CNTs synthesis facility in Roma: techniques and a list of results in various applications

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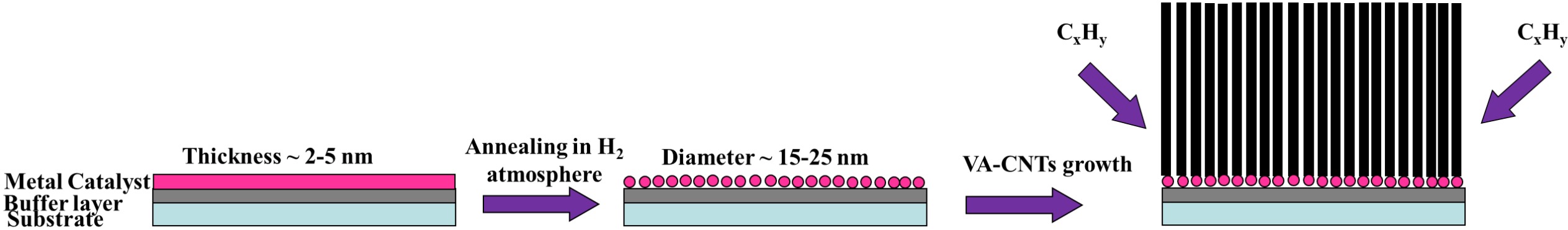
PTOLEMY Collaboration Meeting
06 - 07 October/Zandvoort, NL

A State-of-the-Art CVD facility in INFN/Sapienza Lab

- Thanks to **ATTRACT** funding
- **Operational** since August 2020
- Highly **versatile** CVD chamber with a large reaction zone enabling VA-CNTs growth on an entire wafer (2 inch) or on different samples simultaneously
- Equipped with **Plasma-Enhanced technology operational** since September 2022

Vertically Aligned CNTs (VA-CNTs): growth mechanism

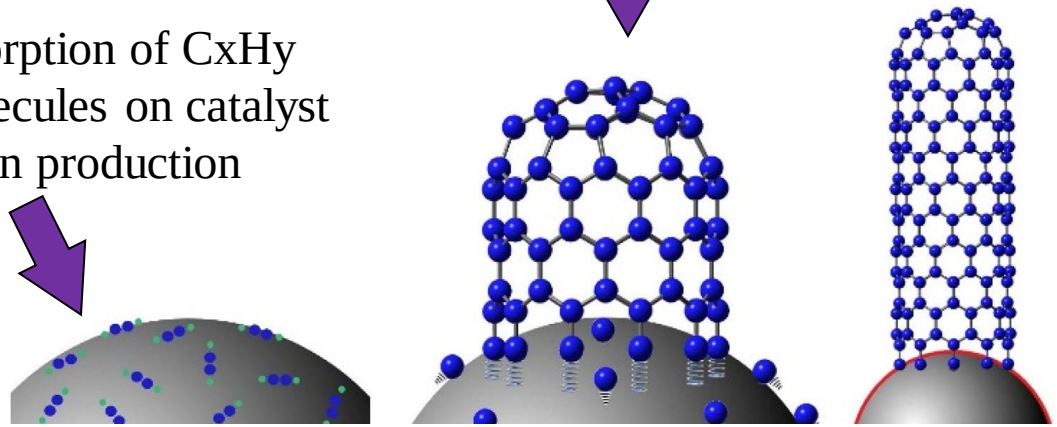
Thermal decomposition of a gaseous precursor on catalytic nanoparticles in a high-vacuum reaction chamber



Diffusion of produced carbon atoms and formation of CNT

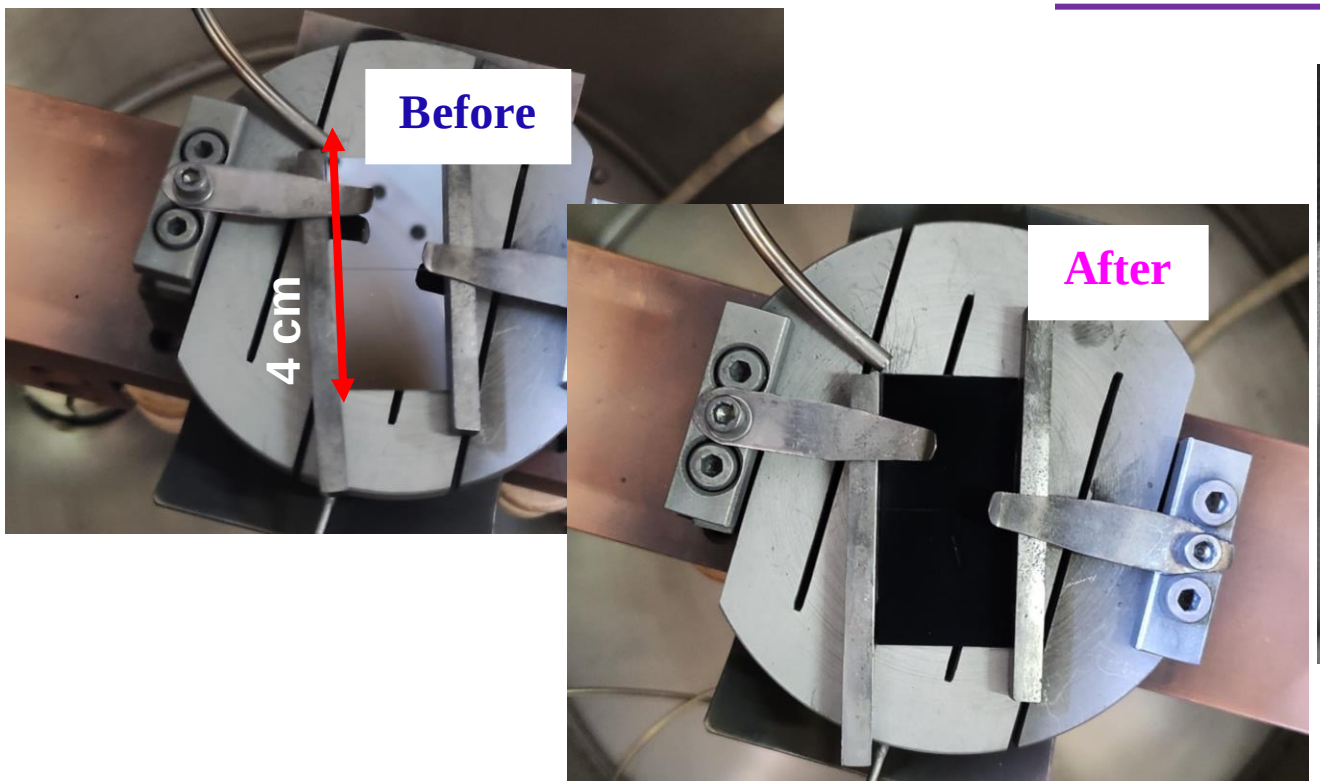
Surface adsorption of CxHy feedstock molecules on catalyst and carbon production

