Experimental report

14/10/2015

Proposal: **DIR-124** **Council:** 4/2014

Title: Neutron reflectivity study of graphene oxide membranes in water/alcohol mixture vapor

Research area:

This proposal is a new proposal

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Samples: C2O

Instrument	Requested days	Allocated days	From	To
D17	2	2	15/09/2014	17/09/2014

Abstract:

Experimental Report. Alexey Klechikov. Umeå University

Graphite oxides can be dispersed in polar solvents into single-layered graphene oxide (GO) sheets. Single-layered GO can then be deposited from solution into thin films or membranes. GO membranes were recently suggested for separation of ethanol from water using a vapor permeation method [1].

The main goal of this project was to study intercalation of solvents into (swelling) of GO thin films. Here we report the neutron reflectivity study of GO thin films deposited on Si substrate and exposed to D_2O, d-Ethanol and D_2O–d-Ethanol vapours.

In this project we continue the study performed on ”Super-Adam” beamline (Vorobiev, Dennison et al. 2014) at the Institute Laue-Langevin, Grenoble, France. During the experiment on D17 beamline we've got a time resolution of 1 point per every 10 minutes, compared to 1 point per 1 hour on "Super-Adam". Besides improving the time resolution, we continuously controlled the humidity inside the experimental cell to verify how it changes after the cell sealing.

Experiments were performed using the same thin film earlier studied on ”Super-Adam” [2]. The film was stored on air for one year between the measurements at "Super-Adam" and D17.

The experiment includes five steps (Figure 1). Step 1: the sample is loaded into experimental cell, D_2O is added and cell sealed. Humidity inside the cell slowly increases starting from ambient to ~70% for the first 30 minutes of the experiment (Figures 2). This results in increase of the GO film thickness due to intercalation of D_2O. Step 2: the cell is opened and the sample is air-dried at ambient humidity. The interlayer distance of GO film decreases to initial value almost immediately after the cell is opened. The same cycles are repeated at Steps 3 and 4 with d-Ethanol instead of D_2O. The intercalation of GO film by ethanol results in increase of the distance as expected from our previous studies [3]. Finally, the sample is exposed to d-Ethanol-D_2O (10:1) mixture to check the selectivity of intercalation of different solvents by the GO film. The thickness of GO film exposed to binary mixture increases stronger compared to pure water (step 1), which demonstrated intercalation by both D_2O and d-Ethanol.

Preliminary analysis of experimental data (Figure 1) shows that the thickness of film increases slowly after the cell is sealed, but instantaneously returns back to the "ground" level typical for ambient humidity. Thanks to the control of humidity it is established that slow kinetic of the film thickness increase is not a property of the GO film, but rather a result of slow increase of humidity inside of the cell.

