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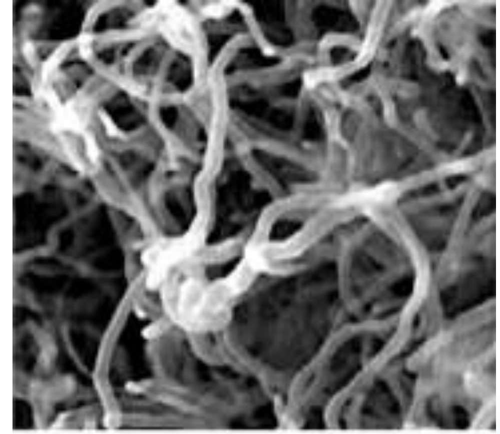
Helium Ion Irradiation Effects in Carbon Nanotubes Based Filters

27-05-2021



Helium Ion Irradiation Effects in Carbon Nanotubes Based Filters

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Objectives

- Investigate the modification Multiwalled Carbon nanotubes (MWNTs) using He ion irradiation.
- Characterization of ion beam irradiated MWNTs using (SEM, EDS, Raman Spectrometry).
- Study the modification mechanisms of irradiated MWNTs.

Work importance

- Investigations on structural change of irradiated CNTs are of great importance to provide insights for interactions between energetic particles and CNTs.
- The ion beam not only is used to introduce defects in nanotubes but also change the tubes diameter which enhances their performance for various potential applications like water filtration.

Introduction

Carbon nanotubes

Carbon nanotubes are allotropes of carbon. These cylindrical carbon molecules have interesting properties that make them potentially useful in many applications, There are different shapes: MWNTs and SWNTs

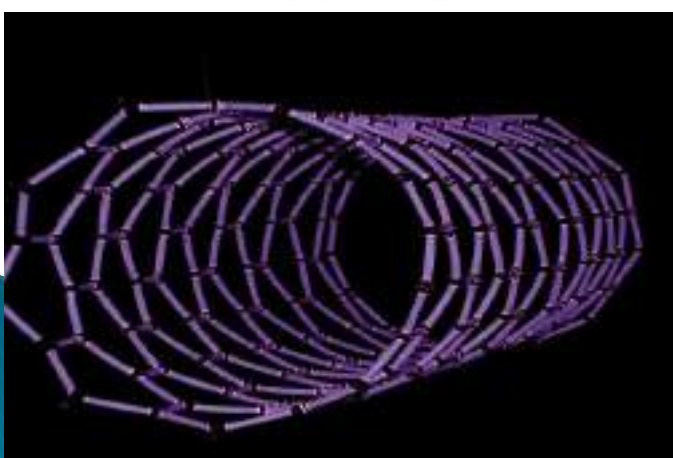
Properties

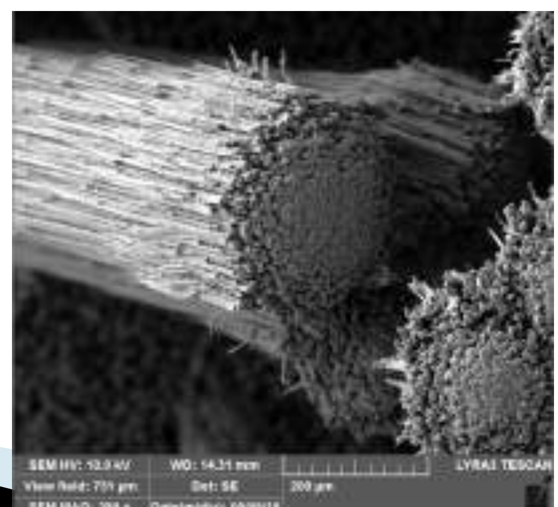
- high surface areas
- smaller pores with high permeability
- good mechanical and thermal stability
- energy saving and low cost
- High adsorption capacity

Applications

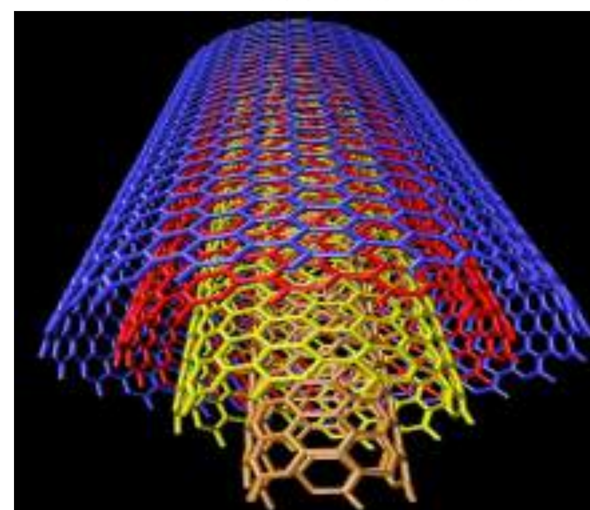
- Composites
- Electronics and batteries
- **Water purification**
- Solar cells
- Space devices

