Carbon nanotubes lined by anodic deposition of MnO_2 for supercapacitor application

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FEMAN Group, IN²UB
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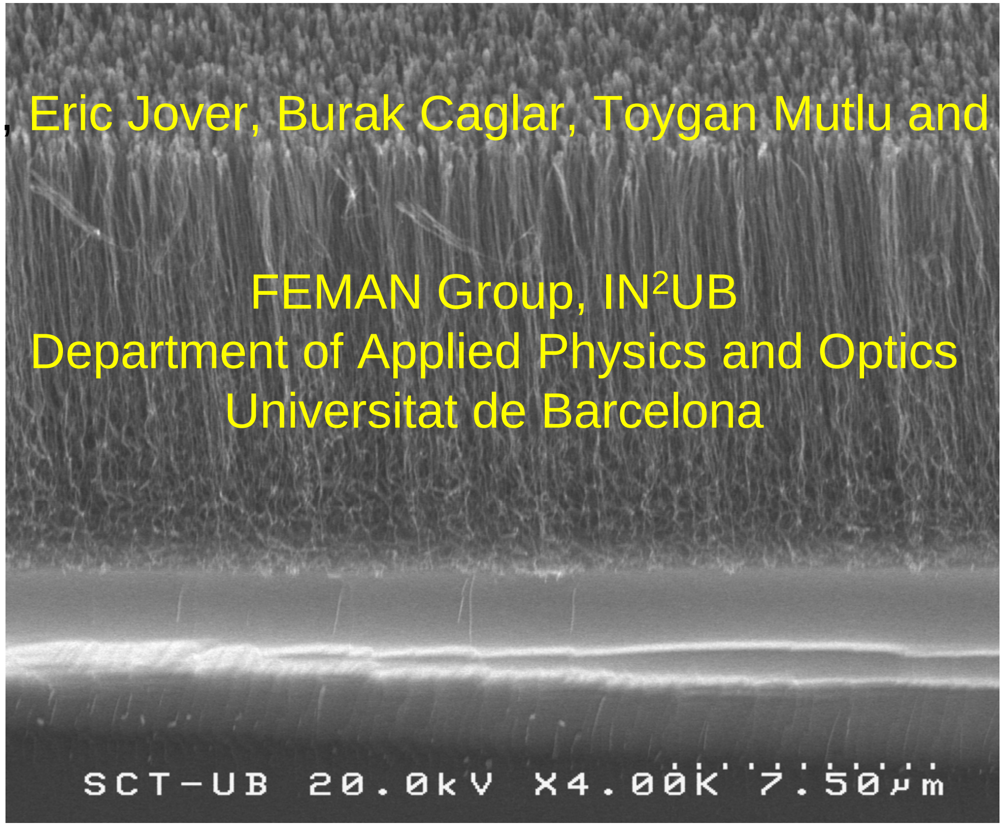
Universitat de Barcelona



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OUTLINE

- INTRODUCTION
- SYNTHESIS AND CHARACTERIZATION OF CNTs
- ELECTROCHEMICAL DEPOSITION OF MnO_2
  - POTENTIOSTATIC DEPOSITION
  - GALVANOSTATIC DEPOSITION
- ELECTROCHEMICAL CHARACTERIZATION OF CNTs/MnO_2
- CONCLUSION AND OUTLOOK

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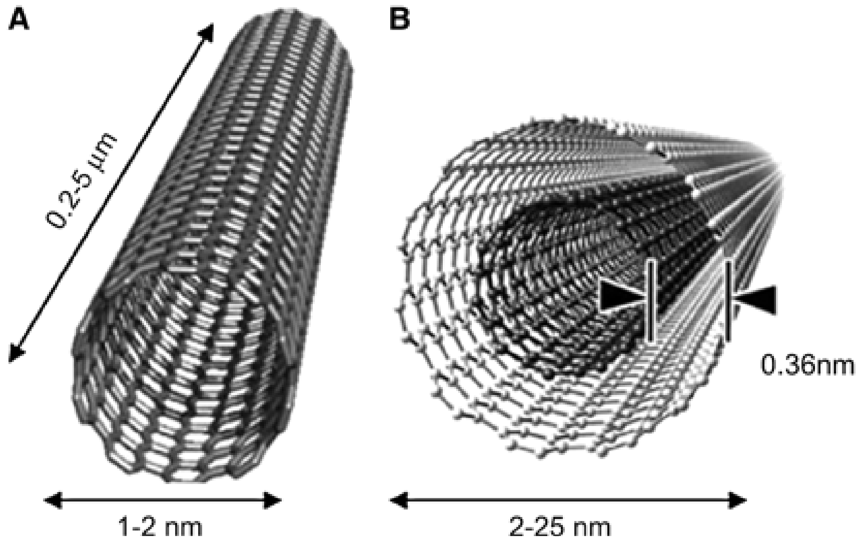
CARBON NANOTUBES

Can be thought as rolled-up **graphene sheets**

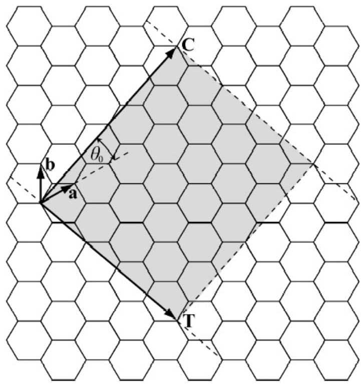
A. Single-walled CNTs
B. Multi-walled CNTs



[1]

Chiral vector:

$$\vec{C}_h = n\vec{a} + m\vec{b} \equiv (n,m)$$

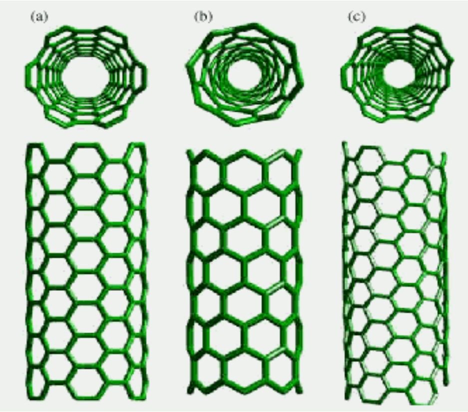


[2]

Atomic structures:

- •Armchair
- •Zig-zag
- •Chiral

armchair zig-zag chiral



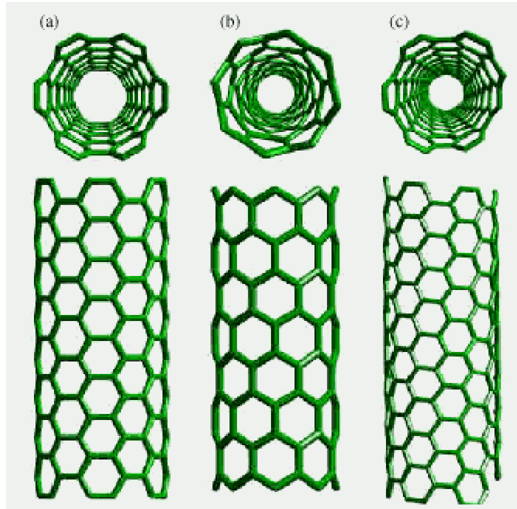
[1] R. M. Reilly, Journal of Nuclear Medicine Vol. 48 No. 7 (2007)1039-1042
[2] Cox, B. J. and Hill, J. M. (2007), *SPIE Newsroom.*

CARBON NANOTUBES

- Properties:
  - Mechanical (strongest fibers in nature)
    Young modulus > 1 TPa
  - In theory CNTs can withstand very high electrical current densities up to 10^9 $A \cdot cm^{-2}$
  - High thermal conductivity > 3000 W/mK
  - High surface area (1 to > 2000 m^2/g)
  - Chemical and thermal stability
  - Can be functionalized

