Microwave and Ultrasound Carbon Nanotubes Functionalization

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Microwaves and Ultrasound for Carbon Nanotubes (CNT) Functionalization

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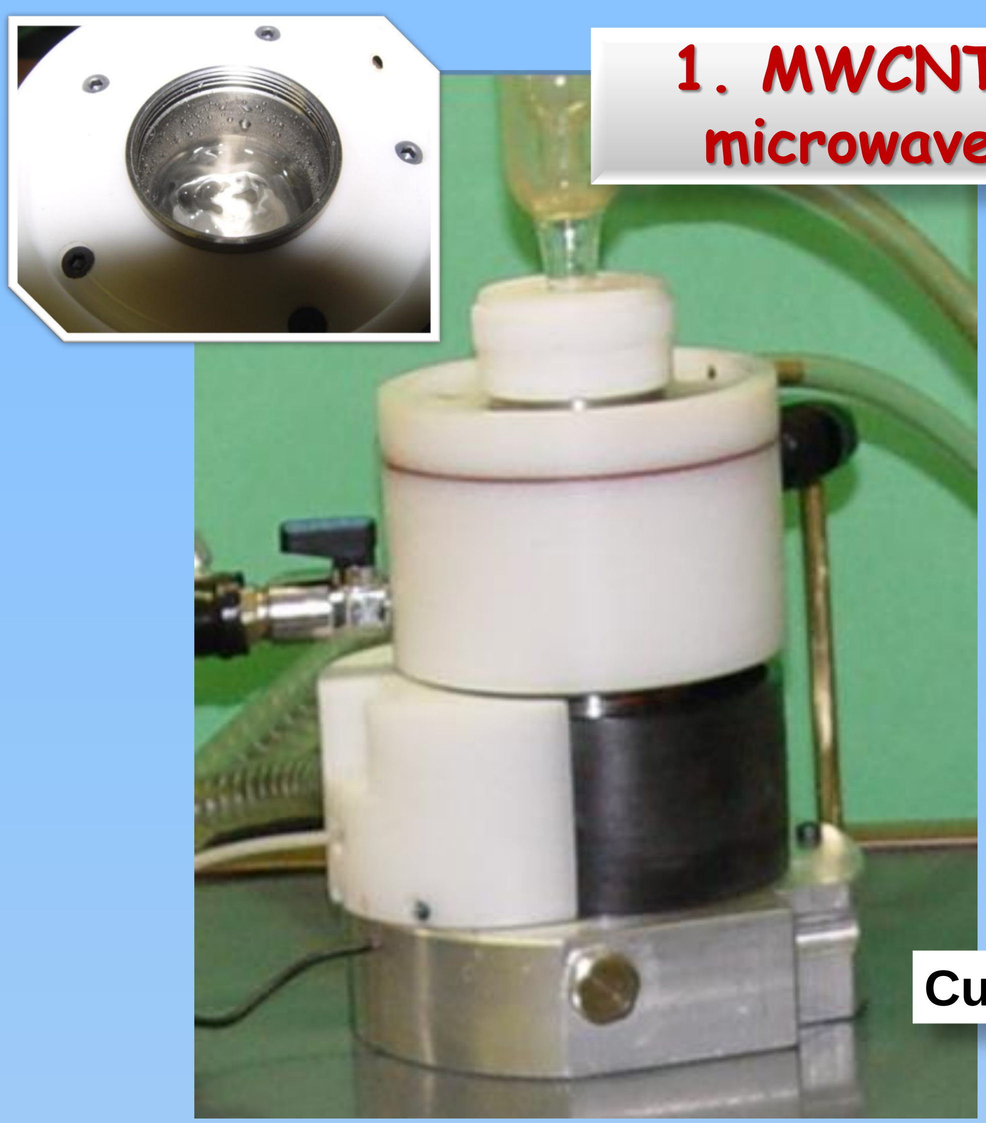
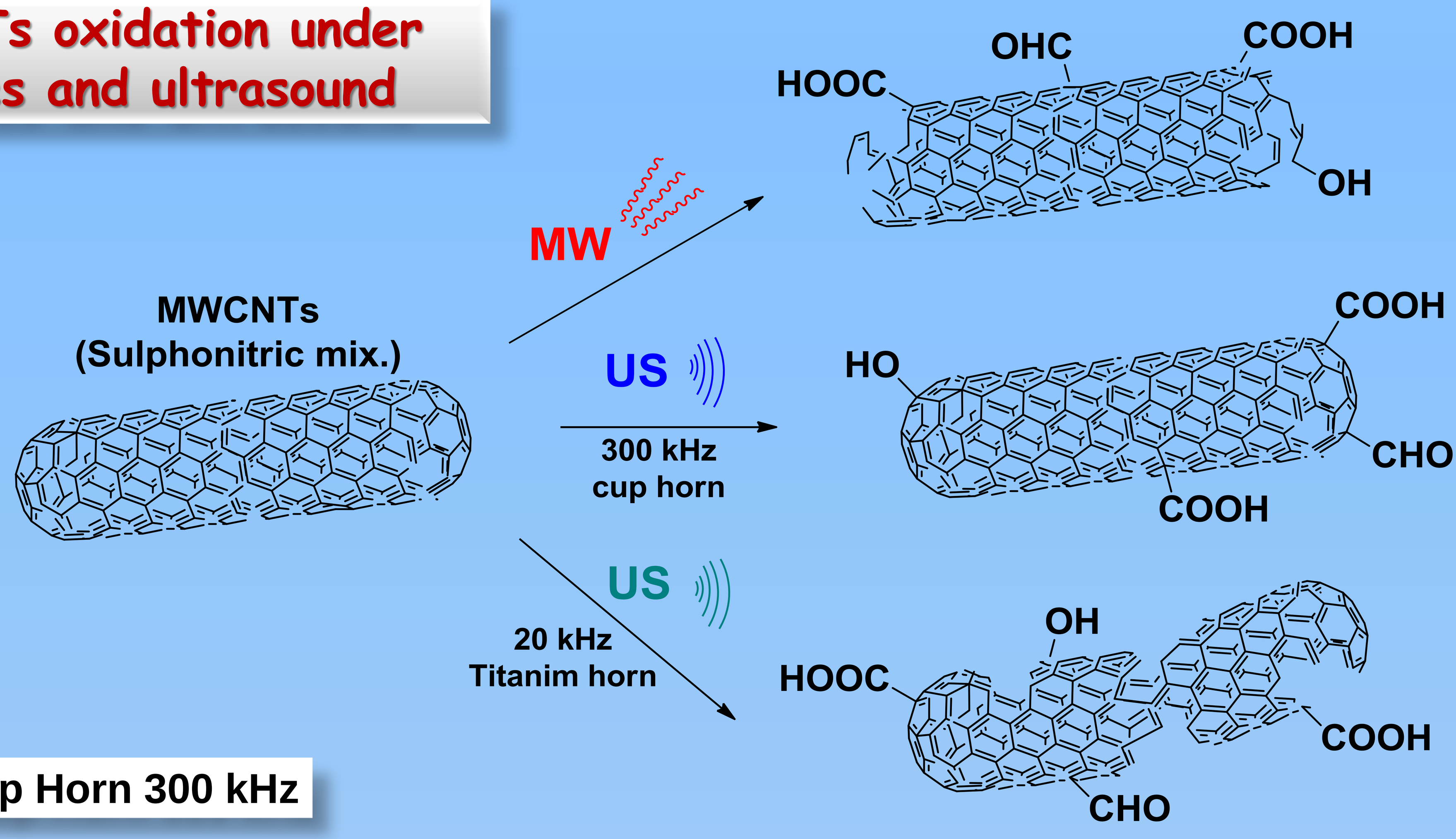
The use of ultrasound (US) and microwaves (MW) in the oxidation and purification of multi-walled carbon nanotubes (MWCNTs) was investigated. These techniques, in particular US at a frequency of 300 kHz, strongly accelerate the process and avoid the heavy structural damage, observed at the 20–35 kHz classic range, even at low power. Due to the residual metal catalyst on the head of MWCNTs, MW heating is strongly absorbed, causing the rupture of the tip and the loss of the metal. All our chemico-physical treatments were performed by suspending the CNTs in a 3:1 H_2SO_4/HNO_3 mixture. The resulting samples were investigated by TEM microscopy, TGA analyses and Raman spectroscopy, while the degree of oxidation was estimated by colourimetric analyses. The aim of our project was mainly focused on the development of new synthetic procedures for the functionalization of CNTs bearing imaging reporters and specific drugs to be used as a teragnostic probe. For this scope, the CNTs surface was chemically modified under ultrasound and/or microwave irradiation.

