SYNTHESIS AND CHARACTERIZATION OF SINGLE WALL CARBON NANOHORNS PRODUCED BY DIRECT VAPORIZATION OF GRAPHITE

Cesare Pagura*, Simona Barison*, Simone Battiston*, Mauro Schiavon**

•Institute for Energetics and Interphases, National Council of Research (CNR-IENI) C.so Stati Uniti, 4, 35127 Padova, Italy, c.pagura@ieni.cnr.it
**Carbonium srl, Via Penghe 28, 35100 Selvazzano (PD), Italy, info@carbonium.it

At a glance: A new method for large-scale production of Single Wall Carbon Nanohorns (SWCNH) is presented. The prototype reactor produce about 100 g/h of soot. The collected soot, characterized by thermogravimetric analyses (TGA), Raman spectroscopy, and transmission/secondary electron microscopies (HRTEM - SEM) revealed conspicuous presence of good-quality SWCNHs. The first results demonstrated the excellent capability of the new approach, that can be easily scaled up to tens the present scale, potentially becoming a powerful method to bring SWCNHs into every day applications

Introduction

Single Wall Carbon Nanohorns [1,2] (SWCNH) represent one of the most interesting carbon nanostructures belonging to the thrived nanotube family.

A key characteristic is their tendency to group together and form aggregates (spherical clusters or bundles) like dahlia flowers or buds, with overall diameters of tens/hundreds nm (see Fig. 1). Advantage of this "self assembling" characteristic is not only the very large surface area, but also an easy permeation of gases and liquids inside their structure.

In spite their tiny tubular structure, SWCNHs maintain many of the typical properties of carbon nanotubes: easiness of functionalization and good electrical and thermal conductivities. Nowadays, SWCNHs therefore represent more than a promise for a very wide range of possible uses, e.g.: methanol fuel cells support; efficient hydrogen storage; super-capacitors; generation of hydrogen by decomposition or steam-reforming of methane; composites for lubrication. Moreover, recent literature [3,4] focussed the important role of SWCNH for photovoltaic applications, since they are considered to be ideal for electron-acceptors hybrid systems.

In addition, many applications in life science were recently reported, e.g. ranging from drug delivery to NIR laser-driven functional CNH complexes used as antiviral materials. Regarding SWCNH toxicity, a very important issue for social sustainability of nanotechnologies, it is widely confirmed that, in experiments using mice and rats, the cytotoxicity was negligibly small [5,6]. Also SWCNH-based hybrid materials and nanofluids with promising properties were reported [7,8].

Not still commercially available, SWCNHs can be produced in laboratory-scale quantities without catalysts, a key feature since they are very difficult to remove, and with high purity starting from graphite by laser ablation/vaporization processes [1,9] or by AC or DC arc discharge [10,11].

For relevant amount, the only known industrial-scale process uses an advanced graphite vaporization method, consisting in spotting a powerful CO_2 laser on a rotating cylindrical rod [12].

With all the foreseen potential market applications, an enormous impact is expected if SWCNHs could become a low-cost raw material thanks to diffusion of methods for massive production.

In this framework, a new method, based on heating of graphite rods by induction of very intense, high frequency, eddy currents (a patented method already tested successfully for fullerenes and carbon nanotubes production [13]) was tailored for mass production of SWCNHs.

Experimental

To produce carbon nanostructures like fullerenes, nanotubes or nanohorns starting from solid precursors (graphite), a very high specific energy (~60 kJ/g) supply is necessary for the vaporization/atomization of precursor. Arc discharge or laser ablation reach such critical energy density, but discharge methods, being limited in the maximum current compatible with a controlled arc current, cannot be easily scaled up and the laser ablation technique requires a very high power and costly CO_2 laser for real mass productions (hg/h of soot), although it is the only actually used.

The process of heating a conductors by electromagnetic induction, where eddy currents are generated within the object itself giving rise to Joule heating, is well known and consolidated for industrial application. One of the most interesting properties of heating by eddy currents is the relevant power density that is possible to concentrate on workpieces, that can reach several $kW \cdot cm^{-2}$, sufficient to reach the temperature (3000-3200°C) necessary to sustain the evaporation of carbon atoms and di-atoms and permits their successive condensation in carbon nanostructures. Moreover, this kind of plant can be scaled up till to MW scale, even increasing the overall efficiency.

Recently, the patented reactor [13] was realized to demonstrate feasibility of induction heating for carbon nanotubes (CNT) production, where a synergic heating of both solid and plasma phases reaches the necessary thermodynamic conditions for the CNT synthesis. A new 30 kW power plant was specifically set up for SWCNH fabrication up to rates around 0.1 Kg/h. A detailed description of the apparatus and typical operational conditions is given in the cited patent. The reactor chamber, cooled by water circulation, is pumped down by primary and turbomolecular vacuum pumps (Edwards and Pfeiffer Vacuum), equipped with a (Air Liquide) gas streaming inlet, controlled by a mass flow controller (MKS). A cooled finger acts as collector to harvest soot production. Since production occurs in dynamic gas flow condition, an exit port drain the excess gas, that is ultra-filtered (0.1 micron mesh, Donaldson) and recycled in the process. A quartz window allows the process to be observed externally. No direct temperature control is used in the process, but off-line measures by an optical pyrometer through the quartz window assured that temperatures over 3000°C on graphite surface were reached and maintained during heating.

Soots were produced under diverse experimental conditions and with different kind of commercial graphite (SGL Carbon Gbmh).

