

**Casting molecular channels through domain formation: High performance
graphene oxide membranes for H₂/CO₂ separation**

Amritroop Achari and Muthusamy Eswaramoorthy*

Nanomaterials and Catalysis Lab, Chemistry and Physics of Materials Unit, JNCASR, Jakkur
P.O, Bangalore 560064, India.

*Correspondence to: E-Mail- eswar@jncasr.ac.in

Supplementary Materials:

Materials and Methods

Figures S1-S12

References (1-6)

Materials and methods

1. Materials and Characterization techniques:

Graphite powder (20 micron) (Sigma Aldrich), NaNO₃ (Sigma Aldrich), KMnO₄ (S D Fine chemicals), H₂SO₄ (98%, AR grade), were used without any further purification. Powder x-ray diffraction (PXRD) patterns were recorded using Rigaku diffractometer using Cu K α radiation, ($\lambda=1.54 \text{ \AA}$). Field-emission scanning electron microscopy (FESEM) images were obtained by using FEI (Nova-Nano SEM-600 Netherlands) equipment. TEM measurements and elemental mapping were performed on a TEM (TECNAI T20) operating at an acceleration voltage (dc voltage) of 100 kV. Samples were prepared by placing a drop of dispersion on a TEM grid (holey carbon). Electronic absorption spectra were recorded on a Perkin Elmer Lambda 750 UV-Vis-NIR Spectrometer. 1 mm path length cuvette was used for recording the spectra.

2. Preparation of Graphene Oxide

Graphene oxide (GO) was obtained from graphite by Hummer's method ¹. In a typical procedure, 23 mL of concentrated H₂SO₄ was mixed with 1 g of graphite and 0.5 g NaNO₃ in a 250 mL round bottom flask cooled in an ice bath at 0 °C. 3 g KMnO₄ was added slowly to the mixture in small portions with vigorous stirring. Temperature was maintained below 20 °C during this time. The ice bath was then removed and the reaction was brought to 30-35 °C, where it was maintained for 30 min. To this 46 mL water was added slowly causing violent effervescence and rise of temperature to 98 °C. The resultant brown coloured suspension was maintained at this temperature for 15 minutes. The suspension was then brought to room temperature and 140 ml water was added. The mixture was then treated with 1 mL of 30% H₂O₂ to reduce any unreacted permanganate. The bright yellow reaction mixture was then

centrifuged at 5000 rpm, washed several times with distilled water and dialysed until pH of the solution turns neutral.

3. Preparation of GO membrane:

In a typical procedure, GO solution (~14 mg/ mL, 0.5 mL) was diluted to 30 mL and centrifuged at 14500 rpm for 15 min. The resultant solution was filtered through a Millipore filter paper to obtain the membranes. For thicker membranes, 1 mL of the concentrated GO solution was diluted to 30 mL, centrifuged and filtered

