Review Article

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Quantum dots synthetization and future prospect applications

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Abstract: Quantum dots (QDs) are nanocrystals of a semiconductor material that exist in a size regime less than 10 nm. QDs have become promising nanoparticles for a wide variety of different applications. However, the major drawback of QDs is their potential toxicity. This review reports on some recent methods for the synthesis of QDs and explores their properties, structures, applications, and toxicity. QDs are extraordinary because their minute size produces a physically confined electron cloud, an effect known as the quantum confinement. Certainly, because of their special properties as they had a great unique optical, electronic, and chemical properties that were not observe in other materials. These unique properties of the QD are an attractive material for a variety of scientific and commercial applications, most of them recently been realized, such as biosensors, bioimaging, photodetectors, displays, solar cells, wastewater treatment, and quantum computers. Finally, but not the end, an interesting potential QD application in future perspectives will expect as light-emitting diode products, biomedical applications, and Li-Fi.

Keywords: quantum dots, zero dimensions, solar cells, photodetectors, biological imaging, Li-Fi

1 Introduction

Russian researchers discovered the level quantization in quantum dots (QDs) in 1981. Moreover, a blue shift in the optical spectrum for nano-CuCl in silicate glass was obtained [1]. Romans and Greeks used lead(II) sulfide (PbS) QDs as hair dye for more than 2,000 years, which prepared these materials using natural materials, such as lead oxide, calcium hydroxide, and water. Also, 4,000 years ago, Ancient Egyptians used nano-PbS for different colors of hair dyeing formulas [2].

While for 100 years, one of the oldest methods to control glass colors is the control of the size of quantum dots in silicate glasses. In the last few decades, cadmium selenide (CdSe) and cadmium sulfide (CdS) combined into silicate glasses to get different color ranged from red to yellow colors. For the first time, X-ray diffraction was used in 1932 to determine that CdSe and CdS precipitated caused the appearance of the red–yellow color. In the period 1982–1993, the quantum size effect played an essential role in controlling the color of glass by changing QD size by several different synthesis methods that were developed during this period [3]. Hence, in 1998, companies started selling QD products, such as Quantum Dot Corporation Company in the USA, which has raised over $37.5 M in venture capital financing.

In the last two decades, QDs have had a mutation in their diversity resulting in the precise control of the QDs nanosizes, which led to the possibility of exploiting QDs in advanced applications. One of these applications revolutionizes the world of display screens and health care, especially in the treatment of serious diseases such as leukaemia, different cancer types and many biomedical applications, [4,5], wastewater treatment and QDS solar cells [6–9].

Today, QDs are a central theme in advanced nanotechnology because of their high variation in most of their chemical and physical properties than their basic semiconductor properties. Potential applications of QDs
include solar cells, transistors, diode lasers, light-emitting diodes (LEDs), biomedical applications [10,11], inkjet printing, wastewater treatment [10], spin-coating [11], and quantum computing.

Zero-dimensional (0D) materials are the first distinguishable fact for nanocrystal materials and are called “QDs” as a result of charge carries confinement in three dimensions, where their electrons are mostly in restricted location; hence, these structures are 0D.

QDs are nanocrystal-semiconducting material having the smallest diameters that can be detected within nanoscale in the range of 2–10 nm (10–50 atoms). QDs are 10,000,000 times smaller than a tennis ball, and they range from glucose to antibody nanosize shown in Table 1. Their optical properties have a distinguishable change according to the different sizes observed [12]. Therefore, QDs have a uniquely powerful ability to convert light to any color in the visible spectrum easily with high efficiency. QDs ≥5 nm are called larger QDs because of red or orange emission color at the longer wavelength.

QDs ≤3 nm are called smaller QDs because of blue or green emission color at a shorter wavelength (Figure 1). That is due to the exact QD composition that decided the specific colors according to their varying sizes.

Artificial atoms are a nickname for QDs because of their small sizes, which can precisely modulate their bandgap and discrete energy levels. So, the color light controlled a quantum dot just by changing its size [13].

