Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for:

Fabrication of Nanoporous Graphene/Polymer Composite Membranes

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A. Additional information on materials and methods

A.1 Sample Preparation

The preparation procedure for the graphene/polymer composite films is depicted in Fig. S1 (a). Graphene/PET membranes were prepared by transferring single layers of chemical vapour deposited graphene (Graphenea, Spain) onto a polyethylene terephthalate (PET) film of 10 or 13 μm thickness (Oxyphen, Switzerland or Goodfellow, England) using a poly(methyl methacrylate) (PMMA; 950K AR-P 672.045 from ALLRESIST, Germany) assisted wet transfer process.[1] After spin coating a ~ 200 nm thick PMMA layer on the graphene, the underlying copper substrate was selectively etched in an aqueous solution of ammonium persulfate (APS; Sigma Aldrich, 7 g dissolved in 200 ml DI water). The resulting graphene/PMMA stack was washed in DI water and attached to the polymer film.

We studied two kinds of samples, i.e. sample set A for which the thin PMMA film employed for the transfer of the graphene layer onto the PET foil was removed before irradiation, and sample set B for which the PMMA film remained on top of the graphene during both irradiation and etching steps.

Exemplary pictures of the process are presented in Fig. S1 (b)-(d). Fig. S1 (b) shows a $1 x 1$ cm^2 graphene sheet that has been transferred onto a PET film with a diameter of 3 cm. The PMMA/graphene/PET sandwich is then mounted into the irradiation holder, see Fig. S1 (c). An additional aluminum mask with an aperture of 1 cm diameter ensures that only the PMMA/graphene/PET area is irradiated. This guarantees that the outer part of the PET support film remains unirradiated and can later be used for handling the sample without damaging the graphene. Successful etching can easily be recognized because the graphene/PET composite changes from transparent to milky-white (Fig. 1 (d)).

