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(Review Article)

A review on quantum dots and their applications

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Abstract

Quantum dots (QDs) are nanosized semiconductor crystals with unique chemical and physical properties, enabling them to emit bright, photobleaching-resistant light. They are classified into three categories: core type QDs, core-shell QDs, and alloyed QDs. Core-type QDs are composed of a single substance, while core-shell QDs have a semiconductor core surrounded by a shell of another semiconductor material. Alloyed QDs are manufactured using high-temperature or wet-chemical processes, while silicon-based QDs display unusual optical and electrical features due to quantum confinement forces. QDs have exceptional optoelectronic capabilities, producing photoluminescence quantum yields of up to 90%. They are useful for various applications, including optoelectronics and photocatalysis. There are three main types of QDs: colloidal, magnetic, and fluorescent. Colloidal synthesis is a widely used technique for creating QDs, offering applications in visible and near-infrared wavelengths. Magnetic QDs display unique magnetic characteristics and can be synthesized using various methods. Fluorescent QDs have high fluorescence quantum yields and are resistant to photobleaching, making them useful in imaging, sensing, and therapies. QDs are being developed to enhance biological imaging capabilities by increasing cellular uptake, reducing toxicity, and enhancing stability. They can be used for intracellular imaging, deep tissue imaging, single-molecule tracking, super-resolution imaging, targeting ligands, selective imaging of mitochondria, pH-responsive fluorescence, responding to specific cellular signals, and self-illuminating systems. However, they have limitations such as toxicity, structural instability, and deterioration due to UV light or aquatic environments.

Keywords: Quantum dots; Composition; Structure; Photoluminicense; Synthesis and Biomedical Applications

1. Introduction

Quantum dots (QDs) are nanosized (2–10 nm) semiconductor crystals with distinguished chemical and physical properties, enabling them to emit a wide range of bright, photobleaching-resistant light . QDs' fluorescence is size tunable, which allows for simple adjustment of QDs' size and composition to achieve desired color . It was found that increased diameter of QDs caused a redshift in fluorescence . Additionally, quantum dots with greater height in dimension display longer photoluminescence lifetime and increased emission wavelength. In higher emission ranges, larger quantum dots hence produce more consistent fluorescence. Along with QD size, QD shape also has a major impact on QD stability and optical properties.Spherical, cylindrical, pyramidal, conical, tetrahedral, and lens-shaped quantum dots are among the different shapes that are most frequently utilised . Tetrahedral QDs were discovered to be more restricted than spherical QDs and their edge absorption is sharper. In contrast, spherical QDs at 3.1 nm demonstrated higher photon absorption efficiency and lower excitation QD shapes [1].

2. Classification of quantum dots

Quantum dots are classified into various types based on composition, structure, type of material used, type of technique used for synthesis [2].

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Three basic categories are used to categorize quantum dots:

- Based on their composition and structure
- Based on the material used
- Based on technique to synthesis

