Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information file

Swelling of graphene oxide membranes in alcohols: effects of molecule size and air ageing.

Artem Iakunkov,[a] *Jinhua Sun,*[a] *Anastasia Rebrikova,*[b] *Mikhail Korobov,*[b] *Alexey Klechikov,*[a,c]
Alexei Vorobiev,[c] *Nicolas Boulanger,*[a] *Alexandr Talyzin*[a]*

[a] Department of Physics, Umeå University, Umeå, SE-901 87, Sweden.

[b] Department of Chemistry, Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russia

[c] Department of Physics and Astronomy, Uppsala University, Uppsala, 751 20, Sweden.

1. Characterization of precursor graphite oxide powder samples.

Powder graphite oxide samples were synthesized using modified Hummers methods, details of the procedure are described elsewhere.[1] Table 1 shows data characterizing elemental composition of precursor graphite oxide powders revealed by XPS: amount of sulphur impurity and C/O ratio. The oxygen from sulphate groups was subtracted in the calculation of C/O ratio (Table S1). All materials were characterized by XRD at ambient air conditions, see Table S1 for d(001) values.

Table S1 Characterization of graphite oxides (from left to right): name of samples, origin of samples, precursor graphite, sulphuur impurity, C/O ratio found using analysis of C1s and O1s XPS spectra, interlayer distance d(001) value found using XRD recorded at ambient air conditions.

Name	Source	Precursor graphite	Sulphur (at%)	C/O	d(001) in ”dry state”
HGO1	ACS Material	Unspecified	0,9	2,47	7,20Å
HGO2	In house synthesis	“Graphexel”, 150-500µm flake	0,4	2,46	7,42Å
HGO3	In house synthesis	“Graphexel”, 0-200µm flake	-	-	7,63Å
HGO4	In house synthesis	“Alfa Aesar”, natural, ~325 mesh, 99.8%	2,1	2,30	7,7Å

FTIR spectra of powder graphite oxide samples were recorded using diffuse reflectance mode at vacuum conditions (Figure S1). The GO powder was mixed with powder of KBr in proportion ~1:10. Except for some change in relative intensity, spectra of all HGO powder samples are similar to each other.

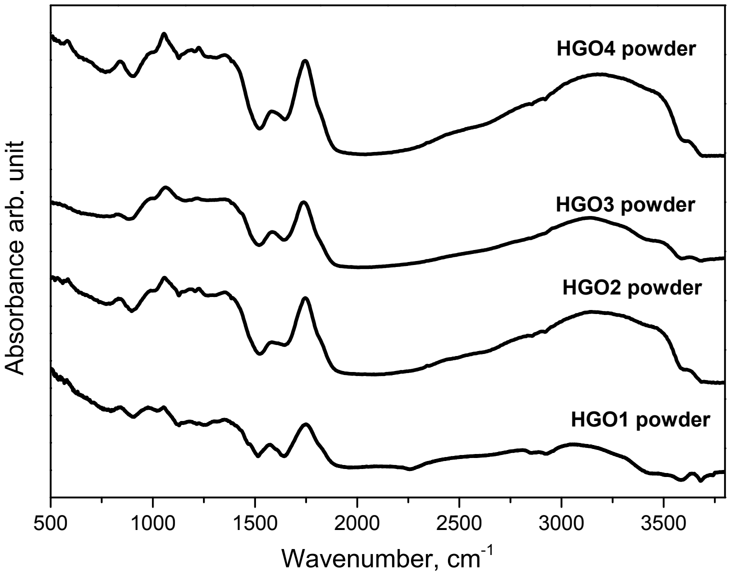


Figure S1 FTIR spectra of HGO1, HGO2, HGO3 and HGO4 recorded in diffuse reflectance mode.

FTIR spectra of precursor GO powder samples and HGO membranes are similar except for change in relative intensity of some peaks. The most pronounced difference is change in relative intensity of C-C (1575-1594 cm^{-1}) and C=O bands (1693-1719 cm^{-1}). Some change in chemical composition of HGO membranes relative to the precursor powders could be expected due to sonication treatment and centrifugation of dispersions.

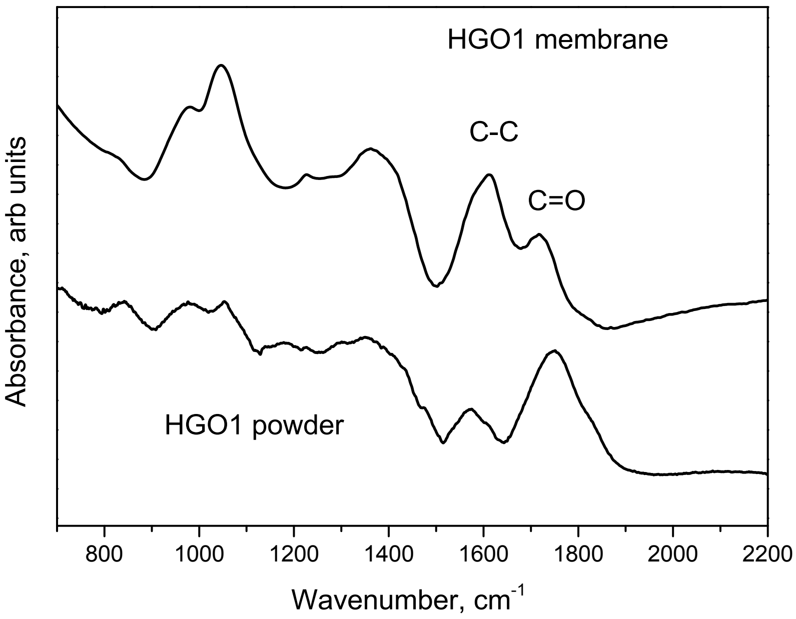


Figure S2. FTIR spectra of HGO1 powder and HGO1 membrane.

2. Experimental details.

Powder samples of commercial ACS Material graphite oxide and several batches of graphite oxides synthesized in our laboratory using slightly modified Hummers method were used to prepare membranes by vacuum filtration of aqueous dispersions. Dispersions were prepared using sonication treatment of HGO powders in water for 24h followed by centrifugation at 4400 rpm. In following, the membrane samples will be named according to the precursor graphite oxides (see **Table S1**). The HGO1 membranes were prepared using ACS Material precursor, these material and membranes were characterized in details in our earlier studies.[2],[3] Some of the membrane samples prepared using this precursor were re-characterized again after 2.5-year and 5-years air storage. In particular, the same piece of membrane which was studied by XPS back in 2012 was re-evaluated in 2018. ACS Material graphite oxide was also used to prepare dispersions spin coated on Si blocks and studied using NR for ethanol and water sorption.[4] Some of the powder from the batch of ACS Material purchased in 2013 was re-evaluated in 2018 for ageing affects as a reference to compare with the HGO1 membrane samples.

Precursor graphite oxide powder was also synthesized in house using Hummer method [5] starting from commercial Graphexel graphite with 150-500µm flake size (**HGO2** membranes) and 0-200µm flake size (**HGO3** membranes). The **HGO4** membranes were prepared using most recently synthesized batch of graphite oxide synthesized using graphite powder purchased from Alfa Aesar (~325 mesh, 99.8% purity). Details of synthesis procedure are available elsewhere.[1] The HGO2 membranes were prepared for our past experiments and some of the samples were stored on air for 1.5-years providing opportunity to study ageing effects. Fresh HGO3 membranes were studied within one week after preparation. Details of membrane preparation procedure were the same as in our previously published studies. [2b]

The air aged sample of HGO1 thin film on Si was characterized several times over past 5 years for sorption of d6-ethanol from vapor. Initial X-ray reflectivity measurements at ambient conditions were performed at the ID10 beamline of the European Synchrotron Radiation Facility (ESRF) , Grenoble, France, using photons with λ=0.654Å. Neutron reflectivity experiments were performed in a specially designed humidity cell at the reflectometer SuperADAM at the Institute Laue-Langevin (ILL), Grenoble, France using a monochromatic beam with wavelength λ=5.19Å.