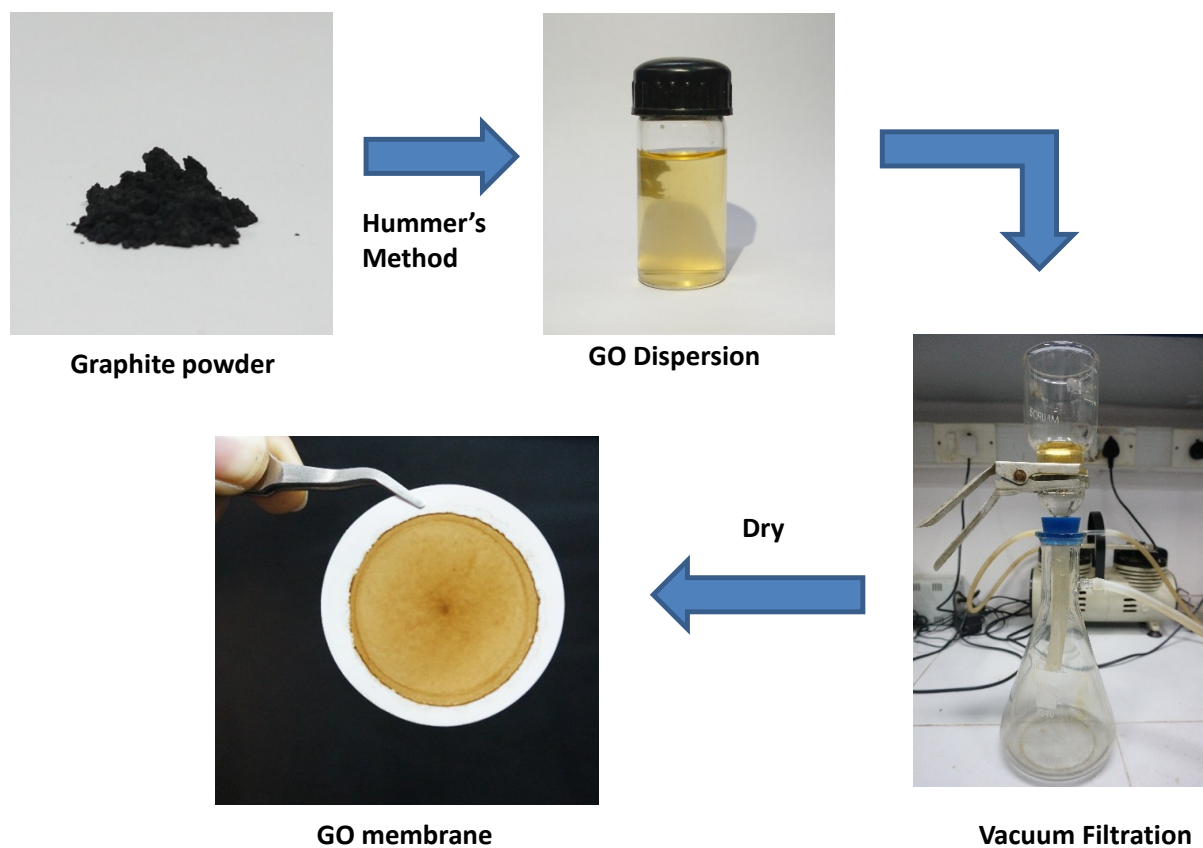


Figure. S1. Preparation of GO membrane

The polycarbonate membranes were purchased from Millipore corp. (Isopore, GTTP 0.2 μm pore size). The pore size of the membranes ranged from 180-250 nm and thickness 7-22 μm . FESEM images and pore size distribution of the membranes are provided below.

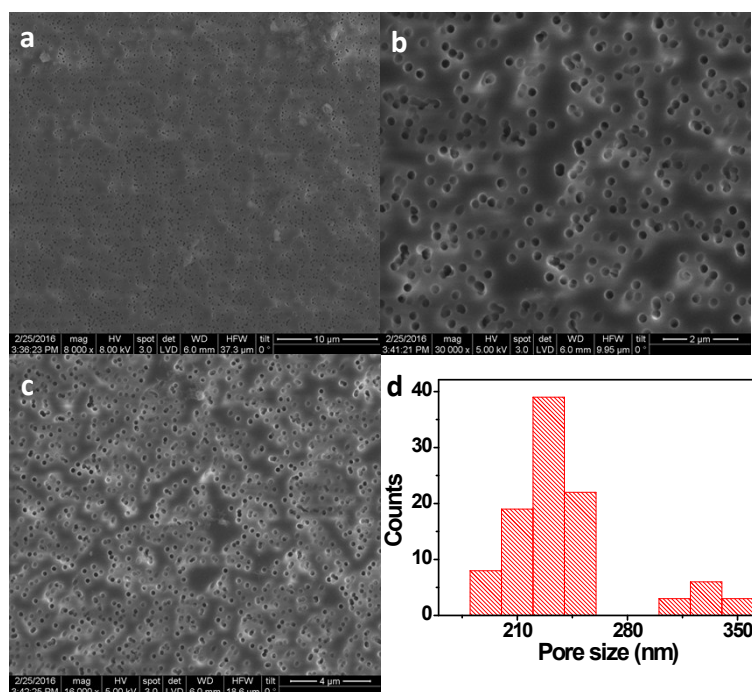


Figure S2. a)-c) FESEM images of the bare polycarbonate membrane and d) pore size distribution of the membrane (100 pores were measured).

4. Gas Permeation Measurements:

Gas permeation measurements were carried out in a custom made permeation cell as shown in figure. S7. Accurate gas flow was maintained through mass flow controllers (MKS and Hitachi). Pure H_2 , O_2 and N_2 were used as feed gases. Gas flow on the feed stream were kept constant at 100 sccm for individual gases and 50 sccm each for mixed gas permeation. On the other hand N_2 was used as sweep gas and the flow was kept constant at 50 sccm. The concentration of the gases in the permeate stream was analysed through gas chromatographs (Agilent 7890 A) fitted with packed molecular sieve columns for H_2 and O_2 separation and capillary molecular sieve columns for CO_2 separation.

The permeation values were calculated according to the following equation ²:

$$P_1(\text{Barrer}) = \frac{x_1 f t 10^{10}}{[1 - (x_1 + x_2)] \cdot A \cdot (p_1 x_1^F - p_2 x_2^F)}$$

Where P_1 = Permeability of gas 1 in Barrer, x_1, x_2 = Mole fraction of gas 1 and 2 in permeate stream, x_1^F = mole fraction of gas 1 in the feed stream, p_1, p_2 = pressure in the feed side and permeate side respectively (cm-Hg), A = area of the membrane (cm²), t = thickness of the membrane (cm), f = flow rate of the sweep gas (mL/s)

And separation factor or selectivity $\alpha = \frac{P_1}{P_2}$

The permeability of Knudsen diffusion can be expressed by the following equation: $P = \frac{D_k}{RT}$
 where P is the permeability, D_k is the Knudsen diffusion coefficient, R is universal gas constant, T is thermodynamic temperature (298 K). The Knudsen diffusion constant was calculated according to this equation.