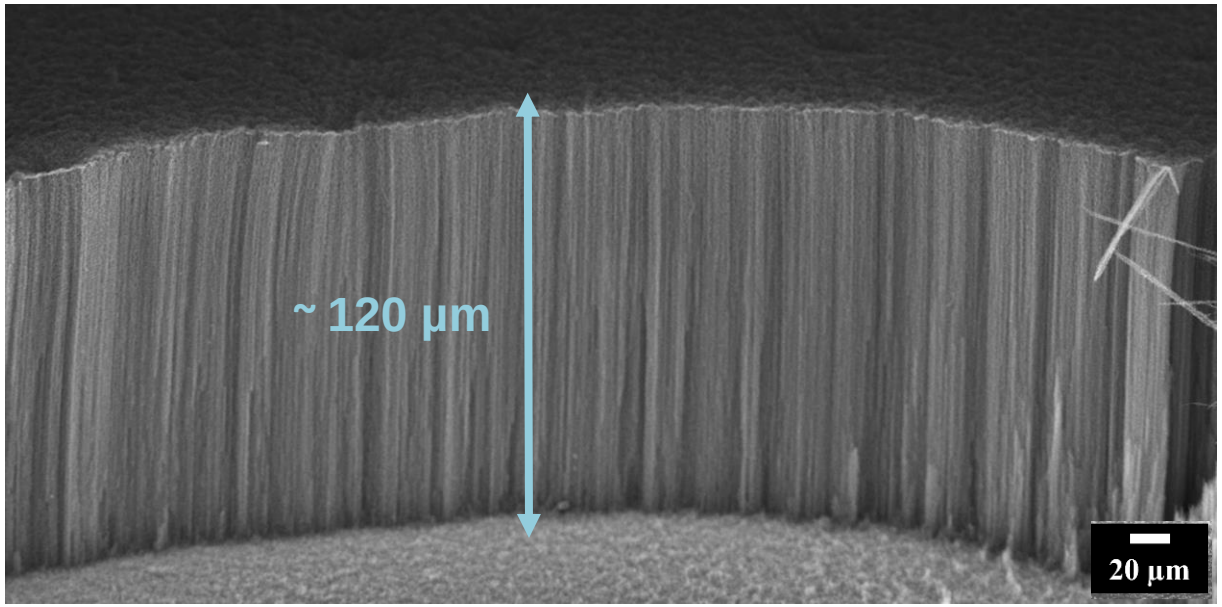
Formation of a carbon layer on catalyst surface (red line) stopping the growth process



H. Shahivandi *et al.*, H (2017), Phys. Stat. Sol. A, 214: 1700101

Optimizing the VA-CNTs Synthesis Process on several substrates





❖ **Optimized** CNTs Growth **Parameters**:

T ≈ 720 – 740 °C

Annealing treatment: 720 °C in H_2 atmosphere for 4 minutes (up to a partial pressure of $8 \cdot 10^{-1}$ mbar);

CNTs growth: 740 °C in C_2H_2 atmosphere for 10 minutes C_2H_2 (up to a partial pressure of 10–20 mbar).

❖ **Optimized** Growth **Substrates**:

- ☑ Fused silica
- ☑ Silicon
- ☑ Basalt, quartz and carbon fibers
- ☑ Metallic supports

Applications of VA-CNTs

1M€ PRIN 2020

❑ Dark Matter Detector

- 'Dark-photocathode' of aligned CNTs

ANDROMEDA

❑ Surface Disinfections

- self-disinfecting surfaces

Collaborating with Sapienza Biology Department

100k€ ATTRACT Grant

❑ Sensors

- Ion sensors
- Gas sensors
- Photo-sensor
- Biosensors

'NanoUV': UV light detectors based on carbon nanotubes

'NanoBio': Carbon Nanotubes for Biosensing

13k€ Sapienza Grant (Collaborating with Sapienza Biology Department)

❑ Challenges

- Control of VA-CNTs properties (diameter, length, density, quality of the tubes)
- Large scale production
- Application development

50k€ Sapienza Grant (Collaborating with Sapienza Engineering Department (DICMA))

❑ Advanced composite materials

- CNTs-based nanocomposites

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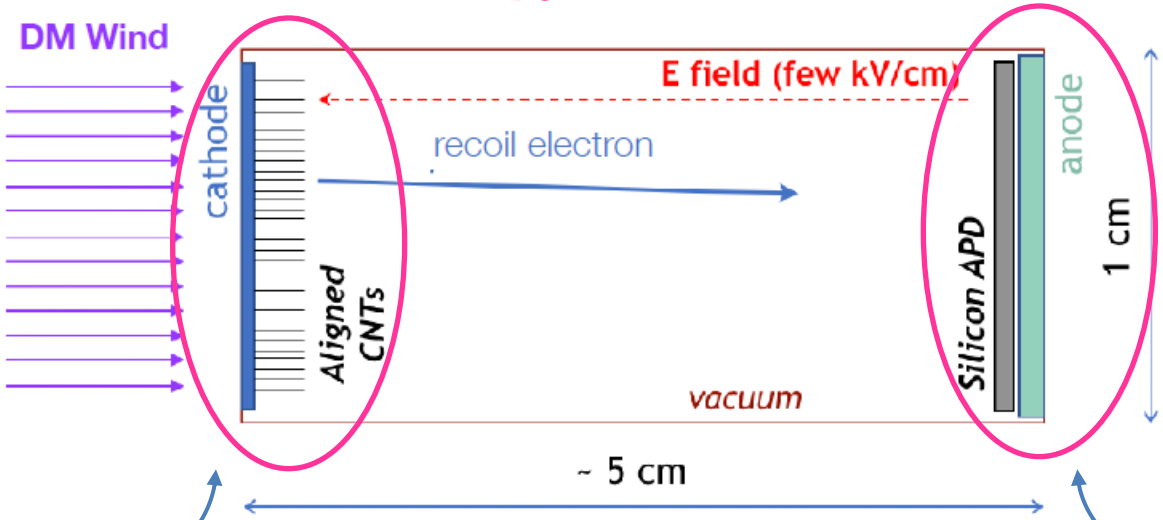
Nanotube Detector Concept: the 'dark-PMT'

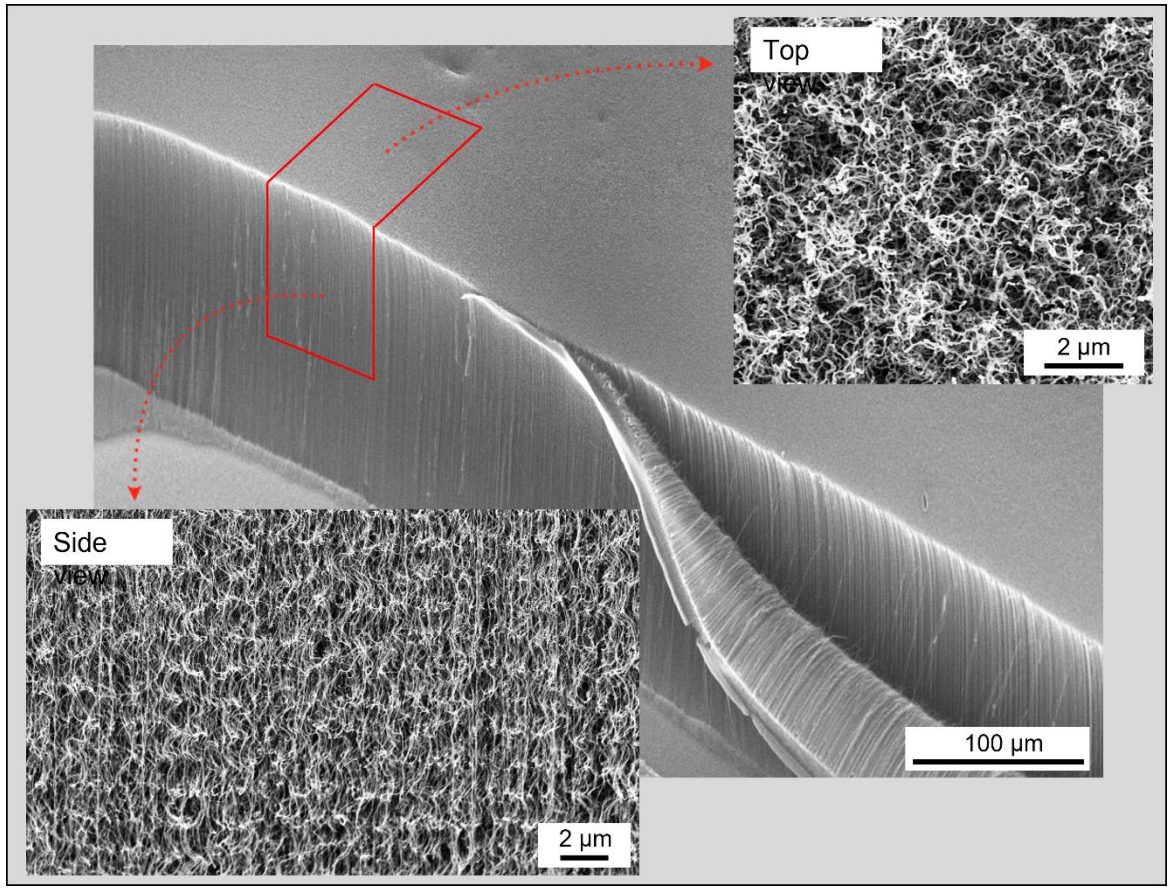
❖ **'Dark-photocathode' of aligned nanotubes**

