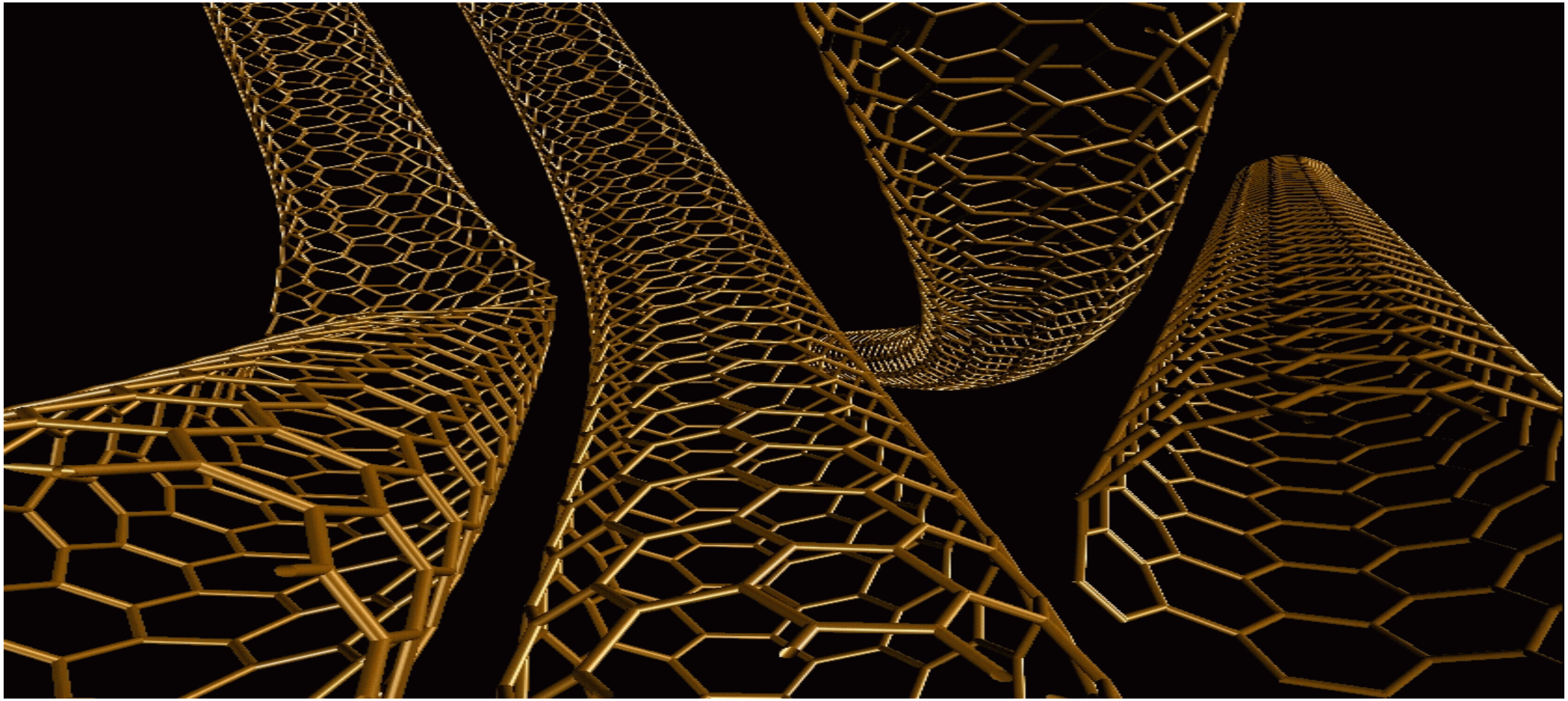


Prof. Maurizio De Crescenzi

Dott. Luca Camilli

Carbon nanotubes photovoltaics devices

Stage Invernale presso il Dipartimento di Fisica

(6 – 10 Febbraio 2012)

Modulo Didattico “Materiali per la Conversione Fotovoltaica”

UNIVERSITÀ DI ROMA TOR VERGATA

The objective is to use forefront nanotechnologies to develop novel solar cells.
Specifically, these cells are formed by Single-Wall-Carbon-NanoTubes (SWCNTs) and Multi-Wall-Carbon-Nanotubes decorated by quantum nanodots metallic and/or semiconductors.

Carbon Nanotubes serve both as e-h charge production and charge transport highways.

The aim is to: (i) Better control of the synthesis of carbon nanotubes and to perform appropriate characterization and photoconduction measurements, as a function of key parameters during synthesis;

(ii) to perform systematic studies to clarify the physico-chemical reasons of the generation of photocurrent in carbon nanotubes/silicon substrates;

(iii) to insert carbon nanotubes into photovoltaic devices and assess their photoconversion performance.

Outline

-Hystory of the photoconductivity with CNTs

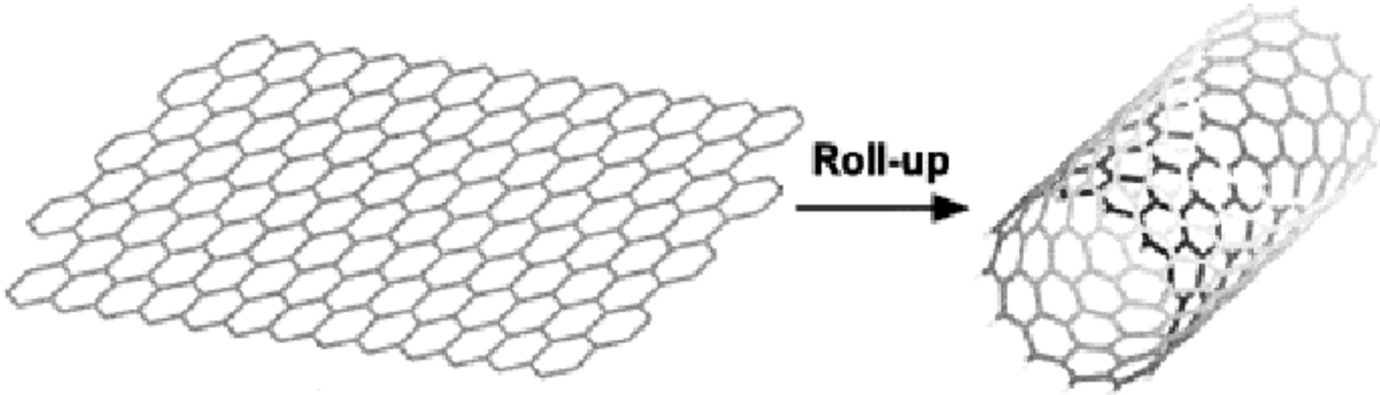
-Methods of Synthesis CVD, Characterization, Devices
-Results on MWCNTs and SWCNTs electrochemical (Graetzel) solar cells, decoration with Cu nanoparticles to enhance the IPCE (%) up to 15%
-Solid state CNT/Silicon solar cell devices

-New routes for production of CNT (on steels)
-CNTs as gas nanosensors (NIRAP project)

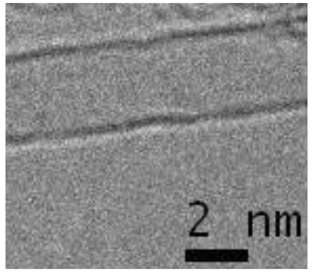
Carbon nanotube structure

Graphitic sheet

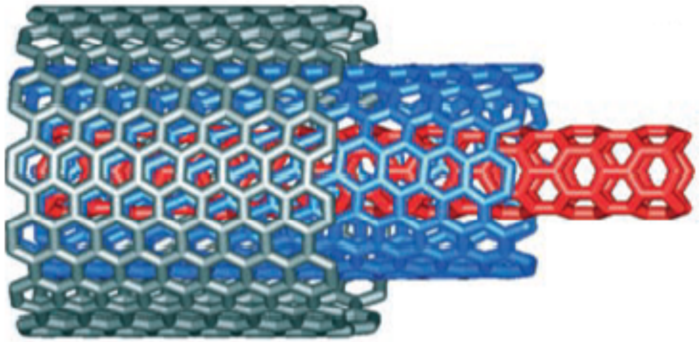
Single Wall CNT



<d> = 1–2,5 nm

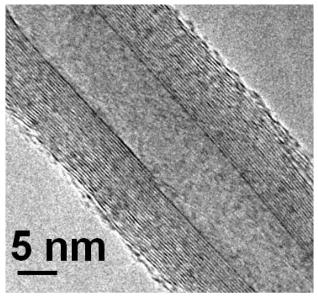


Multi wall CNT

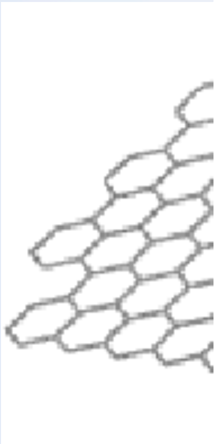


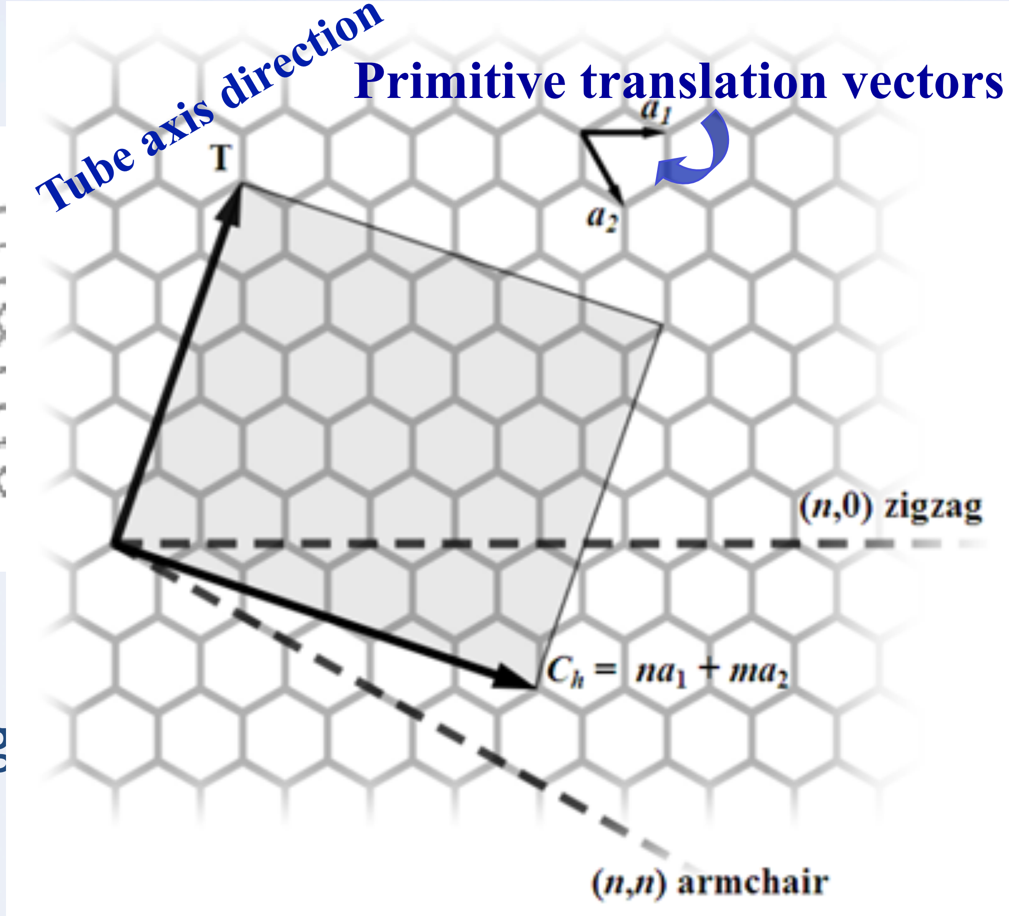
ID > 4-5 nm

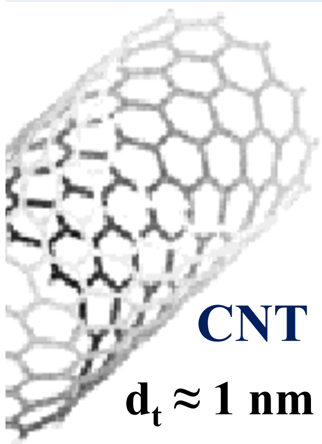
OD < 40-50 nm



Carbon Nanotube (CNT)



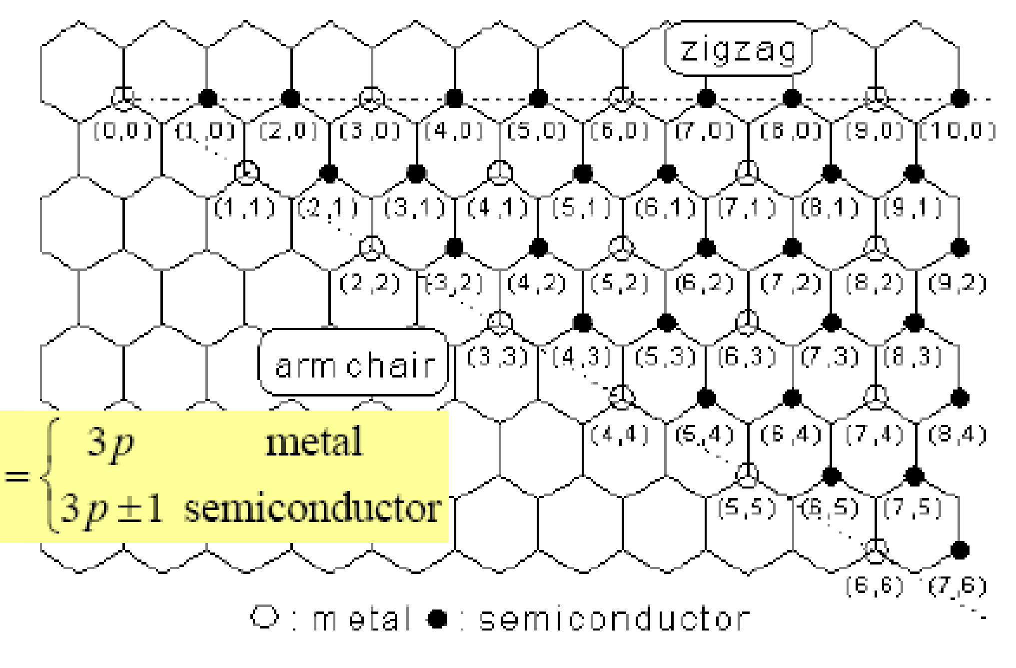




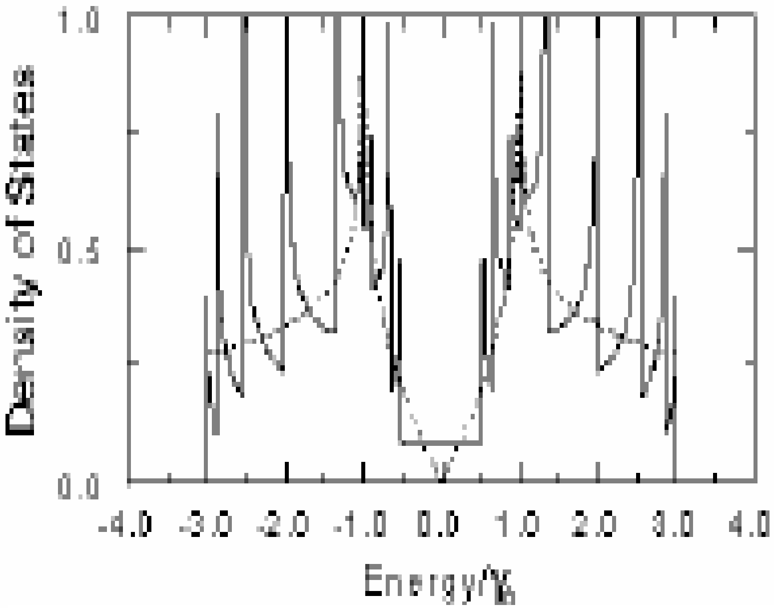
✧ By wrapping … nder: SWCNT

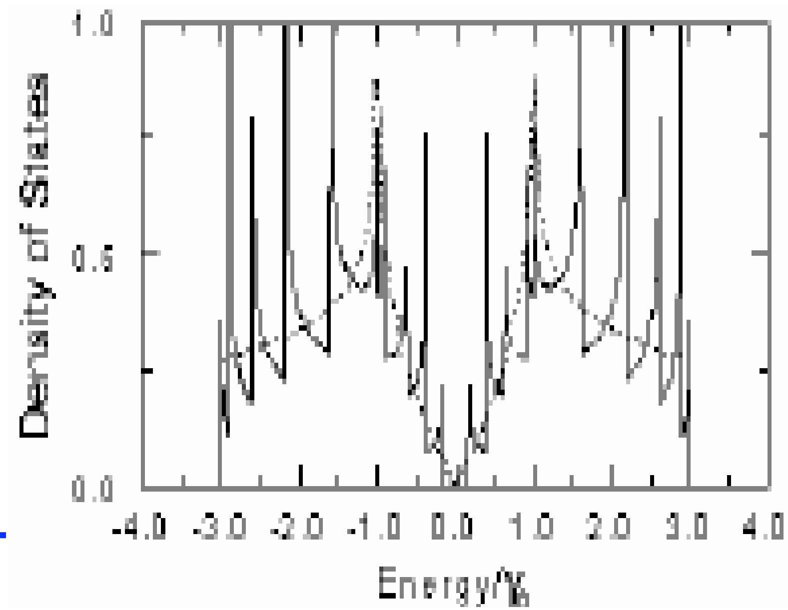
✧ The way this graphene sheet is wrapped is represented by a pair of indices (*n*,*m*) called the chiral vector $\mathbf{C}_h$ thus defining the single-walled nanotube chirality.

METAL OR SEMICONDUCTOR ?



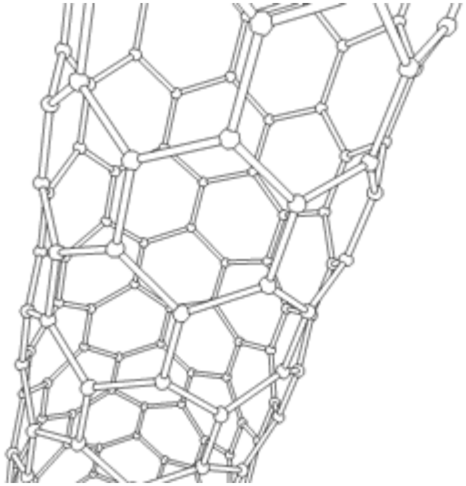
$$n-m=\begin{cases}3p & \text{metal}\\ 3p\pm1 & \text{semiconductor}\end{cases}$$





The energy band gap depends on diameter and elicity spacing and varies from less than 0.1 eV to more than 2 eV depending on nanotube diameter.

Carbon Nanotubes (CNT) as building blocks for solar energy conversion devices



✓Unique opto-electronic properties

✓Wide electrochemical stability window

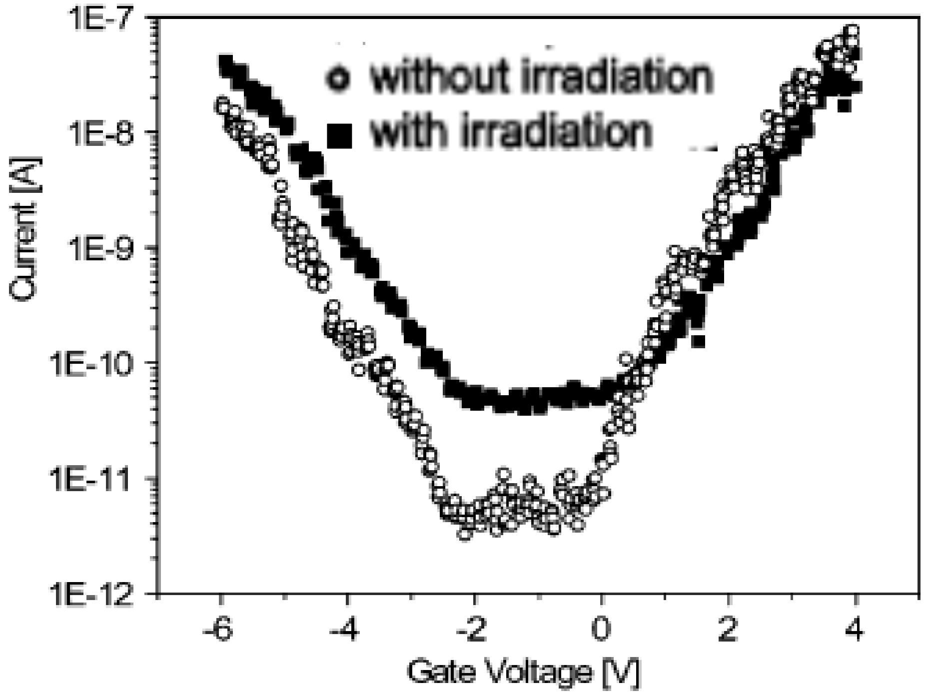
✓High surface area

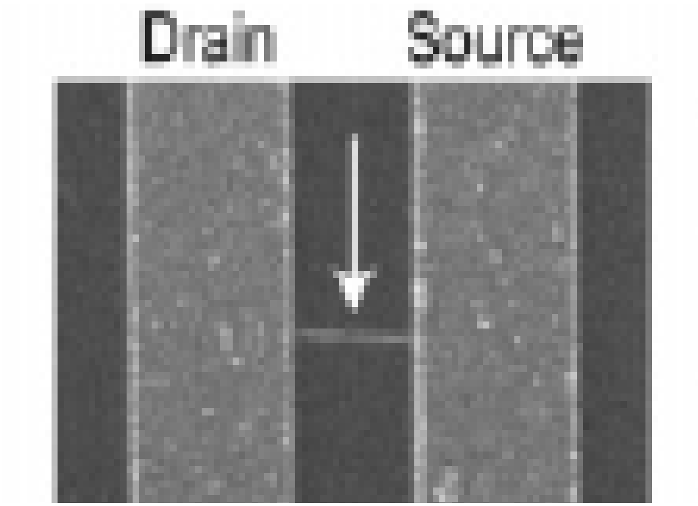
✓Cylindrical morphology provides reactive edges to chemical functionalization and surface modification

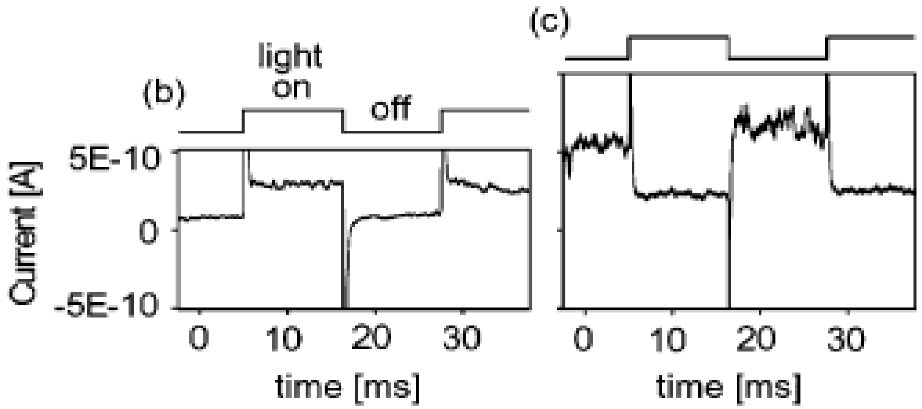
✓Carbon nanotubes have a band-gap in the range of 0-1.1 eV depending on their chirality and diameter

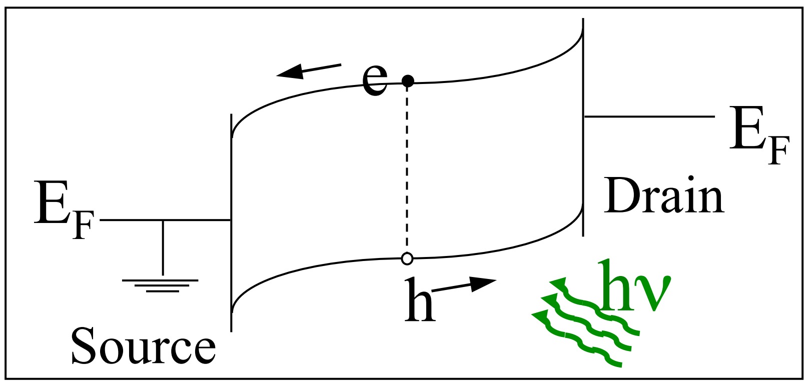
✓No need of selective doping to form p-n junctions