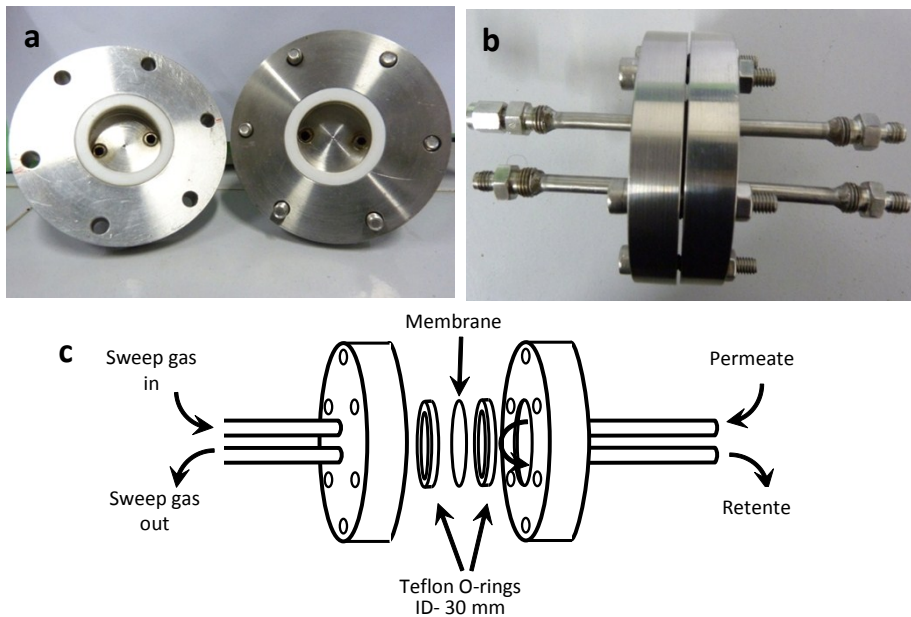


Figure S3. a, b-Images of the permeation cell, c- Schematic diagram of the permeation cell with membrane.

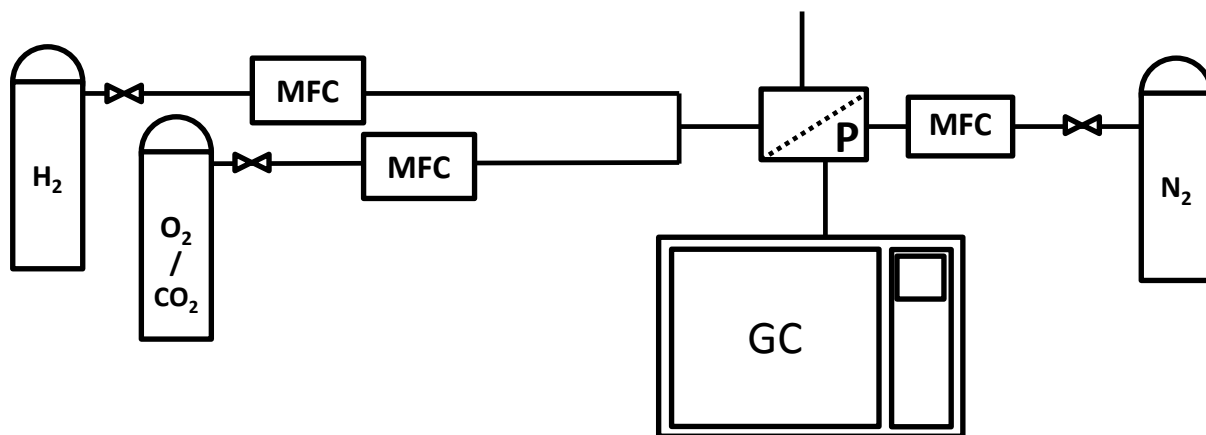


Figure S4. Schematic of the gas permeation setup. MFC- Mass flow controller, P- permeation cell, GC- Gas Chromatograph.

