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transparent and flexible pH sensor

nt06 june 18 – 23, 2006, nagano

outline

I. preparation and performance of transparent and flexible cnt networks
II. preparation of transparent and flexible cnt/polyaniline pH sensors
III. performance
    a. optical pH response
    b. potentiometric pH response
IV. quick summary

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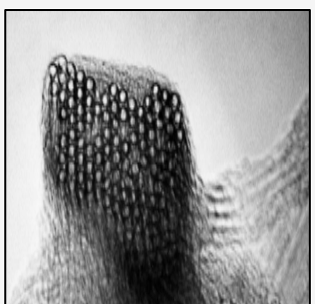
preparation of cnt suspension

1. raw material

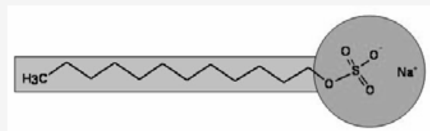
sticky, dusty, maybe toxic,
not soluble.



strong tendency to bundle
(picture from Smalley group, I guess)

2. processing

suspending in aqueous
solution of a surfactant
with aid of ultrasound.

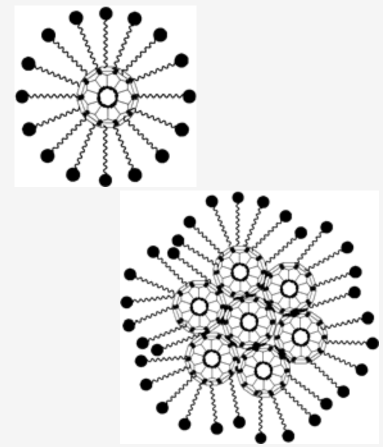


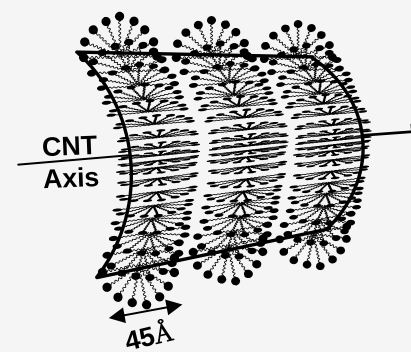
1% sodium dodecyl sulfate (sds)

+ ultrasonic treatment

3. stable cnt suspension

surfactant forms Micelles on both
cnt bundles and individual CNTs,
yielding in a stable suspension.

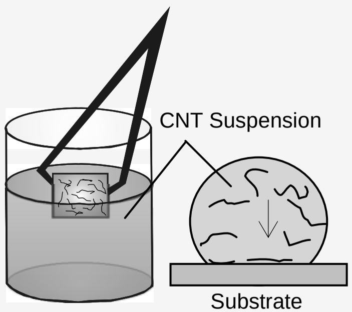




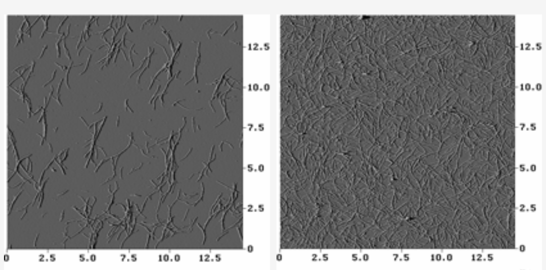
alignment of sds on cnt surface
(C. Richards et al., Science 300, 775, 2003)

preparation of thin cnt networks

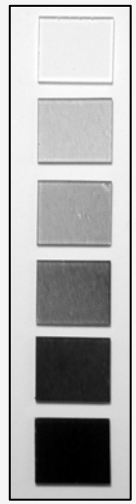
1a) adsorption

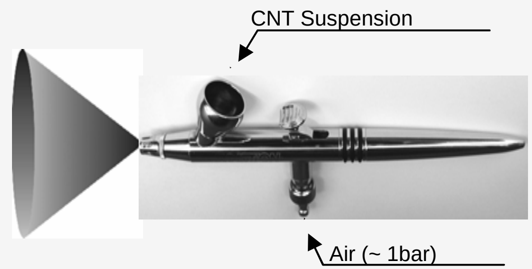


- thin films only
- homogenous covering

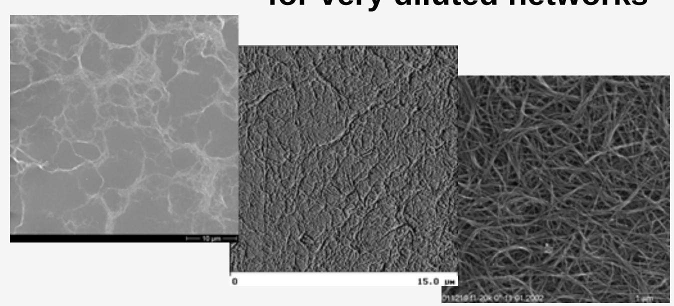


1b) spraying





- large area
- all densities
- less homogenous
  for very diluted networks

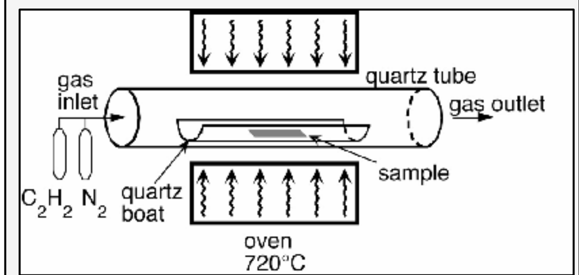


1c) removing surfactant

a) simple procedure by
dipping sample into pure water…

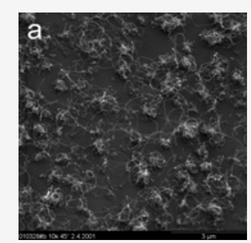
b) … and blowing dry.

2) cvd growth



- thin films only
- sophisticated process
- requires high temperature

=> not suitable for
transparent and flexible substrates



<u>cnt networks for flexible conductive coatings</u>

flexibility test: sheet conductivity remain even after heavy mechanical treatment

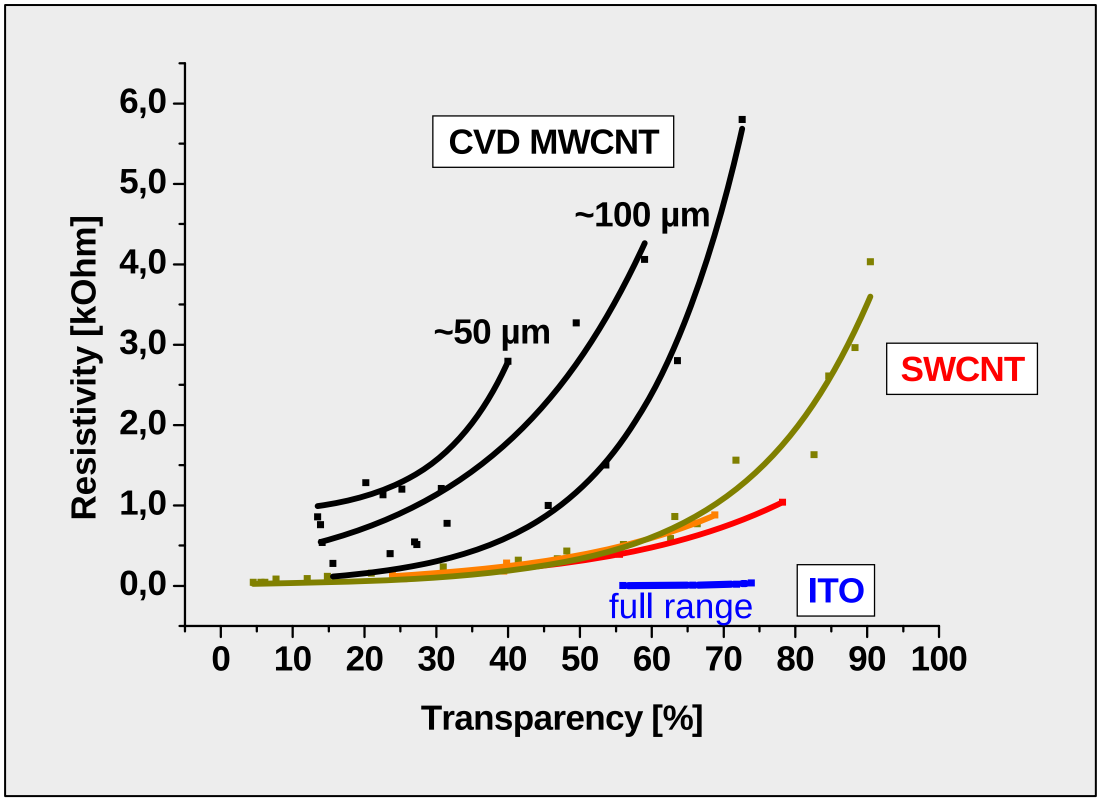
<u>this particular sample:</u>
transmission: T = 98 %
4-probe-resistivity :
before folding = 20 kOhm
after folding = 70 kOhm

note:
the multimeter is used only to demonstrate a conductivity, which is in fact a 2 probe measurement.

