Supporting Information

CO_2-selective PEO-PBT (PolyActive™)/graphene oxide composite membranes

Madhavan Karunakaran, Rahul Shevate, Mahendra Kumar, and Klaus-Viktor Peinemann*

Advanced Membranes and Porous Materials Center, 4700 King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

*Corresponding Author (klausviktor.peinemann@kaust.edu.sa)

Experimental Section

Materials

Poly(ethylene oxide)-poly(butylene terephthalate) (PEO-PBT) copolymer was received from IsoTis Ortho Biologics and used without any further purification. Graphite flakes were purchased from Sigma Aldrich and used as received. Sulphuric acid (H_2SO_4, 97%), hydrochloric acid (HCl, 35% in water), hydrogen peroxide (H_2O_2, 30% in water), and potassium permanganate ($KMnO_4$) were procured from Sigma Aldrich. Porous polyacrylonitrile (PAN) membrane support was used as a substrate to prepare PEO-PBT/GO thin film composite membranes. Tetrahydrofuran (THF) and deionized water were used as a solvent to prepare the PEO-PBT/GO solutions.

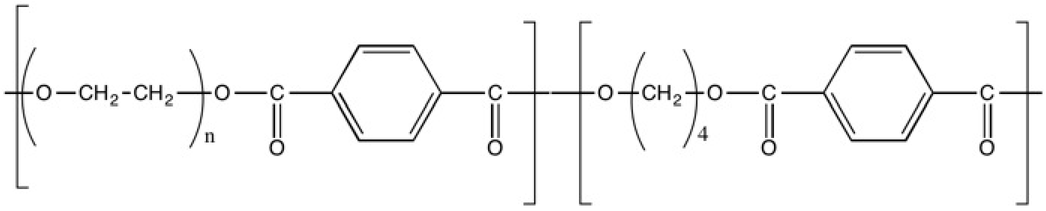

Fig. S1 Schematic representation of poly(ethylene oxide)-poly(butylene terephthalate) (PEO-PBT) copolymer.

Graphene oxide synthesis

Graphene oxide (GO) was synthesized by a modified Hummers method.[1,2] 2 g of graphite flakes were heated in a 100 W microwave oven for 15 s to produce expanded graphite (EG) flakes as the precursor for synthesis of GO. 2g of expanded graphite flakes was taken in a 500 ml three-neck round bottom flask. To this, 250 ml of H_2SO_4 was added at 10^oC and stirred for 90 min. About 10 g of $KMnO_4$ was gradually added to the mixture and stirred continuously for 24 h at room temperature. The resulting mixture along with round bottom flask was then transferred into an ice bath. The mixture of 100 ml H_2O_2 and 500 ml deionized (DI) water was slowly added into the above resulting mixture and the solution temperature was maintained less than 50^oC to prevent thermal explosion. The color of the mixture turned into golden brown from green after addition of H_2O_2 and DI water mixture. The resulting mixture was stirred for another 1 h and then filtered. Then, the filtrate was washed and centrifuged for three times with 10% HCl solution. Subsequently, HCl treated oxidized exfoliated graphite particles were washed and centrifuged with DI water. Centrifugation and washing steps with DI water were carried out until a solution pH was achieved to >5. During washing process, oxidized EG particles were exfoliated to GO nanosheets.

Membrane Preparation

Dense Membrane

About 1 mg/ml of GO was dispersed in DI water, the predetermined amount of GO in DI water was taken in a round bottom flask and diluted with THF/DI water (80/20 wt %). To this about 3wt% of PEO-PBT polymer was added and dissolved the polymer under reflux condition for 4 h. The resulting polymer solutions were sonicated for 3h and then transferred into teflon petridish.

PEO-PBT/GO solutions were evaporated at room temperature for 24 h to make a dense membranes. Afterwards, the membranes were peeled off and dried at 60^{o}C for 8 h in a vacuum oven to remove residual traces of water and solvent from the membranes. The membrane thicknesses were measured by a digital micrometer and were between 50 to 60 µm.

