EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Study of the interface between ionic liquid and graphene oxide sheet using the Langmuir film procedure	**Experiment number:** SC-5199
Beamline:	**Date of experiment:** from: 14/07/2021 to: 19/07/2021	**Date of report:** 17/02/2022
Shifts:	**Local contact(s):** Oleg Konovaov	*Received at ESRF:*

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Report:

Supercapacitors devices based on graphene sheets (as electrode) and ionic liquid (IL) (as electrolyte) appears as very promising for future energy storage devices. However, their properties are mainly driven by the interface between the two compounds. We use the Langmuir film procedure to elaborates and study such interface. We focus on the Graphene oxide (GO) - [C20mim] [NTf2] IL system (*Figure 1*). Our aim is to obtain first a GO / IL interface and then probe it by x-ray surface scattering (XRR, GIXD and XRF).

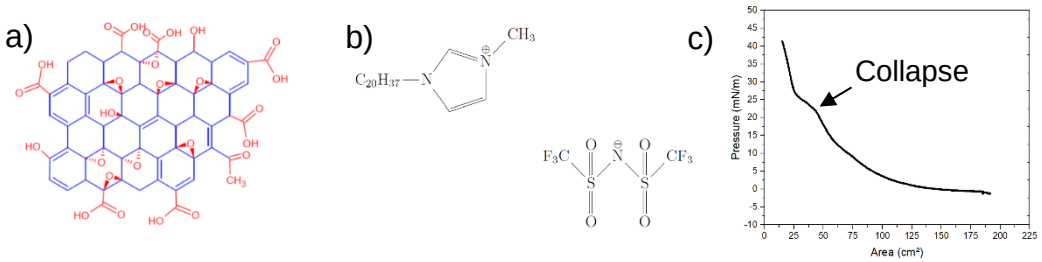

Figure 1 : a) Graphene Oxide (GO), b) Ionique Liquide (IL) : 1-eicosyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and c) Isotherm of mixed GO+IL Langmuir film.

We first studied the film formed by the pure compounds at the air-liquid interface. We have probe, according to the surface pressure, the layers thickness by XRR, the structure by surface diffraction and the amount of compounds adsorbed at the interface by fluorescence. Then, we study mixed film at the air-liquid interface for pressure after and before the plateau of the isotherm (*Figure 1)*. Indeed, this plateau suggest a collapse of one (or both) specie(s). We studied the system for different concentrations.

Pure Ionic liquid:

At low surface pressure (before the collapse of the monolayer) :

- XRR spectra can be adjusted by a single layer of thickness of 15 Å and a rather low density of 1.30 g.cm^{-3}, indicating a not very dense monolayer (*Figure 2 right red curve*).
- No diffraction signal was observed (*Figure 2 left red curve*) indicating a disordered monolayer.

All these results indicates a liquide expensed phase of the IL monolayer.

At high surface pressure (at the end of the plateau) :.

- Fit of the XRR spectra indicates a film thickness of 32 Å, in agreement with a multilayered system.
- Diffraction peaks are orbserved (*Figure 2 left blue curve*) indicating an organization of the chain on a rectangular lattice.

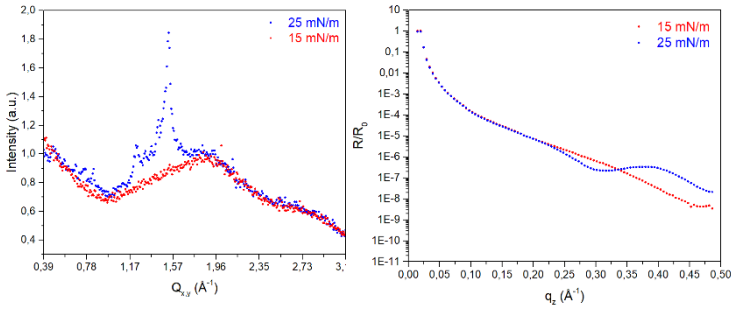

Figure 2 : GIXD (left) and XRR (right) of LI before and after collapse

Pure graphene oxide:

At low surface pressure (before the collapse of the monolayer) :

- XRR spectra can be adjusted by two GO layer, the first one, in contact with water, of thickness of 10 Å and a density of 1.35 g.cm^{-3}, and the second one, above the first one, of thickness of 9 Å but with a density 40% lower than the one of the first layer (*Figure 3 right red curve*).
- No diffractrion signal was observed (*Figure 3 left red curve*) suggesting that the GO sheets density is too weak.