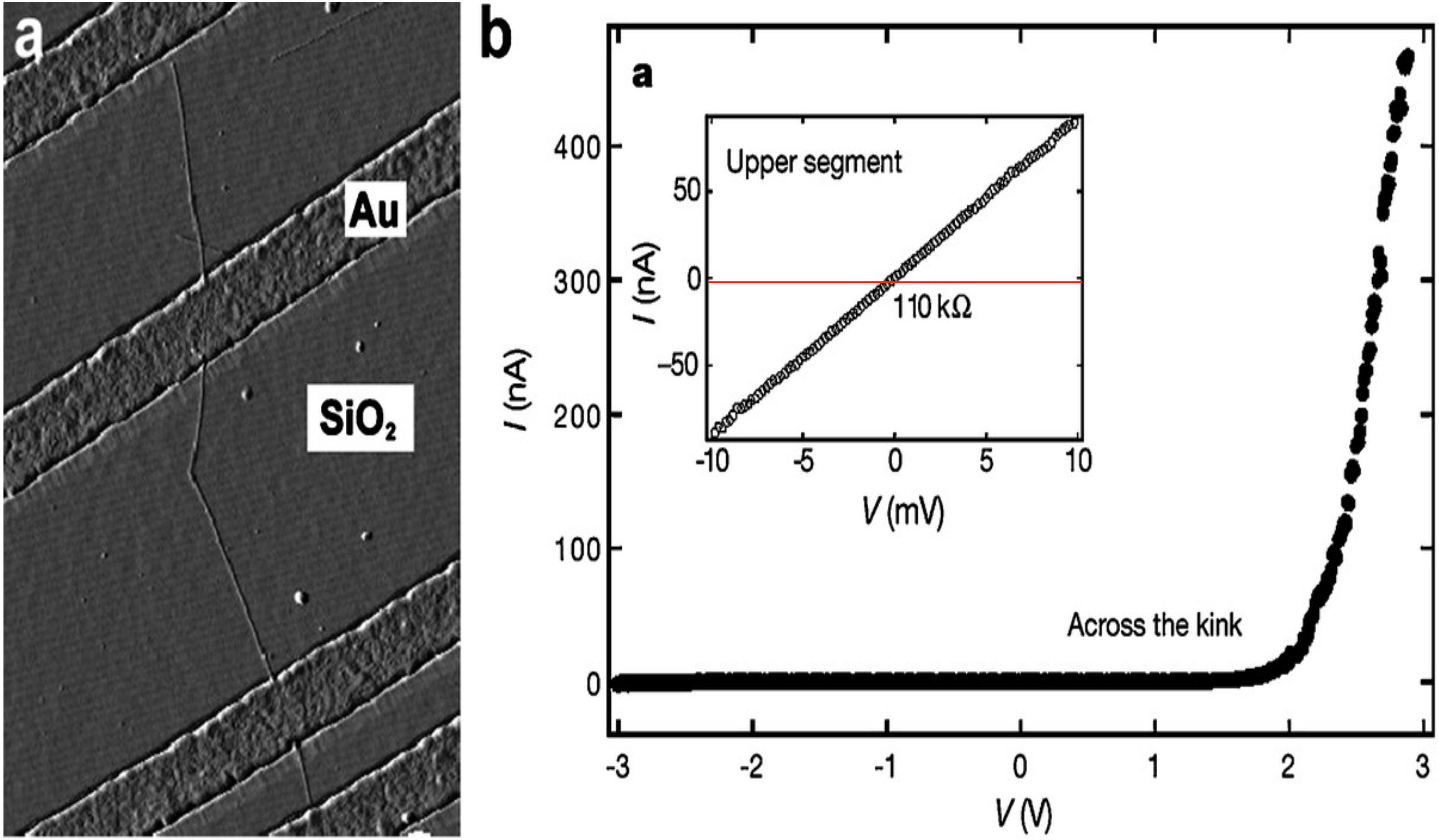
Photoconductivity of Single Wall Carbon Nanotubes
M. Freitag, Y. Martin, J. A. Misewich, R. Martel, Ph. Avouris
Nano Letters 3, 1067 (2003)





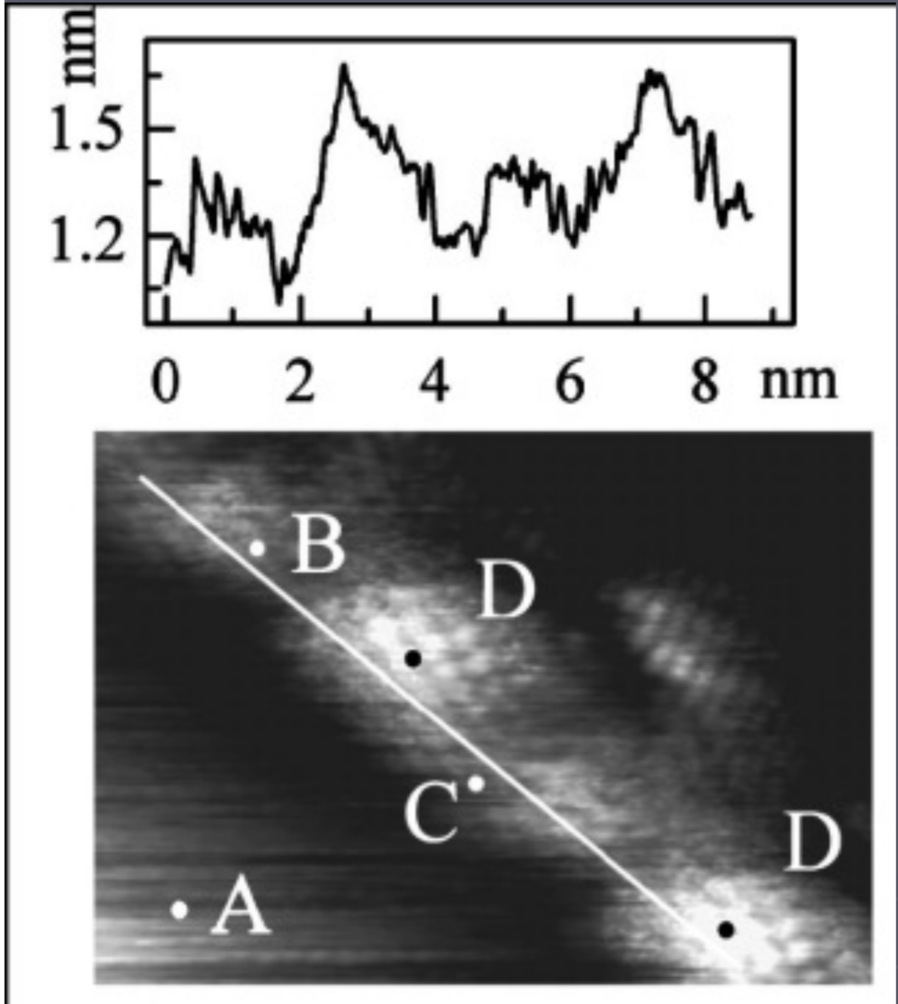


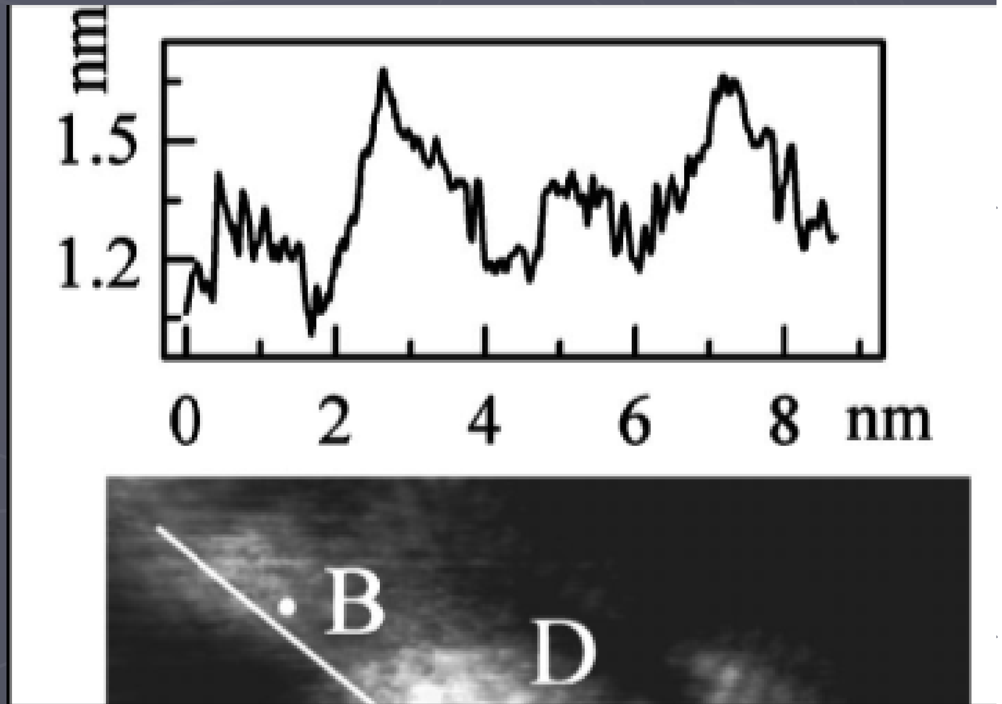




Z.Yao Z, H.W.C.Postma, L.Balents, C.Dekker, *Nature* 402, 273–76 (1999)
Formation of Schottky barrier within the same metal and semiconductor nanotube

The conductance increases at locations where the CNT is squeezed, while it decreases significantly in unsqueezed regions characterized by an unperturbed hexagonal net





P.Castrucci, M.Scarselli, M.De Crescenzi, F.Rosei, A.El Khakani APL 85, 3857 (2004)

Ji Ung Lee, Appl.Phys.Lett. 87, 073101 (2005)

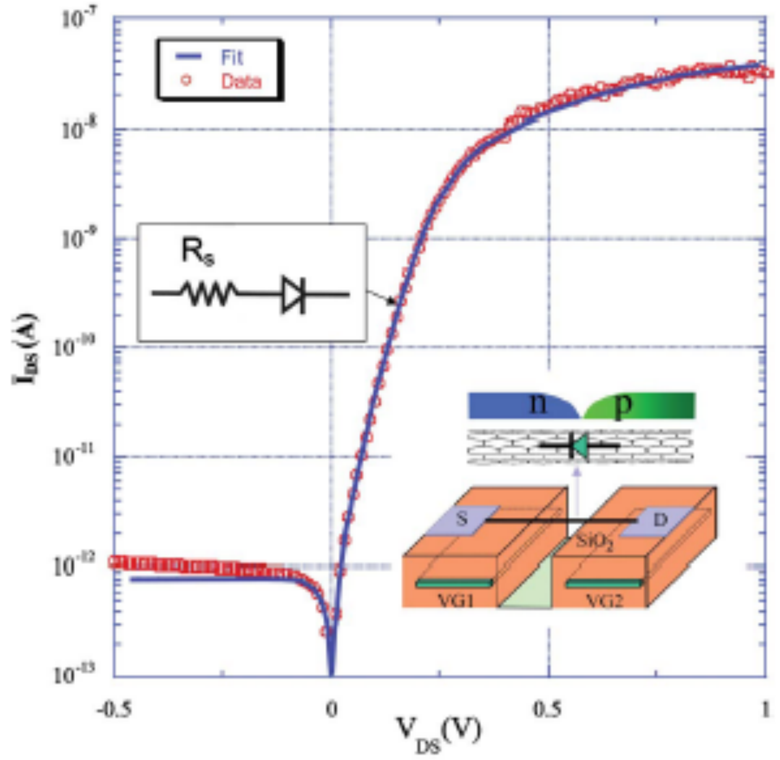


FIG. 1. (Color) The inset shows the split gate device where VG1 and VG2 are biased with opposite polarities (VG1=−VG2=+10 V) to form an ideal *p-n* junction diode along a SWNT. Data are typical dark current-voltage (*I-V*) curve at T=300 K with a fit to Eq. (1) using $I_0=8.0\times10^{-13}$ A, n =1.0 with a series resistance $R_s=18\times10^6$ ohms.

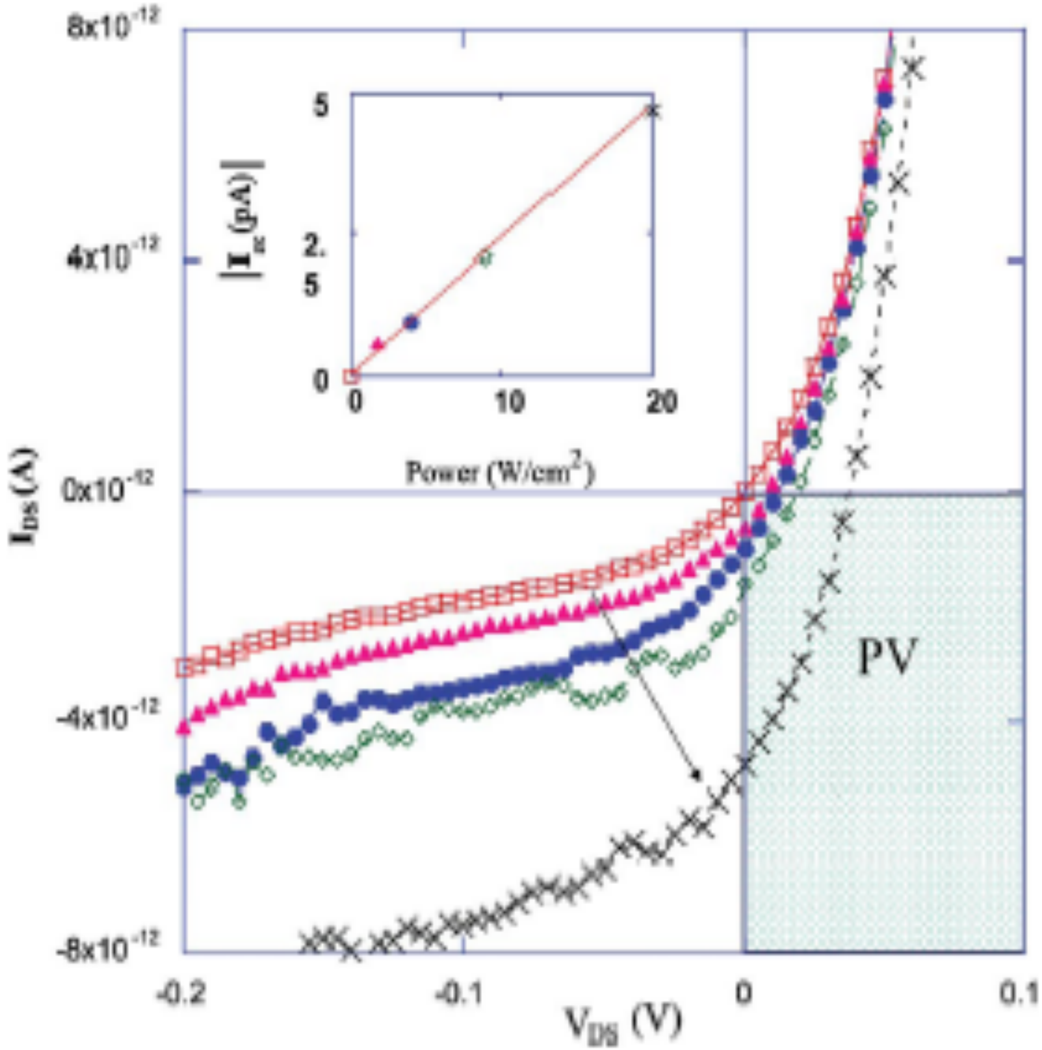
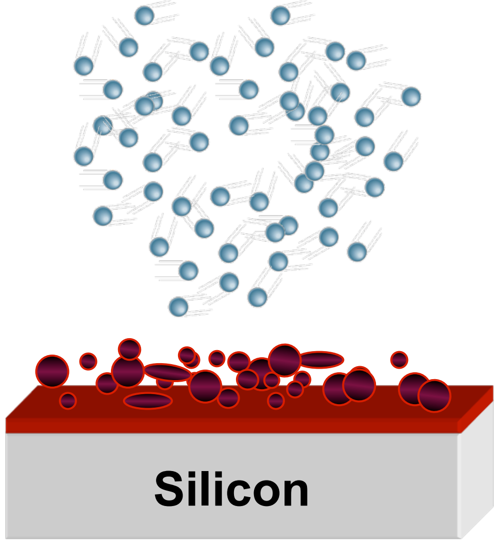


FIG. 2. (Color) *I-V* characteristics under increased light intensity showing a progressive shift into the fourth quadrant (PV) where the diode generates power. The inset shows the expected linear increase in the current measured at V_{DS}=0 (I_{sc}) with illuminated power.

Synthesis of MWCNT in UHV by CVD

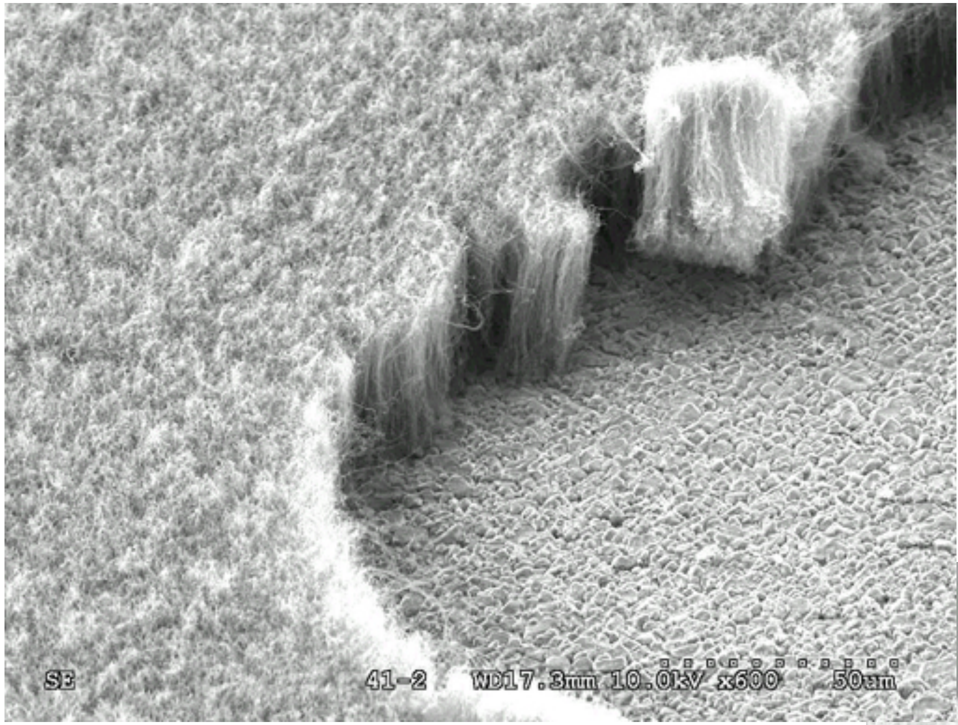


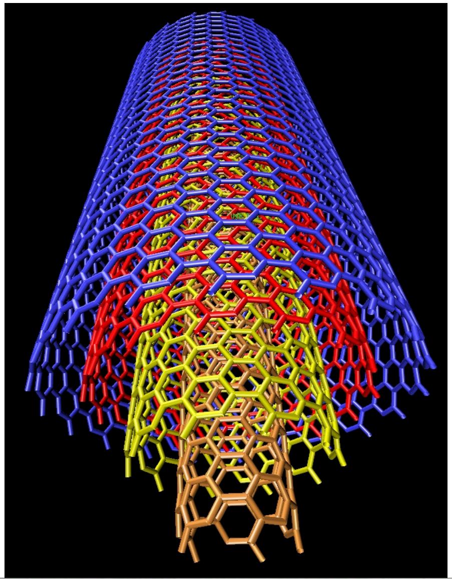
C_2H_2

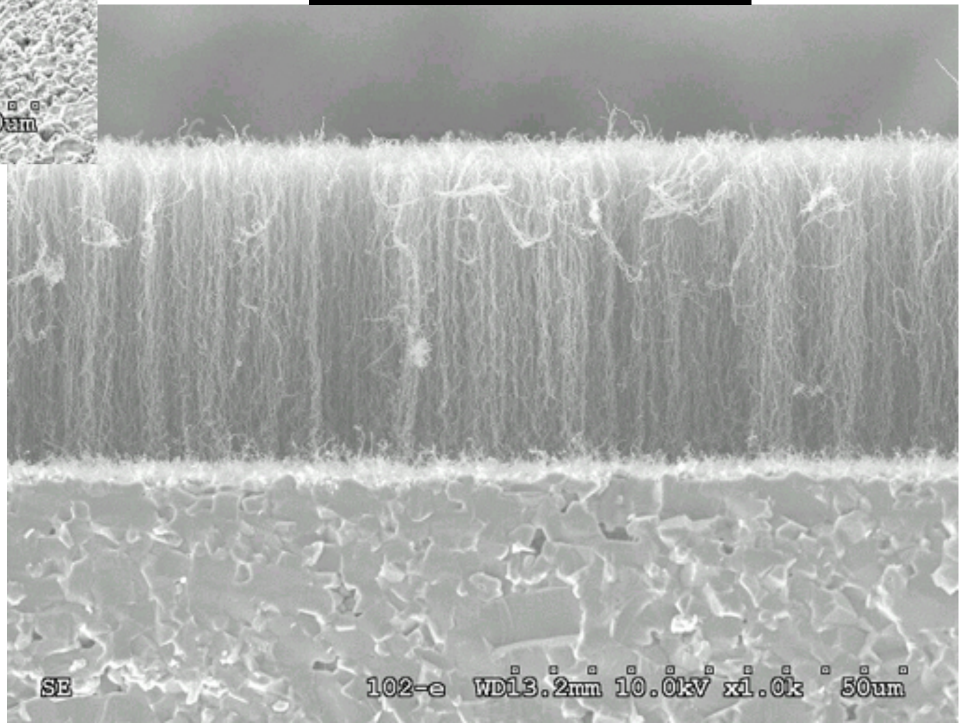
Fe catalyst
0.2 ÷ 1 nm
deposited at RT
in UHV conditions

Substrate temperature during growth:
T = 650°C ÷ 850°C

C_2H_2 atmosphere
C_2H_2 pressure= 10 ÷ 900 Torr

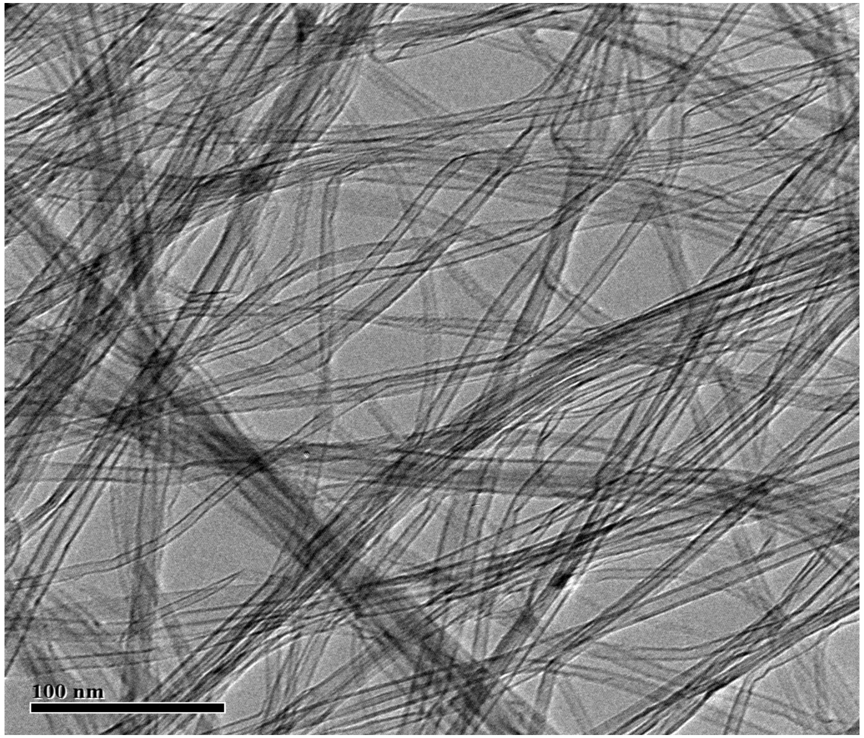


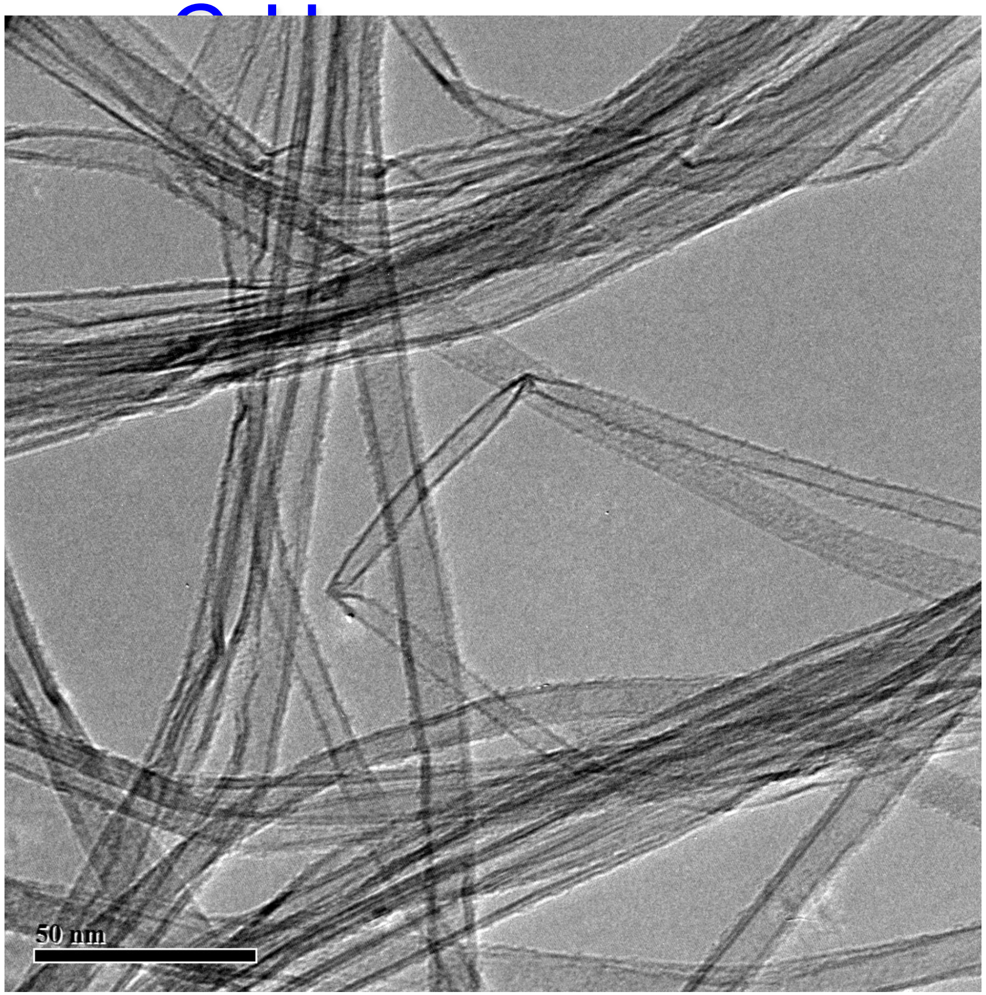


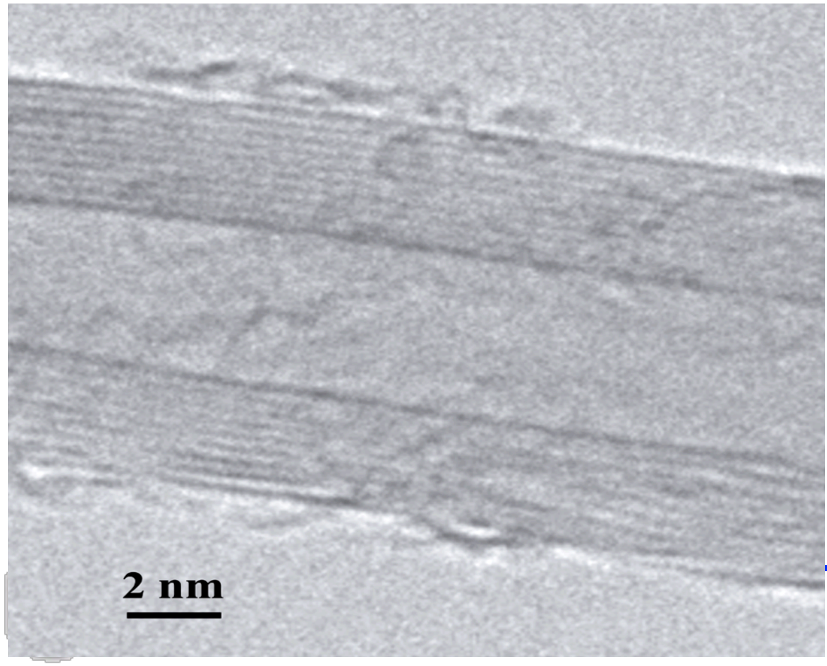


Multiwalled nanotubes (MWNTs)
consist of multiple layers of graphite
rolled in on themselves
to form a tube shape.

