

## Size effects in nanomaterials: Theoretical insights

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### Abstract

Nanomaterials exhibit unique characteristic wherein their physicochemical properties are intrinsically linked to their dimensions. This article examines the core principles underlying the size-dependent properties of nanomaterials, linked to the critical length scales, and attributing them to two primary nanoscale phenomena: the inverse correlation between particle size and surface area-to-volume ratio, and the effects of spatial confinement. Additionally, this paper also discusses the mathematical description of gradual size effects through cluster size equations and identifies instances where discrete size effects become apparent, along with a concise overview of categorizing nanomaterials, the methodologies employed in their fabrication and characterization, thereby enhancing our understanding of their properties and prospective utilization in diverse scientific and technological fields.

**Keywords:** Nanomaterials, size effects, critical lengths, quantum confinement, specific surface area and cluster size equation

### Introduction

The exploration of nanoscale phenomena and nanomaterials, commonly referred to as nanoscience, has emerged as one of the most vibrant and interdisciplinary domains within modern scientific inquiry, and it persists in its advancement at an extraordinary pace and across a multitude of trajectories. Nanoscience is a multidisciplinary field characterized by the convergence of various disciplines. This interdisciplinary nature results in fluid topic boundaries subject to constant refinement and adaptation. It has garnered significant attention from the general populace, as nanotechnology has been acclaimed as one of the pivotal technologies of the twenty-first century. The rapid pace of scientific inquiry in nanoscience generates a substantial volume of new knowledge. But the theoretical insights in the size dependence of the properties of nanomaterials are not usually presented in simple and less mathematical way. This review is an attempt to summarize the core principles behind the tuning of the physicochemical properties of nanomaterials in simple way.

The significance of nanomaterials often lies in their size-dependent properties, in which a change in dimensions can fundamentally alter the inherent characteristics of the material. In essence, possessing a nanoscale size is a necessary but insufficient condition. Nanomaterials are defined as materials with at least one characteristic length scale ranging from 1 nm to 100 nm. Additionally, they exhibit at least one property that significantly differs from that of their bulk counterparts owing to their nanoscale dimensions. The burgeoning field of Nanoscience and Nanotechnology is largely driven by the promise that nanomaterials hold for a vast array of applications, including solar energy conversion, optoelectronics, nanophotonics, spintronics, smart coatings, smart catalysts, and biomedical devices. The defining characteristic of nanomaterials that is their size-dependent physical and chemical properties, enables precise engineering of material characteristics not only through chemical composition but also by manipulating the size, shape, and assembly of nanostructures. This unique attribute stems from

the controlled arrangement of individual building blocks such as atoms or smaller nanoparticles<sup>[1-3]</sup>.

Although the macroscopic properties of materials often appear independent of size, at the nanoscale, these properties can exhibit significant deviations from their bulk counterparts. For instance, the colour of gold, typically yellow in its bulk form, can shift to red or even blue when reduced to nanometre dimensions, as illustrated in Fig.1. This phenomenon underscores the importance of size-dependent effects in understanding and manipulating materials at the nanoscale.

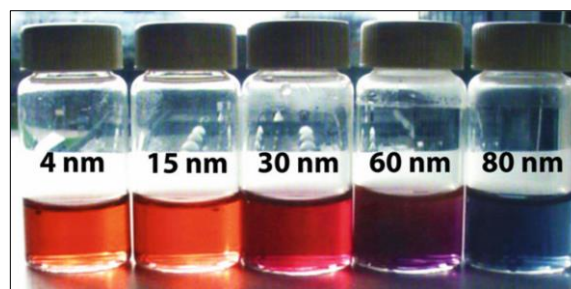


Fig 1: Gold nanoparticles in water<sup>[4]</sup>

In its bulk state, gold is a soft, ductile metal, characterized by a bright yellow colour and a lustrous appearance. It exhibits a relatively high melting point and is known for its chemical inertness. As illustrated in Figure 1, however, gold nanoparticles demonstrate a stark contrast to their bulk counterpart. They exhibit remarkable solubility, readily forming colloidal dispersions in various solvents. When dispersed in transparent media, such as water or glass, these nanoparticles impart intense colours ranging from orange to red, violet, or blue, depending on their size distribution. Furthermore, gold nanoparticles exhibit enhanced chemical reactivity, serving as highly efficient catalysts. A notable characteristic of these nanoparticles is their reduced melting point compared that with of bulk gold. As their size decreases below 50 nm, the melting point progressively diminishes,

reaching values as low as 600 K for nanoparticles with a diameter of 3 nm [5]. This colour changing property is not limited to the metallic particles but it is found in semiconducting materials also. Fig. 2 presents a photograph of the fluorescence emitted by some dispersions of CdSe nanoparticles of varying sizes when exposed to UV radiation in a darkened environment [1].

