Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary Information

Continuous flow fabrication of graphene oxide in aqueous hydrogen peroxide

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Experimental Section

Method and characterization

***Synthesis of gGO*. In a typical experiment, vein graphite flakes were dispersed in 30% aqueous hydrogen peroxide (H_2O_2) (20 mg/mL). The dispersion was allowed to stand in a ventilated fume cupboard overnight prior to processing. The two-step process used the energy efficient thin film microfluidic platform, the vortex fluidic device (VFD).**

***Characterization of the gGO*. The gGO was characterized by Field Emission SEM (FEI Quanta 450, operated at 5 kV at a working distance of 10 mm), AFM (Nanoscope 8.10 tapping mode), TEM (Hitachi HF5000 CS-TEM/STEM, operated at 200 KV and equipped with SSD EDS detectors.), Raman spectroscopy, X-ray photoelectron spectroscopy, zeta potential analysis and the 4-point probe measurement. Raman scattering were recorded at an excitation wavelength of 532 nm (≤ 5mW) at room temperature. Samples for SEM and Raman analysis were prepared on clean silicon wafers. TEM specimens were prepared by drop-casting the dispersion of gGO onto standard holey carbon grids prior to characterization. X-ray photoelectron spectroscopy (XPS) analysis was carried out using the Kratos Axis Ultra, Thermo Scientific, UK, with monochromatic Al Ka X-rays.**

***Tapping mode AFM* Atomic force microscopy (AFM) was performed in air using a Bruker Multimode 8 AFM with Nanoscope V controller, operating in standard tapping mode. The AFM probes used were silicon HQNSC15/AlBS Mikromasch probes (nominal tip diameter and spring constant is 16 nm and 40 N/m respectively). Set-point, scan rate and gain values were chosen to optimize image quality. The AFM topography images have been flattened and height measurements were made using the section analysis tool of Nanoscope Analysis 1.4. The AFM scanner was calibrated in x,y and z directions using silicon calibration grids (Bruker model numbers PG: 1 μm pitch, 110 nm depth and VGRP: 10 μm pitch, 180 nm depth and Mikromasch model TGZ01: 3 μm pitch, 18 nm depth).**

Raman **Raman spectra were acquired using a Witec alpha300R Raman microscope at an excitation laser wavelength of 532 nm with a 100x objective (numerical aperture 0.00). Typical integration times for single Raman spectra were between 30-60 s for 2-3 accumulations. The grating used was 600 grooves mm–1 which has a spectral resolution of ~3 to 4 wavenumbers. Laser power levels were kept as low as possible to prevent sample damage and was approximately 5 mW or below.**

XPS **The X-Ray Photoelectron Spectroscopy (XPS) instrument was provided by SPECS (Berlin). A no-monochromatic X-ray source (12kV-200 W) with Mg anode was used for the measurements. The operation was performed under ultra-high vacuum (UHV) condition with a base pressure of e^{-10} mbar. The samples were mounted on Mo sample holder. Semiconductor-grade Si was used as a substrate. The conductivity of Mo holder and Si substrate was sufficient for the electron compensation due to the X-ray radiation and thus avoiding any charging of the samples.**

Conductivity measurements **Sheet resistance measurements were completed on gGO films (thickness 100 μm) deposited on a glass slide, using a four-point probe (KeithLink Film Resistivity Measurement Tool 1.0). Three readings at various locations on a film were taken and the results were averaged.**

Electrochemical measurements **(Preparation of (Si–H)–gGO and (Si–H)–GO surfaces) Si electrodes were pre-washed with dichloromethane (DCM), isopropanol and Milli-Q water (>18 MΩ cm) followed by incubation in piranha solution (3 H_2SO_4: 1 H_2O_2 (V/V)) at 130 °C for 30 min. The surfaces were then etched with deoxygenated 40 wt% aqueous NH_4F solution in the presence of a small amount of ammonium sulfite monohydrate (~5 mg) for 13 min to remove the native oxide layer on the Si surface and obtain a Si–H surface. The etched surfaces were then rinsed with Milli-Q water and DCM and dried under a stream of nitrogen gas. The freshly prepared Si–H surfaces were then directly incubated in 1 mg/mL aqueous suspension of gGO and GO for 24 h. The surfaces were then washed with Milli Q water before further measurements. All experiments were performed on n-type Si (111) with a thickness of 475-525 μm and resistivity of ~ 0.01–0.1 Ω cm. Electrochemical measurements**

