Electrical Sensing of Biomolecules based Nanomaterials and Carbon Nanotubes

Department of Chemistry
Pohang University of Science and Technology
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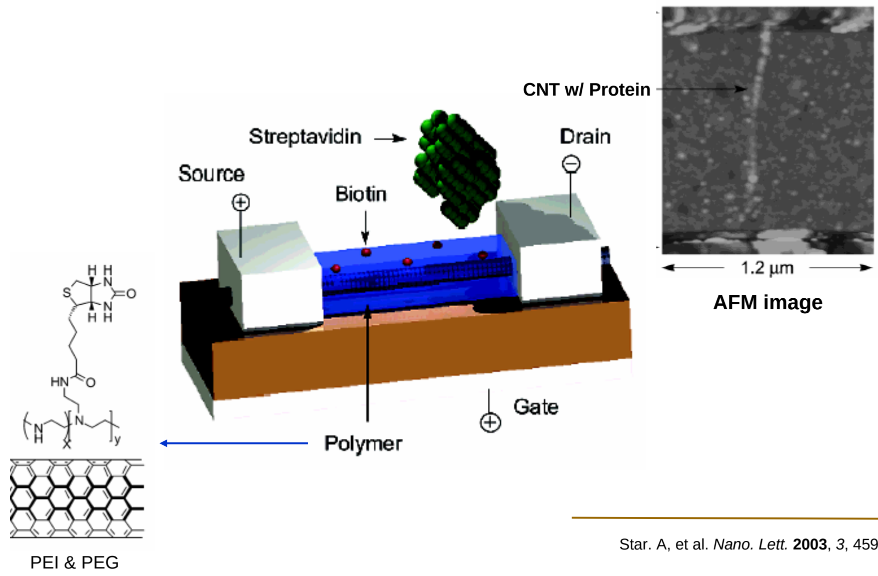
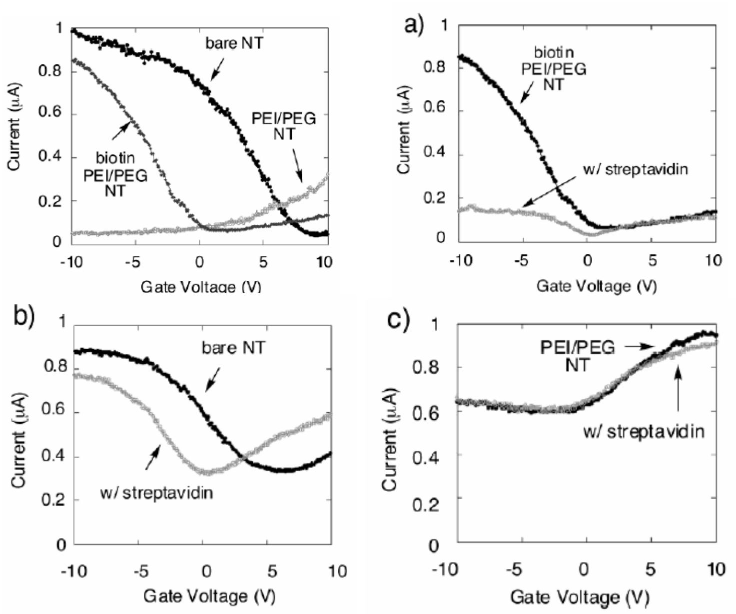
Specific Protein Binding Sensor using SWNT (case 1)

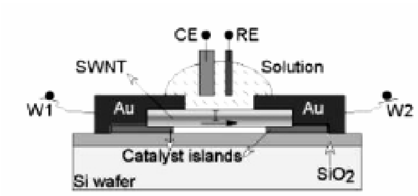


Star. A, et al. *Nano. Lett.* **2003**, *3*, 459

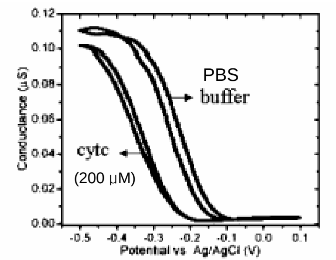


Protein Sensor using SWNT (case 2)

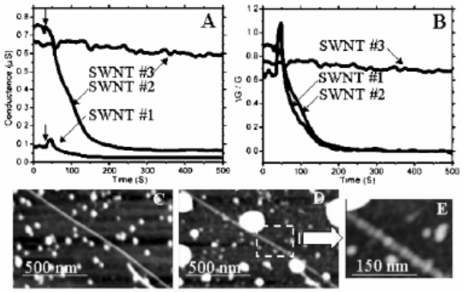
Individual SWNT device



CE : Pt   RE : Ag/AgCl



P-type SWNT

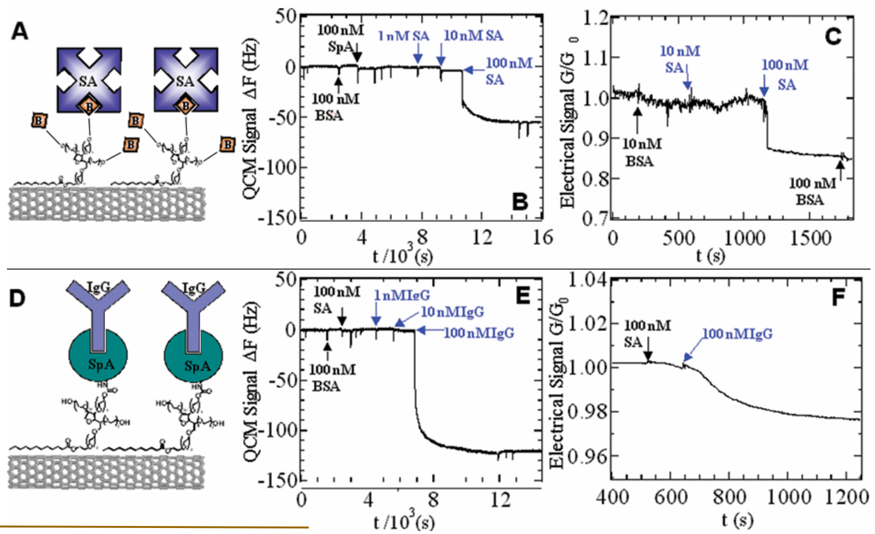


A,B : #1 & #2 : p-type, #3 : metallic SWNT
C : before D & E : after the introduction of the protein(cytochrome c) sol'n

→ Protein adsorption does not change slop but V_{Th}

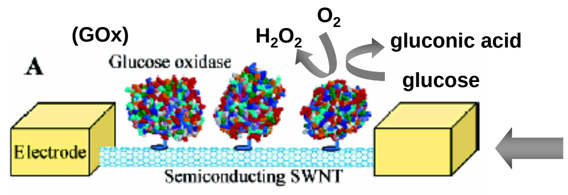
Boussaad. S, et al. *Chem.Comm.* **2003**, *1502.*