M.Kaempgen et al., Applied Surface Science, 252 (2) 2005, 425.

comparison of cnt material

sheet resistivity vs. transmission



conclusions

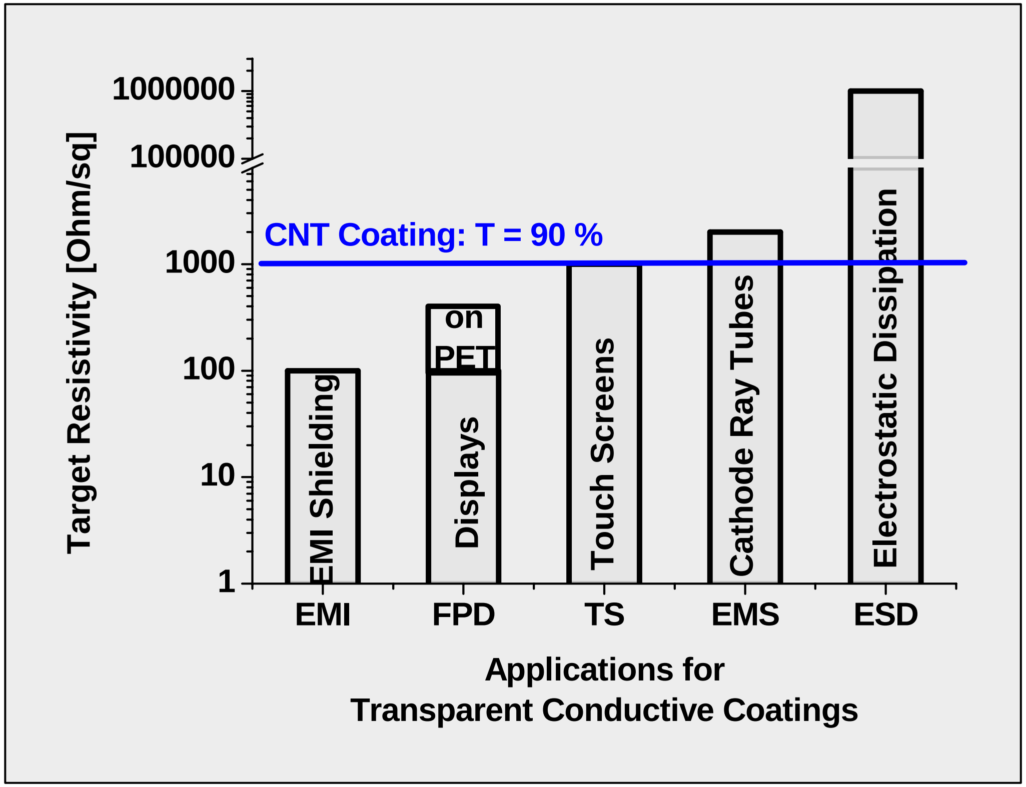
- **swcnts are favorable over mwcnts**
- **the longer the better (fewer tube/tube contacts)**
- **performance of ito cannot be reached currently**

M.Kaempgen et al., Applied Surface Science, 252 (2) 2005, 425.

potential applications

=> cnt networks combine flexibility, transparency, and sufficient conductivity.
They already fulfill the requirements for various applications where the high performance of ito is not needed.

potential applications



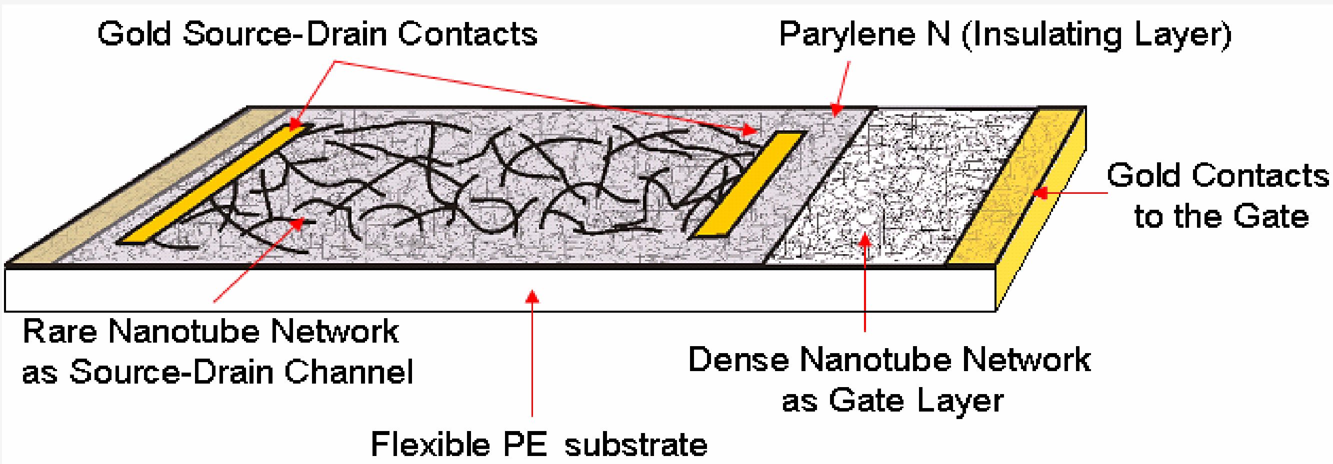
also, ito replacement demonstrated successfully in

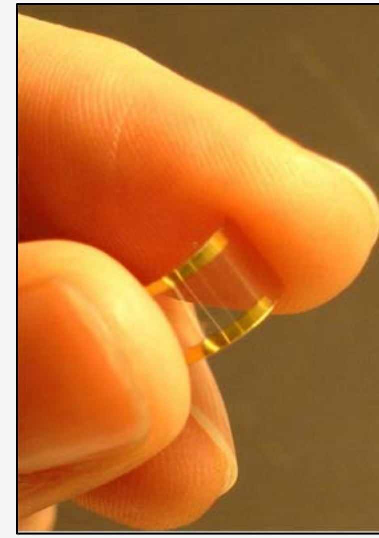
a) solar cells
e.g. *A.D. Pasquer et al., APL, 87, 203511, 2005*

b) oleds
e.g. *C.M. Aguirre et al., APL, 88, 183104 ,2006*

M.Kaempgen et al., Applied Surface Science, 252 (2) 2005, 425.

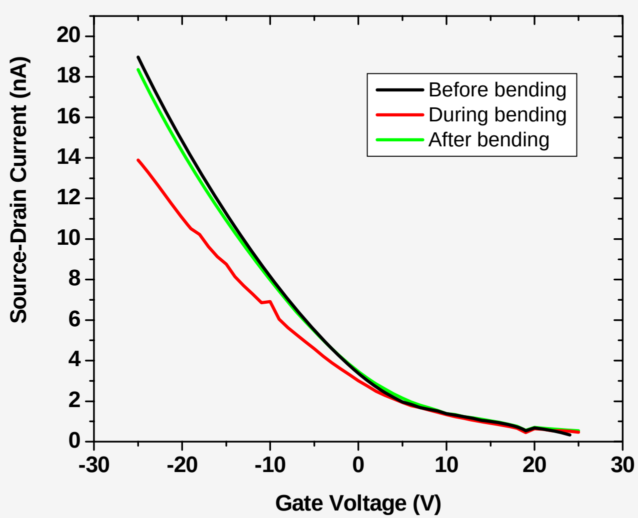
e.g. transparent flexible transistor



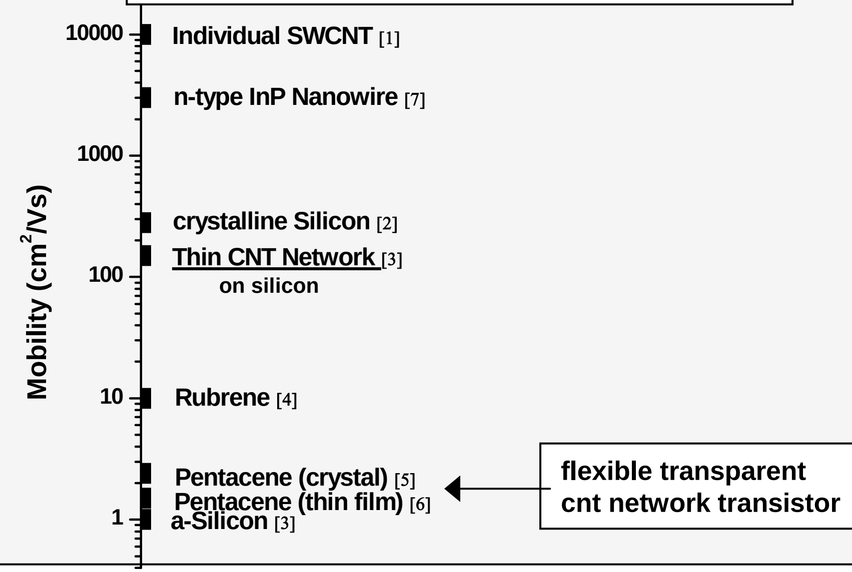


E. Artukovic, M. Kaempgen et al. *Nano Lett.* 2005, **5**, 757.

reversible response upon bending



mobility is competitive to organic TFTs



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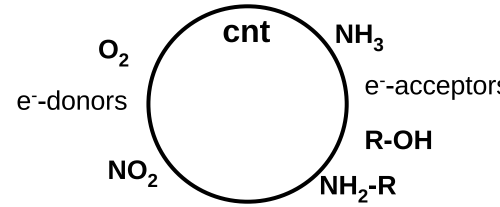
strategies for cnt sensors

The electronic properties of in particular semiconducting CNTs depend strongly on the interaction with the environment (adsorbed molecules, substrate).
Sensing is based on interaction with electron donors/acceptors but is not selective for pure CNTs => Surface modification required.

pure cnt
O_2 *(P.G. Collins, 2000)*
NH_3, NO_2 *(J.Li, 2003)* **cnt networks**
NH_2-R *(J.Kong, 2001, T)*
HO-R *(T.Someya, 2003, T)*

