



Membranes adventures at DESY Hamburg

Sergey Girshevich, Moscow State University, Russia

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Abstract

The structure of graphene oxide (GO) membranes at interaction with different solvents was studied using DESY radiation X-ray diffraction. A series of membranes based on aluminum oxide with GO/fullerenols or carbon nanotubes deposited on it (in different concentrations) was studied in different temperature ranges and at different humidity. The obtained measurement results are presented below.

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1. Introduction

Swelling of graphite oxide (GO) powders in polar liquids is a significant phenomenon from both theoretical and practical viewpoints. Practical interest is associated mainly with possible separation/filtration of liquids and storage of gases by means of thin, tunable, and mechanically strong GO layered structures. Studies of GO membranes were started in 1960s (1) and it still go on (2). The most interesting is the swelling of the oxide and the subsequent transport of water through without transport of other liquids, some of which are polar. In addition, previously, using the data on sorption on the membrane, the presence of pseudo-negative thermal expansion of membranes based on GO was supposed (3). Therefore, to further study the properties of selective GO membranes, the dependences of the d-spacing of the membranes on temperature and humidity were investigated.

The last data of sorption, which were obtained in our laboratory, are presented on the Fig.1. Practical graphs were obtained from measurements of membrane mass, theoretical (teor) data were obtained from measurements of d-spacing, using the equation

$$M = M_0 * (d_0 * \rho_0 + (d_1 - d_0) * \rho_{H_2O})$$

Where M – membrane mass after sorption

M_0 – membrane mass before sorption

d_0 – membrane d-spacing before sorption

d_1 – membrane d-spacing after sorption

ρ_0 – membrane density before sorption

ρ_{H_2O} – water density

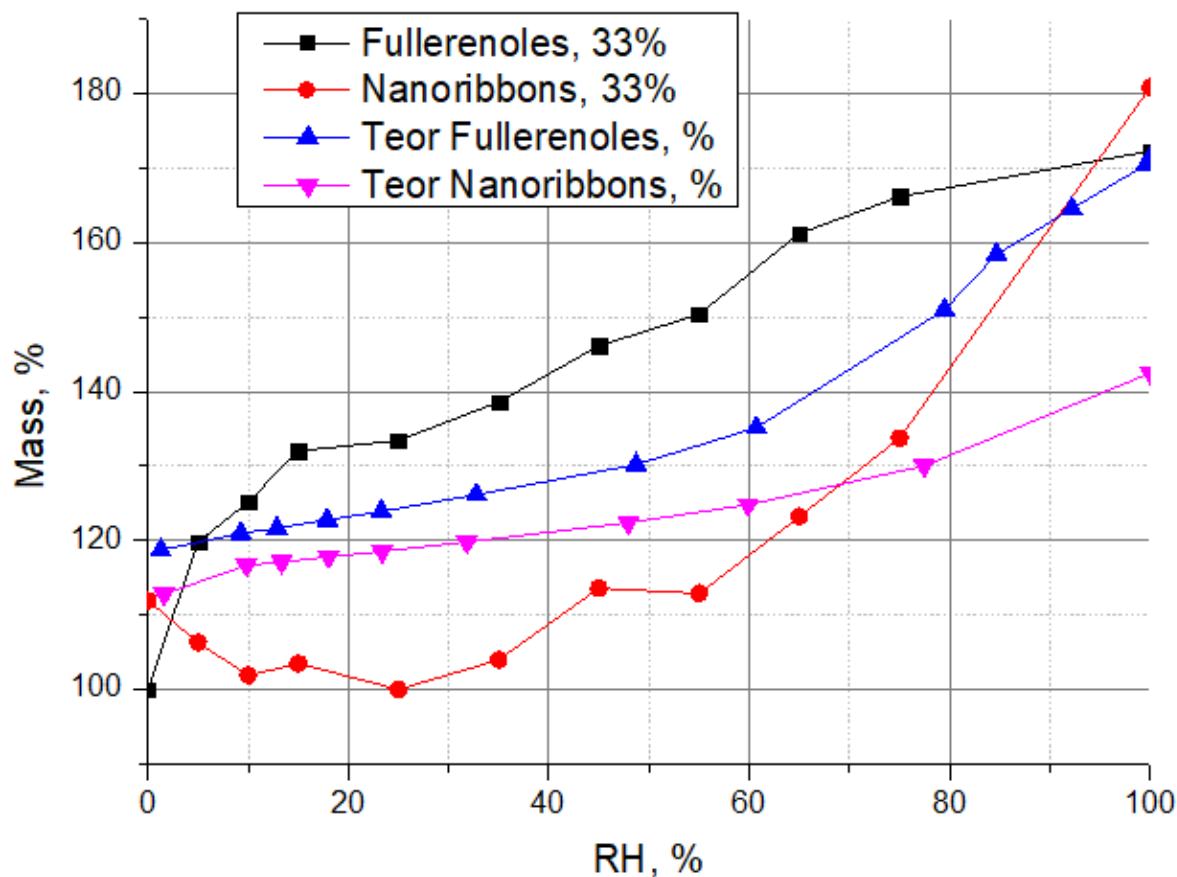


Figure 1: Theoretical and experimental graphs of water sorption for membranes based on GO