Table 1: Scale range in nanometer

| Item       | Scale (nm) | Item       | Scale (nm) | Item       | Scale (nm) |
|------------|------------|------------|------------|------------|------------|
| Water      | 10⁻¹       | Virus      | 10⁷ nm     | A period   | 10⁵ nm     |
| Glucose    | 1          | Bacteria   | 10³ nm     | Tennis ball| 10⁷ nm     |
| Antibody   | 10         | Cancer cell| 10⁶–10⁵ nm |            |            |

1.1 QD size

Every 10 nm contains nearly 3 million QDs when they are lined up together or fitted within the width of a human thumb. According to QDs’ small size, the QD electrons are confined in a quantum box (small space), also when its radii are smaller than exciton Bohr radius, which means that the separation between an electron and a hole in an electron-hole pair is followed by a large splitting in energy levels. This results in more energy being necessary in order to move into an excited state, and more energy is increased upon returning to a rest energy [14].

Generally, as QD size decreases, the energy difference between the highest valence band and the lowest conduction band increases. Hence, dot excitation needs more energy, which is released when their crystal returns to its ground state, due to a color shift from the longer wavelength (red color) to shorter wavelength (blue color) in the emitted light (Figure 2).

Electronic excitation for a nanocrystal semiconductor depends on electron–hole pair location, which is delocalized usually at a longer length than that for lattice constant.

![Figure 1: Variation in QD colors with their size][13]

![Figure 2: Splitting of energy levels in QDs due to the quantum confinement effect, and semiconductor bandgap increases with decrease in size of the nanocrystal][14]
1.2 QD size effect

QD size effect (QDE) occurred when the diameter of the nanocrystal semiconductor approaches to exciton Bohr diameter, which is due to starting change in QD electronic properties. CdS, one of the famous QDs, was investigated 30 years ago; the QDs occur when their nanodiameter is near or below the exciton diameter $\leq 6 \text{ nm}$ ($3,000–4,000$ atoms).

Generally, a large percentage of the atoms in QDs have a small-size regime that are on or near the surface. A $5 \text{ nm}$ quantum dots cadmium sulfide has $15\%$ of its atoms on the surface. The existence of a large interface between the nanocrystal and the surrounding medium affected their properties. Nanocrystals have an imperfect surface and electron–hole traps observed upon optical excitation. Hence, the presence of these trapped electrons and holes led to changes in the optical properties of the nanocrystals.

1.3 Color-changing phenomena

QDs can emit any color of light from the same nanocrystal semiconductor simply according to the changes in its size. That refers to the high level of control possible over the size of QDs, which can be tuned during synthesis processes to emit any color of light [15]. Hence, the bigger dots emit at longer wavelengths like red, while smaller dots emit at shorter wavelengths like green. QD tune (wavelength of the emitted light) has the same behavior as a guitar string because a higher pitch is produced when a guitar string is short and a lower pitch is produced when it is lengthened (Figure 3).

At the same time, the bandgap changes with size while the bandgap is the energy needed to promote an electron from valence band to conduction band and when it lies in the range of visible wavelength spectrum leading to changes in the emitted color. Also, the magnetic memory (coercive force) that needed to reverse an internal magnetic field within the quantum dot depended on its size.

1.4 Quantum confinement

In a smaller nanocrystalline semiconductors size that is twice that of the exciton Bohr radius, the excitons are shrunk, leading to quantum confinement. The most effective essential consequence of the quantum confinement effect is the size dependence of the bandgap, which is tuning to a precise energy depending on confinement degree and nanocrystal dimensionality [16,17]. Hence, there are three confinement regimes according to the QD size, electron Bohr radius and hole wave functions (Scheme 1).

Exciton confinement energy is controlled by varying the quantum dot size. Hence, the splitting of energy levels of both valence and conduction bands refers to a strong quantum confinement effect obtained in small QDs.

The splitting energy levels affect on the stationary wave functions for different QDs shapes (box and

![Figure 3: QD tune behaviors.](image)

![Scheme 1: Different QD confinement regimes.](image)
pyramid). Energy states in box-shaped dots maintain orbital symmetry as more s-type and p-type in character. While in pyramid-shaped dots, the wave functions are mixed due to the asymmetry confinement effect (Figure 4).

