Electronic Supplementary Material (ESI) for Nanoscale

Supporting Information.

The structure of graphene oxide membranes in liquid water, ethanol and water–ethanol mixtures.

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1. Additional characterization of membranes.

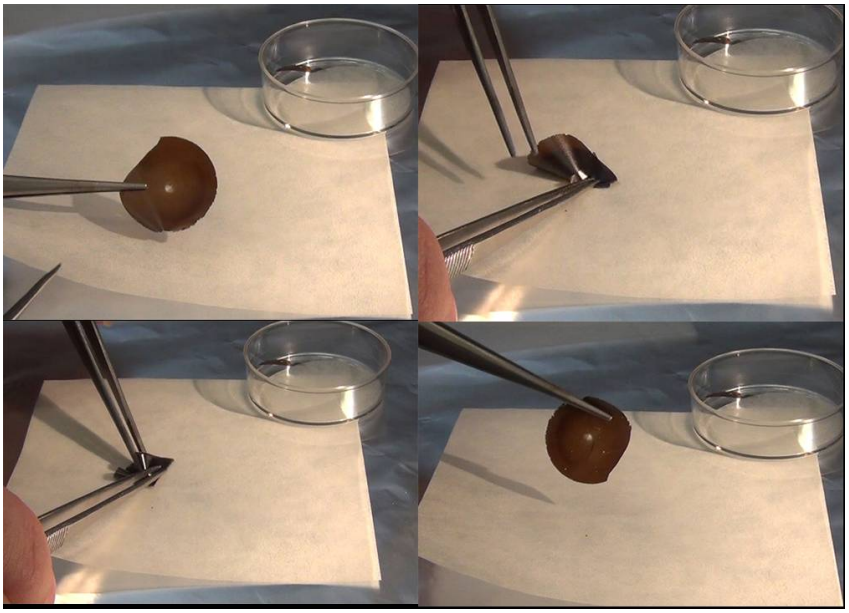


Figure 1S Folding of B-GO membrane does not result in breaking. H-GO membranes can be bend to certain extent but break on pieces when folded. See also video which shows B-GO and H-GO membranes folding difference.

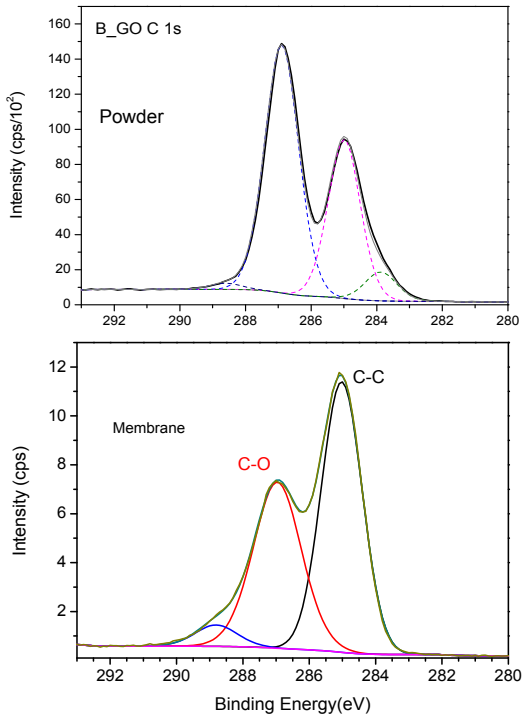


Figure 2S. XPS spectra of B-GO powder and B-GO membrane after washing with 50:50 water/ethanol mixture. Small impurity of Na (0.6 at%) was detected in as deposited dried B-GO membranes but washing with 1:1 water/ethanol removed this impurity below detectable limits. Addition of ethanol is required to prevent the membrane from delamination. The washing procedure removed trace contamination with Na. The relative intensity of peak changed and C/O ratio increased as a result of sonication in NaOH solution and removal of Na by washing.