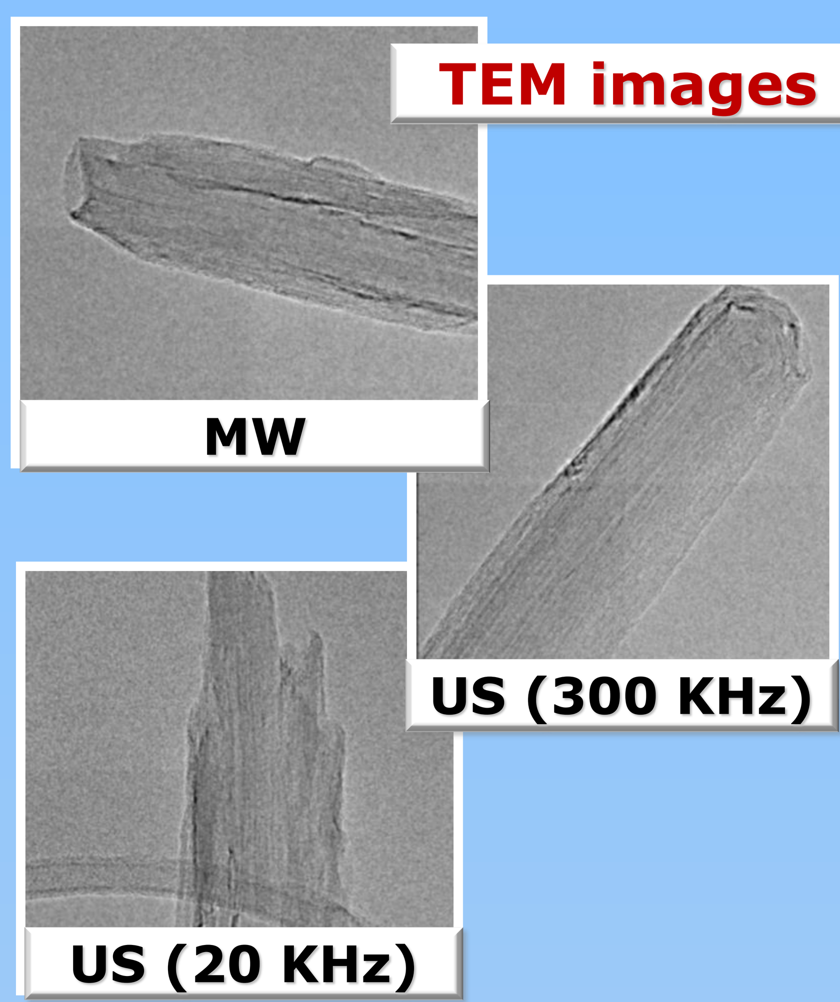
1. MWCNTs oxidation under microwaves and ultrasound



