Nanotechnology
&
Colorants for Coatings

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Contents

What is the potential of nanotechnology ?

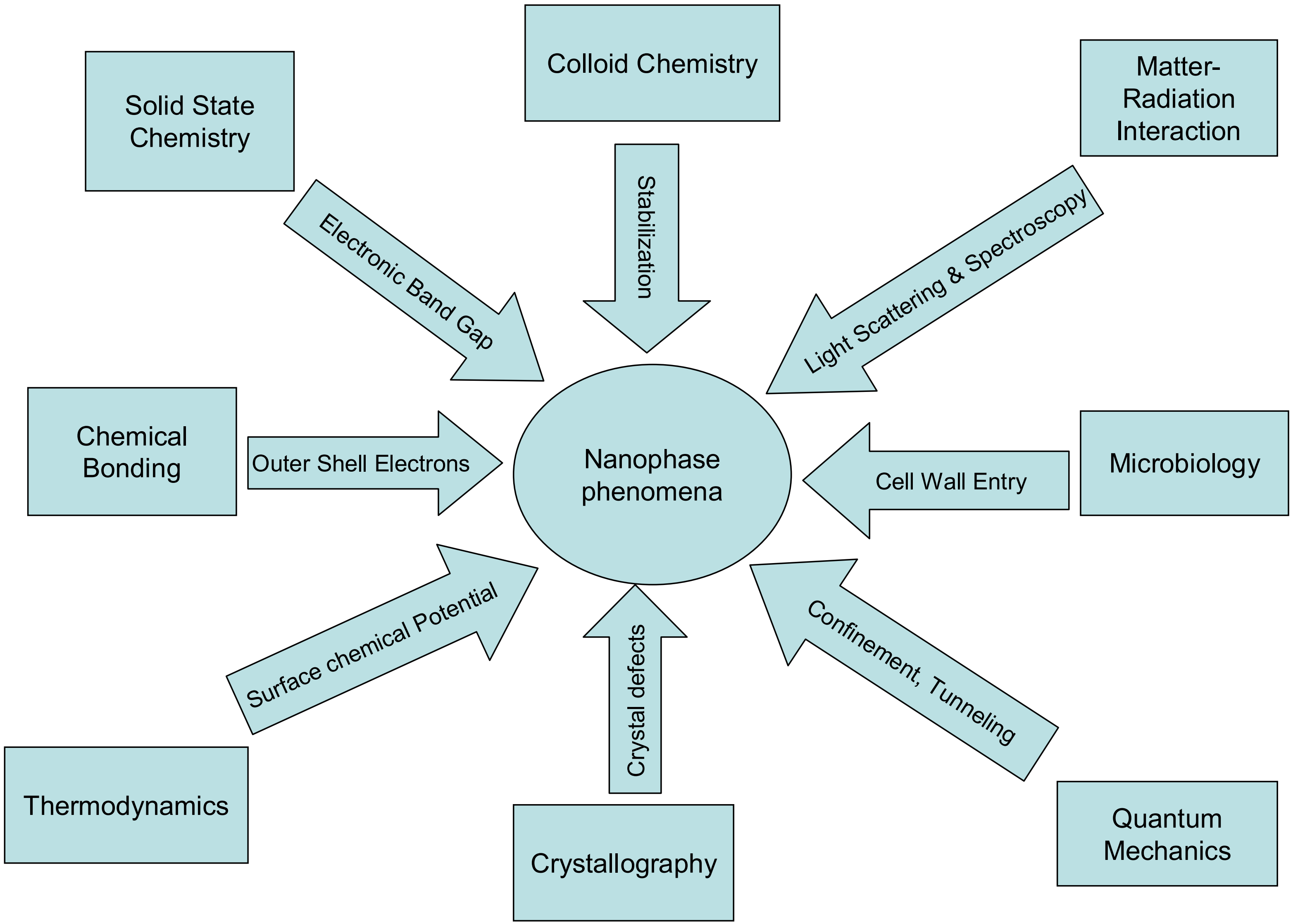
Nanotechnology: Myths

1. It is a distinct field of technology
2. Fine particle technology = Nanotechnology
3. It is unsuitable for products of common use
4. The methods of production are too sophisticated & expensive

Potential

- Breakthrough possibilities in chemistry to fabricate materials with novel mechanical, electrical, thermal, optical, biological properties.
- Nano-industrial revolution like semiconductors
- Will create millions of jobs in next 10 yrs
- NNI of US: 2009 Budget is US $1.5

Interdisciplinary Nature of Nanotechnology



What is the crux of nanotechnology?

