Thermal reduction to control the spacing in graphene oxide membranes: Effect on ion diffusion and electrical conduction

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Procedure for the synthesis of graphene oxide

Graphene oxide was synthesized via the modified Hummer's method. Graphite flakes (~ 325 mesh size, Alfa Aesar) were oxidized using a combination of powerful reagents i.e., sulphuric acid (H₂SO₄), potassium per sulphate (K₂S₂O₈), phosphorous pentoxide (P₂O₅). 3g of graphite flakes were dissolved in 10 ml of H₂SO₄. Oxidizing agents K₂S₂O₈ and P₂O₅ were added to the graphite in sulphuric acid and stirred at 90 °C till the flakes were dissolved. The stirring continued for 4 more hours at 80 °C and the solution was then diluted with 500 ml of Milli-Q MilliporeTM water (Ultrapure water > 18MΩ). After the dilution, the solution was stirred overnight, filtered, washed with de-ionised water and then dried to get the powdered form of graphene oxide.

Pre-oxidized GO powder was then subjected to further oxidation with 125 mL of H₂SO₄ and 15g of Potassium permanganate (KMnO₄) in an ice bath where the solution was stirred for 2 more hours. 130 mL of Milli-Q MilliporeTM water was added to the mixture and this caused the temperature to rise to 95 °C. After 15 minutes, 15 mL of Hydrogen Peroxide (H₂O₂) was added to reduce the manganese in the solution to manganese sulphate (Mn \rightarrow MnSO₄). Finally, the solution was diluted with 400 mL of Milli-Q MilliporeTM water and resultant yellow suspension was stirred overnight. GO was filtered and washed till the rinsed water pH was found to be approximately 7, the brown dispersion was placed in a dialysis membrane to get rid of metal ions and acids.[1, 2] If not specifically mentioned the chemicals were purchased from Sigma-Aldrich Canada and used as received.

All the films were been synthesized via vacuum filtration of the GO suspension (0.5 mg/ml) through anodisc membrane filter (25 mm in diameter, 0.02 μ m pore size), Whatman. The film thickness can be controlled by either the concentration of the GO in the suspension or by the filtration volume.

Apparatus

Field Emission Scanning electron microscopy (FESEM) was done with a LEO 1530 Gemini field emission gun attached with EDX/OIM.

Optical spectroscopy was carried out using USB4000 (ocean optics) spectrometer.

Electrical characterization was done using a custom-built IV setup consisting of Agilent 6614C DC power supply and Hewlett Packard 3458Amultimeter.

Raman spectra were obtained on a J-Y T64000 Raman spectrometer with 514.5 nm wavelength incident laser light.

Glancing angle (0.6°) X-Ray diffraction was done a PANalytical machine using CuK α line as the X-ray source.

TGA was performed in a Q-500 TA instruments. The heating rate was 10° C/min and the experiment was conducted with air as the atmosphere.

FTIR was done in an Bruker Tensor 27 spectrometer.

XPS was done on a Thermo-VG scientific ESCALab 250 microprobe with a monochromatic Al K α source (1.4866 KeV).

Electrochemical experiments were performed in a three electrode set-up with Ag/AgCl as the reference electrode, a Pt wire as the counter electrode and the TrGO film (or the ITO) as the

working electrode. The area of the working electrode was $\sim 1 \text{ cm}^2$. The measurements were performed using an Ivium technologies CompactStat potentiostat. Tensile testing was done on a Rheometric Scientific DMTA V, at strain rates of 5×10^{-5} /sec.

Reduction of the GO films: The GO films made by vacuum filtration are exposed in an oven to the appropriate temperature for thermal reduction. The temperature is increased gradually till the final exposure temperature is reached and the film is exposed for 30 min.

IV testing

Both vertical and horizontal tests on the TrGO membranes were performed by making silver contacts with the film. Identical silver strips were made on the membranes using conductive silver paste (Electron Microscopy Sciences). Following this copper leads were connected from the silver electrode to the power supply and the multi-meter. In case of horizontal testing the spacing between the silver strips was maintained at 5 mm. The width of the strips was 1mm. To ensure proper width a small opening in a filter paper was made through which the silver paste was applied onto the membranes. For vertical testing, the current between two identical strips on the opposite faces of the membrane was measured. The size of the strip was 5mmx1mm. The results were repeated on 3-5 films.







