Chapter

Quantum Confinement Effect of 2D Nanomaterials

Gopal Ramalingam, Poopathy Kathirgamanathan, Ganesan Ravi, Thangavel Elangovan, Bojarajan Arjun kumar, Nadarajah Manivannan and Kaviyarasu Kasinathan

Abstract

Quantum confinement is the spatial confinement of electron–hole pairs (excitons) in one or more dimensions within a material, and also electronic energy levels are discrete. It is due to the confinement of the electronic wave function to the physical dimensions of the particles. In this effect can be divided into three ways, 1D confinement (free carrier in a plane), quantum wells; 2D confinement (carriers are free to move down), quantum wire; and 3D confinement (carriers are confined in all directions), which are discussed in detail. In addition the formation mechanism of exciton and quantum confinement behavior of strong, moderate, and weak confinement have been discussed below.

Keywords: quantum dots, energy level, exciton, confinement, Bohr radius

1. Introduction of quantum confinement

The term "quantum confinement" mainly deals with energy of confined electrons (electrons or electron hole). The energy levels of electrons will not remain continuous as in the case of bulk materials compared to the nanocrystals. Moreover, obtaining the confined electron wave functions, they become a discrete set of energy levels as shown in **Figure 1**. Such kinds of effects appear when the dimensions of the potential approach near to *de Broglie wavelength* of electrons resulting in the changes or discrete levels of energy. The effects are defined as quantum confinement and consequently, for nanocrystals, are often called quantum dots (QDs). Furthermore, this quantum dot effect has an influence in the nanomaterial properties such as electrical, optical, as well as mechanical behavior of the material. It is due to its peculiar nature why nanomaterials possess higher energy electrons than the bulk materials. Depending on the QD size, confined electrons have higher energy than the electrons in bulk materials. The semiconductor nanomaterials exhibit fascinating properties when reducing their dimensionality from 2D to 1D or 1D to 0D. Perhaps, the quantum confinement effect occurs when reducing the size and shape of nanomaterials less than 100–10 nm or even lesser. These changes due to the discrete set of electron energy levels lead to size confinement [1–3] (**Figures 1** and **2**).

In order to understand to know more about quantum confinement, it is necessary to understand the phenomenon of quantum dots (QDs). QDs are the new class of materials in which quantum confinement effects can be evident. QDs are very tiny semiconductor crystals in the order of nanometer size, and also molecules are tightly confined electrons or electron–hole pairs called "excitons" (explained in

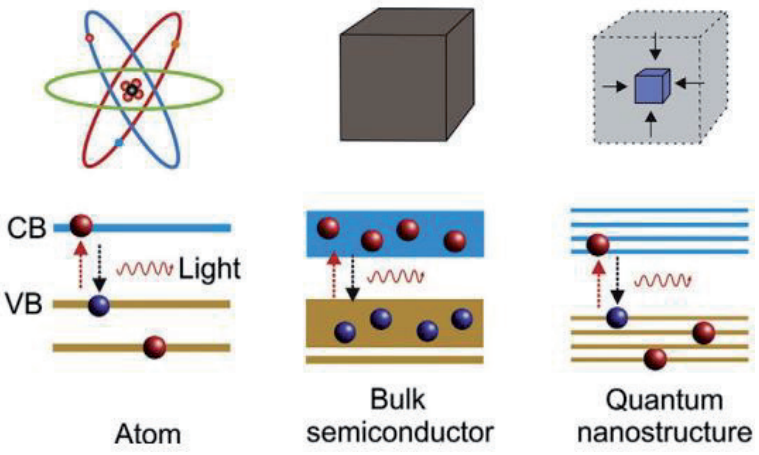

Figure 1.
Schematic diagram showing energy band structures in atom, bulk semiconductor, and quantum nanostructure.

