ESRF	**Experiment title:** Large scale structure of aligned carbon nanotubes membranes	**Experiment number**: MA/958
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Report:

1. Context

Conception of well-controlled nanoporous membranes is a central issue for the developing of chemical separation, drug delivery and wastewater remediation systems [1-3]. Numerous approaches are being investigated, including mesoporous macromolecular architectures and ordered alumina [4]. Nevertheless there is a major challenge: improving the selectivity of the membrane especially by controlling the pore size of the porous structure. This is a particularly difficult challenge in the 1- to 10-nm size range.

Here, we chose to impregnate an aligned nanotube network (named 'carpet') with a polymer to produce such a membrane (FIG. 1). Carbon nanotube carpets are macroscopically ordered systems made of parallel tubes with controlled inner hollow cores e.g. pore diameter. Our objective in the present experiment was to quantify the degree of alignment and the distribution in tube diameters for (i) raw nanotube carpets made under different synthesis conditions (varying synthesis parameters), (ii) carpets after temperature treatment aiming at removing catalyst nanoparticles present inside the nanotubes and (iii) membranes - after polymer impregnation, for two different polymers: epoxy and polystyrene.

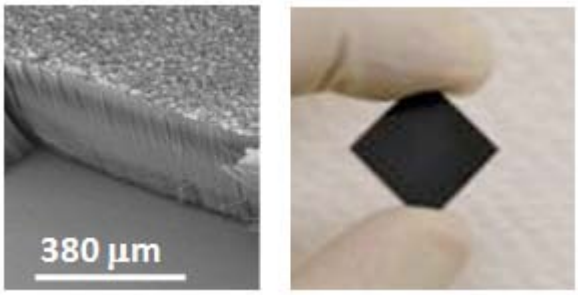

FIG. 1 : *Left: a* carbon nanotube carpet, made of oriented - hundreds of microns long - parallel cylindrical tubes. *Right:* a nanotube membrane (CEA-Saclay). At the end of the polymer impregnation process, it has been mechanically polished leading to a network of open tubes with a final thickness of ~ 100 µm.

2. Experimental

Measurements were performed on the BM02 beamline at energy of 8 keV. We realized two kinds of measurements. The first one consisted in measuring the small angle X-ray scattering signal of our carpets (as-grown and after annealing) and membranes with a sample changer, for two sample orientations, namely for nanotubes parallel to the X-ray beam or rotated by 45°. We studied 4 changers of 18 samples each, i.e. about 70 samples, in the two orientations, to quantify the anisotropy of the scattering for each sample. For the other experimental configuration, we used a goniometer head to finely tune the orientation of the nanotubes with respect to the X-ray beam, in order to be able to refine precisely the values of nanotube diameters from the recorded data.

3. Results

We studied carpet and membrane samples, corresponding to different synthesis conditions, and thus a priori to different diameters and different orientational distributions of the nanotubes. Recorded data are of good quality and after their complete fitting, we should have new results that will help us to understand the role of synthesis conditions and the effect of impregnation by the polymer (epoxy or polystyrene) on tube alignement and tube diameter. It is a pre-requisitive to elaborate membranes adapted to desired goals. Fit of the data is in progress but the first results are promising as shown below.

Concerning nanotube alignement, recorded images in the two configurations used with the passer changers (nanotubes parallel to the X-ray beam or rotated by 45°) are shown: anisotropy is clearly visible.

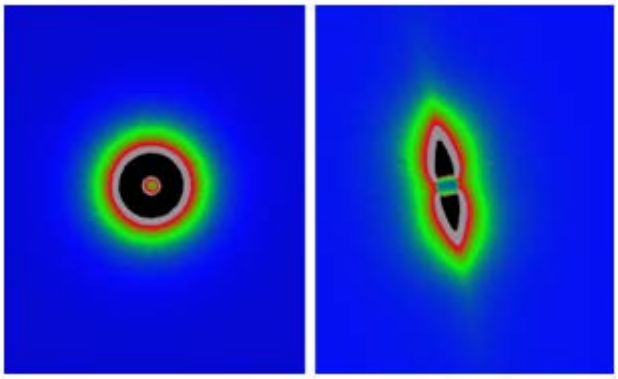

FIG. 2 : *Left:* Isotropic image (mean nanotube axis parallel to the X-ray beam)
Right: Anisotropic one (45° between mean nanotube axis and the X-ray beam)

X-ray scattering diagrams of a raw carpet and of the corresponding membrane, after high temperature treatment, polymer embedding and final polishing step, are reported in FIG. 3. No clear oscillation is visible for the raw carpet while two minima can clearly be identified in the case of the membrane. This first result is very encouraging because it shows that the change in contrast brought by (i) the presence of the polymer

matrix and (ii) the removal of catalytic particles inside nanotubes does allow us to measure intensity oscillations, which should then allow us to determine the nanotube diameter distribution.

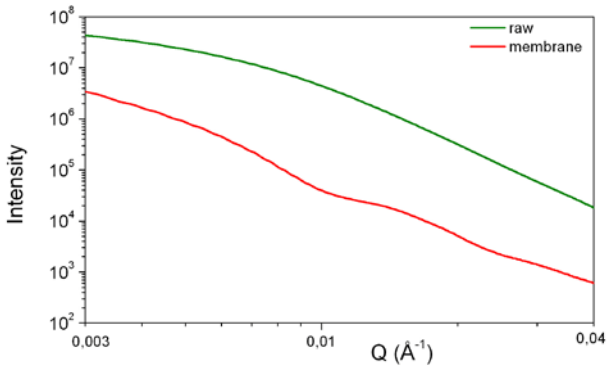

FIG. 3 : Small angle X-ray scattering diagrams of a raw carpet and of a membrane.

[1] B. J. Hinds et al., Science 303, 62 (2004)
[2] M. Majumder, N. Chopra, R. Andrews, B.J. Hinds, Nature 438, 44 (2005)
[3] J.K. Holt et al., Science 312, 1034 (2006)
[4] J. T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, Nature 402, 867 (1999)