Fundamentals:

Basics for Designing Organic Nanomaterials

Chapter 1. Characteristics of Nanomaterials

Chapter 2. Methodology of Nanomaterials

- **2.1 Template Method**
  - **2.1.1. Microemulsion**
  - **2.1.2. Nanostructured Polymer (Copolymer, DNA)**
  - **2.1.3. Nanostructured Ceramics (AAO, Porous Silica, Zeolite)**

- **2.2. Non-template Method**
  - **2.2.1. Sol-gel Method**
  - **2.2.2. Vapor Deposition (Physical, Chemical)**
  - **2.2.3. Electrospinning**

Chapter 3. Structure, Property, and Applications of Organic Nanomaterials

- **3.1. 0-D Organic Materials**
- **3.2. 1-D Organic Materials**
- **3.3. 2-D Organic Materials**
- **3.4. 3-D Organic Materials.**

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Chapter 1. Characteristics of Organic Nanomaterials

1.1. Introduction to nanomaterials

1.2. Size-dependant Properties

- 1.2.1. Comparison of bulk- and nano- material
- 1.2.2. Energy band
- 1.2.3. Conductivity
- 1.2.4. Melting point
- 1.2.5. Magnetism

1.3. Applications

- 1.3.1. Colors
- 1.3.2. Catalysis
- 1.3.3. Nanoelectronics

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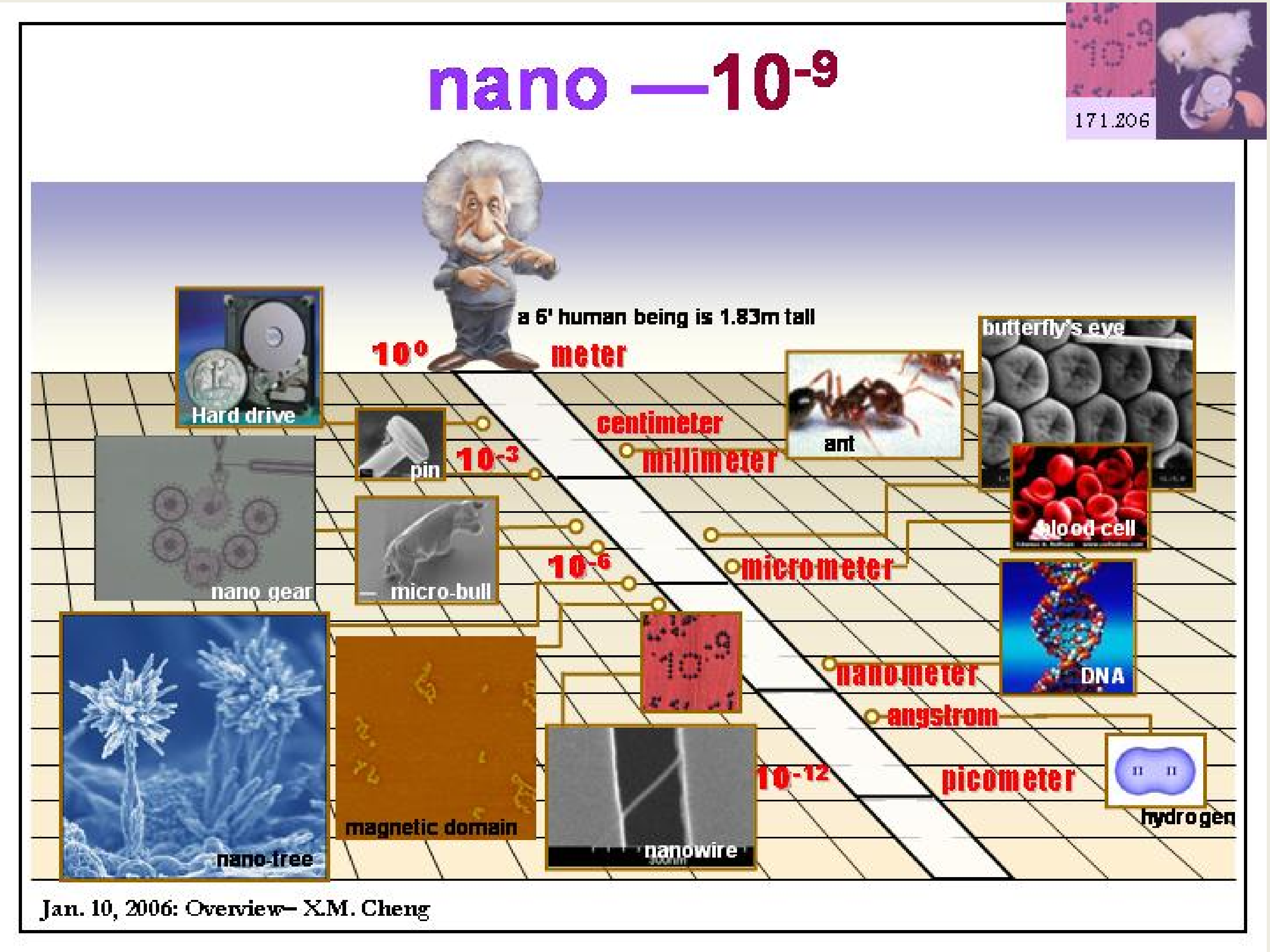
1.1. Introduction

- **What Is Nanoscale ?**



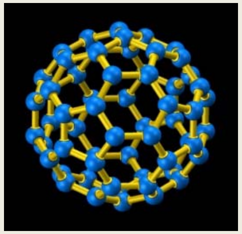
1.1. Introduction

- **The Nanotechnology Movement**

about 1/1000 width
of human hair

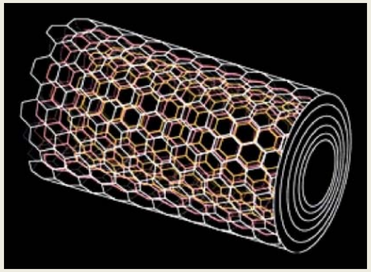
Definition

the systematic manipulation of matter on the length scale 1-100 nm
to produce useful new engineered structures, materials, or devices.



History

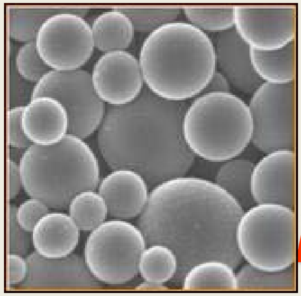
- R. Feynman, 1959, "There's plenty of room at the bottom"
- Kroto, Smalley, Curl, 1985, synthesis of Fullerene, C60
- Sumio Iijima, 1991, discovery of single wall carbon nanotube (?)



© Hyperion catalysis website

Nanotechnology today

- 1600 companies, 700 industrial products
- world-wide investment of 4.8 billion $ / yr



The U.S. National Nanotechnology Initiative (NNI)

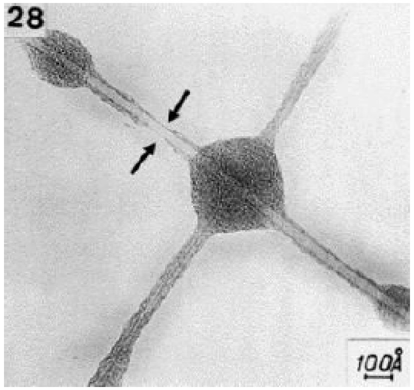
- first passed in 2001
- now ~ 1 billion $ / yr
- optimistic status report: May 2005
- four phases envisioned (now in phase 1)

1.1. Introduction

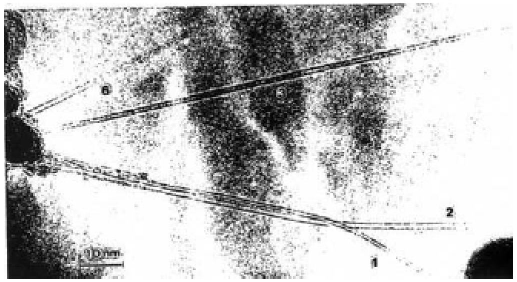
Single-Walled Carbon Nanotubes (SWCNTs)의 발견

1976년 일본의 Endo 그룹에 의해 최초로 발견. Ref: M. Endo *et al*, *J Cryst Growth* **32** (1976) 335–349.

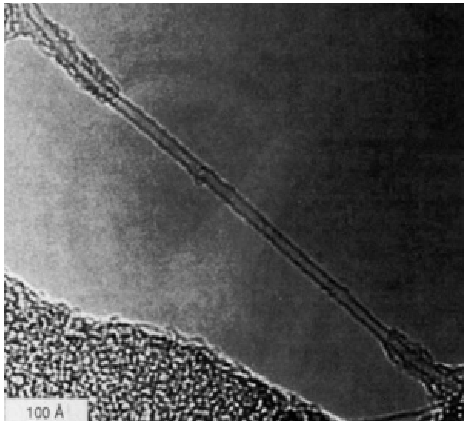
1993년 2편이 동시에 발표 (nature 지 6월 17번째 이슈). Submitting 날짜 : 일본 NEC연구소의 Iijima group (4월 23일), 미국 IBM 연구소의 Bethune group (5월 24일) Ref: S. Iijima *et al.*, *Nature* **363** (1993) 603–605. , D.S. Bethune *et al.*, *Nature* **363** (1993) 605–607.



J Cryst Growth **32** (1976) 335–349



Nature **363** (1993) 603–605



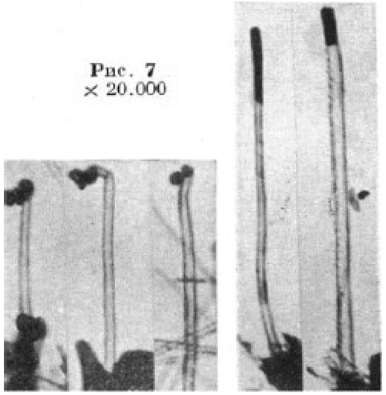
Nature **363** (1993) 605-607

Multi-Walled Carbon Nanotubes (MWCNTs)의 발견

1952년 러시아의 Radushkevich 그룹에 의해 MWCNTs와 흡사한 carbon filament가 발견됨. Ref: L.V. Radushkevich et al., *Zurn Fisic Chim* **26** (1952) 88–95.

1973년 독일의 Boehm과 영국의 Baker 그룹에 의해 여러가지 금속촉매를 이용한 carbon filament 제조에 관한 논문이 발표 되었음. Ref: H.P. Boehm, *Carbon* **11** (1973), pp. 583–590., R.T.K. Baker *et al.*, *J Catal* **30** (1973) 86–95.

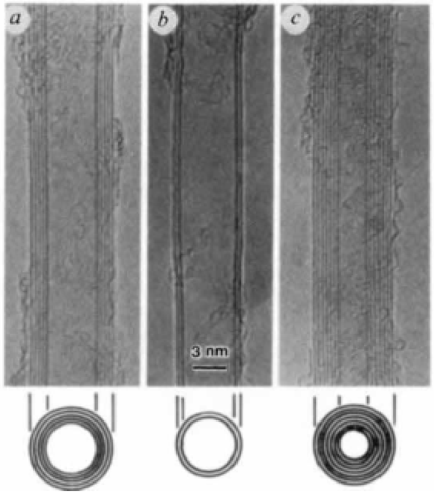
1991년 일본의 Iijima에 의해 MWCNTs에 대한 논문 발표됨. Ref: S. Iijima, *Nature* **354** (1991) 56–58.



Zurn Fisic Chim **26** (1952) 88–95.

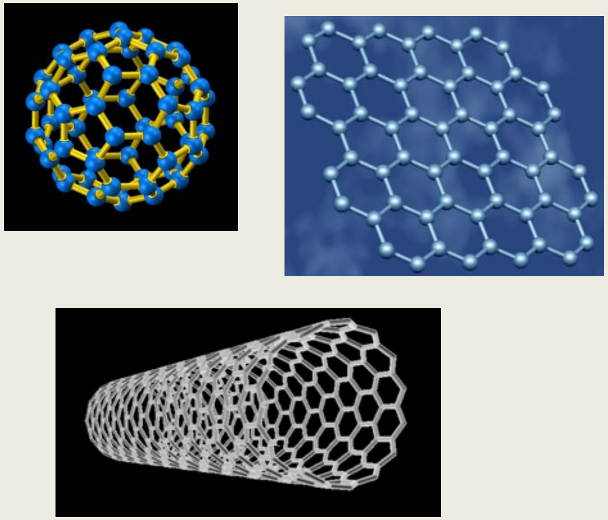
J Catal **30** (1973) 86–95.

Carbon **11** (1973) 583–590.



Nature **354** (1991) 56–58.

1.1. Introduction



Nanoparticles

- buckminster fullerene C_{60}
- metallic nanoparticles (gold, silver, iron, etc)
- glass/ceramic nanoparticles (titania, silica, etc)
- quantum dots (semiconductor nanoparticles)

Nanotubes, nanofibers, nanowires

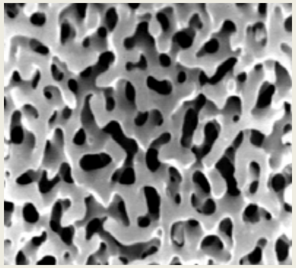
- carbon nanotubes
- nanofibers (carbon, polymer, ceramic)
- nanowires (metallic, semiconducting)

Nanoplatelets

- graphite, clay, graphene
- silica, hydroxyapatite

Nanostructured surfaces

Nanostructured solids



and their application as components for next-generation technologies, including:

batteries, fuel cells, sunscreens, cosmetics, structural materials, implants, drug delivery vehicles, catalysts, sorbents, and much, much more…….

