Nanomaterials in optics, electronics and energy applications

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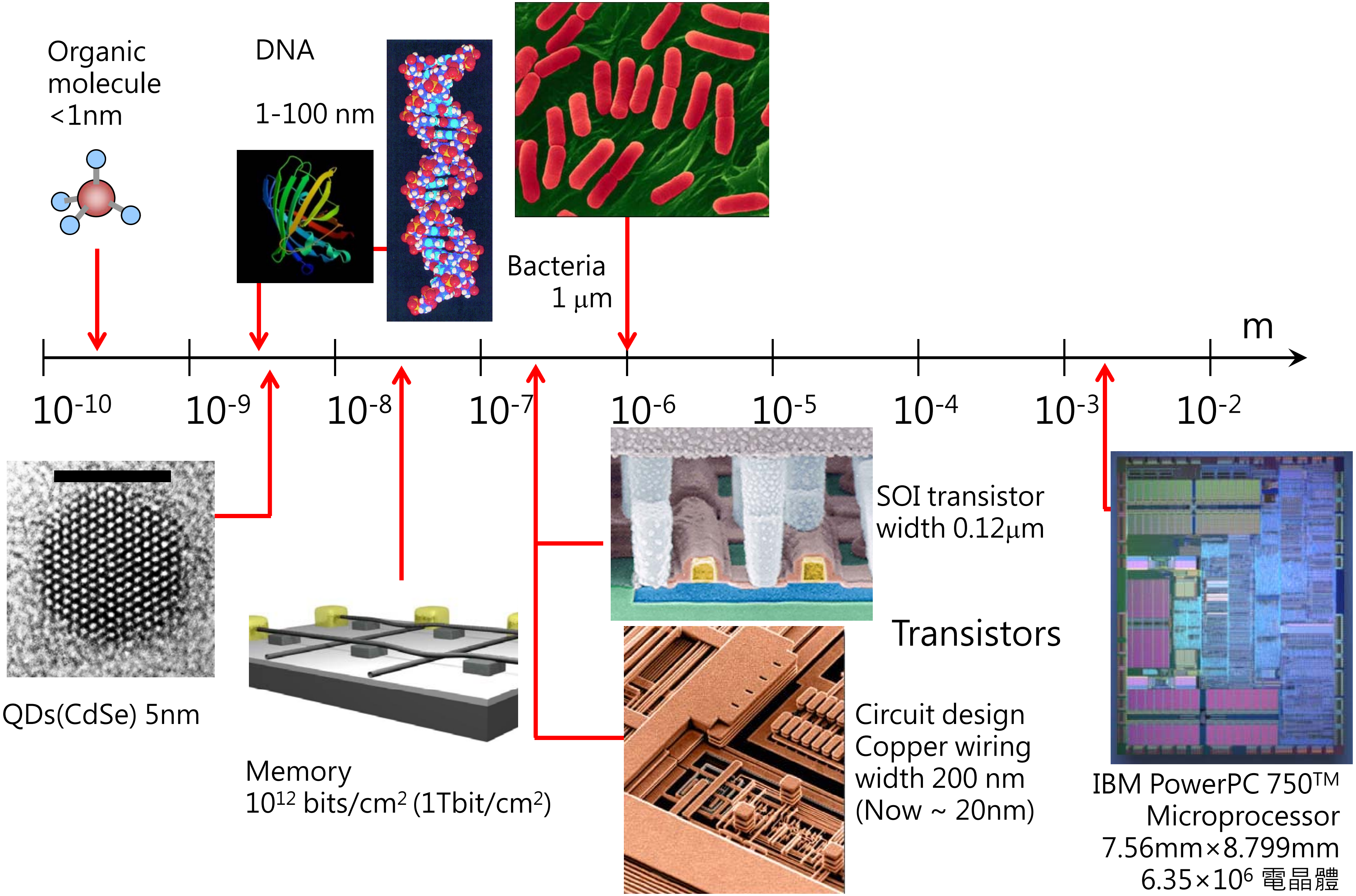
Outline

- **Part I: Optics and electronics of low-dimensioal nanomaterials**

- **Part II: CNTs and graphene**

- **Part III: Nanomatreials in Energy**

Size of Nano??



Organic molecule <1nm
DNA
1-100 nm
Bacteria 1 μm
m
10^-10
10^-9
10^-8
10^-7
10^-6
10^-5
10^-4
10^-3
10^-2
QDs(CdSe) 5nm
Memory
10^12 bits/cm^2 (1Tbit/cm^2)
SOI transistor width 0.12μm
Transistors
Circuit design
Copper wiring
width 200 nm
(Now ~ 20nm)
IBM PowerPC 750TM
Microprocessor
7.56mm×8.799mm
6.35×10^6 電晶體

Definition of Nanomaterial

Original： “quantum size effect” where the electronic properties of solids are altered with great reductions in particle size

。

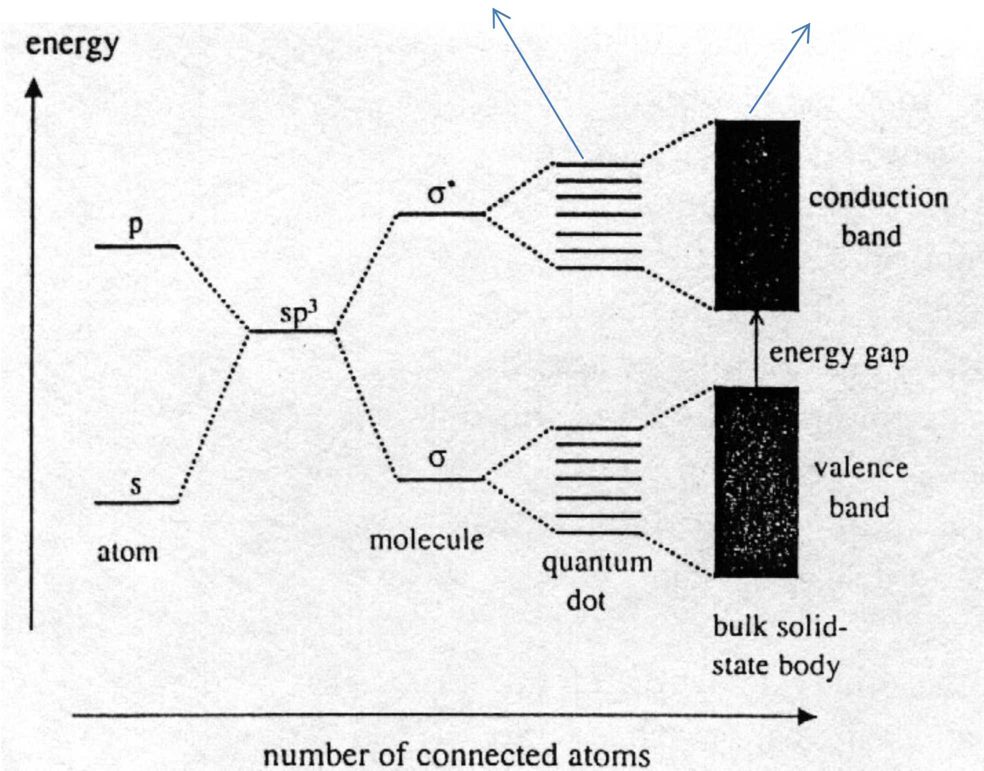
（New）

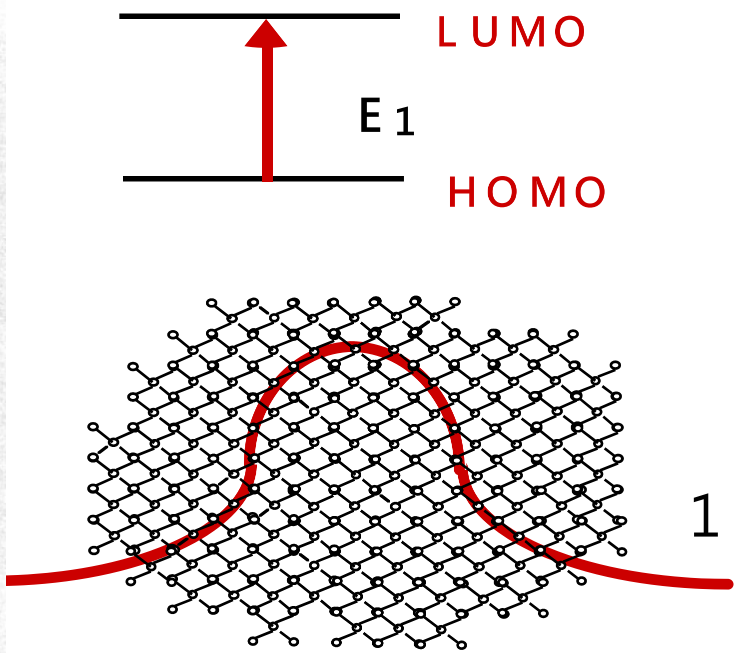
On 18 October 2011, the European Commission adopted the following definition of a nanomaterial:[2]

A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range *1 nm – 100 nm*.

"

Quantum confinement effect



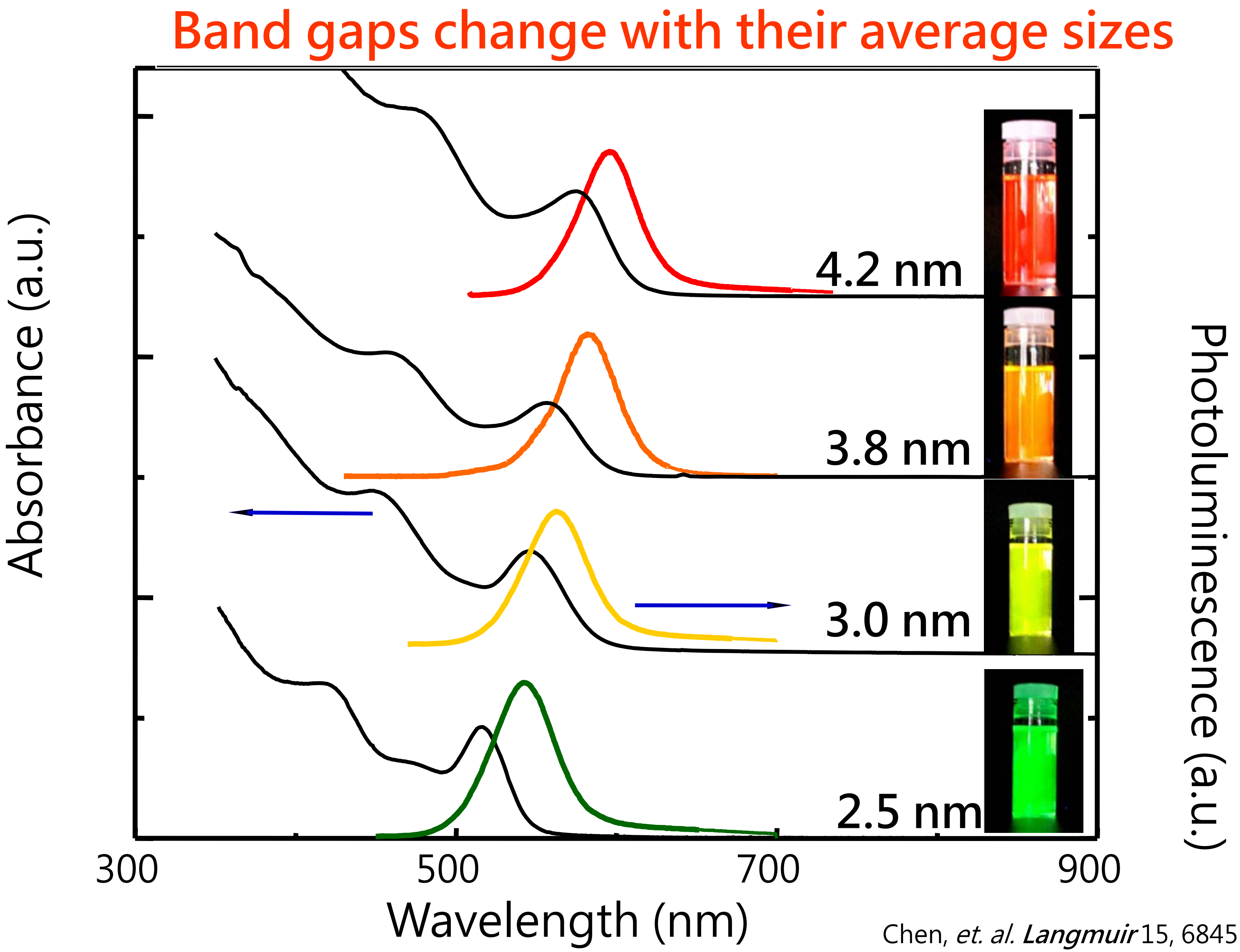


$$E(R) = Eg + \frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon R}$$

m_e and m_h : effective masses

e : bulk optical dielectric coefficient

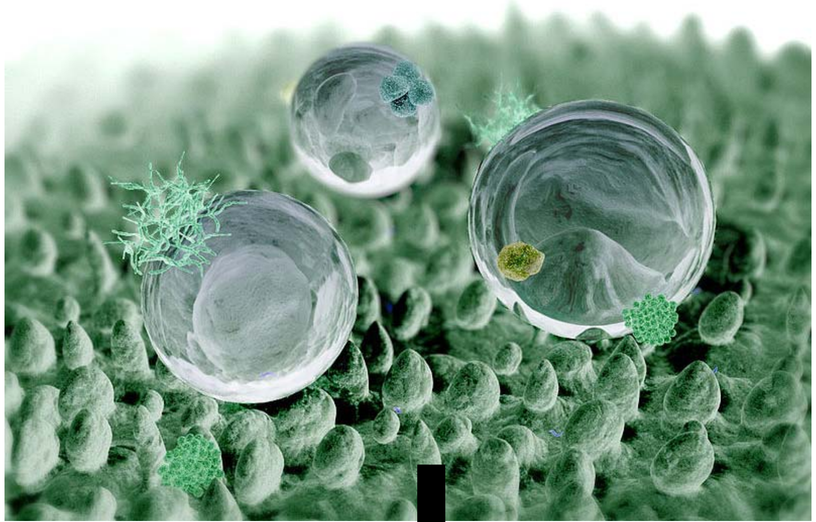
Size-dependent optical properties of CdSe QDs



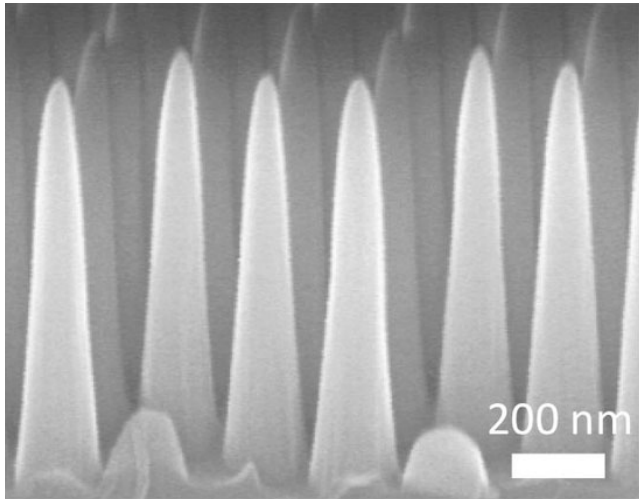
Chen, *et. al.* ***Langmuir*** 15, 6845 (1999)

Lotus Effect

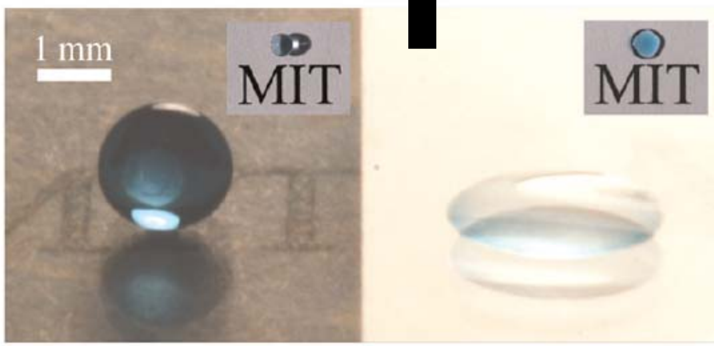
Lotus



Nano array on glass substrate



Self-cleaning



Park, K. C. et. al., *ACS Nano* **2012**, *in ASAP.*

H2O

Protection from the Inside Out.

