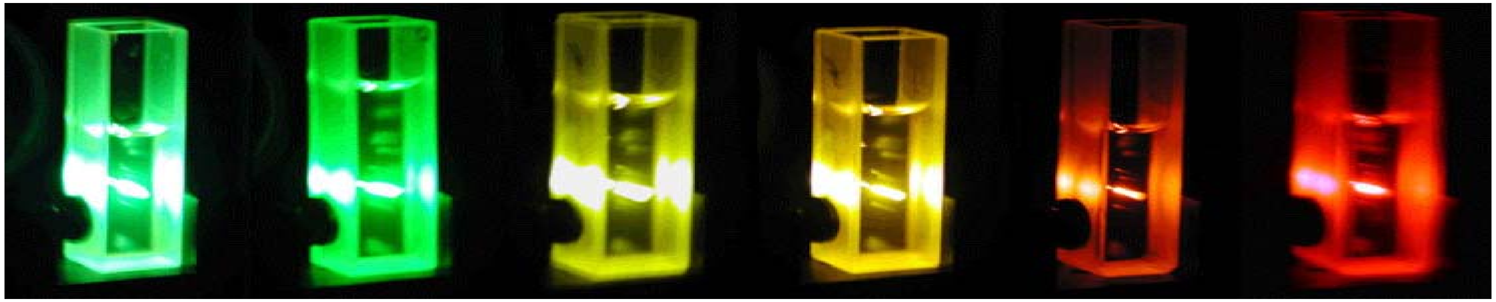
Nano Materials

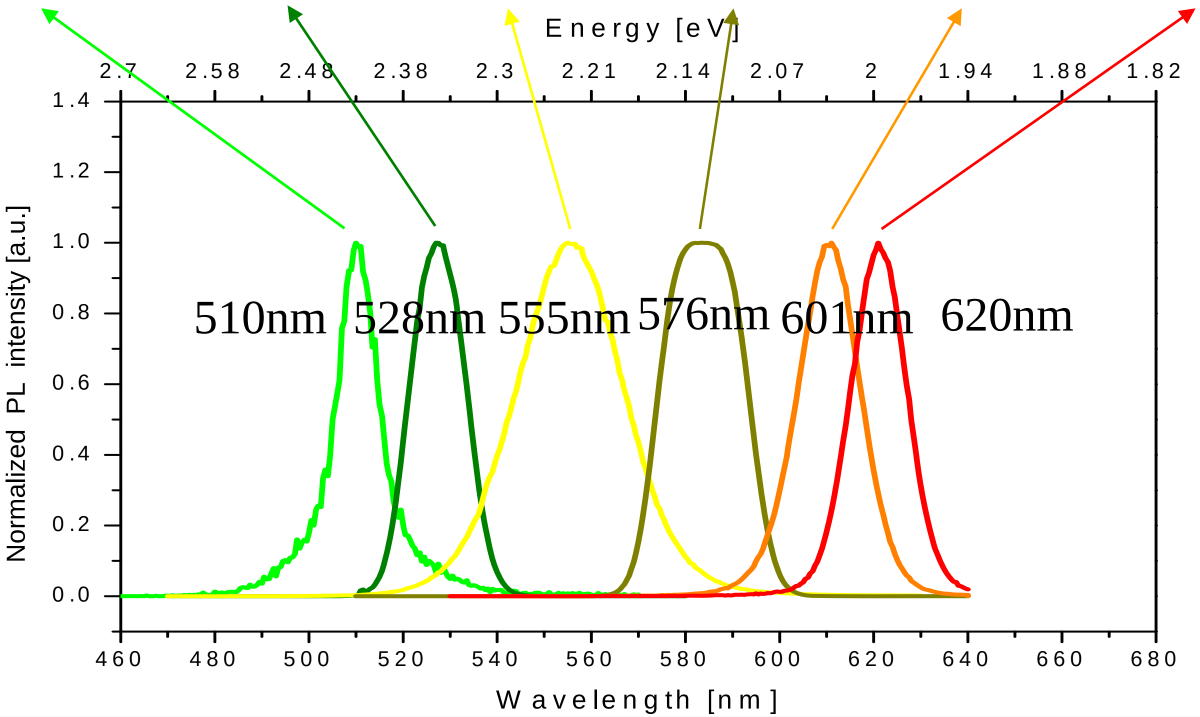
Contents

Properties and Applications- Optical

❑ Optical properties

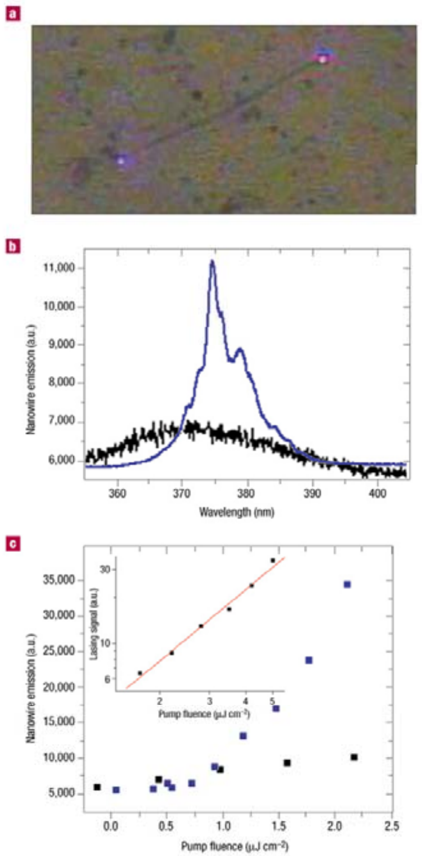
Larger Quantum Dot Size →

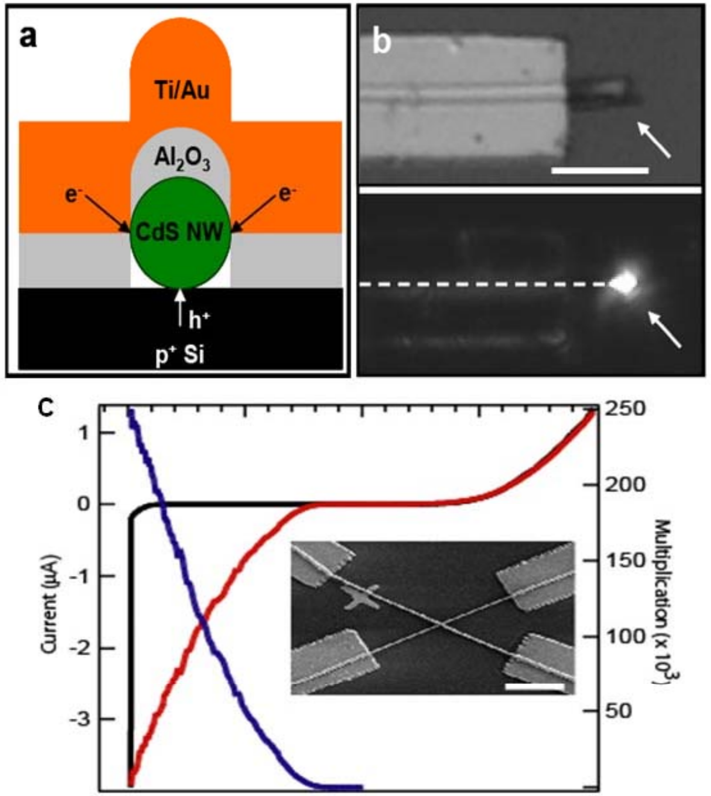




Properties and Applications- Optical

❑ Optical properties

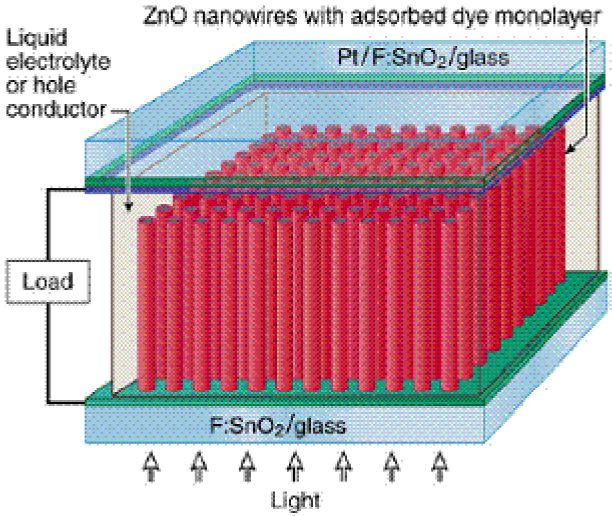




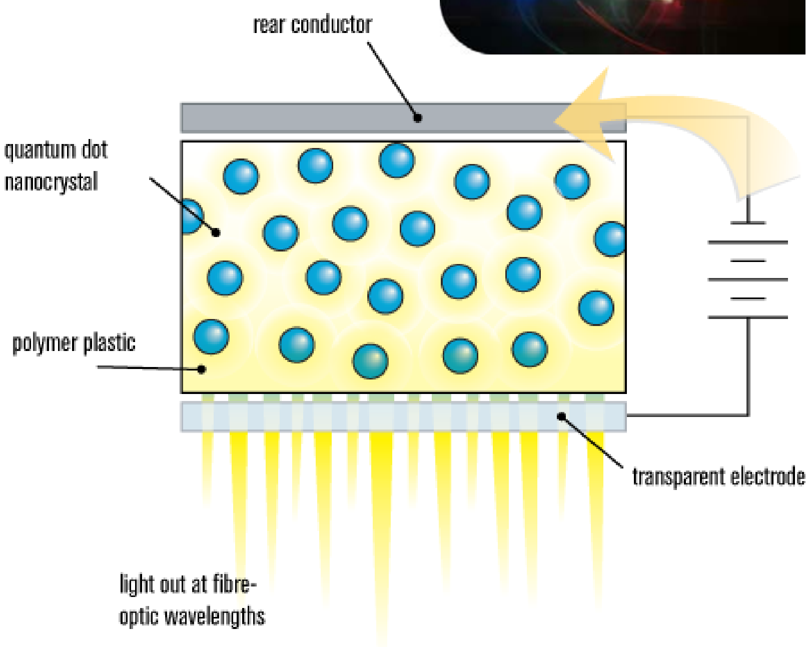
- Nanowires act as a cavity for stimulated emission and laser

Properties and Applications- Energy

❑ Energy applications



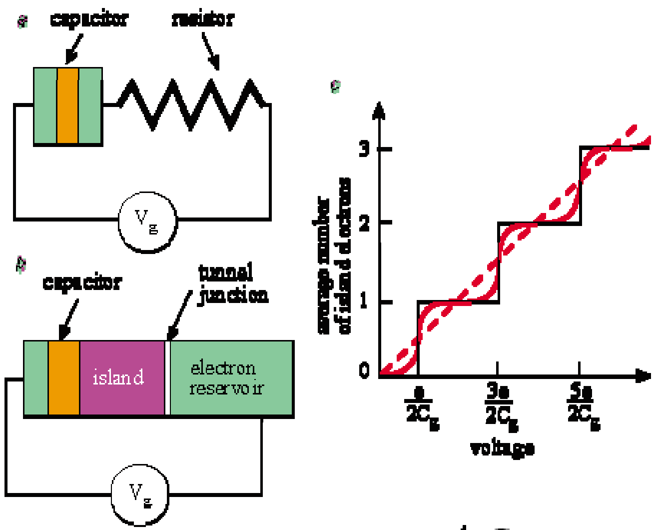
- Nanowires in the solar cell provide direct electrical pathways and ensure good efficiency



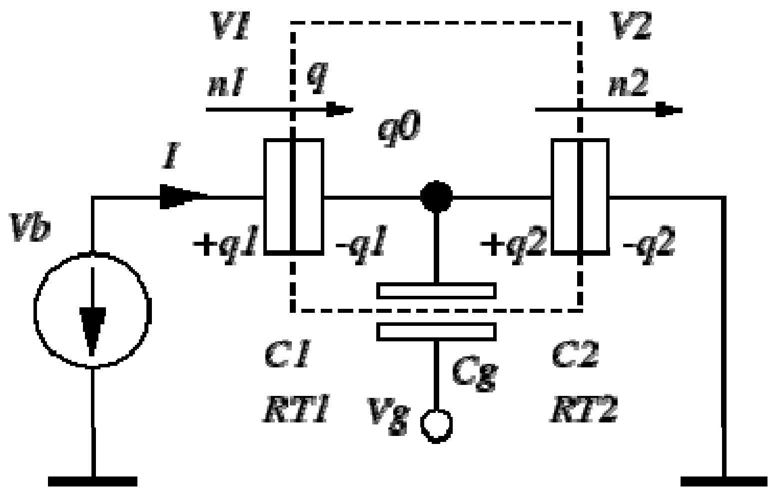
- Quantum dot LED provide various wavelength and high efficiency

Properties and Applications- Electrical

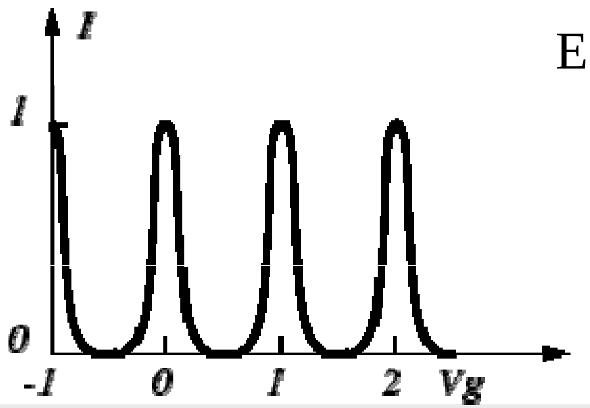
❑ Single electron transistor and Columb blockade



Island in a circuit



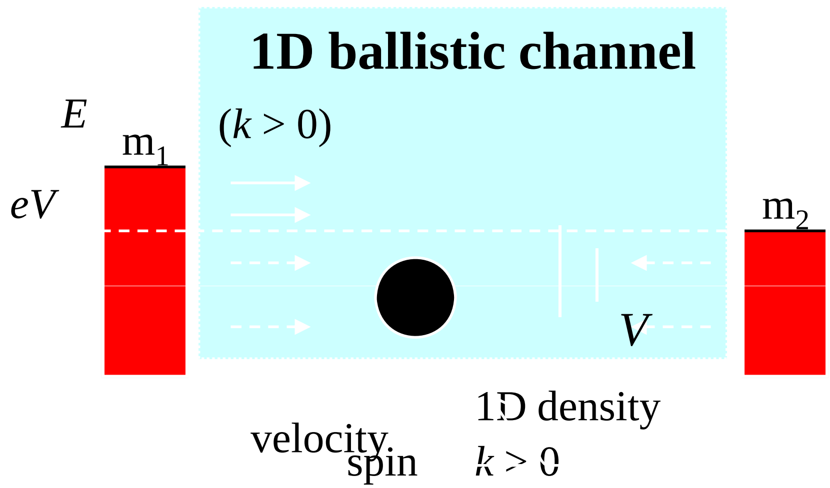
Equivalent circuit of an SET



Coulomb oscillations in a SET transistor

Properties and Applications -Electrical

Conductance of 1D quantum wire



Contacts: 'Ideal reservoirs'

Chemical potential m ~ E_F
(Fermi level)