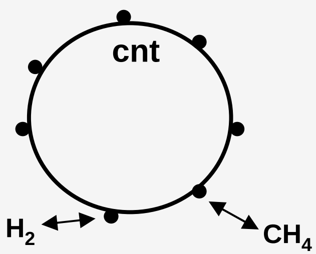


Enhanced selectivity through surface modifications:

metal coating (Pd)
H_2, *(J.Kong, 2001)*
CH_4 *(Y.Lu, 2004)*, **cnt networks**

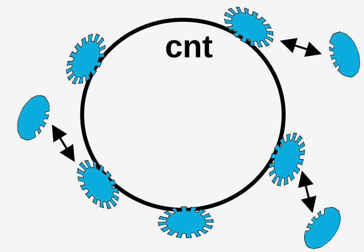
polymer coating

biomolecules
Proteins *(R.J.Chen, 2001)*
Enzymes, *(J.J.Gooding, 2003, …)*
DNA *(C.V. Nguyen, 2002)*



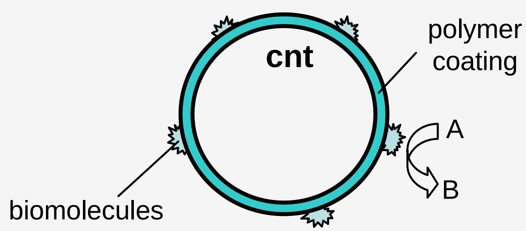
non conducting polymer
Polyethylenimine/NO_2 *(P.Qui, 2003, T)*
Polyethylenimine/CO_2 *(A. Star, 2004, T)*
Nafion/H_2O *(A. Star, 2004, T)*

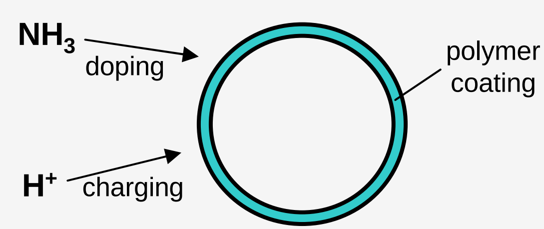
conducting polymer
Polythiophen, -pyrrol- aniline



immobilization of biomolecules
Nafion/tyrosinase/phenol *(Q.Zhao, 2005)*
Polyaniline/GOx/Glucose *(P.Soundarrajan, 2003)*
Polypyrrol/GOx/Glucose *(M.Gao, 2003)*

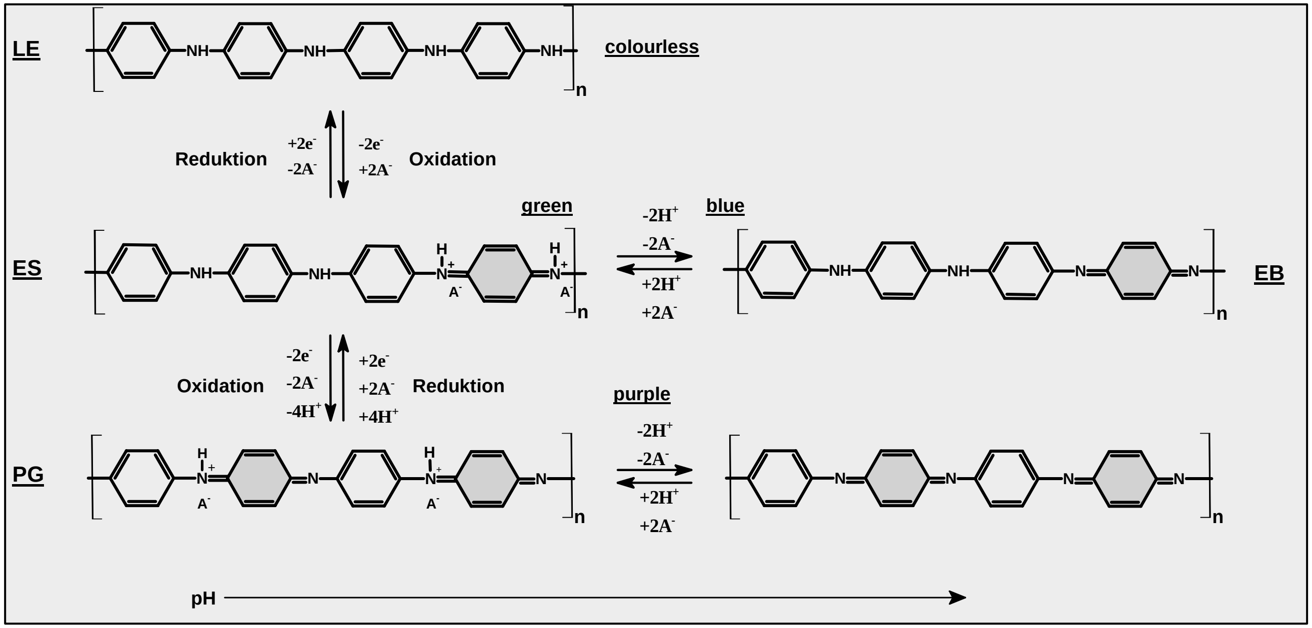
sensing material
Polyaniline sulfonic acid/NH_3,
(E.Bekyarova,2004) **cnt networks**

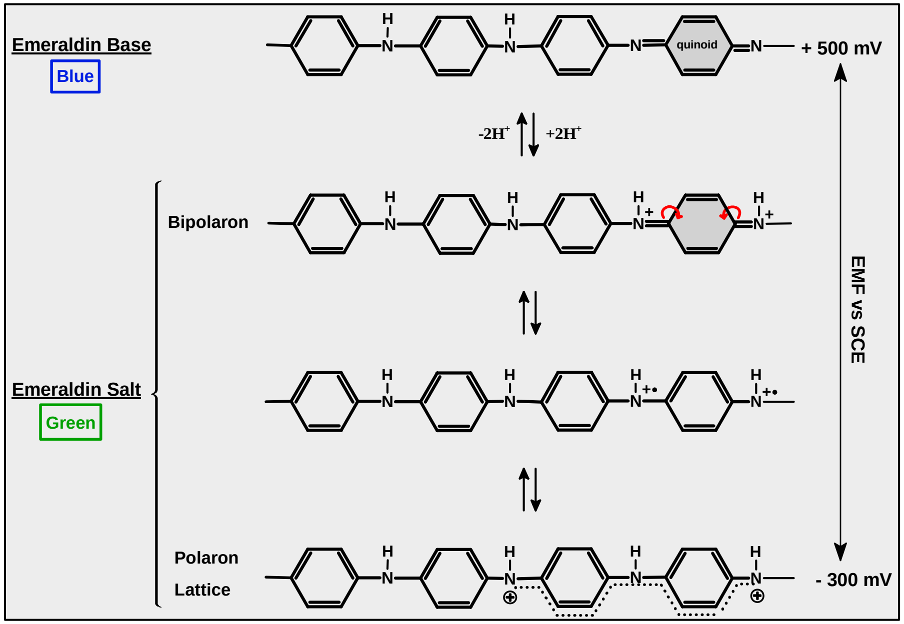




structure of polyaniline

structure, colour, and electronic properties strongly depend on pH value.





LE - Leuco-Emeraldin
ES – Emeraldin Salt
EB – Emeraldin Base
PG - Pernigraniline

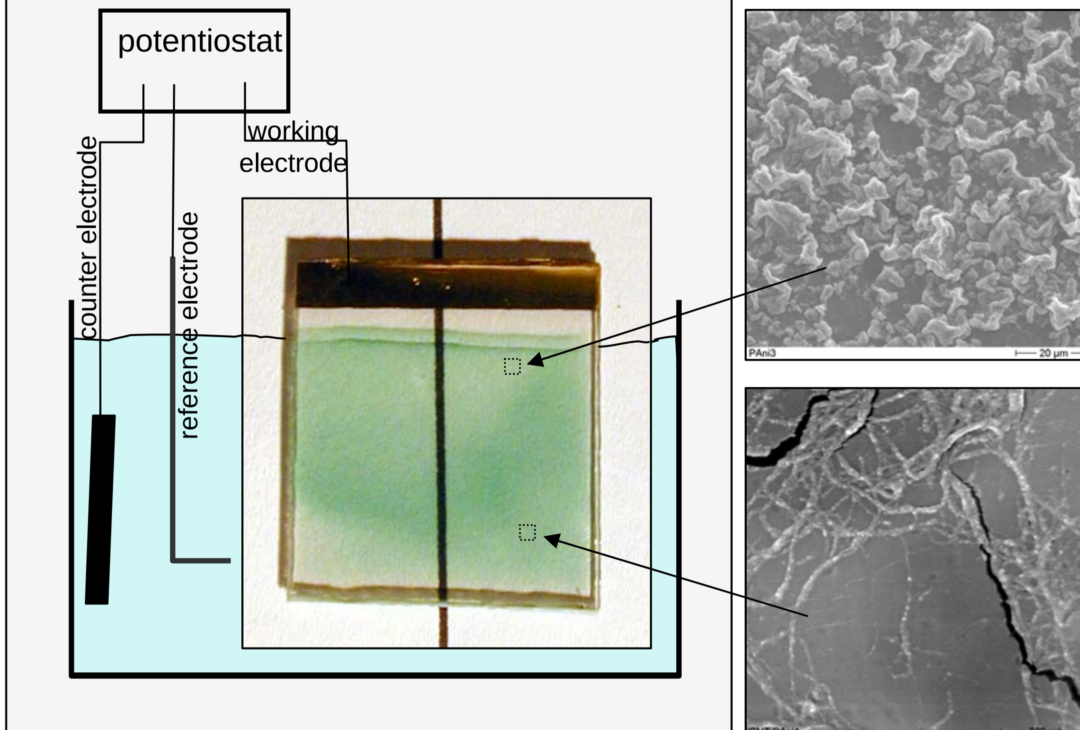
device preparation

how to put polyaniline onto cnts?

pure bulk polyaniline is greasy and sticky
=> a hardly processable material

electrochemical deposition:
polymer grows only onto the cnt networks (no deposition on the substrate)

sem characterization



thickness of polymer coating
varies with immersion depth

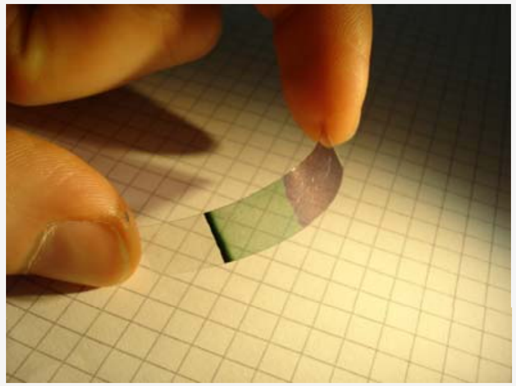
the function of the cnt network is both, electrical contact and mechanical support.