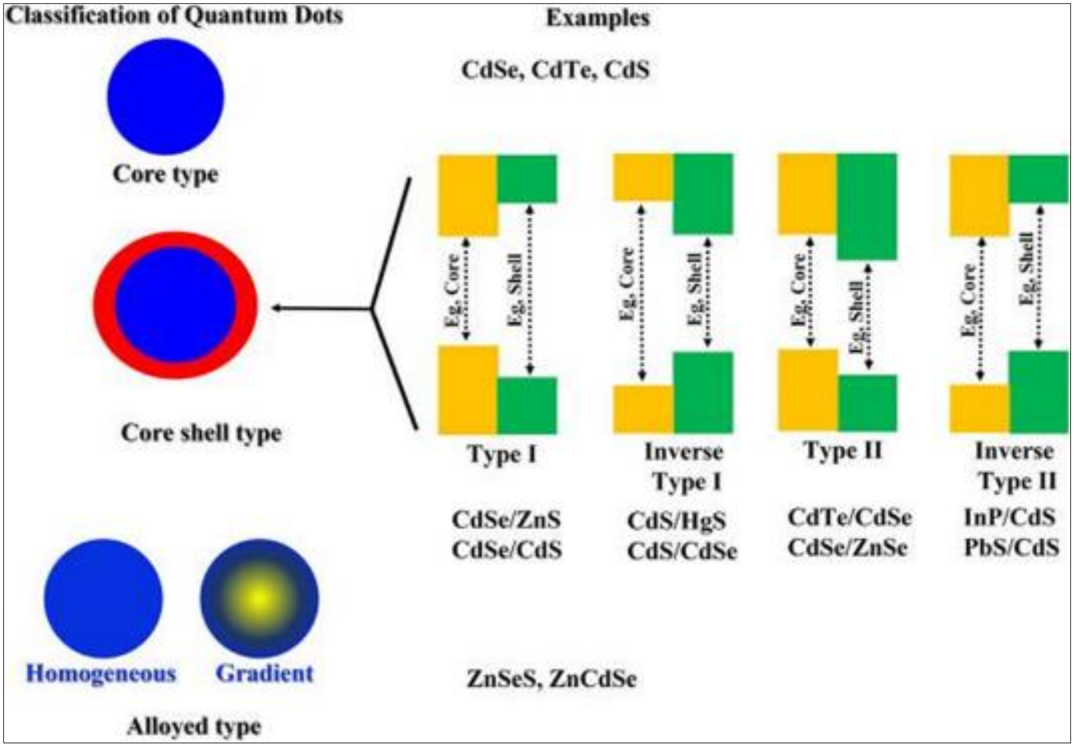

Figure 1 Classification of quantum dots based on their composition and structure

2.1. Based on their composition and structure:

- Core type quantum dots,
- Core-shell type quantum dots,
- Alloyed type quantum dots
    - ***Core-type quantum dots***: Core-type quantum dots are predominantly made of a single substance, often metallic chalcogenides such as cadmium telluride (CdTe) or lead sulfide (PbS) These nanocrystals generally range from 2 to 10 nanometers in diameter, allowing quantum confinement effects that drastically modify their electrical and optical characteristics compared to bulk materials Core-type QDs may emit vivid and pure colors, with the capacity to generate a variety of colors depending on their size. Smaller dots produce light at shorter wavelengths (blue), whereas bigger dots emit longer wavelengths (red) owing to changes in energy levels These QDs have high attenuation coefficients and prolonged photoluminescence lifetimes, making them ideal for numerous applications in optoelectronics and biomedical domains [3]
    - ***Core-shell type quantum dots***: Core-shell QDs consist of a semiconductor core surrounded by a shell of another semiconductor material. This design enhances stability and photoluminescence efficiency by sheltering the core from oxidation and degradation. The production techniques often include high-temperature reactions or aqueous procedures that allow for fine control over the size and content of the QDs, which in turn determines their optical properties. Core-shell QDs have strong emission peaks, making them appropriate for applications needing accurate color outputs.They can absorb a greater spectrum of light, boosting their value in applications like photovoltaics and bio-imaging The shell boosts the quantum yield by restricting excitons inside the core, which decreases non-radiative recombination losses [4-6].
    - ***Alloyed type quantum dots***: Alloyed QDs are often manufactured by high-temperature procedures or wet-chemical processes, allowing for exact control over their size and composition. The synthesis procedures may greatly impact the resultant QDs' features, particularly their optical qualities and stability. Common materials used in alloyed QDs include mixtures of II-VI and III-V semiconductors, such as CdSe(cadmium

selenium), ZnS(zinc sulphur), and InP (indium-phosphide. Alloying may lower non-radiative recombination losses, resulting to greater photoluminescence quantum yields [7- 10]

2.2. Based on the material used

- Silicon-based quantum dots,
- Perovskite quantum dots
    - ***Silicon-based quantum dots***: Silicon quantum dots (SiQDs) are nanoscale semiconductor particles composed mostly of silicon, generally ranging from 1 to 10 nanometers in size. These quantum dots display unusual optical and electrical features owing to quantum confinement forces. The photoluminescence of SiQDs may be modulated throughout the visible spectrum to near-infrared by altering their size. Smaller dots tend to produce shorter wavelengths (blue light), whereas bigger ones emit longer wavelengths (red light). SiQDs may produce photoluminescence quantum yields (QY) of up to 90%, substantially greater than typical silicon materials [11,12].
    - ***Perovskite quantum dots***: Perovskite quantum dots (PQDs) are a family of nanomaterials defined by their unique crystal structure and exceptional optoelectronic capabilities. The band gap of PQDs may be changed by modifying their size and composition, allowing for emission throughout the whole visible spectrum. PQDs may reach photoluminescence quantum yields of 80%, making them very efficient light emitters. They often exhibit narrow full width at half maximum (FWHM) values, which increases color purity in applications like screens. PQDs feature a defect-tolerant structure that enables them to retain excellent performance even in the presence of defects, which is frequently a limiting issue in traditional quantum dots. Their unusual features make them useful for a broad variety of applications, from optoelectronics to photocatalysis [13- 15].