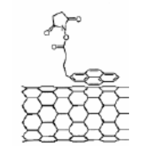
Specific Protein Binding Sensor using SWNT (case 2)



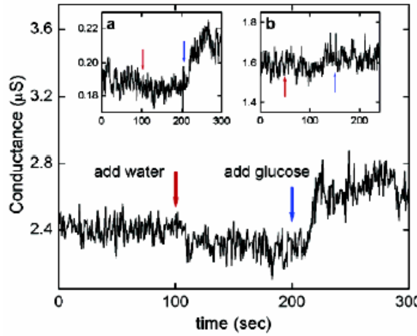
Chen. R, J, et al. *PNAS.* **2003**, *100*, 4984

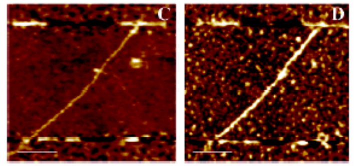
Glucose Sensor using SWNT





Linking molecule
: pyrene group

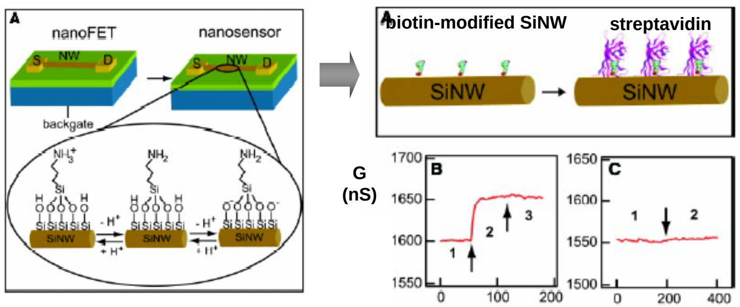




AFM image

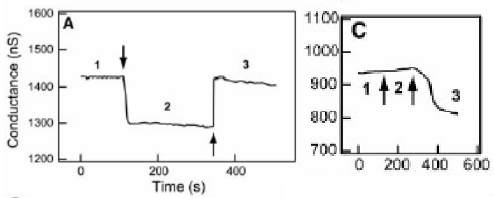
Besteman. K, et al. *Nano. Lett.* **2003**, *3*, 727

Specific Protein Binding Sensor using SiNW



Modified SiNW **Modified SiNW** **Unmodified SiNW**

↑ *1, 3 : buffer   2 : 250 nM streptavidin*



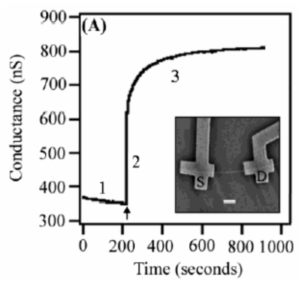
1, 3 : buffer
2 : 3 µM m-antibiotin

1 : buffer   2 : bovine IgG
3 : 3 µM m-antibiotin

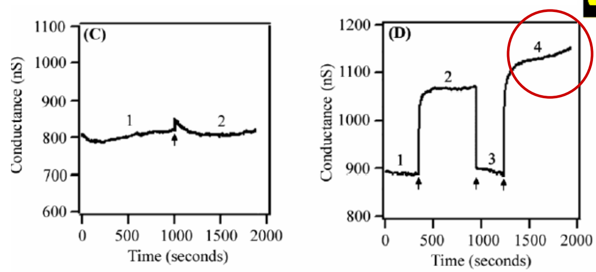
Cui. Y, et al. *Science* **2001**, *293*, 1289

DNA Sensor using SiNW

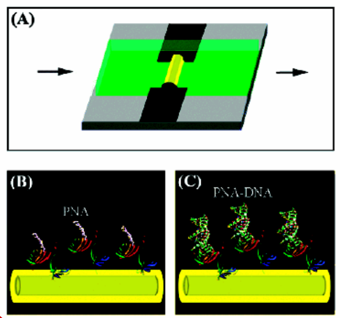
1 : buffer
2 : 60 fM WT DNA →



1,3 : DNA free sol'n
2,4 : 100 fM MU DNA ↓



Static system   **Flowing (buffer) system**

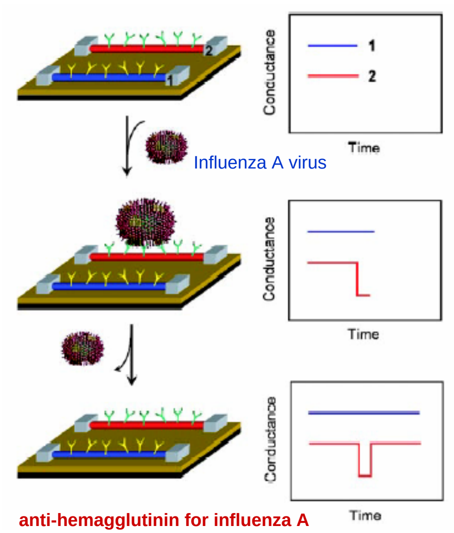


(A) Yellow : sensor device
Green : microfluidic channel
(B) PNA(peptide nucleic acid) surface
(C) PNA-DNA duplex

Hahm. J, et al. *Nano. Lett.* **2004**, *4*, 51

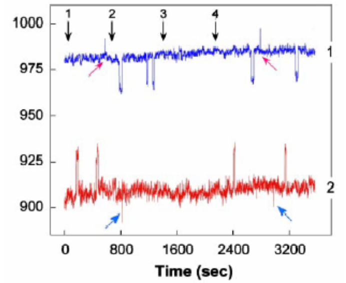
Single Virus Sensor using SiNW

Microfluidic Channel **(100 virus particles per µl)**



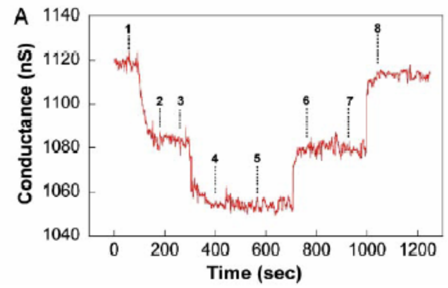
anti-hemagglutinin for influenza A
anti-adenovirus group III

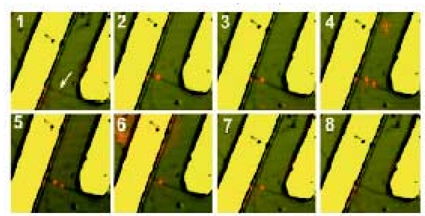
50 virus particles per µl



anti-influenza type A antibody
anti-adenovirus group antibody
Introduce 1: adenovirus
2 : influenza A
3 : buffer
4 : 1 : 1 mixed adenovirus & influenza A