The humidity cell was loaded with several ml of d6-ethanol which evaporates under the sealed aluminum jar until saturation achieved. The saturation vapor pressure was achieved inside of the cell after several hours.[6] The GO film was exposed to d6-ethanol ≥99.5% (Sigma Aldrich) and air dried between exposures to solvent vapors. Details of the NR experiments and data analysis are available elsewhere.[6] Typically, the NR scans were repeated until no further changes in the shape of NR curves observed, typically 4-6 hours. More details about NR experiments are provided in SI file.

XRD characterization of graphite oxides and HGO membranes was performed using in-house diffractometer PANalytical X'pert diffractometer with CuKα radiation in reflection mode. For experiments with swelling, the membrane was immersed into drop of solvent and covered with plastic foil to prevent evaporation. The plastic foil also helps to flatten the membrane to the sample holder surface. Several scans were typically recorded to verify for possibly kinetic effects until the saturated swelling state achieved. Some of the XRD tests were also performed for samples immersed in liquid alcohols for 2 days to study very slow kinetic effects

Part of XRD experiments was done using synchrotron radiation in beamline ID 11 ESRF , Grenoble, France with λ = 0.30996Å. The XRD 2D images were recorded from small strips of HGO membranes (~0.5-0.7 mm wide and 1-3 mm long) cut from larger sample and loaded into

0.7 mm glass capillary. Solvent in excess amount was added to the capillaries which were sealed using torch to prevent evaporation. The membrane strip was then aligned relative to X-ray beam to find (001) diffraction spots. Several scans were typically recorded for solvent immersed samples and the procedure was repeated several times over the period of 23-24 hours. The samples were removed and re-aligned between these tests which mean that the time-dependent set of images was not recorded at exactly the same spot.

Chemical composition of membrane was tested by XPS and Fourier-transform infrared (FTIR) spectroscopy. XPS spectra were recorded with a Kratos Axis Ultra electron spectrometer equipped with a delay line detector. A monochromated Al Kα source operated at 150 W, a hybrid lens system with a magnetic lens, providing an analysis area of 0.3 × 0.7 mm, and a charge neutralizer were used for the measurements. The binding energy scale was adjusted with respect to the C 1s line of aliphatic carbon, set at 285.0 eV. All spectra were processed with the Kratos software.[7]

FTIR spectra were recorded by Bruker Vertex 80v FT-IR spectrometer with DTGS detector at vacuum in Attenuated total reflection (ATR) mode and Bruker IFS 66 v/S FT-IR spectrometer with DTGS and MCT detectors *at vacuum* in diffuse reflectance mode. The spectra range of 500-4000 cm^{-1} and 128 scans were typically used to collect the each spectrum.

3. Neutron Reflectivity experiments.

3.1 Scheme of the Neutron Reflectivity (NR) experiment.

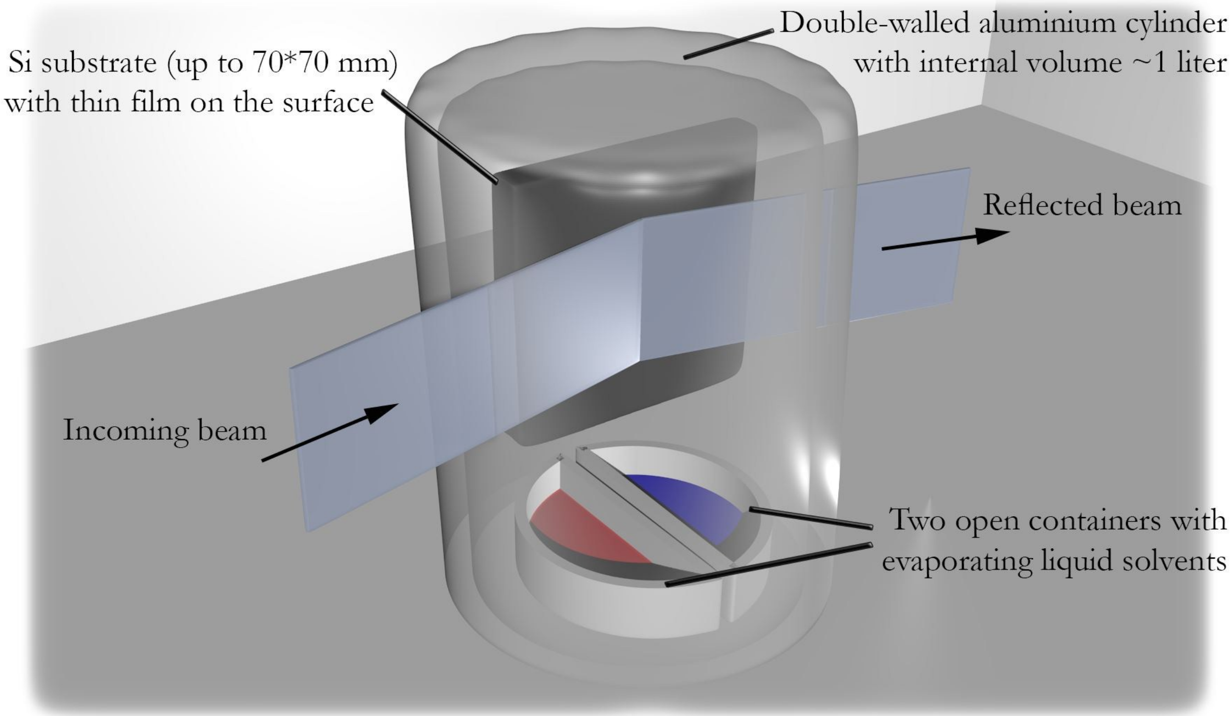


Figure S3: Scheme of the NR experiment.

Standard scheme of NR experiment includes following steps:

1) NR data are recorded first at ambient air conditions to characterize “ambient state.” The ambient state is also characterized using synchrotron XRD in order to evaluate inter-layer distance provided by d(001). The number of layers is calculated using thickness of film evaluated using NR data and inter-layer distance provided by XRD.

2) The film is exposed to solvent vapors in a sealed cell (Figure S2) and the NR patterns are recorded continuously for 6-8 hours (~1-1.5 hours per pattern) following increase of vapor pressure inside of the cell. The patterns are recorded until saturation state is achieved. The NR pattern recorded at saturated vapor conditions is used for modelling, change of film thickness due to swelling and composition of solvent-saturated film are calculated.

3) The film is exposed to ambient air conditions in order to desorb d6-Ethanol and to verify reproducibility of sorption. Typically the ambient state of GO film was recovered within 2-4 hours.

3.2 Modelling Neutron Reflectivity data to extract information about thickness and chemical composition of GO films.

3.2.1 Introduction of parameters, constants and simple relations used for modelling of NR data

ρ – scattering length density (SLD) obtained directly from the fit of the neutron reflectivity curve;

L – thickness of the GO film obtained directly from the fit of the neutron reflectivity curve;

d – spacing between GO monolayers in the direction perpendicular to the film surface;

N – number of GO monolayers in the sample film;

$S_h = 5.246$ Å^2 – area of the carbon hexagon, which assumed to be constant.

b – neutron scattering length (NSL) specific for every isotope (see Table S1);

$B = \sum b_i$ – total NSL of molecules or crystal unit cells consisting of several atoms with corresponding individual b_i (see Table S1);

V – volume of the GO unit cell.

$$\rho = B / V \tag{1}$$

$$d = L / N \tag{2}$$

$$V = d \cdot S_h = L \cdot S_h / N \tag{3}$$

Table S2. Values of neutron scattering length B for relevant chemical elements and molecules.

