Review Article

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Basic Understanding of Quantum Dots: The Artificial Atoms of the Nanoworld

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Abstract

Nanotechnology has been a conversation starter in the scientific communities for decades. The advancement of technologies that have helped humans go beyond the microscale to the nanoscale with its enthralling new concepts in store has opened up various avenues for research. One of the fascinating nanostructures we shall discuss in this paper are Quantum Dots (QDs). QDs are clusters of semiconductor atoms confined in all three dimensions to the nanoscale, resulting in properties quite distinct from molecular structures and bulk materials. The most notable property of quantum dots is the production of narrow and specific wavelengths of emitted light with high spectral resolution and longer lifetimes, making them suitable for real-time in vitro and in vivo imaging. This, coupled with the cost-effective control over the sizes of QDs, leads to the tuning of the emitted wavelengths. Furthermore, carefully coating various functionalities enhances the specificity and makes them suitable for in vivo targeting. QDsare being used for recent development in various fields, such as light-emitting diodes, photovoltaics, etc. This review paper will focus mainly on the various properties of quantum dots, and the reasons behind the same, with akeen focus on the application of QDs in biomedical imaging, biological sensing, and so on. This review hopes to capture a basic understanding of QDs and their properties with a keen focus on understanding the recent developments and biomedical applications.

Keywords - Quantum dots, synthesis, quantum confinement, Q-LEDs, in-vivo imaging

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1. Introduction

In 1981, Russian physicist Alexey Ekimov was credited with the discovery that led to the development of what we now know as quantum dots. Ever since then, significant work has been done to understand their various size and shape-dependent optoelectronic properties; the fact that QDs represent atoms and their basic behaviour and properties has led to a keen interest of researchers in their tunable properties. Quantum dots are crystalline spherical nanoparticles in the core range of 2 to 10 nm, or, of the order of 10 to 50 atomic lengths (Bohr Radius).[3] The most common QDs are made up of semiconductor materials and are incredibly unique since they have electrons confined in all three spatial dimensions.

The unique properties of quantum dots, mainly their large surface-to-volume ratio and size-dependent band gaps,have led to exciting research, especially in the optics and biomedical app fields.

2. Fluorescence of Quantum Dots

The most talked about property of Quantum dots is their specific emission wavelengths. Relaxation is when the electrons return to a lower energy state from a higher energy state. Relaxation is of two main types - radiative and non-radiative relaxation. Generally, the time for non-radiative relaxation (vibration, heat dissipation, photochemical decomposition) is less than the time for radiative relaxation from the excited state. The Jablonski diagram depicts the various singlet and triplet electronic transitions and the vibrational modes of de-excitation. The transition of electrons from the lowest vibrational energy level of the excited state to a lower energy electronic state by emitting photons is called fluorescence.

The energy absorption by QDs excites the electrons to the first excited state from the ground state. Their transition back to the ground state emits bright and narrow emission spectra producing fluorescence, which has a longer lifetime than that of fluorescent organic dyes.

More importantly, unlike bulk solid semiconductors, QDs have discrete energy levels as opposed to the conduction andvalence bands observed in bulk solids. This property is highly desirable in producing specific wavelengths, the cause and occurrence of which has been further discussed under section 3.

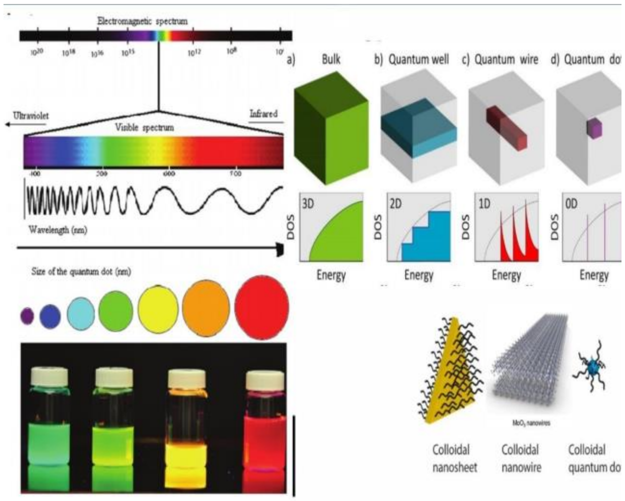
3. Quantum Confinement

In bulk-phase solids, we have large atoms in close vicinity. Extreme energy levels of particles split to give a large number of closely spaced energy levels that appear as a near continuum known as bands. In bulk semiconductors, the bands are classified as conduction (HOMO) and valence bands (LUMO), and their band gap is between that of metals and insulators.[9]