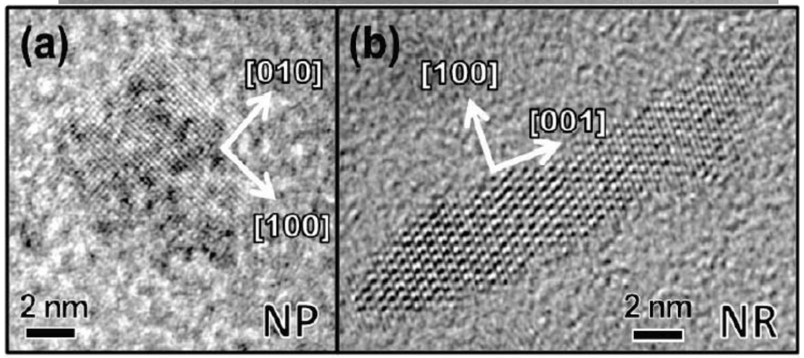
http://www.youtube.com/watch?v=zjsWFvUkh7M

Photocatylysts using Nanomaterials

- Bulk TiO_2 V.S. TiO_2 nanorods/nanoparticles

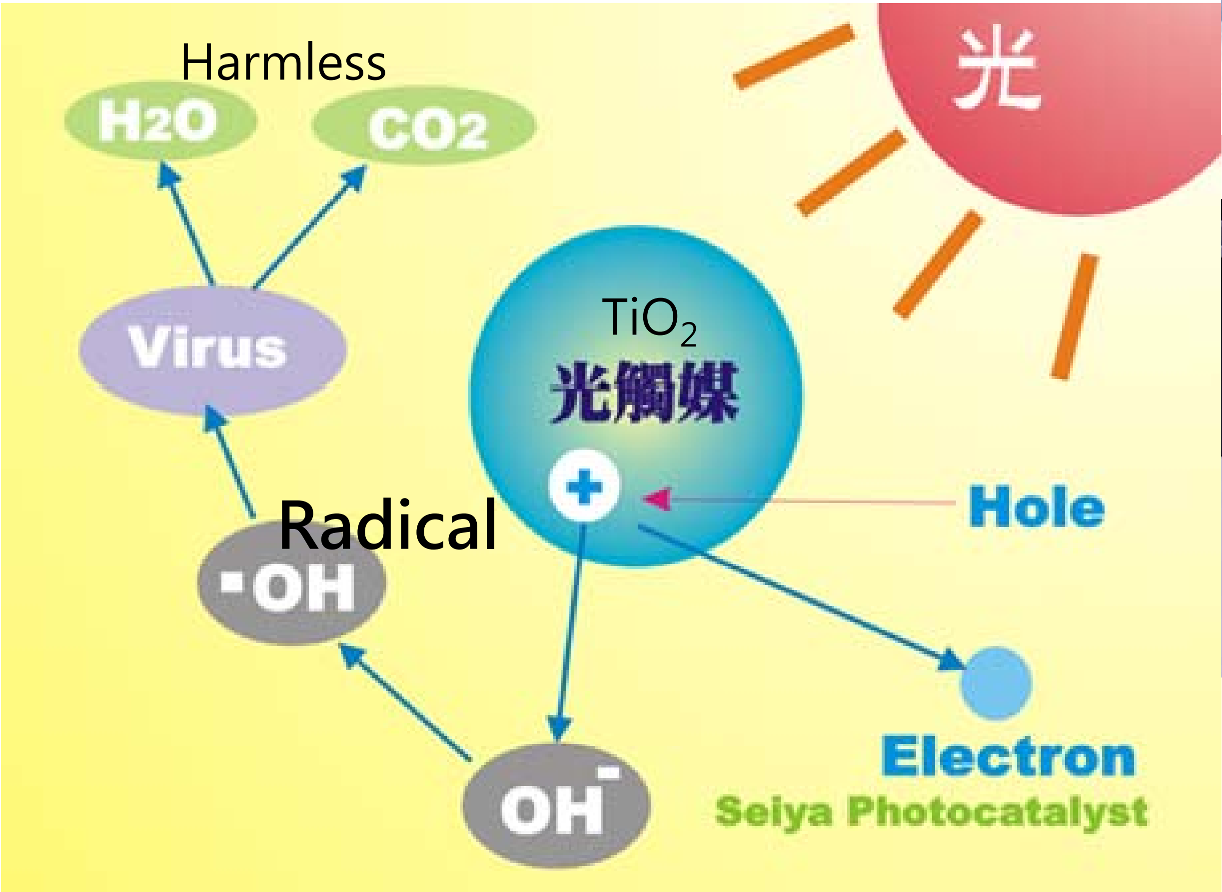
http://www.35664.net/new/public/tag.php?name=%E4%B8%93%E9%A2%98&page=14

http://www.hiwtc.com/products/tio2-ultra-fine-and-high-purity-333573-22847.htm



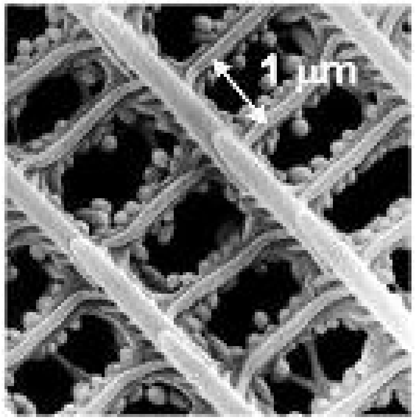
Journal of American Chemical Society, 133,11614, (2011)

Photocatalytic effect

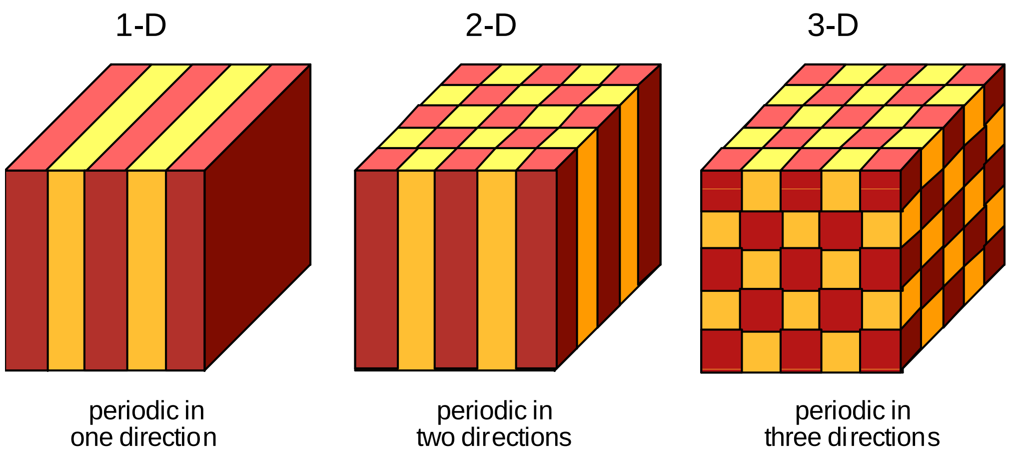


http://proj3.moeaidb.gov.tw/nanomark/Licens

Photonic crystals



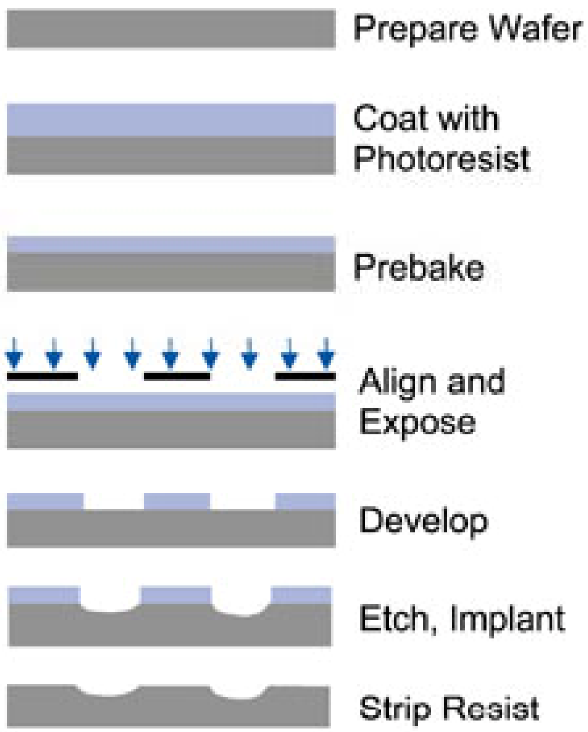
From 《奈米科學網》

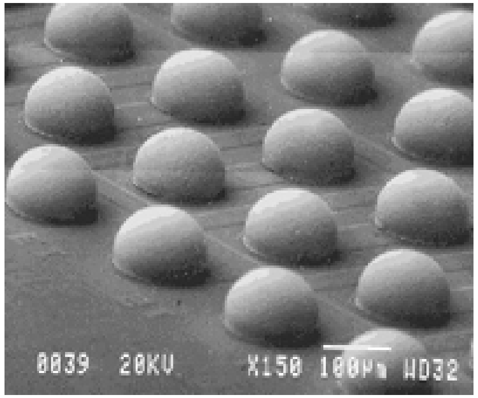


periodic electromagnetic media

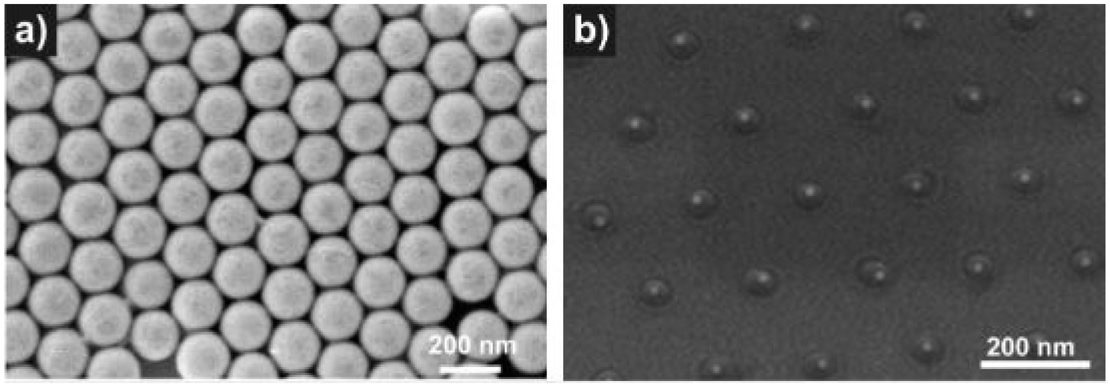
How to make Nanomaterials ??

- Top－down (Physical method): lithography
- Advantage: Easily controlled
- Disadvantage: Expensive



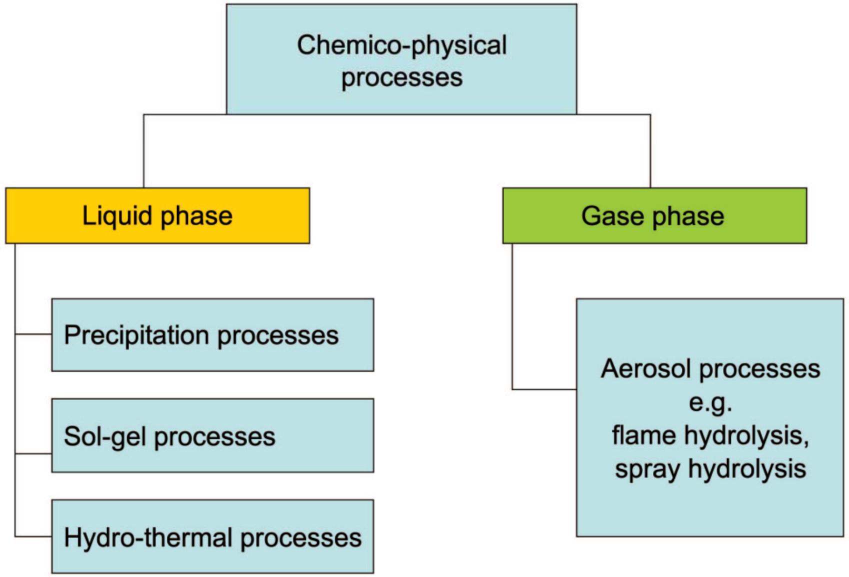


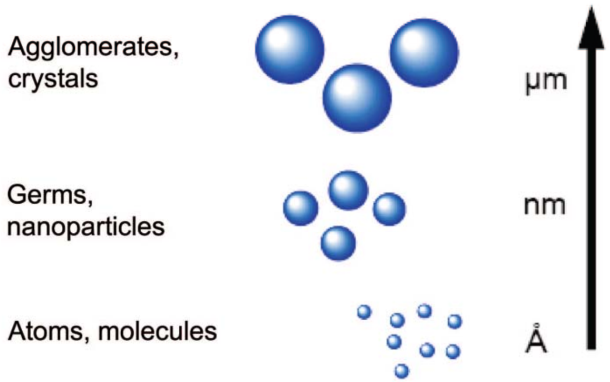
http://www.beilstein-journals.org/bjnano/single/articleFullText.htm?publicId=2190-4286-2-50

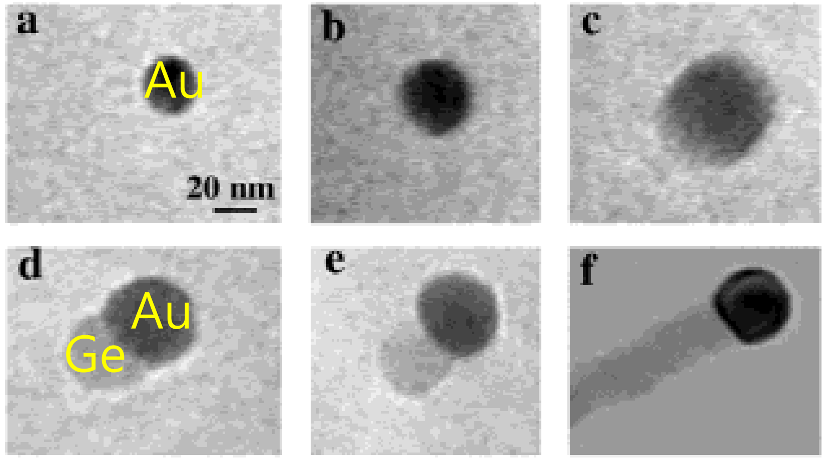


http://spie.org/x32391.xml

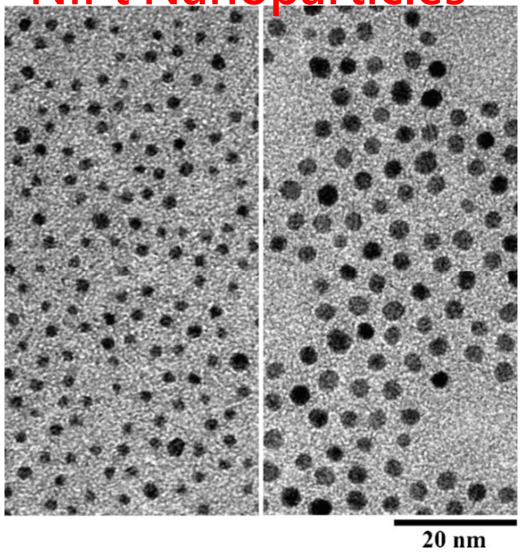
Bottom up (Chemical Method)

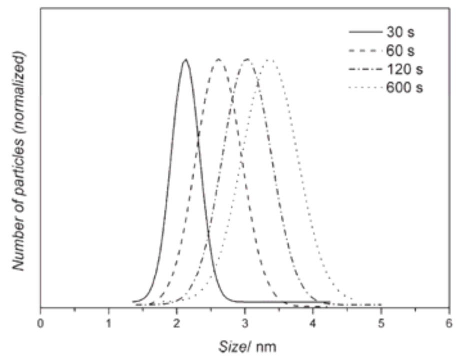






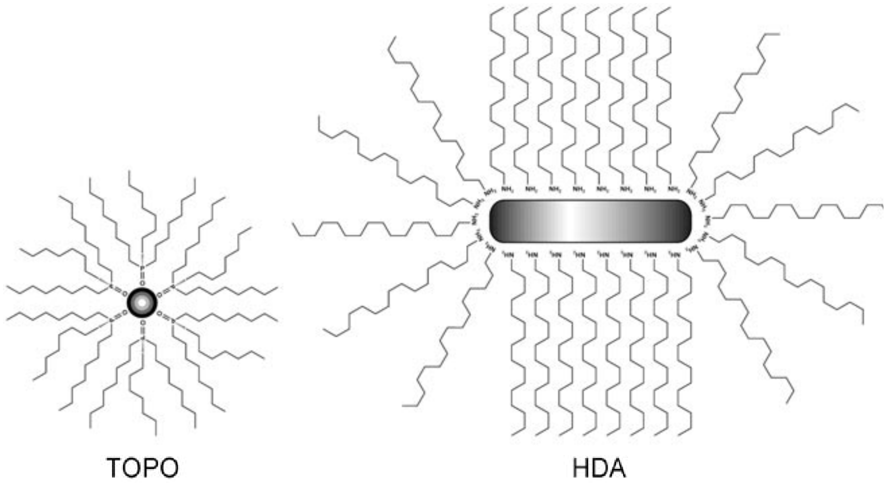
NiPt Nanoparticles



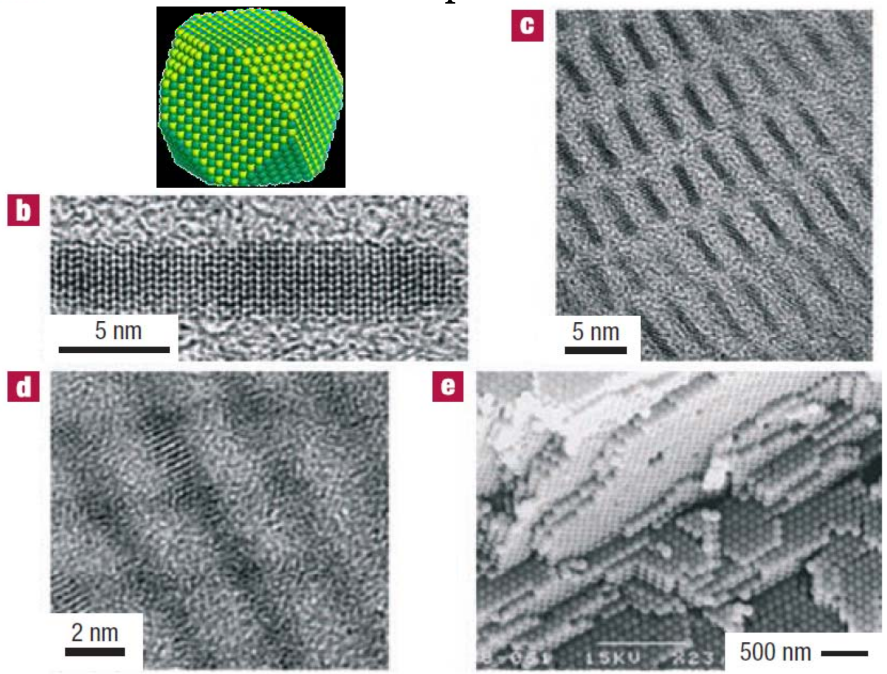


Ahrenstorf, K. et. al., Adv. Funct. Mater. 2008, 18, 3850–3856

Atomic Foundry

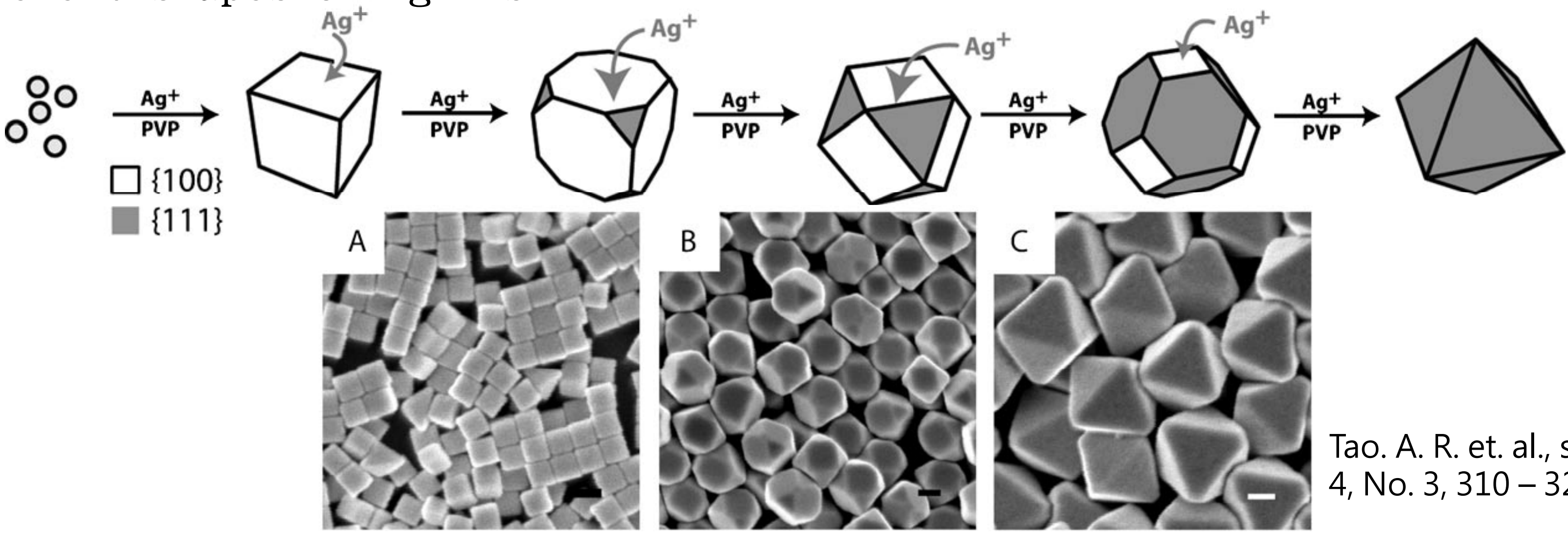


Different shapes of CdSe



Min, Y. et. al., Nature Materials 7, 527 - 538 (2008)