2.3. Based on technique to synthesis

- Colloidal quantum dots,
- Magnetic quantum dots,
- Fluorescent quantum dots.
    - ***Colloidal Quantum dots***: The band gap of CQDs may be modified by modifying their size and composition, allowing for fine control over their absorption and emission wavelengths. CQDs may be manufactured utilizing numerous ways that allow for exact control over their size and content such Hot-injection method, Solvothermal synthesis and Ligand-Assisted Reprecipitation. This tunability offers applications spanning the visible and near-infrared wavelengths. CQDs may reach photoluminescence quantum yields of 80%, making them efficient light emitters suited for displays and lighting applications. They often display narrow Full Width at Half Maximum (FWHM) values, which promotes color purity in applications like light-emitting diodes (LEDs). Many CQDs are built on non-toxic materials, making them safer for biological applications compared to heavy metal-based quantum dots [16].
    - ***Magnetic quantum dots*** : Magnetic quantum dots (MQDs) are nanoscale semiconductor particles that display unique magnetic characteristics alongside their quantum confinement effects. The synthesis of MQDs may be performed using several ways including Colloidal synthesis, Laser ablation, Solvothermal and Hydrothermal procedures. MQDs demonstrate superparamagnetic behavior, where they may become magnetized in the presence of an external magnetic field but do not sustain magnetization after the field is withdrawn. They display Curie-like paramagnetism owing to localized magnetic moments at their edges or flaws. This behavior may be controlled by the size and form of the dots as well as their surface chemistry. The capacity to change their surface chemistry enables for functionalization with biomolecules or polymers, boosting their utility in targeted medication administration and imaging [17-19].
    - ***Fluorescent quantum dots***: Fluorescent quantum dots (QDs) are nanocrystalline semiconductor particles that have received substantial interest in the domains of imaging, sensing, and therapies owing to their unique optical features. QDs have high fluorescence quantum yields, which implies they generate a strong signal when stimulated. The emission wavelength may be carefully controlled by adjusting the size of the QDs. This enables a broad spectrum of hues from blue to near-infrared, making them adaptable for multiplexing applications. Unlike standard organic fluorophores, QDs are very resistant to photobleaching, which boosts their utility in long-term research [20, 21].

3. Synthesis of quantum dots

These fall mostly into four primary groups [22]:

- Biogenic synthesis
- Colloidal synthesis
- Eectrochemical assembly
- Biotemplate-based synthesis.

3.1. Biogenic synthesis:

One promising biotechnology-based approach for generating QDs on a wide scale is termed "biogenic synthesis." In this technology, QDs like CdS (Cadmium sulphide) are manufactured utilizing living bacteria like E. Coli as bioreactors. The first step includes conjugating cadmium ions to cysteine-terminated peptides, which detoxifies the metal, which is toxic to living beings. Subsequently, the ions that have undergone detoxification are given to the bacteria, where they interact with the native sulfide ions to generate CdS QDs, which are then released from the bacterium and collected. Numerous advantages are connected with this method, such as biosafety, economical manufacturing, scalability, and environmental tolerance. Furthermore, the peptide employed in the detoxification step might modify the physico-chemical features of the resulting QDs [23].

3.2. Colloidal synthesis

Colloidal synthesis is regarded as one of the most well-known and widely used techniques for creating QDs. To get the precursor metals into the molecular state, the idea is to inject them into a solvent at a high temperature. Following the nucleation process, the precursor molecules come together to form nuclei, which then develop into nanocrystals (crystal growth step). Adjusting the physico-chemical characteristics of the generated QDs is mostly dependent on the latter stage. QDs are extracted from the solvent (termination step) and the crystallization operation is stopped after the required particle size has been achieved. Because the solvents utilized in this reaction are primarily organic, this process is also known as organometallic synthesis in the literature. CdTe/CdS and PbS QDs are two examples of QDs made using this technique. QDs produced via organometallic synthesis have narrow peak emission, high monodispersity, and high quantum yield, all of which make them ideal candidates for imaging applications. However, the stability and toxicity hazards of residual solvent are increased by the use of organic solvents in this procedure. Furthermore, QDs made using this technique are typically capped with hydrophobic ligands, which means that post-synthesis modifications are required to give the prepared QDs aqueous solubility. These modifications can include silica-based shells, polymeric coatings (like amphiphilic block copolymers), or exchange with hydrophilic ligands (like thiolated compounds). The aforementioned changes are efficient, but they also make the production more complex, which affects scalability and price. Using aqueous solvents instead of organic ones has become popular as a solution to the aforementioned issues.Many QDs, such as CuInS2 QDs, CdS QDs, AgInS2-ZnS QDs, and ZnSe QDs, were created by aqueous solvent-based synthesis. QDs with an average particle diameter of 5 nm are produced by aqueous-based synthesis, which also removes the need for post-synthesis solubilisation techniques. Comparing the generated QDs to those made by organometallic synthesis, however, reveals dismal optical characteristics [24].

3.3. Electro-chemical synthesis

The production of nanomaterials with customized properties can be achieved by the reliable method of electrochemical synthesis of quantum dots. Its environmental advantages and scalability make it a desirable choice for industrial and research applications in a variety of domains, from biology to electronics. Bulk materials, including graphite, are usually exfoliated using this process in an electrolyte solution. For instance, graphite can be electrochemically exfoliated in a potassium persulfate solution to create Graphene Quantum Dots (GQDs), which are uniformly sized and have particular optical characteristics. It is possible to regulate the size and characteristics of the resultant quantum dots by varying factors like the applied voltage, electrolyte content, and reaction time. This makes it possible to adjust the emission properties of the QDs [25].