Channel: 1D, ballistic
(transport without scattering)

$$I = \int_{\mu_1}^{\mu_2} ev(E)\left(2\frac{1}{2}g_{1D}(E)\right)\mathrm{d}E = \int_{\mu_1}^{\mu_2} ev(E)\left(\frac{2}{hv(E)}\right)\mathrm{d}E$$

$$= \frac{2e}{h}(\mu_2 - \mu_1) = \frac{2e}{h}(eV)$$

$$G = I/V = \frac{2e^2}{h}$$

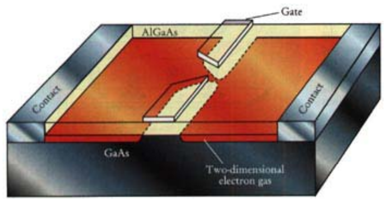
Conductance is fixed, regardless of length *L*,
no well defined conductivity s

Properties and Applications- Electrical

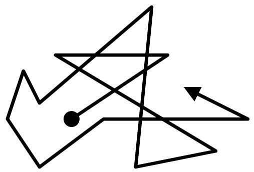
❑ Transport regime

Length scales:	l_F	Fermi wavelength (only electrons close to Fermi level contribute to G)
	L_m	momentum relaxation length (static scatterers)
	L_f	phase relaxation length (fluctuating scatterers)
	L	sample length

- **Ballistic transport**, $L << L_m, L_f$
  - no scattering, only geometry (eg. QPC)
  - when $l_F \sim L$: quantized conductance $G \sim e^2/h$



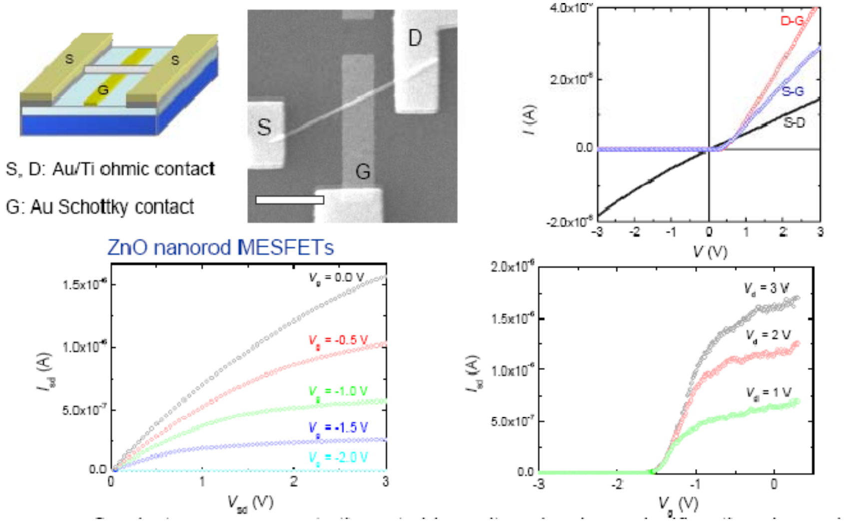
- **Diffusive**, $L > L_m$
  - scattering, reduced transmission



- **Localization**, $L_m << L_f << L$
  - $R \sim \exp(L)$ due to quantum interference at low T
- **Classical** (incoherent), $L_f, L_m << L$
  - ohmic resistors

Properties and Applications- Electrical

❑ Nanowire MEFETs and mobility



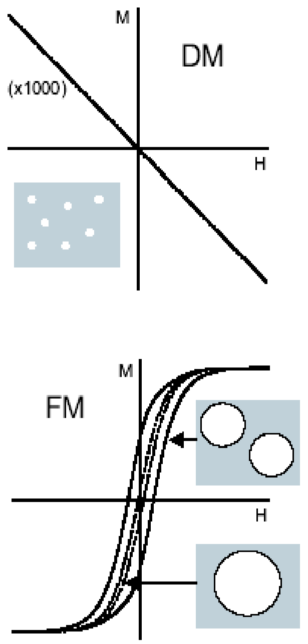
Materials	Mobility (cm^2/Vs)
ZnO nanorods	200–3000
ZnO TFTs	0.1–50
In_2O_3 nanobelts	10–120
Si nanowires	300
Ge nanowires	16–600
GaN nanowires	150–650

- Conductance response to the gate bias voltage has been significantly enhanced: low turn-on voltage of -1.5V
- Individual MEFET operation for integrated circuits

Properties and Applications- Magnetic

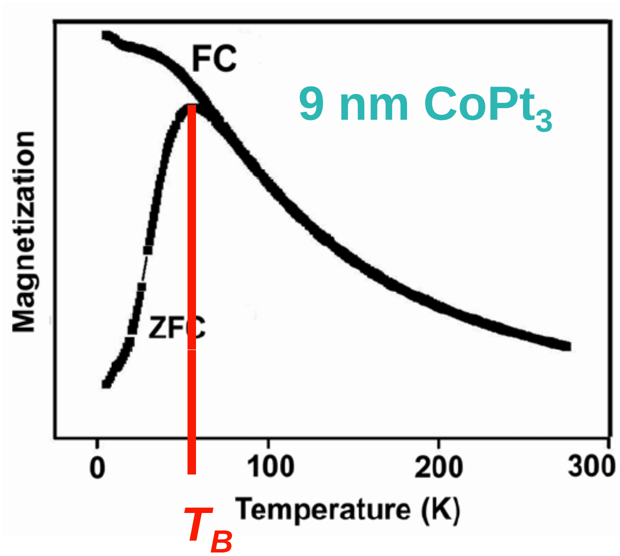
❑ Superparamagnetic Properties of Nanoparticles

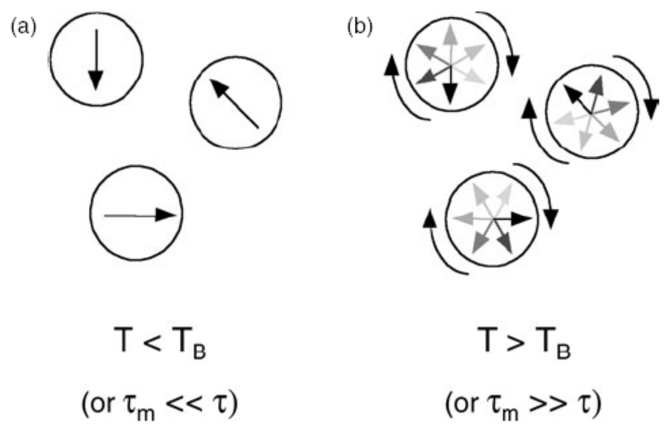
- Magnetism and Relaxation



$$\Delta E = KV$$

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right)$$

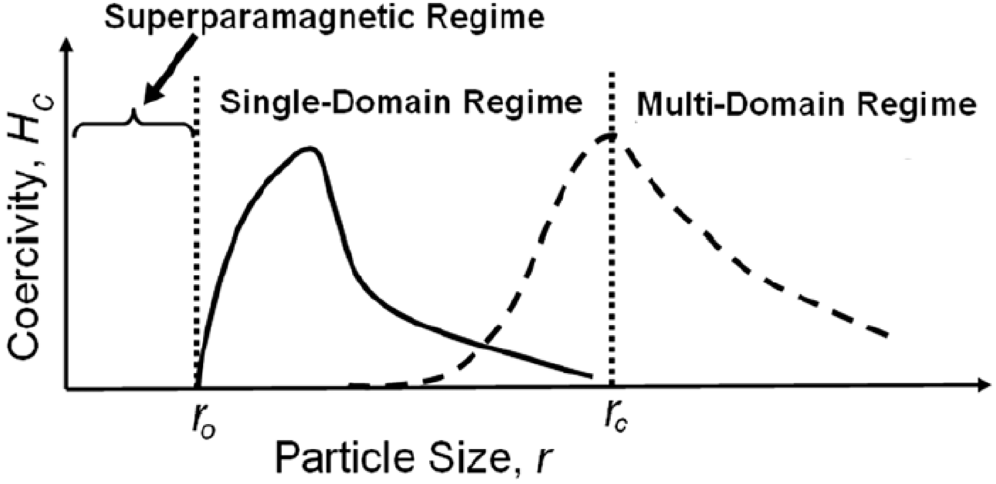




Properties and Applications- Magnetic

Superparamagnetic Properties of Nanoparticles

- Size Dependence on Magnetism



$r_c=(6k_BT/K_u)^{1/3}$

K_u: crystalline magnetoaniosotropy

hard magnets: r_c = ~ 3-4 nm

soft magnets: r_c = ~20 nm

Schematic illustration of the dependence of magnetic coercivity on particle size.
In the single-domain regime, the coercivity can follow either the solid curve for noninteracting particles or the dashed line for particles that have coupling between them.
The coercivity falls to zero for superparamagnetic colloidal particles.

Properties and Applications- Biomedical

- **Superparamagnetic Nanoparticles (Ferrofluids)(5)**
  - (a) Separation and purification
  - (b) GMR sensor
  - (c) MR contrast agent
  - (d) Hyperthermia
  - (e) Magnetic drug delivery

- **Metal Nanoparticles(4)**
  - (a) Dependence of SPR on Size and Shape
  - (b) Colorimetric sensing with SPR
  - (c) SERS

- **Semiconductor Nanoparticles – Fluorescence imaging (1)**

Properties and Applications- Biomedical

- **Drug Delivery Systems (8)**
  - (a) Basics of drug delivery (passive targeting, active targeting)
  - (b) Endocytosis of drug carrier
  - (c) Nucleic acid delivery

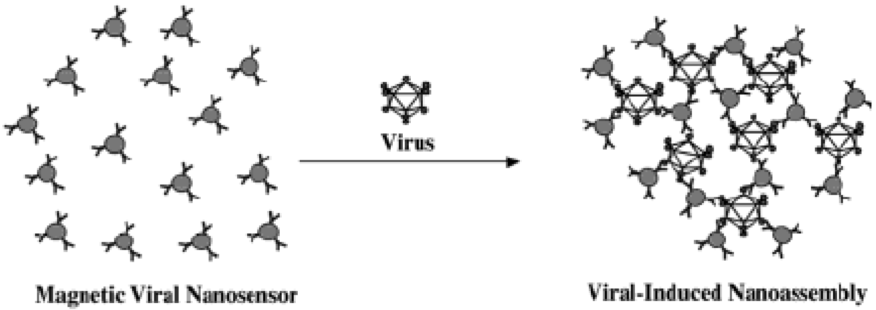
- **Nanofibers – scaffold, wound dressing, drug release control (2)**

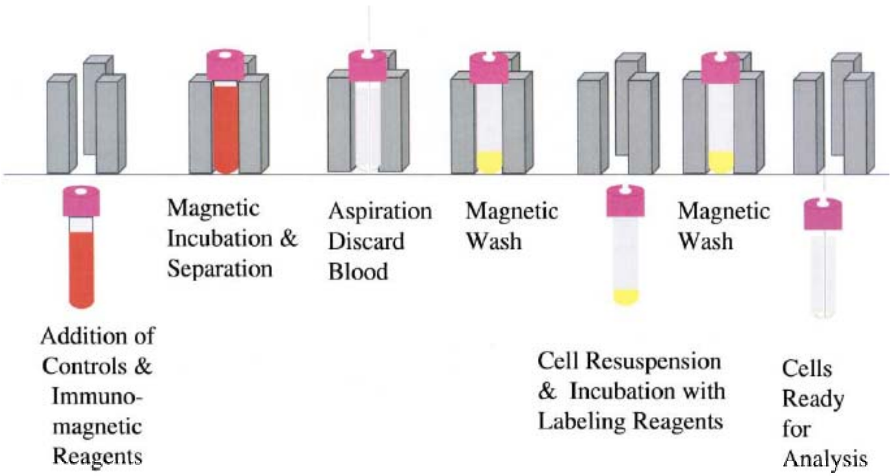
- **Nanowires(5)**
  - (a) Biosensors (semiconductor nanowires, CNT)
  - (b) Chemical sensors
  - (c) Biochips

Properties and Applications- Biomedical

❑ Ferrofluids

- Separation and Purification of Biomolecules





Polymer or SiO2 coated SPM nanoparticles

→ Surface treatment with functional group

→ Biomolecule attachment on the surface

→ Bioconjugation with target biomaterials

→ Magnetic field applied

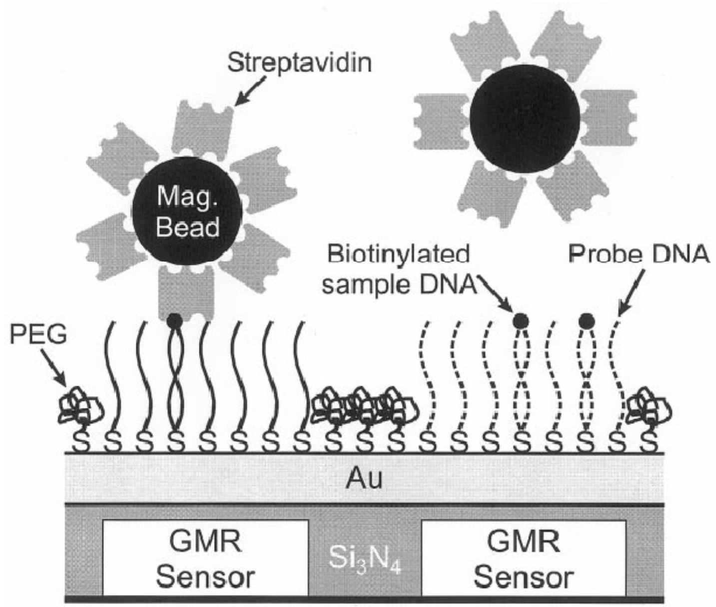
Properties and Applications- Biomedical

❑ Ferrofluids

- Biomolecule carrier for Magnetic Sensors

GMR: Giant Magnetoresistance

Huge change of electric resistance under magnetic field applied



SPM Microbeads

→ Surface treatment with functional group

→ Attachment of target biomolecules at the surface

→ Bioconjuation with biomolecules on the pattern surface

→ Fringed magnetic field detection

→ Sensing the existence of target biomolecules

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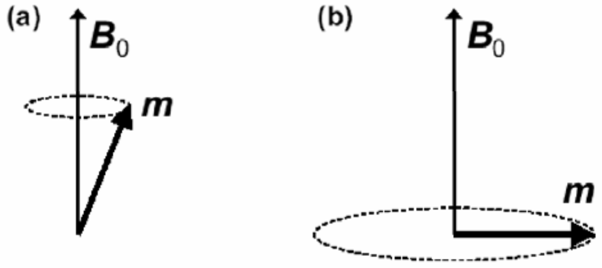
Properties and Applications- Biomedical

❑ Ferrofluids

- MR imaging contrast agent



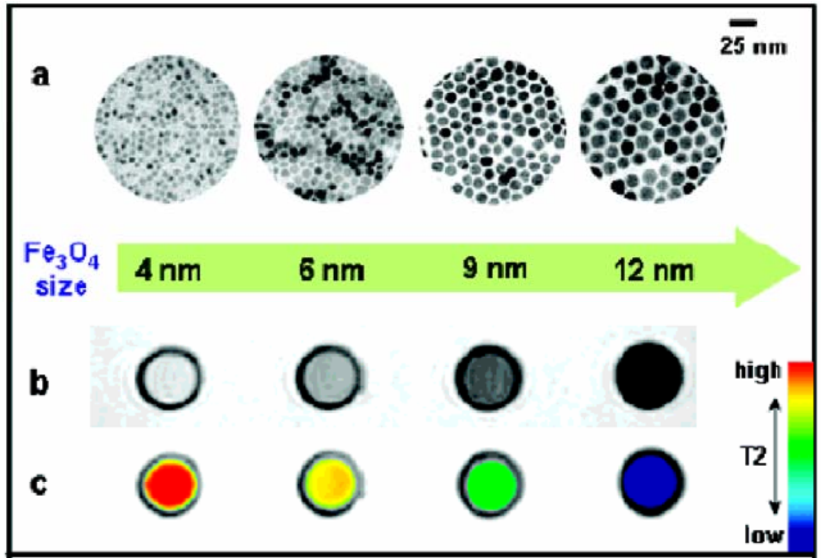
Relaxation of mignetic moments

T_1 relaxation: $m_z = m[1-\exp(-t/T_1)]$

T_2* relaxation: $m_{x-y} = m\sin(w_o t+\phi)\exp(-t/T_2)$

$$\frac{1}{T_2*} = \frac{1}{T_2} + \gamma\frac{\Delta B_o}{2}$$

ΔB_o: lacal magnetic fluctuation



T_1 relaxation (conventional Gd chelates)
→ make the site brighter

T_2 relaxation (SPM nanoparticles)
→ make the site darker

Properties and Applications- Biomedical

❑ Organic Colloids

- Basics of Drug Delivery

Pathways in DDS

1. Oral delivery – the most attractive and widely used, convenient and noninvasive, delivery through the intestinal epithelial cells
2. Transdermal delivery
3. Intraveneous injection

Types of carriers

1. Polymer-based :
- **Micelles from Amphiphilic Block Copolymers (ABC),**
- **Sol-gel types: pH sensitive, temperature sensitive**
- **Crosslinked conjugations**

2. Lipid-based systems: Liposomes, micelles, introduction of polymers for better stability
3. Nanoparticles (dendrimers, inorganic particles)
4. Peptide-enhanced Target delivery

What to deliver ?