2. Experiment condition

Interlayer distance of GO membranes at the controlled humidity levels was evaluated at P03 beamline of PETRA III synchrotron (Deutsches Elektronen-Synchrotron, Hamburg) in grazing incidence geometry (4). An incident photon beam with the energy of 15.01 keV ($\lambda = 0.827 \text{ \AA}$, $\Delta\lambda/\lambda < 3 \cdot 10^{-4}$) was used. The beam was focused at the sample position by \ compound Be lenses to the size of $(31 \times 24) \mu\text{m}^2$. A grazing incidence angle of 0.4° was selected to maximize scattering intensity from the samples. Scattered X-rays were captured using Nexus Lambda 9 M detector (pixel size $55 \times 55 \mu\text{m}^2$). The sample-to-detector distance was set to $SDD1 = 610 \text{ mm}$. A standard calibration of sample-to-detector distance with silver behenate was performed prior to GIWAXS experiment providing an uncertainty in absolute d-spacing of below 0.01 nm^{-1} for d-spacing of 10 nm^{-1} . A specially designed cell with Kapton windows was used to control humidity levels during the experiments (5). A total flow of 1000 mL/min of mixed dry and wet (about 100% humidity obtained by bottle-type humidifier) nitrogen was introduced to the cell with VEMD (Festo) flow controllers. The humidity level was monitored with KIP-20 (Teplopribor, Russia) temperature humidity transducers based on HIH-4000 (Honeywell, accuracy $\pm 3.5\% \text{ RH}$) sensors before and next to the experimental cell. Additionally, the spectra of wetted samples were acquired by placing a water drop onto the sample surface under $>98\%$ humidity. GIWAXS data were analyzed using the DPDAK software package (6).

3. Measurement

3.1. Preparation of samples

MFGO100

Suspensions of GO nanosheets were obtained by an improved Hummer's method according to the procedure described in (7). Firstly, medium-flake graphite (MFG) was carefully intercalated with the mixture of concentrated H_2SO_4 (96%) and H_3PO_4 (87%) (the mass ratio of 9:1) for 30 minutes under simultaneous top-drive and magnetic stirring. Then, the intercalated graphite compound was oxidized by careful stepwise addition of KMnO_4 (99% purity) over the period of 60 min and kept at 50°C for 24 h under constant stirring. After the oxidation stage, the excess of oxalic acid was added to the suspension to reduce all the Mn^{4+} to Mn^{2+} . The GO suspensions were 2-fold diluted by addition of ice, and further stirred for 1 hour. Then, the obtained GO suspensions successively centrifuged (7000 rpm for 10 min, 15-20 times) and washed using double-distilled water until the pH of 4 was reached. Purification of the suspensions from residual inorganic ions was performed by dialysis for 30 days. The extent of sulfate-ions removal from the GO suspensions was controlled using conductometry and XPS techniques.

CNTGO

Graphene oxide nanoribbons (CNTGO) were obtained by oxidation of pure single-walled carbon nanotubes (CNTs) by a modified Hummer's method (8). A detailed description of the CNTGO synthesis is described in our earlier study (9), but in general it is the same as MFGO synthesis. The only difference was the use of single-walled carbon nanotubes as a precursor.

CNT20 and CNT33

GO made of carbon nanotubes and MFGO (graphene oxide made of medium-scale graphite, the size of the exhaust gas sheets is $\approx 800 \text{ nm}$) were mixed in a ratio of 1:4 and 1:2

VAB2 MFGO1:2 and VAB2 MFGO1:4

A mixture of fullerenols and graphene oxide MFGO in the weight ratio of 1:2 and 1:4, respectively, was used as a precursor

3.2. Temperature series

Membranes MFGO100 and the VAB2 MFGO1:2 were studied at different temperatures when interacting with different solvents

