Who does not have a mobile phone?

Who has Nokia mobile phone?

Nokia on the cover of Forbes: “Can anyone catch the cell phone king?", 2007.

Skoltech
Skolkovo Institute of Science and Technology

RSF Russian Science Foundation

Laboratory of NanoMaterials

Single-walled carbon nanotubes: from synthesis to applications

Albert G. Nasibulin

Skolkovo Institute of Science and Technology
Moscow, Russia

Aalto University,
Department of Chemistry and Materials Science, Finland

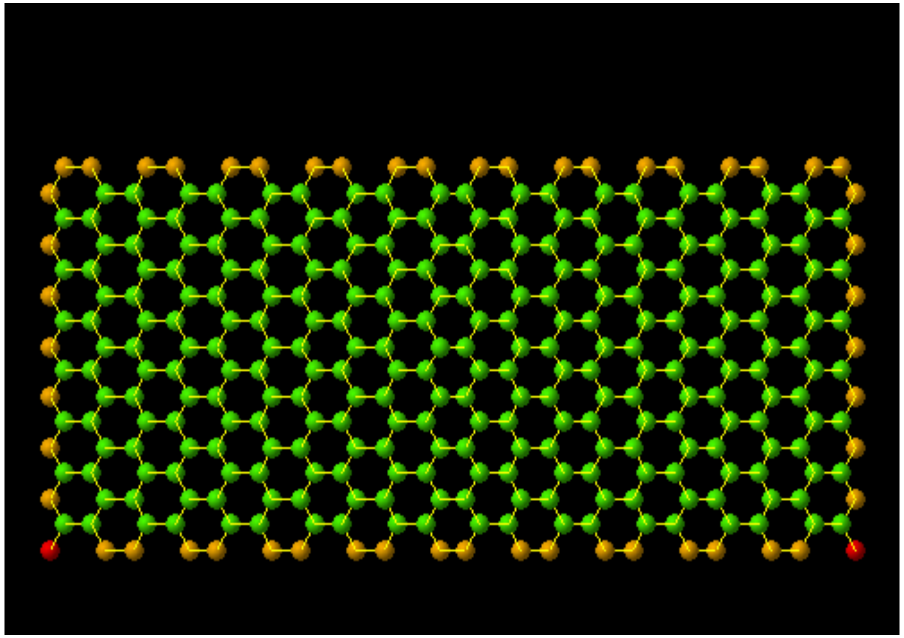
NanoNasibulin.Com

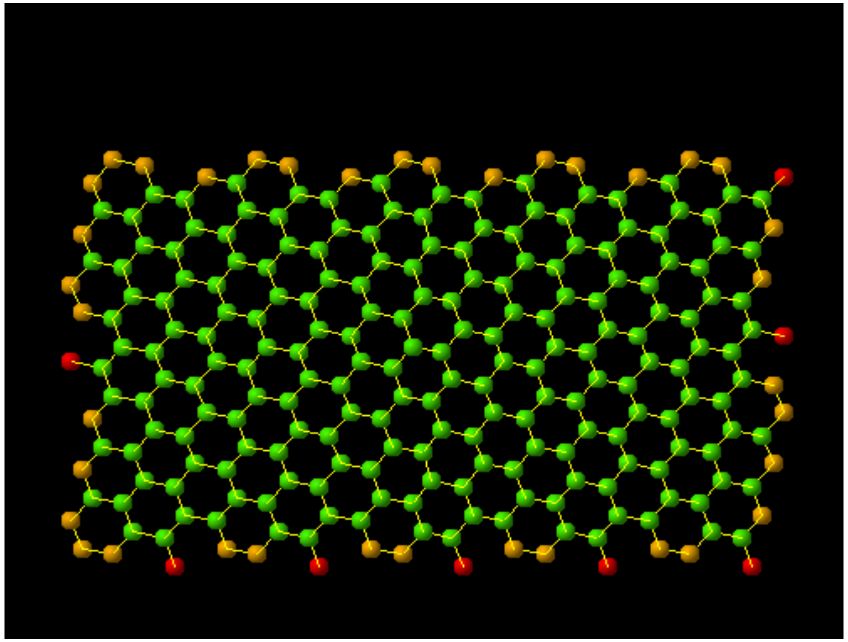
Outline:

1. Carbon nanotubes
2. Synthesis of CNTs
3. Applications

Single-walled Carbon Nanotube (SWCNT):

Roll of carbon sheet one atomic layer thick





Rolling in different directions makes different kinds of tubes

(10,10) armchair tube
METALLIC

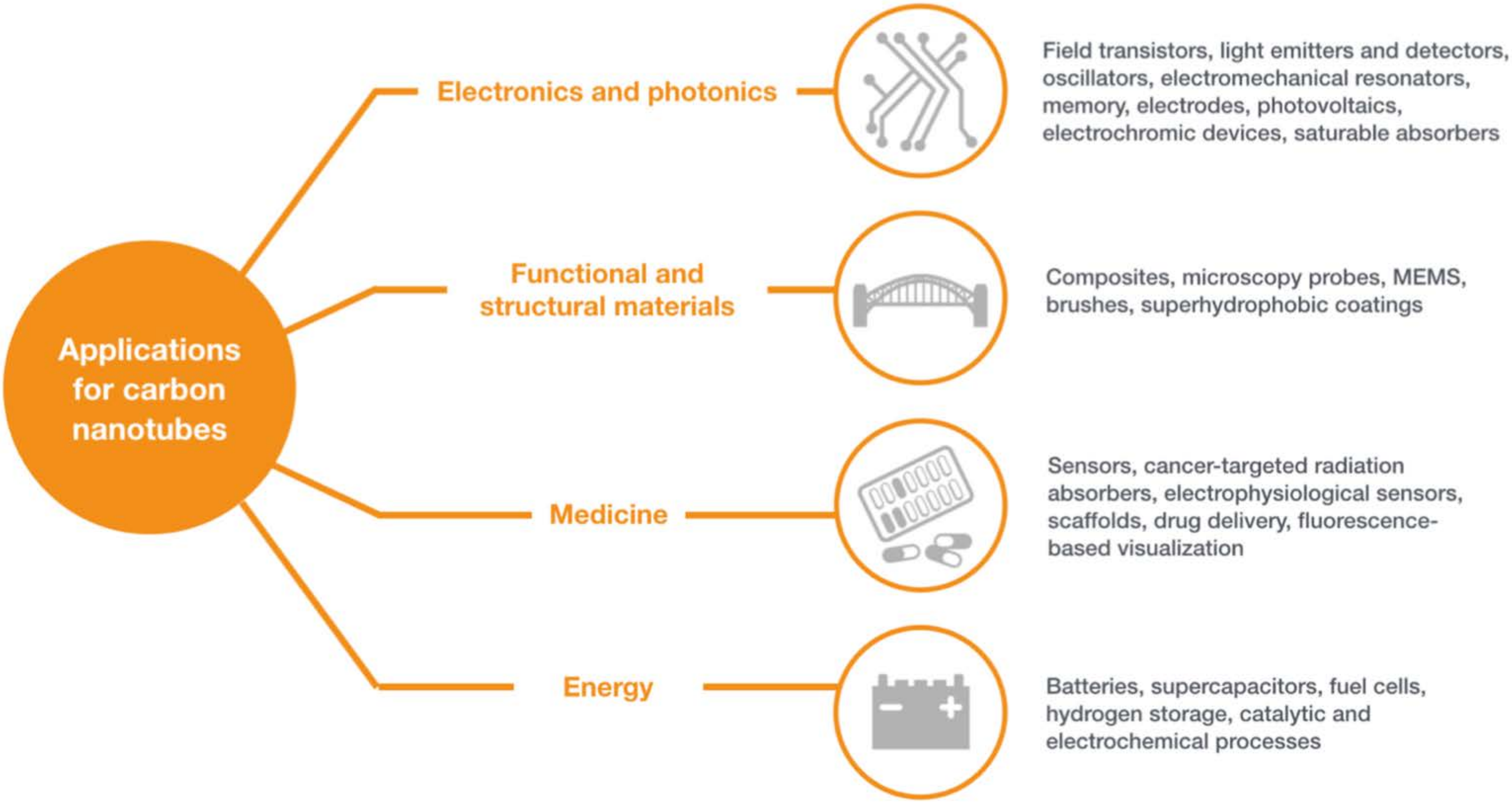
(10,5) helical (chiral) tube
SEMICONDUCTING

Courtesy of Prof. Maruyama

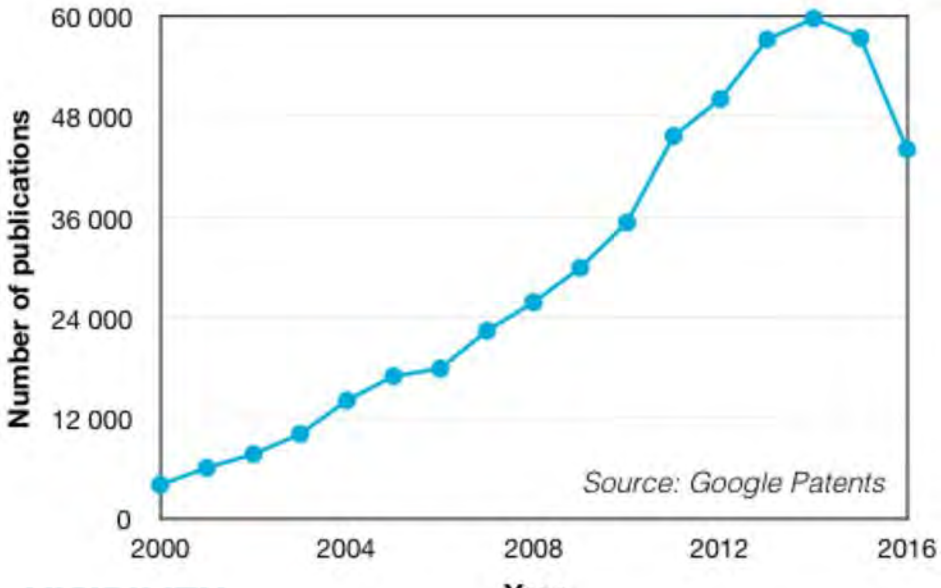
Properties of Carbon Nanotubes

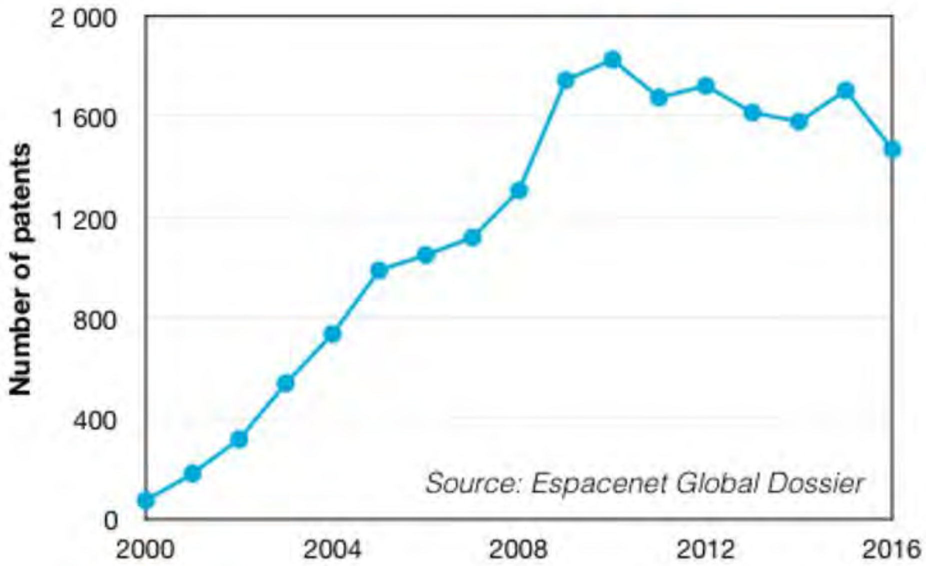
- Better conductor than copper
- Better transistor material than silicon
- Conduct heat twice as efficiently as diamond
- Field emit 500 times as efficiently as molybdenum
- Thermally stable up to 1500 ^{o}C while polymers degrade below 150 ^{o}C
- Half as dense as aluminum
- 25 times stronger than steel

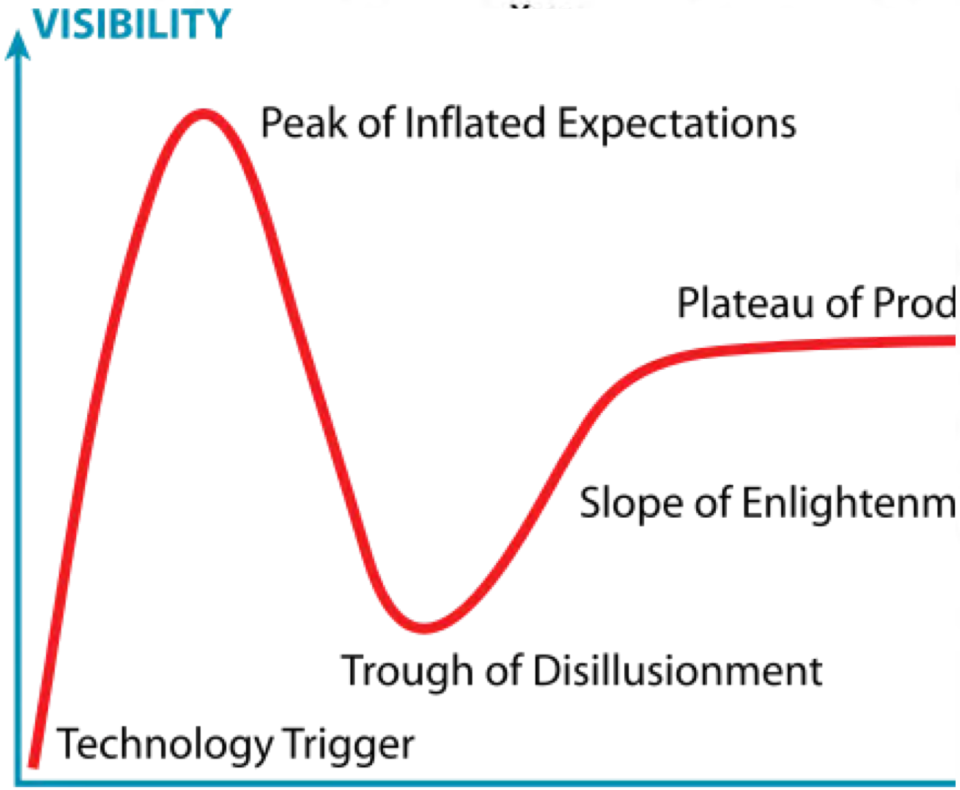
Some applications of CNTs

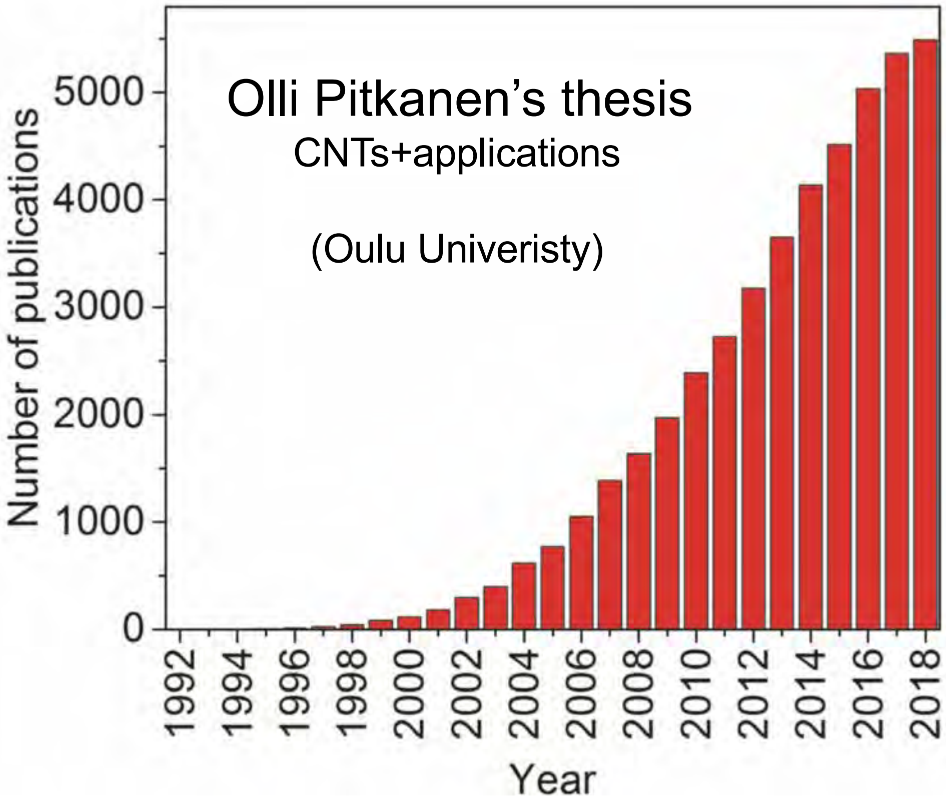


Number of papers and patents related to CNTs









Annual production of CNTs

- Less than 10 t
- 10 -100 t
- More than 100 t

Country	Company	Types of tubes	Production, ton
China	Cnano	MWCNT, SWCNT, DWCNT	200
	TimesNano (Chengdu Organic Chemicals)	MWCNT, SWCNT	350
	Hanwha Nanotech	MWCNT, SWCNT	8
Japan	Showa Denko	MWCNT	400
Korea	Iljin	MWCNT, SWCNT	10
Belgium	Nanocyl	mainly MWCNT, also SWCNT, DWCNT	400
France	Arkema (Graphistrength)	MWCNT	30
USA	Hyperion Catalysis International	MWCNT	10
	Continental Carbon Nanotechnologies	MWCNT, SWCNT, fullerenes	
	Carbon solutions	MWCNT	
	Catalytic materials	MWCNT	0,4
Russia	OCSiAl	SWCNT	60
	NanoTechTsentr	MWCNT	2
	Boreskov Inst. Catalyst	MWCNT	2
Canada	Raymor Industries	MWCNT	1

Currently, carbon nanotubes account for a 28% market share of overall nanomaterials demand.
MWCNTs: Asia-Pacific, followed by North America and the European Union.
SWCNTs: Russia is the leader!

Gorkina and Nasibulin (2016) pp. 117-141. In Public Analytical Report: Development of Photonics in Russia and in the World. Moscow: Bitubi.