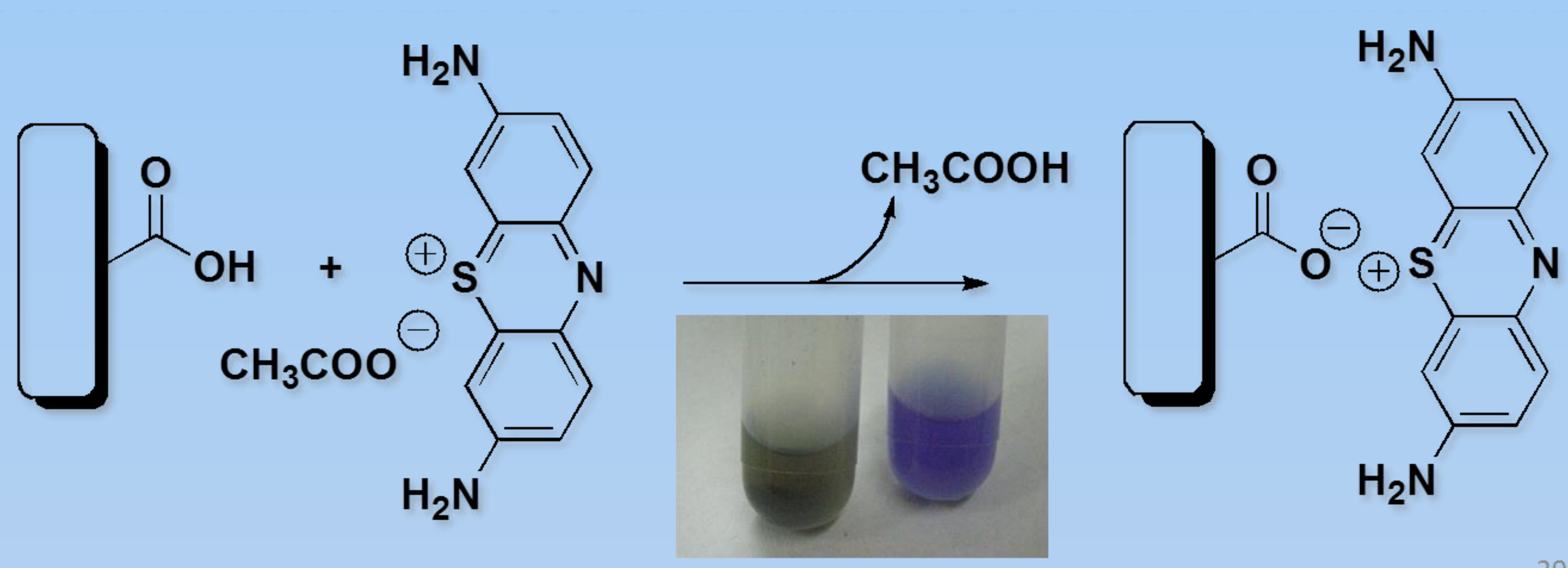
Cup Horn 300 kHz



TEM images

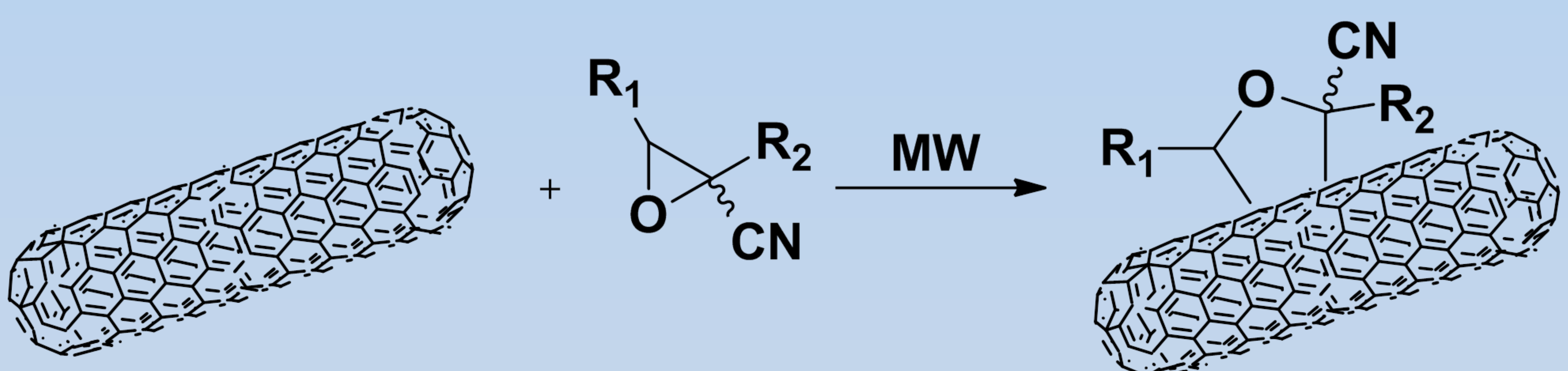


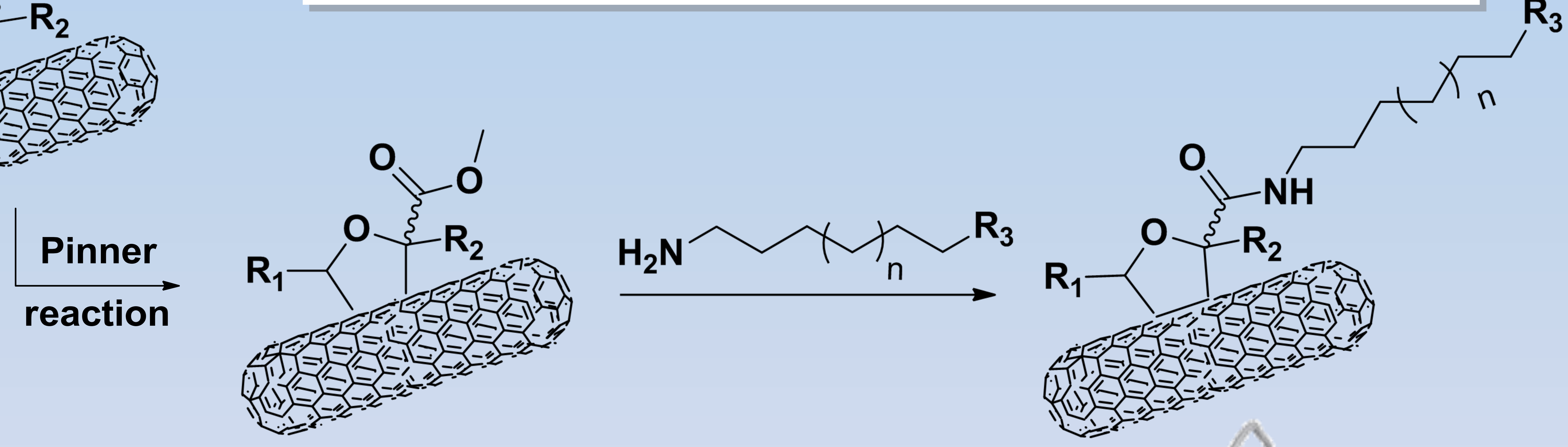
Colourimetric Analyses: Thionin Acetate (THA) EtOH solution (4.3×10^{-6} M)
1:1 ratio (THA cation:oxidized CNT carboxylic groups)