Results

All the SWCNH production methods tend to produce some quantities of byproduct, such as wrapped or unwrapped graphene foils, amorphous carbon and graphite sub-micron particles (aka "giant graphite balls" (GGBs) [14]). Thermo-Gravimetric Analysis (TGA) in air or in oxygen flux is a very efficient tool for determining the overall quality of soot material, providing information on the different carbon structures, due to differences in their decomposition temperatures.

Fig.2 a) and b) represents TGA curves (800°C max, in air flux, 5°C/min ramp, performed with a SDT Q600 - TA Instruments) of production batches of soot "as prepared". According to literature ([7,14]), in the derivative curves of Fig. 2 a) different phases are well observable: an amorphous phase peak at 400°C, followed by peaks related to SWCNHs, and almost two peaks ascribable to residual graphitic structures as in [7] (GGBs and graphene). The residual is quite low, below 4%, compatible with the purity of graphite used in these experiments. For comparison, neat TGA curves of used graphite are reported (blue lines).

Fig.2 b) shows the curves after optimization of synthesis parameters (Ar flow and residual pressure), where amorphous and graphitic phases are strongly reduced and the purity of SWCNH is greatly improved.

TEM is the most accredited technique to evaluate the morphology of the products, even if, visualizing less than few pg of sample, cannot be assertive for overall production quality. Fig. 3 shows TEM images of single particles found in the soot produced by the reported method. The last one, reports a HR-SEM image, showing agglomerates of dhalia- and bud-like nanohorns.

The other acknowledged technique able to evidence the presence of SWCNHs is the Raman spectroscopy. Raman spectra in fig. 4 show typical bands observed for SWCNH of two samples respectively collected from the cold finger inside the reactor and from the residual dust from the chamber walls, with a high intensity D band at 1314 cm^{-1} and the G band at 1594 cm^{-1} with intensity comparable to that of the D band. The spectrum also shows the G' band (overtone of the D band) at 2620 cm^{-1} and a characteristic band at 2895 cm^{-1}.

Conclusion

The presented method demonstrated its remarkable potentiality in large-scale production of SWCNHs with good purity.

The plant can be scaled up to tens the present scale.

Furthermore, by changing the reactor parameters or adding other gases to carrier gas (like nitrogen or diborane), the same plant could be able to produce N-doped or B-doped SWCNHs or graphene sheets or different kind of carbon nanomaterial, i.e. single wall nanotubes, by injecting suitable catalyst (Fe or Co organometallic compounds)

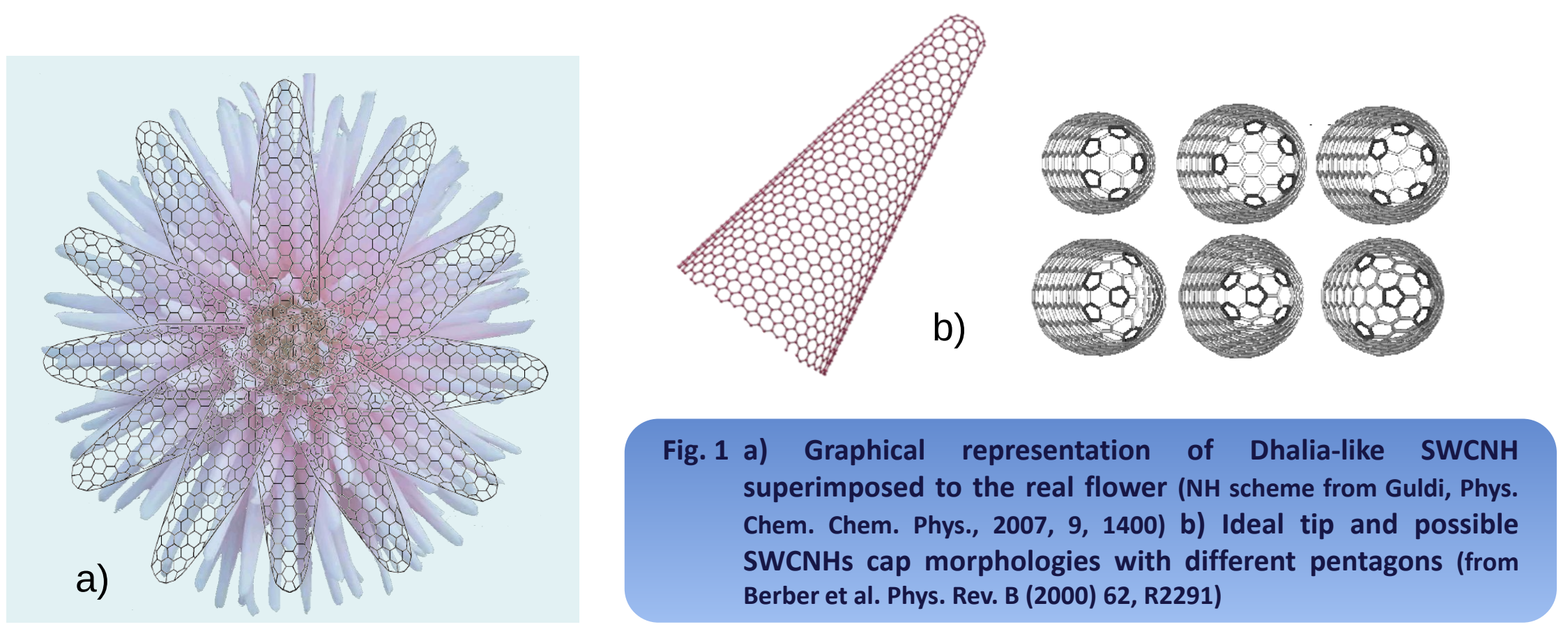


Fig. 1 a) Graphical representation of Dhalia-like SWCNH superimposed to the real flower (NH scheme from Guldi, Phys. Chem. Chem. Phys., 2007, 9, 1400) b) Ideal tip and possible SWCNHs cap morphologies with different pentagons (from Berber et al. Phys. Rev. B (2000) 62, R2291)