Criteria for Nanomaterials

1. The basic structural unit only a few atoms large size along at least one dimension:

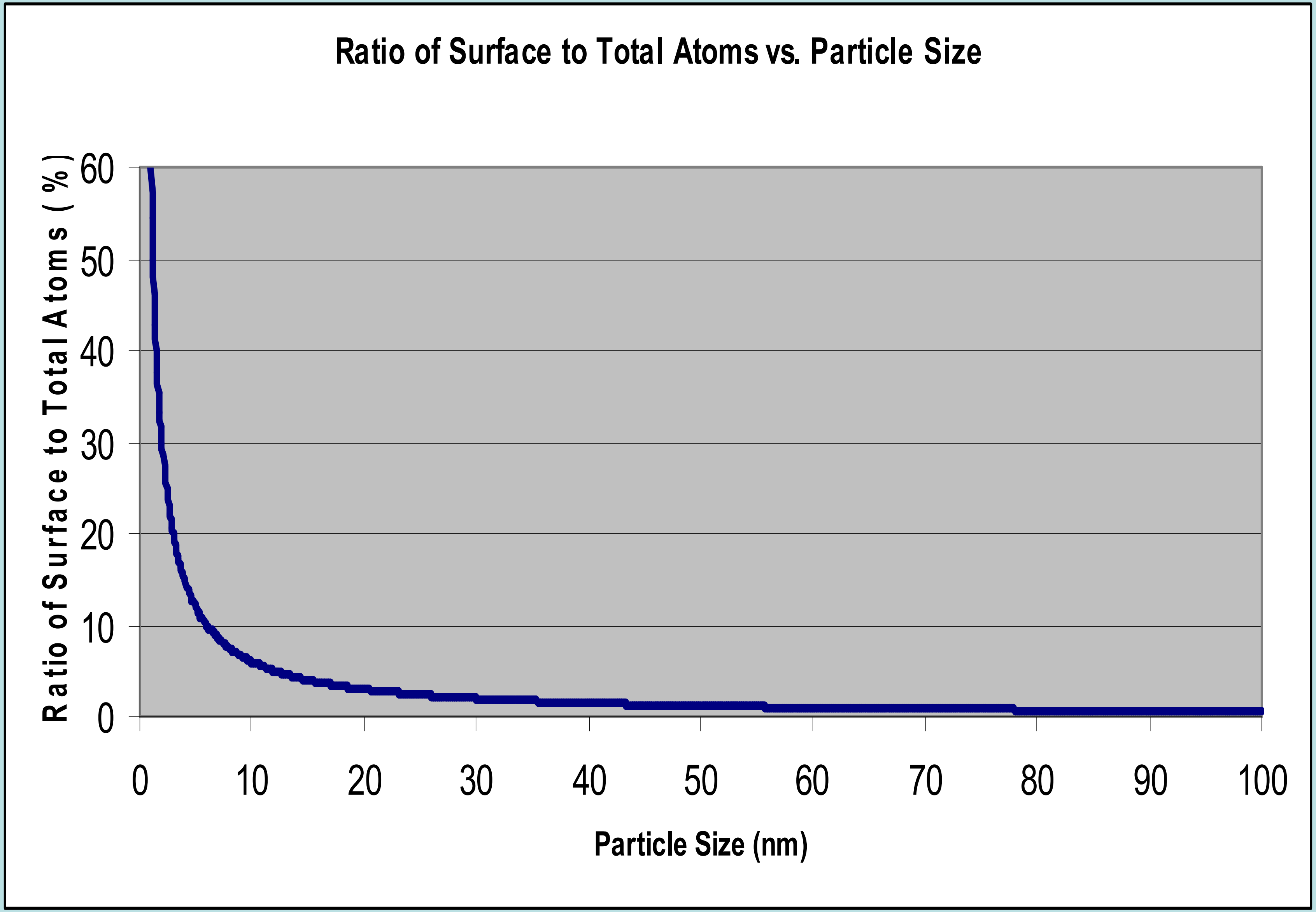
   'Quantum Confinement' (5~50 nm)

2. Properties distinctly different from the bulk material:

   Mere extrapolation of properties, as the particle size decreases into the nanometer region, is not enough for the material to be termed as nanomaterial. Point of inflection is essential.

What Changes at Nanoscale?

1. Number of atoms(molecules) on the surface becomes significant
2. Intrinsic properties become extrinsic
3. Crystalline matter becomes defect free
4. Gravity is inconsequential
5. Polymer particles become almost monomolecular
6. Particles become invisible
7. Mie scattering → Raleigh Scattering
8. Photocatalytic activity changes drastically
9. Particles can enter cell wall


Ratio of Surface to Total Atoms vs. Particle Size
Ratio of Surface to Total Atoms (%)
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
Particle Size (nm)