1. Pharmaceutical drugs
2. Nucleic Acids (DNA, oligonucleotides...) : Gene delivery
3. Proteins

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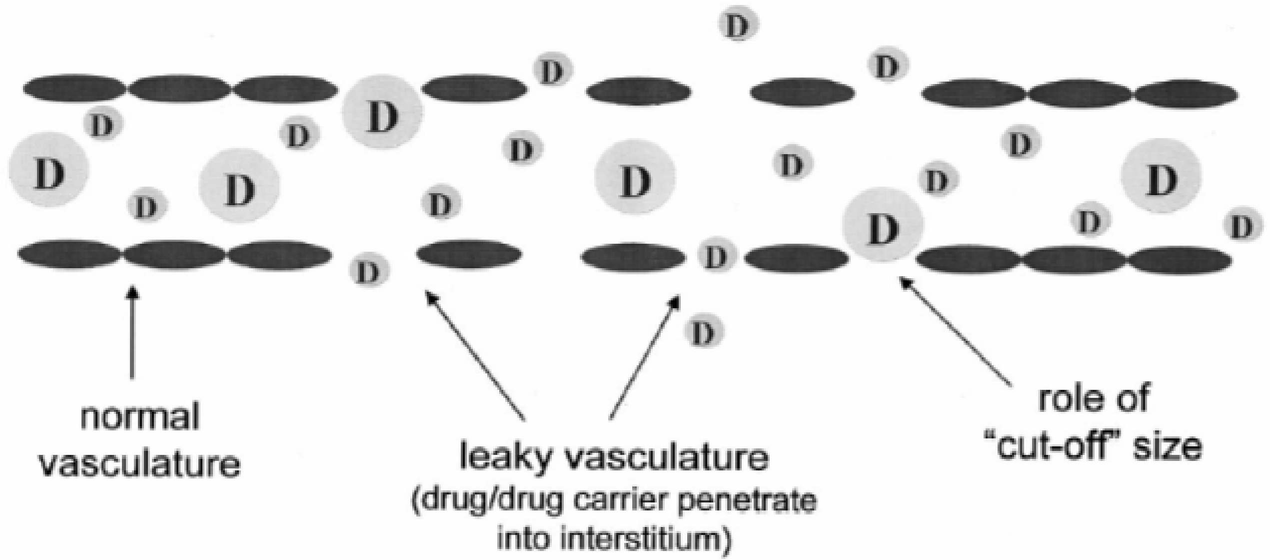
Properties and Applications- Biomedical

❑ Organic Colloids

- Passive Targetting (Enhanced Permeability and Retention)



Tumor area: wider gap between endothelial cells
→ Small drug carriers can penetrate due to the EPR effect

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Properties and Applications- Biomedical

❑ Organic Colloids

- Active Targetting (Surface modification or external force)

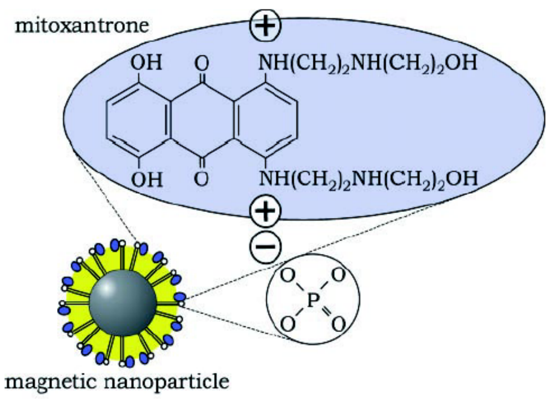
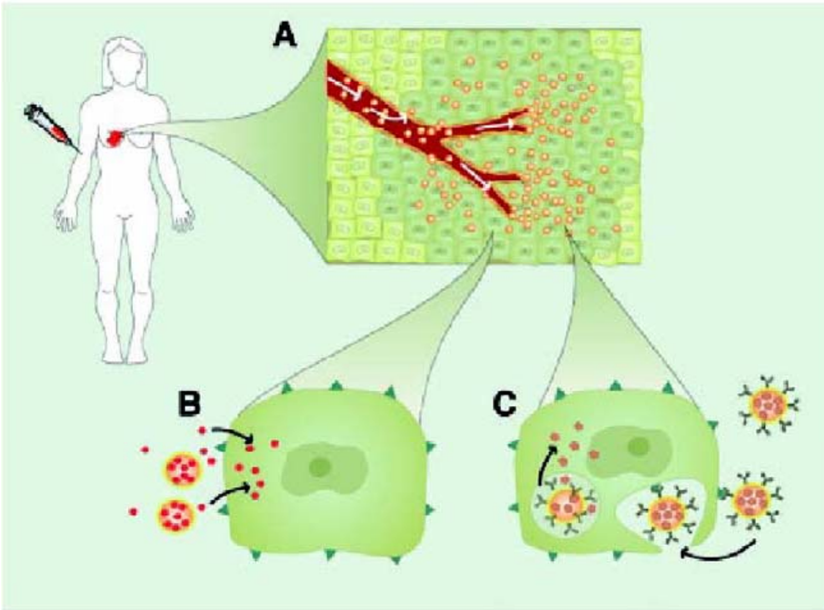


Fig. 1. Structural formula of MTX bound to magnetic nanoparticle.



Surface functionalization

→ target delivery to a specific cells via specific bioconjugation

→ internalization of the carriers (forming endosomes)

→ endosome ruptured (intracellular drug carrying)

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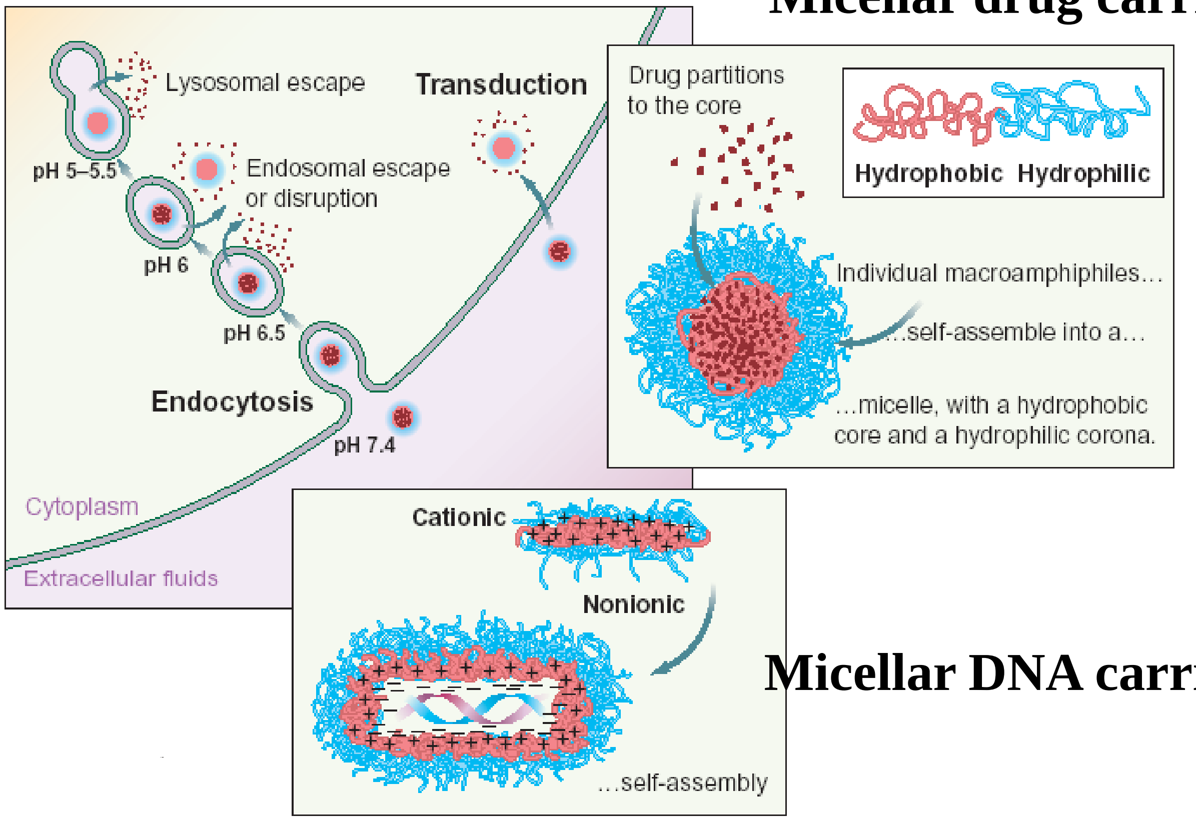
Properties and Applications- Biomedical

❑ Organic Colloids

- Endocytosis of Drug Carrier

Endocytosis and Transduction

Micellar drug carrier



Micellar DNA carrier

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Properties and Applications- Biomedical

❑ Organic Colloids

- Nucleic Acid Delivery – Non-viral Delivery

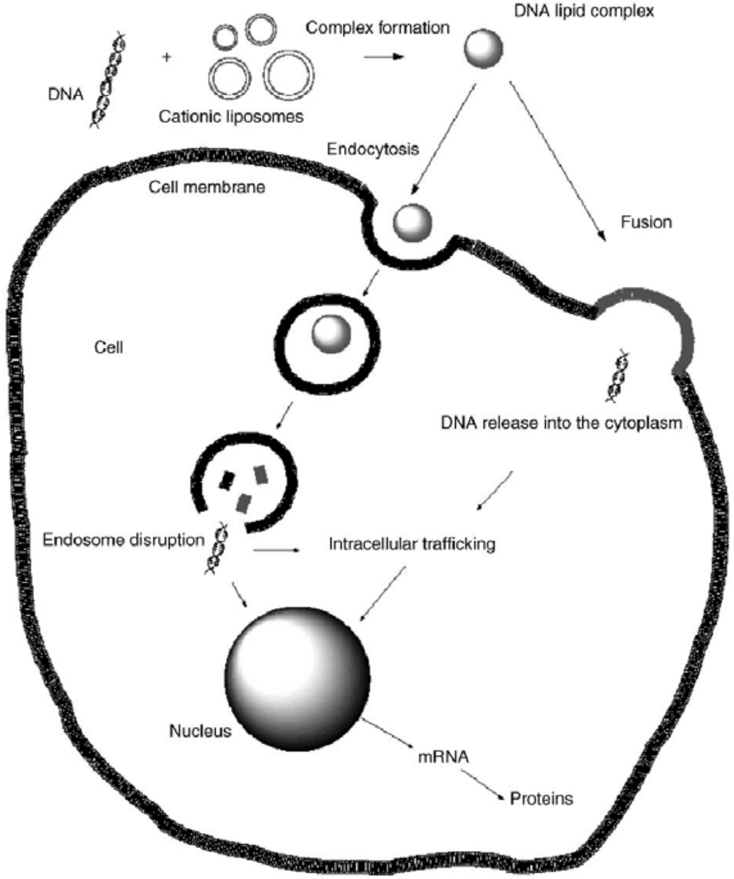
Non-virial Delivery

- Imitating the function and structures of viruses
 for gene delivery.

- Advantages: ease of sythesis, low immunogenicity, ease of quality control

- Disadvantages: solubility, cytotoxicity (polyplexes), low transfection efficiency (lipoplexes)

➔ Few nonviral vectors are in clinical trial.



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Properties and Applications- Biomedical

❑ Organic Colloids

- Conditions of Ideal Delivery

Ideal Nucleic Acid Delivery: high transfection efficiency, biodegradable, nontoxic, non-inflammatory, non-immunogenic, specific targeting capabilities, large material capacity, stable for storage, manufacturable at a low cost

How to increase the transfection efficiency?
→ design functional synthetic vectors

1. pH-sensitive: during endocytosis pH changes
   from 7.4 (extracellular)→ 6.5~6.0 (endosome) → 5.0 (lysosome)
   pH-sensitive moeities: polyhistidine, polylysine, guanidinium, acylhydrazone
2. redox-sensitive: ---SH + HS--- → ---S-S--- intracellular process
3. enzyme-sensitive: charge reversal
4. specific targeting: specific binding with receptors in cell surfaces
   ex) transferrin → T cells
   galactose → cancer cells
5. cell membrane fusion: peptide in lipoplex surface
   ex) TAT peptide

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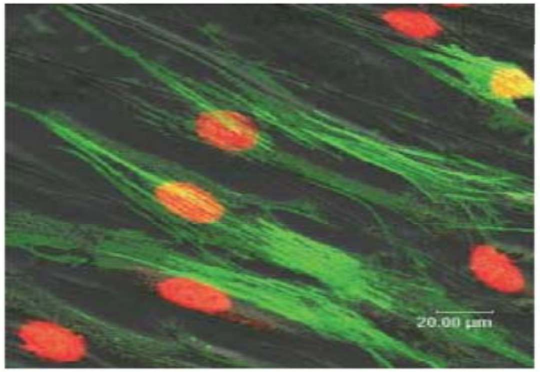
Properties and Applications- Biomedical

