Nanomaterials in optics, electronics and energy applications

Chun-Wei Chen

Department of Materials Science and Engineering, National Taiwan University
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Outline

• Part I: Optics and electronics of low-dimensional nanomaterials

• Part II: CNTs and graphene

• Part III: Nanomaterials in Energy
Size of Nano??

- **Organic molecule** <1nm
- **DNA** 1-100 nm
- **Bacteria** 1 μm

- **QDs(CdSe) 5nm**
- **Memory** 10^{12} bits/cm^2 (1Tbit/cm^2)
- **Copper wiring width** 200 nm (Now ~ 20nm)
- **IBM PowerPC 750\textsuperscript{TM} 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:

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 $1 \text{ nm} – 100 \text{ nm}$. 

"
Quantum confinement effect

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

\( m_e \) and \( m_h \): effective masses
\( e \): bulk optical dielectric coefficient
Size-dependent optical properties of CdSe QDs

Band gaps change with their average sizes

Lotus Effect

Lotus

Nano array on glass substrate

Self-cleaning

With WaterBlock™, you can make a splash wherever you go!

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

• Bulk TiO$_2$ V.S. TiO$_2$ nanorods/nanoparticles

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

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

Harmless

Radical

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

1-D periodic in one direction
2-D periodic in two directions
3-D periodic in three directions

periodic electromagnetic media

From 《奈米科學網》
How to make Nanomaterials??

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

http://spie.org/x32391.xml

http://www.beilstein-journals.org/bjnano/single/articleFullText.htm?pubId=2190-4286-2-50
Bottom up (Chemical Method)

NiPt Nanoparticles


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Different shapes of CdSe


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)


3D STEM Tomography images of P3HT/TiO₂ hybrids

**TiO₂ nano rod (NR)**
- 4nm x 20nm

**TiO₂ nano particle (NP)**
- 5nm x 5nm

*STEM-HAADF electron tomography (2 Å resolution)*
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

Phase separated domain

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

Phase separated domain

Well-dispersed
3D scanning transmission electron microscopy (STEM)
Electron tomography of P3HT/TiO₂ hybrids

**TiO₂ nanorod** (NR)  
4nm x 20nm

**TiO₂ nanoparticle** (NP)  
5nm x 5nm

*STEM-HAADF electron tomography*

**Phase separated domain**

**More dispersed**
Scanning electron microscopy (STM)

Silicon atoms on a surface

(Quantum tunneling effect)

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

http://www.exo.net/~pauld/workshops/Atoms.html
Atomic Force Microscopy (AFM)

Single wall carbon nanotube
Optical and electronic applications of nanomaterials
Bulk crystal
Quantum wire (nanowires, nanorods)
Quantum dot (nanocrystals)

Density of states

Energy

States

3d
2d
1d
"0 d"
Three dimensional system (bulk)

Free electron model in 3D

\[ D(E) \propto \sqrt{E} \]
Two-dimensional system

\[ V = \text{infinite at } z \text{ direction} \]

\[ \lambda = \frac{2}{3} d_z, \quad k = \frac{3 \pi}{d_z} \]

\[ \lambda = d_z, \quad k = \frac{2 \pi}{d_z} \]

\[ \lambda = 2d_z, \quad k = \frac{1 \pi}{d_z} \]

\[ D(E) \propto \text{const} \]

1-D confinement, 2-D free electron
1-D system (Quantum wire)

\[ D(E) \propto \frac{1}{\sqrt{E}} \]

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
\[ e^- + h^+ \rightarrow \text{exciton} \]

- free exciton \( E_b \approx 0.01 \ eV \)
- tightly bound exciton \( E_b > 0.1 \ eV \)
Optical absorption and excitons in semiconductor quantum well

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

(No exitonic effect)
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

Band gaps change with their average sizes

Surface plasmonic effect

Gold nanoparticles

Nano-Size

Silver nanoparticles

Nano-Size
Localized Surface Plasmon (LSP)

External EM field $E_o$

Excited free electron density oscillation $\rightarrow$ LSP

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

Resonant at specific frequency $\rightarrow$ LSPR

- Resonant frequency $\omega_r$ varied with: metals, morphology, and dielectric environment

![Graphs showing normalized extinction vs. wavelength for Ag and Au nanoparticles.](image)

Different Geometries (Gold nanorods)

Plasmons in metallic nanoparticles

The colors of gold nanorods

<table>
<thead>
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<th>AR</th>
<th>1.94</th>
<th>2.35</th>
<th>2.48</th>
<th>3.08</th>
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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

- Field effect transistor gas sensor

Schematic of catalytic sensor

Schematic of MOS-FET sensor
Nanomaterials on gas sensor application

Fabricated by carbon nanotube

Current-voltage curves for electrical breakdown for NH₃, CO₂, N₂, O₂, He, Ar and air

Nanomaterials on gas sensor application

Fabricated by Graphene

Concentration, $\Delta n$, of chemically induced charge carriers in single-layer graphene exposed to different concentrations, $C$, of NO$_2$.

Changes in resistivity, $\rho$, 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

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

Variation in $I_{SD}$ vs $V_G$ for a SiNW array exposed to ammonia NH$_3$ vapor.

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

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.