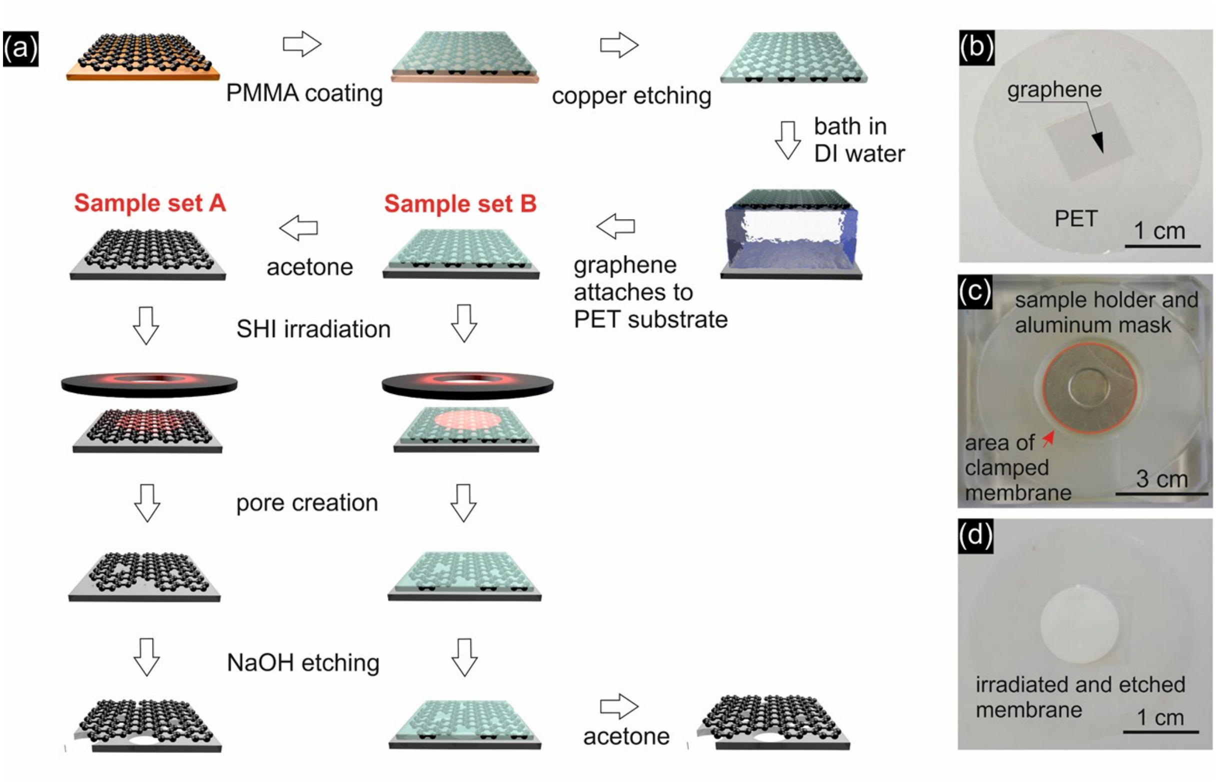

Figure S1: (a) Preparation protocols for sample sets A and B. (b) Graphene (1 x 1 cm^2) transferred onto a 10 or 13 µm thick PET film. (c) Sample holder used at the X0 beamline of the GSI (Darmstadt, Germany) and mask with a 1 cm opening to delimit the irradiation area. (d) Etched nanopores in the PET film result in a milky white contrast.

A.2 Characterization techniques

After etching, the samples were investigated by various characterization techniques.

Atomic force microscopy (AFM) was done with a Bruker Icon AFM using the Peak Force quantitative nanomechanical mapping (QNM) mode.

To visualise the quality of graphene coverage on the PET substrate on a larger scale, we performed scanning electron microscopy (SEM) using the secondary electron detection channel (JSM-6510 series, Joel, operated at 10 kV voltage and MERLIN HR-SEM, ZEISS, operated at 1.5 kV voltage). Prior to this, the membranes were coated with a ~ 5 nm thin gold film.

To confirm that graphene does not suffer during the etching process by unintentional defect creation, Raman spectroscopy (Raman InVia spectrometer with 532 nm wavelength, Renishaw, England) was applied for monitoring spectra for various etching times. Subsequent etching and performing Raman spectroscopy measurements in alternating manner allows us to investigate if defects in graphene are created due to the NaOH etching.

The membrane performance of the graphene/PET composite and PET reference samples was tested by gas/liquid dewetting permporometry (CFP-34RTG8A-X-6-L4, Porous Materials Inc., USA), obtaining values for gas permeability, pore sizes and pore size distribution.

The basic principle is based on the dewetting of a liquid filled pore by applying a certain pressure. The pressure necessary to dewet a given pore depends on the diameter of the most constricted part of the pore and is given by the Washburn equation.[2,3] Pore size distribution is obtained by the differential quotient of the ratio of the gas flux through a dry and a wet membrane and the transmembrane pressure. Measurements were performed with samples having a diameter of 25 mm, Galwick wetting liquid (16 mNm^{-1}, Porous Materials Inc., USA), and compressed air (up to 7 bar) or nitrogen (up to 34 bar).

Gas permeability has been obtained by the same device (CFP-34RTG8A-X-6-L4, Porous Materials Inc., USA). The gas flux of samples having a diameter of 25 mm have been measured by the internal gas flow meter (compressed air up to 7 bar, nitrogen up to 34 bar).

For determining the permeability of pure water a home-made stirred dead-end filtration cell was used. Measurements were performed with samples having a diameter of 25 mm, deionized water and a differential pressure of 0.5 or 2 bar.

A.3 Additional results

A.3.1 SEM analysis

In order to demonstrate the protecting effect of the PMMA for the graphene during the etching step, additional SEM images were taken for samples that were etched in a 1.5 mol/L NaOH solution at 80 °C for 16 min. Fig. S2 presents SEM images of the graphene coverage of a composite membrane where the PMMA was removed after the etching step had been performed. The graphene coverage is close to 100 %.