Electrical behaviour depends on the atomic structure

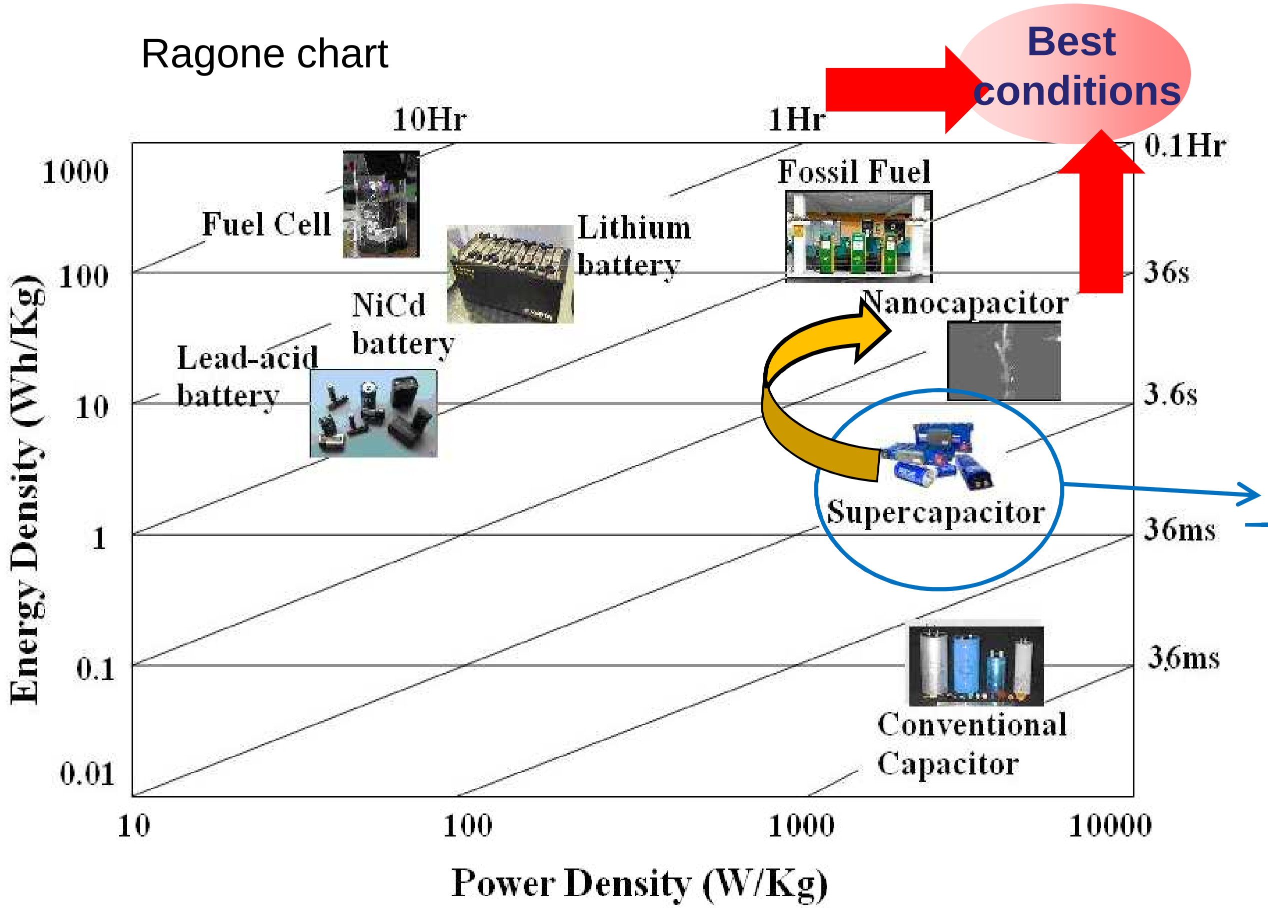
armchair zig-zag chiral



metal semiconductor

SUPERCAPACITORS

Ragone chart



✓Relatively high energy storage densitiy

✓High power density

✓Long cyclic life

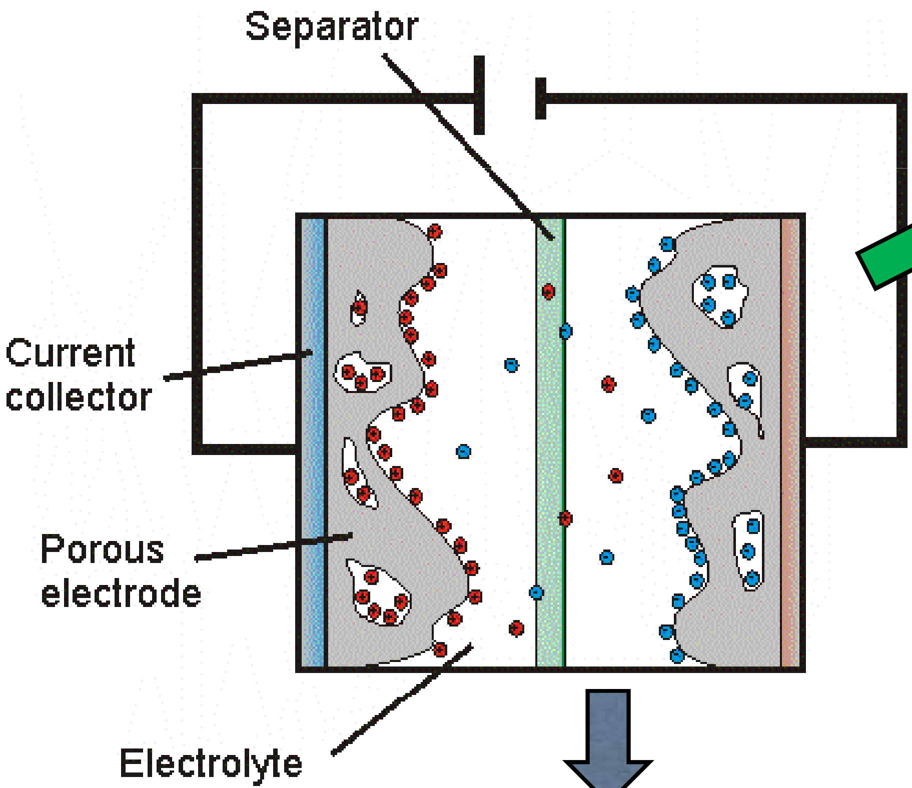
Applications:

•Electric vehicles
•Pulse power applications

http://imechanica.org/node/4939/revisions/11120/view

SUPERCAPACITORS

Electric Double Layer Capacitor



CNTs can improve the performance of supercapacitor due to:

✓Large surface area
✓High conductivity

Mechanisms:

➢Electrostatic charge storage

Activated carbon (~ 100 Fg^{-1})

Improvements in development

➢Pseudocapacitance:

Redox reactions at the surface of active materials (~ 1000 Fg^{-1} for RuO_2)
(RuO_2,MnO_2,Fe_3O_4)

MnO_2:
✓rich redox behaviour
✓Low cost
✓Enviromentally friendlier

SUPERCAPACITORS

CNTs – based electrodes
(from a **suspension**):

- ❑High capacitive currents
- ❑Limited reproducibility
- ❑Spatial heterogeneity
- ❑Low cost technology
- ❑Scalability to large areas

Vertically aligned CNTs - based electrodes:

- ❑ Low contact resistance
- ❑ Large specific surface area
- ❑ Fast electron transfer kinetics
- ❑ Low capacitive currents
- ❑Spatial homogeneity
- ❑Control of surface density
- ❑Confinement to a desired area by photolithography
- ❑Middle cost technology
- ❑Scalable technology at large areas

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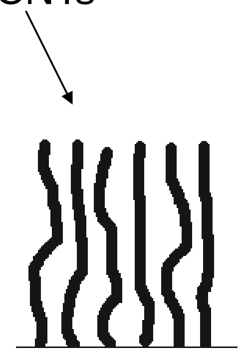
GOAL of this WORK:

1. Synthesis of long, dense and thin VACNTs

VACNTs



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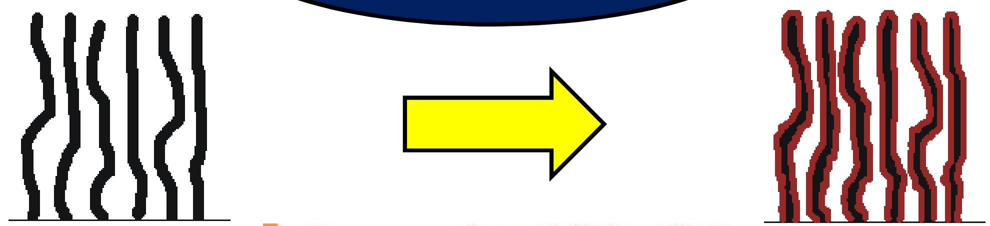
GOAL of this WORK:

1. Synthesis of long, dense and thin VACNTs

2. e-deposition of MnO_2

VACNTs

MnO_2/VACNTs



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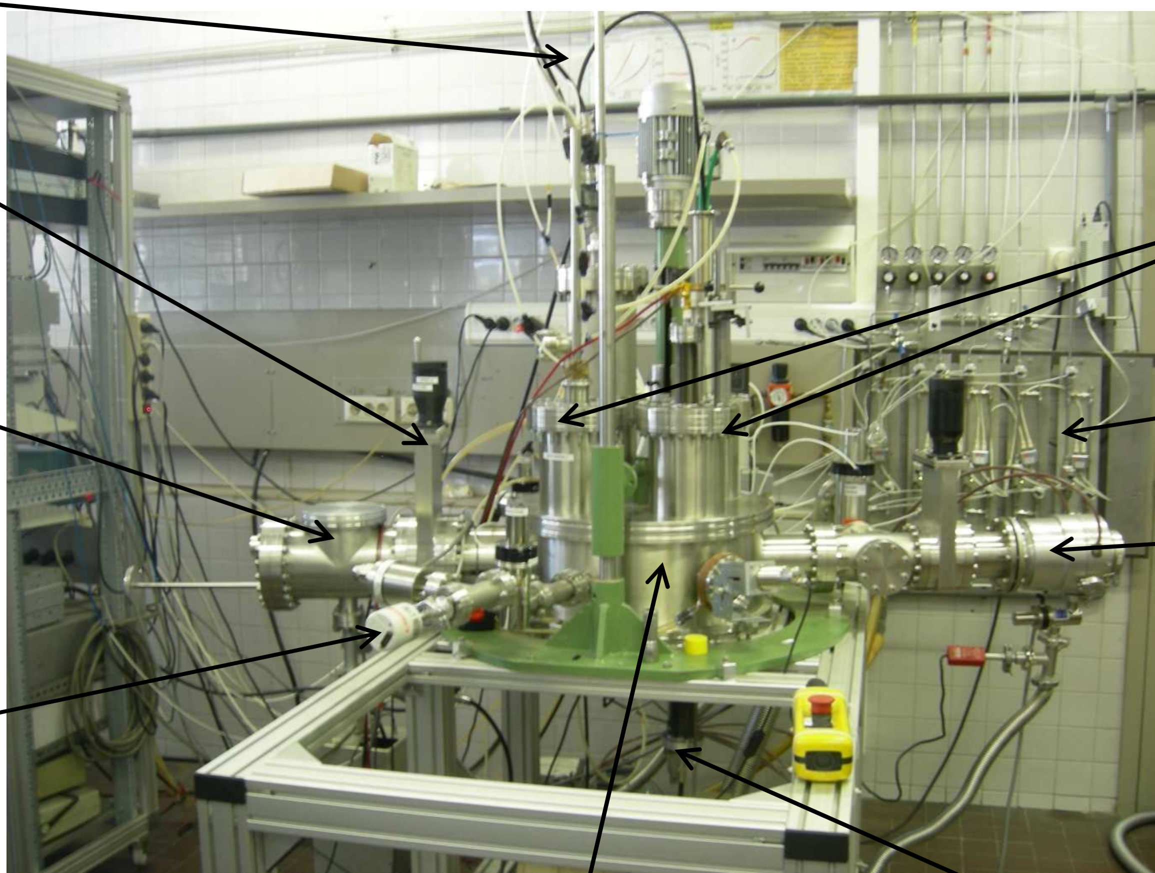
SYNTHESIS OF CNTs

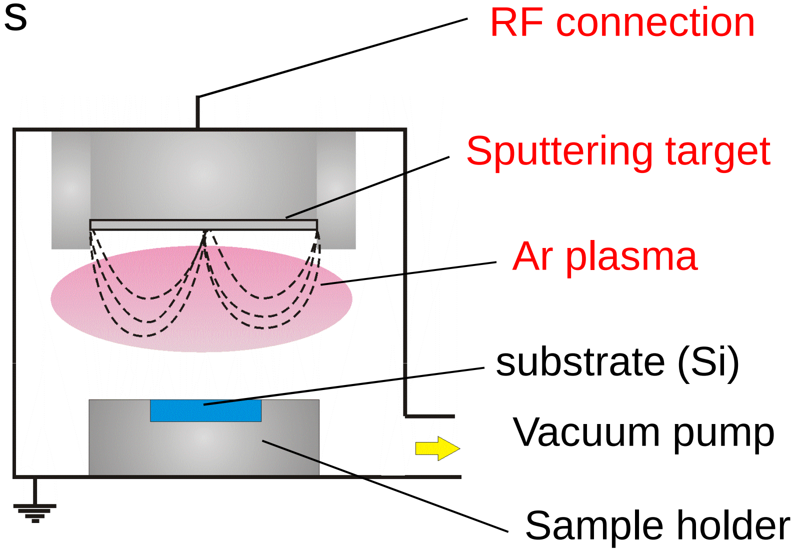
PECVD and CVD reactor of the FEMAN group