Composite Membrane

The composite membranes were prepared by dip-coating process using microporous PAN membrane support. After the dip-coating procedure, the membranes were dried under ambient conditions.

Instrumental Characterizations

ATR-FTIR spectra for the dense membranes were recorded using Nicolet iS10 (Thermo Scientific) spectrometer. The data were collected for 16 scans with a resolution of 4 cm^{-1}. All scans were recorded at ambient temperature.

Raman spectra were recorded on a Jobin-Yvon Horbia LabRam Aramis Raman spectrometer equipped with a 50×Objective lens (Olympus, NA 0.75) with a wavelength of 532 nm. For Raman analysis of GO based membranes, the membranes were mounted on a glass substrate, and then laser beam was focused on the center of membrane surface to record Raman spectra.

Scanning electron microscopy (SEM) images of the dense GO based membranes were recorded on a **Field emission scanning electron microscope (FESEM,** FEI Quanta 200 series**)** . Imaging was carried out at an accelerating potential of 5 kV with a working distance of 10 mm. The dry membrane samples were mounted on aluminum stubs using aluminum tape and coated with gold before recording SEM images of the membranes.

Atomic Force Microscopy (AFM) analysis was performed using an Agilent (Model 5400) microscope in the tapping mode. The tip characteristics are as follows: spring constant 3Nm^{-1}, resonant frequency 60-80 Hz. The GO membrane was imaged using TEM. The GO membrane was embedded in a low-viscosity epoxy resin (Agar R1165) and cured for 24 h at room temperature. About 100 nm ultrathin sections of membrane was prepared using an ultramicrotome (Leica EM UC6) and then placed on a carbon-coated copper grid. Images were obtained using a Tecnai 12 instrument (FEI company) at an operating potential of 120 keV.

Results

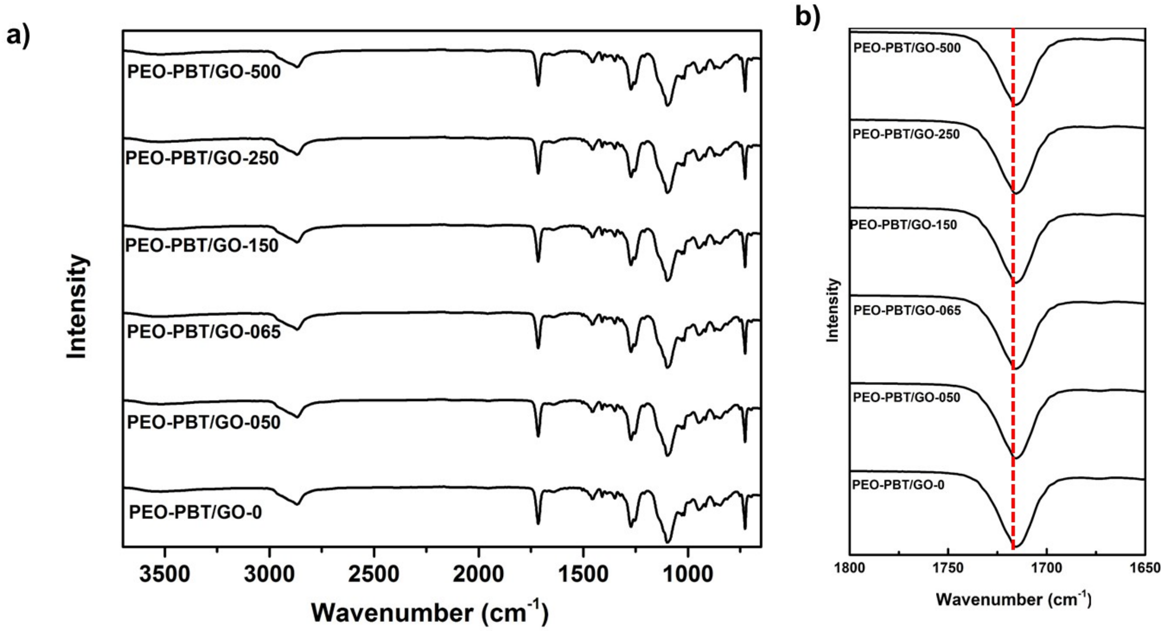

Fig. S2 ATR-FTIR spectra of PEO-PBT and PEO-PBT-GO membranes a) wave number from 3500-650 cm^{-1}, b) wave number from 1800-1650 cm-1 (-C=O).