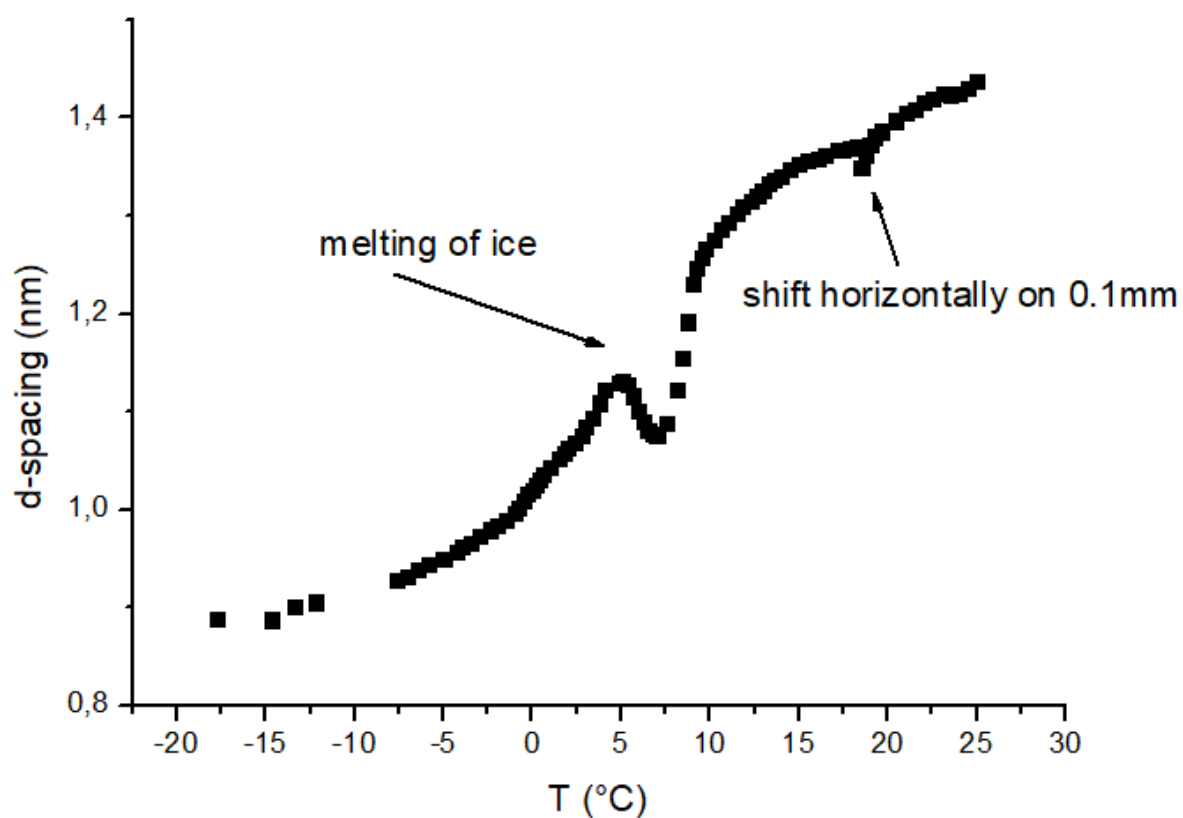


Figure 2: Temperature dependence of the d-spacing for the MFGO10 membrane, on which a drop of H₂O is deposited