- Ejected e^- accelerated by electric field
- Detected by solid state e- counter

Dark-PMT



Not-Aligned Top Layer



'WAVINESS' at the nanoscale

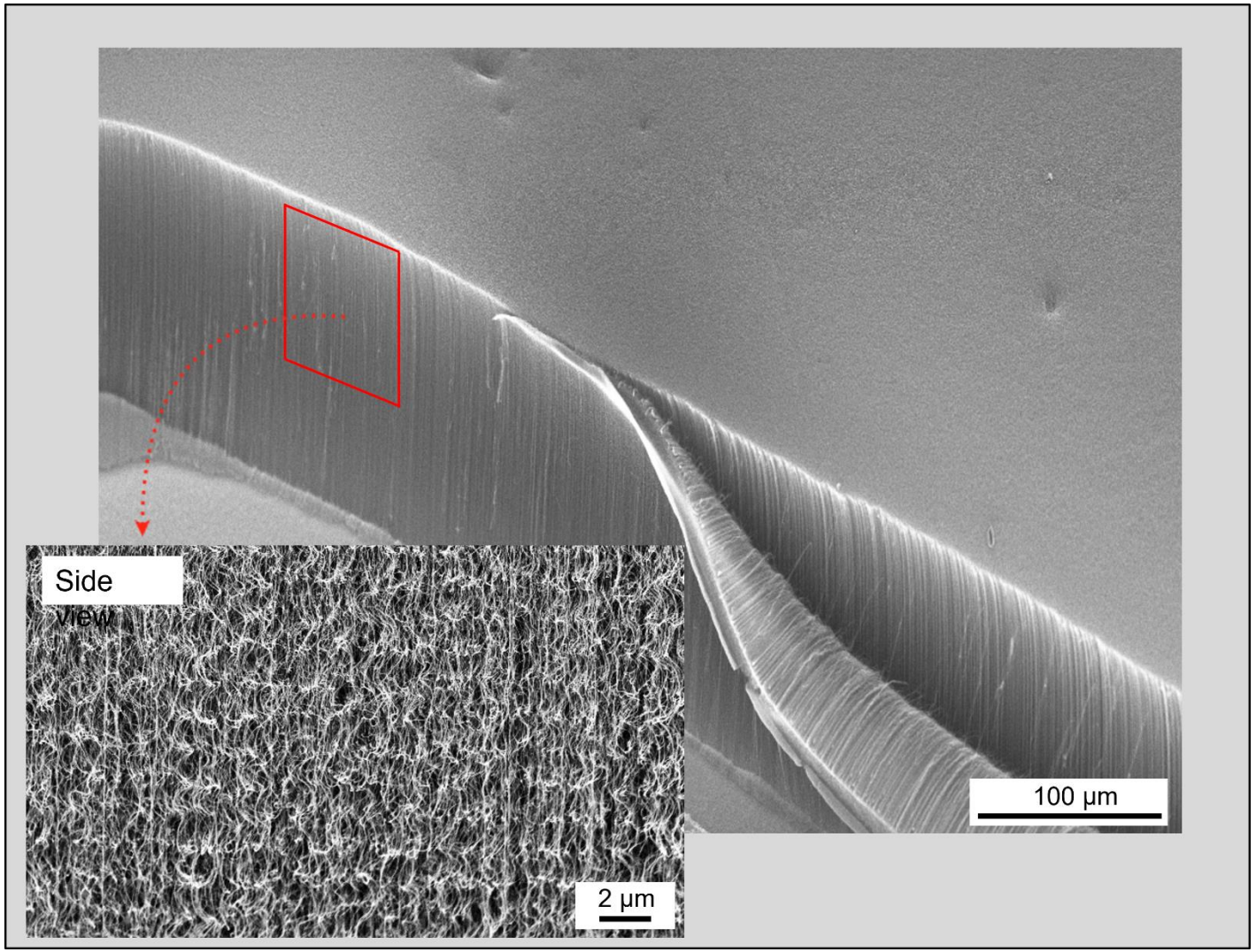
See Alessandro Ruocco's talk

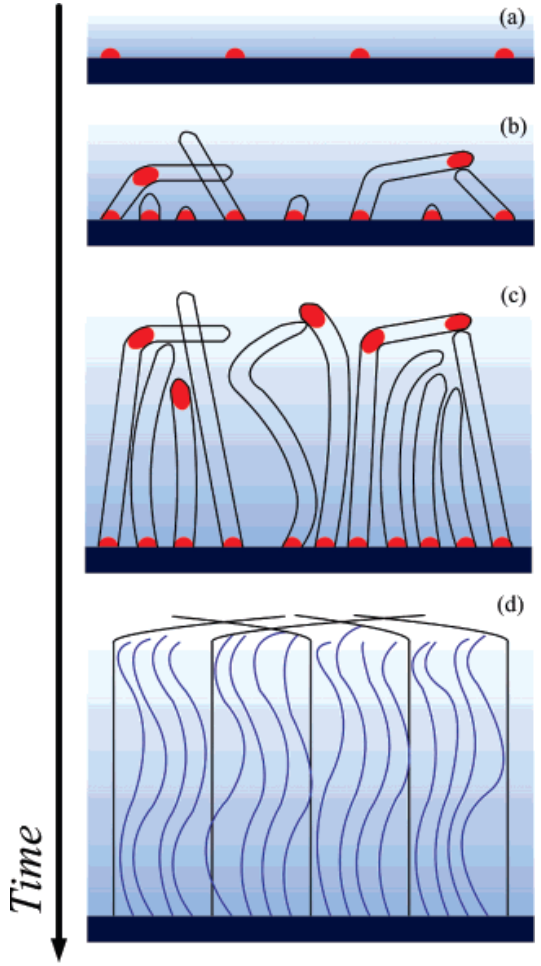
❖ <u>Aligned CNTs:</u>
Optimizing: length, density, morphology

❖ <u>Silicon detector for keV electrons</u>
Optimizing: technology, geometry, distance

Waviness of VA-CNTs at the Nanoscale

❖ Aligned CNTs:
Optimizing: **non-uniformity** and **density** of catalyst nanoparticles





Synchronous synthesis of CNTs with different growth rates leads to **wavy** structures

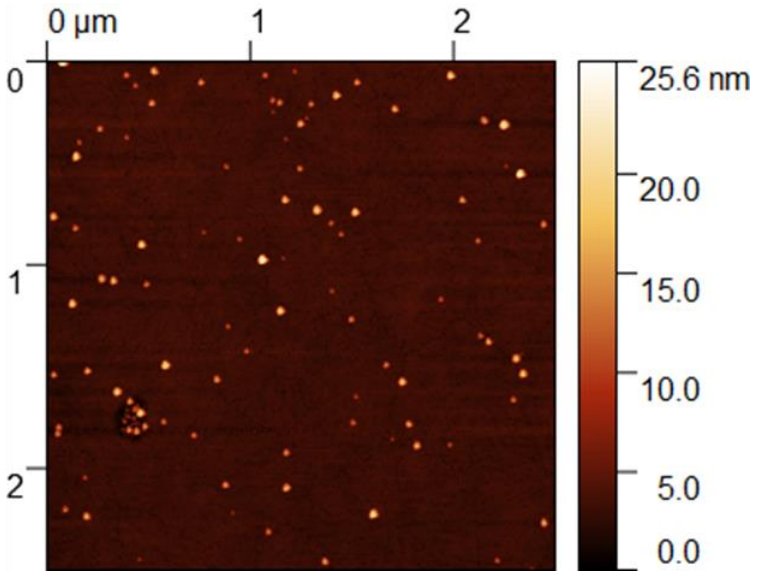
Q. Zhang et al., J. Phys. Chem. C, **2007,** *111,* 14638-14643