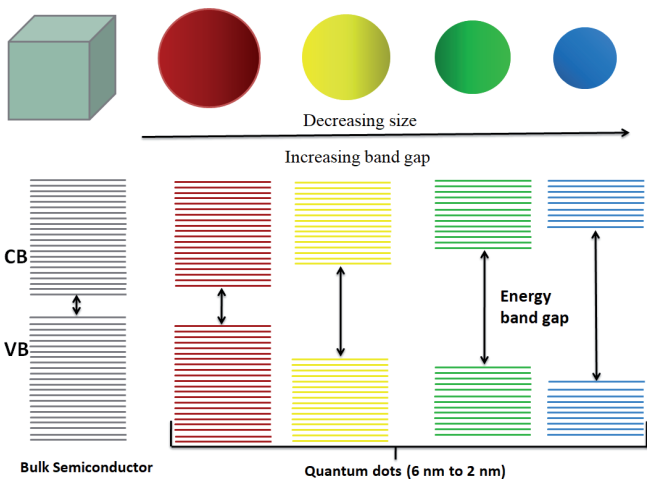

Figure 2.
Schematic diagram showing energy band structures in atom, bulk material, and quantum nanostructure.

the next section) in all three dimensions. QDs are a subatomic group in the family of nanomaterials, which comprises metals, insulators, semiconductors, and organic materials. It's well-known that the quantum confinement occurs only in semiconductor quantum dots because of their tunable bandgap nature than the zero bandgap in metals respectively. As mentioned before the peculiar tunable band gap properties QD are composed only of group II–VI-, III–V-, and IV–VI-based materials. The optical, electrical, and bandgap properties are tunable with respect to changes in particle size that lead to different multiple applications.

The main discussion is that, how bandgap can be tuned with respect to size? For that we need to understand the formation of discrete energy levels and the formation of excitons.

2. Formation of discrete energy level

To understand or recall the formation of discrete energy level, when atoms are brought together in a bulk material, the number of energy states increases

substantially to form nearly continuous bands of states. And also decreasing trend occurred in the amount of atoms in the material, and energy states were delocalized with confinement nature. The phenomena create electron-hole pairs and spatially confined nature when the particles move toward the natural *de-Broglie wavelength* of electrons in the conduction band. As a result the energy difference between energy bands is increased with decreasing particle size dimension as shown in **Figure 3**.

Particle behaves like a free particle when the dimensions of the confining structure are very large in comparison to the *de Broglie wavelength*. On this stage, the energy states are continuous, and the bandgap comes to its original position, and another energy spectrum does not remain continuous and becomes discrete in nature when the dimensions of confining structure is decreased toward nanoscale. Therefore, the bandgap exhibits size-dependent properties and eventually causes a blue shift in the emitted light as the particle's size is decreased. However, this effect demonstrates the consequences of confining the electrons and electron-hole pair

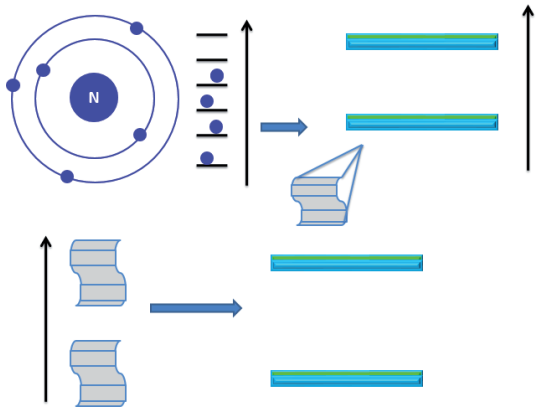

Figure 3.
Schematic diagram for the formation of discrete energy levels.

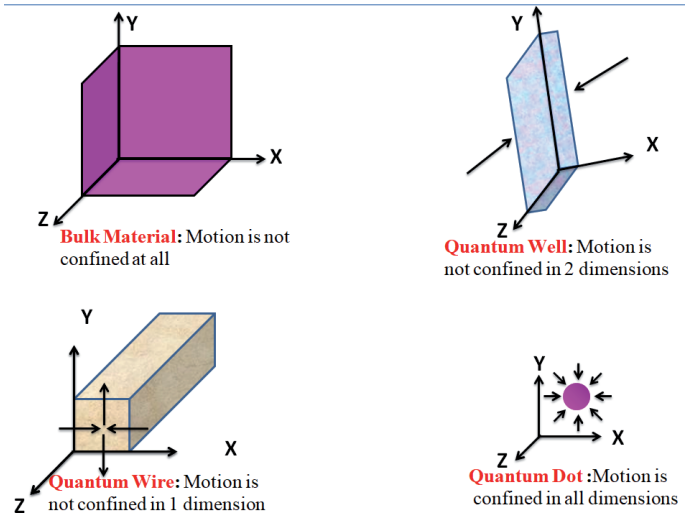

Figure 4.
Schematic representation of quantum confinement in all three directions.