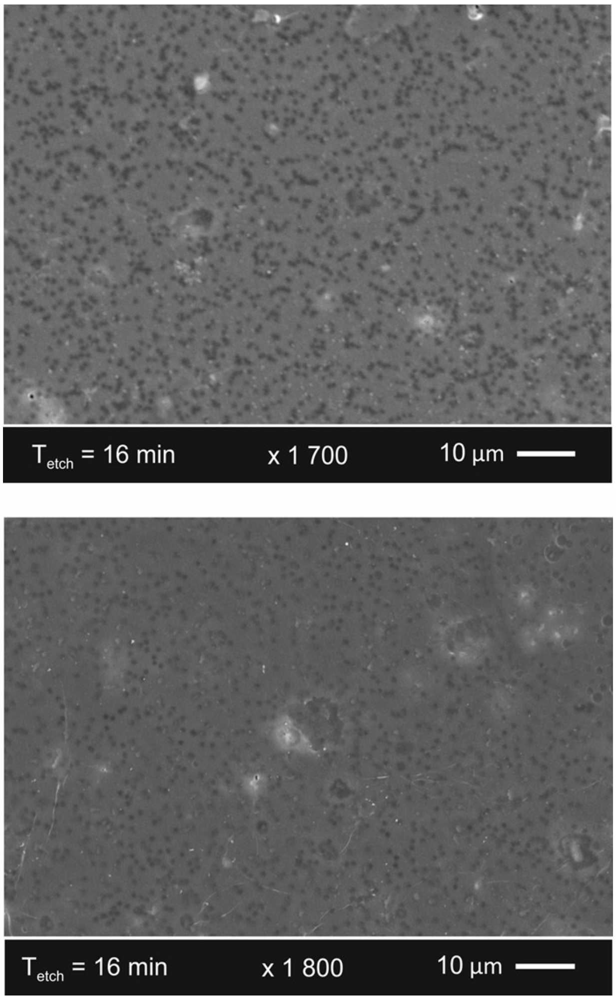

Fig. S2: SEM images of a track-etched graphene/polymer composite membrane at different positions. The presence of PMMA on the graphene during etching suppresses the delamination of the graphene thus enhancing the graphene coverage. Etching was performed in a 1.5 mol/L NaOH solution at 80 °C for 16 min.

A.3.2 Raman Characterization

Fig. S3 shows characteristic Raman spectra of the samples under investigation. Three $SrTiO_3$/graphene samples were irradiated with 1.5 GeV U ions of different fluences ranging from $1.7 \cdot 10^{10}$ ions/cm^2 to $1.7 \cdot 10^{11}$ ions/cm^2. Etching and Raman spectroscopy was performed alternately in order to evaluate the defect density of graphene as a function of etching time. Fig. S3 shows the intensity ratio of the defect (D) and the graphite (G) peak of graphene after different etching times in a 3 mol/L aqueous NaOH solution at 50 °C.