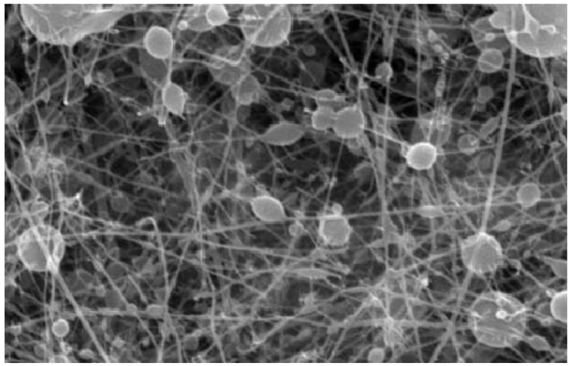
❑ Nanofibers

- Use of Nanofibers

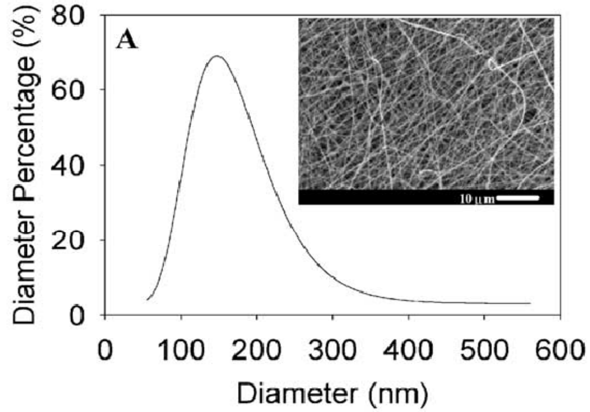
scaffolds for tissue engineering

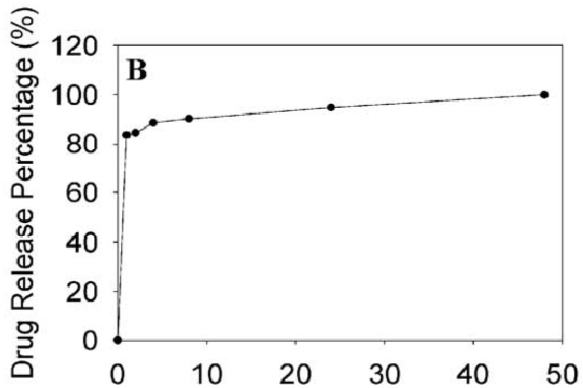


wound dressing



drug release control

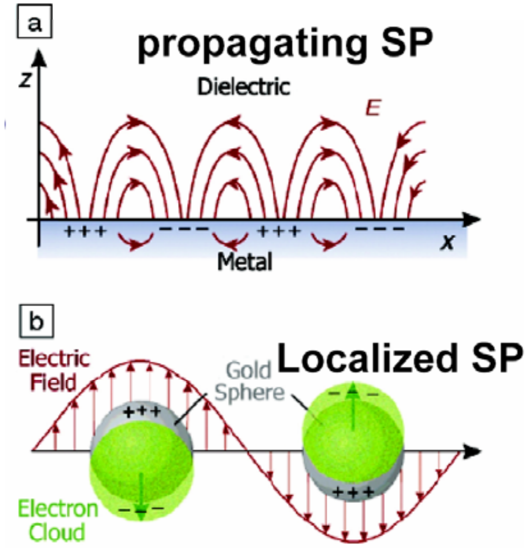




Properties and Applications- Biomedical

❑ Surface Plasmon Resonance (SPR)- metal nanoparticles

External electromagnetic resonates the surface plasmon of metal nanoparticles



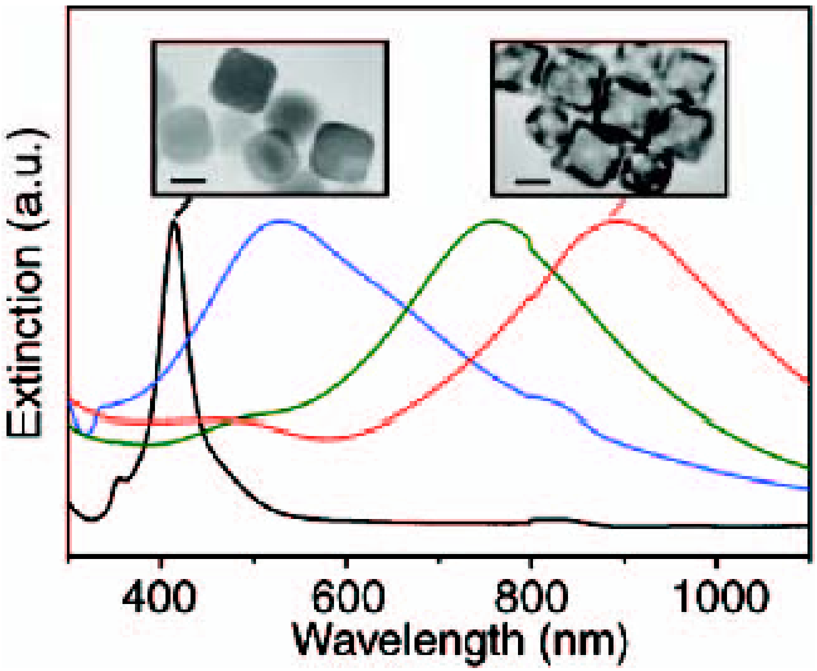
$\omega_p = (Ne^2/\varepsilon_o m_e)^{1/2}$ for 3-D bulk
$\omega_p/\sqrt{2}$ for thin films
$\omega_p/\sqrt{3}$ for nanoparticles

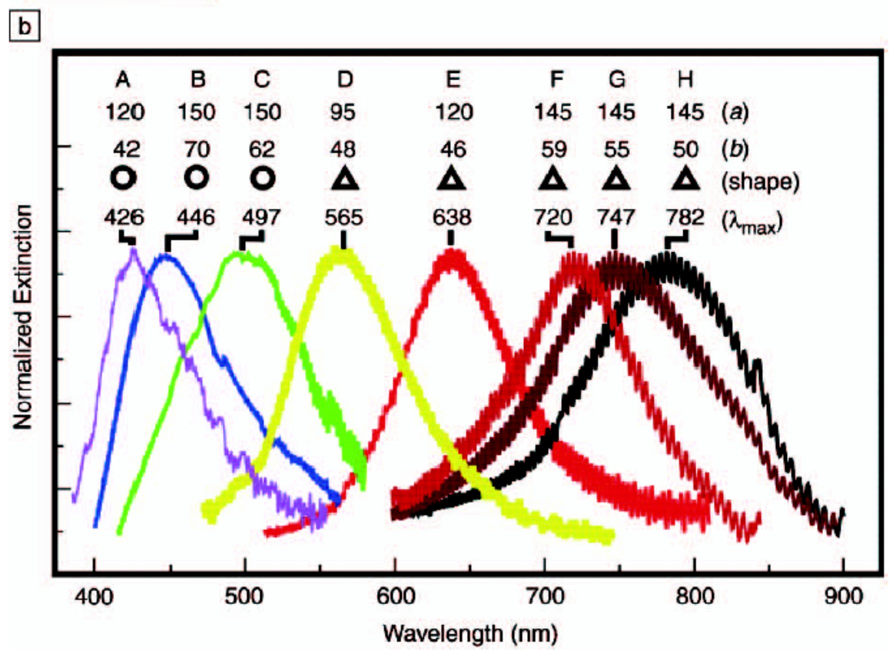
ω_p = plasma frequency
N = number density of electrons
ε_o = dielectric constant
e = charge
m_e = effective mass

→ enhancement of electromagnetic field at the interface (100~10,000 times)
→ Surface-enhanced spectroscopy
(strong local polarization, large local electromagnetic field)
→ **Surface enhanced (Raman, Fluorescence, second harmonic)**

Properties and Applications- Biomedical

❑ Dependence of SPR on size and shape- metal nanoparticles





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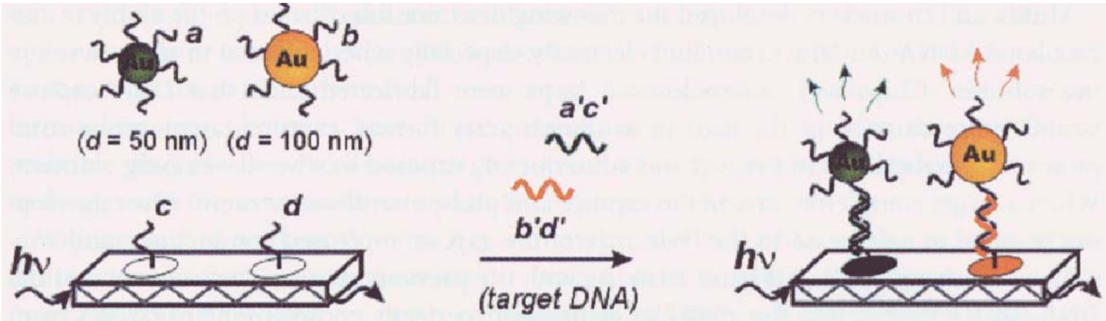
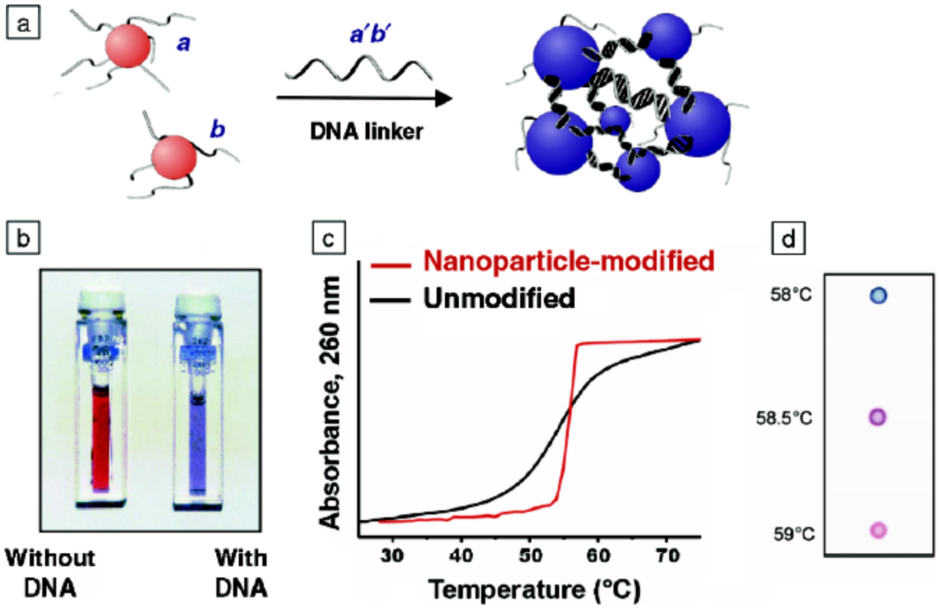
Properties and Applications- Biomedical

❑ Colorimetric Sensing with SPR- metal nanoparticles





Sensing with bare eyes
– portable sensors

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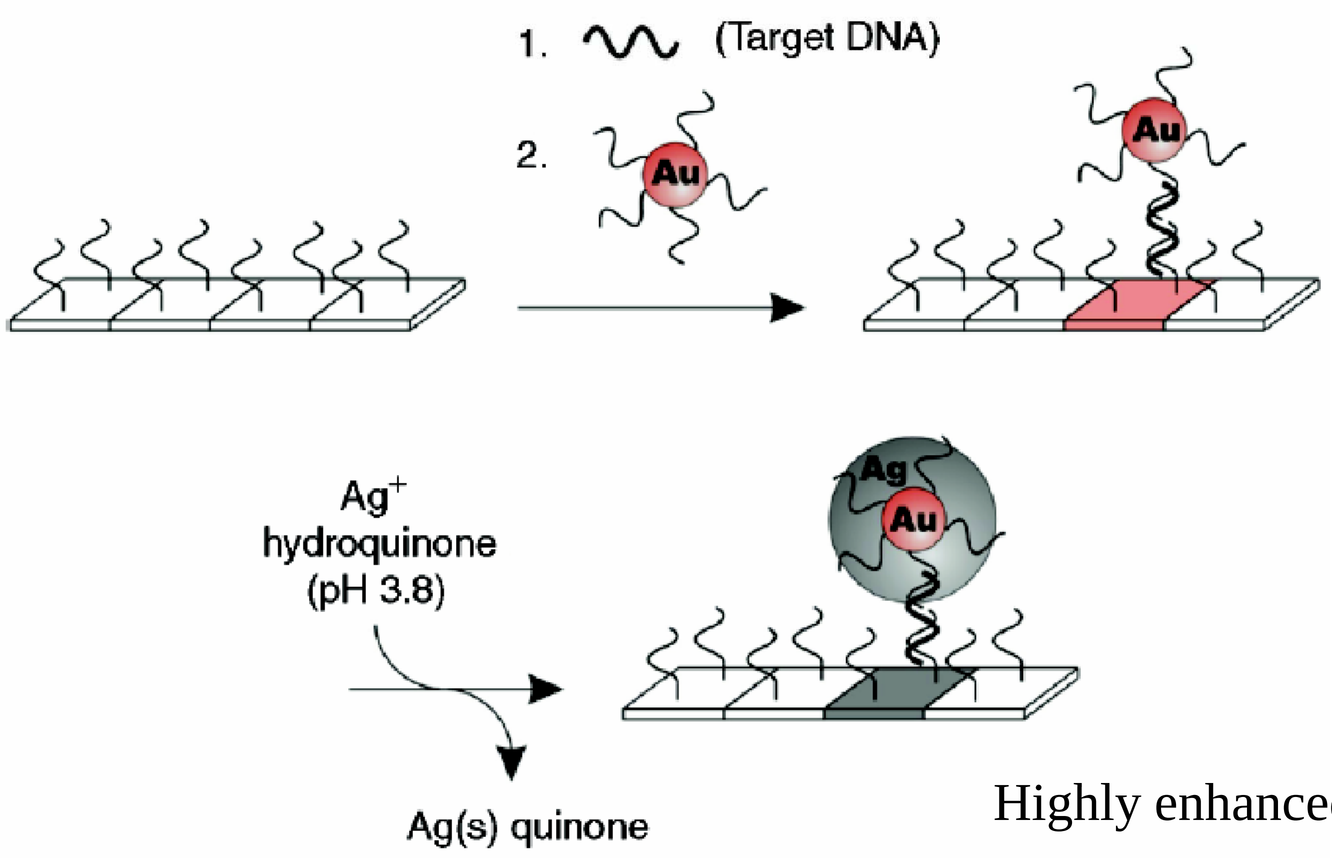
Properties and Applications- Biomedical

❑ Surface Enhanced Raman Spectroscopy (SERS)- metal nanoparticles



Highly enhanced sensitivity

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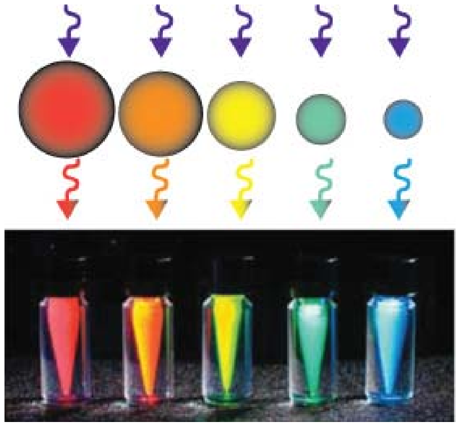
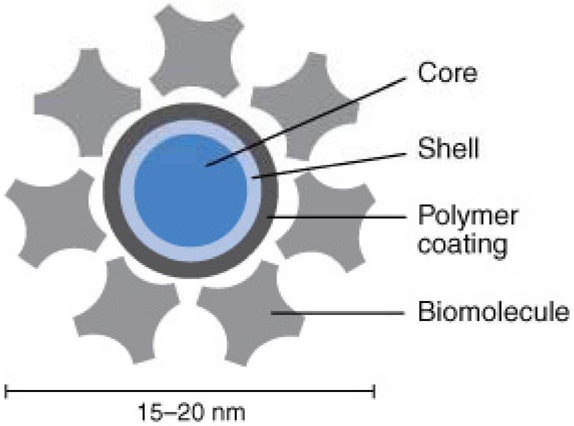
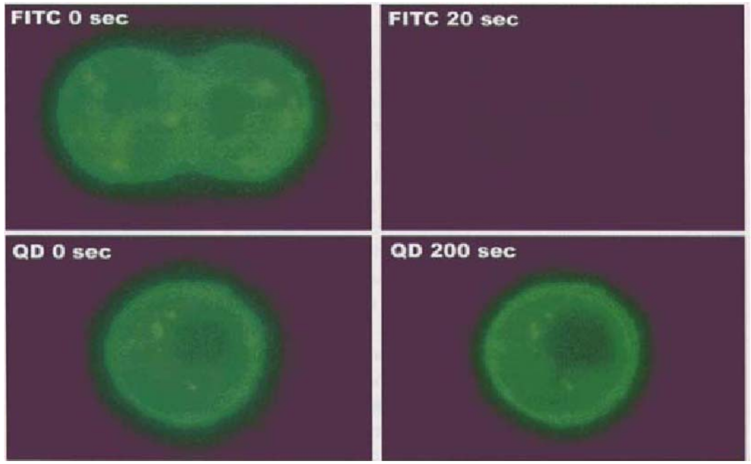
Properties and Applications- Biomedical