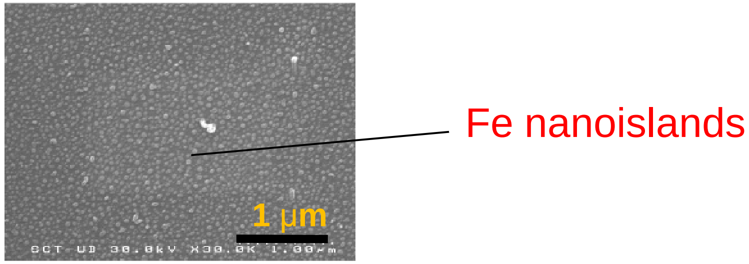
SYNTHESIS OF CNTs

Steps of the synthesis

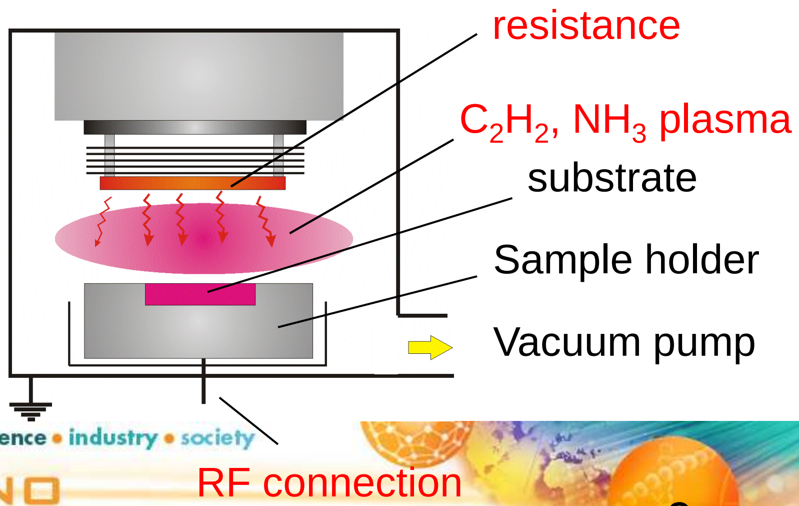
1. **Magnetron sputtering** of Fe (thin film deposition) → **Catalyst layer**
   - RF power: 50 W
   - Pressure: 2 Pa
   - Target material: Fe



2. **Annealing** under H_2 → **Granulation**
   - Pressure: 2 Pa
   - T= 600 – 800 ºC
   - Hold time: 120 s

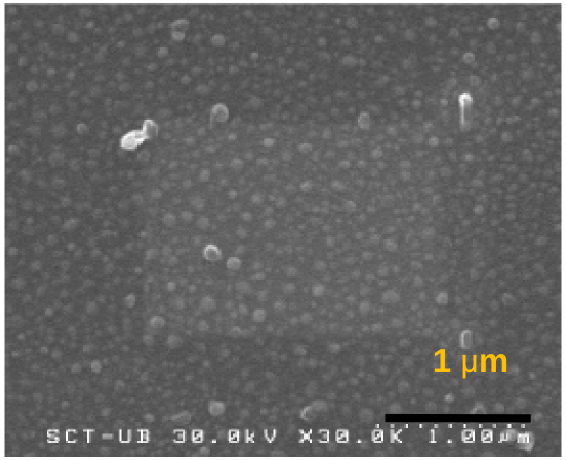


3. Plasma enhanced chemical vapour deposition (**PECVD**) → **CNTs growth**
   - RF Power: 50 W
   - NH_3, C_2H_2 (2:1)
   - Pressure: 100 Pa

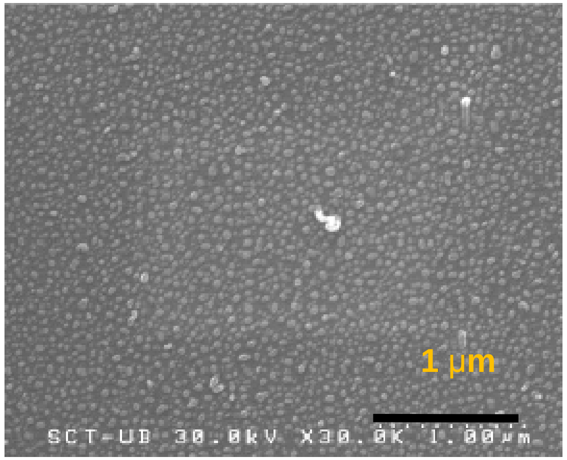


SYNTHESIS OF CNTs

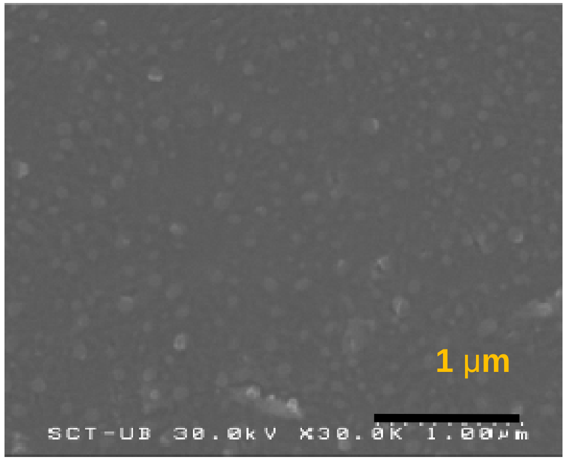
Optimization of the annealing time



10 min, 750 ºC

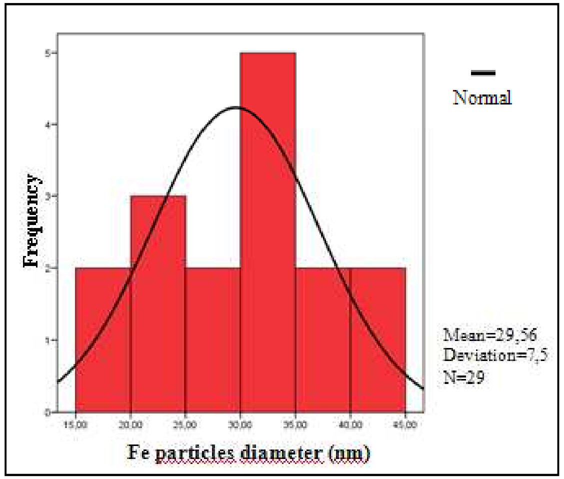


14.5 min, 750 ºC



30 min, 750 ºC

Sample	Fe particle diameter (nm)
10 min	51 +/- 10
14.5 min	32 +/- 8
30 min	83 +/- 20

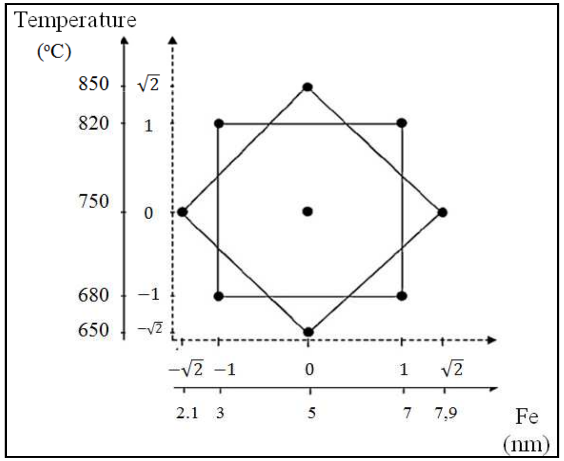


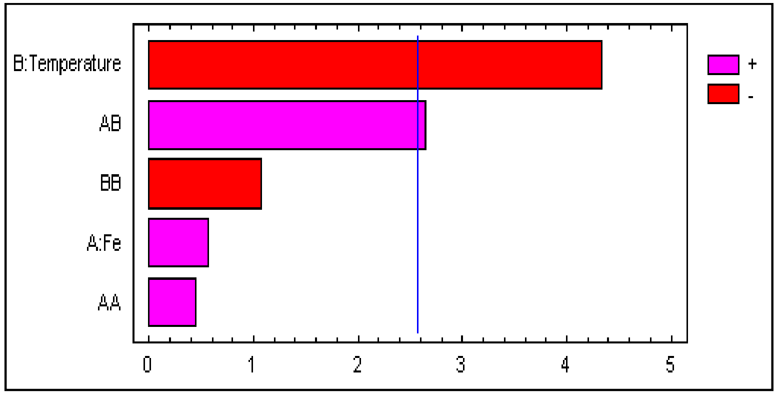
Distribution of the Fe particles' diameter

SYNTHESIS OF CNTs

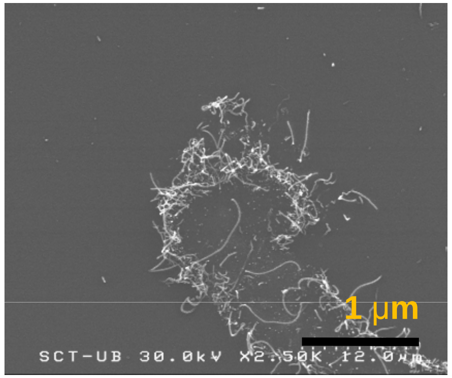
Box –Wilson optimization:

- ✓ catalyst thickness
- ✓PECVD reaction temperature

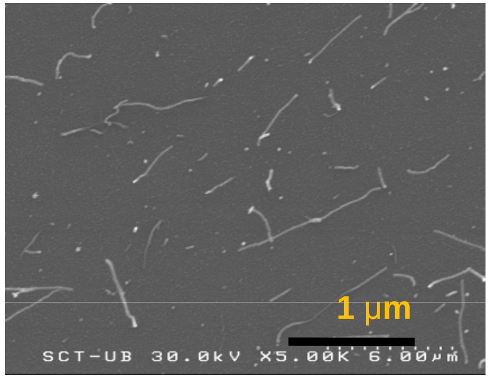




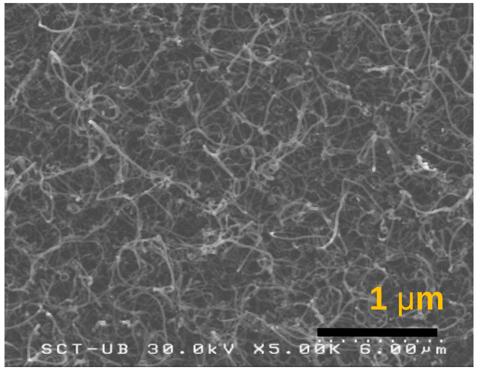
Pareto diagram of the standarized effects of T and catalyst thickness on the CNTs density

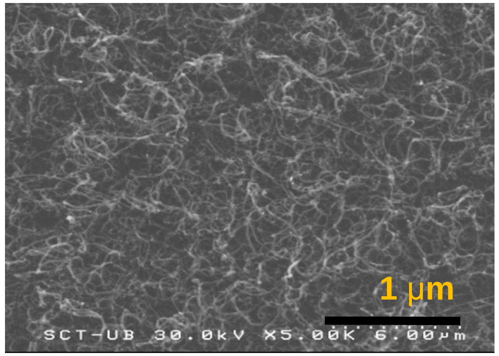


2.1 nm, 750 ºC

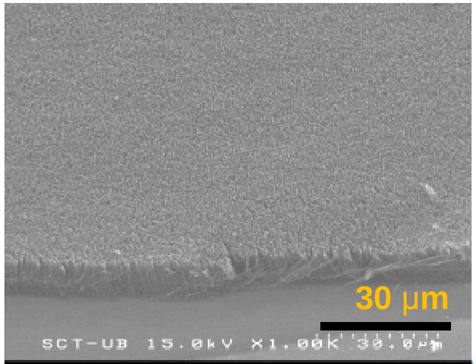


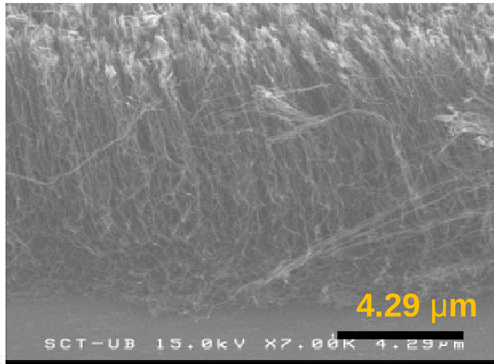
3 nm, 820 ºC





5 nm, 750 ºC



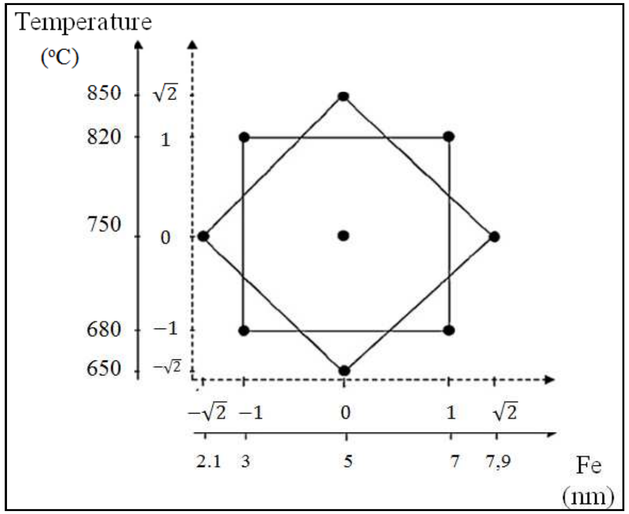


3 nm, 680 ºC

SYNTHESIS OF CNTs

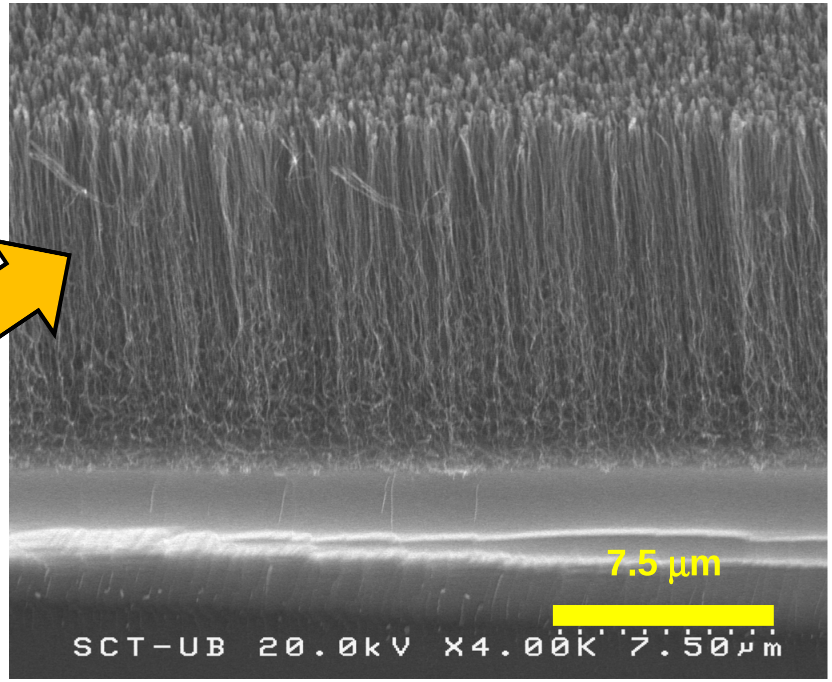
Box –Wilson optimization:

✓ catalyst thickness
✓PECVD reaction temperature



Diameter = $\alpha_0 + \alpha_1 T + \alpha_2 t + \alpha_3 T^2 + \alpha_4 t^2 + \alpha_5 Tt$

T = PECVD reaction temperature
t = catalyst thickness



OPTIMUM CONDITIONS:

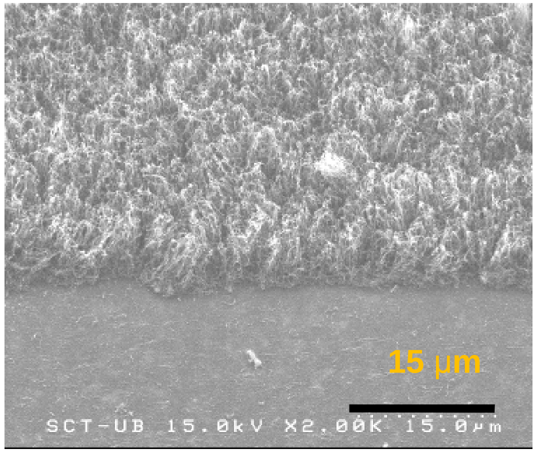
t_{Fe} = 3 nm
T_{PECVD} = 680 ºC

} ~ 30 nm
Length ~ 9 µm
Vertically aligned

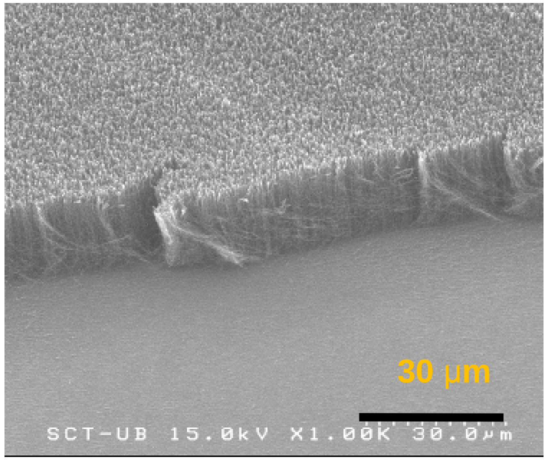
SYNTHESIS OF CNTs

Optimization of the PECVD reaction time

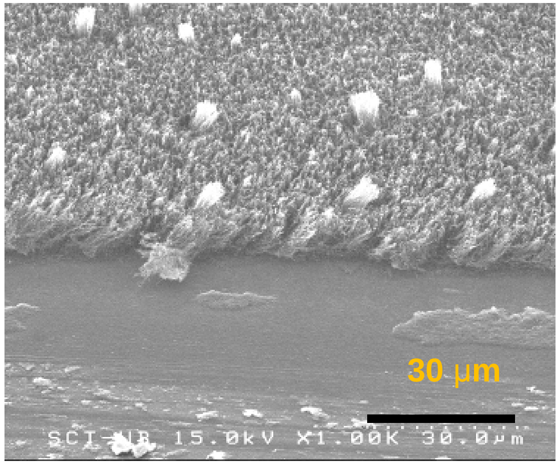
PECVD reaction time (s)	Reaction temperature/ catalyst thickness	CNTs diameter (nm)	CNTs length (μm)
600	680 ºC / 3 nm	45 +/- 10	4 +/- 1
900	680 ºC / 3 nm	22 +/- 9	17 +/- 5
1200	680 ºC / 3 nm	30 +/- 10	10 +/- 2