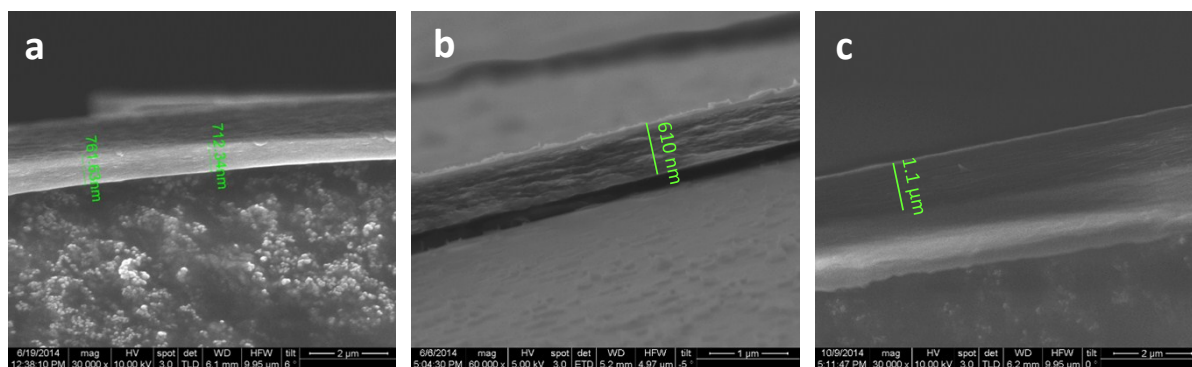


Figure S5. Cross sectional FESEM images of membranes with different thickness. a) membrane with average thickness of approx. 700 nm, b) membrane with average thickness of approx. 600 nm and c) membrane with average thickness of approx. 1000 nm

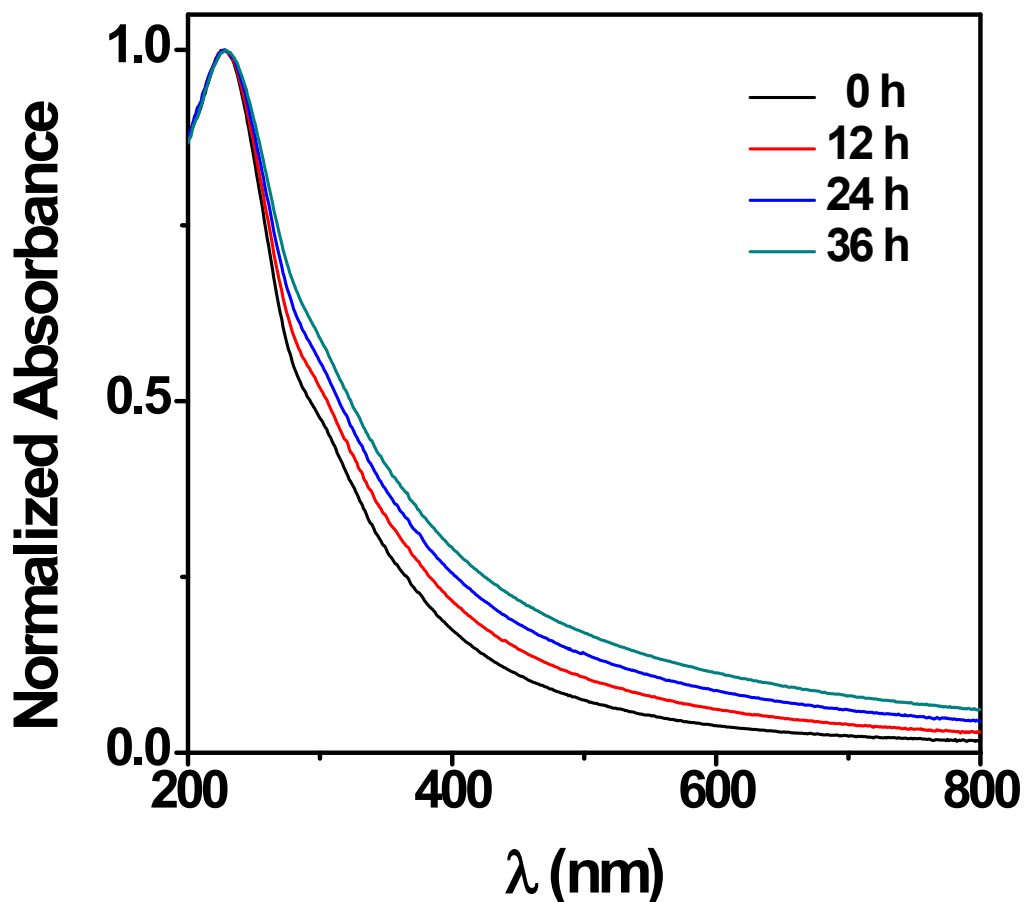


Figure S6. UV-Vis absorbance spectra of GO dispersion heated at 80 C for different times. The spectra has been normalized to the peak at 230 nm. The increase in absorption in the visible range of the spectrum is a direct indication of the darkening of the solution. These as prepared GO samples show a pronounced absorption peak at ~230 nm, attributed to the $\pi - \pi^*$ transition of C=C and a broad absorption at visible region ³. After annealing at 80 °C, the main absorbance peak at 230 nm remains intact while absorbance increases in the visible range, consistent with darkening of colour. This increase in absorbance was attributed to the oxygen diffusion under temperature to form distinct oxidized and graphitic regions, which forms larger π conjugated domains, having higher absorbance in the visible region ⁴.