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1.1. Introduction

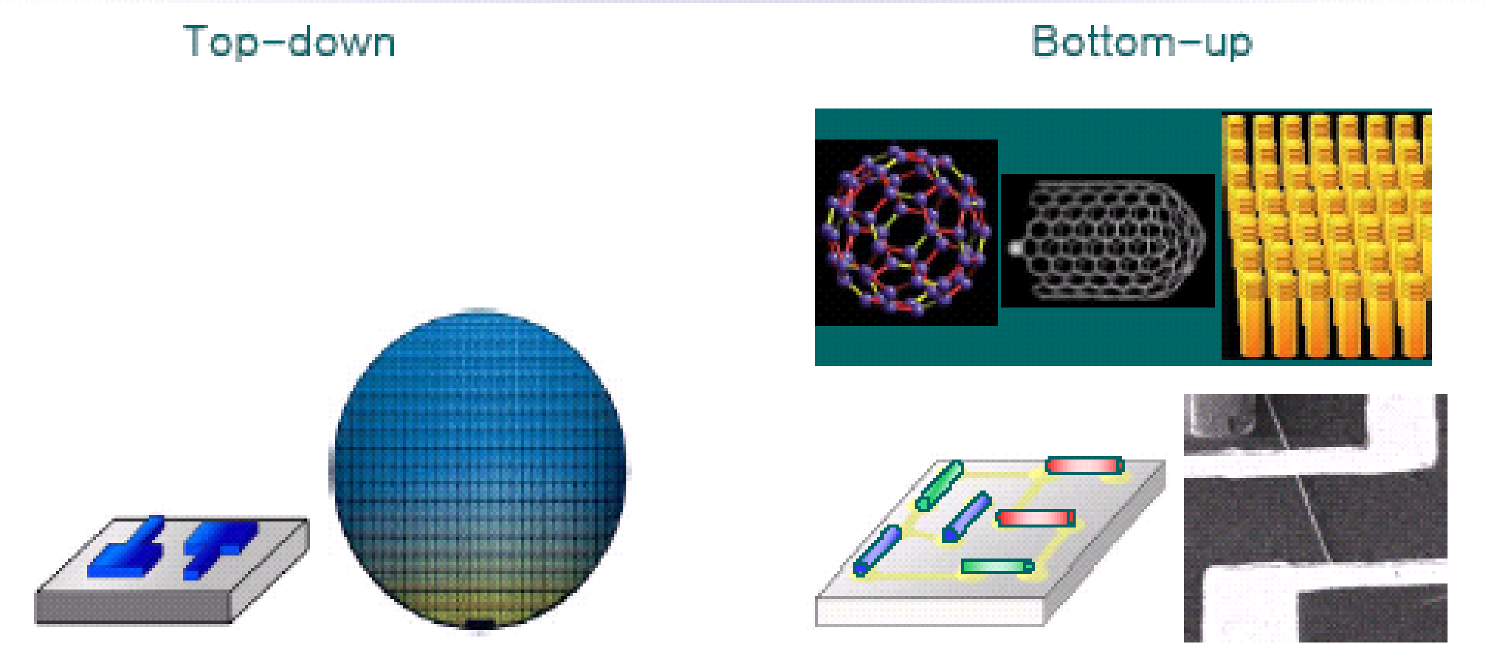
The Nanomaterial Matrix

(some well-known examples)

	0-D materials	**1-D materials**	**2-D materials**
metals	Au nanoparticles Fe magnetic nanoparticles nanopart. catalysts (Pt,Zn,Cu,Ni,Co...)	nanowires	
semiconductors	quantum dots	semiconducting nanowires, nanorods	
ceramics	nanophase powders for low-T sinterable coatings, parts, composite fillers, sorbents	electrospun ceramic nanofibers for composite fillers	nano-clays
carbons	fullerenes, carbon black, nanohorns	carbon nanotubes, nanofibers	graphene
polymers	biodegradable polymer nanobeads for medical applications	electrospun polymer nanofibers	
other	oligomers (e.g. chitosan) branched compounds (dendrimers) surfactant assemblies (liposomes)		

1.1. Introduction

- **Two Approaches in Nanotechnology**



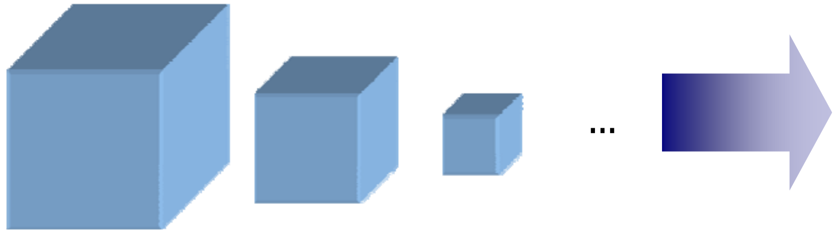
- Fabrication of nanomaterials/nanodevices by lithography
- Ultrahigh density device fabrications
- Complicated and of high cost
- Use of limited materials due to material compatibility

- Fabrication of nanodevices by simple assembly of nanomaterials
- Numerous types of nanodevices
- Use of numerous nanomaterials (Carbon nanotubes, semiconductor nanocrystals and nanowires/nanorods, etc)

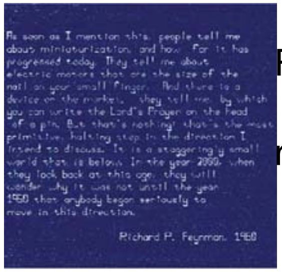
1.1. Introduction

- **Top-down approach**

Bulk Materials



Nano-scale structures



As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

Richard P. Feynman, 1960

R. Feynman, 1959,
"There's plenty of
room at the bottom"

Nano lithography / Patterning

Conventional Lithography

KrF	**ArF**	**F_2**	**EUV**
(λ = 248 nm)	**(λ = 193 nm)**	**(λ = 157 nm)**	**(λ = 11.4 nm)**

Nanolithography

- **E-beam lithography**
- **Nanoimprint Technology**
- **Probe Technology**

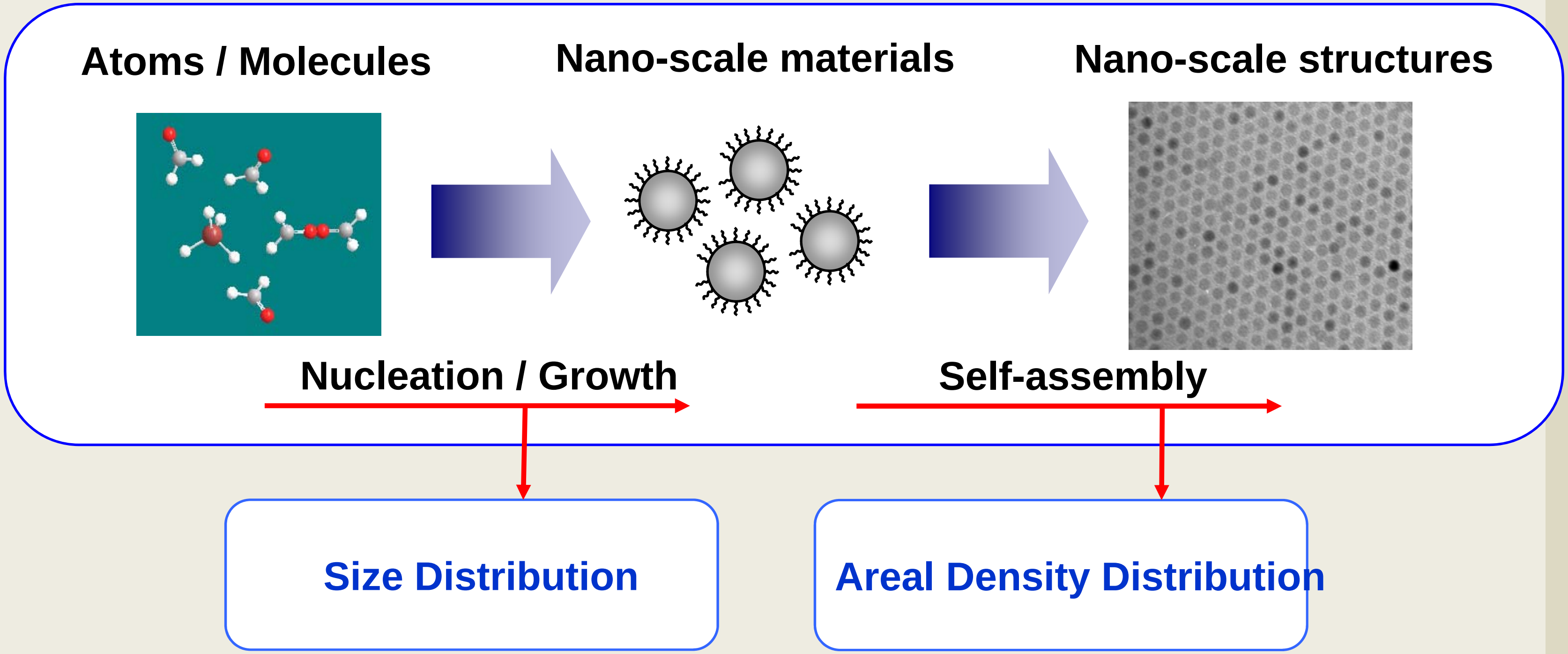
Demand

High controllability

High cost

1.1. Introduction

- **Bottom-up approach**



Atoms / Molecules

Nano-scale materials

Nano-scale structures

Nucleation / Growth

Self-assembly

Size Distribution

Areal Density Distribution

Nucleation, Growth & Self-assembly

- **Thin film technology**
- **Colloid process**
- **Gas phase nucleation**

Cost effective

Low controllability

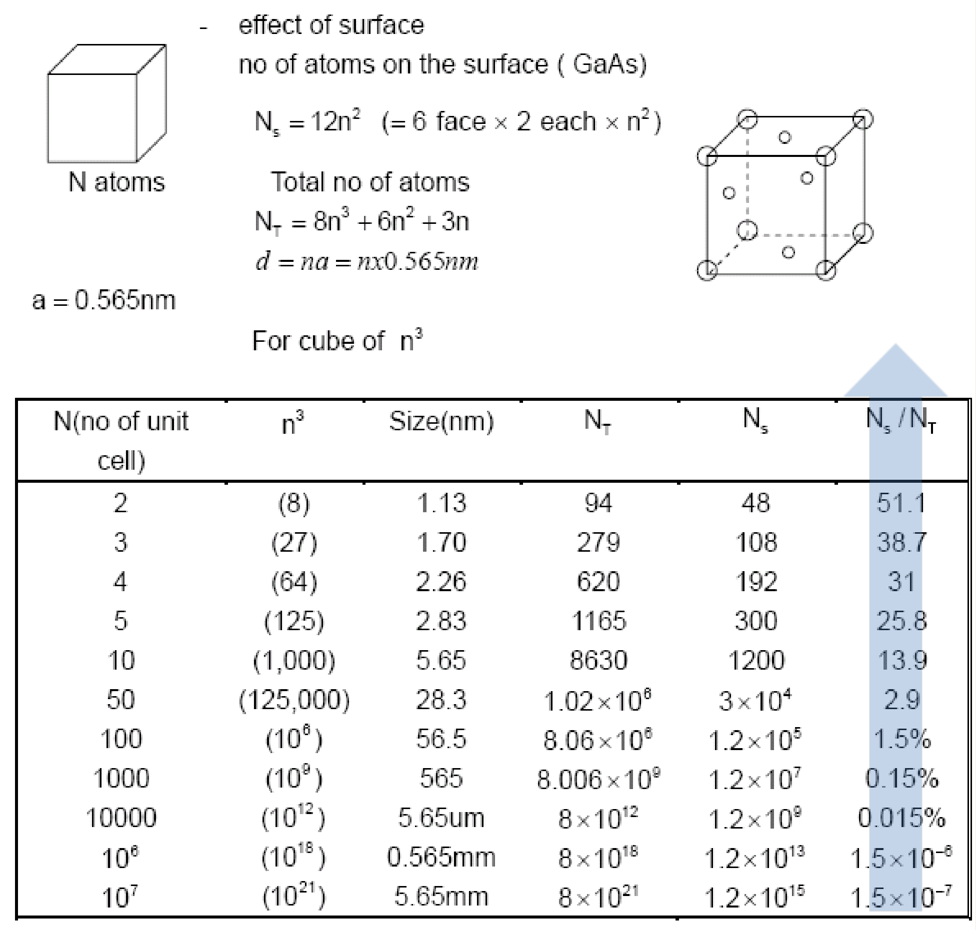
1.2. Size-dependant Properties

1.2.1. Comparison of Bulk- and Nano- material

- **Bulk VS Nano-sized material**

  - The property of such a small object shows a drastic change.

  - The portion of surface layer increases and thus different interaction atoms at the surface become significant.