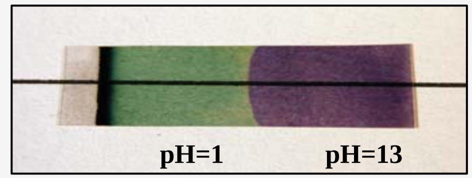
devices

simple preparation: spraying / adsorbing + electrochemical deposition
=> use of almost any user defined substrate

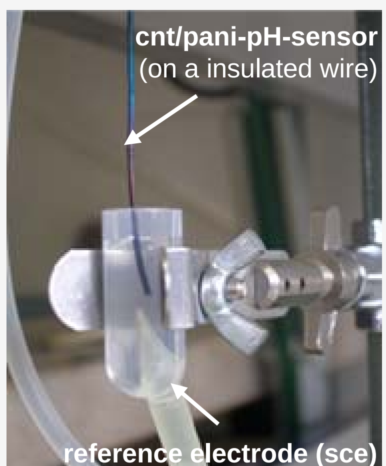
possible devices:

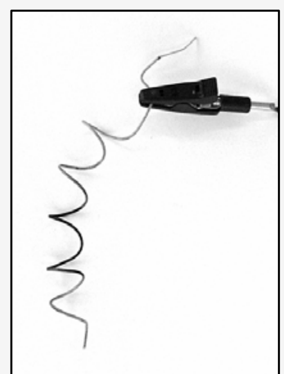
a)
Transparent films
for optical pH measurements





b)
flexible tip-like shape
for demanded potentiometric
pH measurements





<u>in contrast:</u>
commercial pH sensors made from glass are big, stiff, brittle and need more volume of the liquid.

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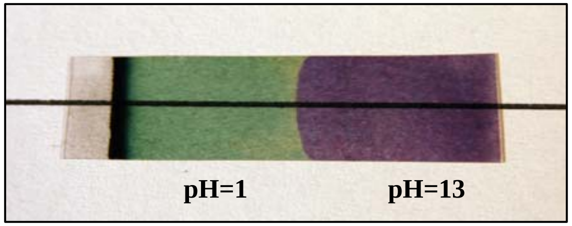
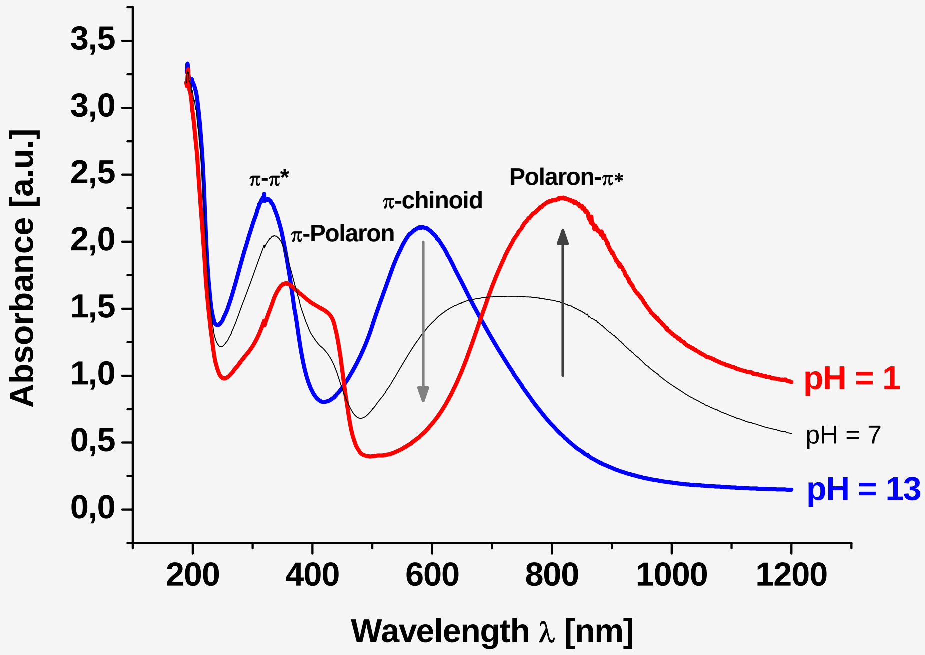
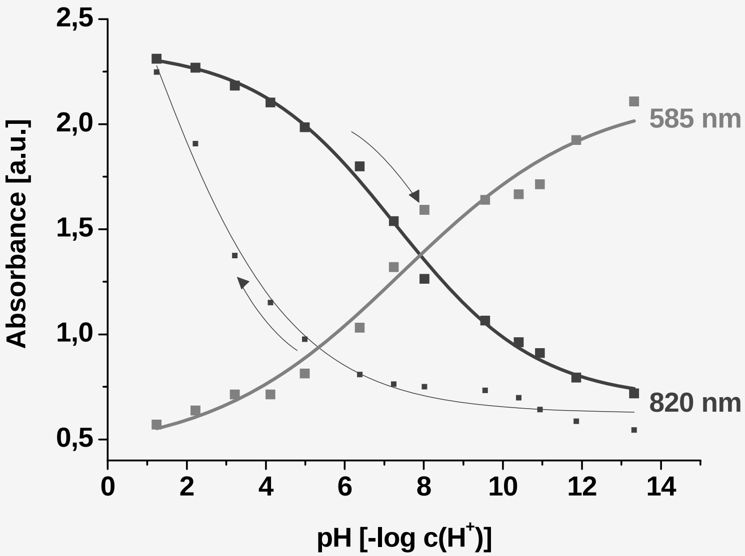
       (linearity, selectivity, reproducibility, signal stability)
IV. quick summary

optical pH response



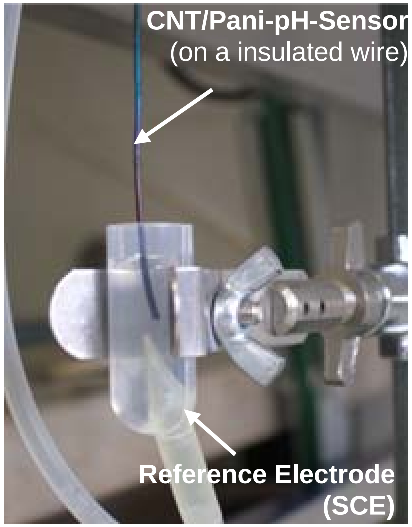
UV/VIS Spectra

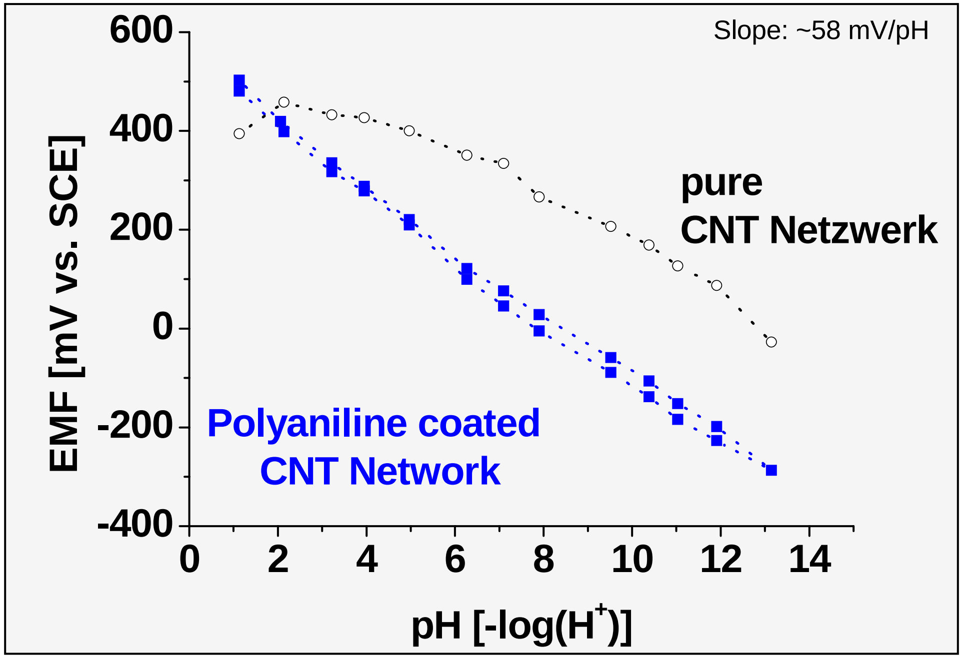




- linear response only in mild pH regime (pH ≈ 4-10)
- but huge hysteresis
=> optical pH sensing is not favorable