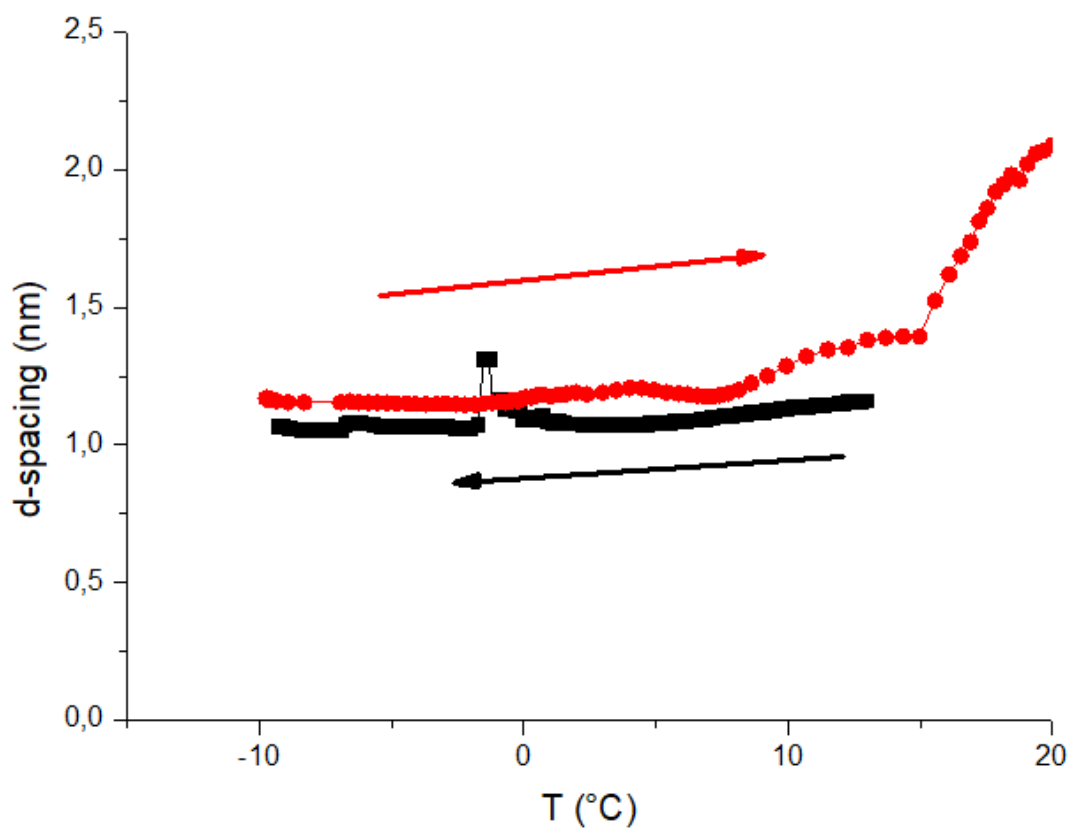


Figure 3

Temperature dependence of the d-spacing for the VAB2 MFGO1:2 membrane, on which a drop of H_2O is deposited

Difference between down and up lines can be explained by horizontal shift of synchrotron beam, that says about inhomogeneity of the d-spacing in the XOY plane.

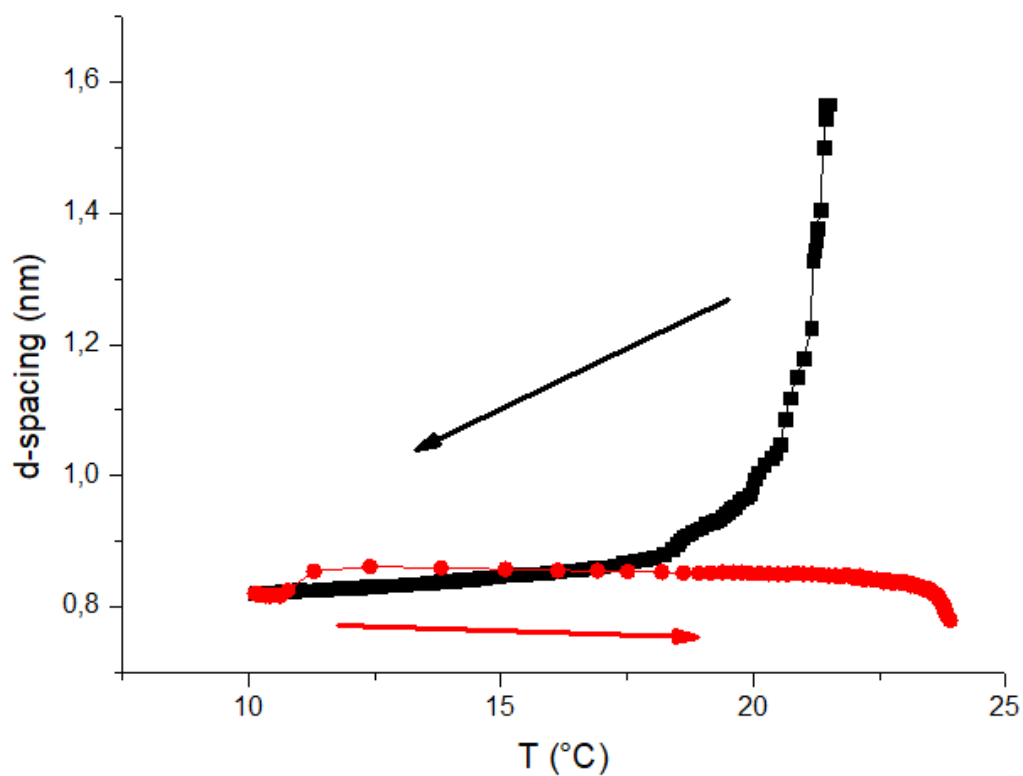


Figure 4: : Temperature dependence of the d-spacing for the VAB2 MFGO1:2 membrane, on which a drop of CH_3OH

Although results of temperature series measurements are a bit strange and need additional analysis, there are no any proofs of pseudo-negative thermal expansion for these samples.

3.3. Humidity series

Membranes CNTGO, CNT33, CNT20, VAB2 MFGO1:2 and VAB2 MFGO1:4 were measured at different humidity: there is one measure with lots of points for VAB2 MFGO1:2 and measures with 3 different point (0, 50 and 100%) for each other.