Compound	**Formula**	**B(10^{-4}Å)**
Carbon	C	0,6648
Oxygen	O	0,5805
Hydrogen	H	-0,3740
Deuterium	D	0,6674
Water	H_20	-0,1675
d6-Ethanol	C_2D_5OD	5.9145

3.2.2 Calculation of ambient state composition of GO film.

Calculation of ambient state for experiment performed in 2018 is detailed below.

Experimental values found for the ambient state:

$L_0 = 228$ Å

$\rho_0 = 3.288 \cdot 10^{-6}$ Å^2

$d_0 = 8.927$ Å

According to (2) number of layers $N = 25.54$

According to (1) experimentally obtained NSL value of the GO unit cell is $B_0 = 1.540 \cdot 10^{-4}$ Å

Assuming GO formula unit as $C_2O_{0.8}H_{0.24}$ it can be found $B = 1.704 \cdot 10^{-4}$ Å which is too high comparing to the experimental B_0. To eliminate this contradiction one has to add in to formula unit of the ground state some elements decreasing B by $\Delta B = 0.164 \cdot 10^{-4}$ Å. The decrease is due to light water absorbed by GO film in quantity 0.164 / 0.1675 = 0.98 molecules per GO unit cell.

Thus our ground state can be written as

$C_2O_{0.8}H_{0.24} + (H_2O)_{0.98}$

This formula is used as an “ambient state” of GO film and reference for calculation of solvent sorption.

3.2.3 Qualitative interpretation of the ρ and L variation in terms of number of intercalated d-Ethanol molecules during vapor exposure.

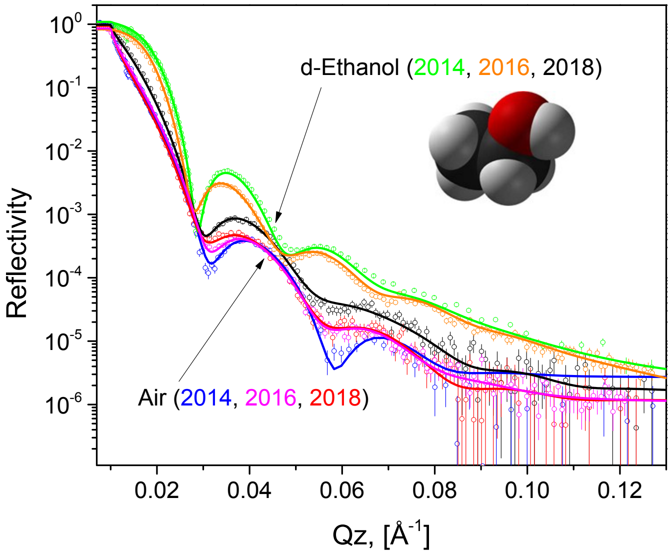


Figure S4: Neutron reflectivity curves recorded from HGO1 film in air and under saturated vapor of d6-ethanol in 2014, 2016 and 2018

Experimental data show that both parameters ρ and L change during the vapor exposure. Intercalation of solvent molecules change *B* and *V* of the GO unit cell.

One can write for the ambient state

$$\rho_0 = B_0 / V_0 \qquad (4)$$

If some molecules with unknown total NSL B_x are intercalated than GO unit cell transforms to a new state with volume V_1 and SLD ρ_1 related as

$$\rho_1 = (B_0 + B_x)/ V_1 \qquad (5)$$

It is easy to see that using Eq-s. (3-5) the unknown additive B_x can be found from four experimentally obtained parameters L_0, L_1, ρ_0 and ρ_1 as

$$Bx = \left(\frac{V1\rho1}{V0\rho0} - 1\right)b0 \qquad (6)$$

Using the value B_x and individual NSL *B* presented in Table S1 one can find exact number *n* of intercalated molecules (atoms etc) as $n = B_x/B$.

	SLD	d-spacing		B	ΔB	mol/f.u.
	HGO1	**2018**				
1	3.288	**8.29**	Air	1.43		
2	4.127	**8.58**	d-Ethanol	1.86	0.43	**0.07**
		2016				
1	3.345	**8.15**	Air	1.43		
2	5.412	**9.89**	d-Ethanol	2.81	1.38	**0.23**
		2014				
1	3.349	**8.11**	Air	1.42		
2	6.034	**10.04**	d-Ethanol	3.17	1.75	**0.30**

Table S2. Summary of neutron reflectivity data recorded using spin coated HGO1 film in air and inside of the sealed cell with saturated d6-ethanol vapor. The d-spacing representing inter-layer distance of HGO1 was calculated using change of film thickness. Solvent sorption is provided in as number of molecules per formula unit (mol./f.u.).

4. Characterization of flake size distribution in GO dispersions.

Several graphite oxide batches were used in our experiments to prepare HGO dispersions. The graphite oxides were synthesized using different graphite precursors or purchased from commercial source. The flake is size is considered as one of important parameters which affect properties of GO membranes. Therefore, we evaluated flake size distribution for HGO dispersions which were used to prepare membranes. The dispersion was spin coated on mica for flake size analysis using AFM. Example of AFM images used for analysis of flake size distribution are shown in Figures S4-S6. The images show mostly single layered flakes not overlapping with each other. Typically 9-10 images were recorded in different spots and analyzed for flake size distribution using Gwyddion software. Broad distribution of particle size was found for all studied samples.

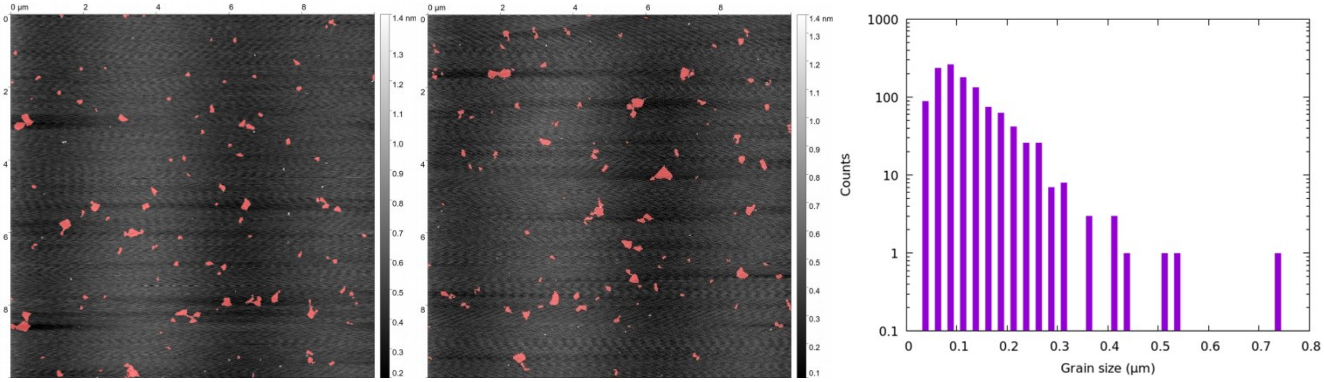


Figure S5. Examples of AFM images recorded using HGO1 dispersion and histogram of flake size distribution which summarizes statistical data on flake size. Average flake size is 116 nm.