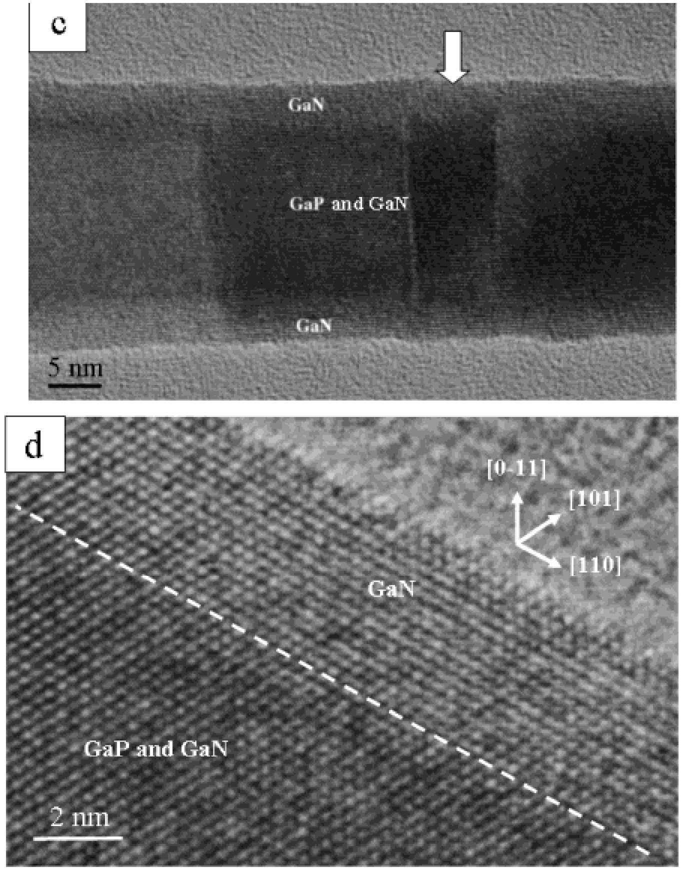
Different shapes of Ag NPs



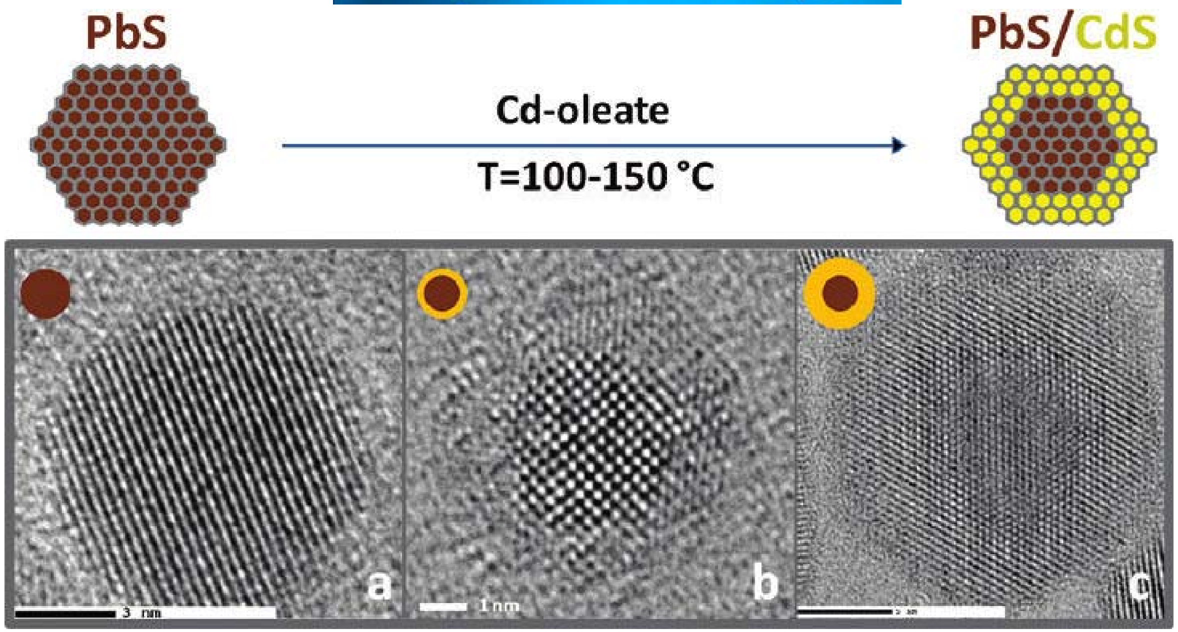
Tao. A. R. et. al., small 2008, 4, No. 3, 310 – 325

How to observe Nanomaterials??

Transmission electron microscopy(TEM)

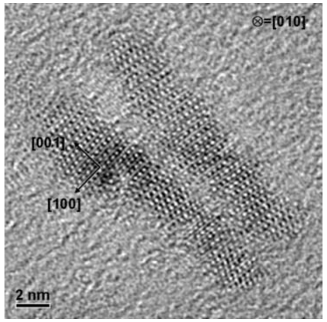


Lin, H. M. et. al., Nano Lett., Vol. 3, No. 4, **2003**



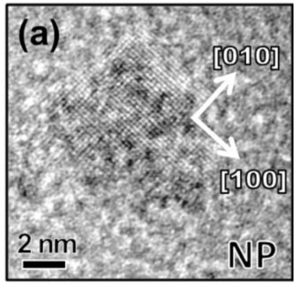
Kinder, E. et. al., *J. Am. Chem. Soc.* 2011, 133, 20488–20499

3D STEM Tomography images of P3HT/TiO_2 hybrids

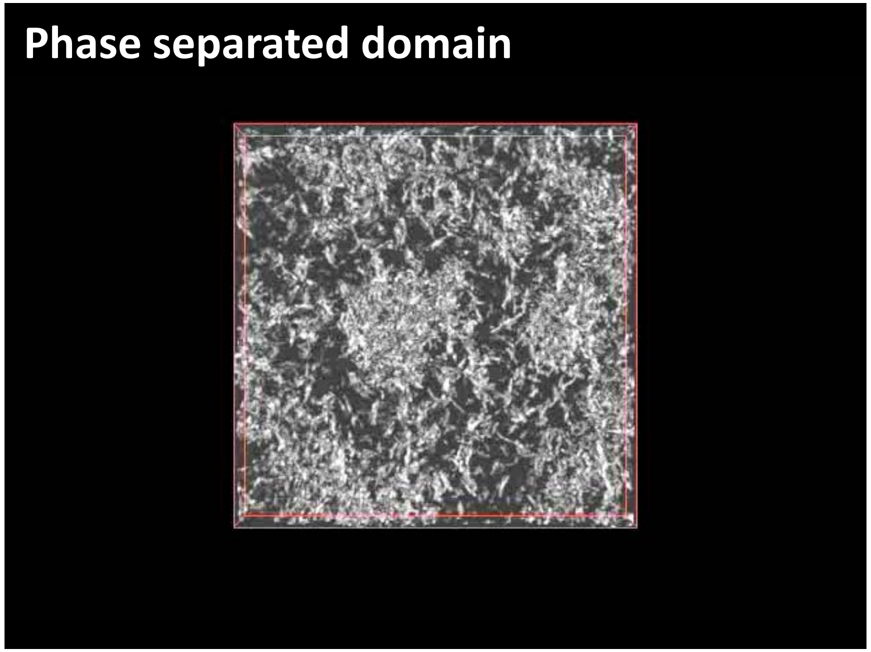


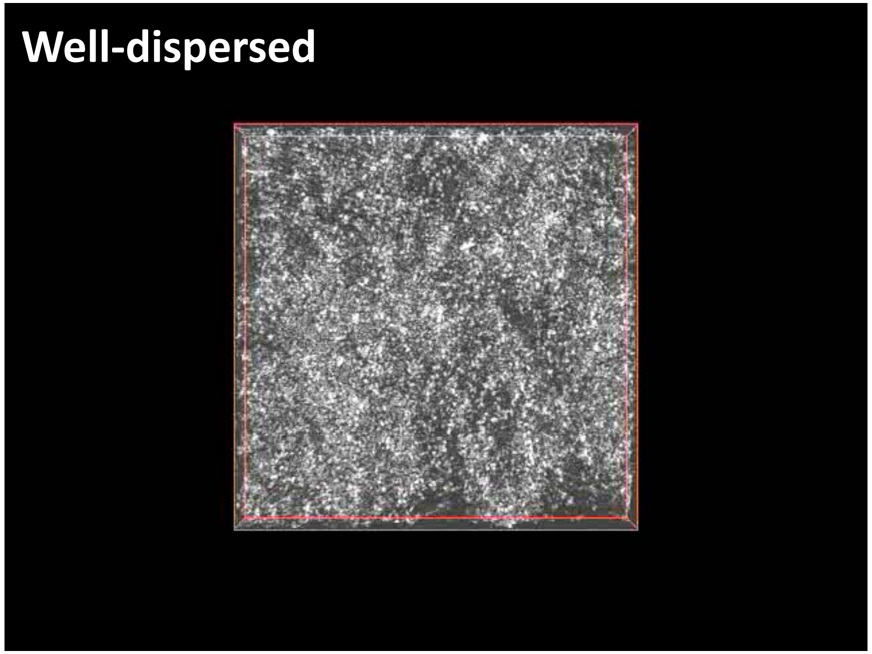
TiO_2 nano rod
(NR)
4nm x 20nm

TiO_2 nano particle
(NP)
5nm x 5nm



STEM-HAADF electron tomography (2 Å resolution)





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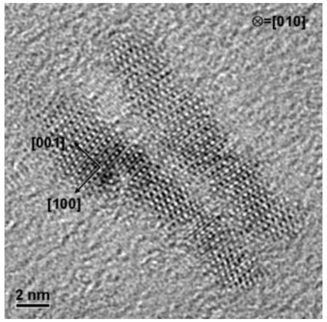

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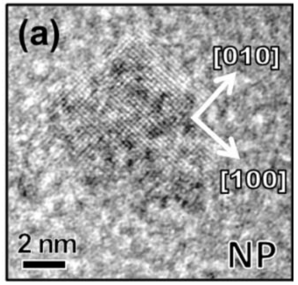

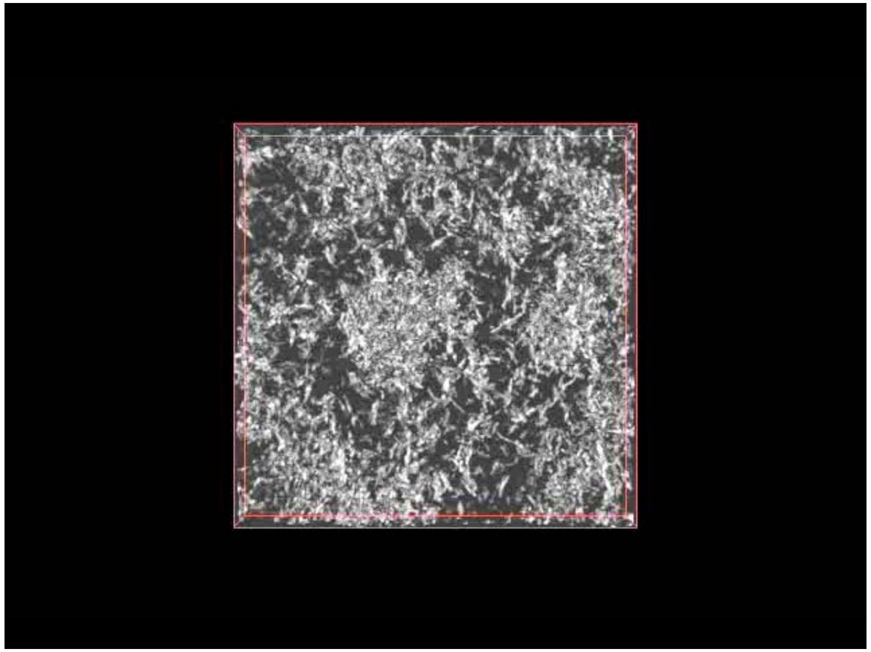

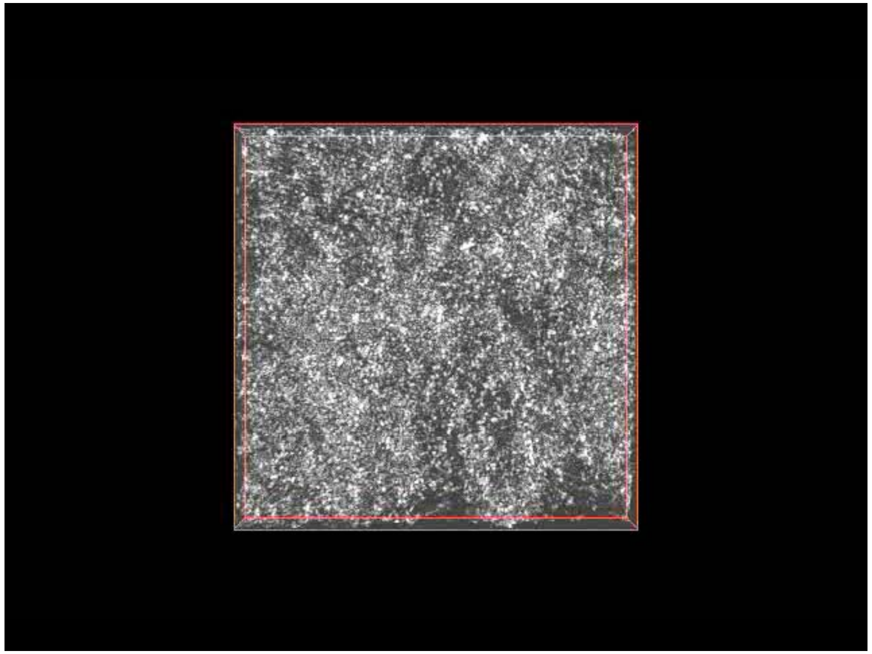

Phase separated domain

Journal of American Chemical Society, 133,11614, (2011)

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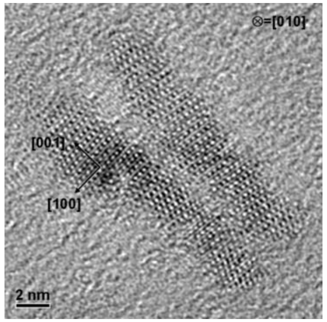

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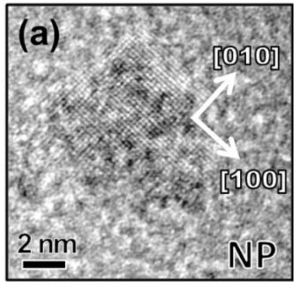
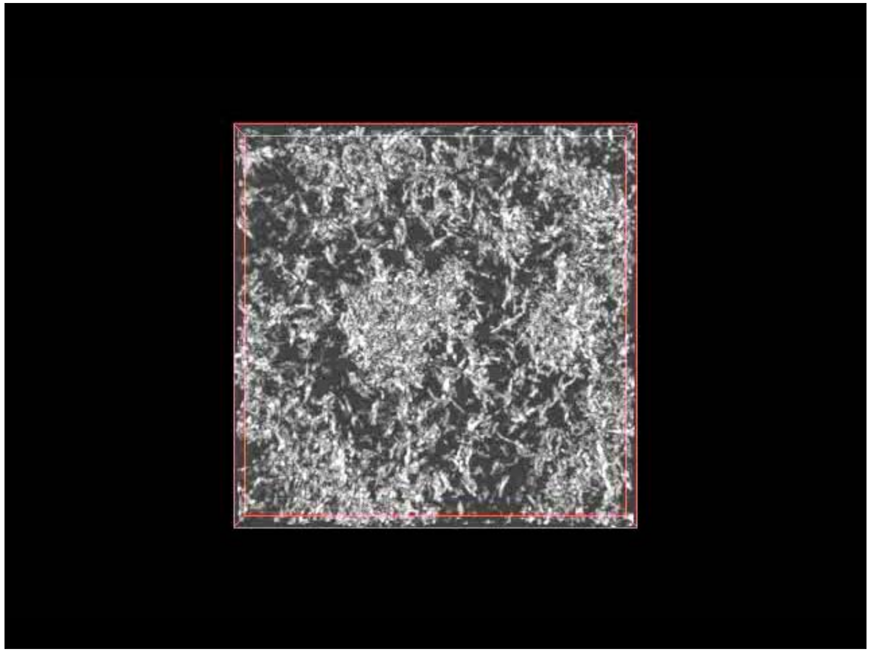
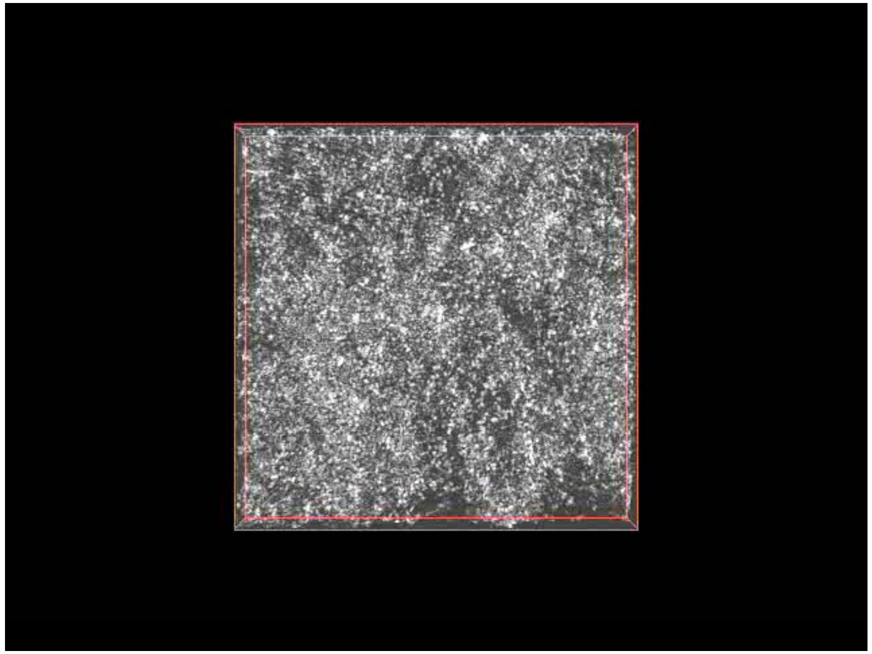


