Electrical Sensing of Biomolecules based Nanomaterials and Carbon Nanotubes

Department of Chemistry
Pohang University of Science and Technology
Hee Cheul Choi

Contents

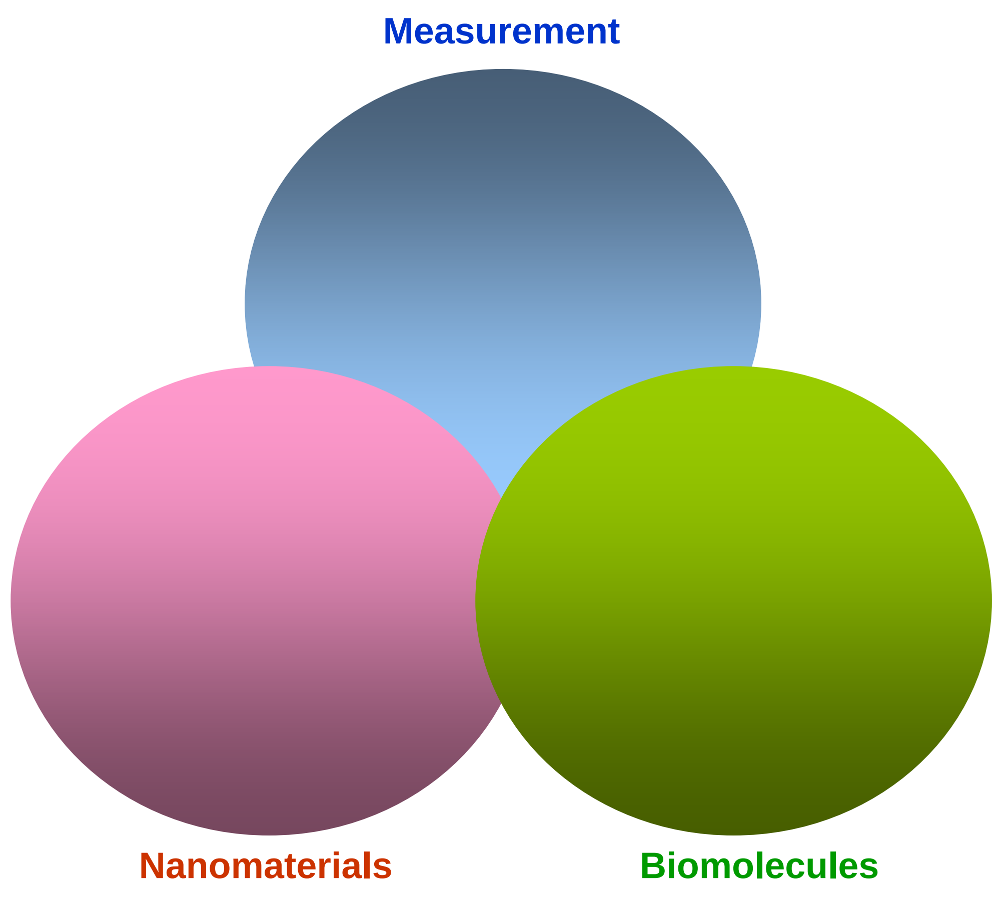
- Part /

Electrical sensing of biomolecules based on Nanomaterials

- Part //

Carbon Nanotubes and applications

Part I



Colorimetric vs. Electrical sensing

Colorimetric detection

Fast
Easy detection (even with naked eyes)
Chemistry oriented (Equipment free~)

Color source required (fluorescent tagging molecule)
Tagging for millions of unknown or known target molecules
Works well for pairs with high binding constant

Electrical detection

Requires electrical equipments
Many assumptions and unresolved phenomena to rationalize the signals
Sensitive to environment (noise, electric shock, etc)

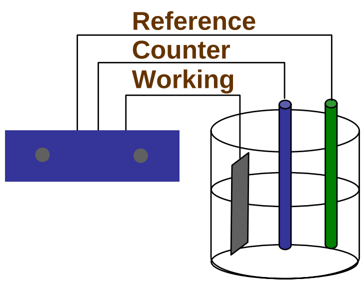
Tagging free system
May work well for the pairs with low binding constant
Fast
Applicable to "Ubiquitous" concept

Electrical sensing

Definition:

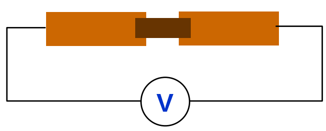
Detection chemical & biological reactions via electrical signal readout

Electrochemical



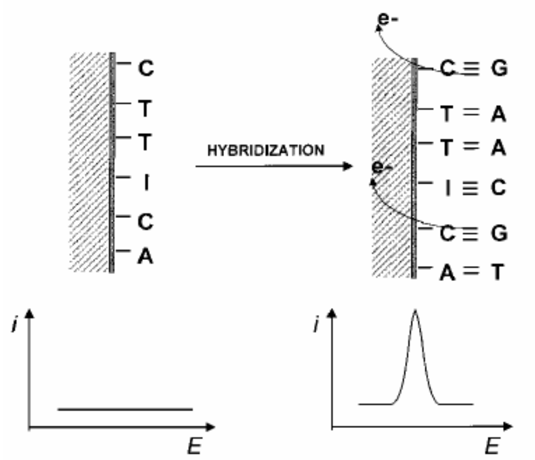
CV (cyclic voltammetry)
PV (pulse voltammetry)

