Experimental report

14/08/2019

Proposal: **EASY-341** **Council:** 4/2018

Title: Internal layer structure a novel lipid/graphene biomembrane superstructure

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Thierry CHARITAT**

Experimental team:

Local contacts: Giovanna FRAGNETO

Samples: 1,2-Dipalmitoyl-sn-glycero-3-phosphocholine

Instrument	Requested days	Allocated days	From	To
D17	24	24	20/09/2018	21/09/2018

Abstract:

Understanding the interactions between lipids and graphene promises to be effective towards measuring experimentally biochemical phenomena within lipid monolayers and bilayers. Our initial results show that the deposition of graphene on a lipid monolayer results in a more ordered and extended monolayer than regions without graphene. The lipid molecules change their conformation in presence of graphene on top, perhaps suggesting that the lipids follow the natural wavy conformation of graphene. Additional studies by Neutron reflectometry helped us to understand the molecular organization within the layered lipid/graphene and lipid/graphene/lipid hybrid monomolecular films. But further insights on how such graphene stabilizes and interacts with lipid monolayers/bilayers will be important to have a successful encapsulation of graphene within a lipid bilayer that could be lifted from their supports without disrupting the lipid-lipid and graphene-lipid interactions.

Experimental Report-Experiment n° 9-13-734

Internal layer structure a novel lipid/graphene biomembrane superstructure

MACEDO Lima[1], MUKHINA Tetiana[2,3], BELYAEVA LIubov[1], ARJMANDI TASH Hadi[1], CHARITAT Thierry[3], SCHNEIDER Gregory[1]

[1] Leiden Institute of Chemistry, Leiden, Netherlands
[2] Institut Laue Langevin, Grenoble, France
[3] Institut Charles Sadron, Strasbourg, France

Local contact: FRAGNETO Giovanna.
DOI: 10.5291/ILL-DATA.EASY-341

1 Context

Graphene is typically supported - sometimes sandwiched - with other two-dimensional (2D) materials to promote higher mobility, to ensure the reproducibility in electrical performances and to prevent environmental contamination [1, 2]. Frequently composed of inorganic, hard and crystalline materials, the so called van der Waals heterostructures have emerged as a route to design new and remarkably complex layer-by-layer films of 2D materials, including graphene [3]. One challenge associated with 2D materials as supporting and sandwiching layers is their limited chemical diversity, functions, and inherent inorganic nature. The possibility of combining graphene with soft, dynamic and molecular self-assembled monolayers is therefore of high interest as an organic alternative to inorganic 2D materials and could provide a versatile platform for applications, such as biosensors, drug delivery systems or cellular devices [4].

Lipids - main constituents of cell membranes - can self-assemble and form stable quasi two dimensional fluid membranes [5]. Lipids can spread on graphene [6], however little is known on the formation, stability and molecular structure of phospholipids molecules surrounding graphene [6, 7]. Mainly, studies focused on graphene oxide (GO), as both lipid vesicles and GO form stable suspensions in aqueous environments [8, 9]. GO is an easily accessible form of graphene, suitable to study the influence of oxidation states on the chemical characteristics of GO-lipid assemblies, at the cost of lower electron mobility, higher chemical reactivity, oxygen doping, and surface/edge inhomogeneities. Being negatively charged, GO has a particular affinity with positively charged lipid head groups [10], highlighting the importance of electrostatic interactions in the assembly process [11]. Pristine graphene, however, does not contain charges on the basal plane therefore minimizing electrostatic interactions and favoring hydrophobic interactions between lipid tails and graphene at the interface [12].

2 Experiments

In this EASY Access experiments on the D17 reflectometer, we have used TOF mode, with a wavelength range from 2 to 20 Å and two incident angles. Samples were prepared by Langmuir-Blodgett and Langmuir-Schaefer techniques using the Langmuir troughs (NIMA611 and NINA121) in the PSCM lab at the ILL. A CVD graphene layer was transferred onto a lipid monolayer by bringing it into contact with graphene floating on ammonium persulfate solution (APS) as described in [13]. The second monolayer of the bilayer system was deposited on top the the DSPC-graphene assembly by LS technique.

We have investigated 3 different samples : (i) 2 samples consisting of a graphene layer inserted in a DSPC supported bilayer at the solid/liquid interface; (ii) one reference DSPC supported bilayer. Samples were characterized in 3 contrasts to enhance the resolution.