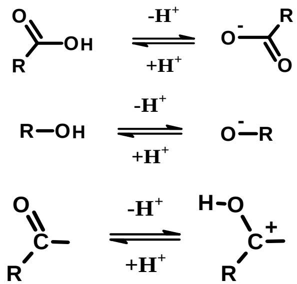
potentiometric pH response: **linearity**





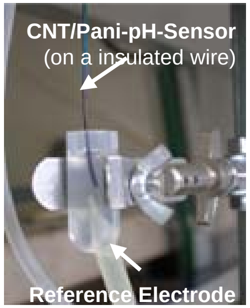
→ **excellent linearity**

pH response of pure cnt network due to functional groups

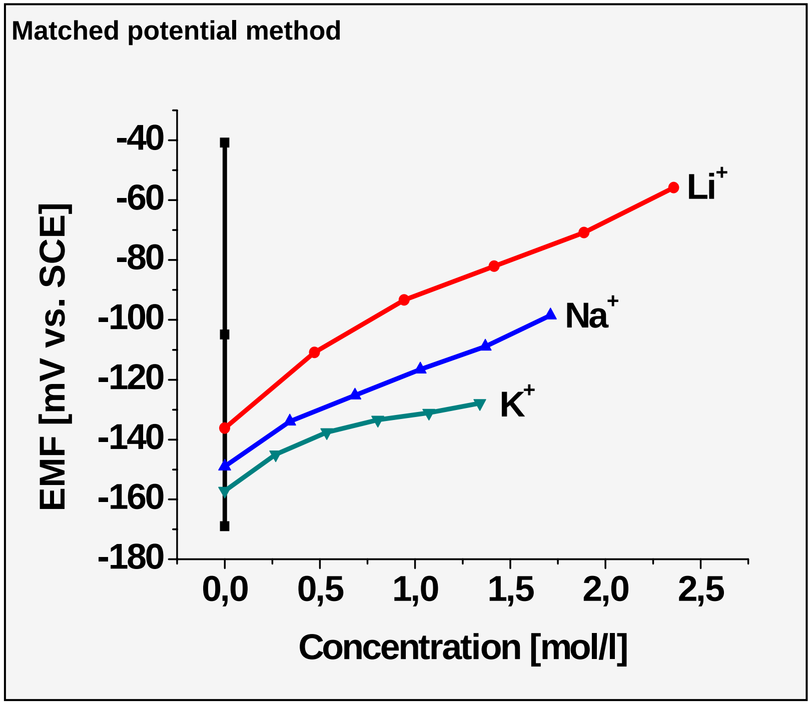


M.Kaempgen et al., Journal of Electroanalytical Chemistry, 586 (1) 2006, 72-76.

potentiometric pH response: **selectivity**



possible interfering ions: Li^+, Na^+, K^+, …



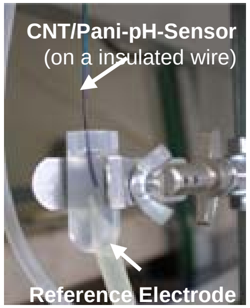
Interfering Ion M^+	Selectivity coefficient $\log(K_{H+,M+})$
Li^+	- 10,0
Na^+	- 10,4
K^+	- 10,5

a value of -10,5 means
signal for K^+ and H^+ is equal when
concentration of K^+ = $10^{10.5}$ x conc. H^+

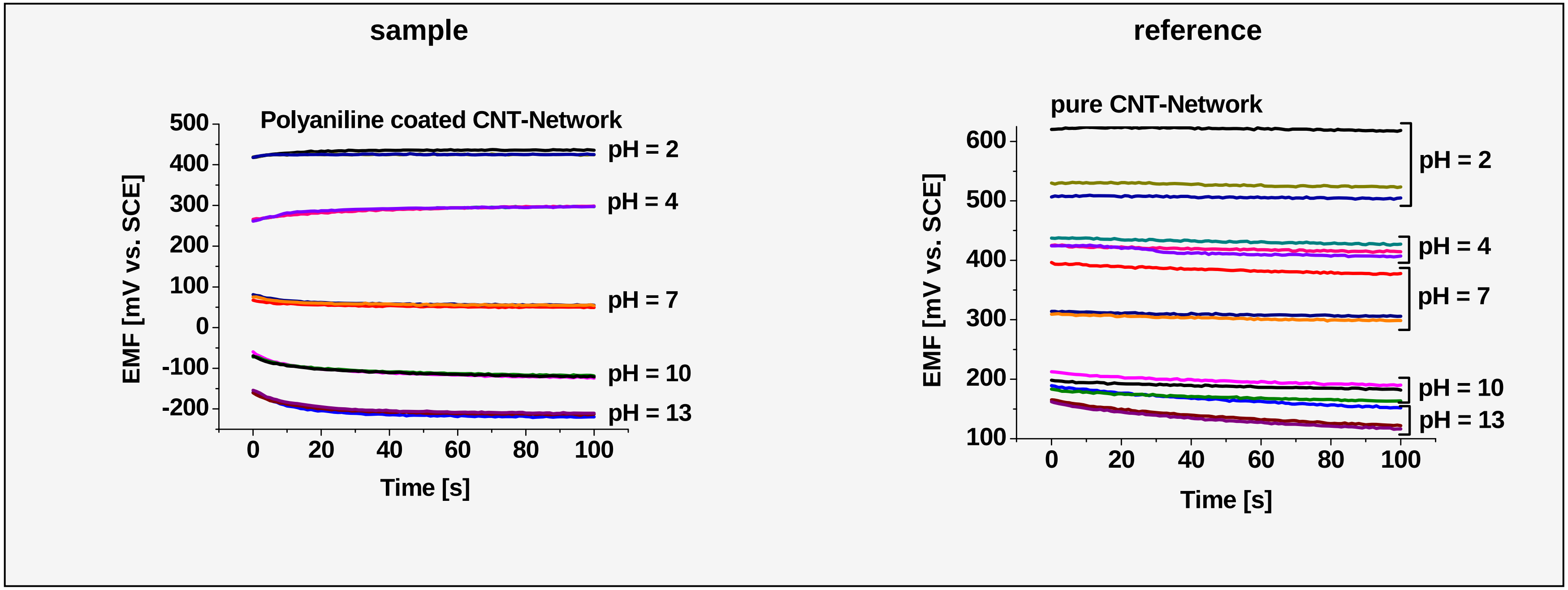
→ excellent selectivity

M.Kaempgen et al., Journal of Electroanalytical Chemistry, 586 (1) 2006, 72-76

potentiometric pH response: **reproducibility**



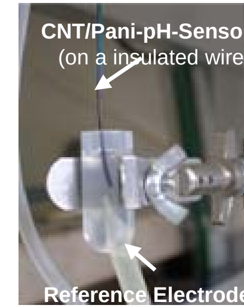
3x subsequent dipping [pH = 2 →7 →12 → 4 →10]



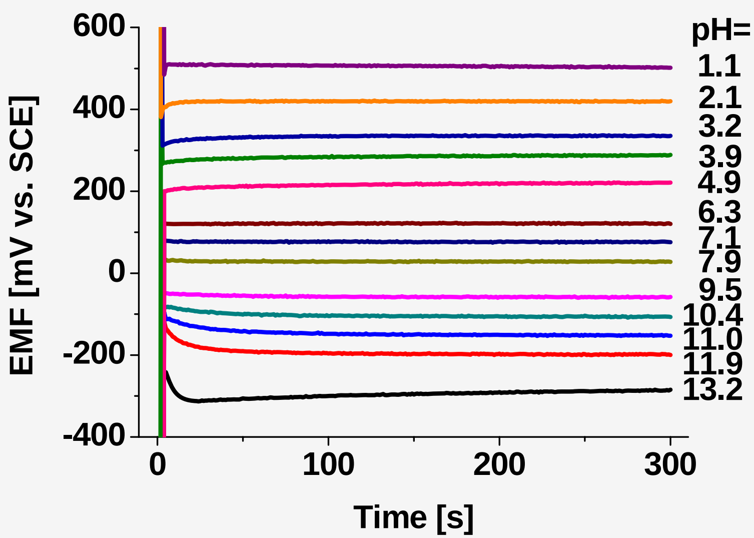
→ excellent reproducibility

M.Kaempgen et al., Journal of Electroanalytical Chemistry, 586 (1) 2006, 72-76.

potentiometric pH response: **signal stability**

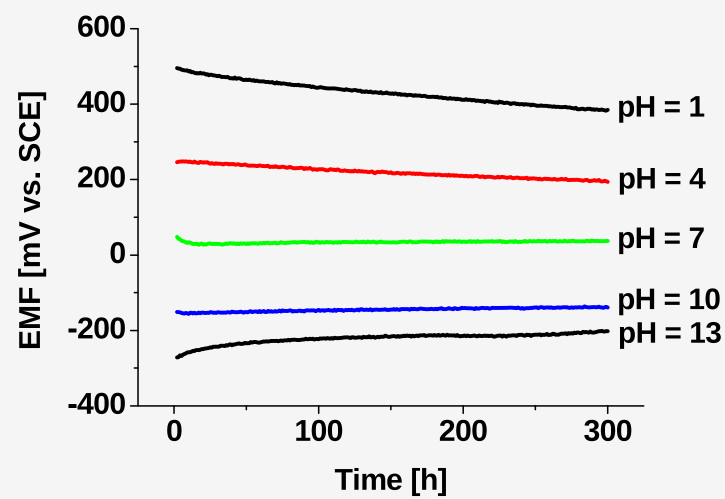


measuring 5 min:



measuring 5 hours:

drift: 2-10 mV/h

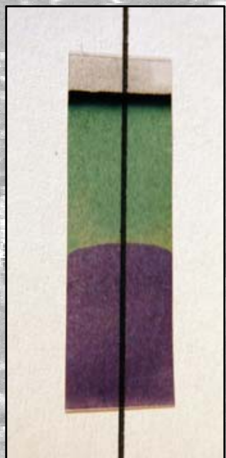


→ higher drift for extreme pH values but still good

M.Kaempgen et al., Journal of Electroanalytical Chemistry, 586 (1) 2006, 72-76.