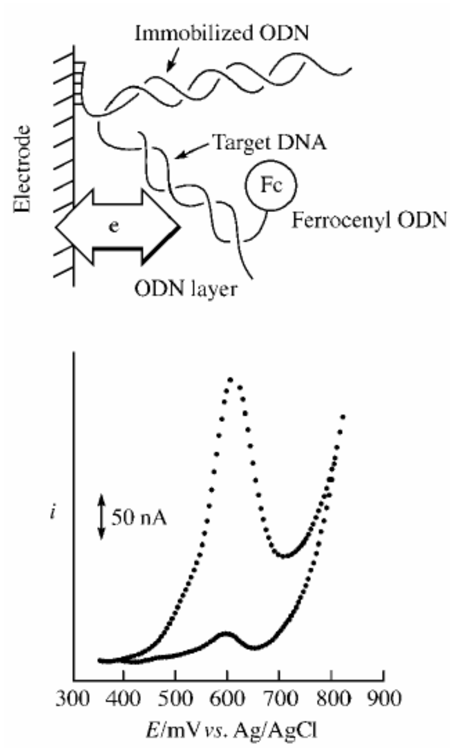
Electrical



I-V (current-bias), I-t (current-time)

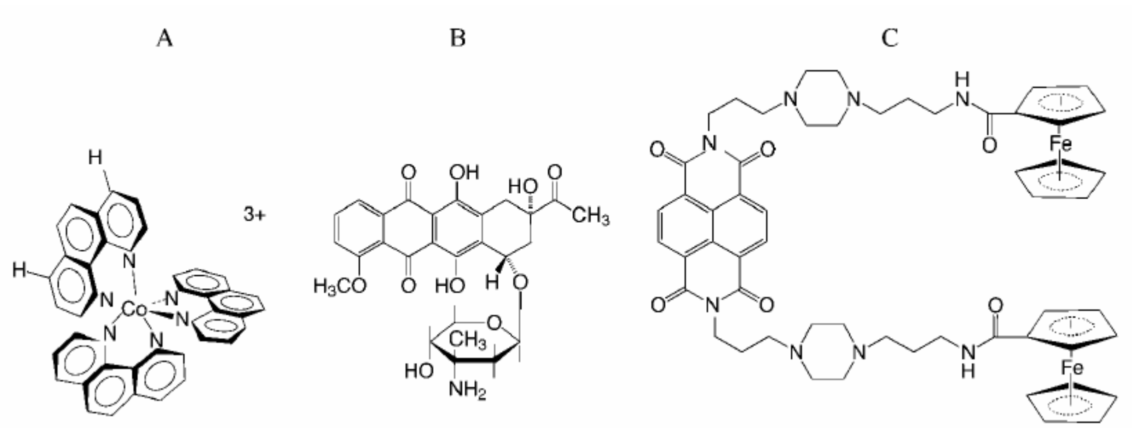
Electrochemical sensing





J. Wang, *Chem. Eur. J*. **1999**, *5*, 1681.

Signal transducer (Active redox markers)



Daunomycine

Tris(1,10-phenanthroline)cobalt(III)

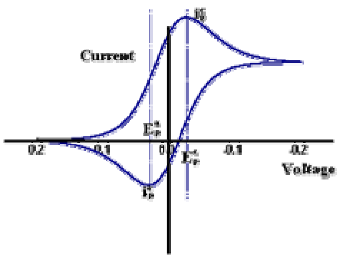
Ferrocenyl naphthalene diimide

J. Wang, *Chem. Eur. J*. **1999**, *5*, 1681.

Cyclic voltammogram and pulse voltammogram

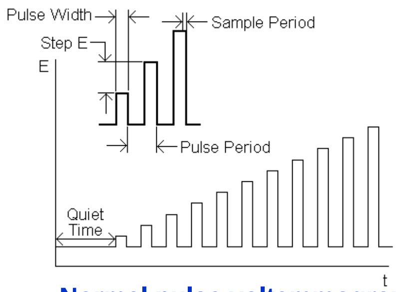
CV: one of the most conventional techniques to analyze redox potentials of complexes

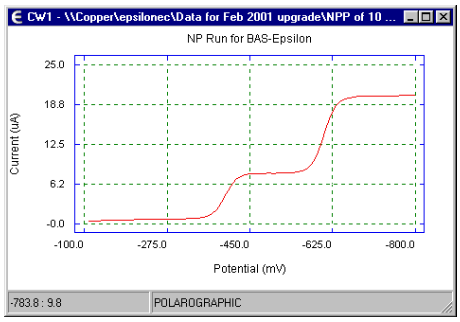
$$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$$