The electrochemical experiments were performed using CH instrument, USA (CHI650) and a conventional three-electrode cell, with an Ag/AgCl aqueous electrode, 1 M KCl and platinum wire as reference and counter electrodes, respectively. The electrochemical reduction of gGO and GO were carried out directly after their attachment to the Si–H surface. All experiments were carried out in 0.1 M phosphate buffer at pH 7.4 and scan rate of 50 mV/s.

Applications methods

1. Cytotoxicity studies

***In vitro* cell viability assays, the MCF-7 breast cancer cells were cultured in 75 cm^2 cell culture flasks (Thermo Scientific) in Dulbecco's Modified Eagle Medium (DMEM, Sigma D8437) supplemented with 1% L-glutamine (Sigma G7513), 1% penicillin/streptomycin (Sigma P4333) and 10% fetal bovine serum (FBS) as complete medium. The flasks were incubated at 37°C in 95% air and 5% CO_2 humidified conditions. *In vitro* cell viability assay was carried out using MTT viability assay. Typically, 10^4 cells were seeded in a flat-bottom 96 well plate for 24 h. After 24 h seeding, the old medium was removed and the cells were treated with various concentrations of gGO suspension in complete DMEM medium, at 0 (as control), 3.125, 6.25, 12.5, 25, 50, 100 and 200 µg/mL, respectively. The cells were incubated for an additional 24 h. After that, the treatment medium was removed and replaced with 0.5 mg/mL methylthiazolyldiphenyl-tetrazolium bromide (MTT, sigma) containing fresh DMEM medium. After 4 h incubation at 37°C, 80 µL of 20% (w/v) sodium dodecyl sulfate (SDS) in 0.02 M HCl was added to each well to dissolve insoluble purple formazan crystals produced by live cells. The plates were incubated in the dark at room temperature overnight for the formazan to dissolve. Thereafter 220 µL of the solution in each well was transferred to a new 96 well plate, in avoiding the residual gGO which could affect the absorbance values at 570 nm. Finally, the absorbance at 570 nm was measured by using a microplate reader (Promega, GloMax). Cell free control experiments were performed as previous method [59] with slight modification. gGO with different concentrations (3.125-200 µg/mL) were suspended in 0.5 mg/mL of MTT solution in DMEM to see if the gGO react with the MTT reagents. After 4-hour incubation at 37°C with 5% CO_2, 80 µL SDS was added to see if any insoluble formazan formed during the incubation process. The gGO suspensions were**

centrifuged and the supernatant for each condition was observed at 570 nm, which was used to ascertain if the MTT reagent reacts with gGO itself.

2. Biocompatibility analysis

The cotton cloth was cut into circles to fit a petri dish with 85 mm diameter. The cotton pieces were laundered and then sterilised by boiling in water for 1hr. Dispersions of GO and gGO were produced at concentrations of 2 g/L. The dispersions were then sonicated for 30 min. The cotton cloths were then placed inside the vials and were further sonicated for 60 min. The cloths were removed from the vials and placed on ceramic plates. The cotton cloths were placed in the oven at 150°C to dry for 30 min. Thereafter 30 µL of *E. coli* JM109 culture of 3.3 x 10^7 CFU/ml were added in the vials containing 1.8 x 1.8 cm of cotton (control), gGO- and GO-coated cotton fabrics and then incubated at 37°C for 4 hrs. Afterwards, 3 mL of 0.9% (w/v) cold sterile saline solution (Merck, Germany) was applied to wash the *E. coli* from the fabrics by spinning in a rotary mixer (LabTek, Australia) for 10 min at 250 rpm. The solutions were diluted and placed onto MacConkey agar (Oxoid Ltd., UK) plates to count the number of *E. coli*. The plates were incubated at 37°C for 18 hrs before observation.