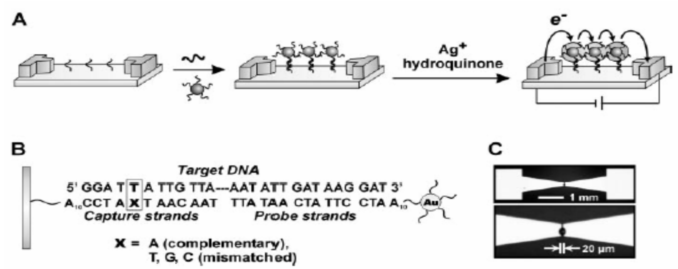
Patolsky. F, et al. *PNAS.* **2004**, *101*, 14017

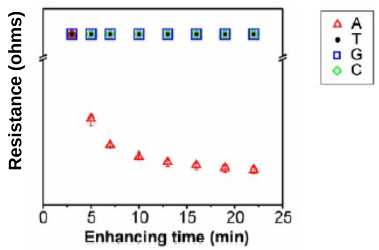




Single Virus Binding Selectivity

Application 2 : DNA array detection



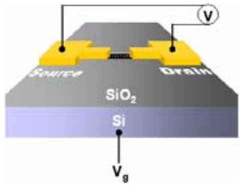


Park. S, et al. *Science* **2002**, *295*, 1503

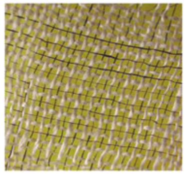
Part II

What applications carbon nanotubes will contribute?

Electromagnetic Shield coating



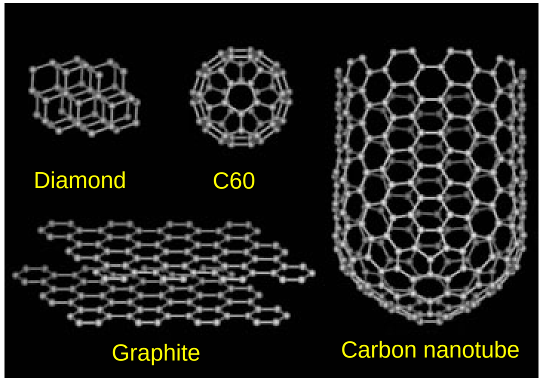
Field emission devices



Ray Baughman, UT Dallas

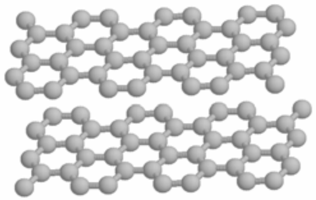
Strong materials

Forms of Carbon

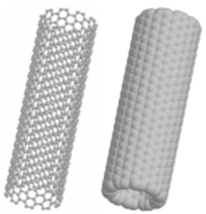


Structure of carbon nanotubes

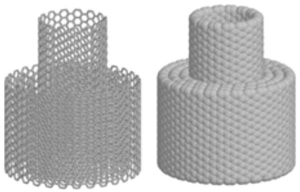
- Nanotubes consist of graphene sheets of carbon
- Rolled into a cylinder
- Some with multiple concentric cylinders



Graphite



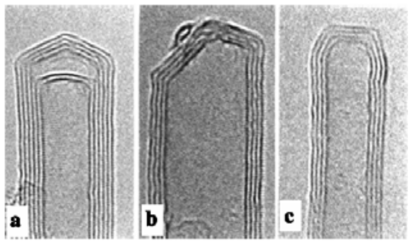
Single-walled nanotube (SWNT)



Multi-walled nanotube (MWNT)

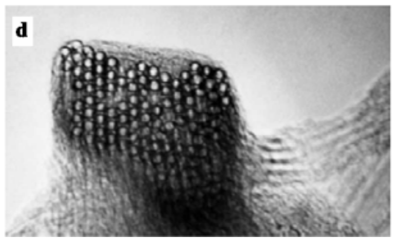
Representatives of carbon nanotubes

Multi-walled (MWNT)



Sumino Iijima

Single-walled (SWNT)

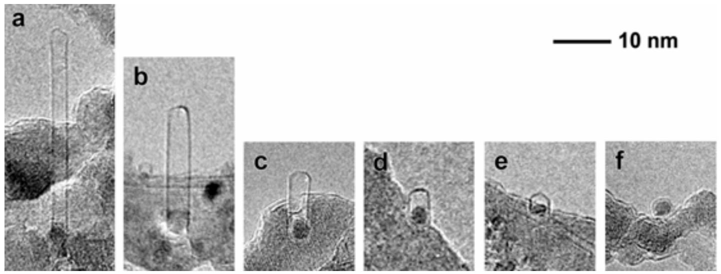


Richard Smalley

SWNTs are all C molecular wires and excellent quasi 1D systems for basic work (synthesis, materials science and physics) and potential applications

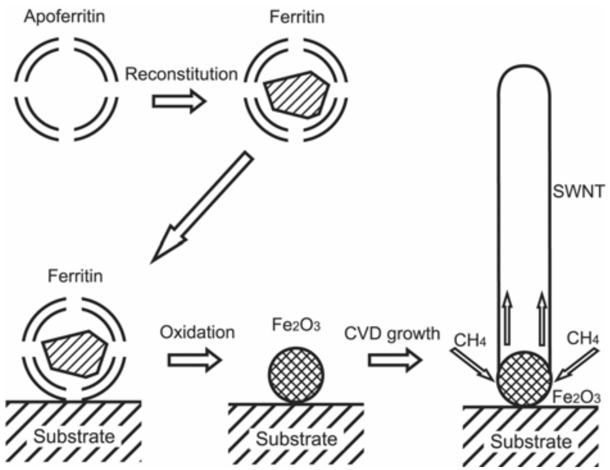
How do SWNTs grow?

Nanotubes at various stages of growth



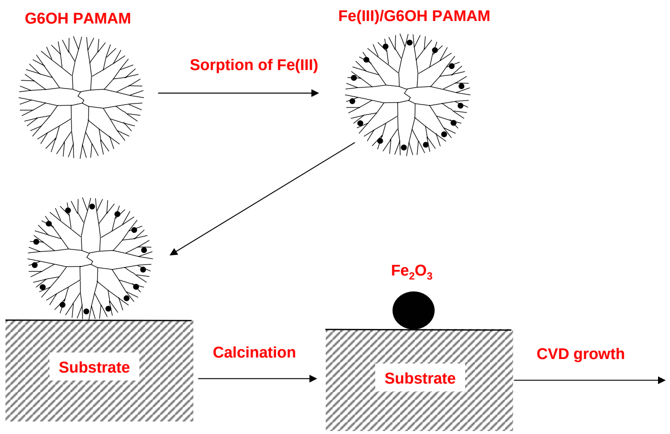
- Particle size ~ tube diameter
- Catalytic particles (active end) remain on support
- The other end is dome-closed
- Base growth (differs from the VLS growth mode)

Diameter Control: Catalytic Nanoparticles Derived in Apoferritin Templates (d~1-3 nm)