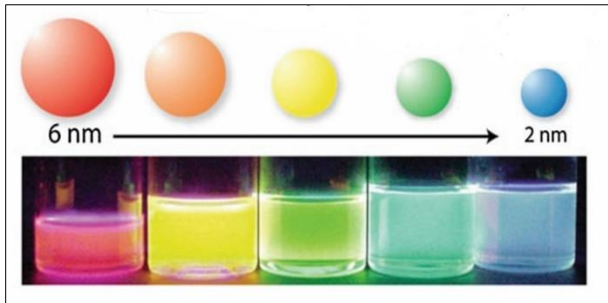


Fig 2: Size-Dependent Fluorescence Properties of CdSe Nanoparticles Dispersions [1]

**Nanoscale Size: An Active Variable!**

In nanoscience, the characteristic length scale of a nanoscale material is a pivotal parameter. This dimension, which is significantly smaller than the other relevant dimensions in the material, defines the unique properties of the system. The

characteristic dimension determines the properties of the system, and is much smaller than the other dimensions encountered in a given material. Thus, the relevant or characteristic size at the nanoscale level becomes an active variable in nanoscience. Table 1 lists the relevant dimensions as active variables for some of the standard shapes studied.

Table 1: Active Length-variables for Standard Geometries

Shapes	Characteristic or Relevant Dimension as Active variable
Nanosphere	Diameter or Radius
Nanosheet	Thickness or Height
Nanowire	Diameter or Radius
Nanocylinder	Diameter or Radius

Each physical phenomenon has a coherence or critical length. When the characteristic length of the sample is comparable to the critical length associated with that property, the physical property is anticipated to exhibit different qualities than those of the bulk state. It is useful to categorize the size of nanocrystals into different regimes specific to different properties, beyond which size dependence would not be relevant. The following table presents some of the critical length scales of the various relevant physical quantities for different phenomena.

Table 2: Critical Length Scales in Various Material Phenomena [6]

Phenomenon	Physical Quantity	Critical Length scale
Thermal	Phonon mean free path	Hundreds of nm at 300 K to very large at low T
Electronic (metals)	Fermi wavelength, $\lambda_F$ ; Scattering length, $l_s$	$\lambda_F \approx 1 \text{ \AA}$ ; $l_s \approx 10 - 100 \text{ nm}$
Fluidic	Boundary layers, molecular dimensions	Always in the low Reynolds number limit: radius of gyration for dissolved molecules
Optical	Half-wavelength of light in medium, $\lambda/2n$	100 - 300 nm
Electronic (semiconductor)	Exciton Bohr radius	$a_B \approx 2 - 50 \text{ nm}$
Magnetic	Range of exchange magnetic field interactions	Exchange interactions: 1-100 $\text{\AA}$ , dipolar interactions, up to microns

Interestingly, the critical length scale for different physical properties and materials is not the same because it relies on both the properties under discussion and the nature of the chemical bonds in the material. The schematic diagram in

Fig. 3 also illustrates this aspect. All the regimes begin essentially with small clusters ( $\geq 1\text{nm}$ ), but their upper boundaries exhibit notable disparities.