1.5 QD structure

QDs usually consist of 200–3,000,000 atoms but only have 100 free electrons or less than that [18]. Many structures can be distinguishable according to their electron confinement. The first QD experiments were done with the planar structures where their electrostatic confinement leads to dimensions of nearly 100 nm, and the confinement structural for vertical QDs is about 10 nm. Although self-assembled QD structures have pyramidal or lens-shaped ≤10 nm, their electrostatic confinement lets that pyramidal QDs are very promising for laser applications than the planar and vertical structures [19].

Figure 4: 3D confined electron wave functions in a quantum dot.
1.6 Quantization effects

Generally, quantization effects in nanocrystalline semiconductor structures have reduced size, depending on the direction of the charge carriers confined in different dimensions (Figure 5) [20].

QD properties differ from its bulk semiconductors due to different quantum confinement effects according to their different sizes and their confinement energies. Hence, QDs have remarkable optical properties for recent bio and laser applications because their three dimensions are reduced to zero (Table 2).

2 QD classification

There are three main groups of QD semiconductors according to the periodic table elements:

2.1 III–V semiconductors

III–V semiconductors are derived from elements of III (B, Al, Ga, and In) and V (N, P, As, Sb, and Bi) of periodic table elements. The outstanding performance appears for gallium arsenide (GaAs), especially in optical data processing that GaAs-QDs serve as a light source used in lasers as a gain medium. However, this class of QDs seems to be reserved for special applications but does not compare with Si-QDs in the semiconductor industry [21].

II–VI semiconductors: They are derived from elements of II (Zn and Cd) and VI (O, S, Se, and Te). Prominent representatives of this QD class are CdSe and CdTe. Currently, ZnO QDs are increasingly prepared [21].

2.2 IV–VI semiconductors

IV–VI semiconductors are derived from elements of IV (C, Si, Ge, Sn, and Pb) and VI (O, S, Se, and Te) of periodic table elements. Although, the development of Si-QDs is not advanced as QDs from another group such as III–V and II–VI semiconductors, which have a great potential for integration into the current silicon electronics. Hence, they are an essential component of processors, optical chips, and optical sensors because Si-QDs used in photovoltaics lead to increases in their efficiency. Recently, they are mainly recommended for use in the aerospace industry due to the high prices of Si materials [22].

Table 2: Comparison of different confinement direction structures

| Item                        | Three dimensions | Two dimensions | One dimension | Zero dimensions |
|-----------------------------|------------------|----------------|--------------|----------------|
| Dimension parameters included | All parameter of length, breadth, and height | Both of length and breadth | Only one parameter either length or breadth or height | Length, breadth, and heights are confined at single point |
| Defined as Electron movement directions | Nanoparticle Three directions | Quantum well Two directions | Quantum wire One direction | Quantum dot Zero directions |
| Restricted directions | Zero restricted directions | One restricted direction | Two restricted direction | Three restricted direction |
| Common examples | Nanometal oxides | AlGaAs | GaN InP | CdSe CdS |
3 QD types

3.1 Core-type QDs

QDs can be single-component materials with uniform internal compositions as selenides or sulfides (chalcogenides). The electroluminescence and optical core-type QDs properties can be tunable by any simple change in QD size.

3.2 Core–shell QDs (CSQDs)

QDs with small regions of one material embedded with another bandgap material are known as CSQDs. QDs with CdSe in the core and ZnS in the shell are available at a high quantum yield of ≥80%. QD shells improve quantum yield and make them more suitable for their synthesis conditions for various applications [23] (Figure 6).

CSQDs are used for improving the efficiency and brightness of semiconductor nanocrystals, and they are growing shells of another higher bandgap semiconducting material around them. Hence, the electroluminescence properties of QDs arise due to exciton decay (recombination of electron–hole pairs) through radiative processes. Also, it can occur through nonradiative processes leading to the reduction of the fluorescence quantum yield.

3.3 Alloyed QDs

Alloyed QDs formed by two nanocrystal semiconductors have different bandgap energies that have exhibited distinguishable properties differently clearly from their parent semiconductor properties. Where this also confirmed by that the alloyed QDs possess a novel tunable properties that were proved clearly to have a clear quantum confinement effects.

