Frozen Polymerization for Aligned Porous Structures with Enhanced Mechanical Stability, Conductivity, and as Stationary Phase for HPLC

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Supporting Information

Experimental Details

Chemicals and Reagents

Tetraethylene glycol dimethacrylate (TEGDMA, assay spec ≥ 90% by GC),ethylene glycol dimethacrylate (EGDMA, 99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), 3-(trimethoxylsilyl)propyl methacrylate (TPM, 98%), hydroxyethyl methacrylate (HEMA, ≥99%), oligo(ethylene glycol) methacrylates 175 and 475, poly(ethylene glycol) dimethacrylate (PEGDMA, Mw 450), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS, 1% aqueous solution), dioxane, camphene, cyclohexane were purchased from Sigma Aldrich and used as received. Graphite flakes were purchased from Alfa Aeser. The HPLC test mixture was from Thermo Fisher Scientific. The molecular structures of some compounds are shown below.
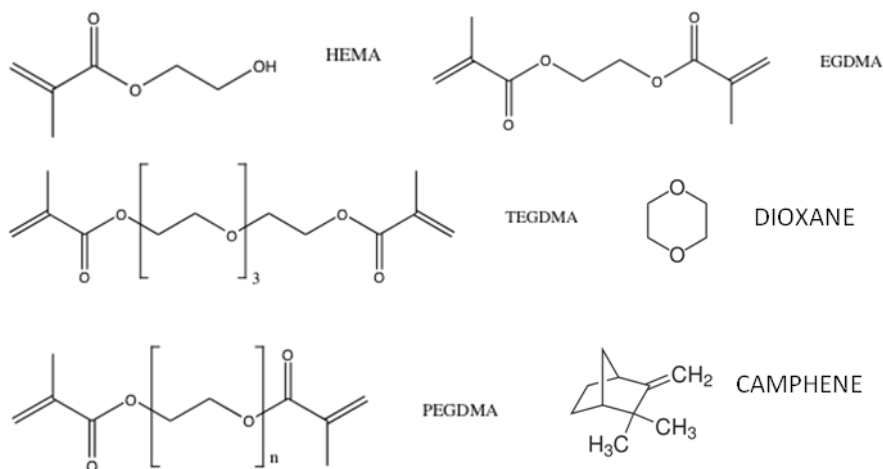
The frozen polymerization process

5 cm^3 solution in a cylindrical glass tube (dimension 75 mm long x 10 mm diameter) was slowly immersed into liquid nitrogen at a rate of around 75 mm min^{-1} until it was fully frozen. The frozen sample was then placed on ice or dry ice under a 40-watt Spectroline ® X-series UV bench and display lamp (wavelength 365 nm) and polymerized for 2 h (unless stated otherwise). The sample was turned every 30 min during the polymerization to ensure complete polymerization. There was no melting observed. After polymerization, the frozen samples was warmed up to room temperature and placed in a vacuum oven overnight at room temperature to remove the solvent and get the dry porous material.

Dioxane solutions: 1:5, 1:10, 1:20 v/v of TEGDMA/dioxane solutions were prepared with 1 wt % initiator DMPA with respect to the monomer. The oligo(ethylene glycol) methacrylate samples were polymerized for 3 h. All the frozen dioxane samples were polymerized on ice under UV light.

Cyclohexane solutions: 1:5 v/v of TEGDMA/cyclohexane solutions were prepared with 1 wt % DMPA initiator. The frozen samples were polymerized on dry ice.

Camphene solutions: 1:5 w/w TEGDMA/camphene solution was prepared with 1 wt % DMPA initiator as before. It was heated to 60°C to get a clear solution. This solution was then transferred into a pre-warmed glass tube for directional freezing. The frozen polymerization was on dry ice to ensure no camphene was polymerized.

Treatment of PTEGDMA with PEDOT-PSS and graphene suspensions.