- Temperature of the substrate
- Time of exposure

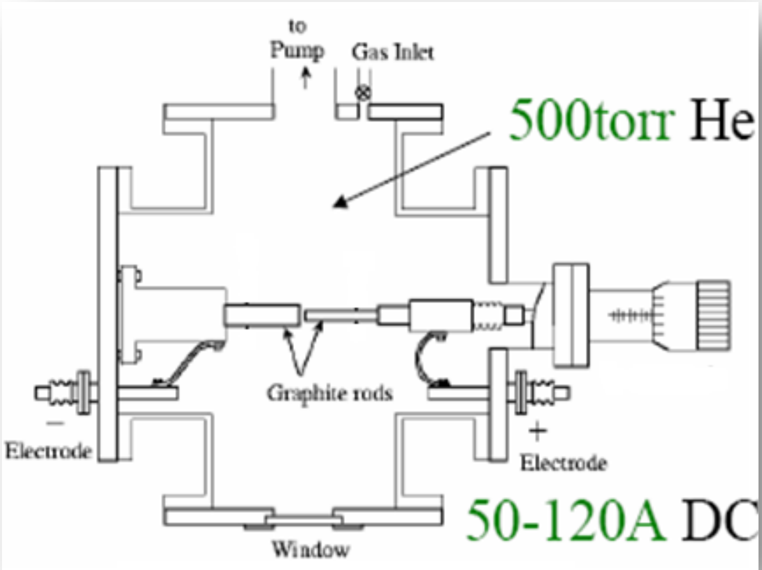




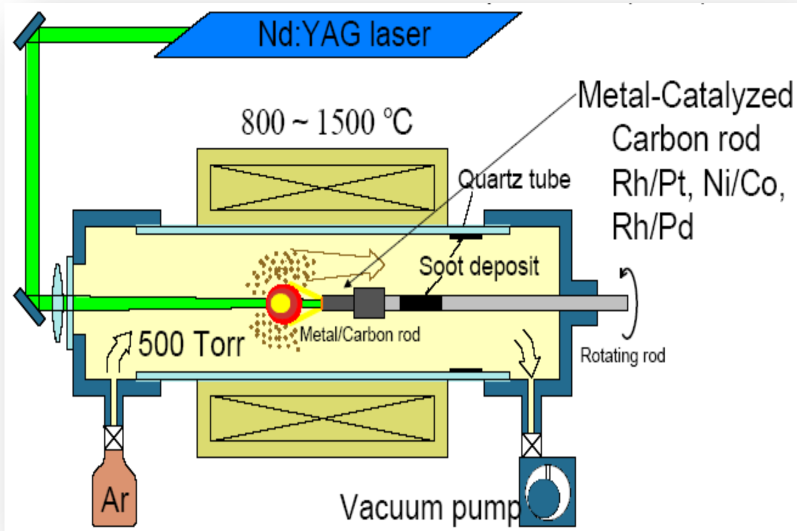


Growth Methods

CVD



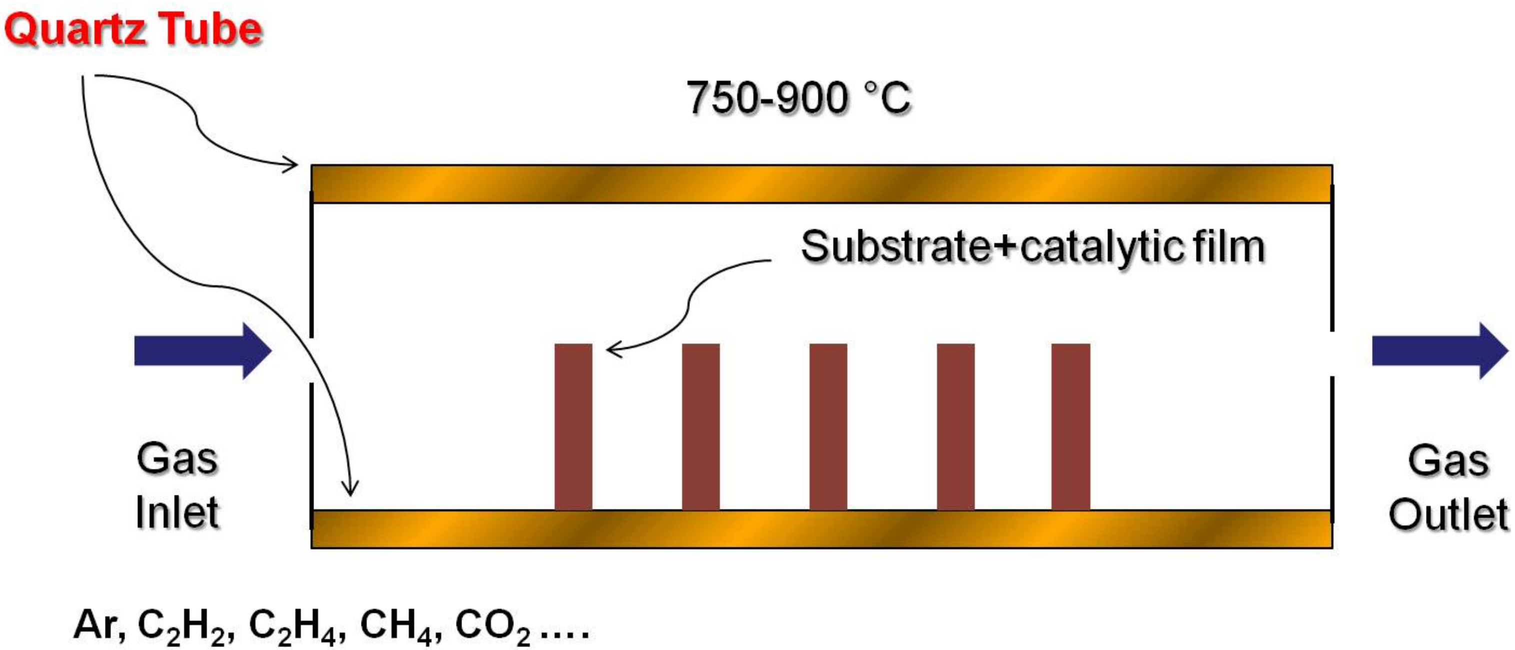
SYNTHESIS



Arc Discharge

Laser Ablation

Chemical Vapor Deposition

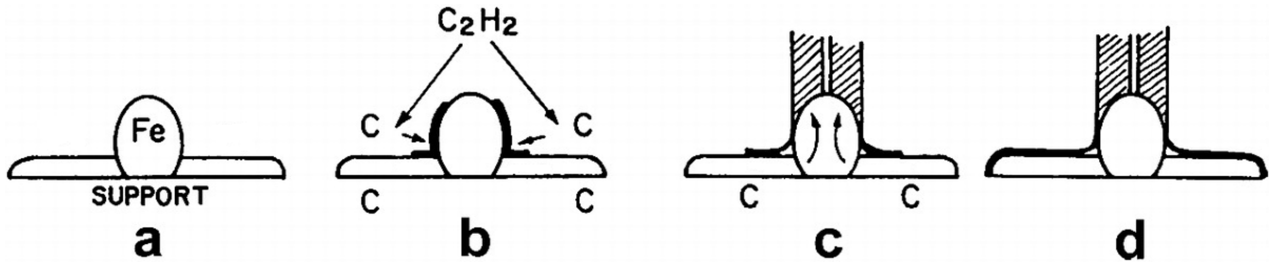


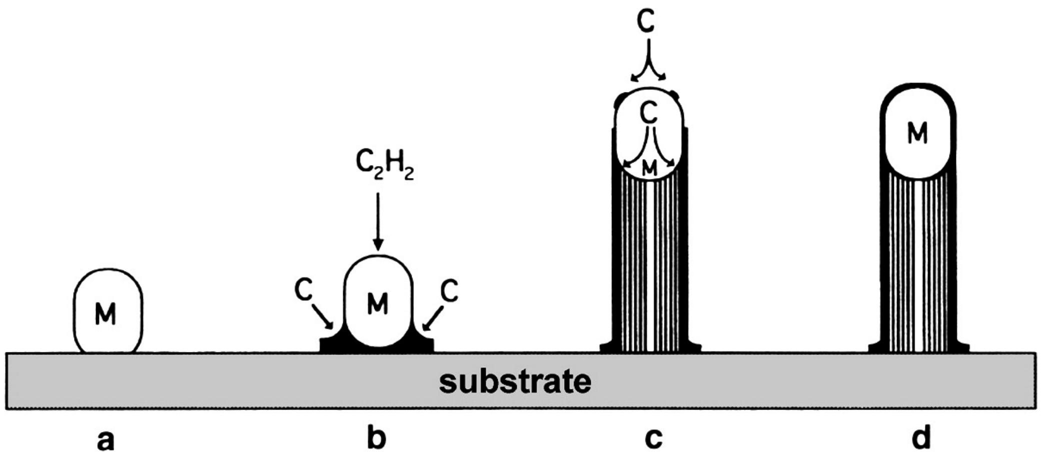
Recipe:

- solid substrate, where the chemical reaction takes place
- gas precursor, acting as carbon source
- catalytic material, favoring the chemical reaction

Growth mechanism

Base-growth

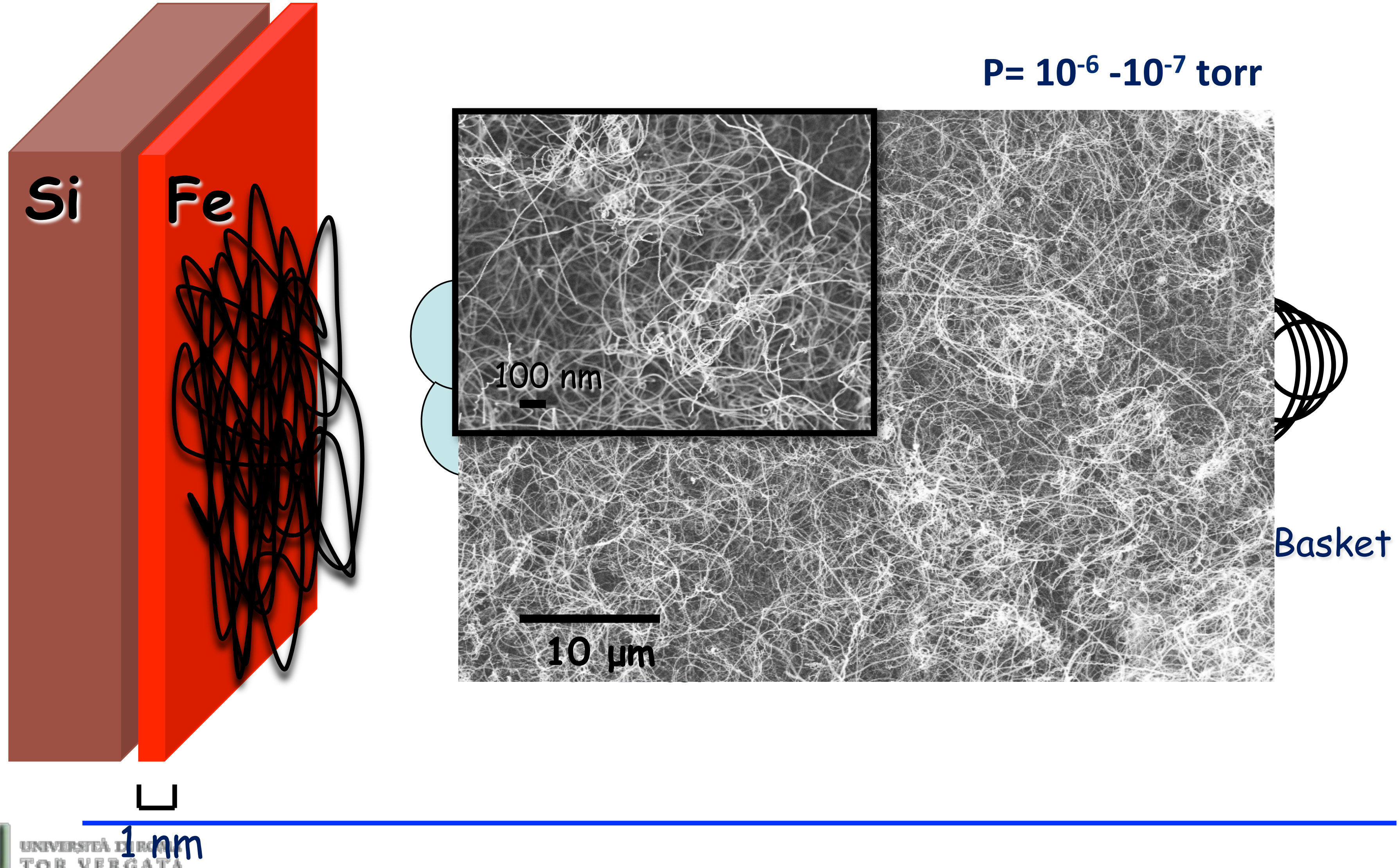




Tip-growth

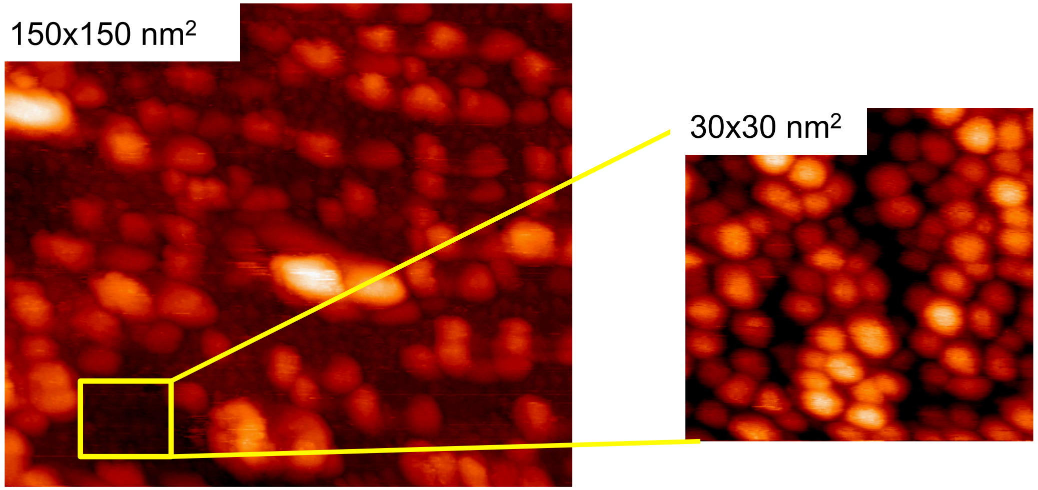
CVD: the classic method

P= 10^{-6} -10^{-7} torr



Why does it work?

- Presence of a catalytic film (i.e. Iron)
- Roughness of the catalytic film (i.e. Iron)



1 nm Fe on Si substrate

How much is it?

Crystalline silicon

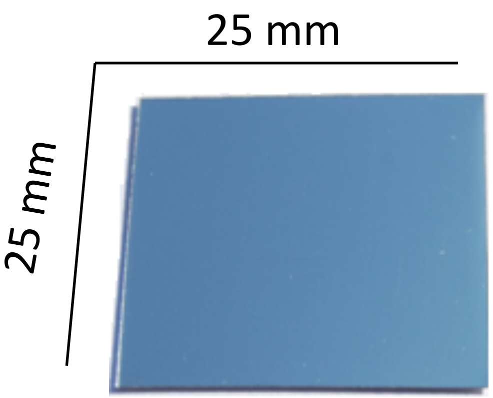
10.000 €/m^2 (from Siltronix)

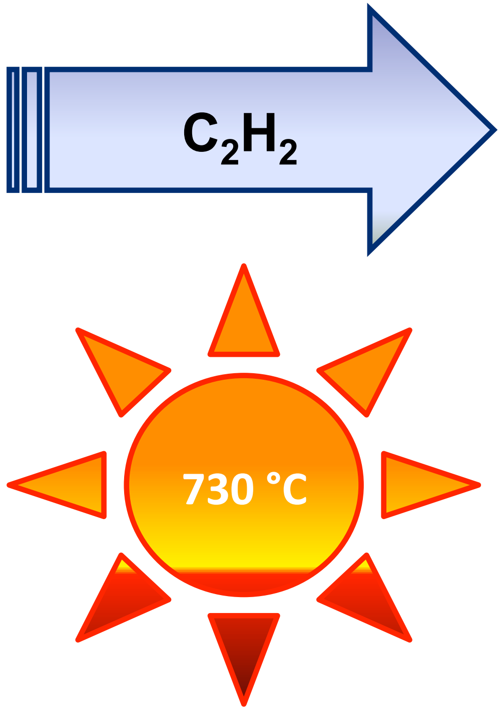
Stainless Steel

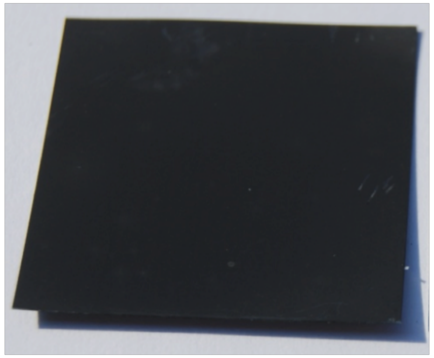
100 €/m^2 (fromGoodfellow)

CNT growth

Before... CVD After







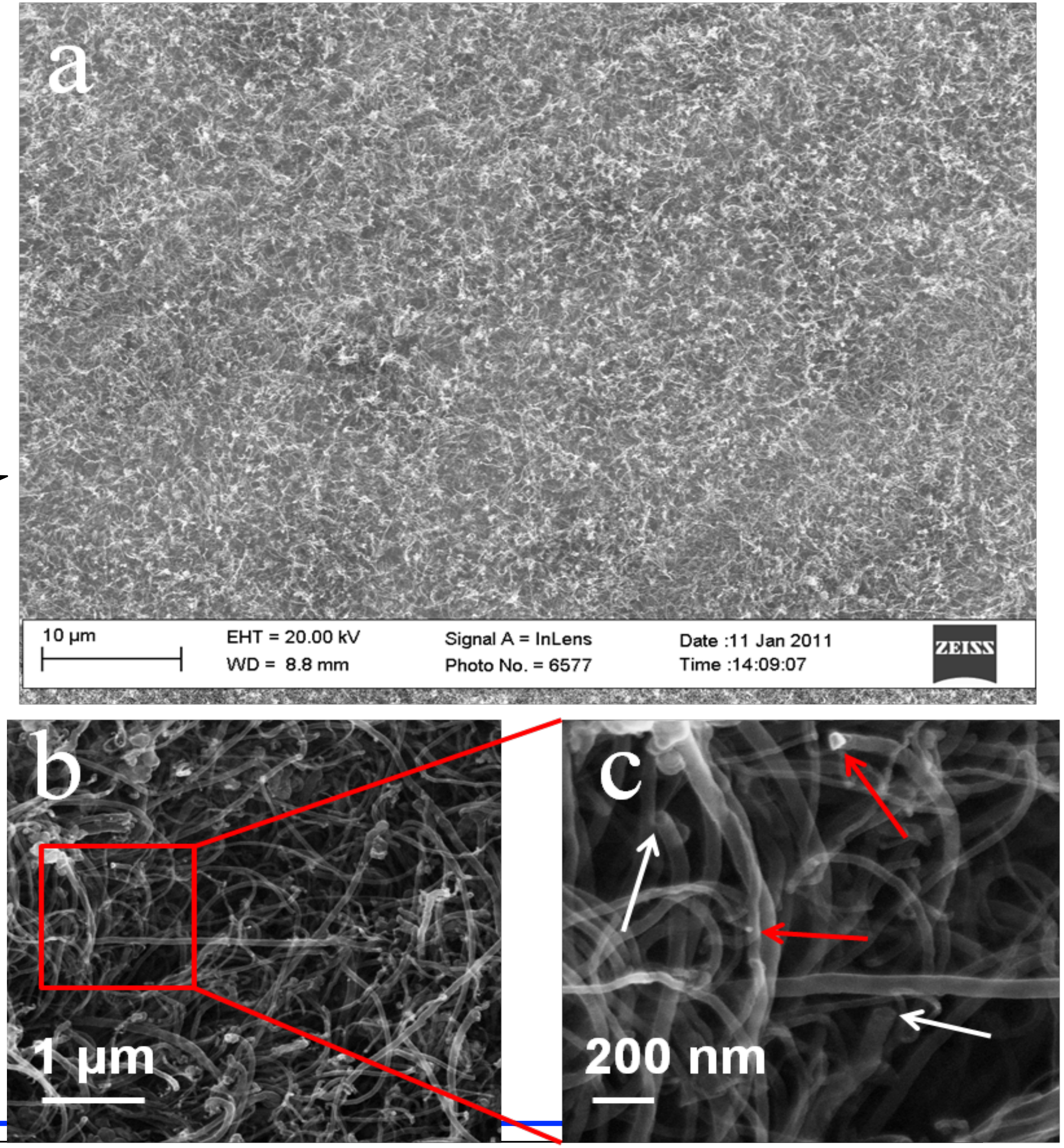
7mg in 10’

Huge production

L.Camilli, M.De Crescenzi et al. Carbon 49, 3307 (2011)

…the quality?