Alloyed QDs have homogeneous and gradient internal structures that their composition and internal structure merely changing without any changing of the size of the nanocrystals as a result of allowing tuning of the electrical and optical properties to take place as alloyed QDs of CdS,Se/ZnS (6 nm diameter) that emits light of different wavelengths according to changing composition as shown in Figure 7 [24].

Tuning effect in electrical and optical properties by changing their nanocrystal size becomes a distinguishable mark of QDs.

4 QD fabrications

QDs are commonly fabricated in solution as colloids suspended and on solid crystalline substrates as epitaxial structures are grown (Figure 8). Epitaxial nanocrystals are easily prepared because they have a wide range of sizes and shapes in regular patterns [25]. Hence, they recommended advanced applications in various fields.
As a result of their epitaxial activity, it is divided into four types (Scheme 2).

Figure 8 shows that colloidal-epitaxial quantum dot where (a) is the electronic energy states of a semiconductor in the transition from discrete molecules to nanosized crystals and bulk crystals, (b) comparison of a colloidal-quantum dot and self-assembled quantum dot epitaxially deposited on a crystalline substrate, and (c) absorption (upper) and fluorescence (lower) spectra of CdSe semiconductor nanocrystals showing quantum confinement and size tunability [26].

5 QD synthesis

Recently, colloid QDs attracted more attention because of their distinguishable optical properties, which make a scientific breakthrough, especially in the optics field where it depends on the QD energy gap by changing QD size. The QD sizes are controlled by their synthesis methods. The most accessible technique for creating QDs is a colloidal synthesis, which chemically produces QDs suspended in solution. Figure 9 shows that cadmium compound is heated to 320°C and dissolves in an organic solvent. At room temperature, selenium compound dissolved in a different organic solvent is injected into the reaction vessel, causing supersaturation of the resultant CdSe solution. As the temperature drops to around 290°C, the nucleation of new crystals stops, and existing crystals grow. After a period of growth, the length of which determines the size of the QDs, the solution is cooled to 220°C, stopping the growth. A small amount of zinc sulfide is injected into the reaction vessel to coat the QDs and prevent them from reacting with the environment [27].

Generally, a saturated semiconductors solution is dissolved in an organic solvent, where each semiconductor material has a suitable chemical synthesis
compatible with its structure. Then the pH or the temperature is changed to a supersaturated solution, which nucleates to produce small nanocrystals.

QD size results from tuning by changing pH, the temperature, or reaction time length. Hence, small quantities of QDs can be carried out in the lab by these processes because there are no need for any exotic reagents, whereas for large quantities of QDs, it is so difficult to produce them because they need advanced control in their temperature.

Cadmium is the easiest semiconductor to synthesize by colloidal process (e.g., CdS, CdSe, and CdTe) although it is a harmful heavy metal to the health and environment. Therefore, cadmium is in the legally restricted material list of the European Union.

Although the colloidal synthesis process is a successful method for QD synthesis, it has some technical disadvantages (Scheme 3). These reactions produce 10–15% of the size distribution of dots. It may reduce to 5% by the
selection and filtration suitable techniques. Colloidal synthesis is unsuitable for applications that require manipulation or careful placement of QDs like quantum computing such as solar cell applications, which require large QD quantities [27].

5.1 QD synthesis techniques

There are two main categories for synthesis techniques of QDs: a top-down and bottom-up approaches [28].

5.1.1 Top-down synthesis processes

There are three top-down synthesis processes: wet chemical etching, reactive ion etching, and focused ion beam. These processes offer a high-efficiency control degree of flexibility in nanostructured system designs (Scheme 4). Hence, any QD shape (wires, tube, or rings) is realized with accuracy separation and periodicity by this technique, which was successfully of II–VI and III–V QDs with nearly about 30 nm.
5.1.2 Bottom-up approach

There are two main bottom-up synthesis processes: wet chemical methods and vapor-phase methods. These different processes are suitable for most elements and produce a high-efficiency control degree of the quantum confinement properties (Scheme 5).