PTEGDMA made from 1:20 dioxane solution was washed at least 3 times with dioxane for 24 h to remove any unreacted monomers, initiator, or oligomers, and then dried in the vacuum oven overnight. PTEGDMA monolith was soaked in 10 cm^3 1 % aqueous PEDOT-PSS solution for 48 h and then dried in a vacuum oven. In another study, the PTEGDMA monolith was soaked in 10 cm^3 0.4 % graphene oxide (GO) suspension for 48 h then dried in the vacuum. The dry GO-PTEGDMA was placed in 1 cm^3 hydrazine monohydrate in 100 cm^3 of distilled water at 120 °C for 48 h. The monolith was then washed thoroughly with distilled water to remove any hydrazine and vacuum dried before the mass was recorded. The mass increase data for both experiments are shown in the table below.

Sample	Concentration of soaking solution	Mass of PTEGDMA	Mass increase after treatment	% mass increase
PTEGDMA-PEDOT-PSS	1 % (10 mg cm^{-3})	0.0476 g	0.0022 g	4.62 %
PTEGDMA-Graphene	0.4 % (4mg cm^{-3})	0.0372 g	0.0018 g	4.84 %

The graphene oxide was prepared using a modified Hummers method similar to the procedure reported before (D.C. Marcano *et al., ACS Nano*, **2010**, *4*, 4806-4814.): Concentrated sulfuric acid (50 cm^3) was added to a mixture of graphite flakes (2 g) and sodium nirate (1 g), and the mixture was cooled using an ice bath to 0 °C. Potassium permangenate (9.0 g) was added slowly in portions to keep the reaction temperature below 20 °C. The reaction was warmed to 35 °C and stirred for 7 h then added to 200 cm^3 of ice cold distilled water and refluxed at 98°C for one week. The reaction mixture was cooled to room temperature and poured onto ice (200 cm^3) with 30% hydrogen peroxide (2 cm^3). The mixture was

then purified via centrifuging and continuously washed with water for 1 week. Then the product was washed with diethyl ether to yield 1.2 g of graphene oxide, which was confirmed by CHN analysis.

Preparation of aligned porous monolithiccolumns

Glass tubes with dimension 88 mm L x3.5 mm O.D. x 2.0 mm I.D. were silanized with 30% of (3-trimethoxysilyl)propyl methacrylate (TPM) in acetone to provide a vinyl group for anchoring of polymer monoliths following the procedure developed by Binghe Gu *et al.* (*Anal. Chem.* **2007**, *79*, 5848). Typically, the tubes were washed with ethanol and water then treated with 2 M HCl and heated at 110 °C for 3 h. The tubes were rinsed with ethanol and dried at 110 °C overnight in a vacuum oven. Silanization of the surface-activated tubes were performed at 25 °C overnight with the TPM solution. After silanization, the tubes were rinsed with acetone and dried at 25 °C in a vacuum oven overnight. To prepare the polymer column, 1 cm^3 TEGDMA + 4.25 g camphene + 1 wt % DMAP was heated to 60 ^{0}C to get a clear solution and then ultrasonicated for 10 s. The silanized glass column was filled with the mixture, directionally frozen, and polymerized on dry ice under UV irradiation.

Characterization

Conductivity: Front panel resistance measurements were taken via a two-probe method using a Keithley 2600A I-V sourcemeter, sourcing 1 mA current and measuring the voltage drop between the same probes. This gives a resistance value on the sourcemeter. Conductive silver glue was used to stick the probes to the porous material. A photograph of the set-up is shown here. The samples with cylindrical shapes were used for the measurement.
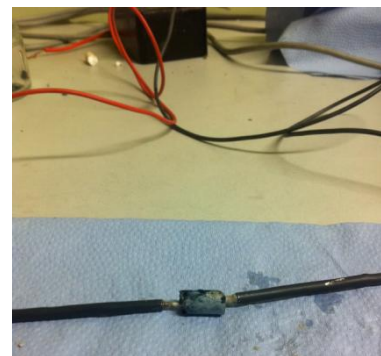
The conductivity values are worked out using volume resistivity formula.