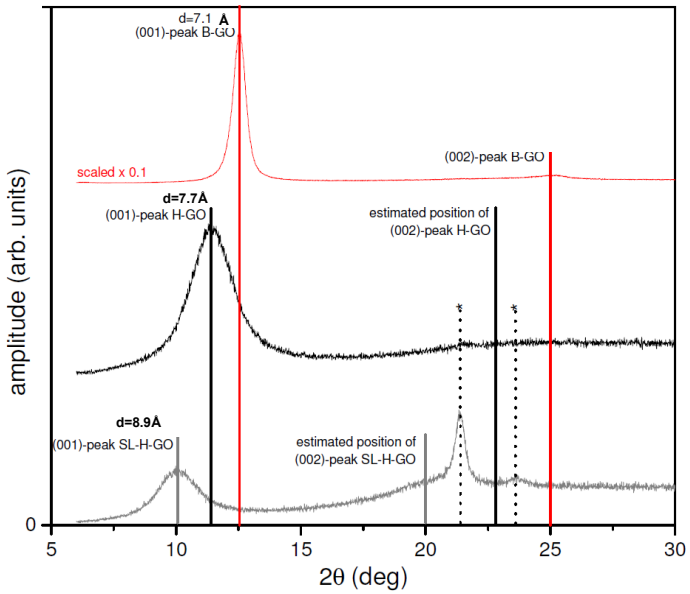


Figure 3S XRD patterns recorded using conventional diffractometer in reflection mode from B-GO and H-GO membranes. XRD from membrane prepared using "single layered" graphene oxide powder (purchased from ACS Materials) is marked as SL-H-GO. The dispersion prepared using the SL-H-GO powder was not stable and aggregated slowly. Using it as precursor for the membrane deposition resulted mostly in inhomogeneous products. Therefore, no further studies of these membranes were performed. Peaks marked by dashed lines and stars are from foil used to attach the membrane for XRD measurements. Note that B-GO membrane shows both (001) and (002) reflections whereas H-GO only (001) reflection. Better crystallinity of B-GO membrane is evidenced also by less broad peaks and higher intensity of all reflections. The patterns were recorded 2-3 days after the membrane deposition. The same H-GO membrane after 5 weeks of on air storage showed d(001) =7.3 nm due to slow de-hydration.