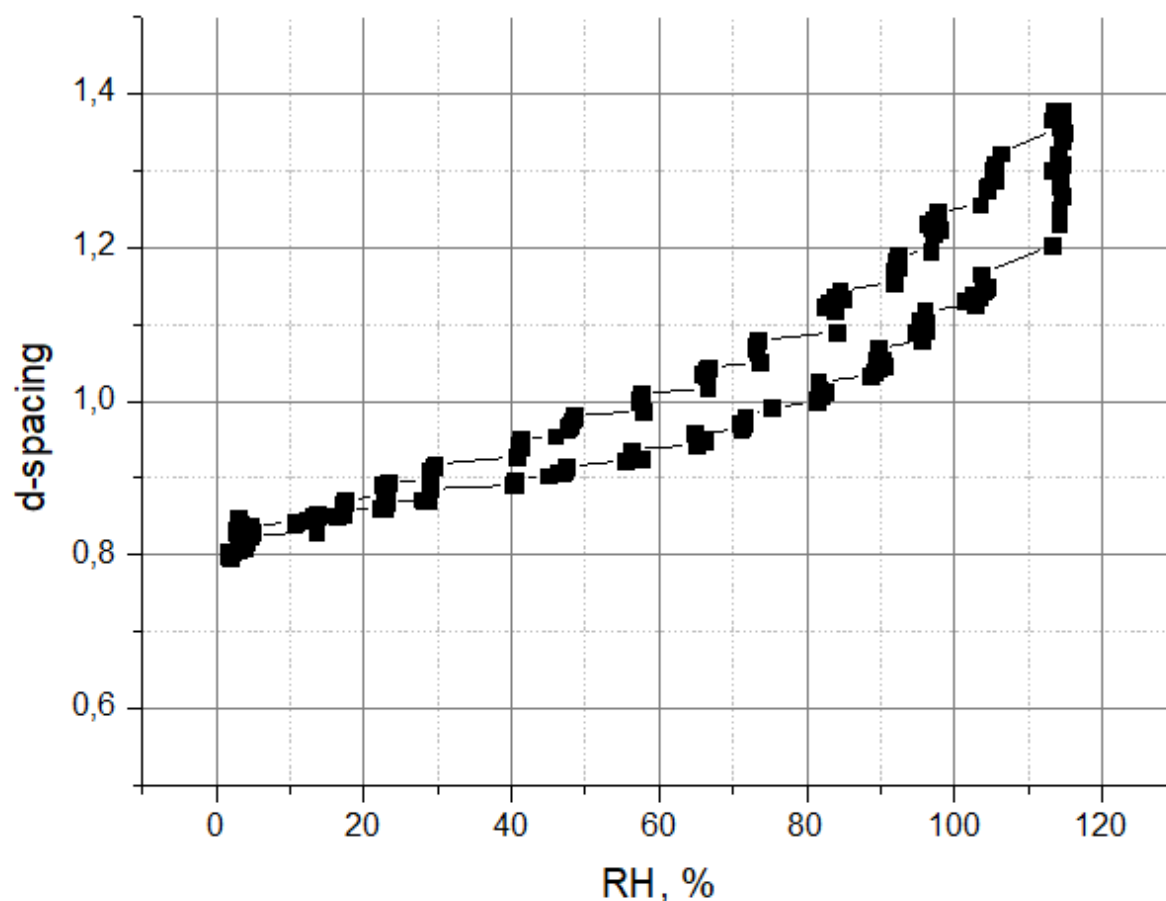
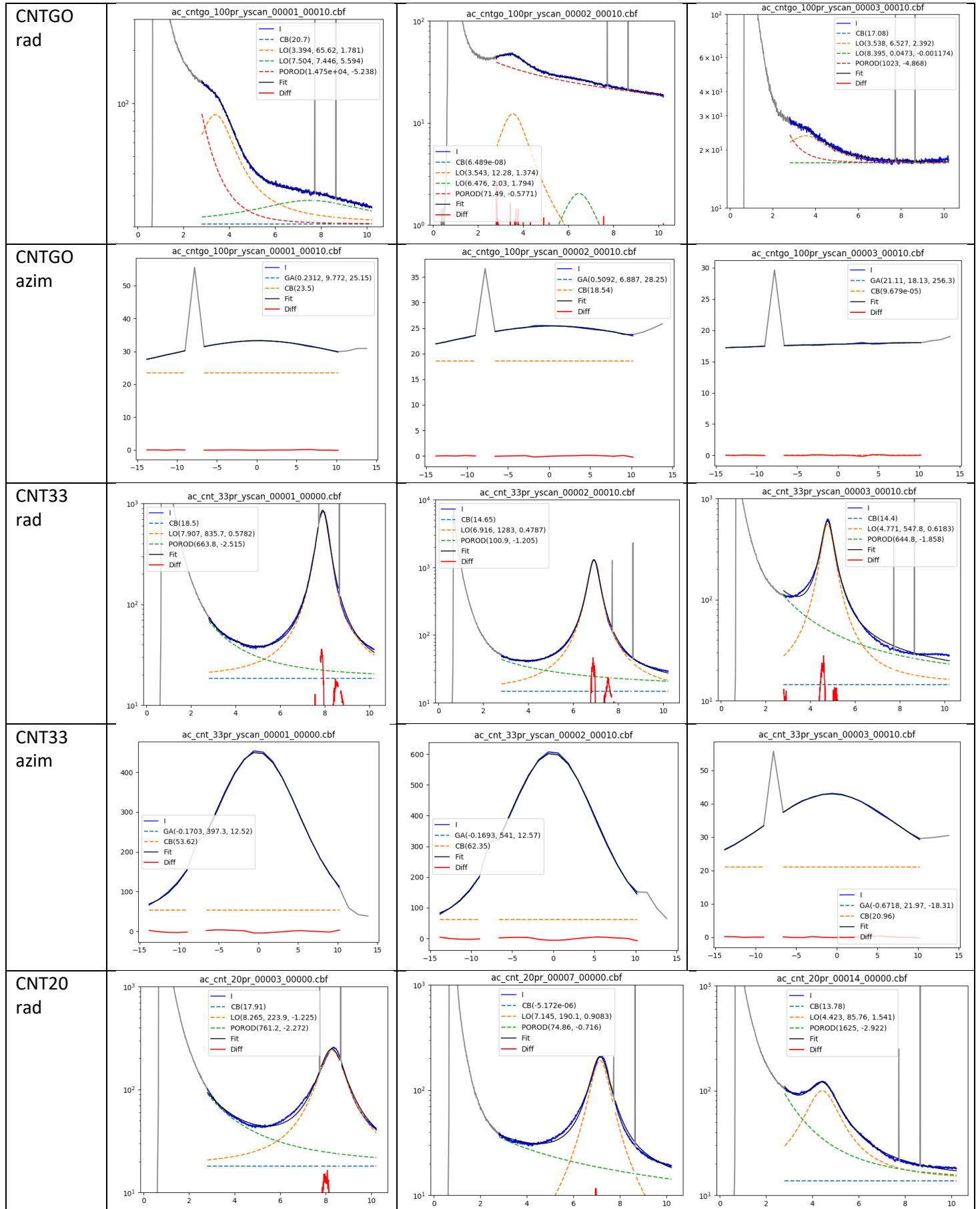