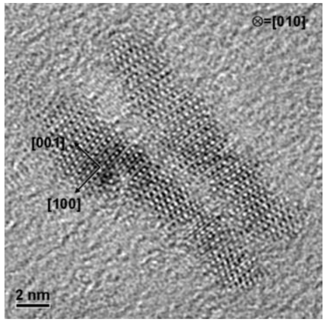




Phase separated domain

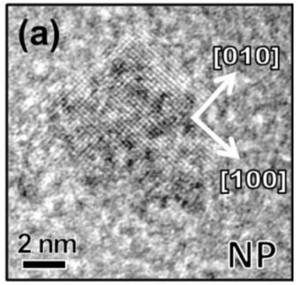
Well-dispersed

3D scanning transmission electron microscopy (STEM)
Electron tomography of P3HT/TiO_2 hybrids

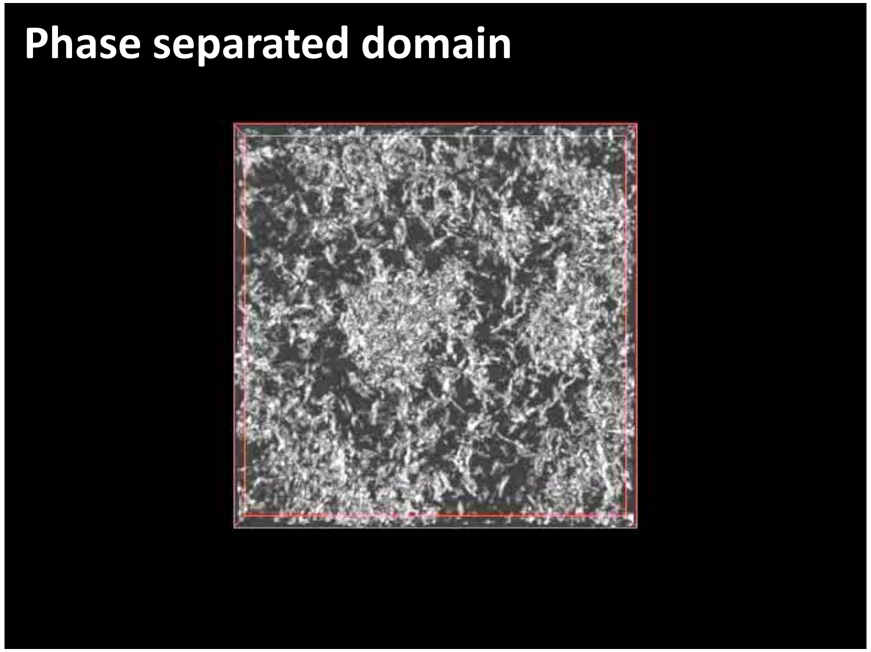


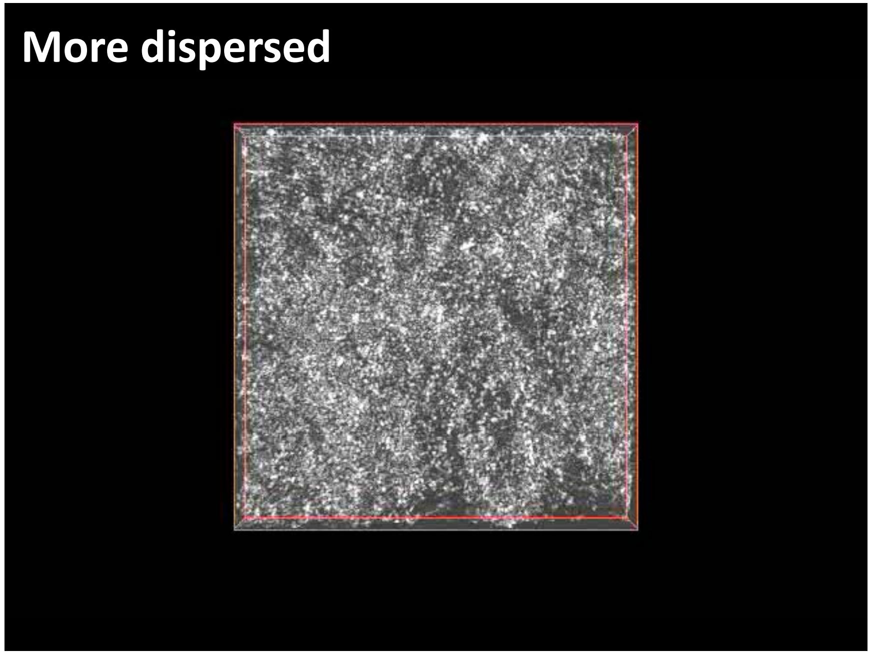
TiO_2 nanorod
(NR)
4nm x 20nm

TiO_2 nanoparticle
(NP)
5nm x 5nm

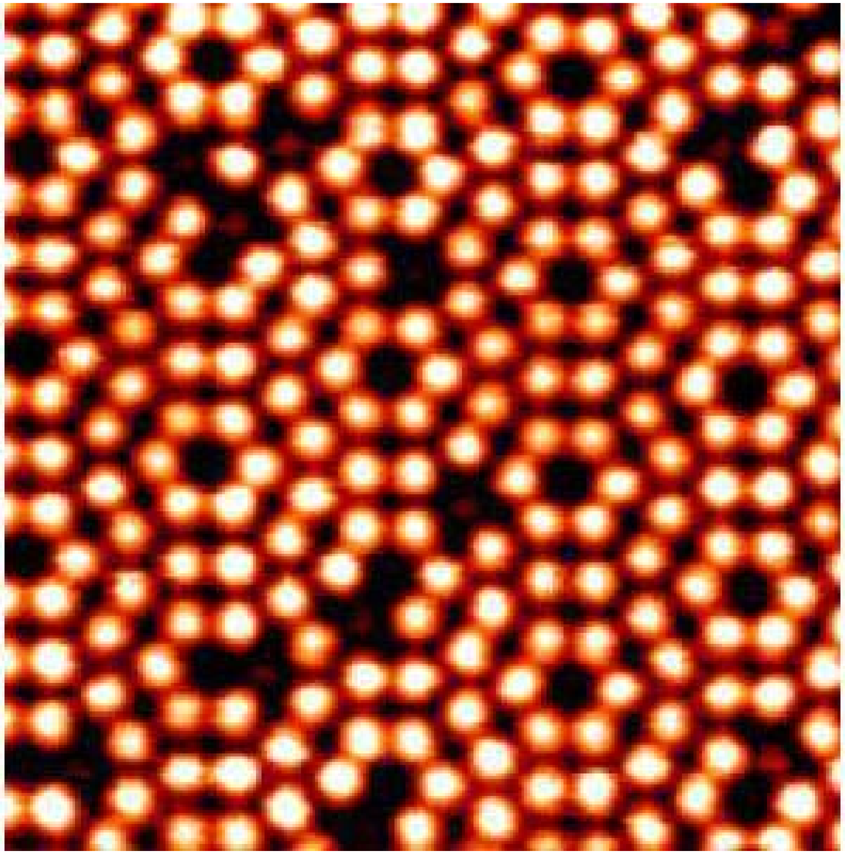


STEM-HAADF electron tomography





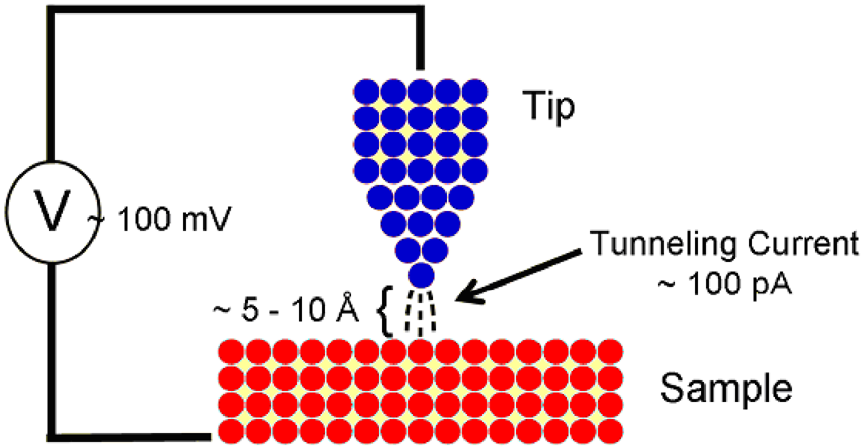
Scanning electron microscopy(STM)



Silicon atoms on a surface

http://www.exo.net/~pauld/workshops/Atoms.html

(Quantum tunneling effct)



http://www.personal.psu.edu/ewh10/ResearchBackground.htm

Atomic Force Microscopy (AFM)

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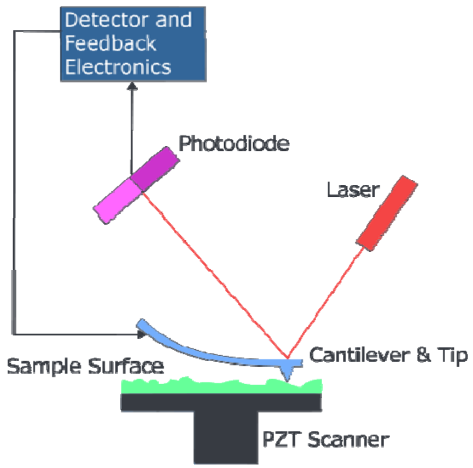
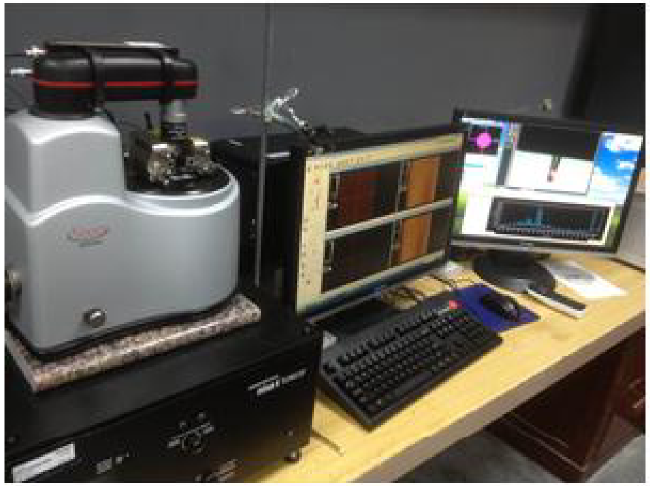
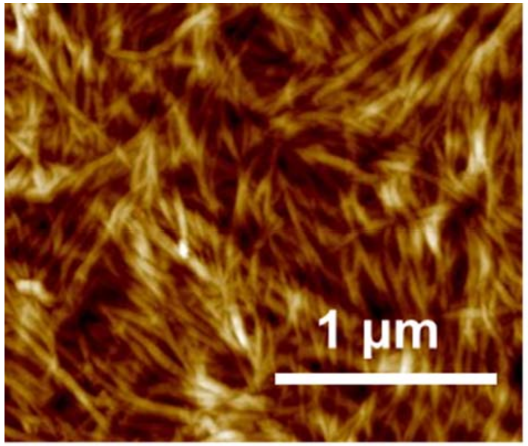
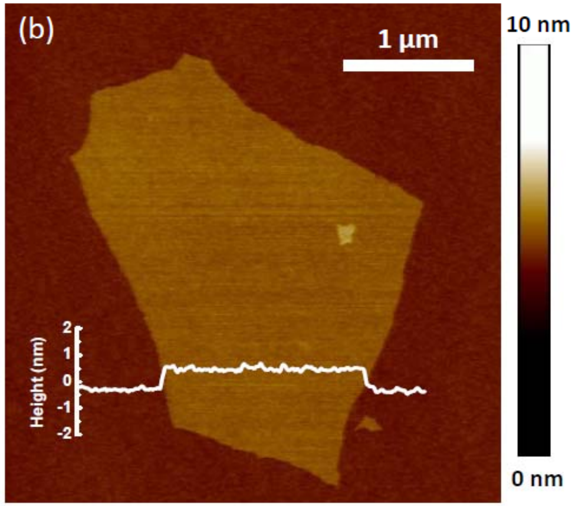




single wall carbon nanotube

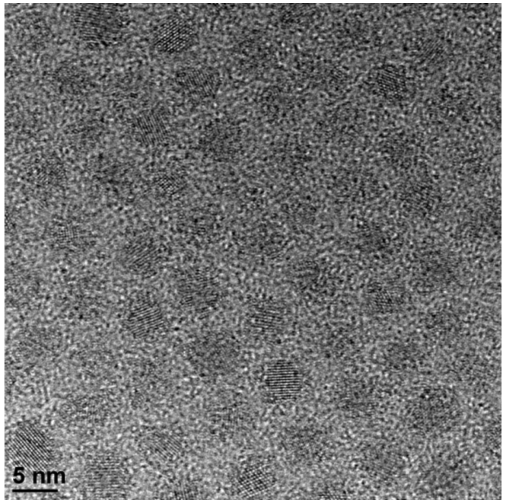


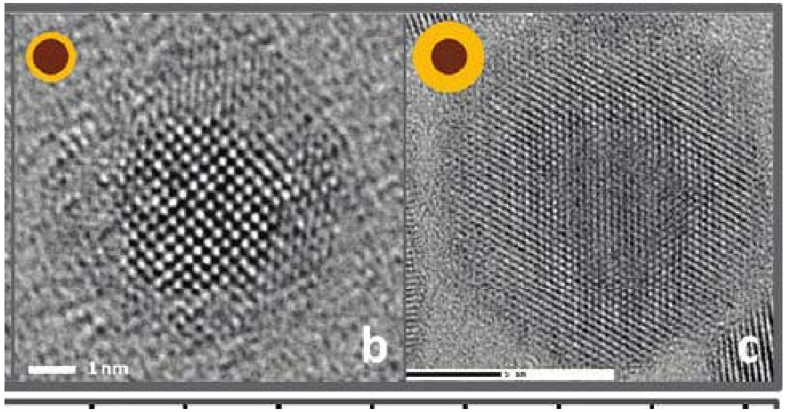
（Graphene oxide)



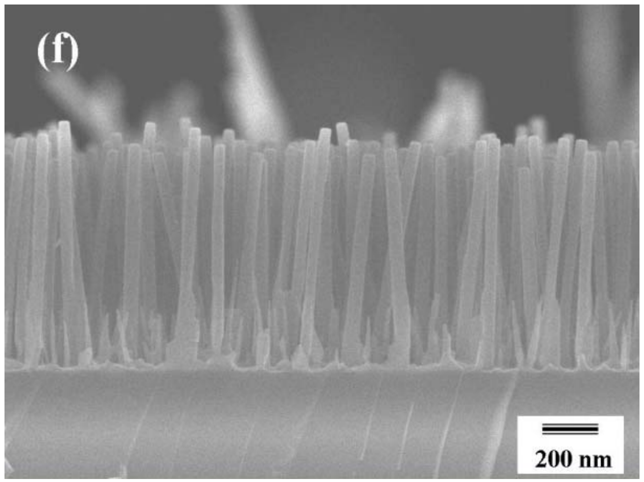
Optical and electronic applications of nanomaterials