SWNT



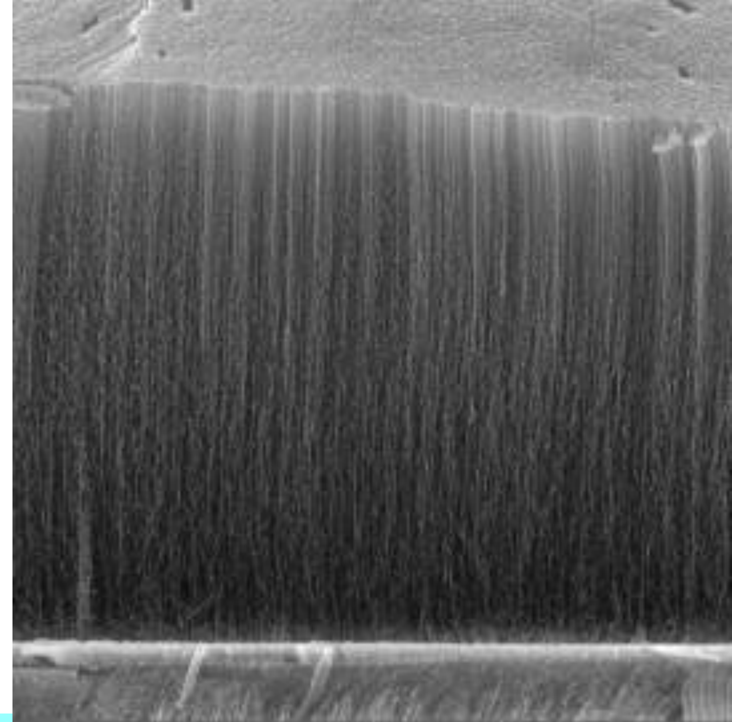


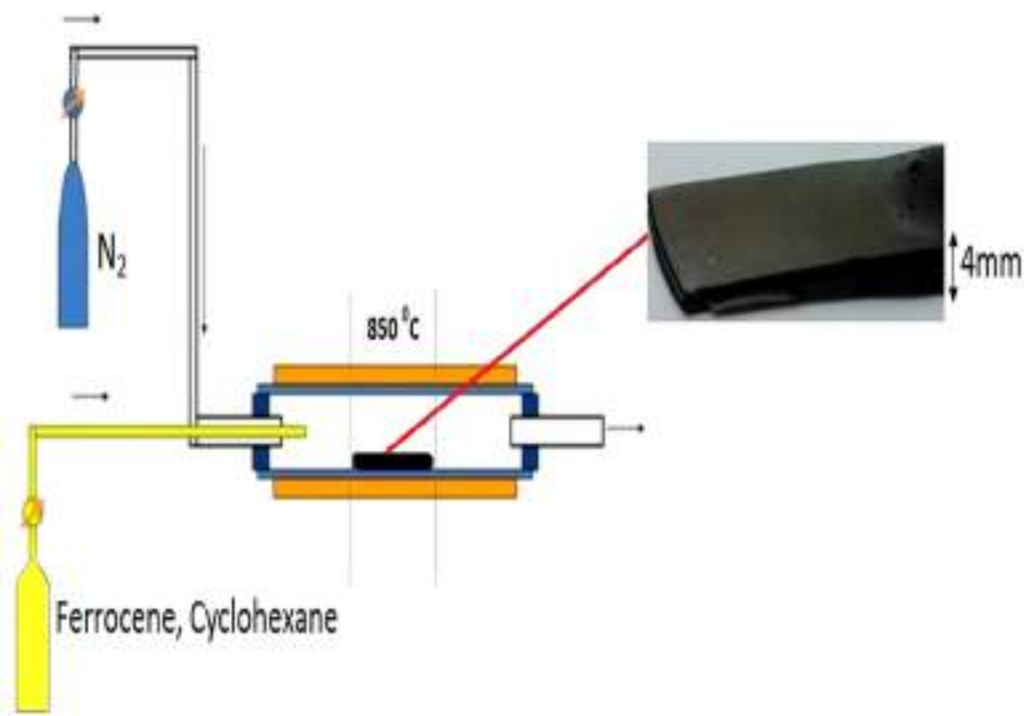
MWNT



Synthesized MWNTs using CVD method

A liquid solution of ferrocene in cyclohexane as soon as the support nitrogen gas were supplied into the Ø 2.5 cm × 100 cm long quartz tube placed in an automatically temperature controlled oven. With the described method uniform forest arrays up to of 20 × 80 mm^2 were systematically obtained on silicon substrate.

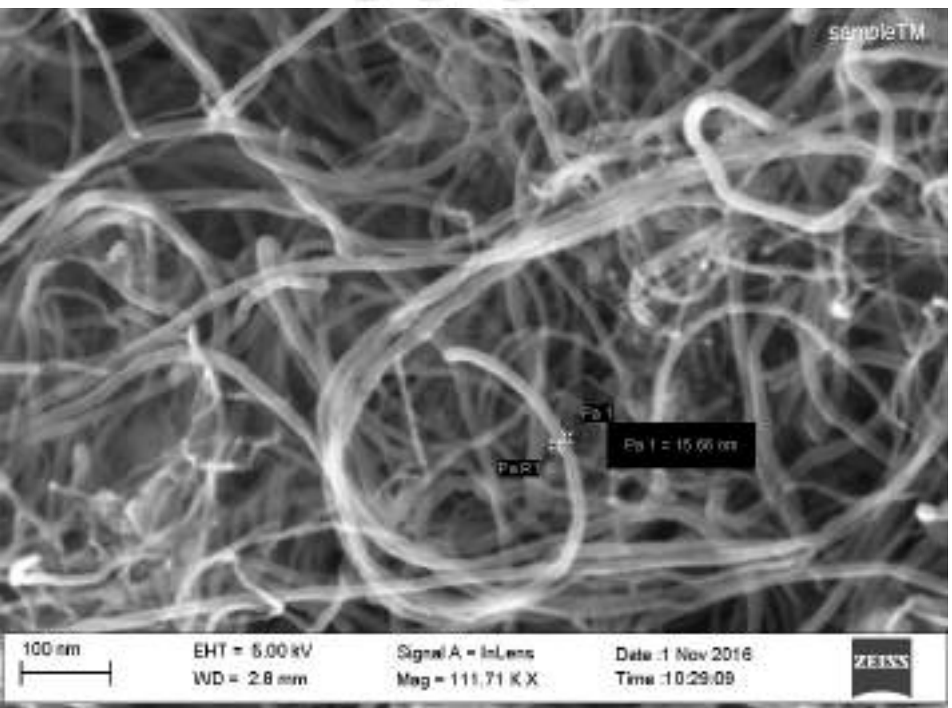




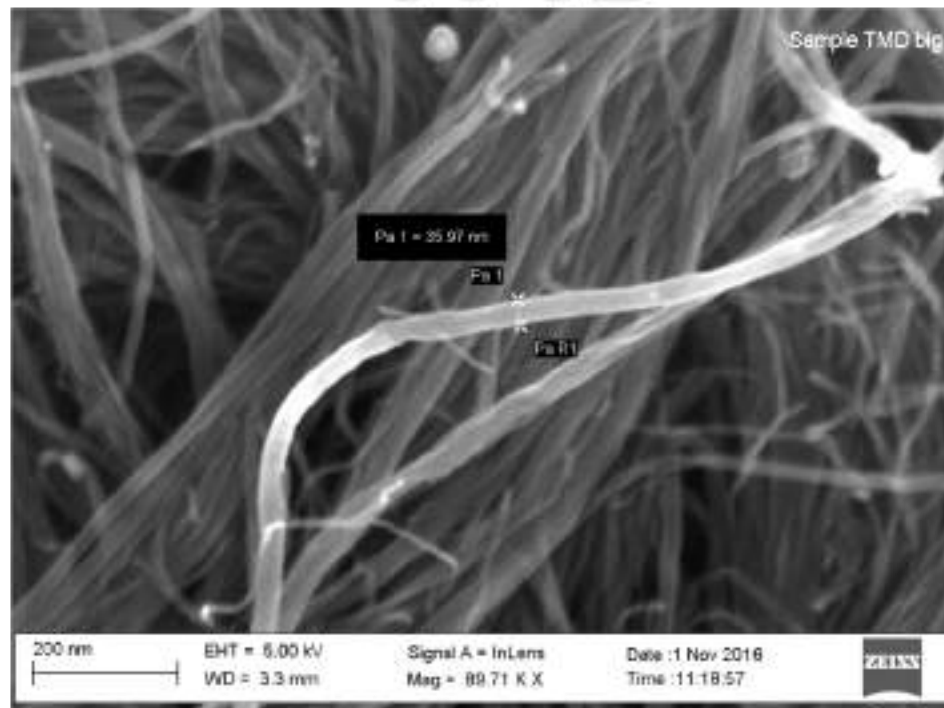
Commercial MWNTs (powder)

Parameter/CNTs	"Taunit-M"	"Taunit-MD"
External diameter, nm	(18-30)	(35-50)
Internal diameter, nm	(4-8)	(10-20)
Length, μm	2 and more	20 and more
Specific surface area, m^2/g	210	(179)

TM



TMD



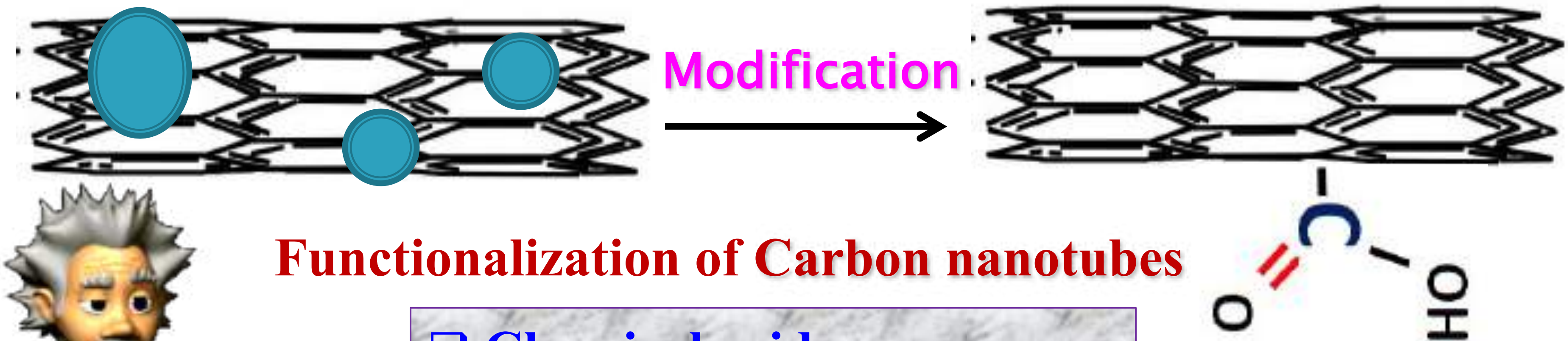
Nickel Ni(II)

- The main source of nickel pollution in the water derives from a number of industrial production processes such as **battery manufacturing**.
  - The toxic effects of nickel include bone nose, and lung cancer, **rapid respiration**, **shortness of breath**.