Figure 5: Dependence of the d-spacing on the humidity for the membrane Vab2 MFGO1:2

This graph has a hysteresis. It can be explained with features of membrane swelling mechanisms.

Table 1: Graphs for different membranes at different conditions, radial and azimuthal profiles
(in radial profile X-axis is $2\pi/d$, 1/nm, in azimuthal profile X-axis is rocking angle, degrees)

	Humidity 0%	Humidity 50%	Humidity 100%
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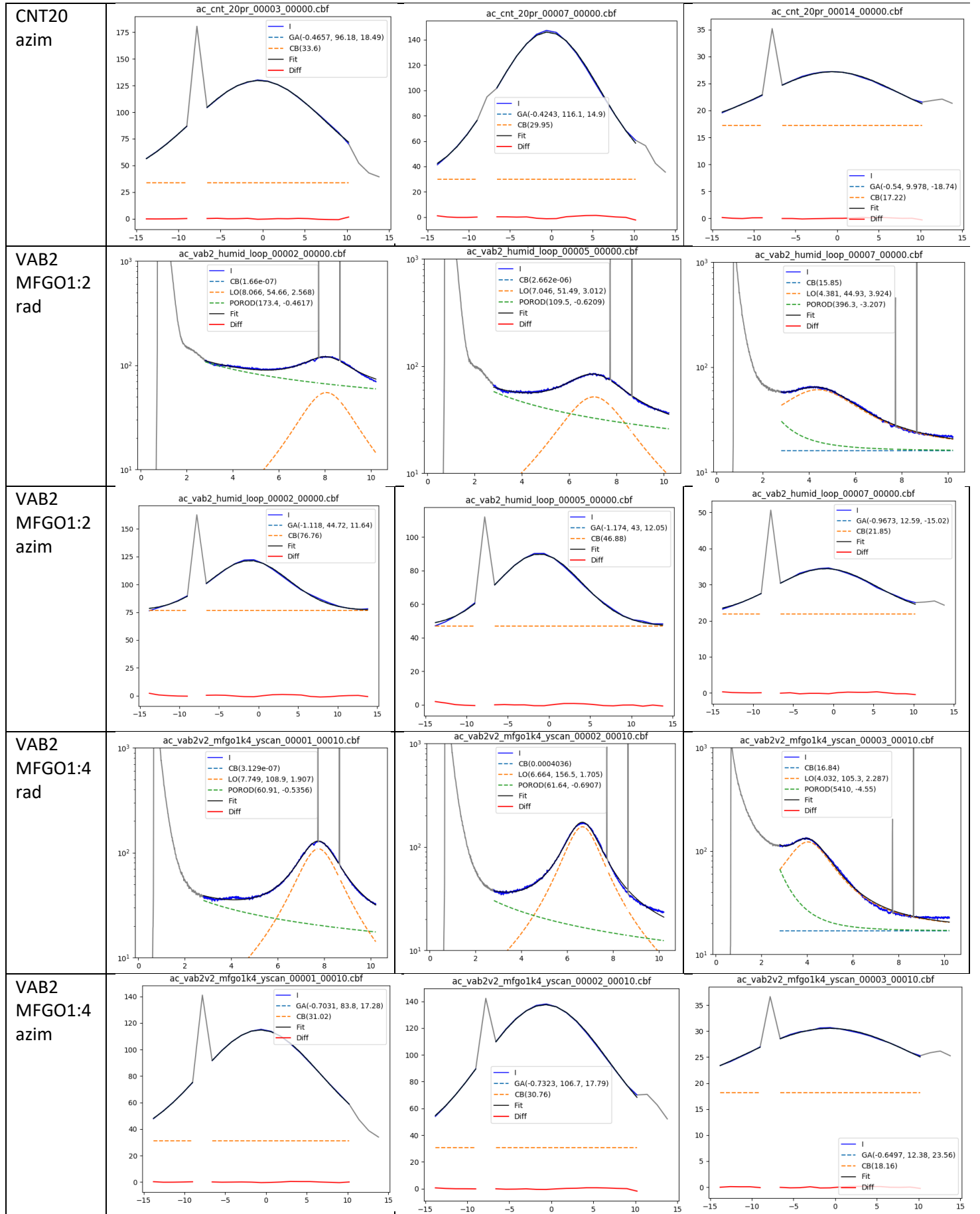


