl aqueous solution was used as the electrolyte, and it was purged with nitrogen for 15 min before the experiment. Cyclic voltammetry measurements were carried out in the potential range of −0.2 to 0.6 V vs. Ag/AgCl at 20 mV s^{-1} and 20, 50, 100, 150, and 200 mV s^{-1} for the scan rate experiment.

Silanisation of glass substrate

To ensure attachment of the 3D microstructures to the substrate, all glass substrates (high precision round cover slips, 30 mm, thickness 170 ± 5 µm; No 1.5 (Thermo-Fisher)) underwent silanisation treatment. First, the slides were cleaned with acetone, isopropanol, ethanol, methanol, and DI water; followed by UV Ozone for 20 min (Ossila, United Kingdom). Slides were then submerged in a solution of 3-(trimethoxysilyl)propyl methacrylate (3 vol.% in ethanol with 0.1 vol.% acetic acid) for 1 h. The slides were removed from this solution, rinsed with ethanol, dried under nitrogen, and baked in an oven at 60 °C for 3 h.

3D design

Several of the 3D structures used in this work were designed using Blender software and adapted as needed in DeScribe software. The Shamrock, Snowflake, and Water Lily structures were adapted from files licensed under the Attribution-Non-commercial 4.0 International (CC BY-NC 4.0 DEED) license and available for download under the links below:
Shamrock by Bjornnijen, https://www.thingiverse.com/thing:749260
Snowflake by protechnordic is https://www.thingiverse.com/thing:563396
Water lily by guppyk licensed under the Creative Commons - Attribution license, and available at https://www.thingiverse.com/thing:4364395

Raman spectroscopy

Raman spectra were obtained for photoresists and microstructures fabricated with each of the photoresists described in this article using a WITec alpha300 RA Raman microscope (Oxford Instruments) with a 532 nm solid laser source of 50 mW power. The microstructures used for RAMAN spectroscopy were cubes fabricated using TPP with designed dimensions of 50 x 50 x 30 µm.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was carried out using the facilities of the Advanced Microscopy Laboratory (AML) in Trinity College Dublin. Samples were coated with a conductive Pd/Au layer using an Ag-Pd target (57 × 0.1 mm) that was purchased from Ted Pella Inc and a Cressington 208Hr high-resolution sputter coater, to improve contrast where static charging interfered with the imaging. Low kV (2-5 kV) SEM was carried out using the Zeiss ULTRA Plus with a GEMINI FESEM column (Zeiss, Germany) and an SE2 detector.

Atomic Force Microscopy (AFM)

A commercial AFM system (MFP-3D, Asylum Research, USA) was used for measuring the swelling and mechanical properties of the micro-fabricated 3D structures. Imaging both in air and water was performed in contact mode, and height and deflection images were recorded. Data were recorded with 256 lines per scan direction and with a scan rate of 0.3 Hz and scan angle of 90°. AFM probe (Electrical all-in-one, BudgetSensors, Bulgaria) with 4 different platinum coated AFM cantilevers on a single AFM holder chip in which cantilever D with tip radius < 25 nm, resonant frequency of ~350 kHz, and a spring constant of ~40 N m^{-1} was used for topography and modulus measurements. The AFM height images were processed using Gwyddion AFM software (version 2.6), all images were 1st order plane fit flattened. Line profile data were obtained following image postprocessing and plotted using Igor pro-6.38. Young's modulus measurements were done in contact mode using force spectroscopy technique in Asylum software. Before carrying out force curves on the sample, the probe was calibrated to obtain the spring constant and deflection InvOLS (inverse optical lever sensitivity). The modulus values were obtained by fitting the extension part of the force curve with Hertz model. Force measurements were done in two different locations over the micro-cubes with a force distance of 3 μm and trigger voltage of 1V. Three force curves were collected at each point and the overall modulus value was reported by averaging 6 different force curves over a single cube fabricated at a specific laser power.

Conductive Atomic Force Microscopy (C-AFM)

C-AFM measurements were performed using an Asylum Research MFP-3D AFM with an ORCA integrated tip-holder and current preamplifier (2 nA sensitivity). The sample bias was applied to the ITO electrodes via a wire from the ORCA holder, and the tip was held at virtual ground via the current preamplifier. The preamplifier converted the current to a voltage (gain 471.9 pA V^{-1}) that was subsequently recorded after analog-to-digital conversion by the AFM hardware. The current preamplifier was within a few centimetres of the tip to minimise electrical noise. Visual tip observation was provided by an overhead mounted CCD camera. The reported sample bias was applied to the substrate, with the tip being grounded through the preamplifier's virtual ground. Platinum-coated (with a Cr adhesion layer) contact-mode AFM probes (Budget Sensors, all in one electrical (AIOE), cantilever B with spring constant 2.7 N m^{-1}) were used for all electrical measurements reported in this work. The contact mode deflection set point was set to maintain a ~10 nN load during imaging. A triangular waveform

going from 0 to +5V to -5V at 1Hz frequency was applied to obtain IV curves. C-AFM images were obtained at +5V and -5V bias applied to the sample.