(or the excitons) within a dimension which approaches the critical quantum limit, often termed as the Bohr exciton radius.

In this view, a quantum dot confines in all the three dimensions; a quantum wire (nanowire) confines in two dimensions; and a quantum well confines only in one dimension. The corresponding structures are also termed as zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D) potential wells, respectively, with regard to the number of dimensions in which the confined particle has freedom of movement. **Figure 4** shows the overview of quantum confinement in nanostructures.

- Electrons confined in one direction, i.e., **quantum wells** (thin films)**:** Electrons can easily move in two dimensions (**2D**), so one dimensional is quantized.

- Electrons confined in two directions, i.e., **quantum wires**: Electrons can easily move in one dimension (**1D**), so two dimensional is quantized.

- Electrons confined in three directions, i.e., **quantum dots**: Electrons can easily move in zero dimension (**0D**), so three dimensional is quantized.

In conclusion, each confinement direction changes a continuous k component to a discrete component characterized by a quantum number n.

3. Formation of excitons

It is very important and necessary to understand the concept of excitons as it is the primary step to understand QDs and quantum confinement in semiconductors. In the case of semiconductor, electrons were shifted from valence band to conduction band when emitting light falling on it, and consequently recombination effect imposes or creates the photon particle. The electron and hole were occupied or created from conduction band and valence band, respectively. However, the charge of hole is equivalent to the electron charge which is helping the implementation of one particle named as excitation. In the abovementioned charges and coulomb exchange interaction, there is an attractive connection between the electron and the hole. Such kind of electron-hole pair is sometimes expressed in a simple term as quasiparticle which is named exciton. It is an electrically neutral quasiparticle that occurs in insulators, semiconductors, and some liquids.

In solid-state physics, the bandgap/energy bandgap is separated between the finite energy level of conduction and valence band. When an electron from the valence band attains sufficient energy to overcome the energy gap, due to thermal excitation or absorption of a photon, and its goes to the conduction band, a hole is created on the left behind on the valence band. The created hole is moving to conduction band; this is formed as an excited electron; the charge carrier in semiconductor device recombines with the hole after the release of energy. The combination between the electron and hole pair combination leads to the formation of excitons.

Because of the different polarity charges and the coulomb force exchange interaction, there is an attractive connection between the electron and the hole, and by a simple way, the electron-hole pair is called as a quasiparticle which is named *exciton*. Due to combination of electron and hole, the resulting neutral quasiparticle nature exits into different material natures like semiconductor, insulator, and some liquids. Furthermore this exciton transports the energy without compromising net electric charge as per condensed matter theory.

However, there is a major difference. Excitons have an average physical separation between the electron and hole, referred to as the exciton Bohr radius. This physical distance is different in each material. In the case of semiconductor nanocrystal (SNC) (QDs), the size of the particles is lesser than the Bohr radius; the electron excited by an external energy source tends to form a weak bond with its hole. This bound state of electron and electron hole, which are attracted by the electrostatic coulomb force, is often called an exciton which is shown in **Figure 5A**, **B**.

Thus, the Bohr radius is the distance in an electron–hole exciton, also called the exciton Bohr radius [4]. Every semiconductor material has a characteristic exciton Bohr radius (**Figure 5C, D**) in which the quantum confinement effect is realized. This unique confinement property causes the "band" of energies to turn into discrete energy levels in QDs (**Figure 6**).

3.1 Excitons

In general the quantum mechanical behavior of semiconductor particle, let us consider the materials in an electron which is stimulated from valence band to conduction band (**Figure 7**).