Upgrade of VA-CNTs synthesis via AFM analysis

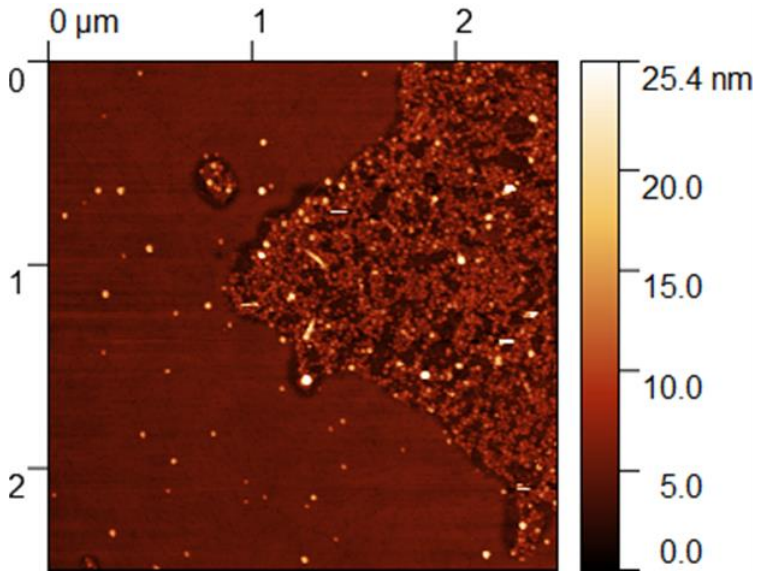
Operational since September 2022

Park NX10 AFM

AFM images of Fe NPs after the **annealing treatment** performed in the high vacuum CVD chamber



Isolated Fe NPs



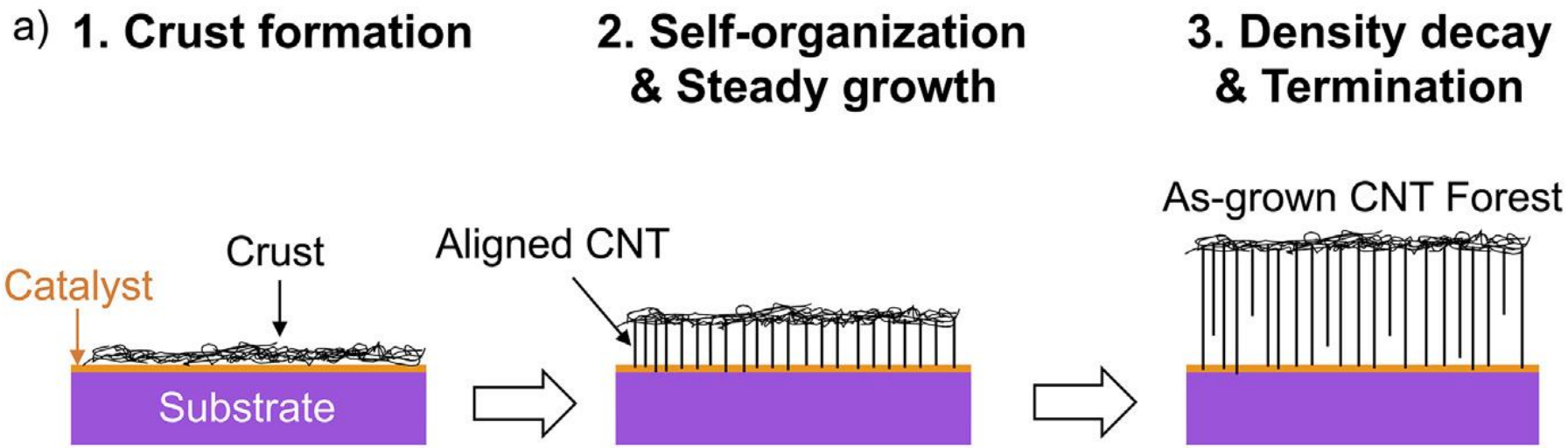
Fe NPs cluster

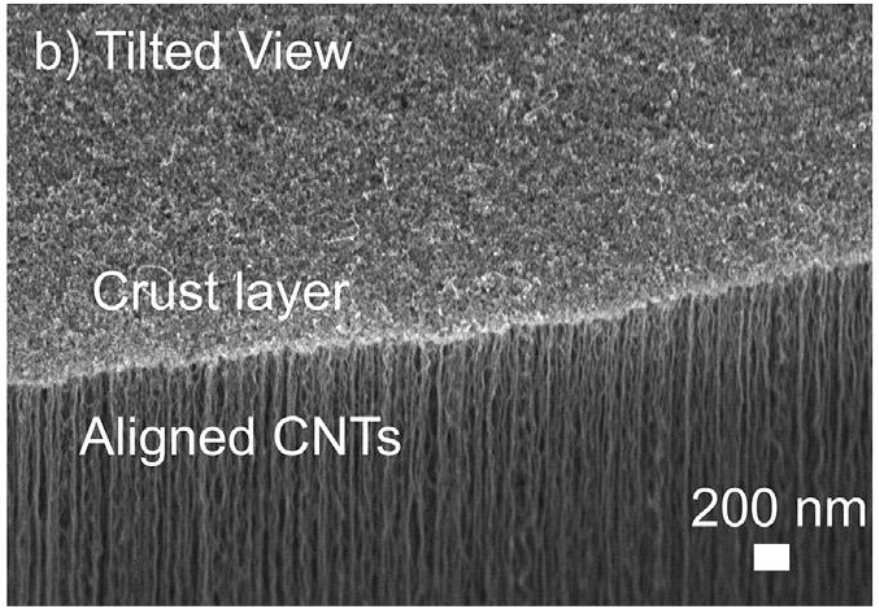
❖ <u>Reducing waviness at the nanoscale:</u>
Maximize: catalyst NPs density and distribution through an **iterative process** combining:

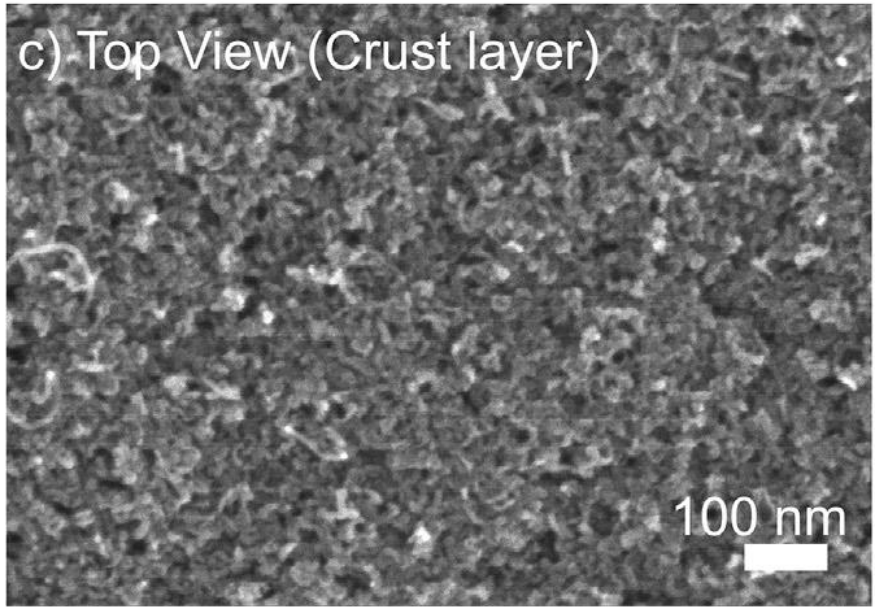
- Optimizing parameters influencing the nucleation of catalyst NPs (from deposition to annealing)
- AFM characterization of NPs size, density and distribution

	Now	Goal
Catalyst NPs density [cm^{-2}]	10^{10}-10^{11}	> 10^{12}
Catalyst NPs size [nm]	15-30	5 (±20%)

Not-Aligned Top Layer: A Problem?