Kelvin probe Force Microscopy (KPFM)

A commercial AFM system (MFP-3D, Asylum Research, USA) was used in this study. Pt/Ir-coated conductive probes (PPP-EFM Nanosensors, with nominal tip radius < 15 nm, resonant frequency of 75 Hz, and a spring constant of 2 N m^{-1}) were used for both topography and KPFM measurements. KPFM scanning was operated in dual pass mode in air, in which the topography of the surface is obtained in the first pass in amplitude modulation mode, while in the second pass the tip is lifted to a defined height (50 nm) and an AC voltage Vac ~3 V is applied to the tip at the cantilever's resonance frequency, generating an electrostatic force between the tip and the sample. Contact potential difference (CPD) of the surface is obtained by monitoring the DC offset (Vdc) applied to nullify the first harmonic in phase electrostatic force between the tip and the sample.

Appendix

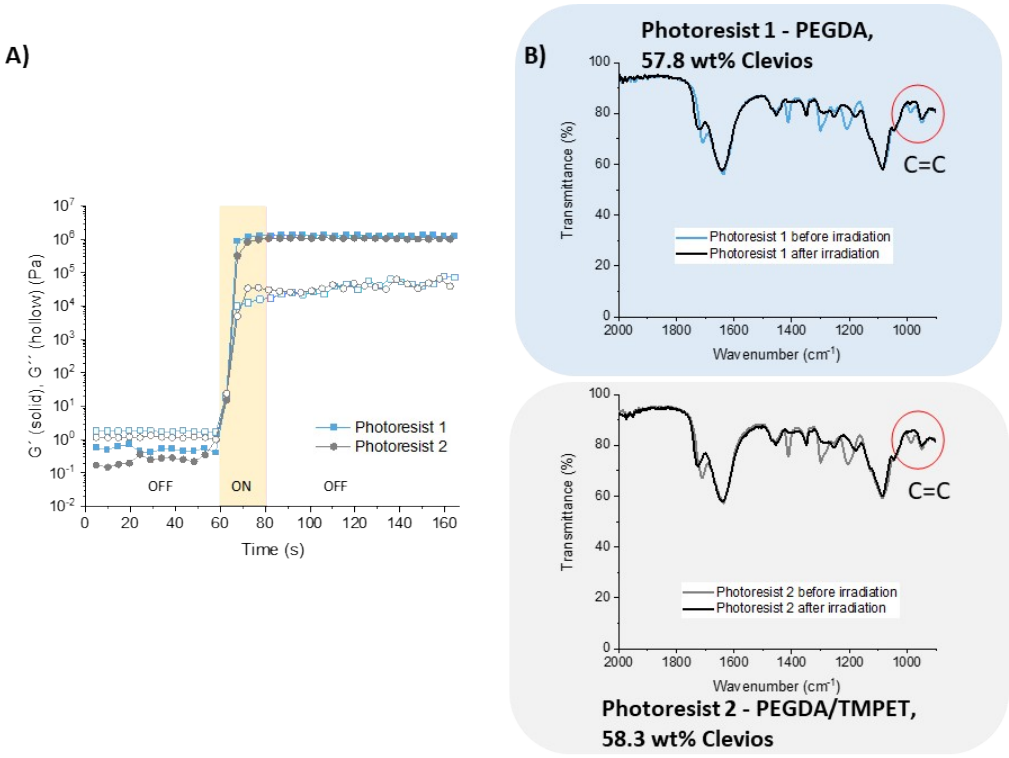

Fig. S1. A) Rheological measurements of the elastic modulus (G′, plain figures) and loss modulus (G″, empty figures) to determine the gel point when the inks are irradiated (λ = 365 nm, power 1 mW cm^{-2}) for 20 s (in the interval from 60 to 80 s). B) ATR-FTIR spectra of photoresists 1 - PEGDA, 57.8 wt% Clevios (top) and 2 - PEGDA/TMPET, 58.31 wt% Clevios (bottom) before and after irradiation.

