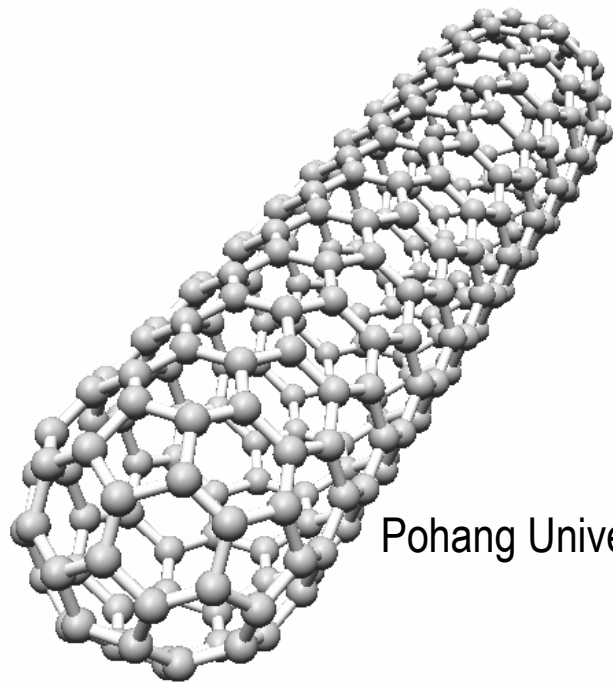


# Carbon Nanotubes for Transistor Type-Biosensor and Therapeutic Applications



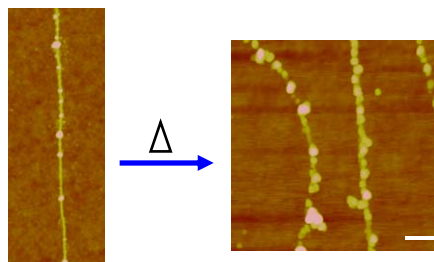
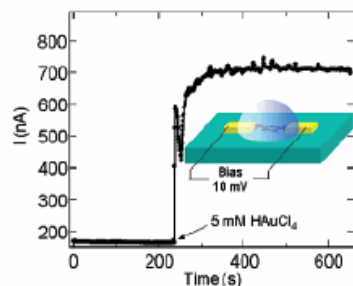
Hee Cheul Choi

Department of Chemistry,  
Pohang University of Science and Technology (POSTECH)  
South Korea, 790-784



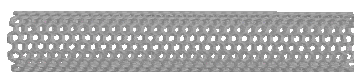
# Surface Chemistry of Carbon nanotubes: Hybrid structures

## Facile and spontaneous synthetic approaches



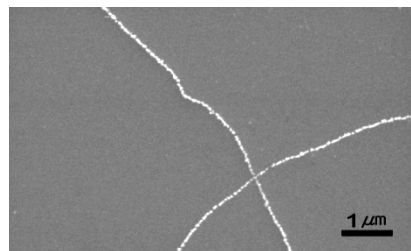
Choi, et al., *JACS* 2002, 124, 9059.

Noble metal-SWNT composites

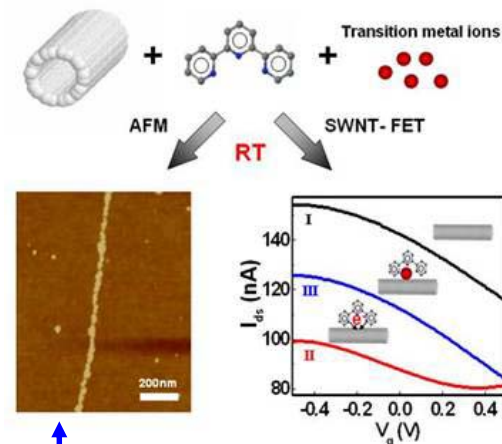


Transition metal-SWNT

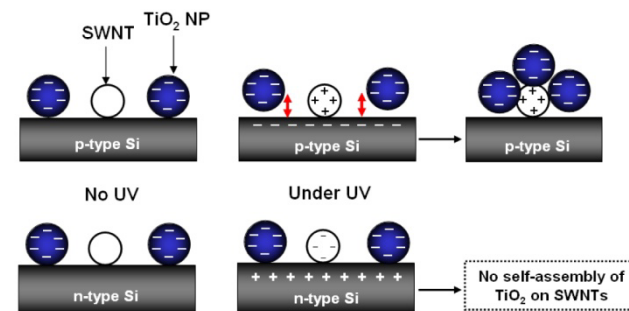
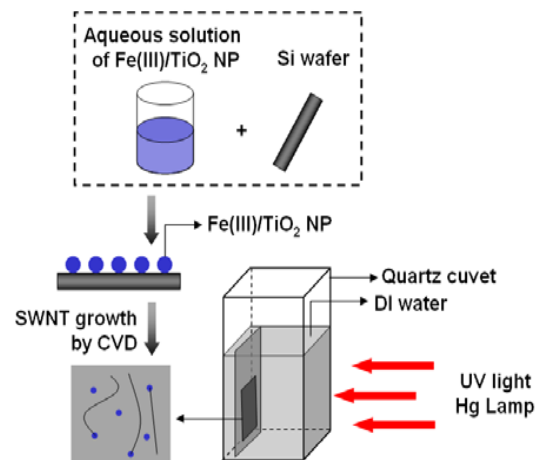
$\text{TiO}_2$ -SWNT composites



Shin and Choi, et al., *Adv. Mater.* 2007, 19, 2873.



Lee and Choi, et al., *Small* 2005, 1, 975.