- effect of surface

no of atoms on the surface (GaAs)

$N_s = 12n^2 \quad (= 6 \text{ face} \times 2 \text{ each} \times n^2)$

Total no of atoms

$N_T = 8n^3 + 6n^2 + 3n$

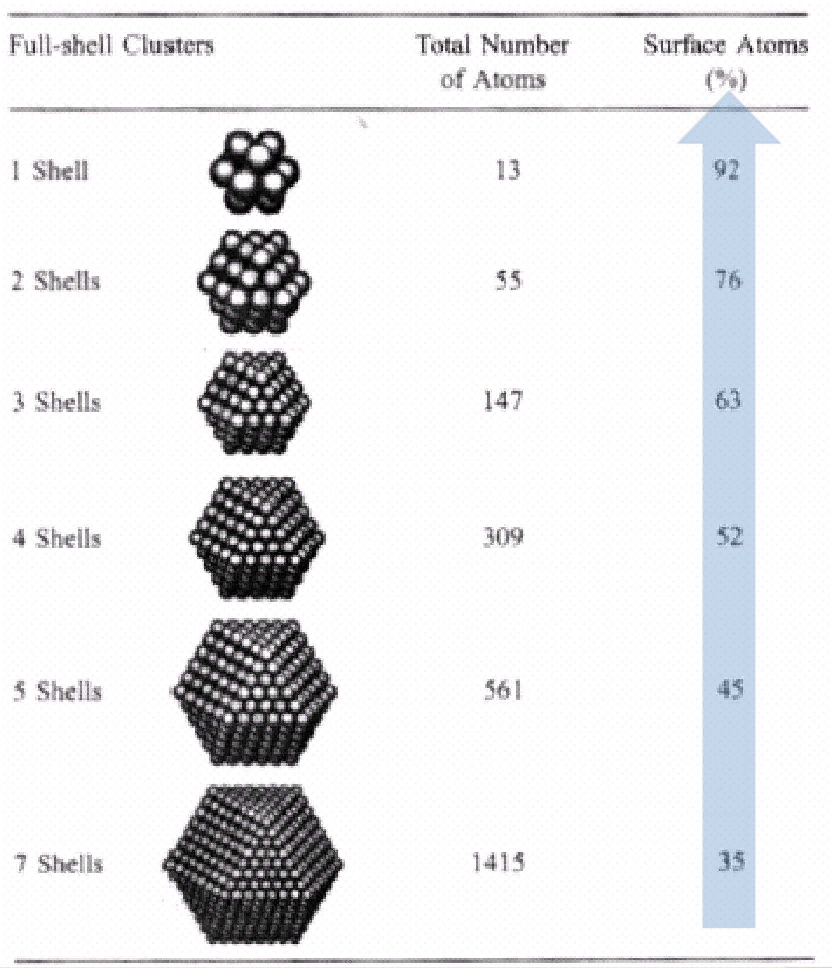
$d = na = nx0.565nm$

N atoms

$a = 0.565\text{nm}$

For cube of n^3

N(no of unit cell)	n^3	Size(nm)	N_T	N_s	N_s / N_T
2	(8)	1.13	94	48	51.1
3	(27)	1.70	279	108	38.7
4	(64)	2.26	620	192	31
5	(125)	2.83	1165	300	25.8
10	(1,000)	5.65	8630	1200	13.9
50	(125,000)	28.3	1.02×10^6	3×10^4	2.9
100	(10^6)	56.5	8.06×10^6	1.2×10^5	1.5%
1000	(10^9)	565	8.006×10^9	1.2×10^7	0.15%
10000	(10^{12})	5.65um	8×10^{12}	1.2×10^9	0.015%
10^6	(10^{18})	0.565mm	8×10^{18}	1.2×10^{13}	1.5×10^{-6}
10^7	(10^{21})	5.65mm	8×10^{21}	1.2×10^{15}	1.5×10^{-7}



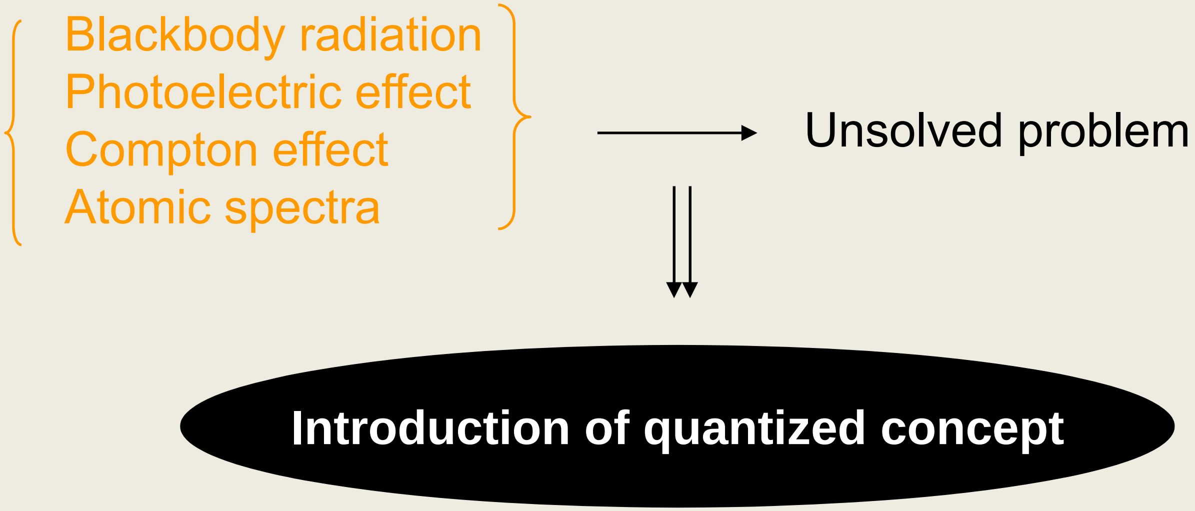
Full-shell Clusters	Total Number of Atoms	Surface Atoms (%)
1 Shell	13	92
2 Shells	55	76
3 Shells	147	63
4 Shells	309	52
5 Shells	561	45
7 Shells	1415	35

1.2. Size-dependant Properties

1.2.1. Comparison of Bulk- and Nano- material

- **Nanoscale System**

Newton mechanics – particle deterministic description



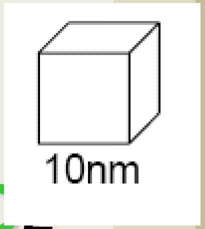
Blackbody radiation
Photoelectric effect
Compton effect
Atomic spectra

Unsolved problem

Introduction of quantized concept

Quantum size effect

As the size of system decrease, new effects begin to appear
- # of charge carrier
n type semiconductor, $n_d = 10^{18}/cm^3$ is required to transport information
but in nanosystem, $n_d = 1/(10nm)^3$ only one electron is required.



1.2. Size-dependant Properties

1.2.2. Energy band

- Energy band theory of solid

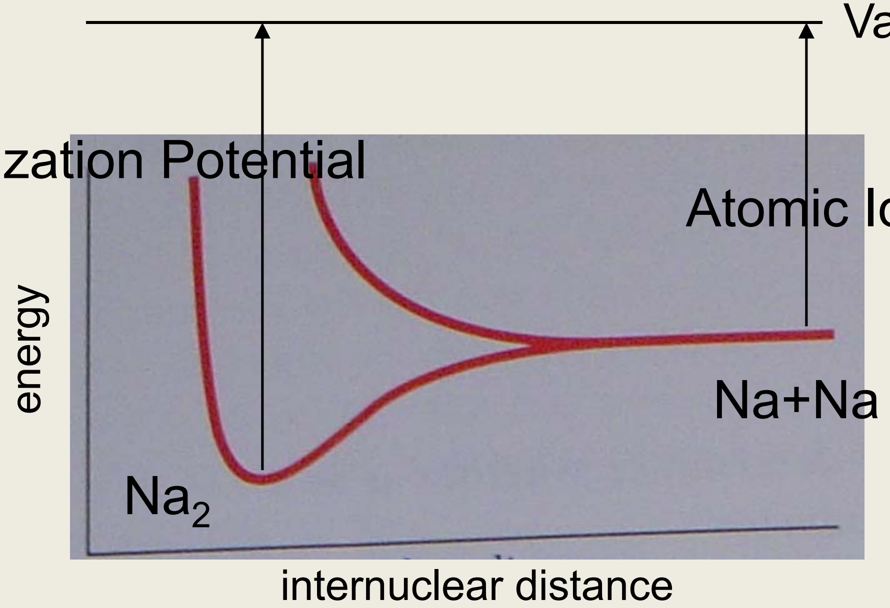
conductivity of solids varies strongly:
•Cu resistivity(ρ) = 1.7×10^{-8} Ωm (good conductor)
•quartz resistivity(ρ) = 7.5×10^{17} Ωm (good insulator)

•explanation: electron bands!

How energy bands arise?

example: 2 Na atoms

1 attractive
and 1 repulsive state



Vacuum level

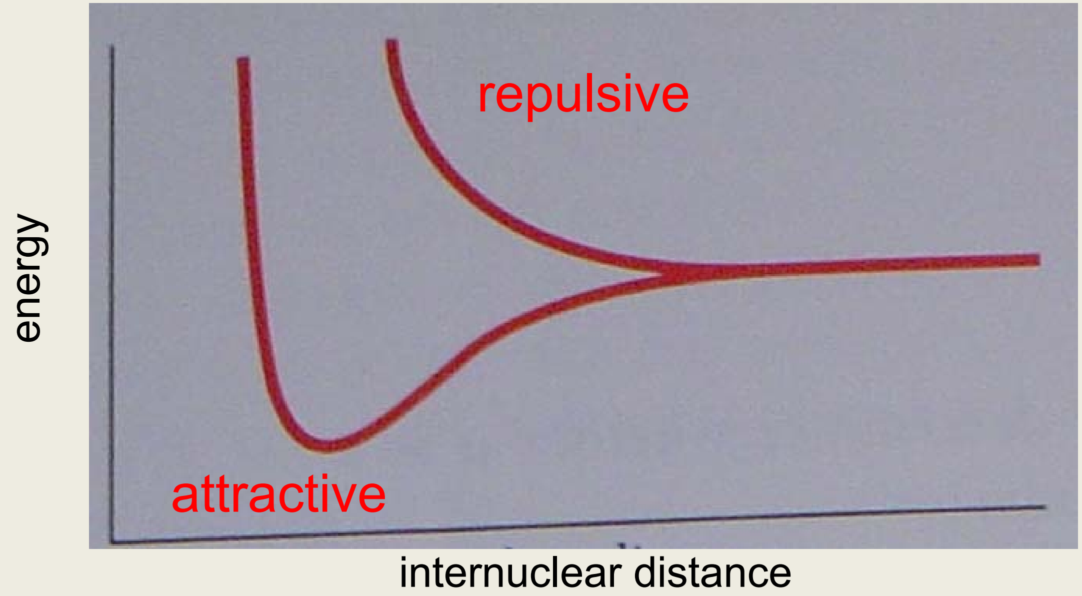
Molecular Ionization Potential

Atomic Ionization Potential

1.2. Size-dependant Properties

1.2.2. Energy band

- Energy band theory of solid



overlapping wave functions lead to splitting of the state”:

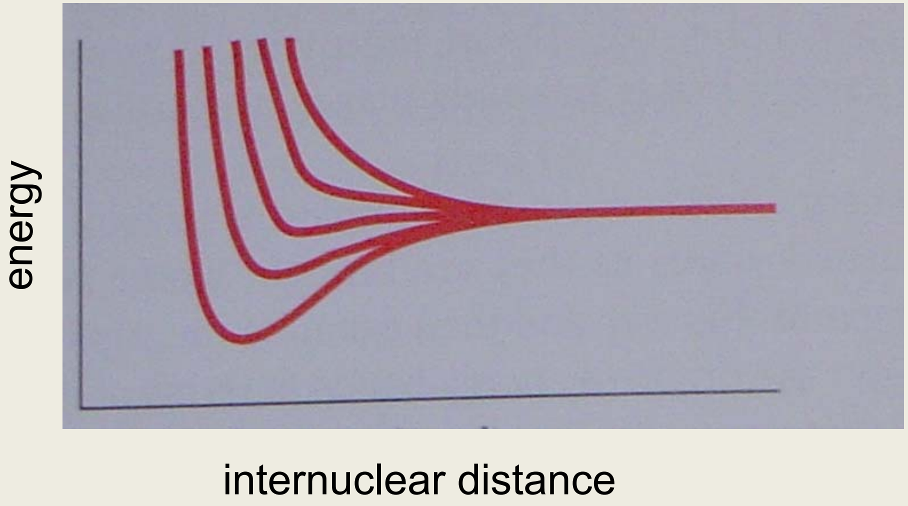
- attractive state: more electron density between atoms, more screening
- repulsive state: less electron density between atoms, less screening

1.2. Size-dependant Properties

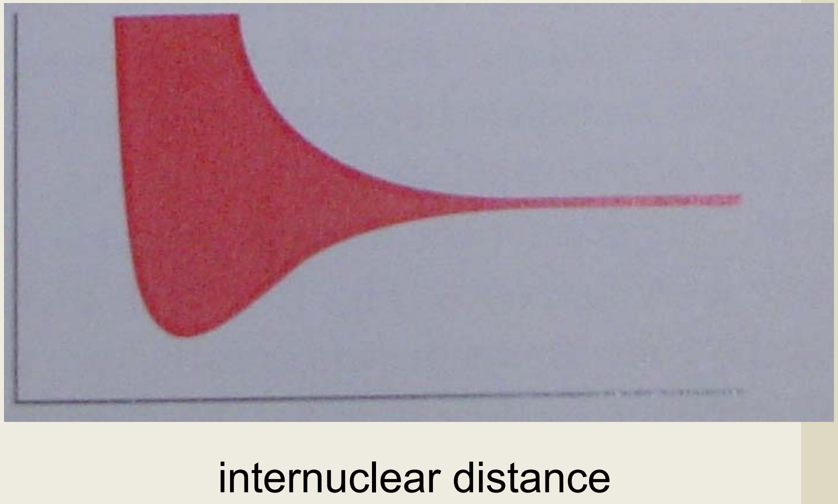
1.2.2. Energy band

- Energy band theory of solid

5 Na atoms:



10^{23} Na atoms:



as many states as atoms involved!