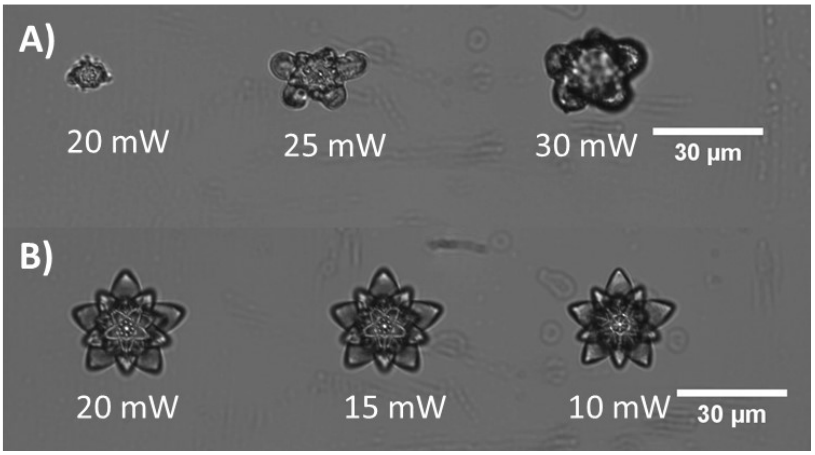

Fig. S2. Microscope images of waterlilies fabricated by DLW-TPP A) after 8 minutes and B) after 30 minutes of evaporation using the photoresist 2 - PEGDA/TMPET, 58.31 wt% Clevios.

Table S1. Summary of weight loss during evaporation experiments of photoresist 1- PEGDA, 57.8 wt% Clevios.

Experiment number	weight loss (%) relative to initial weight
1	18.3
2	17.6
3	19.6
4	15.1
5	15.1
6	16.2
7	16.6
8	16.8
Average	16.9

Table S2. Summary of weight loss during evaporation experiments of photoresist 2 - PEGDA/TMPET, 58.31 wt% Clevios.

Experiment number	weight loss (%)
1	16.9
2	17.6
3	13.6
4	16.9
5	14.9
Averages	15.97

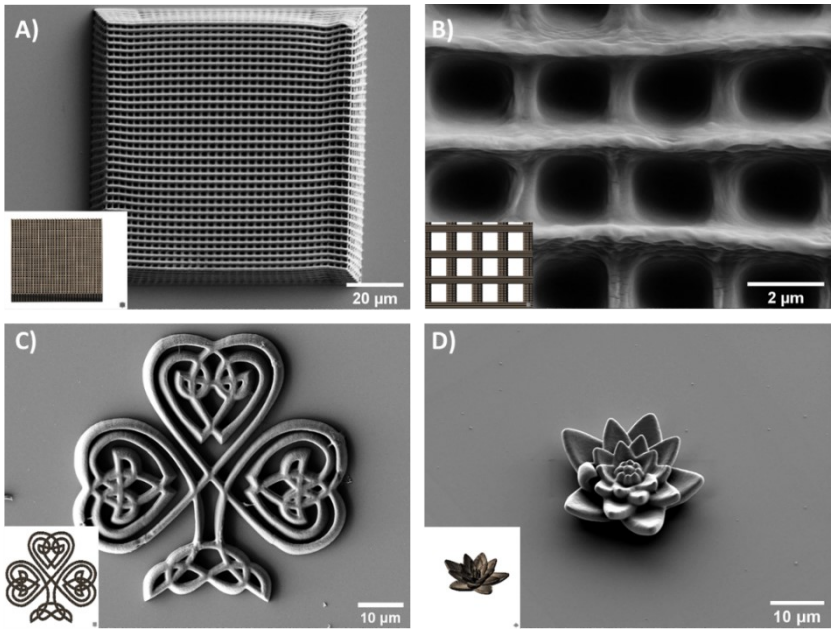

Fig. S3. A) and B) SEM pictures of 16 layers woodpile, C) Shamrock, and D) waterlily fabricated using photoresist 1- PEGDA, 57.8 wt% Clevios. Scale bar representing A) 20 µm, B) 2 µm, C) 10 µm and D) 10 µm.