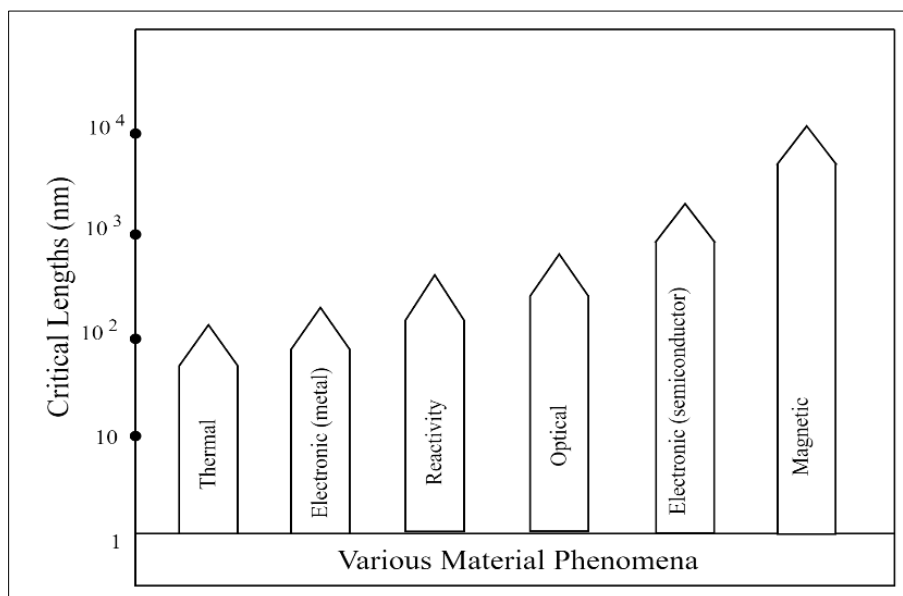


Fig 3: Property Specific Nano-regimes [7]

Atomic quantum clusters (AQC), comprised of a finite number of atoms with dimensions below 1 nm, exhibit nonmonotonic properties that are highly sensitive to their exact atomic composition. In contrast, nanomaterials ranging from 1 to 100 nm display a more gradual variation in properties with size, remaining largely unaffected by the addition of individual atoms. As depicted in Fig. 4, small nanoparticles demonstrate pronounced size effects, while larger particles exhibit a smoother dependence on size, eventually converging towards bulk behaviour. This transition from discrete to continuous size-dependent properties is evident in a variety of nanoparticle characteristics, including the thermal, electronic, optical, mechanical, magnetic, and chemical properties. Thus, the size effects fall into two categories.

- **Specific Size Effects:** These involve self-selection and the existence of “magic numbers” for small and moderately sized clusters and nanostructures. A property  $\chi(N)$ , which depends on the number of constituents ( $N$ ), exhibits irregular variations as the size of the nanostructure increases. Consequently,  $\chi(N)$  does not follow a predictable size-scaling behaviour.
- **Smooth Size Effects:** For large nanostructures, a quantitative model can be developed to describe the

transition of their physical and chemical properties towards those of the bulk material. This transition can be expressed using size equations in terms of the number of atoms, represented by the following equation, known as the Cluster Size Equation

$$\chi(N) = \chi(\infty) + BN^{-\beta}$$

Here,  $\chi(\infty)$  denotes the property of the infinite bulk system,  $B$  is a constant, and  $\beta$  is a positive exponent. By adopting a spherical cluster model, where an  $N$ -atom cluster is approximated as a sphere of radius  $R$ , this smooth transition can be described by a simple scaling law expressed in terms of the cluster radius:

$$\chi(R) = \chi(\infty) + AR^{-\alpha}$$

In this equation,  $A$  is another constant and  $\alpha$  is again a positive exponent. Many, but not all, properties of a cluster depend on the ratio of surface to bulk atoms. This ratio is proportional to  $(1/R)$ . Consequently, the exponents  $\alpha$  and  $\beta$  are commonly 1 and  $1/3$ , respectively. These equations are based on the principles of cluster packing and excluded volume effects.