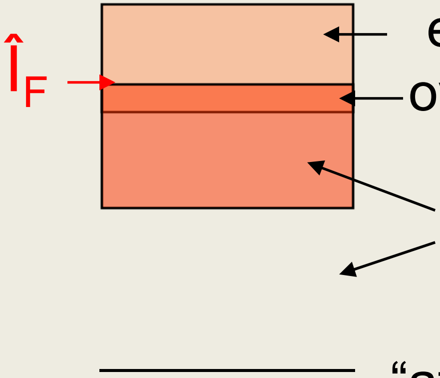
“continuous”energy band of closely spaced levels

1.2. Size-dependant Properties

1.2.2. Energy band

- Energy band theory of solid

conductor



Î$_F$

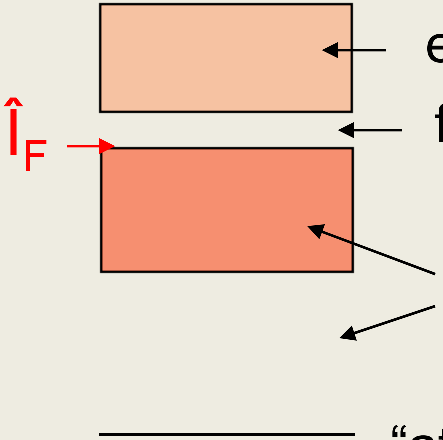
empty band

overlapping bands

filled bands

“atomic” state

semiconductor or insulator



Î$_F$

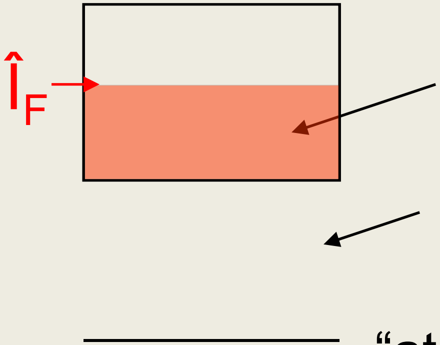
empty band

forbidden band
“gap”

filled bands

“atomic” state

conductor



Î$_F$

partially filled band

filled band

“atomic” state

“small” gap (~1 eV):
→ semiconductor
“large” gap (several eV):
→ insulator

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1.2. Size-dependant Properties

1.2.2. Energy band

- Energy band in semiconducting nanomaterial

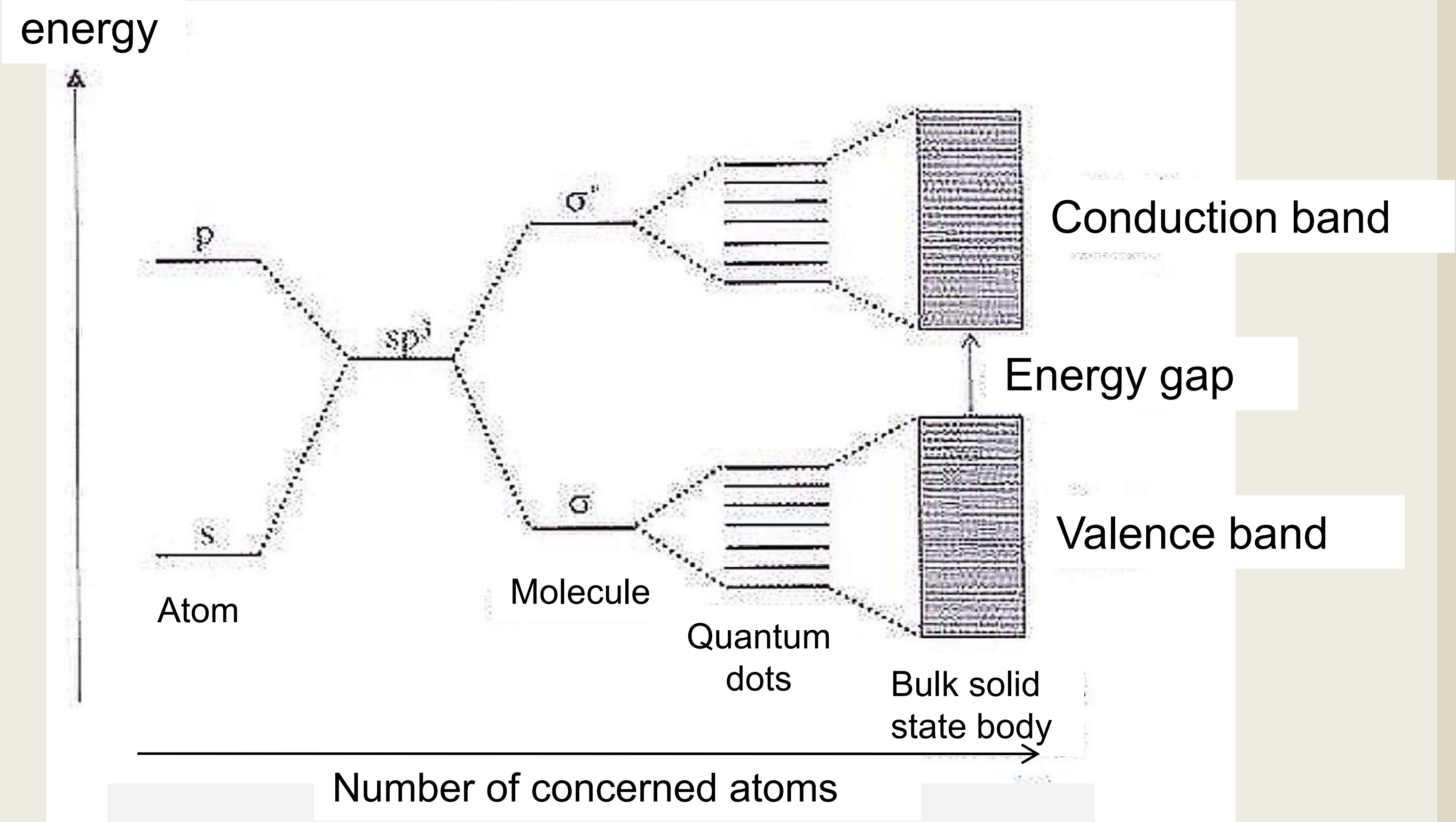


Figure. Electronic energy levels depending on the number of bound atoms. By binding more and more atoms together, the discrete energy level of the atomic orbitals merge into energy band.

1.2. Size-dependant Properties

1.2.2. Energy band

- Energy band in semiconducting nanomaterial

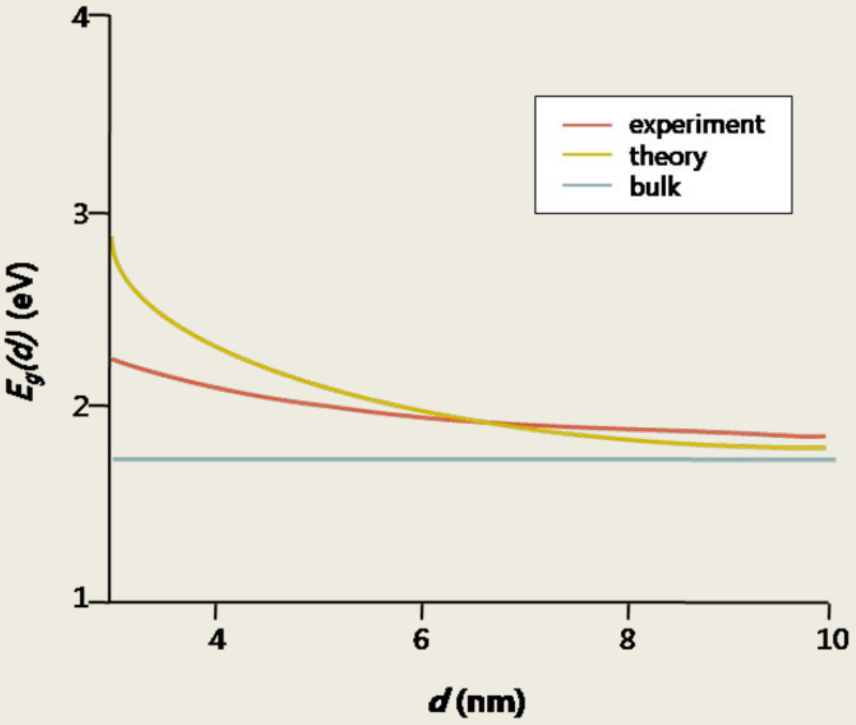


Figure. Size dependence of the energy gap E_g(d) for colloidal CdSe quantum dots with diameter d. The experimental values were obtained by recording the absorption spectra of CdSe quantum dots of different size

- In the early 1980s, Efros described the size-dependent electronic properties of quantum dots,

$$E_n = E_g + \frac{h^2\pi^2}{2\mu R^2}$$

E_g = band gap of bulk semiconductor
h = Planck`s constant
R = radius of the quantum dots
μ = reduced mass of exciton

- This model was expanded by Brus and coworkers to include Coulombic interaction of excitons and the correlation energy

$$E_n = E_g + \frac{h^2\pi^2}{2\mu R^2} - \frac{1.786e^2}{\varepsilon R} + 0.284E_R$$

$$E_R = \frac{\mu e^4}{2\varepsilon^2\varepsilon_0^2 h^2} = 13.56\frac{\mu}{\varepsilon^2 m_e}$$

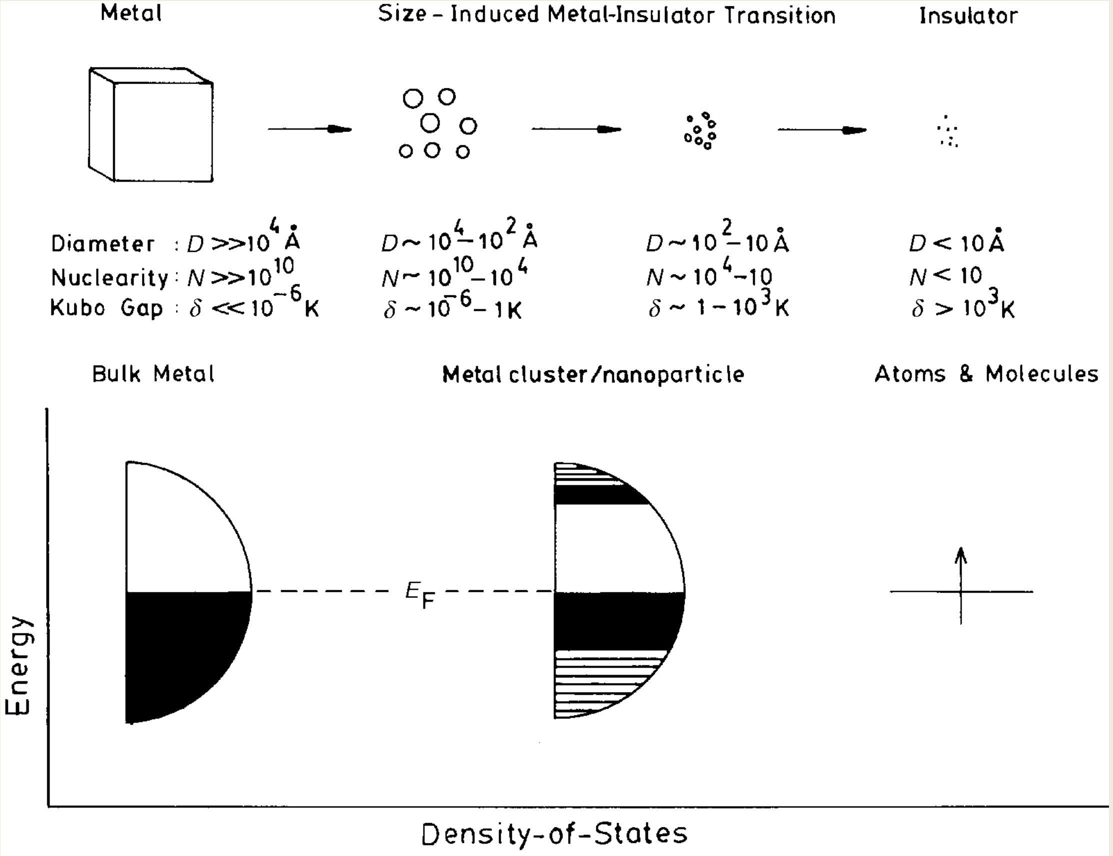
ε_0= permittivity of free space
ε = dielectric constant of the bulk semiconductor
m_e = mass of the electron

Chem. Mater. **2001**, 13, 3843.

1.2. Size-dependant Properties

1.2.2. Energy band

- Metal nanoparticle (Metallic → Insulator transition)



So few atoms comprise discrete nanoclusters of this size, the spacings between adjacent energy levels (referred to as the Kubo gap, δ) become comparable to the thermal energy, kT –especially at lower temp and smaller diameter

$$\delta = \frac{3E_f}{2N}$$

δ = Kubo gap, energy spacing between adjacent E level
N = the nuclearity, the number of atoms
E_f = the energy of Fermi level

Figure. Schematic of the density of states exhibited by bulk metal relative to increasingly smaller nanoclusters. As the nanocluster size decreases, the energy continuum of the bulk metal is transformed into discrete energy levels, especially at band edge.

Chem. Soc. Rev. **2000**, *29*, 27.

1.2. Size-dependant Properties

1.2.3. Conductivity

- If the conduction band of metal is only partially occupied by electrons, they can move without resistance in perfect metallic crystal lattice. But they are scattered by the wave character of the electrons.

- The mobility of electrons : $\mu = \dfrac{e\lambda}{4\pi\varepsilon_0 m_e V_F}$

where,

λ = mean free path between collisions
m_e = effective mass of the electron
V_F= speed of the electrons (Fermi speed)
ε_0 = dielectric constant of vacuum

- Mean time between two collisions $\tau = \lambda / V_F$

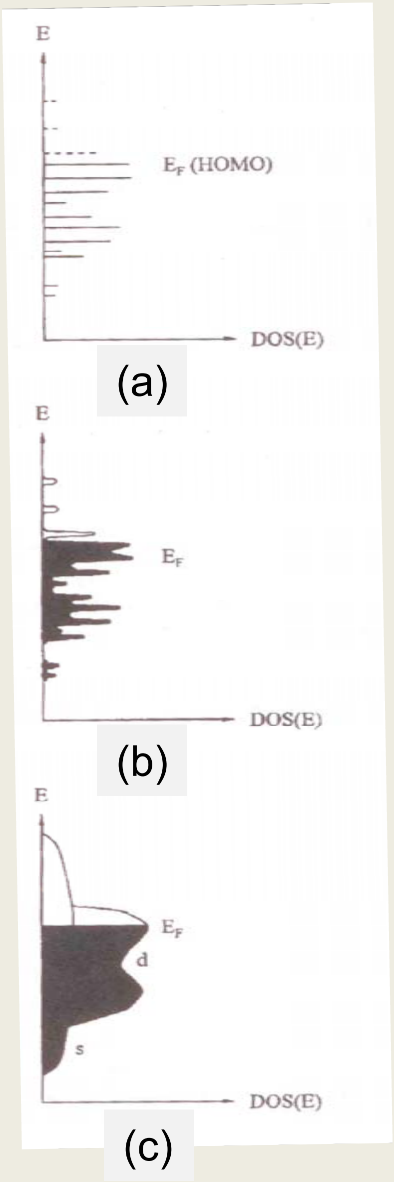
Ex) Copper at RT : $V_F = 1.6 \times 10^6\ \mathrm{ms}^{-1}$, $\lambda = 4.3 \times 10^{-8}\mathrm{m}$. $\therefore\ \tau = 2.7 \times 10^{-14}\mathrm{s}$

- Scattering mechanisms : 1) dislocation, stacking disorders, etc.
  2) scattering at thermal vibrations of lattice (phonon)

- Ohm's law describes the linear relation between U and I in **bulk metal** ; U = IR

1.2. Size-dependant Properties

1.2.3. Conductivity



- The band structure begins to change if the dimension of a metal particle becomes small.

