Chapter 1. Introduction to Nanoparticle Technology

"Nanoparticles – the small particles with a big future."

1.1 Definitions

Definition by size

- Particles having sizes less than 0.1μm (100nm)

1^{st} generation nanoparticles: <100nm

2^{nd} generation nanoparticles: <10nm

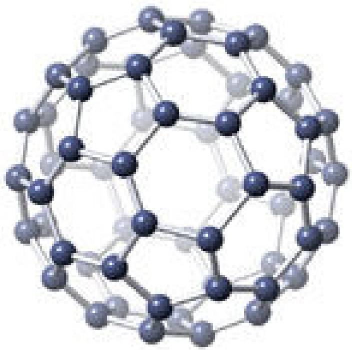
- Lower limit of nanoparticles: ~1nm

*Other names of nanoparticles

- ultrafine particles, clusters, nanocrystals, quantum dots

cf. colloids, aerosols, hydrosols, organosols..

Size Ranges of Particle
- Coarse particles : >10μm
- Fine particles : ~1 μm
- Ultrafine (nano) particles : <0.1 (100nm)



Buckminster fullerene

Football

Planet earth

if a buckyball (60 carbon atoms arranged into a sphere with a diameter of approximately 1nm) were expanded to the size of a football, the football would correspondingly be expanded so that it was much bigger than the size of Earth (becoming approximately the size of Neptune or Uranus – about 50,000km in diameter).

<u>Definition by properties</u>

: whose properties becomes discontinuous as the bulk contracts

- less than the characteristic length of some phenomena*

cf. Mean free path of gases, wavelength of light, electron wave, distance between electro-hole pair (exciton)

<u>Characteristics of nanoparticles</u>

-*Difficult to produce by breakdown process:*

- *-Formation by growth (buildup or bottoms-up)*

-*Small size effect (quantum size effect)*

- *-Contain very small number of atoms(or molecules): size effect*
- *-Electronic states quite different from those of bulk: size effect*

-Large surface effect

- *- Contain large portion of surface atoms(or molecules) : High surface activity*

1.2 Field of Nanoparticle Technology

(1) Design and preparation of nanoparticles with high functionality

What?

Size, shape, chemical properties, crystallinity, structures if composites

How?

Bottom-up: nucleation and growth in liquid phase and/or gas phase

Top-down: ultrafine milling

Mixed: spray pyrolysis in aerosol phase

(2) Characterization of nanoparticles

Size and morphology(shape): TEM, SEM, STM , LPA, DMA

Chemical/crystalline properties: FT-IR, NMR, ACP-IES, XRD

Surface properties: BET, XPS, Auger, AFM

Composite structures: TEM, element mapping

(2) Dynamics of nanoparticles

- *Movement of nanoparticles*
- *Formation and growth of nanoparticles*

(4) Handling(Unit Operation) of Nanoparticles

- *Storage, transport, crushing and mixing**
- *Separation*

(5) Dispersion, Consolidation and Device(Value Addition) Technology

- *Particle-particle interaction*
- *Surface modifications*
- *Assembly: 1-, 2-dimensional, porous, densification*
- *Device for application*

(6) Adverse Effect of Nanoparticles

- *Dust explosions*
- *Respiration hazards/Effect in human bodies*
- *Particle contamination and cleaning in industries*

1.3 History of Nanoparticle Research

4c, Roman glassmakers, **glasses containing nanosized metal particles*

- Lycurgus cup

In diffused light In focused light

- Explained by Michael Faraday(1857) and Gustav Mie(1908)..

**18-19c, H.Davy, C.Maxwell(1861), G.Eastman(1883),*

***Photographic films** using silver*

halide photochemistry(silver nanoparticles)

1905, A.Einstein "the existence of colloid(Big atoms)", discovered Brownian motion.

1958, **Richard Feynman, a lecture entitled "There are plenty of room at the bottom."* http://qubit.plh.af.mil/RelatedArticles/related/Feynman59.pdf

- predicted the existence of electron beam lithography, scanning tunneling microscope and building circuits on the scale of nanometer for powerful computers

**1960s~1970s, preparation of nanoparticles by gas evaporation-condensation method*

Quantum confinement (Kubo) effect

** 1981-1986 Japan, Ultra-Fine Particle Project under the auspices of the Exploratory Research for Advanced Technology program (ERATO)*

- preparation, characterization, properties, applications

**1981 G.K. Binnig H. Roher(IBM Zurich): invented scanning tunneling microscope (1985 Nobel prize)*

- *allows atomic-scale three-dimensional profiles of surfaces to be obtained*

**1985 R.Smalley, R.Curl and H.Kroto discovered* C_{60} *(Nobel Prize in 1996).*

-*Officially known as buckminsterfullerene (exactly like a football).*

1987 B.J. van Wees and H. van Houten (Netherlands)/D. Wharam and M.Pepper (Cambridge U.), observed* ***quantization of conductance* *(step in I-V curve)*

- Coulomb blockade, single electron transistor

1991, Yablonovitch, 3-D photonic crystals

*1991, Iijima made **carbon nanotubes** (multi-walled)**,** Single-walled(1993)*

1993, Murray, Norris and Bawendi synthesize the first high quality quantum dots of nearly monodisperse CdS CdSe and CdTe. they emit different colors depending on their size.