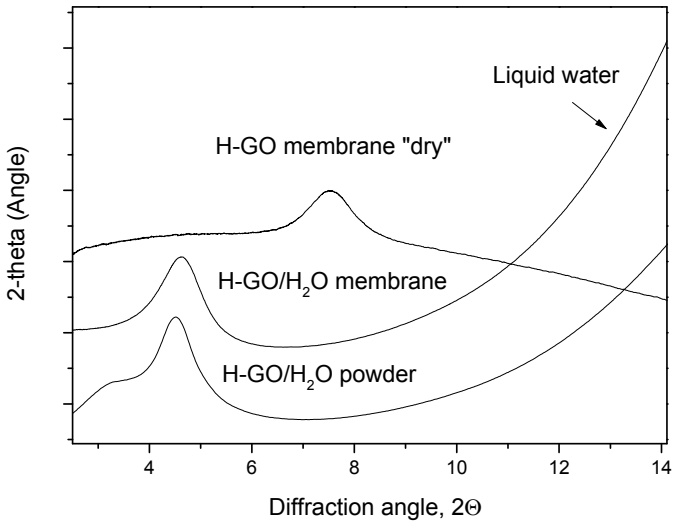
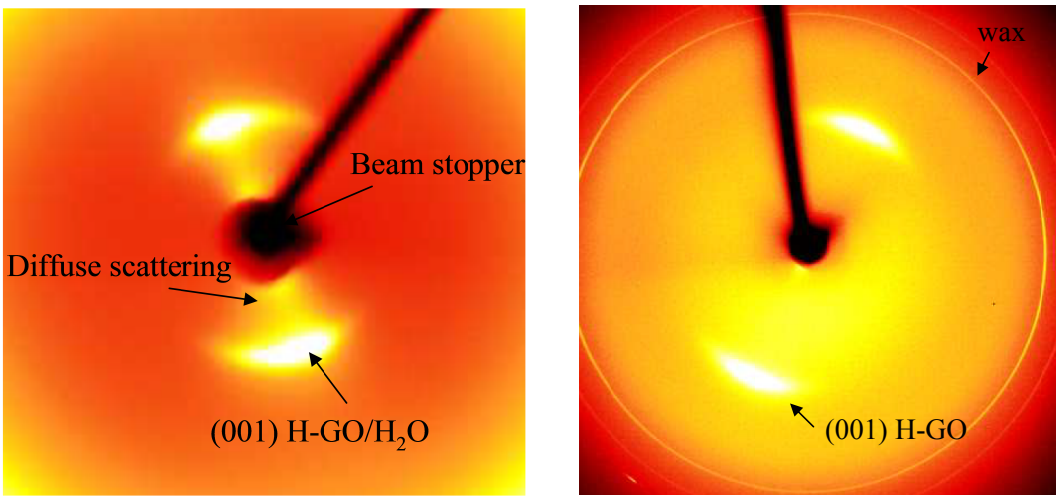
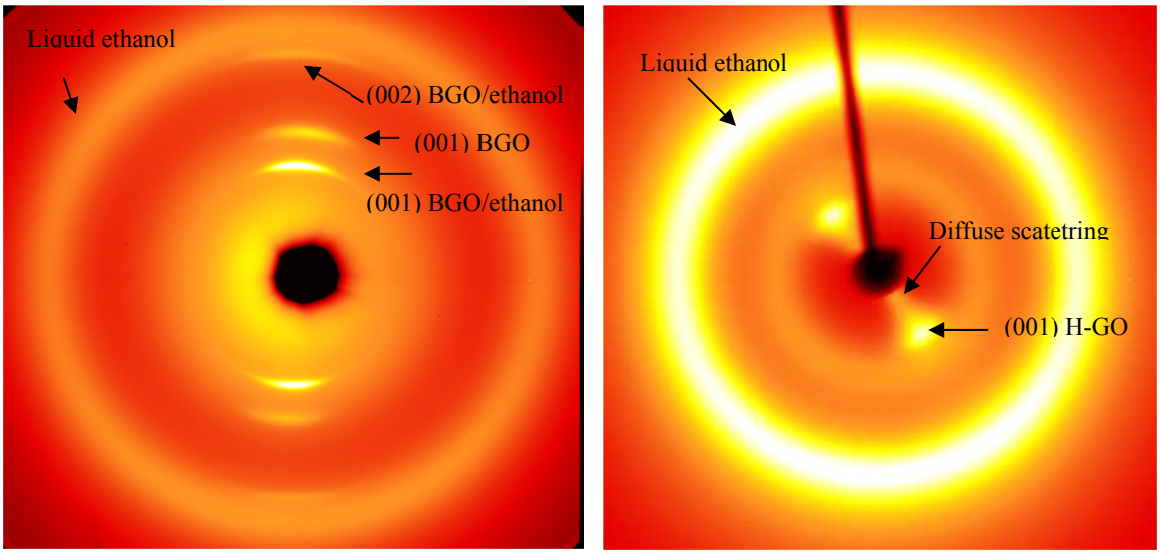


Figure 4S. Integrated XRD patterns of H-GO membrane in "dry" state (air exposed), H-GO membrane water immersed and reference sample of water immersed precursor H-GO powder. The background which starts above ~8 degrees is part of broad reflection from liquid water. Patterns recorded at 290K, radiation wavelength 0.99258Å.



a) b)

Figure 5S. a) Fragment of XRD image recorded from H-GO membrane immersed in water (inside of glass capillar) at 290K. Two bright spots correspond to (001) reflection (d=12.26Å) while the bright diffuse scattering region connects these two spots and extends to d-spacing above 40Å.
b) Fragment of XRD image recorded from solvent free "dry" H-GO, d(001)=7.17Å. Diffraction rings marked by arrow are from wax used to attached the tiny piece of membrane. Dry membrane sample shows no strong diffuse scattering similar to the water immersed sample.



a) b)

Figure 6s XRD images recorded for ethanol immersed samples of : a) B-GO membrane, no strong diffuse scattering is visible, only part of membrane is in solvated state, d(001)= d=9.05Å and d(002)= 4.52Å for solvated phase, d(001)=6.95Å for not solvated B-GO phase ; b) H-GO membrane, diffuse scattering similar to H-GO/water sample (**Figure 5sa**) is also observed.