→ Ohm’s law is no longer valid.

→ Single nanoparticles have to be investigated.

- Different density of state between bulk and nanosized material.

Figure. Formation of a band structure (a) from a molecular state, (b) from a nanosized particle with broadened energy states, and (c) the fully developed band structure consisting of *s* and *d* band. E_F = Fermi energy, DOS = density of states. In (a) E_F corresponds to the highest occupied molecular orbital (HOMO)

1.2. Size-dependant Properties

1.2.3. Conductivity

- Quantum mechanically describe by the quantum Hall resistance RQH and the capacity of the particle

$$E_{C,QH} = \frac{h}{R_{QH}C}$$

- The current-voltage characteristic for an ideal quantum dot shows no current up to

$$U_{Coulomb} = \pm \frac{e}{2C}$$

- Following this an electron tunneling process occurs if the Coulomb energy of the quantum dot is compensated by external voltage of U = ± ne/(2C)

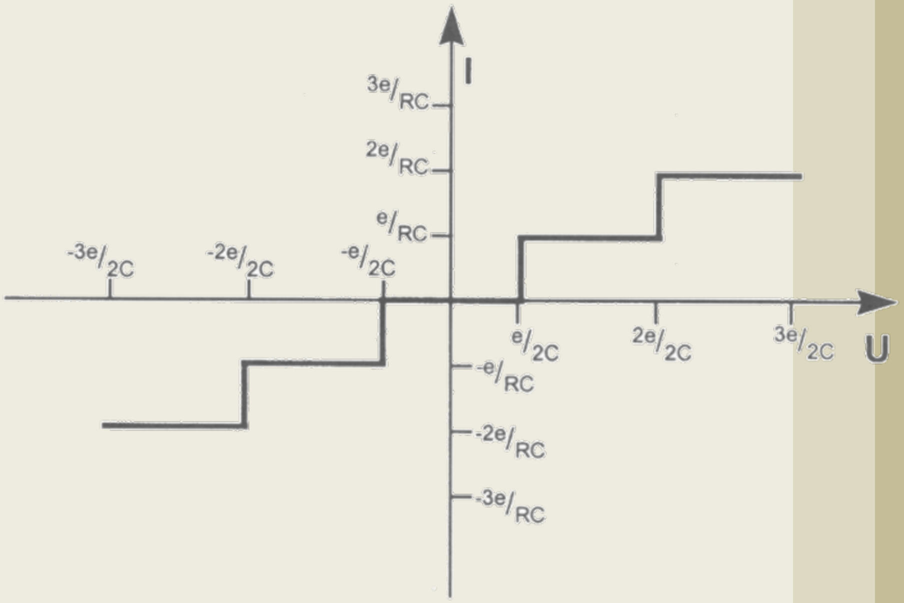


Figure. I-U characteristic of ideal single electron transport

1.2. Size-dependant Properties

1.2.3. Conductivity

- SEM image of an experiment

- 17nm palladium particle is trapped between two Pt tips, separated from them by a thin shell of organic molecules(p-H_2N-C_6H_4-SO_3Na).

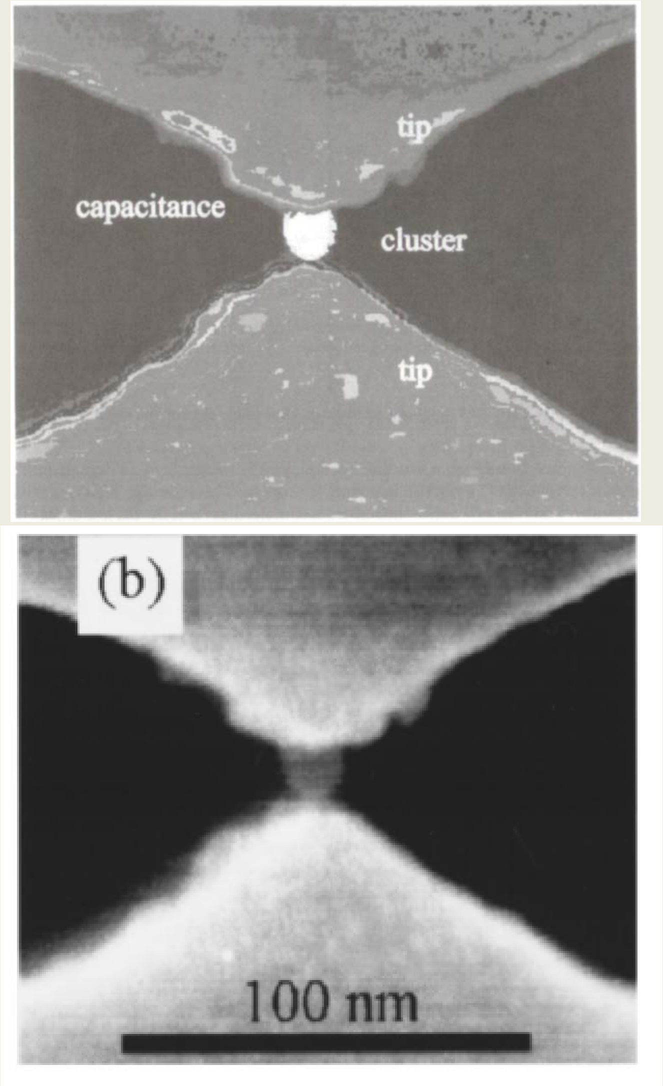


Figure. Scanning electron microscopic image of a 17nm ligand-stablized palladium cluster, trapped between two platinum tips.

Appl. Phys. Lett., **1997**, *71*, 1273.

1.2. Size-dependant Properties

1.2.3. Conductivity

❖ I-U characteristic of the 17nm palladium

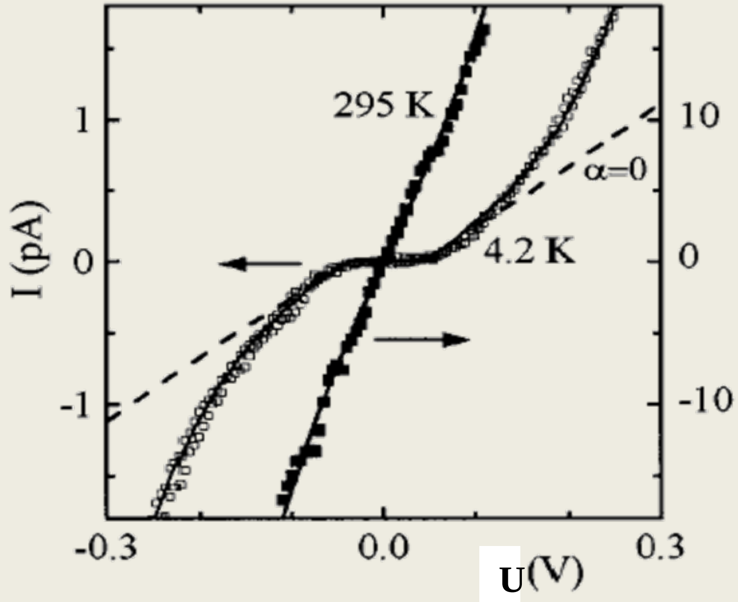


Figure. I-U characteristics of the 17nm palladium cluster. At 295K it behaves in a bulklike manner, following Ohm's law. At 4.2K a pronounced Coulomb blockade is observed. *Appl. Phys. Lett.*, **1997**, *71*, 1273.

- At 295K, there is a linear relation between I and U, corresponding to Ohm's law.

- At 4.2K, a typical Coulomb gap of ~55mV is observed, indicating that the condition $kT \ll e^2/2C$ is fulfilled.

- To make quantum size behavior of small metal particles available at RT we have to further reduce their size, as the capacitance C of the particles depends directly on their diameter.

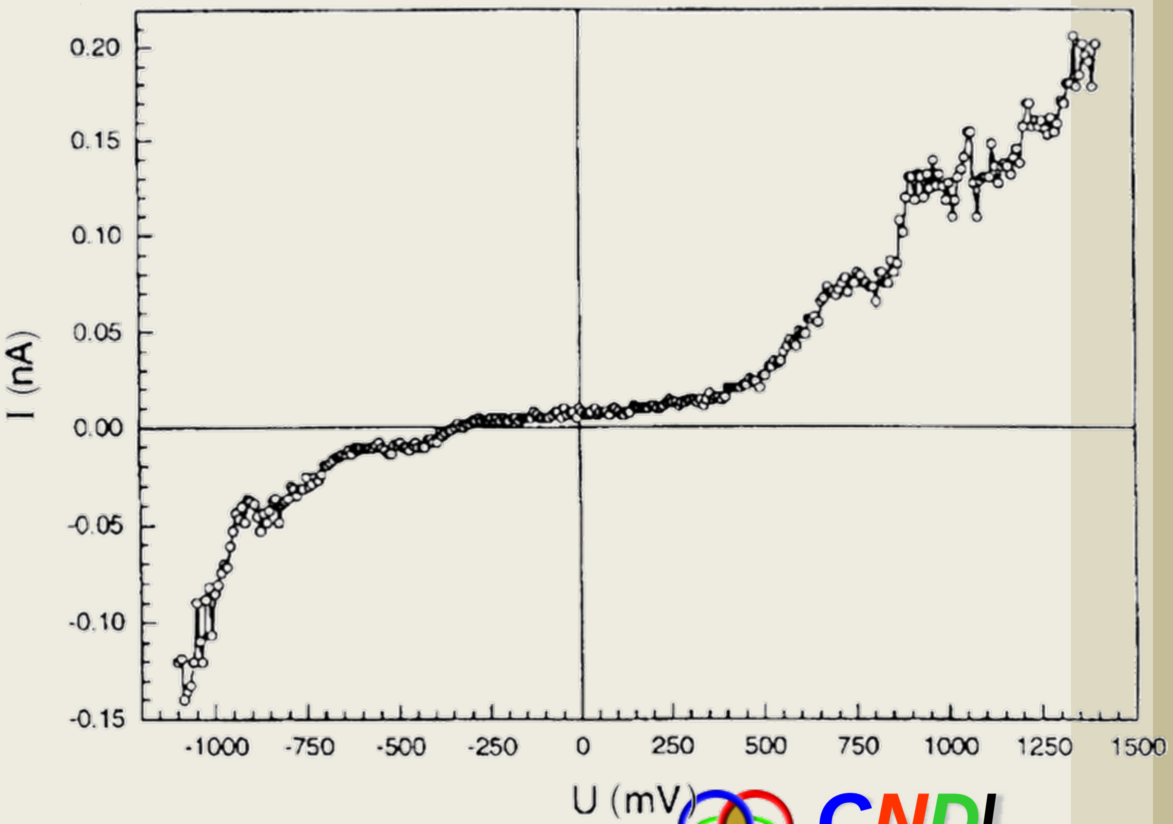
1.2. Size-dependant Properties

1.2.3. Conductivity

- ❖ I-U characteristic of the 1.4nm gold particle

Figure. I-U characteristics of a ligand-stabilized Au55 cluster at room temperature. *Appl. Phys. A.* **1998**, *66*, 189

- The gold cluster compound $Au_{55}(PPh_3)_{12}Cl_6$ shows typical Coulomb blockade even at RT



1.2. Size-dependant Properties

1.2.4. Melting points

- The melting point of solid is reached when the order of the lattice is beginning to be destroyed.

- Bulk vs. Nanoparticles
  - Bulk : For a distinct solid, the melting point is a physical constant.
  - Nanoparticles : When the number of surface atoms becomes equal to or even exceeds the number of inner-core atoms, the melting process starts earlier.

    → As the coordination number of surface atoms is 9 or smaller, these atoms are more easily rearranged than those in the center of the particles.

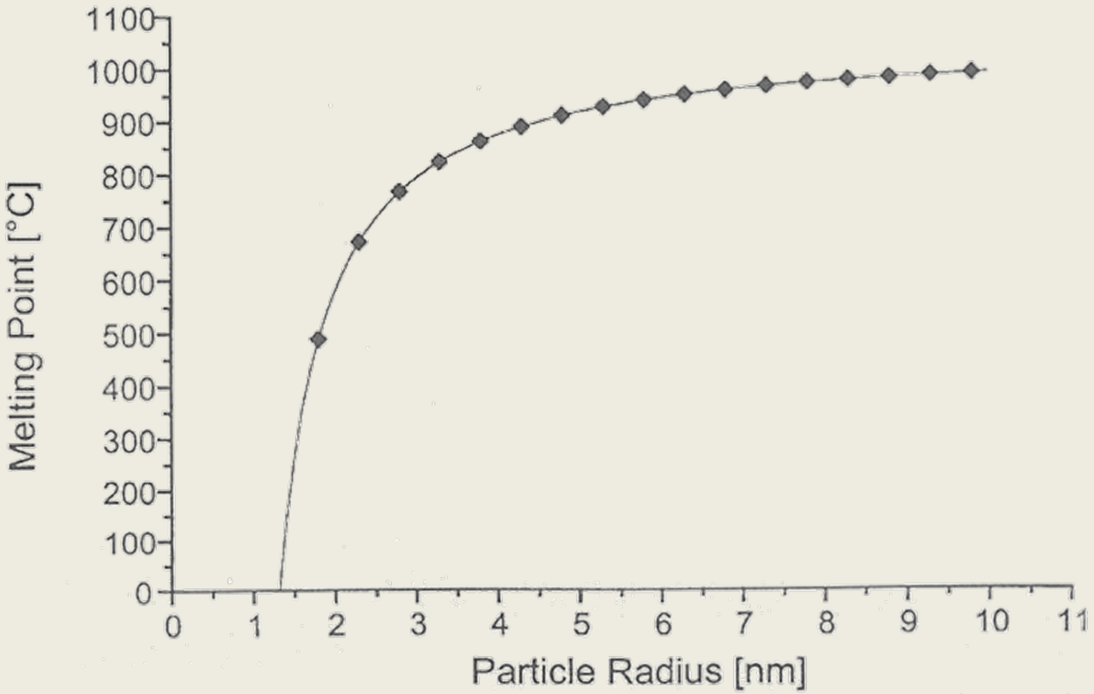
- In Figure, the relation between particle size and melting point of gold particles is shown.