*1999**, Self assembly** of molecules on metal nanoparticles*

*1996 NSF et al., **assessed current worldwide status of nanoscience and nanotechnology***

*2000.2 B. Clinton, **National Nanotechnology Initiative***

Followed by Japan, EU and other countries..

2003, Prototype solar cells (Nanosolar Inc.) with conducting polymers and nano-based particles.

- much cheaper and easier to make.

- produced in flexible sheets, making them suitable for many applications

**2004, Silica nanoshells coated with gold (Rice University and the University of Texas)*

- killed cancerous tumours, when exposed to an external source of near-infrared light.

**2004, NanoScale Materials Inc., neutralizer for chemical hazards*

- dry powder formulation (Reactive Nanoparticle (RNP™)) to bind with a variety of chemical warfare agents and toxic chemicals, and chemically convert them to safer by-products

1.4 Applications and Perspective of Nanoparticles

Dispersed state

Fillers, paints, ferrofluids, magnetic recording media, drugs, cosmetics, phosphors, rocket propellant, fuel additives

Consolidated state

- Porous structure

Catalysts, electrodes of solar cells and fuel cells, sensors, adsorbents, synthetic bone, self-cleaning glass

- Ordered assembly

Quantum electronic device, photonic crystals, DNA chips, biosensors

- Dense phase

Flexible/dense ceramics and insulators, harder metal, CNT in tennis racquet

** Present and future application of nanoparticles*

<u>Biomedicals</u>

- Pharmacy in a cell- controlled release

- Solubilized therapeutic drugs

- Tagging of DNA and DNA chips

<u>Information Tech</u>

- Information storage (nanoparticles, nanopens)

- Chemical/Optical computers(2-D,3-D assembly- photonic crystals)

- Quantum (molecular) electronic devices

<u>Materials</u>

- Flexible/dense ceramics and insulators: replacing metals

- Harder metal materials(5 times that of normal metals)

- Nanometallic colloids as film precursors

- *Fillers for improved polymers (stronger, lighter, wear resistant, tougher lame retardant) - replacements for body parts and metals*
- *Unusual coloring in paints*
- *Smart magnetic fluids (vacuum seals, viscous dampers, cooling fluids, nanoscale bearings, heat conductors, magnetic separations)*

<u>Energies</u>

- *Magnetic refrigeration (magnetocaloric effect)*
- *Nanostructured electrodes and magnetic metals with soft magnetic properties*
- *Better batteries- metal nanoparticles*

<u>Environmental/green chemistry</u>

- *solar cells (photovoltaic, water splitting)*
- *photo-remediation (pollutant destruction, water decontamination)*
- *Destructive adsorbents (acidic gases, polar organics)*
- *Self cleaning*

Catalysis

- Chemical catalysts (particle size and dispersion, crystal faces, edges, corners, defects)

- Sensors (porous aggregates of semiconductor particles)

R&D by US government for nanotechnology

Estimated government sponsored R&D in $ millions/year
using NNI nanotechnology definition (without MEMS, other microstructures)

Fiscal Year	1997	2001	2002	2003	2004R
W. Europe	126	~ 225 (270)	~ 400	~ 650	
Japan	120	465	~ 720	~ 800	
USA	116	422 (465)	~ 600 (697)	770	849
Others	70	~ 380	~ 550	~ 800	
Total	*432* 100%	*1492 (1580)* 365%	*2250 (2367)* 547%	*3020* 700%	*849*

Others: Australia, Canada, China, E. Europe, FSU, Israel, Korea, Singapore, Taiwan
Note: ( ) Actual budget

Key areas of relevance in FY 2004 Request
(single counted, without cross-cutting, all in $ million)

- Materials 141
- Electronics 179
  total 320
- Energy 12
- Environment 25
  total 37
- Bio-medical 109
- Societal and Educational Implications 19
  total 138

World market for nanotechnology

❑ **New technologies and products: ~ $1 trillion / year by 2015**
(With input from industry US, Japan, Europe 1997-2000, access to leading experts)

Materials beyond chemistry: $340B/y
Pharmaceuticals: $180 B/y
Aerospace about $70B/y
Electronics: over $300B/y
Chemicals (catalysts): $100B/y
Tools ~ $22 B/y

Est. in 2000 (NSF) : about $40B for catalysts, GMR, materials, etc.
Est. in 2002 (DB) : about $116B for materials, pharmaceuticals and chemicals

Would require worldwide ~ 2 million nanotech workers