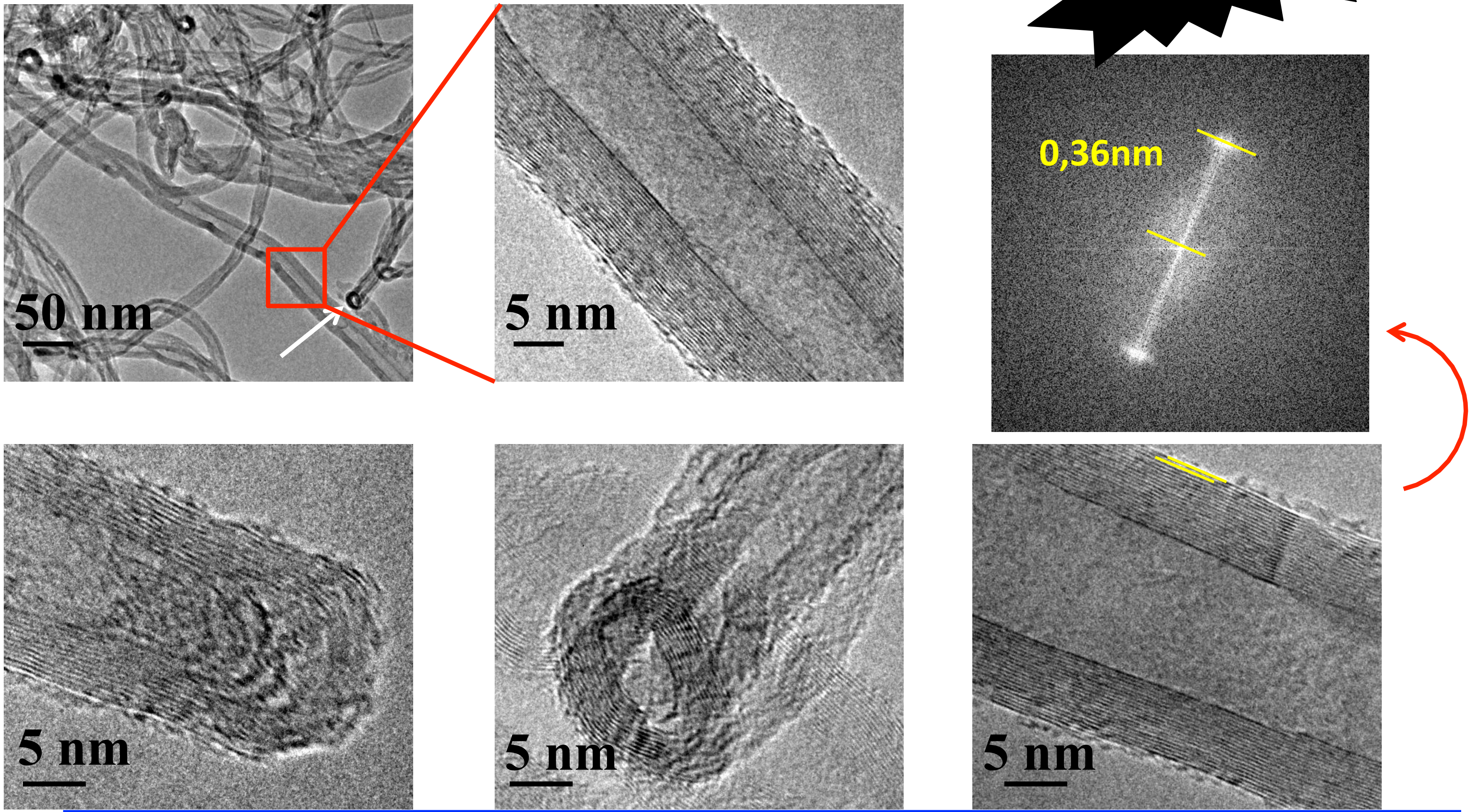
SEM



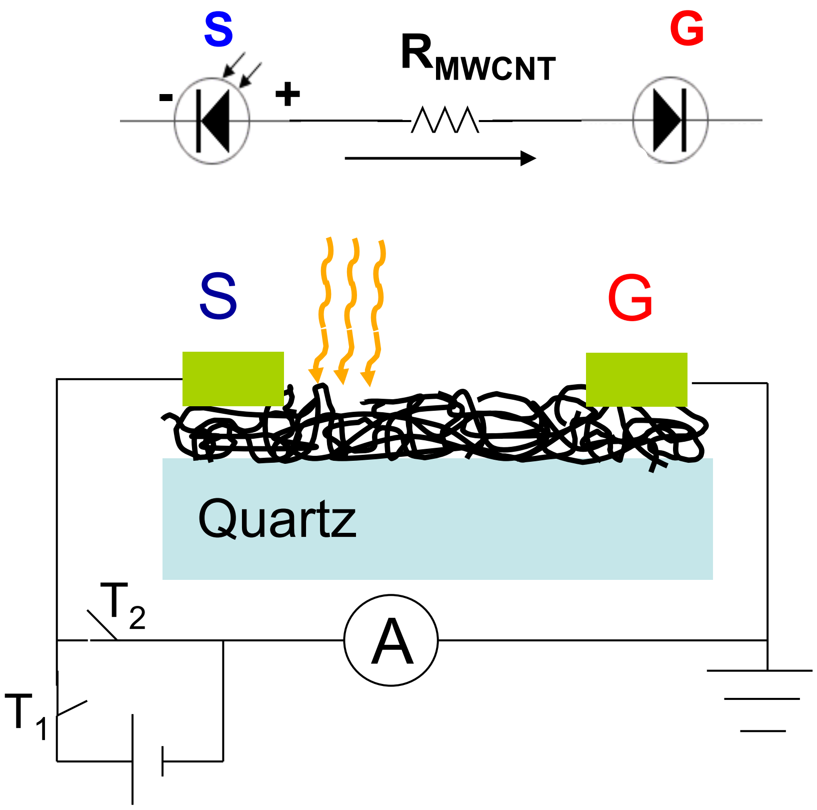
…the quality?

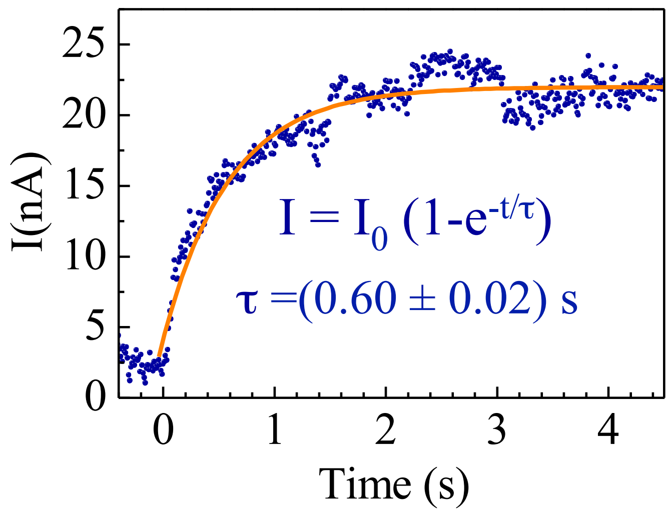
23 walls

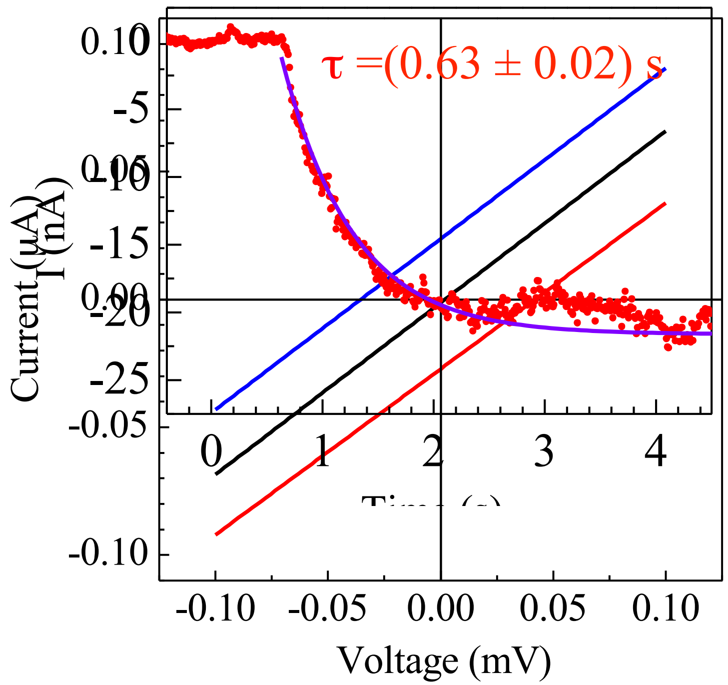
TEM



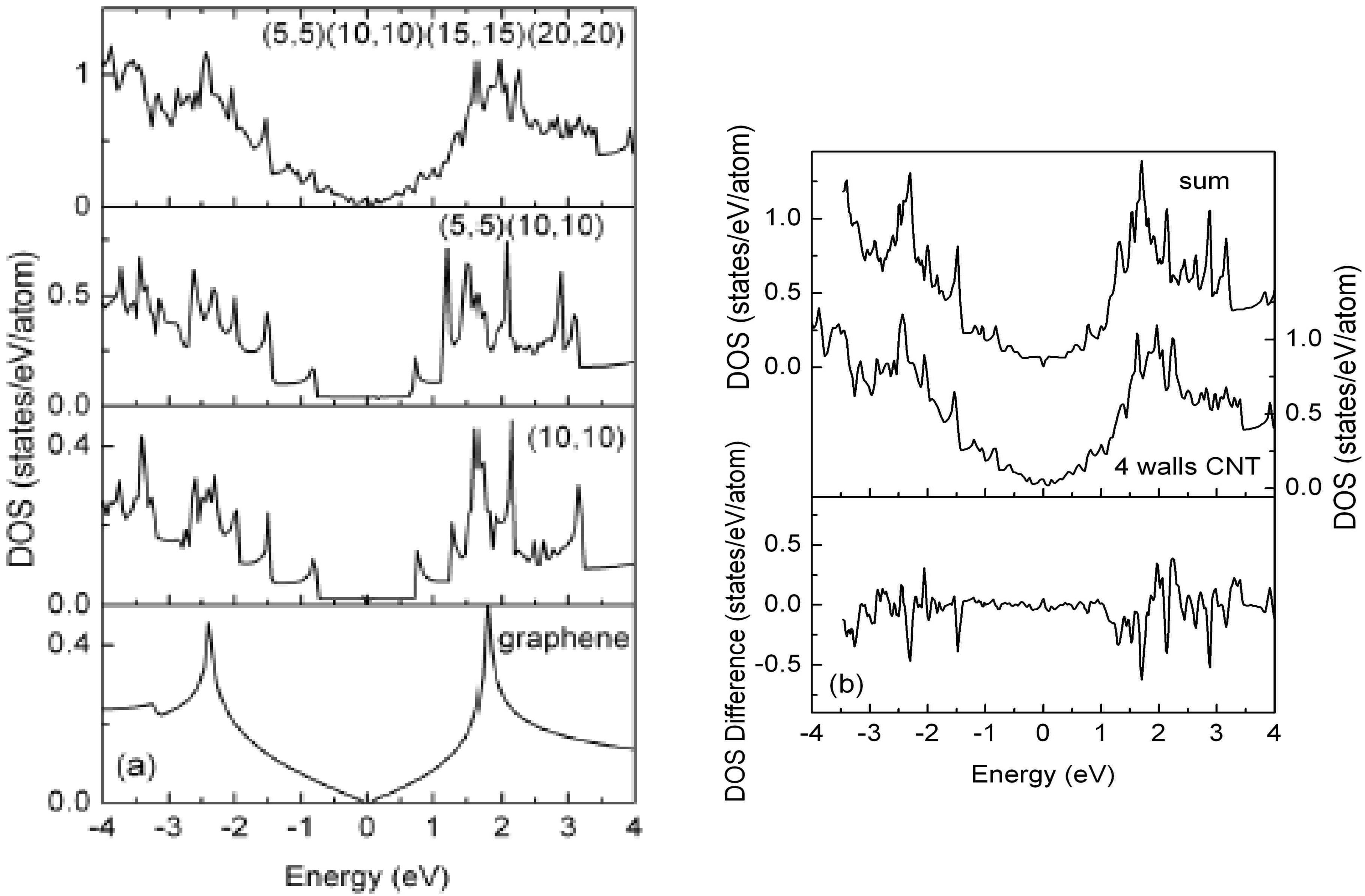
Which device to fabricate?





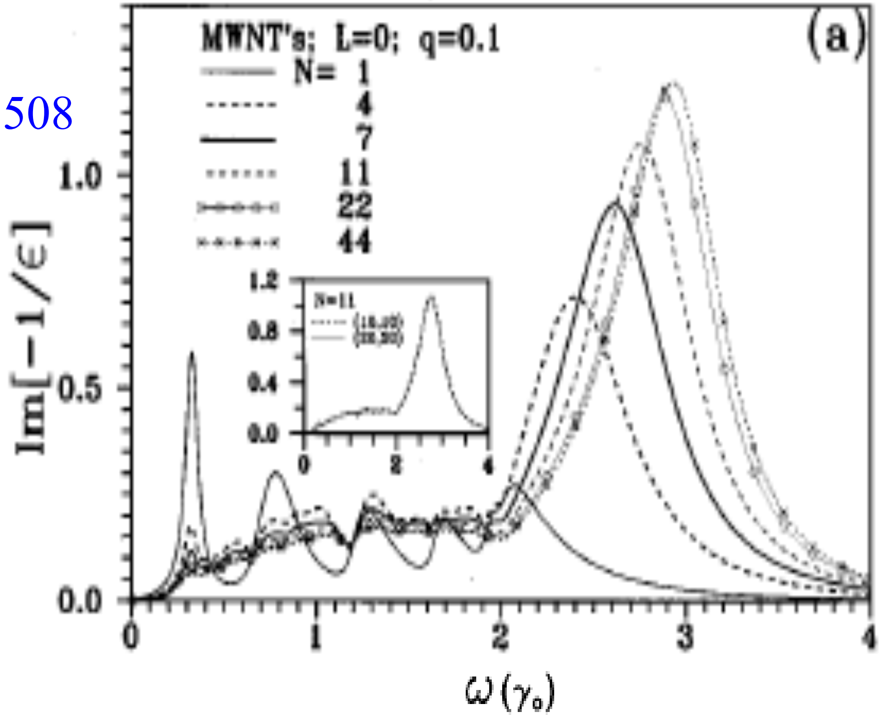


- MWCNTs generate e-h pairs upon illumination
- Two Schottky junctions opposite each other form between CNTs and metal electrode separate e-h pairs and drive separated carriers.
- Carriers moves through a diffusion mechanism
- Ohmic character of MWCNTs



Computation by A.Continenza, L'Aquila University (Italy)
P.Castrucci, M.DeCrescenzi et al., Nanotechnology 22, 115701 (2011)

F. L. Shyu, M. F. Lin, P.R.B 62 (2000) 8508



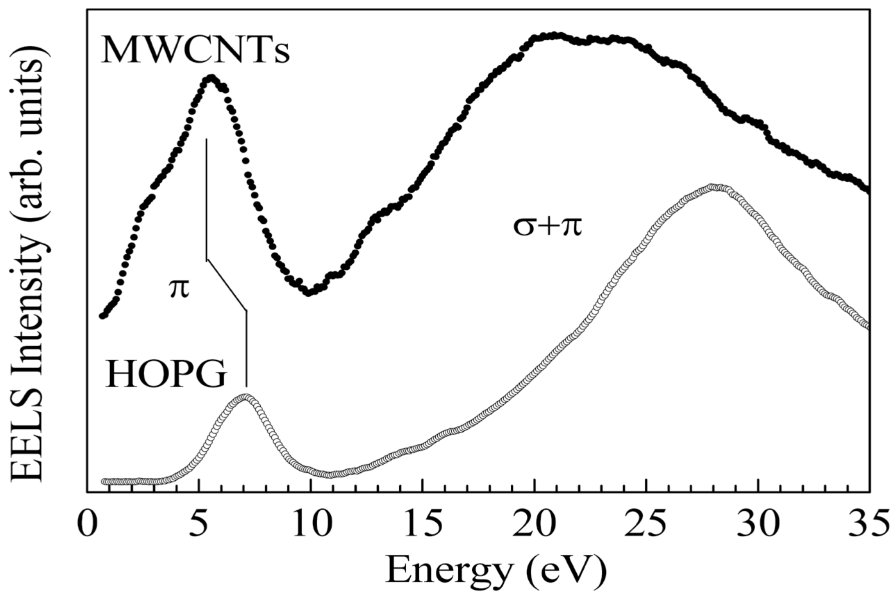
The quantum confinement of the charged carriers within the nanotubes

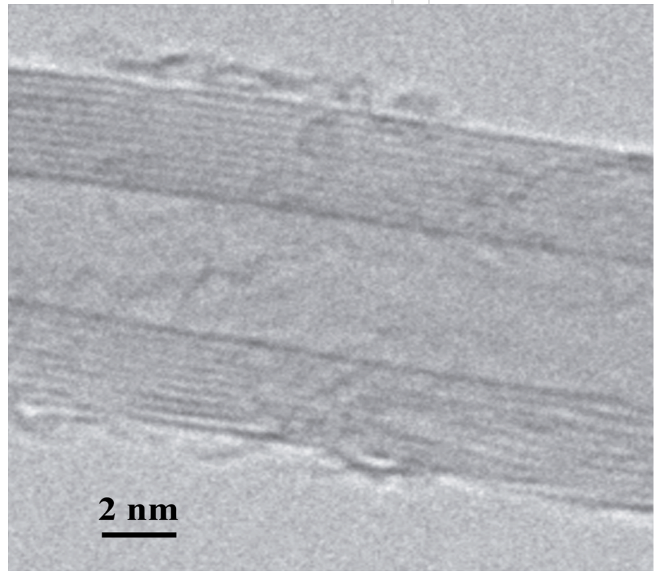
➡highly localized states in the infrared and visible energy region

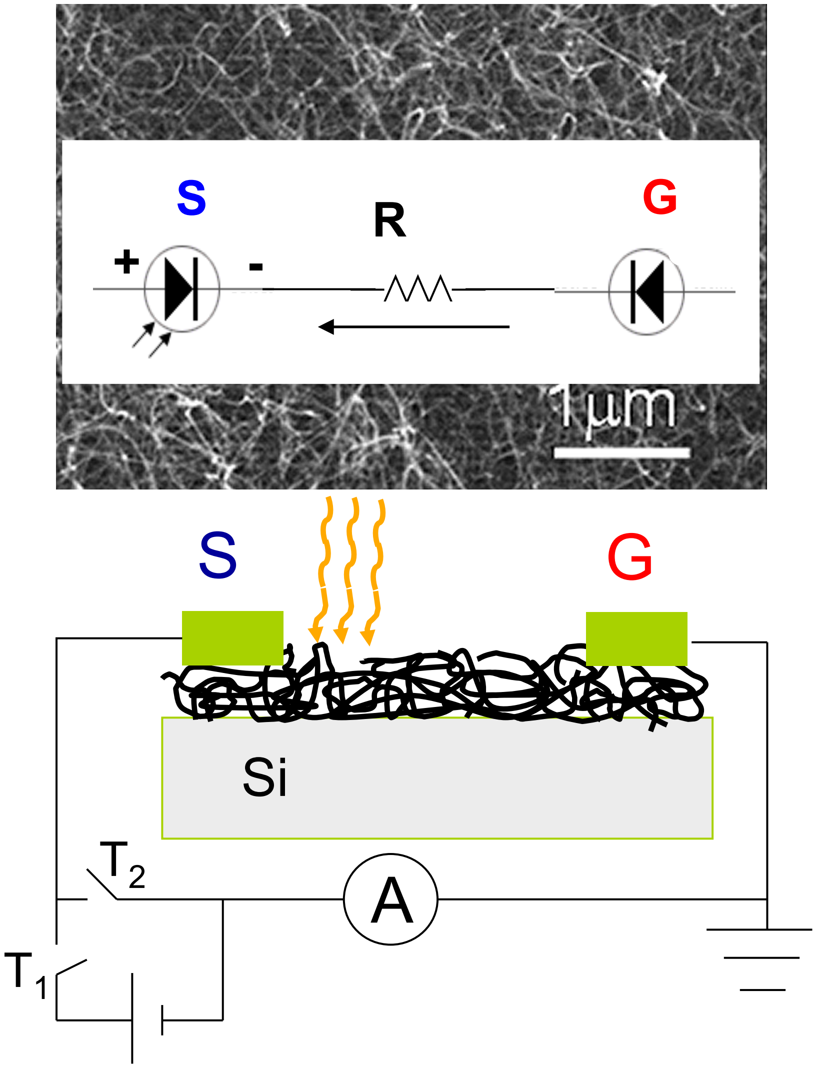
➡ strongly-bound excitons which modify the electronic behaviour

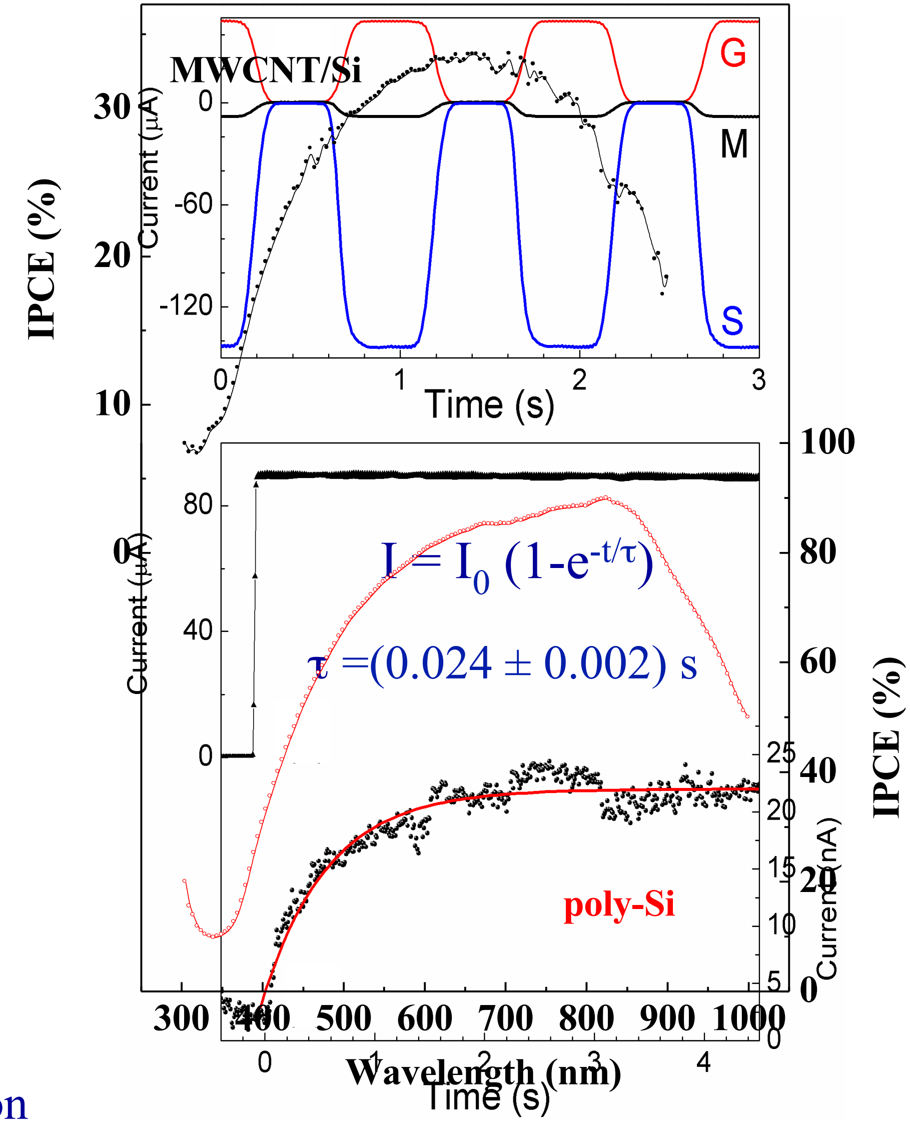
➡interband excitation channels.

This finding was theoretically predicted and evidenced by energy loss measurements.



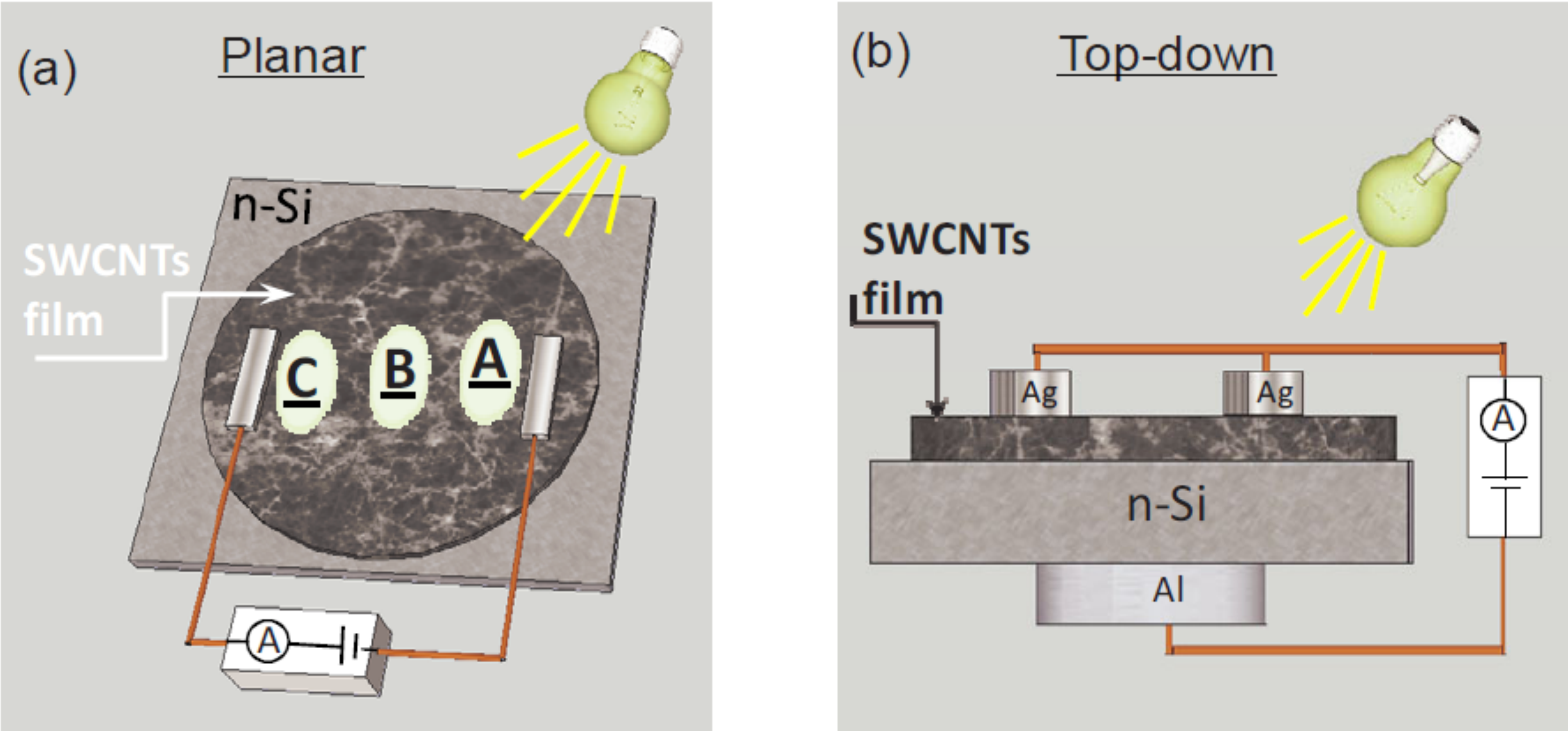






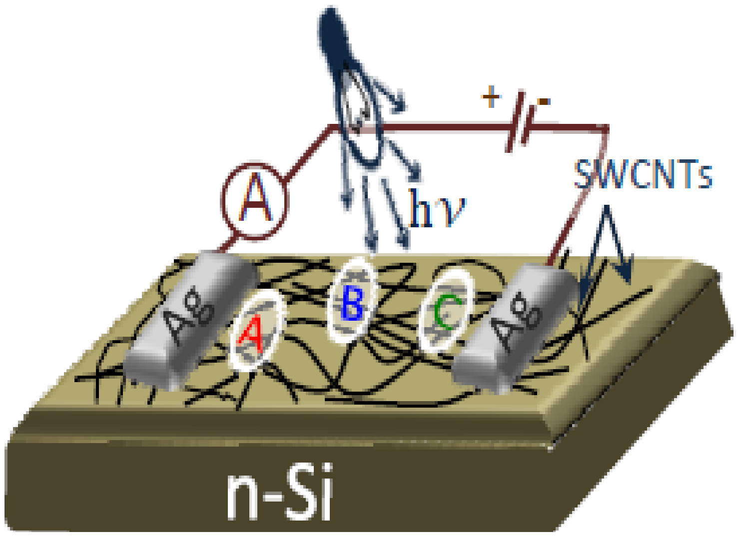
- MWCNTs generate e-h pairs upon illumination
- Si takes part to the e-h generation process, to the charge carriers separation and transport
- The system shows a photovoltaic character, with an IPCE of about 34%