❑ Fluorescence Imaging- semiconductor NPs

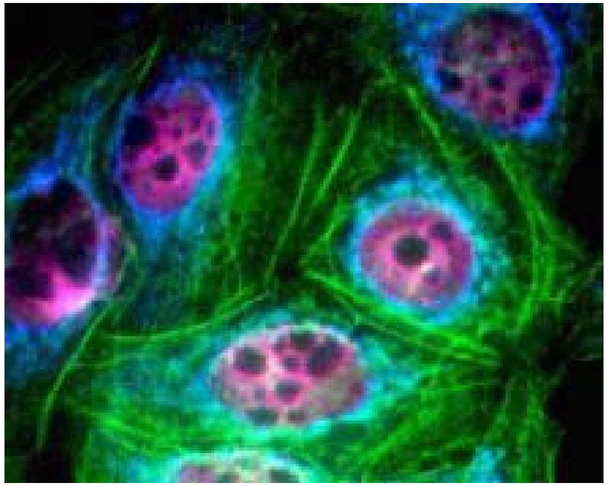




Surface treatment for biocompatibility



Advantage:
Long-time fluorescence



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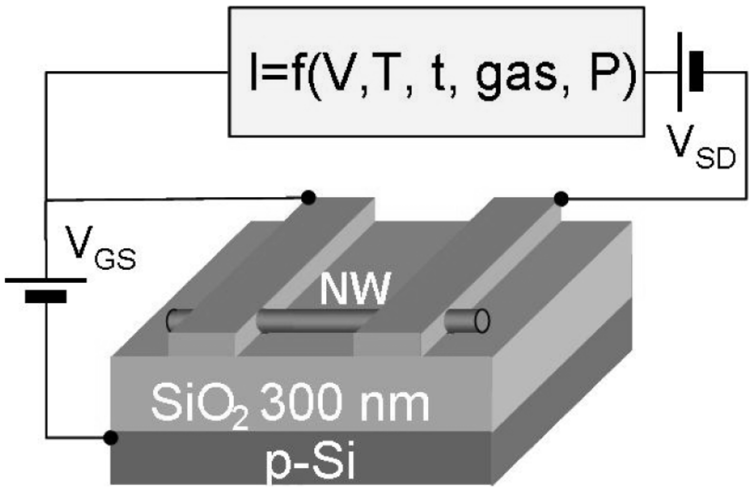
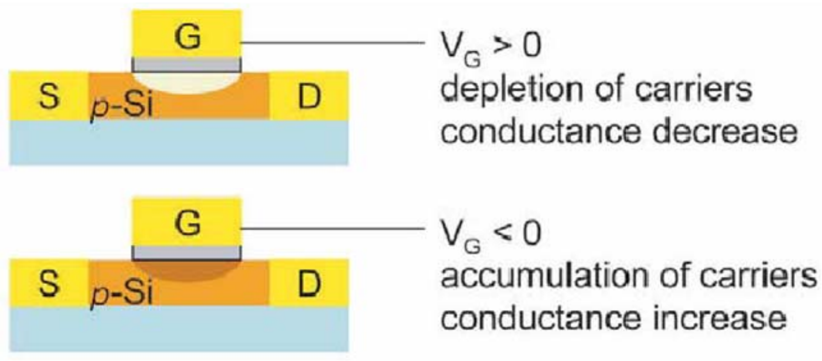
Properties and Applications- Biomedical

❑ Nanowire Sensors

- ✓ Highly Sensitivity of poisonous gas detection
- ✓ Real time detection of Selective poisonous gas
- ✓ Turn out the portable gas sensor
- ✓ Gas sensors properties
  long-term monitoring applications and real-time measurement



- Chemical Gating Effect
- Chemical Reduction and Oxidation



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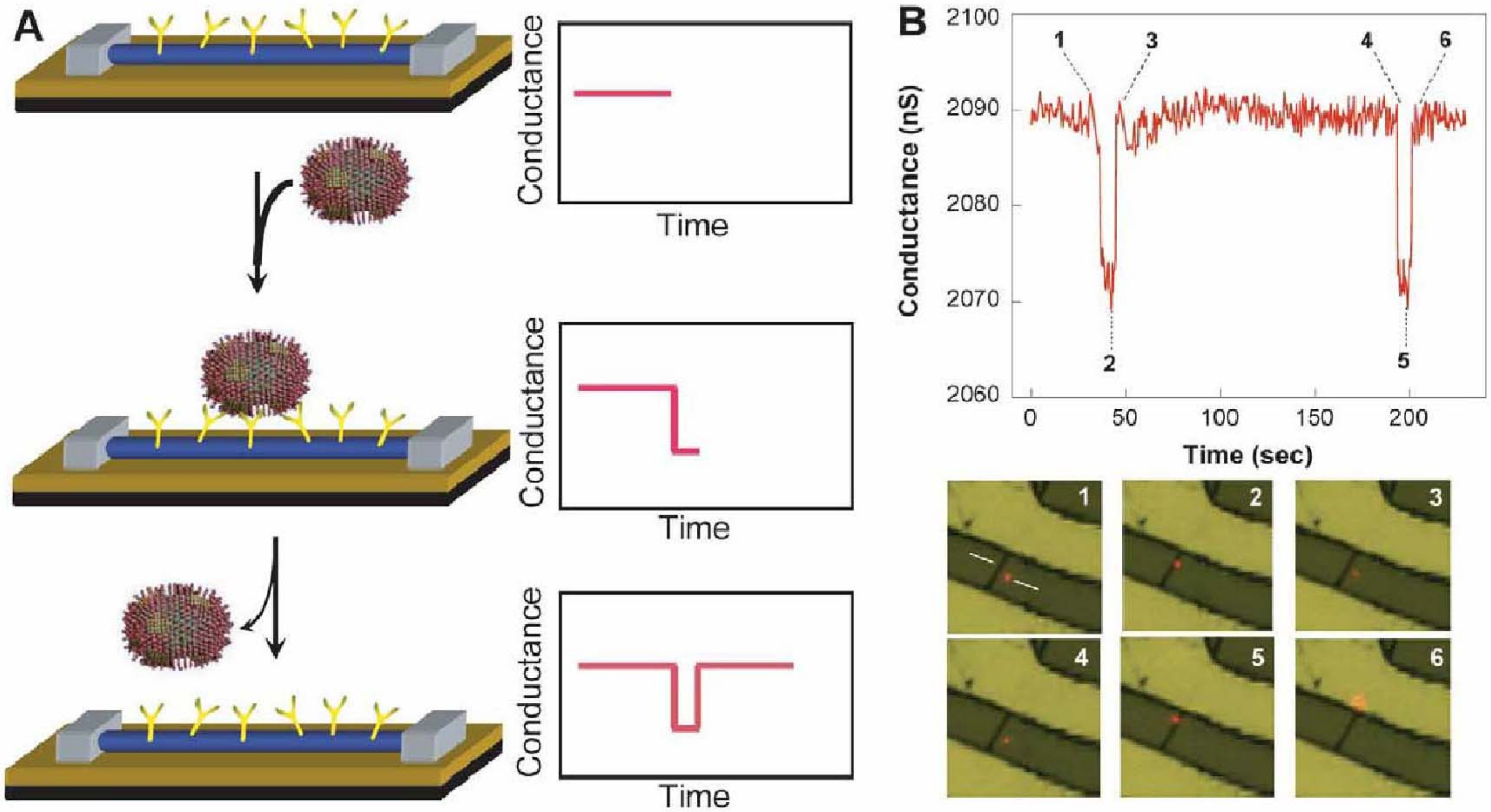
Properties and Applications- Biomedical

❑ Biosensor Using Semiconductor Nanowires



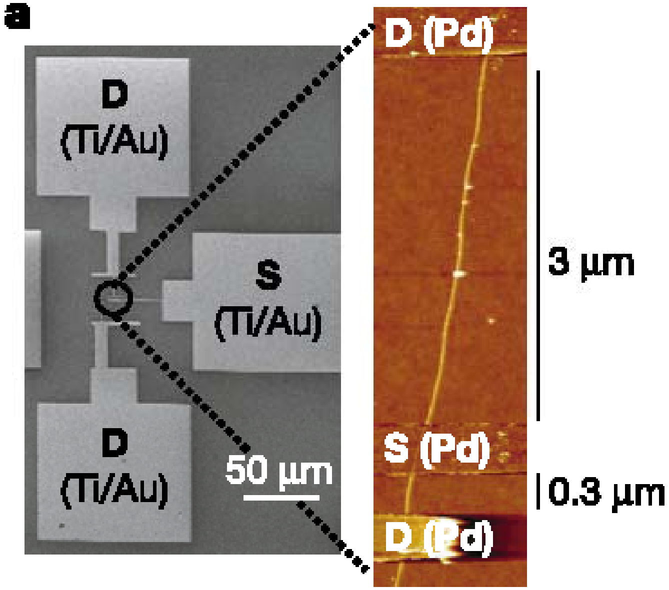
PNAS 2004, 101, 3208

Properties and Applications- Biomedical

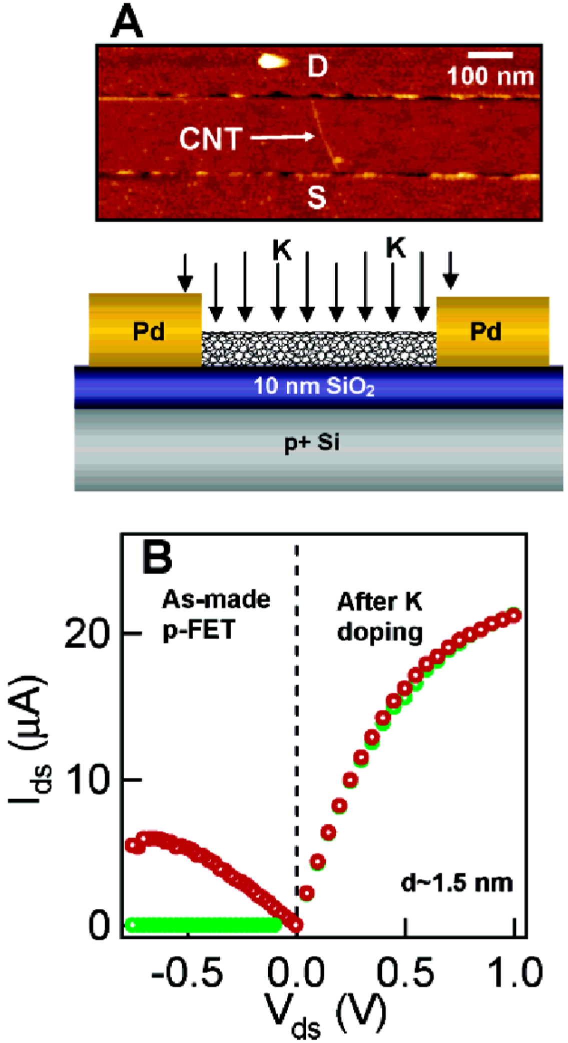
❑ Biosensor using CNT

1. Gate Field Effect
2. Schottky Barrier

Which is more effective ?



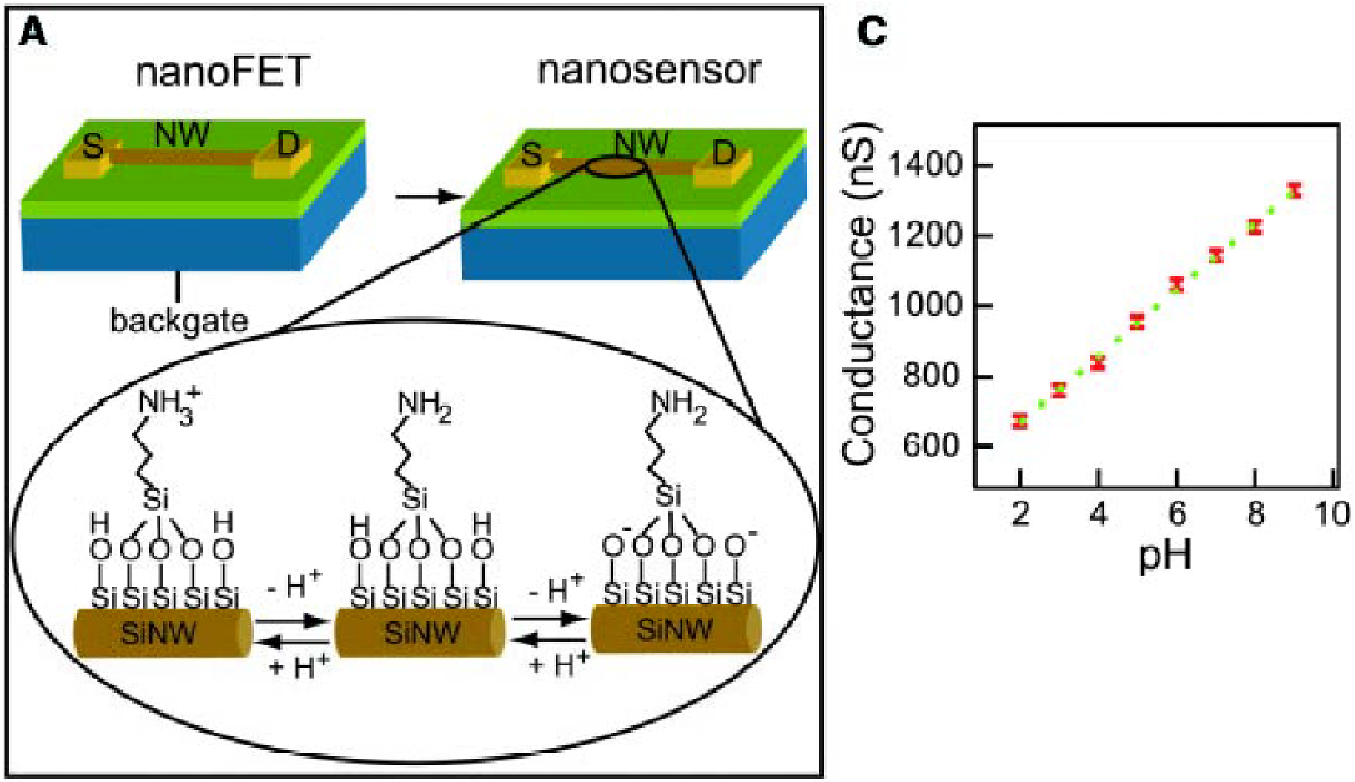
Nature 2001, 424, 654



Nano Lett. 2005, 5, 345

Properties and Applications- Biomedical

❑ Sensing Chemical Reactions – pH Sensor- nanowire



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Properties and Applications - Catalysis

❑ Nanomaterials in Catalysis

Surface chemistry is important in catalysis. Nanostructured materials have some advantages:

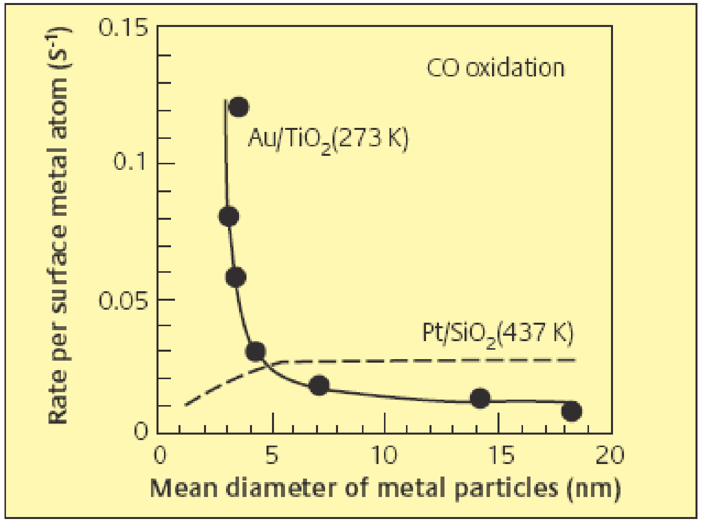
- Huge surface area, high proportion of atoms on the surface
- Enhanced intrinsic chemical activity as size gets smaller which is likely to changes in crystal shape
- Ex: When the shape changes from cubic to polyhedral, the number of edges and corner sites goes up significantly
- As crystal size gets smaller, anion/cation vacancies can increase, thus affecting surface energy; also surface atoms can be distorted in their bonding patterns
- Enhanced solubility, sintering at lower T, more adsorptive capacity

Properties and Applications - Catalysis

❑ Catalysis by Gold Nanoparticles

Bulk gold is chemically inert and thus considered to be not active or useful as a catalyst. However, gold nanoparticles can have excellent catalytic properties.