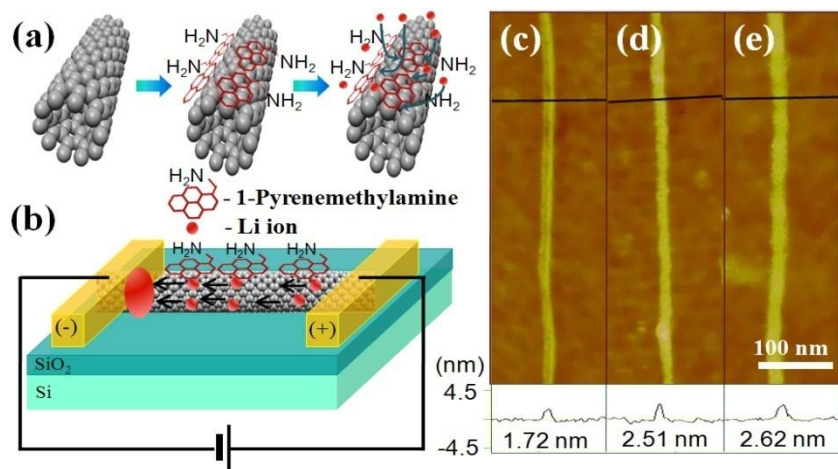


Mechanism

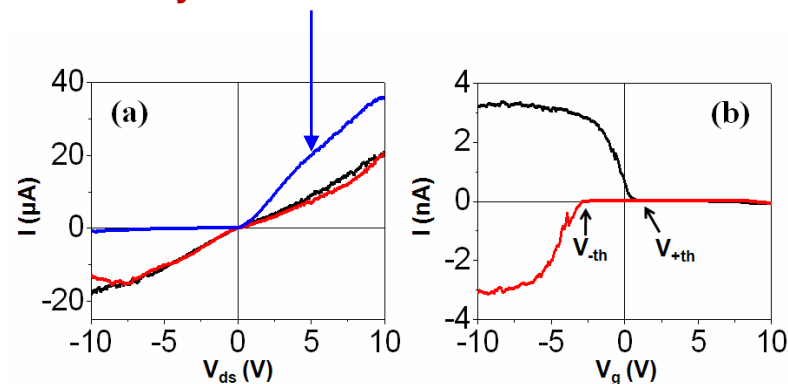


# Surface Chemistry of Carbon nanotubes: Schottky diodes

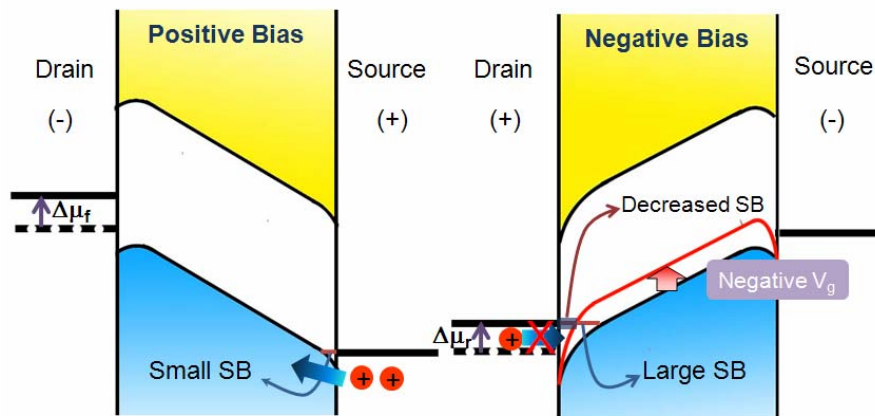
## Intercalation of Li ions in pyrene-functionalized SWNT



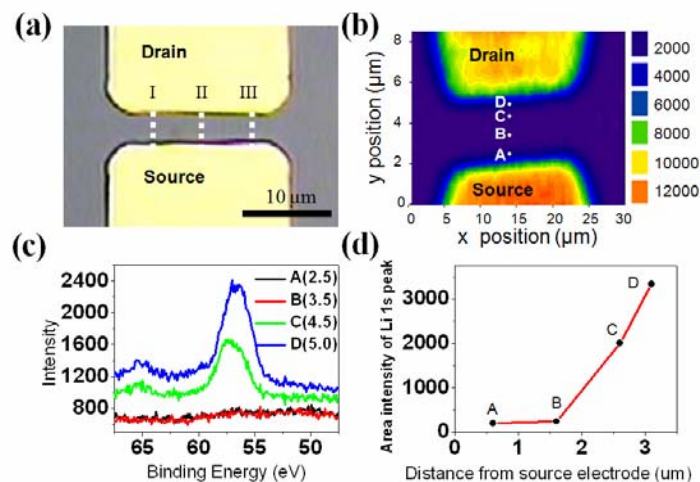
## Schottky diode behavior



## Modulation of band energy

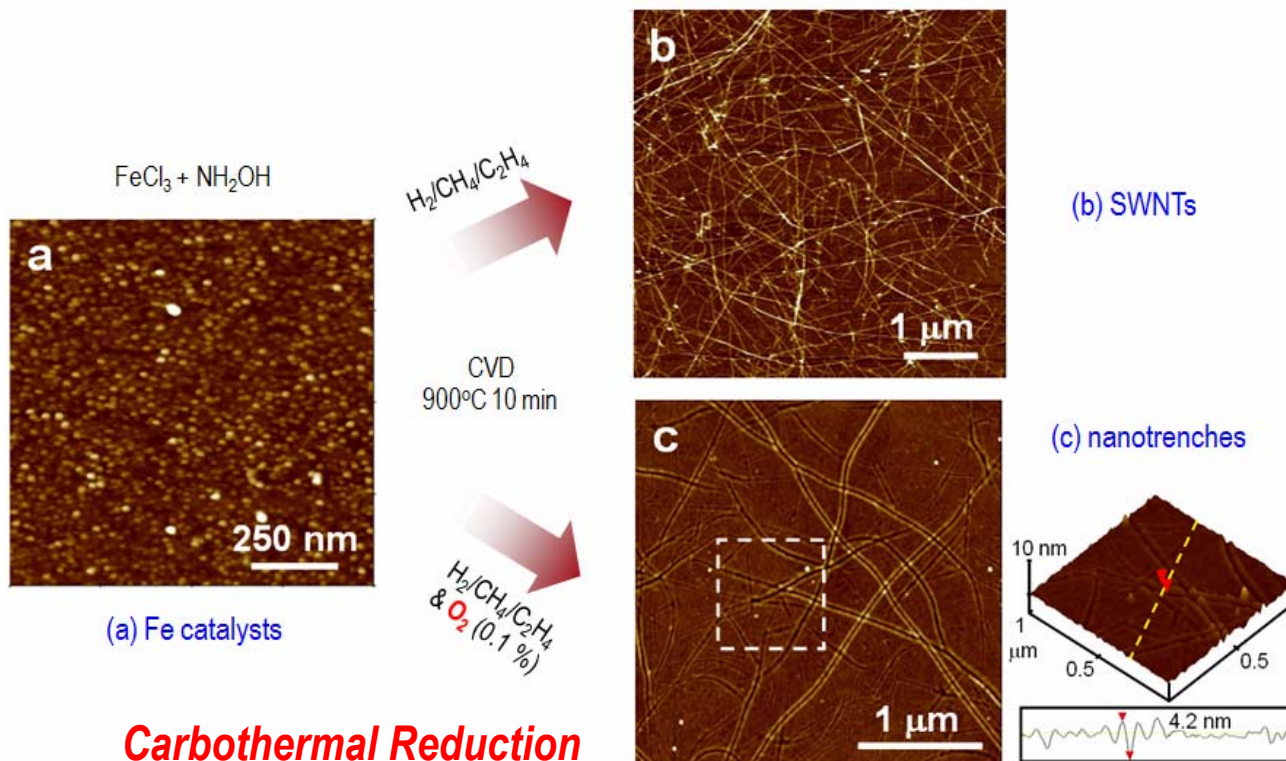
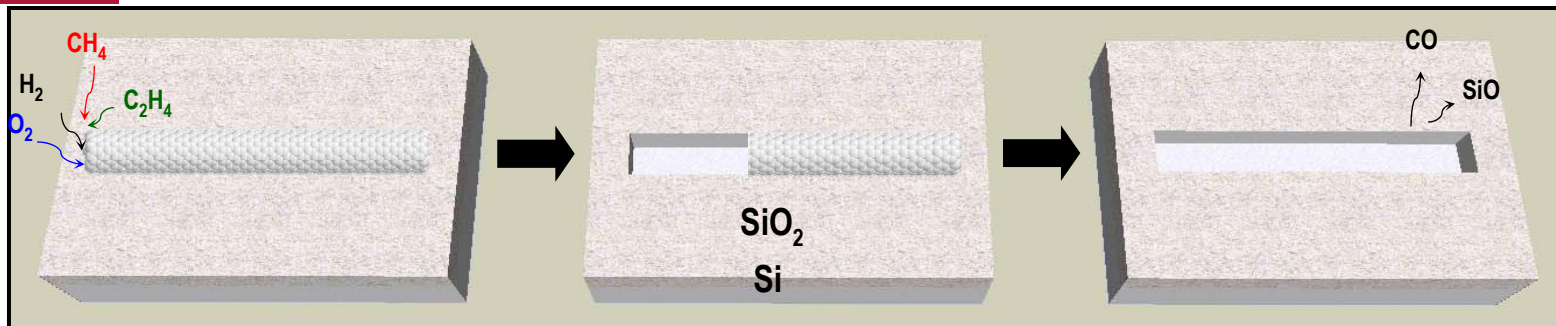