$\rho = R (A/L)$

Where ρ is the static resistivity (measured in ohm-metres, Ω m), R is the electrical resistance of a uniform specimen of the material (measured in ohms, Ω), L is the length of the piece of material (measured in metres, m), A is the cross-sectional area of the specimen (measured in square metres, m²). Resistivity is the reciprocal of conductivity.

Sample	Cylindrical dimension	Resistance	Resistivity (To 3 sf)	Conductivity
PTEGDMA-PEDOT-PSS	Length: 1cm Diameter.: 0.7cm	500 kΩ	192000 Ωcm	5.2×10^{-6} S/cm
PTEGDMA-Graphene	Length: 1cm Diameter: 0.7cm	3.43 kΩ	1320 Ωcm	1.91×10^{-4} S/cm

Compression test: The tests were taken along the direction of pore alignment. The test samples had a cylindrical shape with dimension 10 mm (height) x 7 mm (diameter). An Instron 4204 with a 5kN loading cell was employed and the velocity of compression was 0.5 mm min^{-1}. The stress-strain graphs were obtained. Young modulus was defined as the stiffness of an elastic material and calculated by dividing stress/strain from the initial linear part of the stress-strain curve. Stress strain takes into account length and diameter.

FTIR measurement: Fourier transform infrared spectroscope (FTIR) measurements were conducted using the Bruker Tensor 27. The frozen samples were taken off dry ice at specific times. All the solvent was removed in a vacuum oven at room temperature overnight. They were all sliced in the same position and the material was ground up using a pestle and mortar. KBr pellets were made by placing 200 mg KBr into a mortar and grinding with 2 mg of the ground polymer material. These were then compressed into pellets by compressing at 2 tonnes pressure for one minute then at 10 tonnes for another minute.

Scanning electron microscope (SEM) imaging: The pore structure of the monoliths was observed by a Hitachi-S4800 SEM. A small piece was cut from the monolith using a blade and then adhered to a stud using Araldite resin. The samples were coated with gold using a sputter-coater (EMITECH K550X) for 2 minutes at 30 mA before SEM imaging.
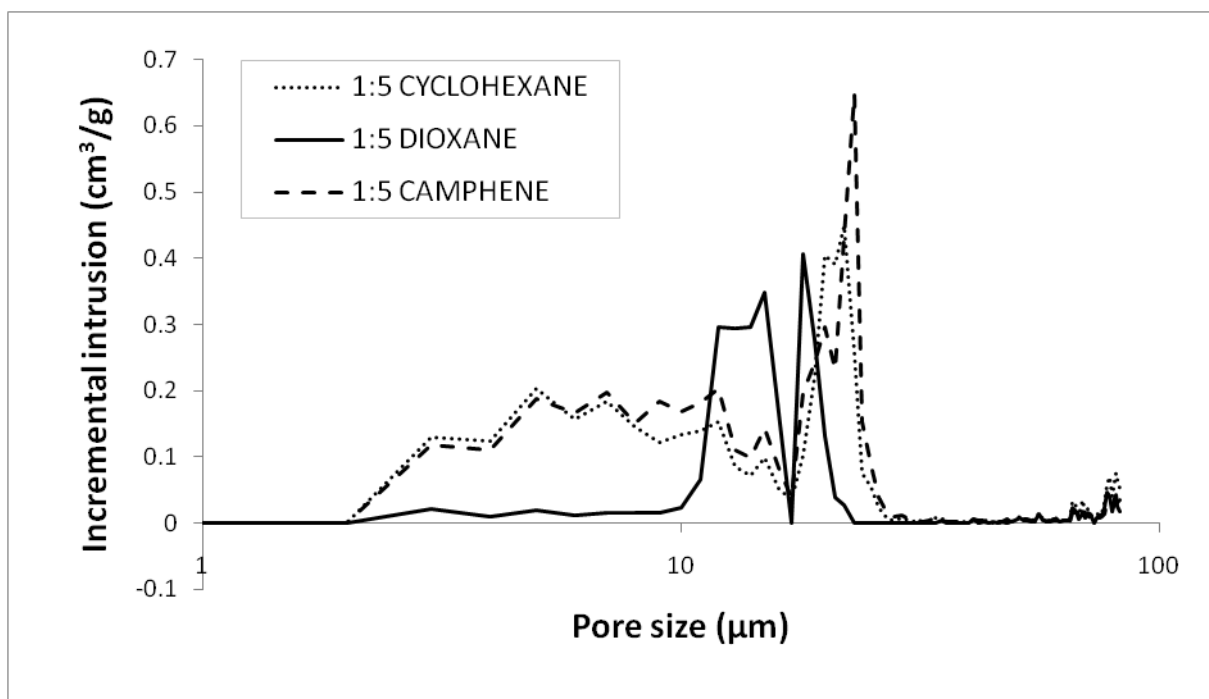
Hg intrusion porosimetry: The intrusion volume and macropore size distribution were measured using a Micromeritics Autopore IV 9500 porosimeter over a pressure range of 0.10 – 60000 psia. The intrusion volume was calculated by substracting the intrusion arising from mercury interpenetration in large spaces (> 150 μm) from the total intrusion.