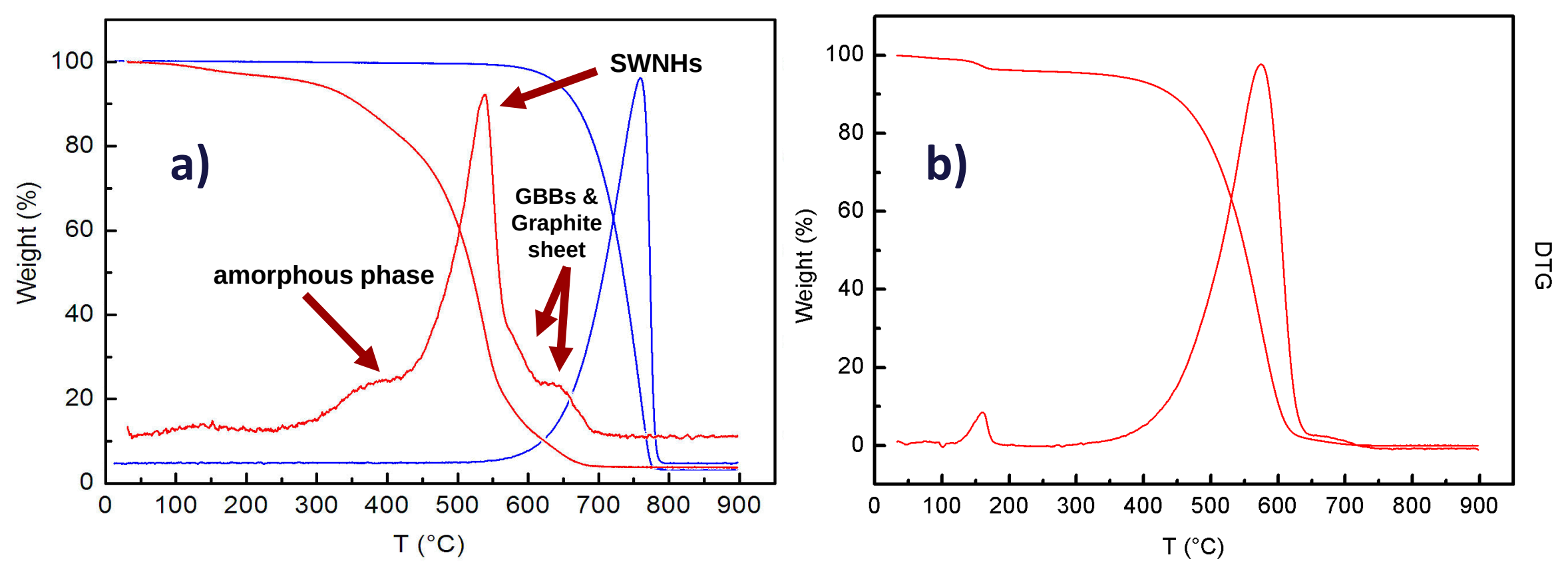


Fig. 2 TGA curves of untreated soot (red)
a) before parameter optimization (pure graphite in blue for comparison)
b) after parameter optimization, where the amorphous phase and graphitic phases are strongly reduced