## Lithium intensity distribution (SP-TEM, Li 1s)





# Surface Chemistry of Carbon nanotubes: Carbothermal Reduction – *Etching SiO<sub>2</sub>*



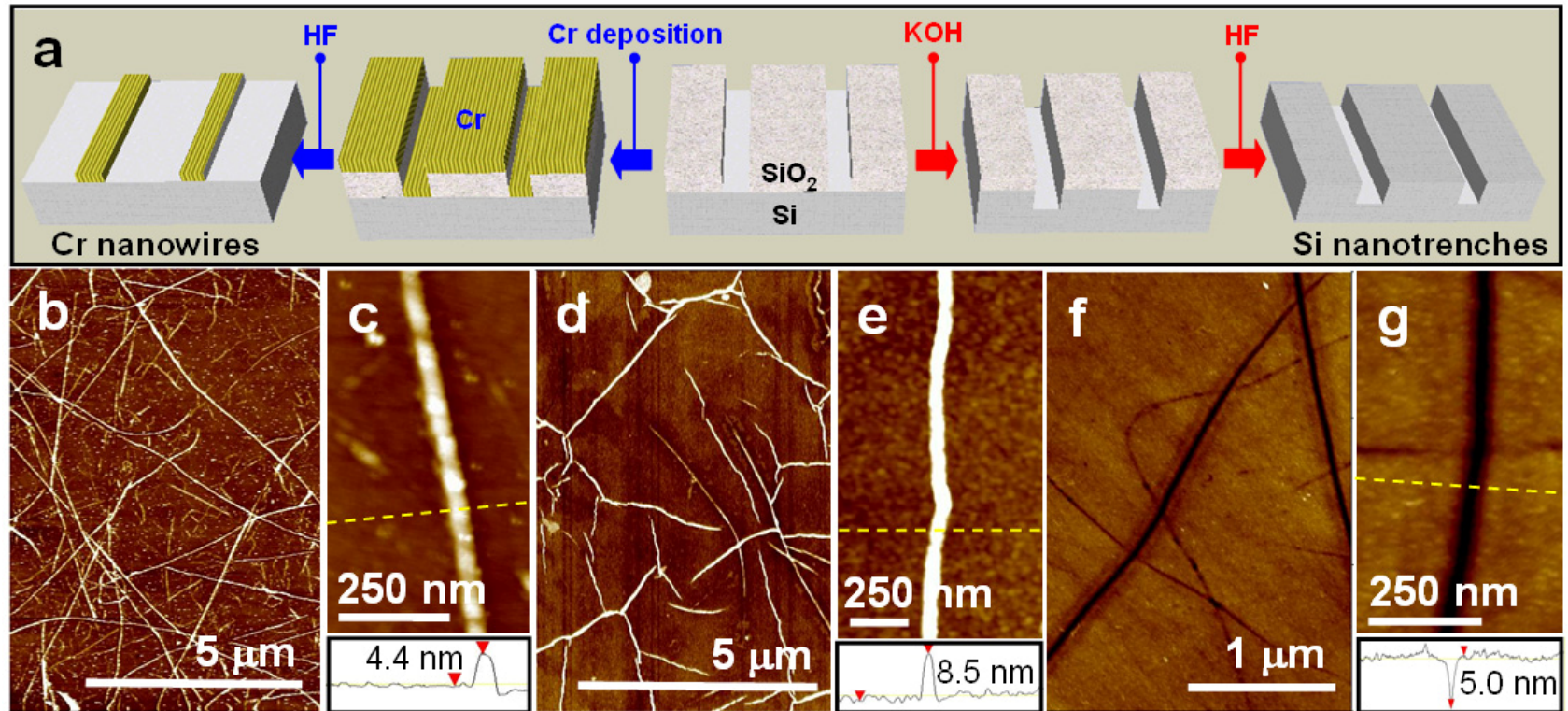
Byon and Choi, *Nature Nanotech* 2007, 2, 162.

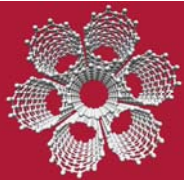
Byon and Choi, *Nano Lett.* 2008, 8, 178.





## Sub-10 nm scale Lithography using Nanotrenches



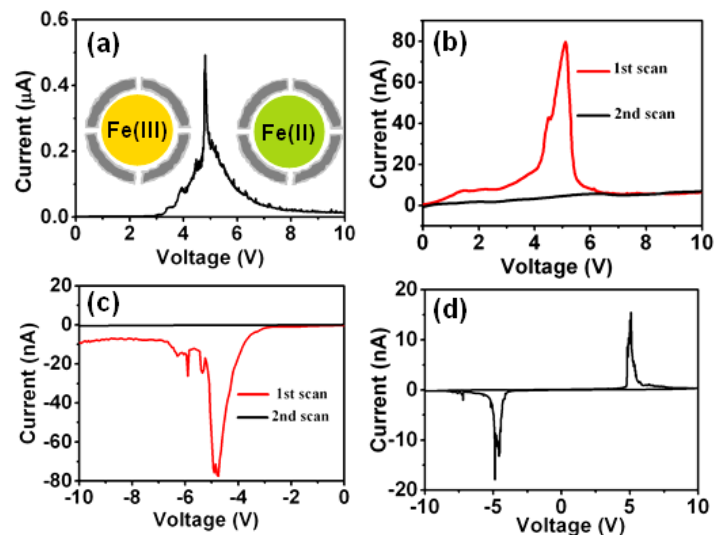
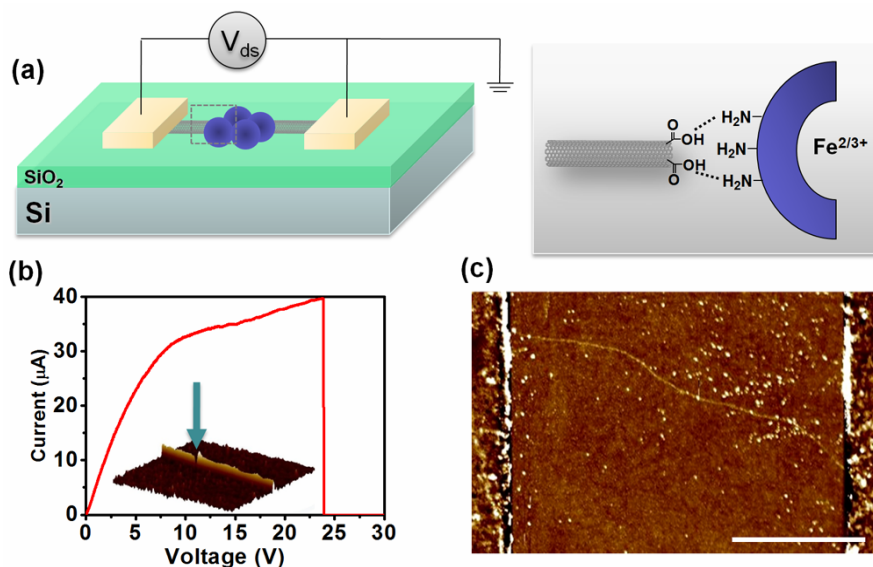


# Carbon nanotube electronics:

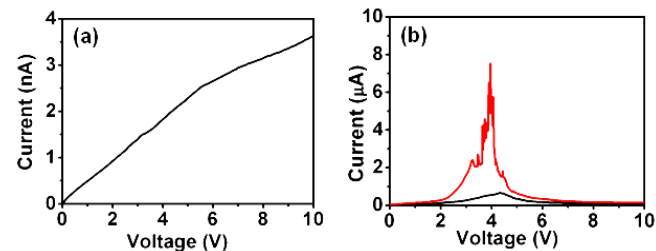
## Carbon nanotube/protein-based memory device

### Negative Differential Resistance (NDR) device

- Ferritin captured in metallic SWNT nanogap electrodes

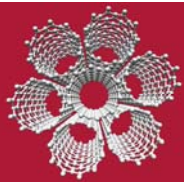


- Electrically cut m-SWNT (gap = ca. 20 nm)
- Electrostatically captured Ferritins
- Peak current density:  $4.0 \times 10^6$  A cm<sup>-2</sup> (record)
- Peak-to-Valley Ratio (PVR): ~ 40 (@ scan rate of 26 mV/s)
- NDR is 1.2 μohm cm<sup>2</sup>