Figure S1: Raman and FTIR spectrum showing
0.060 the changes in the TrGO membranes on thermal reduction. (a) The Raman spectrum shows that
0.045 the increase in the ratio of the D to G band on thermal reduction. (b) The Raman spectrum of
0.030 graphite for comparison. (c) The FTIR spectrum shows the that the peaks associated with O-H at 3400 cm⁻¹ and C-O at 1060 cm⁻¹ decrease on thermal reduction.

The Raman analysis of the GO and Tr-GO membranes is presented in Fig. S1a. Similar to reduction of GO with chemicals such as hydrazine and ascorbic acid, an increase in I_D/I_G (the relative intensity of the D band at ~1350 cm⁻¹ and G band at 1590 cm⁻¹) is observed. The ratio of these two peaks is inversely proportional to the size of the ordered regions in the reduced graphene oxide. On reduction it is stipulated that new ordered region are formed in GO and these are smaller in length scale leading to an increase in the I_D/I_G ratio.^[3-5] The ratio increases from 0.85 at 60 °C to ~ 0.95 at 225 °C.

The FT-IR data presented in Fig. S1c shows the effect of the thermal reduction on the functional groups present in graphene oxide. The prominent absorption peaks observed are namely: O-H at 3400 cm⁻¹ (a very broad peak), C=O at 1726 cm⁻¹, C-O at 1250 cm⁻¹ & 1060 cm⁻¹ (epoxy and alkoxy), C=C at 1600 cm⁻¹ (due to sp2 hybridized carbon), the peaks in the 2300-2400 cm⁻¹ are from C=C or C=N. Being in the fingerprint region the peak at 1370 cm⁻¹ is hard to specify to a functional group but can arise due to -CH₃ or N=O. On thermal reduction at 60 °C no other major change in the spectrum is observed, as the expected due to insufficient thermal activation for the removal of the functional groups. Starting with reduction temperatures of 180 °C, 200 °C, 225 °C and 250 °C, we start observing that the peaks at 3400 cm⁻¹, 2300-2400 cm⁻¹, 1370 cm⁻¹ and 1060 cm⁻¹ start to decrease in intensity. The intensity of the decrease varies with functional groups. For the O-H at 3400 cm⁻¹ and C-O at 1370 cm⁻¹ a gradual decrease is observed till 200 °C and these peaks completely disappears at 225 °C, and 250 °C. While the absorbance band at 2300-2400 cm⁻¹ and 1060 cm⁻¹ disappears at 200 °C and higher temperatures.^[6-7] This leads to the conclusion that the primary reduction of the GO membranes occurs between the temperatures of 180 °C to 225 °C.

XPS analysis

The XPS spectrum for the C1s region for the GO films was conducted to analyze the change in the ratios of the C-C (non-oxygenated ring C, ~ 284.6 eV) to that of the C-O (at 286 eV) and carboxylate C (O-C=O, 289 eV). We observe that the ratio is ~ 1.09 for 60 °C films, this increase very slightly to 1.122 for films processed at 180 °C and increase to 3.85 when the films are processed at 250 °C. These observations are consistent with the FTIR, XRD and TGA results.



Figure S2: The C1s XPS spectra for GO films thermally processed at different temperatures. (a) Films processed at 60°C. (b) at 180°C and (c) at 250°C.

Diffusion Testing

Diffusion characteristics of the TrGO membranes were tested in a home build set-up. It consisted of two reservoirs that were separated by placing the TrGO membrane in between. One of the reservoirs was filled with Millipore water (Ultrapure water > 18M Ω) and the other with appropriate salt solution. The conductivity of the MilliQ water was tested periodically to measure the increase in its salt concentration due to diffusion across the TrGO membrane.

Diffusion model

The diffusion across the membrane separating two stationary reservoirs of fluids can be modelled as follows:



Figure S3: The schematic showing the model used for diffusion across the GO membranes.