Table 2: d-spacing (nm) for different membranes at different humidity

	Humidity 0%	Humidity 50%	Humidity 100%
CNTGO (1 st peak)	1,85±0,97	1,77±0,69	1,78±1,20
CNTGO (2 nd peak)	0,84±0,62	0,97±0,27	0,75±0,00
CNT 33	0,79±0,06	0,91±0,06	1,32±0,17
CNT 20	0,76±0,11	0,88±0,11	1,42±0,49
VAB2 MFGO1:2	0,78±0,25	0,89±0,38	1,43±1,28
VAB2 MFGO1:4	0,81±0,20	0,94±0,24	1,56±0,88

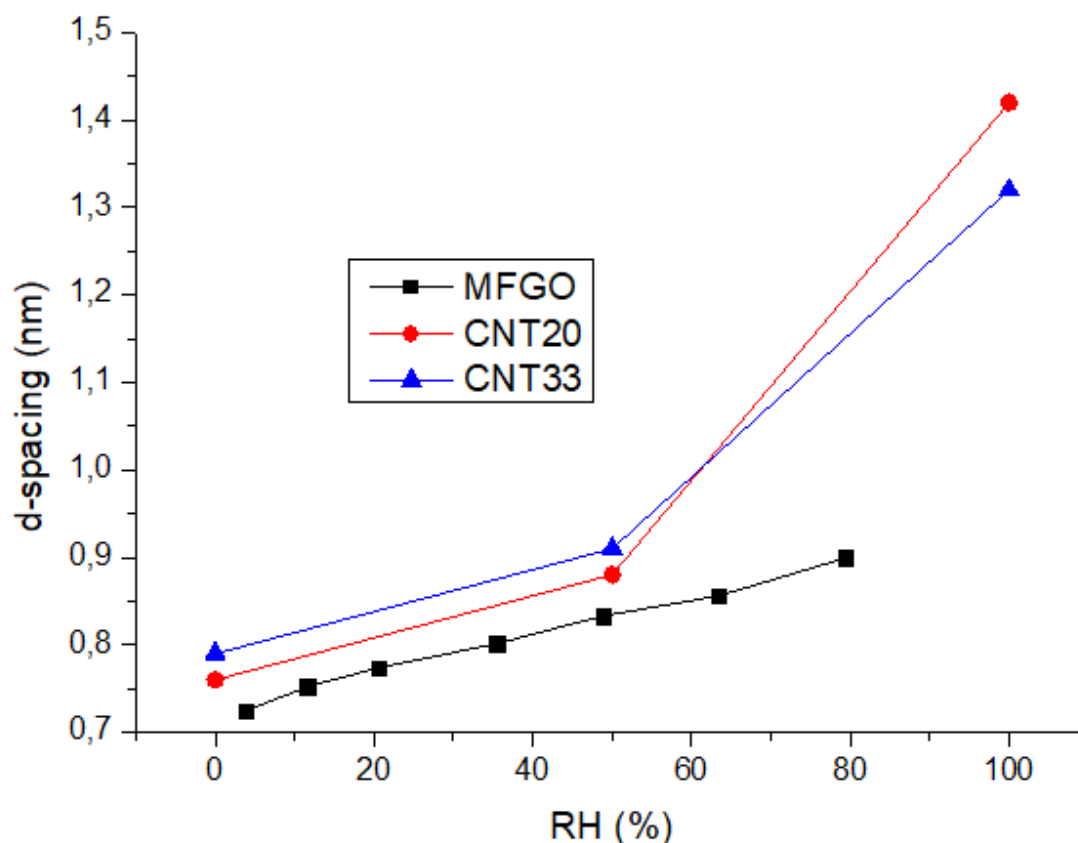


Figure 6: Dependence of the d-spacing on the humidity for the membrane

Comparing M\measurements at different humidity points for samples CNT20 and CNT33 with measurements for MFGO (which were made earlier) shows increase of d-spacing after adding on membranes modified carbo nanotubes.