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CNT Synthesis Techniques

According carbon atomisation
all methods can be divided into

Physical

Carbon
sublimation-desublimation

- Arc-discharge
- Laser ablation
- Solar energy
- Induction heating

Chemical

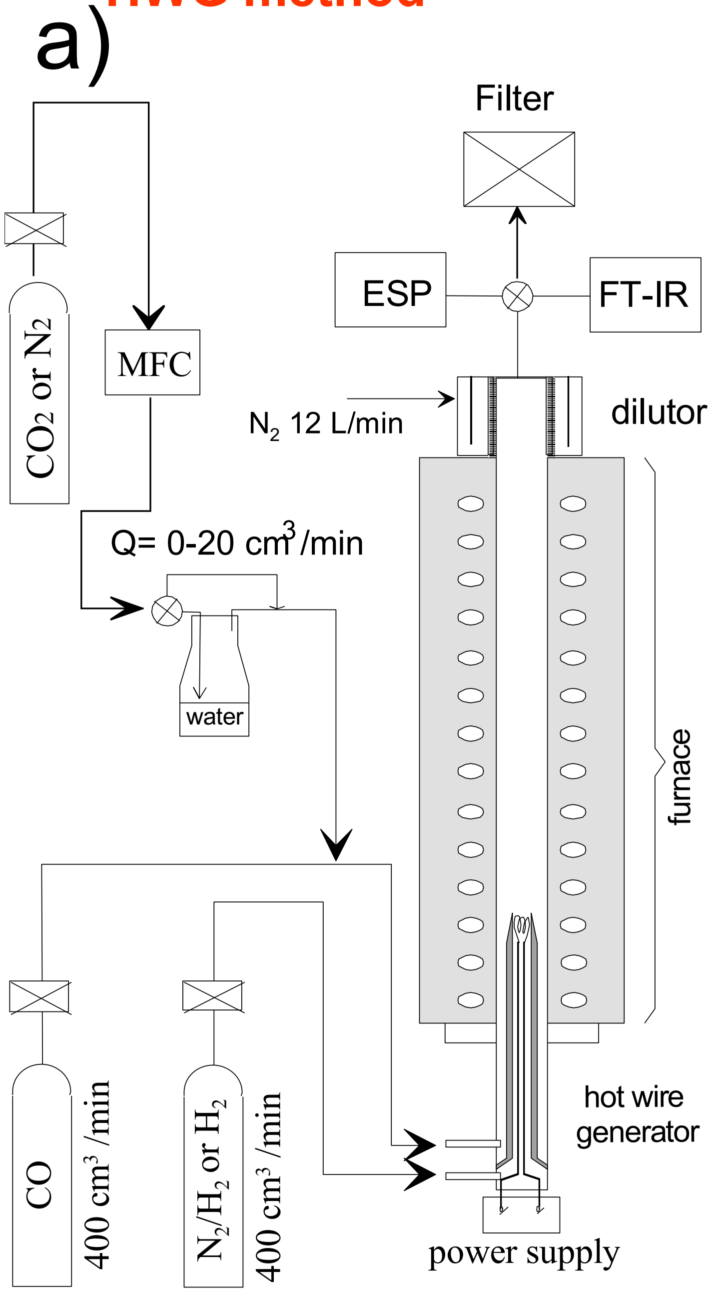
Decomposition of carbon Compounds
(hydrocarbons, CO, alcohols, *etc.*)

Substrate supported CVD
(Thermal, plasma enhanced)

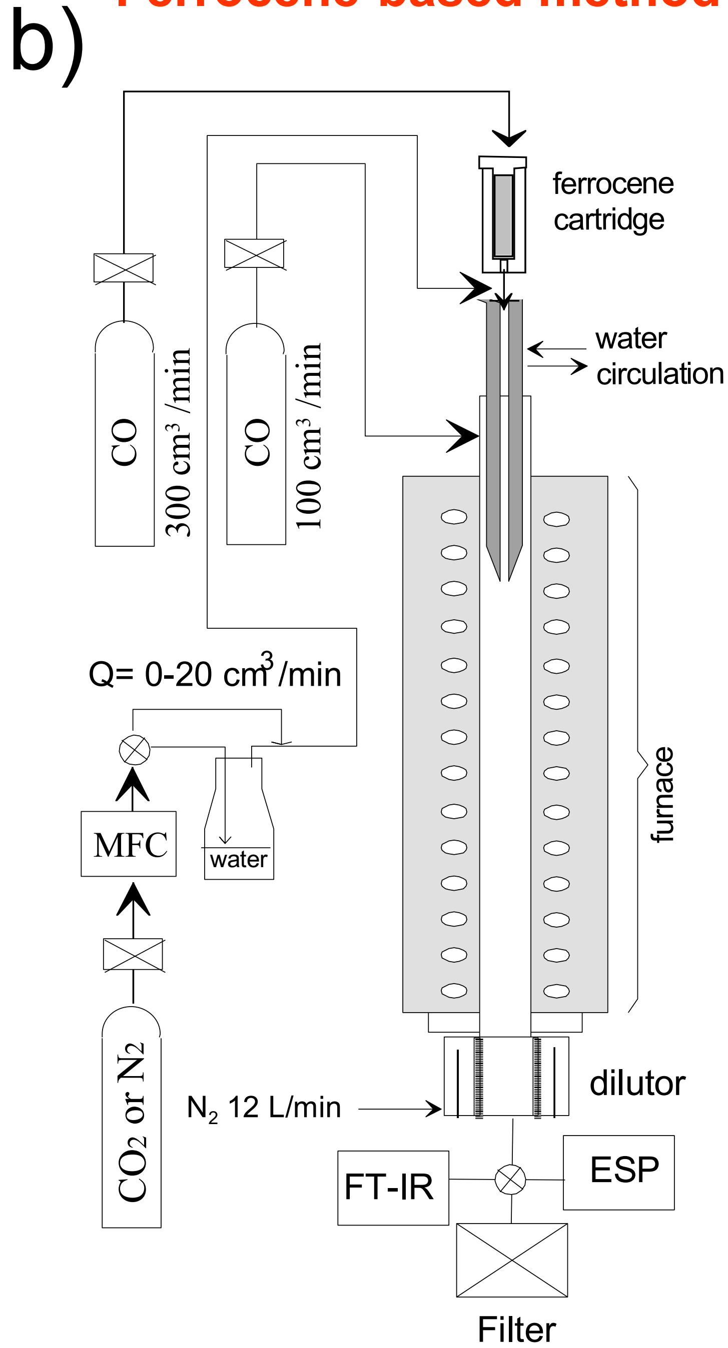
Aerosol CVD (floating catalyst) method

Aerosol CVD Methods for CNT Synthesis

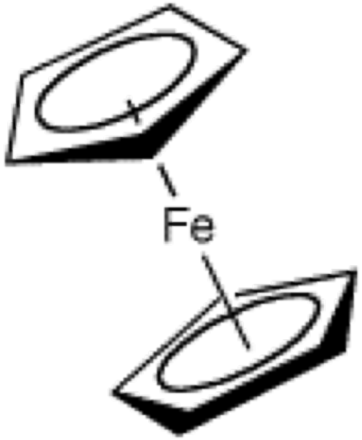
HWG method



Ferrocene-based method

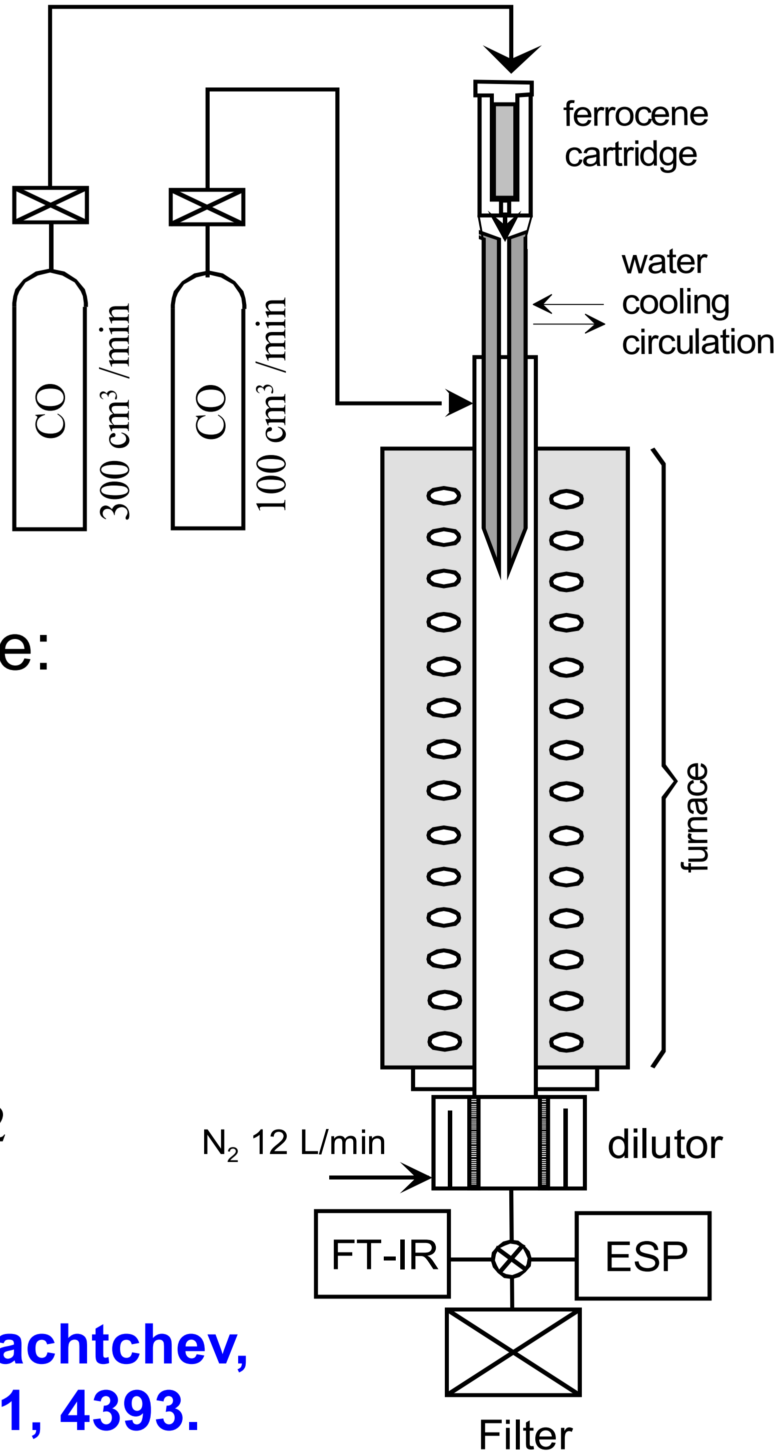


Experimental setup: Ferrocene Reactor



Ferrocene molecule:
$FeC_{10}H_{10}$

$$CO + CO \overset{Fe}{=} C(s) + CO_2$$

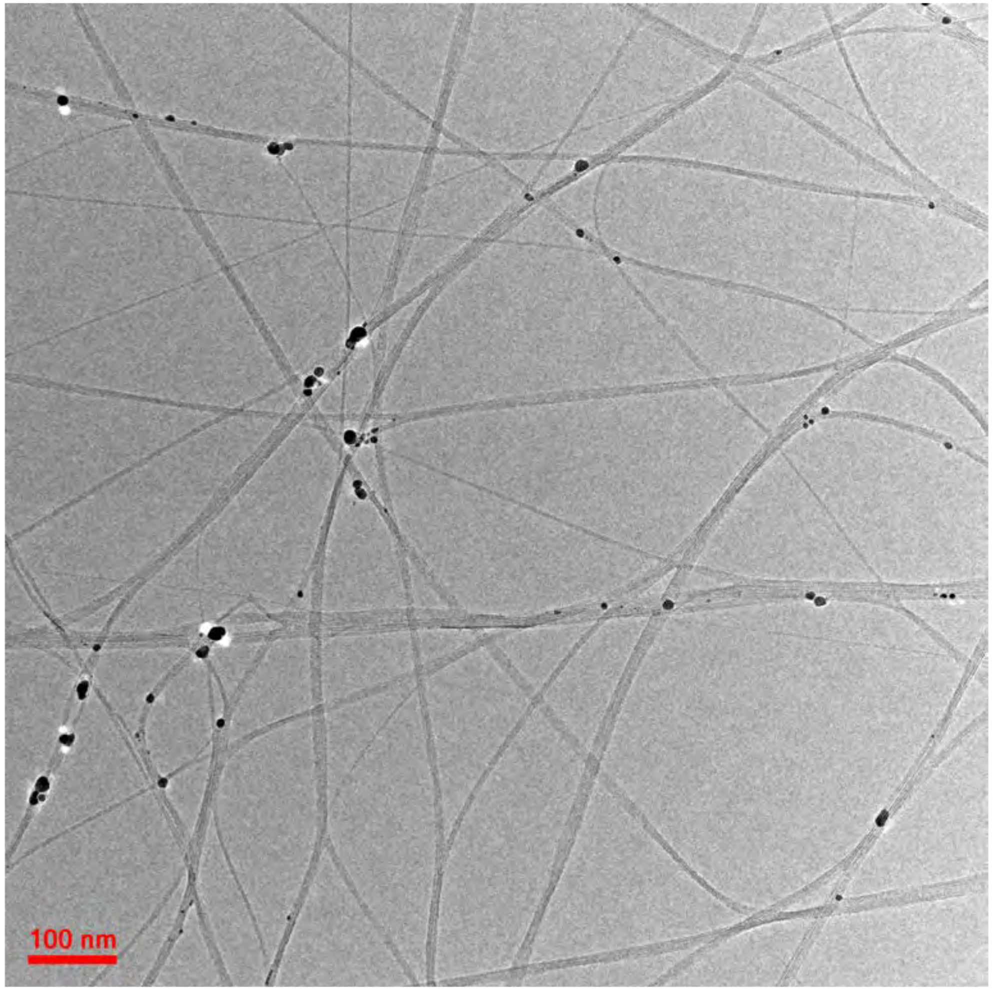


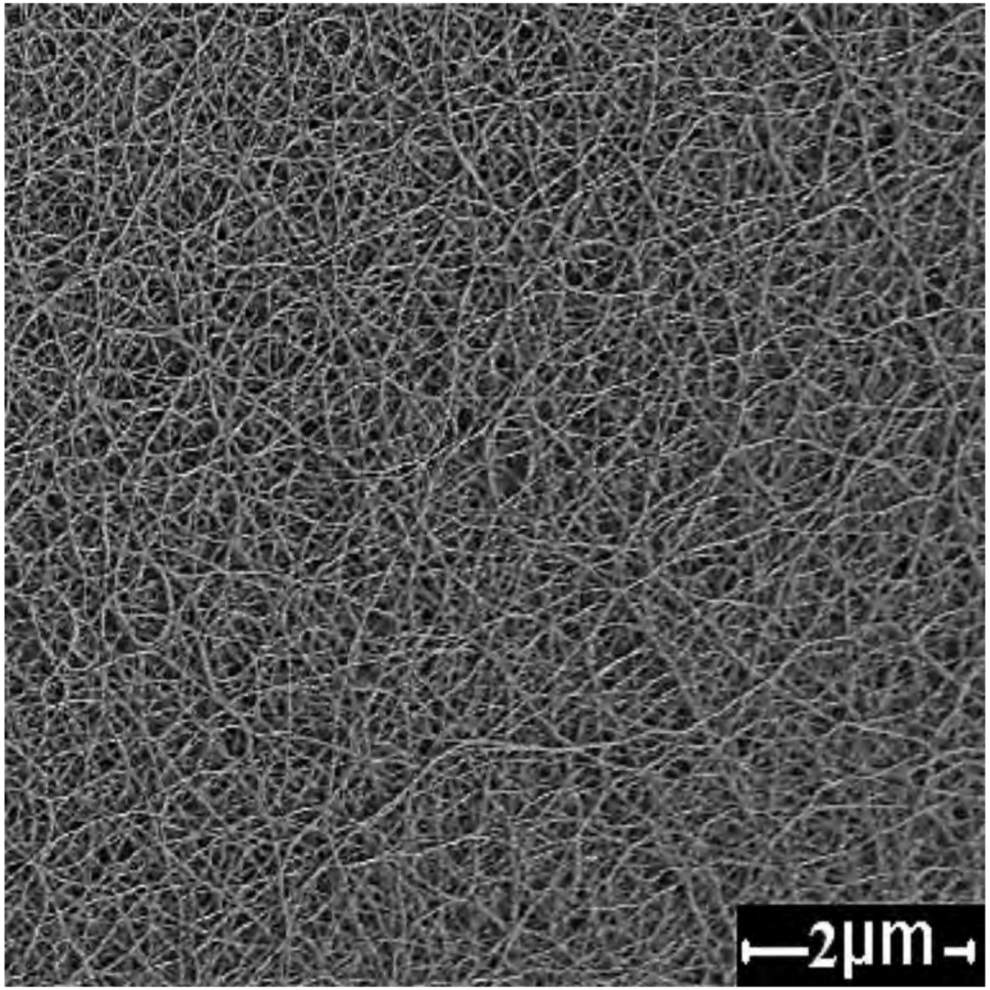
Moisala, Nasibulin, Brown, Jiang, Khriachtchev, Kauppinen, (2006) *Chem. Eng. Sci.* 61, 4393.

Novel dry, direct deposition method

Kaskela, Nasibulin, Timmermans et al. (2010) *Nano Letters.* 10(11), 4349

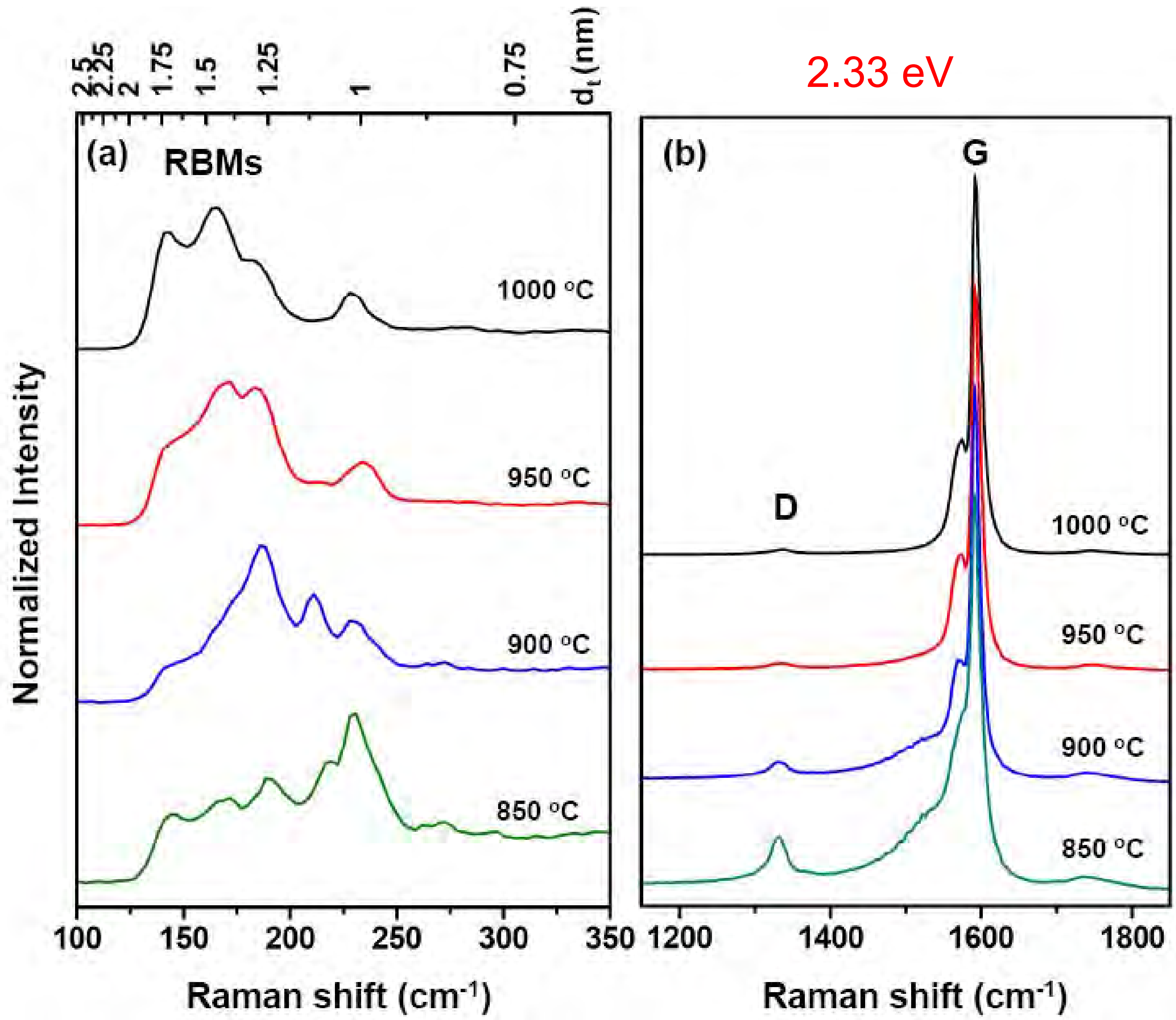
TEM and SEM images of SWCNTs
by aerosol CVD method