Surface Energy & Particle Size

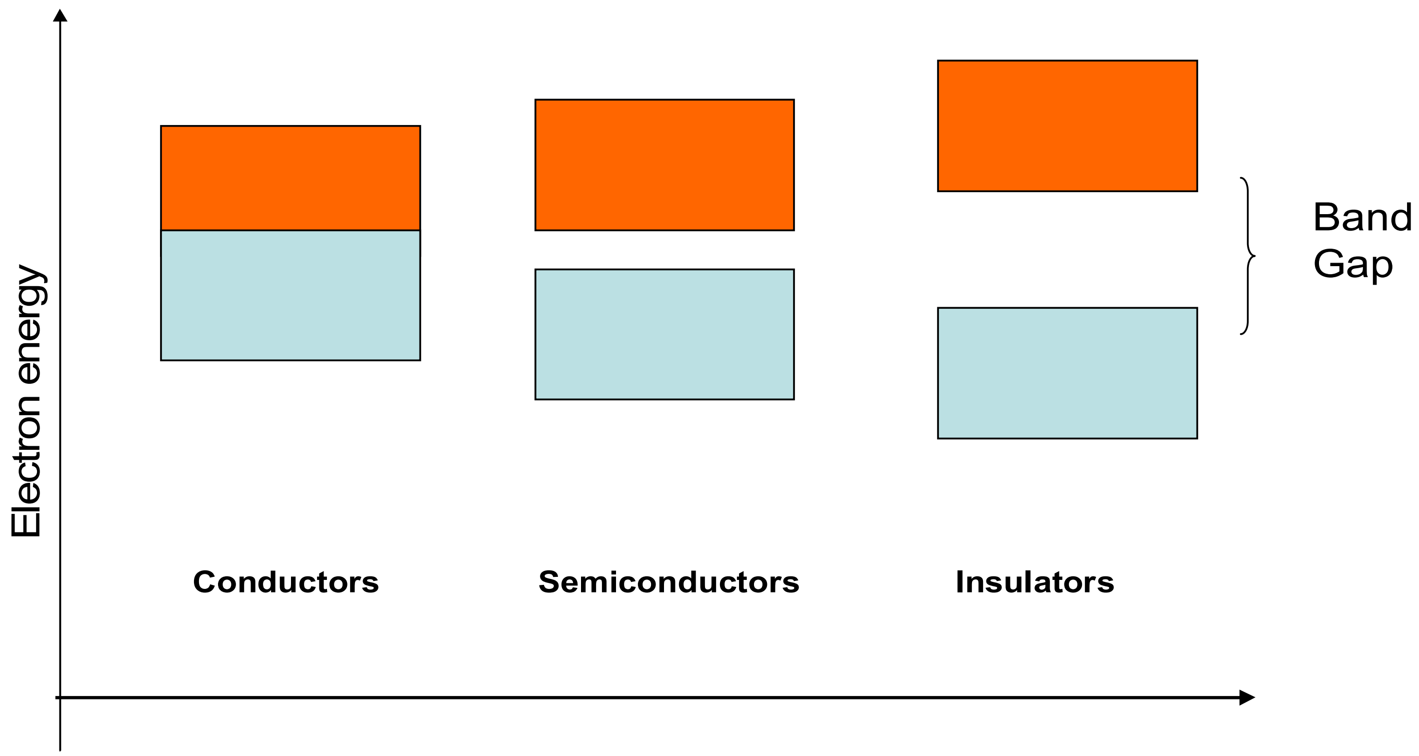
Side	Total Surface area	Total Edge	Surface Energy	Edge Energy
nm	sq. cm/g	cm/g	J/g	J/g
1000	2.8 x 10^4	5.5 x 10^8	0.56	1.7 x 10^-4
1	2.8 x 10^7	5.5 x10^14	560	170

Nanostructures and Nanomaterials: Synthesis Properties & Applications : Guozhong Cao