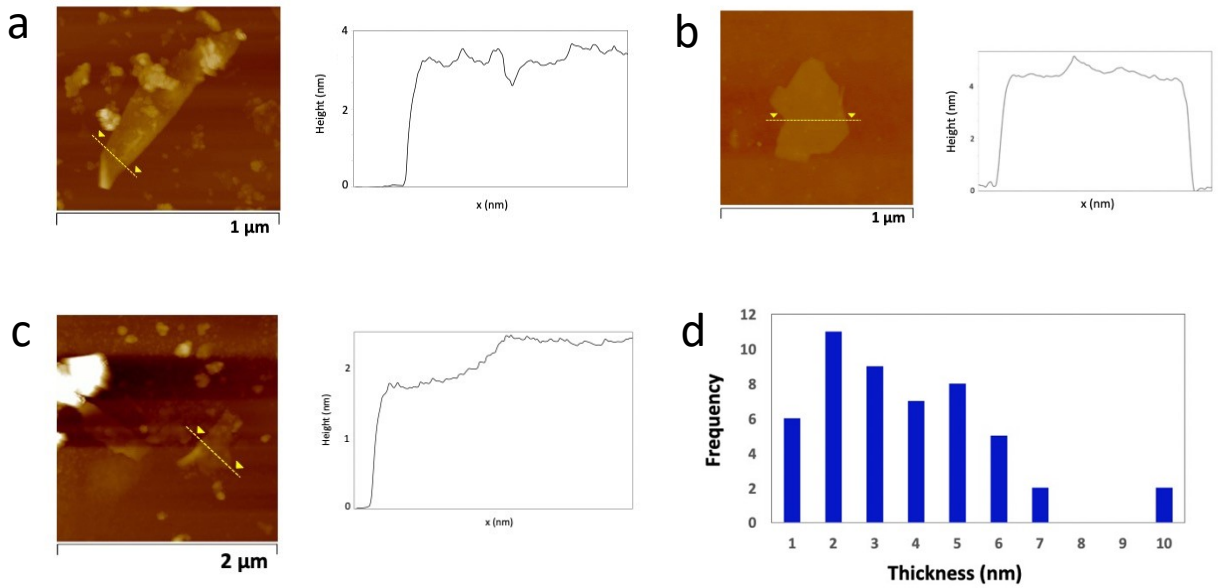
3. Organic photovoltaics

Materials and OPV device fabrication and characterization

PM6 was purchased from Lumtec (Luminescence Technology Corp.), and IT-2Br was synthesized following the reported procedure [70]. OPV devices with the structure of ITO/ZnO/gGO/BHJ/MoO_3/Ag or ITO/ZnO/BHJ/MoO_3/Ag were fabricated. Patterned ITO-coated glass substrates (10 Ω/sq, purchased from Xin Yan Technology Ltd) were cleaned using the procedure described elsewhere [71]. ZnO films were prepared using the Zn sol-gel solution, followed by annealing at 280 °C for 10 minutes in air to offer a 25 nm film [74]. When gGO is used, ~0.1 mg/mL gGO dispersed in ethanol was spin-coated under 3000 rpm for 1 min on top of ZnO layer. The annealing of gGO was done in a nitrogen filled glove-box. The bulk-heterojunction (BHJ) layer was spin-coated from PM6:IT-2Br (1:1 weight ratio) 20 mg/mL chlorobenzene solution. MoOx (12 nm) layer was thermally evaporated on top of

the BHJ layer at 1.5 E-6 torr, followed by the deposition of Ag electrode (80 nm) through a shadow mask, which defined the device area to be 0.1 cm^2. The OPV devices were measured in air by an Oriel solar simulator fitted with a 150 W xenon lamp (Newport), filtered to give an irradiation of 100 mW/cm^2 at AM1.5 and calibrated using a silicon reference cell with NIST traceable certification. The photocurrent density–voltage (*J-V*) characteristics of devices were measured through a Keithley 2400 source meter unit. External quantum efficiency (EQE) measurements were performed in air by a Cornerstone 260™ motorized 1/4 m monochromator (model 74125, Newport) and TracQ basic software for data acquisition. UPS analysis The work function was characterized using Ultraviolet photoelectron spectroscopy (UPS) as described elsewhere[71]. The measurements were performed under an ultra-high vacuum (UHV) apparatus built by SPECS (Berlin, Germany) using a low intensity UV light source (HeI) with an excitation energy of 21.21 eV. The UPS samples were prepared the same way as the device fabrication.