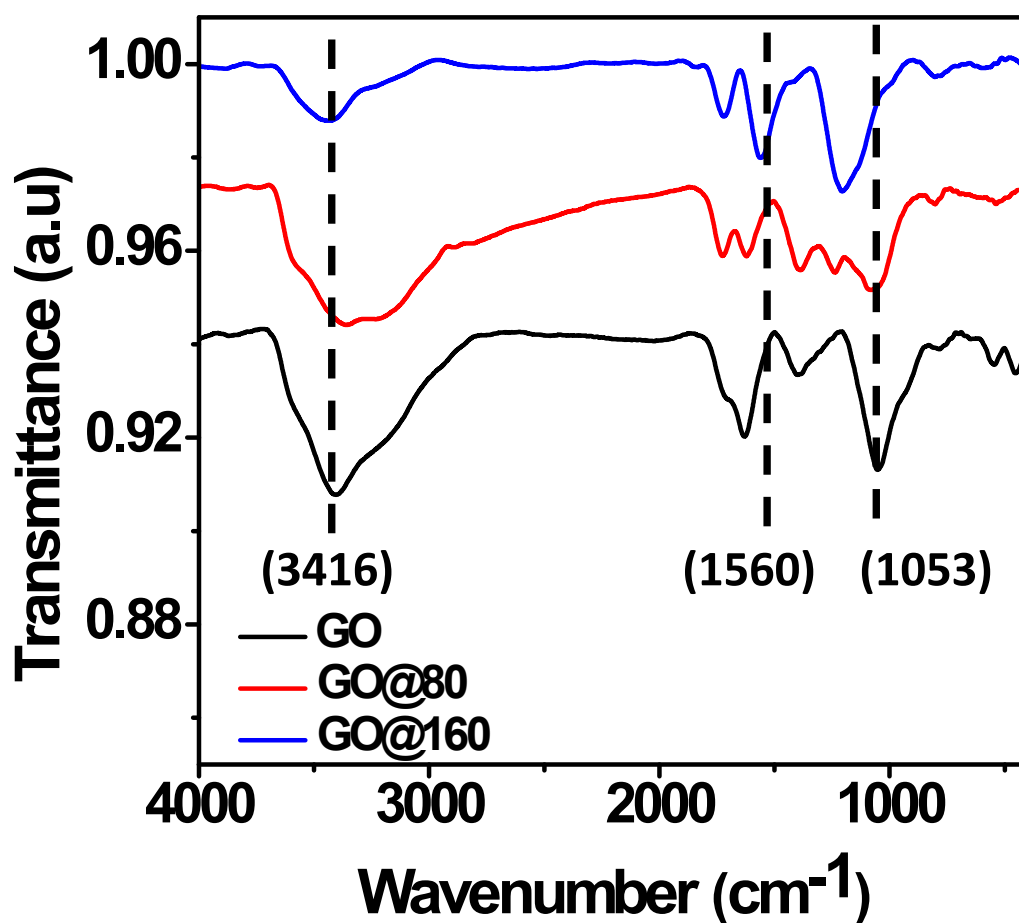


Figure S7. IR spectra of as prepared GO, GO annealed at 80 °C and 160 °C for 42 h. GO shows typical IR peaks at frequencies 1053 cm⁻¹, 1724 cm⁻¹ and 3416 cm⁻¹, corresponding to C-O and C-OH stretching, C=O stretching from carbonyl and carboxylate groups and O-H stretching from adsorbed water and hydroxyl groups respectively⁵. In the sample after 42 h heating at 80 °C (GO@80) all these peaks are retained, while after heating at 160 °C for 42 h (GO@160) the oxygen functional group peaks diminish and new peak at 1560 cm⁻¹, corresponding to skeletal vibrations of graphene domains arise.