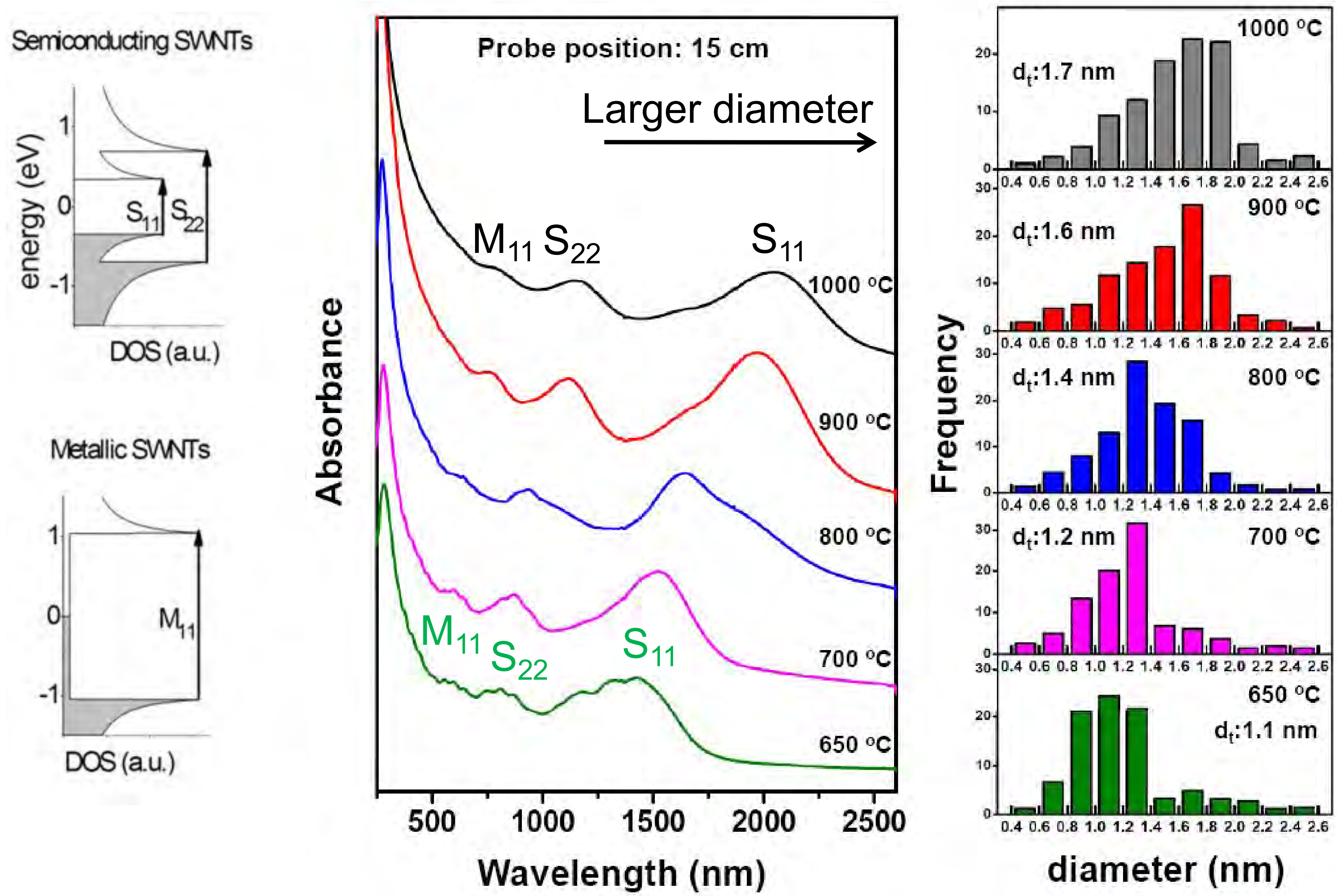


Raman spectra in the regions of (a) RBMs and (b) G and D bands of the SWCNT samples collected at probe position of 6.5 cm **as a function of T_{set}**

2.33 eV



UV-Vis-NIR absorption spectra and corresponding fitted diameter diagrams of the SWCNT **as a function of T_{set}**

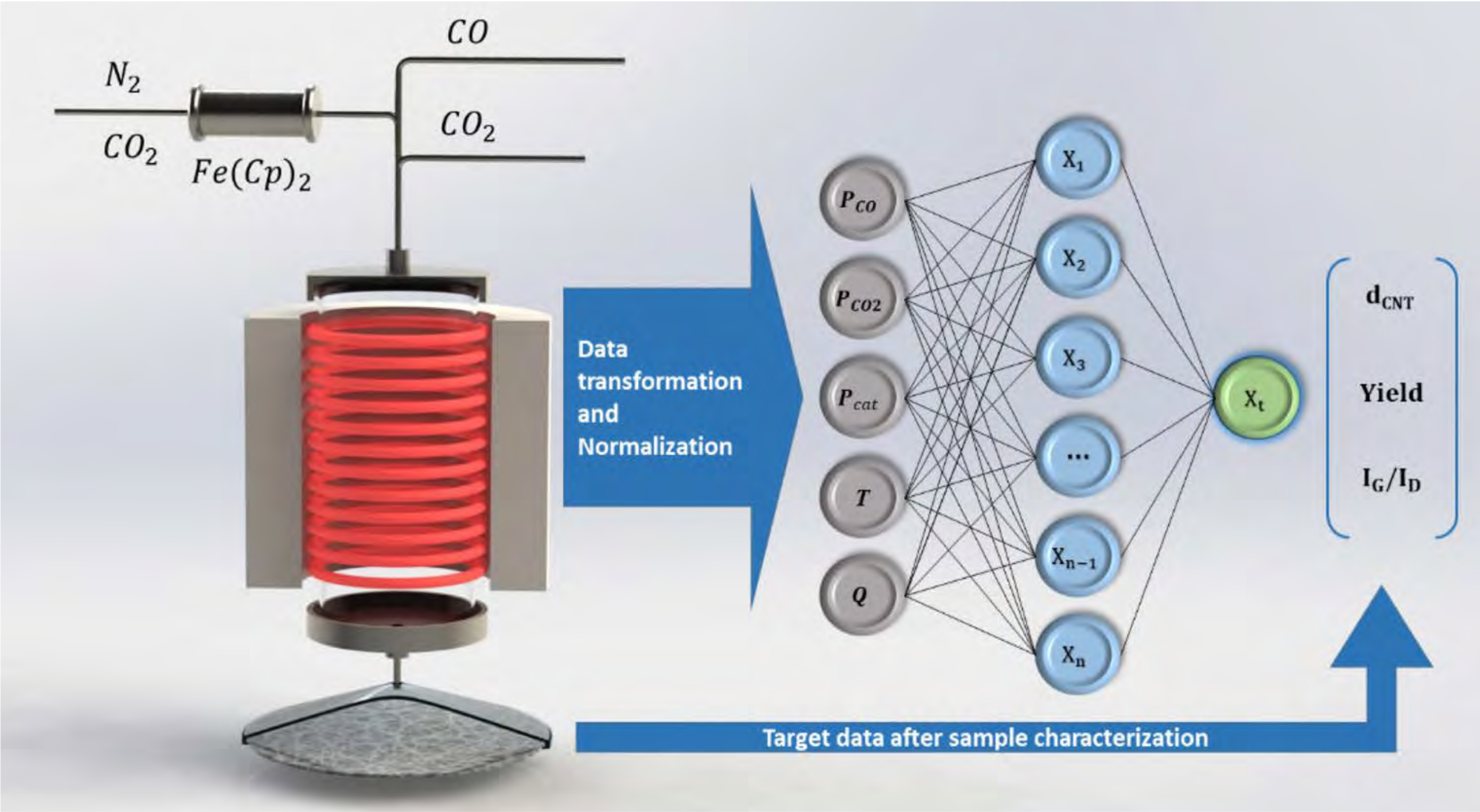


Tian, Nasibulin et al. (2010) *J. Phys. Chem. Letters* **1**(7), 1143

Vsevolod Iakovlev

PREDICTION OF SYNTHESIS OUTCOME
Artificial Neural Network

Dmitry Krasnikov



Iakovlev, Nasibulin *et al.* (2019) **Carbon 153,**100.

Outline:

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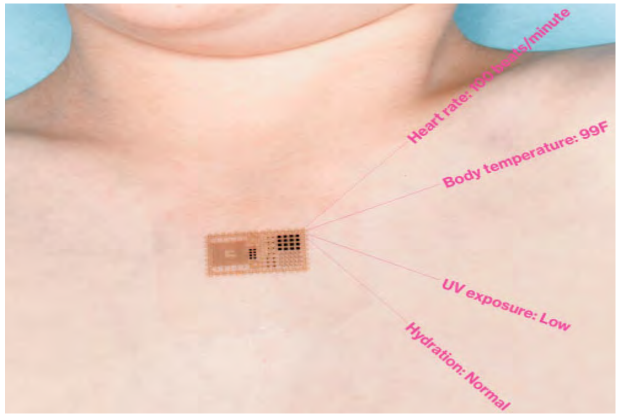
Applications of flexible, transparent and elastic electrodes

Future flexible devices based on transparent conductors and thin film transistors

http://www.concept-phones.com/?s=flexible

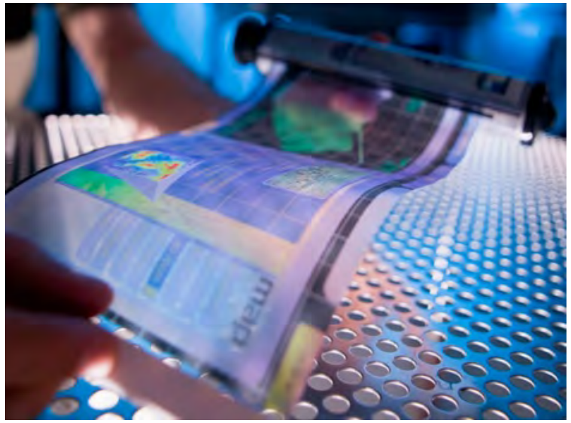
Real time high-quality, human body wellness monitoring system



Requirements to materials for flexible and stretchable electronics

Fabrication on plastic substrate

Room temperature process



Hewlett-Packard

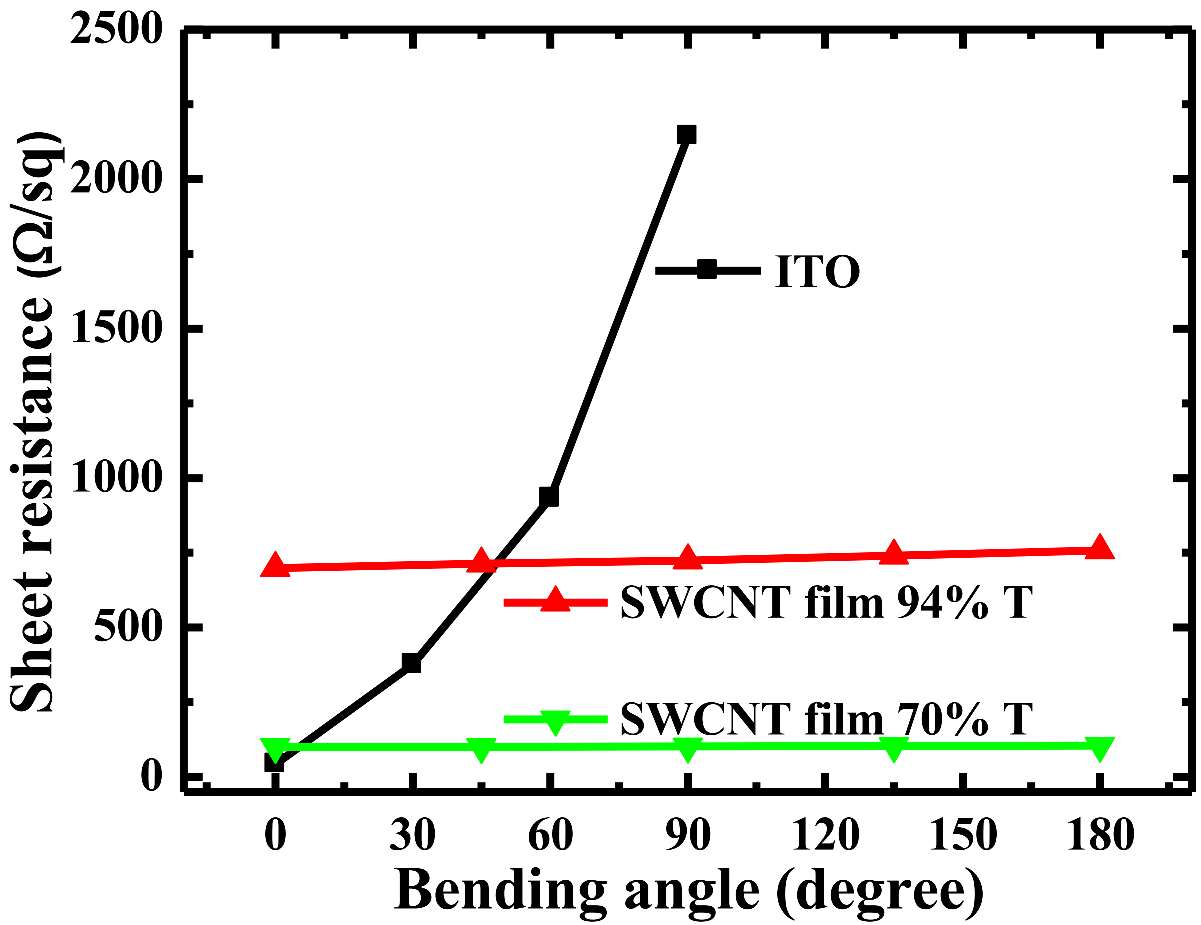
Low-cost fabrication

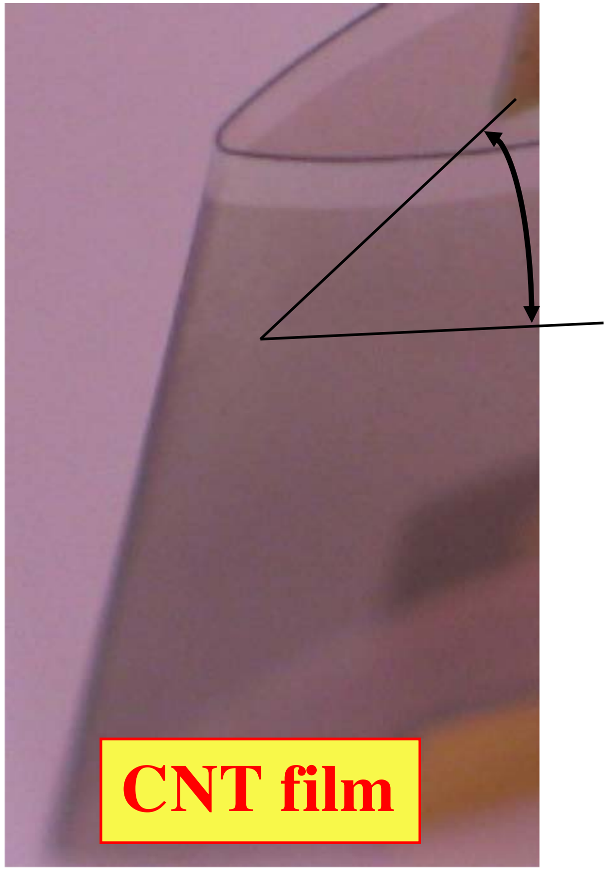
Atmospheric pressure process
High-speed printing method
Roll-to-roll manufacturing

Currently used materials such as silicon and transparent conducting oxides (ITO, ZnO, Cd_2SnO_4…) cannot be used! Alternative materials are required!!!

ITO (indium tin oxide) vs. CNT films

ITO: Excellent transmittance and conductivity

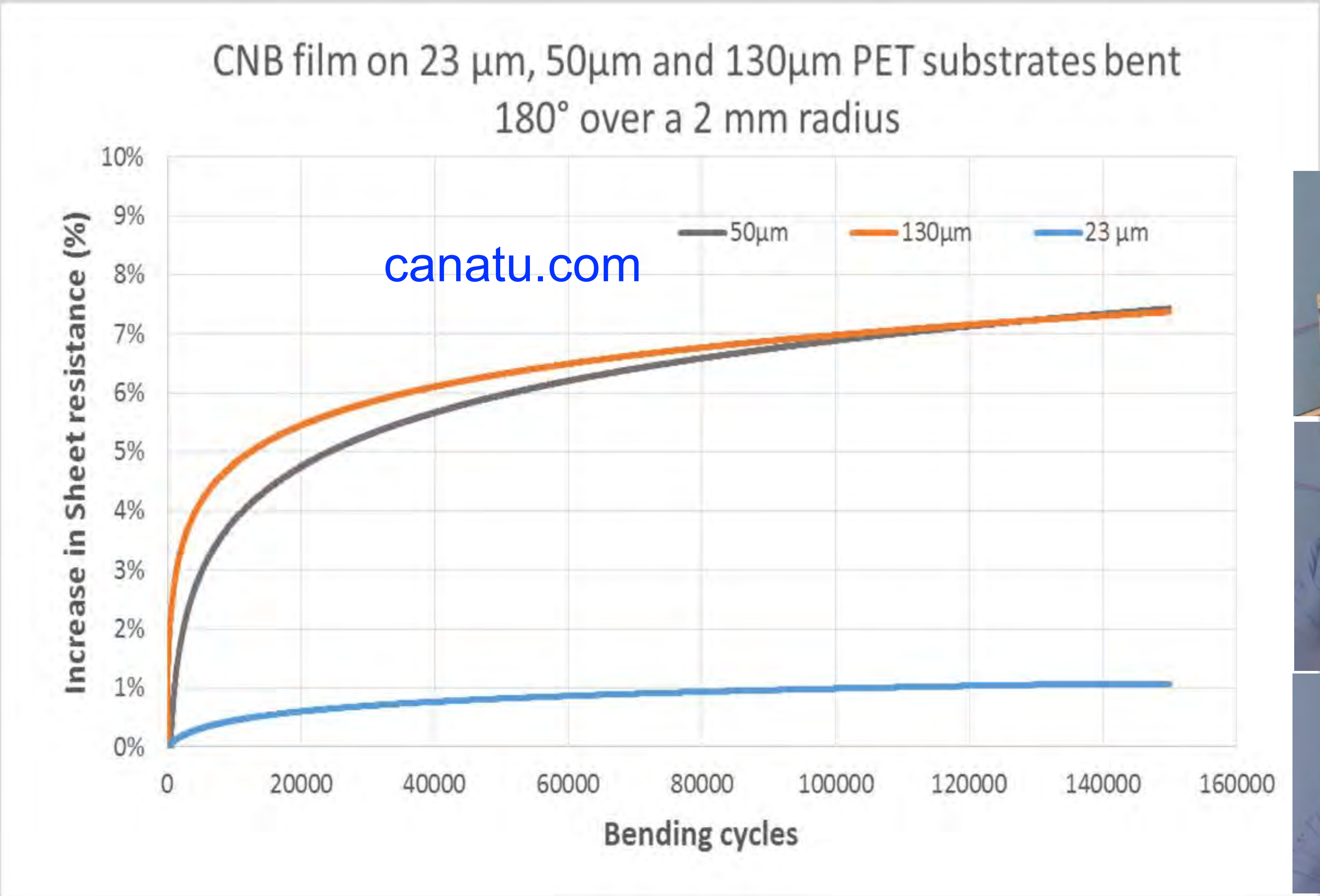


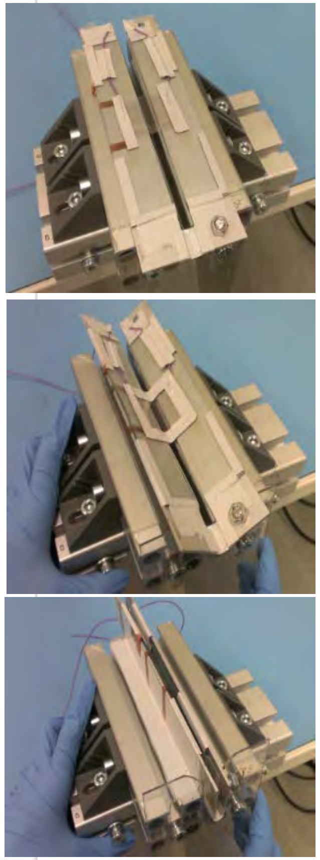


- Indium is limited natural resource!
- ITO can be cracked easily against bending, yielding poor flexibility

Courtesy Prof. Young-Hee Lee, SKKU University, Korea

Thin and flexible SWCNT films





Alexey Tsapenko

State-of-the-art of transparent electrodes based on CNTs

2010: R_{90} = 108 Ω/sq. (Kaskela *et al. Nanoletters* **10**, 4349)