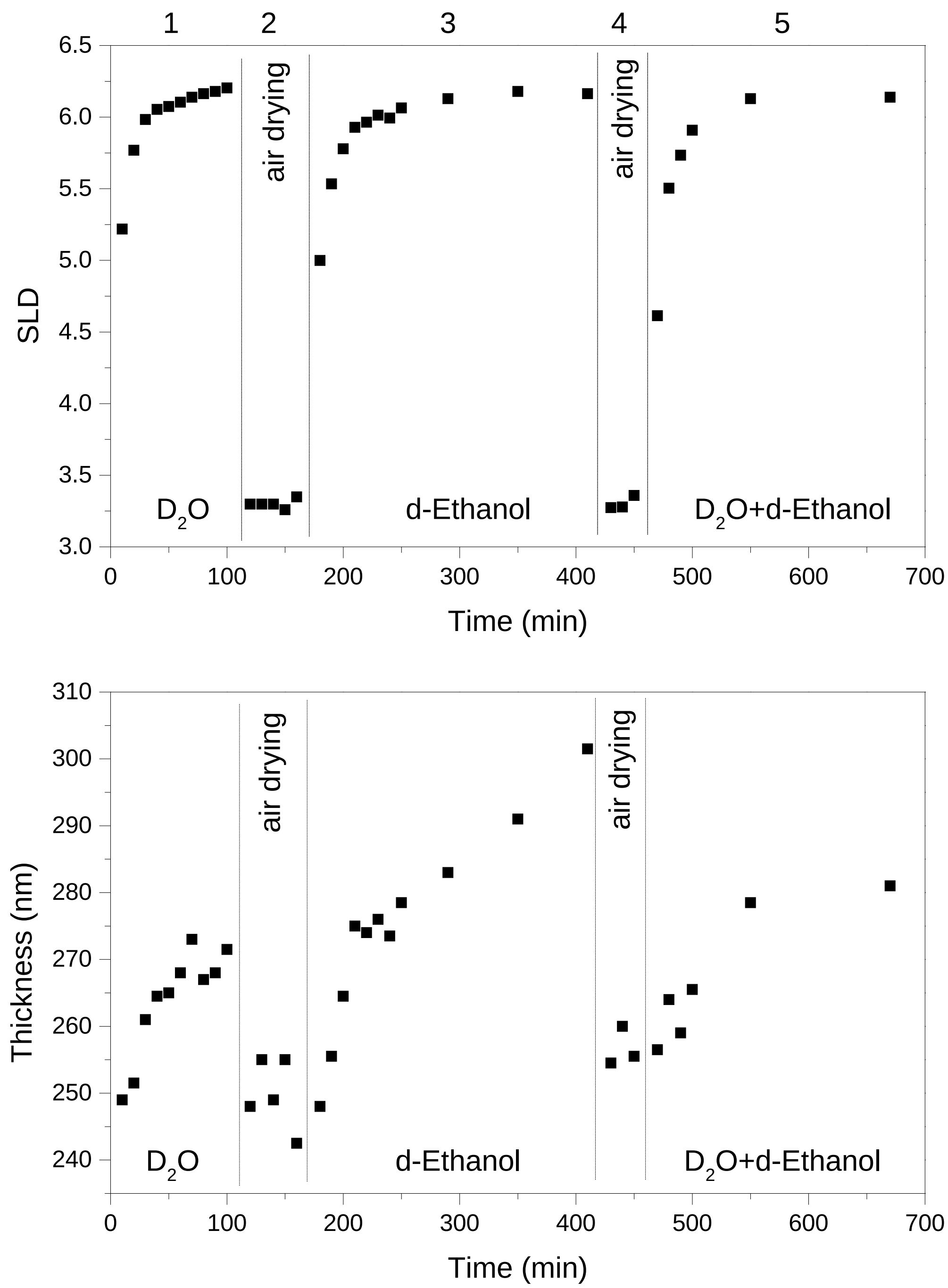

Figure 1: Evolution of GO film SLD (a) and Thickness (b) exposed to vapors of D_2O, d-ethanol and D_2O/d-ethanol 10:1 mixture with intermissions for air drying.

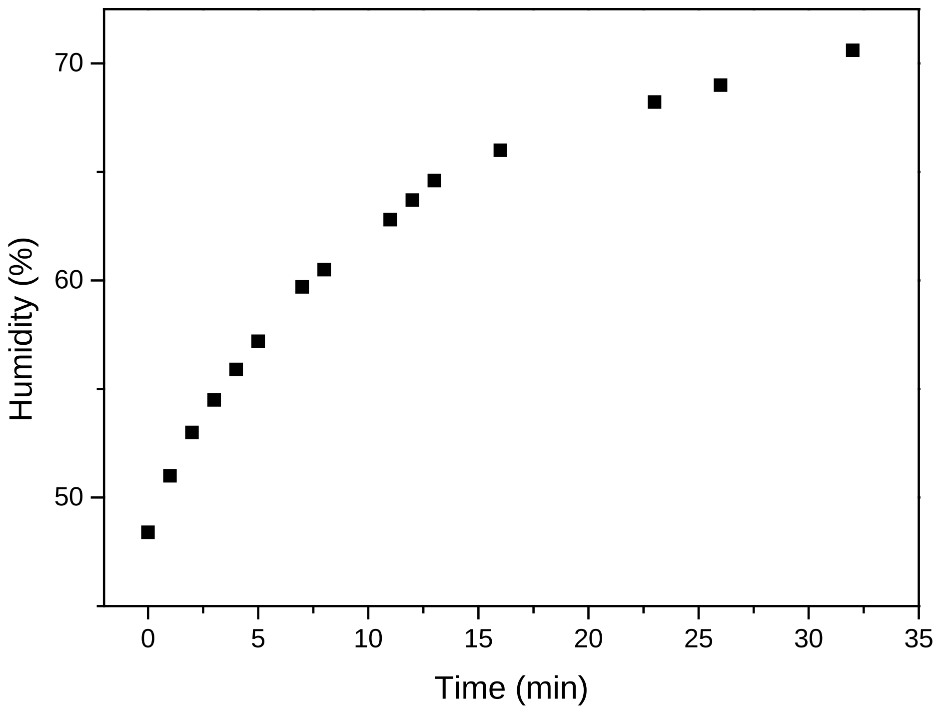

Figure 2: Humidity increase inside of experimental cell after sealing with D_2O. Initial value corresponds to ambient humidity.

It can be concluded that slow kinetics of D_2O intercalation into GO films reported in our earlier study is not confirmed. The films thickness is following change of vapor pressure inside of the experimental cell. However, slow intercalation of ethanol observed in this study cannot be explained by simple increase of vapor pressure. Saturation of film thickness in ethanol vapors was not observed even after 400 minutes while for water it stabilized after ~50-60 minutes.

Remarkably, the swelling properties of GO film remain almost unchanged after 1 year on air storage while the absence of precise selectivity in absorption of ethanol from binary water/ethanol vapor is confirmed.

References.

1. Nair, R. R.; Wu, H. A.; Jayaram, P. N.; Grigorieva, I. V.; Geim, A. K., Unimpeded Permeation of Water Through Helium-Leak-Tight Graphene-Based Membranes. *Science* **2012,** *335* (6067), 442-444.
2. Vorobiev, A.; Dennison, A.; Chernyshov, D.; Skrypnychuk, V.; Barbero, D.; Talyzin, A. V., Graphene oxide hydration and solvation: an in situ neutron reflectivity study. *Nanoscale* **2014,** *6* (20), 12151-12156.
3. Talyzin, A. V.; Hausmaninger, T.; You, S. J.; Szabo, T., The structure of graphene oxide membranes in liquid water, ethanol and water-ethanol mixtures. *Nanoscale* **2014,** *6* (1), 272-281.