Pristine MWNTs

- amorphous carbon
- metallic catalyst
- Low reactivity
- solvophobic

This limits the performance of CNTs for practical applications like water filtration



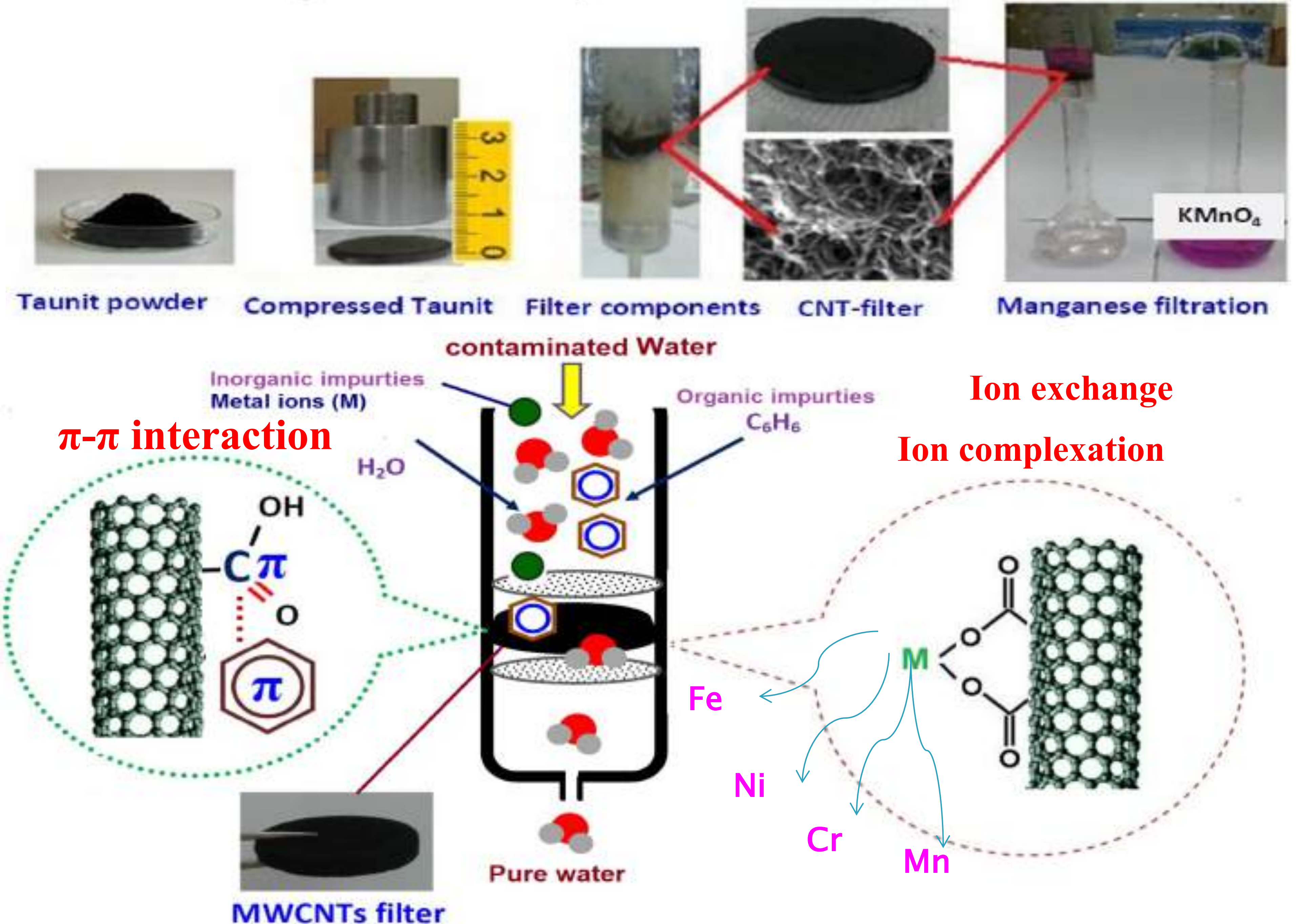
Functionalization of Carbon nanotubes

- ❑ Chemical acids
- ❑ Ozone treatment
- ❑ Electron beam annealing
- ❑ Ion beam irradiation

B. Purification and functionalization of MWNTs surface

Treatment used	Process	effect
1- Nitric acid (HNO_3)	CNT powder added into 100 ml of concentrated nitric acid 60%. Then the mixture solution was sonicated in water bath at 80°C for 10 hours.	➢High oxygen content ➢Relatively high purified MWNTs ➢Weight loss 25%
2- Potassium permanganate ($KMnO_4$)	CNT powder dispersed in a flask with 20 ml of 0.5 M sulfuric acid, 1g of potassium permanganate were dissolved in 20 ml of 0.5 M sulfuric acid.	➢ Very high oxygen content ➢Low purified MWNTs ➢Weight loss 40%
3- mixture of (HCl+ H_2O_2)	0.1 g of synthesized MWNTs was mixed directly with 20 ml of 5M hydrochloric acid and 20 ml of 30% H_2O_2. the mixture was sonicated in water bath at 60°C for 2 h.	➢Low oxygen content ➢High purified CNTs ➢Weight loss 10%
4- Electron beam annealing	Irradiation of MWNTs by 20 KeV electron beam in scanning electron microscope	➢Low oxygen content ➢High purified CNTs ➢No Weight loss
5- Ion beam irradiation	Irradiation of MWNTs by 80 KeV He ion beam	➢High purified CNTs ➢No Weight loss

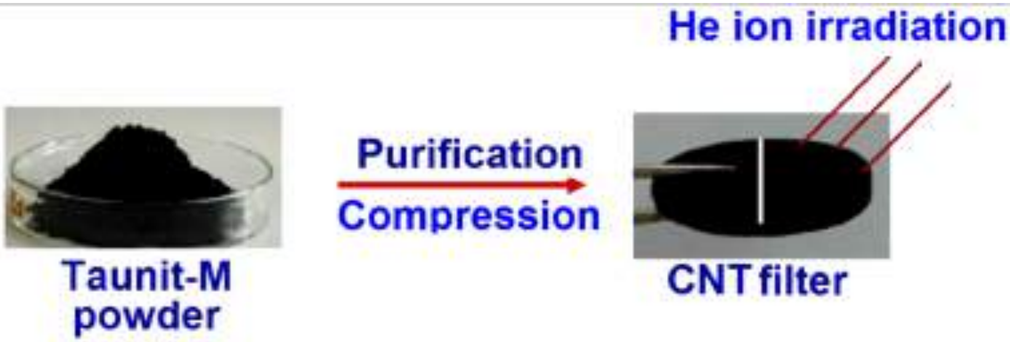
Filter design and Adsorption mechanisms of MWNTs



Preparations & Methods

Ion beam irradiation

- Purified Taunit-M was compressed using high pressure piston to the form of circular tablet with the diameter 20 mm and the thickness of 2 to 4 mm.