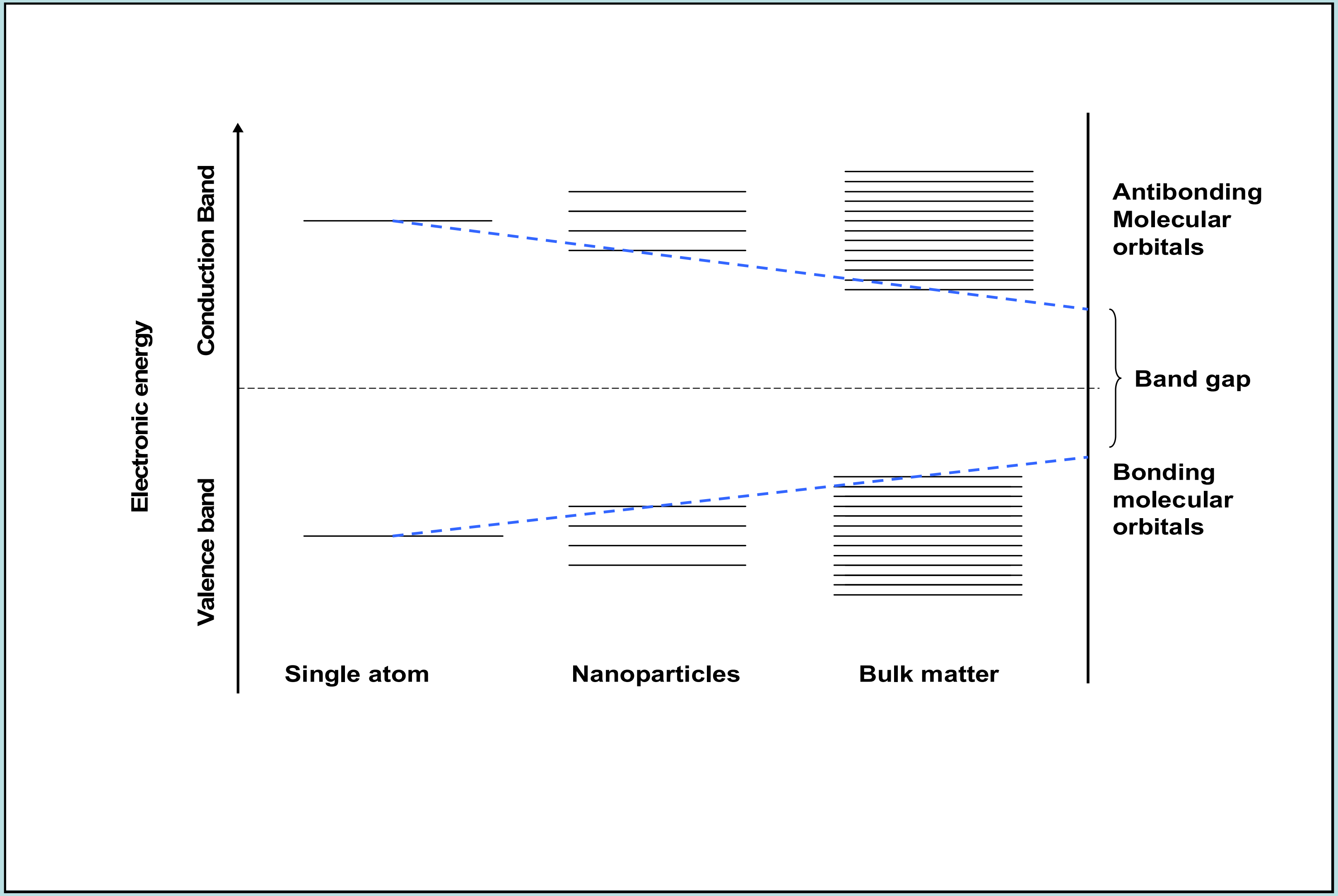
Relaxation of High Surface Energy

1. Surface contraction, change of crystal shape and purification
2. Chemisorption
3. Self Assembly
4. Re-aggregation

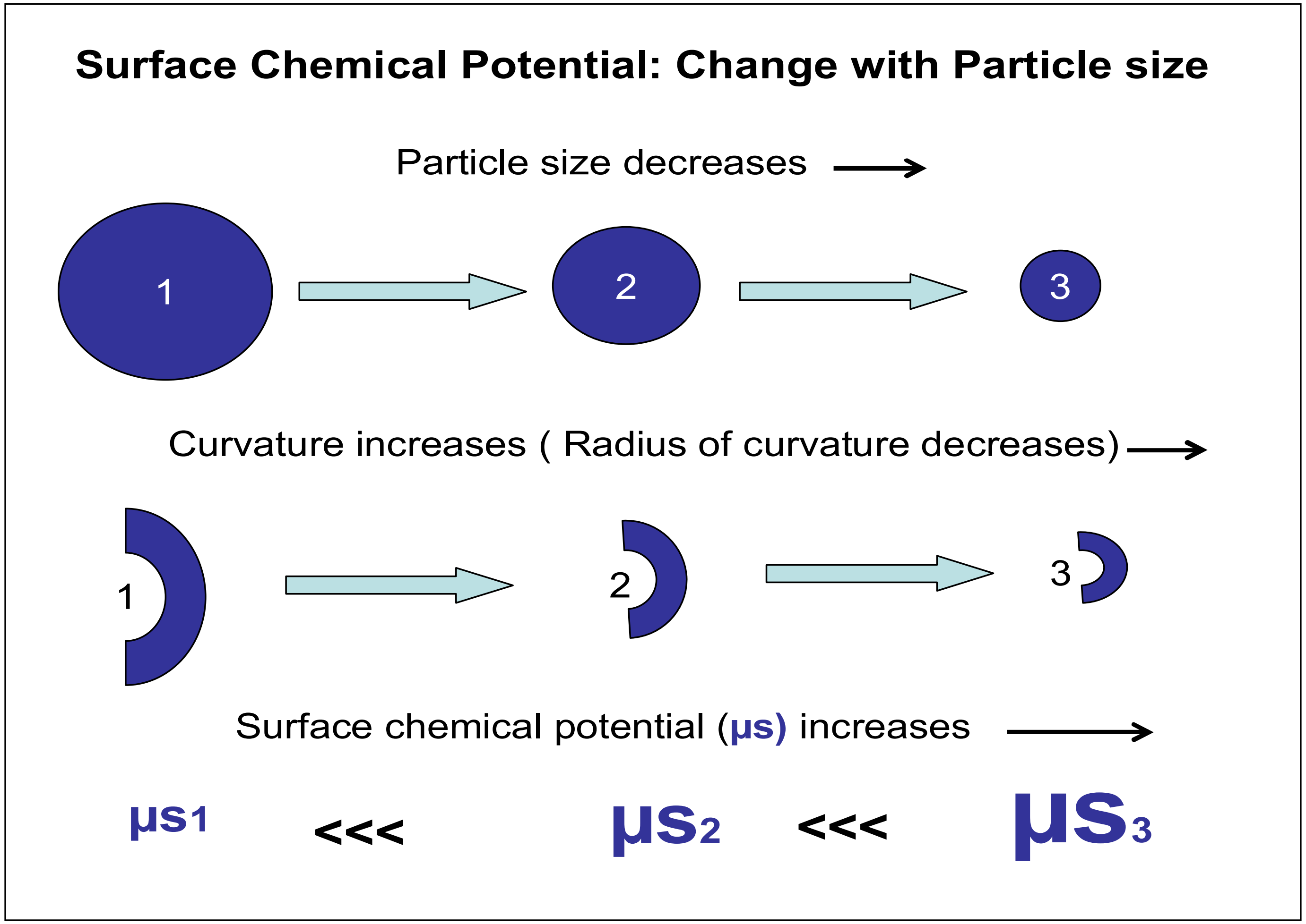
Band Structure of Matter