P.Castrucci, M. DeCrescenzi, A.Continenza et al., Nanotechnology 22, 115701 (2011)



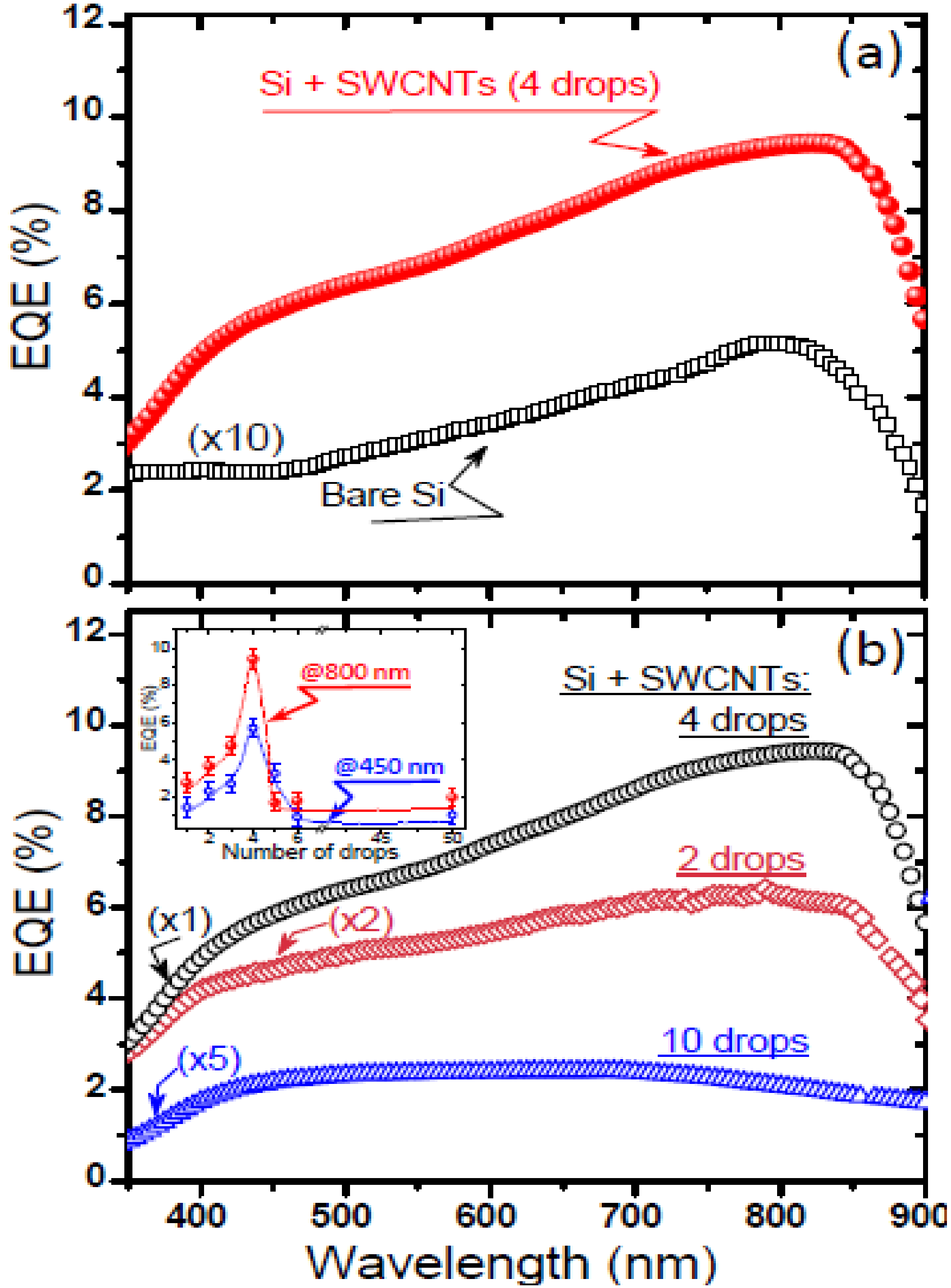
Schematics of both (a) planar and (b) top-down configurations of the SWCNTs/n-silicon hybrid devices. A, B and C correspond to the different light spot locations (ground electrode, center and signal electrode) investigated on the planar device surface.

Planar geometry



$$EQE(\lambda) = 100\ h\ c\ I(\lambda)\ /e\ \lambda\ P(\lambda)$$

External Quantum Efficiency



V.LeBorgne, P.Castrucci, S.Del Gobbo, M.Scarselli, M.DeCrescenzi, M.A.El Khakani, Appl.Phys.Lett. **97**, 193105 (2010); Appl.Phys.Lett. 95, 083114 (2009)

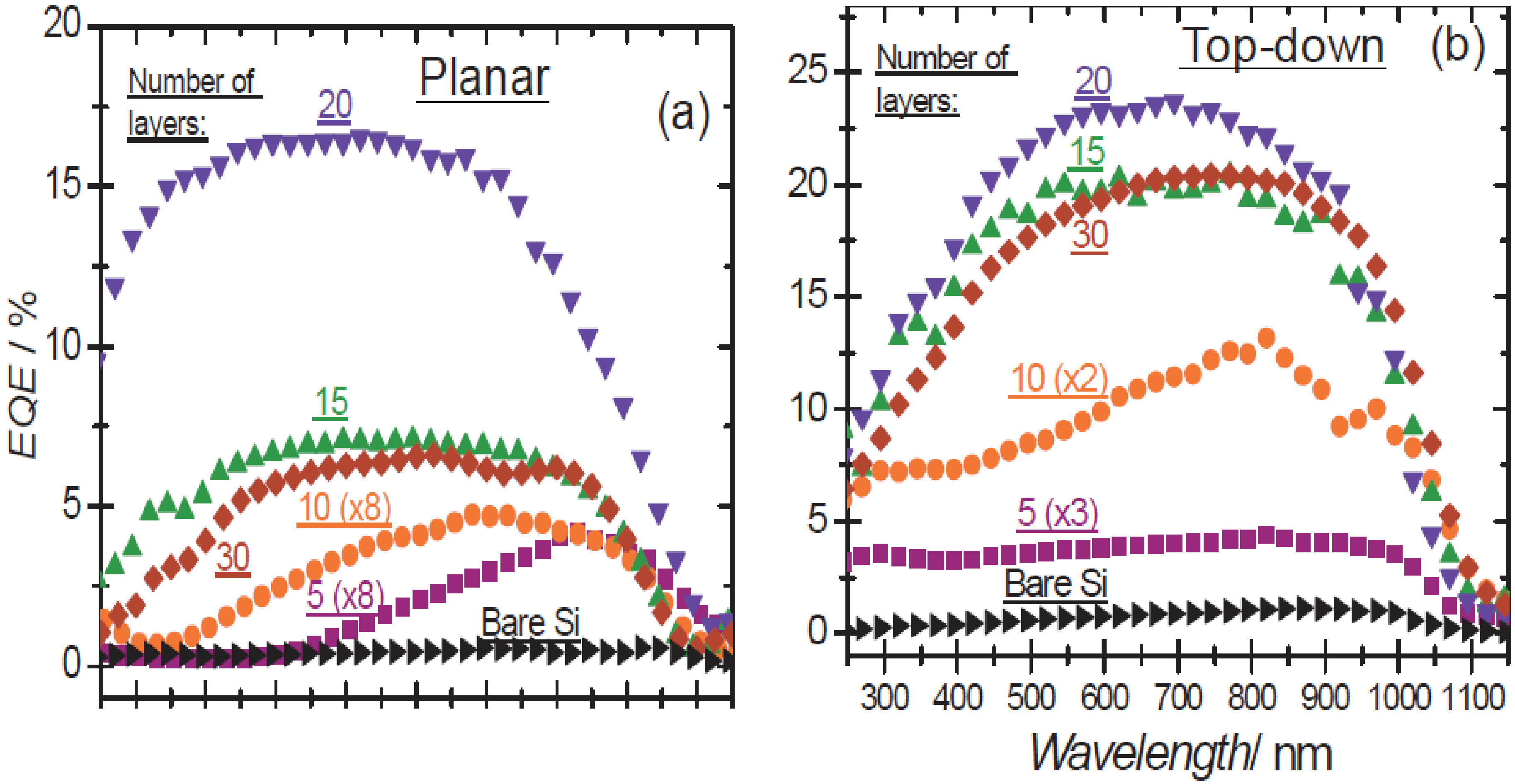
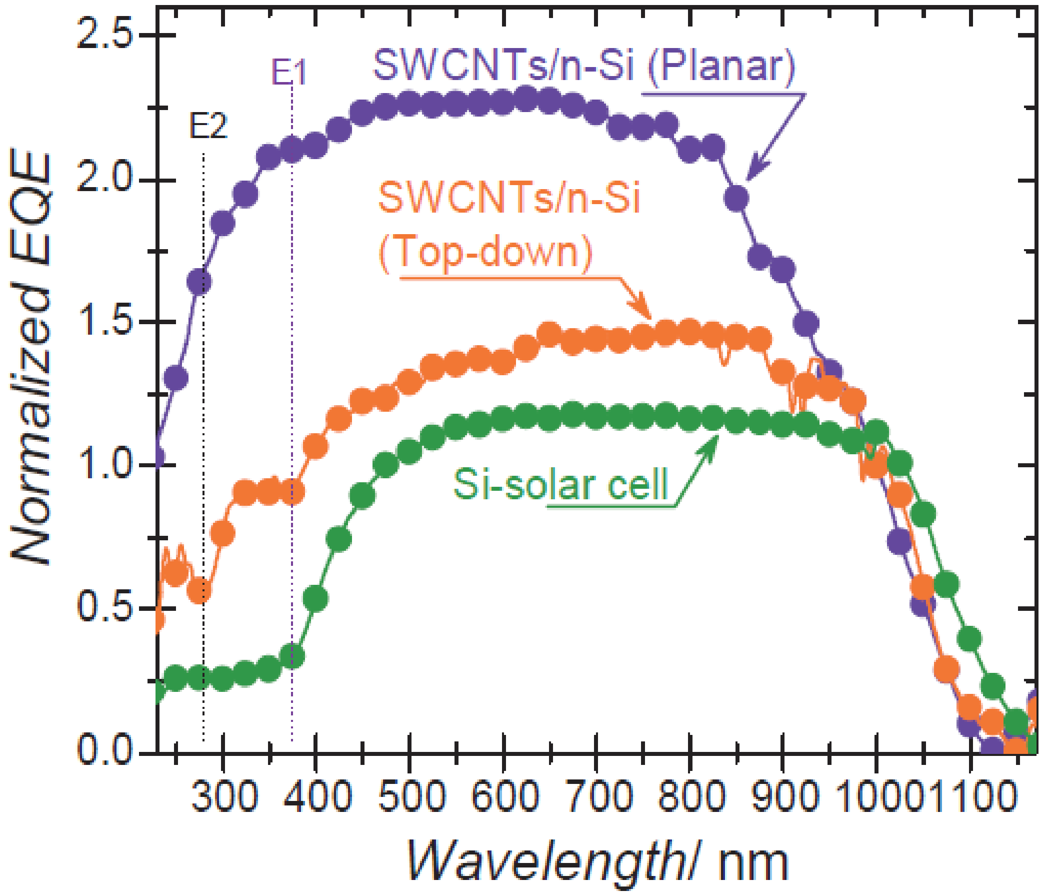
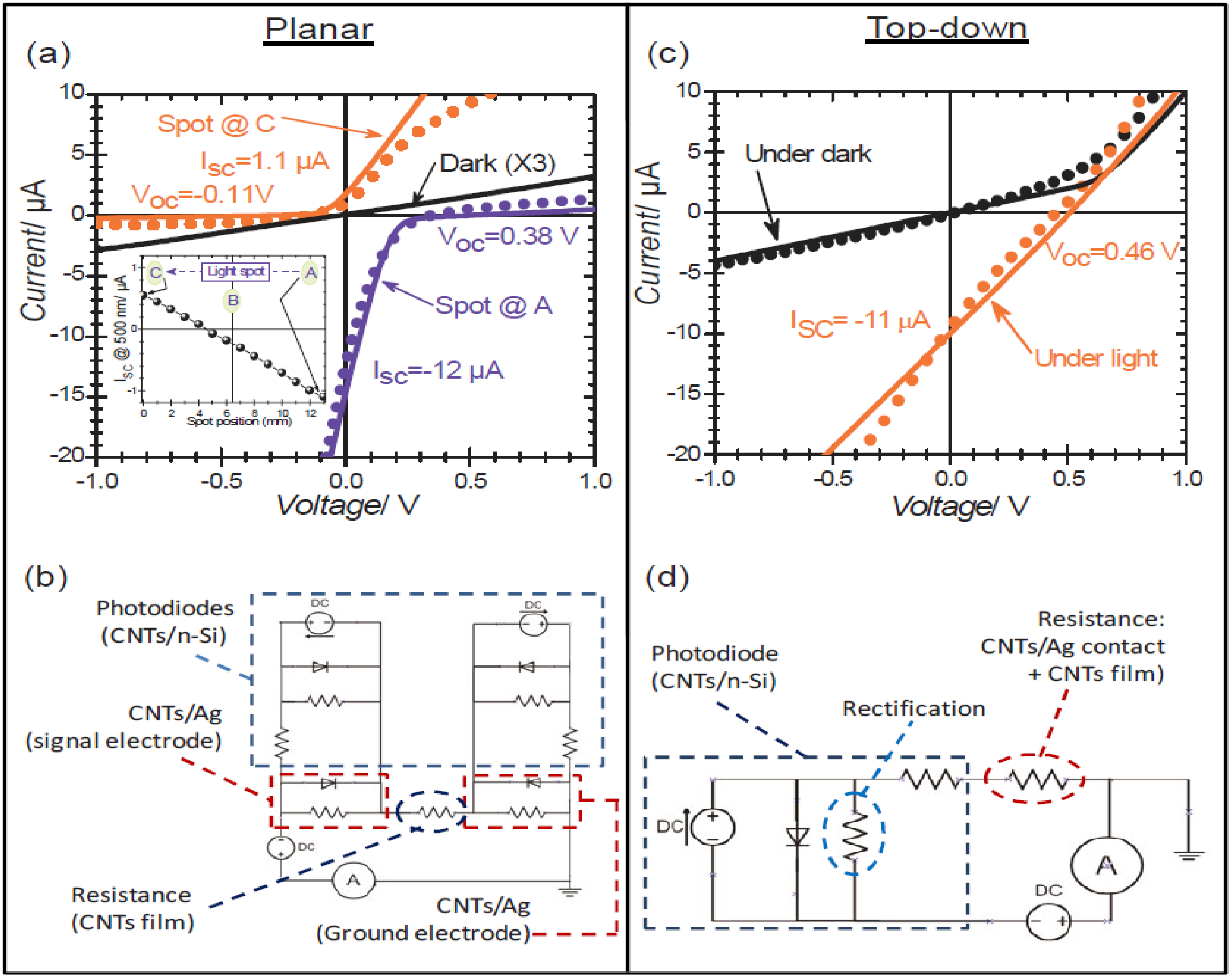


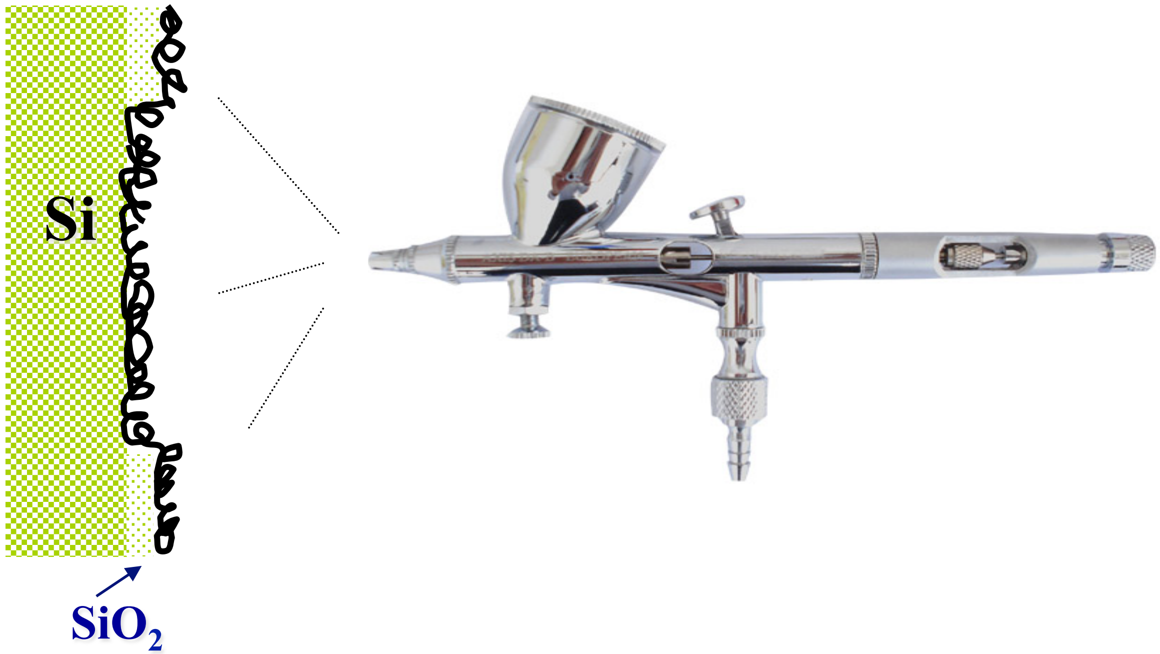
Figure 4. EQE spectra of the SWCNTs/n-Si devices as a function of the number of spin-coated layers of SWCNTs for both (a) planar and (b) top-down configurations.



Comparison of normalized EQE spectra of both planar and top-down SWCNTs/n-Si PV devices (fabricated with 20 spin-coated layers of SWCNTs) with that of standard polycrystalline silicon solar cell. The EQE spectra were normalized to their respective EQE value at 1000 nm.



Planar
(a)
Spot @ C
Isc=1.1 µA
Voc=-0.11V
Dark (X3)
Voc=0.38 V
Spot @ A
Isc=-12 µA
Light spot
C
B
A
Isc @ 500 nm/ µA
Spot position (mm)
Current/ µA
Voltage/ V
Top-down
(c)
Under dark
Voc=0.46 V
ISC= -11 µA
Under light
Current/ µA
Voltage/ V
(b)
Photodiodes
(CNTs/n-Si)
CNTs/Ag
(signal electrode)
Resistance
(CNTs film)
CNTs/Ag
(Ground electrode)
DC
A
(d)
Resistance:
CNTs/Ag contact
+ CNTs film)
Photodiode
(CNTs/n-Si)
Rectification
DC
A

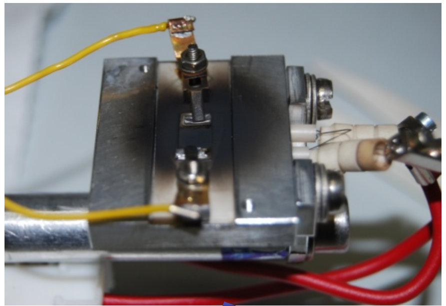


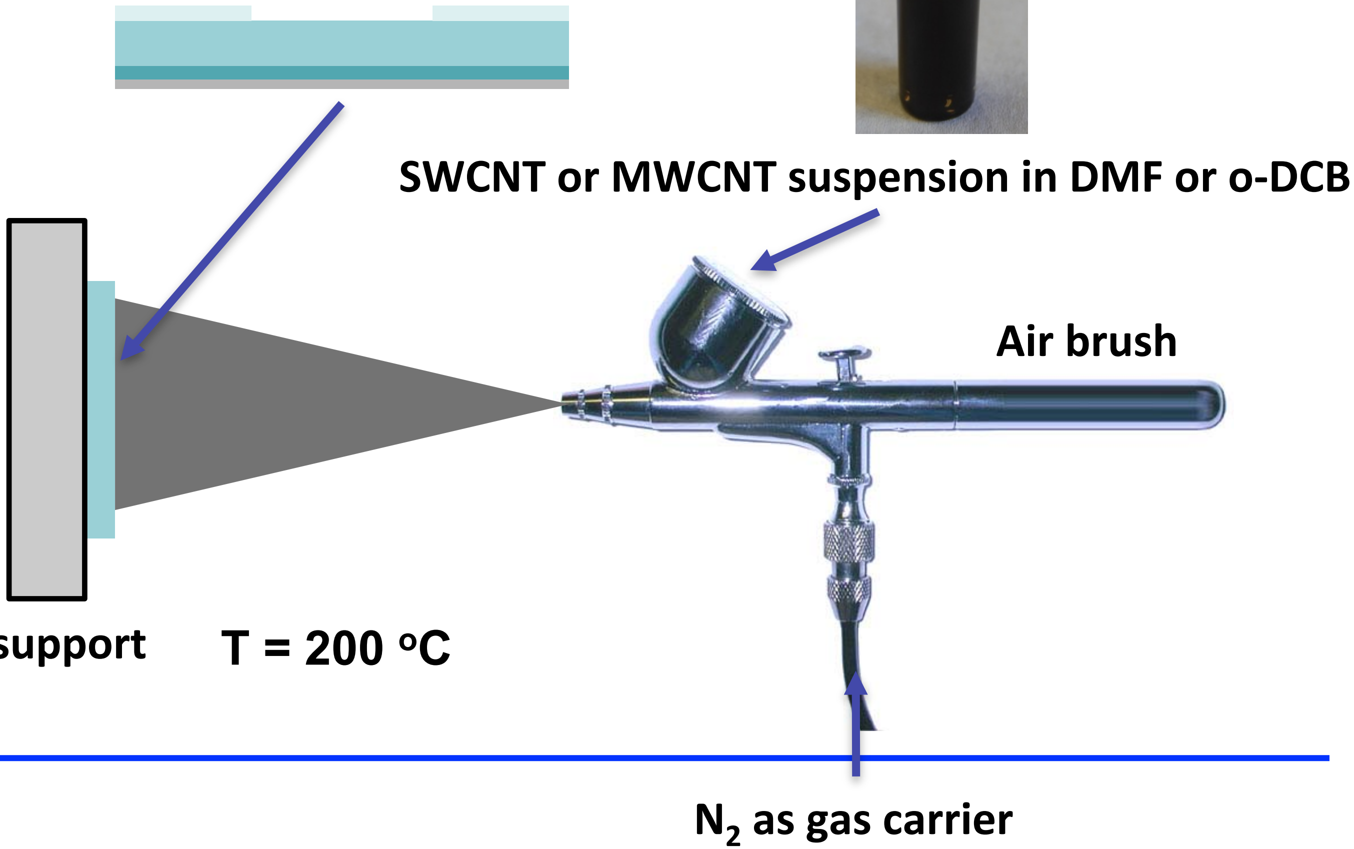
- Sonication of MWCNTs/Si in 1,2 diclorobenzene
- Selective etching of a 300 nm SiO_2/Si substrate
- By airbrushing: MWCNTs dispersion on a SiO_2 etched substrate and quartz substrate
- Optical absorption measurements
- Ag electrodes deposition

MWCNT/SWCNT deposition

Dispersion in N,N-Dimethylformamide (DMF) or o-dichlorobenzene (o-DCB) 1h in ultrasound bath (conc. 1-10 µg/ml)

Airbrush deposition on hot patterned Si substrates (200 °C)