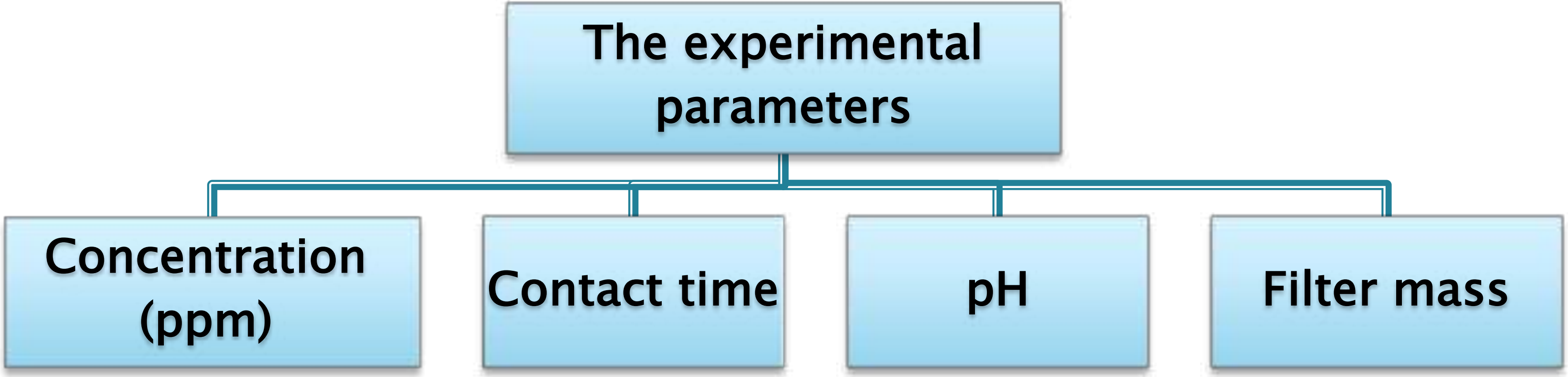


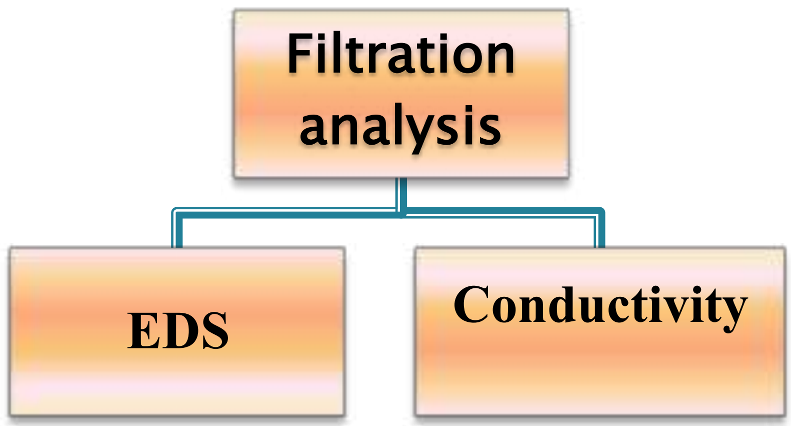
- The pressed tablets of MWNT taunit and arrays were irradiated at HVEEE-500 ion accelerator at SINP MSU with He ion beam of the energy E= 100 keV with fluencies $1x10^{16}$ ion/cm^2.

Ion Beam Laboratory Irradiation Facility
SINP (MSU)

Experiment parameters and its variation

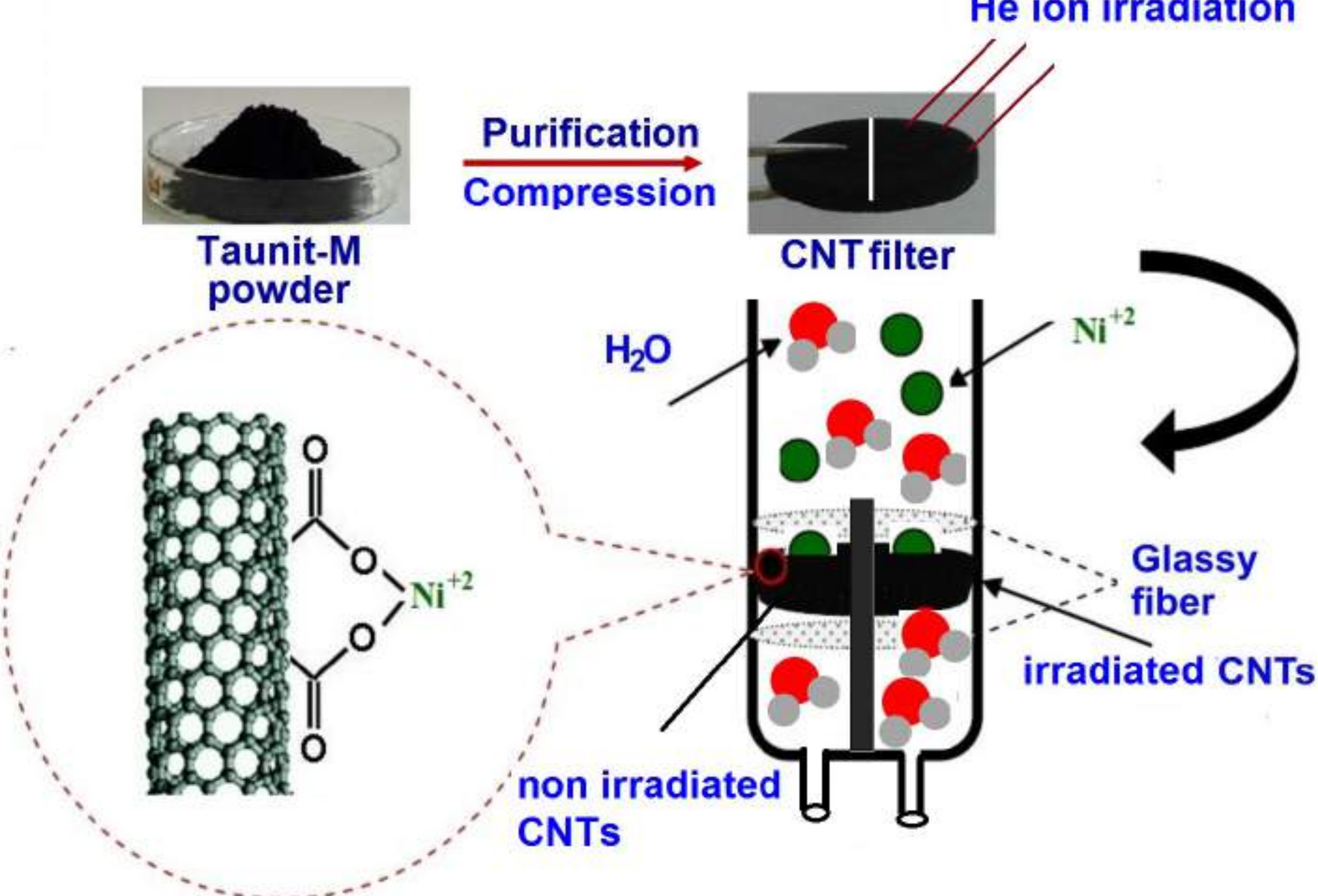
Parameter	Variation		
	Low	Medium	High
1. Concentration of Ni (II) in initial aqueous solution (ppm)	10	50	100
2. pH of Ni (II) aqueous solution	4	7	10
3. Taunit-M filter mass (in g per 50 ml of solution)	0.1	0.2	0.3





$$R\ (\%) = \frac{C_0 - C}{C_0} \times 100$$

where C_0 and C are the concentrations before and after filtration


He ion irradiation
Purification
Compression
Taunit-M powder
CNT filter
H2O
Ni+2
Ni+2
Glassy fiber
irradiated CNTs
non irradiated CNTs