High performace liquid chromatography (HPLC) test: The columns were assessed on a HPLC instrument (Agilent 1200 series), comprising of a vacuum degasser, quaternary pump, ALS auto-sampler, heated column compartment and UV-Vis detector. Data analysis was performed using Agilent Chemstation software, version B.02.01 (Agilent Technologies, USA). The test mixture contains uracil, caffeine, toluene, ethylbenzene and phenylene.

Supporting Figures
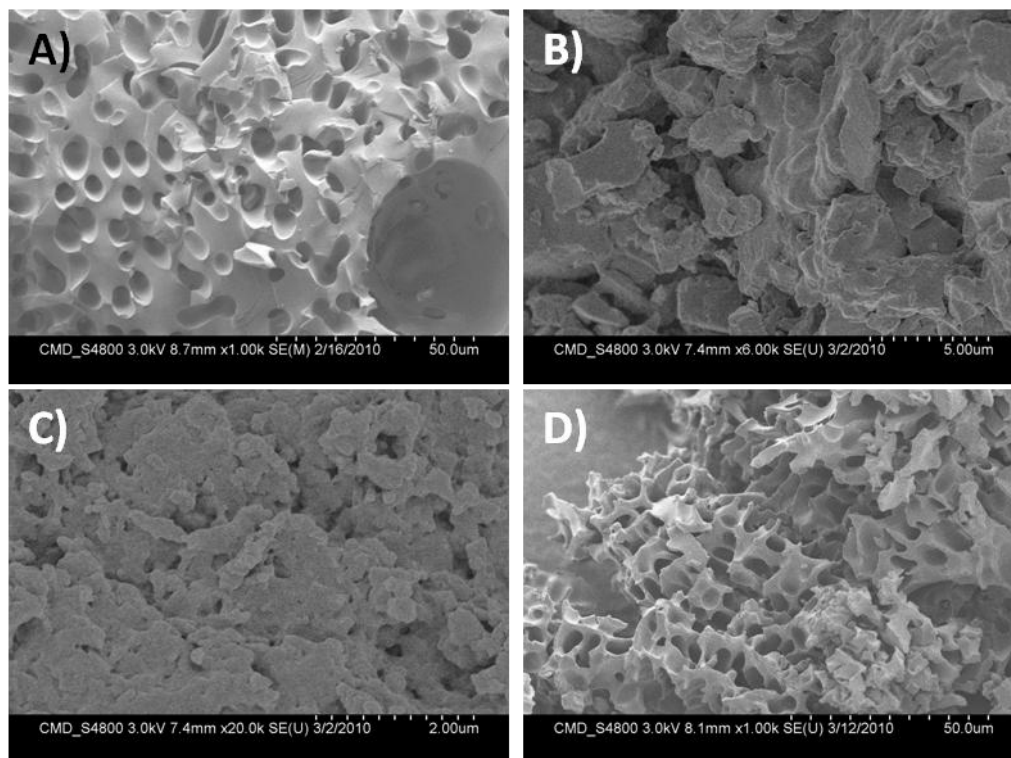
Fig. S1 A) TEGDMA was mixed with camphene (1:1 w/w) by mass and heated to 60°C until dissolved, then 1 wt % DMPA initiator was added. This was then frozen randomly in freezer (-20 ^{0}C) and then polymerized on dry ice under UV lamp for 2 hours. The polymerized sample was then heated to 200 ^{0}C in a furnace for 3 hours to vaporize camphene. B) Similar procedure as in (A), but after freezing the cold sample was allowed to warm up and polymerize at room temperature. C) Similar procedure as in (A) but the cold sample was warmed