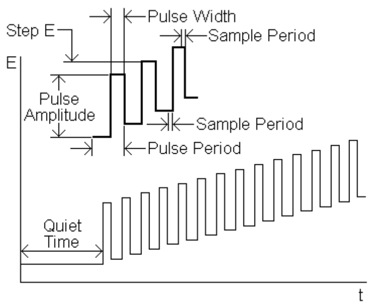
Why pulse? – to discriminate charging current and faradic current (diffusion controlled) utilizing the difference in decaying time

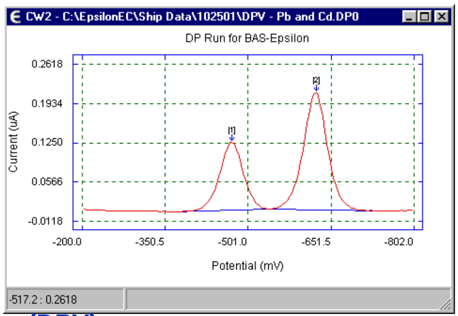
t decay of cc << t decay of fc





Normal pulse voltammogram (NPV)

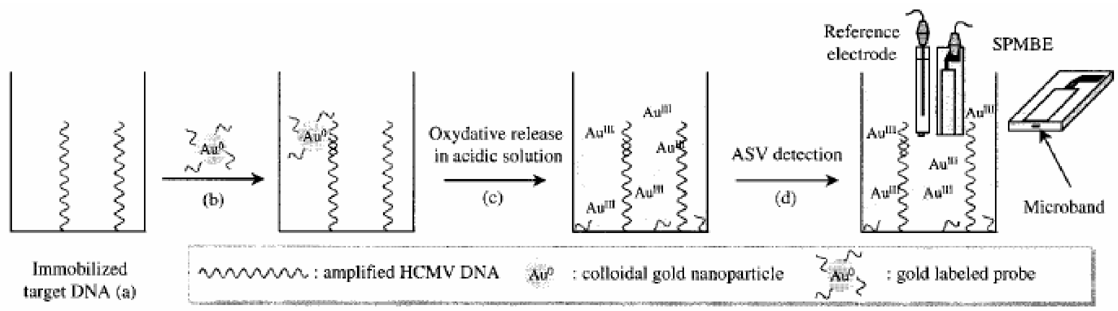




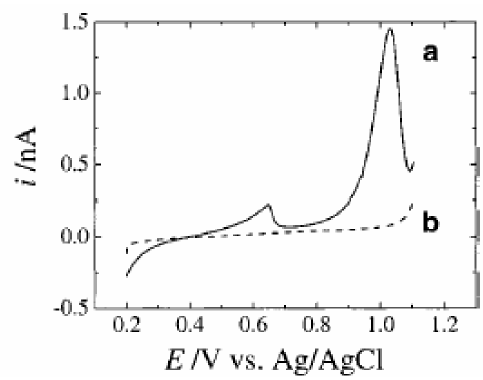
Differential pulse voltammogram (DPV)

DNA sensor using Au nanoparticles (case 1)

Au nanoparticle-based electrochemical detection of HCMV-amplified DNA



Anodic stripping voltammetry curve



a : Au probe/HCMV DNA-coated SPE
b : Au probe/SPE

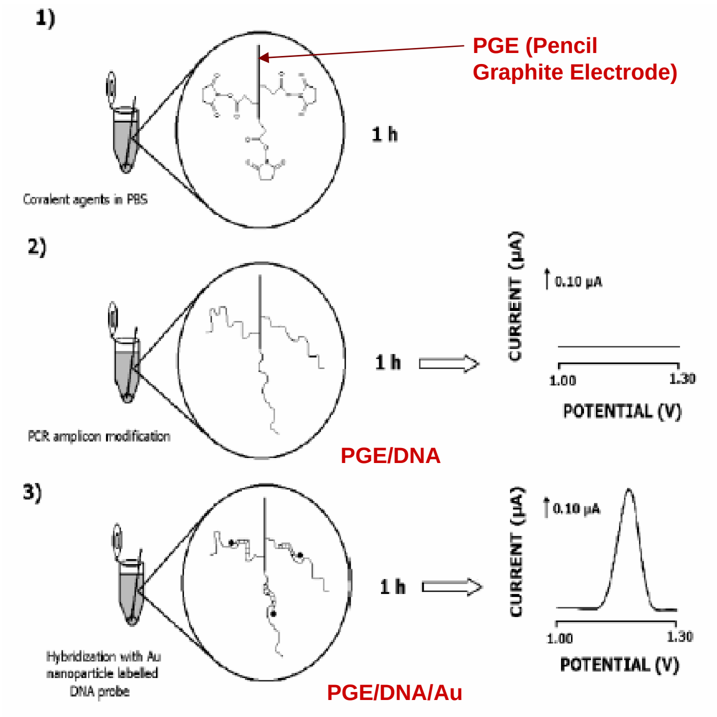
scan rate : 50 mV/s

** HCMV DNA : Human Cytomegalovirus DNA*
** SPE : Screen-Printed Electrode*

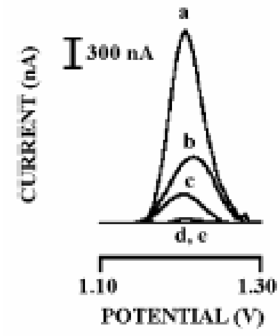
Authier. L, et al. *Anal. Chem.* **2001**, 73, *4450.*