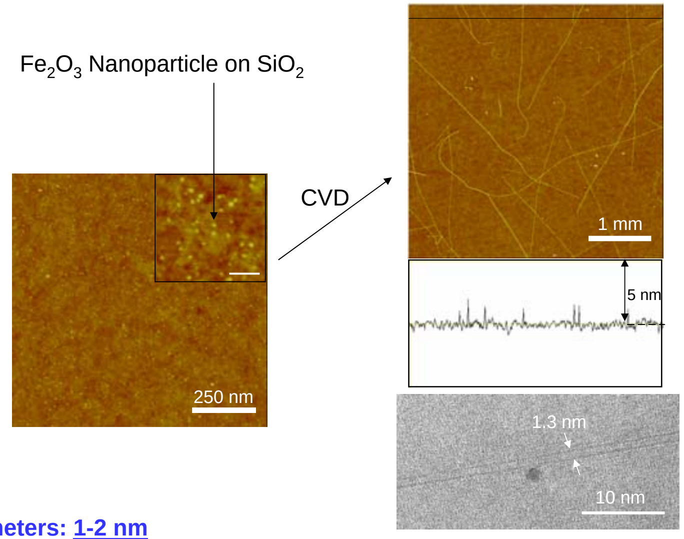
Y. Li, et al.,*J. Phys. Chem.*, ***105***, *11424, 2001*

Diameter Control: Catalytic Nanoparticles Derived in Dendrimer Templates (d~1-2 nm)



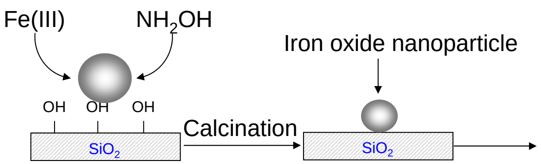
Choi, H. C. et. al *J. Phys. Chem. B* **2002**, *106*, 12361.

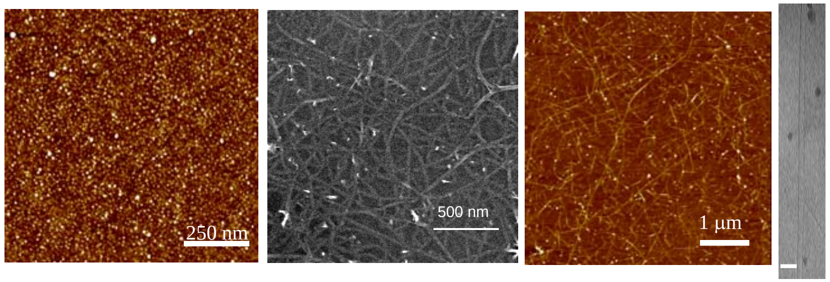
Nanotubes Grown From Dendrimer Templated Nanoparticles



- Diameters: 1-2 nm
- (1-5 nm with conventional supported catalyst)

A Simple Approach to Monolayer Catalytic Nanoparticles: Clean Tube Films



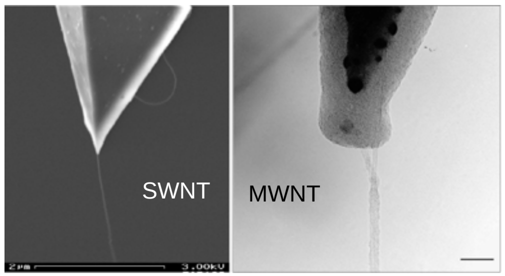


Choi, H. C. et al., *Nano. Lett.* **2003**, *3*, 157.

Applications

- AFM tip for high resolution images and fabrication
- Electrical devices
- Electro-mechanical devices
- Gas and biosensors

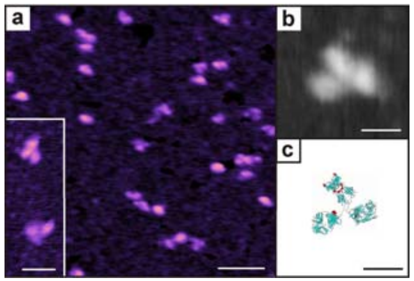
For better resolution



Nanotube at the apex of Si tip
- Direct growth for SWNT
- Glue attached for MWNT

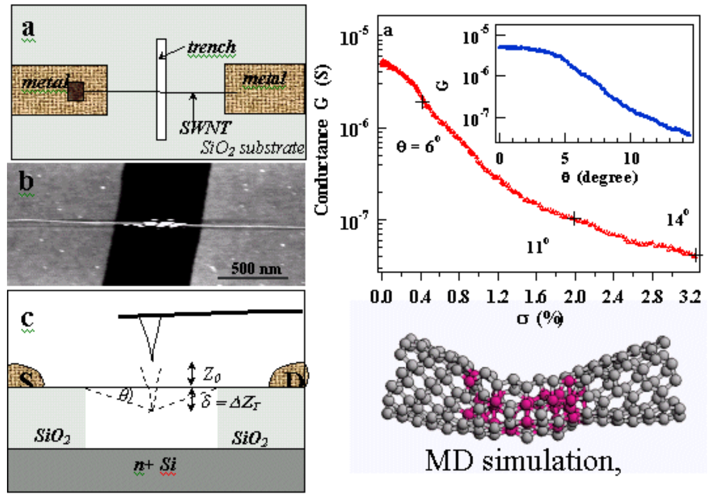
Nature **398**,761-762, 1999
PNAS **97**, 3809-3813, 2000

Immunoglobin G (IgG)
- consists of 4 polypeptide chains (Y-shpe)
- Two antigen binding fragments (Fab)
- One Fc site

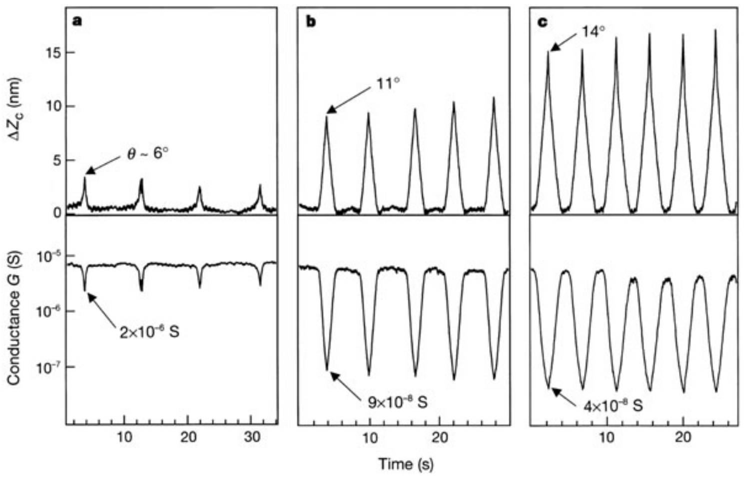


J. Am. Chem. Soc. **120**, 603-604 (1998)

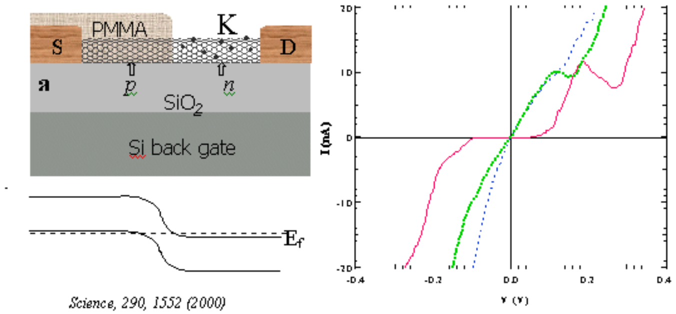
Tube deflection and Conductance change



Deflection and corresponding conductance changes: "reversible"