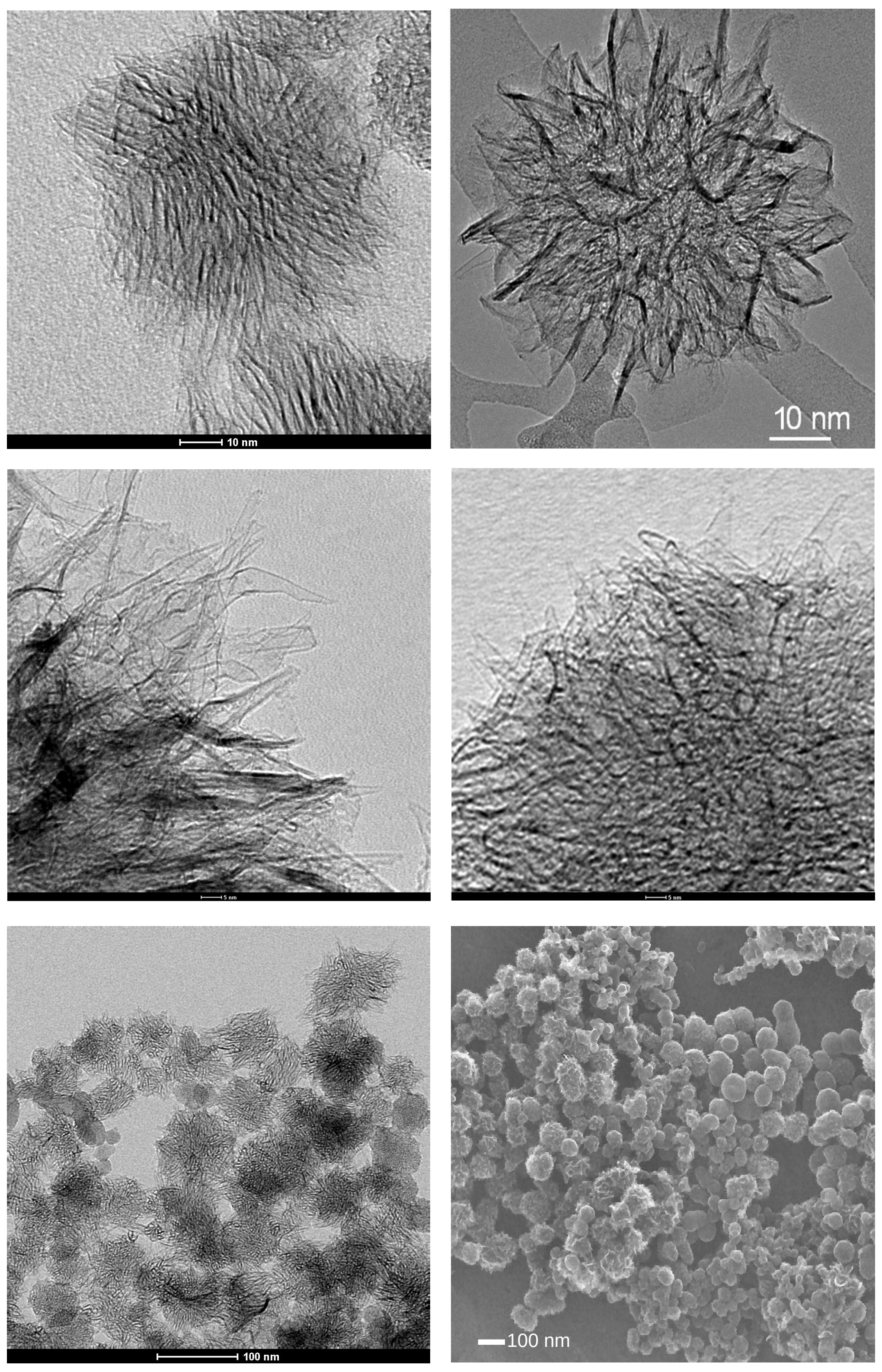


Fig. 3 Images by TEM and HRSEM of nanohorn particles: when the synthesis parameters are optimized the typical Dhalia-like structures are prevalent

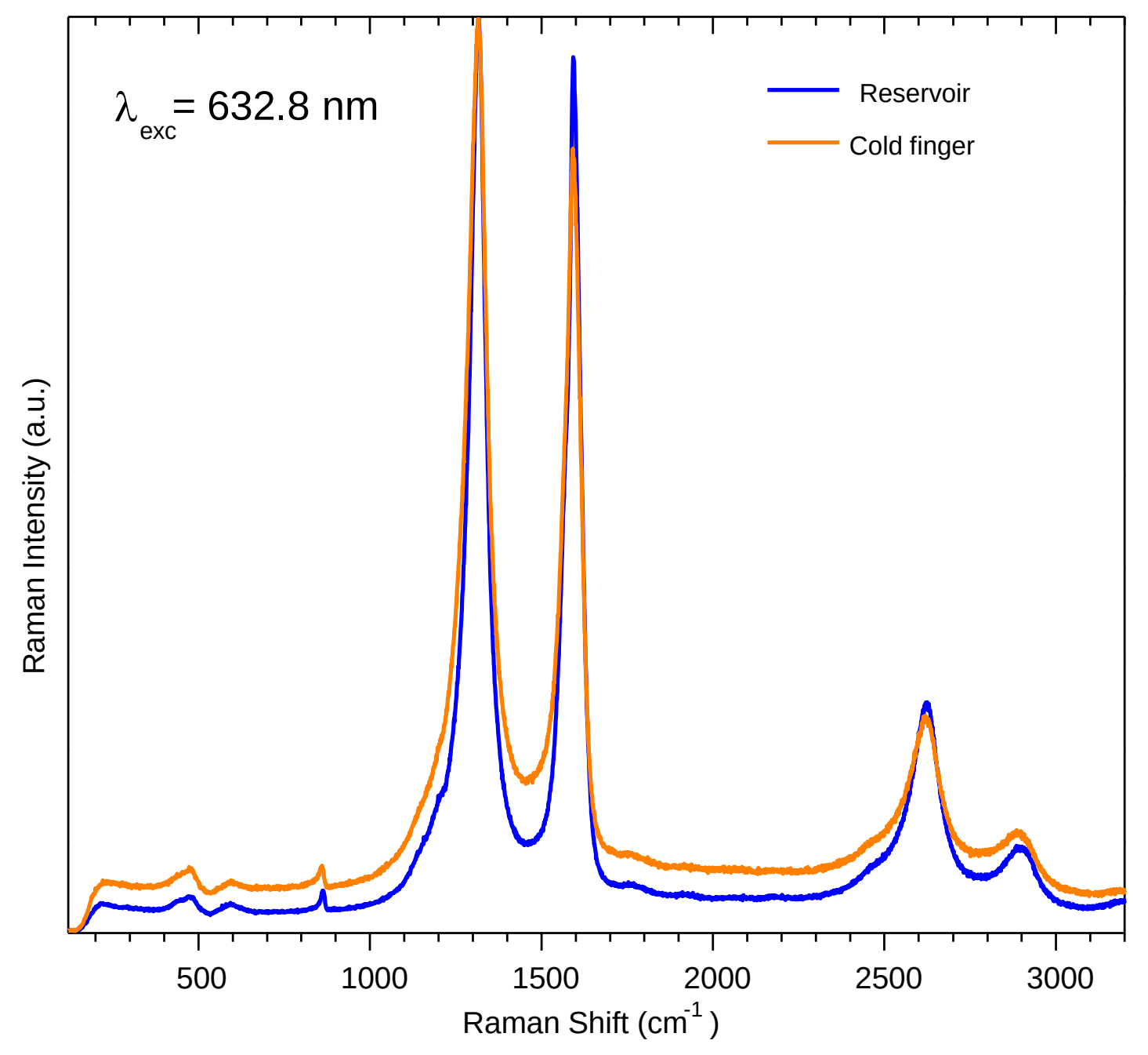


Fig. 4: Raman spectra of soot sampled in two zones of reactor chamber. Typical bands for SWCNH are observed in both samples