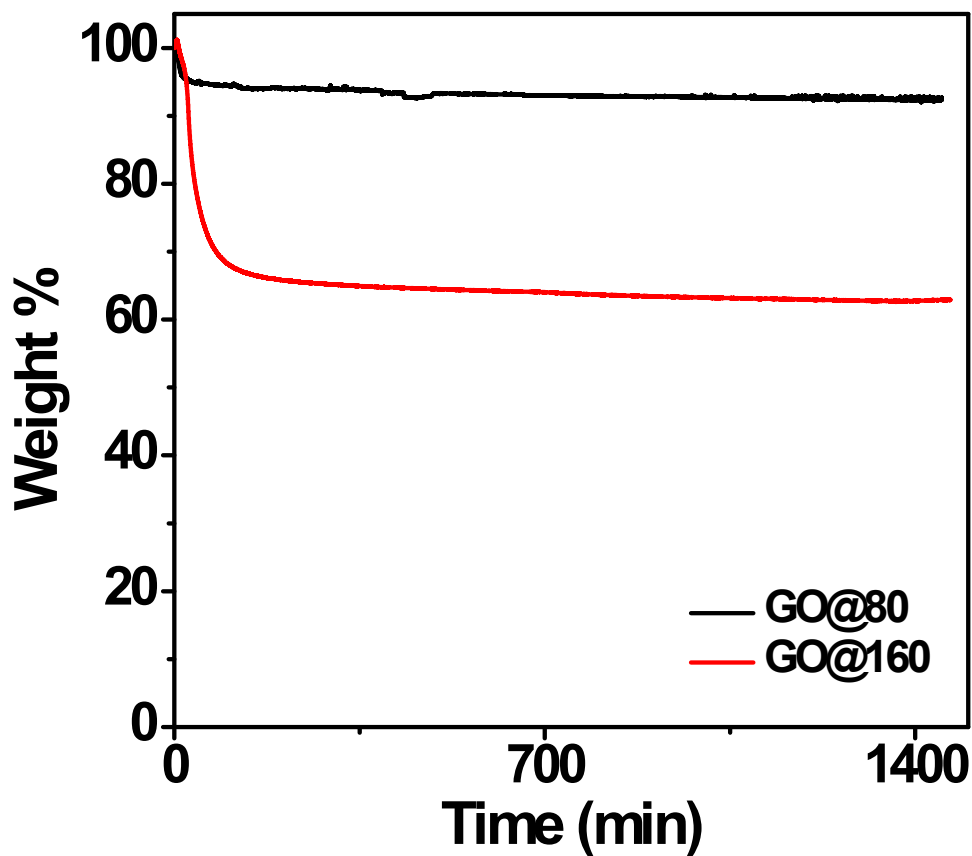


Figure S8. Isothermal TGA studies of GO samples at 80 C and 160 C for 24 h. GO annealed at 80 °C show minimal weight loss (~10 %), which can be attributed to the loss of water molecules physisorbed on the surface. On the other hand, at 160 °C about 40% weight loss is observed. As most of the structural oxygenated functional groups are lost, the sample converts to thermally reduced rGO.

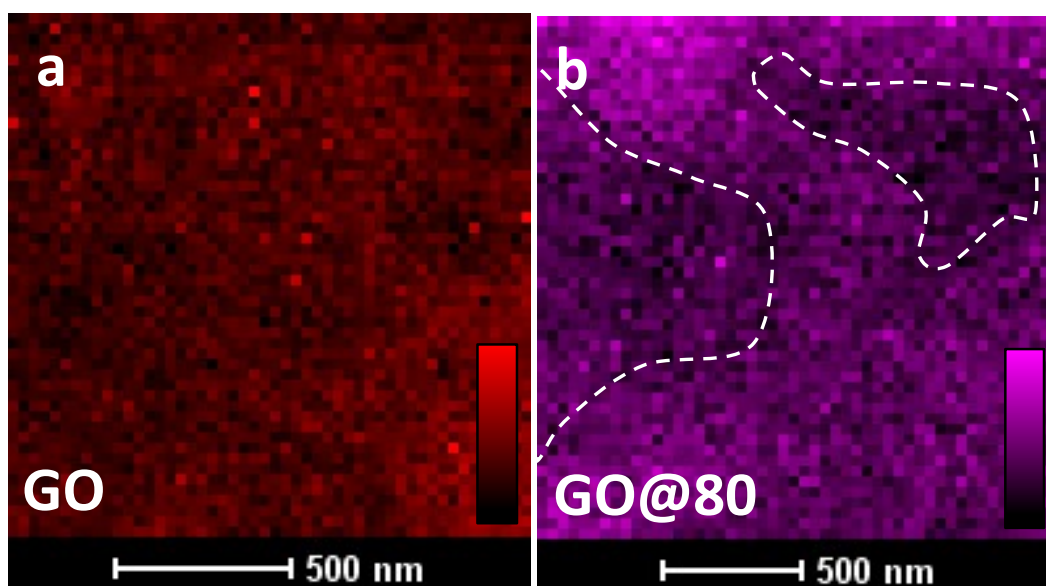


Figure. S9. Elemental mapping of oxygen on GO sheets a) before and b) After heating at 80 °C for 42 h. The colored regions represent oxygen rich domains. Distribution of oxygen is uniform on the as-prepared GO, whereas there is clear indication formation of oxygen rich and oxygen deficient regions after annealing.