up and polymerized at 60 ^{0}C. (D) The same monomer mixture was heated to 60 ^{0}C, directionally frozen in liquid nitrogen, polymerized on dry ice, placed in a vacuum oven at room temperature to remove camphene.
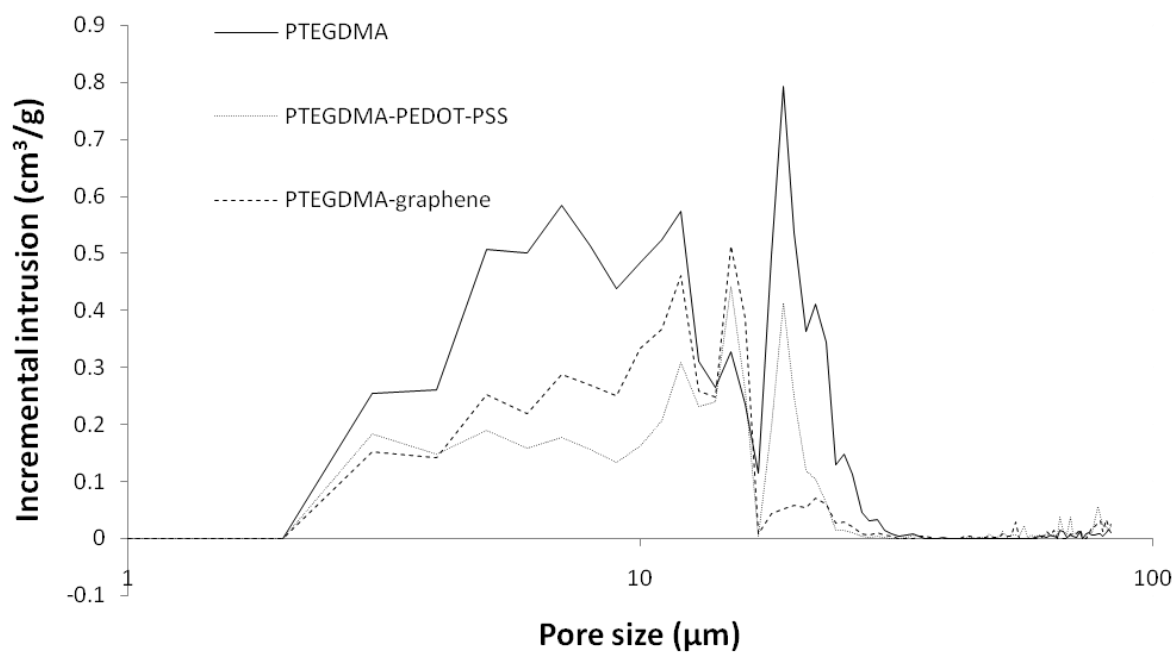
Fig. S2. Macropore size distributions as measured by Hg intrusion porosimetry for the samples shown in Fig. 1. The materials made from cyclohexane and camphene show similar pore size distributions: in the range of $2 - 17$ μm (peak at 5 μm) and $17 - 25$ μm (peak at 20 μm). The material from dioxane solution shows a narrow pore size distribution: $10 - 17$ μm (peak at 15 μm) and $17 - 22$ μm (peak at 18 μm). Intrusion pore volume for 1:5 cyclohexane is 5.55 cm^3 g^{-1} and for 1:5 camphene 5.40 cm^3 g^{-1}.
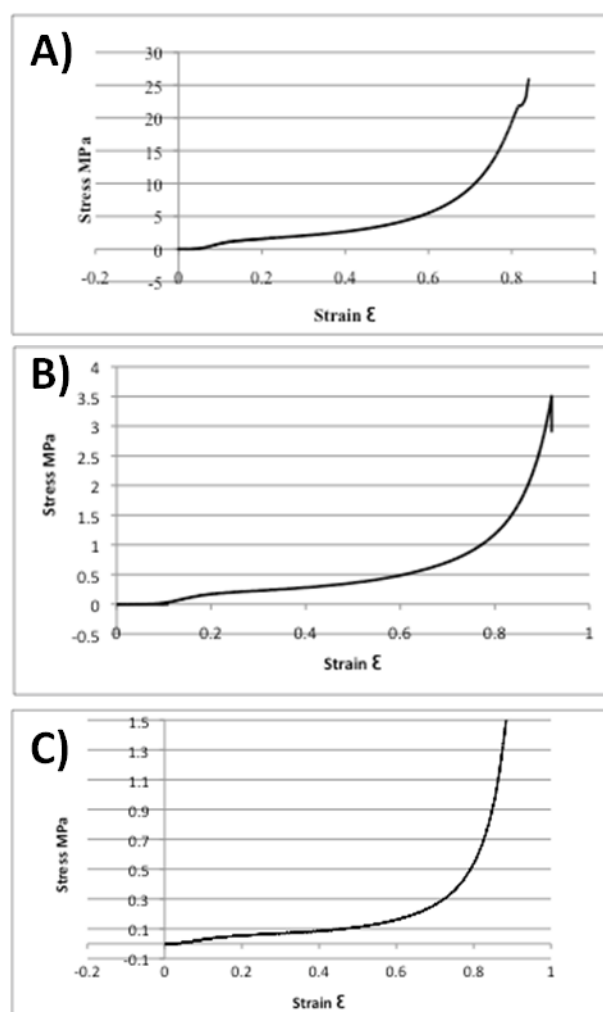
Fig. S3. Full plots of compression test curves for aligned porous PTEGDMA made from solutions of 1:5, 1:10, 1:20 dioxane solutions. The same plots but zoomed in the initial linear parts are shown in Fig. 2B.