6 Toxicity of QDs

QDs are diverse materials different from their normal chemical substances, which lead to most significant research efforts for assessment of QD toxicity that has a big challenge. Many studies indicate that the cytotoxicity of CdTe QDs not only comes from the Cd\(^{2+}\) ions released but also from QDs intracellular distribution in cells and related nanoscale properties [29]. In a recent study case, the genotoxic response to CdTe QDs in human breast carcinoma cells was observed [30]. In some in vitro studies, QD toxicity may derive from their physical and chemical properties (size, concentration, shape, charge, composition, surface functional groups, mechanical stability, surface charges, and photolytic stability) and environment. Evaluation of their potential toxicity is complex as these factors include properties such as QD size, concentration, chemical composition, charge, and capping ligands and also on their oxidative, mechanical, and photocatalytic stabilities [31].

Also it was investigated the mode of toxicity use of QDs in the nucleus of the cell, where it was discovered that the QDs induce on DNA mutation, which leads to block the propagation process in the future for the generation of new cells that may carry the same diseases [32]. In the future, QDs will be used in the identification of different cancer cell categories and molecular mechanisms of diseases and will also find their role in new drug action process mechanisms and availability of finding new biochemical assays methods. Hence, on one day, QDs might be safely used for biological imaging as fluorescent probes, targeted drug-delivery monitoring, and controlling any modifications of functional and structural properties of their intracellular components.

7 QD applications

QDs are considered a new trend in the nanoscience world, so QDs concerned with specific unique fields are shown in Scheme 6.
7.1 Displays

Displays with QD technology have brighter colors and pure colors and are more power efficient and incredibly vibrant [33]. QDs have a significant optical property such as their pure colors and bright appearance. Hence, displays are the most field investment in the QD technology for different display types shown in Table 3 [34]. Quantum-dot light-emitting diodes (QDLEDs) emit light from their nano semiconductors unlike traditional displays from a vacuum of the gas tube.

QDLED development technologies use flexible substrates by solution-based processing. QDLEDs have many advantages over traditional displays such as brightness, saturated color, high color tuning, large displays area, and modern designs [35].

7.2 Photodetectors

Advanced integrated circuits using quantum dot photodetectors (QDPs) via their substrate integration produced from their single crystalline semiconductor or solution processed. QDPs are used in surveillance, machine vision, spectroscopy instruments, and industrial inspection [36].

7.3 Biosensors

Many recent biosensors depend on the unique optical properties of the QDs in various fields, such as zinc sulfide QDs used for food toxin detection [37].

Many QD-based sensors are used for monitoring pesticides [38]. In live-cell nitrogen, phosphorus graphene QDs (N, P-GQDs) are used for detection of NO$_2^-$, which have carcinogenic effects because it is commonly used as a food additive or a preservative agent [39]. Therefore, it can easily interact with the proteins and then form the carcinogenic N-nitrosamines, which increases the possibility of deformities and cancer [40,41] (Figure 10).

7.4 Biological imaging

Biological research considered as one of the main branches of QD applications where QDs are used as tracers injected into targeted living cell tissues. QD applications can be designed for advanced cancer treatments because they can orient to a specific organ such as the liver, not by applying traditional chemotherapy [42].

Also, QDs can be used for the earlier detection of cancer cells with high precise diagnoses (Figure 11) [43].

Silver QDs designed to detect a DNA sequence related to the human oncogene [44]. Generally, most of QDs are based on cadmium, so silicon QDs have a great priority in biological imaging and diagnostic applications than cadmium sulfide quantum dots and cadmium selenide quantum dots (CdSeQDs) because of low toxicity of silicon compared to cadmium. Also, some diseases such as mental retardation can be detected by Gd-QDs as an effective probe for this disease [45–49].

7.5 Solar cells

QD-sensitized solar cells (QDSSCs) represent the third generation of solar cells whose efficiency reaches about 60%, whereas the maximum efficiency for traditional
solar cells is 33% [50,51]. There are several distinguishable properties of QDs that let them inexpensive and highly efficient for solar cell applications:

- Selection of synthesis-based solution and fabrication process helps in the suitable substrate selection that leads to decreasing the manufacturing cost of solar cells.
- High crystallization of solar cells can fabricate at low temperature that leads to decreasing their energy cost used.
- Improve visible light absorption due to the wide tunable band gap property that enable to harvest the visible light.
- High efficiency of QDSSC may refer to using multiple carrier generation during the fabrication process.
- Organic–inorganic hybrid solar cells combine organic represented as polymers and inorganic nanoparticles, with the intent of incorporating the advantages associated with both material groups.