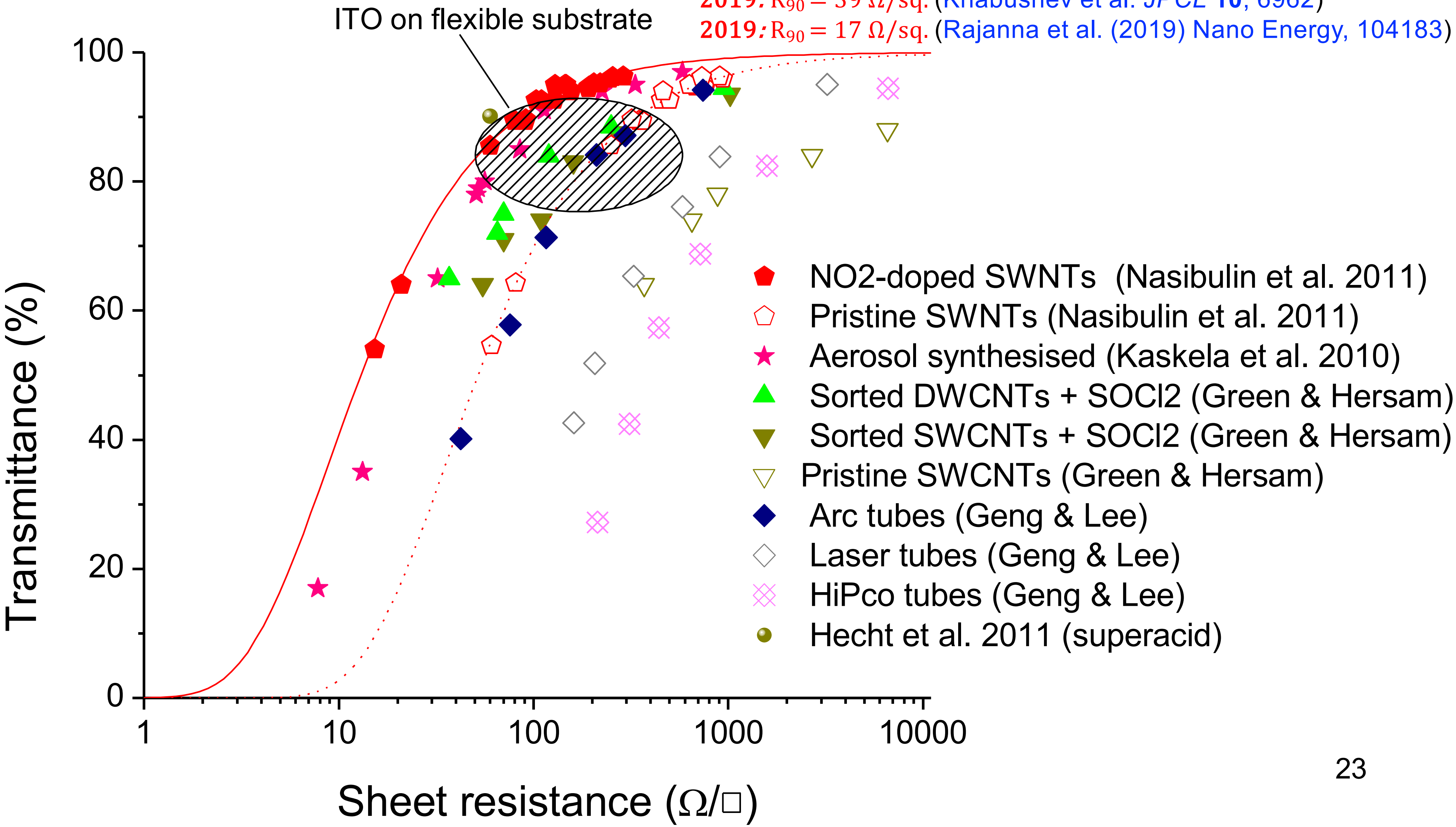
2011: R_{90} = 84 Ω/sq. (Nasibulin *et al. ACS Nano* **5**, 3214)

2015: R_{90} = 65 Ω/sq. (Mustonen et al. APL **107**, 143113)

2018: R_{90} = 42 Ω/sq. (Tsapenko et al. *Carbon* **130**, 448)

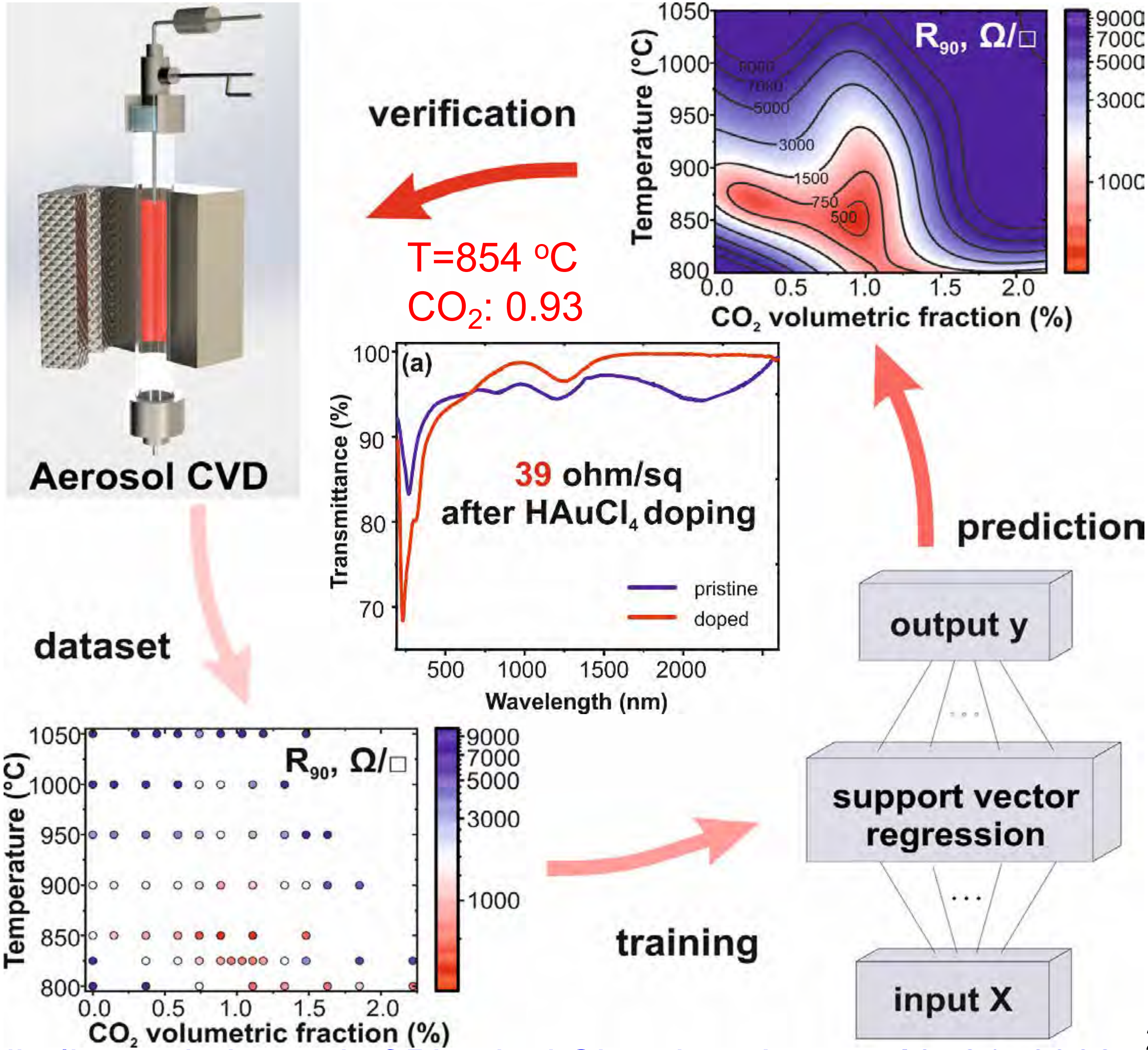
2019: R_{90} = 39 Ω/sq. (Khabushev et al. *JPCL* **10**, 6962)

2019: R_{90} = 17 Ω/sq. (Rajanna et al. (2019) Nano Energy, 104183)



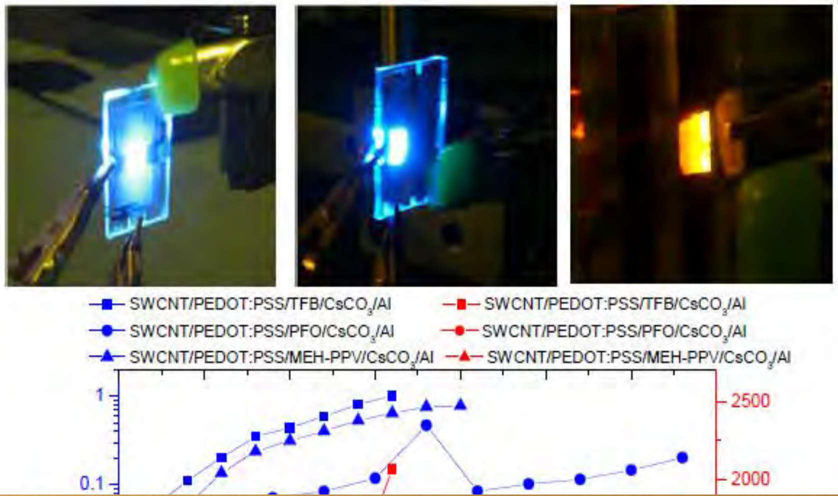
Machine learning: Support Vector Regression

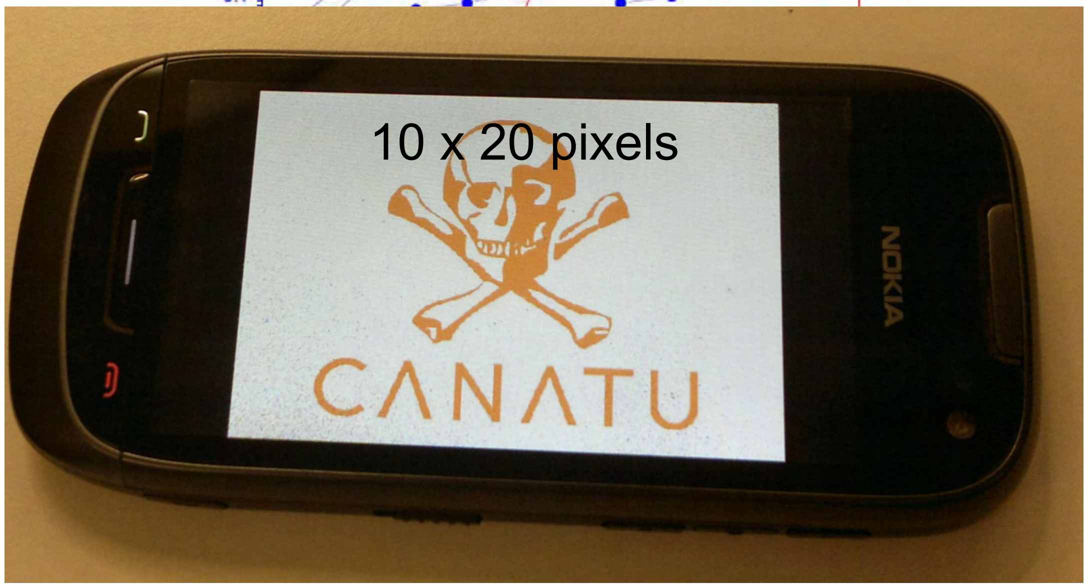
Eldar
Khabushev



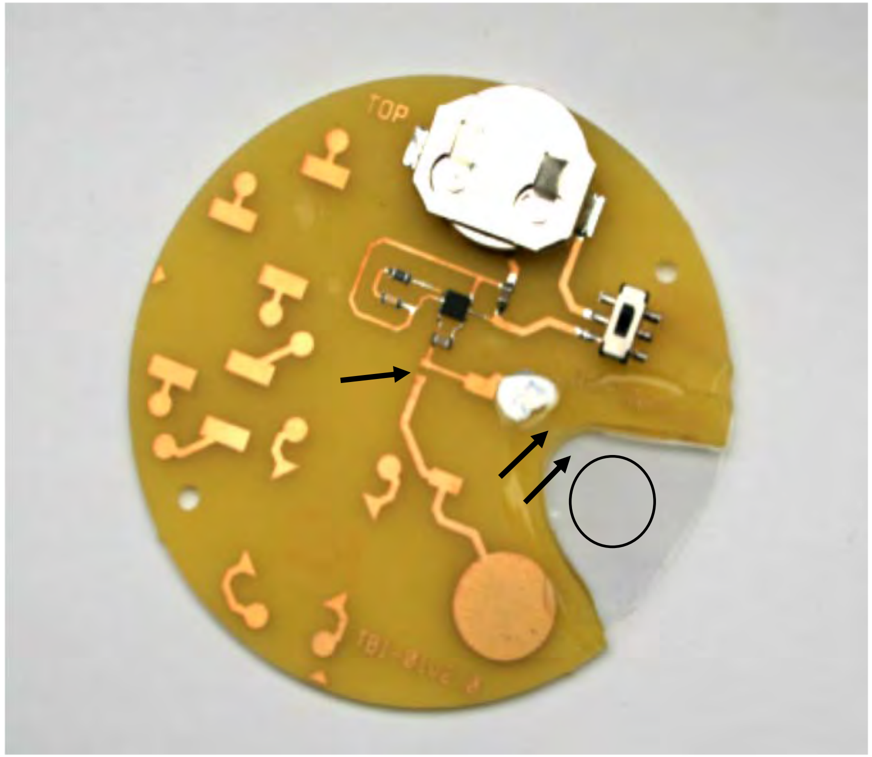
Khabushev, Nasibulin *et al. Journal of Physical Chemistry Letters* **10**, 21, 6962

Applications:
OLEDs and capacitive touch sensors





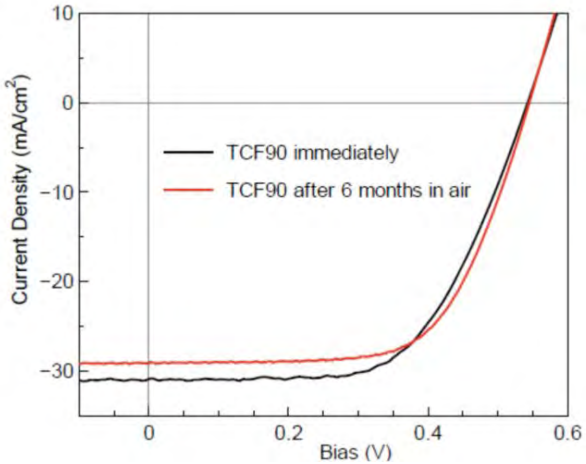
Touch sensor

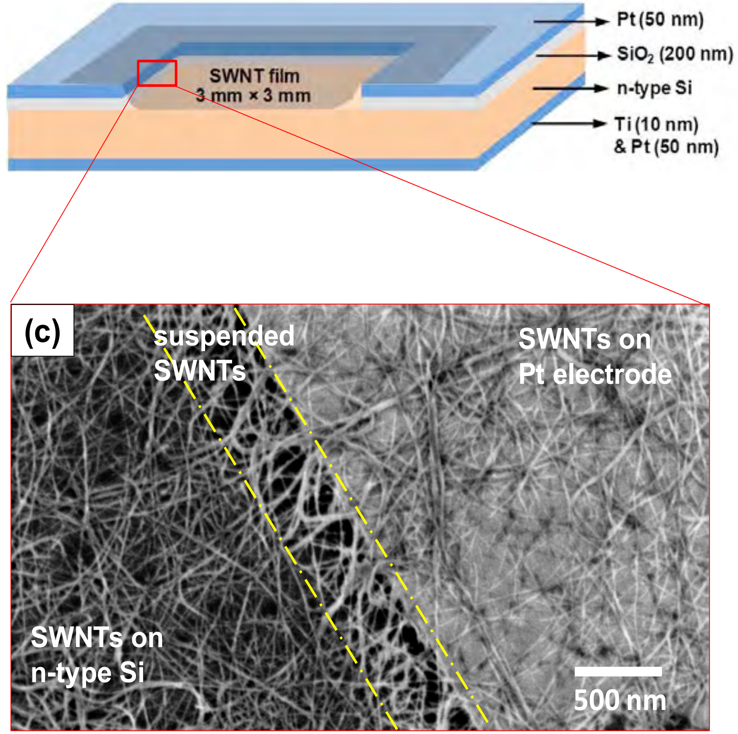


Kaskela, Nasibulin *et al.* (2010) *Nano Letters.* 10(11), 4349.

Canatu Ltd. (canatu.com)

Air-Stable High-Efficiency Solar Cells with Dry-Transferred Single-Walled Carbon Nanotube Films





Films		Experimental Results				
		Time of Measurement	PCE (%)	FF (-)	J_{sc} (mA/cm^2)	V_{oc} (mV)
TCF70		Immediately	9.3	0.68	25.7	535
TCF80	A		10.6	0.68	29.3	535
	B		10.7	0.67	29.6	535
	C		10.8	0.68	29.7	535
	D		10.6	0.67	29.6	535
TCF90			10.1	0.61	30.9	535
		6 Months in Air	10.2	0.64	29.2	540

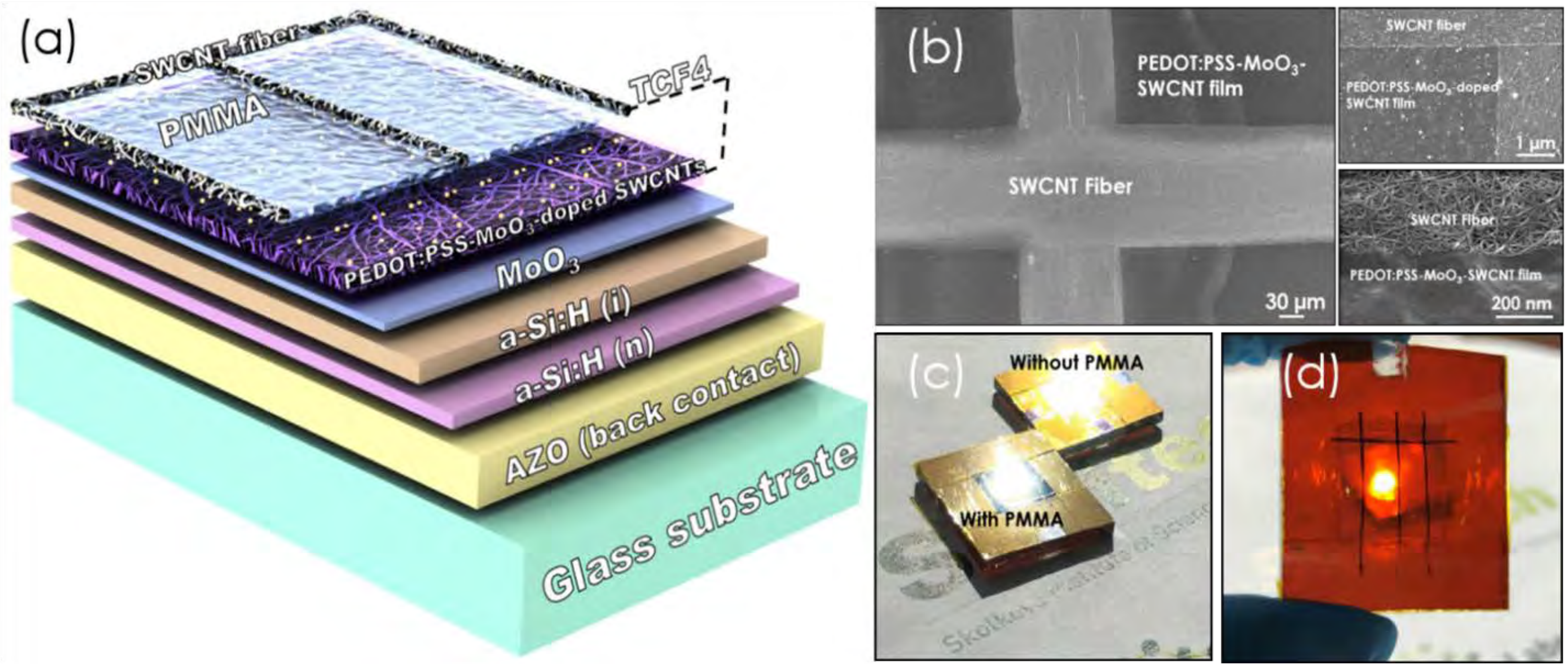
Cui, Nasibulin, Maruyama et al. ***J. Mater. Chem. A***, 2014,**2**, 11311-11318