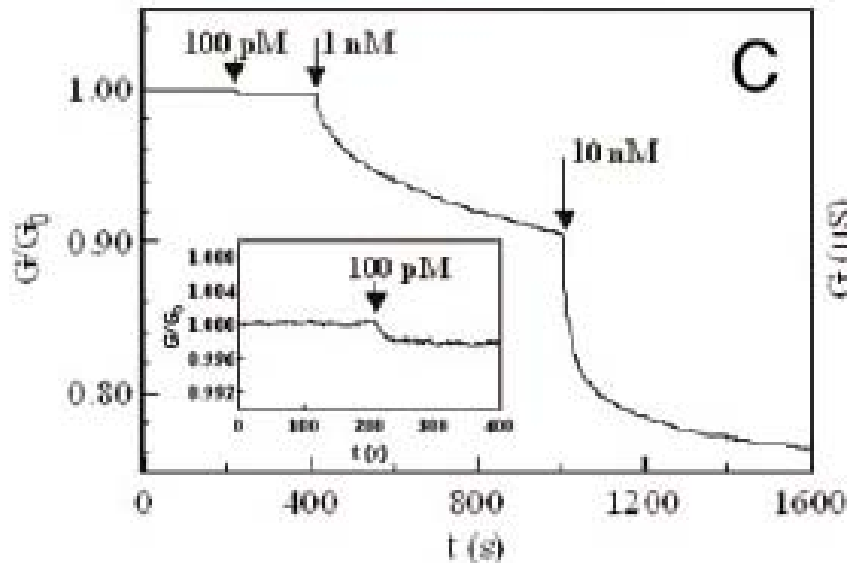
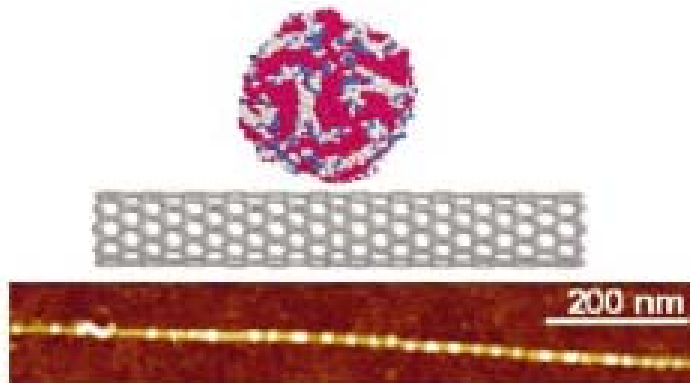
Apoferritin

Apoferritin + Fe(III)

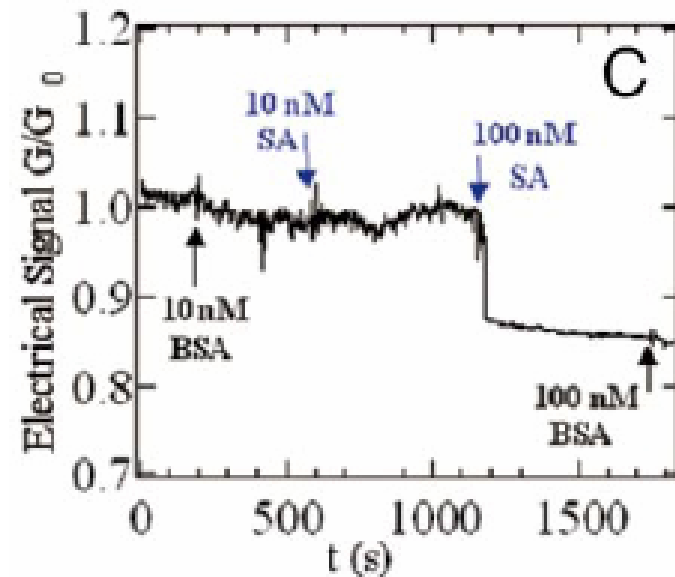
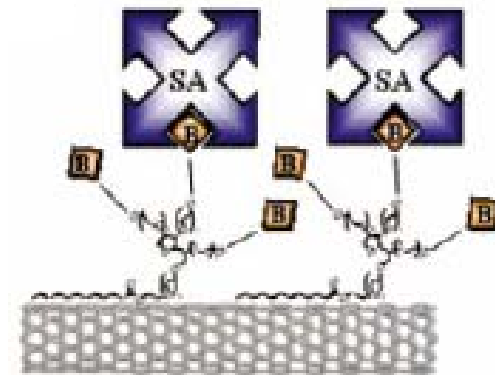


# Electronic sensing of biomolecular recognitions using SWNTs-FETs

## ▪ Nonspecific Binding



## ▪ Specific Binding (*using CDI-Tween20*)





### Sensitivity

- At least  $\sim$  pM, grateful if it can go lower.
- Protein detection limit of SWNT-FET:  $>10$  nM  
(c.f. Lieber group:  $\sim 10$  fM detection limit of proteins using SiNW devices-*Nat. Biotechnol.* **2005**, 23, 1294.)

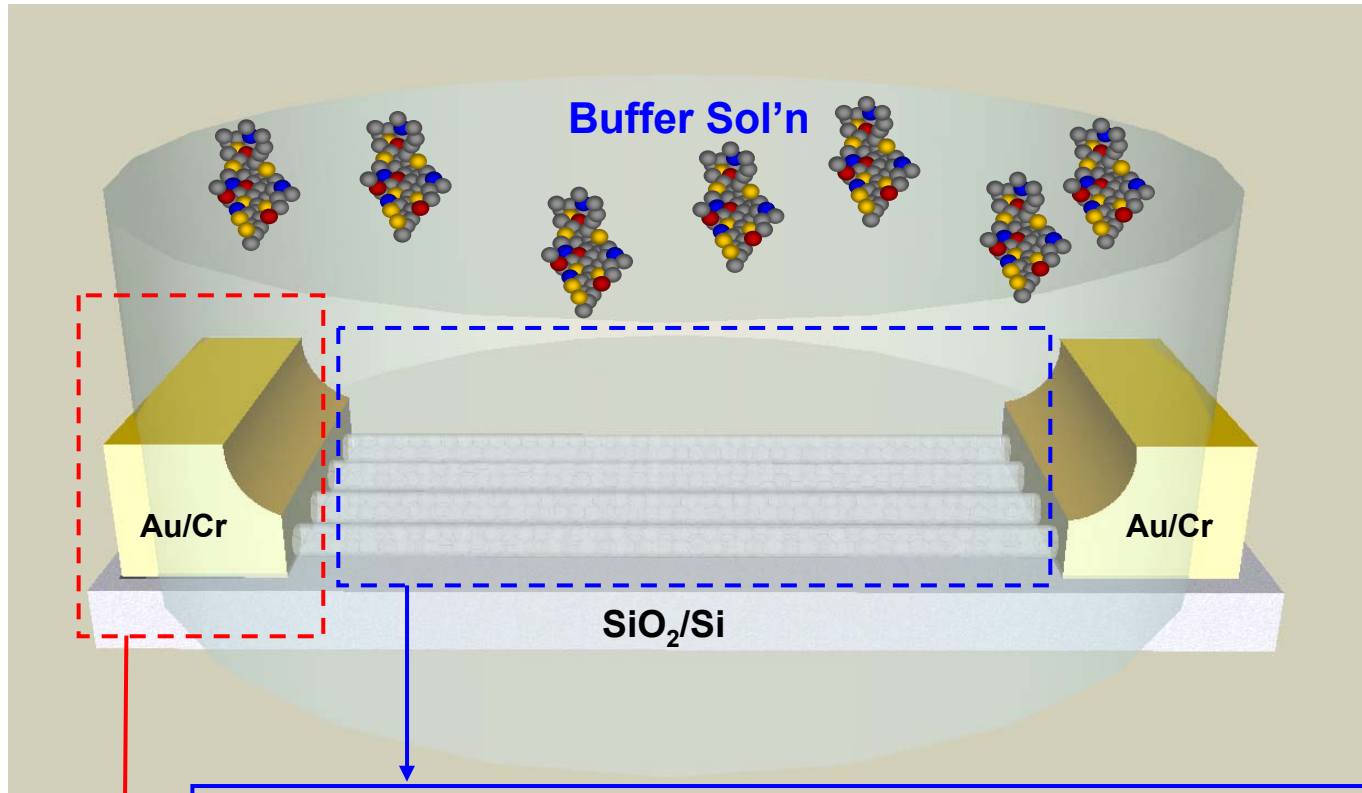
### Feasibility

- Prompt use: currently too long stabilization time
- Nonspecific binding: perfect protection of devices with efficient chemical blocking is mandatory.