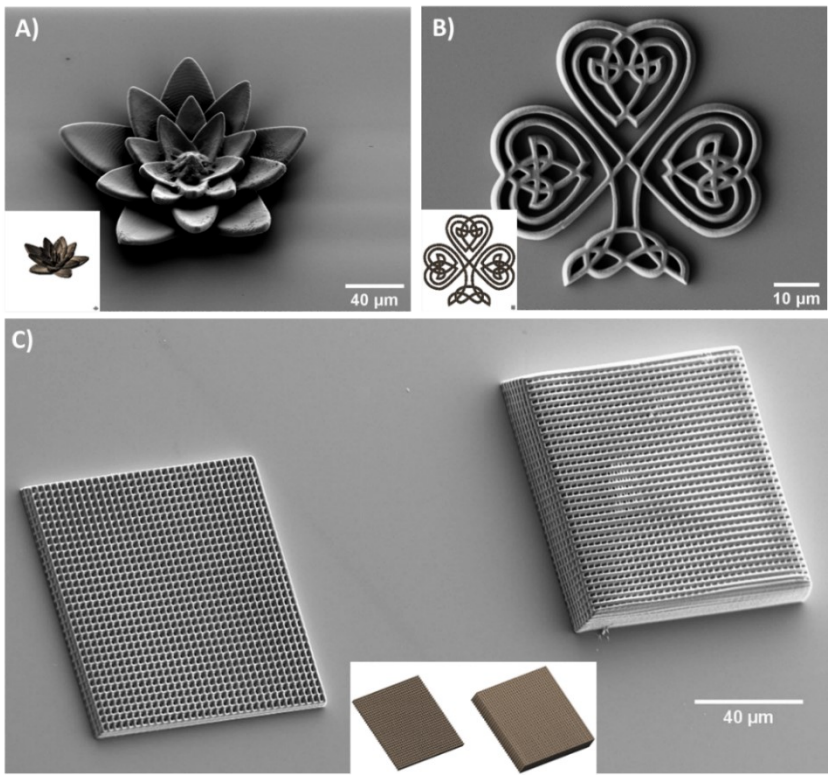

Fig. S4. SEM images of A) Waterlily, B) Shamrock, and C) 5 layers (left) and 16 layers (right) woodpile fabricated using the photoresist 2 - PEGDA/TMPET, 58.31 wt% Clevios with a scale bar representing A) 40 µm, B)10 µm, C) 40 µm.

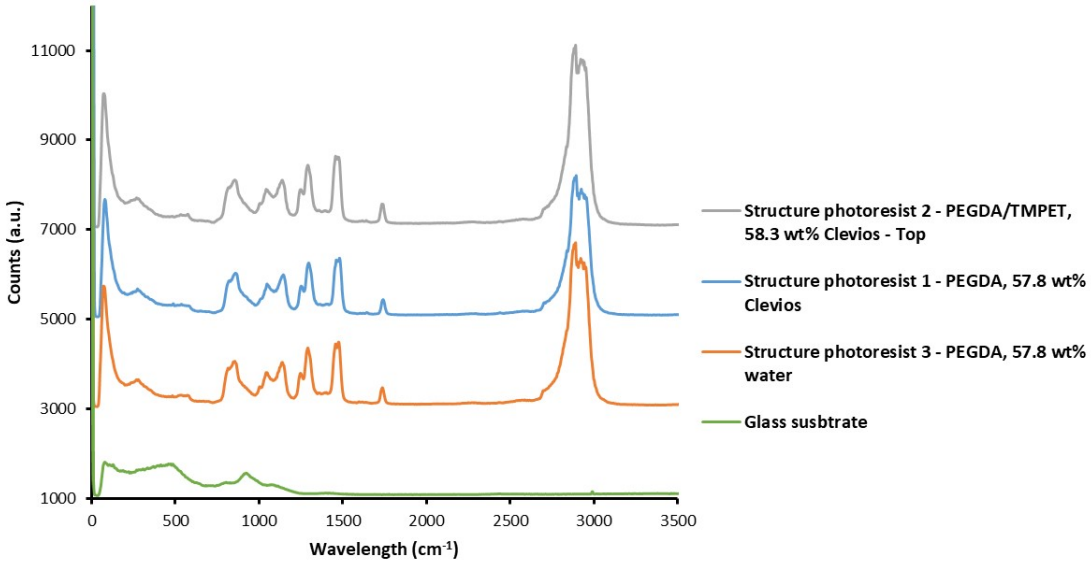

Fig. S5 Raman spectra of glass used as the substrate for the fabrication of microstructures, cubes (50×50×30 µm) fabricated by TPP using photoresist 3 - PEGDA, 57.8 wt% water (which has the same composition as photoresist 1 but uses only water instead of Clevios PH1000); photoresist 1 - PEGDA, 57.8 wt% Clevios; and photoresist 2 - PEGDA/TMPET, 58.31 wt% Clevios.

Table S3. Composition of photoresist 3 - PEGDA, 57.8 wt% water.