600 s



900 s

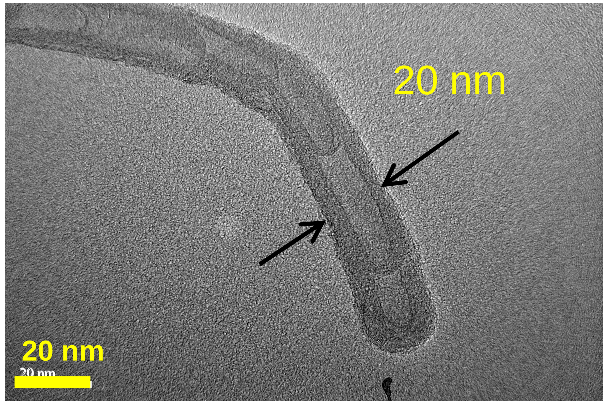


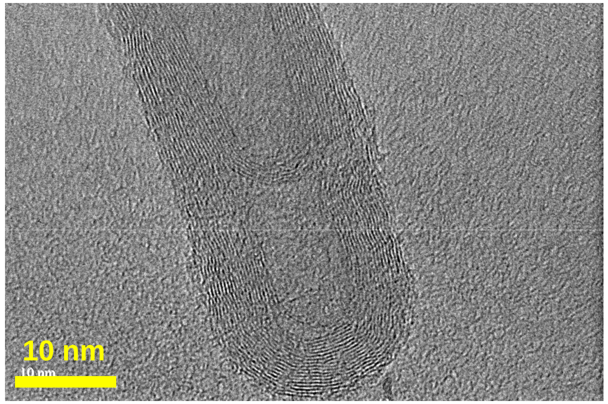
1200 s

CHARACTERIZATION OF CNTs

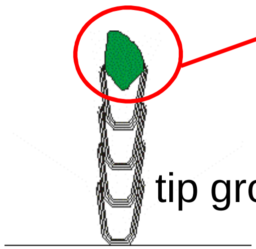
TEM images of the CNTs

- Multi-walled CNTs
- “Bamboo-like” structure

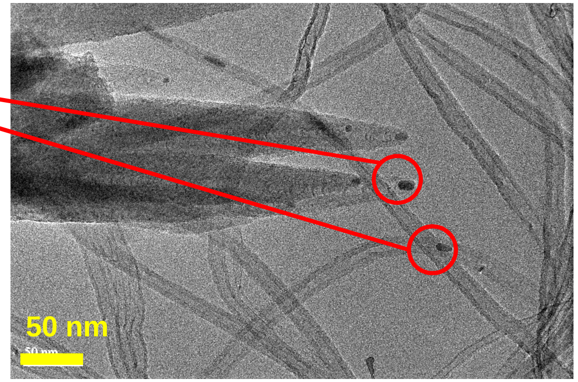




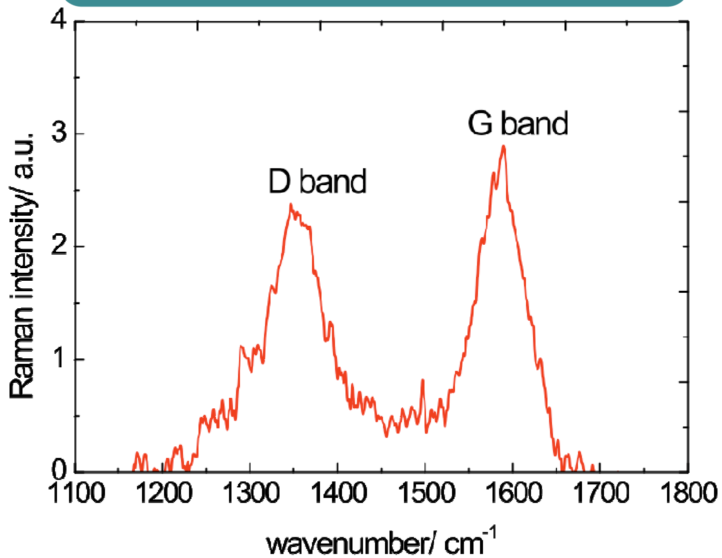
Fe nanoparticles



tip growth mechanism



Raman spectroscopy



$I_D/I_G = 0.84$
D band: 1351 cm^{-1}
G band: 1584 cm^{-1}

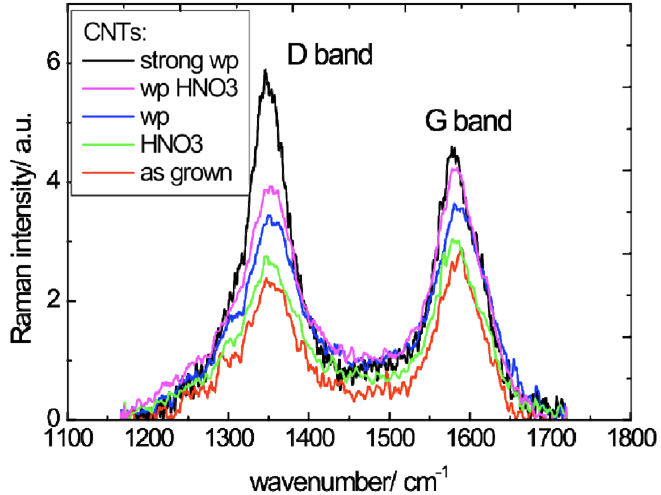
CHARACTERIZATION OF CNTs

Raman spectroscopy

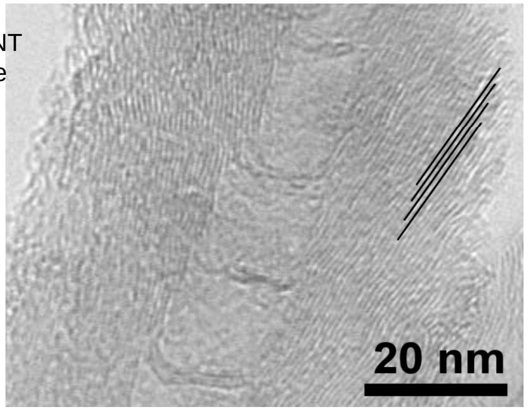
Surface treatments:

- Water plasma
- Immersion in nitric acid

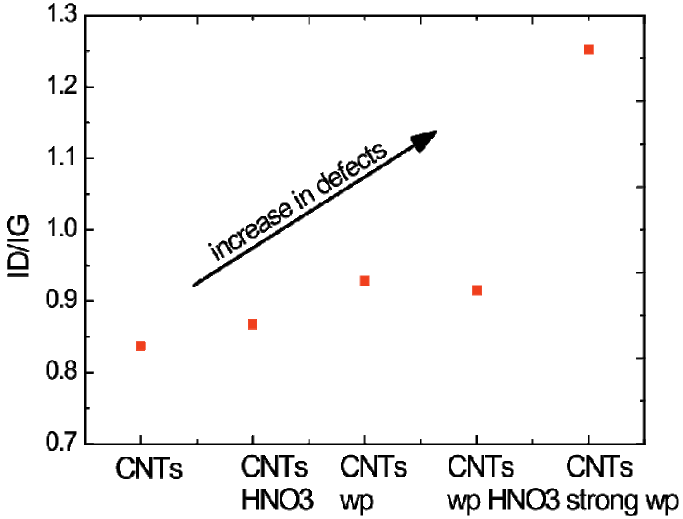
- **Remove amorphous carbon**
- **Clean CNTs structures**
- **Expose graphitic edge planes**
- **Open the tips of the CNTs**
- **Improve electron transfer electrode/electrolyte**



HRTEM image of the body of a CNT showing its bamboo-like structure



Crystalline graphitic planes



[3] F.J. del Campo, J. García-Céspedes, F. Xavier Muñoz, E. Bertran, Electrochemistry Communications 10, 1242-1245 (2008).

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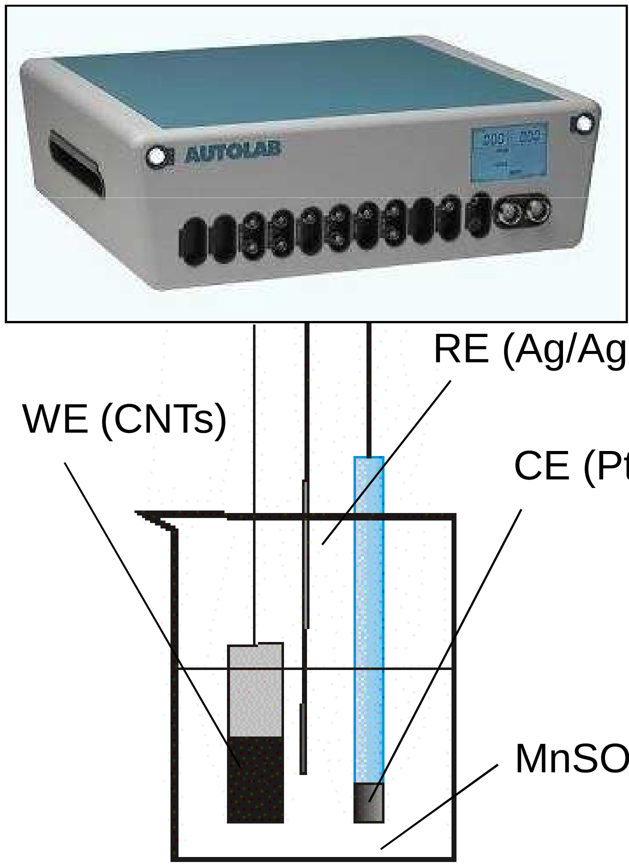
ELECTROCHEMICAL DEPOSITION OF MnO_2

Potentiostatic deposition of MnO_2

- 0.6 V vs. Ag/AgCl
- 0.2 M $MnSO_4 \cdot H_2O$
- 3 minutes



ELECTROCHEMICAL DEPOSITION OF MnO_2

Potentiostatic deposition of MnO_2

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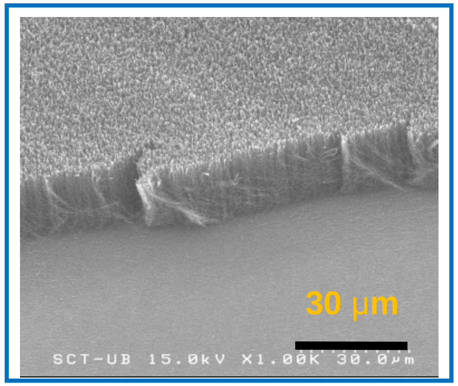
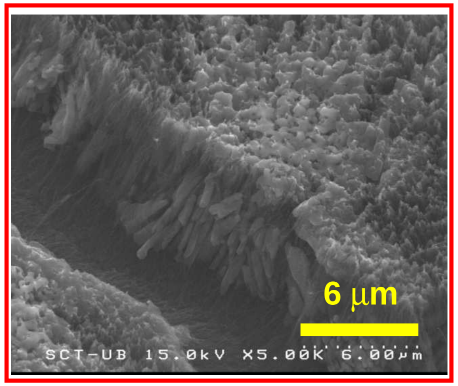
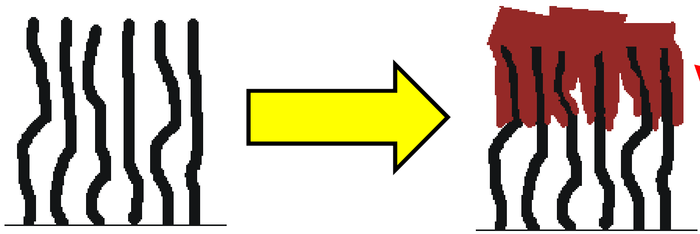
- ➢0.2 M $MnSO_4 \cdot H_2O$
- ➢3 minutes