DNA sensor using Au nanoparticles (case 2)

Detection of hybridization using Au nanoparticle -tagged capture probes



Differential pulse voltammograms



a : WT-Au(p) + WT(t)
b : MT-Au(p) + WT(t)
c : WT-Au(p) + no (t)
d : WT-Au(p) + non complementary DNA(t)
e : bare PGE

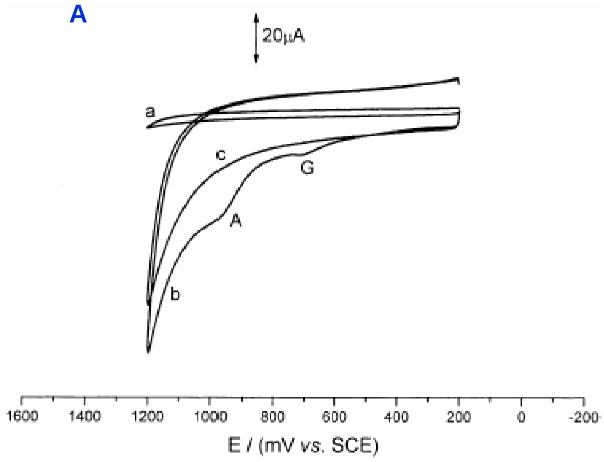
** WT : wild type, MT : mutant type Factor V Leiden DNA*
** (p) : probe, (t) : target*

Ozsoz. M, et al. *Anal. Chem.* **2003**, 75, *2181.*

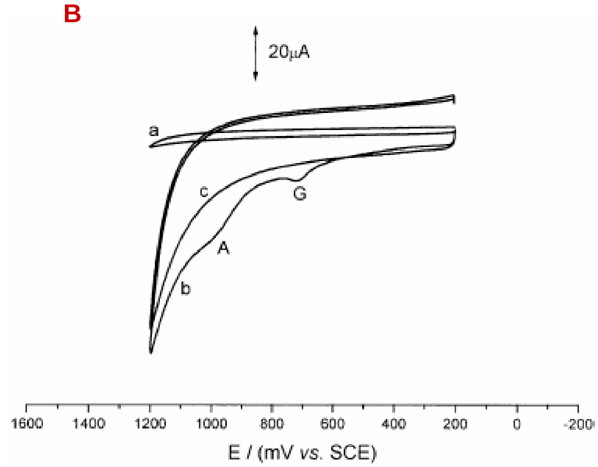
DNA sensor using Glassy carbon (GC) vs. GC/CNT

Cyclic voltammograms

A



B



a : bare GC electrode
0.3 mg/mL natural DNA (denatured DNA) in 0.1 M PBS buffer
b : SWNT modified GC electrode
0.3 mg/mL natural DNA (denatured DNA) in 0.1 M PBS buffer
c : SWNT modified GC electrode
absence of natural DNA

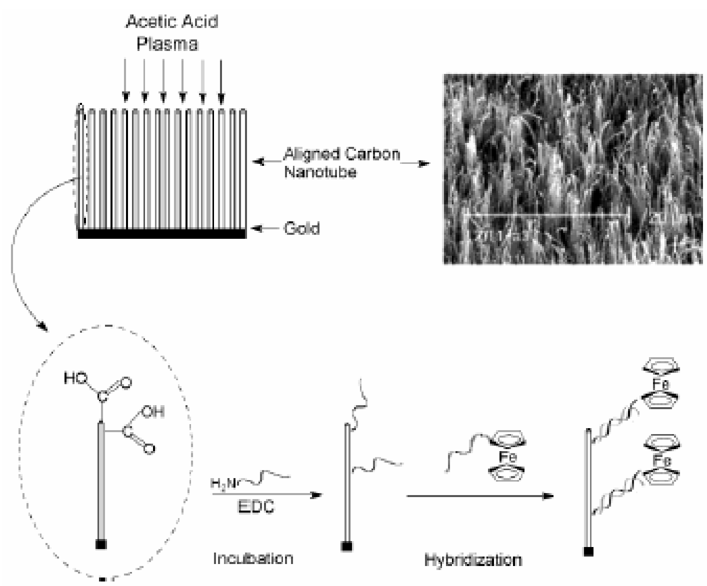
A : adenine
G : guanine

Wang. J, et al. *Electroanalysis* **2004**, 16, *140.*

CE : Pt, RE : SCE

DNA sensor using aligned CNTs (case 1)