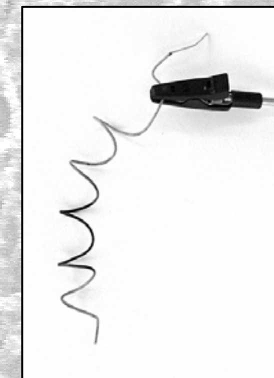
conclusion

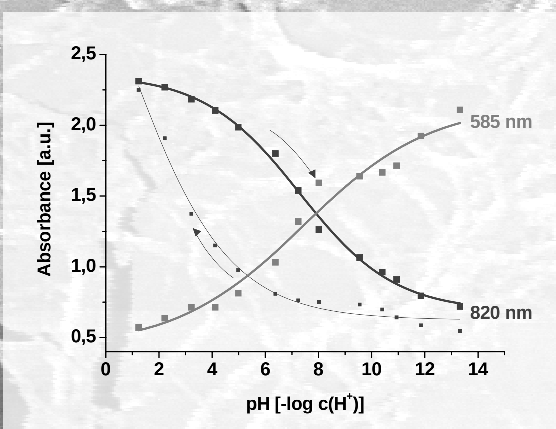
cnt / polyaniline pH sensor



- simple preparation
- use of any user defined substrate
- excellent performance
  (linearity, selectivity, stability, reproducibility)

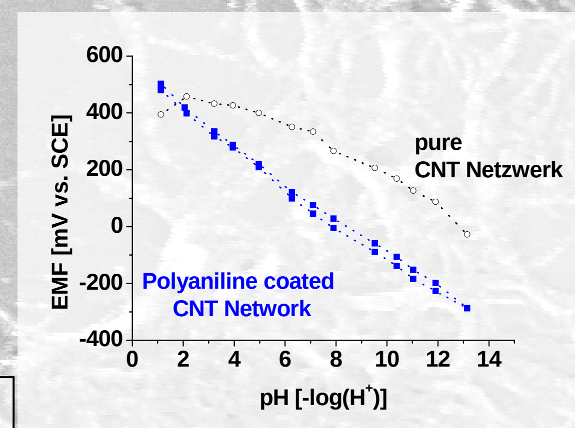
- optical and electronic investigations on various coatings possible
- for demanding applications

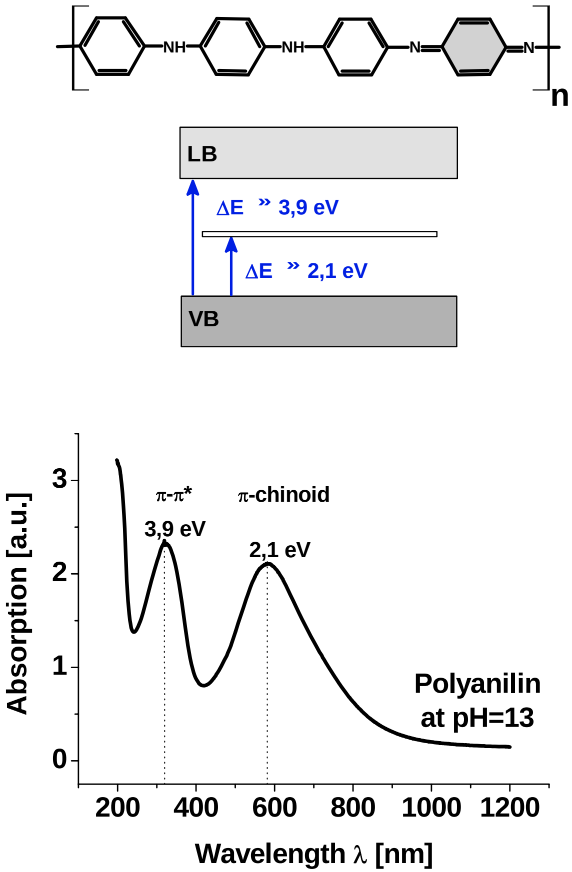


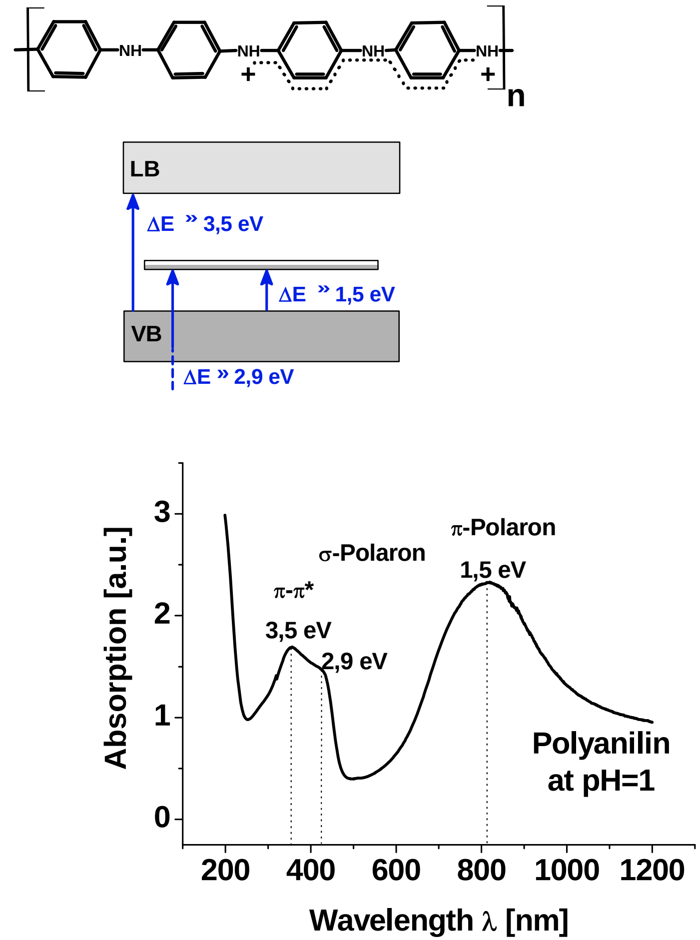


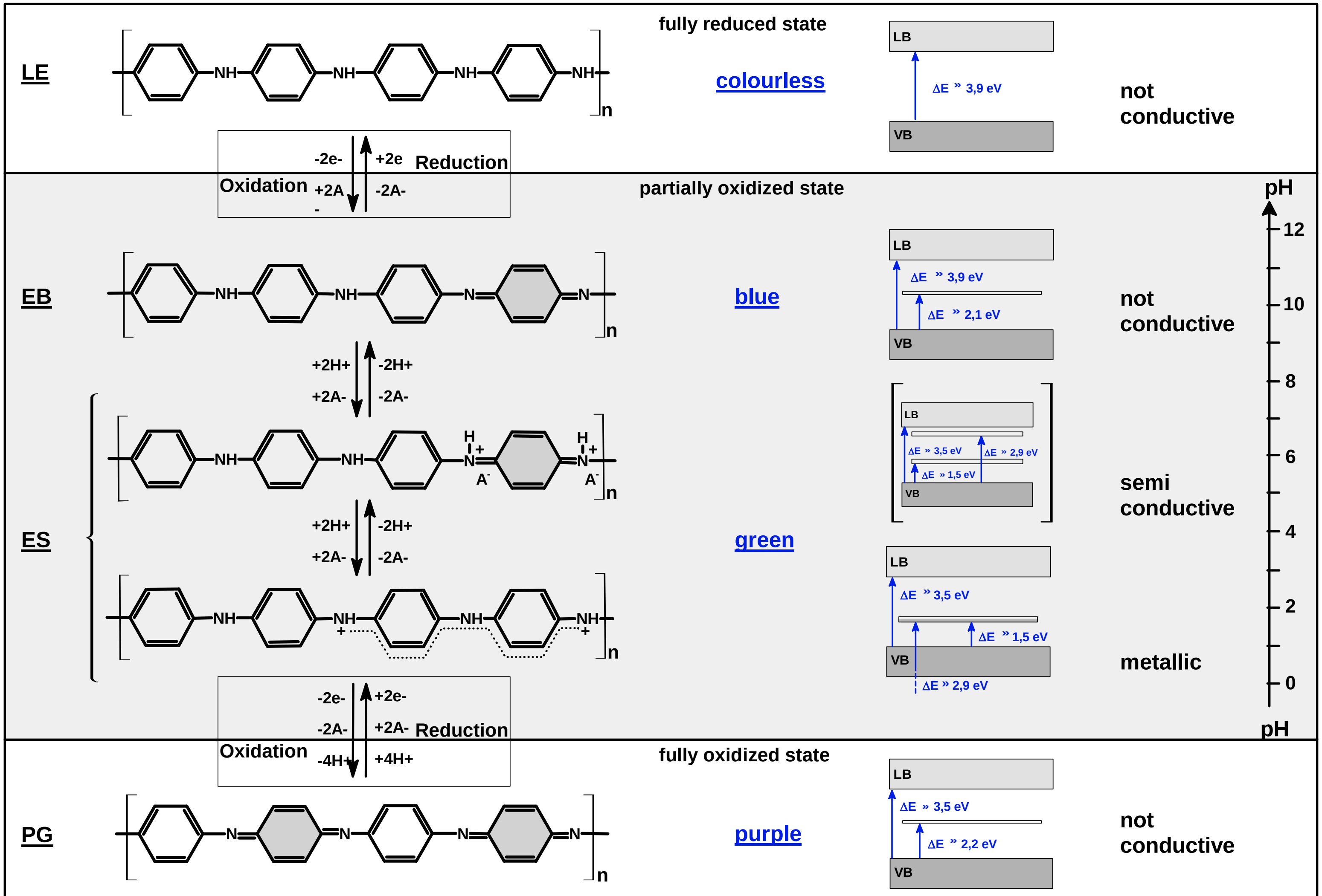
domo arigato for attention!
sayonara!