At high surface pressure (at the end of the plateau) :

- XRR indicates that the thickness of layers increase with respect to the increase of the surface pressure (*Figure 3 right blue curve*).
- Diffraction peak of the hexagonal lattice in the GO sheets is observed (*Figure 3 left blue curve*).

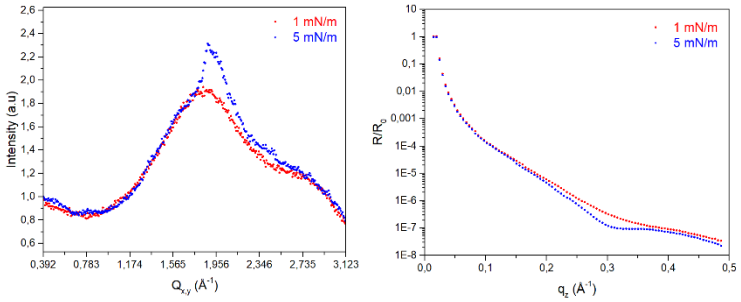

Figure 3 : GIXD (left) and XRR (right) of GO

For mixed of graphene oxide and Ionic liquid film :

At low surface pressure (before the collapse) :

- XRR can be adjusted by a two layers model (*Figure 4 right red curve*). The first layer, in contact with water, have a thickness of 12 Å and a density of 1.2 g.cm^{-3} indicating a pure IL composition. The second layer, above the previous one and in contact with air, have a thickness of 8 Å and a density of 0.88 g.cm^{-3} indicating a GO composition.

At high surface pressure (at the end of the plateau) :

- XRR can be adjusted by a three layer model with the first one of thickness 16 Å and formed by ionic liquid molecules, the second one with a thickness of 9 Å in agreement with the thickness of GO sheets and the third one in contact with air with a thickness of 30 Å (*Figure 4 right blue curve*). The thickness of the first layer increases from 12 to 16 Å with a density of 1.1 g.cm^{-3}.

No diffraction signal is detected (*Figure 4 left curves*) for both pressure. That could be due to a low signal/noise ratio n but a more detailled analysis (varying the q_z integration) will be done

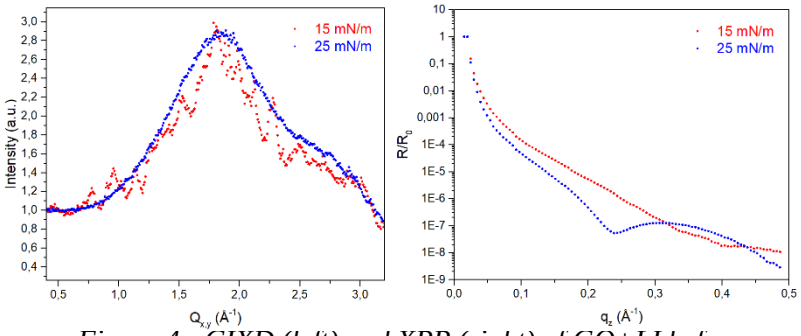

Figure 4 : GIXD (left) and XRR (right) of GO+LI before and after collapse

A model of the film structure is presented on figure 5

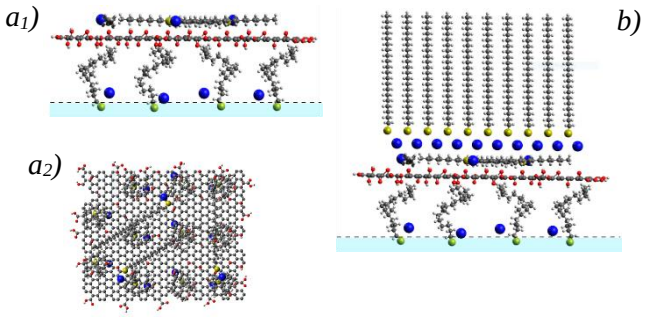

Figure 5 : Illustratyion of the configuratiob of GO+IL stacking at the air-water interface before (a_1 & a_2) and after (b) the collapse

Fluorescence spectra were simultaneously recorded for the differents surface pressure. As one can notice on the spectrum, one can detect a variation of the peaks intensities. This will allows in estimating the variation of concentration of the adsorbed species at the surface,. The sulfure intensity appears weaker after the collapse than before the collapse. This suggest that the [NTf2] do not collapse as much as the [C20mim] molecules.