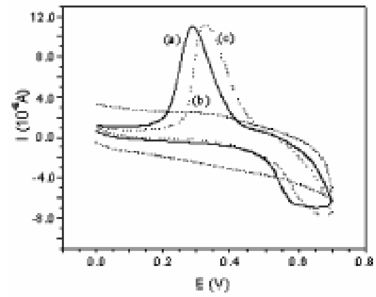
Aligned nanotube-DNA electrochemical sensor



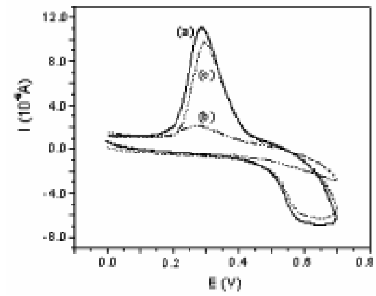
FCA : ferrocenecarboxaldehyde

He. P, et al. *Chem.Comm.* **2004**, 348

Cyclic voltammograms



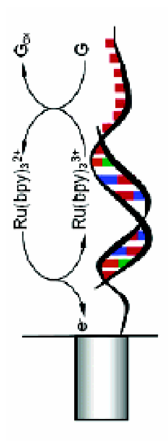
a : ssDNA + FCA-complementary DNA
b : w/ FCA-noncomplementary DNA
c : w/ target DNA (+b)



reversible →
In 0.1 M H_2SO_4 sol'n
Scan rate 0.1 V/s
FCA-DNA 0.05 μg/mL

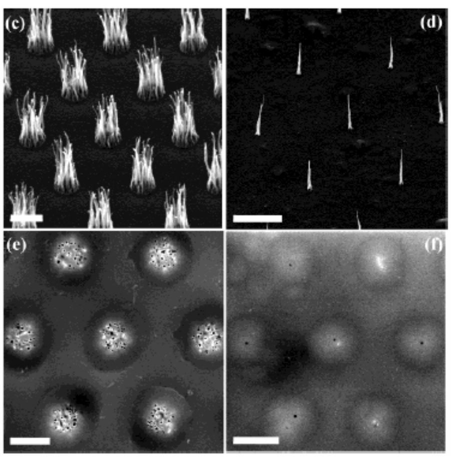
a : ssDNA + FCA-complementary DNA
b : denature (thermal)
c : w/ FCA-complementary DNA

DNA Sensor using aligned CNTs (case 2)



SEM images

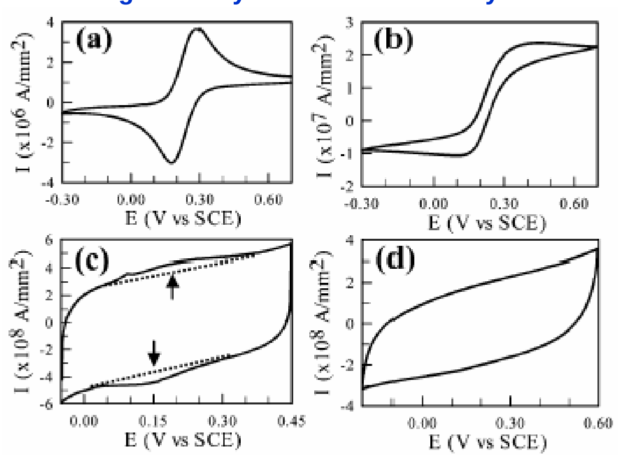
high density **low density MWNTs**



top : array of MWNTs
down : after polished MWNTs
scale bar : 2, 5, 2, 2 μm

Cyclic voltammograms

high density **low density MWNTs**



(a), (b) : 1 mM $K_4Fe(CN)_6$ & 1.0 M KCl
(c), (d) : Fc-MWNT array in 1.0 KCl

scan rate 20mV/s

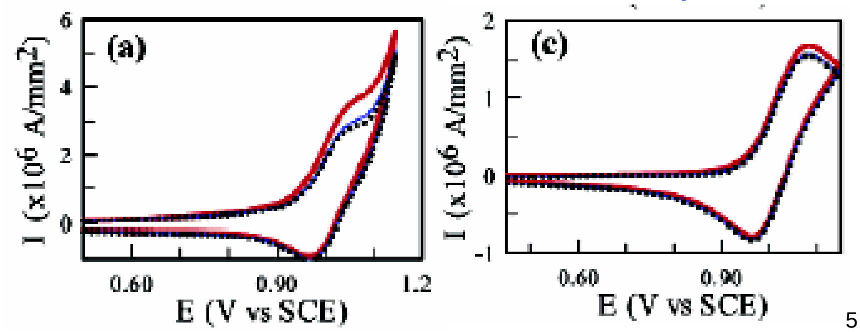
He. P, et al. *Chem.Comm.* **2004**, 348