## The two regions effecting to a biosensor sensitivity



**Nanotube aspect:** Direct charge communication between proteins and nanotubes

**Metal-nanotube contact aspect:** Schottky barrier modulation by protein adsorptions on metal surfaces



# The origin of conductance changes: Schottky Barrier

- Nanotube aspects:

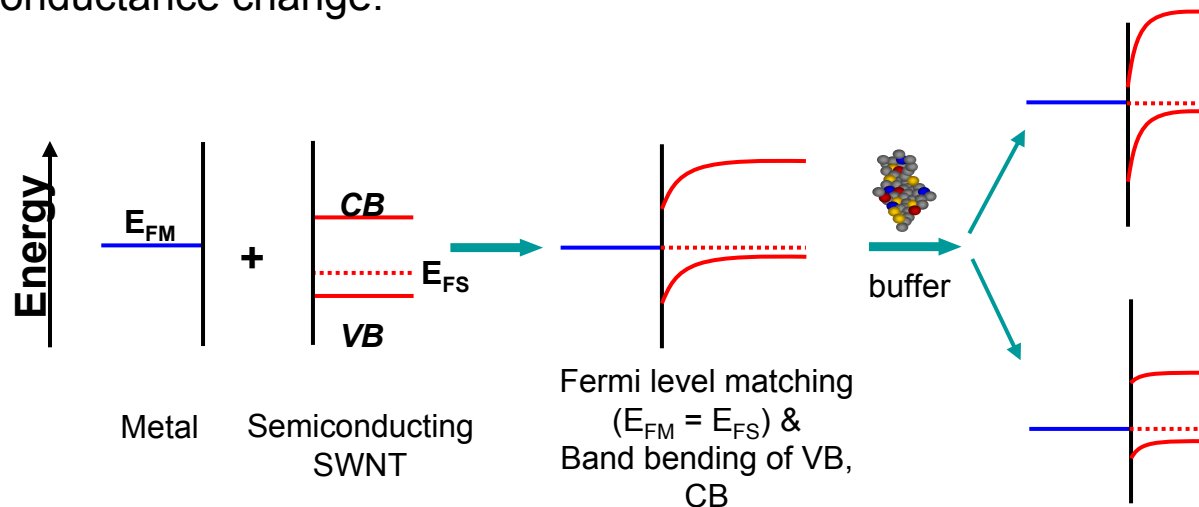
Charge injection from biomolecules

Electric double layer field modulation caused by biomolecules

**→ Strongly depending on the  $pI$  (isoelectric point) values of proteins**

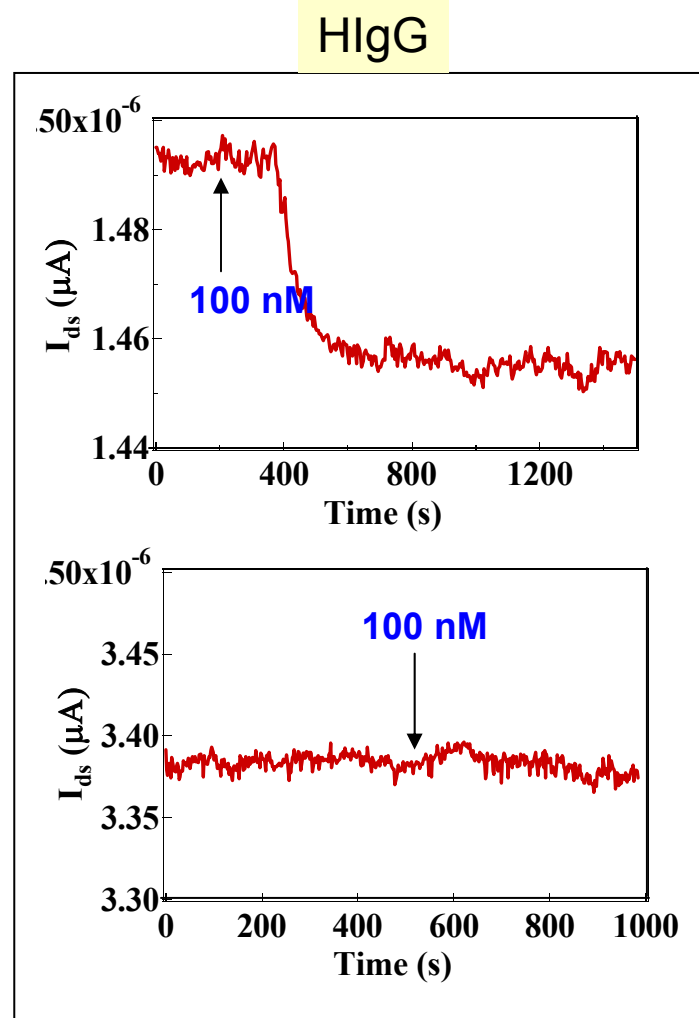
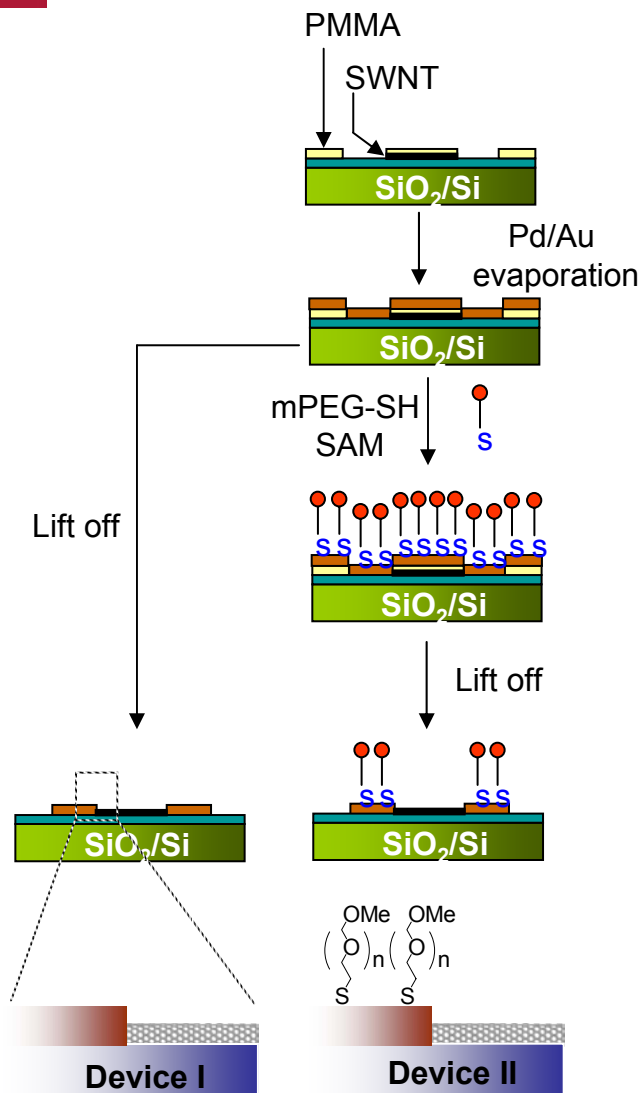
- Metal-nanotube contact aspect:

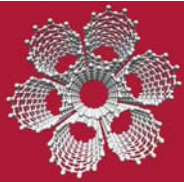
Adsorbed chemical species may modulate work function level of contact metals, which consequently change the Schottky barrier height resulting in the conductance change.