Results & Discussions

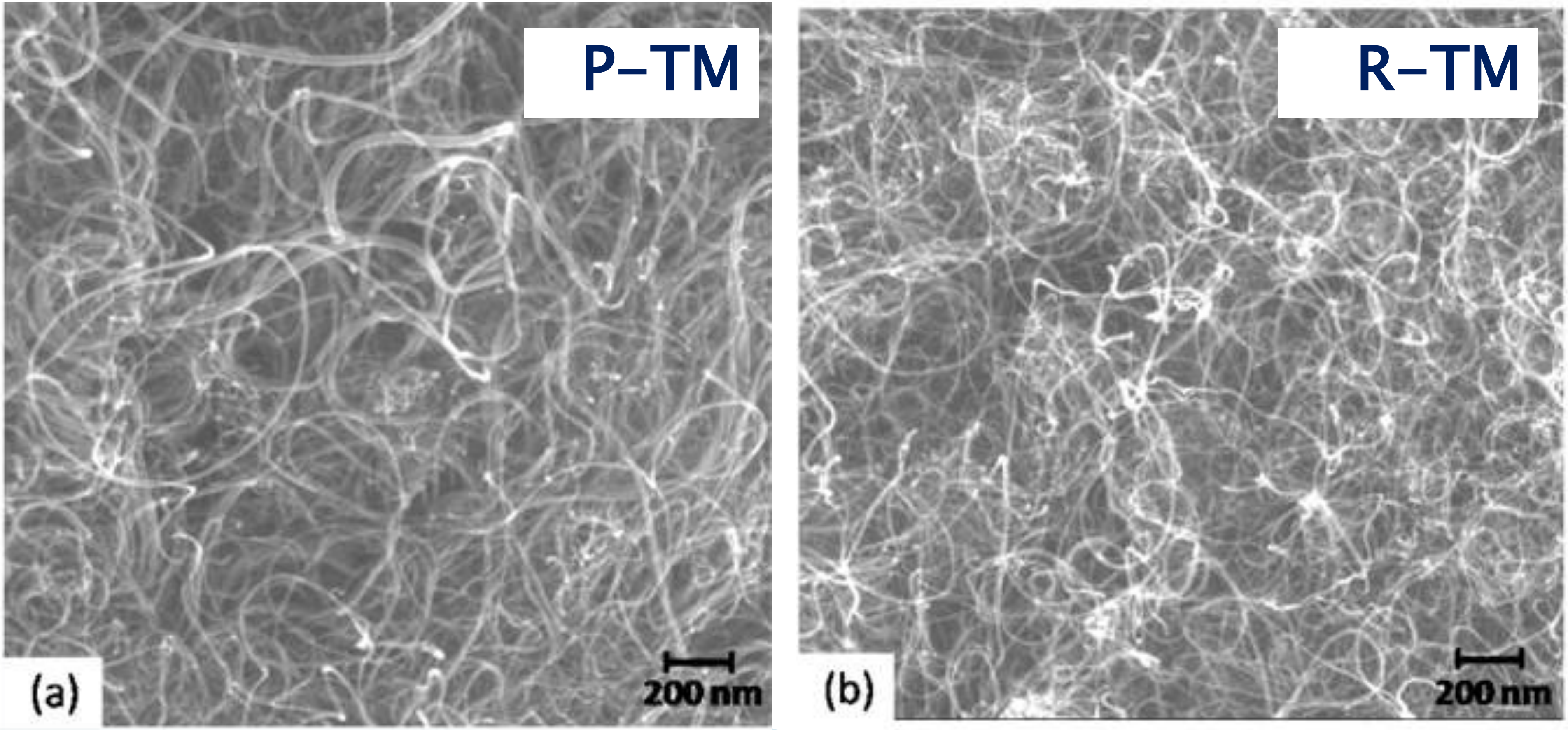
Characterization of MWNTs

- Scanning Electron Microscopy (SEM)
- Raman Spectrometry (RS)
- Energy Dispersive X-ray Spectroscopy (EDS)

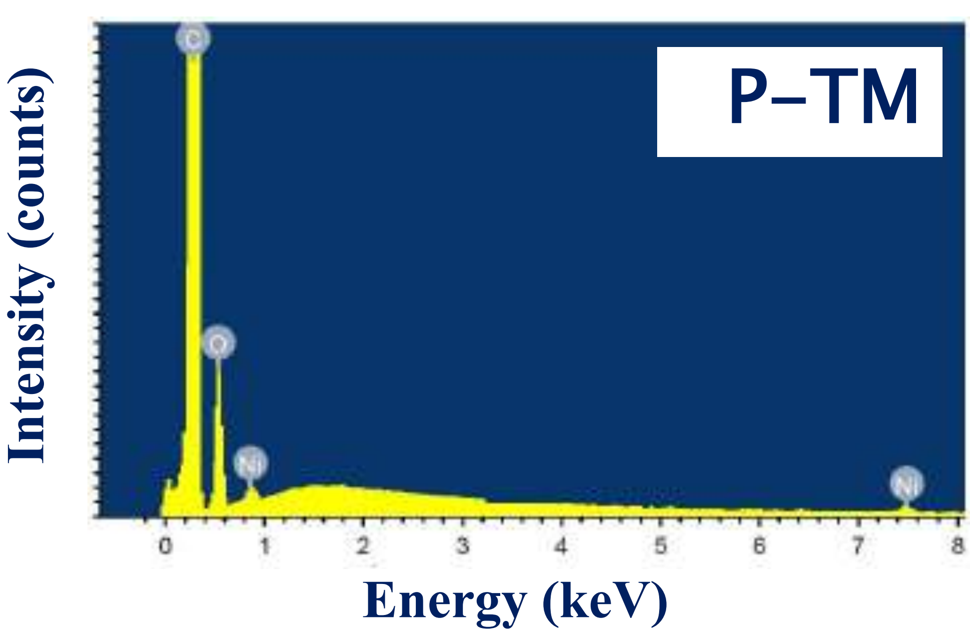
Morphology of P-TM and R-TM filters was characterized by SEM