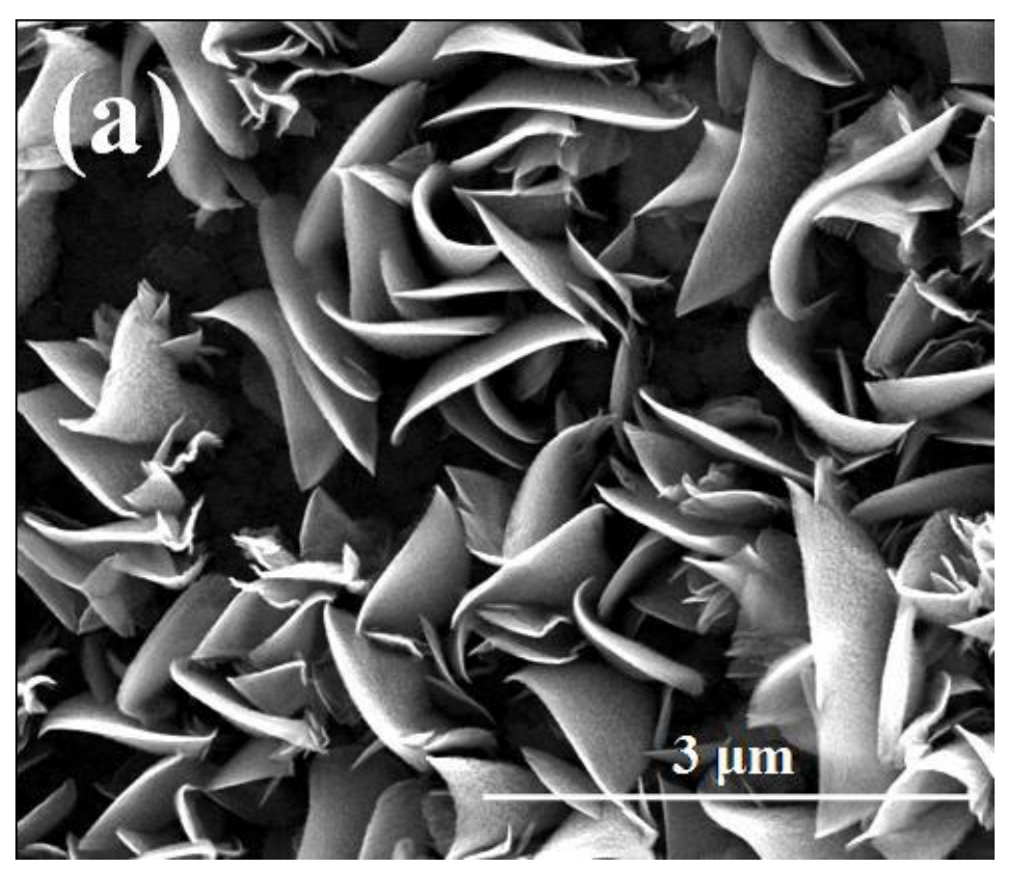
QR Codes

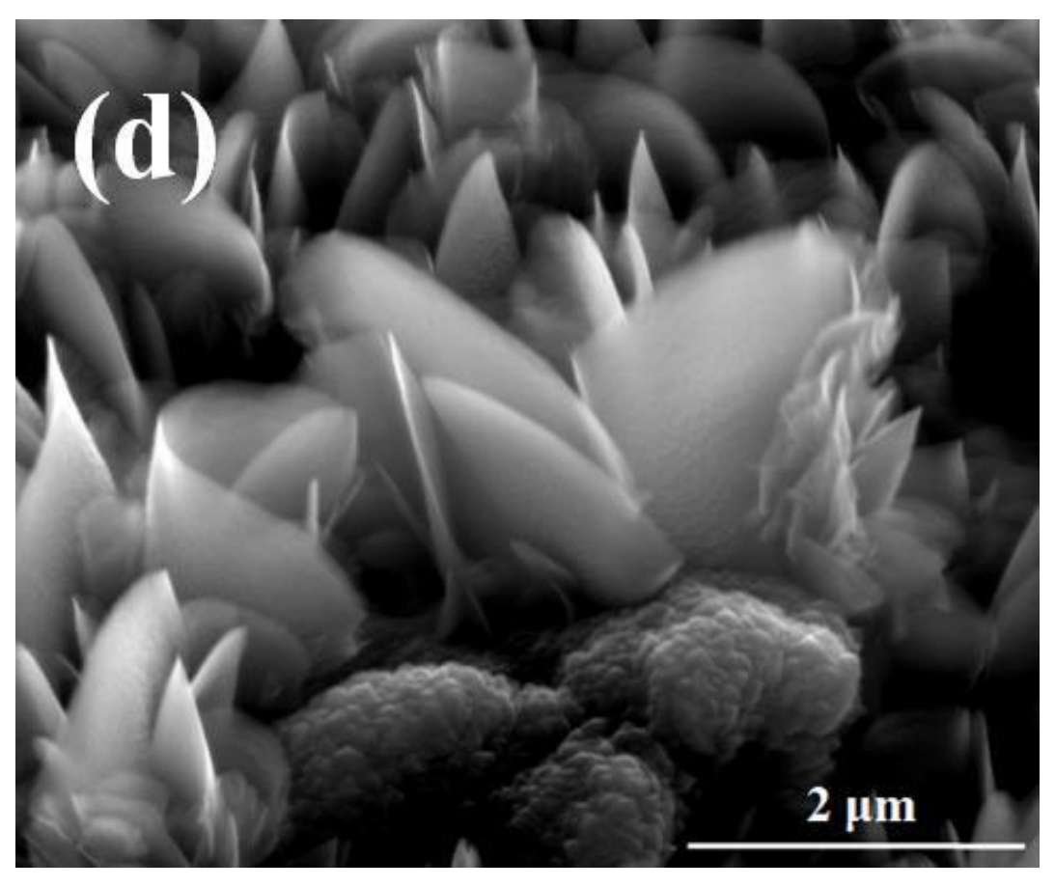
Application of SWCNHs

In our labs we are testing many possible applications for SWCNH.

