

Controlled deposition of carbon nanotubes within a smectite nanoclay by means of a modified Langmuir-Schaefer approach

A. Kouloumpis¹, P. Zygouri¹, K. Spyrou^{1,2}, T. Tsoufis², P. Stathi², P. Rudolf² and D. Gournis¹

¹ Department of Materials Science and Engineering, University of Ioannina, 45100 Ioannina, Greece

² Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747AG Groningen, the Netherlands

Much of the research effort concerning the nanoscopic properties of layered materials focuses on their use as building blocks for the development of new hybrid nanostructures with well-defined dimensions and behaviour. The objective of this work is the synthesis of a new type of clay-based hybrid materials for application in gas storage/separation, heterogeneous catalysis and sensing: nanometer-sized clay platelets are sandwiched with carbon nanotubes through layer-by-layer deposition and intercalation chemistry to yield novel pillared carbon nanotube-clay structures.

A bottom-up approach (Fig. 1) was applied for the production of hybrid materials where smectite clay nanoplatelets act as the structure-directing interface and reaction media. This method, based on combining self-assembly with the Langmuir Schaefer technique [1], uses the clay nanosheets as a template for the grafting functionalized carbon nanotubes in a bi-dimensional array, and allows for perfect layer-by-layer growth with control at the molecular level.

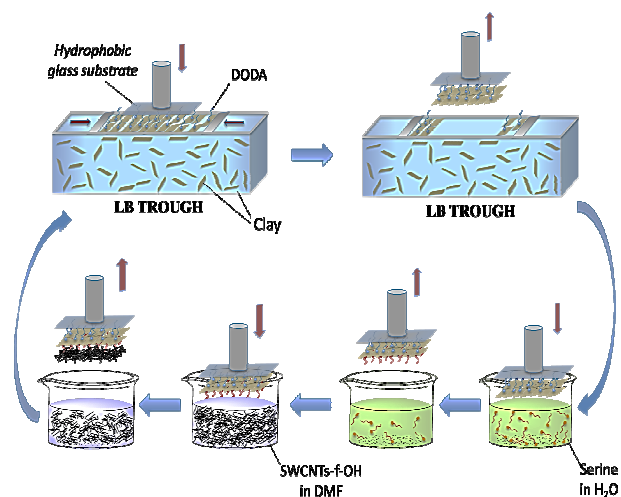


Fig. 1. Schematic representation of the synthetic procedure

Initially, CNTs were functionalized with phenol groups via 1,3-dipolar cycloaddition in a single step using commercially available reagents [2]. Sidewall functionalization provided stable dispersions of CNTs in water and other polar solvents. A dilute water solution of clay was used as subphase on the Langmuir-Blodgett deposition system while an appropriate amino surfactant (that binds electrostatically to the clay surface) was applied for the formation of hybridized organo-clay. After the horizontal lift of a hydrophobic substrate, a surface modification of the clay platelets was performed by

bringing the surface of the transferred Langmuir film in contact with a second amino surfactant solution (capable of interacting strongly with the functionalized nanotubes). In the final step, the hybrid organo-clay film was lowered in the solution of the functionalized CNTs. Multilayer films were constructed by repeating this procedure.

Hybrid clay/CNT thin films deposited on various hydrophobic substrates were characterized by X-ray diffraction (XRD) and reflectivity (XRR), FTIR, Raman and X-ray photoelectron spectroscopies as well as Atomic Force Microscopy.

[1] LM Toma, RYN Gengler, EB Prinsen, D Gournis and P Rudolf. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12188

[2] RYN Gengler, D Gournis, AH Aimon, LM Toma and P Rudolf. *Chem. Eur. J.* **2012**, *18*, 7594.

[3] V Georgakilas, A Bourlinos, D Gournis, T Tsoufis, C Trapalis, A Mateo-Alonso and M Prato. *J. Am. Chem. Soc.* **2008**, *130*, 8733