Supplementary Figure 1



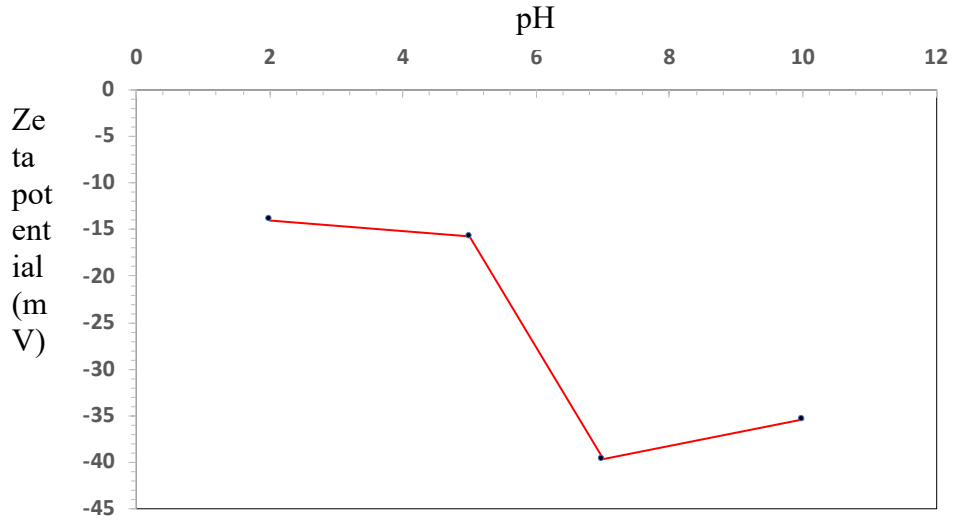
Supplementary Figure S1| (a-c) AFM height images of individual gGO sheets with its corresponding cross-sectional analysis and (d) Average thickness distribution plot based on the AFM cross sectional analysis (calculated from an average distribution of 50 sheets)

Supplementary Figure S2

	sp^2 (%)	sp^3 (%)	C-O (%)	C=O (%)	O-C=O (%)	Total % oxidation
Graphite flakes	87.17	8.82	4.01	0.00	0.00	4.01
Graphite/H_2O_2	79.54	12.20	8.26	0.00	0.00	8.26
Control 1: Low NIR irradiation (260mJ)	75.27	5.75	10.70	4.45	3.83	18.98
Control 2: High NIR irradiation (650mJ)	59.28	7.76	20.21	7.37	5.38	32.96
Control 3: UV irradiation only	62.20	10.36	12.84	6.84	4.76	24.44
UV/NIR irradiation (260mJ)	47.12	13.63	25.15	9.16	4.94	39.25
UV/NIR irradiation (650mJ)	42.61	9.54	20.23	20.45	7.17	47.85

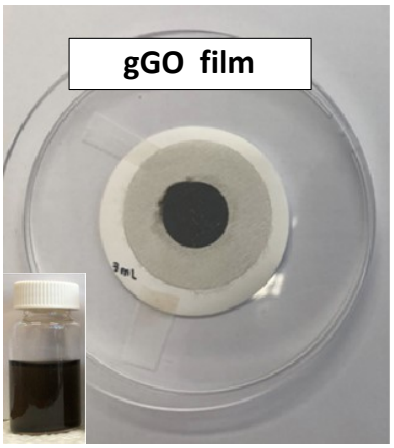
Supplementary Figure S2| XPS analysis based on the deconvolution of the C1s peak of the oxidized graphene generated under the different operating conditions

Supplementary Figure 3



Supplementary Fig. S3| Zeta potential of the gGO aqueous dispersion as a function of pH