Chemical	Amount (mg)	Weight %
Poly(ethylene glycol) diacrylate (PEGDA-700)	305	35.26
Ethylene Glycol	20	2.31
LAP	40	4.63
Water	500	57.80

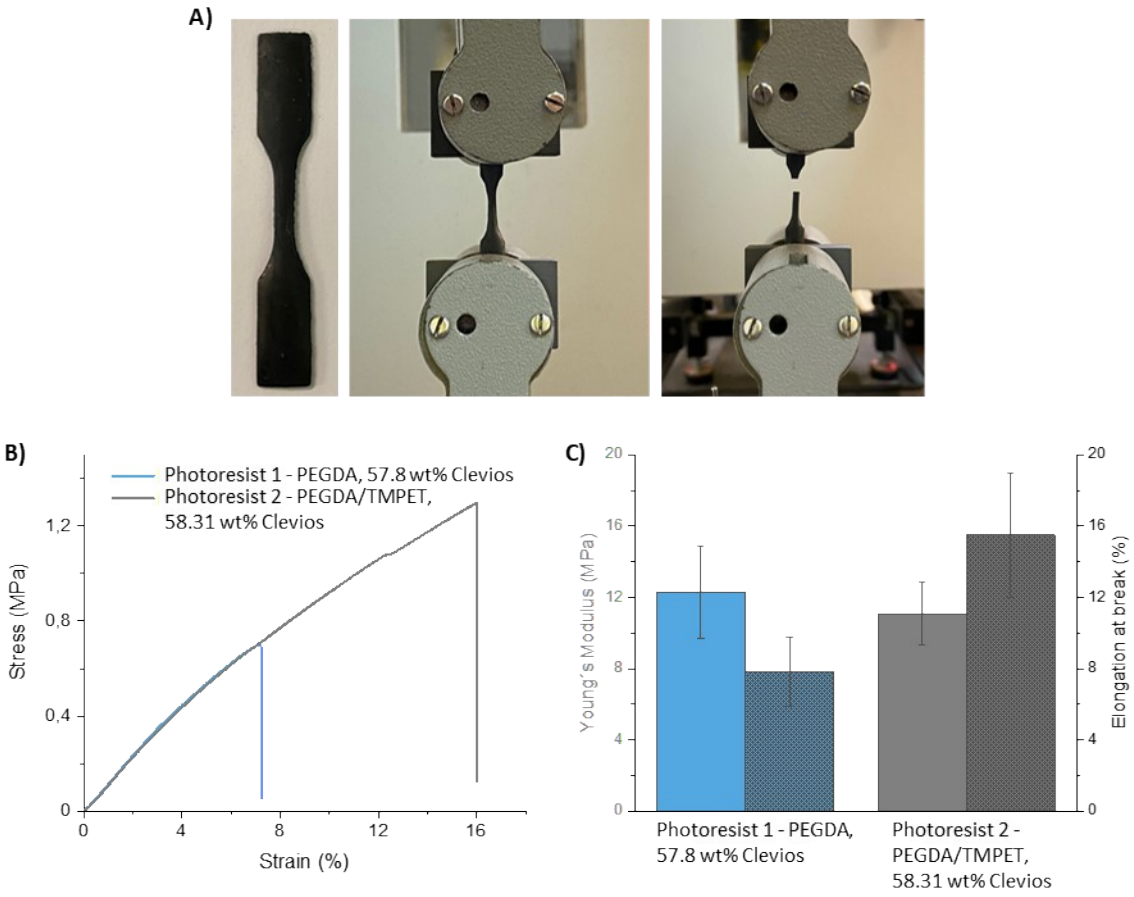

Fig. S6. A) Pictures of the macrogel structures used in tensile tests, before (left), during the test (middle), and after the sample broke (right). B) Stress–strain curves of macrogels using photoresist 1 - PEGDA, 57.8 wt% Clevios; and photoresist 2 - PEGDA/TMPET, 58.31 wt% Clevios. C) The Young's modulus (plain) and elongation at break (dotted) were obtained from the strain–stress curves of macrogels.

Table S4. Composition of photoresist 4 - PEGDA, 20 wt% Clevios.