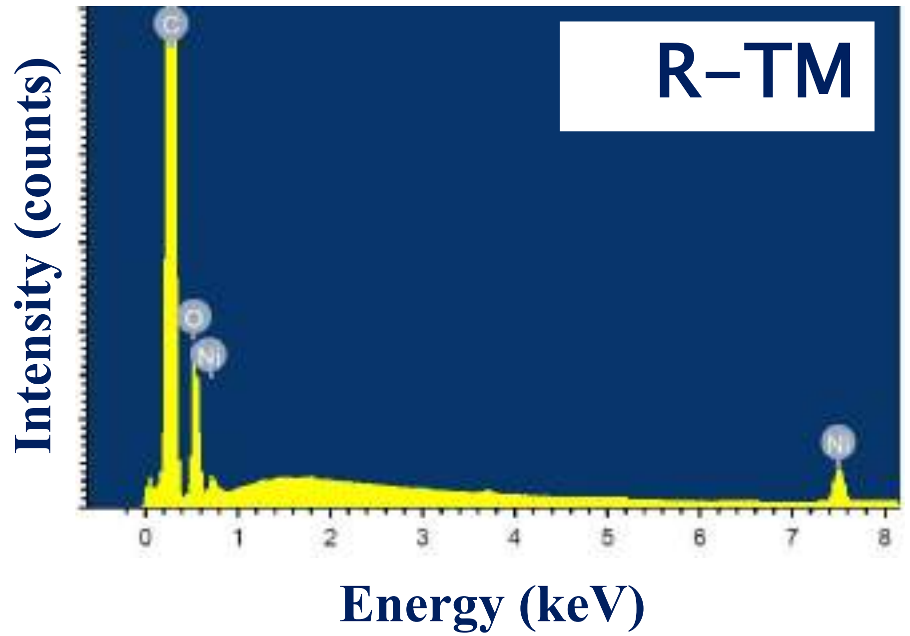
TM- FILTER

Average diameter = 26 nm → Irradiation → Average diameter = 14 nm



EDS Analysis

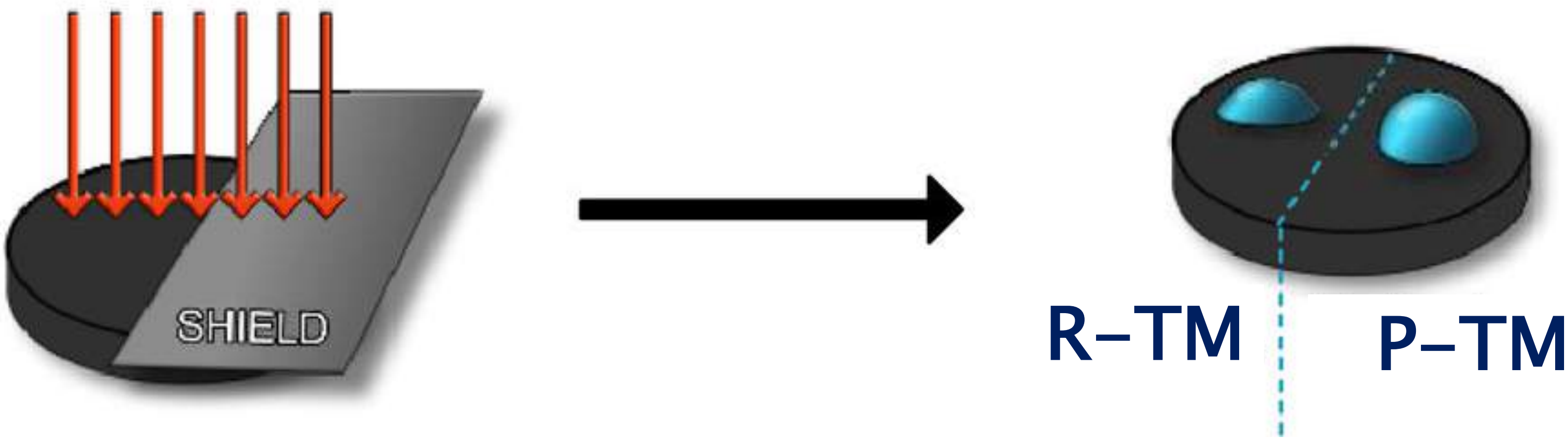


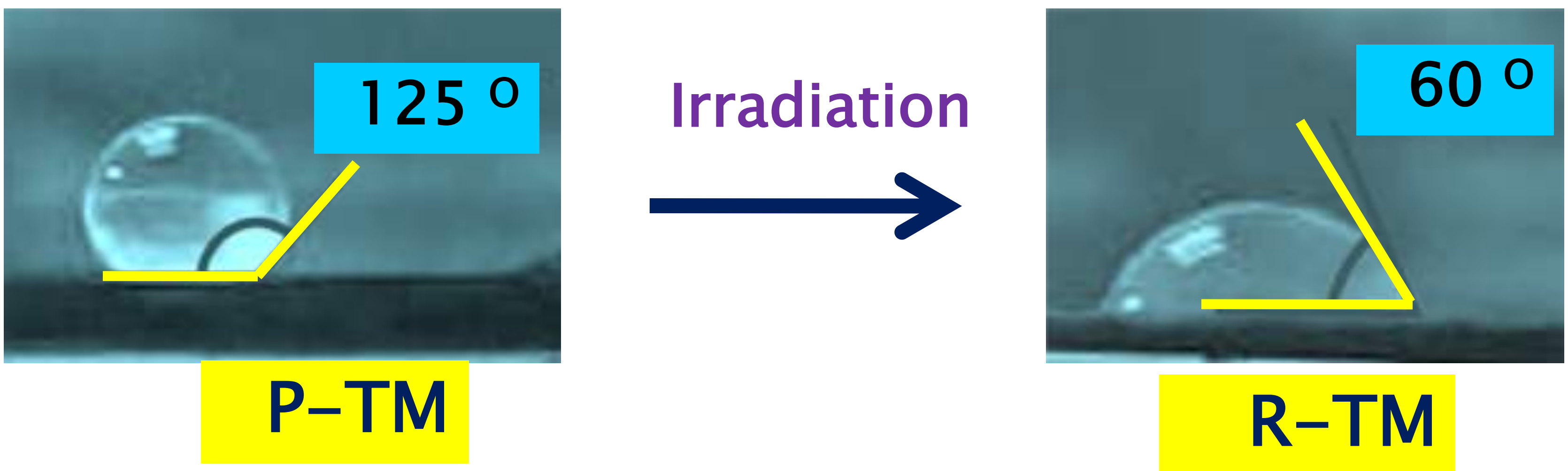


Element	Weight %
C	89.2
O	10.15
Ni	0.65

Element	Weight %
C	85.0
O	12.35
Ni	2.65

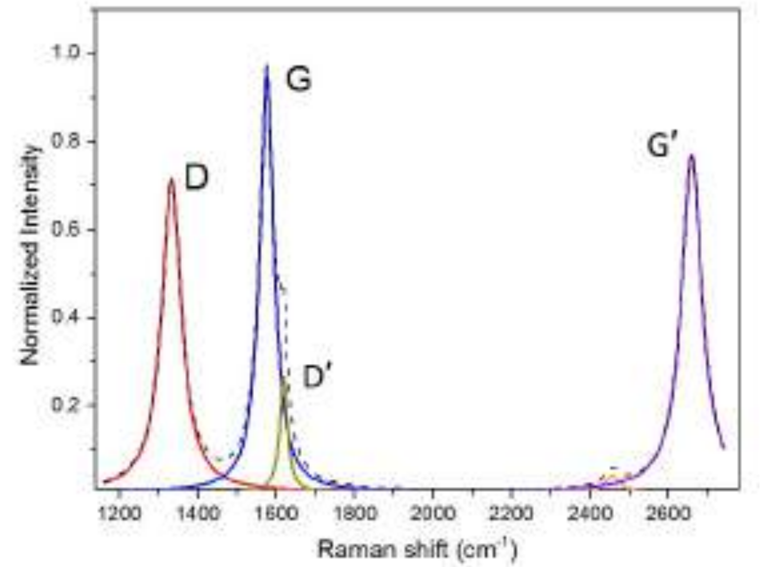
Wettability investigation of the irradiated CNT surface





Raman Spectroscopy

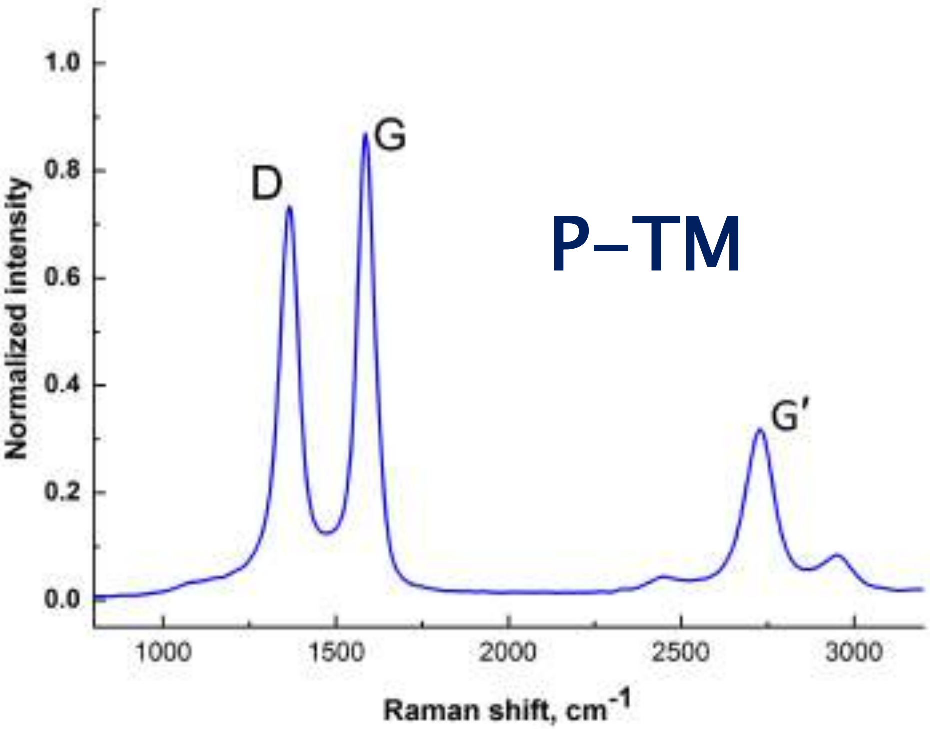
❑ The structure defects were characterized by analysis of Raman spectra which were measured using micro Raman NTEGRA Spectra system with 473 nm excitation laser wavelength