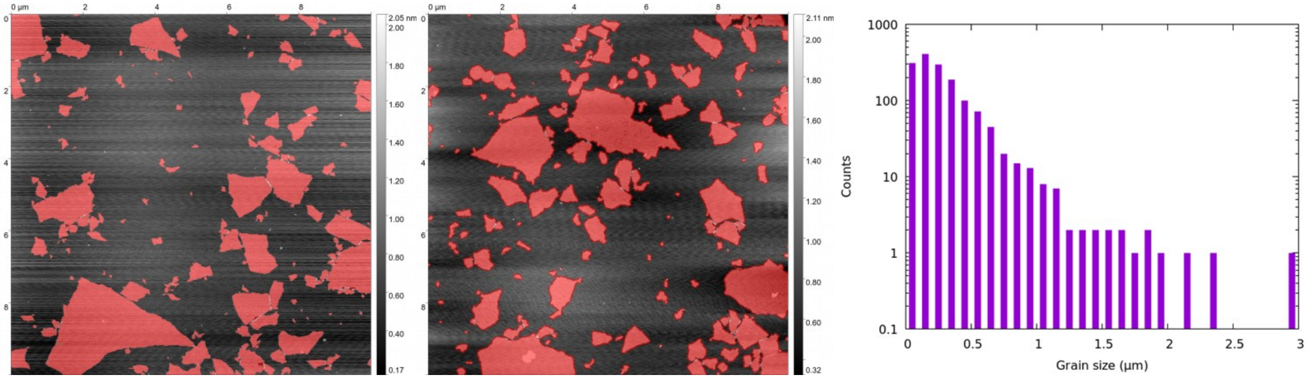


Figure S6. Examples of AFM images recorded using HGO2 dispersion and histogram of flake size distribution which summarizes statistical data on flake size. Average size of flakes is 279 nm.

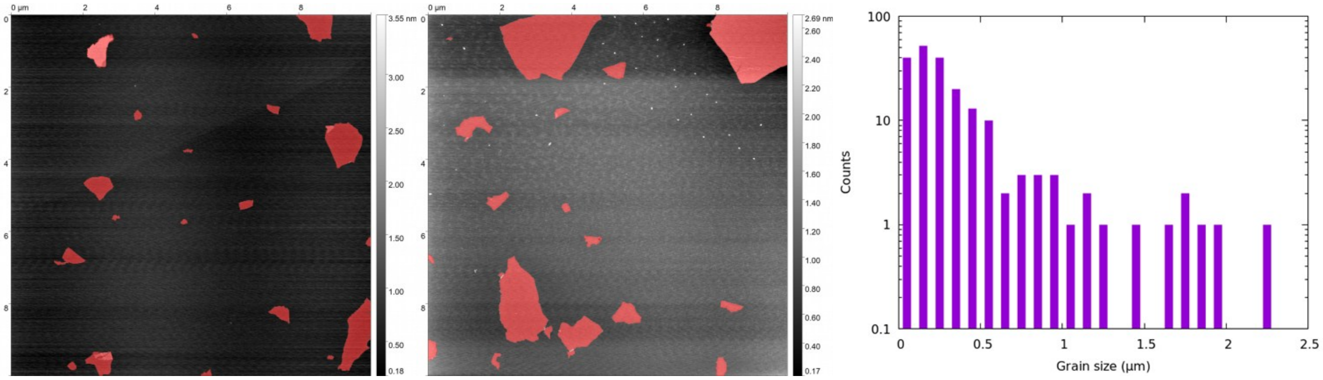


Figure S7 Examples of AFM images recorded using HGO3 dispersion and histogram of flake size distribution which summarizes statistical data on flake size. Average size of flakes is 328 nm.

The data shown in Figures S4-S6 demonstrate that HGO2 and HGO3 dispersions exhibit similar flake size distribution with minor difference in average flake size value. The precursor graphite oxides were synthesized using graphite powders with significantly different flake size (150-500μm for HGO2 and 0-200μm for HGO3). Strong decrease of flake size is likely a result of prolonged sonication treatment which was used for preparation of GO dispersions. It is known that prolonged sonication of aqueous dispersions results in breaking of GO flakes and decrease of average flake size.[8]

5. Additional data for XRD experiments with swelling of graphite oxide powders and HGO membranes in alcohols.

5.1 Swelling HGO1 membranes aged for different periods of time

HGO1 membrane aged for 2,5 was studied in alcohols with number of carbon atoms from 1 (methanol) to 8 (1-octanol). Most intensive (001) reflection was used to calculate average inter-layer distance. Pattern of membrane recorded after 2 days of immersion in alcohols to achieved saturation, exception is patterns in methanol and ethanol, where data were recorded until no change in patterns could be found. Usually 2-3 scans, time of scan was 15 min, see Figure S7.

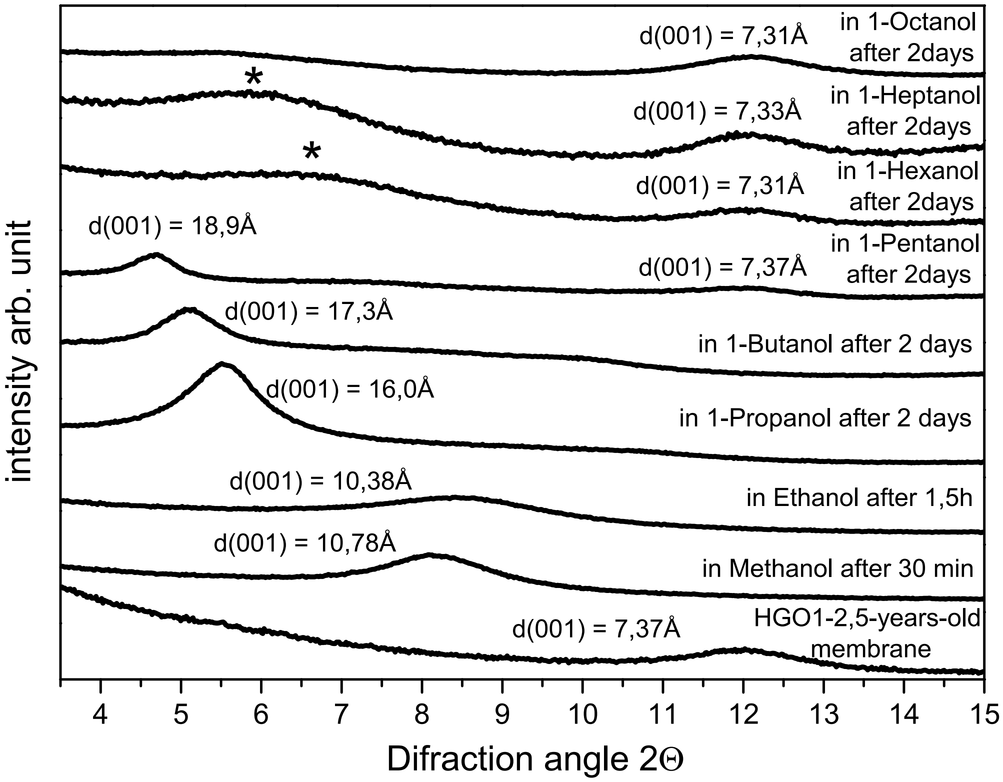
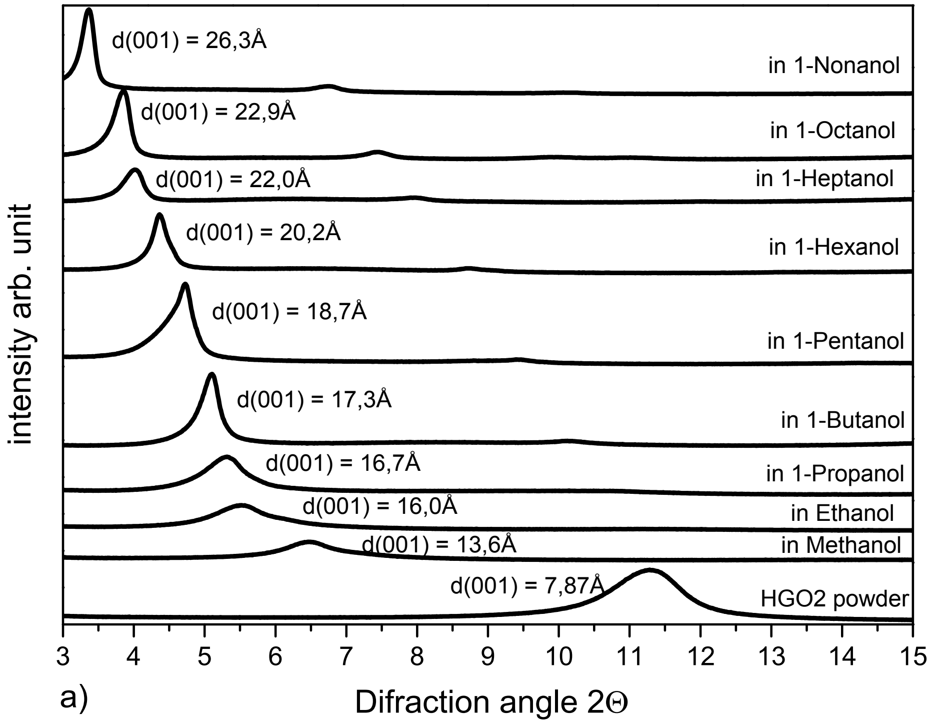