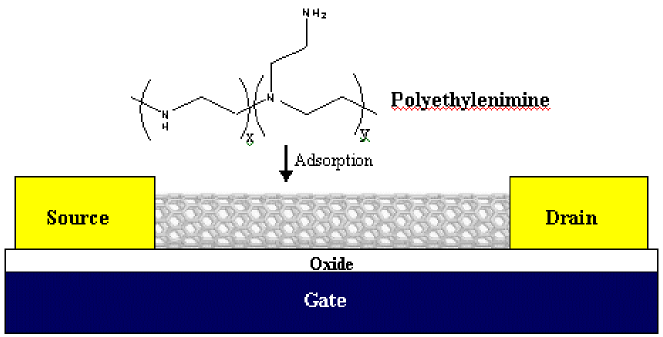


Chemical Profiling of Single Nanotubes: Intra-Molecular p^+n^+ junction Nanotube Esaki Diode:

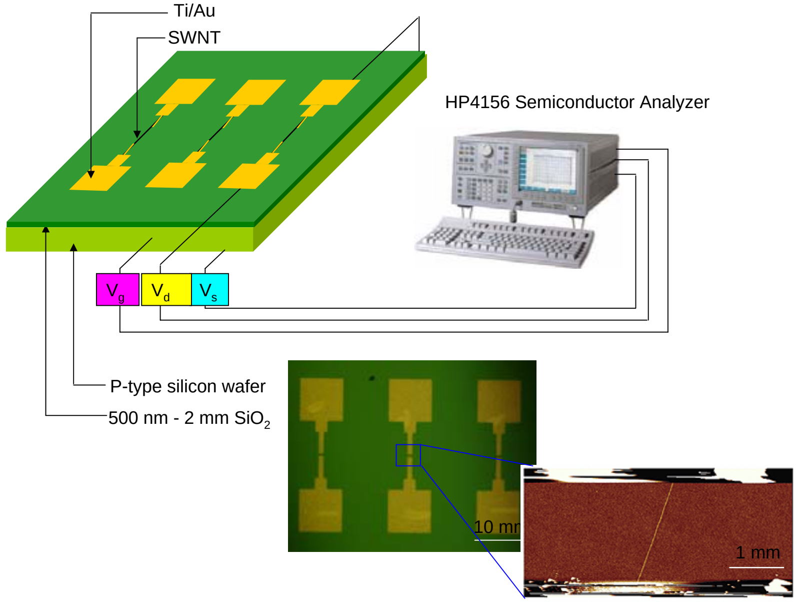


Science, 290, 1552 (2000)

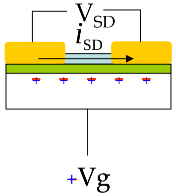
Polymer functionalization for Air Stable n-type SWNT FET (JACS, 2001):

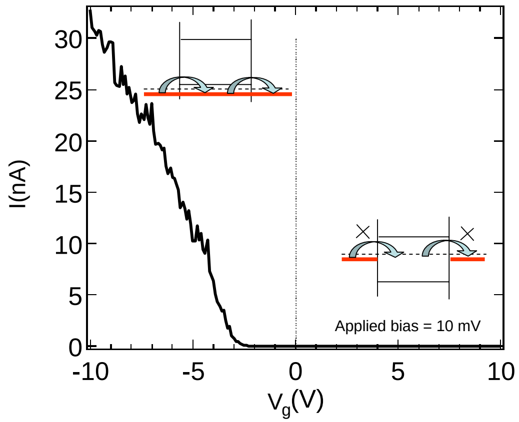


Carbon nanotube based Field Effect Transistors (SWNT-FETs)

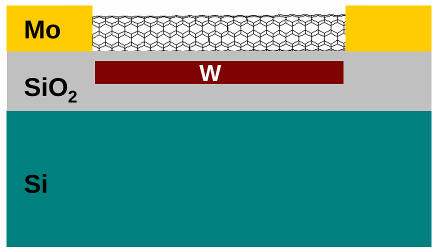


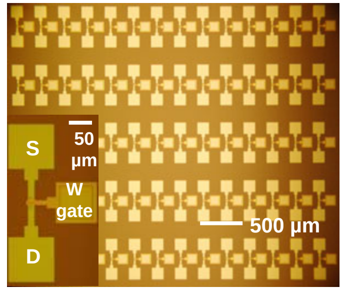
I-Vg characteristics of SWNT-FETs





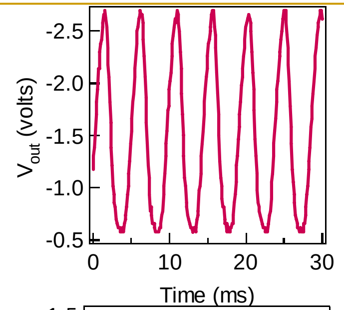
Integrated Nanoelectronics: *Nanotube Transistor Arrays with Local W/ SiO_2 gates*

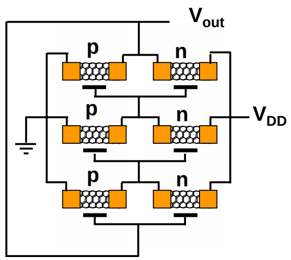


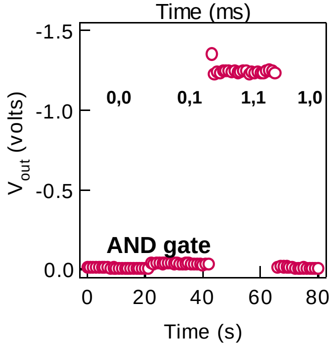


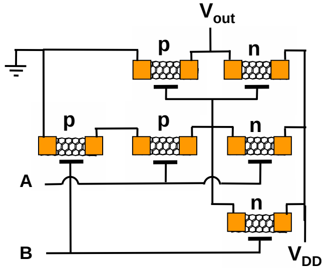
- **Derived by patterned growth of nanotube arrays**
- **Percentage of semiconducting tubes: ~ 70% by CVD**
- **High yield of transistors**
- **Ability in obtaining p- and n- arrays on same chip for Complementary Devices**