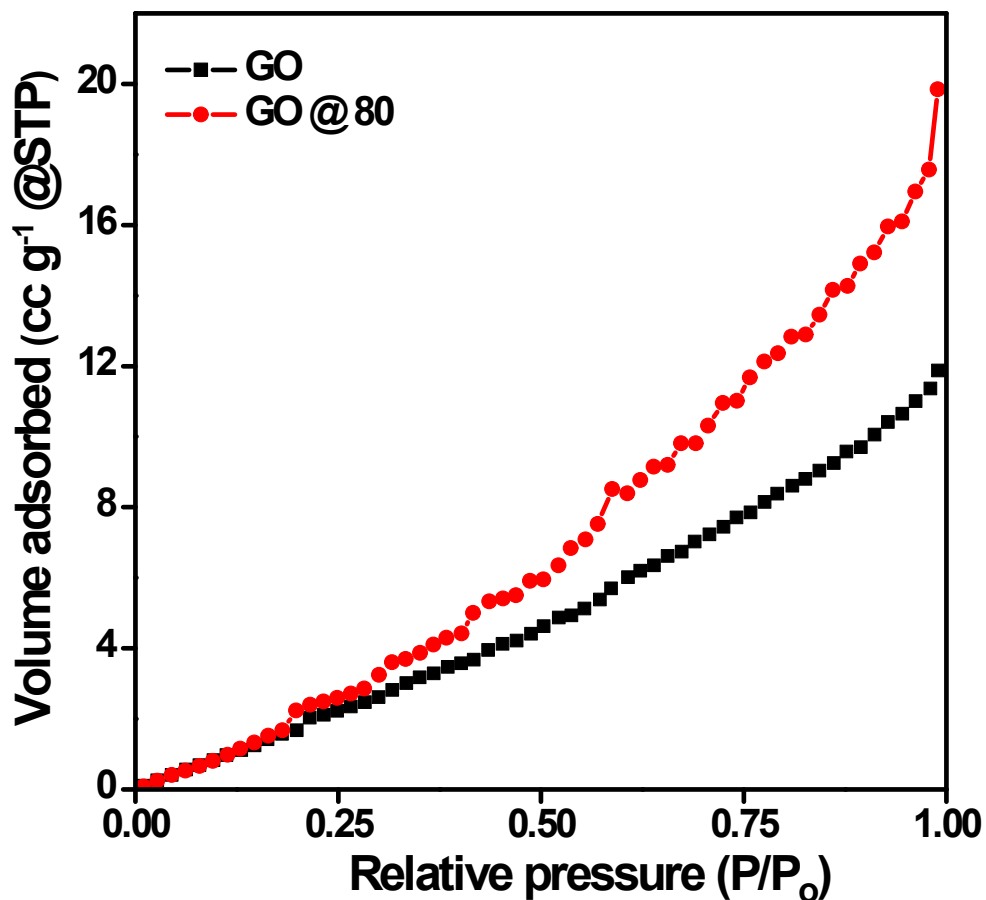


Figure S10: N₂ adsorption isotherms (77 K) of as-prepared GO membrane and GO membrane heated at 80 °C. Continuous increase in N₂ uptake above P/P₀ > 0.3 indicate enhanced pore openings of GO membranes annealed at 80 °C (Pore volume 3.026x10⁻² cc/g) compared to as prepared GO membranes (Pore volume 1.837x10⁻² cc/g). Note: total pore volumes were calculated at relative pressure of 0.98.