Before

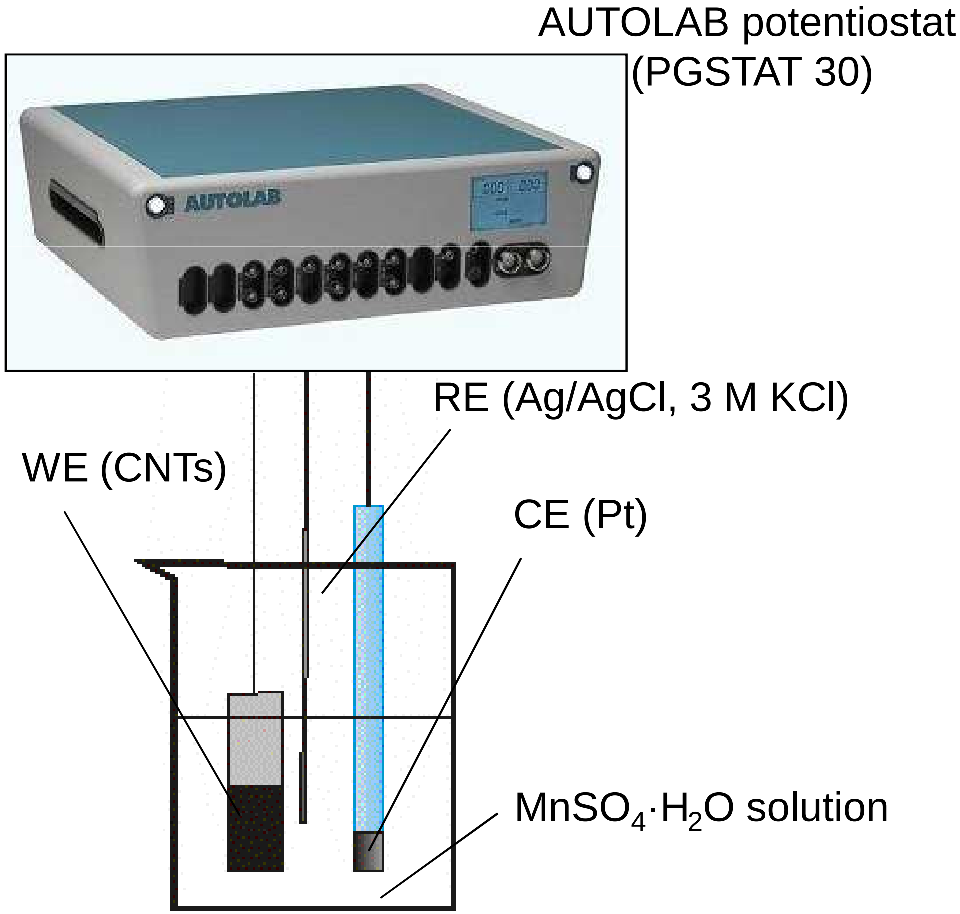


After





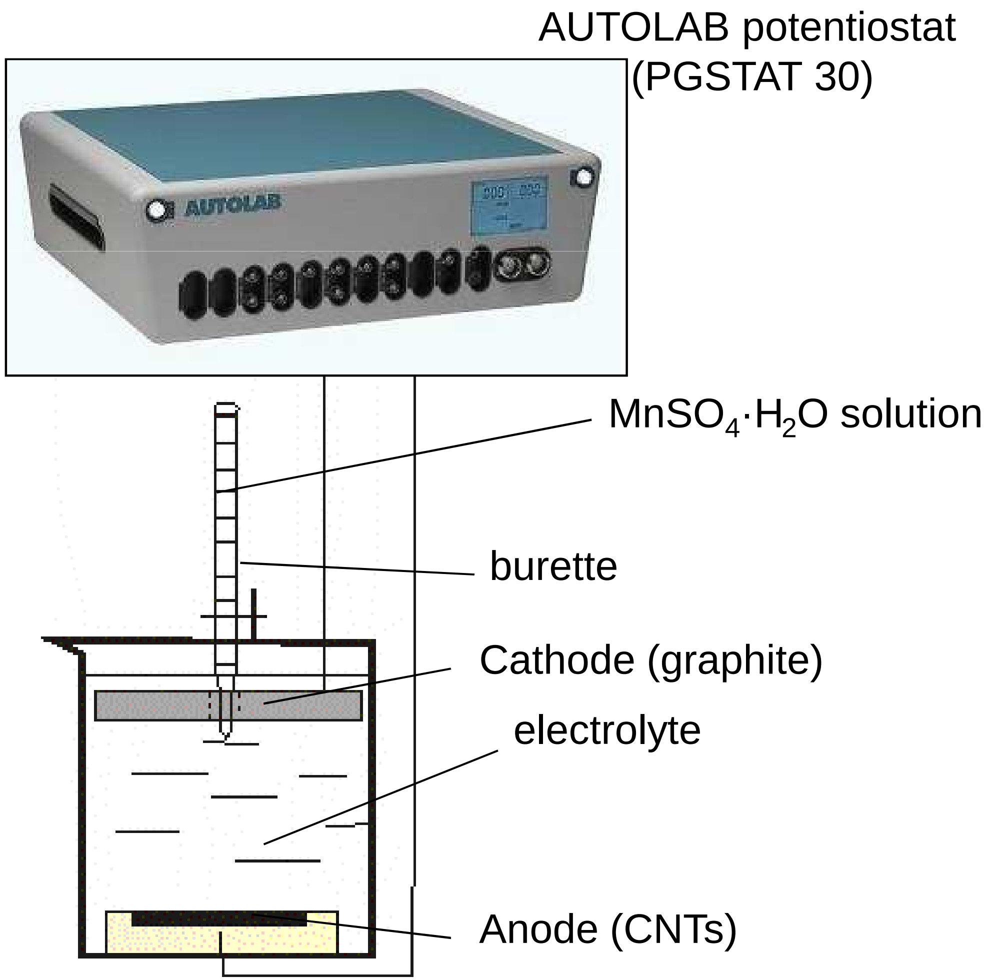
A thick layer of MnO_2 is deposited on top of the CNTs



ELECTROCHEMICAL DEPOSITION OF MnO_2

Galvanostatic deposition of MnO_2

- 1 mA/cm^2
- 0.5 mL 0.2 M $MnSO_4 \cdot H_2O$
- 2 minutes



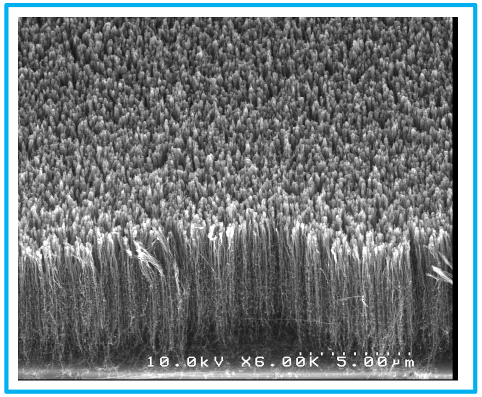
Fan et al., Diamond and related materials 17 (2008) 1943-1948

ELECTROCHEMICAL DEPOSITION OF MnO_2

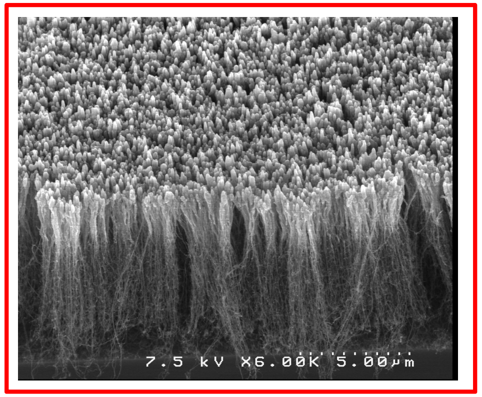
Galvanostatic deposition of MnO_2

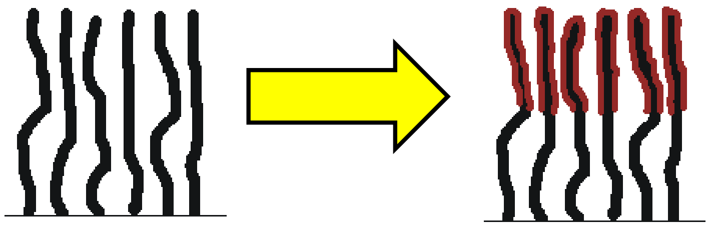
- 1 mA/cm^2
- 0.5 mL 0.2 M $MnSO_4 \cdot H_2O$
- 2 minutes

Before

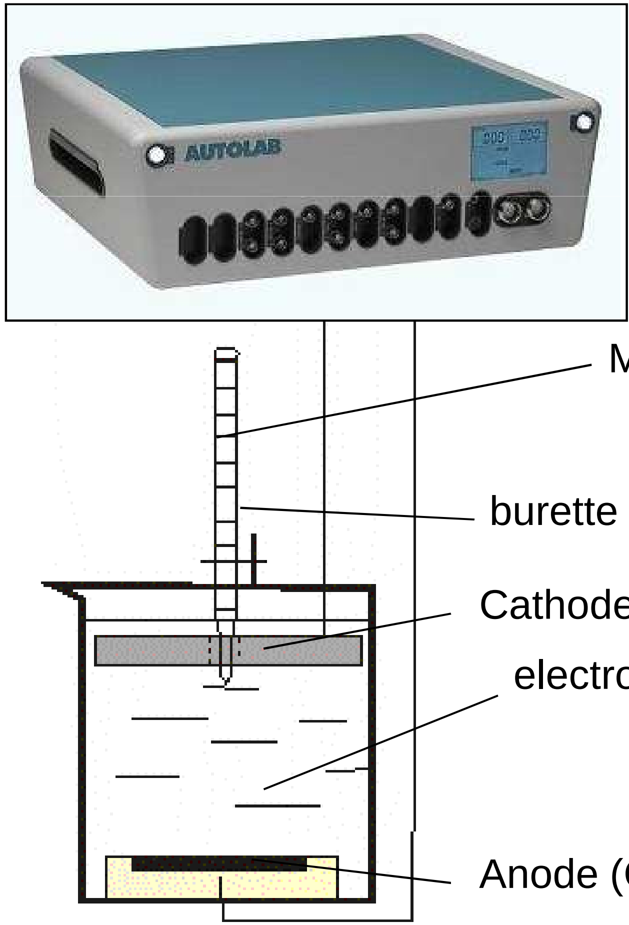


After





AUTOLAB potentiostat (PGSTAT 30)