Fig. S4 Macropore size distributions of PTEGDMA and its composites as measured by Hg intrusion porosimetry. The intrusion pore volumes are 10.61, 8.12 and 7.30 cm^3 g^{-1} for porous PTEGDMA, PTEGDMA-PEDOT-PSS and PTEGDMA-graphene, respectively.
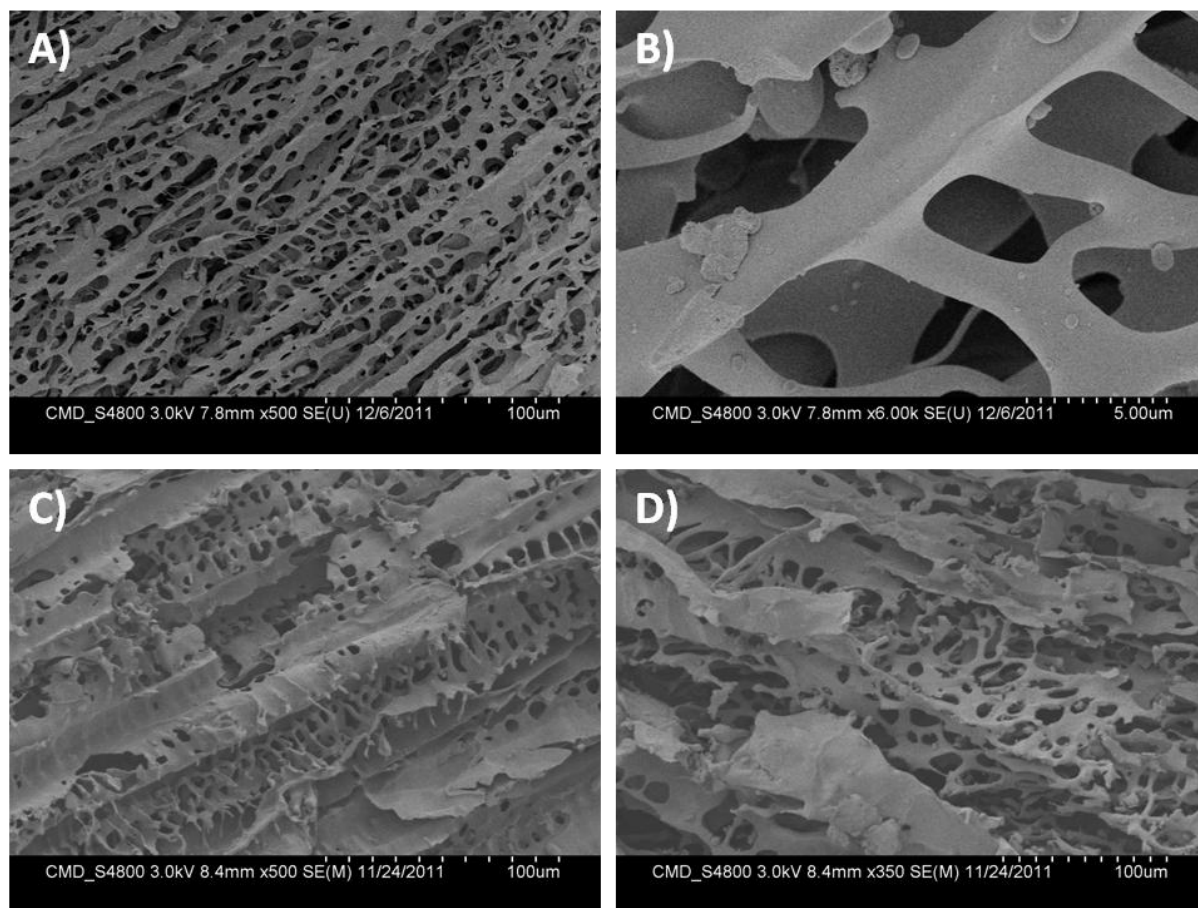