The valance band left behind electron is a 'hole', which can be thought of as a particle with its own charge (+1) and effective mass. The bound states of electron and hole are considered to be quasiparticles known or called as "exciton." Electron–hole pair formation is due to coulombic attraction. The exciton can be considered as a hydrogen-like system, and the exciton radius is easily compared with Bohr radius approximation which is used to calculate the spatial separation of the electron–hole pair:

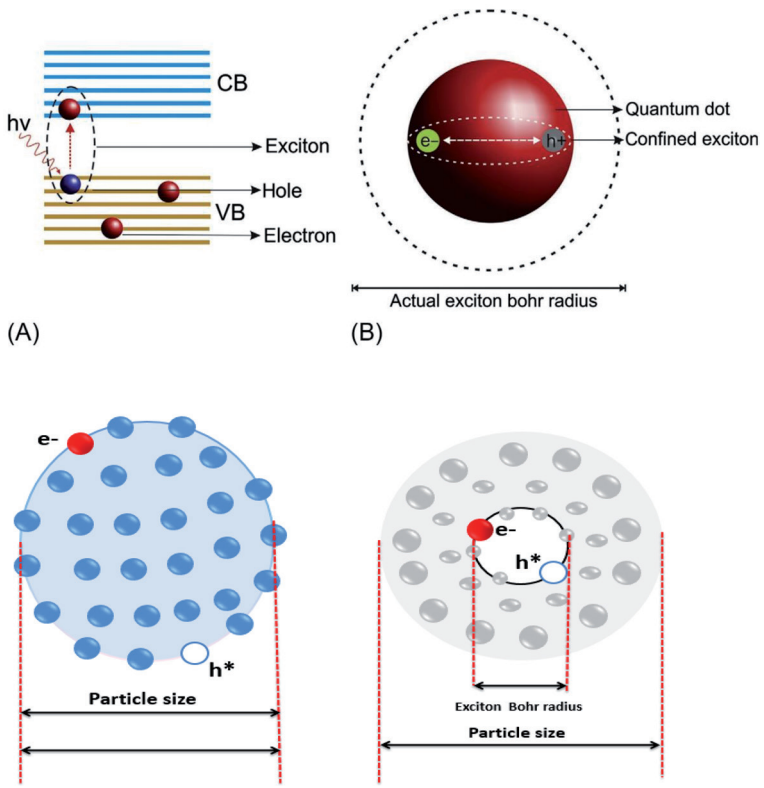

Figure 5.
(A) Formation of excitons. (B) Comparison of exciton radius and QD size.

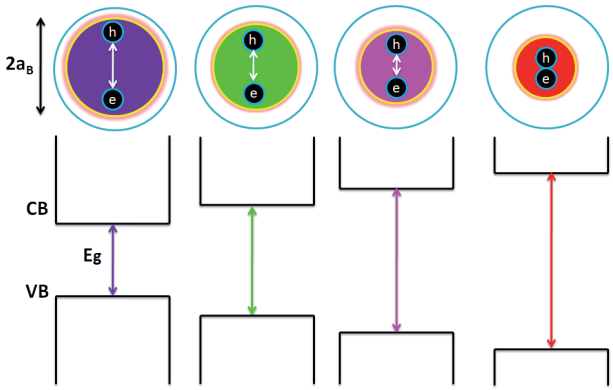

Figure 6.
Quantum confinement in semiconductor crystal.

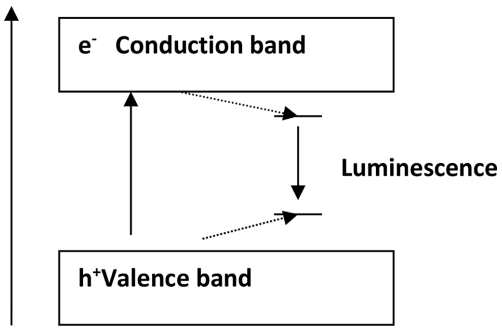

Figure 7.
Energy-level diagram showing promotion of an electron from valence band to the conduction band leaving a hole behind.

$$r = \frac{\varepsilon h^2}{\pi m_r e^2} \tag{1}$$

where r is the radius of a three-dimensional sphere containing excitation, m_r is the reduced mass of the excitation, ε is the dielectric constant of the given material, e is the charge of the electron, and h is Planck's constant. Ion cyclotron resonance is a powerful technique to find the effective mass of the hole and electron with a range of 0.1–3 m_e (m_e is the mass of the electron). Furthermore, the empirical radius and mass calculation suggest that the electron-hole pair spatial separation is around about 1–10 nm for most of the semiconductors.