The excellent catalytic property if gold nanoparticles is a combination of size effect and the unusual properties of individual gold atom, which are are attributable to the so-called relativistic effect that stabilizes the 6 s^2 electron pairs.



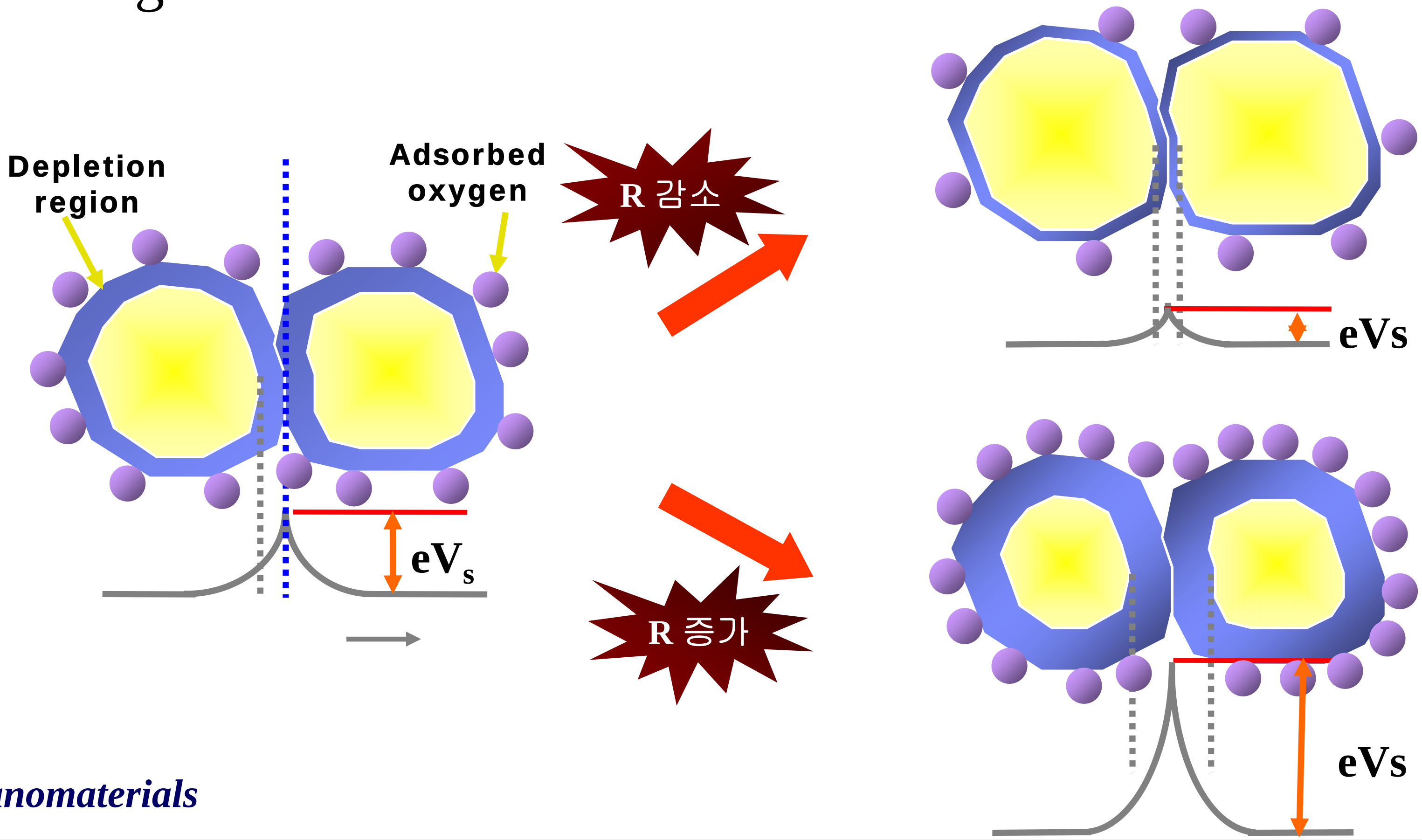
Turnover frequency (TOF) for CO oxidation overPt/SiO2 and Au/TiO2.

Haruta, M., *Gold Bull.* **2004,** 37, 27

Properties and Applications- Gas Sensors

❑ Semiconductor-type Gas Sensors

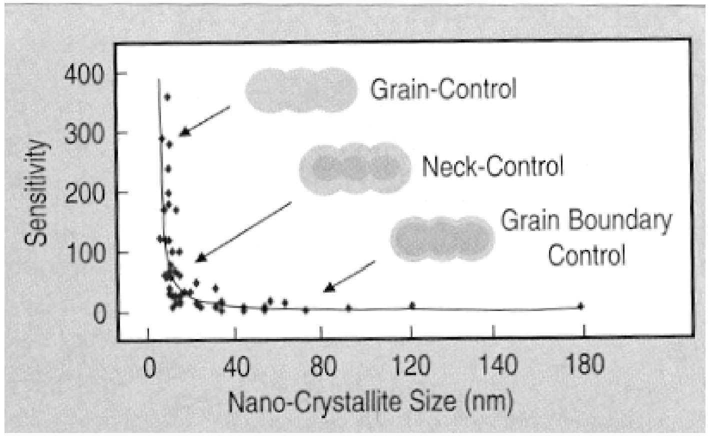
- SnO_2, TiO_2, ZnO, etc
- sensing mechanism

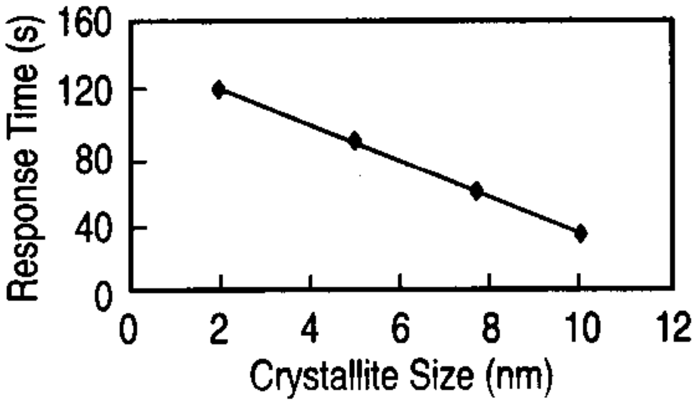


Properties and Applications- Gas Sensors

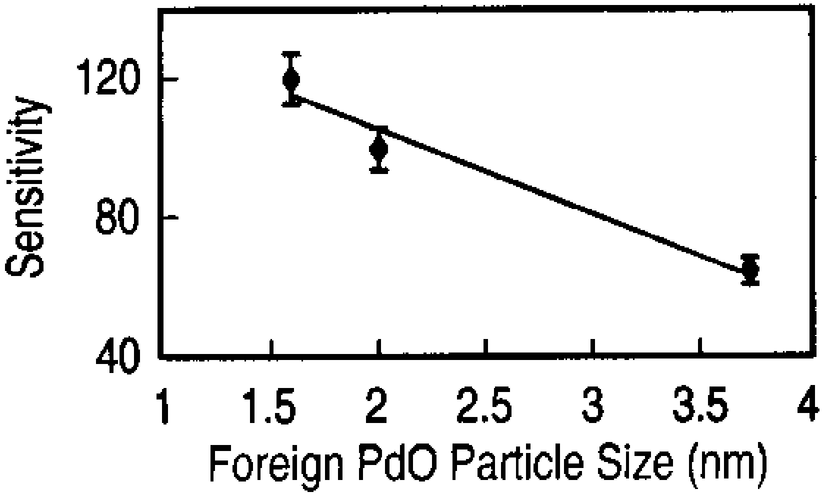
❑ Semiconductor-type Gas Sensors

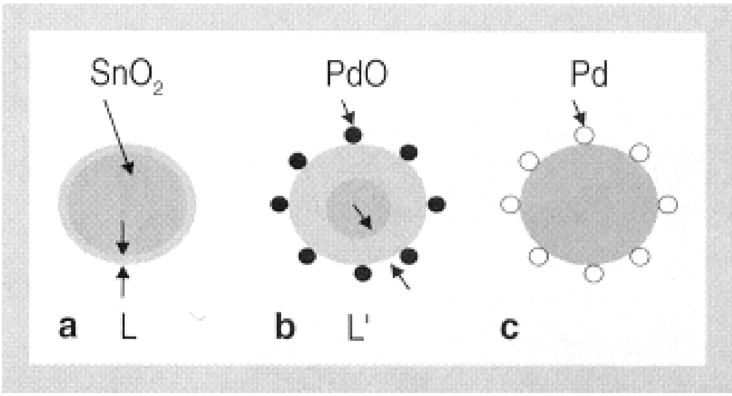
- effect of particle size





catalyst

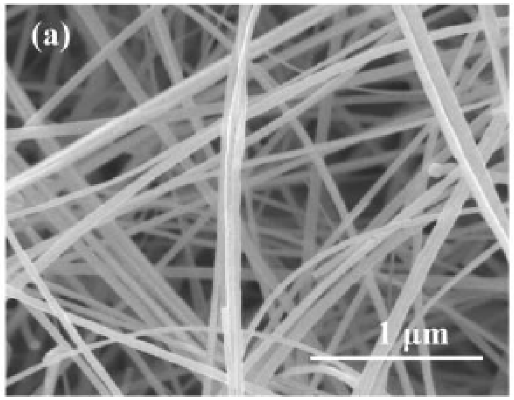


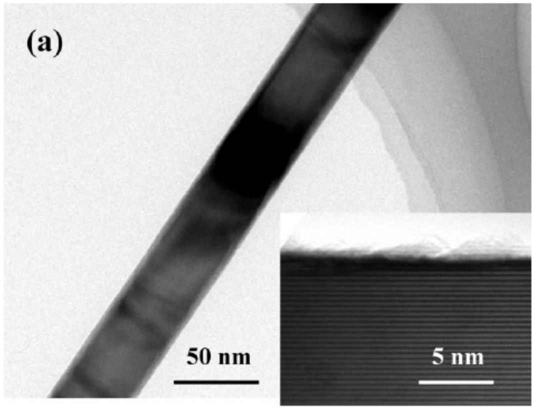


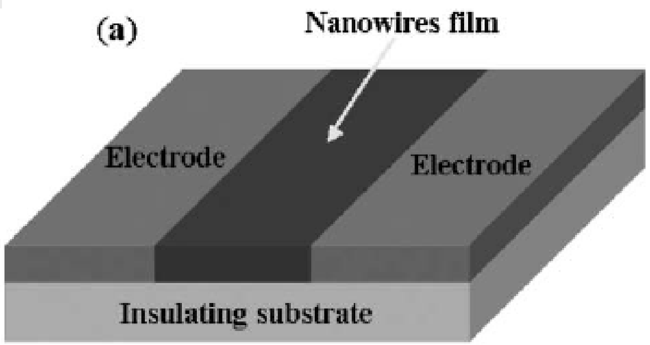
S. Seal and S. Shukla, Journal of Metal, 54(2002)35

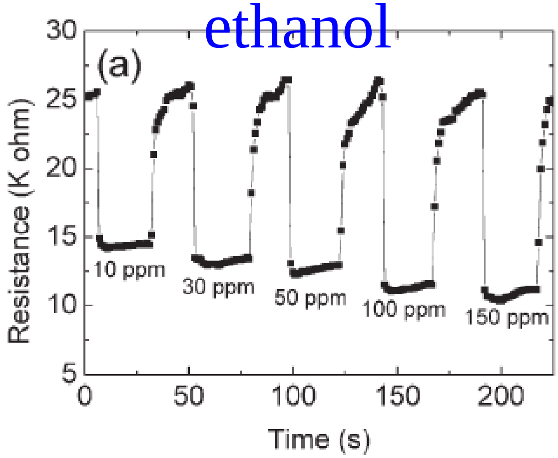
Properties and Applications- Gas Sensors

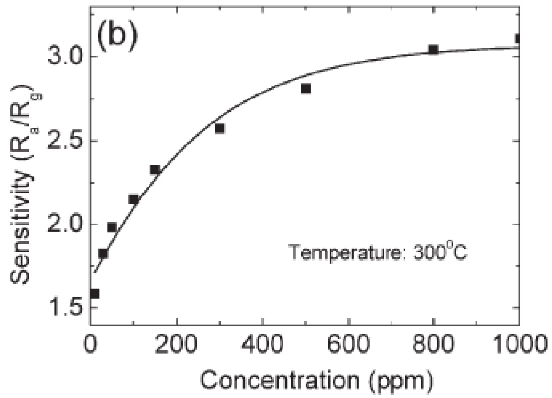
❑ Assembly of SnO_2 nanowires







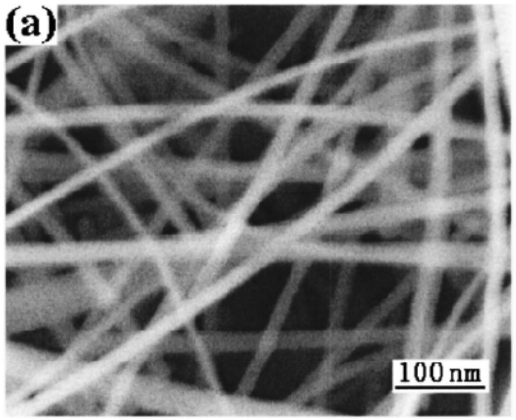


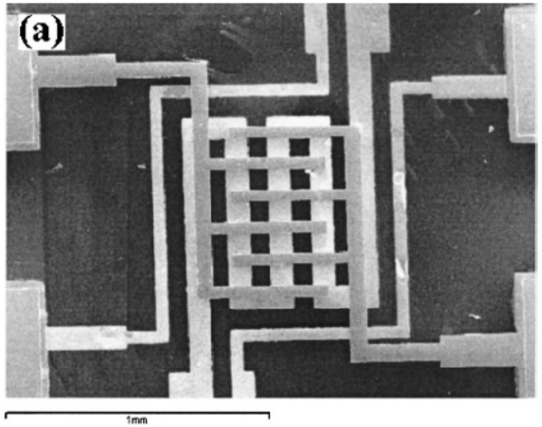


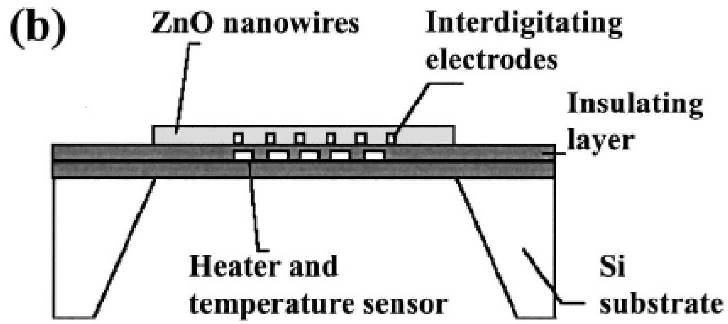
Q. Wan, T. H. Wang, Chem. Commun. (2005) 3841–3843