Jeon, Nasibulin et al. **JACS,** 2015, **137**, 7982

Solar cells based on amorphous Si and SWCNTs

Efficiency of the cell : 8.8%

Pramod Rajanna

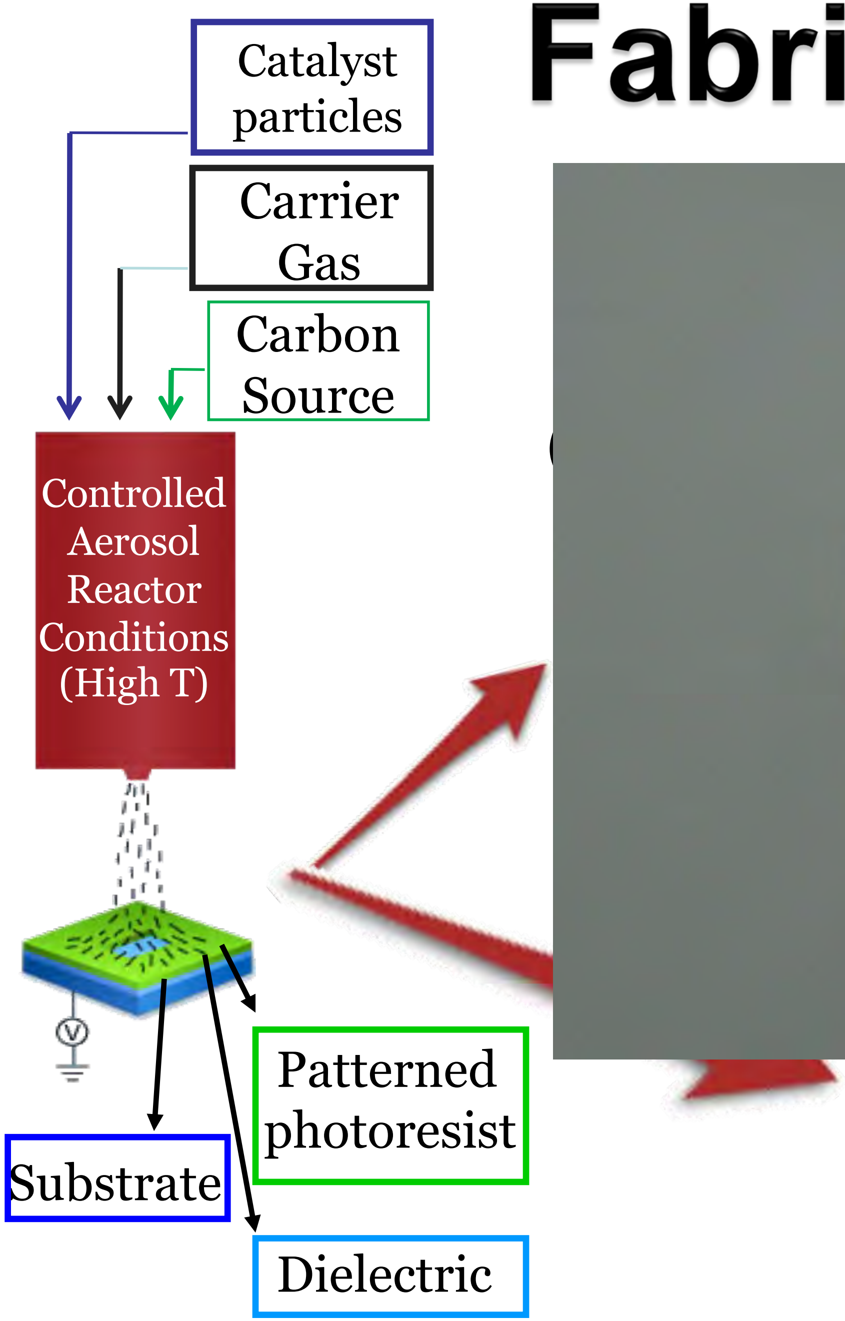


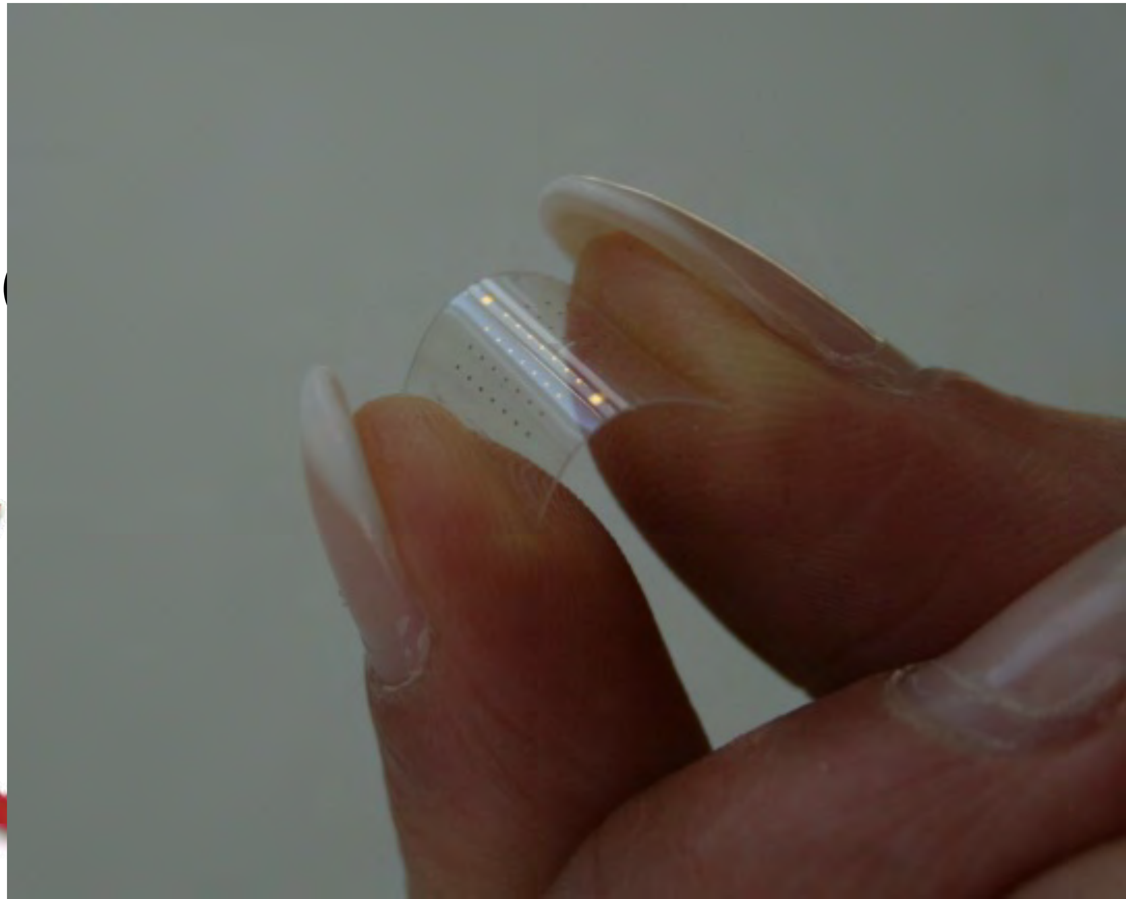
Funde, Nasibulin *et al.* (2016) *Nanotechnology* **27**(18) 185401 — PCE= 1.5%

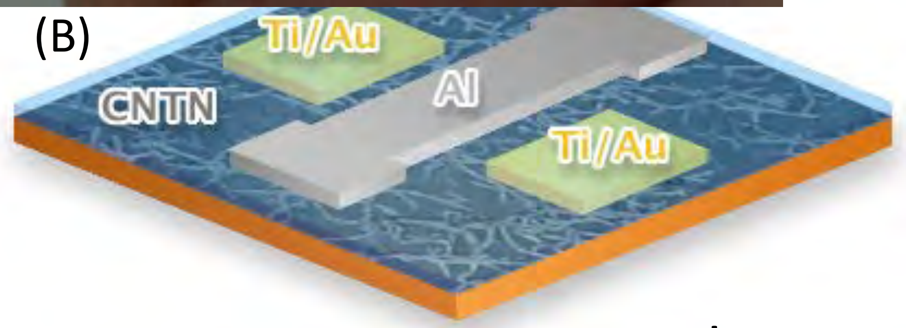
Rajanna, Nasibulin *et al.* (2018) *Nanotechnology* **29** 105404 — PCE= 3.4%

Rajanna, Nasibulin *et al.* (*2019*) *Nano Energy* 104183 — PCE= 8.8%

Fabrication of TFT

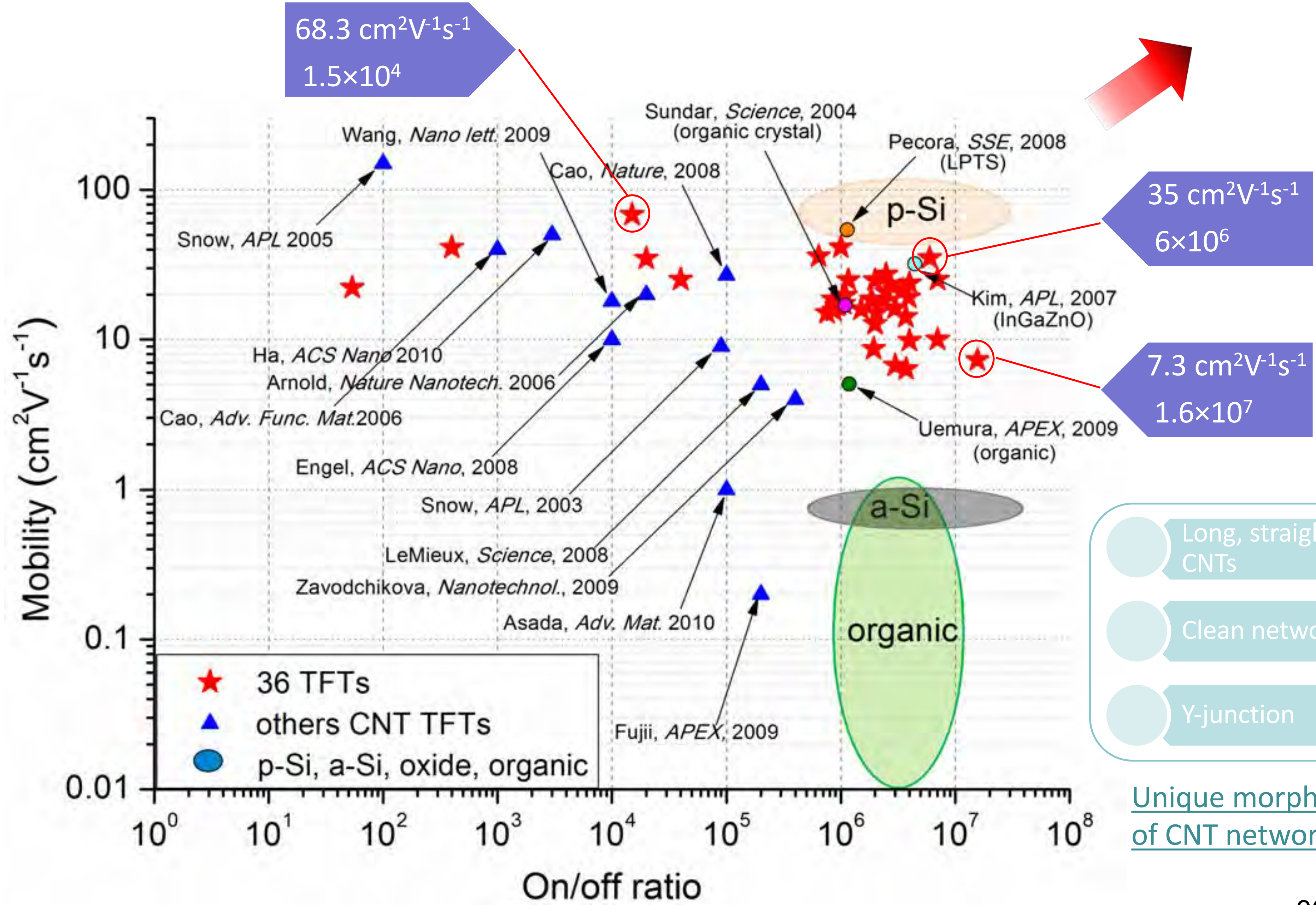






Top-gate structure on polymer

Thin film transistors based on SWCNTs



Long, straight CNTs

Clean network

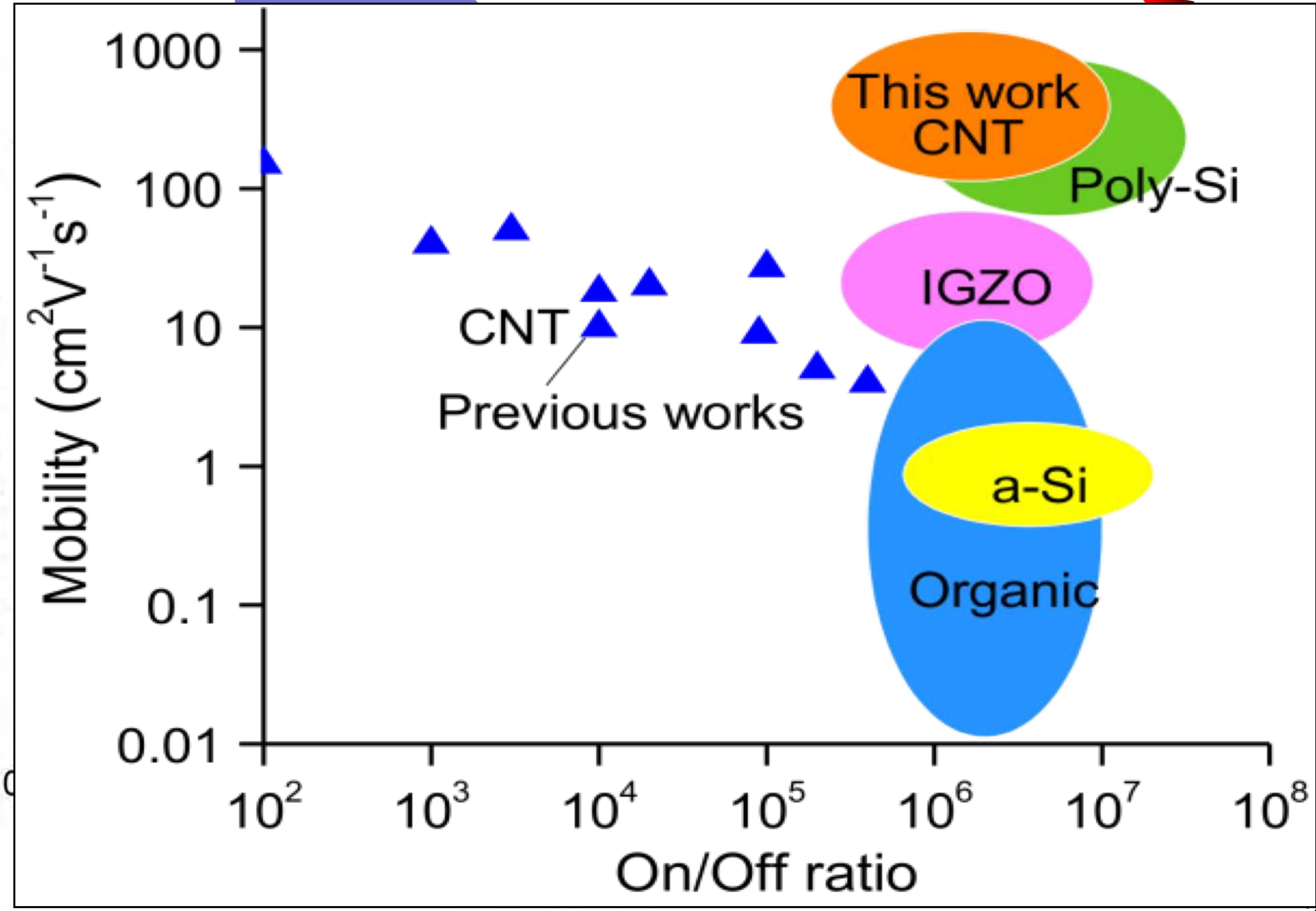
Y-junction

Unique morphology of CNT network

Sun, Timmermans, Tian, Nasibulin *et al.*, *Nature Nanotechnology* (2011) **6**, 156.

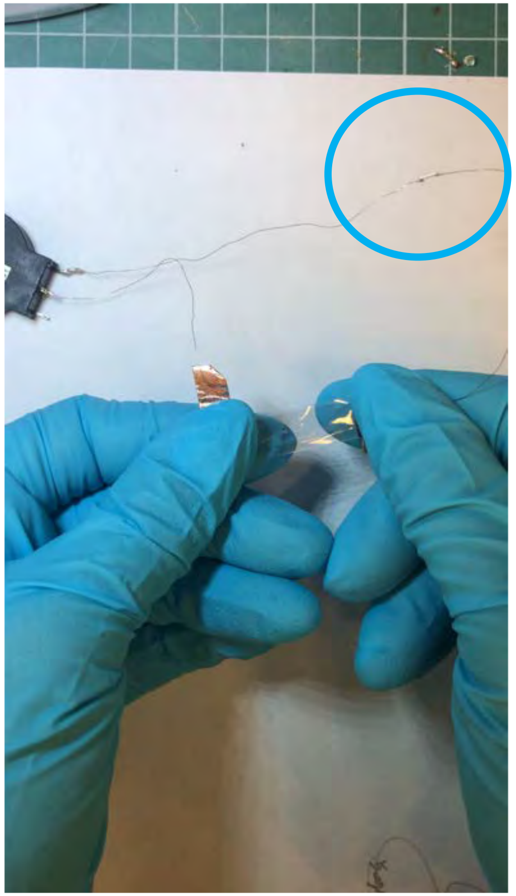
Thin film transistors based on SWCNTs

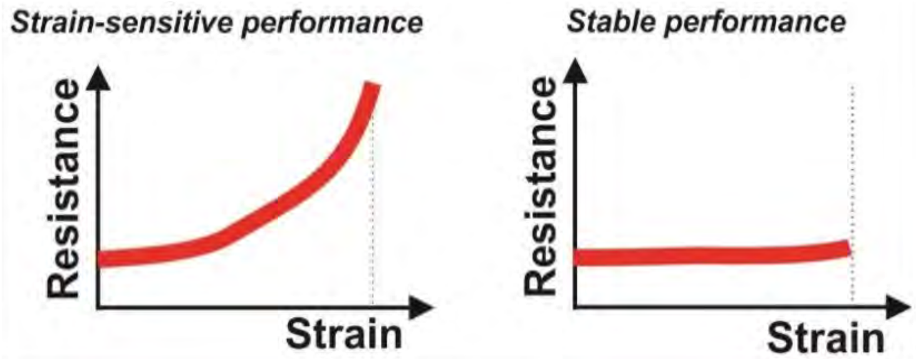
68.3 $cm^2V^{-1}s^{-1}$

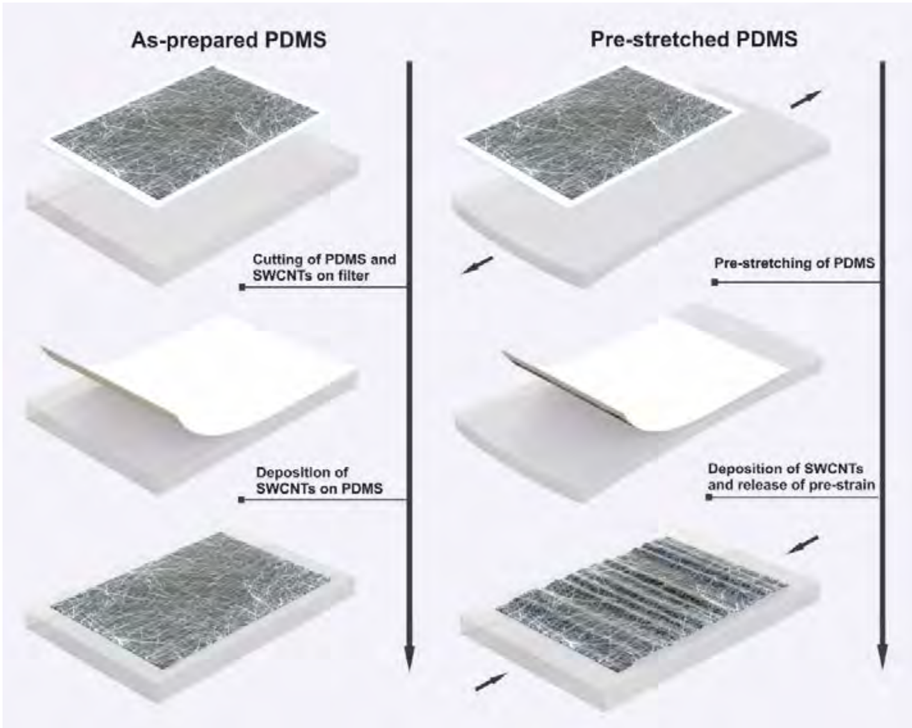


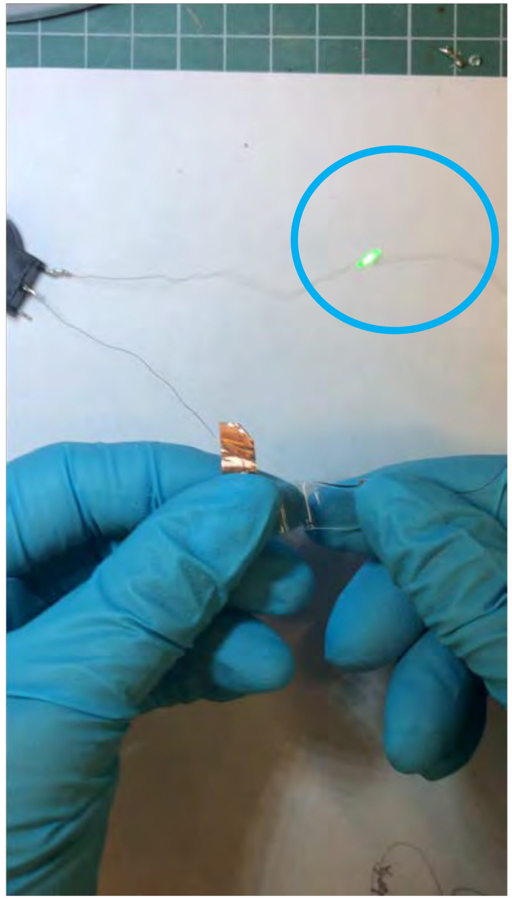
Sun, Kaskela, Nasibulin *et al.*, *Nature Communications* **4**, 2302 (2013).

