Experimental report

24/06/2022

Proposal: **6-07-72** **Council:** 4/2020

Title: SANS CHARACTERIZATION OF PILLARED GRAPHENE-BASED MATERIALS FOR SUPERCAPACITORS

Research area: Materials

This proposal is a new proposal

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Samples: graphene samples (Carbone in majority, H, N, O)

Instrument	Requested days	Allocated days	From	To
D22	2	2	25/05/2021 24/06/2021	26/05/2021 25/06/2021

Abstract:

The aim of the proposal is to investigate the hierarchical porosity within pillared graphene-based materials for supercapacitors as well as the polarization driven electrolyte ions adsorption (tetraalkylammonium cation-tertafluorofoborate anion in acetonitrile as electrolyte).
We want
(i) to gain a deeper understanding of the complex nanostructure of these composite materials (bridged and graphitic components), using hydrogenated or deuterated pillars to disentangle the different contribution,
(ii) to demonstrate the electrosorption of electrolytic ions by comparing their localization within the different porosities before and after polarization, taking advantage of the sensitivity of neutrons to H and B.
(iii) to compare the effect of static vs alternative polarization on the sample nanostructure.
This SANS experiment will shed light on the ion adsorption/electrowetting processes in such multiscale composite materials and will allow gaining better understanding of ion sorption for optimizing the design of these promising materials, serving as model systems to probe structure-property relationships for a wide range of applications (energy storage, filtration, separation).

SANS characterization of Pillared Graphene-based Materials for Supercapacitors

Experimental team: Hakima MENDIL-JAKANI, Florence DUCLAIROIR, Yassine BEN CHERIFI.

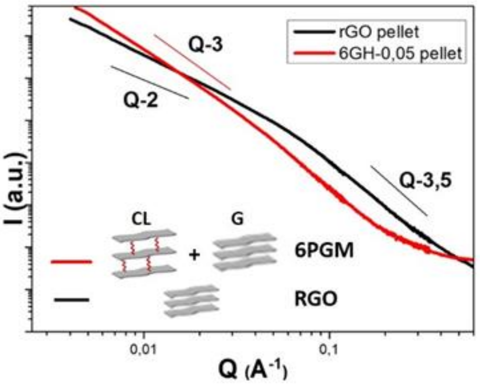

Fig. 1 SAXS profile of RGO (black) and 6PGM (red) with a scheme of their local structures

The aim of the present study was to investigate the **morphology** and the **hierarchical porosity** of **pillared graphene materials** (PGM) for supercapacitors (SC) and energy storage applications. **Graphene based materials** are studied for SC as they –theoretically- display **large surface area** to maximize the number of adsorbed ions together with a **hierarchical porosity** to favor ions diffusion. However, experimentally the achieved capacitance (C_{SP}) remain limited because graphene sheets tend to re-aggregate. Our group succeeded in limiting this issue by **bridging/cross-linking** and separating the sheets using aliphatic diamine pillars resulting in an expanded graphene structure[1,2], called **pillared graphene material (PGM).** WAXS analysis was performed to give evidence of the expanded structures (d_{CL} spacing value of the cross-linked arrangements) and showed that they coexist with partially stacked graphene sheets (d_G) (biphasic material, **Fig.1.a)**. SAXS profile (**Fig.1.b**) recorded for the reference reduced graphene oxide (RGO, grey), revealed an extended small angle Q^{-2} behavior, which is the signature of 2D objects (lamellae of long graphitic-like particles). At larger angles, a ~$Q^{-3.5}$ Porod’s law was observed indicating rough interfaces between air and particles. The SAXS profile of the **PGM** displayed a steeper **Q^{-3} slope** in the small angle range (red) which can be attributed to **mass fractal scattering.** Although those preliminary SAXS data gave useful structural information on the architecture of graphene-based material, **only neutrons can provide insights on the density of the solid phase** and on the proportion of **open vs closed pores at different length scale**.

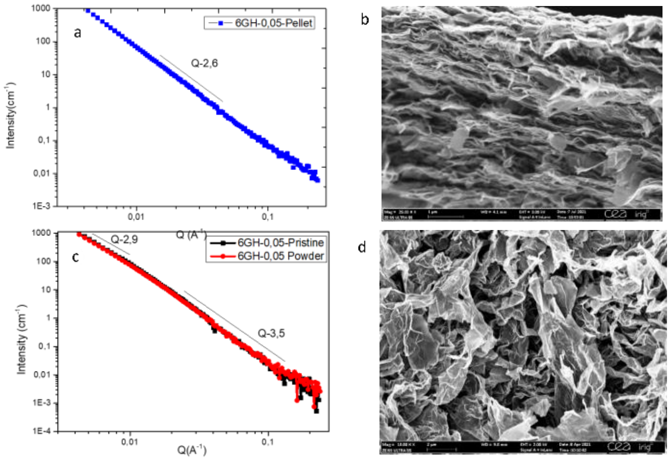

Fig. 3 (a) SANS profile of 6GH-0.05-pellet (b) SEM image of the pellet profile of 6GH-0.05 (c)

Samples preparation: Pillared and references materials were prepared using two different synthesis methods (reduced powders and hydrogels). PGM are labeled: X-RP-Y for reduced powders and X-GH-Y for graphene hydrogels with X being the number of C atoms in the alkyldiamine pillar and Y the equivalent number of the pillar. Specifically the following reference samples have been studied: RGO and GHG and the following PGM materials: 6GH-0.05, 6RP-0.2.