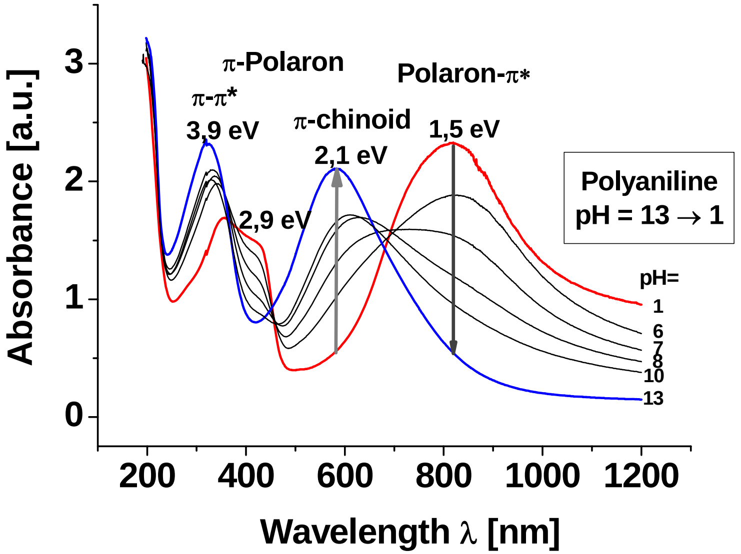
contact: m.kaempgen@fkf.mpg.de



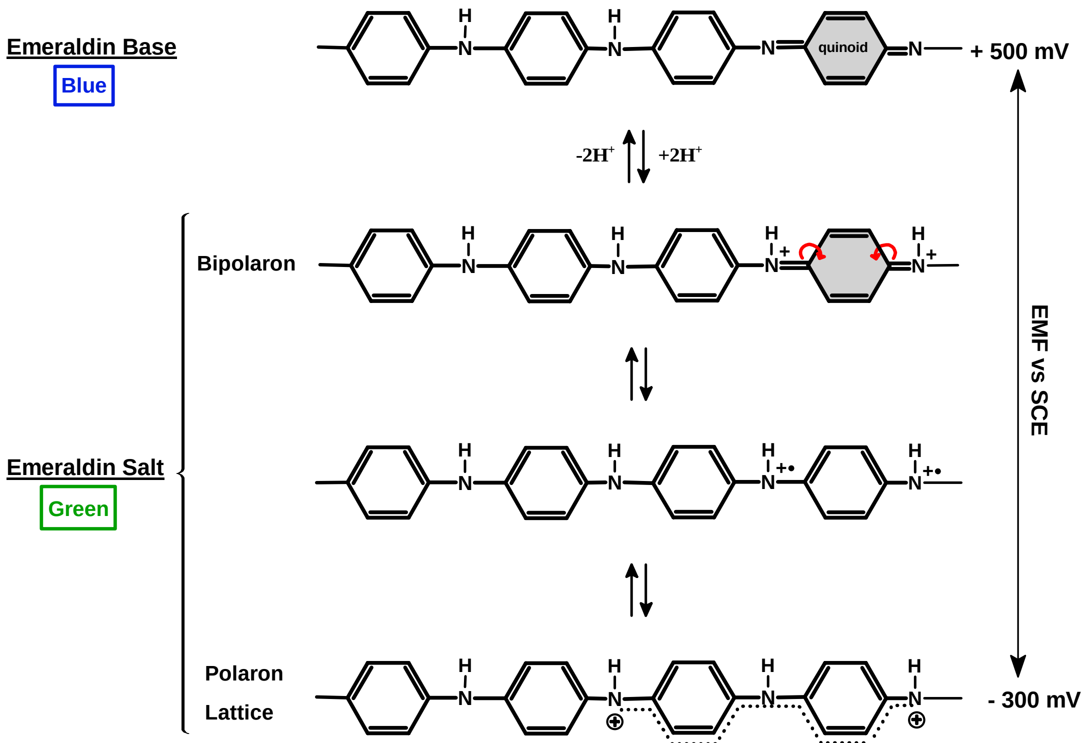

NH
NH
N
N
n
LB
ΔE » 3,9 eV
ΔE » 2,1 eV
VB
π-π*
3,9 eV
π-chinoid
2,1 eV
Polyanilin
at pH=13
Absorption [a.u.]
Wavelength λ [nm]
0
1
2
3
200
400
600
800
1000
1200


NH
NH
NH
NH
+
+
n
LB
ΔE » 3,5 eV
ΔE » 1,5 eV
VB
ΔE » 2,9 eV
σ-Polaron
π-Polaron
π-π*
3,5 eV
2,9 eV
1,5 eV
Polyanilin
at pH=1
Absorption [a.u.]
Wavelength λ [nm]
0
1
2
3
200
400
600
800
1000
1200


LE
fully reduced state
colourless
LB
VB
ΔE » 3,9 eV
not conductive
-2e-
+2e
+2A-
-2A-
Oxidation
Reduction
partially oxidized state
EB
blue
ΔE » 3,9 eV
ΔE » 2,1 eV
not conductive
+2H+
-2H+
+2A-
-2A-
ES
green
ΔE » 3,5 eV
ΔE » 2,9 eV
ΔE » 1,5 eV
semi conductive
metallic
ΔE » 3,5 eV
ΔE » 1,5 eV
ΔE » 2,9 eV
pH
12
10
8
6
4
2
0
pH
-2e-
+2e-
-2A-
+2A-
-4H+
+4H+
Oxidation
Reduction
fully oxidized state
PG
purple
ΔE » 3,5 eV
ΔE » 2,2 eV
not conductive
NH
N
A-
n



Absorbance [a.u.]
Wavelength λ [nm]
π-Polaron
π-π*
3,9 eV
2,9 eV
π-chinoid
2,1 eV
Polaron-π*
1,5 eV
Polyaniline
pH = 13 → 1
pH=
1
6
7
8
10
13

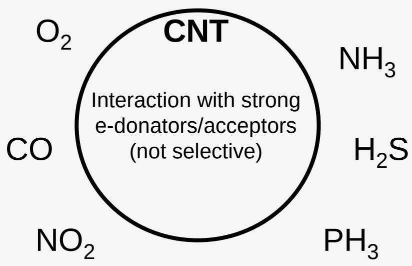


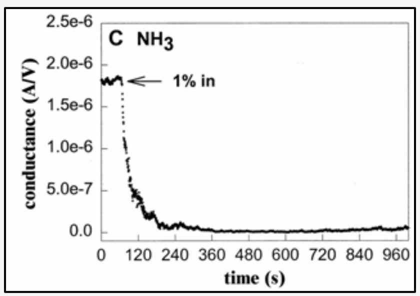
Emeraldin Base
Blue
quinoid
+ 500 mV
-2H+
+2H+
Bipolaron
Emeraldin Salt
Green
Polaron
Lattice
EMF vs SCE
- 300 mV

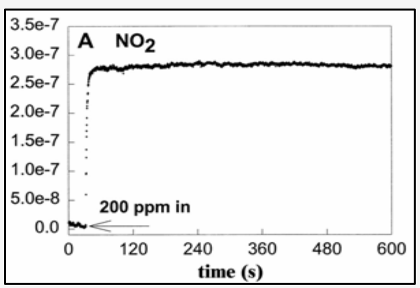
Strategies for CNT Sensors

Enhanced selectivity through …

a) Surface not modified

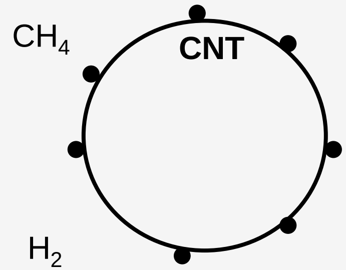


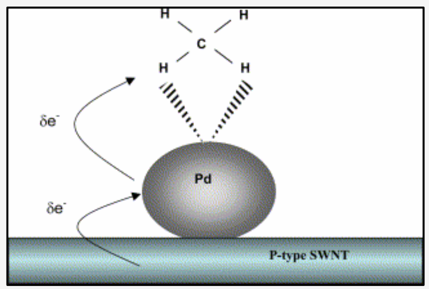




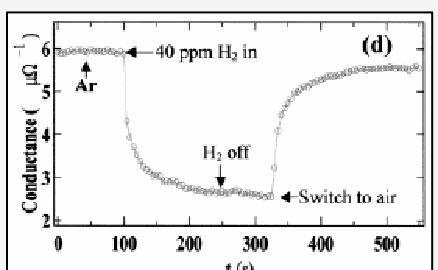
NH_4/NO_3-Sensor (not selective)
J. Kong et al.,
Science 287, 622, 2000

b) …attached metal cluster



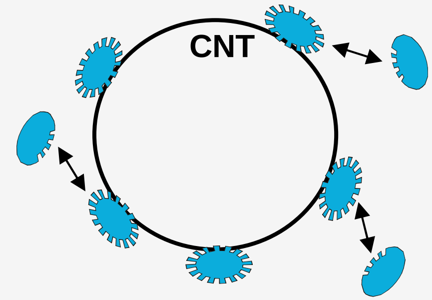


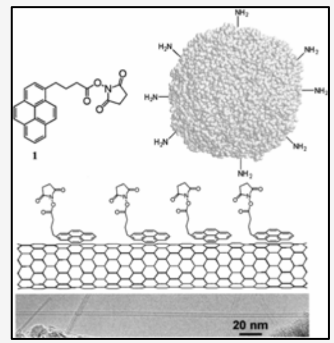
Methan Sensor (network)
Y. Lu et al
Chem. Phys. Lett.391, 344, 2004



