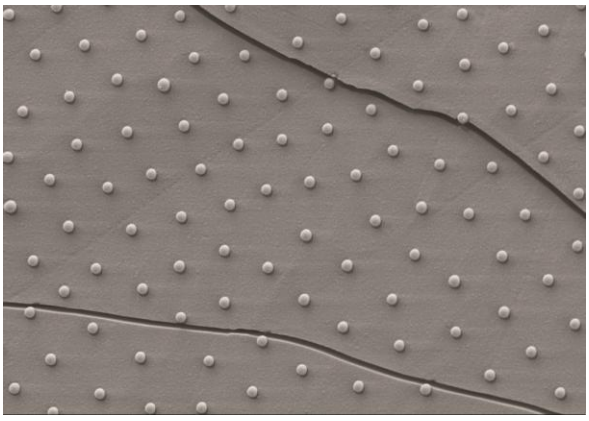
1. PUBLISHABLE SUMMARY MC-IEF-252926 (SALINAME)

The autonomous organization of micro- and nanoparticles (MP/NP self-assembly) is a process with huge potential for robust, cost-effective and parallel fabrication of materials whose macroscopic properties and structure are controlled by the properties of their nano(micro)-constituents. MPs and NPs can be used as additives to improve the performance of existing materials (e.g. mechanical strength, thermal properties) but they can also be used as the building blocks to obtain new materials and impart them additional properties (e.g. optical, electrical, magnetic). Despite the upsurge in the synthesis of novel and increasingly more sophisticated types of MPs and NPs, large scale demonstration of their use as building blocks for self-assembled materials is currently falling short of our expectations. The main obstacle to rapid progress is the fact that many aspects of the fundamental behavior on MPs and NPs during self-assembly are to date still not fully understood and hold the key to true control of material fabrication. Therefore, true progress in material fabrication can only be achieved after such fundamental knowledge is disclosed. This statement is especially true for ultra-thin, two-dimensional (2D) materials obtained by MP/NP self-assembly at the interface between two liquids, where many basic aspects remain to date unexplored. 2D materials find vast use in a host of technological applications ranging from biomaterials and microelectronics to optics, solar cell technology and drug delivery. On the other hand, liquid interfaces (as for instance the interface between water and an immiscible solvent, e.g. oil) constitute and ideal *locus* for 2D self-assembly: MPs and NPs can be trapped at the interface and interact to spontaneously form 2D structures.

The main objective of this project was to shed light on the fundamental properties of NP self-assembly at liquid interfaces, with the aim to pave the way for the fabrication of ultra-thin nanoparticle membranes obtained by *in situ* crosslinking after self-assembly.

The main result of this project has been the development of a novel method to measure the properties of individual NPs directly and *in situ* at a liquid interface. The technique is based on a development of freeze-fracture, shadow-casting (FreSCa) cryogenic scanning electron microscopy (cryo-SEM) and it pushes the boundaries of pre-existing techniques down of two orders of magnitude, making it possible to measure for the first time the three-dimensional position (and thus the wetting properties) of individual NPs as small at 10nm *in situ* at the interface between oil and water (see figure). This major result, published in *Nature Communications*, has attracted great interest in the scientific community and spawned several international collaborations. In particular it enabled the possibility to answer both fundamental and applied open questions, e.g. in relation to emulsion stabilization, charge and shape effects in NP wetting, as well as disclosing the presence of significant heterogeneity in the NP wetting properties which have important consequences in directing material fabrication.



FreSCa cryo-SEM of 200nm polysyterene NPs at the water/oil interface

Another important objective reached in this project has been the detailed study of the behavior of composite NPs at liquid interfaces. In particular we focused our attention to iron oxide NPs surrounded by a thick polymer shell which constitute an ideal model system for the self-assembly of membranous materials. Before proceeding to cross-linking such interfacial assemblies into mechanically stable membranes, we realized that several basic questions needed to be answered first. In particular optimization of the time scales for NP adsorption, determination of the NP arrangement and the conformation of the polymer shell at the interface are all key issues which have to be answered before proceeding to material fabrication. We successfully investigated these aspects by a combination of novel experimental approaches (entailing also measurements at the EU synchrotron facility ESRF), numerical simulations and theoretical modeling in collaboration with other research groups. The main outcomes of these investigations relate to the fact that we highlighted a significant deformation of the polymer shells at the interface which has direct consequences on cross-linking strategies and that time scales for NP adsorption are affected by collective dynamics of the particles already residing at the interface.

The results obtained in this project have high relevance in the broad field of Soft Matter Science and Materials, both as they have contributed to significantly further our fundamental knowledge in NP self-assembly at liquid interfaces and as they clarified practical aspects necessary to convert such basic knowledge into real applications. Given the present status of this research, it is expected that in the near future the first demonstrations of cross-linked NP membranes obtained by self-assembly at liquid interfaces will be produced. In addition to the scientific results, this project has also enabled great personal and professional development of the grantee. Dr. Isa has been able to experience a top research environment, intellectual freedom and has had the possibility to supervise students and write research grants. Currently he holds a prestigious Senior Researcher Fellowship of the Swiss National Science Foundation, to obtain which this Marie Curie Fellowship played an instrumental role. This research work has also enabled extensive scientific communication across European countries and the US, favoring the establishment of a precious network of collaborations and increasing the visibility of EU research in Soft Matter Science. The results of the projects have been made available through several publications in international peer-reviewed journals and have been disseminated to the scientific community through seminars and presentations at international conferences and to the general public on the host institution’s dedicated webpage. Finally, the positive reputation achieved by Dr. Isa at the end of this fellowship made it possible for him to be nominated as a participant to the Global Young Scientists Summit (Singapore 20-25.01.2013) where he will meet other young researchers from across the world to discuss the impact that science can have on global development.