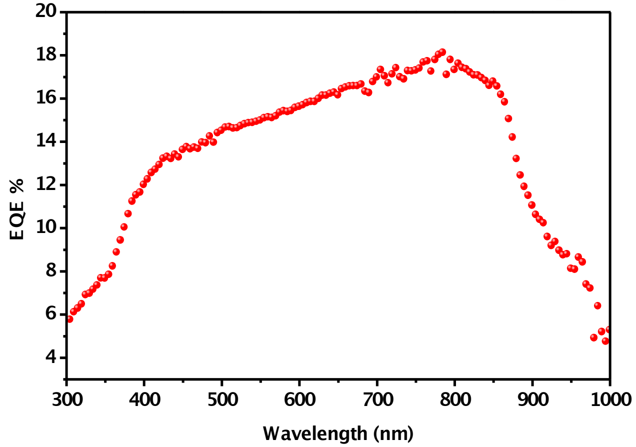


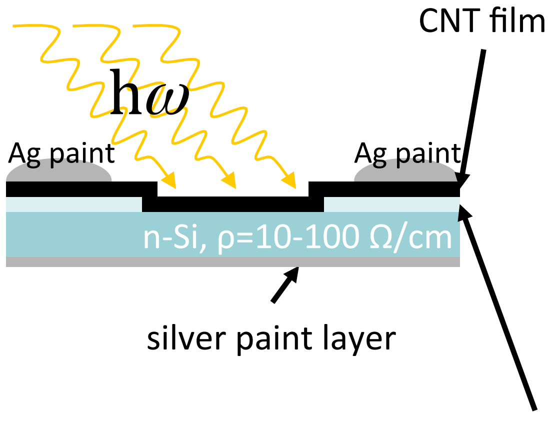


$$\theta_C \propto \frac{1}{R_S} = \frac{W}{L} R^{-1}$$

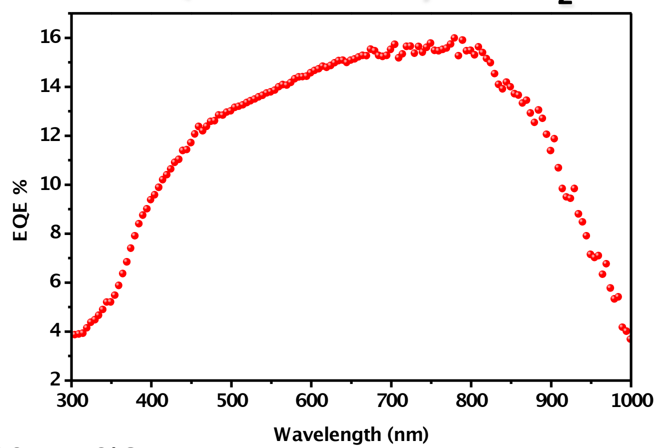
MWCNT and SWCNT on n-Si

EQE of MWCNT/Si-SiO_2

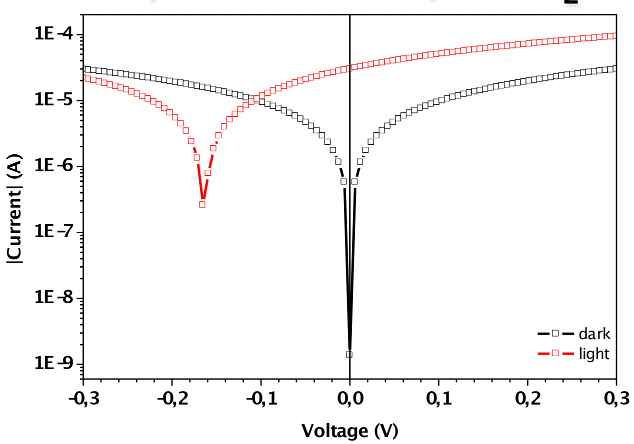




EQE of SWCNT/Si-SiO_2



I/V of MWCNT/Si-SiO_2

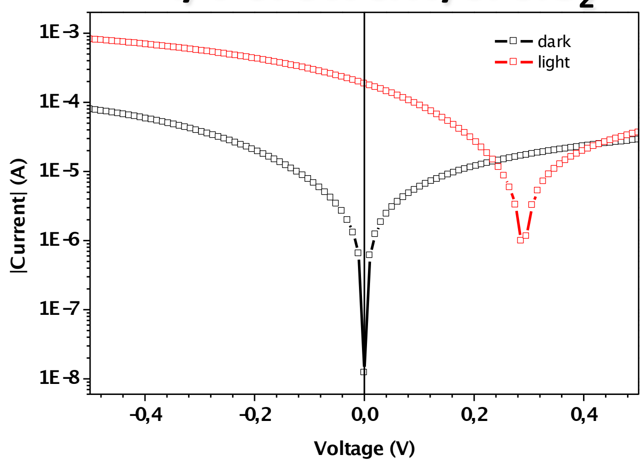


$I_{SC} \approx 10^{-3}$ mA

V_{0C}=200-500 mV

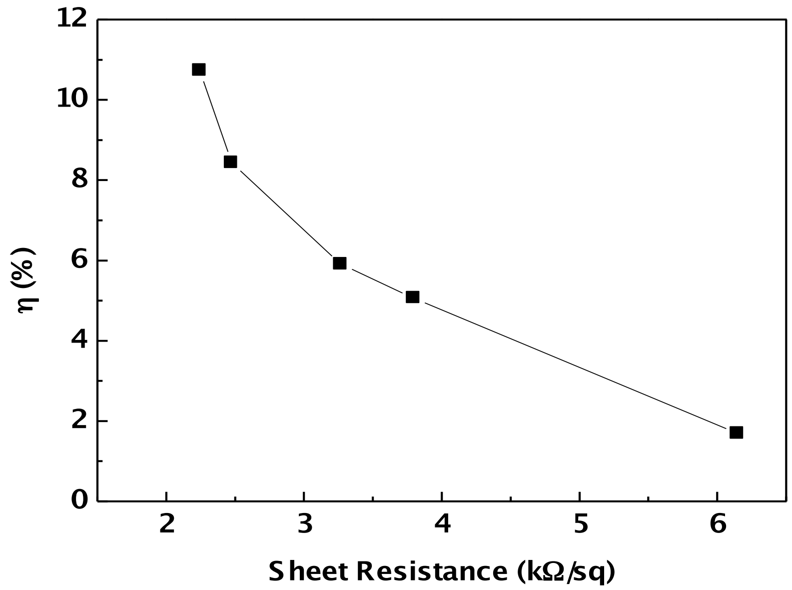
EQE≈ 20 - 70%

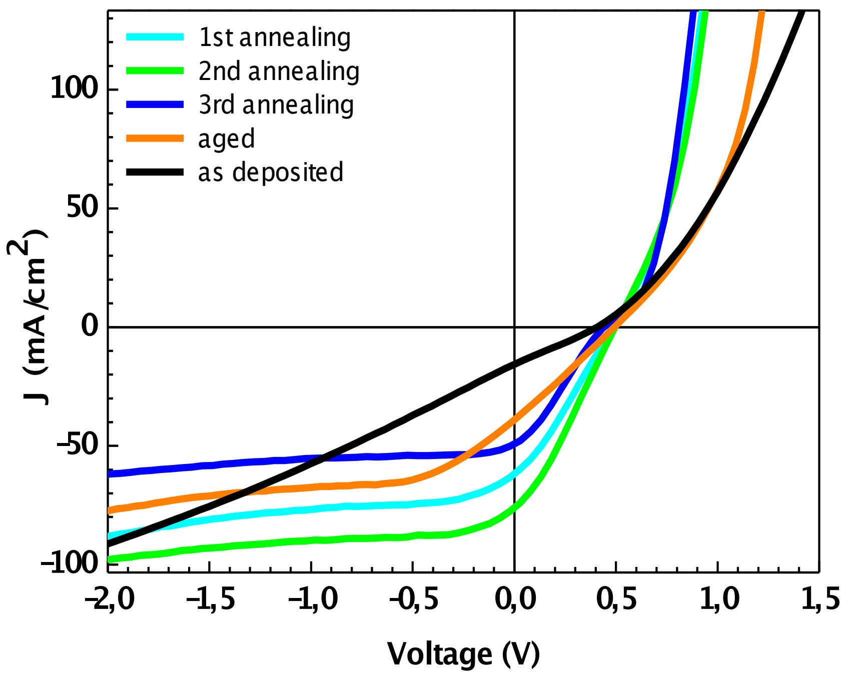
I/V of SWCNT/Si-SiO_2



Efficiency of CNTs Solar cells

	R (kΩ)	R_{sheet}(kΩ)	FF	η (%)
As deposited	3.725	6.15	0.26	1.7
Aged (15 gg)	2.3	3.8	0.26	5.06
1st Ann. @ T=280°C	1.5	2.5	0.28	8.43
2nd Ann. @ T=280°C	1.36	2.2	0.29	10.73
3rd Ann. @ T=280°C	1.98	3.3	0.27	5.90





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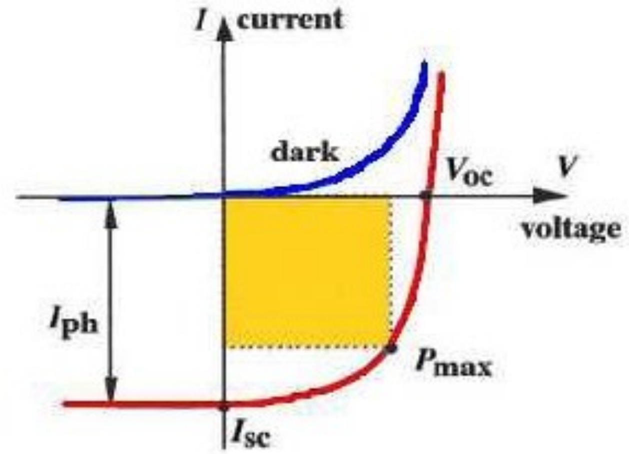
I-V measurements



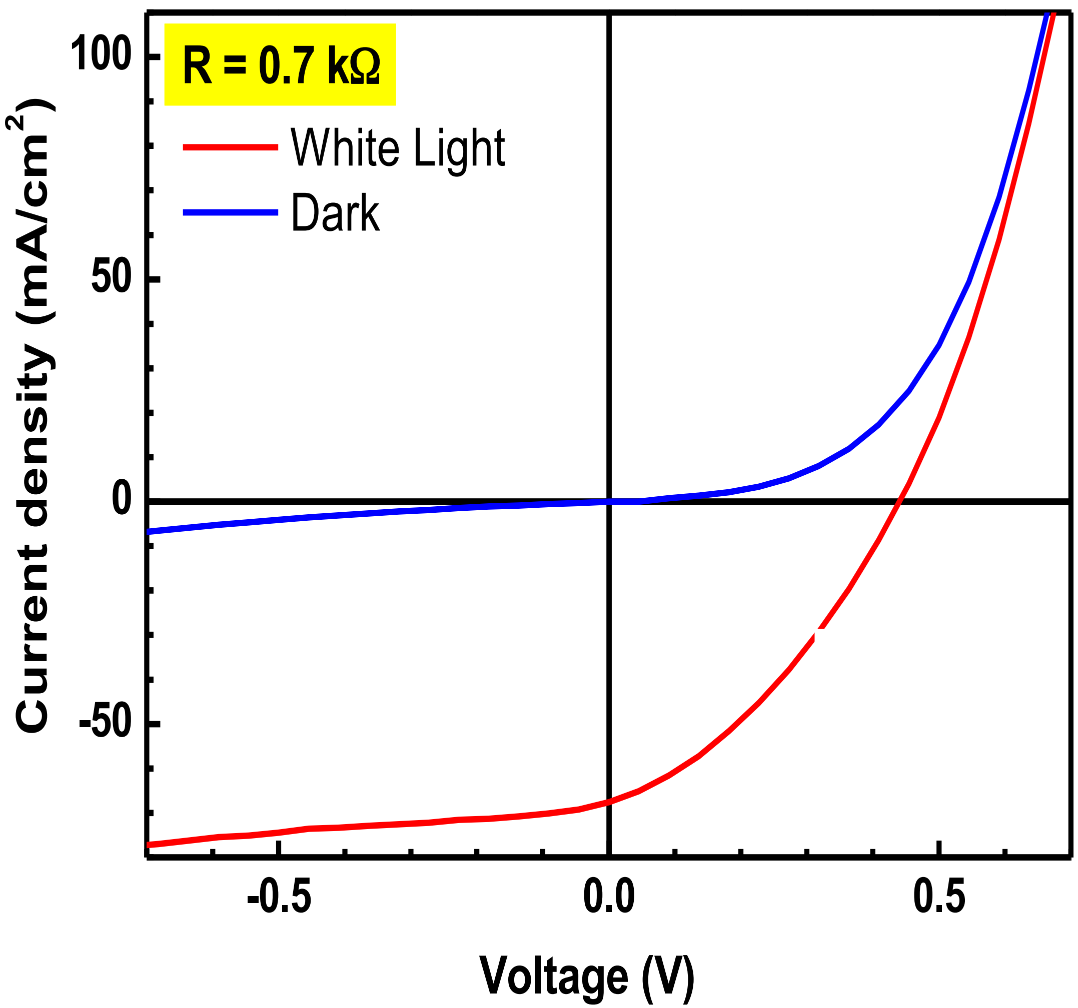
$$FF = \frac{I_{PM} * V_{PM}}{I_{SC} * V_{OC}}$$

It is a measure of the cell quality

$$\eta = \frac{I_{SC} * V_{OC} * FF}{P_{light}} \%$$

It is a measure of the efficiciency

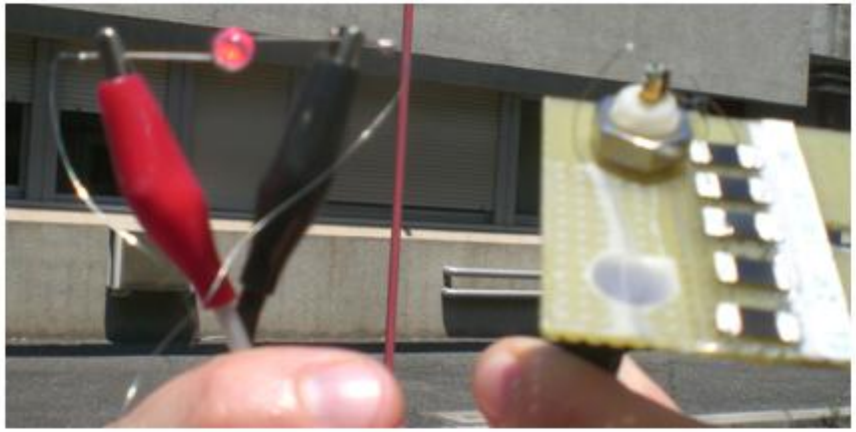
The maximum of Isc occurs by using a thickness which miximises the number of photons that reach the silicon and the number of Schottky junctions which minimise the Resistance.



At the sunlight (h = 12:00 a.m.) estimated incident power,
P_{in} = 100mW/cm^2
Voc = 0.44 V, Jsc = 5.2 mA/cm^2

Under Xe lamp white light,
P_{in} = 80mW/cm^2 :
Voc = 0.44 V, Jsc = 43.7 mA/cm^2

FF = 36%
Efficiency 1.5%



Sun illumination

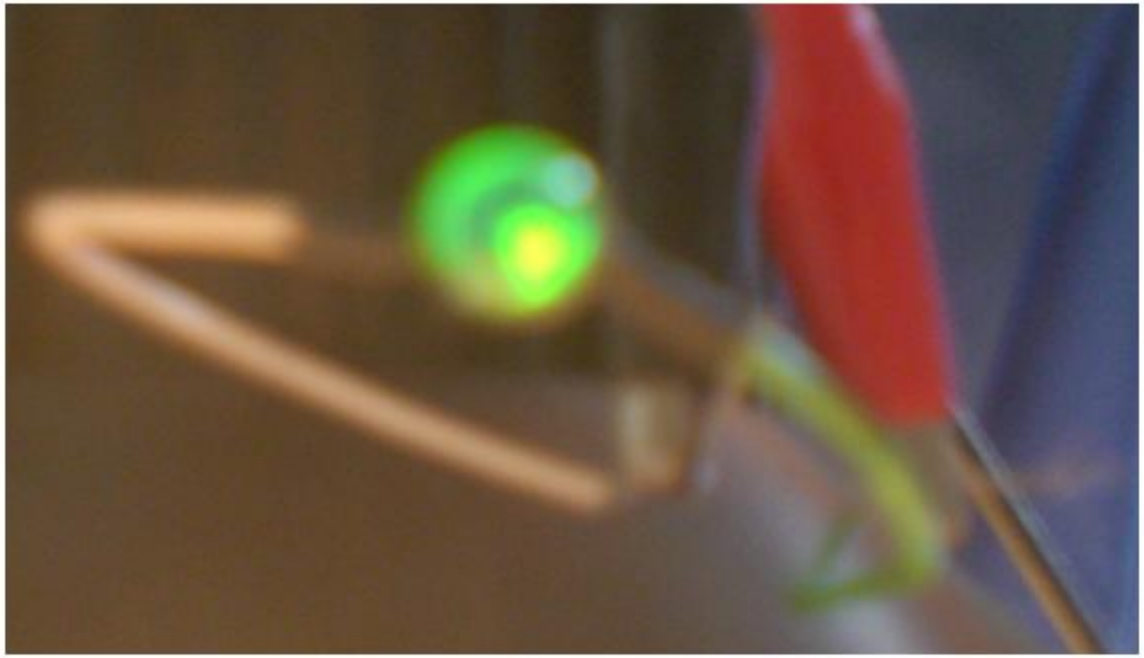
Red LED

Green LED

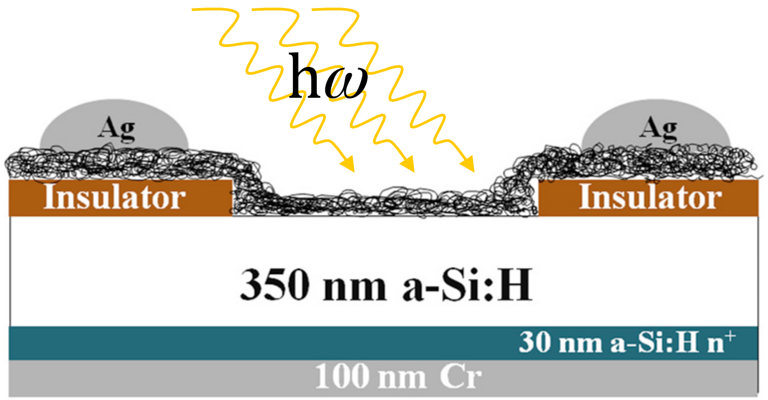
Technical data:

5 n-silicon substrates covered
by 0.1 micron of sprayed
Single Wall Carbon Nanotubes
connected in series
Total Voltage 2.2 V,
Intensity 1.5 mA, power 3.3 mW

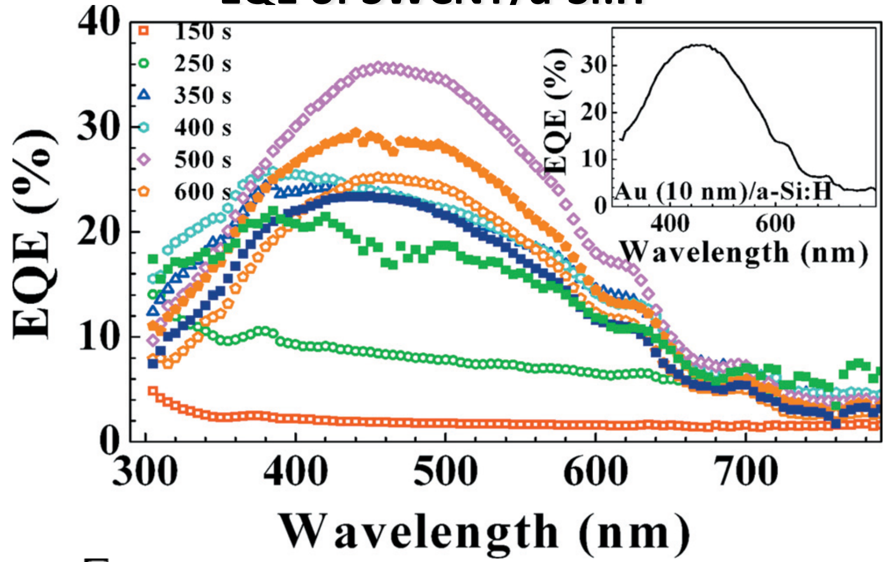
lamp illumination



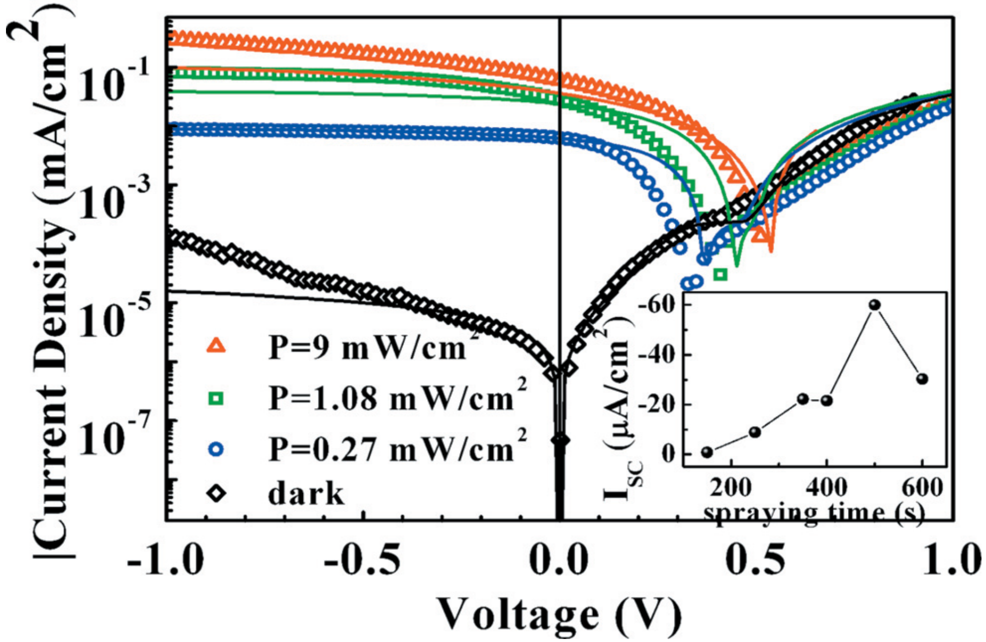
SWCNT/amorphous Si (a-Si:H)

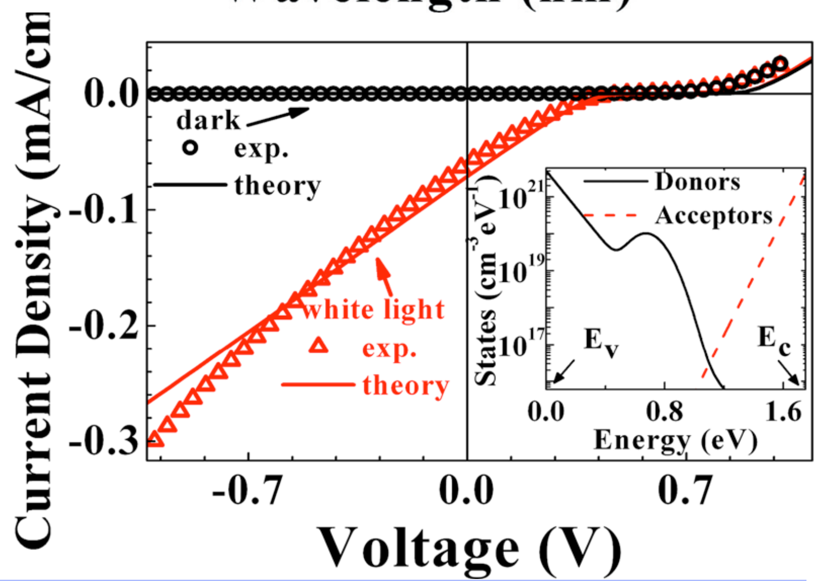


EQE of SWCNT/a-Si:H



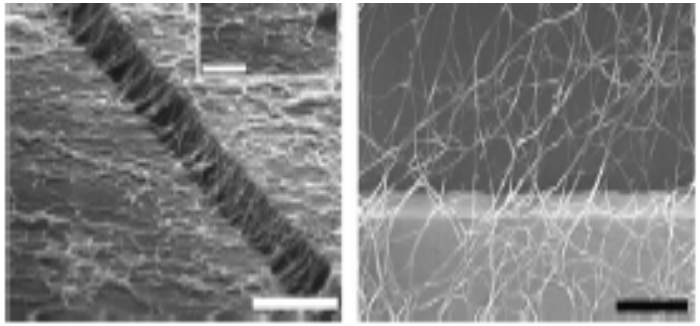
I/V of SWCNT/a-Si:H

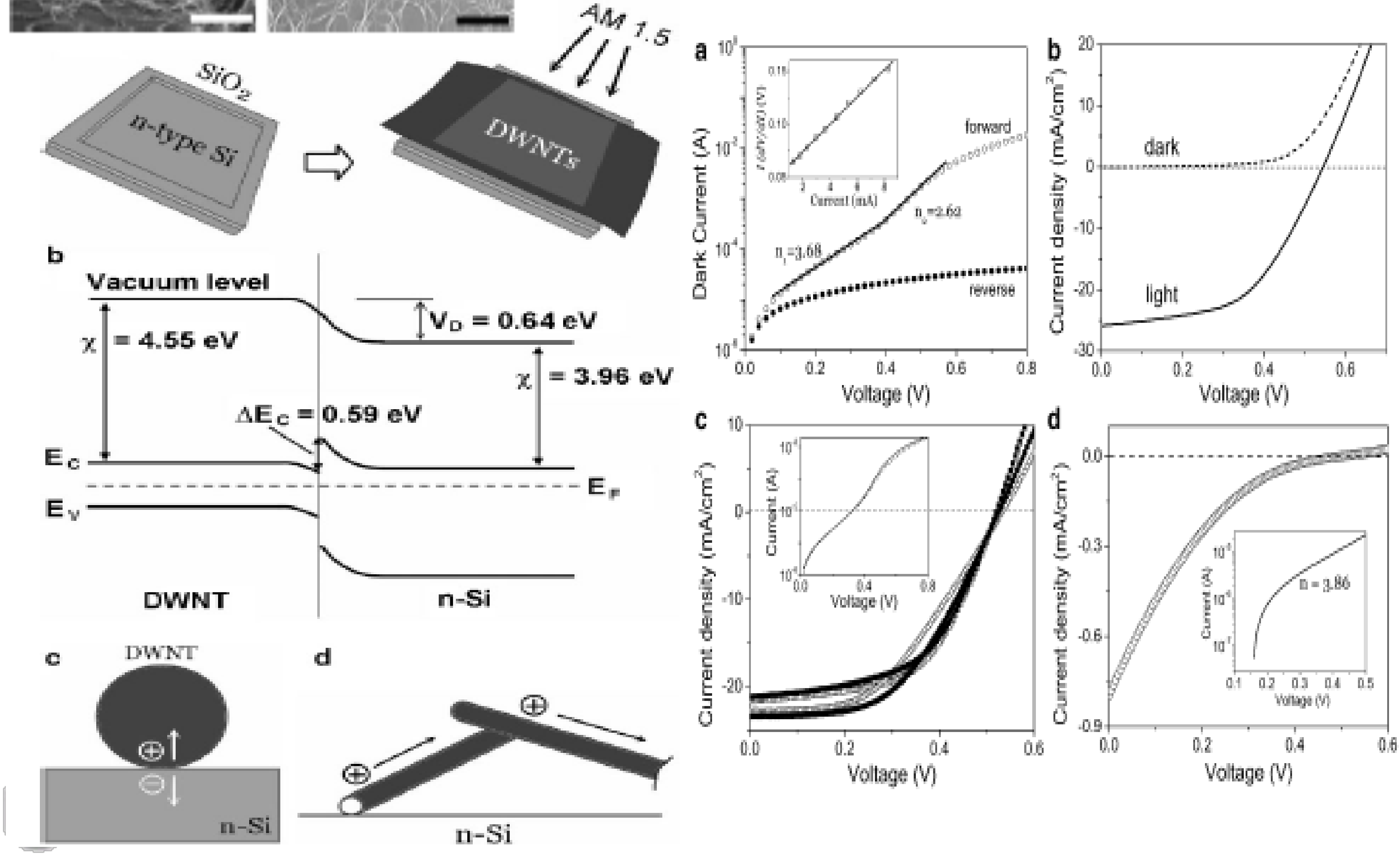




S.Del Gobbo, P.Castrucci, M.DeCrescenzi , G.Fortunato et al. *Appl. Phys. Lett.* 98 (2011) 183113