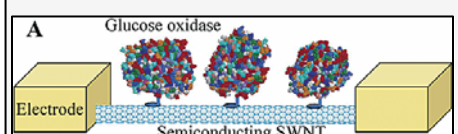
H_2-Sensor
J. Kong et al.,
Science 287, 622, 2000

c) …single (bio)molecules



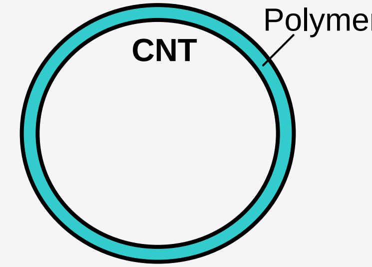


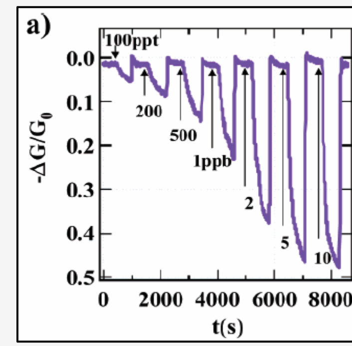
Enzym/pH-Sensor
R.J. Chen et al.,
J. Am. Che. Soc. 123, 3838, 2001



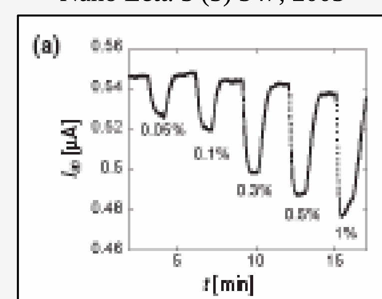
Glucose-Sensor (Transistor)
K. Besteman et al.,
Nano Lett. 3 (6) 727, 2003

d) …entirely coated surface





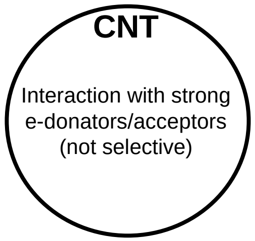
Selective NH_4/NO_3-Sensor
P, Qui et al.,
Nano Lett. 3 (3) 347, 2003



CO_2-Sensor (network)
Y. Lu et al
Chem. Phys. Lett.391, 344, 2004

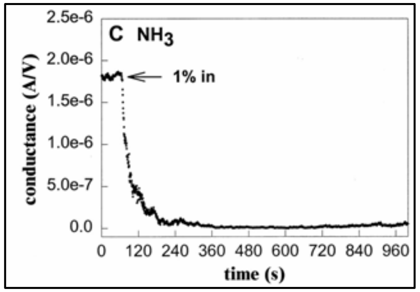
Strategies for CNT Sensors

The electronic properties of (in particular semiconducting) CNTs depend strongly on all kinds of interaction with the environment (e.g. adsorbed molecules, surface chemistry of substrate).

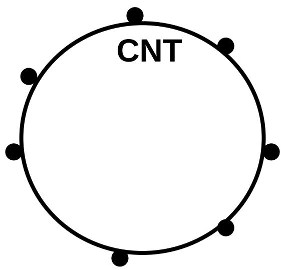


NH_3, H_2S, CO_2, PH_3, … (donor molecules)

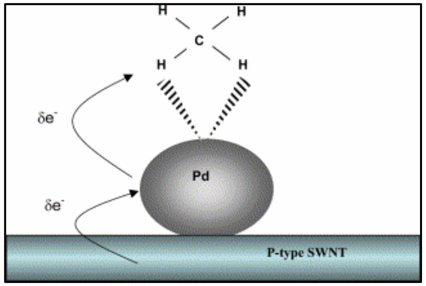
O_2, NO_2, SO_2, … (acceptor molecules)



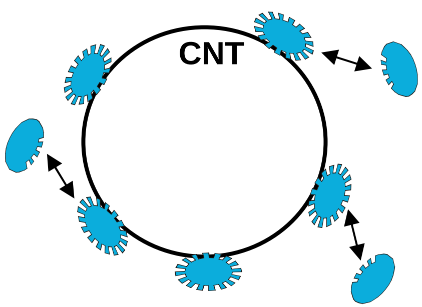
J. Kong et al., Science 287, 622, 2000



H_2, CH_4, …



Y. Lu et al., Chem. Phys. Lett.391, 344, 2004



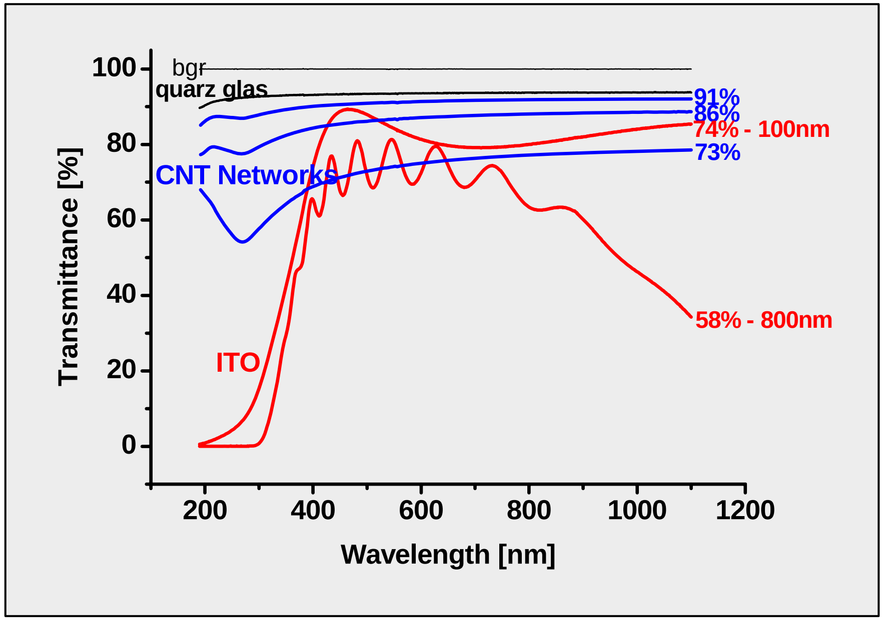
Individual CNT

Gas sensor

Individual CNT

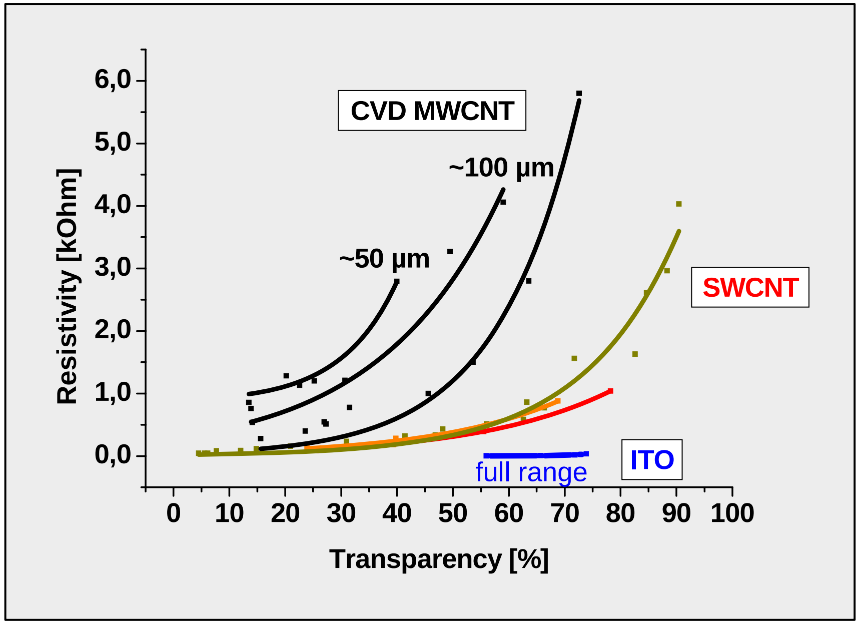
Comparison to ITO

UV/VIS Spectra



Transparency in ITO is limited
(band edge and plasma edge).

Resistivity vs. Transmission



Surface Resistance for T = 90%

- ITO : ~10 Ohm
- CNT Network : ~ 1000 Ohm

Towards a transparent and flexible <u>All CNT Network Transistor</u>

Lithographically defined CNT Network Electrodes

Line width: 10µm

Gap wide: 5µm (left)
20µm (right)