: dramatic decrease of melting points for particles smaller than 3-4 nm

1.2. Size-dependant Properties

1.2.4. Melting points

Figure. Relation between the size of gold particles and their melting point



- We can see that even thermodynamic properties of matter, which classically described are natural constants, change with the dimension of the material.

1.2. Size-dependant Properties

1.2.5. Magnetism

- Diamagnetic materials have only spin-paired electrons.

- In practice a macroscopic piece of a diamagnetic metal can have one or unpaired electrons.→ No way to measure because of the effectively infinite number of atoms and electrons.

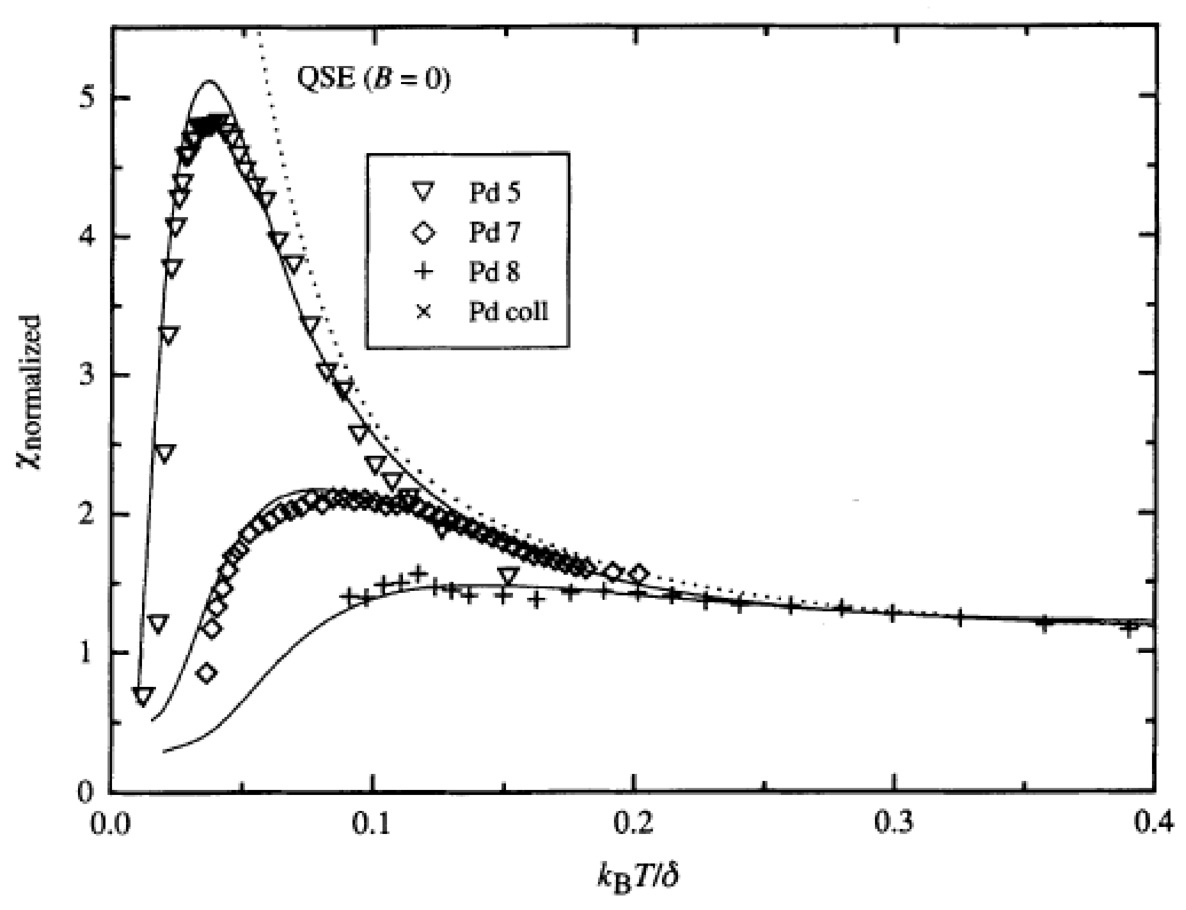
- However, the particle size → small enough to make one unpaired electron measurable → the predicted so-called "odd-even effect" become visible

※ Odd-even effect : Among small diamagnetic metal particles, there should be a 50:50 distribution of odd and even numbers of electrons

CNDL

1.2. Size-dependant Properties

1.2.5. Magnetism



χ = electronic magnetic susceptibility
k_BT = mean thermal energy
QSE = quantum size effect
δ = average energy gap

Figure. Electronic magnetic susceptibility of the Pd clusters in the quantum-size regime

Nature, **1996**, *384*, 621.

CNDL

1.3. Applications

1.3.1. Colors

- Semiconductor (Size-dependant; Exciton)

- Exciton (main mechanism light emission in quantum dots at lower temperature)

  - When an electron is promoted from the valence to conduction bands, an electron-hole pair known as an *exciton* is created in the bulk lattice.

  - The physical separation between the electron and hole is referred to as the *exciton* Bohr radius (r_B) that varies depending on the semiconductor composition.

  - In a bulk material, r_B is significantly smaller than the overall size of the crystal; hence, the *exciton* is free to migrate throughout the lattice.

  - However, in a quantum dot, r_B is of the same order of the diameter (D), giving rising to quantum confinement of the *exciton*. Strong *exciton* confinement at $D \leq r_B$

- Since the dimensions of a quantum dot are extremely small, the addition/subtraction of a single atom will significantly change the nanocrystal band gap. Table lists the r_B values for semiconductor crystals whose band gap may be easily fine-tuned.

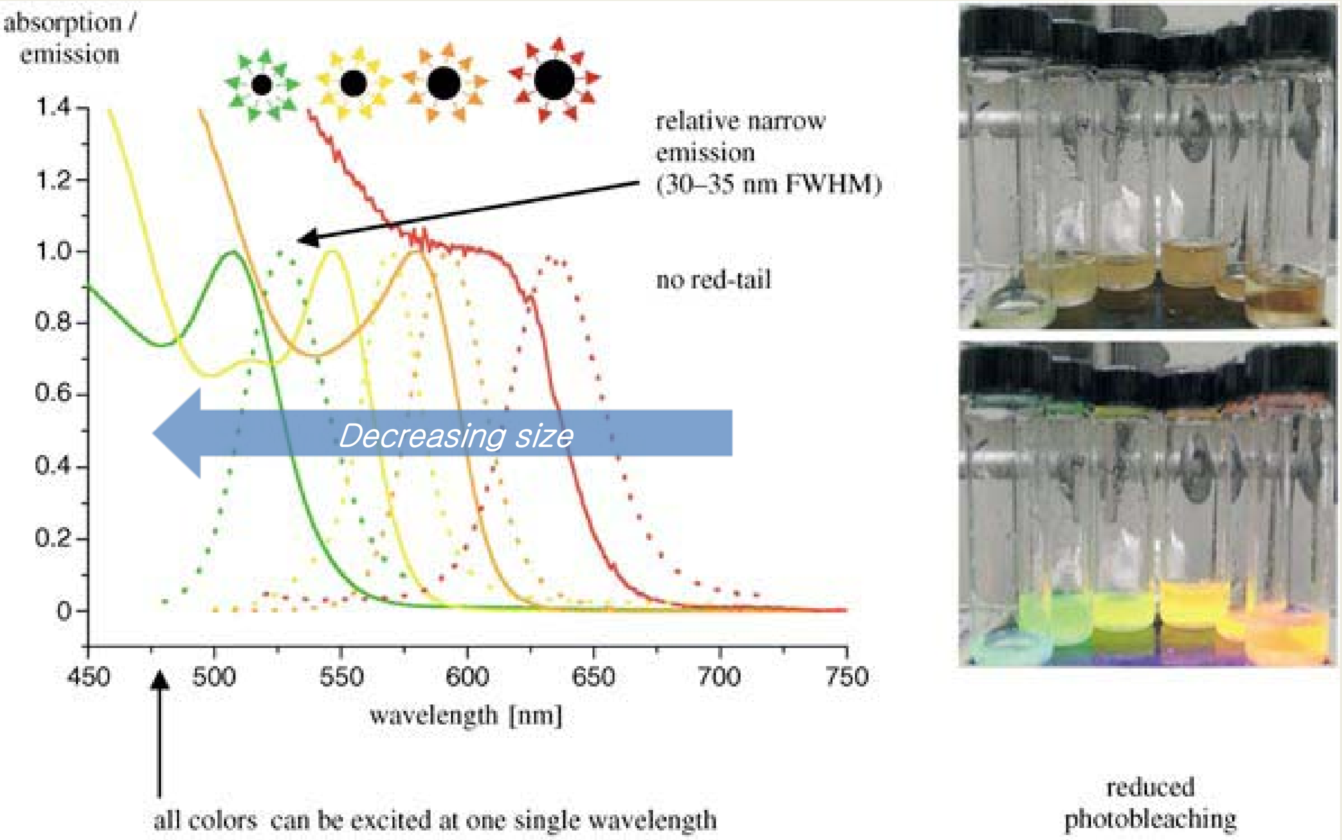
Table. Calculated Exciton Bohr Radii

Material	Si	CdS	CdSe	CdTe	ZnO	ZnS	PbS	InAs	InSb
r_B(Å)	55	28	61	100	18	50	204	340	540

1.3. Applications

1.3.1. Colors

- Semiconductor (Size-dependant)



$$E = h\nu$$

$$c = \lambda\nu$$

$$E(eV) = \frac{1.24}{\lambda(\mu m)}$$

λ = wavelength
ν = wave number
h = planck`s constant

Figure. The size-dependency on the optical properties of CdSe (Semiconductor) nanocrystals. With decreasing size, the fluorescence peak Is shifted to shorter wavelength.

Small, **2005**, *1*, 48.

1.3. Applications

1.3.1. Colors

- Metal (> 2nm; Size- and Shape- dependant)

- The operating principle is different from semiconductor quantum dots, since there is no band gap and the energy states form a continuum analogous to bulk material.
- Another phenomenon known as *surface plasmon resonance* is active, involving specific scattering interactions between the impinging light and the nanostructure
- The oscillating electric field of the incoming light causes the coherent oscillation of the conduction electrons, resulting in a concomitant oscillation of the electron cloud surrounding the metal nuclei.

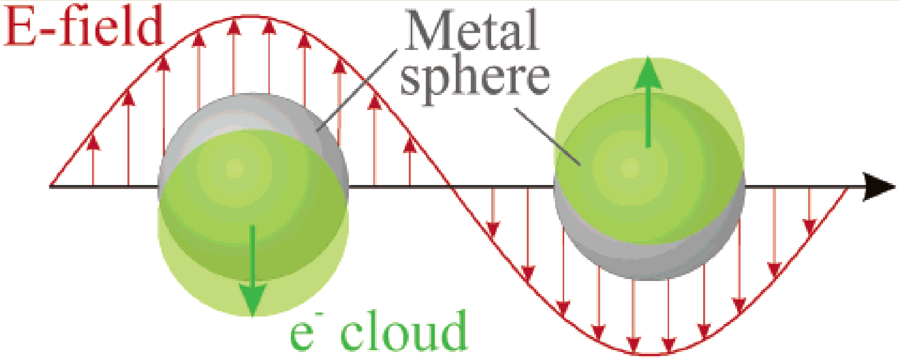


Figure. Schematic of localized surface plasmon resonance (LSPR) for a nanosphere, showing the induced oscillation of the electron cloud relative to the nuclei.

J. Phys. Chem. B, **2003**, *107*, 668.

1.3. Applications

1.3.1. Colors

- Metal (> 2nm; Size- and Shape- dependant)

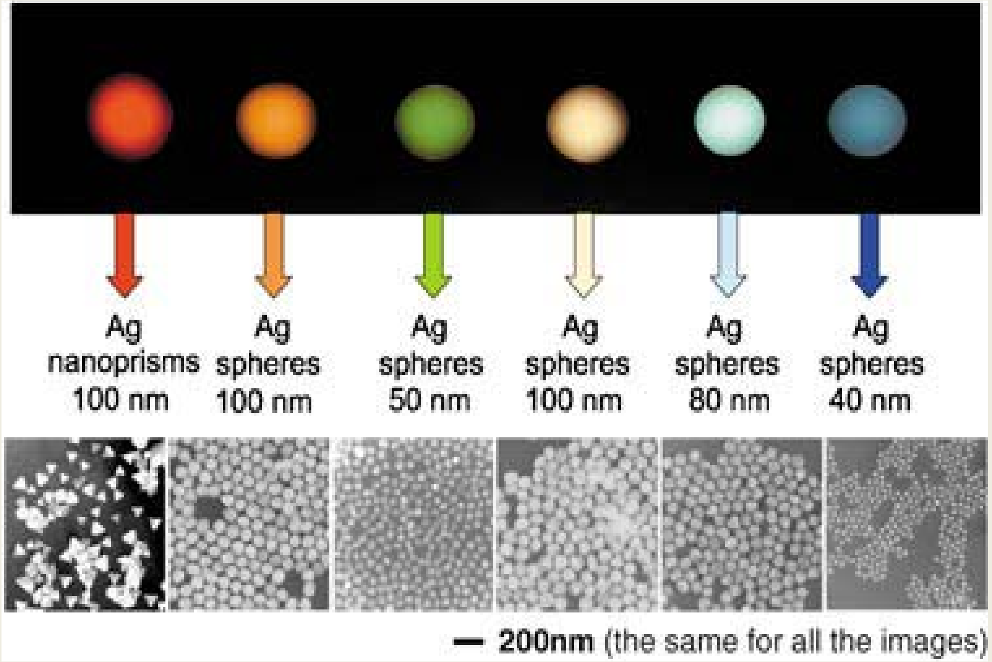


Figure. The influence of size and shape on the light scattering, and resultant colors, of silver nanoparticles.