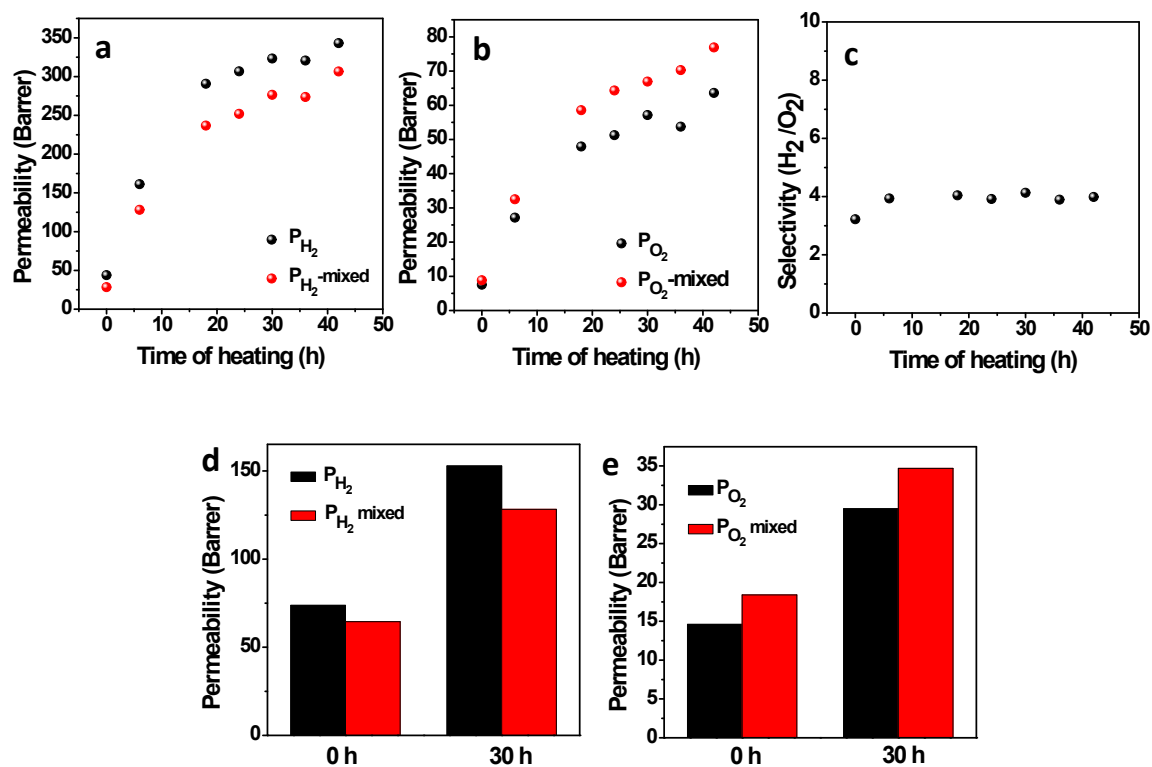


Figure. S11. a)-c) Permeability and selectivity of H₂ and O₂ as individual gases and as 1:1 gas mixture through a GO membrane of 1000 nm thickness. Figure a) and b) shows permeability of H₂ and O₂ respectively as individual gases and 1:1 gas mixture after different intervals of heating at 80 °C. Figure c) shows the variation of separation factor for H₂/O₂ for 1:1 gas mixtures after different intervals of heating at 80 °C. d), e) Permeability of H₂ and O₂ as individual gases and as 1:1 gas mixture through an as prepared 700 nm thick GO membrane and after heating the membrane at 160 °C for 42 h. The permeation through 1000 nm membrane followed the same trend as other less thicker membranes. On the other hand, after heating the membrane at 160 °C there is no significant increase in permeability.

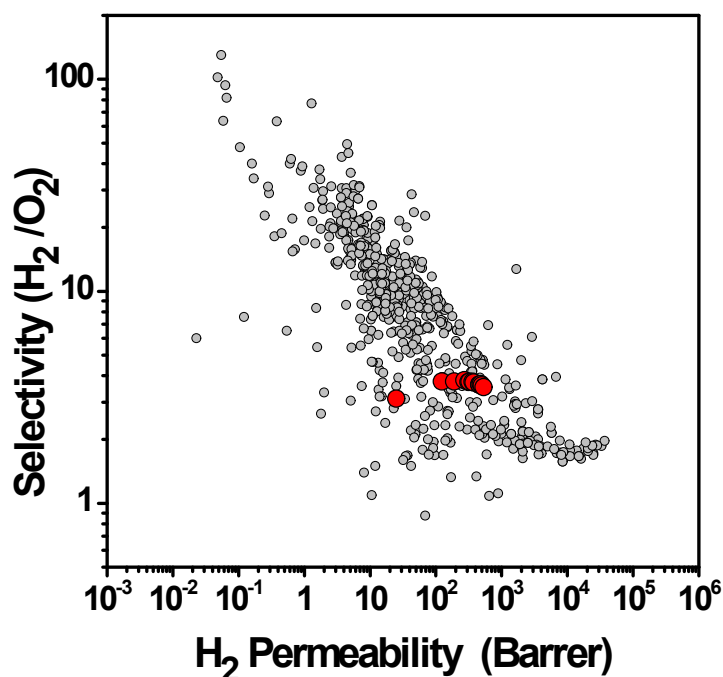


Figure. S12. Comparison of H₂/ O₂ separation with respect to other membranes. The red dots indicate the permeability and selectivity for current report during the course of heating at 80 °C. The grey dots indicate previously reported values for polymeric membranes⁶.

References:

1. W. S. Hummers Jr and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-2678.
2. S. Wiederhorn, R. Fields, S. Low, G.-W. Bahng, A. Wehrstedt, J. Hahn, Y. Tomota, T. Miyata, H. Lin, B. Freeman, S. Aihara, Y. Hagihara and T. Tagawa, in *Springer Handbook of Materials Measurement Methods*, eds. H. Czichos, T. Saito and L. Smith, Springer Berlin Heidelberg, 2006, ch. 7, pp. 283-397.
3. G. Eda, Y.-Y. Lin, C. Mattevi, H. Yamaguchi, H.-A. Chen, I. S. Chen, C.-W. Chen and M. Chhowalla, *Adv. Mater.*, 2010, **22**, 505-509.
4. P. V. Kumar, N. M. Bardhan, S. Tongay, J. Wu, A. M. Belcher and J. C. Grossman, *Nat. Chem.*, 2014, **6**, 151-158.
5. G. Yang, G. Zhang, P. Sheng, F. Sun, W. Xu and D. Zhang, *J. Mater. Chem.*, 2012, **22**, 4391-4395.
6. *Membrane Society of Australasia*, <http://www.membrane-australasia.org/polymer-gas-separation-membranes/>.