0D: nanoparticles

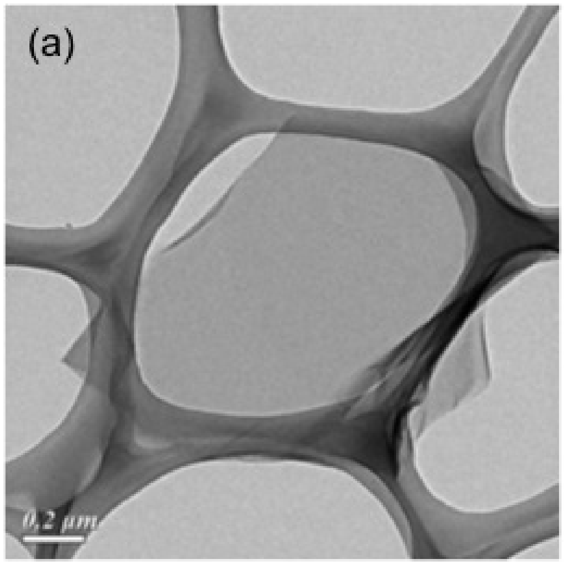


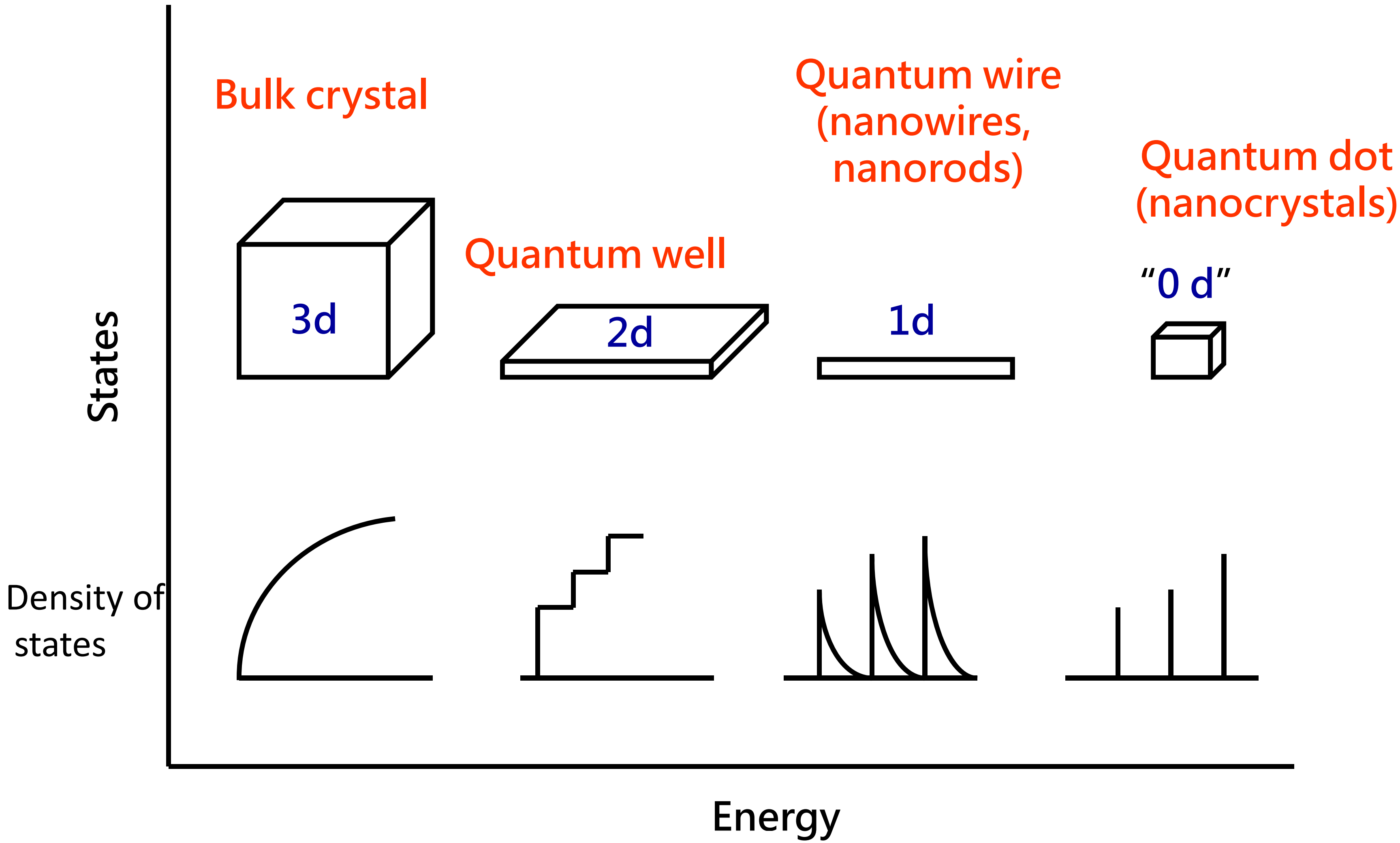


1D: nanowires

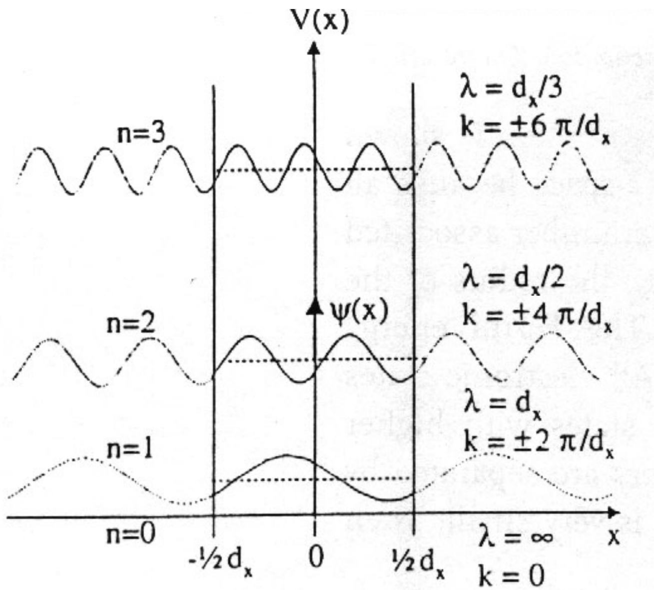


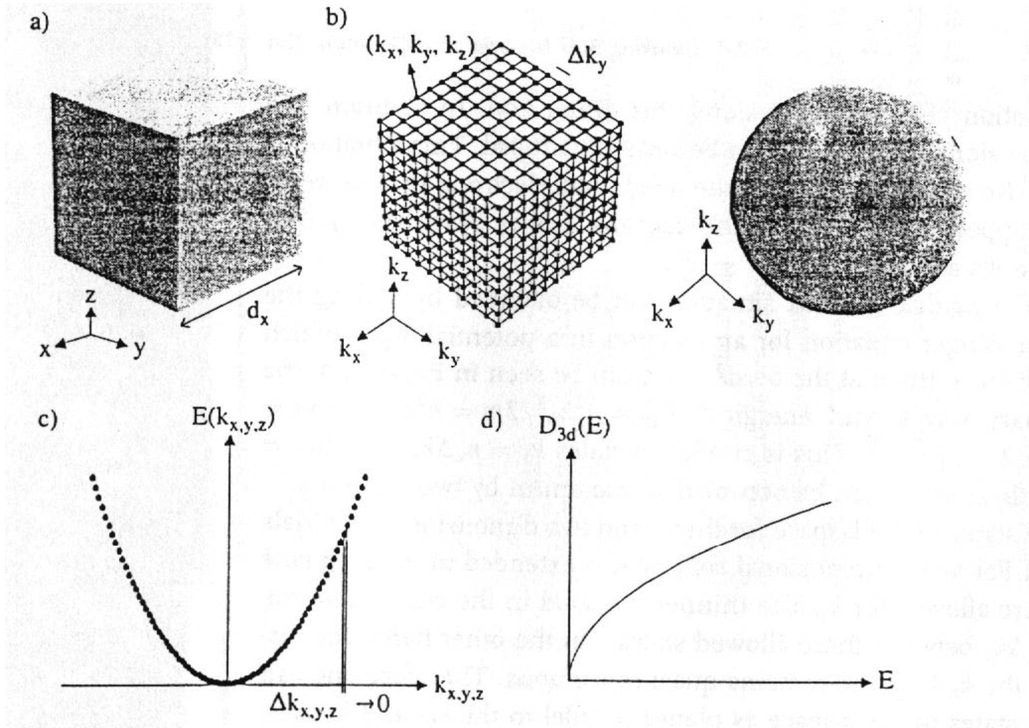
2D: nanosheets




Bulk crystal
Quantum well
Quantum wire
(nanowires,
nanorods)
Quantum dot
(nanocrystals)
3d
2d
1d
"0 d"
States
Density of
states
Energy

Three dimensional system (bulk)



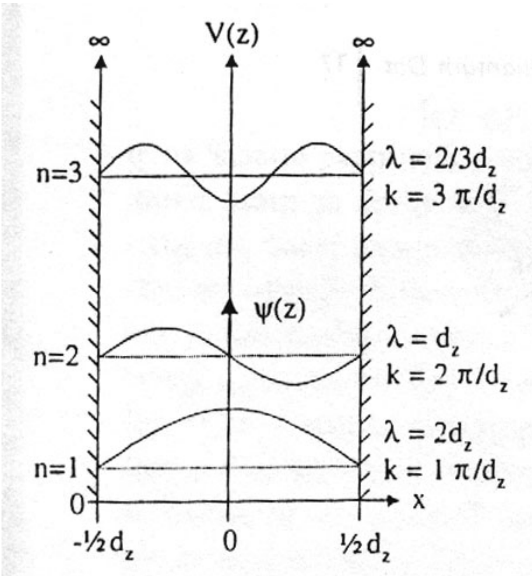


V=0

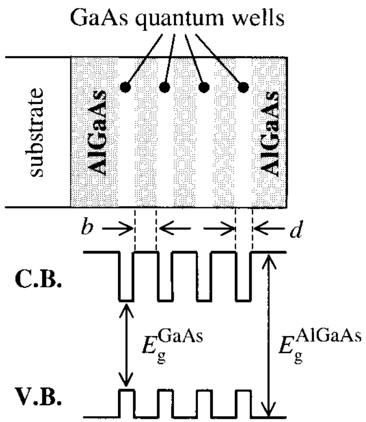
Free electron model in 3D

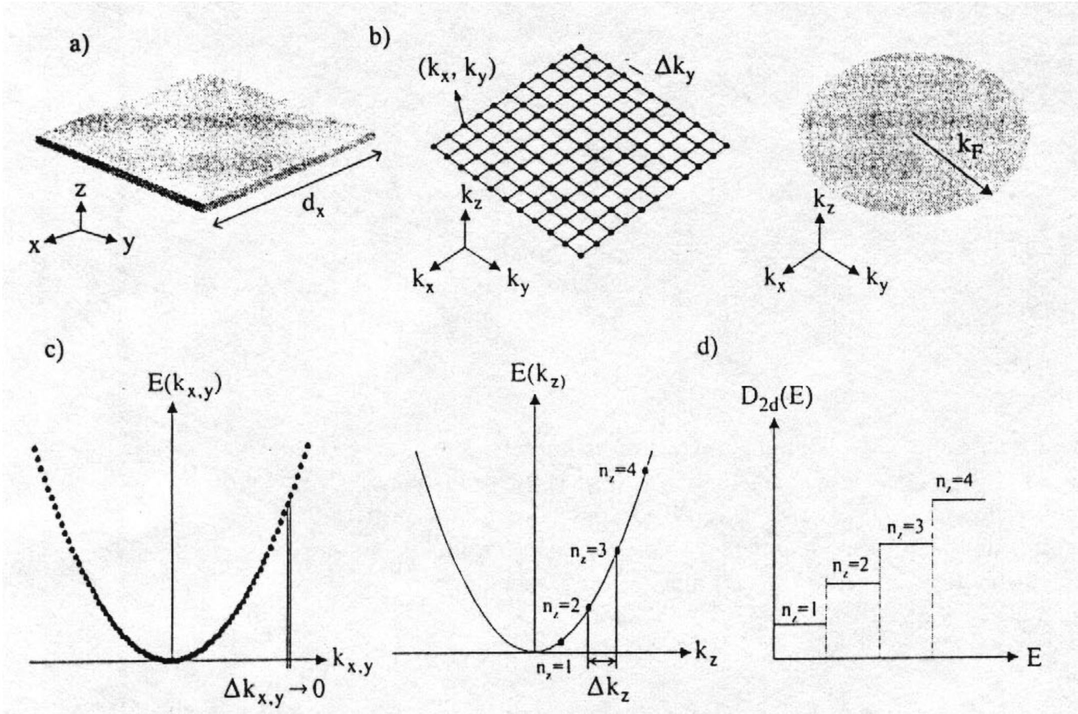
$$D(E) \propto \sqrt{E}$$

Two-dimensional system



V=infinite at z direction

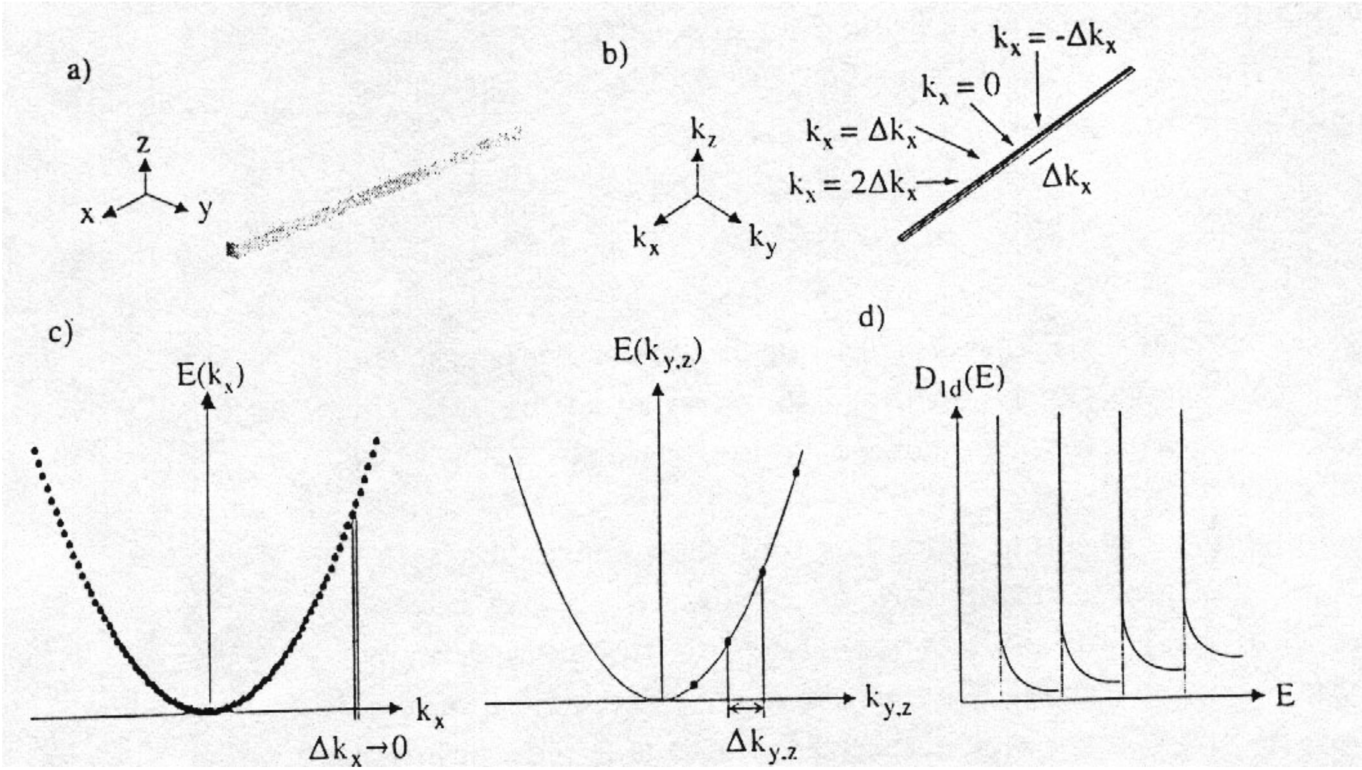




$$D(E) \propto const$$

1-D confinement, 2-D free electron

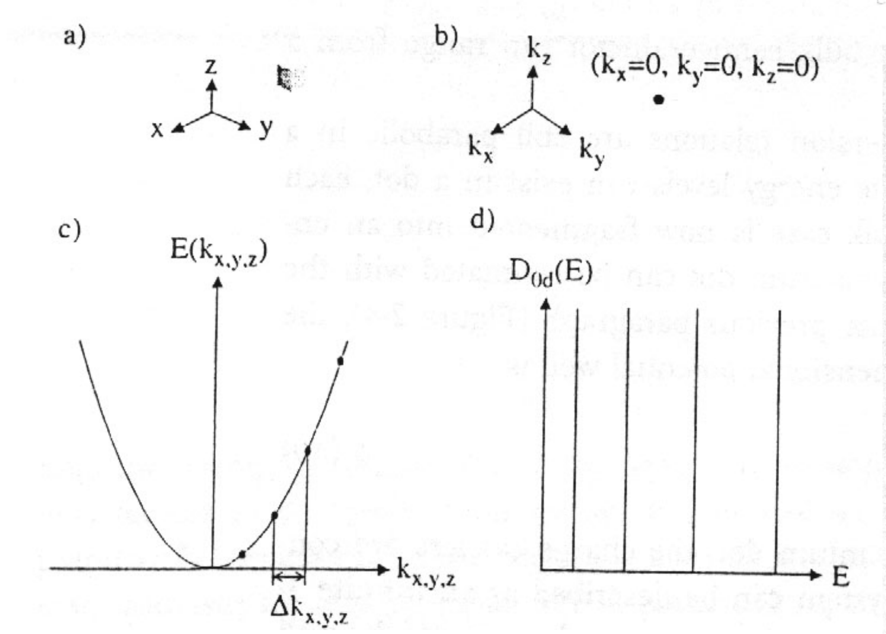
1-D system (Quantum wire)

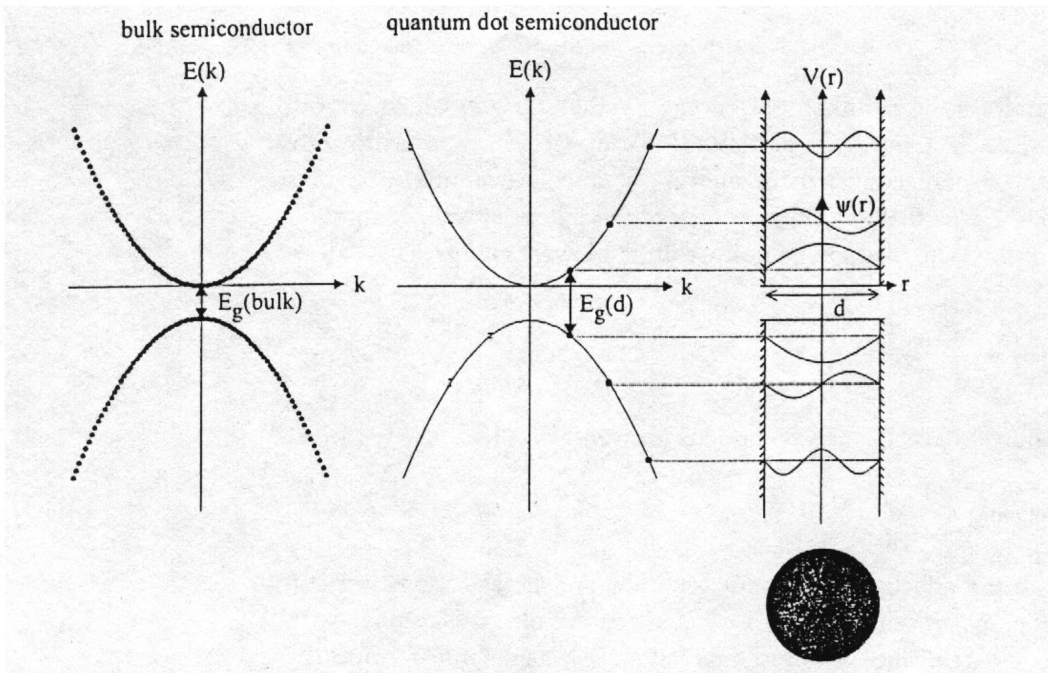


$$D(E) \propto 1/\sqrt{E}$$

2-D confined, 1-D free electron

0-D system (Quantum dot)