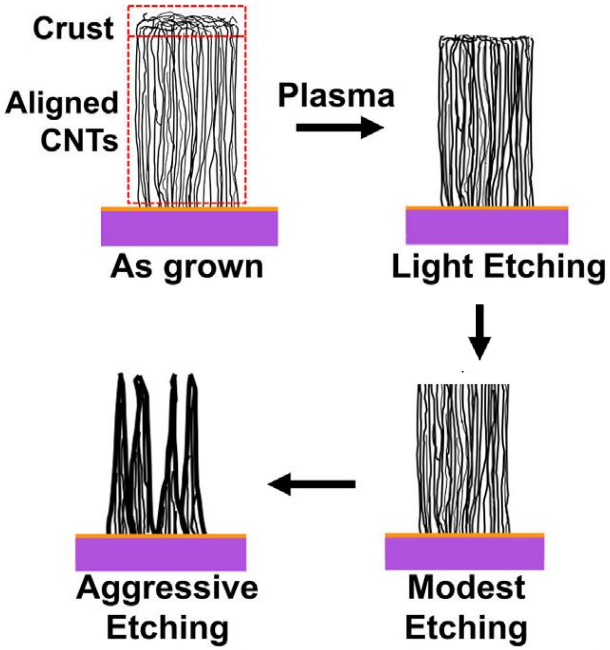


*S. Seo, Carbon 180, **2021**, 204e214*

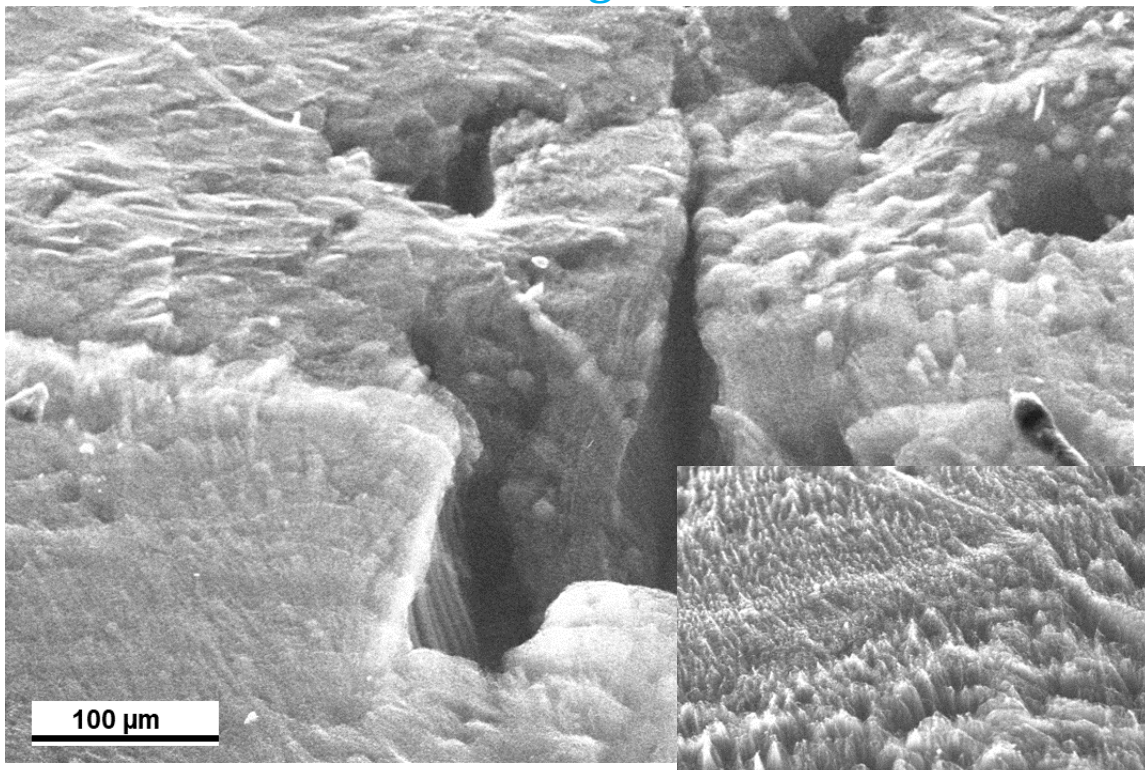
Tailoring the surface morphology of VA-CNTs via O_2 plasma etching