Figure S8. XRD patterns (CuKα) recorded using HGO1 membrane aged for 2,5 years immersed in liquid alcohols. Broad features marked by stars originate from liquid solvents. Some scaling was applied for selected patterns

5.2 HGO2 powder and membranes aged different period of time

HGO2 powder and membranes aged different period of time were studied alcohols with number of carbon atoms from 1 (methanol) to 9 (1-nonanol). Part of analysis was done at ID 11 ESRF, Grenoble, France. To study kinetics of swelling patters for HGO2 membrane aged for 6 months recorded until no change in intensity, position or drying membrane could be found. HGO2 membrane aged for 6months was interpreted as age-not-affected, because of high swelling in ethanol up to 14,5Å, see Figure S8.



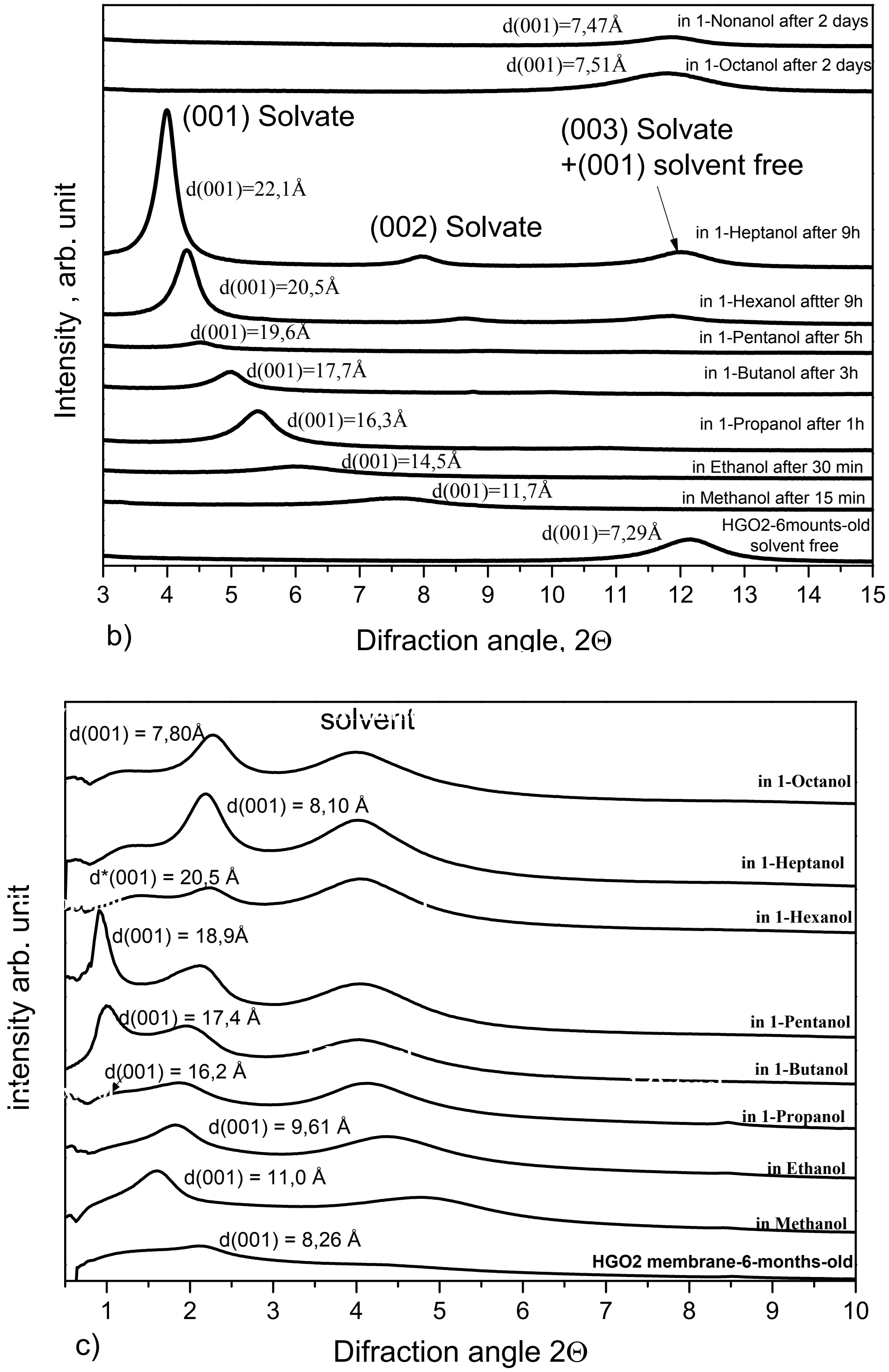
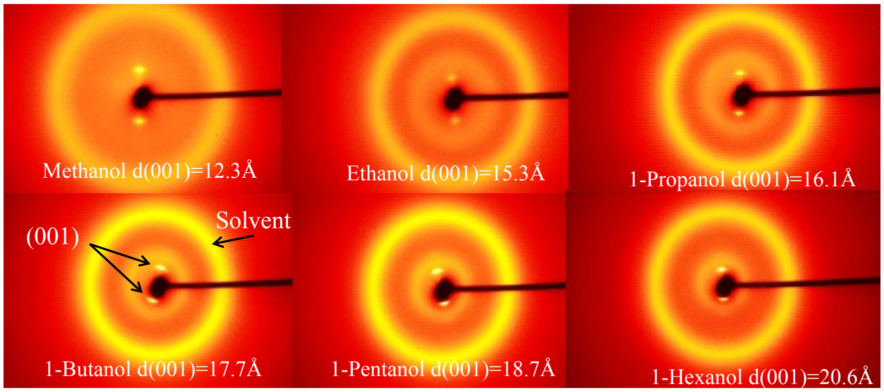


Figure S9. a) XRD patterns recorded from precursor graphite oxide powder used for preparation of HGO2 membranes in different alcohols (CuKα). b). XRD patterns recorded from HGO2 membrane aged for 6 months and immersed in different alcohols (CuKα). c) Integrated patterns for HGO2 1.5-year old membrane (see original 2D images in the main part , Figure 3b.