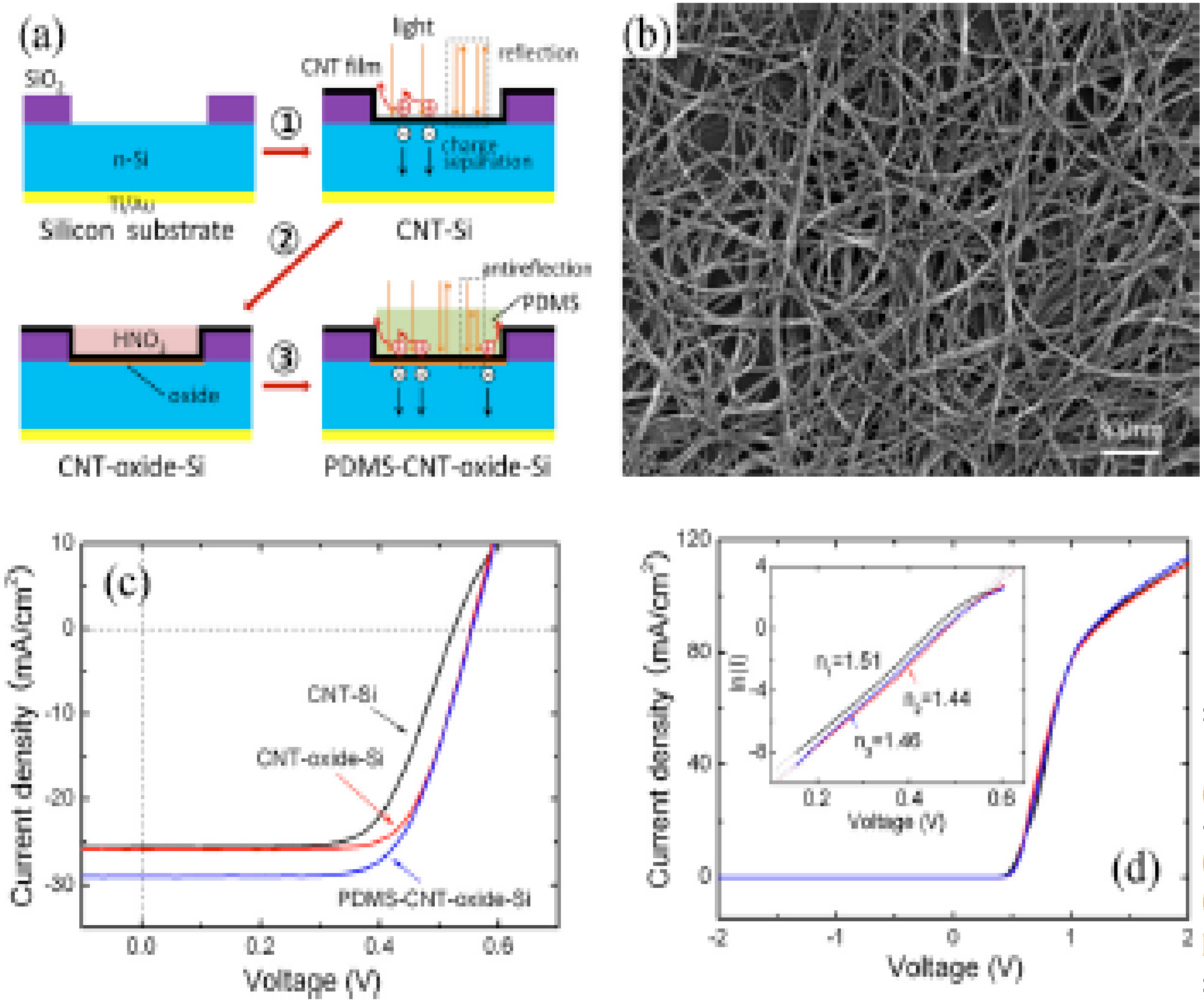
Nanotube–Silicon Heterojunction Solar Cells
Wei et al, Advanced Materials 20, 4594 (2008)





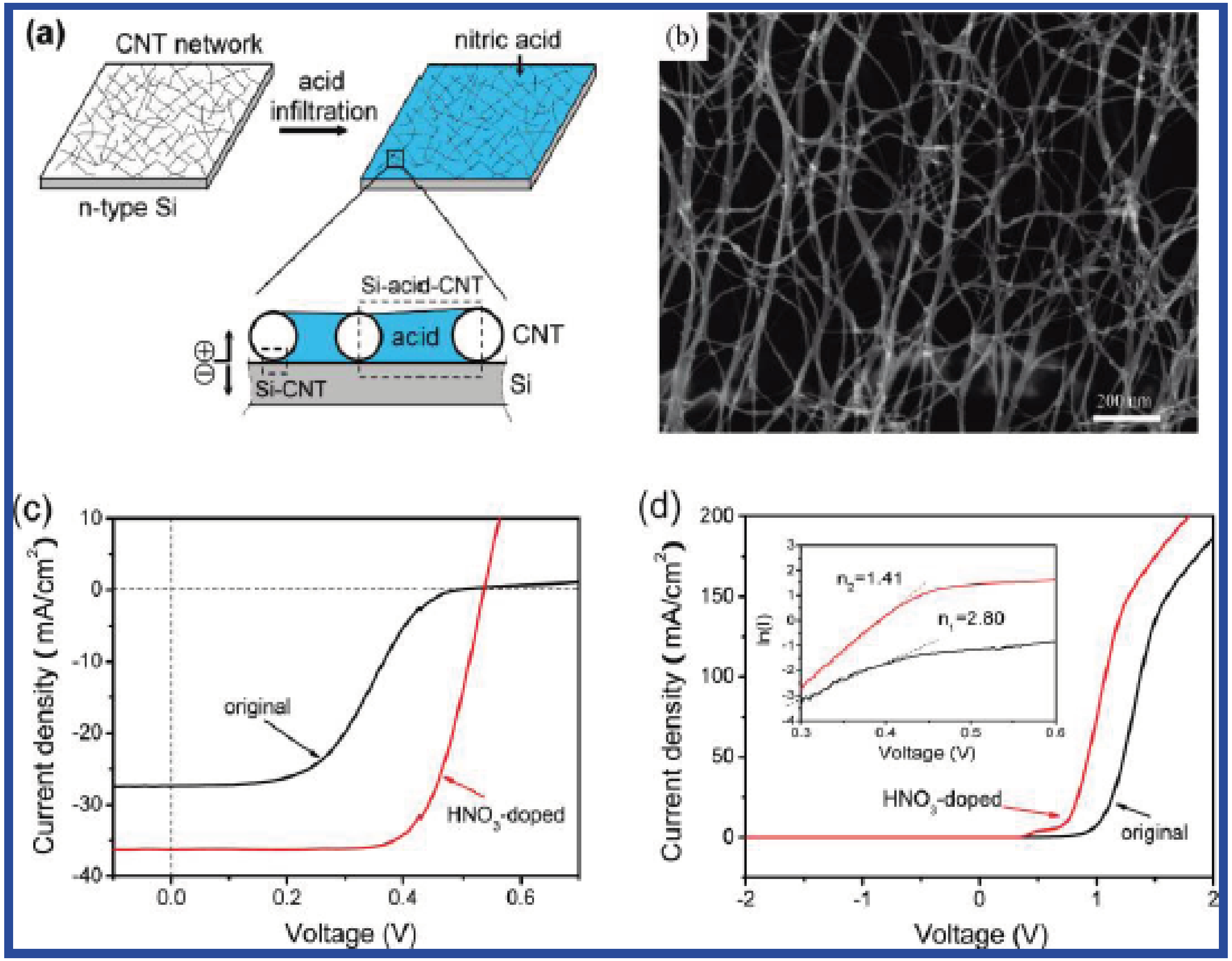
Encapsulated carbon nanotube-oxide-silicon solar cells with stable 10% efficiency

Y.Jia,D. Wu et al. Appl.Phys.Lett. 98, 133115 (2011)

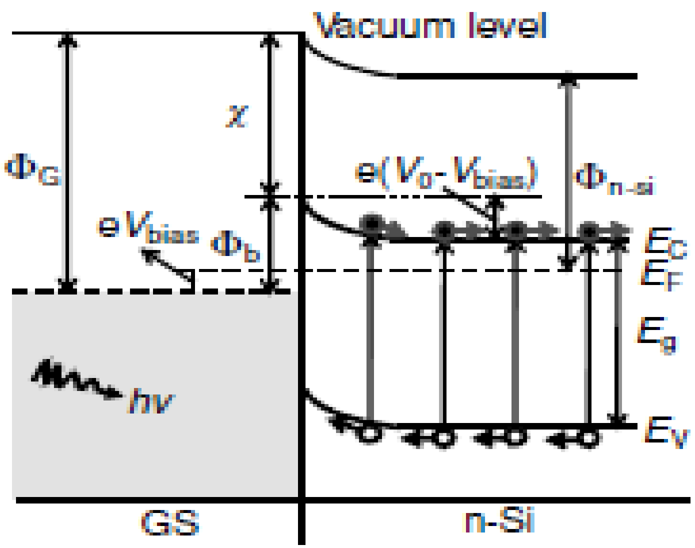


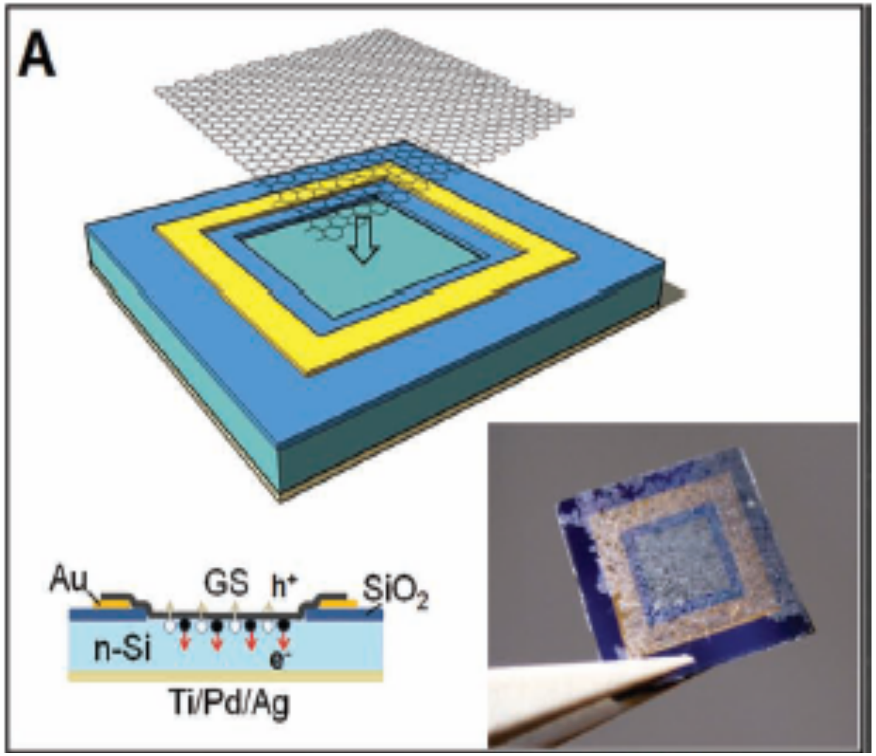
Cell structure	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	R_s (Ω cm^2)	n	η (%)
CNT-Si	0.52	25.6	67.3	6.4	1.51	8.9
CNT-oxide-Si	0.55	25.8	71.5	5.9	1.44	10.1
PDMS-CNT-oxide-Si	0.56	29.0	67.6	6.0	1.46	10.9

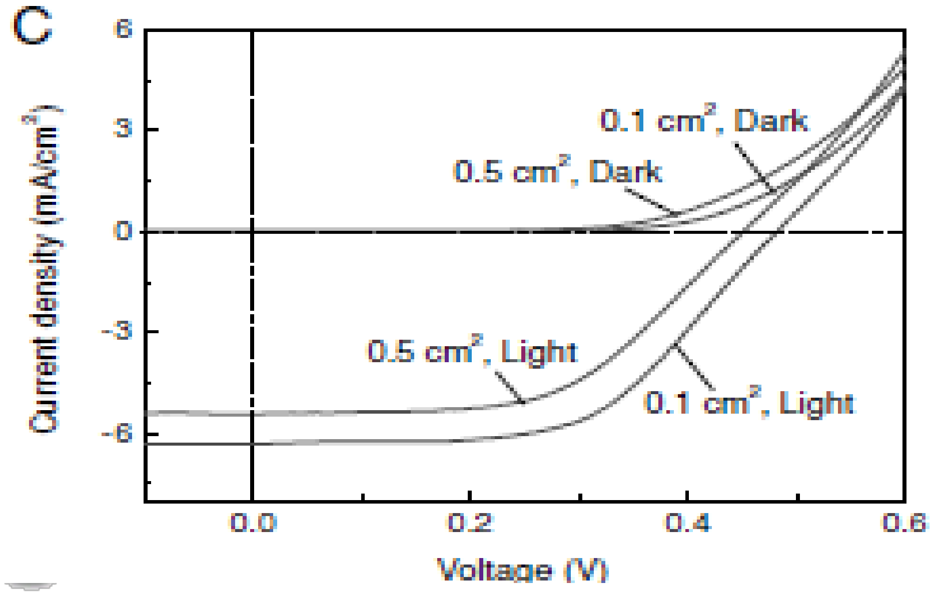
P.Wadhawa et al., Nanoletters 10, 5001 (2011)

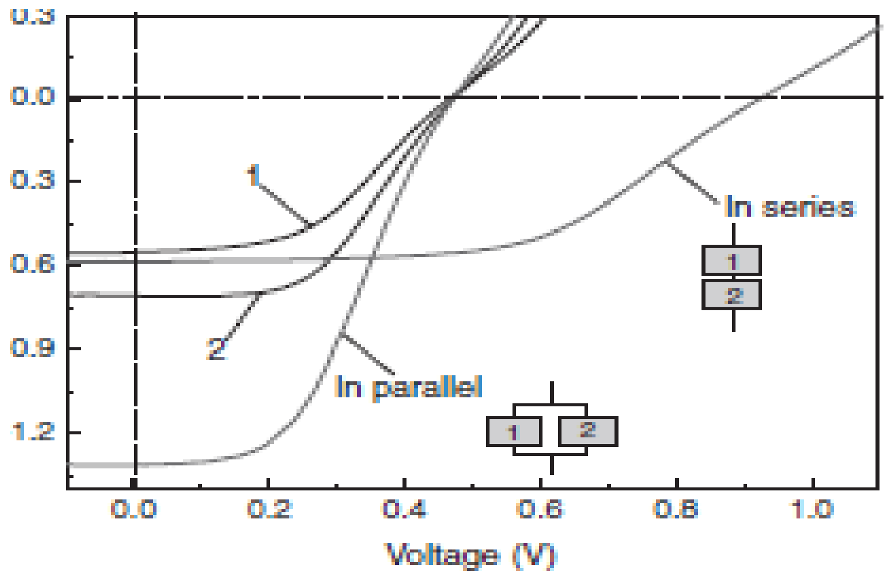


Graphene-On-Silicon Schottky Junction Solar Cells
Li, Wu et al., Adv. Mat. 22, 2743 (2010)



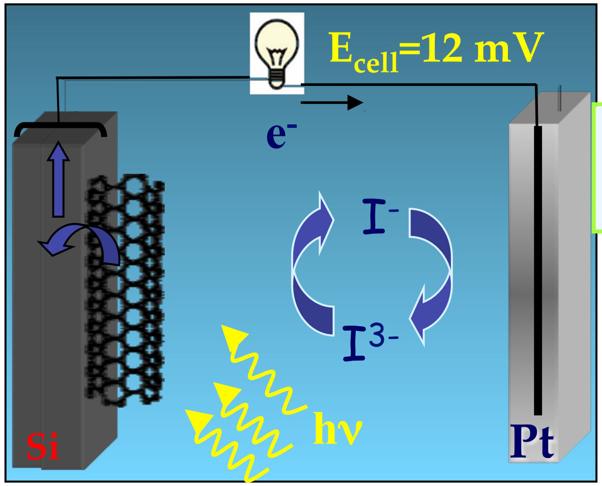






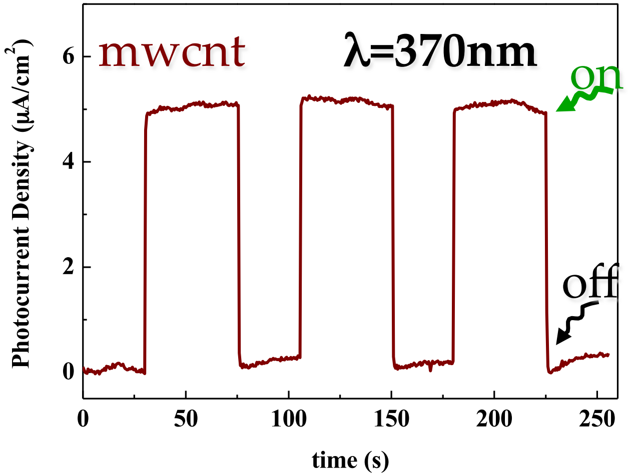
Graetzel cell

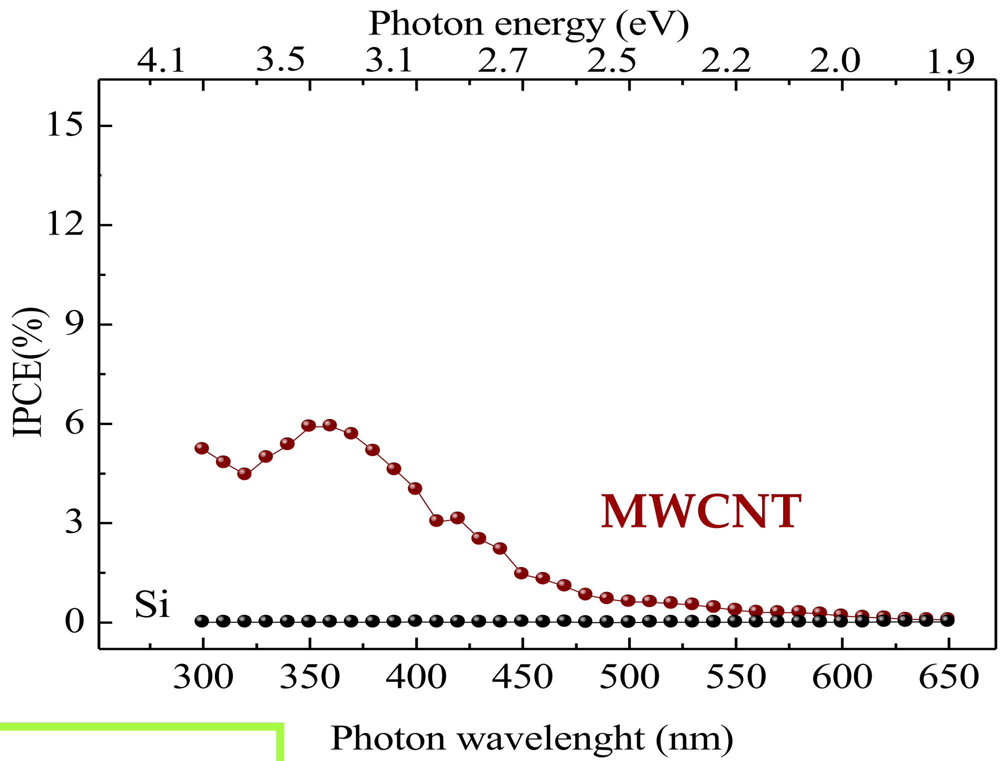
Electrolyte 0.5 M NaI + 0.01 M I_2 in acetontrile 150W Xe lamp (λ > 300 nm) equipped with a monochromator, Ecell= 12 mV



$$IPCE(\%) = \frac{100\, i(A/cm^2)\, 1240}{I(W/cm^2)\, \lambda(nm)}$$

incident photon-to-charge carrier generation efficiency
i = short circuit photocurrent
I = incident light intensity
λ = incident photon wavelength



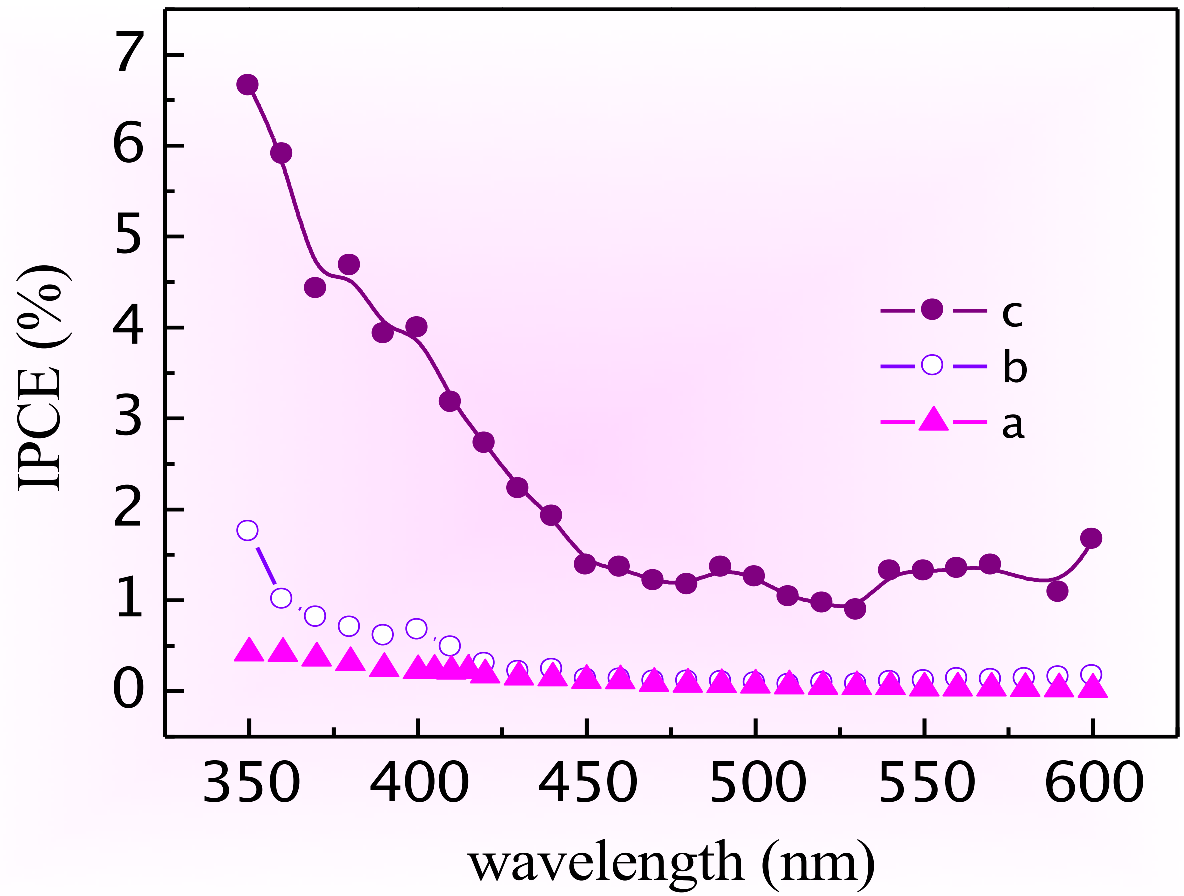


negiglible contribution from Si substrate
IPCE (at 370nm) MWCNTs 6%>> SWCNTs 0.2%