Delving deeper into atomic and subatomic levels, general Newtonian physics starts giving results that do not match experimental observations of the actual properties of the particles. In such cases, a quantum mechanical approach has to be adopted, i.e., solving the Schrodinger equation to obtain the allowable energies for electrons.

Electrons can occupy any of these specific energy levels, and no electron can exist between the forbidden energy gap (E_g) of these energy levels. Electronic excitation can occur in a semiconductor when a photon with energy equalto or greater than E_g is absorbed. The promoted electron leaves behind a vacancy, which behaves like a positively charged particle known as a hole. When this excitation happens, the generated electron-hole pair is called an exciton. The separation between the electron and hole is called the Bohr exciton radius. Its value is minimal compared to the crystal size in bulk materials but becomes significantly comparable as we move to the nanoscale.

When a material's size is altered to enhance its properties, the electrons and their transitions within the material are confined depending on the dimensionality. This is known as Quantum Confinement. The schematic representation of quantum confinement is given below in figure 3.1



11Figure 3.1 (a) Shows the variation of Band Gap with Size of QDs, (b) The various coloured emissions of colloidal QDs, (c) The visualization of spatial confinement in various nanoparticles[22]

Thus, a quantum well confines in only one dimension, and the other two dimensions are delocalized; quantum wires confine the electrons in two dimensions, and in quantum dots, all three dimensions are confined.

The energy of an electron and a hole in a given energy state is given by the following equation

$$= \frac{h^{22}\ 8^{22}}{} \qquad (1)$$

$$h \quad = \frac{h^{22}}{8^2{}_h^2} \qquad (2)$$

Here m_e is the mass of electron, m_h is the hole's mass, h is Planck's constant, n represents the quantum energy state, and d represents the diameter of the particle.[26] Given a value of n, the energy of an electron will be more than that of a hole because of the higher mass of holes compared to the electrons. This also corresponds to our understanding that electrons get excited and move up to the conduction band while holes are in the valence band. Given a specific value of 'n', the difference between the energies of the electron and hole equals the band gap. With the decrease in the value of d, it goes beyond the levels in which quantum confinement takes place; the change in the value of d has more profound changes on the particle's energy. In this region, a slight shift in d changes the corresponding values for holes and electrons and dramatically alters the difference in their energies (band gap) for the same n value. Thus, we are implying that in the nanoscale, the changes that alter a single atom or a few atoms have significant implications on the particle. It is also noted that this inverse dependence of d and band gap leads to the blue shift we observe in quantum dots.[8]

4. Variation of band gap energy with size of QDs

$$() = (uk\ )\left(1+\frac{2}{}\right) \qquad (3)$$

The above equation is based on a straightforward model which has been developed to investigate the impact of size and shape on the energy band gap of semiconductor nanomaterials. d is the diameter of an atom, and D is the diameter of the spherical nanosolids.[29]

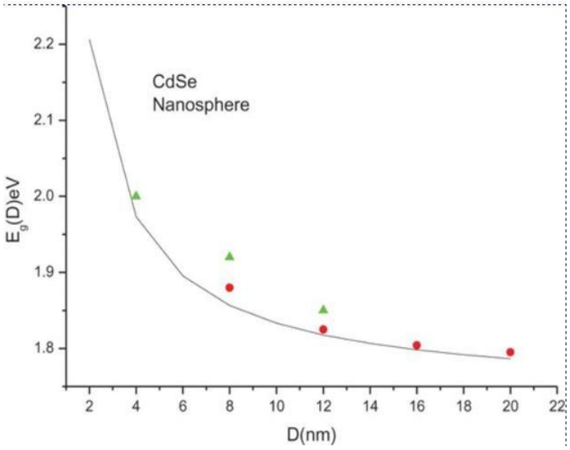


Figure 4.1 Variation of energy band gap of CdSe nanosphere with size[29]