Hybrid materials

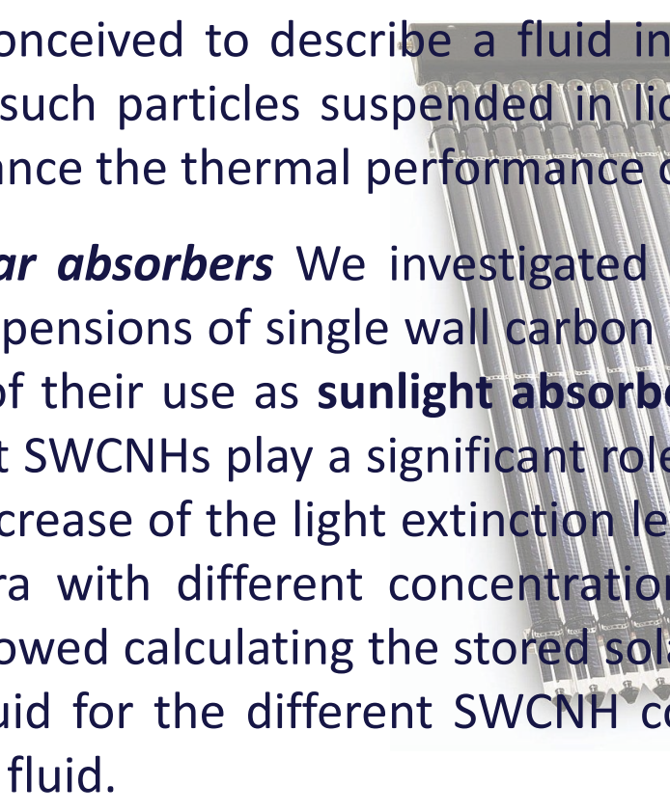
A novel titanium dioxide architecture, called titanium dioxide nanopetals (see below two SEM images), was obtained through two sequential vapour techniques, metal-organic chemical vapour deposition (MOCVD) and magnetron sputtering (PVD) on a single wall carbon nanohorn (SWCNH) bed, resulting in a surprising synergistic effect. The photocatalytic degradation of phenol under UV light irradiation demonstrated that this novel material exhibited a significant increase of photoactivity due to the increased active surface area and also to the presence of heterojunctions between the carbon nanohorns and titanium dioxide, and between the anatase and rutile phases, which helps separation of the photogenerated excitons.





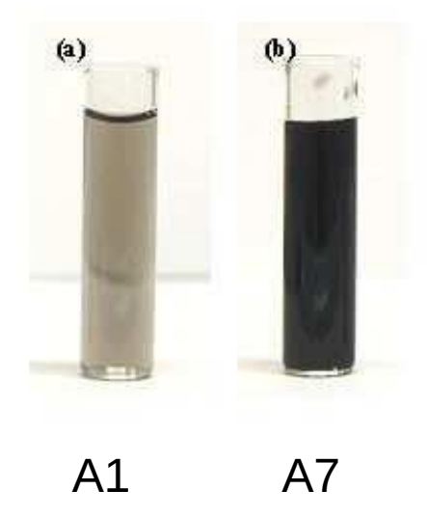
The characteristics and functionality of this novel and intriguing titanium dioxide composite material, which can be easily deposited onto any kind of material (either metals or oxides), could make it appealing for use in photocatalytic applications such as the photodegradation of organic compounds in aqueous solutions and energy devices like the dye sensitized solar cells. [7]