1. The exceptional interest in single- and multi-walled CNTs (SWCNTs and MWCNTs) resides in their possible technological applications in many fields. In particular, the potential applications of CNTs in medicinal chemistry are of great interest, because of their capacity to interact with macromolecules such as proteins and oligosaccharides.[1] The main difficulty regarding the integration of such materials into biological systems derives from their lack of solubility in physiological solutions.[2] To avoid solubility issues, in this work, the CNTs surface was modified under US and/or MW irradiation, investigating the effects of these non conventional techniques, in chemical oxidation of CNTs and further functionalization. As widely recognized, the formation of defects on CNTs structure originates covalent functionalization.[3] Nevertheless, the aim of the applied oxidative treatment with the sulphonitric mix was to induce local defectivity, preserving the CNT structure. US irradiation at 20 kHz showed a marked mechanical effect and a partial breaking up of the structure, while the 300 kHz US allowed for oxidation and maintained the structural integrity of oxidized CNTs providing an excellent oxidation rate.[4] Despite the fact that MW irradiation allowed to achieve a high oxidation degree, it caused the systematic rupture of the CNT tip, due to the superheating initiated by the higher metal concentration of the residual catalyst, on which the CNT was grown.

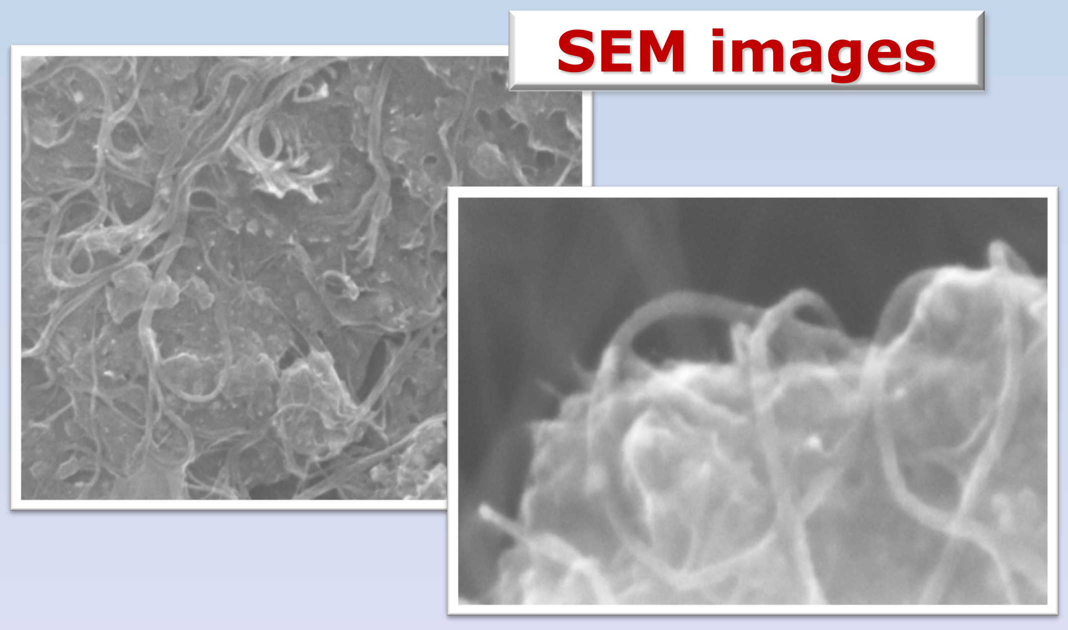
2. SWCNTs grafting solvent-free MW-assisted epoxides cycloaddition





submitted work

SEM images



2. The development of optimized synthetic procedures for the preparation of properly functionalized CNTs was focused on the SWCNTs. Surface modification of SWCNT may be performed by introducing reactive chemical groups through the exposure of the nanotubes, under MW irradiation (CEM oven at 180°C, 60 min), with carbonyl ylides,[5] able to react with SWCNTs via 1,3-cycloaddition.

CONCLUSION

In this work, the effectiveness of the MWCNTs oxidation under MW and/or US in the presence of sulphonitric mixture has been proved. The higher oxidative capacity, able to maintain the structural integrity of oxidized CNTs, was assigned to the 300 kHz-US irradiation. This excellent oxidation rate at this frequency was referred to a higher generation of free radicals, and compared to the 20 KHz a lower mechanical effect that preserve the integrity of the tubular structure was observed. Work is in progress to apply our findings to the emerging field of sonochemical and microwaves protocols for the modification and functionalization of CNTs.

References

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