The diffusional problem can be solved in 1-D using Fick's second law:^[8]

$$\frac{\partial C}{\partial t} = P \frac{\partial^2 C}{\partial x^2}$$

Where P is the effective diffusional resistance that includes the characteristics of the TrGO membrane and the ion characteristics.

The solution is:

$$C = \frac{1}{2}C_o erfc\left(\frac{x}{2\sqrt{Pt}}\right)$$

Where C_o is the initial concentration of the salt solution.

The model assumes both the reservoirs to be of identical volume. Hence the final concentration is $C_0/2$.

The net concentration of the Milli Q water as a function of time can be calculated as the net amount of salt transferred, S_t , as a function of time.

$$S_t = \int_0^t J_o.A.dt$$

Here J_o is the instantaneous diffusional flux across the membrane and A is the cross-sectional area of the membrane. J_o is given by:

$$J_o = \left. -P \frac{\partial C}{\partial x} \right|_{x=0}$$

Solving this it is established that the net amount of salt transferred St is:

$$S_t \propto t^{1/2}$$

Where the proportionality constant will be dependent on the exact experimental conditions and the resistance of the membrane. For identical experimental set-up if only the membrane is changed then the changes in the proportionality constant should reflect the changes in the characteristics of the membrane.

Typical fits for diffusion of 100mM NaCl across a TrGO membrane processed at 60°C (Fig S4a) and at 180°C (Fig. S3-b), show that the basic evolution of the diffusion is captured by this equation.



Figure S4: The fit of experimental diffusion data to the model presented in Fig. S2. The line is the fit from the model and the data points are measured experimental values for 100 mM NaCl. (a) For TrGO membrane processed at 60° C (b) For TrGO membrane processed at 100° C.

Similarly the fits for diffusion of 100 mM CaCl₂ across the TrGO membrane processed at 60°C and 200°C (Fig. S5-a&b).



Figure S5: The fit of experimental diffusion data to the model presented in Fig. S2. The line is the fit from the model and the data points are measured experimental values for 100 mM CaCl_2 . (a) For TrGO membrane processed at 60° C (b) For TrGO membrane processed at 100° C.

From these fits the proportionality constant can be calculated and a comparison among different Tr-GO membranes can be analyzed. Effectively we are able to observe that with increasing thermal reduction temperatures the diffusional resistance of the TrGO films increases significantly.

The results of diffusion for 100 mM CsCl are reported below, Figure S6; the diffusional resistance behaves very similar to that for NaCl. We observe a rapid rise in resistance above 180°C. The slight differences in the behavior may be the result of the higher mobility of Cs+ ion and its slightly smaller hydrated radii.^[9, 10]



Figure S6: The evolution of the diffusional resistance of the TrGO membranes with temperature for salt solution of CsCl. (a) For diffusion from an 100mM CsCl solution, the diffusion rate decreases significantly on thermal reduction and the effect of temperature can be clearly observed. (b) Modelling the diffusion as being proportional to $t^{1/2}$ the diffusional resistance of the film is calculated and plotted. The resistance increases by over 2 orders of magnitude on reduction above the temperatures of 180°C.

Cyclic Voltammetry Analysis

CV's were performed on the Tr-GO films in a solution of 5mM K₃Fe(CN)₆ with 50 mM KCl as the supporting electrolyte. Different scan rates were analyzed for each sample. As seen in Figure S7 & S8, the Tr-GO films processed at 60 °C & 180 °C show significantly lower currents than films reduced at 250 °C. Further in both the films we do not observe both the oxidation and reduction peaks corresponding to K₃Fe(CN)₆ as were clearly observed with films reduced at 250 °C and on plain ITO. Further at high scan rate (50 mV/sec) the observed linear response in the scan's is the result of the high resistance of the films.



Figure S7: The CV plot of the Tr-GO film reduced at 60 °C. We do not observe a clear oxidation and reduction peaks corresponding to $K_3Fe(CN)_6$. Further the current are reduced at more than an order of magnitude in comparison to the films reduced at 250 °C.



Figure S8: The CV plot of the Tr-GO film reduced at 180 °C. We do not observe a clear oxidation and reduction peaks corresponding to $K_3Fe(CN)_6$. Further the current are significantly reduced in comparison to the films reduced at 250 °C.

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