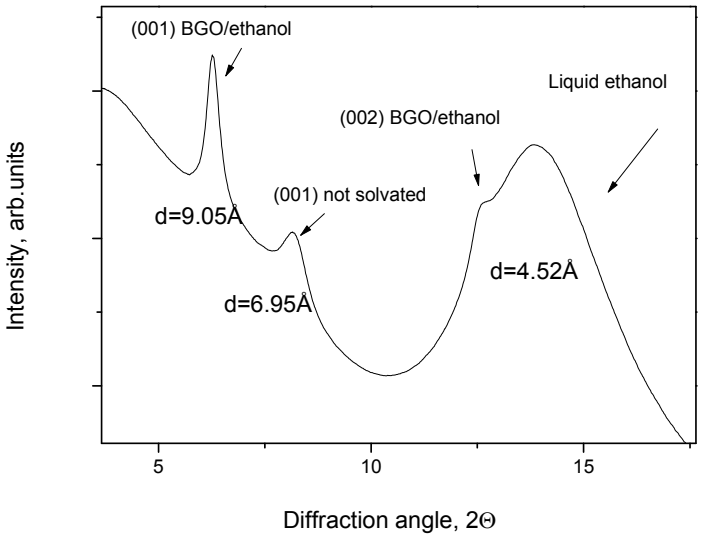


Figure 7s. Integrated patterns for XRD image of B-GO membrane immersed in liquid ethanol. Both solvated and not solvated phases identified in this sample, no change of relative intensity was observed for reflections form these phases with time. The data are interpreted as partial solvation of outer shell of the membrane while ethanol could not penetrate into inner core part of the membrane.

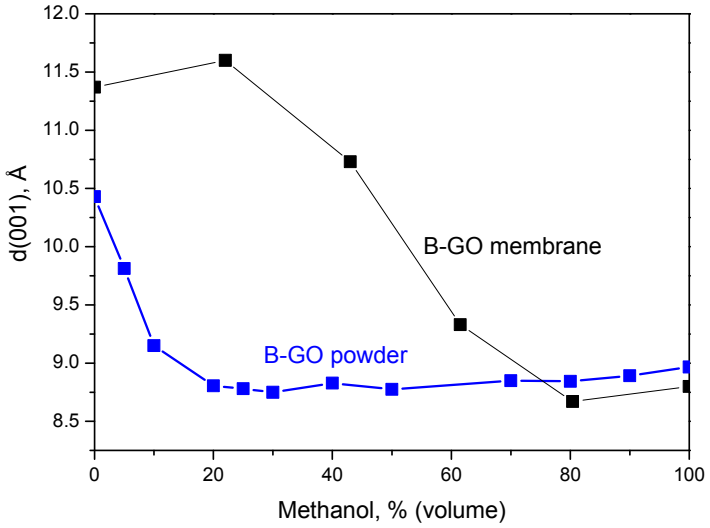


Figure 8S. Interlayer distance, d(001), measured at 300K for GO in liquid water/methanol binary solvents: B-GO membrane ■ and B-GO powder ■.