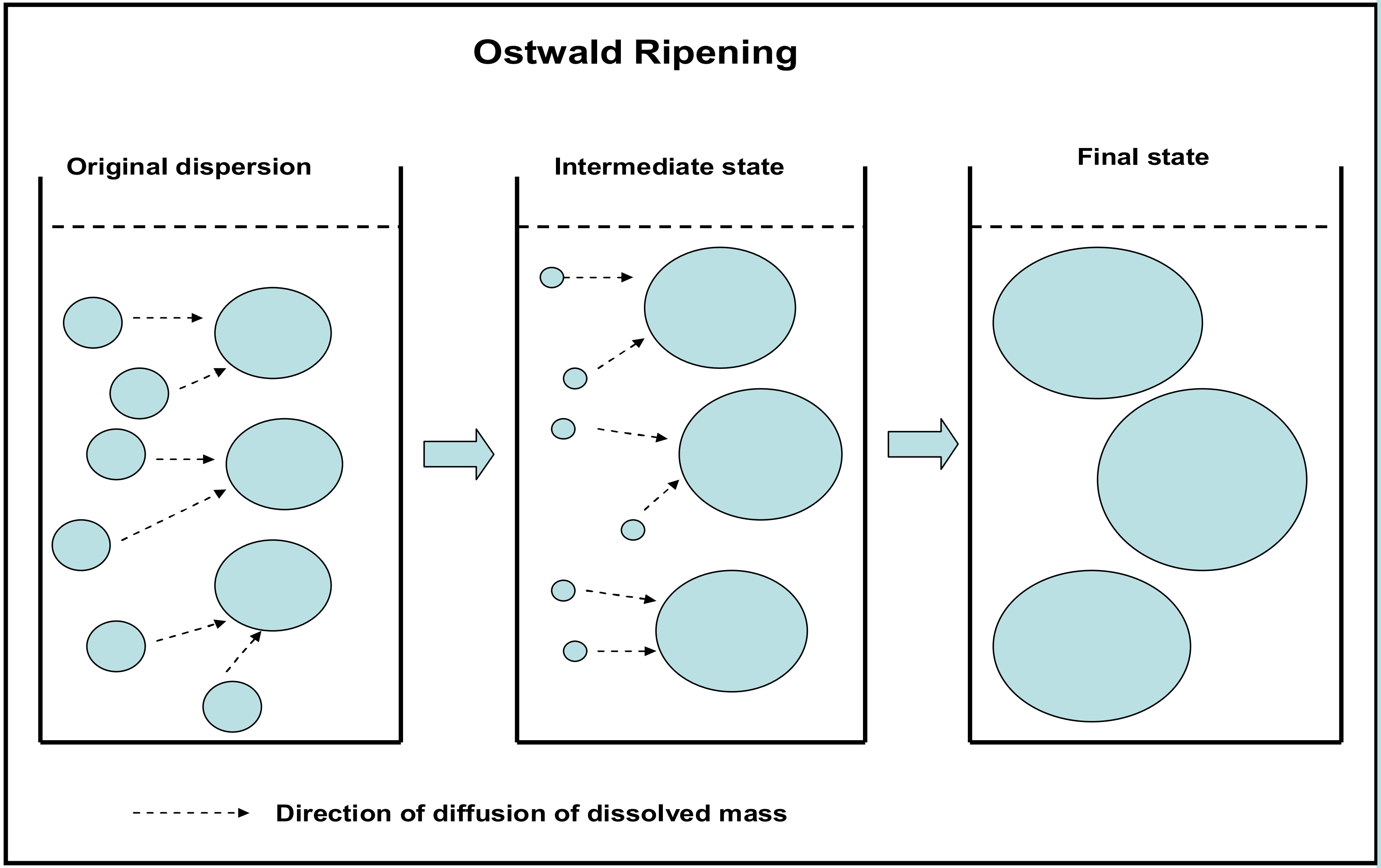
Electronic band gap widens at nanoscale



Surface chemical potential (reactivity) increases at nanoscale



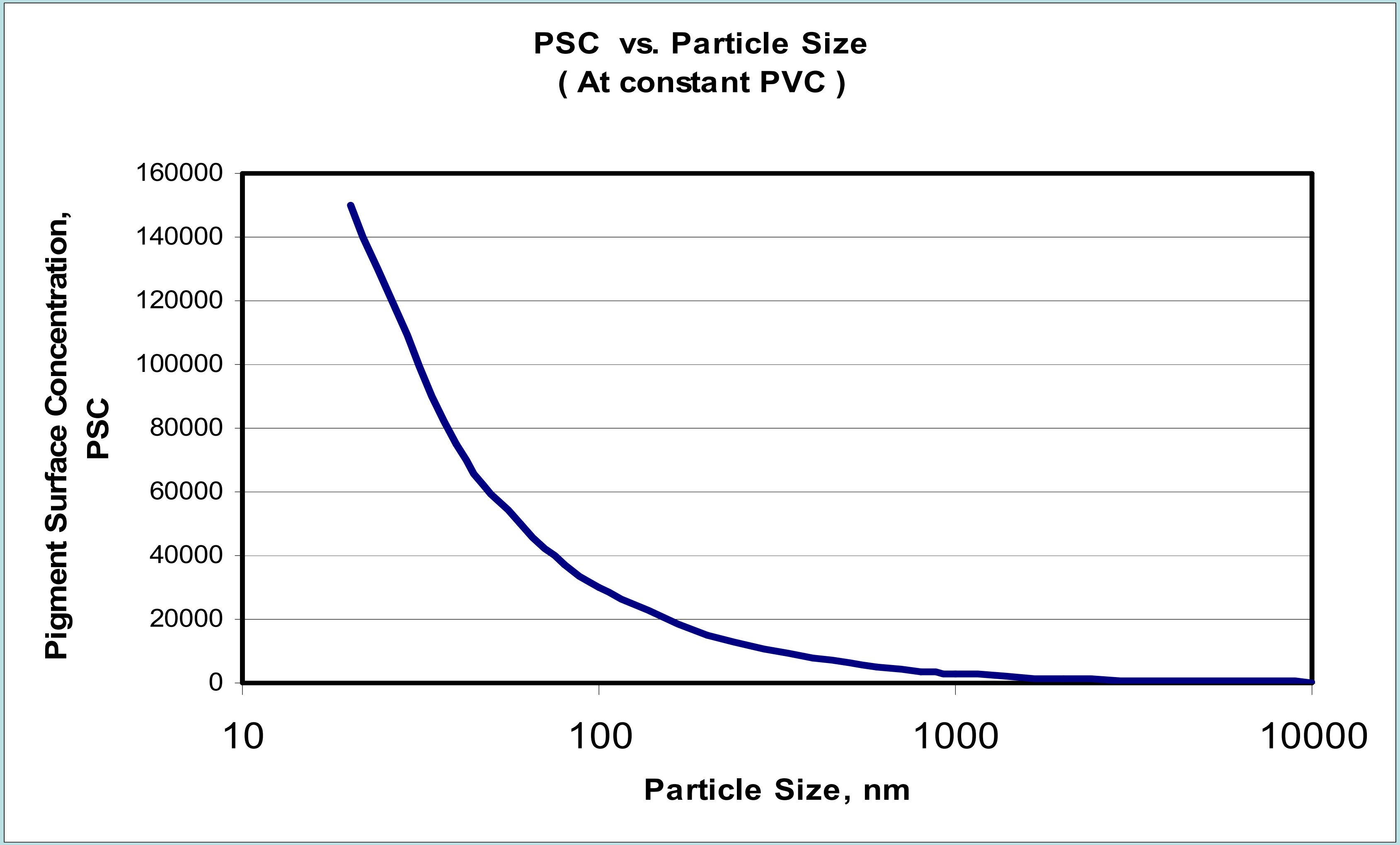
Polydisperse particles coarsen rapidly at nanoscale