ON-GOING

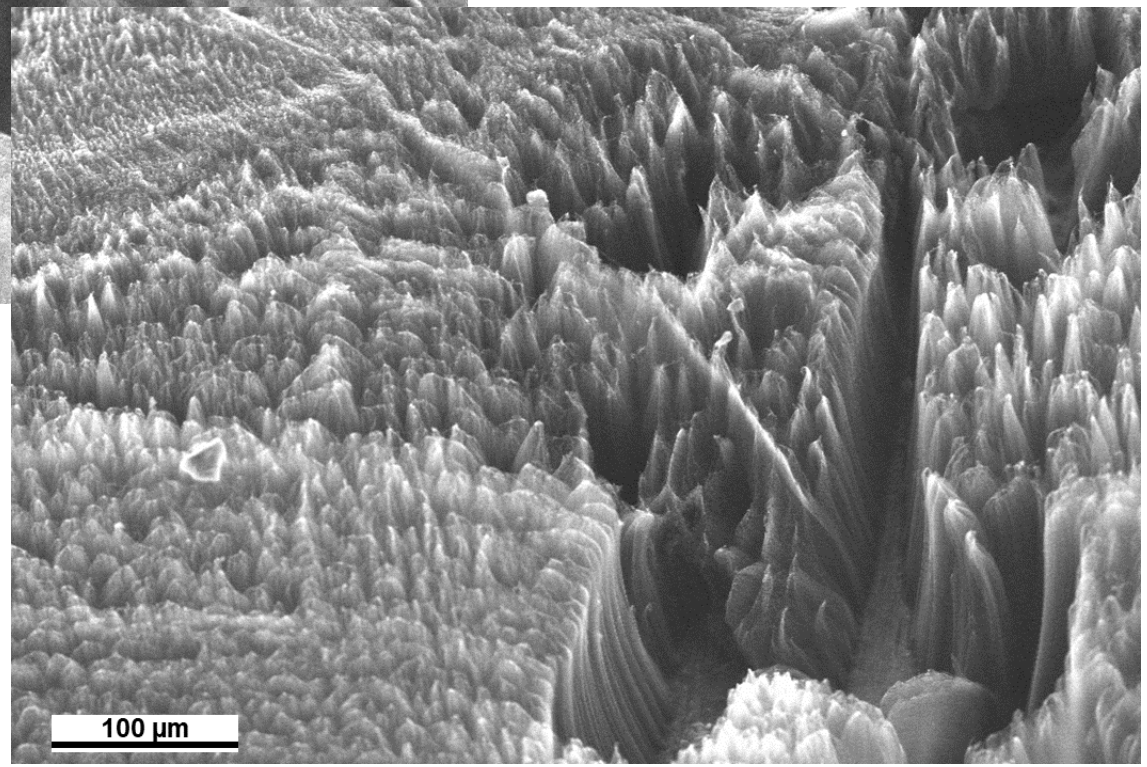
*S. Seo, Carbon 180, **2021**, 204e214*



As-grown



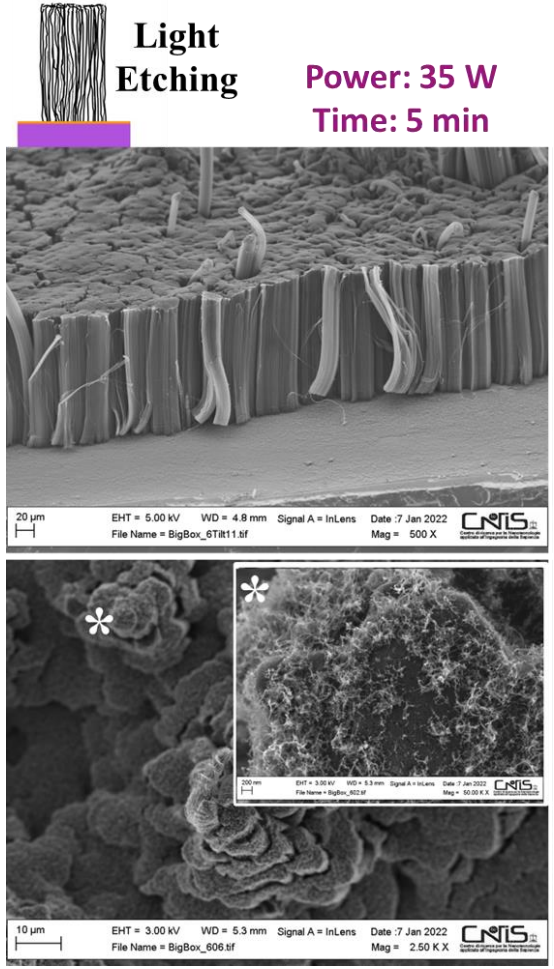
After O_2-Plasma Etching

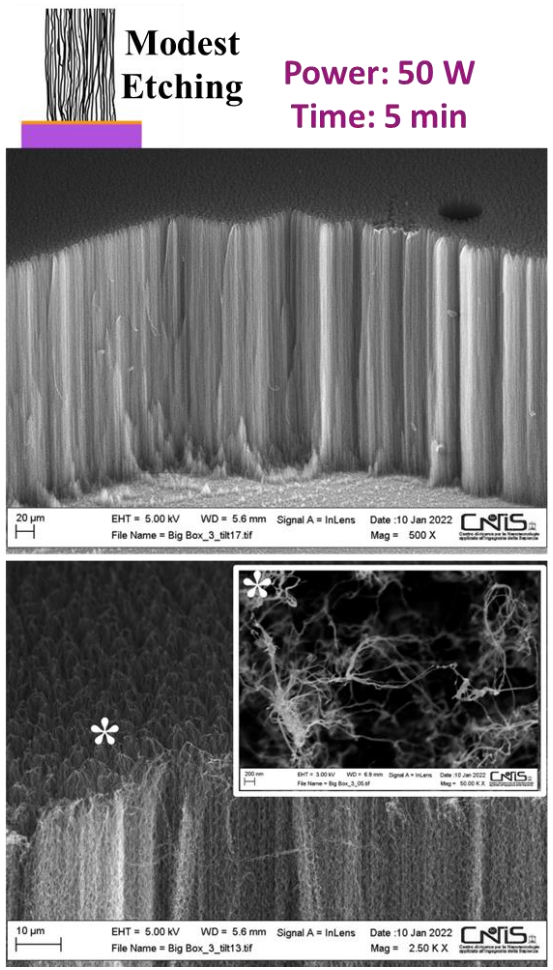


Evaluation of the **effect of O_2-Plasma Etching parameters** (*i.e.*, etching time, plasma power, frequency, pressure) on **CNTs morphology** and, consequently, on their properties (*i.e.*, **electron emission**)

*In collaboration with Giorgio **Pettinari**, CNRIFN,Rome, Italy

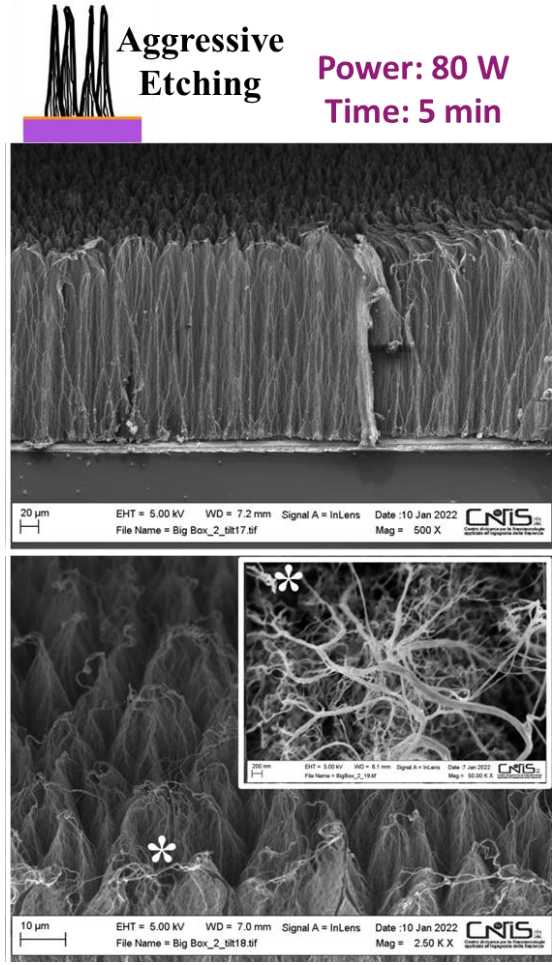
Optimizing Ar/O_2 plasma etching parameters to remove the top crust layer





❖ **Removal of the crust layer:**

- Optimizing plasma etching parameters
- Measuring morphology (SEM), roughness (AFM) and electron emission



ON-GOING

*In collaboration with Giorgio **Pettinari**, CNRIFN,Rome, Italy

Applications of VA-CNTs

1M€ PRIN 2020

❑ Dark Matter Detector

- 'Dark-photocathode' of aligned CNTs

❑ Surface Disinfections

- self-disinfecting surfaces

Collaborating with Sapienza Biology Department

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❑ **Advanced composite materials**