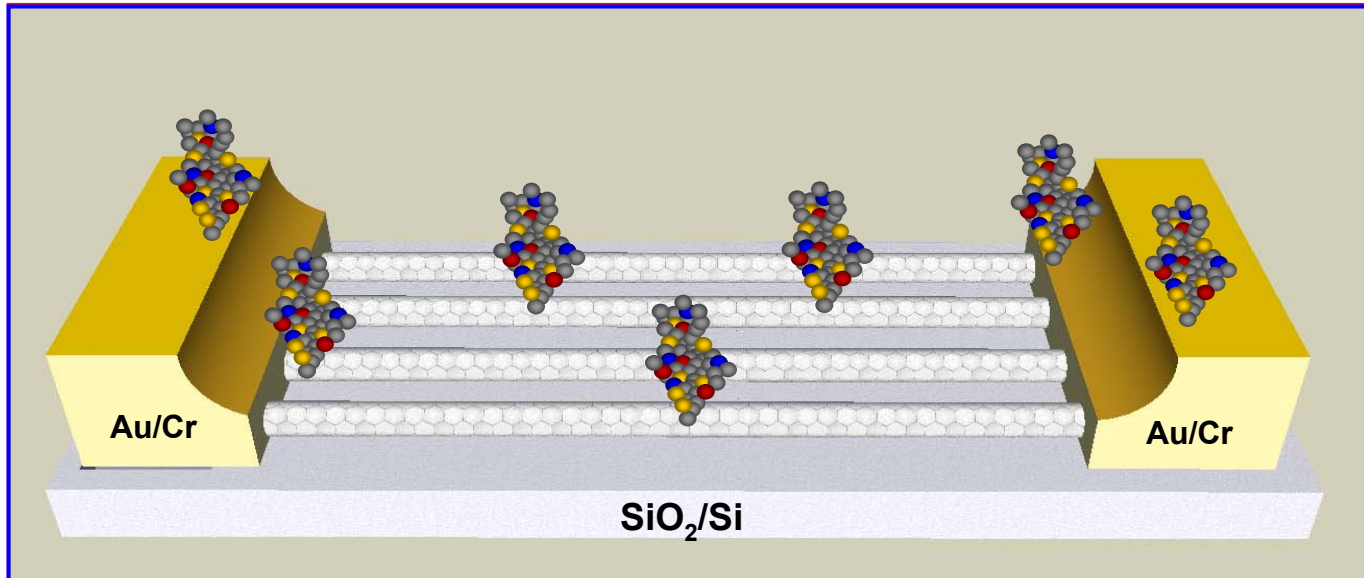


# Experimental evidence for the detection mechanism



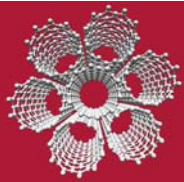


## Increased Schottky contact area for high performance

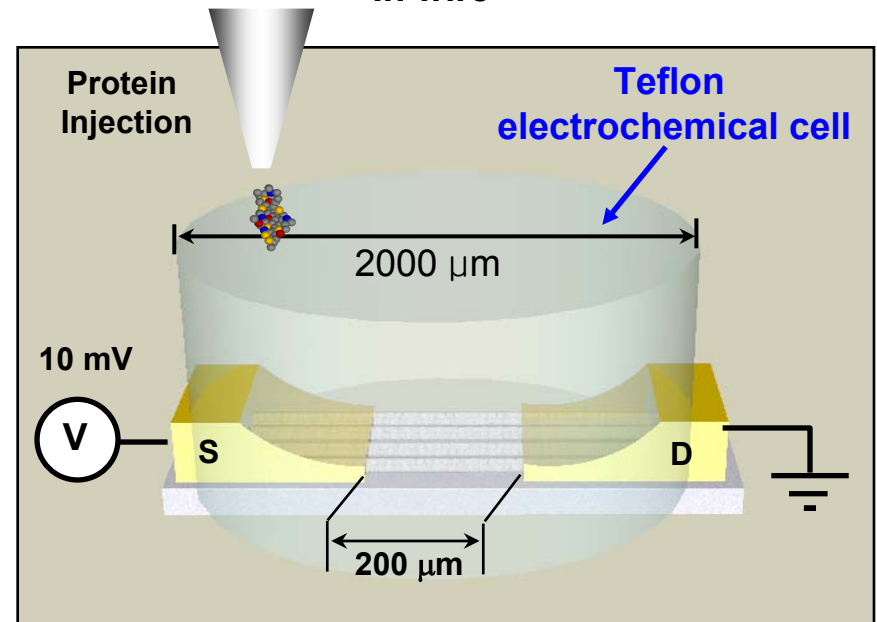
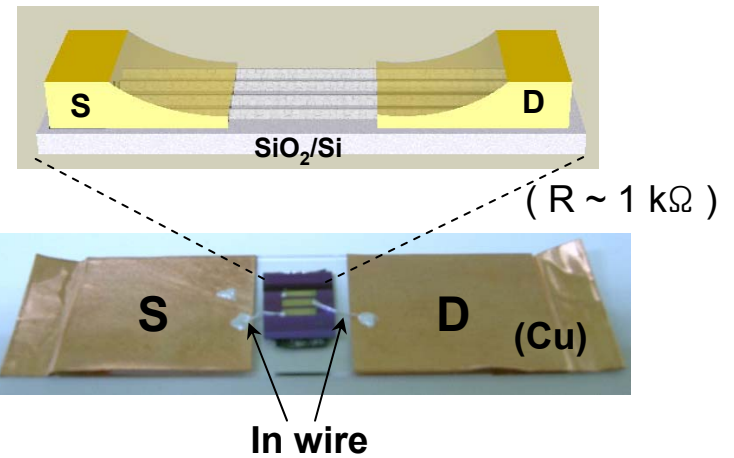
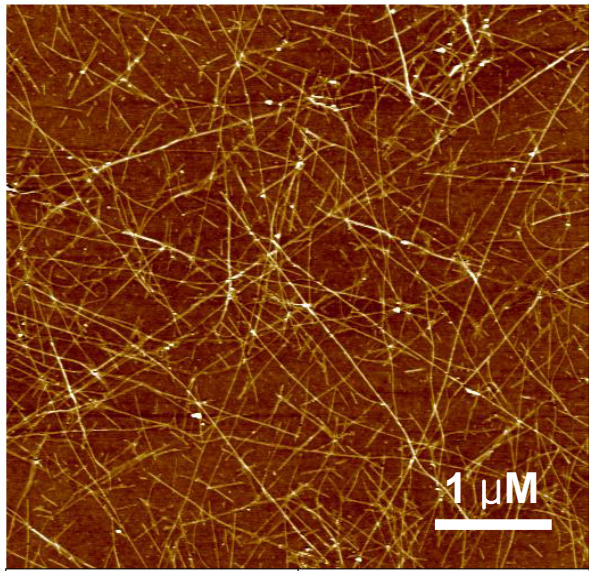
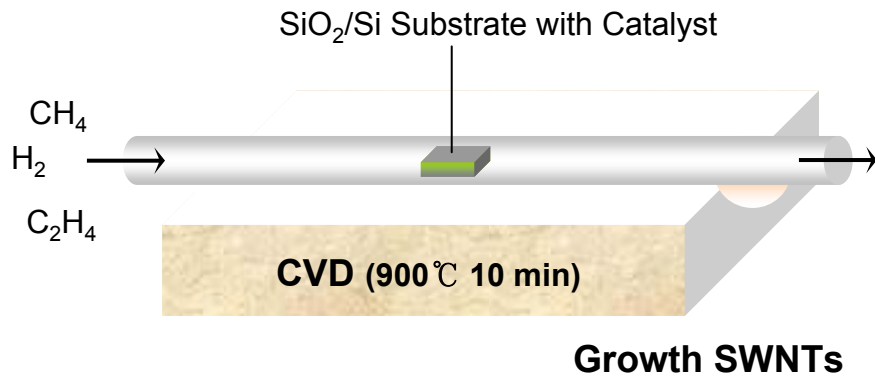