Figure 4.1 shown above showcases the model's predictions for the size-dependent energy band gap of spherical CdSe semiconductor nanomaterials, guided by equation (3). A comprehensive examination of the predicted outcomes in relation to documented experimental data underscores a systematic escalation in band gap energy as particle size diminishes, notably accentuated when the size is below 6 nm.[30,31] These findings align with the quantum confinement theory, which associates the rise in band gap energy with the confinement of electrons and holes due to potential barriers at the surface or potential well of the quantum box. The size dependence of the band gap energy for CdTe nanospheres exhibits a rise in band gap energy as particle size decreases. The model's predictions align well with available experimental observations. [32,33,34] The graphical representation of band energy increase with shape and size underscores the significance of both factors at the nanoscale. The volume-to-surface area ratio, varying with shape and size, influences the number of surface atoms, thereby altering cohesive energy and, consequently, the band gap energy. Quantum mechanically, this can be explained as the particle size reaches the nanoscale, resulting in a reduction in the number of overlapping orbitals or energy levels, leading to a thinner band thickness and a higher energy band gap between the valence band and the conduction band. This phenomenon elucidates the higher energy band gap observed in semiconductor nanomaterials compared to their bulk counterparts.

Tuning the size of quantum dots is pivotal for exploiting their diverse applications. Larger quantum dots exhibit a spectral shift toward the red, making them valuable in technologies like LEDs, while also displaying reduced quantum effects for applications requiring more classical behavior. Conversely, smaller quantum dots leverage subtle quantum effects, crucial in areas such as quantum dot transistors and quantum computing. The size of these semiconductor nanoparticles significantly influences their electronic properties, impacting solar cell efficiency and transistor functionalities. In biomedical and environmental realms, quantum dots of specific sizes find applications in drug delivery, biosensing, and environmental sensing, showcasing the versatility of tailored quantum dot sizes in addressing diverse technological and scientific challenges.

5. Materials and Functionalities

Group 12-16 semiconductors, called II-VI semiconductors, are materials whose cations are from Group 12 and anions are from Group 16 in the periodic table. Some examples of Group 12-16 semiconductor materials are cadmium selenide (CdSe), zinc sulfide(ZnS), cadmium telluride (CdTe), zinc oxide (ZnO), and mercuric selenide(HgSe) among others. The most common is CdSe QDs.[28]

In the bottom-up approach to producing Quantum Dots, nano-sized particles are formed through the controlled agglomeration and binding of their semiconductor precursors. The bottom-up approach is adopted to make QDs with high monodispersibility and better control their sizes.[27] Most syntheses yielding colloidal suspensions of QDs involve the introduction of semiconductor precursors under conditions that thermodynamically favour crystal growth in the presence of semiconductor-binding agents. These agents kinetically control crystal growth to maintain their size within the nanoscale, often achieved by coating with a protective inorganic shell of non-toxic material like ZnS. The central synthesis methodology to produce a wide variety of QDs has been well defined in the literature; a primary trend can be observed:

a. Synthesis of the QD core in a high-temperature organic solvent;
b. Growth of an inorganic shell (usually zinc sulfide, ZnS) epitaxially on the core to passivate the core against photobleaching and to improve quantum yield. It is worth noting that the shell size can be controlled by varying various experimental parameters such as growth temperature, concentrations of reactants and the rate of their addiction.
c. Capping their surfaces with hydrophobic agents like TOP or TOPO to improve stability in an organic phase like toluene, cyclohexane, etc.[3]
d. Phase transfer of the QD from the organic liquid phase to the aqueous solution;