CdSeQDs are rarely used for solar cell fabrication because of their hazardous, expensive, unstable, and nonenvironmental nature. Although quantum dot superlattice (QDSL) such as B-doped nc-Si:H/a-SiC:H has a

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Figure 10: Different QDs for pesticides in food and in environment [38].

Figure 11: (a) Cancer cells marked with standard methods (white circle) compared with quantum dot tagged cancer cells (bright orange) and (b) different types of QDs injected beneath the skin of a mouse [43].
significant potential to increase the high-conductivity performance of the silicon solar cells’ thin film, bandgap width, and antireflection effect (Figure 12) [52].

The highest power conversion efficiency of QDSSCs based on graphene is increased by 37.5% on graphene/Zn-TiMMO (graphene/zinc-titanium mixed metal oxide) than on Zn-TiMMO due to the presence of graphene that increases the adsorption properties of the QDs and decreases their internal resistance.

8 Future prospect applications

Future QD displays will provide high-quality pictures for both TVs and monitors using QD materials. TVs are using QD technology from 2015, and they have 1.3 million shipping worldwide. Shipments of quantum dot TVs were expected to grow to 18.7 million in 2018. We forecast by 2025, 60% of TVs will have QDs, and 51% of monitors will adopt QDs [52,53] (Figure 13).

Also, recent prototype products will appear in the market during the following 3 years, like the cicret bracelet and iWatch.

There are other security important products such as those that have anticounterfeiting capabilities with a unique signature. Hence, this ability to control their absorption and emission spectra of QD injection to it. Moreover, QDs may be used in defense applications or counter espionage such as protection against friendly fire events by integrating quantum dots into dust that tracks enemies.

Cancer was the ghost of death in the world until now, so the early diagnosis and treatment of cancers are at the forefront of cancer QD research. These studies include treatment besides detection for cancer diseases, such as leukemia, ovarian cancer, prostate cancer, breast cancer, and pancreatic cancer [36].

Future research expects to seek less toxic QDs such as GQDs having unique optical properties, and it involves many applications such as different types of bioapplications (biosensing and bioimaging) [38,39], solar cells [40,41,54], LEDs [55,56], and photocatalysis [57].

In the future, it expects the integration of materials or techniques, such as magnetic and electric material or signal application techniques, that lead to powerful biosensing QDs. Now, researchers will continue the synthesis of QDs in a green approach that demands better stability, biocompatibility, and unique optical properties.

As a result of the lightning capabilities of LED, it is applicable in transferring data between computers. Li-Fi passes the bottleneck of data transmission technology with more advances than that obtained from using Wi-Fi technology. Li-Fi uses visible light (a wide range of

| Item               | Li-Fi                  | Wi-Fi                 |
|--------------------|------------------------|-----------------------|
| Speed              | 1–3.5 Gbps             | 54–250 Mbps           |
| Range              | 10 m                   | 20–100 m              |
| Spectrum range     | 10,000 times than      | Radio spectrum range  |
| Data transfer      | Use light as a carrier | Use radio spectrum    |
| medium             |                        |                       |
| Frequency band     | 100 times of THz       | 2.4 GHz               |
| Healthy effect     | Nonhazardous           | Hazardous             |

Figure 12: The detailed deposition process of boron doped nc-Si:H/a-SiC:HQDSL samples [52].

Figure 13: QD devices and components ($ million) 2016–2026 [53].
wavelengths) as the carrier in data transmission and networking, whereas Wi-Fi uses radio wavelength.

In the future, Li-Fi may be applicable because of its unique properties (Table 4), so it can be safely used in hospitals, aircraft, and underwater communications. At the same time, it speeds up to 10 Gbps [58,59]. The Li-Fi market will reach more than $6 billion in 2018, and it is expected to be used in the space soon [58].

9 Conclusion

Future QD material applications exceed any expectation limits that refers to their advanced photophysical and chemical properties. The quantization size effect considers the key of variation of the QD properties due to which QDs are suitable for different types of recent applications. QD materials are applicable in the future, especially, in QD solar cells, biosensors, bioimaging, quantum computers, Li-Fi, photodetectors, and photocatalysis.

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