Chemical	Amount (mg)	Weight %
Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)	1.57	0.26
Poly(ethylene glycol) diacrylate (PEGDA-700)	305	50.41
Ethylene Glycol	152	25.13
LAP	27	4.46
Water	119.4	19.74

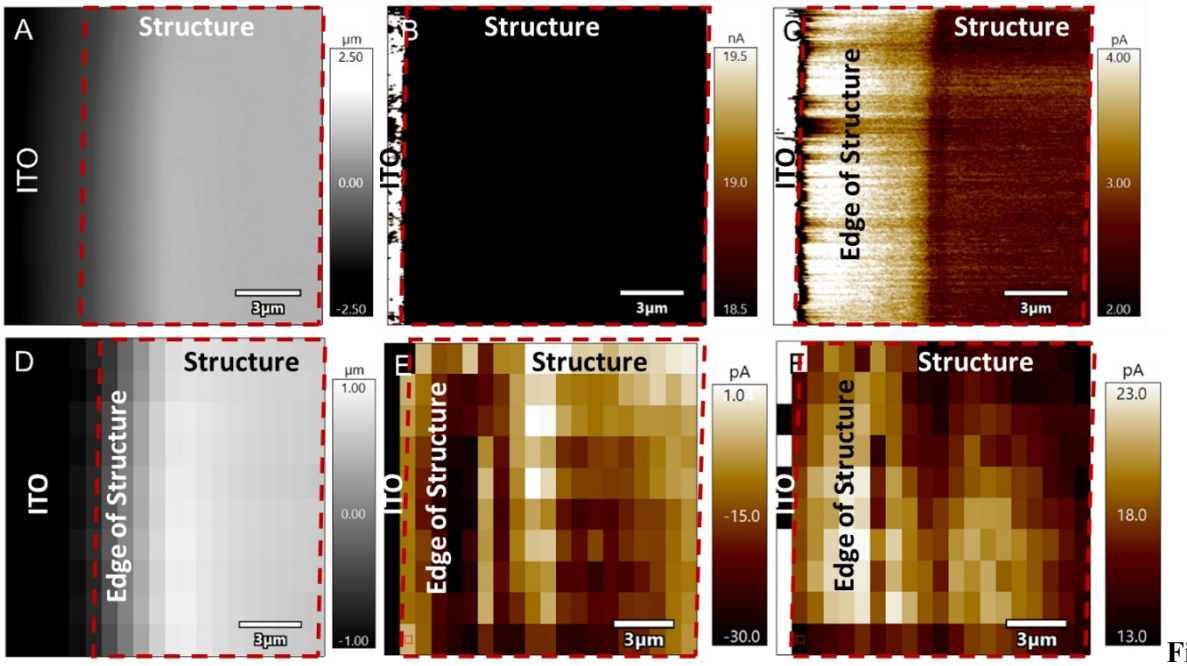

Fig. S7. A) Topographic image of square structure (20×20×3 µm) fabricated on ITO substrate with photoresist 4 - PEGDA, 20 wt% Clevios (Table S3). B and C) current mapping image at +5V DC bias in the same location with maximum color scale adjusted to ITO and structure, respectively. D) Force mapping (20 x 10 points) with I-V curves current measured at E) -5 V and at F) +5 V. The area delimited in the dashed red shape corresponds to the structure.