The GO containing PEO-PBT membrane shows similar bands as the pure PEO-PBT membrane, confirming that no chemical reaction occurred between the GO nanosheets and polymer during the membrane formation. Moreover, the absorption band at 1714 (-C=O) is shifted to 1709 cm^{-1} (Fig. S2b, ESI) for the GO containing membranes revealing possible hydrogen bonding between the carbonyl group of polymer and the polar hydroxyl group present on the basal plane and edges of GO nanosheets. The hydrogen bonding association of polymer and GO nanosheets aids to achieve a stable dispersion of GO nanosheets in the PEO-PBT copolymer solution.

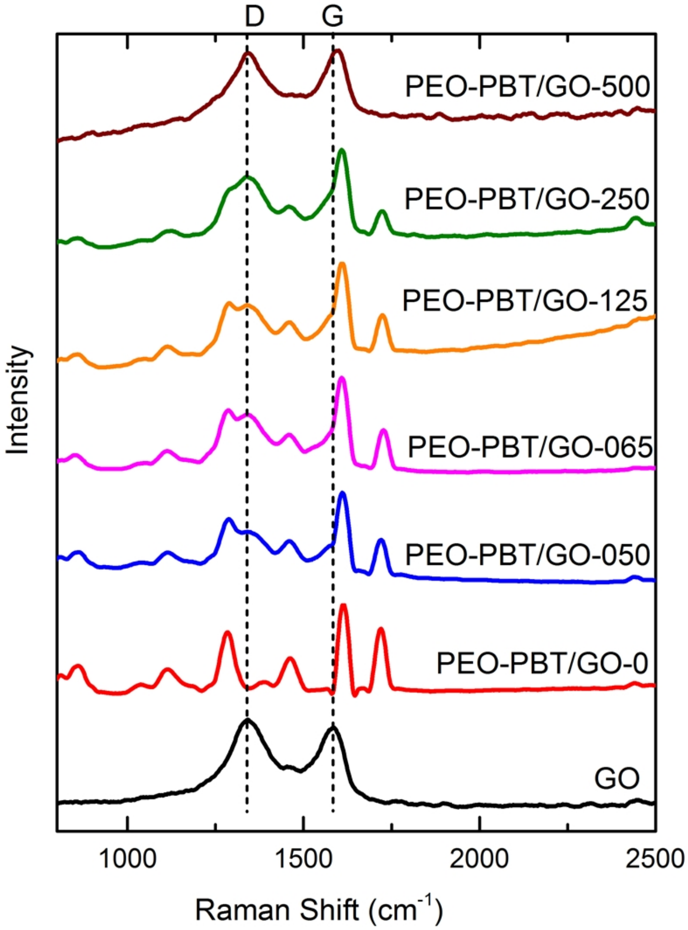

Fig. S3 Raman spectra of GO, PEO-PBT and PEO-PBT/GO membranes.

In the present case, the two characteristic D and G bands of GO were observed in the PEO-PBT/GO membrane at 1345 and 1580 cm^{-1}, which broadens and merge with bands of PEO-PBT polymer. These data confirm the incorporation of GO in the membrane matrix. In addition, the slight shift from 1339 to 1345 cm^{-1} for D band of the composite membrane confirms the good dispersion of GO in the membrane matrix. For PEO-PBT/GO membranes, the D band becomes slightly broader because of the higher level disorder of the graphene oxide layers by the polymer matrix through hydrogen bonding interaction between oxygen containing functional groups (hydroxyl, epoxide and carboxyl) of GO and carbonyl group of PEO-PBT polymer. In addition, the G and D peaks and the polymer peaks are completely suppressed at very high concentration of GO in the composite membrane, which confirms the presence of GO layered on the membrane surface.