4. Quantum confinement effect

In literature, semiconductor quantum dots are also known as semiconductor nanocrystals or nanoparticles. A semiconductor nanocrystal (SNC) or quantum dot (QD) is a semiconductor whose excitons are confined in all three spatial dimensions. As a result, they have properties that are between bulk semiconductors and those of discrete molecules. Size effects are observed in semiconductor crystals measuring 10–100 nm, whereas quantum size effects are usually the characteristics of nanocrystallites measuring less than 10 nm. The physicochemical properties of nanocrystalline particles are different from those of the bulk materials for two

specific reasons. First, the high surface-to-volume ratio results in many atoms at the surface of the crystalline lattice. Second, the electronic bands are split up into discrete energy levels as the result of three-dimensional confinement of the charge carriers that occurs. This leads to quantum confinement of charge results in the increased bandgap with decreasing particle size.

The quantum confinement effect in low-dimensional semiconductor systems was described about 25 years ago. The bulk crystalline structure is preserved in a nanocrystal. However, due to quantum confinement, nanocrystals have molecule-like discrete electronic states which exhibit strong and size-dependent properties. In the last decade, comprehensive investigations were made to explore size-dependent properties of semiconductors with emphasis on optical properties, including absorption and luminescence.

Detail knowledge of the optical properties of the nanostructured materials is important for understanding the photophysical and photochemical process that follows the absorption of light quanta. Bawendi et al. [5] used quantum mechanical molecular orbital calculations to explain quantum confinement effect on optical absorption, accounting the well-established blue shift in the absorption spectra with decreasing particle size. Bawendi et al. [6, 7] has also provided a recent overview of this field. As discussed previous the spectral shifts during the early stages of inorganic semiconductor particle growth, molecular orbital (MO), and linear combination of atomic orbital coupled with molecular orbital (LCAO-MO) procedures provide information for the construction of energy level diagrams for clusters of several molecules up to size characteristic of bulk semiconductor.

Addition of the filled and empty orbitals of the multiple energy levels can increase the molecules level in a cluster. A decreasing trend in energy differences between the not only filled orbitals and as well as empty orbitals too. Also, a decreasing trend into the energy gap was observed between the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO). For a bulk semiconductor, the filled and empty states form separated continuums, i.e., the valence and conduction bands. However, for quantum dot (Q-size) regime region, energy levels were within the empty and filled states and remain discrete, and the bandgap energy levels were in higher states between the HOMO and the LUMO than that of the bulk materials as shown in the schematic diagram (**Figure 8**).

The bandgap, E_g, increases in magnitude as the semiconductor particle radius decreases in size to the point where it becomes comparable or smaller than the exciton radius [6]. These properties have led to the applications in a wide range of fields, i.e., semiconducting quantum well and super lattice devices, nonlinear optical materials, photocatalysis, and imaging systems. For II–VI compounds, maximum radii for the onset of quantum confinement effect (Q-size effects) leading to the bandgap increase have been determined by Dabbousi et al. [7] to be 10 to 100 Å. Wideband photoconductors such as TiO_2(rutile) and ZnO undergo increase in bandgap as radii approach in the range of 50 Å. It is interesting to note that a blue shift in the long-wavelength optical absorption edge with decreases in particle size was first observed by Berry [8] for AgBr samples with radii of 65 and 350 Å. It's very clear that quantum confinement effect-based semiconductor nanocrystals were produced with tremendous optical and electrical properties than that of the bulk materials which are due to the reduced behavior of characteristic length called as exciton Bohr diameter. And a characteristic length is usually in the range of few nanometers when the material reveals size-dependent optical and electrical properties.