Nanotube Ring Oscillators & Logic Gates



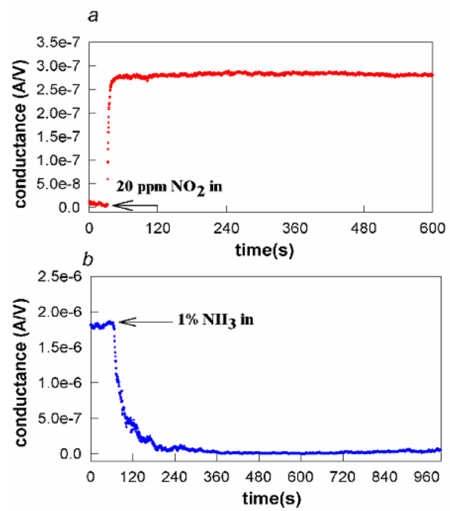






Javey et al. Nano Lett., 2002

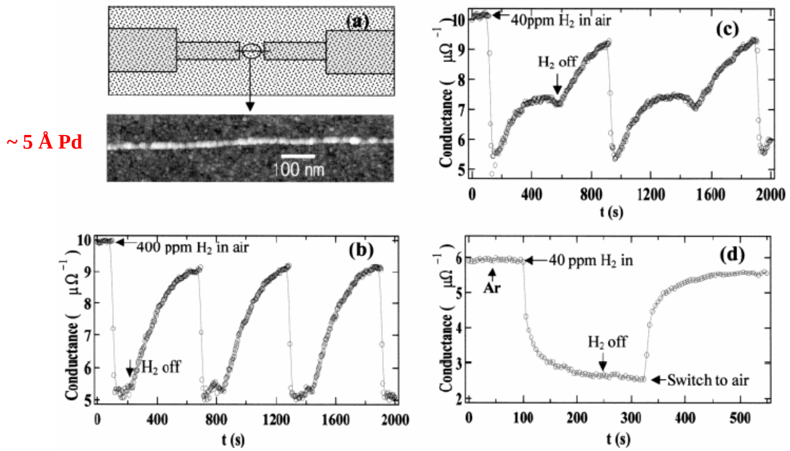
Nanotube Chemical Sensors



- **Orders of magnitude conductance response**
- **Room temperature**
- **NO_2: near chemisorption**
- **NH_3: physisorption**

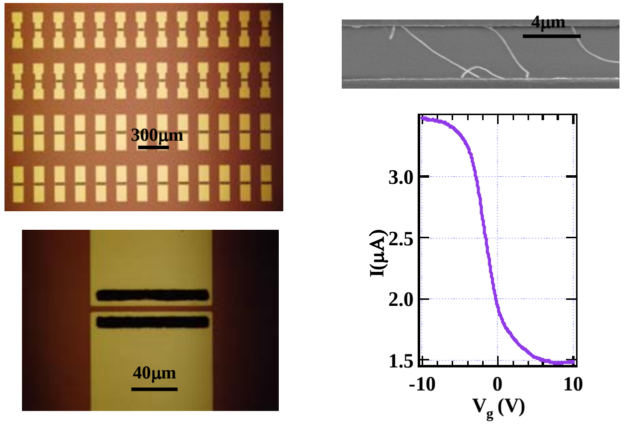
Science, 287, 622, **2000**

H_2 sensing with SWNT/Pd single device



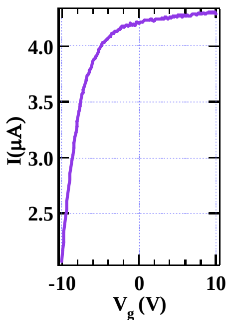
J. Kong et. al., Adv. Mater. 13, 1384, **2001**

Nanotube sensor array with 100% yield

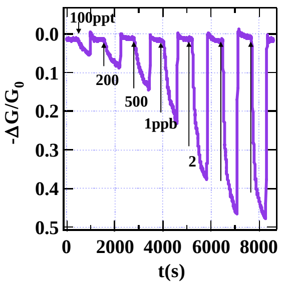


- Grow multiple tubes for each device in a large array
- Semiconducting tubes dominant (70%)
- Excellent electrostatic gating and chemical gating sensitivity
- Large sensor arrays obtained (100% yield, low noise)

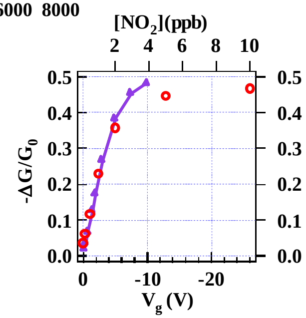
Enhanced sensitivity of NO_2 detection for polymer (PEI) coated n-type devices



I-Vg of n-type device



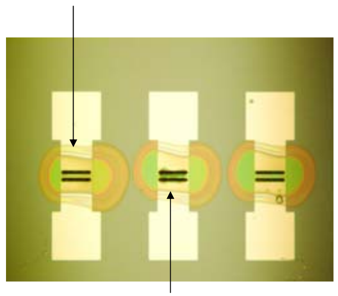
- **NO_2 sensing: Down to 100 ppt sensitivity**
- **Sticking coefficient PEI/tube ~ 0.3 No PEI/tube ~0.001**



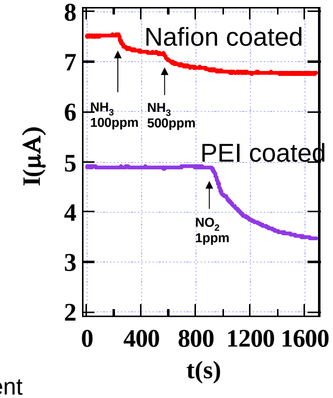
Enhanced selectivity as well:
No response to NH_3, CO, CO_2, H_2, CH_4, O_2

Multiplex-functionalized sensor array capable of detecting multiple molecules in a gas mixture

PEI coated



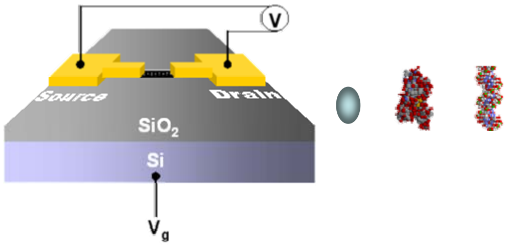
Nafion coated



- Micro-spotting used for coating different devices with different polymers

P. Qi, et al, Nano Lett. 3, 347, **2003**

CNT-FET as a smart sensor



Conventional CNT-FET

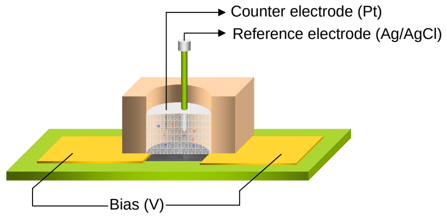
- Change of I_{DS} by the effect of V_{GS}
- V_{GS} by electric field