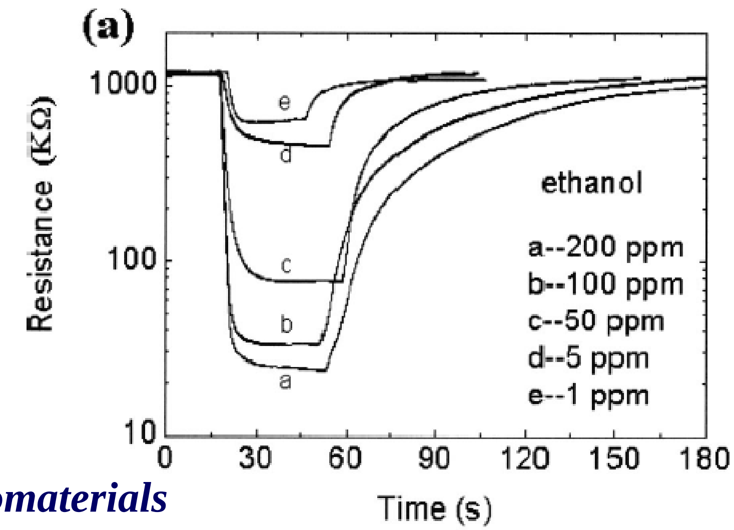
Properties and Applications- Gas Sensors

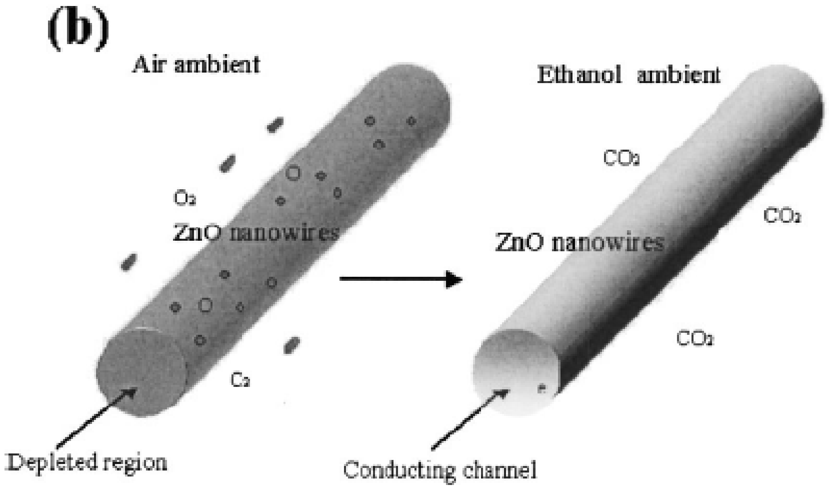
❑ Assembly of ZnO nanowires







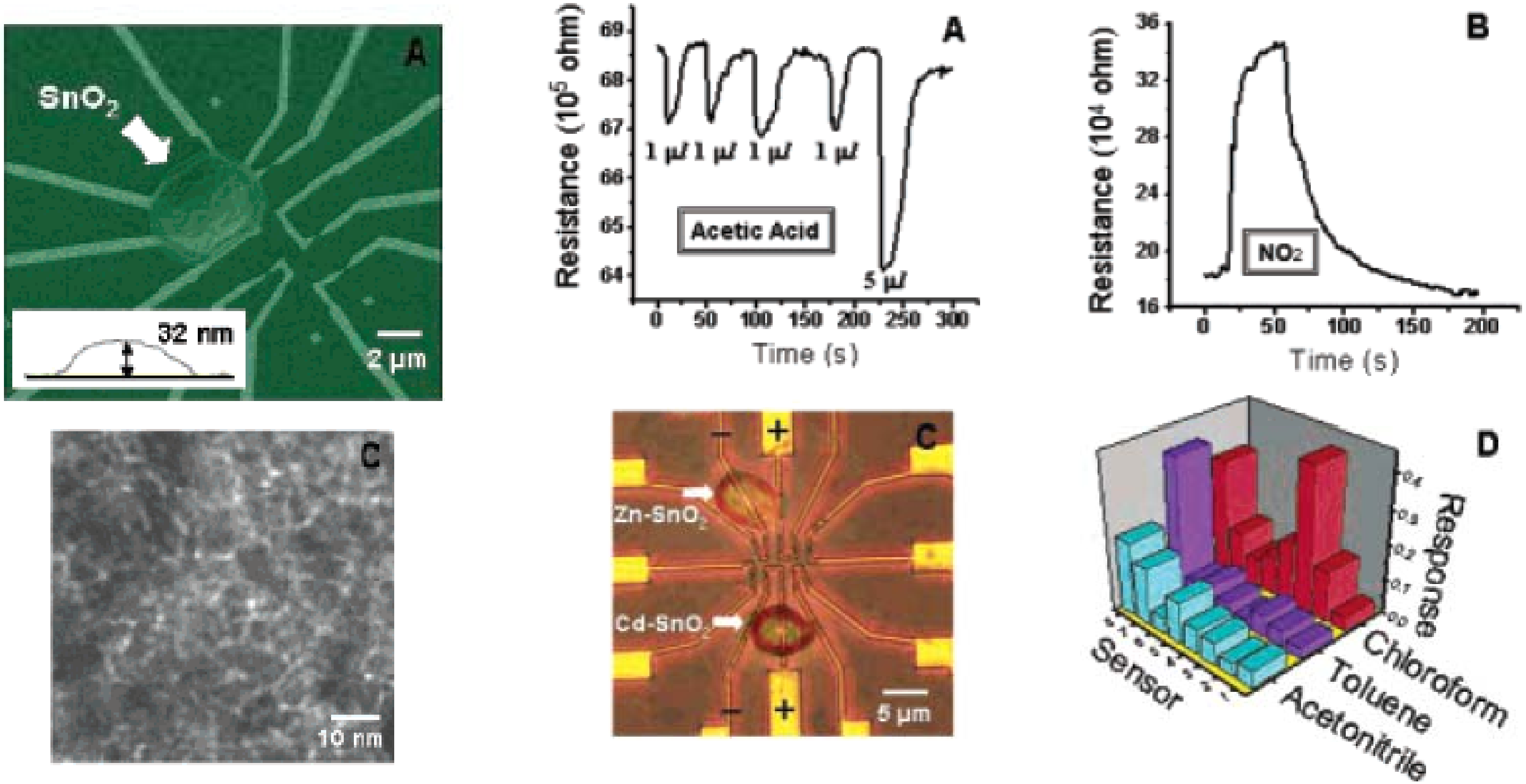




Q. Wan, Appl. Phys. Lett., 84 (2004) 124

Properties and Applications- Gas Sensors

❑ Miniaturized SnO_2 sensor

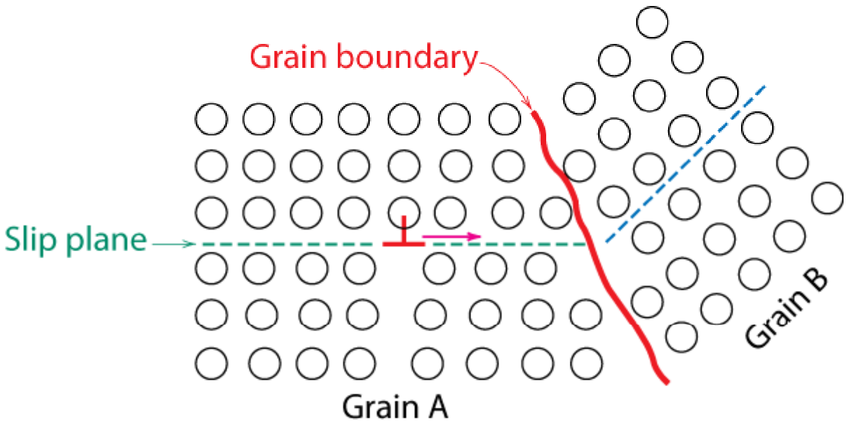


M. Su, J. AM. Chem. Soc., 125(2003)9930

Properties and Applications- Mechanical

❑ Yield Strength & Hardness vs. Grain Size

- grain boundary acts as a barrier to dislocation motion
- fine-grained material- harder and stronger



Hall-Petch relation

$$\sigma_d = \sigma_o + \frac{K}{d^{1/2}}$$

$$H_d = H_o + \frac{K}{d^{1/2}}$$

- Nanomaterials such as whiskers- no dislocation

Is Hall-Petch model valid in nanometer regime?

Properties and Applications- Mechanical

❑ Strength & Hardness vs. Grain Size

Two models

- **grain boundary sliding**
  (H. Hahn et al, Nanostructured Materials, 9, (1997) 603)
- **rule of mixture (bulk, grain boundary)**
  (D.A. Konstantinidis et al.)

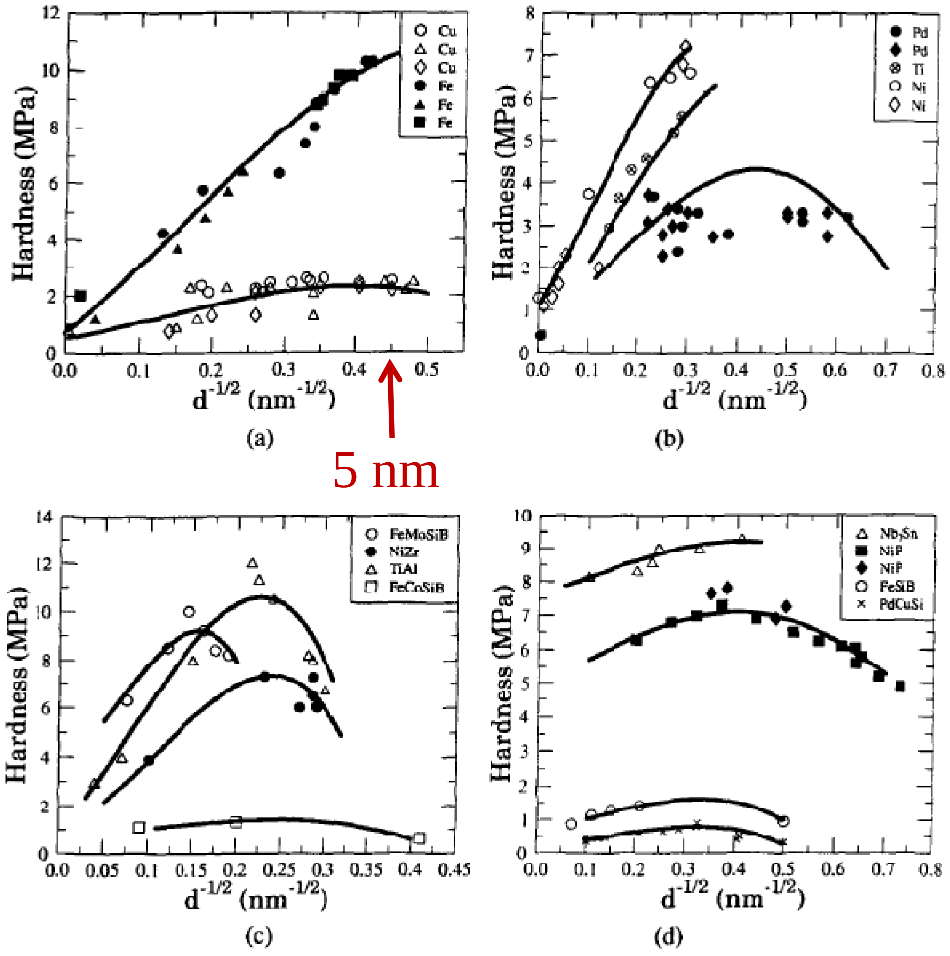


Figure 1. Hardness of coarse grained and nanocrystalline metals [(a),(b)] and intermetallics [(c),(d)]. Experimental data found in the literature (3-31).

D. A. Konstantinidis, Nanostructured Materials, 10(1998)1111

Properties and Applications- Mechanical

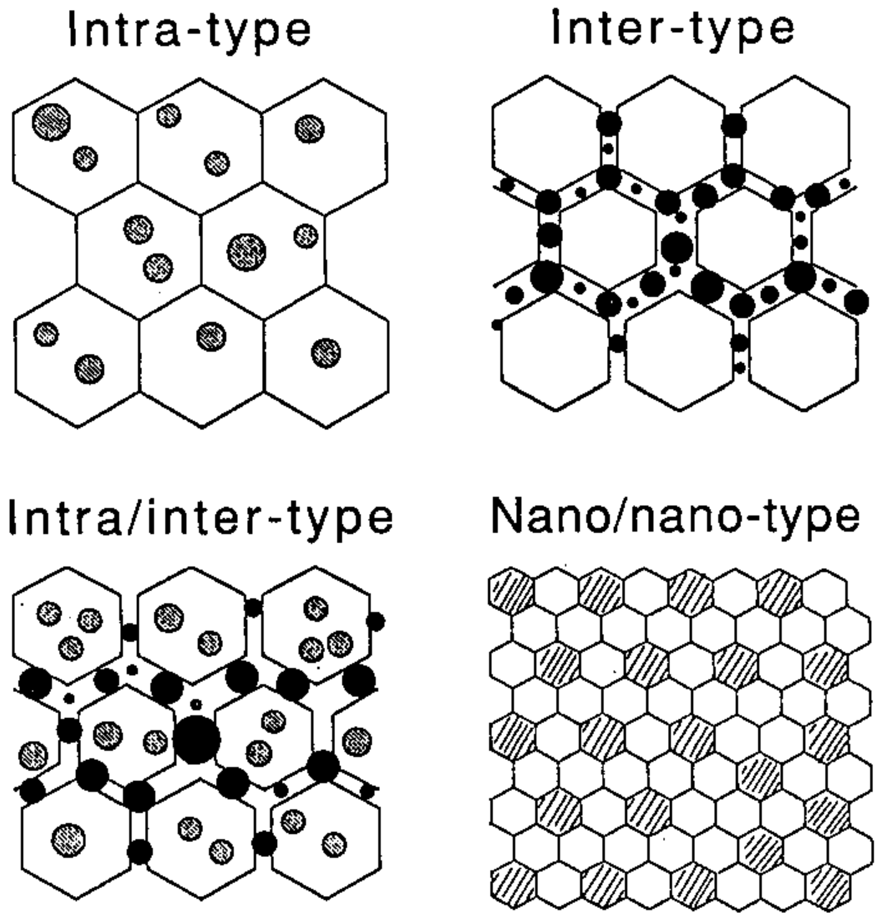
❑ Nanocomposite

- microcomposite

micro-sized second phases
(particulate, platelet, whisker, fiber)
are dispersed at g. b. of matrix
→ improve fracture toughness

- nanocomposite

intragranular
intergranular
nano/nano composite
→strength/toughness
high temp. properties
new functionality
(machinability, superplasticity



K. Niihara, Jpn J. Ceram. Soc., 99 (1991) 974

Properties and Applications- Mechanical

❑ Nanocomposite

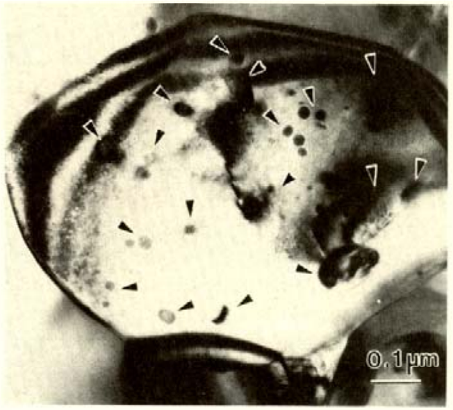


Fig. 3. Transmission electron micrograph for the Al_2O_3/5 vol% SiC nanocomposites.