5.3 Swelling of freshly prepared HGO3 membrane and graphite oxide powder used as a precursor.



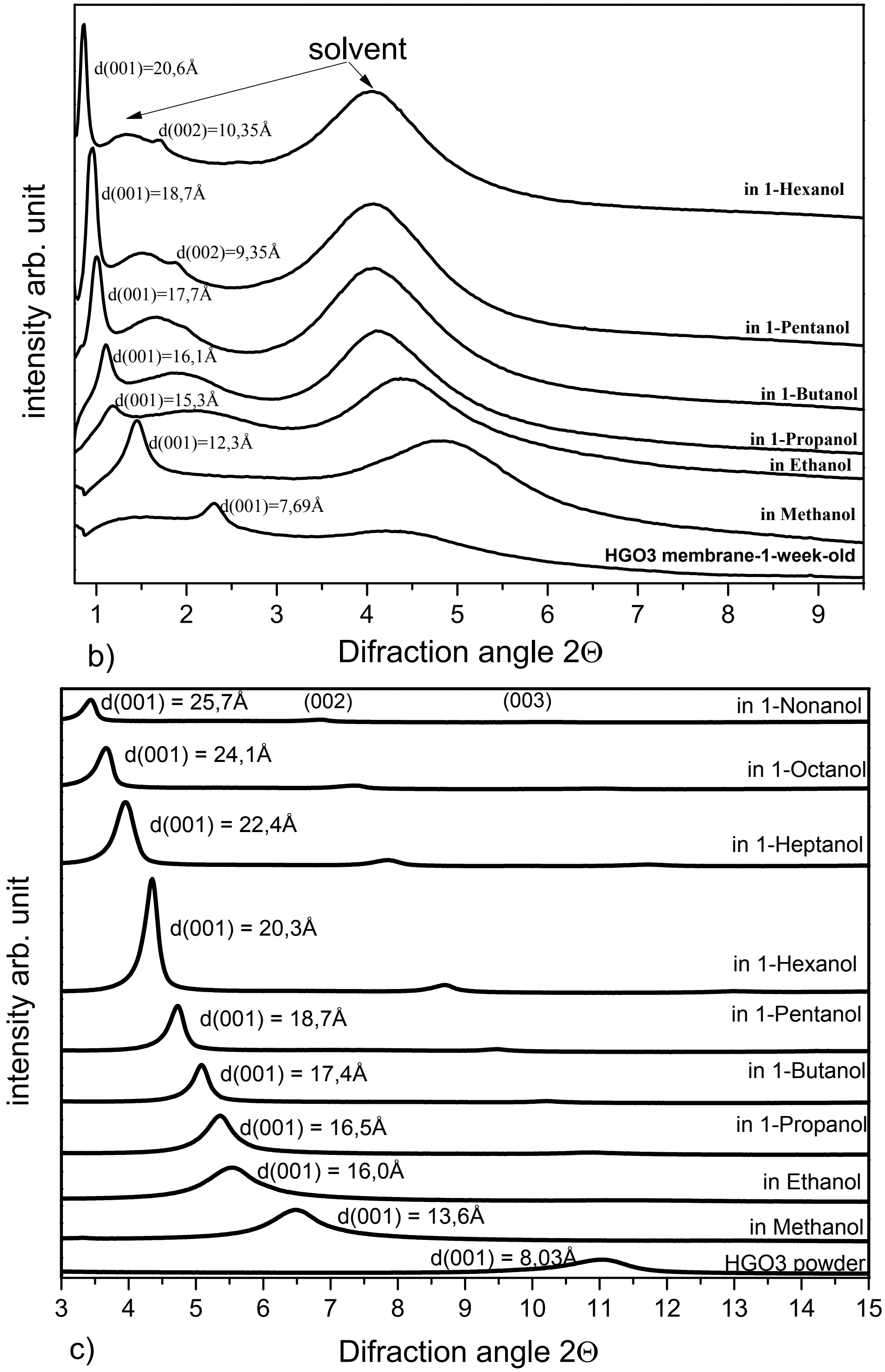


Figure S10. a) XRD images (λ = 0.30996Å) recorded from HGO3 membrane after 23-24 hours of immersion in liquid alcohols b) XRD patterns integrated using 2D images recorded using synchrotron radiation (λ=0.30996Å) from HGO3 membrane aged for 1 week. b) Swelling of graphite oxide powder (HGO3) in alcohols with carbon number C=1 to 9 (methanol to 1-nonanol), XRD patterns recorded using CuKα radiation .

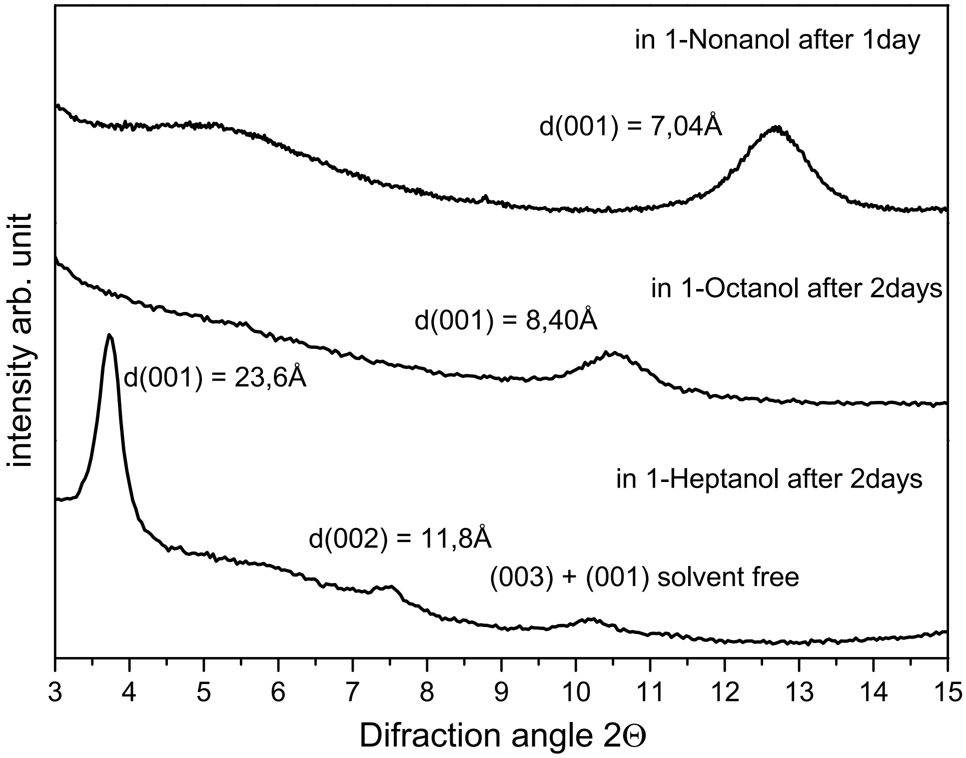


Figure S11. Additional XRD data recorded for HGO3 membrane aged for 1week using in house diffractometer with CuKα radiation. The set of data shown in the main part of the paper for HGO3 membrane was recorded using synchrotron radiation (λ = 0.30996Å) only for alcohols with C=1 to 6.