Point (3) highlights that organic ligands like trioctylphosphine (TOP) or trioctylphosphine oxide (TOPO) render QDs stable in a hydrophobic environment. However, to use QDs for biosensing and bioimaging applications, their extraction in the aqueous phase is essential. This is done by attaching hydrophilic functional groups to their surfaces. Some of them include bifunctional ligands like phosphine, thiols, mono or multidentate ligands like 11-mercaptoundecanoic acid (MUA), polymaleic acid n-hexadecanol ester (PMAH), mercaptoacetic acid (MAA), hydrophilic or amphiphilic polymers (having both a hydrophilic chain and a hydrophobic side chain) such as polyethylene glycol (PEG), etc.[2]

The two main factors which influence the selection of such hydrophilic ligands are:

a. Sizes or the hydrodynamic radii of the QDs - large-sized polymer-coated QDs are not preferred as optical properties are size-dependent. For example, PEG-coated QDs show resistance-specific binding, but there is asignificant increase in the hydrodynamic size, often more than double.[2,5]
b. Non-specific binding to biomolecules - the ligands attached to QD surfaces, including proteins, amino acids, and carboxylic acids, tend to link to biomolecules resulting in low specificity for immunostaining and detection sensitivity.

6. Some Interesting Properties

Group 12-16 semiconductors exhibit bandgap energy within the UV-visible range. That is, ultraviolet light or visible light can be used to excite an electron from the ground valence states to the excited conduction states.

A significant advantage that quantum dots have over traditional organic dyes is their absorption spectra.[3,18]

Generally, materials show typical absorption spectra in which the substance's extinction or absorption coefficient remains low over most of the electromagnetic spectra and peaks to give a substantial amount of absorbed light in a particular small wavelength range characteristic of the material. In the figure 5.1, it is seen that quantum dots show substantial absorbance over more extensive wavelength fields. The intensity of light emitted is directly proportional to the power of absorbed light. Improved emission intensity helps better detect and classify quantum dots from otherfluorescent materials that may be present in the cell. The property mentioned above is shown by all quantum dots irrespective of their size and the wavelength of light they emit. This allows us to irradiate various quantum dots with a single light source. This can be further utilized in multiplex imaging using QDs. In multiplex imaging, we have different QDs with specialized linkages that allow them to bind to other biological markers within the cell. Due to the same light source exciting all of these QDs, the various biological markers can all be detected simultaneously.

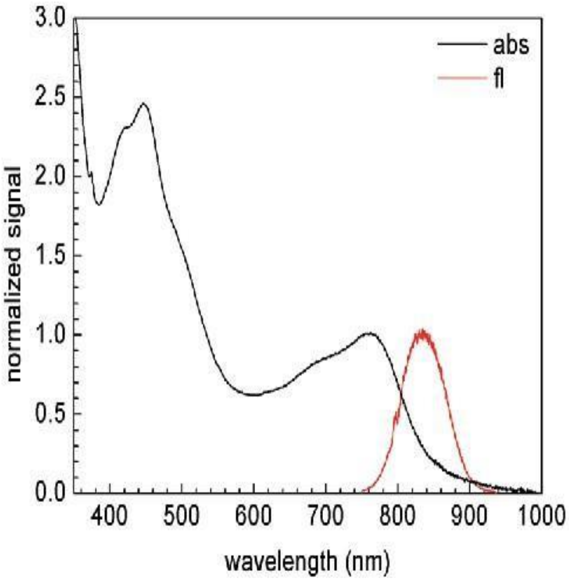


Figure 5.1 The Absorption and Emission Spectra of typical QDs[35]

The peak width of the absorption spectrum represents the monodispersity, i.e., the proportion of same-sized QDs. The larger the absorption peak width, the lower the monodispersity and vice-versa.[21] For example, to use QDs in solar cell applications, Si QDs with specific sizes must be produced to achieve maximum photon absorption from the sun. Information about the surface coatings on the QD shell also can be obtained. More significantly, the surface coverage reduced the recombinations. The images of the produced quantum dots are obtained using TEM and other techniques.[19]

7. Applications

7.1. Display Technology

Quantum Dots are being widely utilized in the display sector. Q-LEDs (Quantum Dot-based LEDs) are creating quite a buzz these days, with many famous brands bringing out new products to incorporate them into their display systems. Q-LEDs utilize QDs to light up their displays rather than the micro-organic dyes used by their O-LED counterparts. The ability of QDs to emit light of particular wavelengths allows the display to have the desirable wavelengths and to cover most of the wavelengths humans can perceive well.[10]

Moreover, their efficient inorganic crystals can undergo more absorption emission cycles without undergoing photochemical breakdown, thus rendering QDs photostable.