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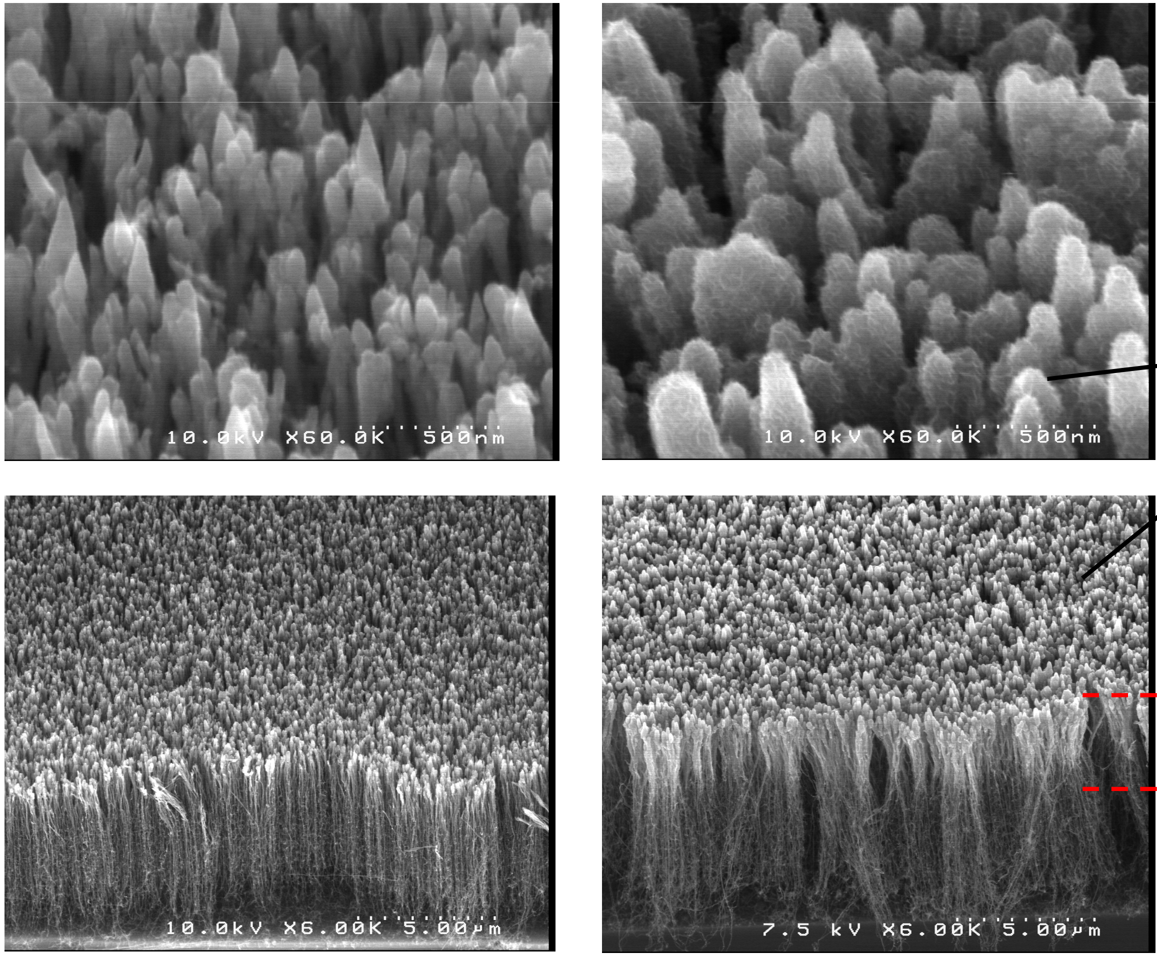
Thinner and more homogeneous layer of MnO_2

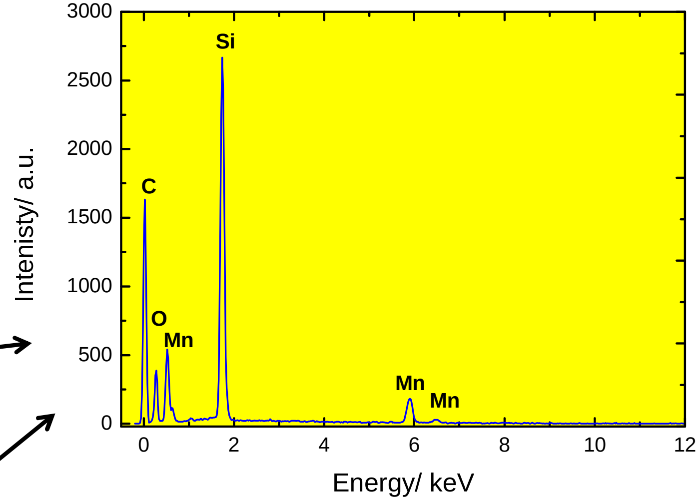
ELECTROCHEMICAL DEPOSITION OF MnO_2

SEM images

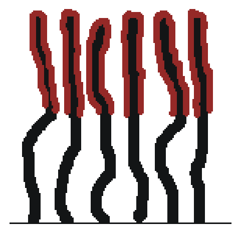
Before After



EDS spectrum



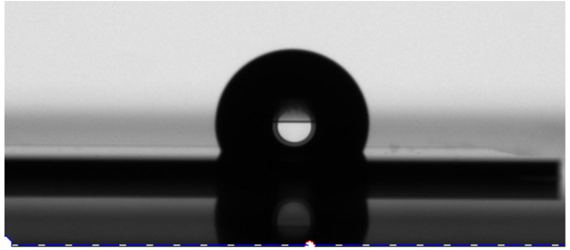
MnO_2 layer



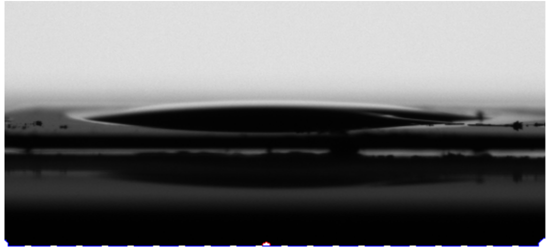
WATER PLASMA TREATMENT

Hydrophylicity of the nanotubes can be increased by a water plasma treatment

untreated sample:



Water plasma treated sample:



- ❑ The surface of the CNTs is functionalized with different chemical groups such as C-OH, C=O and COOH

- ❑ The amorphous carbon and Fe catalyst particles are removed

Poster:
S.Hussain et al., Functionalization and characerization of CNTs by means of water plasma

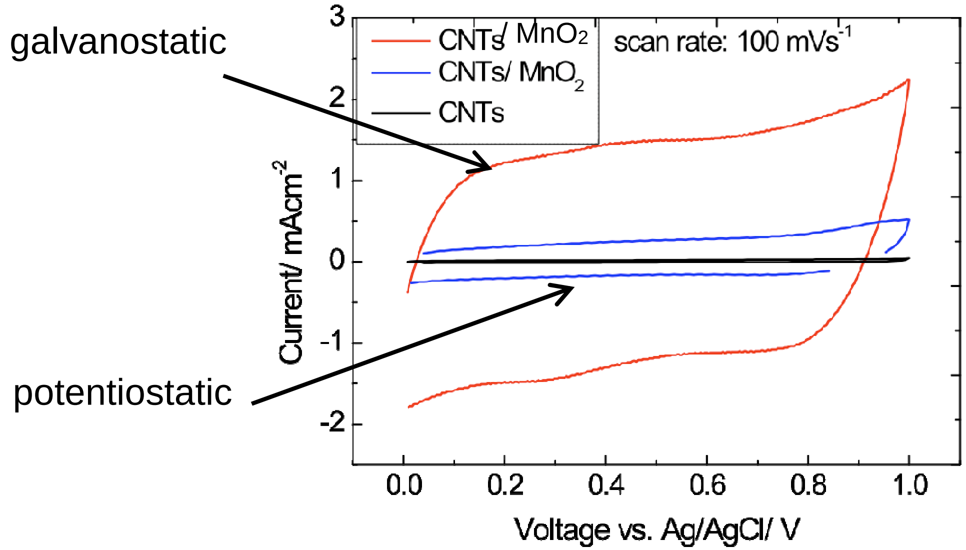
OUTLINE

- INTRODUCTION
- SYNTHESIS AND CHARACTERIZATION OF CNTs
- ELECTROCHEMICAL DEPOSITION OF MnO_2
  - POTENTIOSTATIC DEPOSITION
  - GALVANOSTATIC DEPOSITION
- **ELECTROCHEMICAL CHARACTERIZATION OF CNTs/MnO_2**
- CONCLUSION AND OUTLOOK

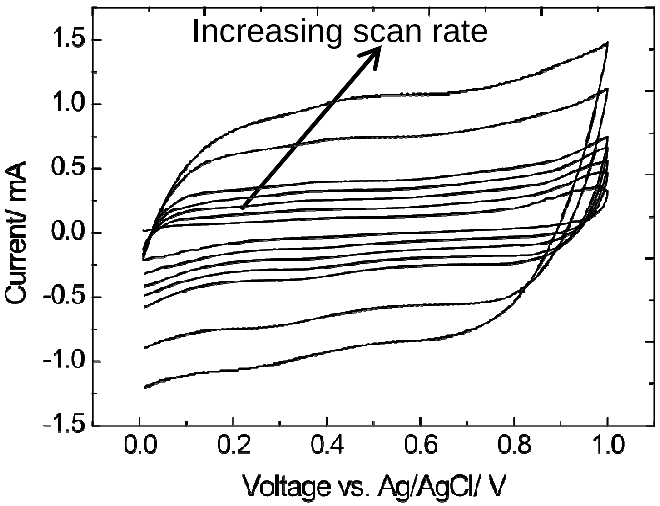
ELECTROCHEMICAL CHARACTERIZATION OF CNTs/MnO_2

Cyclic voltammetry:

- CNTs/MnO_2 electrodes obtained by galvanostatic electrochemical deposition show higher capacitance. Up to **643 F·g^{-1}** at 10 mV·s^{-1} scan rate.