Fig. S5. A &B) SEM images at different magnifications for aligned porous PTEGDMA made from 1:20 with dioxane. C) The porous PTEGDMA loaded with graphene. D) The porous structure loaded with PEDOT-PSS.
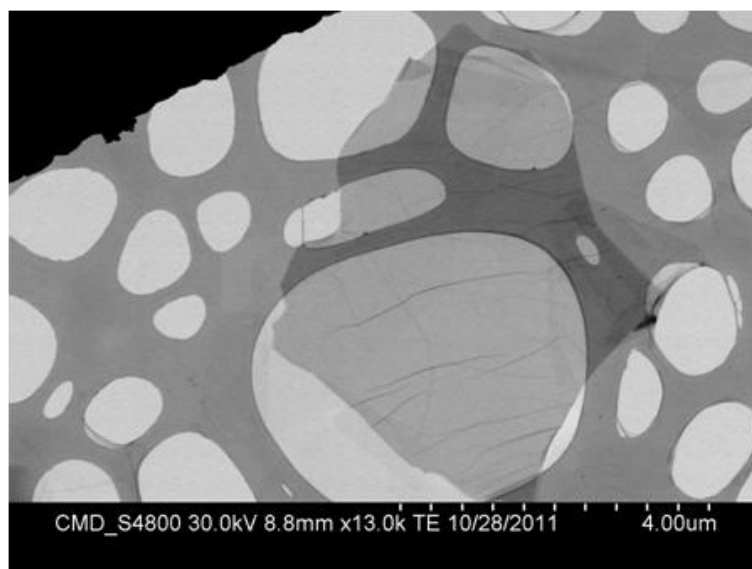
Fig. S6 TEM image of the prepared graphene oxide sheet.