<u>Contrast variation SANS (CV-SANS)</u>: PGM and reference materials (pellets and pristine) were immersed in acetonitrile (ACN) and deuterated acetonitrile (d-ACN) or a mixture of both (0/100, 20/80…) for 24h and 4 days, in order to vary the contrast between the solid phase and the solvent. Theses CV-SANS studies have been performed on the following samples: rGO, 6GH-0.05, and 6RP-0.2.

Main results: *Morphology investigation using SANS:*

SANS profiles recorded on hydrogels (pellets) show one slope $\mathbf{Q^{-2.6}}$ (**Fig 3.a**) which is the signature of mass fractal scattering characterized by high degree of branching points and crosslinks. No slope break was noticed which mean that we observe always the same fractal structure, because of the material pressing to form pellets. These observations were confirmed by SEM images showing stacked wrinkled graphene sheets on a large length scale (**Fig 3.b**). On the other hand pristine (powder) materials (**Fig 3.c**) show two slopes with a slope break assigned to a persistence length. This was confirmed by SEM images (**Fig 3.d)** displaying crooked 2D graphene sheets forming a 3D network.

Contrast variation: Six mixtures of acetonitrile (ACN) and deuterated acetonitrile (d-ACN) (SLD varies from 1.13 to 4.89 10^{10} cm^{-2}) were selected as they cover the SLD calculated using the density of **<u>pellets</u>** measured by He pycnometry. For all samples (references and pillared materials, pristine and pellets) a decrease in the scatteredintensity was noticed with increasing the proportion of d-ACN. However, no matching was observed (see **Fig.3.b**, $I^{0.5}$ vs %(d-ACN) : the intensity never vanishes).

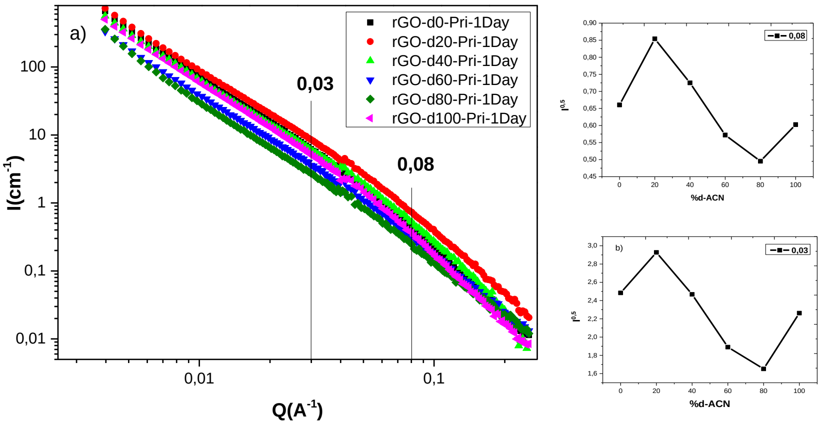

Fig. 2 (a) CV-SANS on RGO pellet in ACN/d-ACN mixtures (immersed 1 day) (b) $I^{0.5}$ vs %(d-ACN) at Q=0.03 A^{-1} and Q=0.08 A^{-1}

The mismatching was tentatively assigned to (i) wettability issues of the pores of different sizes and accessibility; (ii) an underestimated density of the pellets, measured by He pycnometry and used for SLD calculation. Indeed, the processing of pellets is probably associated with the closure of porosities which become inaccessible to the solvent.

After this first SANS run, the material density was measured using pristine materials (powder-like) rather than pellet densities. The associated SLDs are higher (6.2 10^{10} cm^{-2}< SLD< 6.9 10^{10} cm^{-2}). For further CV-SANS experiments, mixtures of **cyclohexane/d-cyclohexane** (SLD varies from -0.28 to 6.8 10^{10} cm^{-2}) will be used instead of ACN/d-ACN to address the issues of open vs closed porosities at different length scales, kinetics of pores wettability …

<u>References :</u>

[1] M. Salanne, *et al, Nat. Energy* **2016**. [2] H. Banda, *et al, J. Power Sources* **2017**.