# Tailoring the morphology and properties of carbon-based materials by *in situ TEM*

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In the actual context of the fast development of nanotechnologies, the industry is confronted with the production of materials and structures with well-defined sizes, geometries and morphologies. The carbon-based structures like graphene, carbon nanotubes (CNTs) and nanofibers (CNFs) are promising candidates for the development of nanodevices which strongly demand for a close control of materials properties at the nanoscale at each step of synthesis, manipulation and further implementation in the process. Owing to the high resolutions developed achieved by transmission Electron Microscopy (TEM), the recent development of the associated in-situ methodologies allow to follow the evolution of nanomaterials from the early synthesis stages up to their functioning under operation conditions. In this work, two in-situ TEM methodologies are employed. The first one, the gas assisted environmental approach is employed for the controlled "synthesis" of CNFs by nano-patterning of Few Layer Graphene (FLG) sheets, whereas the STM-TEM in-situ approach permits to take advantage of the CNTs conduction properties to design an original methodology for a nano-printing/erasing experiments.

The in-situ Environmental TEM as developed in an adapted closed cell (E-cell) allows to perform real time observations of materials evolution under gaseous environments in the high temperature/pressure ranges at with the atomic resolution. The nanopatterning of FLG has the potential of creating nanosheets with well-defined shapes and edge configurations which can be transformed in single-layer GNRs by simple techniques as for instance the chemical exfoliation. To initially characterize the channeling process and the obtained nanostructures we used a system consisting in $Fe_3O_4$ nanoparticles dispersed onto FLG sheets, which has undergone an ex-situ heating treatment (800°C) in $H_2$ atmosphere. The TEM-based results give extensive 2D and 3D insights on both the cutting process and the properties of the nanostructures obtained by catalytic nanopatterning [1]. The in-situ E-TEM methodology was further employed to re-create the very same nano-patterning conditions in an effort to accede to finer patterning characteristics such as the cutting speed or the correlation between the channels directions and the catalysts crystallographic orientations [2]. Indeed, the possibility of building up appropriate experimental conditions allowed to advance the cutting mechanisms by considering the behavior of a complex NPs/FLG support system in the high temperature/pressure conditions and a hydrogen environment.

The scanning tunneling microscope (STM) is an attractive alternative to move single atoms with incredible precision, but this approach is not adapted for assembling nanodevices with thousands of atoms. The use of CNTs as "nanopipetts" able to transport femtograms of mass to predefined spots can be envisaged, an approach based on the Joule assisted electromigration phenomenon, when a high current pass through a metal phase encapsulated inside a CNT. We propose here a highly precise method for delivering nanoparticles (NPs) to the graphene and few-layer graphene (FLG) edges and surfaces using a CNT filled with $Fe_{3-x}O_4$ NPs as a nanopipette. The experiment is realized inside a TEM by using a STM-TEM holder allowing high precision sub-nanometer movement and high voltage supply. A nanoprinting-like experiment highlights the possibility to deposit NPs on the surface of a FLG sheet with a radial distribution relative to the CNT/FLG contact point, or to control the NPs deposition at the FLG edge. The in-situ TEM observation of the experiment has made possible a real time analysis of the structural and chemical properties of both the NPs and the supporting CNT.

The STM-TEM approach can be extended to the CNFs synthesized by the E-TEM methodology in order to get a complete and close control of the sizes, morphologies, NPs distribution and location within the composite systems to be utilized for specific nanodevices.

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