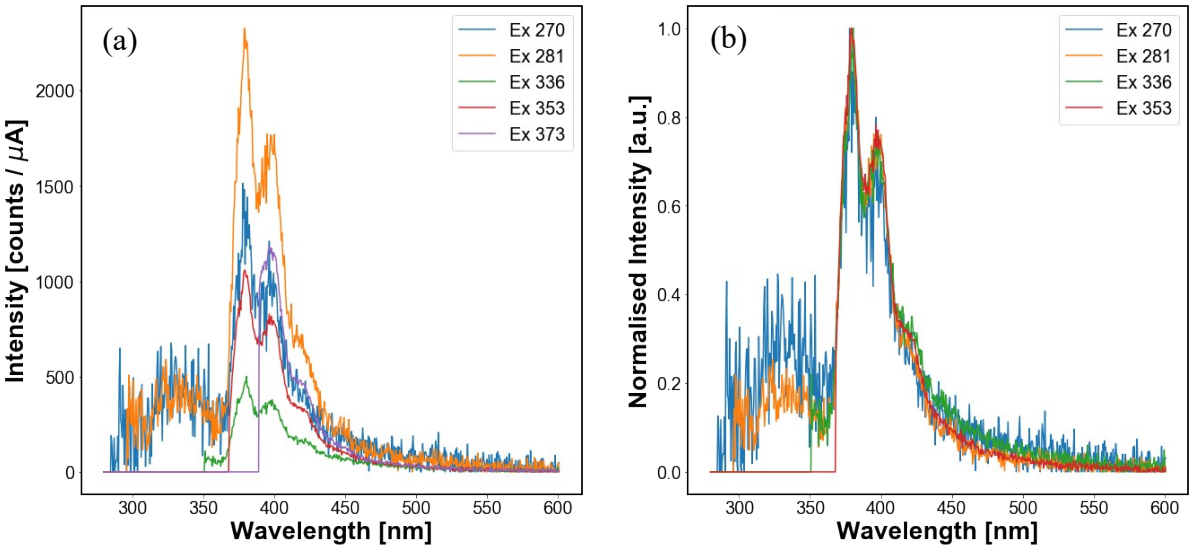
Supplementary Figure 4



Measurements	gGO
Resistance (MΩ)	0.71 ± 0.19
Sheet resistivity (MΩ)	3.25 ± 0.79
Conductivity (Siemens)	320 ± 85.8

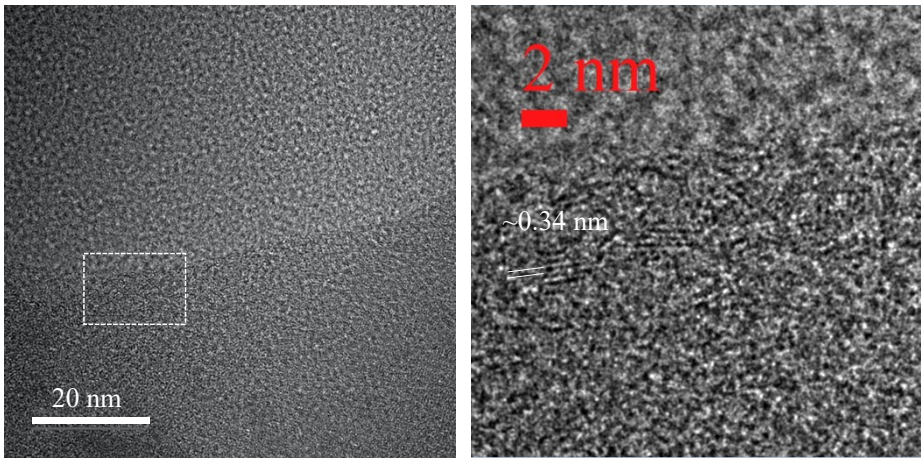
Supplementary Fig. S4| Conductivity, sheet resistivity and resistance measurements of the gGO films. All conductivity measurements were conducted in triplicates using a 4-point probe system.