Microdispersions vs. Nanodispersions

Parameter	**Micro-dispersion**	**Nano-dispersion**
Particle size	0.2 ~ 2.0 microns	10 ~ 70 nm
Interfacial area	Moderate	Very high
Amount of stabilizer	Moderate : 1~3 %	High 10 ~ 15 %
Rheology (equal PVC)	Mildly pseudoplastic	More pseudoplastic
Color	Original spectral	Blue shift
Sedimentation	Moderate. Often irreversible	Very negligible. Reversible
Stability	Kinetic	Thermodynamic
Centrifugability	Relatively easy	Difficult
Examples	Colourants for paints, Polymer Emulsions	Nano Inkjet printing inks, Nano polymer emulsions

High particle surface concentration requires very low dosage of nanoparticles to alter a property



PSC & Coating Properties

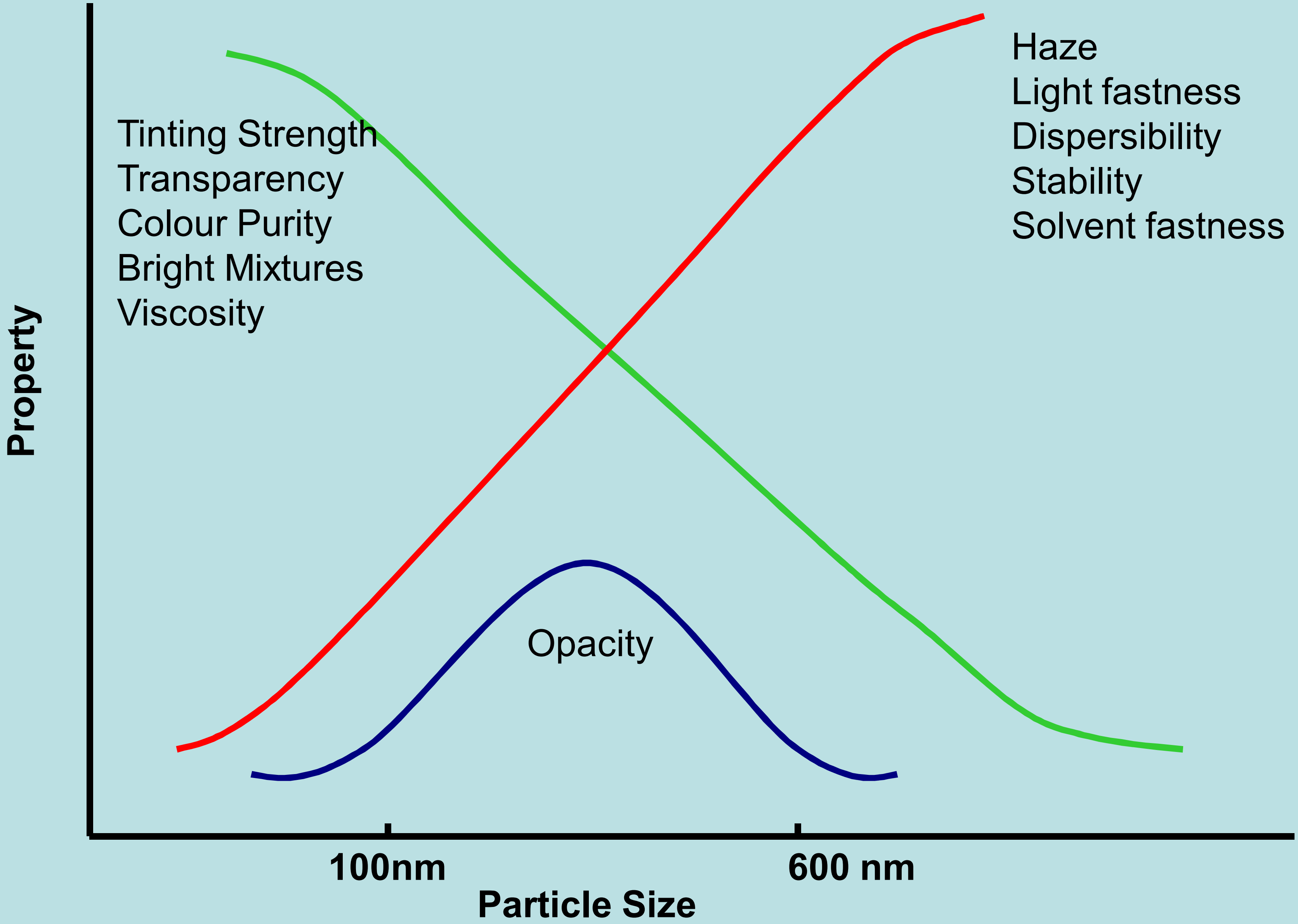
- Optical: Color, Opacity, Gloss
- Photocatalytic: Light fastness
- Mechanical: Hardness, flexibility
- Barrier: Corrosion resistance, Efflorescence, Permeability
- Rheological: Flow leveling, sagging

How do nanopigments differ in properties?