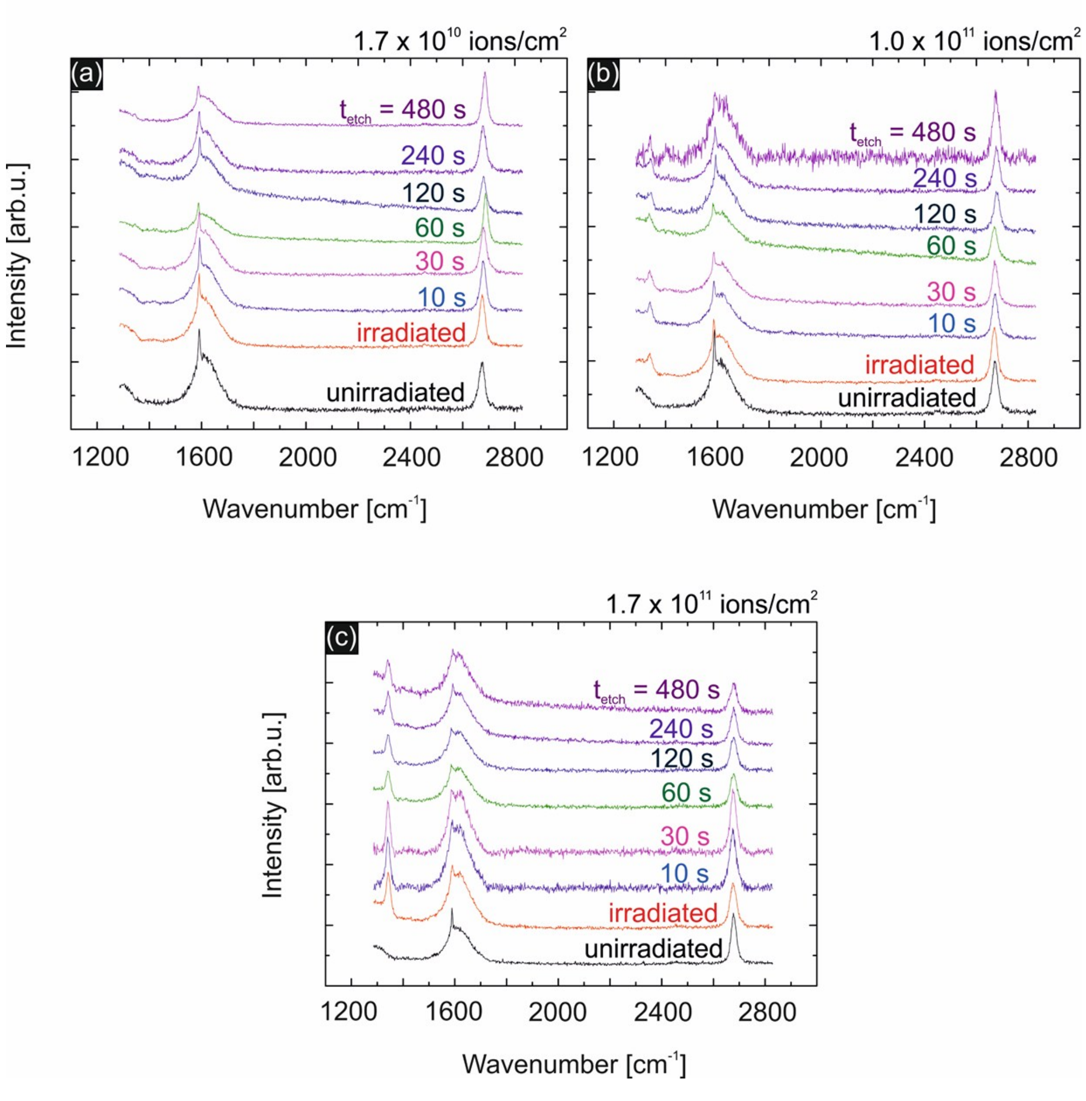

Fig. S3: Raman spectra of irradiated graphene samples after different etching times in a 3 mol/L NaOH solution at 50 °C. The fluences were chosen as $1.7 \cdot 10^{10}$ ions /cm^2 in (a), $1.0 \cdot 10^{11}$ ions/cm^2 in (b) and $1.7 \cdot 10^{11}$ ions/cm^2 in (c).

B. Calculation of water permeability of bare PET and graphene/PET composite membranes

Exemplary calculation of the permeability P_{PET} and resistance R_{PET} of PET track-etched membranes by combining equations (1) and (2) and applying equation (4), respectively.

Pore creation efficiency of 100 % is assumed ($N = 1.7 \cdot 10^{11}$ m^{-2}). Pore size deduced from permporometry ($r = 1.22 \cdot 10^{-7}$ m) and length of the pore equal to membrane thickness ($l = 1.3 \cdot 10^{-5}$ m) are inserted. Viscosity is $\mu = 0.001$ Pa s ($T = 20$ °C).

$$P_{PET,7min} = \frac{\pi\,(1.22 \cdot 10^{-7} m)^4 \cdot 1.7 \cdot 10^{11} m^{-2}}{8 \cdot 0.001\, Pa\, s \cdot 1.3 \cdot 10^{-5}\, m} = 1.14 \cdot 10^{-9} m\, Pa^{-1} s^{-1} = 410\, L\, m^{-2} h^{-1}\, bar^{-1}$$

$$R_{PET,7min} = \frac{8 \cdot 0.001\, Pa\, s \cdot 1.3 \cdot 10^{-5} m}{\pi\,(1.22 \cdot 10^{-7} m)^4} = 1.49 \cdot 10^{20}\, Pa\, s\, m^{-3}$$

Calculation of the resistance $R_{Graphene}$ of a graphene pore by equation (6).

Pore size of 20 nm ($r = 10^{-8}$ m) is used because of observation in SEM images and corresponding to biggest mode in permporometry measurement.

$$R_{graphene} = \frac{3 \cdot 0.001\, Pa\, s}{(1 \cdot 10^{-8} m)^3} = 3.00 \cdot 10^{21}\, Pa\, s\, m^{-3}$$

Calculation of the permeability P_c of the graphene/PET composite membrane by combining equations (3), (4), and (6).

Pore creation efficiency of 100% is assumed in PET and graphene layer.

$$P_C = \frac{1.7 \cdot 10^{11} m^{-2}}{1.49 \cdot 10^{20} Pa\, s\, m^{-3} + 3.00 \cdot 10^{21}\, Pa\, s\, m^{-3}} = 5.4 \cdot 10^{-11}\, m\, Pa^{-1} s^{-1} = 19.4\, L\, m^{-2} h^{-1} bar^{-1}$$

For the transport through track-etched membranes and through nanoporous graphene, errors of calculated values follow the standard propagation of errors according to formula S1.

$$\delta\mu = \sqrt{\sum_i \left(\frac{\partial N}{\partial x_i}\right)^2 \delta x_i} \qquad \text{(S1)}$$

References

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