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.
Single-walled carbon nanotubes: from synthesis to applications

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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 °C while polymers degrade below 150 °C
• Half as dense as aluminum
• 25 times stronger than steel
Some applications of CNTs

- Electronics and photonics
  - Field transistors, light emitters and detectors, oscillators, electromechanical resonators, memory, electrodes, photovoltaics, electrochromic devices, saturable absorbers

- Functional and structural materials
  - Composites, microscopy probes, MEMS, brushes, superhydrophobic coatings

- Medicine
  - Sensors, cancer-targeted radiation absorbers, electrophysiological sensors, scaffolds, drug delivery, fluorescence-based visualization

- Energy
  - Batteries, supercapacitors, fuel cells, hydrogen storage, catalytic and electrochemical processes
More than 100 companies around the world today are manufacturing carbon nanotubes and this number is expected to increase to more than 200 within the next five years, while there are more than 1,000 companies and institutions that are actively engaged in CNTs Research and Development (R&D).

Olli Pitkanen’s thesis
CNTs+applications
(Oulu University)
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!

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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

1. CO₂ or N₂
2. MFC
3. N₂ 12 L/min
4. Q = 0-20 cm³/min
5. CO
6. water
7. Filter
8. ESP
9. FT-IR
10. dilutor
11. furnace

Ferrocene-based method

1. CO
2. 300 cm³/min
3. water circulation
4. ferrocene cartridge
5. water circulation
6. MFC
7. power supply
8. CO₂ or N₂
9. 400 cm³/min
10. N₂ 12 L/min
11. N₂/H₂ or H₂
12. 400 cm³/min
13. FT-IR
14. ESP
15. Filter
Experimental setup: Ferrocene Reactor

Ferrocene molecule: $\text{FeC}_{10}\text{H}_{10}$

$$\text{CO} + \text{CO}^\text{Fe} = \text{C(s)} + \text{CO}_2$$

Novel dry, direct deposition method for electrode manufacturing

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 $T_{\text{set}}$

2.33 eV
UV-Vis-NIR absorption spectra and corresponding fitted diameter diagrams of the SWCNT as a function of $T_{\text{set}}$

PREDICTION OF SYNTHESIS OUTCOME
Artificial Neural Network

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Applications of flexible, transparent and elastic electrodes

Future flexible devices based on transparent conductors and thin film transistors

Real time high-quality, human body wellness monitoring system

http://www.concept-phones.com/?s=flexible
Requirements to materials for flexible and stretchable electronics

Fabrication on plastic substrate

Room temperature process

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, Cd₂SnO₄...) 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

CNB film on 23 μm, 50μm and 130μm PET substrates bent 180° over a 2 mm radius
State-of-the-art of transparent electrodes based on CNTs

- **2010**: $R_{90} = 108 \, \Omega/\text{sq.}$ (Kaskela et al. *Nanoletters* **10**, 4349)
- **2011**: $R_{90} = 84 \, \Omega/\text{sq.}$ (Nasibulin et al. *ACS Nano* **5**, 3214)
- **2015**: $R_{90} = 65 \, \Omega/\text{sq.}$ (Mustonen et al. APL **107**, 143113)
- **2018**: $R_{90} = 42 \, \Omega/\text{sq.}$ (Tsapenko et al. *Carbon* **130**, 448)
- **2019**: $R_{90} = 39 \, \Omega/\text{sq.}$ (Khabushev et al. *JPCL* **10**, 6962)
- **2019**: $R_{90} = 17 \, \Omega/\text{sq.}$ (Rajanna et al. (2019) *Nano Energy*, 104183)

**Graphical Representation:**
- ITO on flexible substrate
- Transmittance (%) vs. Sheet resistance ($\Omega/\square$)
- Different types of CNT-based transparent electrodes are plotted:
  - NO2-doped SWNTs (Nasibulin et al. 2011)
  - Pristine SWNTs (Nasibulin et al. 2011)
  - Aerosol synthesised (Kaskela et al. 2010)
  - Sorted DWCNTs + SOCl2 (Green & Hersam)
  - Sorted SWCNTs + SOCl2 (Green & Hersam)
  - Pristine SWCNTs (Green & Hersam)
  - Arc tubes (Geng & Lee)
  - Laser tubes (Geng & Lee)
  - HiPco tubes (Geng & Lee)
  - Hecht et al. 2011 (supercritical)
Machine learning: Support Vector Regression

T = 854 °C
CO₂: 0.93

Khabushev, Nasibulin et al. Journal of Physical Chemistry Letters 10, 21, 6962
Applications:
OLEDs and capacitive touch sensors

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


Jeon, Nasibulin et al. JACS, 2015, 137, 7982
Solar cells based on amorphous Si and SWCNTs

Efficiency of the cell: 8.8%

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

- Substrate
- Dielectric
- Catalyst particles
- Carrier Gas
- Carbon Source
- Controlled Aerosol Reactor Conditions (High T)
- Patterned photoresist
- Carrier Gas

Top-gate structure on polymer
Thin film transistors based on SWCNTs

Sun, Timmermans, Tian, Nasibulin et al., Nature Nanotechnology (2011) 6, 156.
Thin film transistors based on SWCNTs

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

Sun, Kaskela, Nasibulin et al., Nature Communications 4, 2302 (2013).
Two approaches for fabrication of stretchable electrodes

Hybrid materials: hydrogel/SWCNTs

Application of hydrogel/SWCNT structures as active components

Application of hydrogel/SWCNT structures as passive electrodes

Fibers of SWCNTs

SWCNT thin film about 80nm on filter

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

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

Maria Goncharova

Mechanical and electrical properties

- Tensile strength around 400 MPa, Density around 0.2g/cm³,
average elongation at brake 25%
- Conductivity with 4 contact method around 400 S/cm
- Conductivity of doped fibers with AuBr3 - 2300 S/cm

Supercapacitor

Flexible and transparent

Kanninen et al., Nanotechnology 27 (2016)

Flexible, transparent and stretchable

Gilshteyn et al., RSC Adv. 6, 93915 (2016)
Gilshteyn et al., Nanotechnology 29(32), 325501 (2018).
Ionic liquid gating

Experimental setup

Light

Quartz

SWCNT (WE)

Ag (Ref)

Au (CE)

ionic liquid

Potential

Solvated ions

Diffuse layer

Electrode

Separator

Distance

outer Helmholtz plane

$R_t \gg R_{CNT}$

$U_{out}$

$U_{in}$
Tailoring electronic structure by IL gating

Dr. Daria Kopylova

Kopylova et al. 2020 Carbon 167, 244

$R_{90} = 50 \text{ Ohm/sq.}$
Electrical gating to control pulse generation regime

Dr. Yury Gladush

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

Femtosecond fiber laser development

Electrical control of nonlinear optical properties of carbon nanotubes:
- Laser pulse generation
- Wavelength conversion

Fabrication of freestanding SWNT films

a) 1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11.

Asibulin 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


Romanov et al. (2019) *Nanoscale Horizons* 4, 1158.
Flexible thermoacoustic generator based on SWCNTs

State-of-the-art performance

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

- high TCR up to -2.8% K\(^{-1}\) at liquid nitrogen temperature.
- high sensitivity in a wide IR range 3-50 \(\mu\)m (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 (\(\leq 3\) ms).

Conclusions

High-performance CNT films

CNT field effect transistors

Technique:

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

Result:

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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Thank you! Any questions?