Quantum dots also allow us to produce brighter displays; that is, they have high luminance. This refers tohow bright the screen looks on display. The brighter the screen, the better contrast between dark and light colours (contrast ratio). It has been proven that quantum dots have around 30 to 40 percent more luminance efficiency than OLEDs.[23,24]

7.2. In Vitro Imaging

Experimental observations have shown that QDs or nanoparticles, in general, can penetrate a cell's cytoplasm and that nanoparticles are engulfed by various cells. This observation is of great importance in utilizing the unique properties of QDs in the field of in vitro imaging.[3,5,11]

Thus, QDs can be absorbed in cells and then the cells can be illuminated using UV light. The QDs would disperse through the cell and produce fluorescence emissions, their individual intensities being dependent on their relative positioning within the cell thickness, thus helping us map the parts of cells present at different thicknesses. This technique can be employed in Bright Field Microscopy of cells that do not emit strong fluorescence of their own. Moreover, we can also have QDs with desired functional groups that can attack a specific part of the cell and be scanned.[1,8,11]

7.3. In Vivo Tumour Targeting

These days, the ever-increasing complexity of various tumours calls for novel targeting and detection systems. These can aid the preexisting treatments and therapies using the novel properties of targeting and imaging agents.[2]

Growing cancer or tumour cells require a constant blood supply to increase in size beyond a particular range. Tumours account for this blood supply by producing chemicals that promote angiogenesis.[17] Angiogenesis is the process of the formation of blood vessels. Healthy cells have tight junctions with the blood vessels that do not allow foreign material, such as nanoparticles, to enter the surrounding cells when traveling through the bloodstream. But, the constantly growing cancer cells have leaky blood vessels; that is, they do not have a continuous line of endothelial cells (the cells that form the lining of blood vessels and regulate interactions between the blood flowing and surrounding tissues). This phenomenon is called EPR, which is the enhanced permeability and retention effect (see figure 6.1).[1] EPR allows nanoparticles and even macrostructures of specific sizes to enter the tumour cells selectively. The extracellular fluid in the body is called lymph, and it is transported via lymphatic vessels.[5] These vessels help in the removal and drainage of unwanted substances from the cells; most tumours and cancers lack well-developed lymphatic vessels, thus reducing the drainage of nanoparticles away from them and hence leading to their retention.

Water soluble quantum dots have a hydrophilic ligand coating, which can specifically allow specific proteins to bind to them. These proteins are further attached to tumor-specific antibodies or anti-cancer drugs.[1,7]

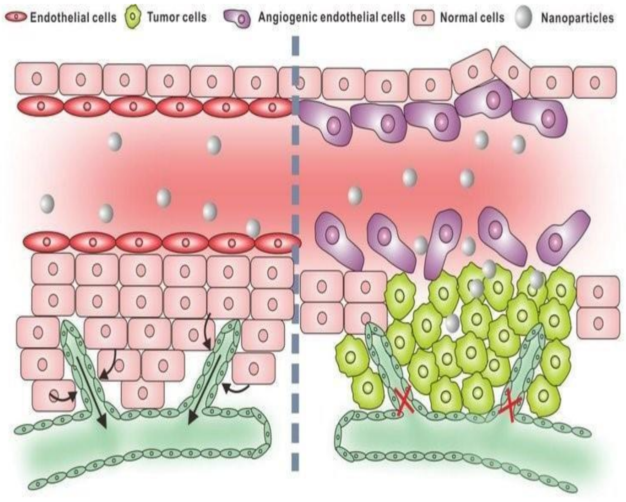


FIGURE 6.1 The EPR effect in tumour cells[25]