Nanosize Organic & Inorganic Pigments
Conventional :100~300 nm→ Nanо: 30~60nm

Phenomenon	**Property@ nanoscale**	**Effect**
Light Scattering	Transparency	↑
	Colour purity	↑
	Haze	↓
Increased Surface Chemical Potential	Dispersibility	↓
	Stability	↓
	Adsorptivity	↑
	Solvent fastness	↓
Increased surface area	Tinting Strength	↑
	Light fastness	↓
Elimination of crystal defects	Photocatalysis	↑
Increased band gap	Hue shift	Blue shift (Angle dependent)

Change in Properties with Particle Size



Production Methods for Nano-Colorants

Top Down Methods

- Nano-media mills
- Micro fluidics
- Ultrasonic dispersion
- Intercalation

Bottom-up Methods

- Sol- gel Technique
- Reverse Micelle

Applications of nano-colorants dispersions

- Metallic effect paints to get high flip-flop effect: Trans-iron oxides, Nano titania, HP organic pigments
- Transparent stains for wood coatings
- Candy-tone finishes for motorcycles
- Inks for ink-jet printers
- Metal decoration coatings
- Opto-electronics

Which are the novel nano colorants?

- Coloured Metal nanoclusters
- Dye intercalated clays
- Quantum Dots
- Photonic Crystals

Coloured Noble Metal Nanoclusters

- Colloidal gold nanoparticles are Red
- Silver nanoparticles are Yellow
- Have been used for centuries in lithography: stained glass in cathedrals
- Various other applications are being discovered: catalysis, cancer detection

Dye Intercalated Clays

- Smectite clays can be intercalated
- Existence of a gallery or interlayer gap of 1 nm: Inserting other molecules like a dye

- Nano clay pigments: Nano clay particles intercalated with dyes act as bright colored pigments
- Good fastness properties due to shielding by inert layers (Planocolors).
- Devoid of heavy metals like lead, chromium, cadmium and mercury.

Quantum Dots: Concept

- Some of the first commercial nano-colourants
- Semiconductor nanoparticles 2~10 nm (~20 atoms) e.g. CdSe, ZnS, PbS
- Quantum confinement in 3D -> Fluorescence
- Absorption in UV-Vis range & emission in Vis-IR
- Emission wavelength = f (Particle size, Distribution, Temp)
- Emission band is narrow: Bright Colours

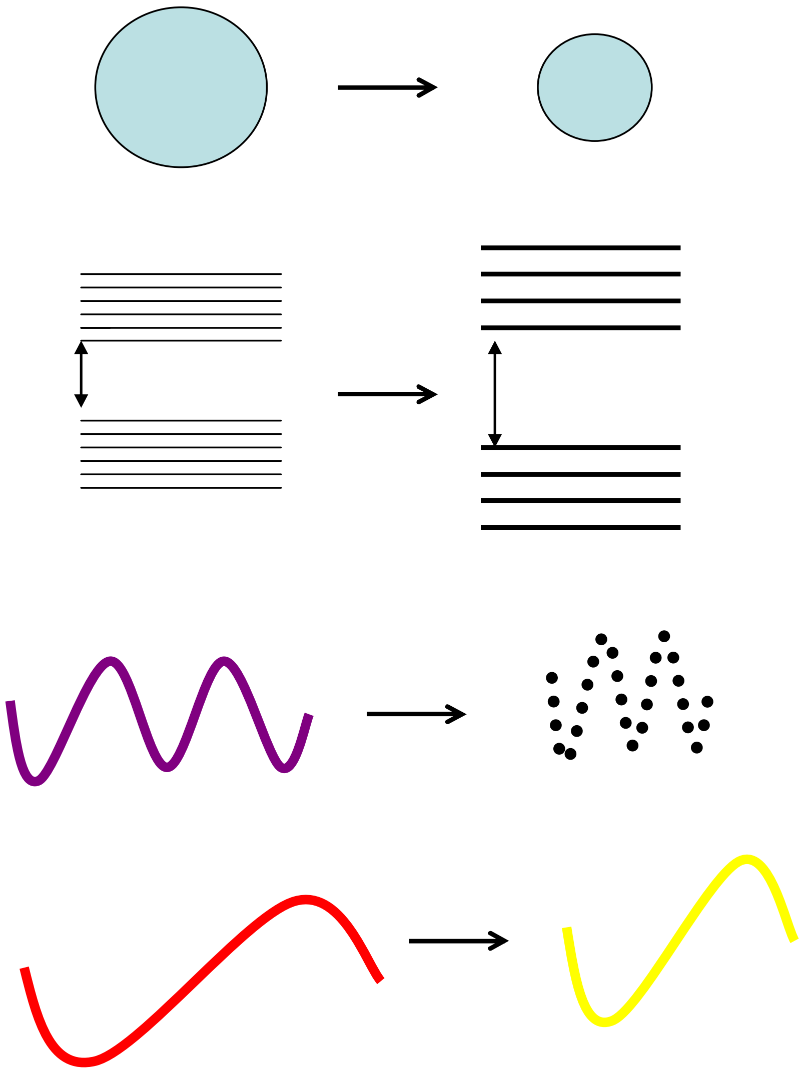
Change of Color with Particle Size in Quantum Dots