After hybridizing the 20 bp polyG targets

Cyclic Voltammograms

high density

low density MWNTs

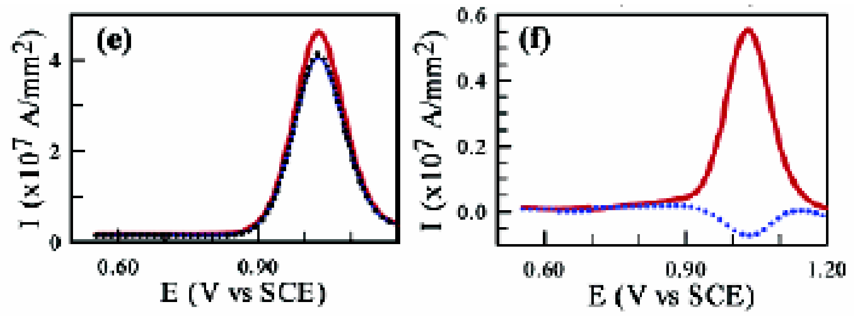


5 mM $Ru(bpy)_3^{2+}$
0.20 M NaOAc buffer
scan rate 20mV/s

Low density MWNTs
(lower limitation)

AC Voltammetry

Differential pulse voltammetry

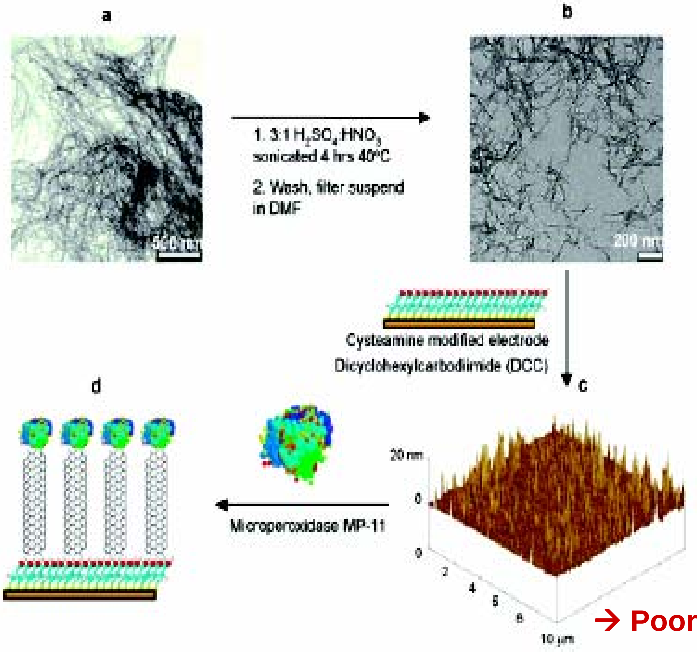


-- 1st , -- 2nd, -- 3rd scan

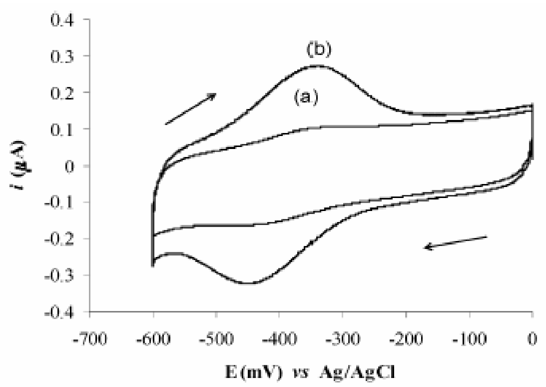
-- subtracting 2nd scan from 1st one
-- substrating 3rd scan from 2nd one

Protein Sensor using aligned SWNTs (case 1)

Fabrication of aligned shortened SWNT arrays



Cyclic voltammograms



a : Au/cysteamine/MP-11 sol'n
b : Au/cysteamine/SWNTs/MP-11 sol'n
In 0.05M phosphate buffer sol'n pH 7.0
w/ 0.05M KCl under Ar(g)
scan rate : 100 mV/s vs. Ag/AgCl

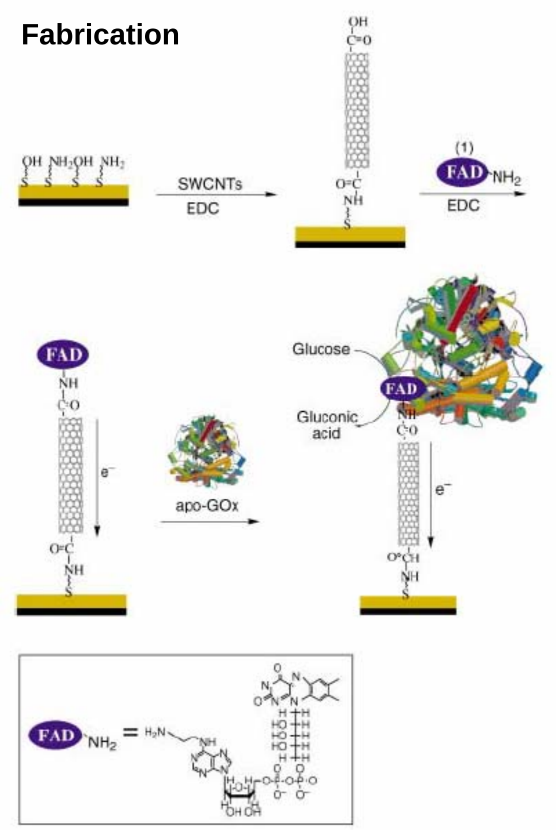
→ **Poor electron transfer across SWNT to MP-11**