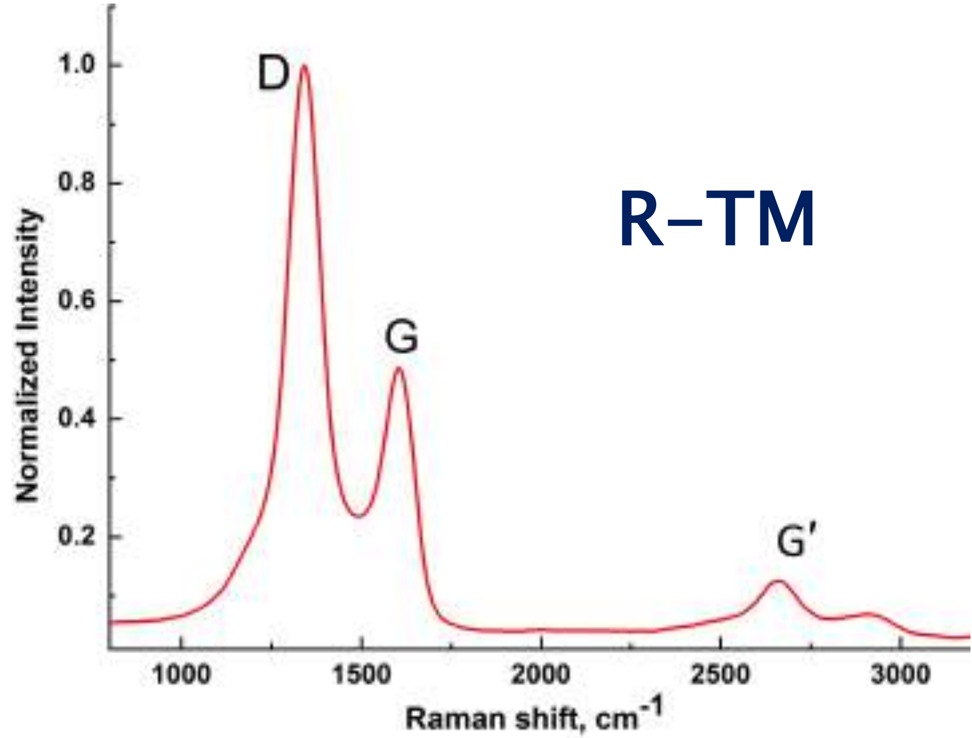


❑ Three characteristic peaks, the D band (disorder band of sp^3-hybridized carbon), the G band (graphite band of sp^2-hybridized carbon) and the G′ band (second overtone of the defect induced D band and is related to the three dimensional order) appeared at 1340, 1580and 2700 cm^{-1}, respectively.

❑These peaks are important for determining the graphitic nature and structural ordering of the tubes

Raman modes of MWNTs filters and the removal efficiency enhancement

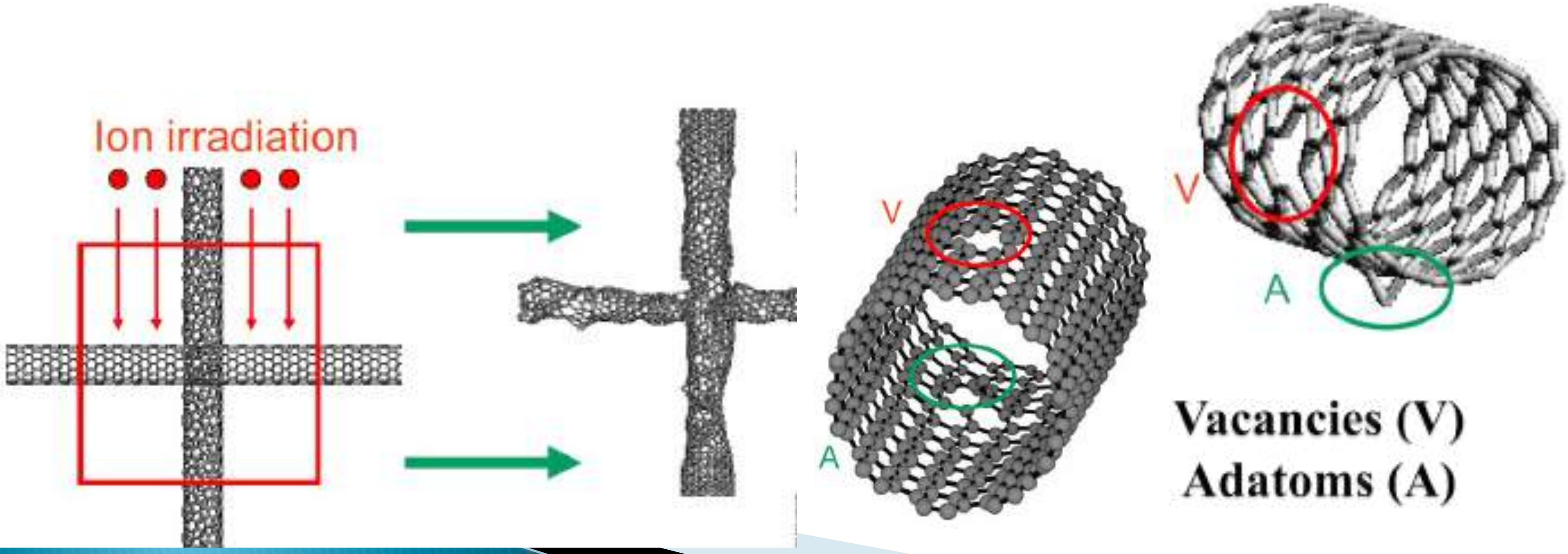




Samples	I_G / I_D	$I_{G'} / I_D$
Before irradiation	1.2	0.41
After irradiation	0.5	0.1

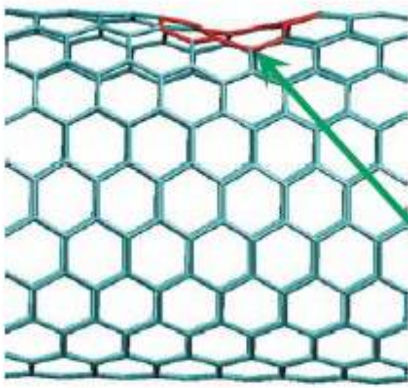
He ion beams to modify properties of carbon nanotubes

- We explore the defect formation in MWNTs pressed samples caused by He ions irradiation with different doses.
- The irradiation effects are characterized using scanning electron microscopy (SEM) and Raman spectroscopy.
- The thermal and athermal mechanisms of the irradiation effects are discussed.