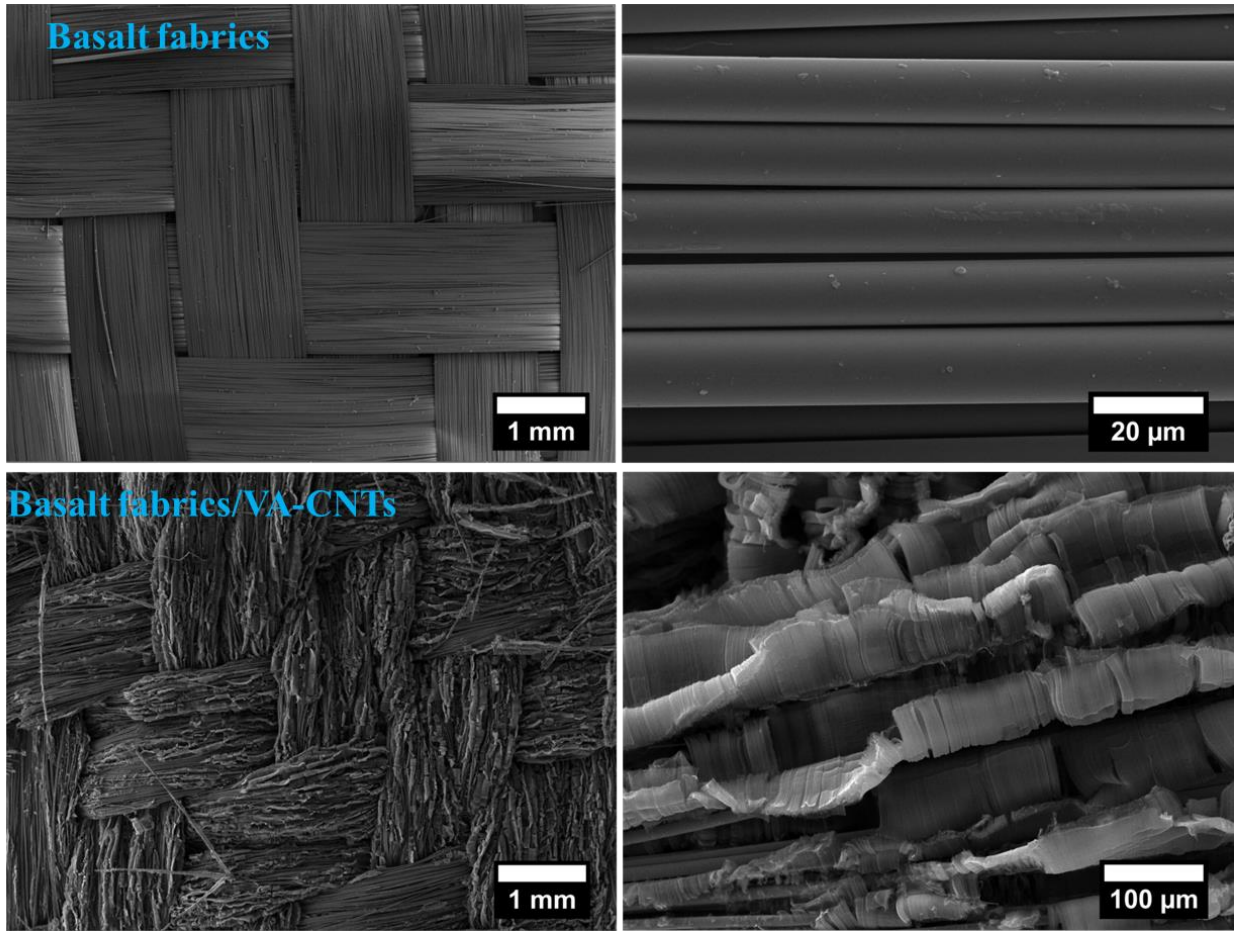
- CNTs-based nanocomposites

CNTs-based Nanocomposites: Basalt Fibers with VA-CNTs

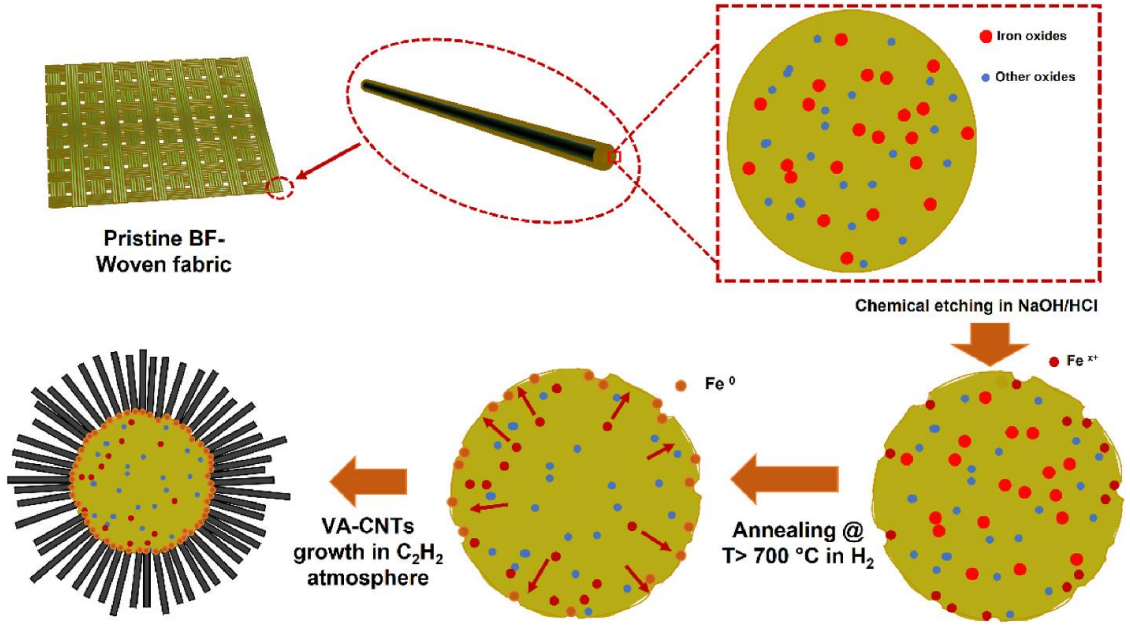
*In collaboration with Sapienza Engineering Department (DICMA)

❖ **Basalt fibers (BF)**, manufactured from natural basalt rock and typically used as **mechanical reinforcement in polymeric matrix composites**, are a **green material** exhibiting:

- high chemical resistance and stability;
- excellent mechanical properties;
- Much cheaper than carbon fibers.



❖ We synthesized, for the first time, VA-CNTs directly on BF without external catalyst by exploiting iron oxides of BF.

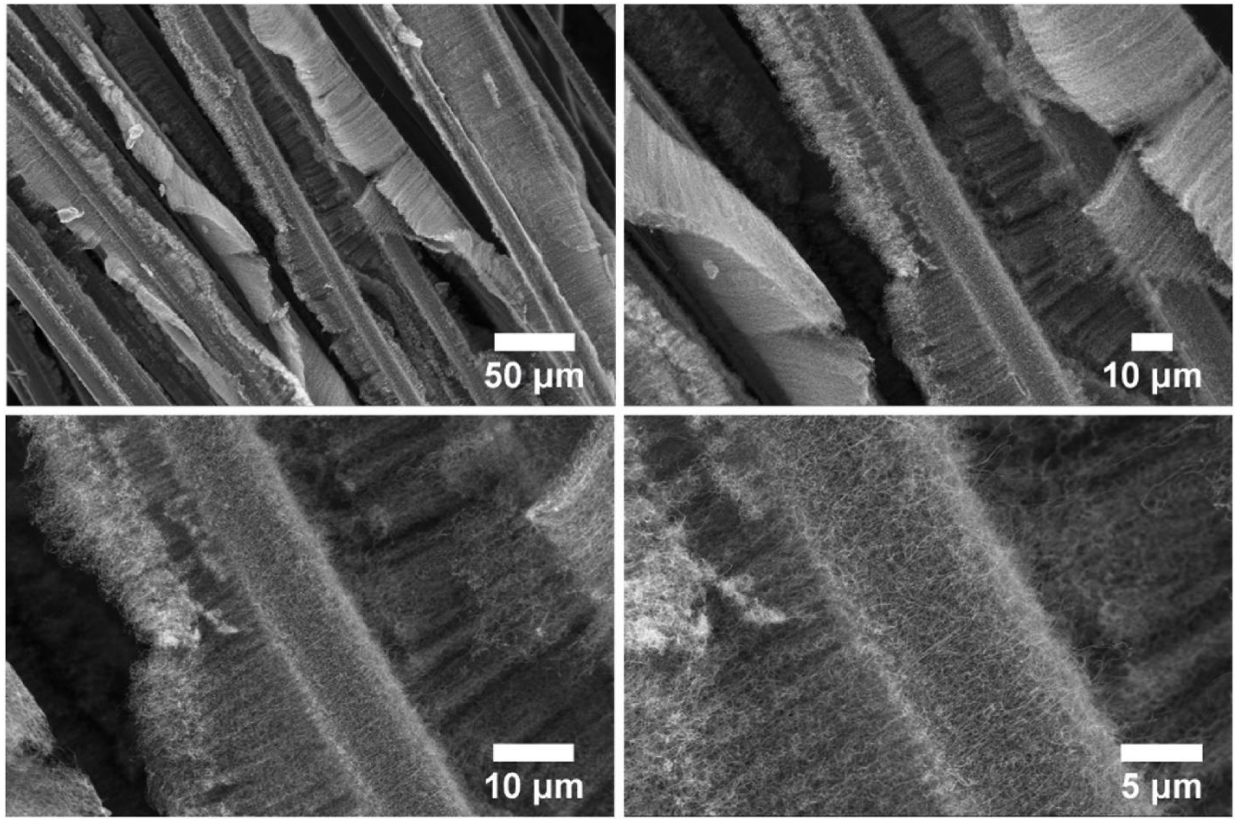


*F. Sarasini et al., Composites Part B: Engineering **2022**, 243.*

CNTs-based Nanocomposites: Basalt Fibers with VA-CNTs

*In collaboration with Sapienza Engineering Department (DICMA)

SEM micrographs detailing the morphology of CNT-modified basalt fabric



- CNTs act as **structural reinforcement** of polymer matrices with enhanced interfacial adhesion and add new functionalities

- VA-CNTs turn BF (intrinsically insulating) into an electrically conductive (~260 S/m) fabric

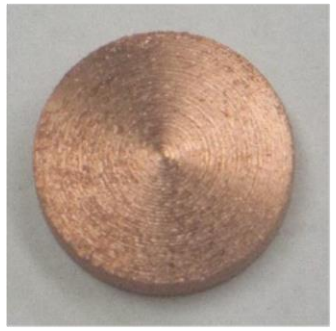
- New application fields for BF:
  - smart textiles;
  - structural reinforcement of polymer matrices
  - Wearable and highly stretchable supercapacitors.