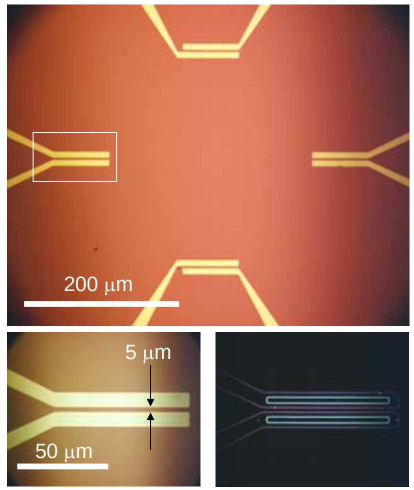
CNT-Chemical Effect Transistor (CET)

- Change of I_{DS} NOT by the effect of V_{GS}
- Why not by chemical effects?
  * Charge transfer from molecules to CNT

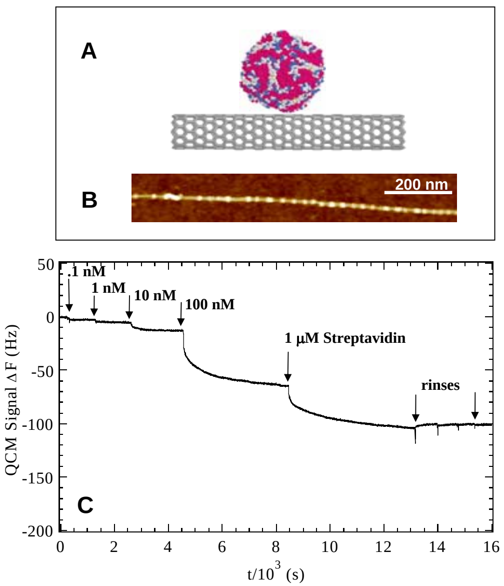
CNT-FET device for biosensor applications

-Teflon based electrochemical cell-





Non-specific interaction of SWNT with proteins

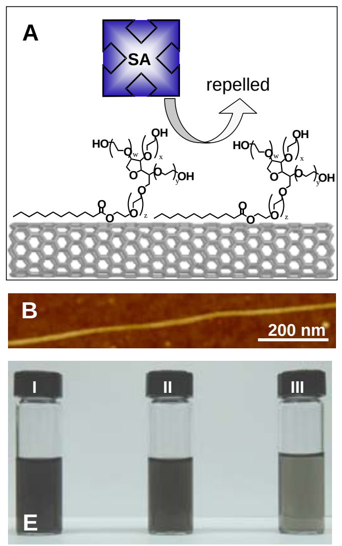


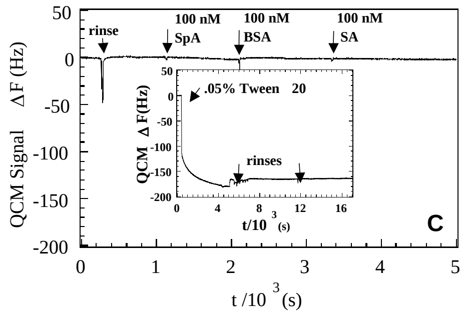
Turns out to be generic:

Streptavidin, Protein A, Glucosidase, Bovine Serum Albumin, IgG…

Chen et al, *PNAS* **2003**, 100, 4984

Hydrophobic/vdW anchoring of Tween20/PEG





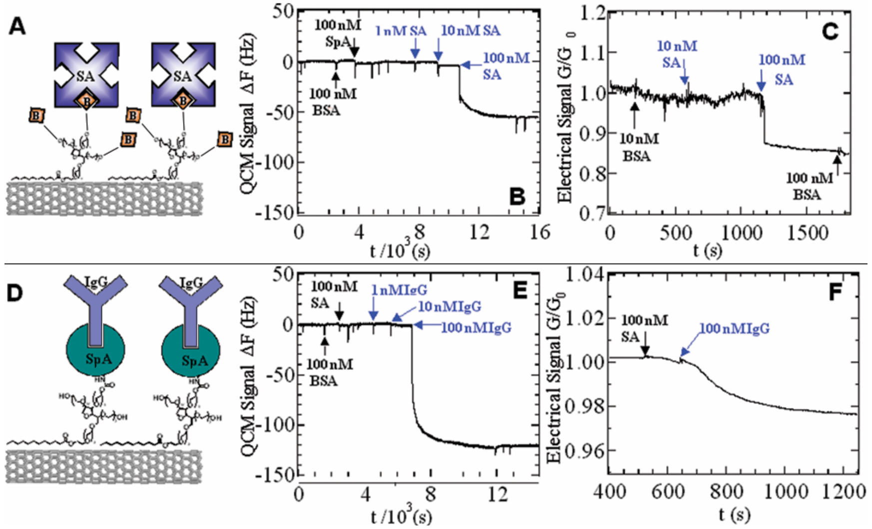
❖Non-covalent irreversible adsorption

❖Water solubility, highly stable

❖Protein resistant

❖Tween 20 & Pluronic block copolymer P103 are the best

Selective electronic biosensor



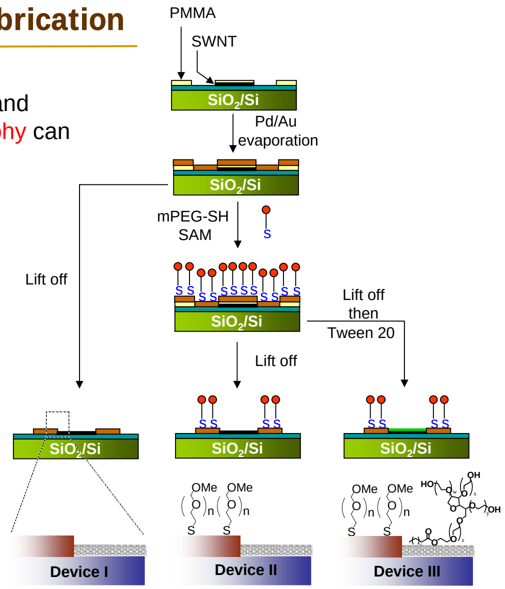
Origin of the conductance change

Where does the conductance change come from?

- Nanotube aspects:
  - Charge injection from biomolecules
  - Electric double layer field modulation caused by biomolecules
- Metal-nanotube contact aspect:
  - Adsorbed chemical species may modulate work function level of contact metals, which consequently change the Schottky barrier height resulting in the conductance change.