- Synthesis of network SWNTs
- Usage of the thin shadow mask
- Thermal evaporator with tilted angle stages





# Fabrication of SWNT-FET having increased Schottky contact area

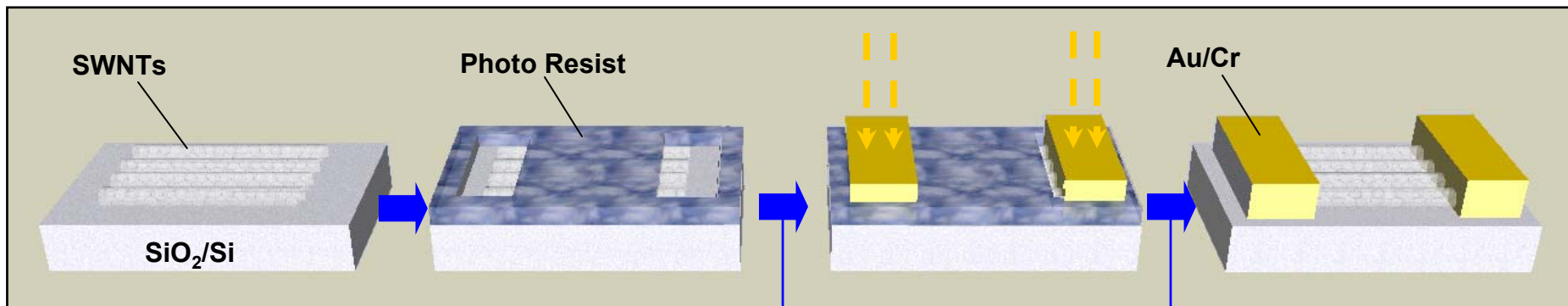


Choi and Dai et al. *Nano Lett.* 2003, 3, 157.  
Yang and Choi et al. *Langmuir* 2005, 21, 9198.



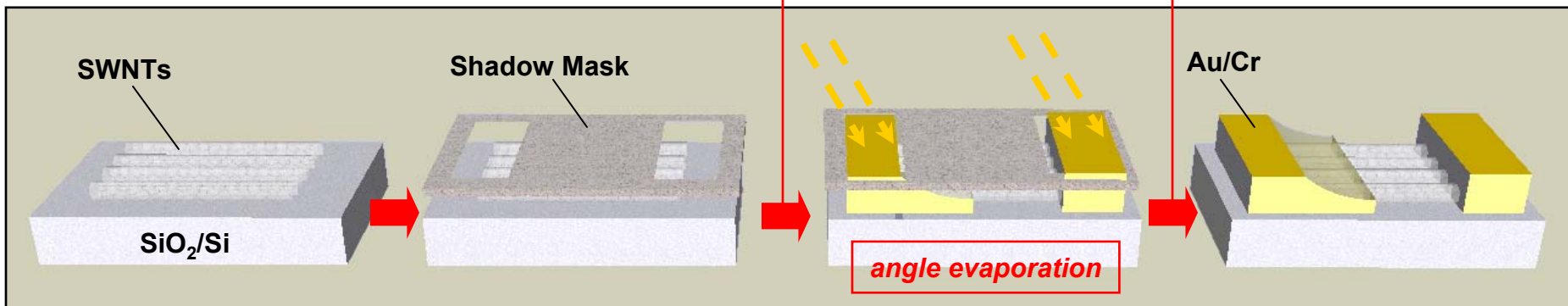
# Fabrication of SWNT-FET having increased Schottky contact area

(a) SWNT FET device fabricated by a **photolithography**



(1) Metal Evaporation

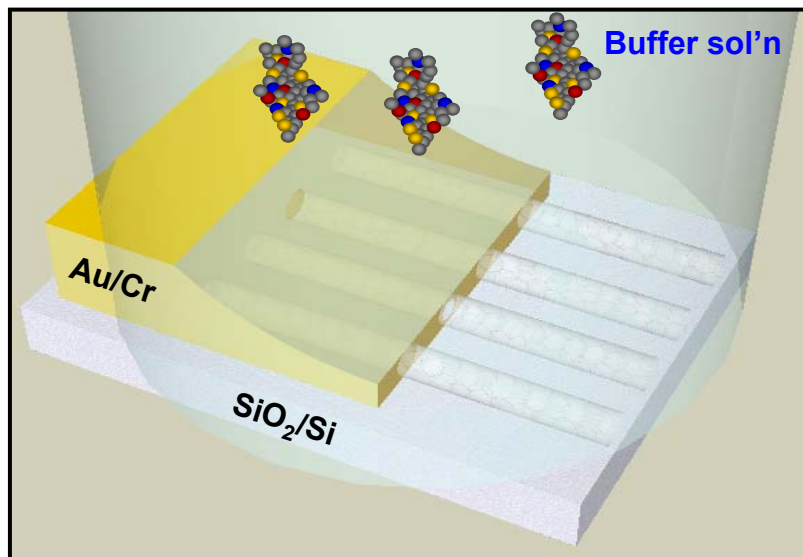
(2) Lift Off



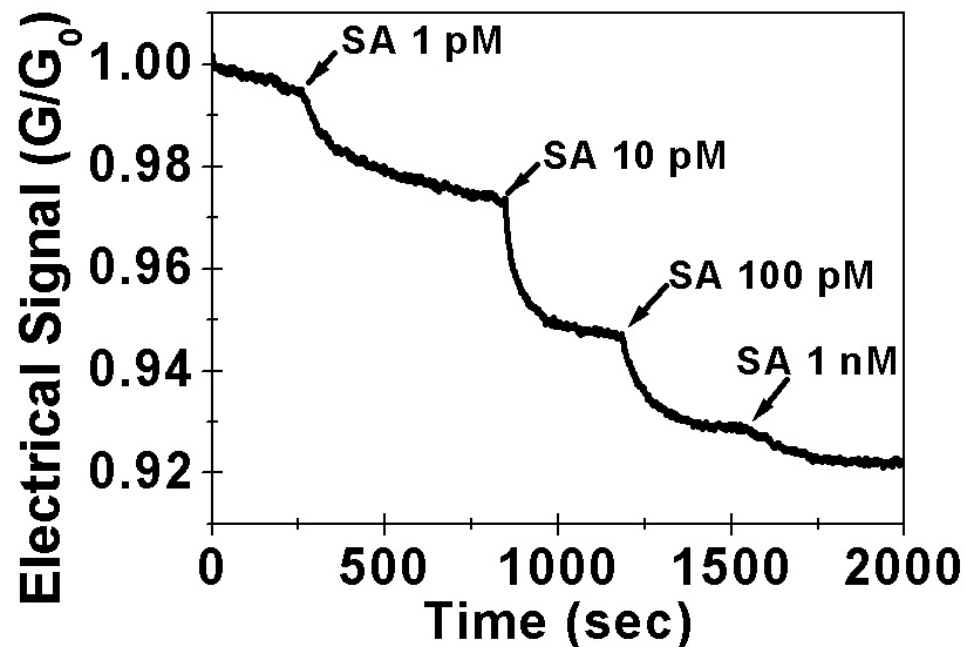
(b) SWNT-FET device fabricated by a **shadow mask at tilted angle**