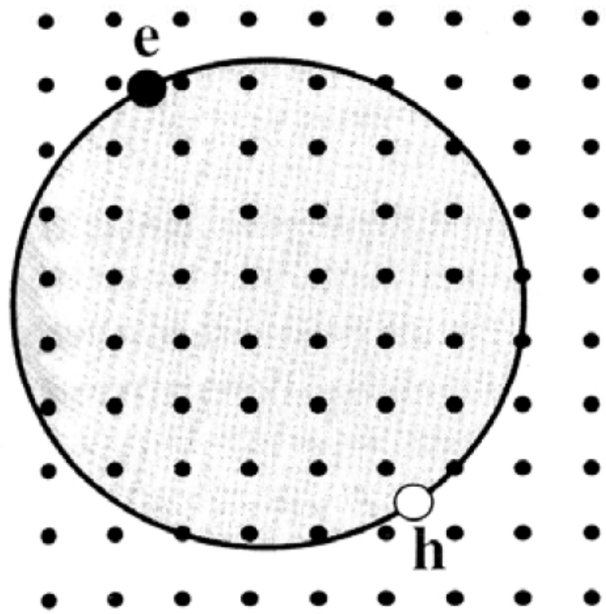




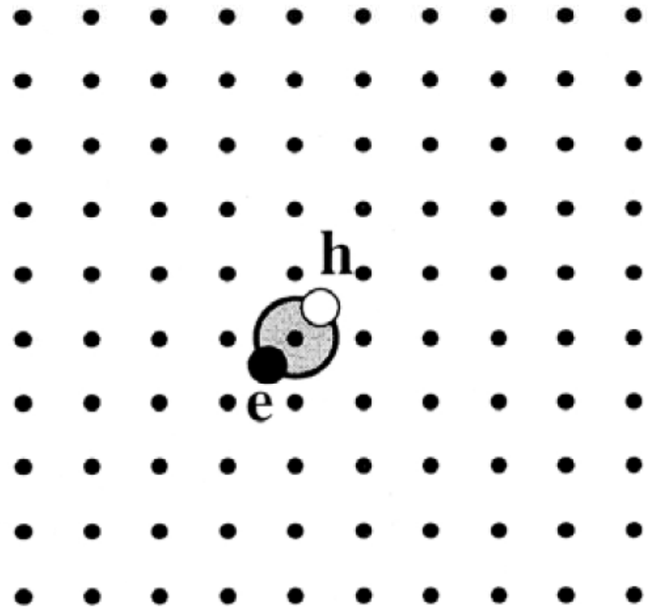
Discrete energy level

3-D confined

Exciton



(a) Free exciton



(b) Tightly bound exciton

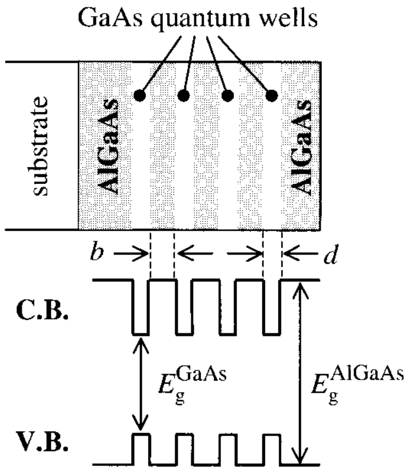
Binding energy and Bohr's radius

$e^- + h^+ \rightarrow$ exciton

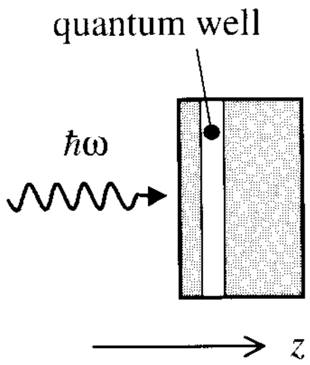
- free exciton $E_b \approx 0.01\ eV$

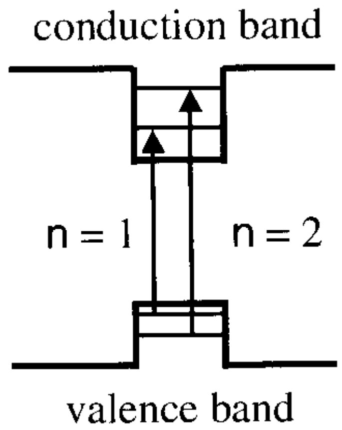
- tightly bound exciton $E_b > 0.1\ eV$

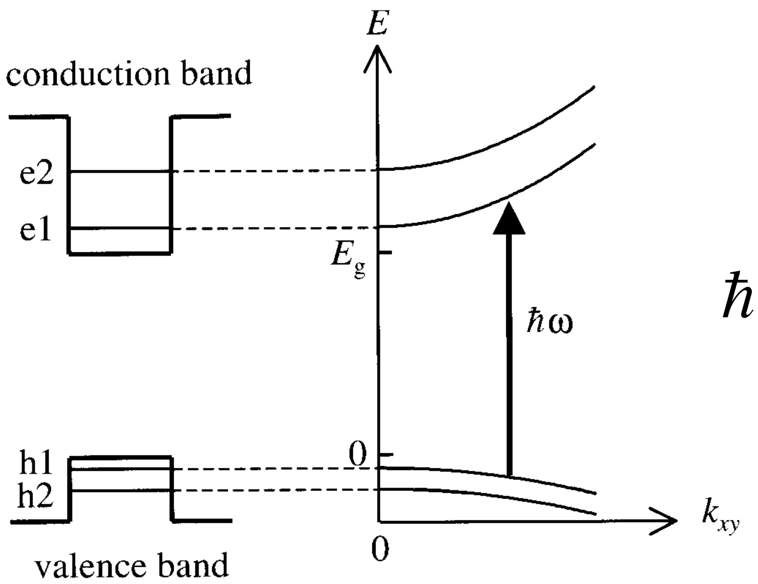
Optical absorption and excitons in semiconductor quantum well



Superlattice

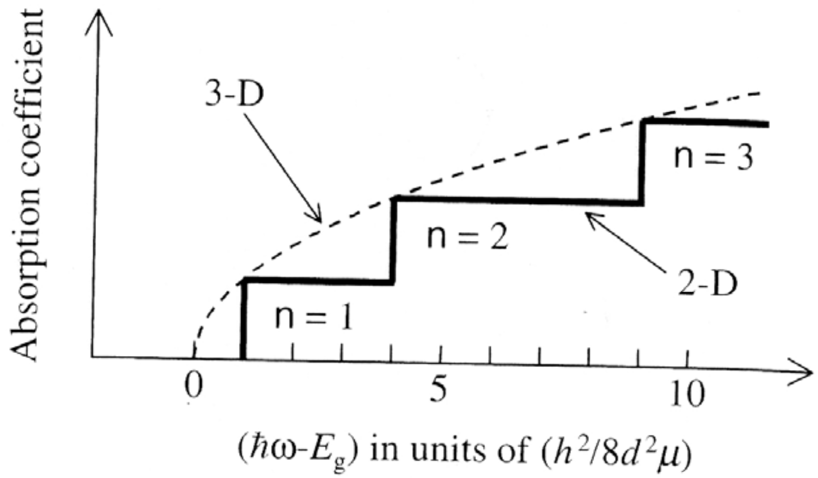




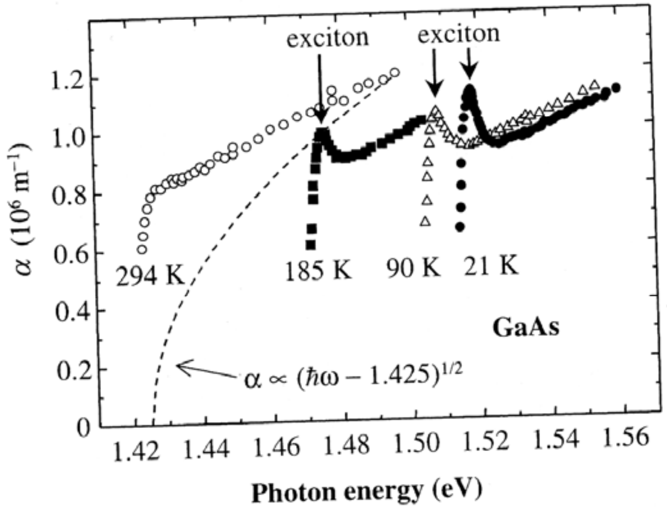


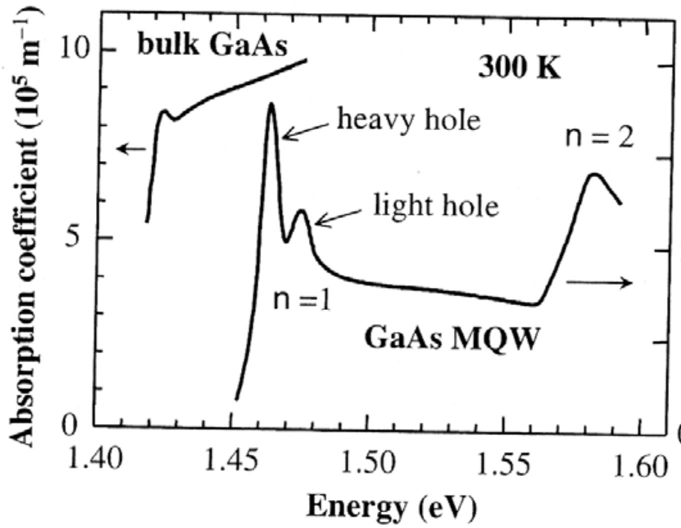
$$\hbar\omega = E_g + \frac{\hbar^2 n^2}{2\pi^2 \mu d^2}$$

(No exitonic effect)

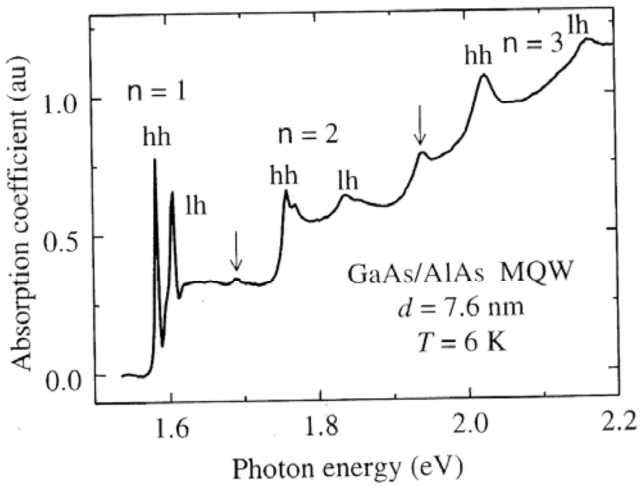


Bulk





Quantum well

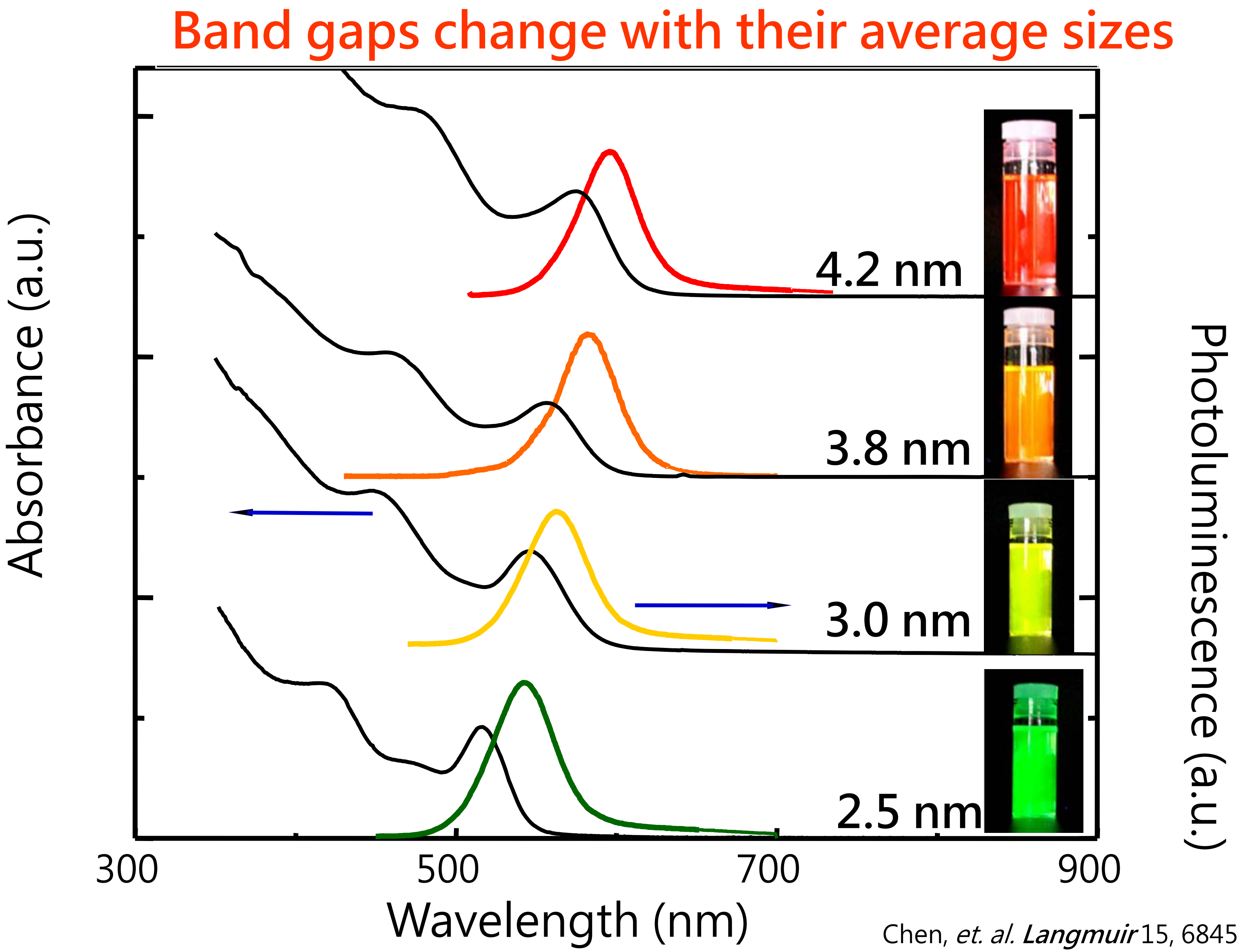


Room T exciton effect is observed.

Strong Coulomb interaction as the e-h distance decreases.

Binding energy increases from 4 meV (bulk) to 10 meV (QW)

Size-dependent optical properties of CdSe QDs



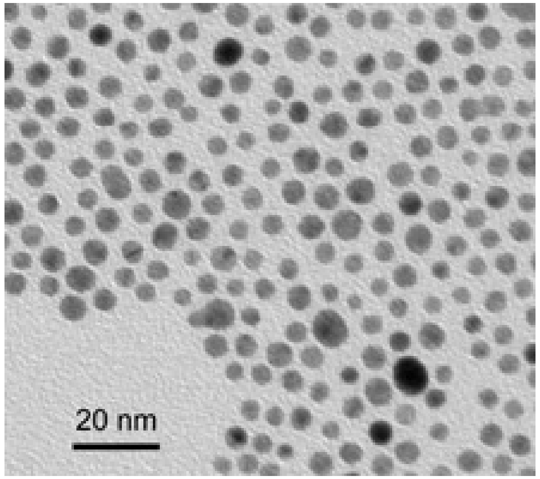
Chen, *et. al.* ***Langmuir*** 15, 6845 (1999)

)

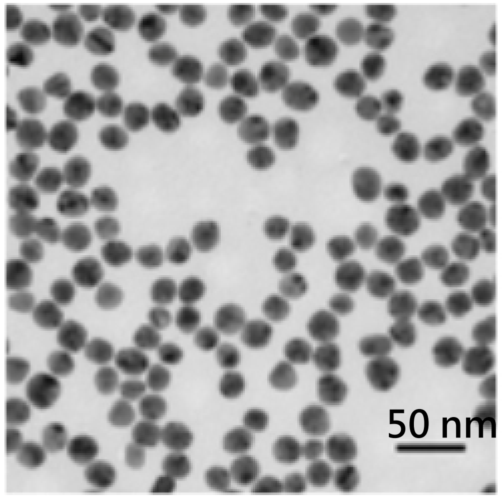
Surface plasmonic effect

Gold nanoparticcels

Nano-Size



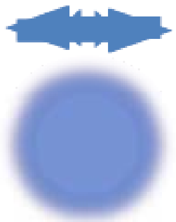
Nano-Size



Silver nanoparticles

Localized Surface Plasmon (LSP)

External EM field E_o



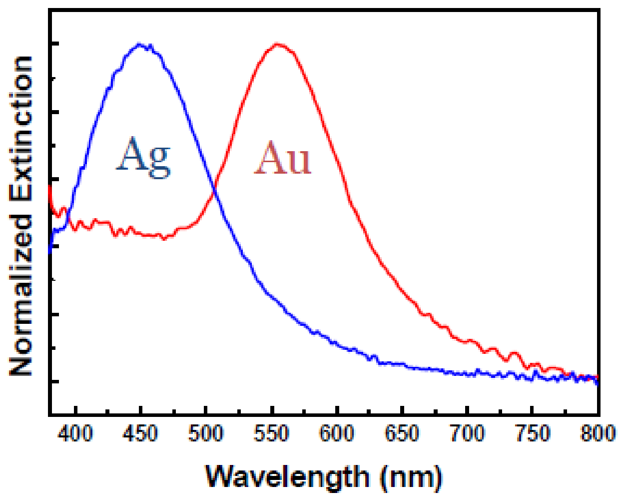
Metal NP

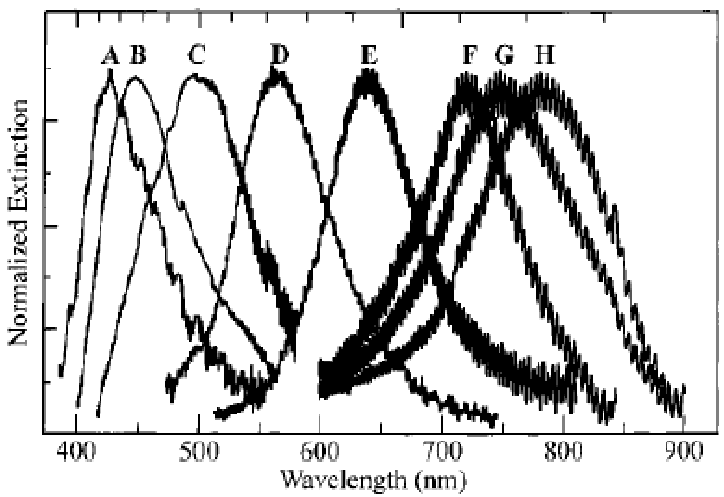
Excited free electron density oscillation → LSP

When particle size $a \ll \lambda$ → dipole oscillation

Resonant at specific frequency → LSPR

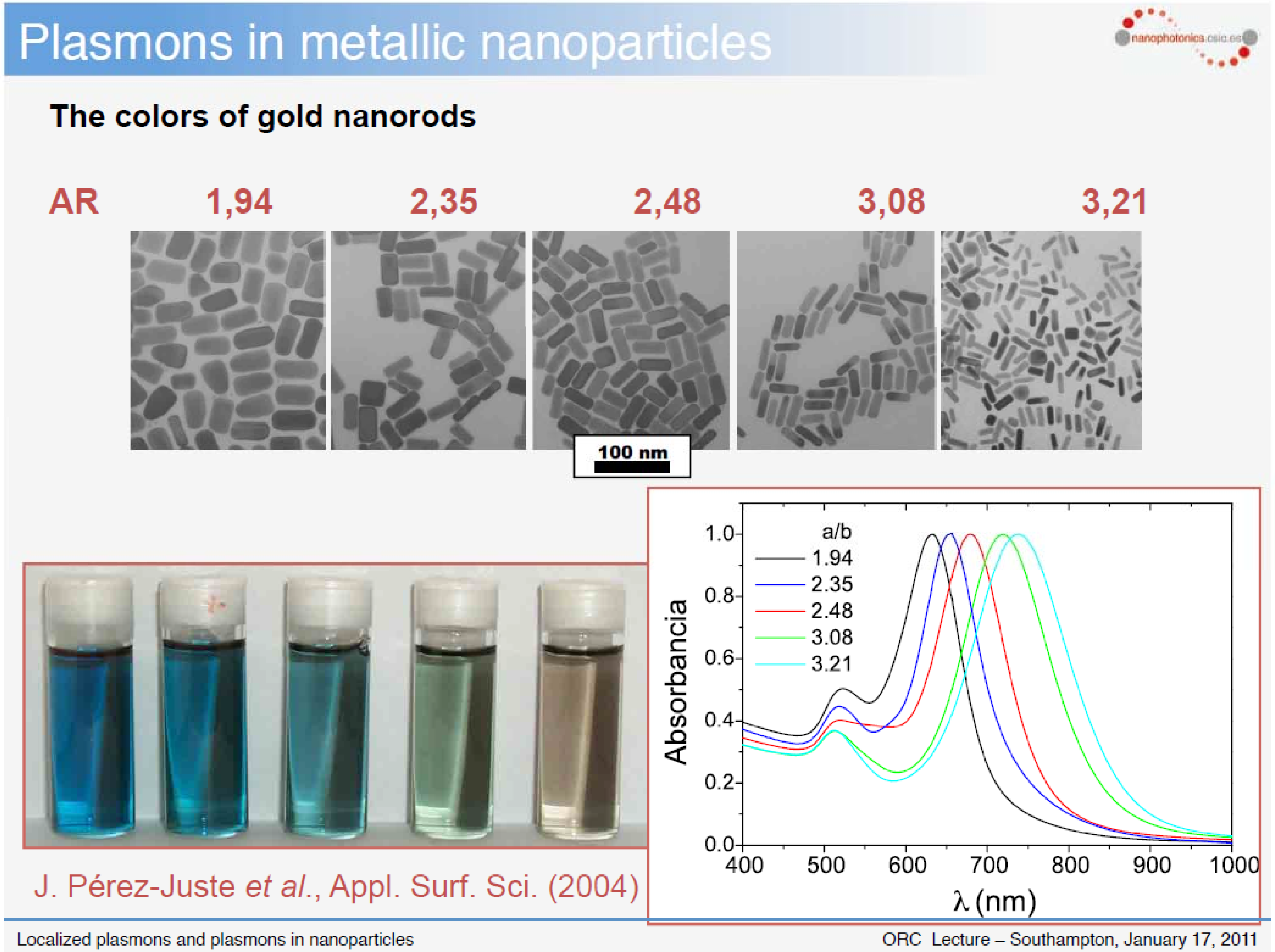
- **Resonant frequency ω_r varied with:**
  metals, morphology, and dielectric environment