5.5 Swelling of aged HGO1, HGO2 and HGO3 membranes in water.

The swelling of GO membranes in water become somewhat smaller as a result of ageing but remains to be significant even after 5 years after preparation, see Figure S11

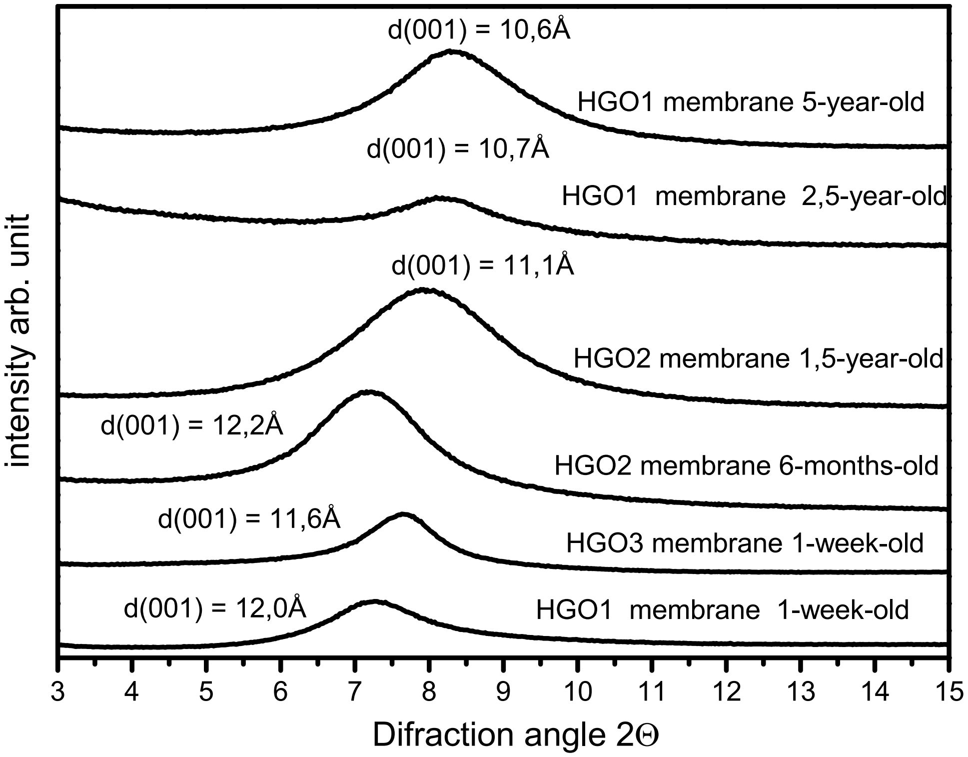


Figure S12. XRD patterns recorded from aged HGO1, HGO2 and HGO3 membrane samples immersed in water.

5.5 XRD data for HGO4 membrane aged for 6 month, swelling in water and ethanol.

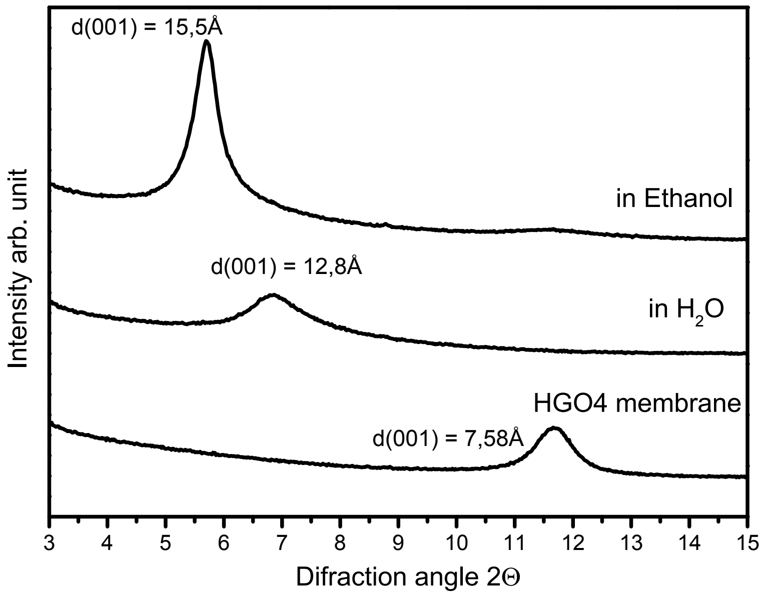


Figure S13 XRD patterns of HGO4 membrane sample aged for 6 months recorded on air (solvent free), immersed in water and in ethanol.

5.6 Kinetics of swelling of HGO1 and HGO2 membranes aged for 1 week and 6 months in 1-heptanol.

Slow kinetics of swelling was observed for membranes in large alcohols (6 carbon atoms and higher). XRD patterns recorded after immersion of freshly prepared HGO membranes in 1-hexanol and 1-heptanol showed reflections from both swollen and pristine phases. The relative intensity of swollen phase was increasing over the period of several hours. Complete swelling of the membrane was not achieved even after ~12 hours of immersion (**Figure S15**).

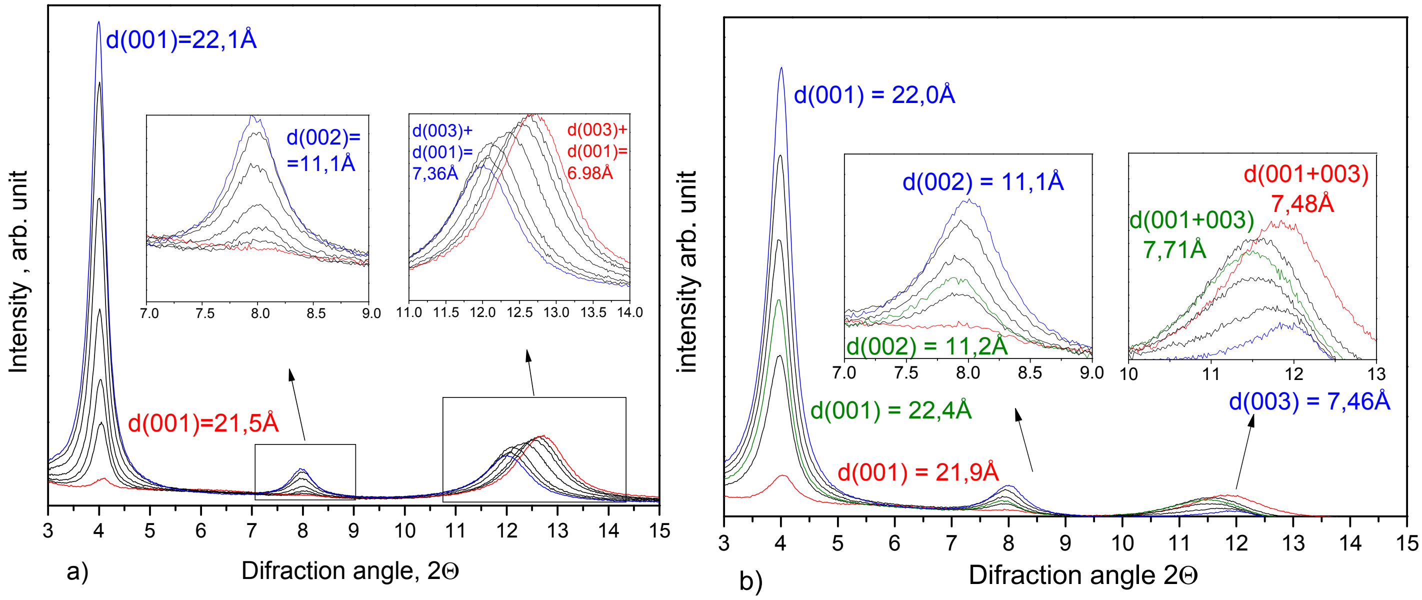


Figure S14. Set of XRD patterns recorded in liquid 1-heptanol from a) 6-month-old HGO2. Red line represents the first pattern recorded 15 min after immersion into solvent; blue line– 9h after immersion b) 1-week old HGO1 membrane red line– 25 min after immersion into solvent; green line – 70 min after immersion, blue line – 12h after immersion.. The (001) reflection from swollen phase is increasing in intensity while the peak position do not shift with time.