Gas permeation measurement

A pressure increase test unit designed and built at KAUST was used to measure the permeance of single gases. The permeability of gases were measured at 25^{o}C by using a constant volume/variable pressure method with a feed pressure of 500 mbar for all gases. The apparatus is shown in Fig. S4.

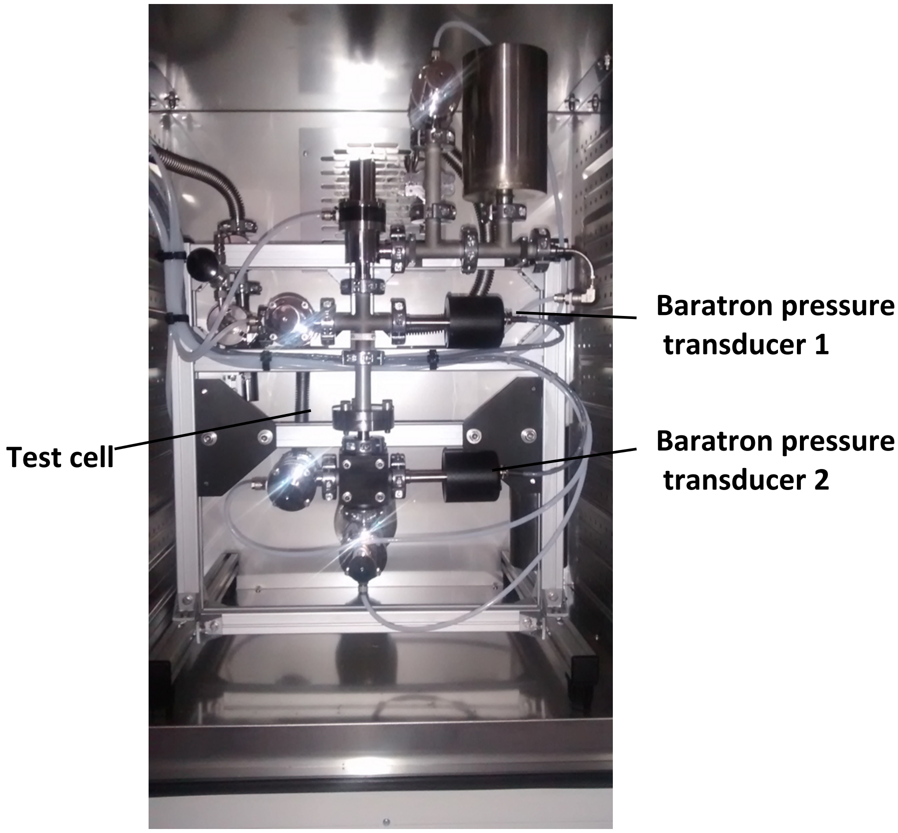

Fig.S4 Constant volume/variable pressure apparatus for gas permeability measurement

Pressure transducer 1 is a Baratron 121AA-0500 model, pressure transducer 2 is a Baratron 121AA-00010 model. The permeate chamber was evacuated using a HiCube 80 Eco turbo pumping station.

The permeance values of a membrane with an unknown thickness of the selective layer can be calculated by using eqn (1):

$$J = \frac{V.\ 22.4}{R.\ T.\ A.\ t} \ln\left(\frac{p_F - p_0}{p_F - p_{P\,(t)}}\right) \tag{1}$$

where V (l) is the permeate volume, R (0.0831 bar l mol^{-1} K^{-1}) is the ideal gas constant, T (K) is the temperature, A (m^2) is the membrane area and t (s) is the time of measurement. p_F, p_0, and $p_{P(t)}$ (bar) are the pressures at the feed, permeate side at beginning, and permeate side at the end of measurement, respectively.