## Highly sensitive SWNT-FET devices: Nonspecific bindings of proteins



- SA
- SpA

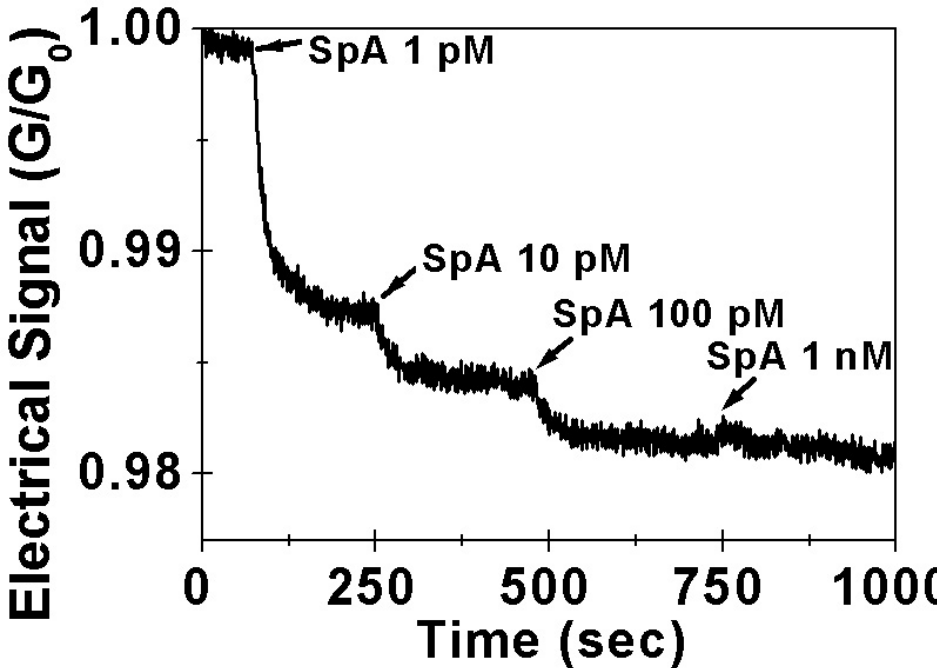


a SWNT-FET fabricated by a **shadow mask**  
**at tilted angle**

→ **1 pM sensitivity**

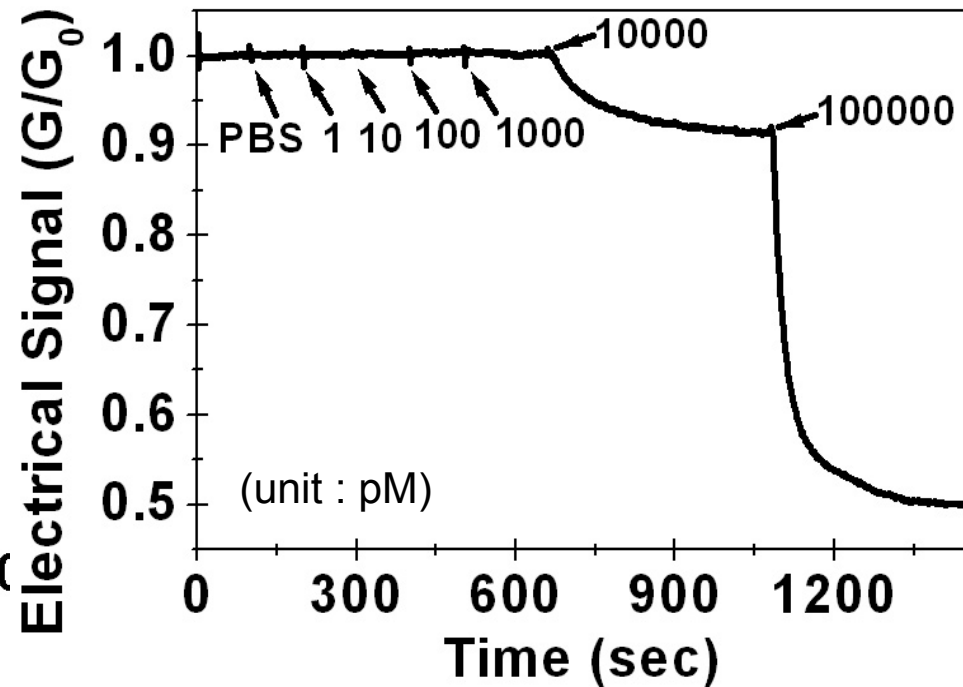


## Highly sensitive SWNT-FET devices: Nonspecific bindings of proteins



a SWNT-FET fabricated by a shadow mask  
at tilted angle

→ 1 pM sensitivity



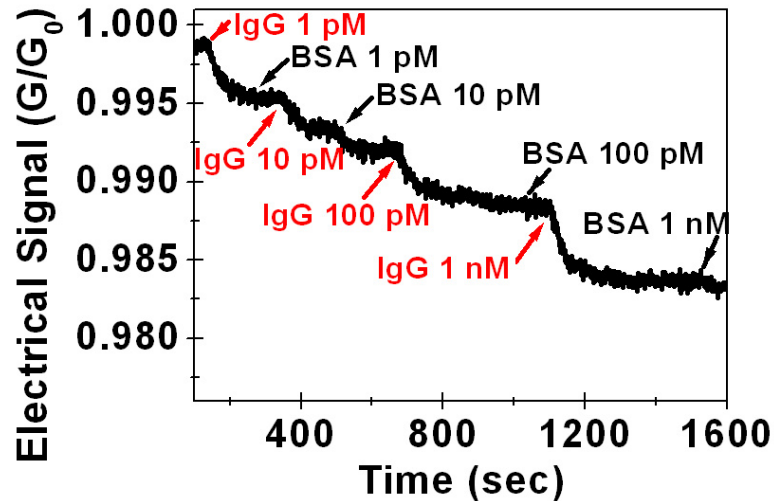
a SWNT-FET fabricated by a shadow mask  
<Protein : SpA>

→ 10 nM sensitivity

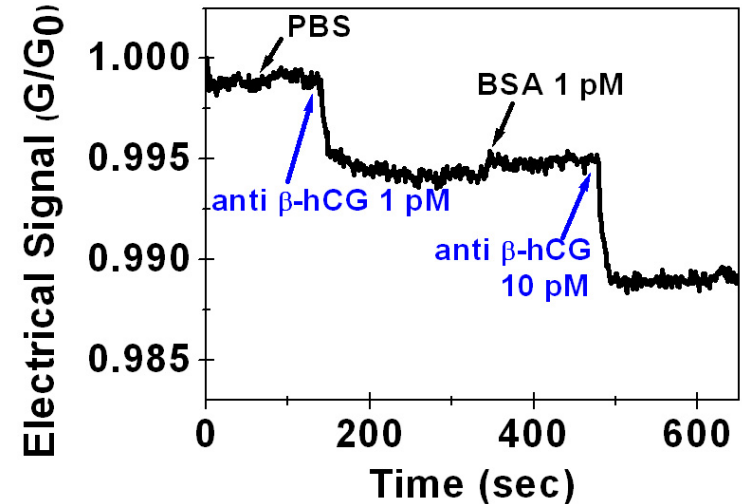




## Highly sensitive SWNT-FET devices: Specific bindings of proteins



- Probe protein: Protein A
- Target protein: rabbit IgG



- Probe protein: hCG
- Target protein: anti  $\beta$ -hCG

Treatment of 0.05% Tween20 after immobilizing probe proteins

→ 1 pM sensitivity



## Acknowledgement



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Dr. Hye Ryung Byon

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Yoonmi Lee

Hyun Jae Song

Hyunseob Lim

Hye Kyung Moon

Suphil Kim

Kyoung Ok Kim

Ji Eun Park

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Prof. Seunghun Hong (SNU)

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