Two approaches for fabrication of stretchable electrodes





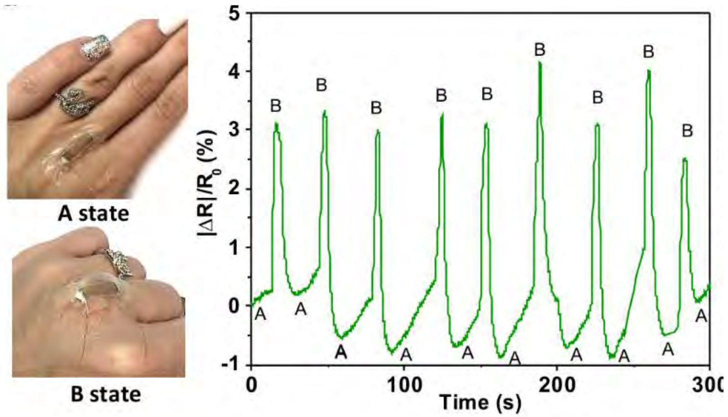


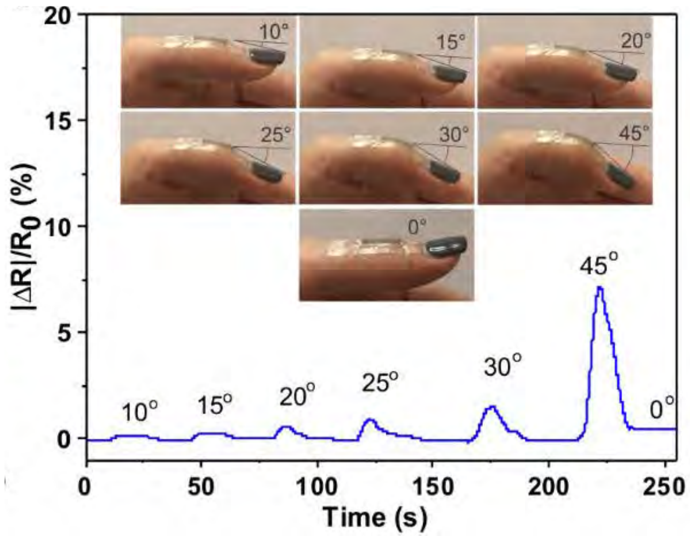


Gilshteyn *et al. (2019) ACS Applied Materials & Interfaces* 11(30) 27327.

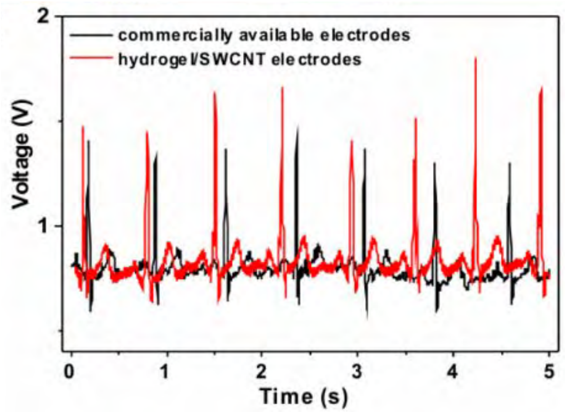
Hybrid materials: hydrogel/SWCNTs

Application of hydrogel/SWCNT structures as active components





Application of hydrogel/SWCNT structures as passive electrodes

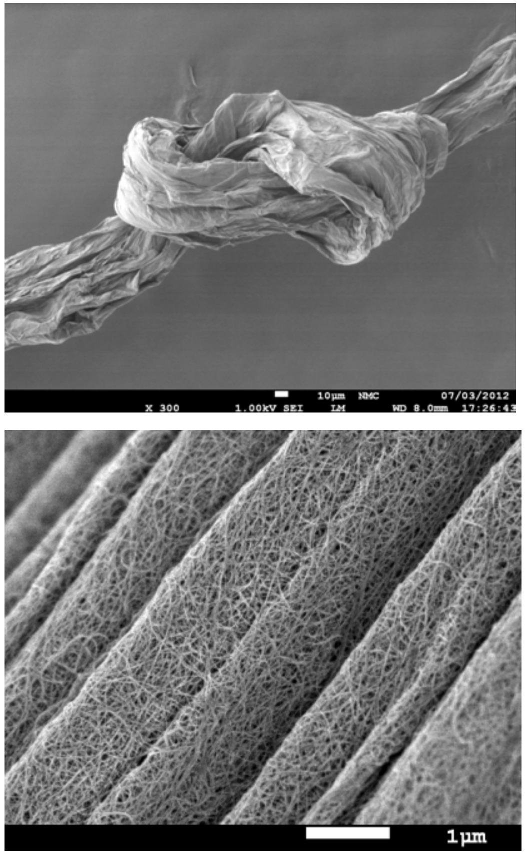


Hydrogel/SWCNT-based ECG electrodes

Gilshteyn *et al.* (2018) ACS Appl. Mater. Interfaces 10, 28069.

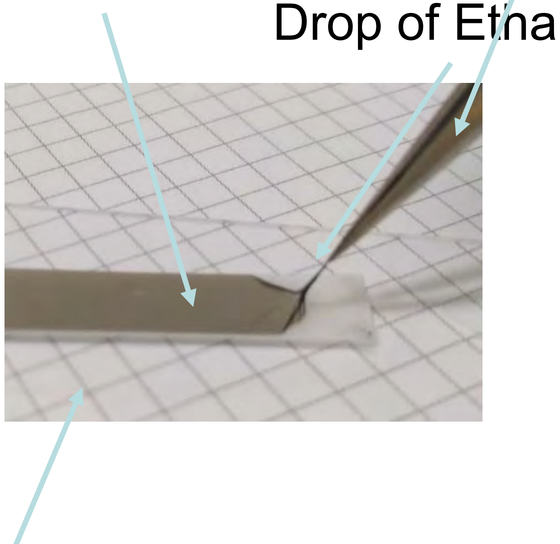
Maria Goncharova

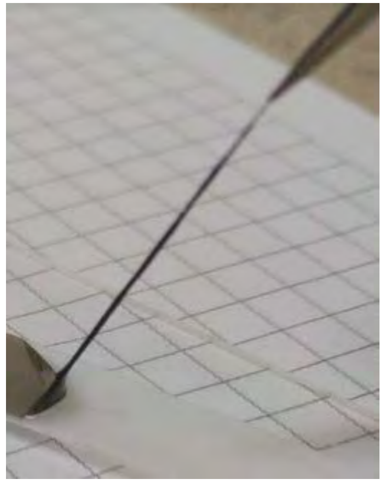
Fibers of SWCNTs



SEM images of CNT fibers, a. fiber knot, b. close-up

SWCNT thin film about **<u>80nm</u>**, on filter



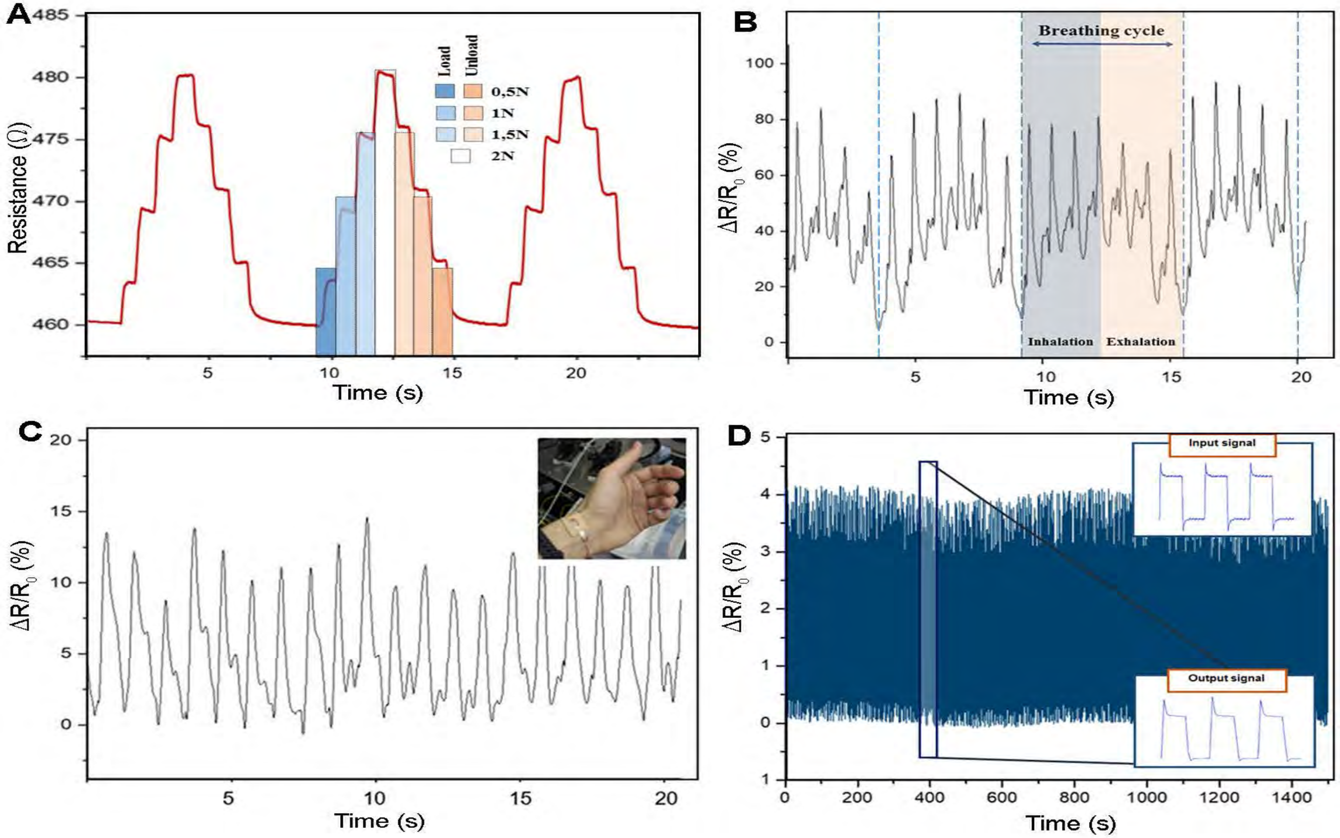


Optical diameters of fibers are in range of 20 to 100 microns, depending on CNT strip thickness and width

Zhilyaeva, Shulga, Shandakov, Sergeichev, Gilshteyn, Nasibulin (2019) *Carbon*, **150,** <u>69</u>.

Mechanical and electrical properties

Maria Zhilyaeva



Extremely sensitive

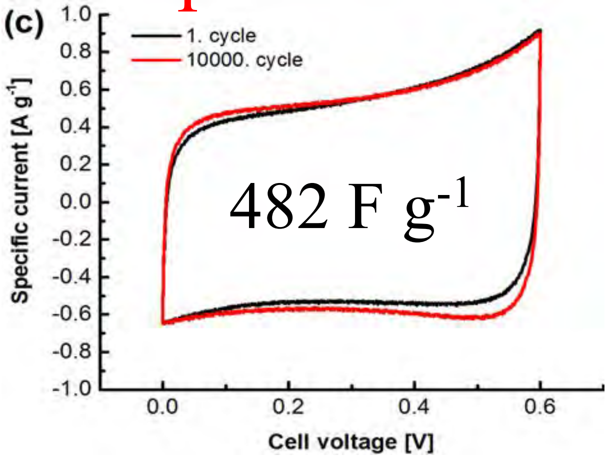
- **Tensile strength** around **400 MPa, Density** around 0.**2g/cm^3** , average **elongation** at brake 25%
- **Conductivity** with 4 contact method around **400 S/cm**
- Conductivity of doped fibers with **AuBr3** - **2300 S/cm**

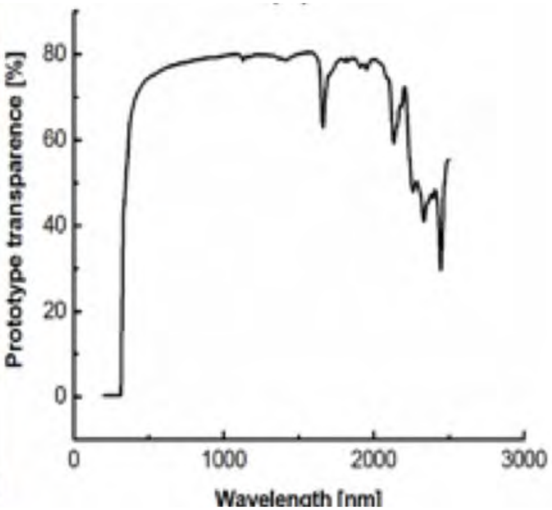
Zhilyaeva, Shulga, Shandakov, Sergeichev, Gilshteyn, Nasibulin (2019) *Carbon*, **150,** 69.

Supercapacitor

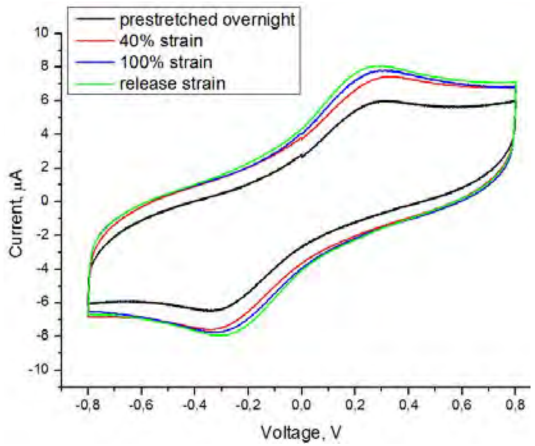
Tanja Kallio

Flexible and transparent





Flexible, transparent and stretchable



Kanninen *et al.*, *Nanotechnology* 27 (2016)
Gilshtein *et al.*, (2020) *Journal of Energy Storage* 30, 101505.

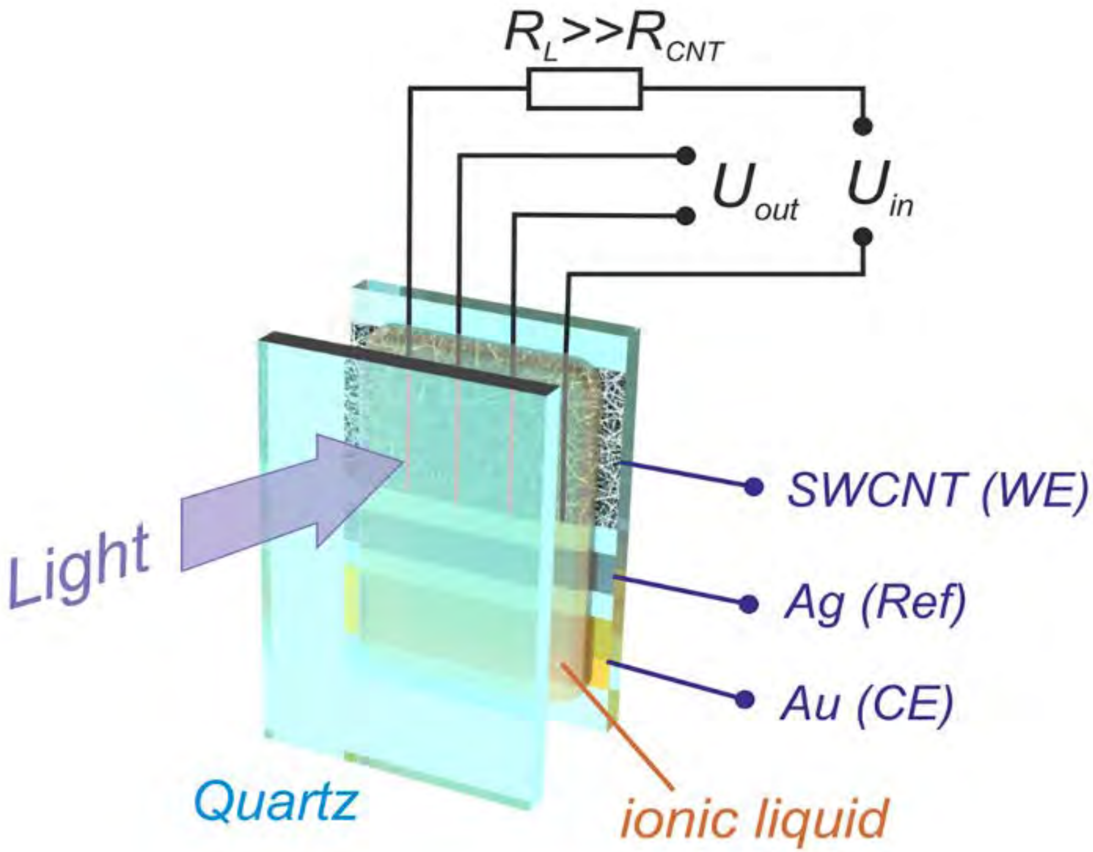
Gilshteyn *et al.*, *RSC Adv.* 6, 93915 (2016)
Gilshteyn *et al.*, *Scientific Reports* **7**, 17449 (2017).
Gilshteyn *et al.*, *Nanotechnology* **29**(32), 325501 (2018).