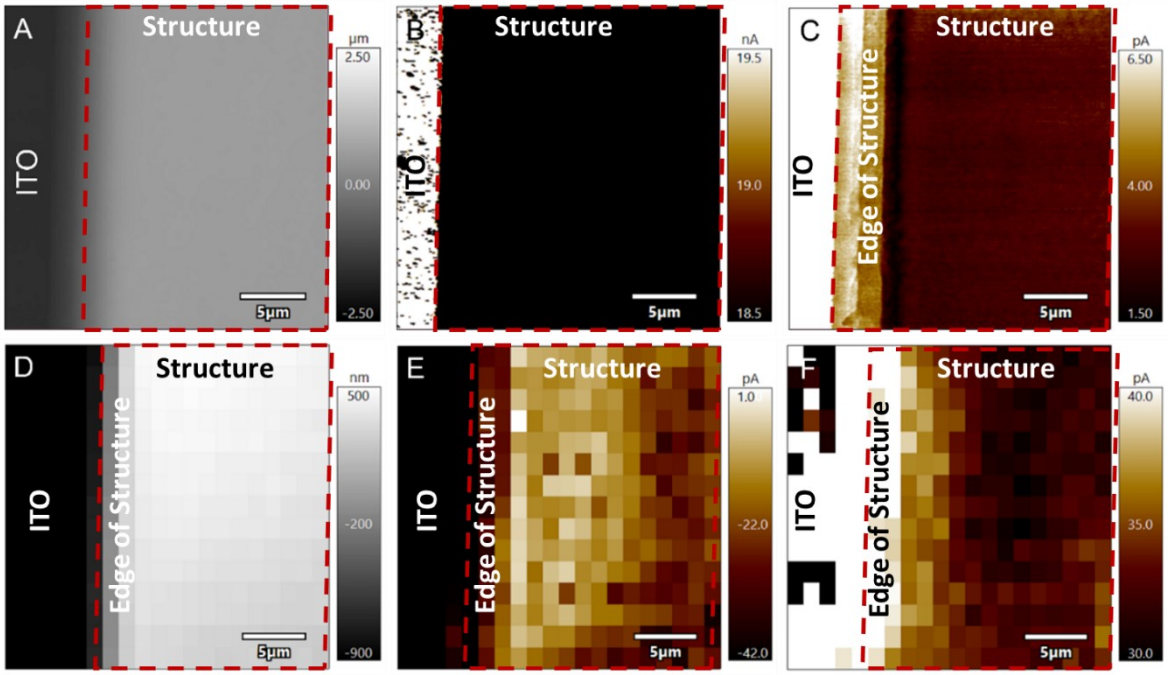

Fig. S8. A) Topographic image of square structure (20×20×3 µm) fabricated on ITO substrate with photoresist 1 - PEGDA, 57.8 wt% Clevios. B and C) current mapping image at +5V DC bias in the same location with maximum color scale adjusted to ITO and structure, respectively. D) Force mapping (20 x 10 points) with I-V curves current measured at E) -5 V and at F) +5 V. The area delimited in the dashed red shape corresponds to the structure.

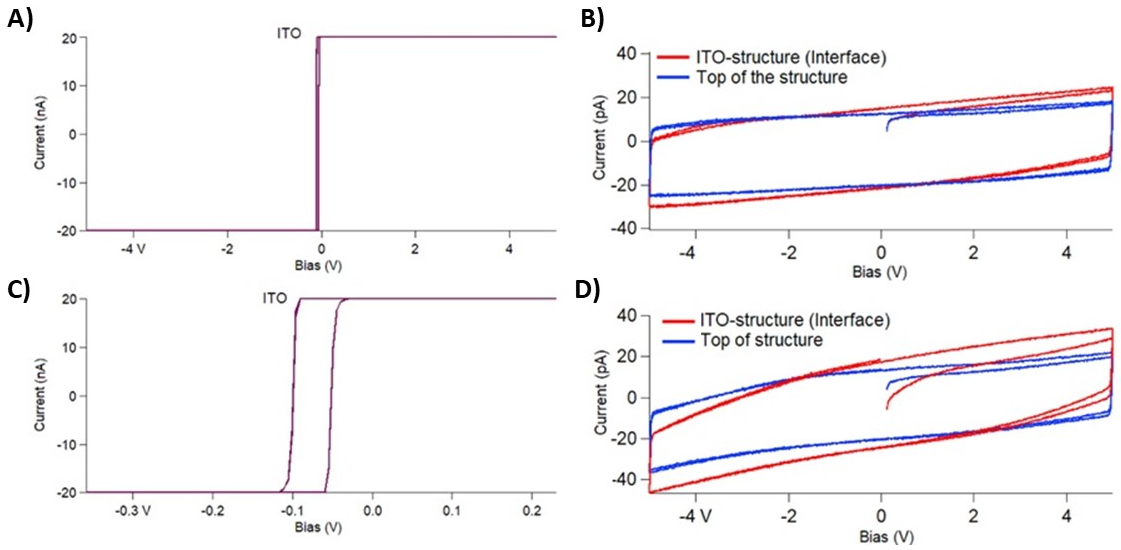

Fig. S9. I-V plots obtained from force mapping. A) I-V plots on ITO surface and C) Zoom in I-V plot of ITO electrode. I-V plots on ITO-structure interface and top of structure fabricated with photoresists B) 4 - PEGDA, 20 wt% Clevios and C) 1 - PEGDA, 57.8 wt% Clevios.

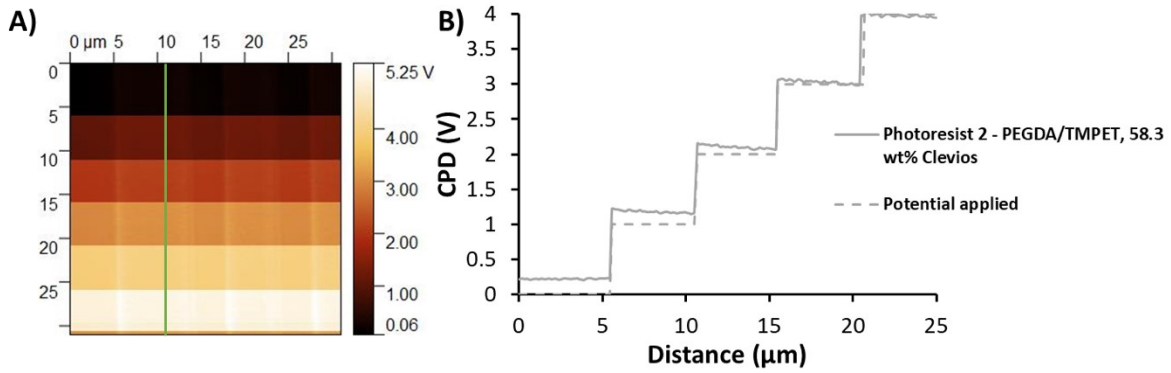

Fig. S10. A) Image of the structures used for KPFM experiment with the substrate bias, fabricated using photoresist 2 - PEGDA/TMPET, 58.31 wt% Clevios. The green line represents the scanning path. B) Plots of the contact potential difference as a function of the bias applied to the structures fabricated using photoresist 2 (grey).