*F. Sarasini et al., Composites Part B: Engineering **2022**, 243.*

DRAGON COPPER: High-Performance 3D-Printed CNTs-reinforced copper matrix nano-composites

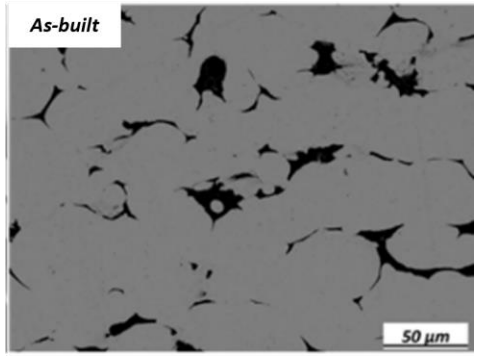
Patent Pending

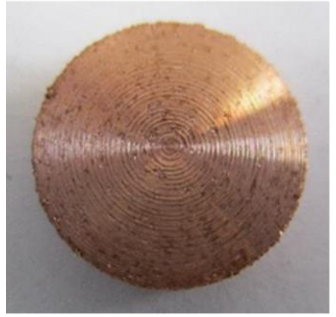
https://www.uniroma1.it/it/brevetto/102022000010511



3D-printed copper

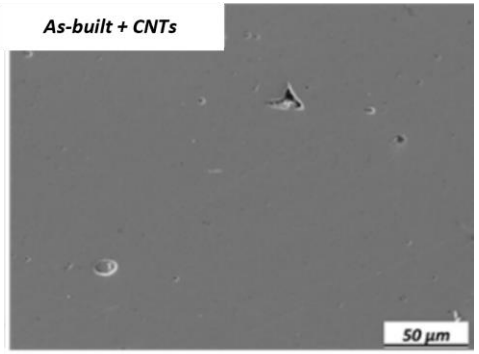
Microstructural defects
Porosity
Density < 90%





Dragon Copper

Uniform fusion
No porosity
Density > 99%



- Small fraction of **CNTs** added to copper powder
- Overcomes limitations of selective laser melting (*i.e.*, microstructural defects, porosity, low density)
- Achieved **uniform fusion** and very **high density** (>99%)
- **Greatly improved** mechanical properties

KEY FEATURES

+113%
breaking strength

+64%
elastic module

+5%
thermal conductivity

(compared to 3D-printed pure copper)

With only
0.1 wt%
Carbon Nanotubes

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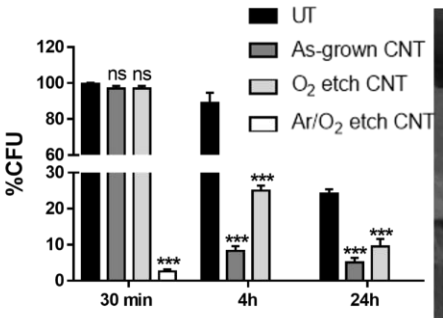
❑ Advanced composite materials

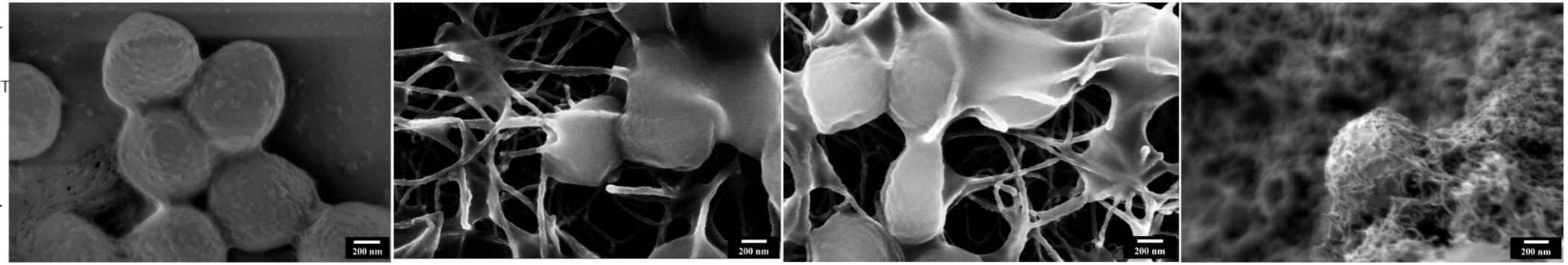
- CNTs-based nanocomposites

Antibacterial properties of CNTs

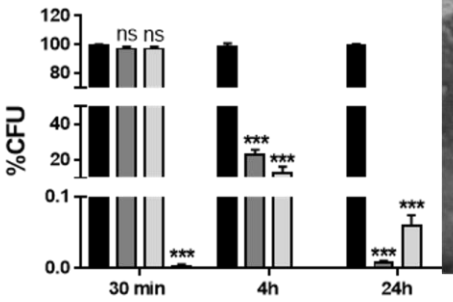
*In collaboration with D. Uccelletti (Sapienza Biology Department)

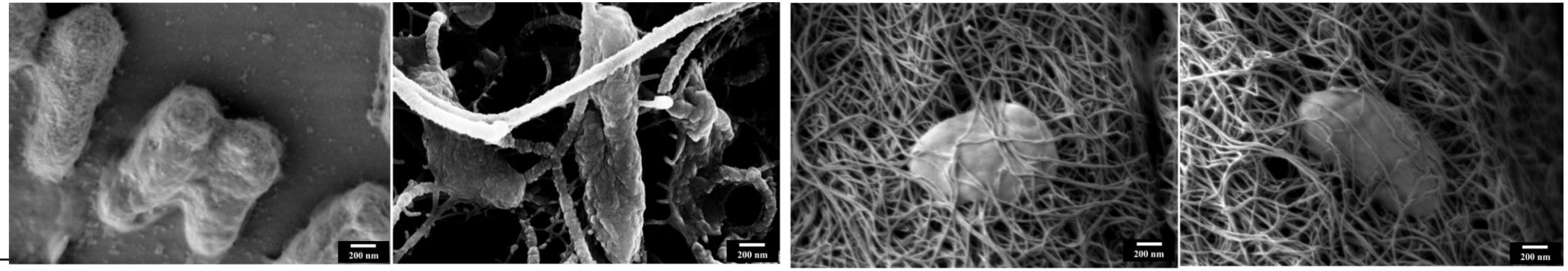
S.aureus





P. aeruginosa





- Bacterial cells adhere tightly to CNTs and become crumpled
- CNTs act as needles penetrating the bacterial cell wall
- Development of self-cleaning surfaces for biomedical devices, filtering systems, solid–air and –liquid interfaces in healthcare units

Conclusions and perspectives

Our CVD chamber successfully synthesizing VA-CNTs since August 2020;

CNT-based carpets show uniform distribution on the underneath catalyst support, typical diameter of around **20 nm** and lengths up to **300 µm**;

Highly aligned MWCNTs can be synthesized on both **opaque** (*i.e.*, silicon) and **transparent** (*i.e.*, fused silica) substrates, but also on non-conventional supports (*i.e.*, basalt, quartz and carbon fibers)

Thanks to the optimization of the CNTs' synthesis process different R&D activities on different application fields were developed :

- **NanoUV**: **UV light** detectors based on carbon nanotubes;
- **Andromeda**: DM detectors built around a target of VA-CNTs;
- **NanoBio**: carbon nanotubes for **biosensors**
- Development of novel **composite materials** made with carbon nanotubes

H (D) upload on VA-CNTs

Precise tuning of VA-CNTs density, distribution, length and alignment by using both *in-situ* and *ex-situ* approaches;

Removal of the crust layer and optimization of non-uniformity and density of catalyst nanoparticles to reduce waviness at the nanoscale

⁞ ON-GOING

Acknowledgement

- Prof. Gianluca Cavoto
- Prof. Carlo Mariani
- Ravi Prakash Yadav (PhD student)

- Prof. Daniela Uccelletti (Sapienza Biology Department)
- Prof. Fabrizio Sarasini (Sapienza Engineering Department (DICMA))
- Giorgio Pettinari (CNR-IFN)

- Francesco Pandolfi

- Valerio Pettinacci (INFN Roma)
- Donato Orlandi (LNGS)
- Daniele Cortis(LNGS)

- Prof. Alessandro Ruocco
- Alice Apponi (PhD student)