Table 3: The broadening of the azimuthal profile approximation is a measure of the non-parallelism of the laying of sheets in the plane (°)

	Humidity 0%	Humidity 50%	Humidity 100%
CNTGO	25,15	28,25	-
CNT 33	12,52	12,57	18,31
CNT 20	18,49	14,9	18,74
VAB2 MFGO1:2	11,64	12,05	15,02
VAB2 MFGO1:4	17,28	17,79	23,56

All samples except CNTGO shows increasing of d-spacing with increasing of humidity. Also inhomogeneity of d-spacing and non-parallelism of sheets increase with increasing of humidity. This perfectly confirm the theoretical description of the process of swelling of GO membranes.

Measurements of CNTGO shows 2 peaks. It's a bit strange result, that need a check. But this may be evidence of the presence of an additional structure in the carbon nanotubes.

4. Conclusion

Finally, the following results were obtained:

- There is a sharp decrease of d-spacing when freezing around 0 degrees
- All membranes show an increase in d-spacing with increasing humidity that confirms the theoretical predictions about the swelling process
- Replacing MFGO with CNT leads to an increase of d-spacing
- There is no evidence of pseudo-negative thermal expansion for GO membranes, which was previously assumed in literature.

References

1. **Boehm, H.-P., Clauss, A. and Hofmann, U.** Graphite Oxide and Its Membrane Properties. *J. Chim. Phys. Phys. Chim. Biol.* . 58, 1961, 141-147.
2. **Anastasiya T. Rebrikova, Alexey Klechikov, Artem Iakunkov, Jinhua Sun, Alexandr V. Talyzin,.** Swollen Structures of Brodie Graphite Oxide as Solid Solvates. *J. Phys. Chem. C.* 124, 2020, 23410-23418.
3. **Zhu, J., et al.** Pseudonegative Thermal Expansion and the State of Water in Graphene Oxide Layered Assemblies. *ACS Nano.* 6, 2012, 8357–8365.
4. **A. Buffet, A. Rothkirch, R. Döhrmann, V. Körstgens, M.M. Abul Kashem, J. Perlich, G. Herzog, M. Schwartzkopf, R. Gehrke, P. Müller-Buschbaum, S.V. Roth.** P03, the microfocus and nanofocus X-ray scattering (MiNaXS) beamline of the PETRA III storage ring: the microfocus endstation. *J. Synchrotron Radiat.* 19, 2012, 647-653.
5. **AnA., Eliseev, Poyarkov A.A., Chernova E.A., Eliseev ArA., Chumakov A.P., Konovalov O., Petukhov D.I.** Operando study of water vapor transport through ultra-thin graphene oxide membranes. *2D Mater.* 6, 2019.
6. **G. Benecke, W. Wagermaier, C. Li, M. Schwartzkopf, G. Flucke, R. Hoerth, I. Zizak, M. Burghammer, E. Metwalli, P. Müller-Buschbaum, M. Trebbin, S. Förster, O. Paris, S.V. Roth, P. Fratzl.** A customizable software for fast reduction and analysis of large X-ray scattering data sets: applications of the new DPDAK package to small-angle X-ray scattering and grazing-incidence small-angle X-ray scattering. *J. Appl. Crystallogr.* 47, 2014, 1797-1803.
7. **Marcano, D.C., Kosynkin, D. V., Berlin, J.M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L.B., Lu, W., Tour, J.M.** Improved Synthesis of Graphene Oxide. *ACS Nano.* 4, 2010, Vol. 8, 4806–4814.
8. **DV, K., Higginbotham AL FAU - Sinitskii, A., Sinitskii A FAU - Lomeda, J.R., Lomeda JR FAU - Dimiev, A., Dimiev A FAU - Price, B.K., Price BK FAU - Tour, J.M., JM, T.** Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. *PG - 872-6 LID - 10.1038/nature07872 [doi]. N.1476-4687 (Electronic).*
9. **Petukhov, D.I., Chernova, E.A., Kapitanova, O.O., Boytsova, O.V., Valeev, R.G., Chumakov, A.P., Konovalov, O.V., Eliseev, A.A.** Thin graphene oxide membranes for gas dehumidification. *Journal of Membrane Science.* 2019, Vol. 577, 184–194.