Supplementary Figure 5



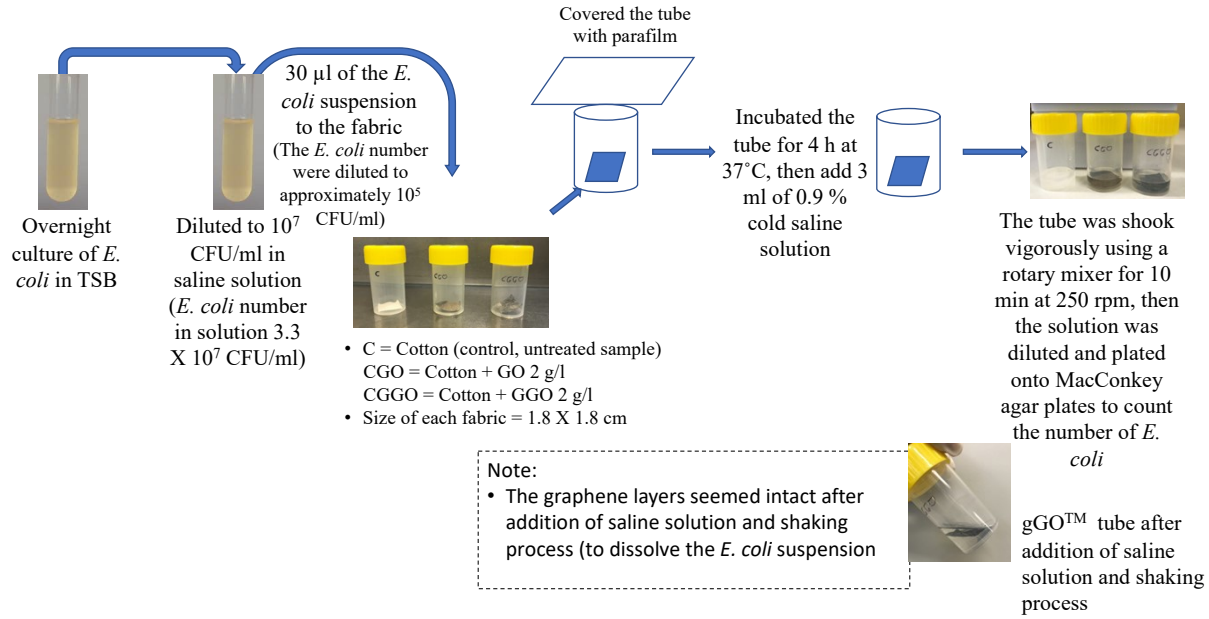
Supplementary Fig. S5| (a) The un-normalised photoluminescent emissions spectra at each of the main excitation frequencies, displaying the relative intensities (b) Normalised PL emissions spectra demonstrating unchanged emissions frequencies.

Supplementary Figure 6



Supplementary Fig. S6| HRTEM images focused on the edge of the gGO nanofilms. Layered lattices were observed at the edge, with average lattice distance of ~0.34 nm, corresponding to a single graphene sheet

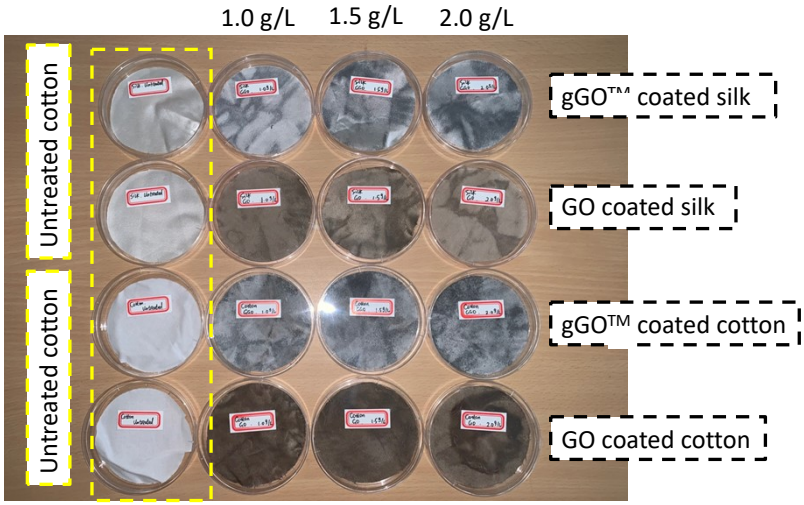
Supplementary Figure 7



Supplementary Fig. S7| Schematic of the method used to prepare the GO and gGO coated sterilised cotton fabrics to understand the biocompatibility properties of the gGO

Supplementary Figure 8

(a)