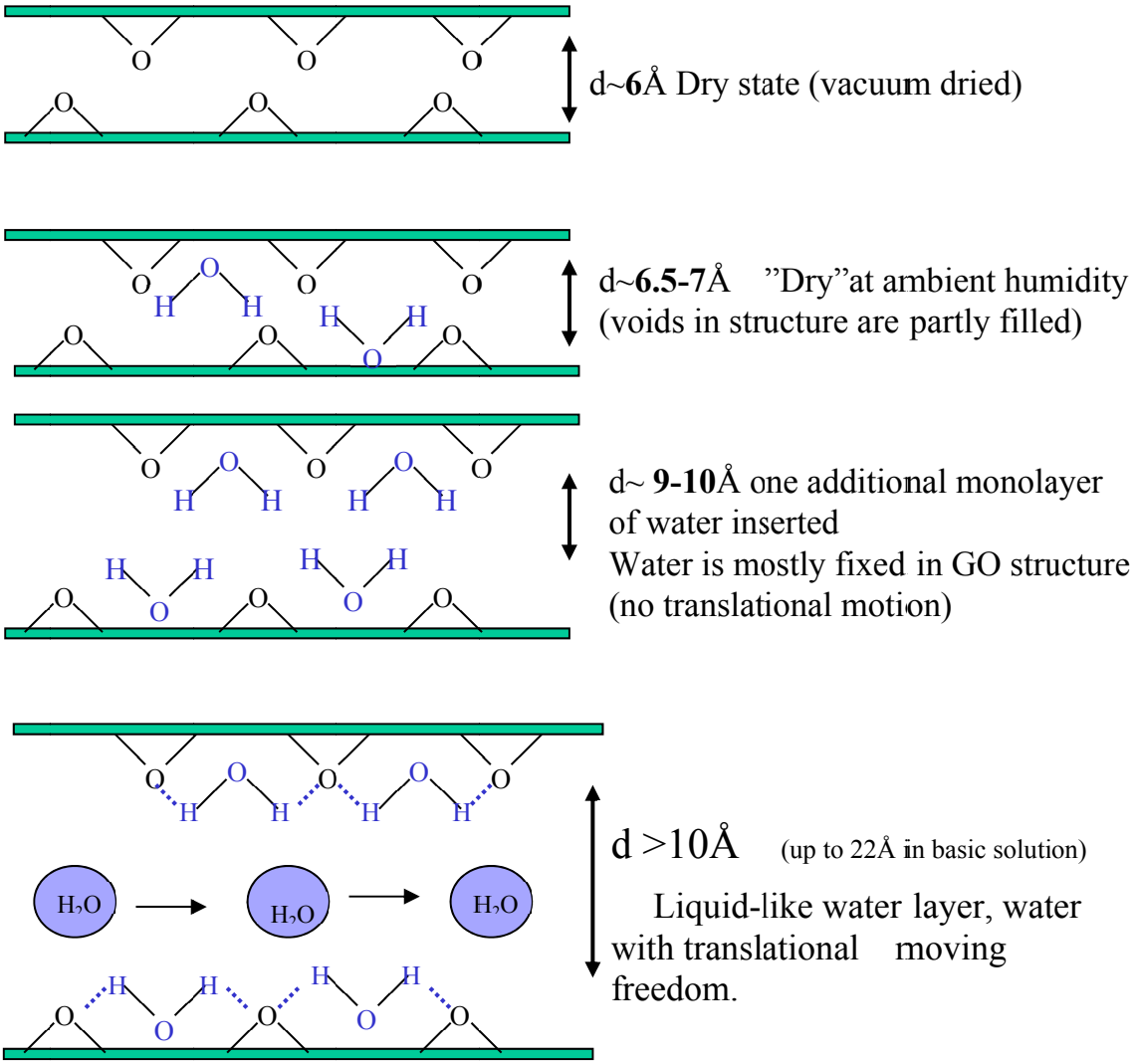


Figure 9s. Diagram which represents summary of structural data for hydration of graphite oxide structure in powder [1] and graphene oxide membranes. Different stages of hydration are drawn schematically with suggestion how liquid-like layer of water could be inserted into the GO structure: hydrophilic graphene oxide planes are covered by more strongly attached water molecules on each side of interlayer and next water layer is inserted in liquid-like state. Note that in basic solutions we observed lattice expansions (under GPa pressures) up to 22Å [1] which corresponds to multilayer water insertion or "osmotic swelling".

[1]. A. V. Talyzin, S. M. Luzan, T. Szabo, D. Chernyshev and V. Dmitriev, *Carbon*, 2011, **49**, 1894-1899.

[2].A. V. Talyzin, B. Sundqvist, T. Szabo and V. Dmitriev, *J Phys Chem Lett*, 2011, **2**, 309-313.