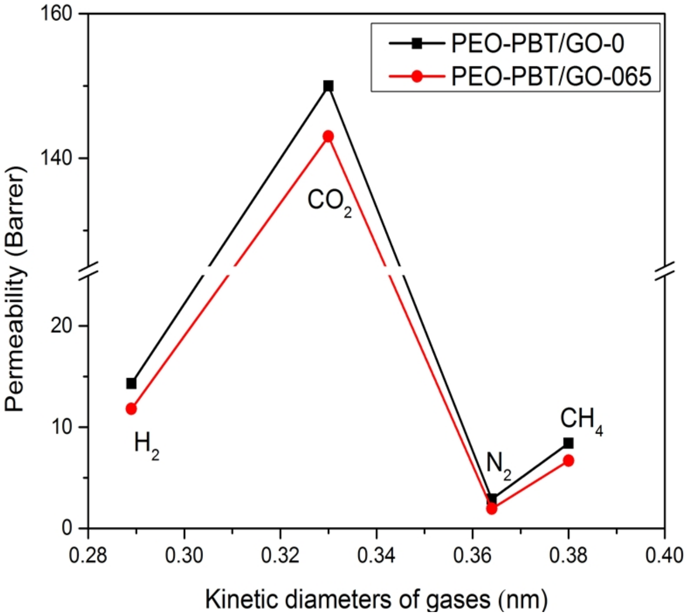

Fig. S5 Gas permeability of PEO-PBT and PEO-PBT/GO membranes as a function of kinetic diameters of gases.

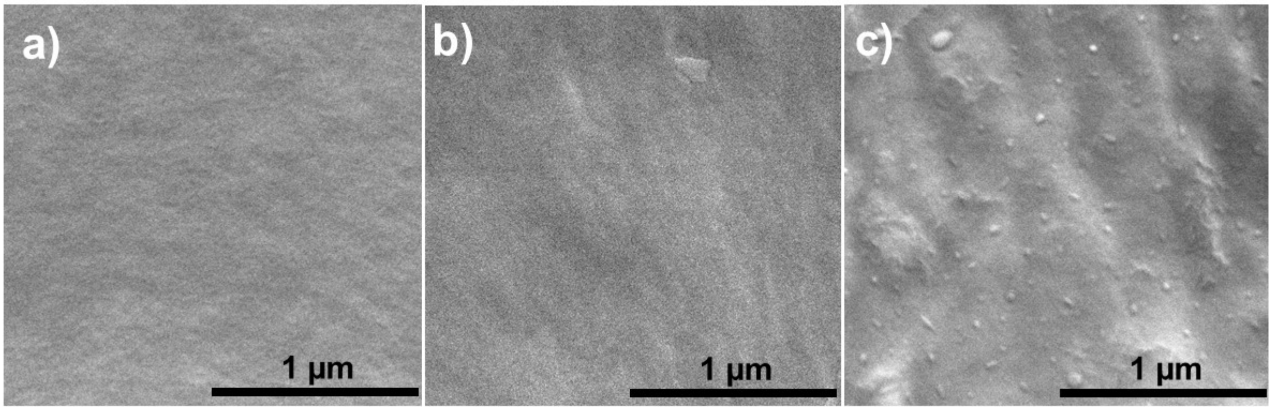

Fig. S6 SEM images of dense membrane a) PEO-PBT/GO-0, b) PEO-PBT/GO-065, c) PEO-PBT/GO-500.

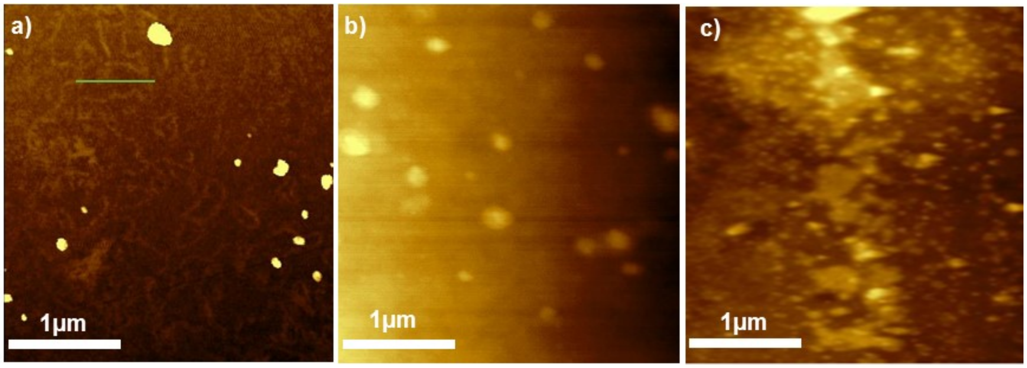

Fig. S7 AFM images of GO and dense membrane a) GO, b) PEO-PBT, c) PEO-PBT/GO-500.