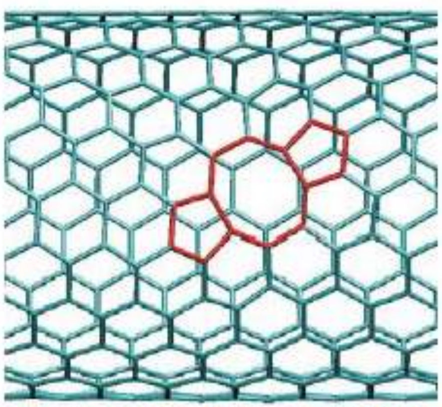
Individual divacancy

Side view



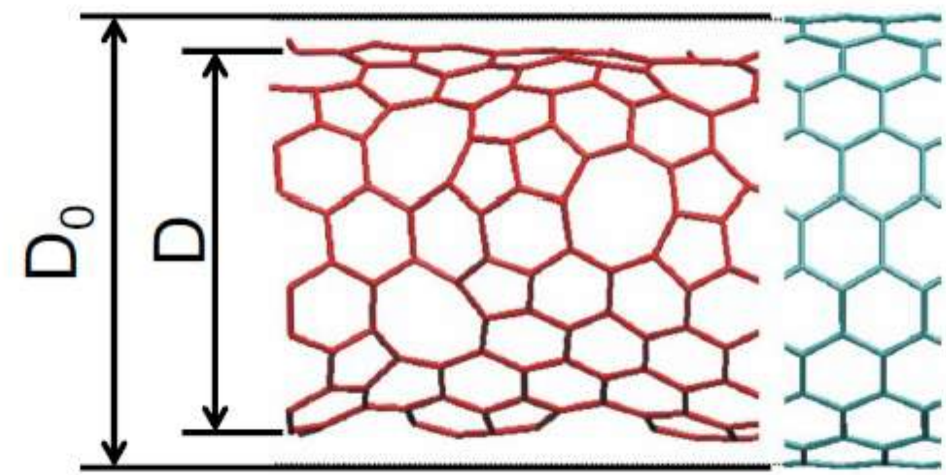
Local decrease in the diameter

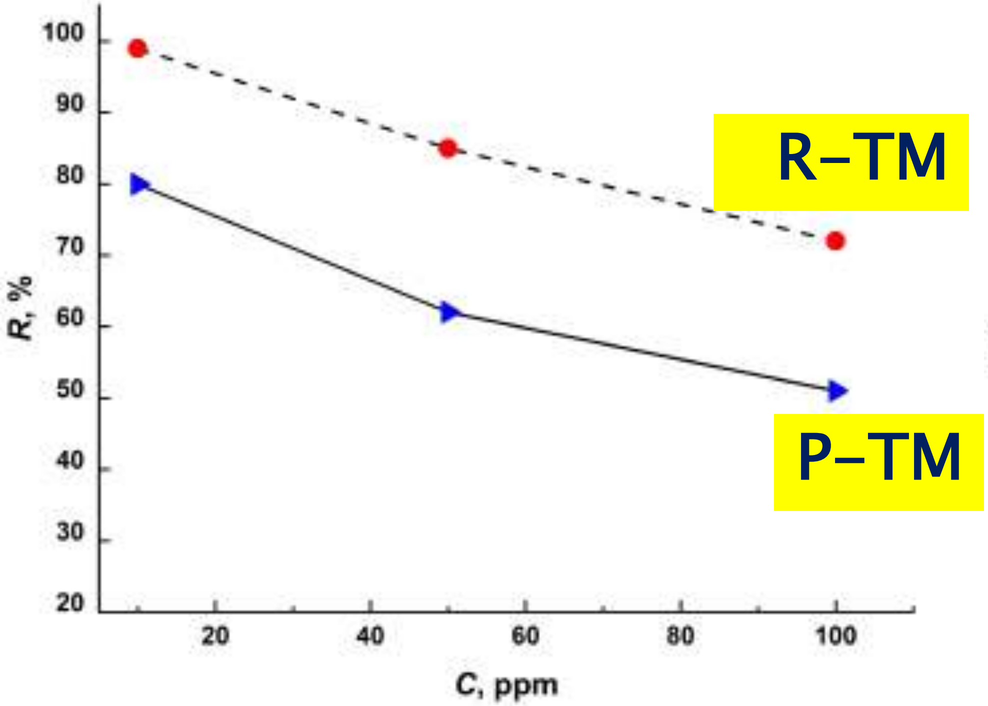
Top view

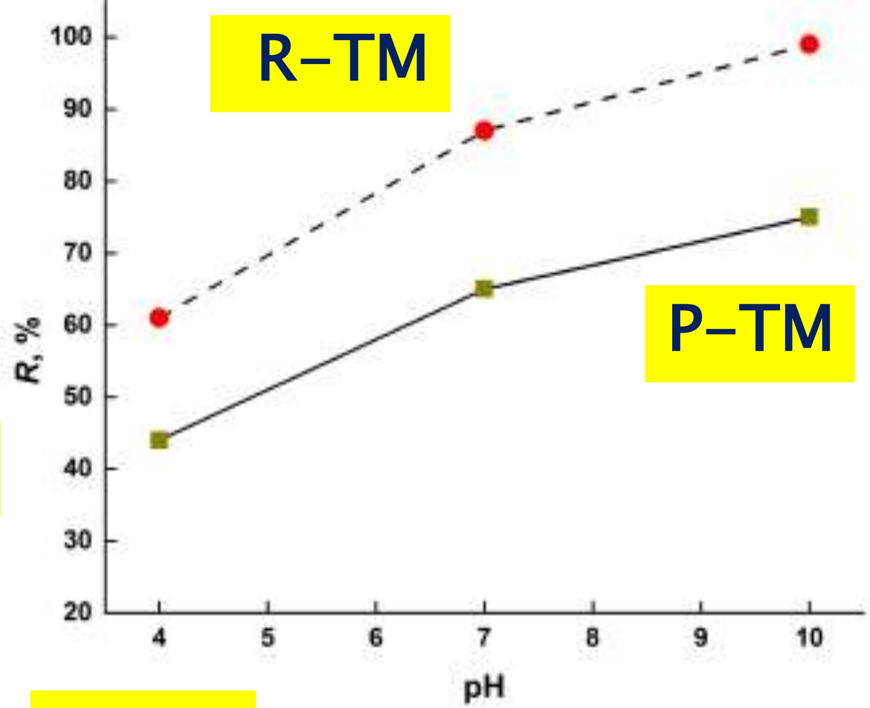


Many divacancies

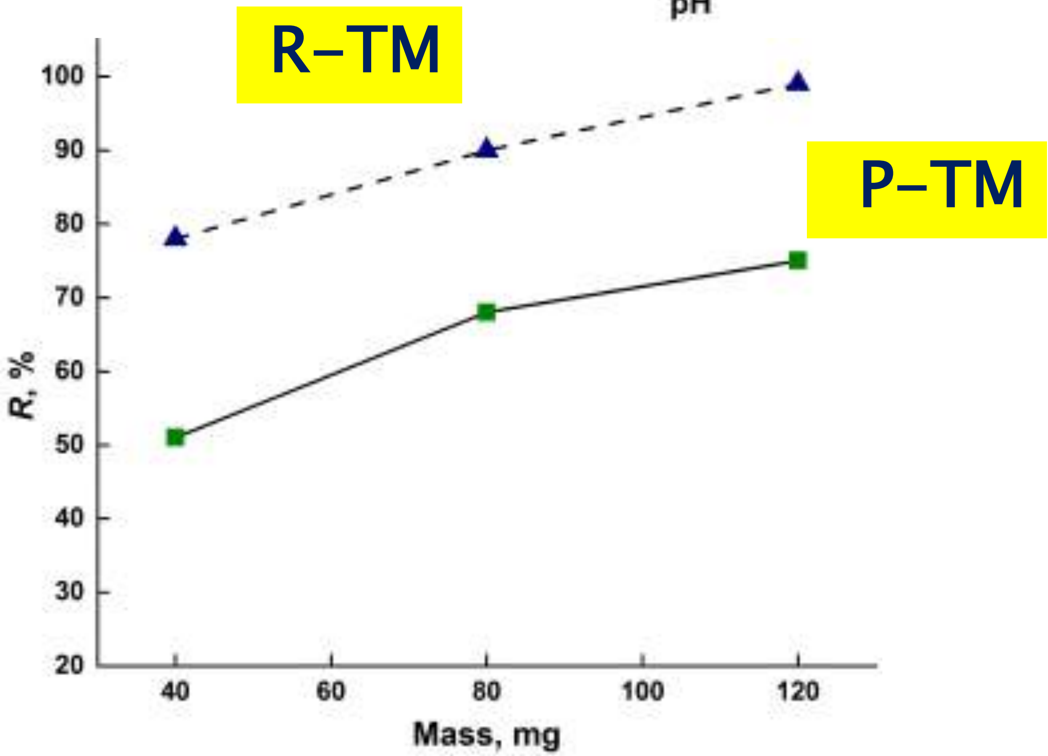
Diameter decreases!







At concentration of 10 ppm, R of irradiated TM is around 99%



Filtration efficiency and contact time

The adsorption efficiency is correlated to the contact time between heavy metal ions in the solution and the CNTs in the filter.

The contact time (t_c) can be roughly estimated in our filtration experiment as the thickness of the filter (h_f) divided by the solution flow rate (f_s) through the filter as follow:

$$t_c = \frac{h_f}{f_s} = \frac{h_f}{h_s / t_s} = \frac{h_f . t_s}{V_s / A}$$

h_s is the solution height in the filtration syringe

t_s is the total time required for filtration,

V_s is the volume of the solution (50 cm^3) with the cross-section *A* of the syringe

	Filtration time (min)	*Flow rate (cm/min)*	*Contact time (min)*	*Removal efficiency (%)*
P-TM	**27**	**0.67**	**0.85**	**78**
R-TM	**16**	**0.98**	**0.39**	**99**

Conclusion

- The application of carbon nanotubes (CNTs) for water purification is one of the pioneer studies.

- In order to enhance the performance of CNT-based filters for this application, ion irradiation of the CNT surface is essential feature.

- The SEM, and EDS analyses show that physicochemical properties of the MWNTs such as structure and surface properties were greatly improved after irradiation, which resulted in high adsorption capacity and filtration efficiency.

- Our investigations showed that ion beam irradiation can improve the surface functionality of MWNTs by creating disorder sites.

- Although, pristine CNTs has showed good adsorption potential for some of these pollutes, the irradiated CNTs (R-TM) showed the maximum adsorption capacity for the most of these contaminates.

- R-TM filters with reduced diameters are highly hydrophilic, have a high solution flux, and absorption ability

- It was noted that, the key factors favoring the removal efficiency are low pH and low initial concentration. At pH=10 and Ni (II) concentration of 10 ppm the removal efficiency could reach 99% in the R-TM filters


THANK YOU