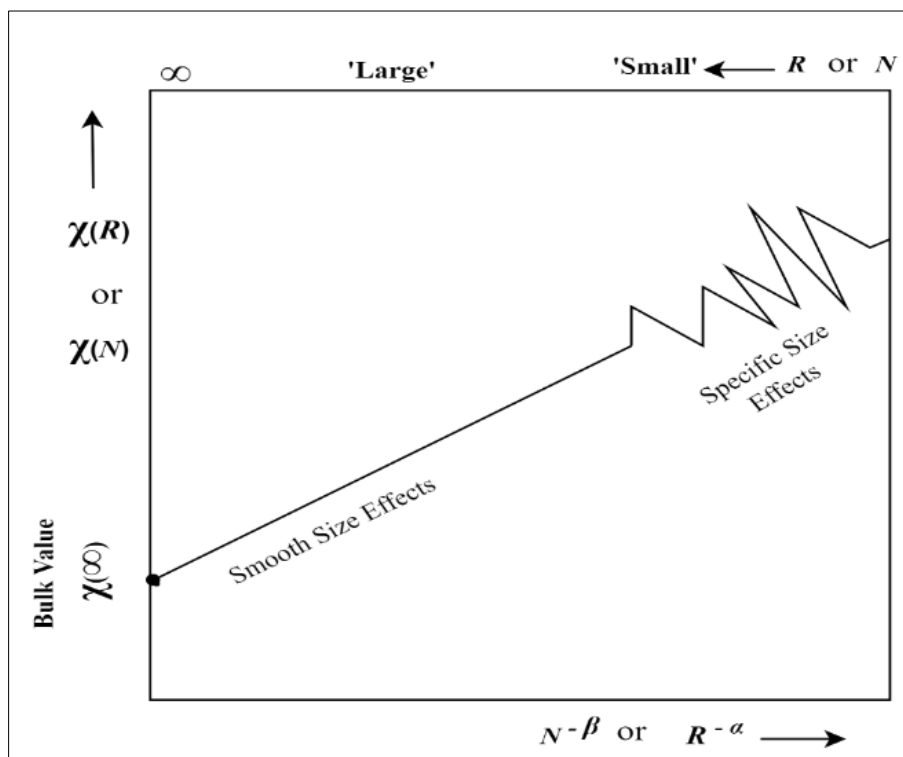


Fig 4: The cluster size dependence of a cluster property  $\chi(N)$  or  $\chi(R)$  [8]

The observed size-dependent properties of nanomaterials, as illustrated in Fig. 4, can be attributed to two primary nanoscale phenomena [1-3, 5]. First, as the particle size decreases, the proportion of surface atoms to bulk atoms (surface-to-volume ratio) significantly increases. Secondly, the constrained dimensions of nanomaterials introduce spatial confinement effects that can influence a wide range of material properties. These finite-size effects are comprehensively explored in the subsequent subsections.

**Spatial Confinement: Reduction in the degrees of freedom:** The phenomenon of spatial confinement, a direct

result of the quantum mechanical behaviour of matter, becomes increasingly pronounced as the dimensions of a system decrease below a critical length scale. While macroscopic objects, composed of a vast number of atoms (e.g., a 1  $\mu\text{m}$  gold particle containing approximately  $10^{11}$  atoms), exhibit classical behaviour, quantum effects become more prominent at nanoscale dimensions.

It is important to note that this critical length scale varies depending on specific physical properties and material composition. For instance, the transition from mesoscale to nanoscale behaviour is not identical for different materials or properties. The most dramatic manifestation of quantum

effects occurs at length scales of 0.1-1 nm, where quantum properties dominate. However, long-range electromagnetic interactions within the 10-100 nm range can significantly influence certain properties. Consequently, the impact of spatial confinement is not uniform across materials or properties. For example, confinement effects on the magnetic properties of nanoparticles only become apparent when their dimensions approach or exceed the critical magnetic single-

domain size, which typically ranges from 20 to 100 nm depending on the material [9, 10]. Furthermore, in the case of semiconductor nanoparticles, such as CdSe, the relevant length scale is the exciton Bohr radius, a dimension characterizing the spatial extension of excitons (i.e., electron-hole pairs) in solids, which ranges from 2 to 50 nm depending on the material [2].