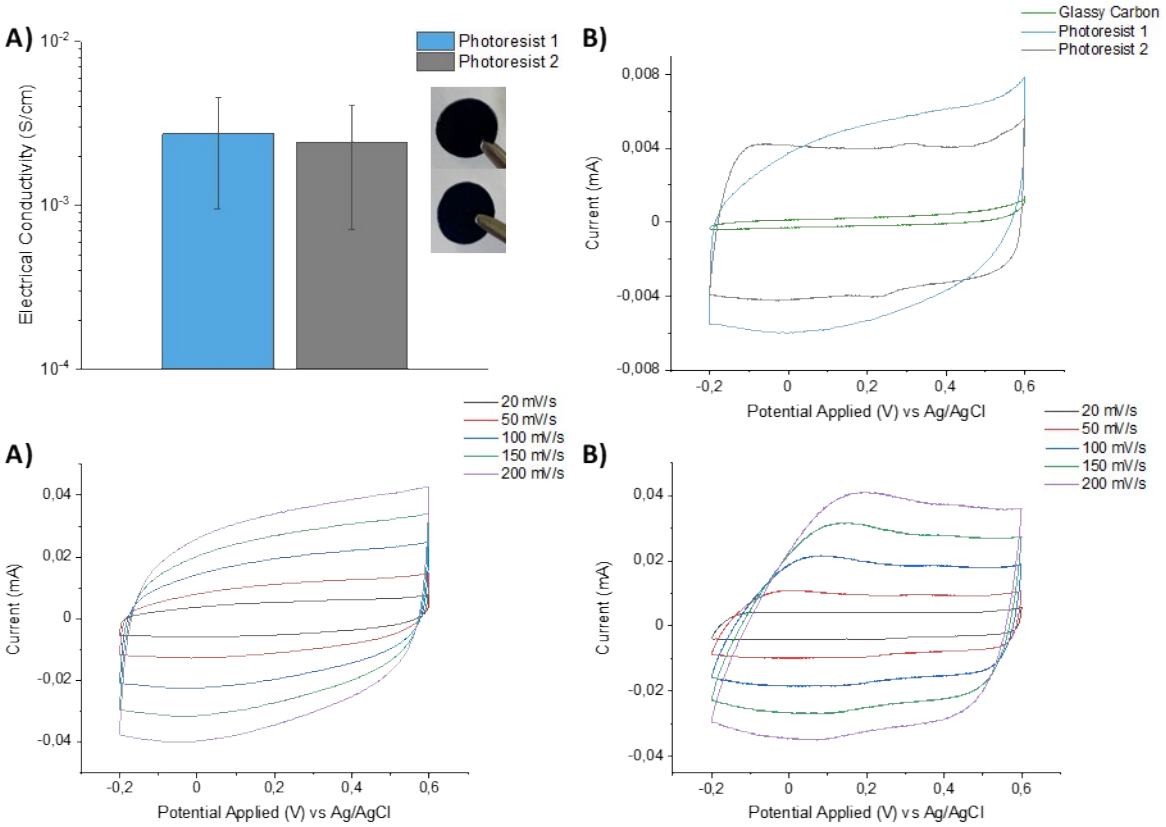

Fig. S11. A) Electrical conductivity of macrogels fabricated using photoresist 1 - PEGDA, 57.8 wt% Clevios (blue bar) and photoresist 2 - PEGDA/TMPET, 58.31 wt% Clevios (grey bar). Inset: Photographs of the printed macrogels. Cyclic voltammograms of gels prepared with: B) photoresist 1 - PEGDA, 57.8 wt% Clevios, and photoresist 2 - PEGDA/TMPET, 58.31 wt% Clevios at 20 mV/s, C) photoresist 1 - PEGDA, 57.8 wt% Clevios at variable rates, and D) photoresist 2 - PEGDA/TMPET, 58.31 wt% Clevios at variable rates, in 0.1 M NaCl aqueous solution.