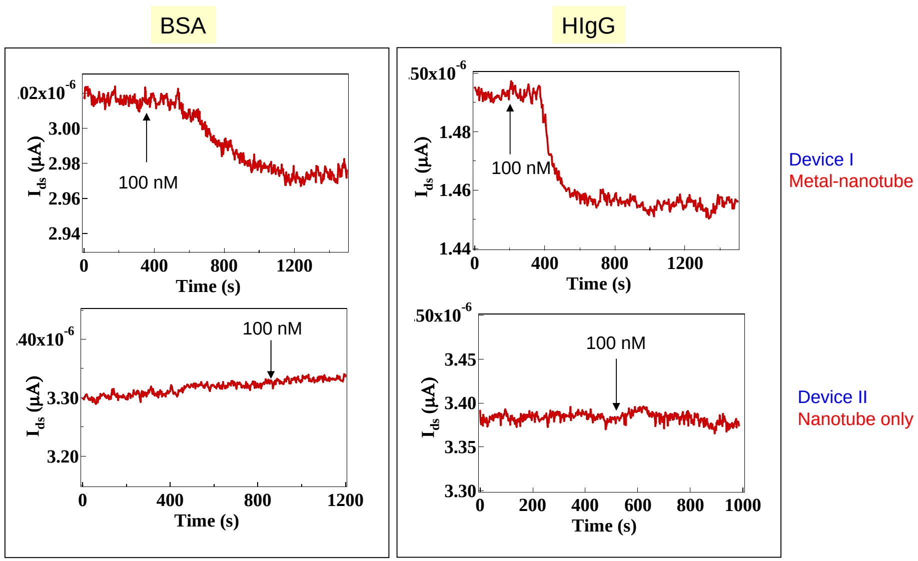
CNT-FET device fabrication

Both photolithography and electron-beam lithography can be used

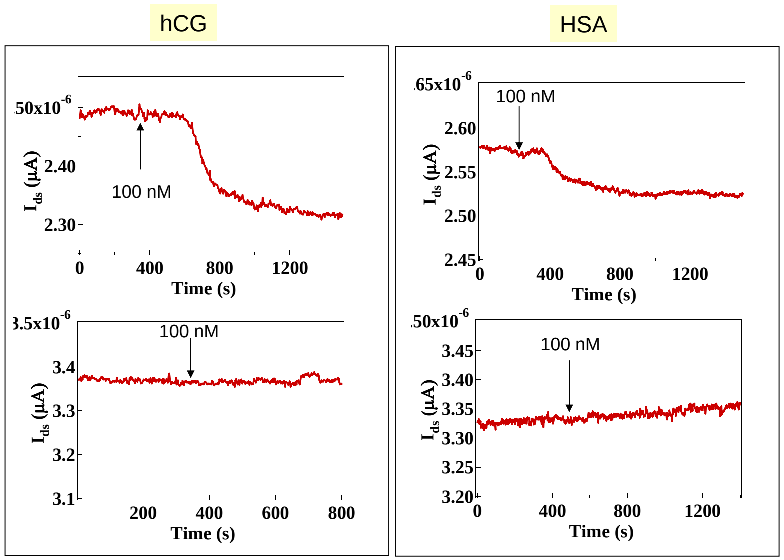


Chen, Choi et al *J. Am. Chem. Soc.* **2004**, *126*, 1563

Nanotube vs. metal-nanotube contact



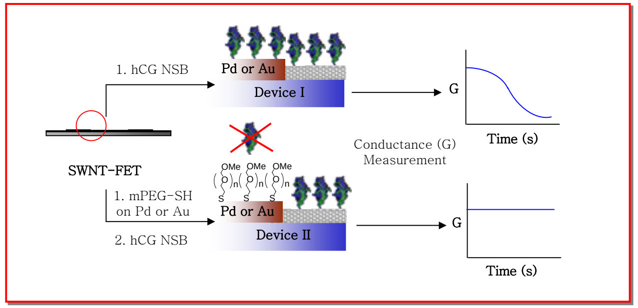
Nanotube vs. metal-nanotube contact



Device I
Metal-nanotube

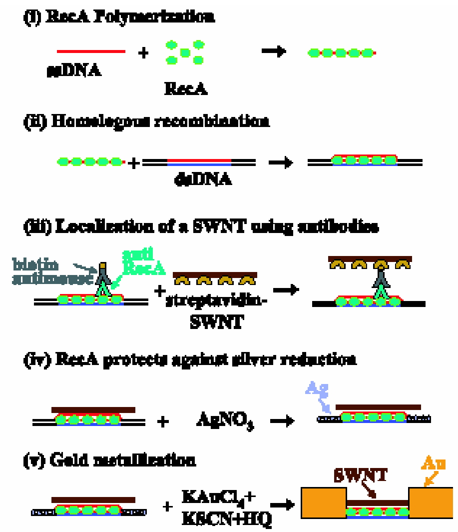
Device II
Nanotube only

Summary of biomolecule sensing mechanism

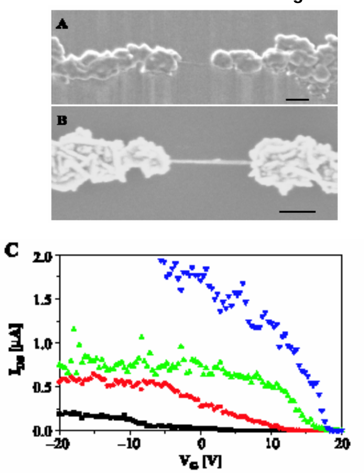


Effective functionalization of metal surface with appropriate chemical species will lead high sensitive and selective nanotube-biosensor.

Application 1 : DNA-templated CNT-FET

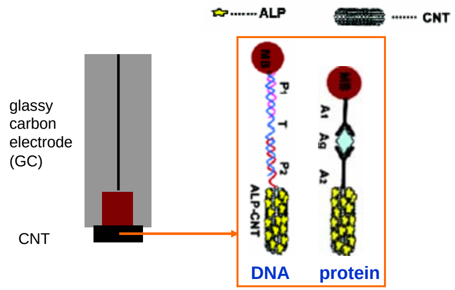


DNA-templated CNT FET
& metallic wires contacting it

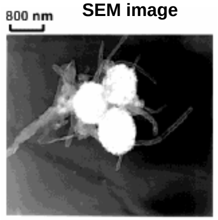


Keren. K, et al. *Science.* **2003**, *302*, 1380

DNA and Protein Sensor using GC/CNTs (case 3)

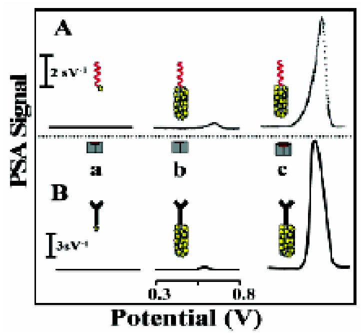


SEM image



Magnetic beads-DNA-CNT + 10 pg/mL target sample

Chronopotentiometric signals



A (DNA) : 10 pg/mL target oligonucleotide
B (protein) : 80 pg/mL IgG
(a) single ALP tag
(b) CNT-multiple ALP tags
(c) CNT-ALP tags modified GC electrode

50 μL α–naphthyl PBS sol'n(50 mM) w/ enzymatic rxn

Wang. J, et al. *J. Am. Chem. Soc.* **2004**, 126, *3010*.