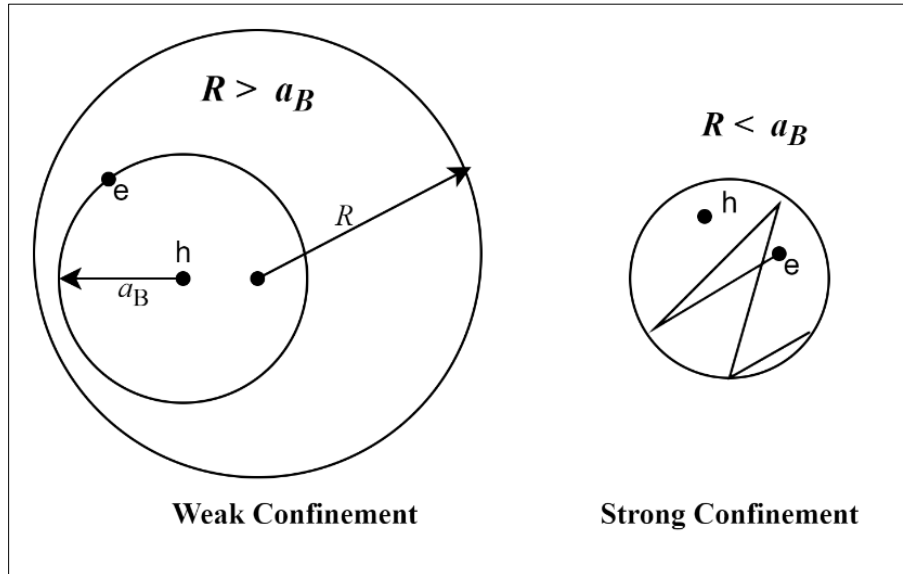


Fig 5: Spatial confinement in a nanoparticle [11]

Three distinct quantum confinement regimes are postulated based on the relative magnitudes of the nano-crystallite radius ( $R$ ) and the bulk exciton Bohr radius ( $a_B$ ) as illustrated in Fig. 5. In the strong confinement regime ( $R/a_B \ll 1$ ), the Coulomb electron-hole interaction is negligible compared to confinement energies, allowing for the treatment of electrons and holes as independent particles. Conversely, in the weak confinement regime ( $R/a_B > 1$ ), the electron and hole motions are strongly correlated due to the Coulomb interaction. The intermediate confinement regime ( $R/a_B \sim 1$ ) is characterized by a delicate balance between quantum confinement and electron-hole interactions, governing the underlying physical processes. As the size of semiconductor nanoparticles approaches the exciton Bohr radius, confinement effects become increasingly pronounced, leading to modifications of the exciton wavefunction and electronic states. This effect is known as quantum confinement. It manifests experimentally as a systematic increase in bandgap energy (blue shift) with decreasing nanoparticle size.

The optoelectronic properties of semiconductor nanoparticles exhibit a strong dependence on their size and shape due to spatial confinement effects. This allows for precise tuning of photoluminescence across a broad spectral range by carefully selecting the nanoparticle composition, size, and morphology. The relationship between emitted photon energy ( $\Delta E$ ) and particle radius ( $R$ ) is generally described by a power law equation:

$$\Delta E = E_0 + \frac{K}{R^\gamma}$$

Where  $E_0$  and  $K$  are constants, and  $\gamma$  is typically a non-integer exponent [11]. The non-integer nature of  $\gamma$  can be attributed, in

part, to the presence of particle size distributions rather than a single, well-defined size.

In contrast to semiconductors, optical excitations in metals do not result in the formation of excitons. Instead, they induce collective oscillations of the free electron gas, known as plasmon resonances. Consequently, the relevant length scale for observing spatial confinement effects on the optical properties of metals is the free electron mean free path. For gold, this characteristic length is approximately 50 nm [5].

Atomic quantum clusters (AQC) exhibit unique and intriguing properties that deviate from the size-dependent behaviour observed in larger metal nanocrystals. This arises when the nanoparticle dimensions approach the Fermi wavelength of an electron, leading to the formation of a bandgap at the Fermi level. This bandgap results from quantum mechanical effects and transforms metal AQC into atomic-level semiconductors. Unlike larger nanocrystals, the properties of AQC cannot be solely attributed to an increase in surface area but rather stem from these novel electronic characteristics. For metal particles comparable to the Fermi wavelength, continuous energy bands transform into discrete energy levels, separated by the Kubo gap [12]. This gap is predicted to depend on the number of electrons ( $N$ ) within the cluster, following the relation [7, 13, 14].

$$\delta = \frac{4E_F}{3N}$$

Where  $E_F$  represents the Fermi energy. The Kubo gap corresponds to the inverse of the average density of electronic states at the Fermi energy for a single spin. In approximately spherical particles with radius  $R$ , the level spacing scales as  $R^{-3}$ , reflecting the proportionality between the density of electronic states and volume.