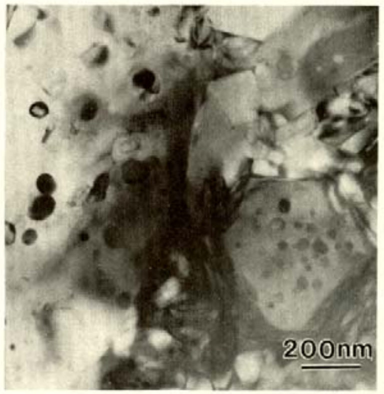
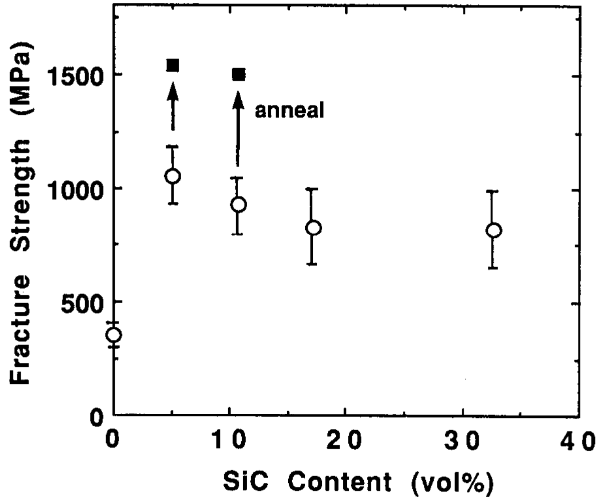
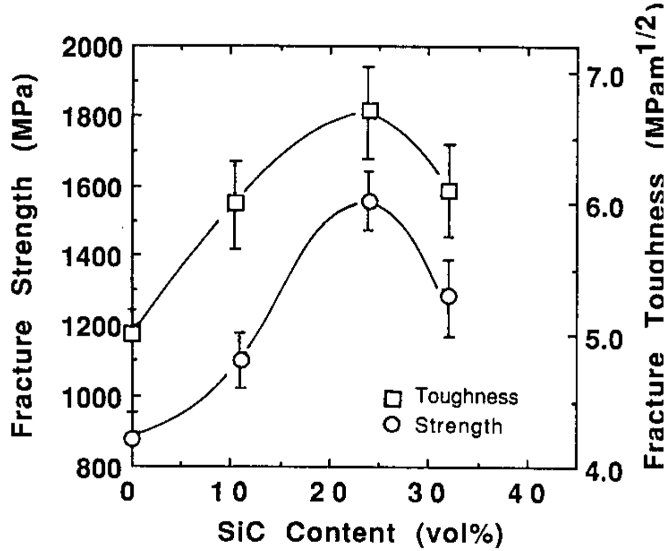


Fig. 4. Transmission electron micrograph for the Si_3N_4/10 vol% SiC nanocomposite.





K. Niihara, Jpn J. Ceram. Soc., 99 (1991) 974

Properties and Applications- Mechanical

❑ Nanocomposite

- nano/nano composite

machinability **superplasticity**

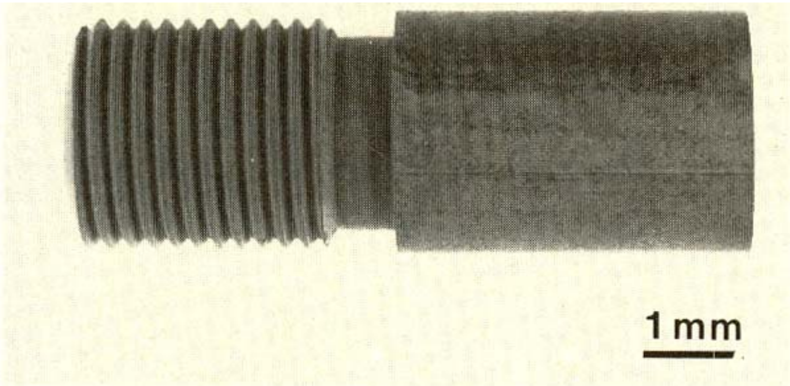


Fig. 17. The intergranular-type SiC/SiC nanocomposite machined by a lathe using WC/Co tools.

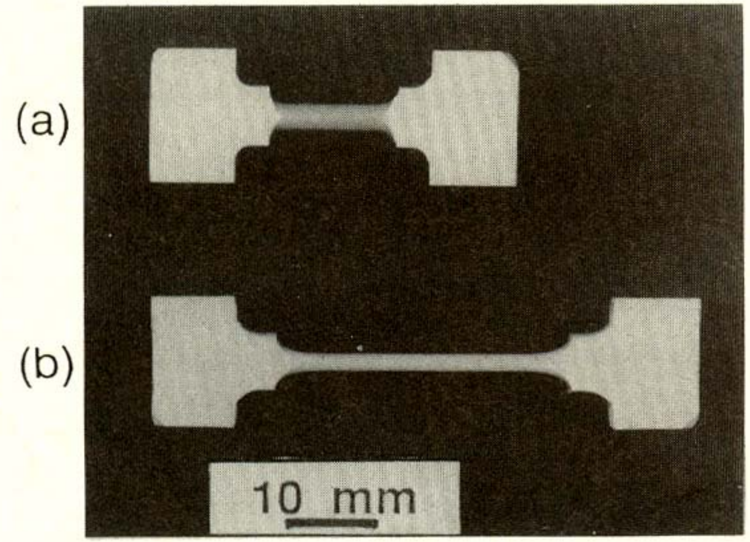


Fig. 18. Superplastic deformation for the Si_3N_4/SiC nano/nano composite. (a) before and (b) after deformation.

K. Niihara, Jpn J. Ceram. Soc., 99 (1991) 974

Properties and Applications- Mechanical

❑ Superplasticity

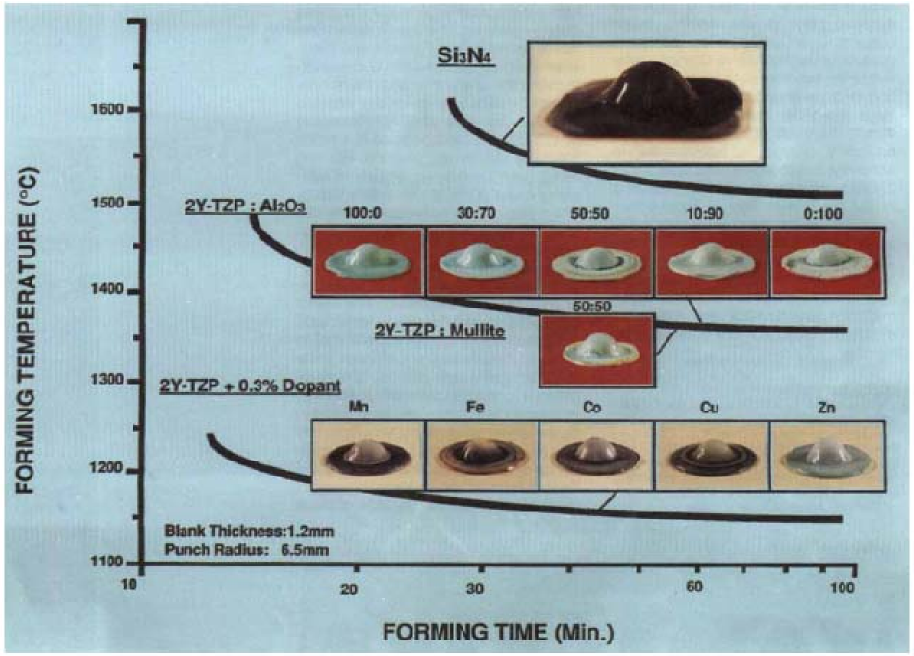


Fig. 1. Superplastic forming temperatures and times of structural ceramics. Hemispherical punch with a 6.5-mm radius was used to stretch the initialy flat, 1-mm-thick disks into the shape shown. Surface finish was excellent and glossy for silicon nitride, zirconia, and zirconia-rich composites. Surface of alumina, although free of visible defects, appeared dull. Under optimal conditions, forming operation can be competed at even lower temperatures and shorter times.

I.-W. Chen, J. Am. Ceram. Soc., 73 (2005)2585

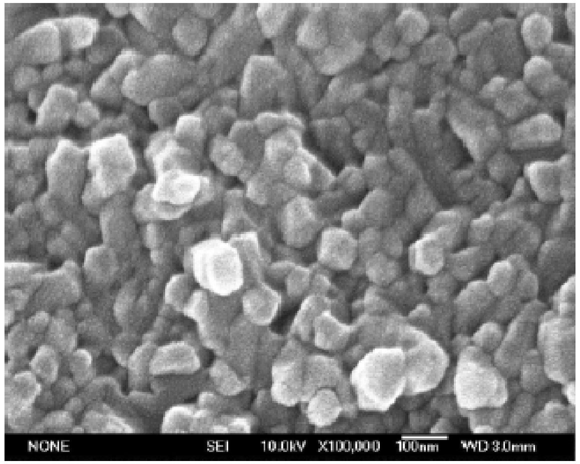
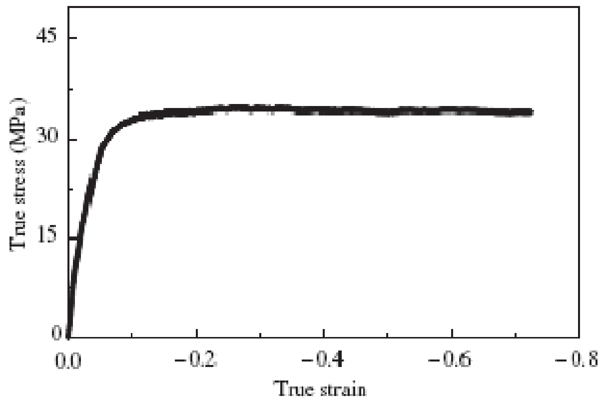


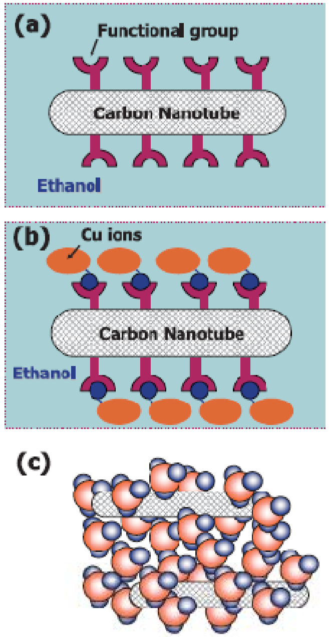
Fig.5. Fractural surface of P2 sample after sintering at 1600°C for 5 min.

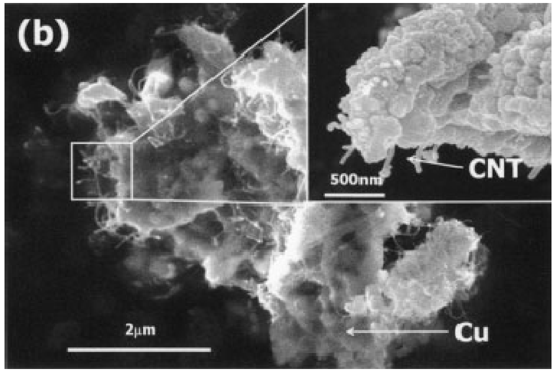


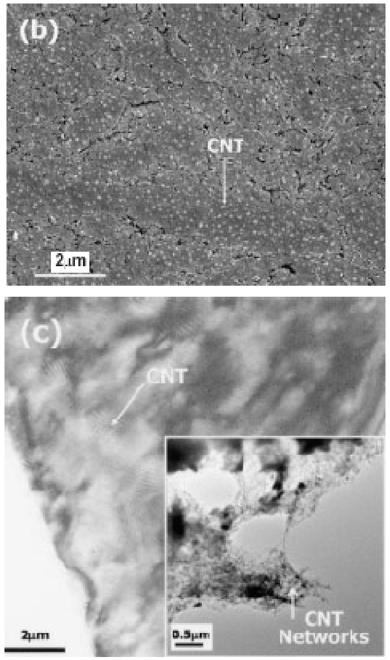
X. Xu, J. Am. Ceram. Soc., 88 (2005) 934

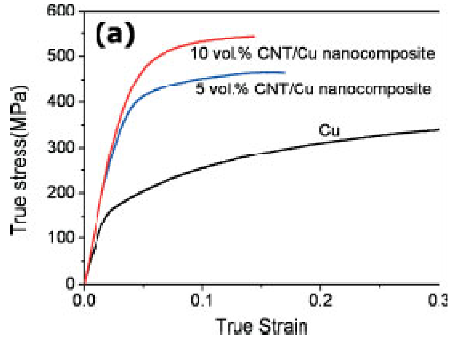
Properties and Applications- Mechanical

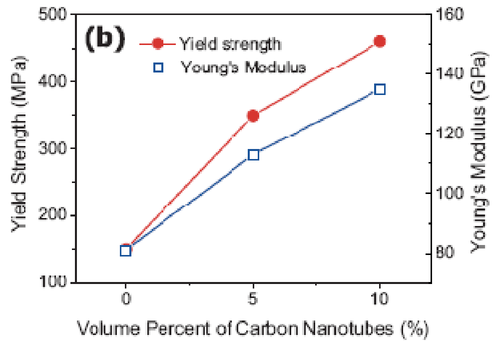
❑ CNT/Cu nanocomposite- tensile stress

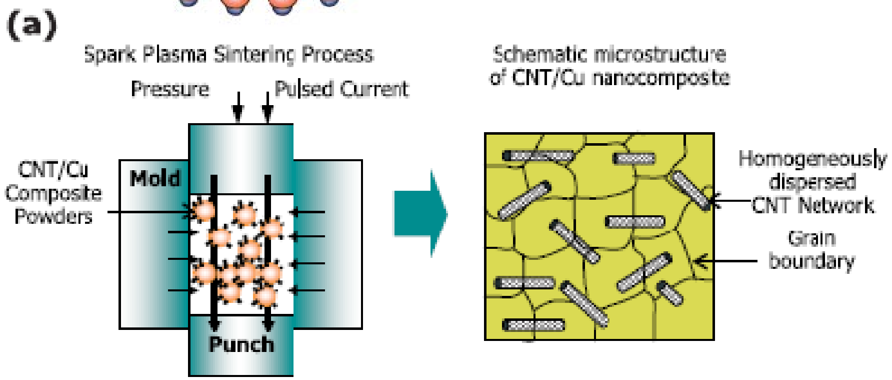












S. I. Cha, Adv. Mater. 15 (2005)1377