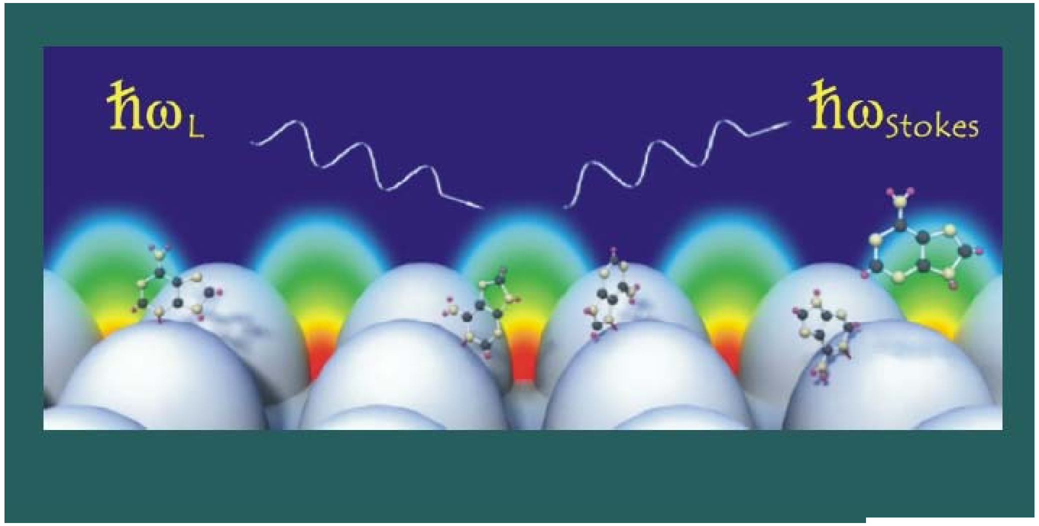


T. R. Jensen et al. JPCB, 104, 10549 (2000)

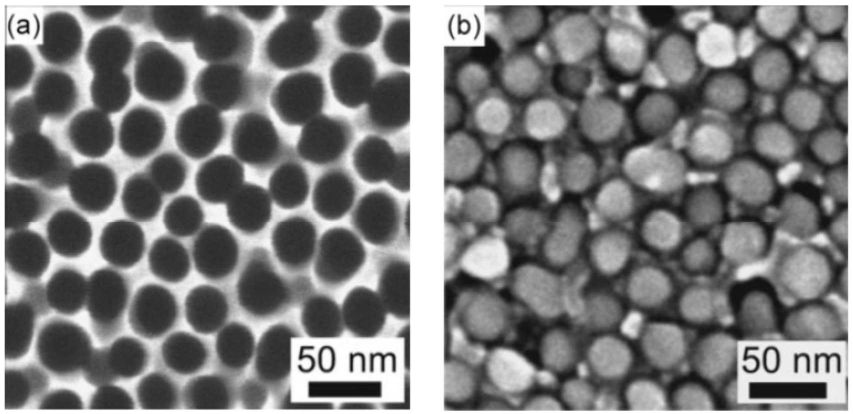
Different Geometries (Gold nanorods)

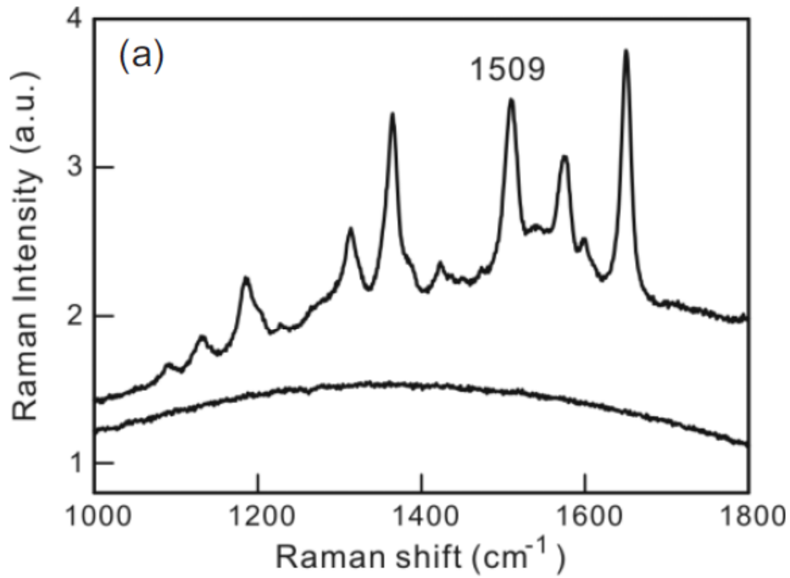


Surface plasma enhanced Raman (SERS)



Dr. W.L.Wang,
IAMS, Academic Sinica





Adv. Mater, 2006, 18, 491

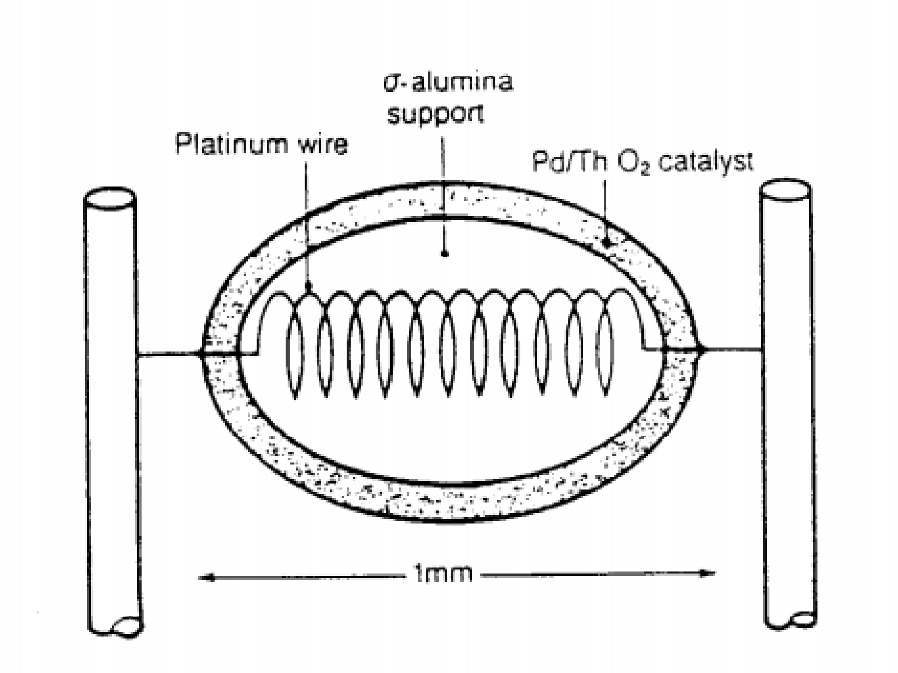
Gas sensor

For detecting Combustible, flammable and toxic gases, and oxygen depletion.

Portable gas detector

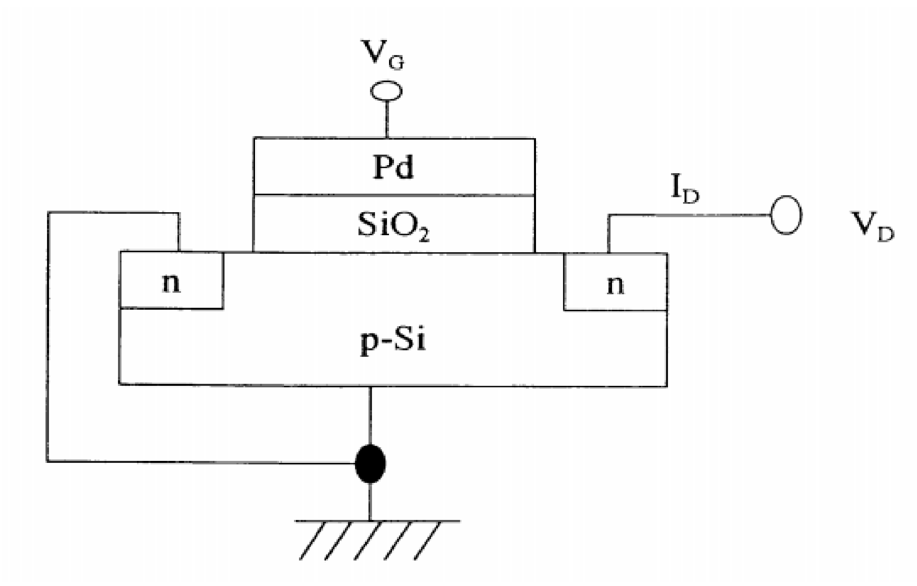
Classification of gas sensor

- Thermal gas sensor: flammable gas, CH_4, Cl_2, H_2, CO



Schematic of catalytic sensor

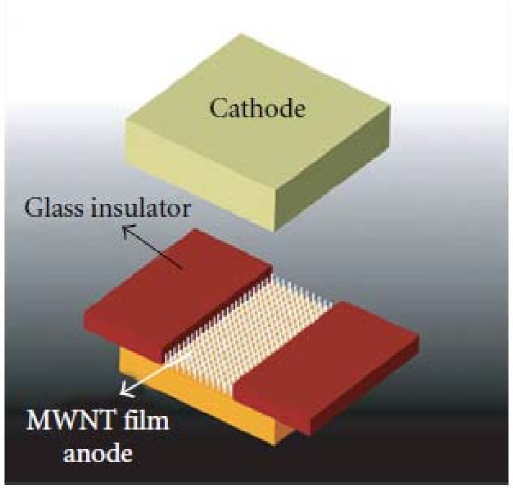
- Field effect transistor gas sensor



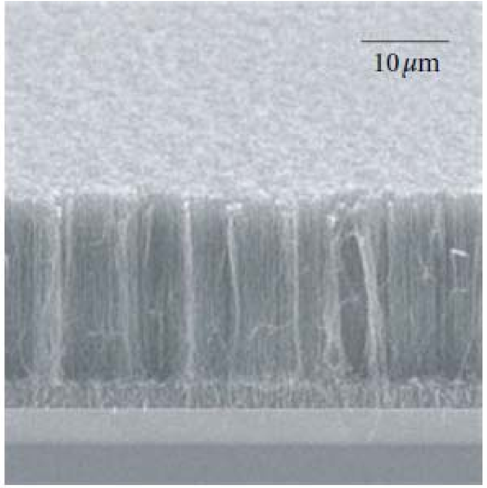
Schematic of MOS-FET sensor

Nanomaterials on gas sensor application

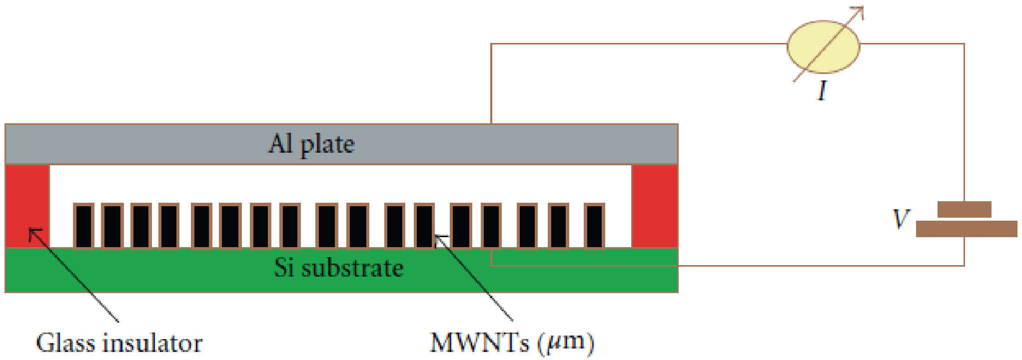
Fabricated by **carbon nanotube**

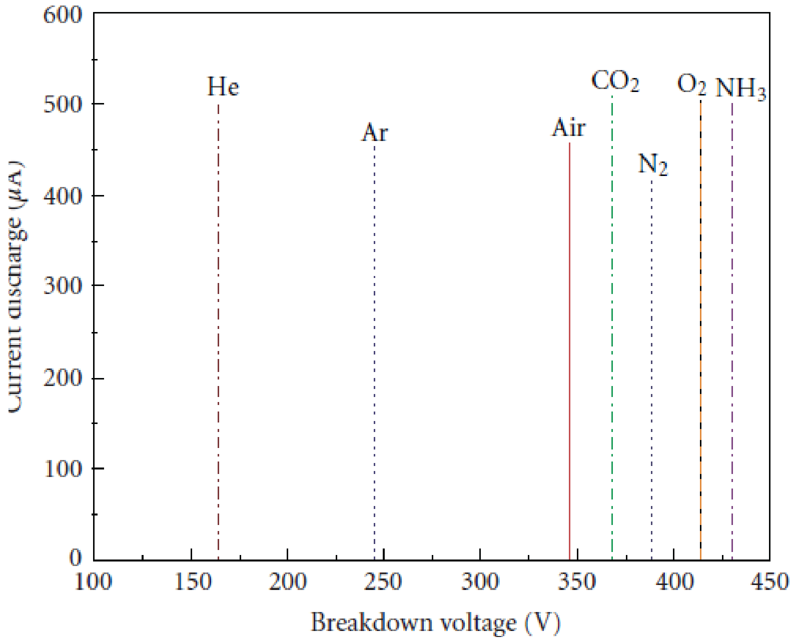


(a)



(c)



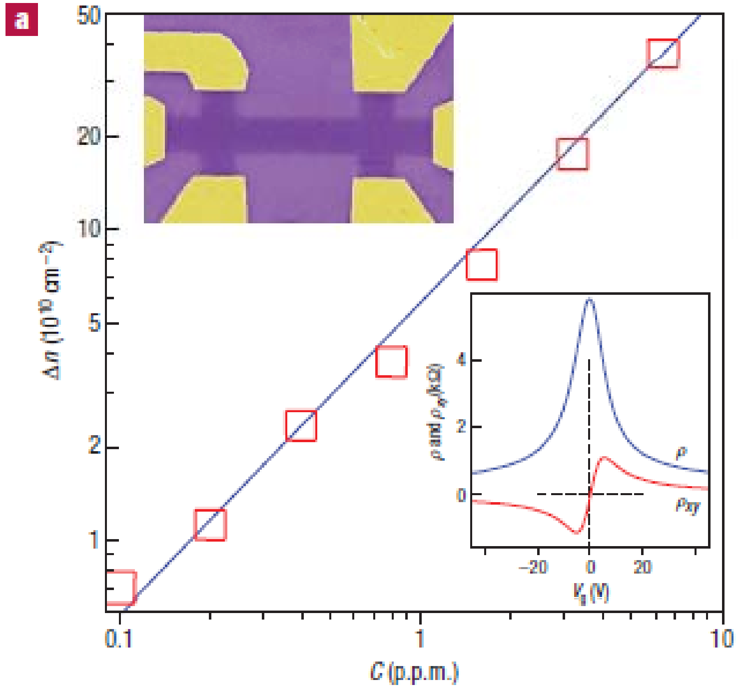


Current-voltage curves for electrical breakdown for NH_3, CO_2, N_2, O_2, He, Ar and air

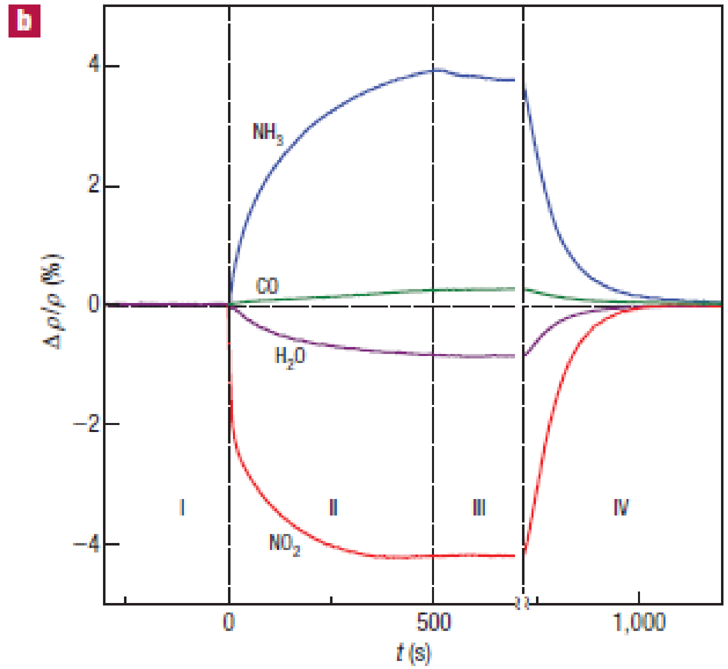
A. Modi, N. Koratkar, E. Lass, B. Wei, and P. M. Ajayan, “Miniaturized gas ionization sensors using carbon nanotubes,” *Nature, vol. 424, no. 6945, pp. 171–174, 2003.*

Nanomaterials on gas sensor application

Fabricated by **Graphene**



Concentration, Δn, of chemically induced charge carriers in single-layer graphene exposed to different concentrations, C, of NO_2.