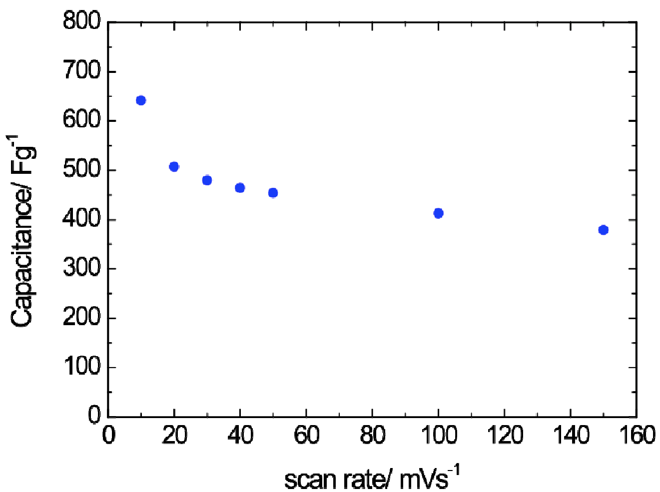


VACNTs/MnO_2 galvanostatic deposition:



$$C_S = \frac{q_a + q_c}{2 m_{MnO_2} \Delta V}$$

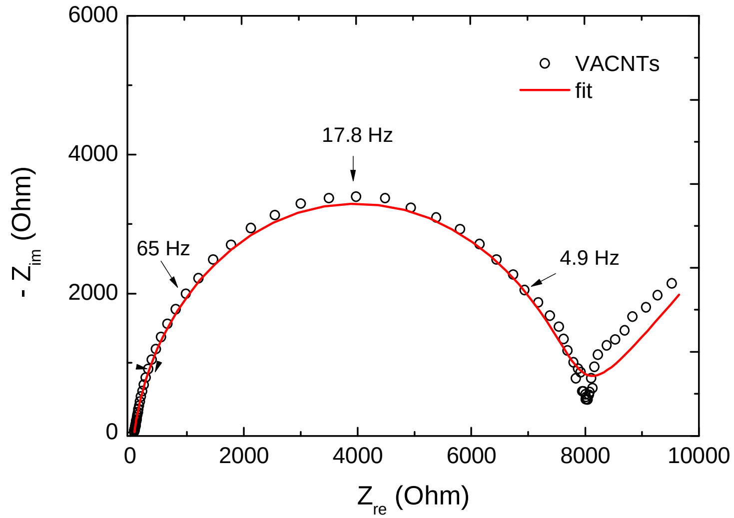
The MnO_2 mass was calculated from UV-vis light absorption of MnO^{4-} obtained from the sample oxidation

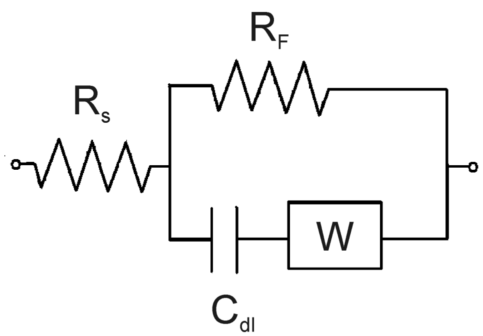


ELECTROCHEMICAL CHARACTERIZATION OF CNTs/MnO_2

Impedance spectroscopy:

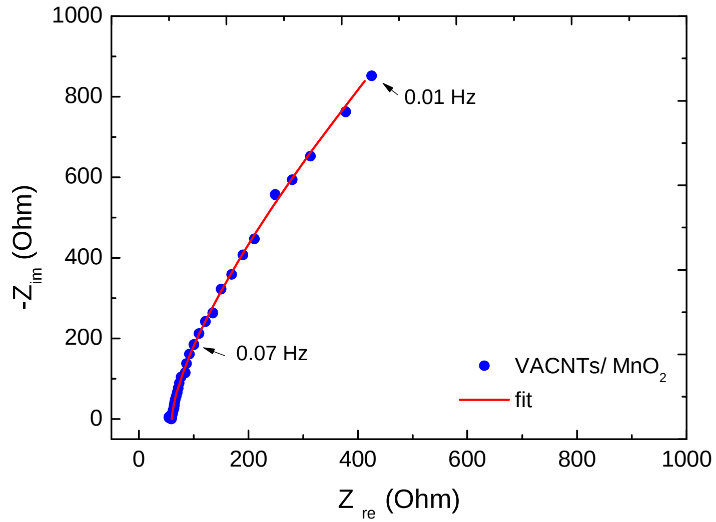
VACNTs:

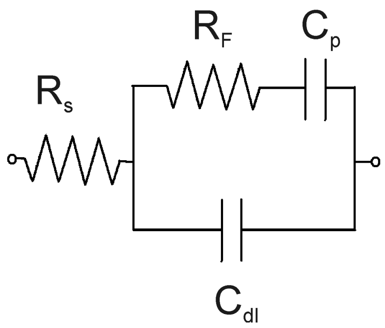




➢The value of the double-layer capacitance of the CNTs is 2 μF·cm^{-2}

VACNTs/MnO_2 galvanostatic deposition:





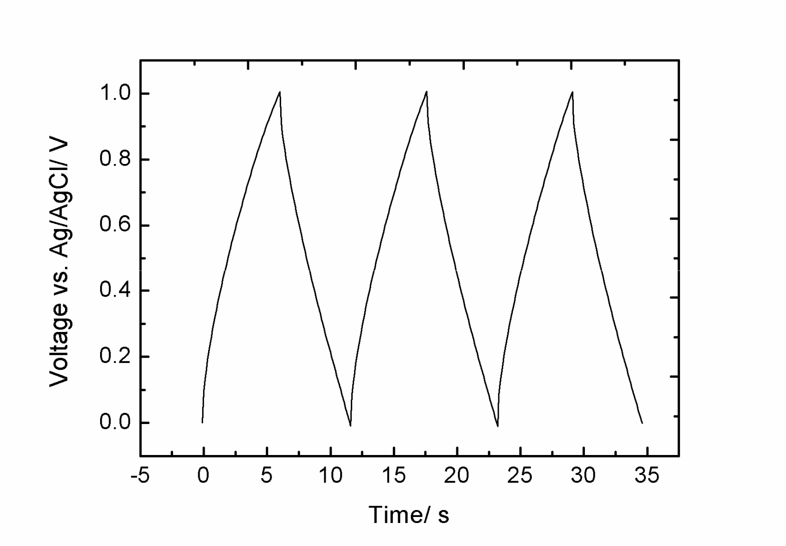
➢The value of the pseudo-capacitance is similar to that obtained with CV; 550 F·g^{-1} (9 mF·cm^{-2})

ELECTROCHEMICAL CHARACTERIZATION OF CNTs/MnO_2

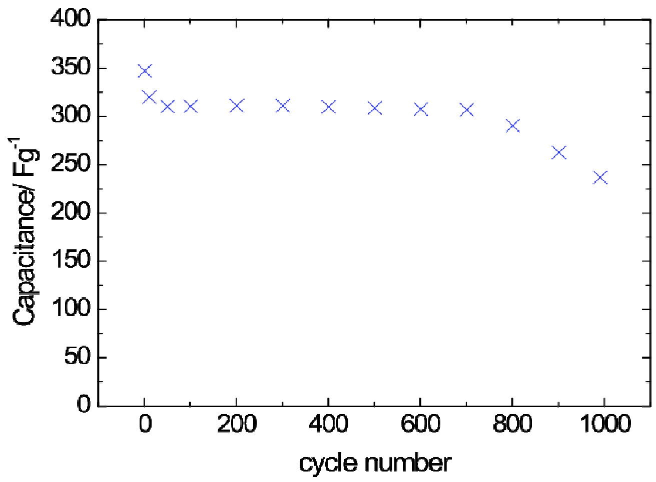
Galvanostatic charge/discharge curves:

$$C_s = \frac{I}{(\Delta V / \Delta t) \cdot m_{MnO_2}}$$

i = 1mA·cm^{-2}



Cycle stability:



- The CNTs/MnO_2 based electrodes show good cycle stability during the first **800 cycles**

- Measurements in a three-electrode cell using 0.2 M Na_2SO_4 as electrolyte

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CONCLUSION

❑ Optimum conditions for the production of dense, thin and vertically aligned CNTs were found to be:

✓Fe catalyst: 3 nm
✓Annealing time: 14.5 minutes
✓PECVD temperature: 680 ºC
✓PECVD time: 900 s

❑ A thin layer of MnO_2 lining the surface of the CNTs is achieved by galvanostatic deposition of MnO_2

❑ A specific capacitance of 643 $F \cdot g^{-1}$ was obtained for CNTs/MnO_2 based electrodes at 10 $mV \cdot s^{-1}$ scan rate

OUTLOOK

- Improve cycle stability of the electrodes (*e.g.* by heat treatment)
- Optimize water plasma/ acid treatment to improve the electrochemical deposition of MnO_2
- Use of ionic liquids to increase the voltage window (up to 3.5V)
- Electrochemical characterization in a two-electrode cell

ACKNOWLEDGMENTS

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THANK YOU !

Electrode material	CNT morph.	CNT diameter	Composite material/Deposition tech.	Spec. Cap.
Polished graphite plates	MWCNT	10–20nm	PSS/PEDOT/MnO_2	375F/g
Si wafer	MWCNT		RuO_2(electrochemically deposited)	1170 F/g
Nickel foam	MWCNT	15nm	manganese dioxide nanofibers	155 F/g
Si wafer	MWCNT	15 to 40 nm	MnO_2(electrodeposition)	471 F/g
Si wafer (Ti film 200 nm)	MWCNT		RuO_2	1380 F/g
Ni foam		20 nm	MnO_2	522 F/g
Ni foam	MWCNT		MnO_2(in situ coating)	250.5 F/g
Graphite	MWCNT		RuO_2	628 F/g
Ti foil	MWCNT	20nm	MnO_2(coprecipitation method)	250 F/g
Si wafers	MWCNT		Polypyrole (PPy)	250 F/g
Graphite substrate	MWCNT	50-100 nm	y-MnO_2 (electrochemically induced deposition)	579 F/g
Si wafer	MWCNT		NiOx (electrochemical deposition)	1701 F/g
Graphite substrate	MWCNT		Mn-oxide (electrophoretic deposition technique, EPD)	260 F/g
Stainless-steel	MWCNT	70–80 nm	Manganese dioxide (electrodeposition)	356 F/g
Ni-foam	MWCNT	30-70 nm	Nickel oxide	160 F/g
Platinum foil	MWCNT	50-100 nm	MnO_2 (thermally decomposing manganese nitrates)	568 F/g