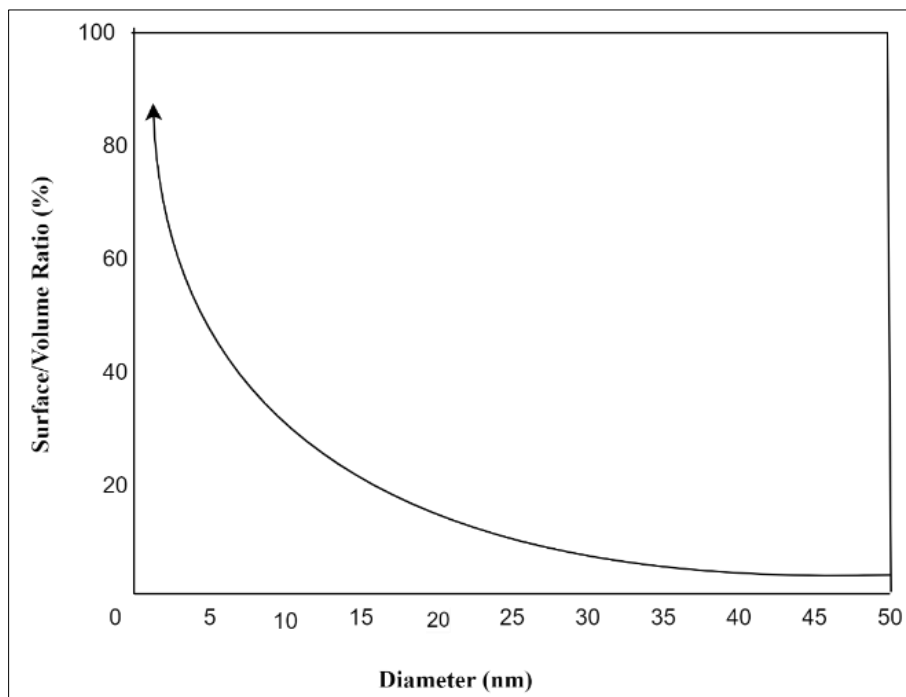
### Higher Specific Surface Area: Surface as a Special State of Matter

As the size of nanoparticles diminishes, there is a corresponding decrease in the total number of atoms present (e.g.,  $1 \times 10^7$ ,  $1 \times 10^4$ , and 100 for nanoparticle radii of 50 nm, 5 nm, and 1 nm, respectively), while the proportion of atoms situated at the surface increases (Fig. 6) [1-3]. This phenomenon can be attributed to a scaling effect; specifically, the surface-to-volume ratio of an object with a fixed amount of material escalates as its dimensions decrease. For instance, the surface area of a sphere varies with the square of its radius  $R$ , whereas its volume varies with  $R^3$ . Consequently, since the total number of atoms in a nanoparticle scales linearly with its volume, the fraction of atoms located at the surface of a spherical nanoparticle scales inversely with its

radius. This relationship similarly applies to elongated cylinders with radius  $R$  and to thin plates with thickness  $d$ . It can be further mentioned that for a fixed volume of a nanomaterial, the number of the surface atoms also depends on the shape thereby affecting the surface to volume ratio. The fraction of atoms on the surface of the particle ( $P_s$ ) can be approximated using the simple relation,

$$P_s = 4N^{-1/3}$$

where  $N$  is the total number of atoms in the particle [7]. This formula effectively captures the increasing dominance of surface atoms as the particle size decreases, highlighting the enhanced surface effects in nanoscale material.



**Fig 6:** Surface to volume ratio for spherical gold nanoparticles

The enhancement of the surface-to-volume ratio significantly influences various properties of nanoparticles, primarily due to the distinct characteristics of surface atoms compared to those located within the particle's interior. Surface atoms have fewer neighbouring atoms, resulting in unsatisfied chemical bonds, commonly referred to as dangling bonds. This leads to an increase in their free energy, reactivity, and mobility. As nanoparticle size diminishes, the influence of surface atoms on the overall free energy and properties of the nanoparticles becomes more pronounced. This shift results in several alterations: a decrease in melting and evaporation temperatures, alongside an increase in reactivity, elasticity, and plasticity. Furthermore, the increased surface area enhances the nanoparticles' ability to form stable colloidal dispersions through mechanisms such as charge or steric stabilization. The surface can be conceptualized as a unique state of matter, which has significant implications; notably, it facilitates the dispersion of nanoparticles in solvents, thereby enabling fabrication and processing in solution. The pronounced contribution of the surface may also induce modifications in interatomic distances—either contraction or expansion—and bond angles, potentially stabilizing crystal structures that are metastable compared to their bulk