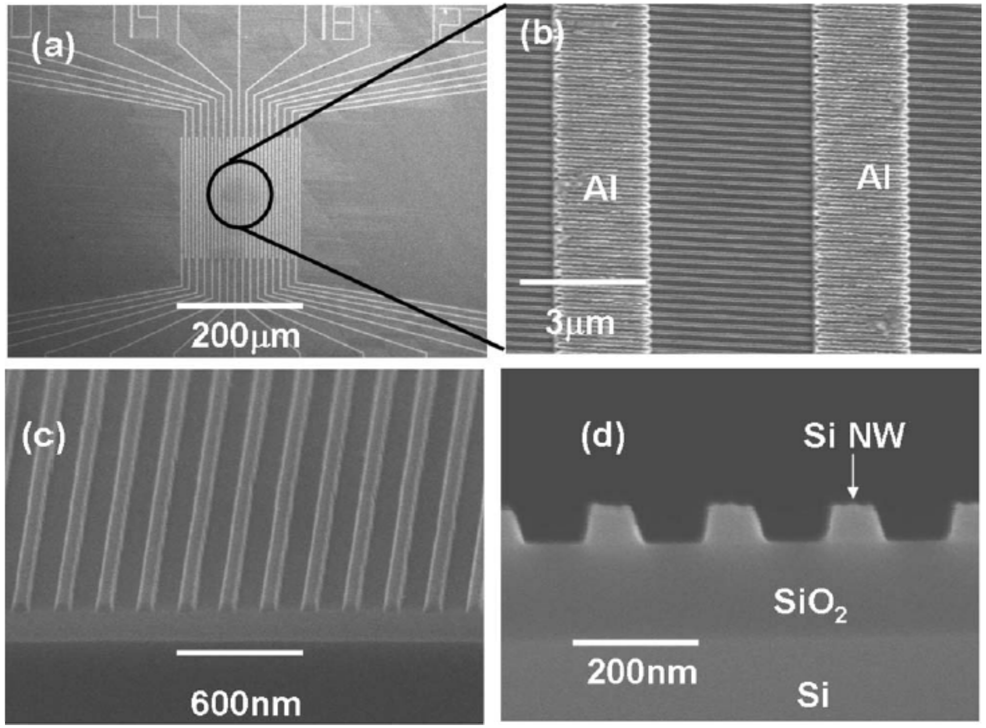
Changes in resistivity, , at zero B caused by graphene's exposure to various gases diluted in concentration to 1 p.p.m.

graphene is an exceptionally low-noise material electronically for chemical detectors.

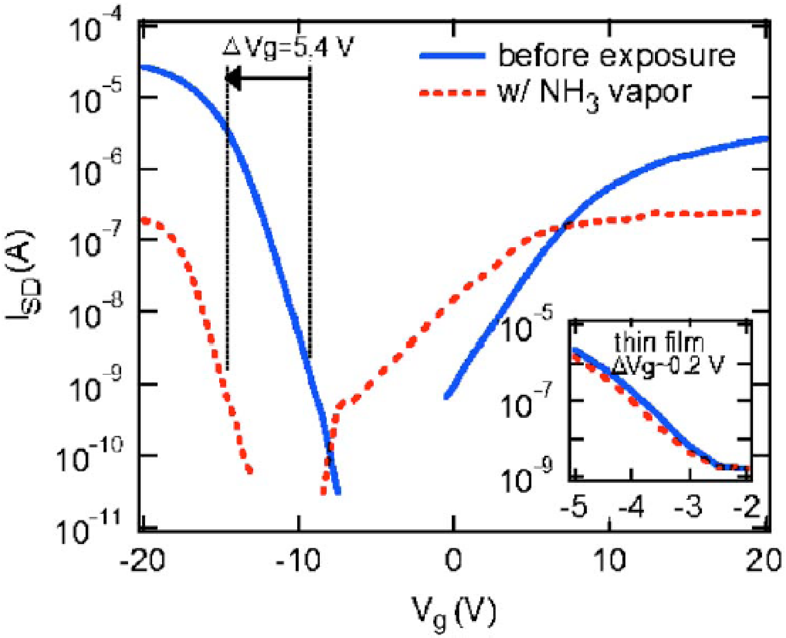
F. SCHEDIN, et. al., nature materials 2006, *6*, *652*

Nanomaterials on gas sensor application

Fabricated by **Silicon nanowire**



Dense arrays of silicon nanowires over large areas created by nanoimprint lithography



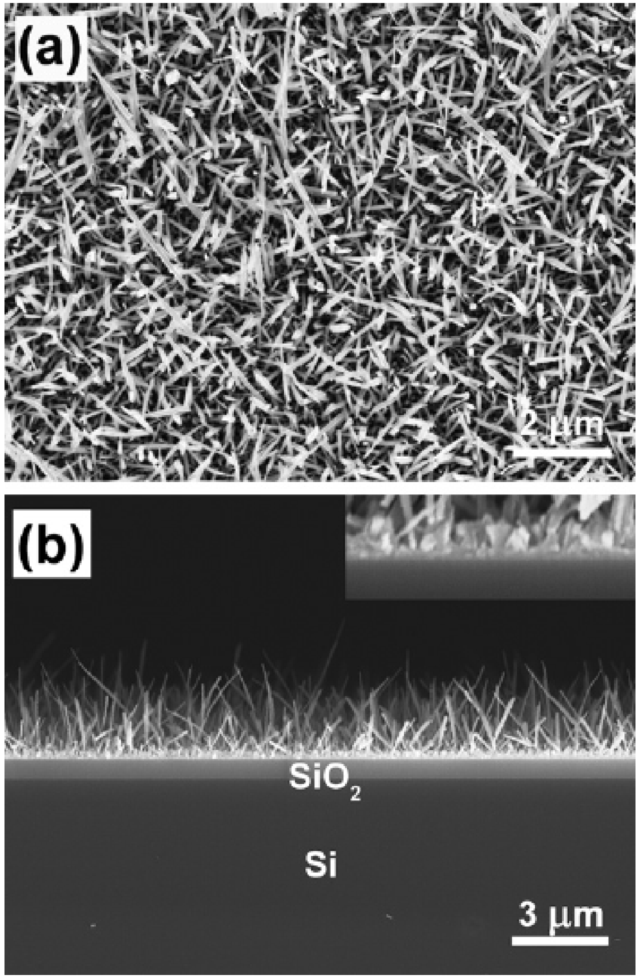
Variation in I_{SD} vs V_G for a SiNW array exposed to ammonia NH_3 vapor.

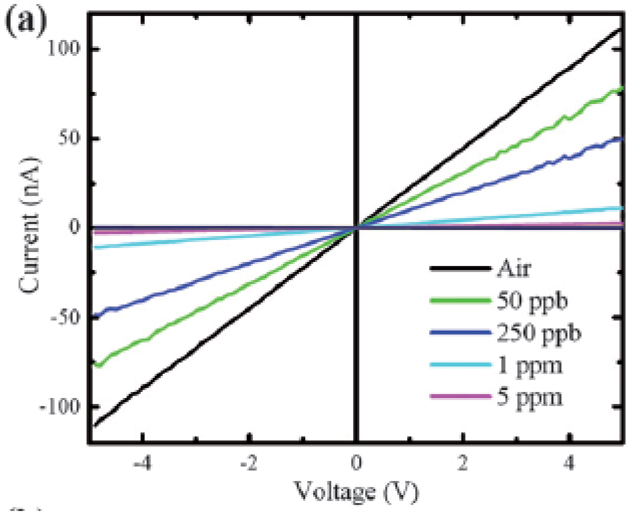
Talin, A. A., *Appl. Phys. Lett*. 2006, **89,** 153102

the shifted threshold voltage of the field-effect transistor
→ a signature of charge transfer between the analytes and the nanowires.

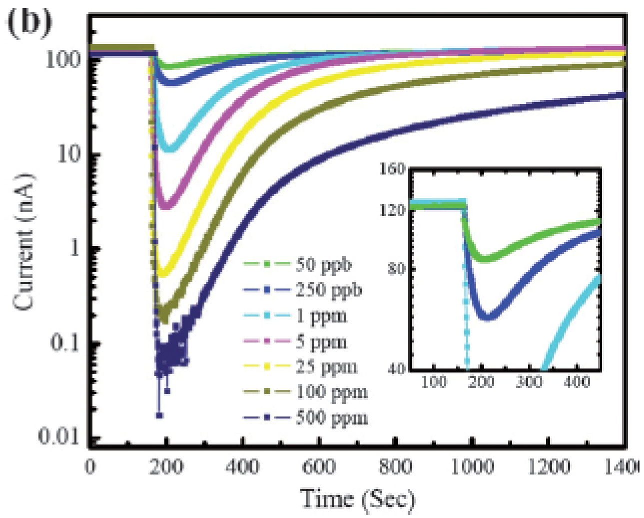
Nanomaterials on gas sensor application

Fabricated by **WO_3 nanowire**





IV curves of gas sensors based on the WO_3 nanowire array being exposed to air-diluted NO_2 with different concentrations.



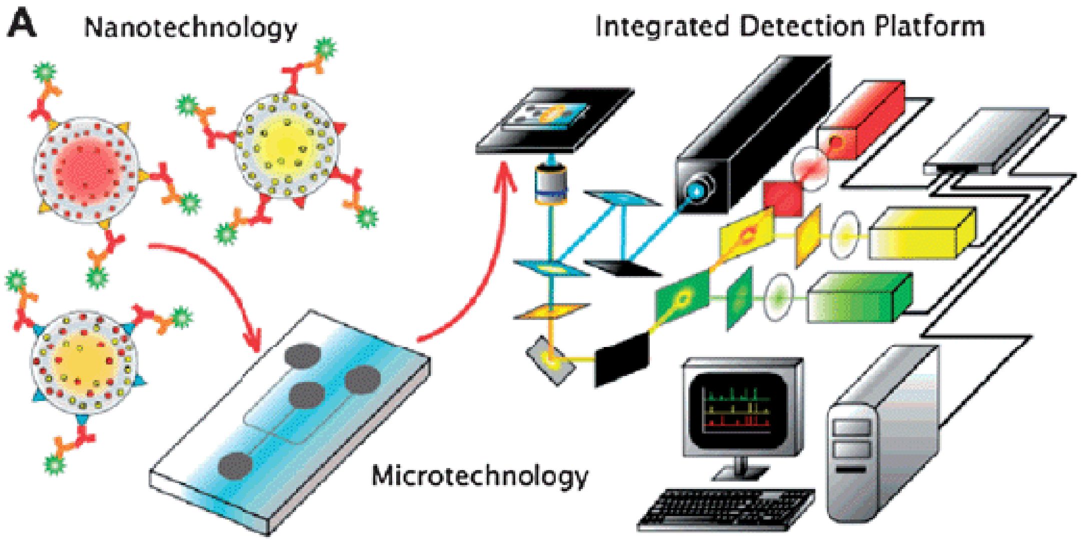
Sensing response curves of the sensor.

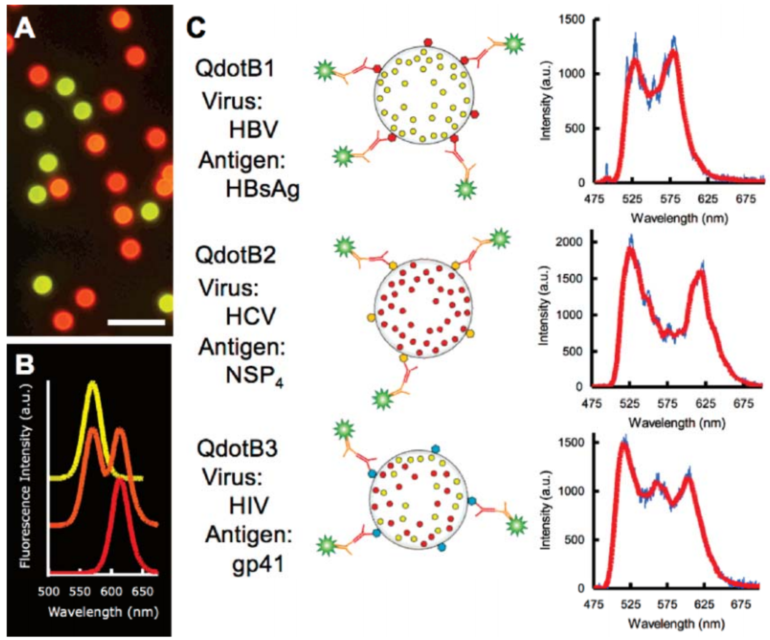
highly sensitive to NO_2 (50 ppb)

Cao, B. et. al., J. Mater. Chem., 2009, 19, 2323–2327

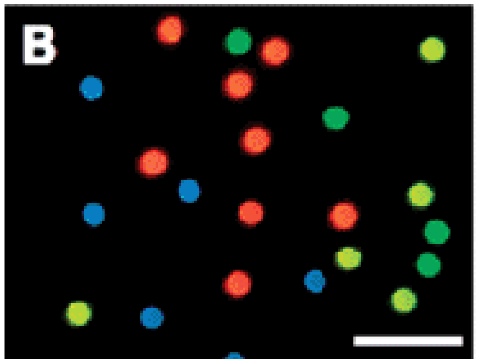
Quantum dot barcodes for multiplexed immunosensing in a microfluidic device with external optical detection.

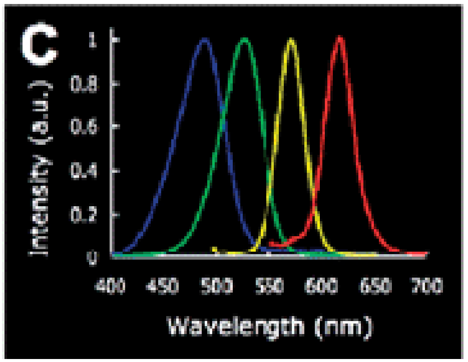
QDs with their corresponding surface conjugated antigens and fluorescence spectra



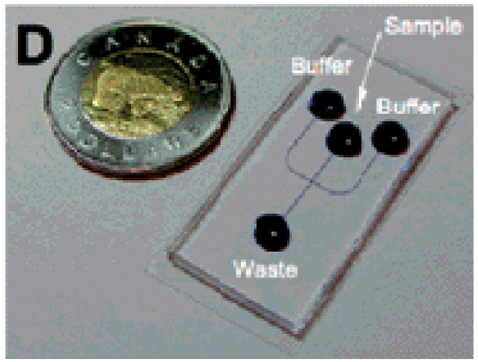


Fluorescent image of quantum dots on chip





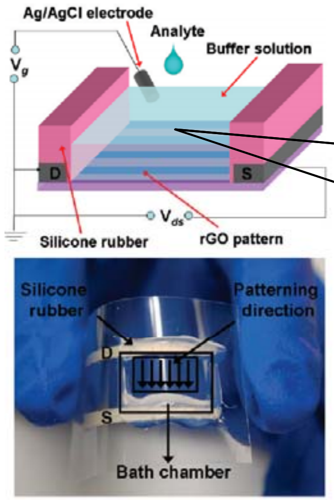
Microfluidic chip



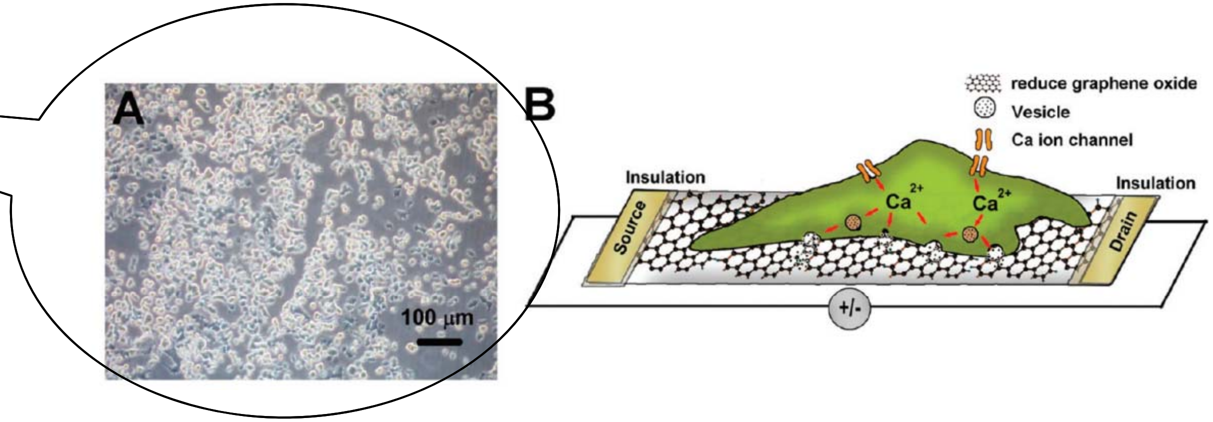
Klostranec, J. M. et. al., *Nano Lett.*, **2007**, *7* (9), pp 2812–2818

Using **reduced graphene oxide FET** as detecting hormonal catecholamine molecules and their dynamic secretion from living cells

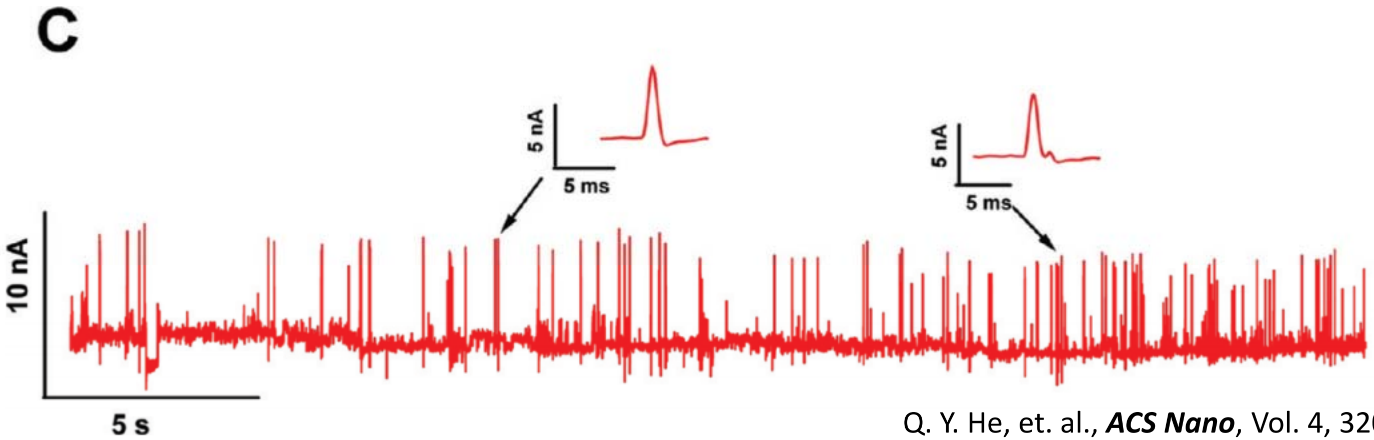
the setup of front-gate Graphene FET for sensing application



Optical image of PC12 cells grown confluently on poly-L-lysine coated rGO PET device



Real-time response of rGO/PET FET to the vesicular secretion of catecholamines from PC12 cells stimulated by high K^+ solution.



Q. Y. He, et. al., ***ACS Nano***, Vol. 4, 3201-3208 (**2010**)