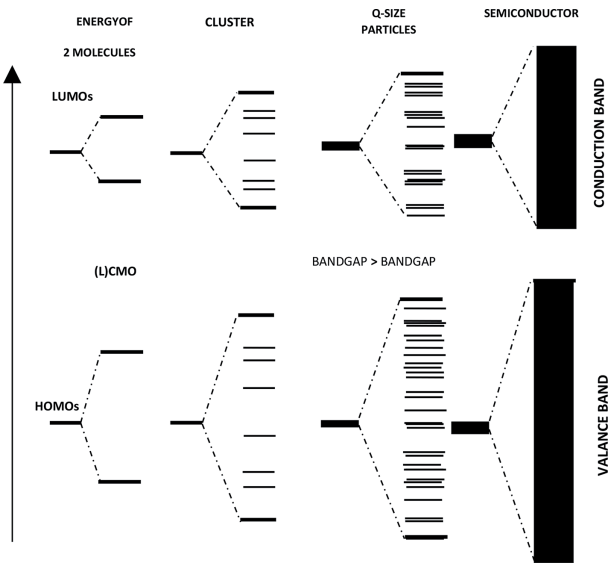

Figure 8.
A schematic diagram of the molecular orbital model for band structure.

One of the most important consequences of the spatial confinement effect is an increase in energy of the band-to-band excitation peaks (blue shift) as the radius R of a microcrystallite semiconductor is reduced in relation with the Bohr radius. However due to significant spatial confinement effect, there is an increase in energy of band-to-band excitation peaks which is called blue shift. The microcrystallite of Radius (R) ranges in semiconductor having less relation with than of the Bohr Radius. Some of minor difference would have happened between the theoretical and experimental of confine effect it is due to electron electron–hole interaction energy, in coulomb term and the confinement energy of the electron and hole in the kinetic energy.

4.1 Weak confinement regime

To observe this regime, the radius (R) of a crystallite should be greater than the bulk exciton Bohr radius (a_B). In this region of weak confinement, the dominant energy is the Coulomb term, and they already occur in size quantization of the exciton motion. The exciton energy states are shifted to higher energies by confinement, and shifts in energy ΔE are proportional to $1/R^2$. The shift "ΔE" of the exciton ground state is given approximately by

$$\Delta E \approx \frac{\hbar^2 \pi^2}{2MR^2} \tag{2}$$

where M is the mass of the exciton and it is given by $M = m_e^* + m_h^*$, with m_e^* and m_h^* being the effective masses of the electron and hole, respectively.

4.2 Moderate confinement regime

Taking another point of view of quantum confinement, especially II–VI semiconductor region, the Bohr radius is equal (a_B) to the material radius (R) which is called moderate confinement regime, and also the following term conditions should satisfy $a_h < R < a_e$ for moderate confinement regime process. A processes were observed in small QDs and a well-restricted motion of a photo-excited hole.

4.3 Strong confinement regime

Finally, the strong confinement regime was confirmed by satisfying the following condition such that $R << a_B$ and $R << a_h$. Due to these conditions, excitations are not formed, and separate size quantization of an electron and hole is the dominant factor. To strong confinement regime, must need two different reasons: the first one is the Coulomb term of electron–hole interaction is small and it's acting as a perturbation, and the second one is independent behavior of electron and holes when the above condition is applied. The optical spectra should then consist of a series of lines due to transition between sub-bands. This factor was confirmed experimentally, and the simple model gives shift in energy as a function of crystallite size as

$$\Delta E \approx \frac{\hbar^2 \pi^2}{2\mu R^2} \tag{3}$$

in which the exciton mass M is replaced by reduced exciton mass μ, where

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \tag{4}$$

The electrons and holes in QDs are treated as independent particles, and for the excited state, there exists a ladder of discrete energy levels as in molecular systems.

5. Summary

Recently quantum dot-based nanomaterials play a major role in the applications many field such as Q-LEDs, transistors, solar cells, laser diodes for displays, medical imaging, quantum computing, etc. In particular the QDs exhibit significant role in the optoelectronic application, its changes because of precisely controlling the size, shape, emission of color and bandgap tuning. These properties are changing inside the quantum dots, and that leads to different applications from energy harvesting to biomedical application. This entire physical and chemical phenomenon could be explained through theoretical model by using quantum confinement behavior.

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Conflict of interest

The authors declare no conflict of interest.

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