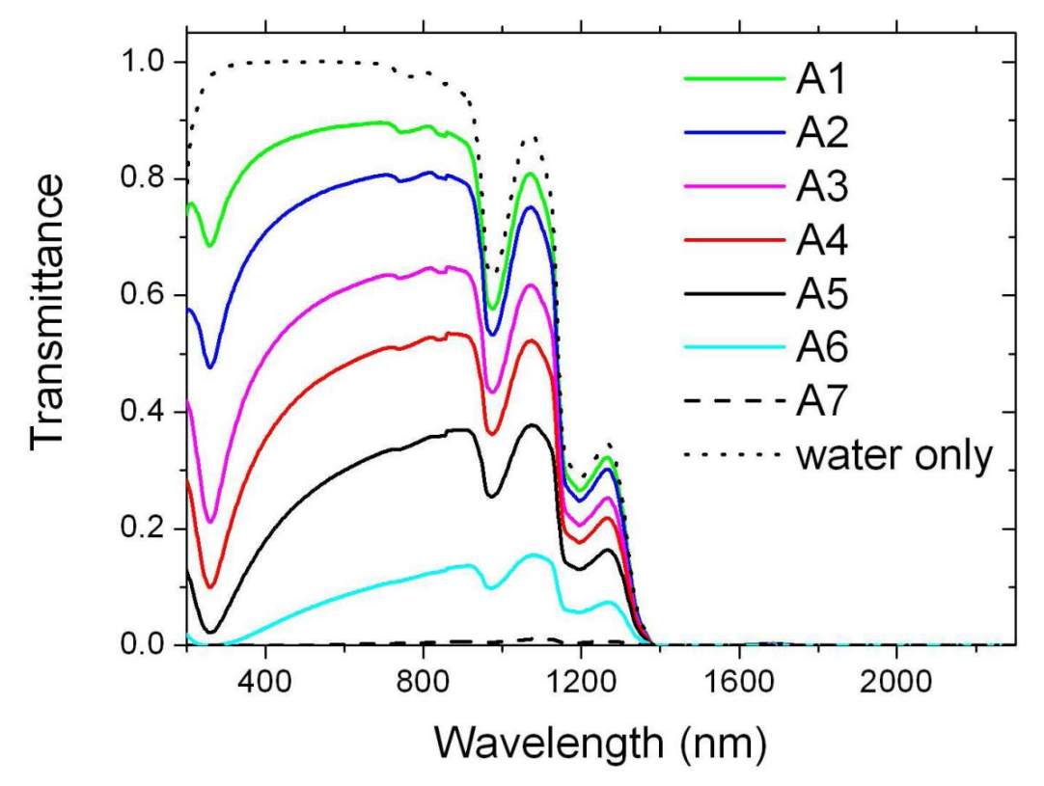
Nanofluids

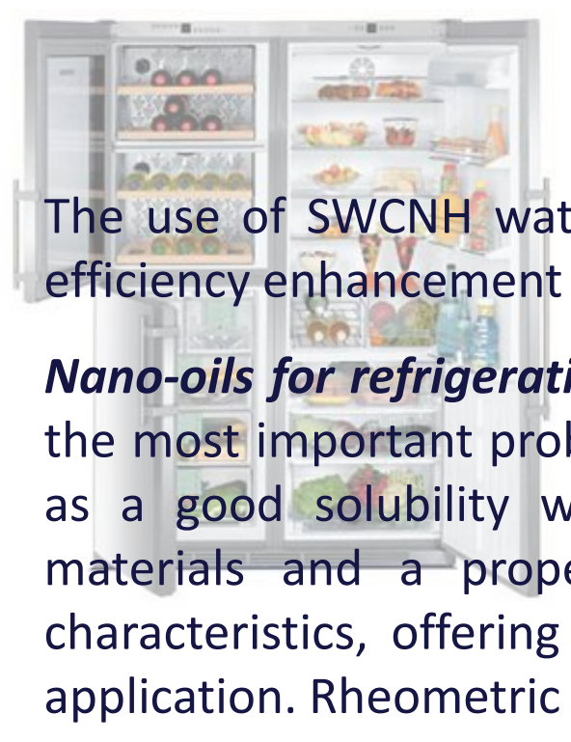


Nanofluid is the name conceived to describe a fluid in which nanometer-sized particles are suspended. Nanofluids consisting of such particles suspended in liquids (typically conventional heat transfer liquids) have been shown to enhance the thermal performance of the base liquids .

Nanofluids as direct solar absorbers We investigated the optical and thermal properties of nanofluids consisting in aqueous suspensions of single wall carbon nanohorns. The characteristics of these nanofluids were evaluated in view of their use as **sunlight absorber fluids in a solar device**. The measured spectral transmission showed that SWCNHs play a significant role in improving the photonic properties of the fluid, leading to a significant increase of the light extinction level even at very low concentrations (see below for the transmittance spectra with different concentration from A1-0.001 g/l to A7-0.050 g/l). Measured extinction coefficients allowed calculating the stored solar energy fraction, as a function of the penetration depth within the nanofluid for the different SWCNH concentrations, and the stored energy distribution within the cold and static fluid.

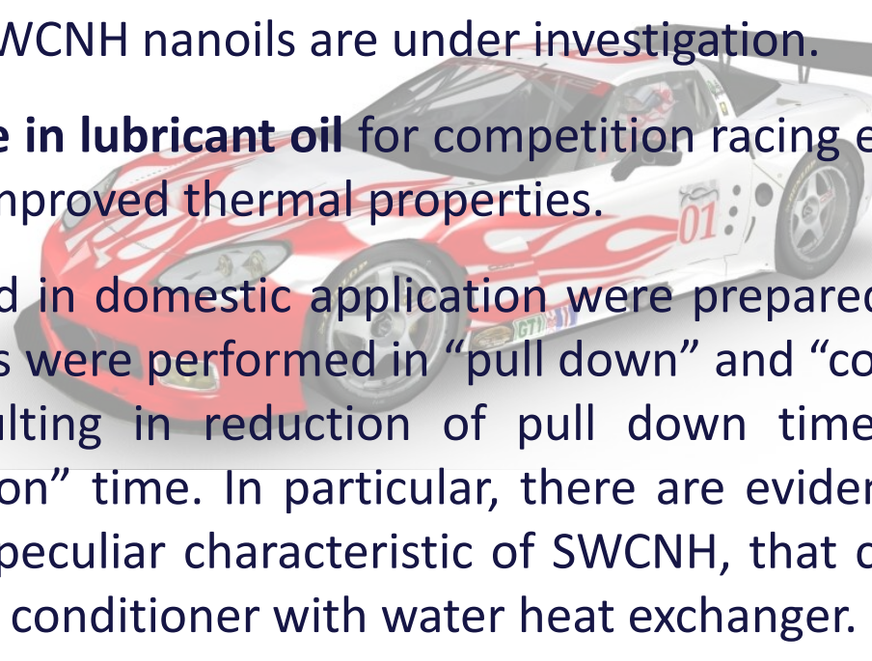






The use of SWCNH water nanofluid as absorber in solar devices seems a very promising step towards efficiency enhancement and more compact and integrated designs. [8]