counterparts or leading to global structural reconfiguration. Additionally, it is important to recognize that the presence of dangling orbitals on the surface of semiconductor nanoparticles introduces energy levels within the bandgap. This phenomenon adversely affects the photoluminescence quantum yield by promoting non-radiative recombination of excitons. To mitigate these effects, it is crucial to address the presence of dangling bonds on semiconductor nanoparticle surfaces through a process known as surface passivation. This can be accomplished by either overgrowing a shell of a semiconductor with a wider bandgap or by applying suitable organic ligands to coat the surface.

All properties that are influenced by the surface-to-volume ratio exhibit a continuous change and gradually approach bulk values. Prominent phenomena observed in nanomaterials, such as magnetic surface effects in magnetic nanoparticles and super-paramagnetism, as well as size-dependent surface plasmon resonance and melting points, are primarily scalable effects resulting from the significant surface-to-volume ratio of lattice ions in small particles. These properties exhibit a smooth scaling behaviour, demonstrating that the influence of surface ions varies



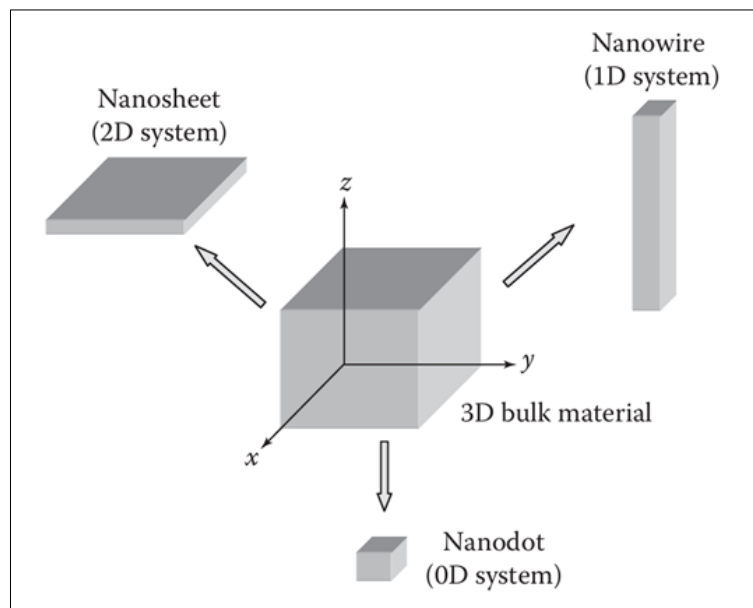
inversely with particle size and progressively approaches bulk values.

The discrete energy levels and shell-like characteristics, referred to as magic numbers, observed in atomic quantum clusters arise from quantum confinement effects. These effects become significant when the dimensions of the particle fall below critical physical lengths, mentioned in the Table 2. Quantum phenomena are particularly pronounced in smaller clusters and frequently overlay a smoothly varying background of scalable effects.

### Types of Nanomaterials

In nanomaterial classification, the concept of dimensionality plays a crucial role. Dimensionality pertains to the number of spatial directions in which a material extends beyond a

specific length scale. Zero-dimensional (0-D) nanomaterials, such as nanoparticles and nanopores, are confined to dimensions smaller than 100 nm in all directions. In contrast, one-dimensional (1-D) nanomaterials, like nanorods, nanowires, and nanotubes, are constrained to less than 100 nm in two directions. Two-dimensional (2-D) nanomaterials, including thin films and nanoplates, have dimensions below 100 nm only in their thickness. It is important to note that the relevant length scale is not universally set at 100 nm, as it can vary depending on the material and the specific property being considered. For instance, a CdSe nanoparticle with a diameter of 50 nm would be regarded as bulk-like, or three-dimensional, from the perspective of the exciton due to the exciton Bohr radius of CdSe being only 3.5 nm.