- Spherical

$$E(\lambda)=\frac{24\pi N_A r^3 \varepsilon_m^{3/2}}{\lambda \ln(10)}\left[\frac{\varepsilon_i(\lambda)}{\boxed{(\varepsilon_r(\lambda)+2\varepsilon_m)^2}+\varepsilon_i^2(\lambda)}\right]$$

E(λ) = the extinction(sum of absorption and scattering
N_A = the density of the nanostructure
r = the radius of the nanostructure
ε_m= the dielectric constant of the metallic nanostructure
λ = the wavelength of absorbing radiation
ε_i, ε_r = the imaginary and real portions of the λ dependent dielectric function of the nanostructure

- Nonspherical : χ may range from a value of 2 (perfect sphere) to 17 (5:1 aspect ratio nanostructure)

$$(\varepsilon_r(\lambda)+\chi\varepsilon_m)^2$$

Small, **2005**, *1*, 14.

1.3. Applications

1.3.1. Colors

- A very obvious property of nanoparticles, at least of some metals, is their specific color.

1) Gold colloids → color glasses
ex) ruby glass : finely dispersed gold colloids

2) silver, copper → attractive colors in glassy materials

- The use of alloys in particular has broadened the availability of nanometals for coloring transparent materials.

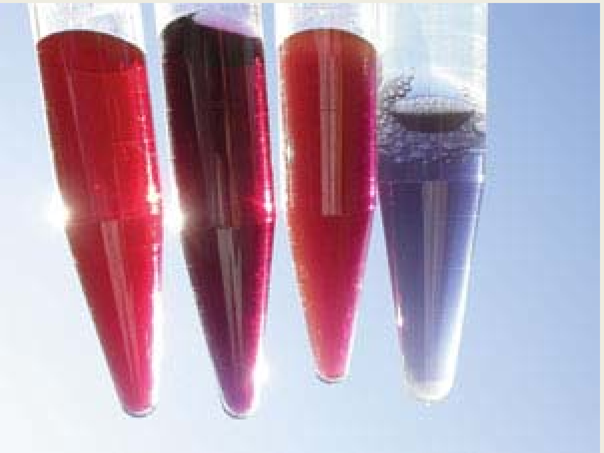


Figure. Dispersions of discrete gold nanoparticles in transparent media have an interesting and flexible color gamut that has only recently been exploited for paints and coatings. These colors depend on how the particles are viewed and on their shape. The gold particles in the test tubes above are being viewed in transmitted light.

1.3. Applications

1.3.2. Catalysis

- The increasing proportion of surface atoms with decreasing particle size

: small metal particles become highly reactive catalysts
: surface atoms are the active centers for catalytic elementary processes
: the percentage of edge and corner atoms also increases with decreasing size

→ Very small metal particles are preferred as catalysts.

- Catalysts based on the activity of metal nanoparticles

: the heterogeneous type only

- Industrial process

The particles are generated on supports such as alumina, silica, or charcoal.
→ various sizes → larger particles will be less active than smaller ones

- Particles are synthesized not on the support but in separate procedures

→ **uniform nanoparticles** the goal

1.3. Applications

1.3.2. Catalysis

- Ligand-protected clusters and colloids

: ligand molecules occupy catalytically active sites
: tune a catalyst with respect to optimized selectivity
: Never cover a particle surface completely
→ Enough channels to allow reactants and products to reach the metal surface and to desorb after the catalytic process

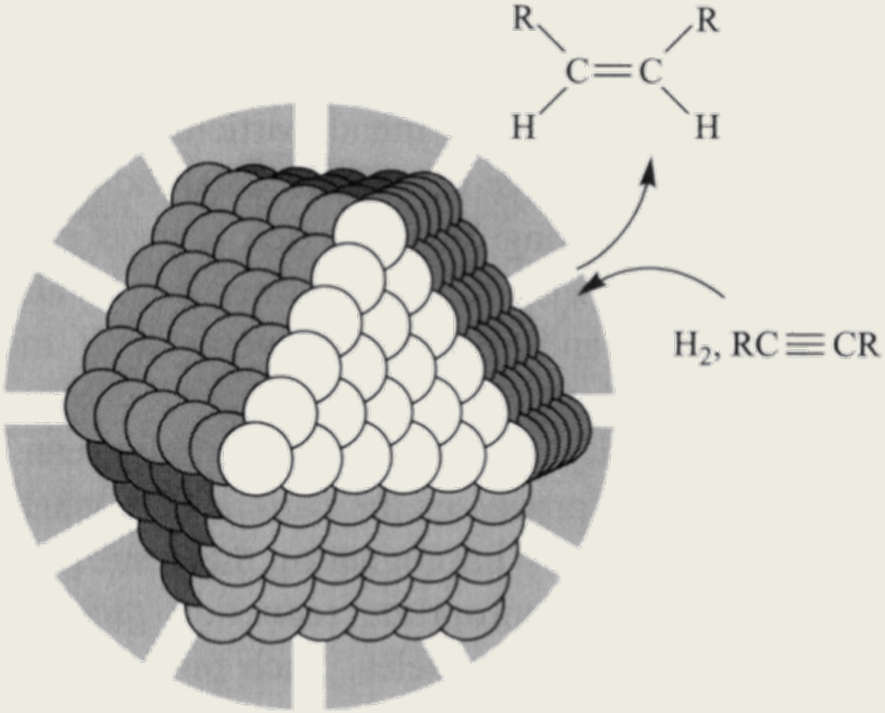


Figure. Sketch of a ligand-stabilized metal cluster indicating channels between ligand molecules admit reactants and allow products to leave.
J. Chem. Soc., Dalton Trans., **1996**, *5*, 589.

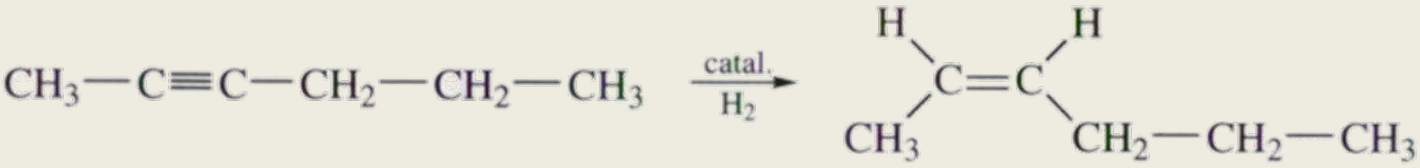
1.3. Applications

1.3.2. Catalysis

- Good catalyst

→ enable semihydrogenation

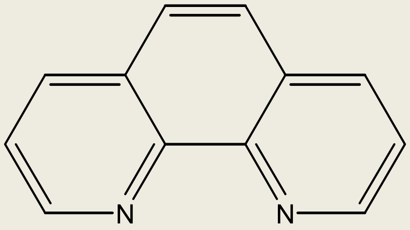
→ selectively determine *cis*- or *trans*-configuration of the resulting alkene.



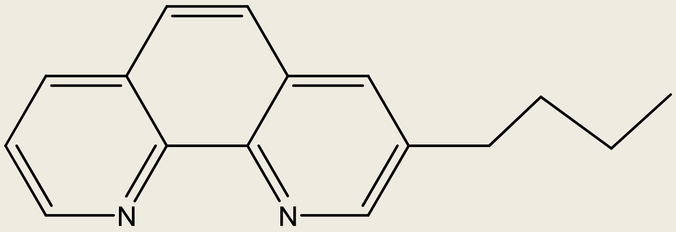
2-hexyne   *cis*-2-hexene

well-tuned catalyst   (2.7)

- Other possible products(trans-2-hexene, hexane, and olefinic isomers) should be avoided.



1,10-Phenanthroline



3-Butyl-[1,10]phenanthroline

1.3. Applications

1.3.2. Catalysis

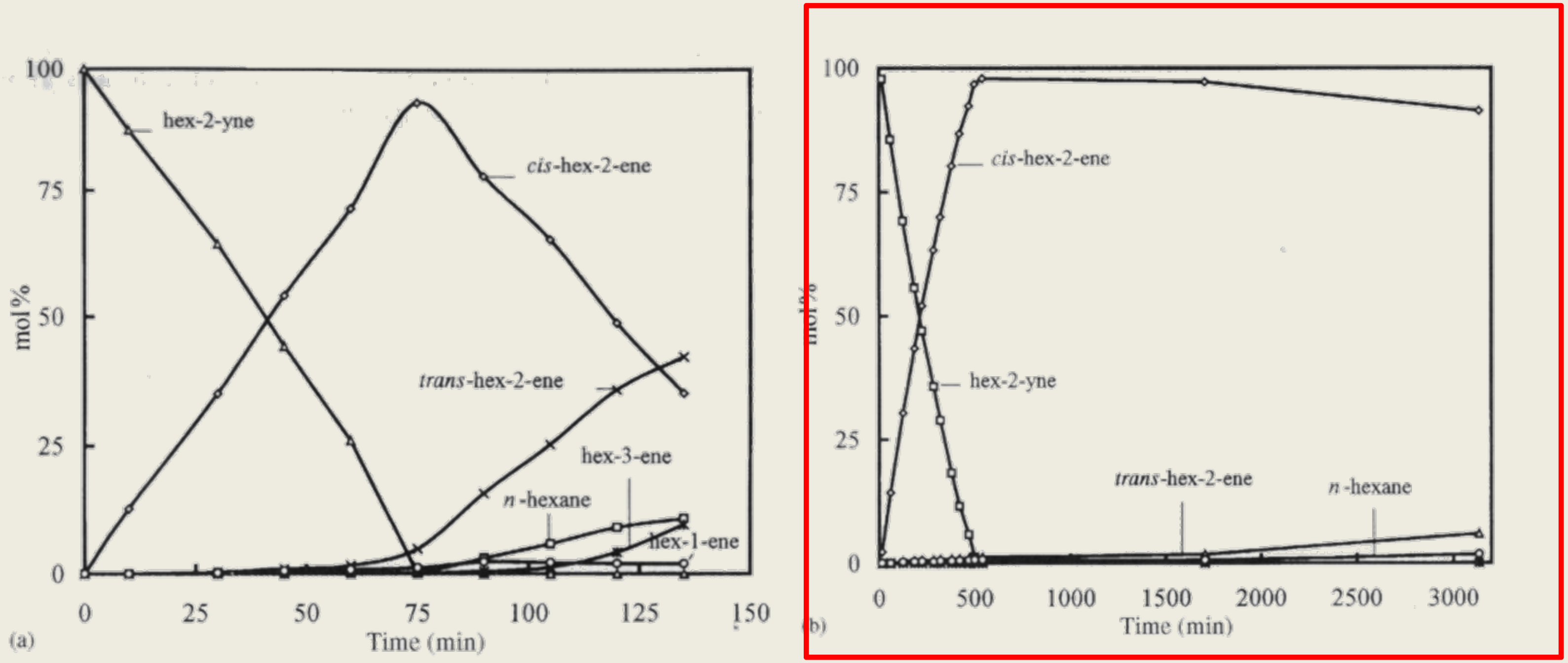


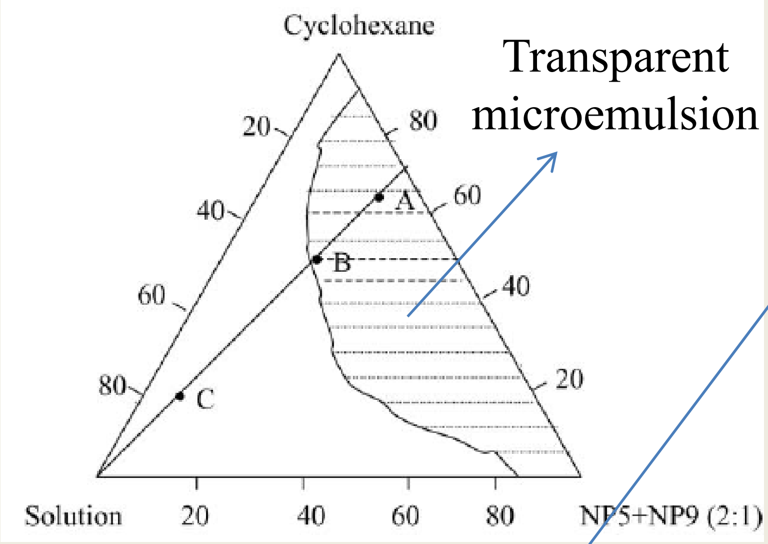
Figure. (a) Course of the semihydrogenation of hex-2-yne to cis-hex-2-ene with phenanthroline-stabilized palladium clusters as catalysts on TiO_2 as a support. (b) The same reaction with 2-butylphenanthroline as ligands on the same palladium clusters. Compared with the reaction in (a) the activity has decreased dramatically, whereas the selectivity has increased 100%. Formation of other product starts after ~25-30 hours.