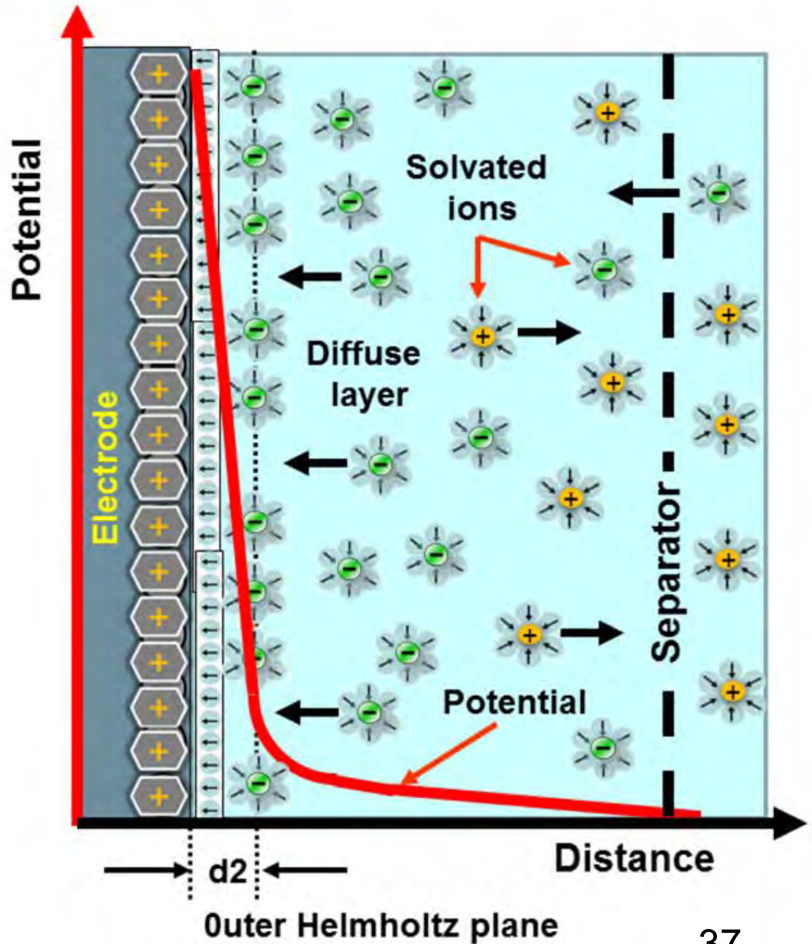
Dr. Daria Kopylova

Ionic liquid gating

Prof. Tanja Kallio

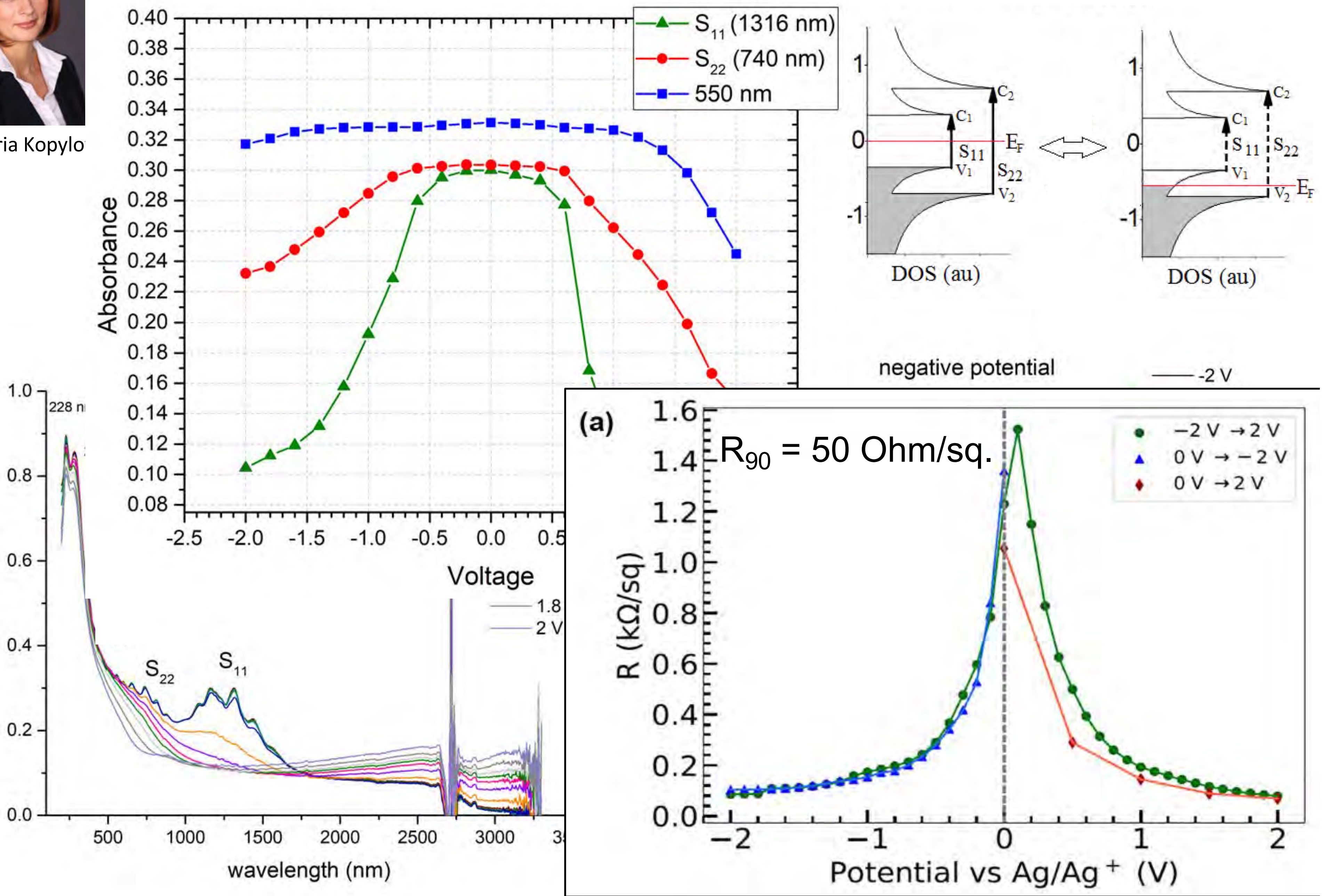
Experimental setup



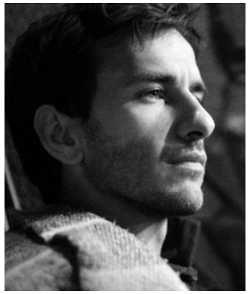


Tailoring electronic structure by IL gating

Dr. Daria Kopylo



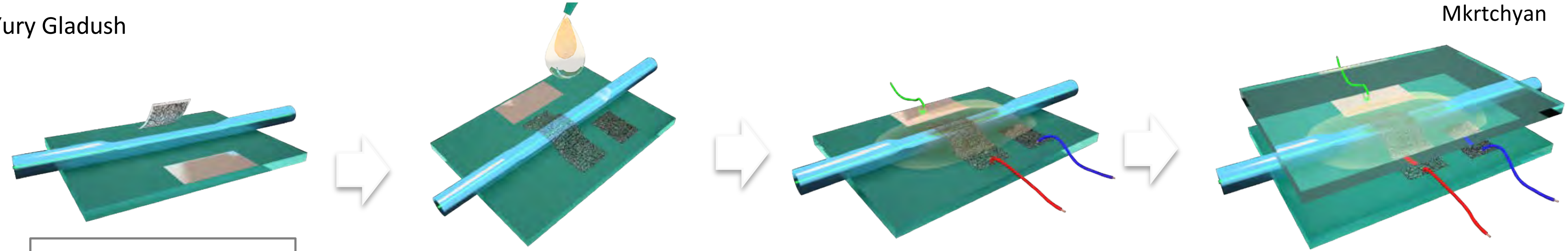
Kopylova *et al*. 2020 Carbon **167**, 244



Dr. Yury Gladush

Electrical gating to control pulse generation regime

Aram Mkrtchyan

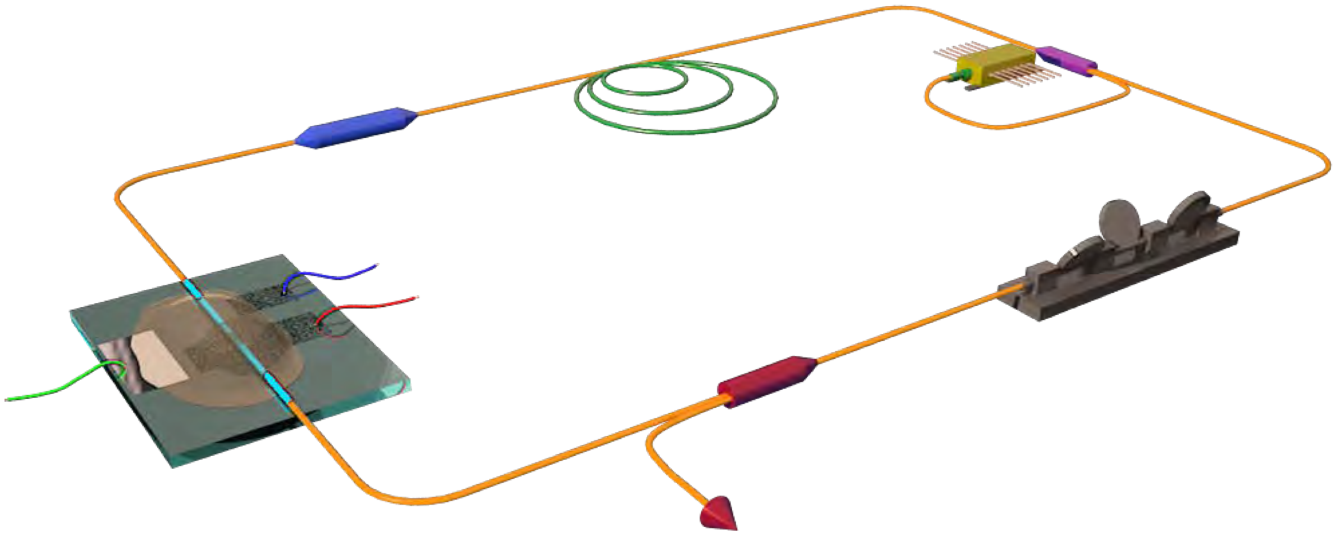


Side-polished fiber fixed and silver electrode fixed on the glass stripe

20 nm thick SWCNT films transferred

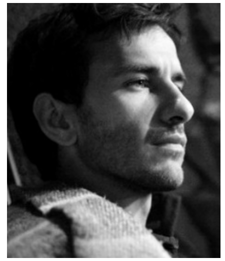
Ionic liquid DEME BF_4 added

Encapsulate from air



Mkrtchyan *et al.* (2019) *Opt. Mater. Express* **9**(4), 1551

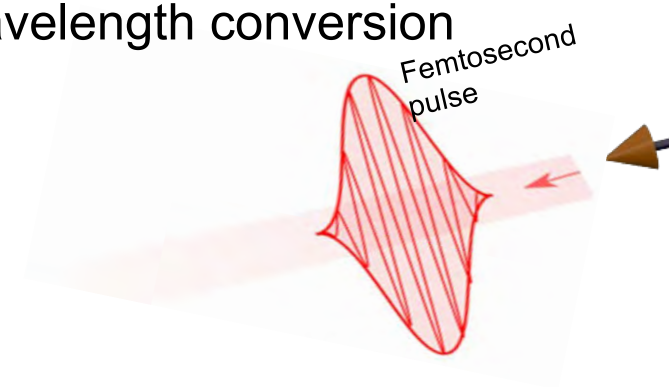
Femtosecond fiber laser development

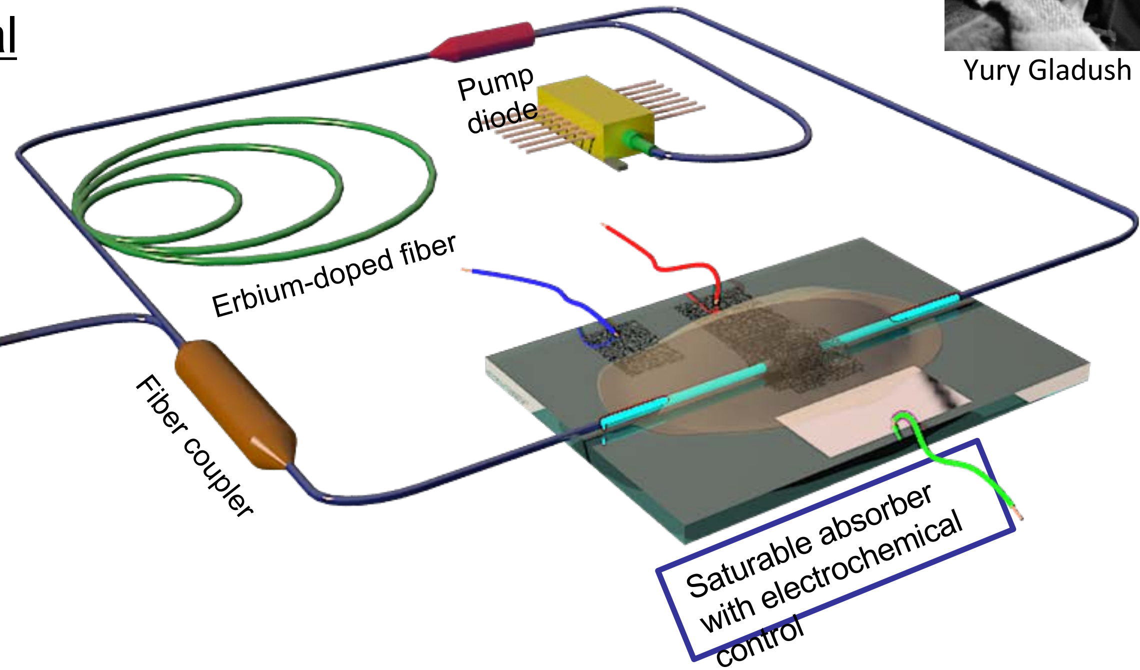


Yury Gladush

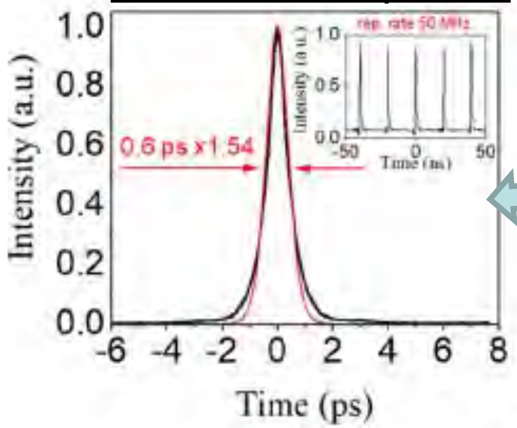
Electrical control of nonlinear optical properties of carbon nanotubes:

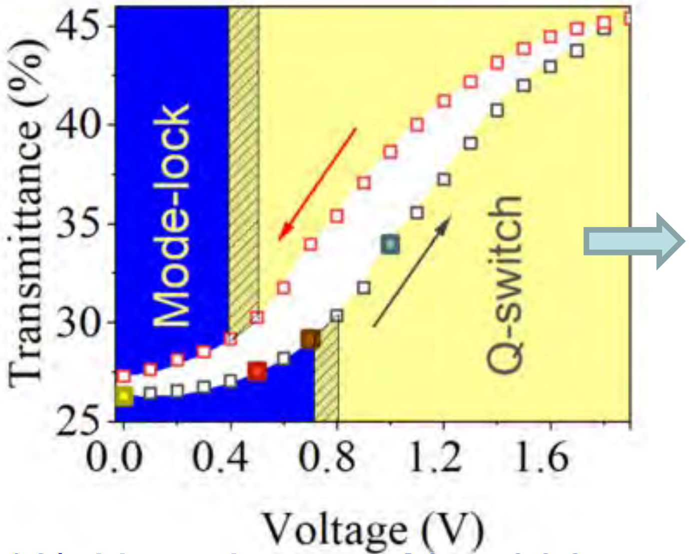
- Laser pulse generation
- Wavelength conversion



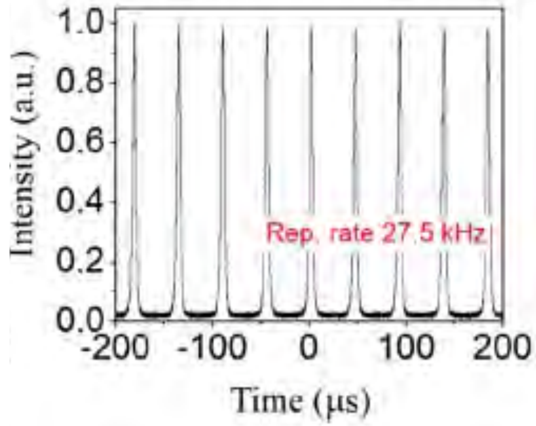


Mode-locked femtosecond pulses



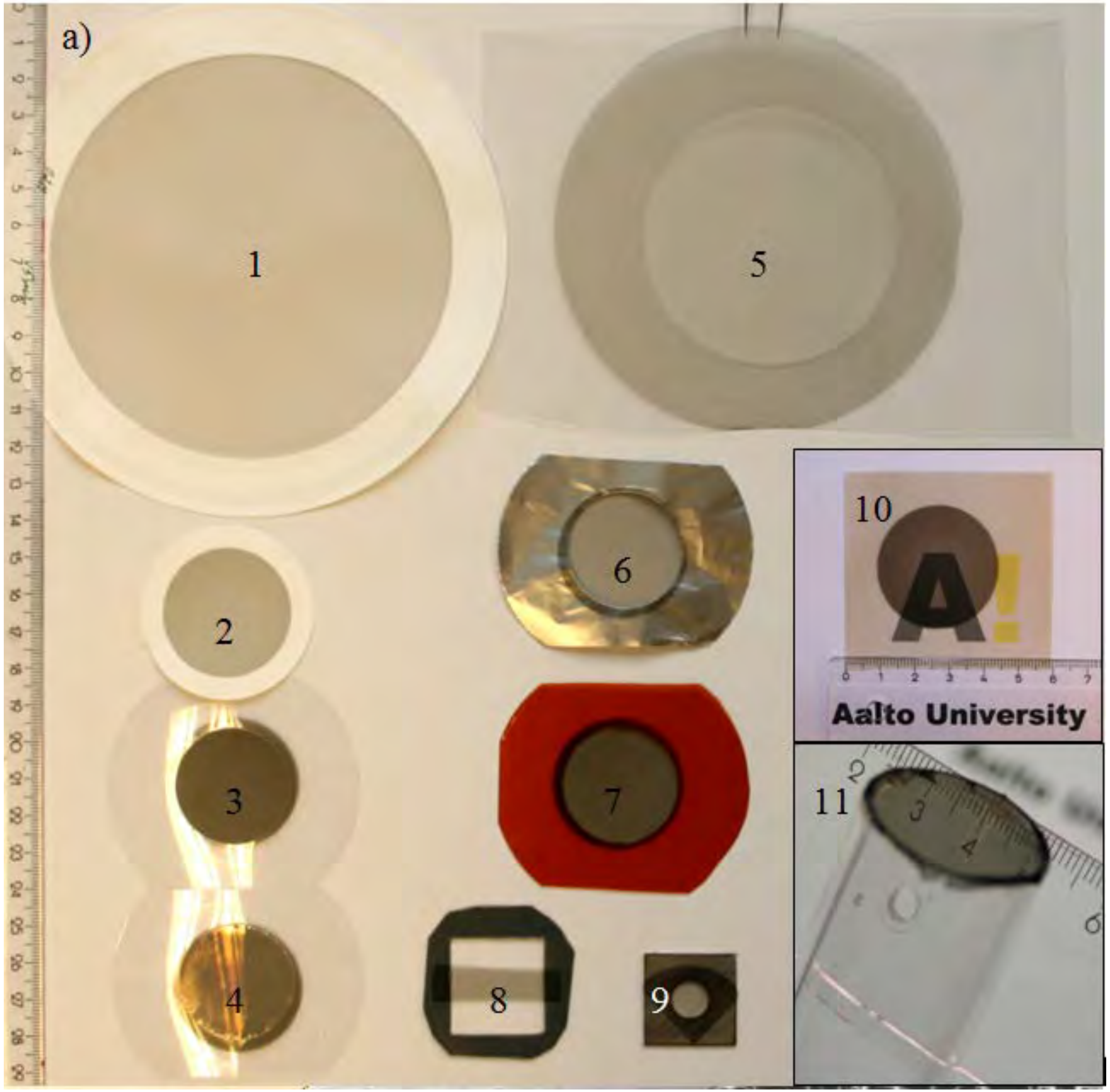


Q-switched microsecond pulses



Gladush, Nasibulin *et al.* (2019) *Nano Letters* **19**, 5836.