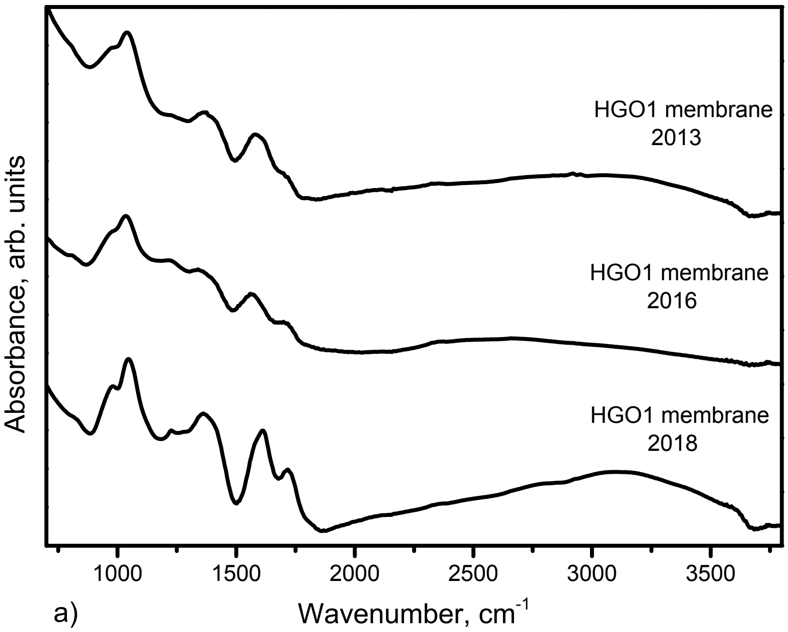
Note that position of the (001) reflection from solvated phase does not shift significantly with time (21.5Å in the first scan and 22.1Å after 9h) but the elative intensity of the (001) reflections of swollen and not swollen phases is changing over the period of hours.

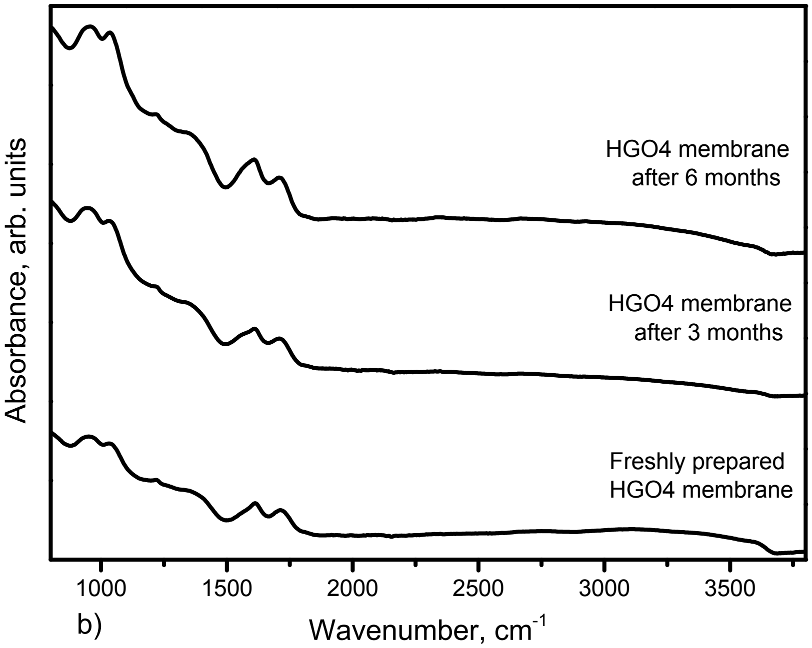
The XRD data shown in **Figure S14** can be interpreted by suggesting that the immersion of membrane sample in to liquid 1-heptanol results in formation of solvate phase first at near surface layers of GO structure while the inner part remains unaffected by swelling. It takes several hours for the solvent to penetrate into the full depth of the micrometer thick membrane. The diffusion of solvent between GO layers is slow, but filling of interlayer space occurs rapidly and to full extent as it follows from the position of d(001) which correspond to full saturation.

It is remarkable that the absence of swelling in largest alcohols was observed only for two out of three types of HGO membranes. All three precursor graphite oxides were synthesized using Hummers oxidation. The graphite oxides showed similar oxidation degree (C/O in the range of ~2.30-2.47), similar structure by XRD and similar FTIR spectra (**Table S1**and **Figure S1-2**). Therefore, the difference in swelling properties of HGO membranes is likely to be related to certain features of GO flake packing in relation with the size/length of molecules. The packing of GO layers and flexibility of the assemblies in response to swelling can also be affected by the flake size.

To verify possible correlation of HGO membrane swelling with size of GO flakes we analyzed flake size distribution using precursor dispersions. Droplets of diluted solutions were dried on mica surface and imaged using AFM. (SI file, **Figures S5-S7**). The average flake size of HGO2 and HGO3 was found to be 0.28µm and 0.33µm respectively, while for HGO1 it was significantly smaller (0.12µm). Therefore, we hypothesize that smaller flakes might pack in somewhat different arrangement compared to larger flakes providing less interlocked structure.

6.0 XPS and FTIR characterization of aged HGO1 and HGO4 membranes.





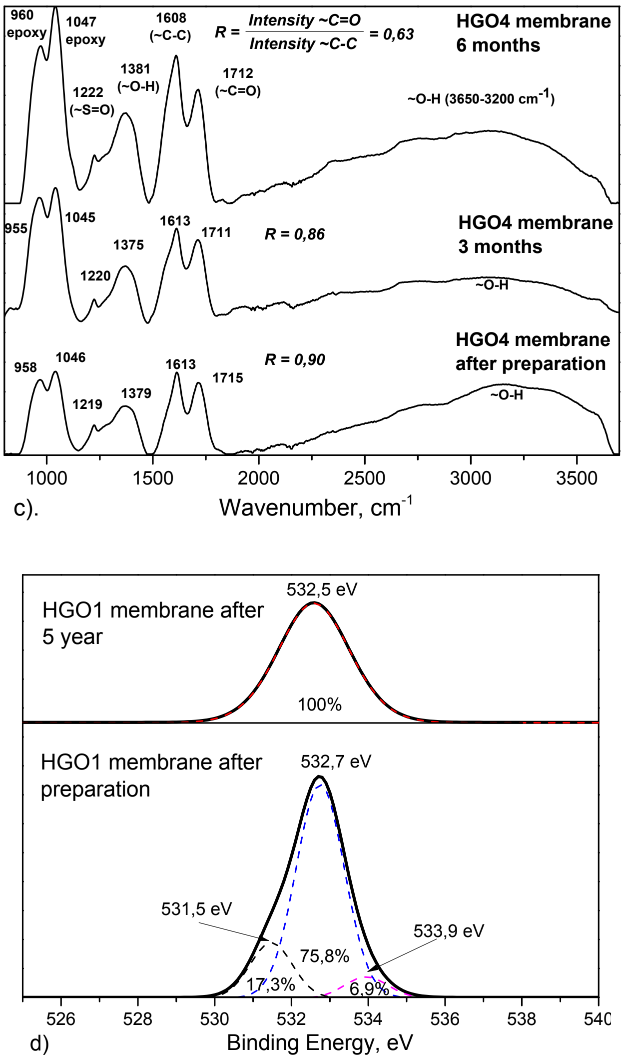


Figure S15. FTIR spectra (recorded in ATR mode) recorded in the range 500-3800 cm^{-1} from a) HGO1 membranes aged for different periods of time b) HGO4 membrane aged up to 6 months c) spectrum with base line correlation for HGO4 membrane and the same sample after 3 month and 6 months of ageing. Relative intensity (R) is provided for peaks typically assigned to C=O and C-C. Spectra were recorded under vacuum conditions to eliminate adsorbed water. d) XPS spectra of HGO1 membrane measured shortly after preparation back in 2013[2a] and after 5 years of ageing at ambient conditions. O1s part of spectra The percent values correspond to the part of area related to particular fitting component (100% is for area of all O1s peaks)

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