J. Chem. Soc., Dalton Trans., **1996**, *5*, 589.

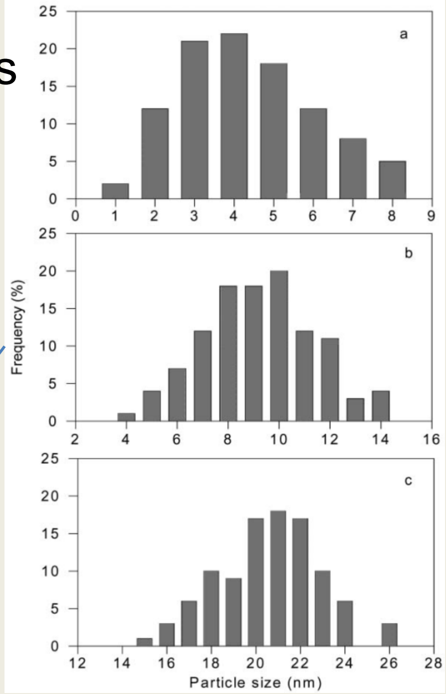
1.3. Applications

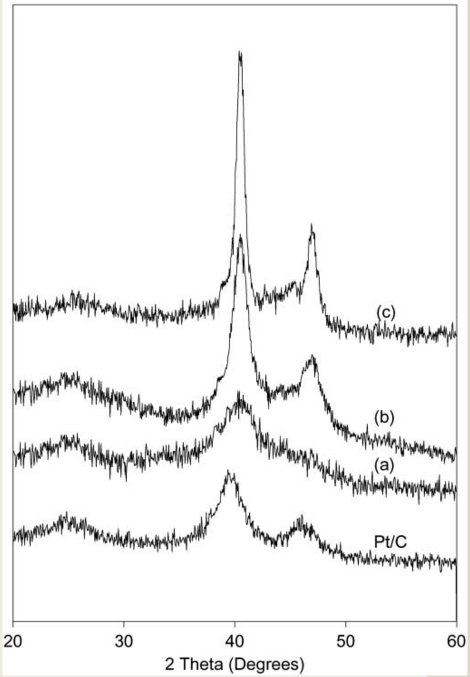
1.3.2. Catalysis

PtRu/C catalysts from microemulsions

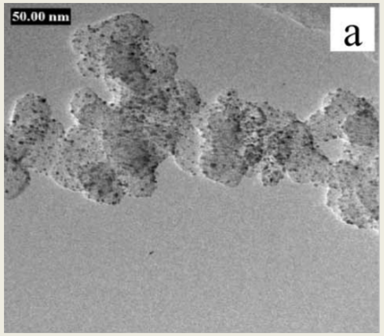


Transparent microemulsion

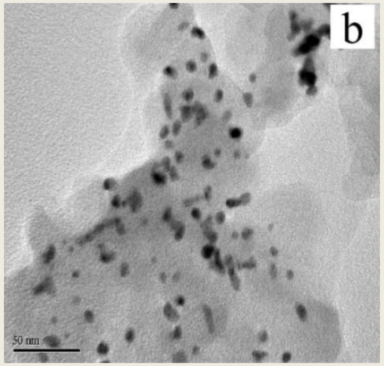




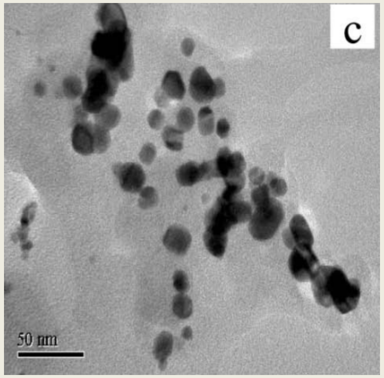
XRD pattern



4.3 ±1.6 nm



9.2 ± 2.1 nm



20.6 ± 2.2 nm

J. Mater. Chem., **2002**, 12, 2453.

1.3. Applications

1.3.2. Catalysis

PtRu/C catalysts from microemulsions and emulsions

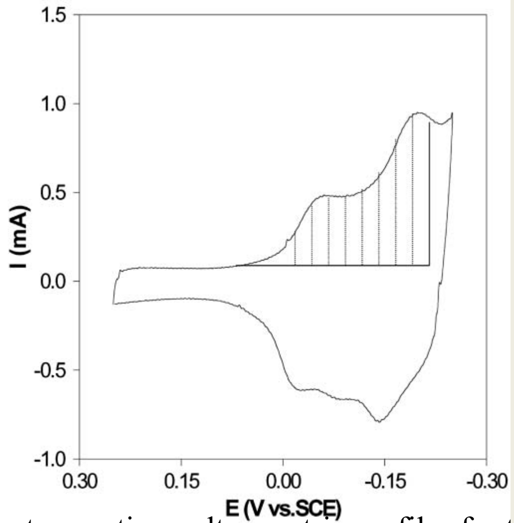


Fig. Hydrogen electrosorption voltammetric profiles for the PtRu/C catalysts obtained from composition A. The hatched area represents the amount of charge of the electrosorption of hydrogen on Pt.

A_{EL} (m^2 g^{-1} Pt) ~ $Q_H/(0.21*10^{-3}C$ * amount of catalyst)

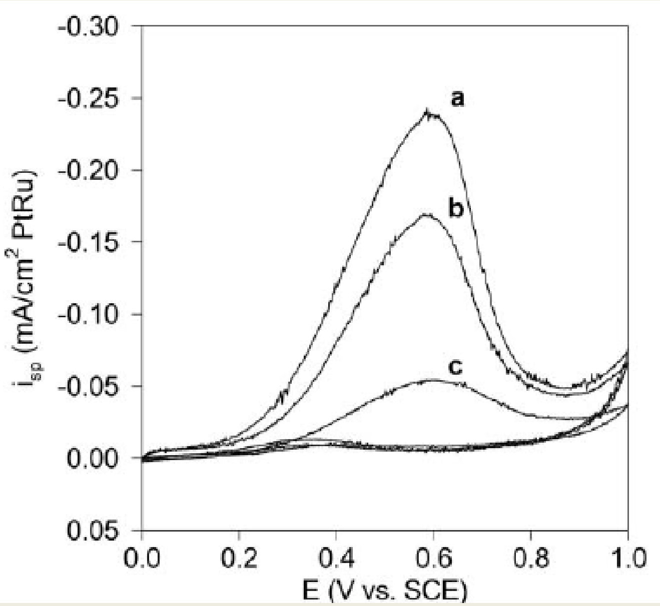
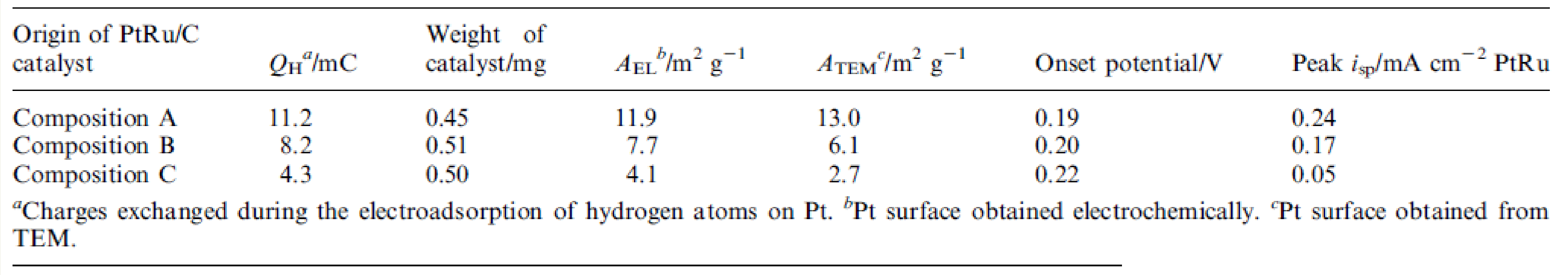


Fig. Cyclic voltammograms for PtRu/C electrodes in Ar-saturated 1M H2SO4 with 2 M methanol present in the electrolyte at 10 mV s^{-1}.



Origin of PtRu/C catalyst	Q_H[a]/mC	Weight of catalyst/mg	A_{EL}[b]/m^2 g^{-1}	A_{TEM}[c]/m^2 g^{-1}	Onset potential/V	Peak i_{sp}/mA cm^{-2} PtRu
Composition A	11.2	0.45	11.9	13.0	0.19	0.24
Composition B	8.2	0.51	7.7	6.1	0.20	0.17
Composition C	4.3	0.50	4.1	2.7	0.22	0.05

[a] Charges exchanged during the electroadsorption of hydrogen atoms on Pt. [b] Pt surface obtained electrochemically. [c] Pt surface obtained from TEM.

J. Mater. Chem., **2002**, 12, 2453.

1.3. Applications

1.3.3. Nanoelectronics

- The most valuable electronic properties of small metal particles have not yet been realized in working system.

- The metal clusters as quantum dots

→ the ability to enable single-electron storage and tunneling

→ behave ultimately as miniaturized transistors, working at room temperature

- Tremendous scientific and technical problems

- No way to address these incredibly small dots

- Electrical connections of the same size range must be developed

- The quantum dots must be specifically arranged on suitable substrates

- contemporary silicon transistor ≒ 1000 x cluster quantum dots

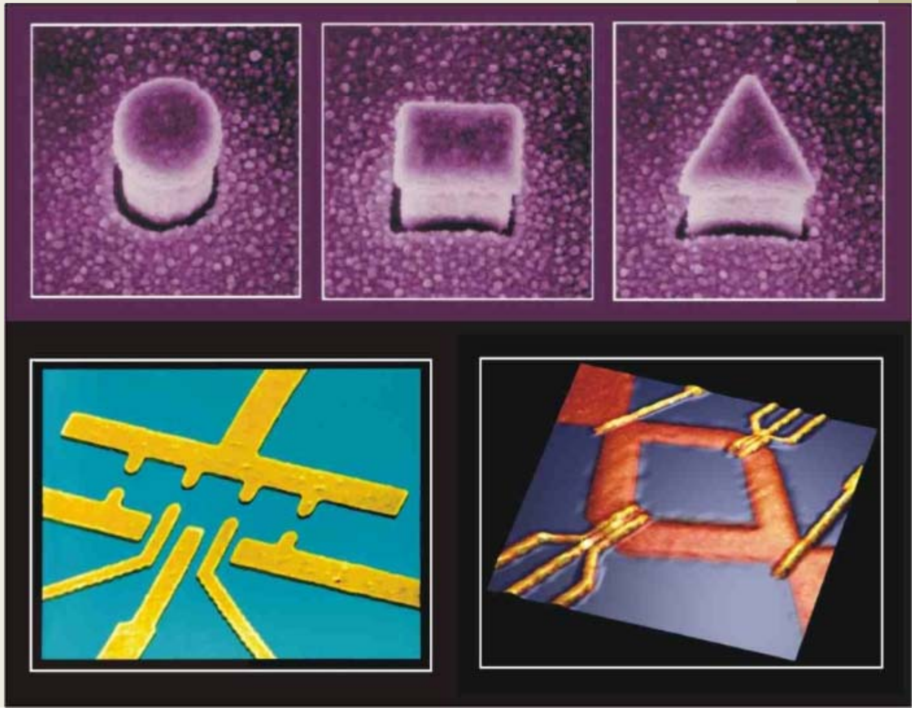
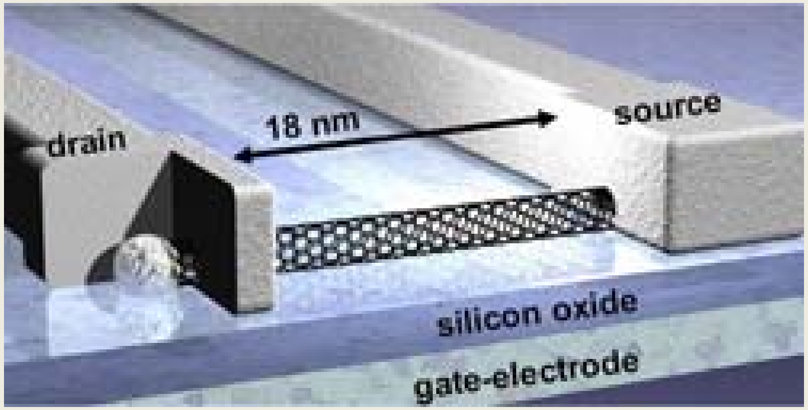


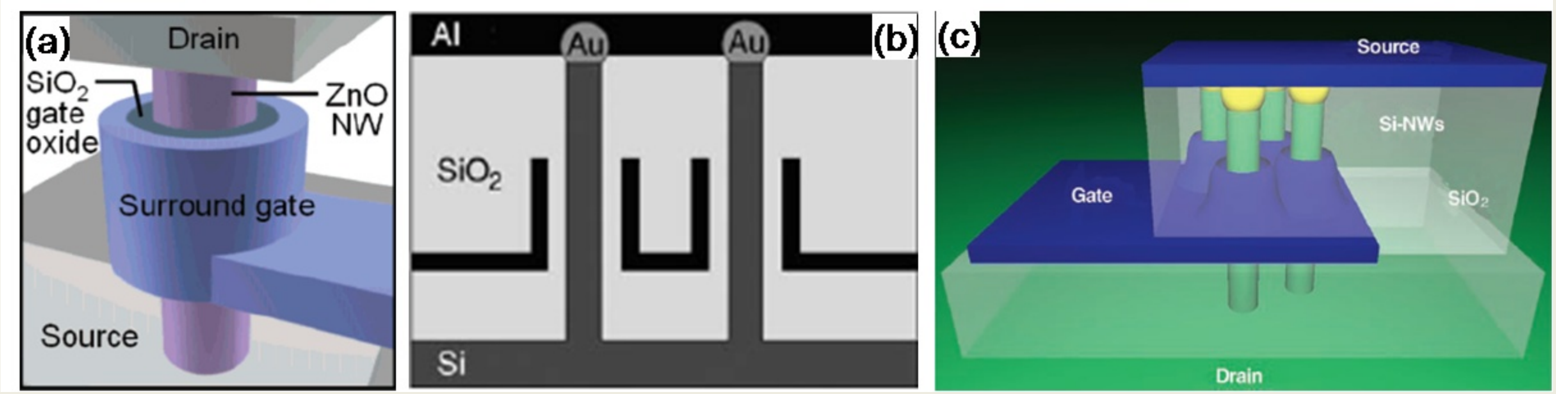
Figure. Quantum dot devices. *Science*, **2000**, *289*, 2105

1.3. Applications

1.3.3. Nanoelectronics

- Nano-Transistor
- Physical limitations of photolithography are becoming a problem
- Bottom-up approach allows smaller geometries





Small **2006,** *2,* 85

1.3. Applications

1.3.3. Nanoelectronics

- FED (Field Emission Display)

- Each pixel of FED has own electron gun

→ Electron gun should be very small

- CNT - Nanosize
  - High aspect ratio
  - High electric conductivity

→ one of the best candidate


In a CRT, the electron gun sits far from the display

In a FED, the electron gun array sits only a millimeter from the display