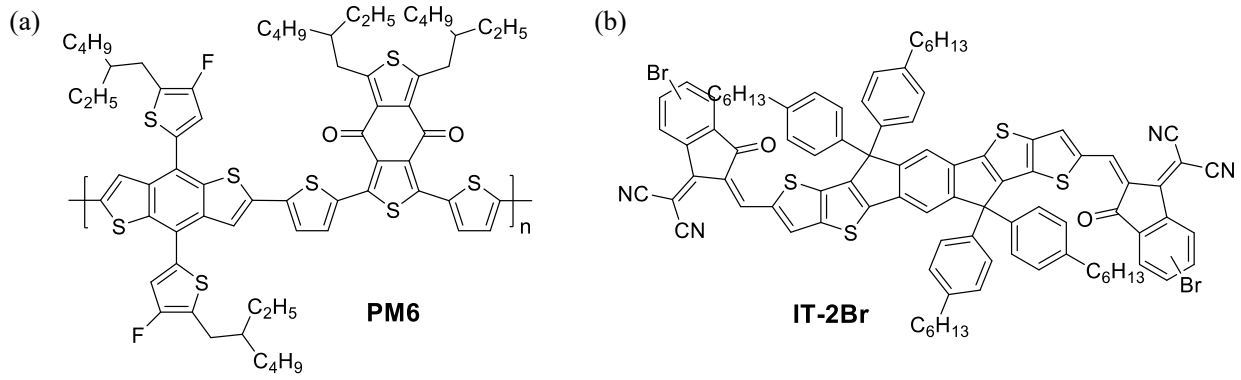


(b)

1: Fitting the cloth	The cotton cloths were cut into 1.8 X 1.8 cm squares
2: Sterilisation	The cotton was sterilised by boiling in water for 1hour.
3: Solution preparation	Dispersions of GO and gGO™ were produced at concentrations of 0.5g/L, 0.1g/L and 0.25g/L. The dispersions were then sonicated for 30 min.
4: Cloth infusion	The cotton cloths were then placed inside the vials and were further sonicated for 60 min.
5: Drying	The infused cloths were then placed in gamma sterilised petri dishes without their lids. These petri dishes were then placed inside a vacuum desiccator over night to dry.
6: Storage	The prepared cloths were labelled, and the lids were replaced on the gamma sterilised petri dishes.

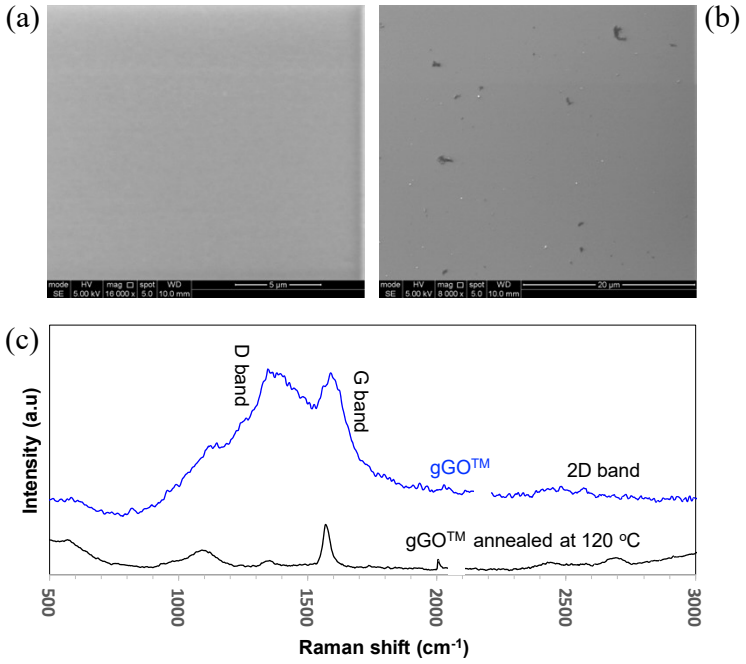
Supplementary Fig. S8| (a) Images of the GO and gGO prepared on both silk and cotton at different concentration and (b) Method used for coating of the GO and gGO on both silk and cotton fabrics.

Supplementary Figure 9



Supplementary Fig. S9| Chemical structures of PM6 and IT-2Br used as the electron donor and acceptor respectively in the OPV device

Supplementary Figure 10



Supplementary Fig. S10| (a) SEM image of ZnO on ITO, (b) SEM image of gGO deposited on the surface of ZnO/ITO and (c) Raman analysis of the gGO before and after thermal treatment at 120 ^{0}C.