Table S1: Gas permeation data for PEO-PBT/GO dense membranes.

Membrane	Permeability (Barrer)[a]				Selectivity α		
	CO_2	N_2	CH_4	H_2	CO_2/N_2	CO_2/CH_4	CO_2/H_2
PEO-PBT/GO-0	150	2.88	8.40	14.30	52	18	10
PEO-PBT/GO -025	150	2.56	8.02	12.50	58	19	12
PEO-PBT/GO -050	149	2.20	7.07	12.20	68	21	12
PEO-PBT/GO -065	143	1.95	6.68	11.80	73	21	12
PEO-PBT/GO -075	130	1.88	5.99	10.60	69	22	12
PEO-PBT/GO -125	123	1.78	5.71	9.95	69	21	12
PEO-PBT/GO -250	95	1.38	4.48	8.21	68	21	11
PEO-PBT/GO -500	76	1.13	3.50	6.56	67	21	11

[a] 1 Barrer = 1×10^{-10} cm^3 cm (STP) cm^{-2} s^{-1} $cmHg^{-1}$

Feed Pressure < 500mbar; Membrane thickness 50-60µm.

Table S2: Gas permeation data for PEO-PBT/GO coated PAN composite membranes.

Membrane	Flux[a]				Selectivity α		
	CO_2	N_2	CH_4	H_2	CO_2/N_2	CO_2/CH_4	CO_2/H_2
CPEO-PBT/GO-0	2.20	0.043	0.12	0.22	51	18	10
CPEO-PBT/GO -025	2.01	0.031	0.11	0.19	64	18	10
CPEO-PBT/GO -050	1.96	0.027	0.092	0.17	72	21	11
CPEO-PBT/GO -065	1.85	0.0256	0.088	0.165	72	21	11
CPEO-PBT/GO -075	1.65	0.023	0.076	0.134	72	21	12
CPEO-PBT/GO -125	1.57	0.023	0.073	0.134	68	21	12
CPEO-PBT/GO -250	1.24	0.018	0.061	0.112	68	20	11
CPEO-PBT/GO -500	0.66	0.01	0.031	0.061	66	21	11

[a](10^{-1} m^3/m^2.h.bar)

Feed Pressure < 500 mbar.

Correction of GO permeability data given in the literature[2,3]

The very high CO_2-permeability of more than 8000 Barrer given in the literature is based on a miscalculation. From Fig. 3C in the Science publication we extract a CO_2 permeance of the GO composite membrane of about 110 GPU. The permeance of the coating of a two-layer composite membrane can be calculated by the resistance model:

$$Permeance_{coating} = \frac{1}{1/Permeance_{composite} - 1/Permeance_{\sup port}}$$

With 110 and 400 GPU for composite and support membrane we then get 152 GPU permeance for the GO coating. Taking the 5 nm coating thickness mentioned on page 1 one gets for the permeability of the GO coating a permeability of 0.76 Barrer ($10^{-10} cm^3 cm/cm^2 s\ cmHg$). This is of course very different from the 8000 to 9000 Barrer given in the references.

References

1. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339−1339

2. H. W. Kim, H. W. Yoon, B. M. Yoo, J. S. Park, K. L. Gleason, B. D. Freeman and H.B. Park, *Chem. Comm.*, 2014, **50**, 13563

3. H. W. Kim, H. W. Yoon, S.M. Yoon, B. M. Yoo, B. K. Ahn, Y. H. Cho, H. J. Shin, H. Yang, U. Paik, S. Kwon, J. Y. Choi and H. B. Park, *Science*, 2013, **342**, 91.