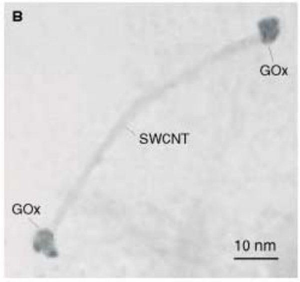
a, b : SWNTs
c: shortened SWNT aligned to the electrode surface by SAM(cysteamine) on gold electrode
d: microperoxidase MP-11 (a small redox protein obtained
by proteolytic digestion of horse heart cytochrome c)

Gooding J.J, et al. *J. Am. Chem. Soc.* **2003**, *125*, 9006

Glucose Sensor using aligned SWNTs (case 2)

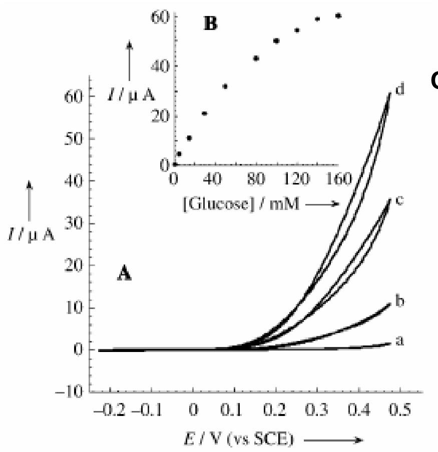
Fabrication





HRTEM image

SWNT modified at
its ends w/ GOx units



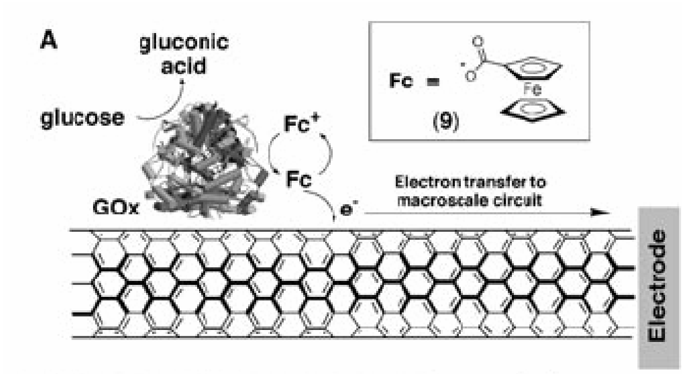
Cyclic voltammogram

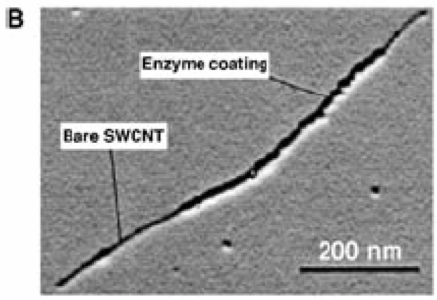
A : 25 nm long
FAD-modified CNTs
(a : 0, b : 20, c : 60,
d : 160 mM glucose)
in PBS buffer, 0.1 M,
pH 7.4, scan rate 5mV/s

B : calibration curve

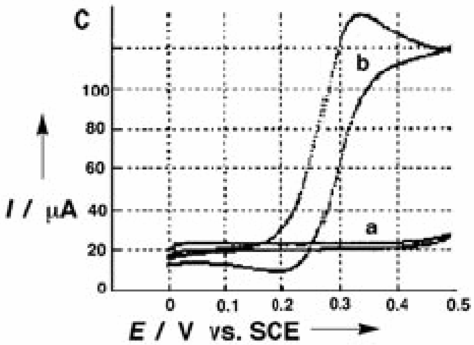
Patolsky. F, et al. *Angew. Chem. Int. Ed.* **2004**, 43, *2113*

Glucose Sensor using SWNT (case 3)





AFM image
Gox-modified SWNT



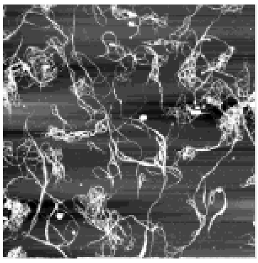
Cyclic voltammogram

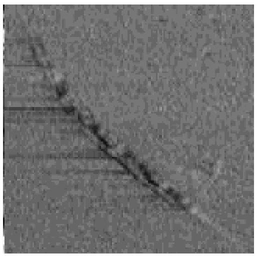
a : absence
b : presence of glucose
in ferrocene mono
-carboxylic acid

Davis.J.J, et al. *Chem. Eur. J.* **2003**, 9, *3732*
Katz. E, et al. *ChemPhysChem.* **2004***, 5,* 1084

Glucose Sensor using Pt Nanoparticles and SWNTs (case 4)