**Fig 7:** Dimensionality of Nanomaterials

Nanomaterials may also include larger objects that possess nanoscale features either within their structure or on their surface. Such materials are commonly termed nanostructured materials. A notable example of this category is nanoporous materials, where the overall size of the material is significantly larger than 100 nm, yet the pores themselves exist at the nanoscale. Nanomaterials cover a broad spectrum of compounds and can be classified into various types. For example, proteins, enzymes, and DNA meet the aforementioned criteria and are often classified as bionanomaterials.

Nanoparticles can exist in various forms, including as free-standing entities (either in colloidal suspension or as dry powders), supported on solid substrates, or embedded within a bulk matrix of a different material. The nanoparticles in colloidal form are often specifically termed "nano colloids." Moreover, handling collections of free-standing individual nanoparticles can be challenging, which is why supported nanoparticles are frequently synthesized. For optical applications, nanoparticles are often embedded within a transparent matrix, such as polymers or glass, to create nanocomposites. Additionally, colloidal nanoparticles can serve as fundamental building blocks for nanoparticle solids or superlattices, which hold great potential for thin-film applications.

### The Nanoscale Tool Kit

#### Techniques for Fabricating Nanomaterials

Nanomaterials can be synthesized through a variety of techniques, which are generally categorized into two main approaches<sup>[15]</sup>:

- 1. Top-down methods:** Where larger materials are systematically reduced to create nanostructures. This approach includes techniques like lithography, which utilizes electron beams, ion beams, or X-rays to remove material. Lithography is extensively employed in the semiconductor industry for the production of integrated circuits and optoelectronic devices. Additionally, top-down methods can involve breaking down larger particles into progressively smaller ones until reaching the nanoscale, such as through high-energy ball milling, a process commonly used to produce nanomaterials in powdered form.
- 2. Bottom-up methods:** Where smaller building blocks, such as atoms or molecules, are assembled into larger structures that eventually reach the nanoscale. These methods can be performed in various ways, producing a wide range of nanomaterials. Common techniques in this category include vapor-phase deposition, the Vapor-Liquid-Solid (VLS) method, and liquid-phase synthesis techniques.

### Techniques for Investigating Nanomaterials

The interdisciplinary nature of Nanoscience is evident in the diverse array of techniques employed to explore and comprehend the characteristics of nanomaterials.

The dimensions and morphology of nanomaterials can be analyzed through Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron Microscopy (HRTEM). Additionally, X-Ray Diffraction (XRD) serves to identify the crystal structure of nanomaterials, while also providing insights into their size.

Surface characterization methods traditionally applied to bulk materials, such as X-Ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectroscopy (RBS), possess penetration depths that align with the typical dimensions of nanomaterials, thus offering comprehensive information regarding the entire nanostructure [1]. The internal strain and disorder within nanomaterials can be directly assessed through a combination of Small-Angle X-Ray Scattering (SAXS) and High-Energy Wide-Angle X-Ray Scattering (WAXS) techniques, as well as Extended X-Ray Absorption Fine Structure (EXAFS).

Moreover, Scanning Tunnelling Spectroscopy (STS) is an effective method for elucidating the electronic energy levels of nanomaterials, demonstrating its applicability to both metallic and semiconductor types.

### Concluding remarks

The preceding overview serves to provide a glimpse of the causes of the size dependence of nano structured materials. Each physical property is associated with a specific coherence or critical length. When a sample's characteristic dimension becomes comparable to this critical threshold, its physical properties may deviate significantly from those observed in bulk materials. The size-dependent properties of nanostructured materials can be attributed to two primary nanoscale phenomena: increased specific surface area and spatial confinement. These effects, when combined, give rise to the unique characteristics observed in nanomaterials at varying dimensions.

Size effects in nanomaterials can be broadly categorized into two types: those specific to particular species and those exhibiting smooth transitions with size. The latter category can often be described using cluster size equations. In metallic nanostructures, the discretization of energy bands leads to the formation of atomic quantum clusters.

To advance the field of nanomaterials and capitalize on its immense potential, it is crucial to develop simple yet reliable cluster size equations. These equations would enable researchers to predict the size-dependent physicochemical properties of nanomaterials more accurately, thereby facilitating their practical applications and further scientific exploration.

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