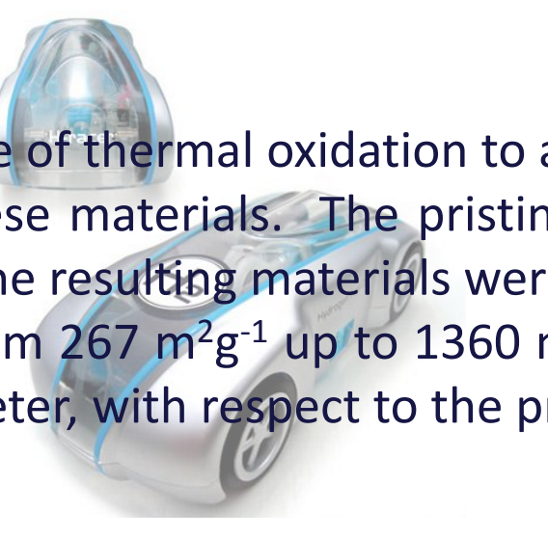
Nano-oils for refrigeration The choice of the best commercial oil employed in compressors is still one of the most important problems in the refrigeration field. This lubricant should satisfy several requirements, as a good solubility with refrigerants, excellent tribological properties, high compatibility with the materials and a proper viscosity. The **dispersion of SWCNH in oils** promises to improve their characteristics, offering a good opportunity in the selection of the most suitable lubricant for a given application. Rheometric and thermal properties of POE/SWCNH nanoils are under investigation.



Nano-oils for automotive Addition of SWCNH as **additive in lubricant oil** for competition racing engines is under investigation, in view of their cleaning action and improved thermal properties.

Nanorefrigerant Nanofluid to be used as refrigerant fluid in domestic application were prepared by high pressure mixing of SWCNH in liquid R600a and R134. Tests were performed in "pull down" and "continuous running" modes in different domestic apparatus resulting in reduction of pull down time, energy consumption saving, and reduction in the "compressor on" time. In particular, there are evidences of a **dramatic increase of pool boiling heat transfer**, due to peculiar characteristic of SWCNH, that candidate these nanorefrigerant as ideal for industrial chiller and air conditioner with water heat exchanger.

Hydrogen Storage



We investigated the use of thermal oxidation to alter the structure of SWCNHs and so modify the hydrogen storage capacity of these materials. The pristine nanohorn sample was thus oxidised at 673 K in air for different periods and the resulting materials were characterised. The BET data revealed a **marked increase in the surface area**, from 267 m^2g^{-1} up to 1360 m^2g^{-1}, and accessible pore volume as well as a decrease in the average pore diameter, with respect to the pristine sample.

References

[1] Iijima S., Yudasaka M. et al., "Nano-aggregates of single-walled graphitic carbon nano-horns", Chemical Physics Letters, 1999;309(3-4):165-70.
[2] Iijima S., "Carbon nanotubes: past, present, and future", Physica B: Condensed Matter, 2002;323(1-4):1-5.
[3] Cioffi C., Campidelli S. et al., "Synthesis, characterization, and photoinduced electron transfer in functionalized single wall carbon nanohorns", Journal of the American Chemical Society, 2007;129(13):3938-45.
[4] Pagona G. et al., "Covalent functionalization of carbon nanohorns with porphyrins: Nanohybrid formation and photoinduced electron and energy transfer", Advanced Functional Materials, 2007; 17(10):1705-11.
[5] Miyawaki J., Yudasaka M., Azami T., Kubo Y., Iijima S., "Toxicity of Single-Walled Carbon Nanohorns", ACS Nano, 2008;2(2):213-26.
[6] Lynch R.M. et al., "Assessing the pulmonary toxicity of single-walled carbon nanohorns", Nanotoxicology, 2007;1(2):157-66.
[7] Battiston, S. et al. "Growth of titanium dioxide nanopetals induced by single wall carbon nanohorns", Carbon, 2010; 48 (9): 2470-2477
[8] Sani, E. et al., "Carbon nanohorns-based nanofluids as direct sunlight absorbers" (2010) Optics Express, 18 (5), pp. 5179-5187.
[9] Azami T. et al. "Production of small single-wall carbon nanohorns by CO2 laser ablation of graphite in Ne-gas atmosphere" Carbon, 2007;45(6):1364-7.
[10] Gattia D.M., Vittori Antisari M., Marazzi R., "AC arc discharge synthesis of single-walled nanohorns and highly convoluted graphene sheets", Nanotechnology, 2007;18(25).
[11] Gattia M., Antisari M.V., Marazzi R., Pilloni L., Contini V., Montone A., "Arc-discharge synthesis of carbon nanohorns and multiwalled carbon nanotubes", Materials Science Forum 2006; 2006. p. 23-8.
[12] Azami T., Kasuya D., Yuge R., Yudasaka M., Iijima S., Yoshitake T. et al., "Large-scale production of single-wall carbon nanohorns with high purity", Journal of Physical Chemistry C, 2008;112(5):1330-4.
[13] Schiavon M., "Device and method for production of carbon nanotubes, fullerene and their derivatives" U.S. Pat. 7,125,525 - EP 1428794 2006.
[14] Fan J., Yudasaka M., Kasuya D., Azami T., Yuge R., Imai H., et al., "Micrometer-sized graphitic balls produced together with single-wall carbon nanohorns", Journal of Physical Chemistry B, 2005;109(21):10756-9.