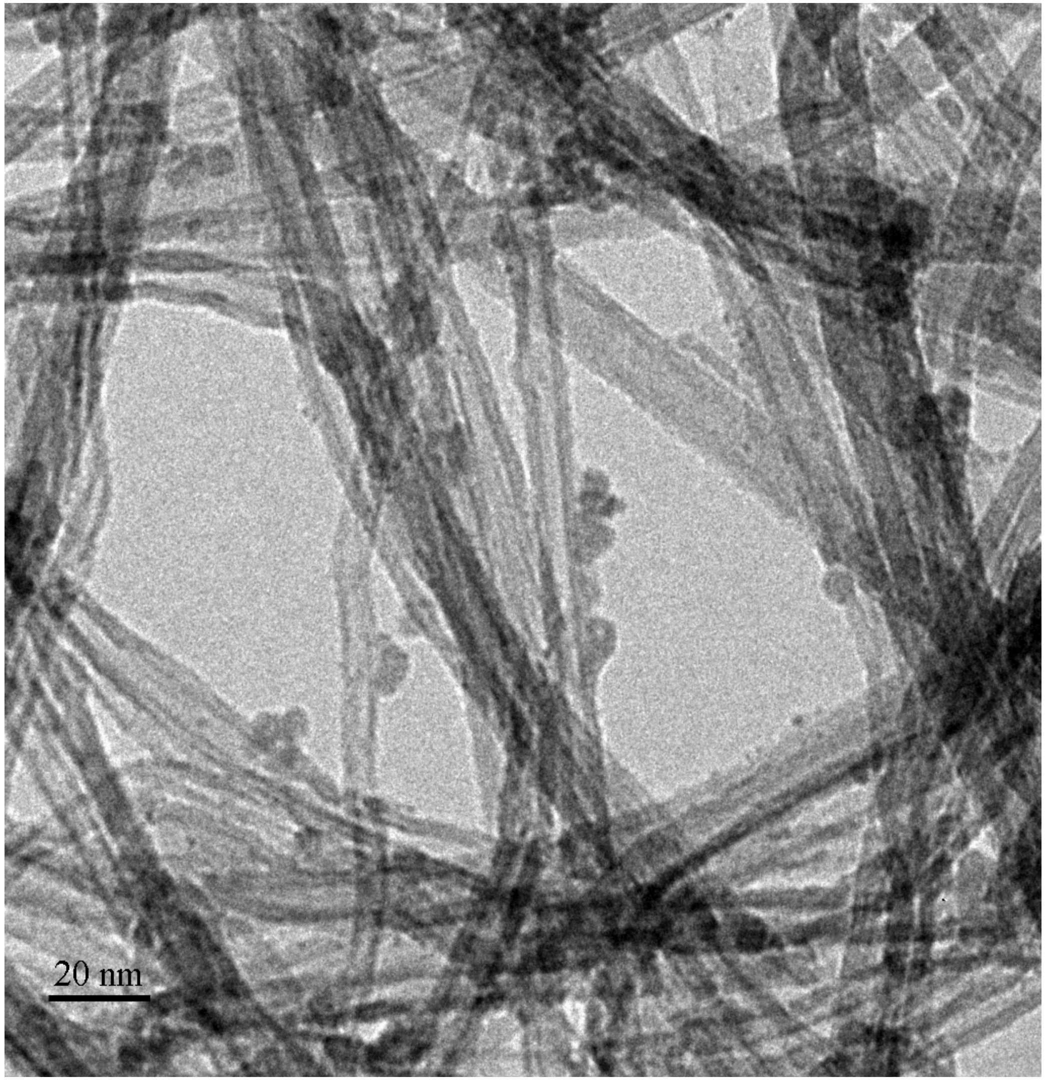
S. Barazzouk, et al., J. Phys. Chem. B 108 (2004) 17015

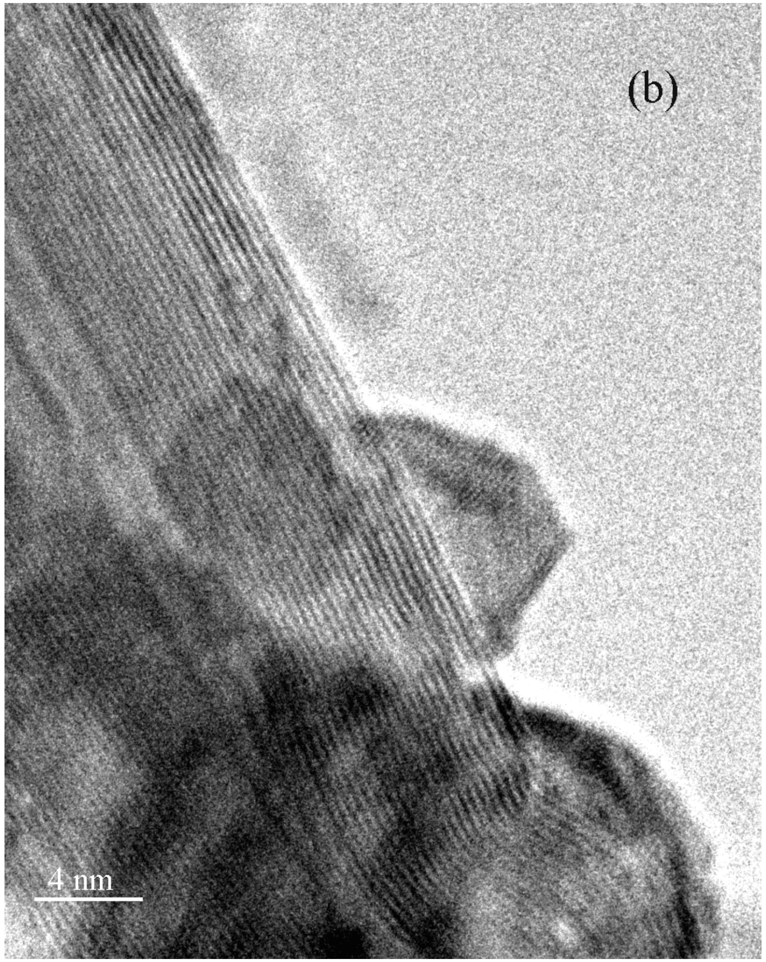
P.Castrucci, M.Scarselli, M.Venanzi, E.Gatto, M.Diociaiuti, E.Speiser, W.Richter, M.De Crescenzi, Appl.Phys.Lett. 89, 253107 (2006)

Sample	N (walls)	D (nm) outer diameter	d (nm) inner diameter
(a)	14 ± 5	20 ± 8	11 ± 5
(b)	10 ± 3	13 ± 2	7 ± 2
(c)	9 ± 2	12 ± 4	6 ± 2

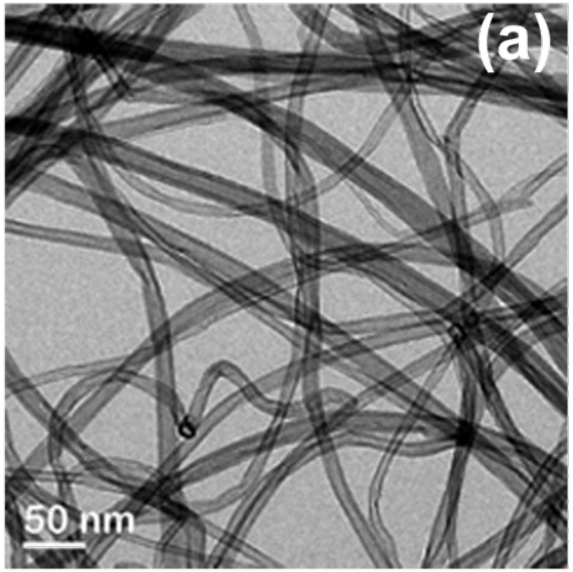


TEM MWCNTs decorated with Cu Nanodots

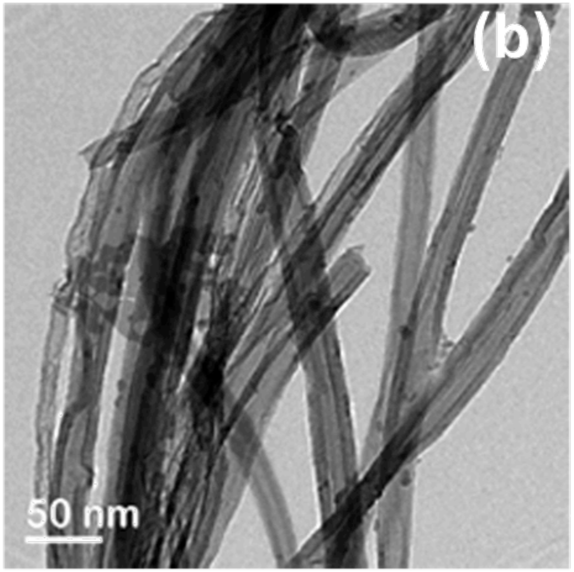




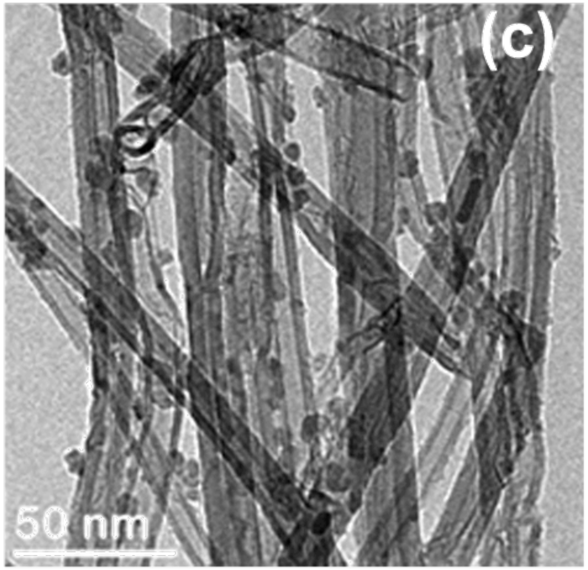
M.Scarselli , P.Castrucci, M.De Crescenzi al., J. Phys. Chem. C 113, 5860 (2009)



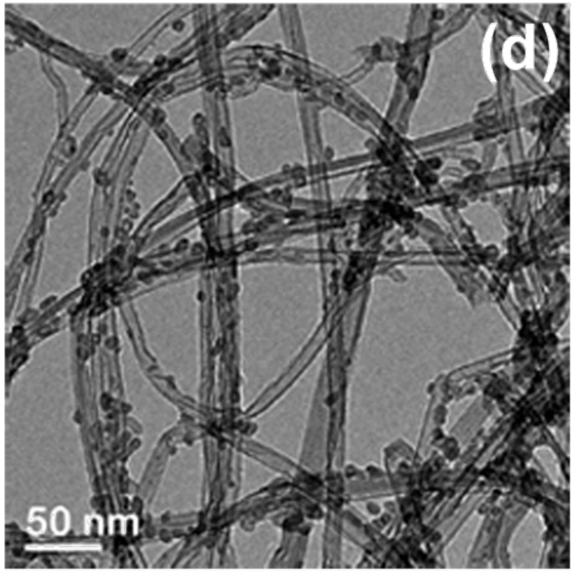
clean CNT



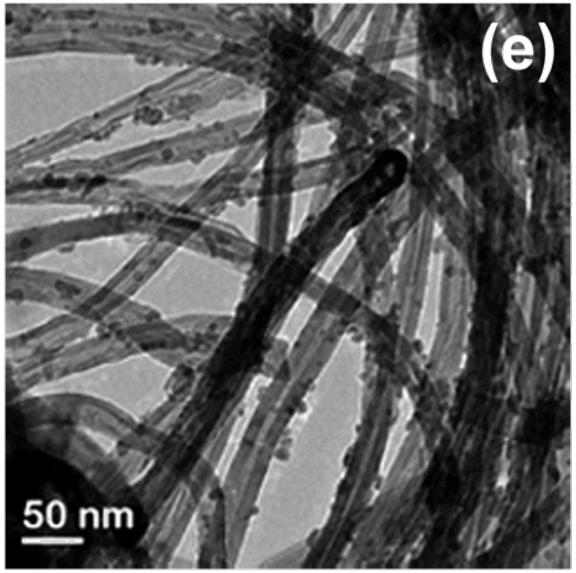
0.1 nm



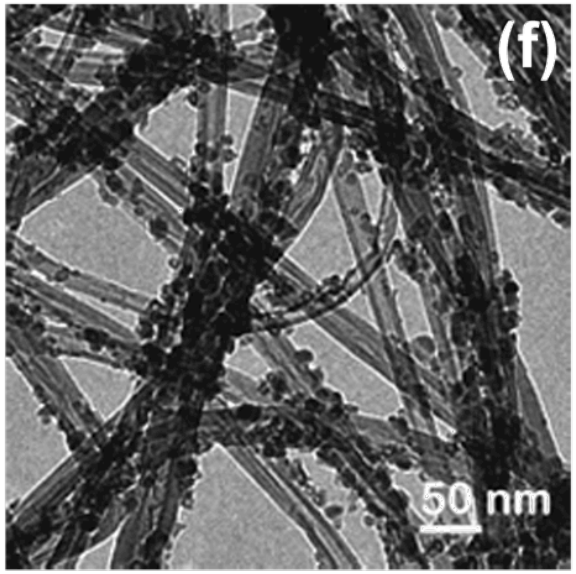
0.2 nm



0.5 nm



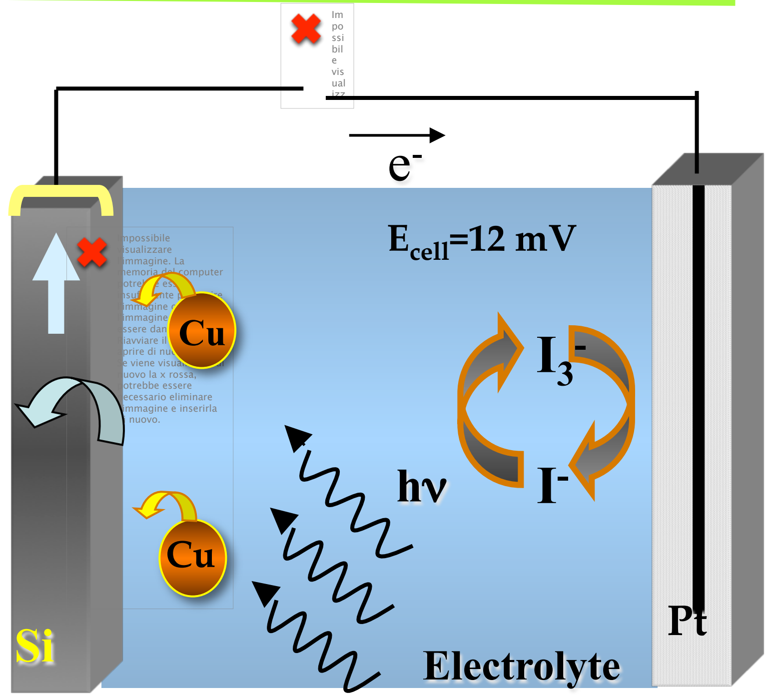
1 nm



3 nm

M.Scarselli, P.Castrucci, M. DeCrescenzi et al., Nanotechnology 22, 115701 (2011)

Photocurrent from Cu-MWCNT

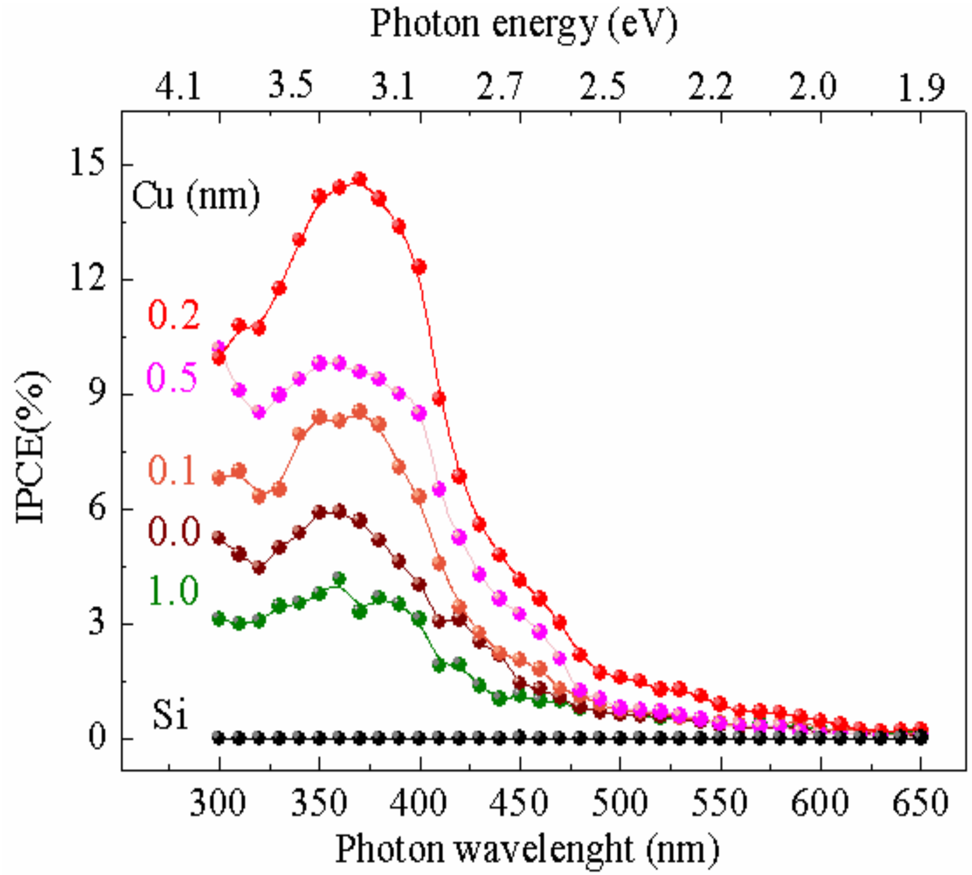


Impossibile visualizzare l'immagine. La memoria del computer potrebbe essere insufficiente per aprire l'immagine oppure l'immagine potrebbe essere danneggiata. Riavviare il computer e aprire di nuovo il file. Se viene visualizzata di nuovo la x rossa, potrebbe essere necessario eliminare l'immagine e inserirla di nuovo.

λ=370nm

on

off



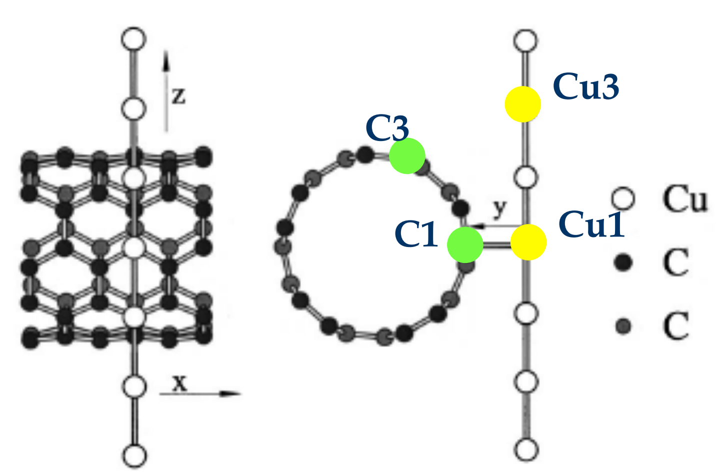
(~ 370nm) IPCE 14.6 % for 0.2 nm Cu (•) vs 5.6 % for MWCNT (•)

0.2 nm Cu (•) average particle size 5.6 nm

- anodic photocurrent generation
- enhanced photocurrent for Cu NPs on MWCNTs

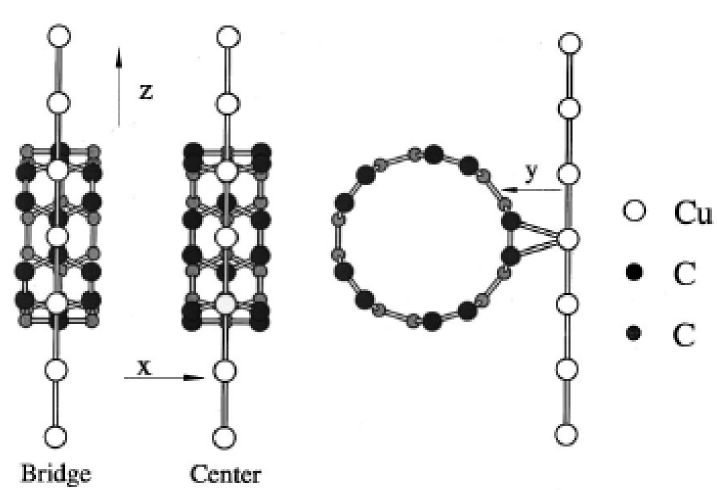
Theoretical investigations

Calculations performed at a level of *ab initio* pseudopotential calculations on a model system which consists of a metallic tube in contact with a copper chain lying perpendicular to it.



on-top geometry

the on-top position is the most stable with some energy gain



bridge and center geometry

the bonding character of the on-top geometry may be regarded as IONIC

K. Kong, S. Han, J. Ihm, *Phys. Rev. B* 1999, *60*, 6074

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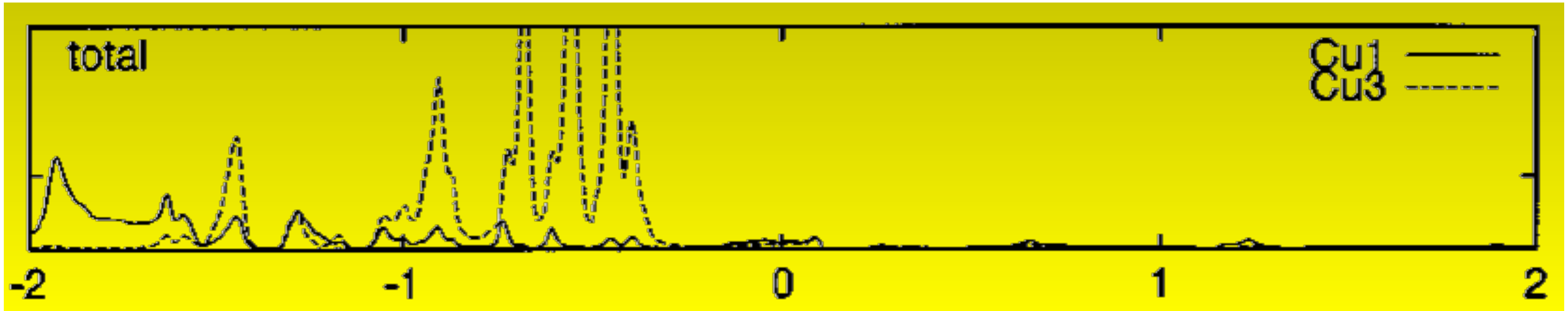
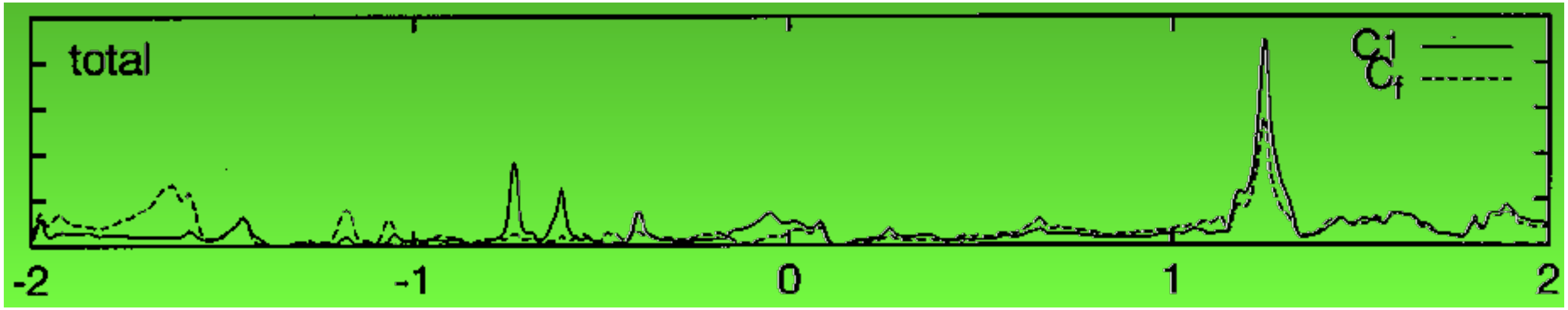
LDOS from theoretical calculations



The 3s and 3*d* electrons in the LDOS of Cu1 vs. Cu3 in the (-1.5 ÷ - 0.5) eV energy range are depleted



On the other hand the LDOS of C1 vs C3 increases thus a higher number of electronic states is made available

the electrons are transferred from the Cu chain to the CNT

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Conclusions

- Carbon nanotubes generate photocurrent in the near ultraviolet and visible spectral range (solid state photocurrent measurements and electrochemical cell Graetzel-type). The EQE for MWCNTs can reach similar values than that from SWCNTs.

- The photogenerated current depends on several effects: formation of e-h in the CNTs, Schottky barrier with the electrodes, heterojunction formation with substrate. EQE of SWCNTs/Si reached 70%. Crystalline as well as amorphous silicon substrates have been used.

- The IPCE grows when CNT's are decorated with Cu nanoparticles.

- The high conversion efficiency of Carbon nanotubes deserves further theoretical as well as experimental investigation in view of the integration of these nanostructures as building blocks in photovoltaic nanodevices.

Collaborations :

P.Castrucci, M.Scarselli, S.Del Gobbo, L.Camilli, W.Richter, B.Buik
(Physics Department, Roma TorVergata, Italy)

M. Venanzi, E. Gatto (Chem. Dept., Roma TorVergata, Italy)
Photoelectrochemical current measurements

M. Diociaiuti (ISS, Italy), **S.Casciardi** (INAIL, Italy)
SEM, TEM images & transmission EELS spectra

V.Le Borgne, M.A.El Khakani
(Université du Québec,Varennes, Canada)
SWCNTs by laser deposition

International Collaborations and projects:

M.A.El Khakani
(Université du Québec,Varennes, Canada)
SWCNTs by laser deposition (MAE project)

N.Motta, John Bell…
(QUT University, Australia) NIRAP project

S.Lefrant
(Nantes University, Nantes, France) Galileo Project

S.V.Bhoraskar
(Pune University, India) Silicon nanotubes synthesis

I.Berbezier
(CNRS, Marseille, France) Ge nanodots for solar cells

Thanks for your attention