3 Results

3.1 Hybrid graphene-trilayer system

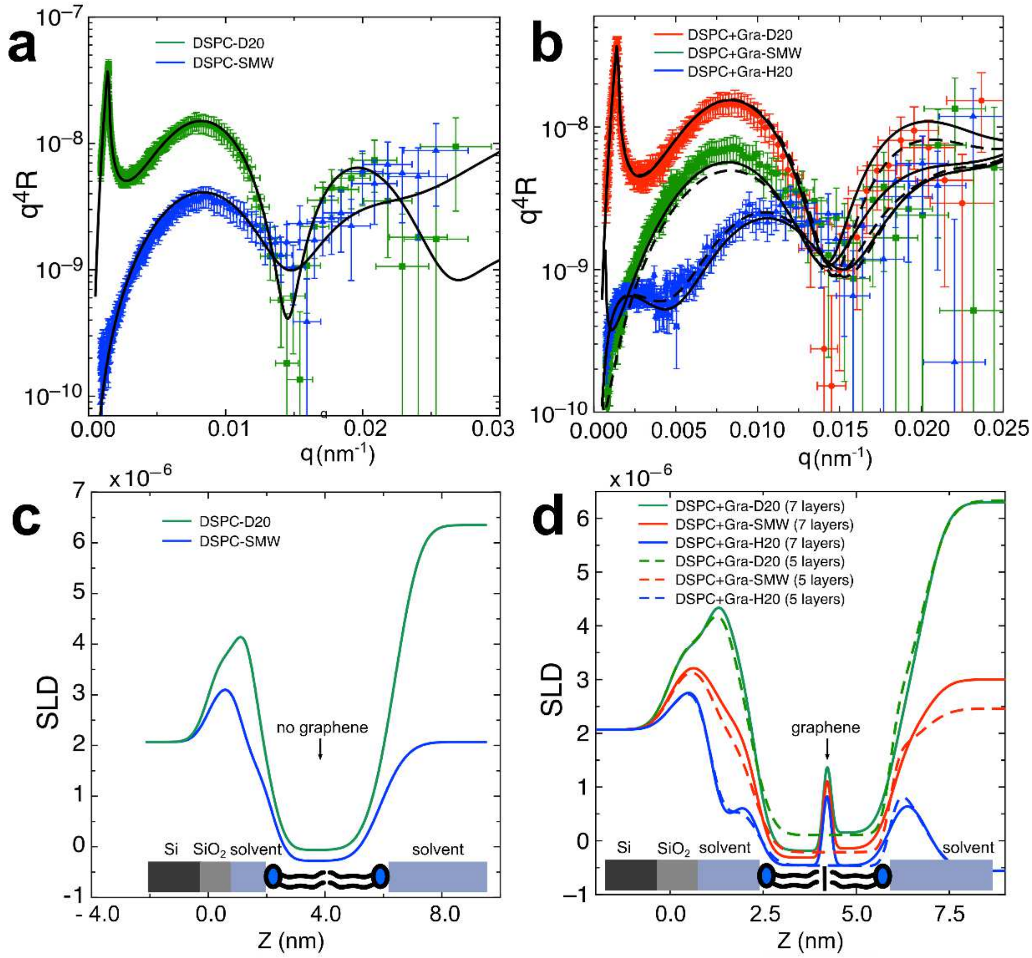

Figure 1: a) Neutron reflectivity profiles displayed as Rq^4 vs q (where R is the reflectivity and q is the wave vector transfer) from a DSPC bilayer at 25°C in D_2O (green line) and silicon matched water (SMW, blue line). b) Neutron reflectivity profiles from a DSPC bilayer at 25°C with inserted graphene in H_2O (blue), SMW (green) and D_2O (red). The black lines correspond to the best fit to the measured data and the dashed black lines correspond to a fit of the bilayer without graphene. c) SLD profiles corresponding to the fits of the data in a). d) SLD profiles corresponding to the fits of the data in b). The dashed black lines correspond to a model of the bilayer without graphene.

We were able to characterize an hybrid DSPC-graphene-bilayer in both gel (T=25°C) and fluid (T=60°C) phases and in 3 contrasts: D_2O, SMW and H_2O with good statistics. Data in gel phase and best fits are shown in Fig. 1. The results are very interesting: (i) the off-specular signal is very low, indicating that the sample is laterally homogeneous and that the graphene does not affect the bilayer dramatically; (ii) the reflectivity data are compatible with a model assuming the presence of a graphene layer in the bilayer (see Fig. 1).

4 Conclusion

The main objectives of this EASY Access experiment was to determine with high resolution the structure of hybrid lipid/graphene systems. Although the analysis of reflectivity data is consistent with the presence of a graphene layer between the two lipid leaflets it does not provide an unequivocal evidence as data can be fitted also with a model excluding this layer. Nevertheless it clearly demonstrates that the integrity of the bilayer is preserved after inclusion of graphene. A publication entitled *Encapsulation of graphene in the hydrophobic core of a lipid bilayer* by Lia M. C. Lima, Liubov A. Belyaeva, Hadi Arjmandi-Tash, Tetiana Mukhina, Giovanna Fragneto, Alexander Kros, Thierry Charitat, and Grégory F. Schneider will be submitted soon.

References

[1] K. S. Novoselov et al, *Science*, 306, 666-669 (2004).
[2] L. Wan et al, *Science*, 342, 614-617 (2013).
[3] A. K. Geim and I. V. Grigorieva, *Nature*, 499, 419-425 (2013).
[4] A. C. Ferrari et al, *Nanoscale*, 7, 4598-4810 (2015).
[5] G. van Meer et al, *Nature Rev. Mol. Cell. Biol.*, 9, 112-124 (2008).
[6] M. Hirtz et al, *Nature Commun.*, 4 (2013).
[7] Y. Y. Wang et al, *ACS nano*, 8, 4228;4238 (2014); P. K. Ang et al, *ACS nano*, 4, 7387-7394 (2010); L. S. Connelly et al, *ACS Appl. Mater. Interf.*, 6, 5290-5296 (2014); K. Yamazaki et al, *J. Phys. Chem. C*, 117, 18913-18918 (2013); Y. Tu et al, *Nature Nanotechnol.*, 8, 594-601 (2013); B. Luan et al, *Nanoscale*, 8, 5750-5754 (2016).
[8] H. P. Boehm et al *Z. Anorg. Allg. Chem.*, 316, 119-127 (1962).
[9] W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 80, 1339-1339 (1958).
[10] S. H. Li et al *J. Phys. Chem. B*, 117, 16150-16158 (2013).
[11] R. Frost et al, *Nano Letters*, 12, 3356-3362 (2012).
[12] L. Rodriguez-Perez et al, *Chem. Commun.*, 49, 3721-3735 (2013).
[13] L. Lima et al, *Nanoscale*, 8 (44), 18646-18653 (2016).