7.4. Immunotherapy

Antibodies are Y-shaped proteins that activate by attaching to the antigen in the tumour cells through the lock and fundamental mechanisms. When antibody-coated QDs are injected into the body, the immunoglobulins on the antibody bind to the specific antigen, thereby leading to antibody-antigen reactions that produce an immune response against the tumour. This therapy is used in combination with surgery, chemotherapy, and radiation therapies.[18]

7.5. Anti-cancer drug delivery

Like antibodies, anti-cancer drugs can be precisely delivered to the target cells. These drugs alter proteins within cancer cells, prevent blood supply to the tumour, and provide toxins that destroy cancer cells without harming the healthy cells.[1,7] Thus, QDs are a promising tool for simultaneous imaging and targeting.

In applications in vivo, quantum dots with high photostability, adequate circulating lifetime, minimal non-specific deposition, and higher capacity for retaining fluorescence for a longer time are required. Surface modifications of the QDs can help enhance these properties.

7.6. Solar Cells

Quantum dots (QDs) have emerged as a prominent technology in solar energy conversion to electricity, particularly in the context of third-generation photovoltaics. Colloidal QDs, known for their cost-effectiveness and relatively high efficiency, show promise for further advancements in renewable energy. The notable growth in the power conversion efficiency of QD-based solar cells, coupled with evolving fabrication technologies, suggests an expanding role for colloidal QDs in the renewable energy sector. They have the potential to significantly surpass the theoretical peak efficiency of silicon-based cells by utilizing dots of varying sizes stacked on top of each other, with the largest band gaps positioned at the top. This innovative approach holds the key to enhancing the efficiency of solar energy conversion and underscores the potential for broader integration of colloidal QDs in renewable energy applications.[39]

7.7. Hydrogen Production

The expansive surface area and abundant edge surface space of Carbon Quantum Dots (CQDs) facilitate rapid electron transfer. The diverse applications of CQDs in photocatalysis and hydrogen production stem from their distinctive photoluminescence characteristics. Notably, these particles exhibit environmental friendliness, characterized by low toxicity and exceptional luminescence. Therefore, they hold promise as a potential resource for the photocatalytic splitting of water. The process of water splitting into H_2 and O_2 not only aligns with environmental considerations but also offers the prospect of harnessing hydrogen as a future fuel source.[36]

7.8. CO2Sequestration

The issue of climate change, which is majorly caused by CO_2 emissions, calls for large-scale carbon sequestration. One innovative approach involves employing carbon quantum dots (CQDs) as materials to enhance pore structures of carbon surfaces, facilitating selective carbon dioxide (CO_2) adsorption from gas mixtures. These CQDs undergo modification through either nitrogen doping of the interior aromatic structure or functionalization with amine groups. In all instances, CQDs exhibit preferential adsorption for CO_2 over nitrogen (N_2) and oxygen (O_2). The degree of selectivity is contingent upon CQD size and the extent of doping and functionalization. Crucially, the synthesis of CQDs involves non-toxic, renewable precursors and solvents.[36] Thus, the CQDs produced through this process are confirmed to be both non-toxic and chemically stable, presenting an environmentally friendly solution for improved CO_2 sequestration.

8. Discussion

Quantum dots have a large number of possible applications in the future. With improved technology, QDs can be utilized in intelligent and adaptable lighting systems. These lighting systems promise to give varying light depending on the environment around and needs, e.g., it is observed that blue light from computer screens leads to sleep deprivation, and adaptive lighting systems will change the light coming from the screen depending on the time of day, and this can be realized with the aid of QDs. It is also known that plants grow well in specific kinds of light, and QDs can be engineered to give only desirable wavelengths.

9. Conclusions

There has been concern around using CdSe-based QDs in humans and living organisms, due to the possible cytotoxicity of Cd^{2+} .[3,18,20] Researchers are coming up with unique solutions to solve the issue. It has been observed that a ZnS coating on CdSe quantum dots makes them relatively safe. Moreover, with the field's growth, various other QDs are coming up on a large scale. It can be concluded that QDs have a broad market ahead of them in the display sector. QDs are currently in the preliminary stages of their applications in biomedical engineering, and there are tremendous opportunities and possibilities.

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