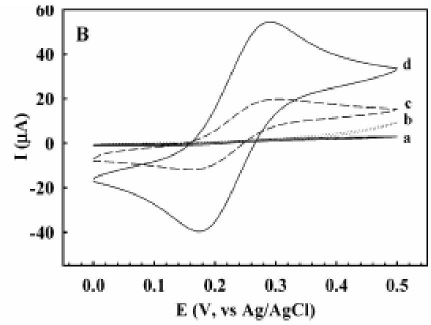
AFM images





SWNTs (scale : 10 nm) **SWNT in Pt particles** (scale : 20 nm)

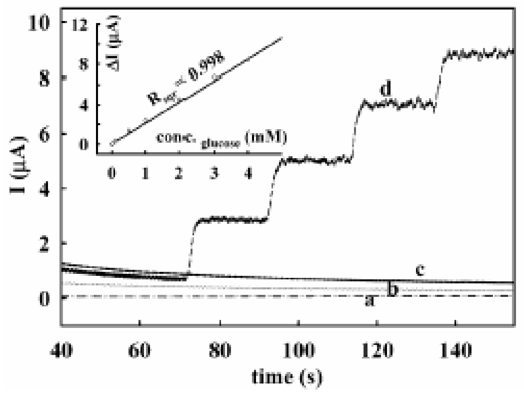
Cyclic voltammograms



a : GC
b : GC/CNT
c : GC/Pt_{nano}
d : $GC/CNT + Pt_{nano}$

20 mM $Fe(CN)_6^{4-}$
+ 0.2 M KCl
scan rate : 20 mV/s
RE : Ag/AgCl

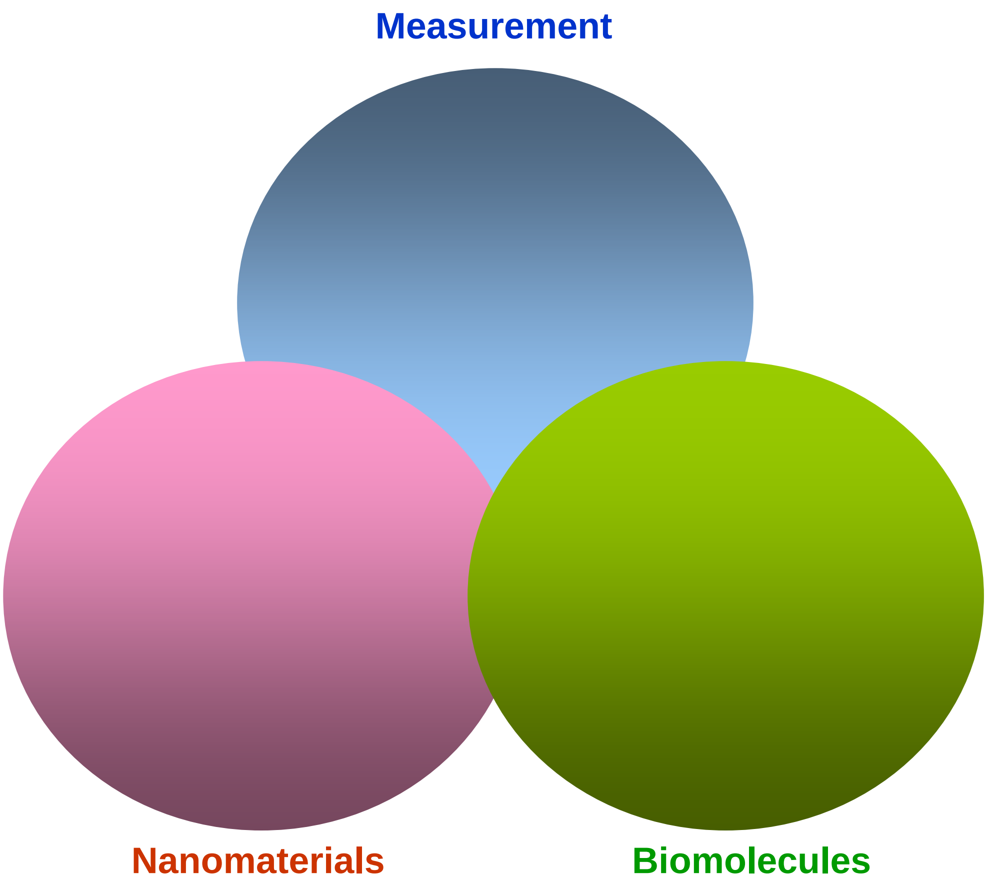
Amperometric detection



a : GC + GOx
b : GC/CNT + GOx
c : GC/Pt_{nano} + GOx
d : $GC/CNT + Pt_{nano}$ + GOx

1 mM glucose sol'n in 50 mM PBS buffer

Hrapovic. S, et al. *Anal. Chem.* **2004**, 76, *1083*



Why transistor and Why nanotube or nanowire?

Transistor: provides direct electrical signals

Nanotube or nanowire:

Impressive not just by its size!!
But by its high performance (charge carrier mobility)

Electrical sensor with high sensitivity