Particle size decreases

Band gap widens & levels become discrete

Absorption at shorter wavelength

Emission at shorter wavelength : Change of color



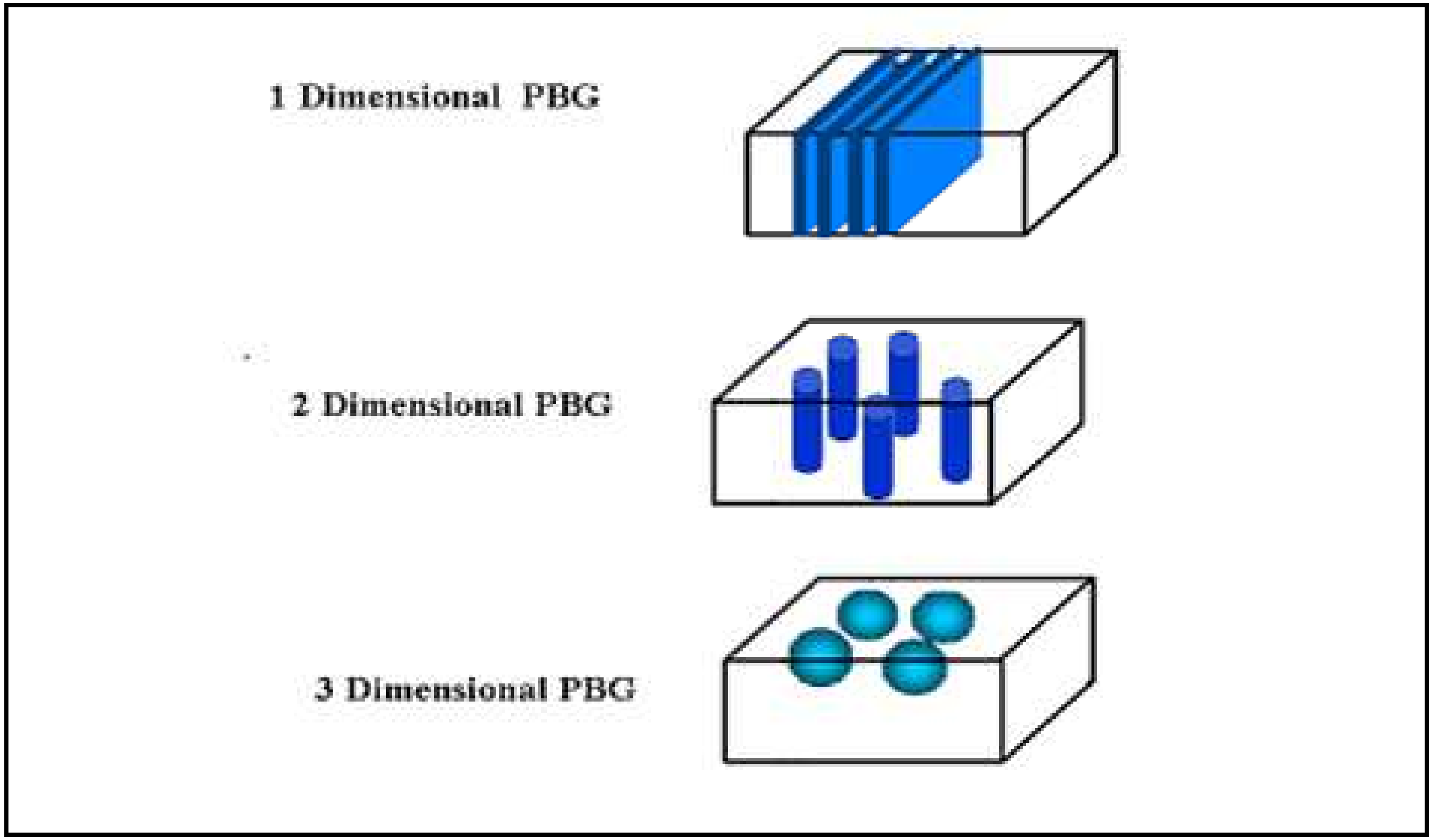
Quantum Dots: Preparation & Uses

- Prepared by colloidal precipitation: Reverse Micelle
- Opto-electronics, displays, LEDs
- Photovoltaic and solar cells
- Security inks: Anti-counterfeiting
- Bright color paints: Selective highlight areas of structures, vehicles, path markings and escape-ways.
- Sighting of the distant objects like tractors in the field and highway markings.
- Night vision paints: Patrolling aid with NVG

Photonic Band Gap (PBG) (Photonic Crystals)

- Spatial periodicity of optically dense and rare domains like gemstone Opal
- Dimension of individual domain ~ wavelength of light
- High contrast of RI between the alternate domains (of the order of 2.5~3.0). Hence the air can be one of the domains.
- Pronounced back scatter followed by interference produces the resultant frequencies or ‘colors’.
- e.g. Chromaflair pigments

Photonic Band Gap 1D, 2D & 3D



Photonic Crystals: Preparation

- Layer by layer nanofabrication
- X-ray lithography
- Laser holography
- Use of di-block copolymers
- Colloidal self assembly
- Thin film coatings

Photonic Crystals: Applications

- 1D photonic band gap are already in use in the form of thin films like colour changing pigments: Chromaflair
- 2D photonic crystals are emerging in the area of communication through photonic crystal fibers.
- 3D photonic dielectrics : Area of intense research; applications in optical computers.

Arthur Clarke's Third Law of Future

"Advanced technologies are
indistinguishable from magic"

Thank you!