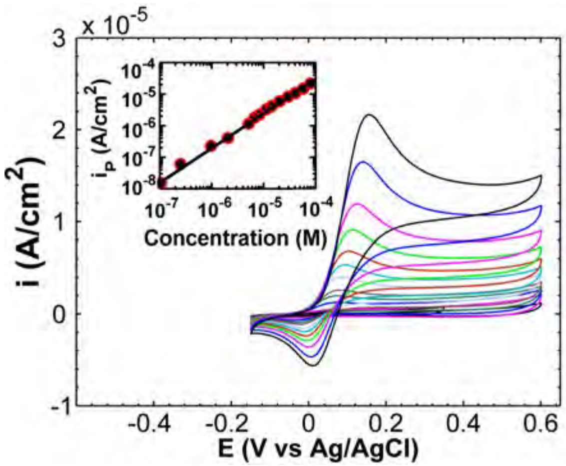
Fabrication of freestanding SWNT films



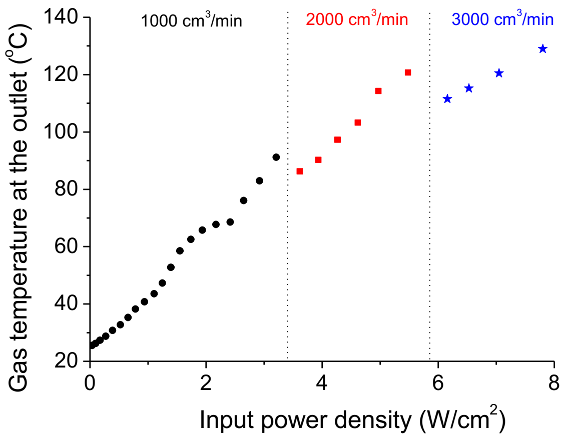
ısibulin et al. (2011) *ACS Nano* **5**, 3214.

Free-standing film: applications

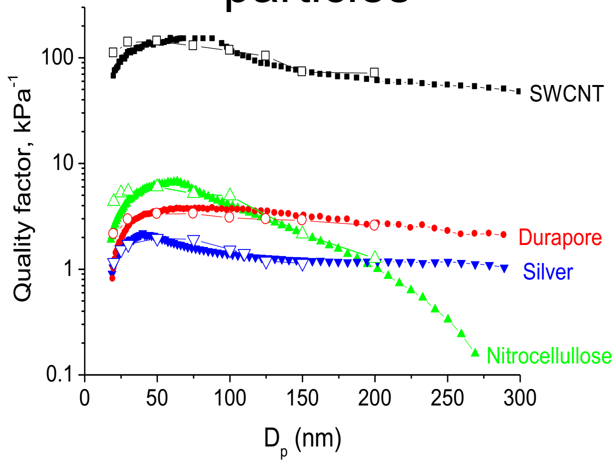
Electrochemical sensor



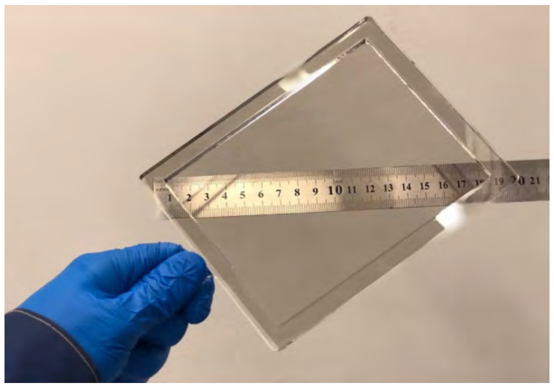
Air heater (sterilization)



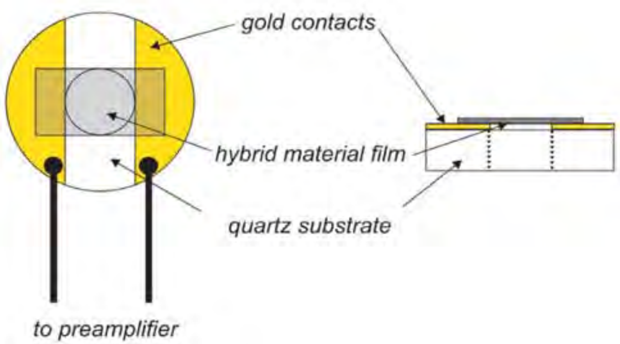
Filter of aerosol particles



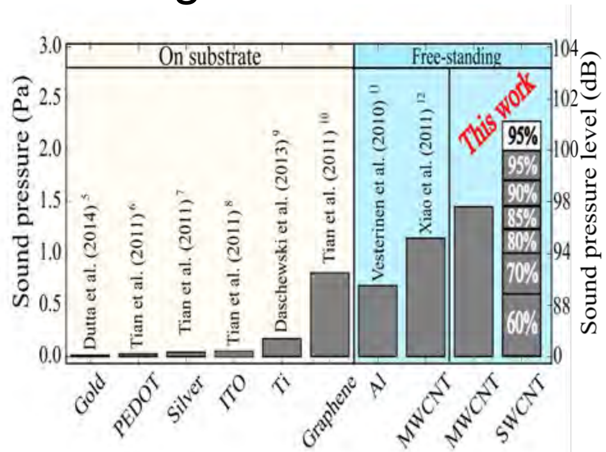
Pellicle for EUV lithography



Bolometer



Ultrasound generator



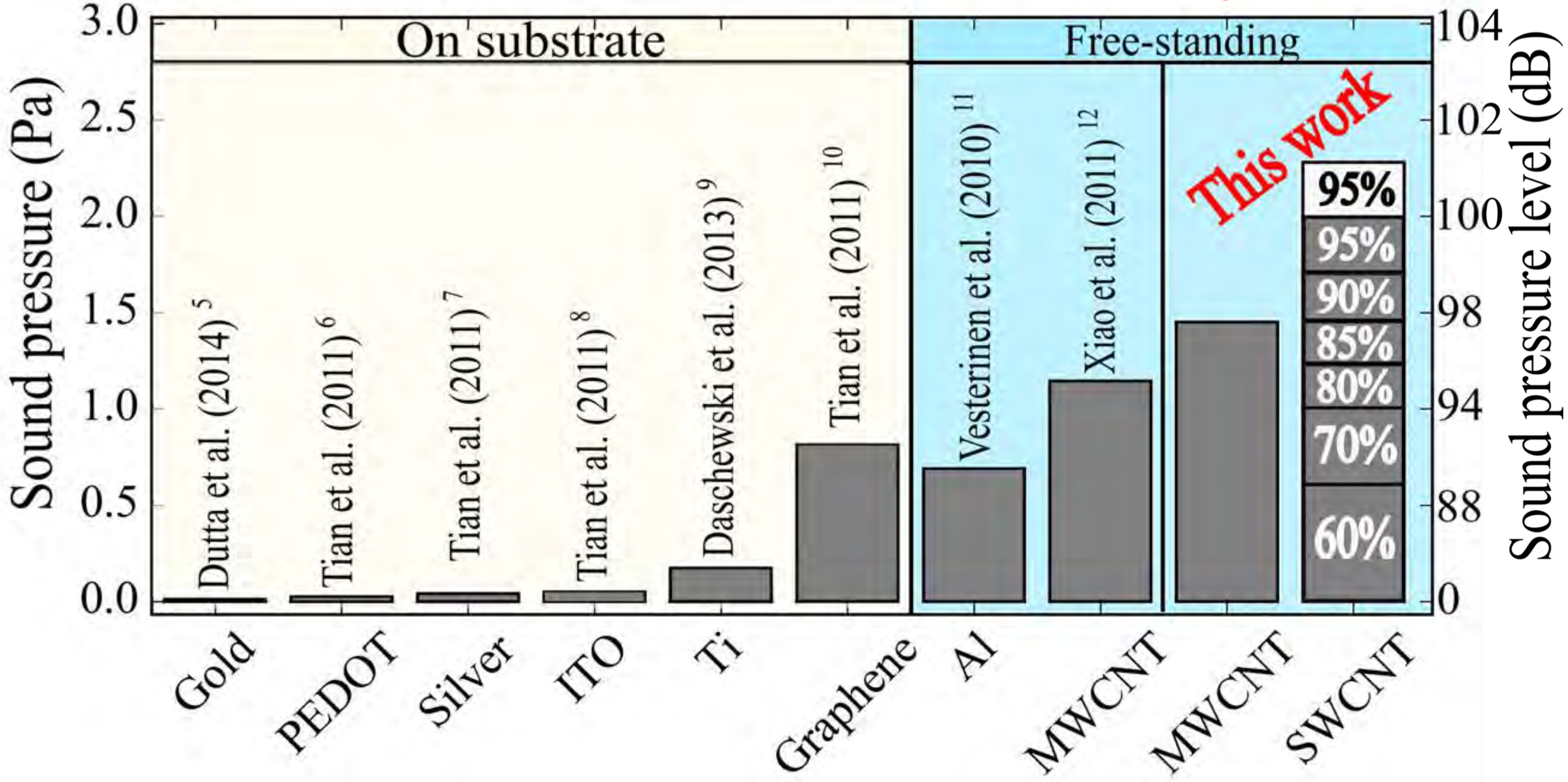
Nasibulin et al. (2011) *ACS Nano* **5**, 3214.
Gubarev et al. (2019) *Carbon* **155**, 734.

Romanov *et al.* (2019) *Nanoscale Horizons* **4**,1158.
Kopylova *et al.* (2018) *Nanoscale* 10, 18665.

Stepan Romanov

Flexible thermoacoustic generator based on SWCNTs

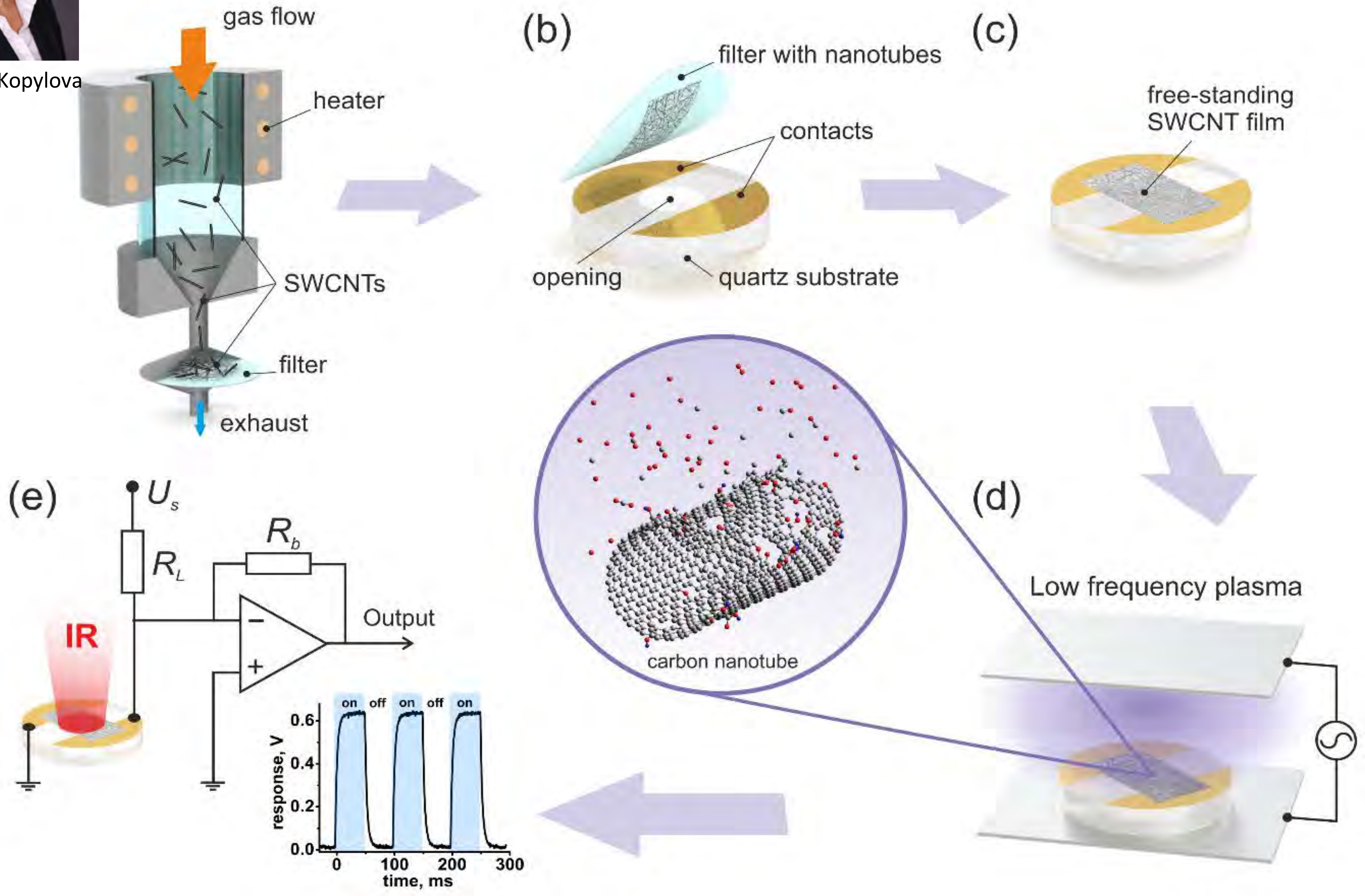
State-of-the-art performance



Romanov *et al.* ***Nanoscale Horiz.***, 2019, **4**, 1158-1163

Dr. Daria Kopylova

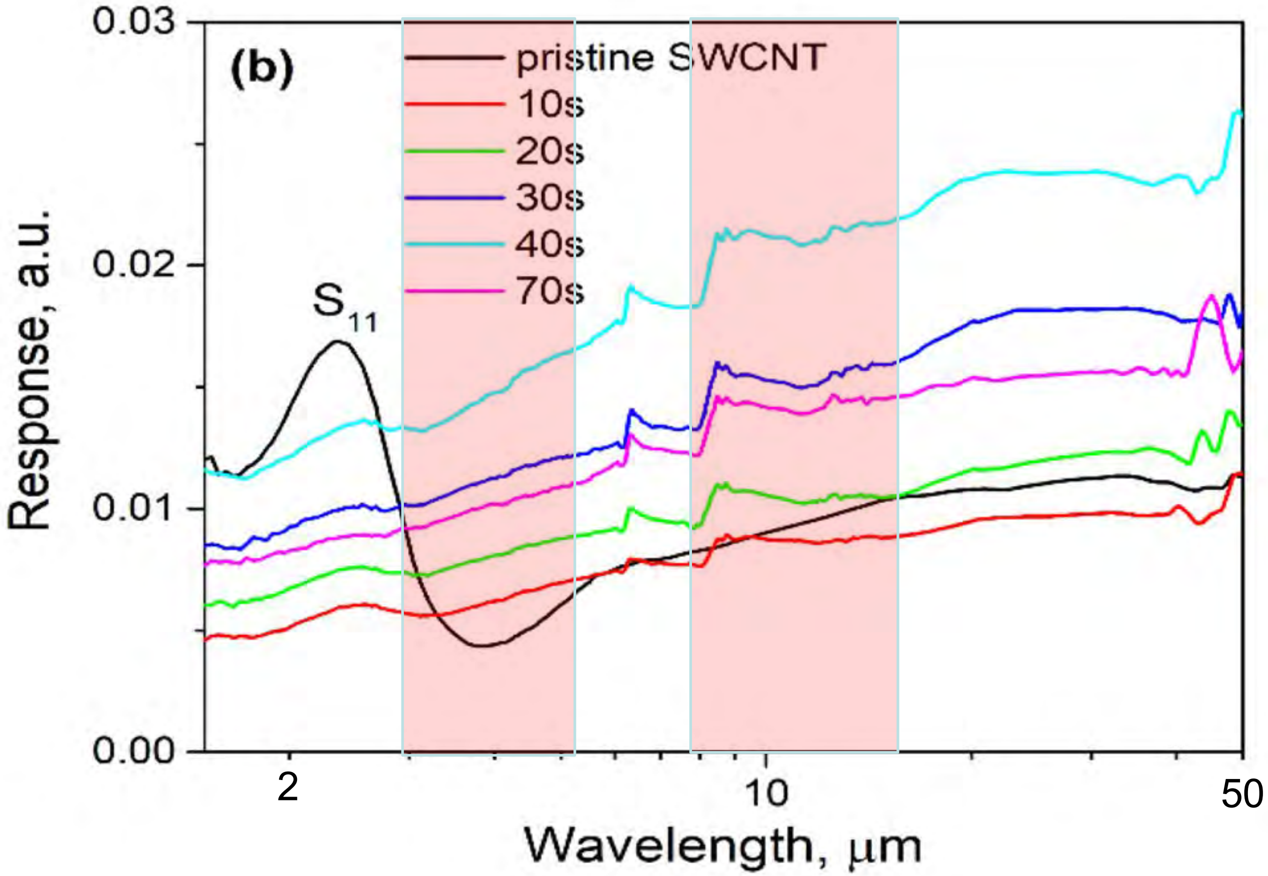
Bolometers



Kopylova, Nasibulin *et al.* (2018) *Nanoscale* 10, 18665.

Dr. Daria Kopylova

Bolometric response



- high TCR up to -2.8% K^{-1} at liquid nitrogen temperature.
- high sensitivity in a wide IR range 3-50 μm (3.3 times higher at RT and 33 times at 100 K),
- smooth spectral characteristics of IR absorption and relatively low noise level and ultrafast (Б3 ms).

Kopylova, Nasibulin *et al.* (2018) *Nanoscale* 10, 18665.

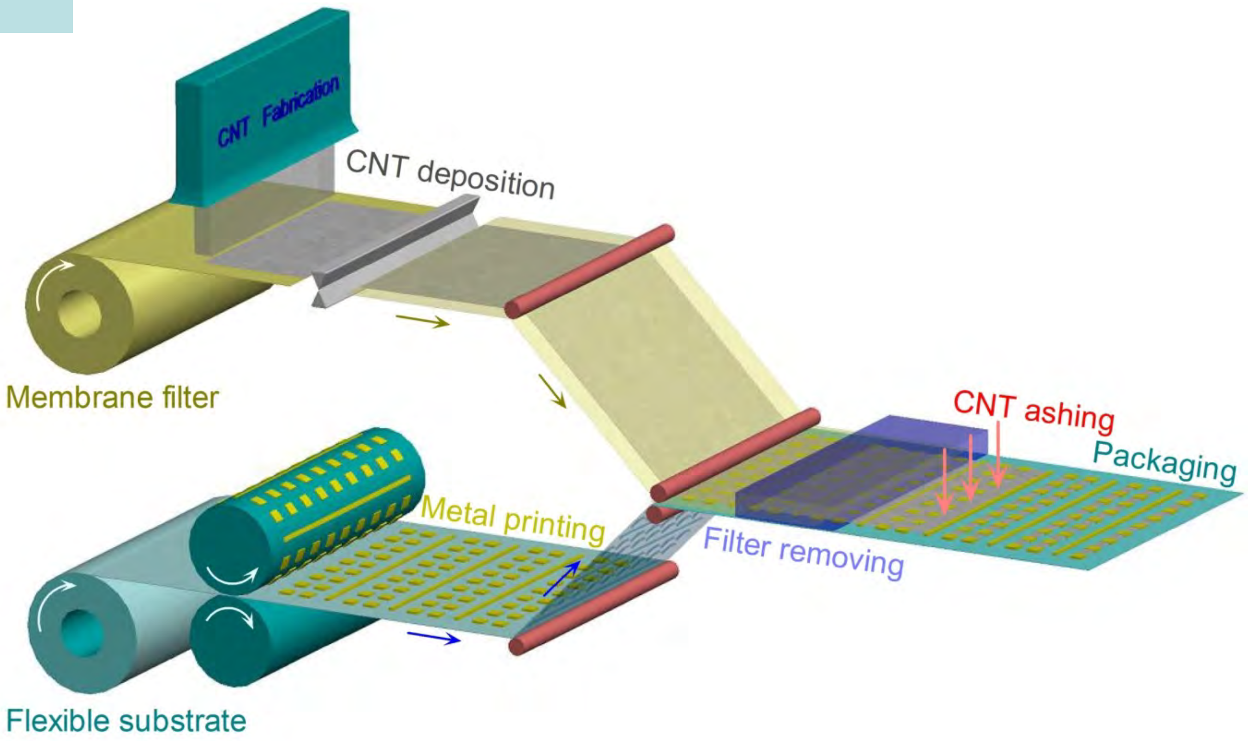
Conclusions

Result:

- High-performance CNT films
- CNT field effect transistors

Technique:

- Low-temperature
- Non-vacuum
- Simple-fast-process
- Low-cost



Future:

- A way to our ambitious goal: large-scale, low-cost, and flexible electronics manufacturing

Sun, Timmermans, Tian, Nasibulin, Kauppinen, Ohno *et al.*, *Nature Nanotechnology* (2011) **6**, 156.

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Dr. Patrik Laiho
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Welcome to LABORATORY OF NANOMATERIALS!

Thank you! Any questions?