3.4. Bio-template synthesis

Creating quantum dots with specific properties appropriate for various uses in nanomedicine and biotechnology can be achieved through the promising process of bio-template synthesis. Biological components are utilized in this process to improve the stability and biocompatibility of quantum dots while also improving their performance. As scaffolds, this technique incorporates a variety of biological materials, including peptides, DNA, RNA, and viruses (like bacteriophages). Quantum dots are assembled more easily thanks to these biomolecules. Through interactions like adsorption or covalent bonding, the precursors are assembled on the surface of the biotemplates. It's advantageous for preserving the integrity of the template and the QDs because this assembly can take place under mild circumstances [26].

4. Applications and future prospectives [27]

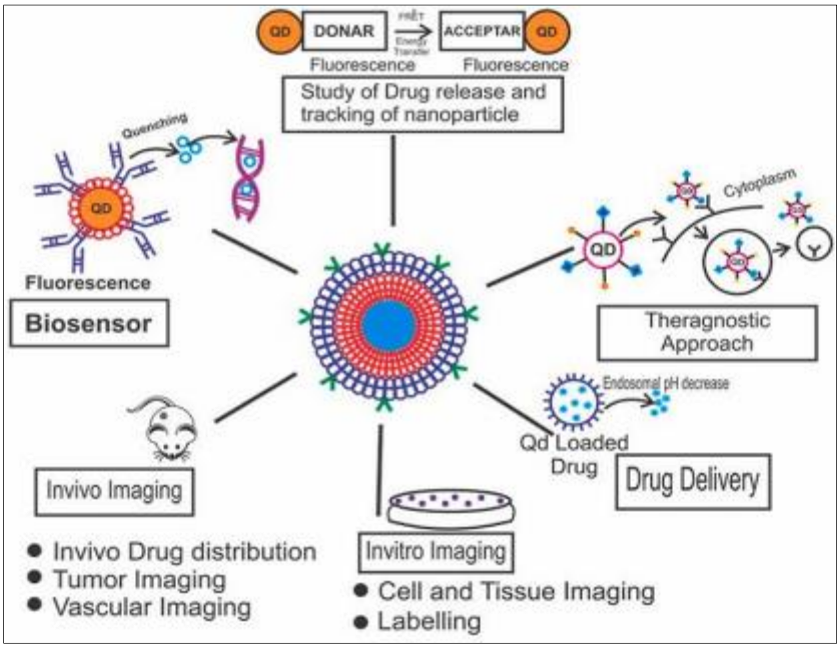

Figure 2 Various biomedical applications of quantum dots

Quantum dots as light-emitting diodes (LED): QD-LED technology is being explored for various advanced applications, including augmented reality, flexible displays, and automotive lighting. The ability to produce a wide color gamut makes them suitable for high-resolution displays.

Integrating different functional groups onto the surfaces of quantum dots to create multifunctional ones. These functional groupings could comprise medicinal compounds, imaging agents, and ligands that target particular cells.

Creating QDs that combine therapeutic and diagnostic imaging features in a theragnostic manner. To distribute medications in a targeted manner, QDs can be loaded with medication or therapeutic agents.

Table 1 Examples of surface modifications of QD's and their applications

Core/Multilayer Shell	Surface Modification	Target receptor
CdSe/CdS/ZnS QD's	Folic acid	Folate receptors
Graphene QD's	Anti-EGFR antibody	EGFR
Cd/Se	Aptamer 32	EGFRVIII in glioma cells
CdSe/ZnS	Dendrimer linked to PEG-folate	Folate receptors
Cd/Se QD's	PEG-folic acid	Folate receptors
CdSe/ZnS	Pepride E5	Chemokine receptor-4
Gold QD's (AuQDs)	Cold atmosphere plasma	Fas/TRAIL-mediated cell death receptor
Carbon QDs	Retinoic acid receptor responder protein 2	Retinoic acid receptor
Cd/Se	Anti-VEGFR antibodies	VEGFR
Ag_2S QD's	ZEGFR1907 antibody	EGFR
GQD's	Reduced graphene	Aryl hydrocarbon receptor
Cd/Se	Synaptic proteins	Neurotransmitter receptors

Creating QDs with hydrophilic and biocompatible surface coatings will increase their cellular uptake, decrease toxicity, and increase stability in biological settings.

By using cell-penetrating peptides as surface alterations to improve QDs' cellular internalization, effective intracellular imaging of processes and structures is made possible.

QD's allows the real-time visualization of biological processes in living things. Because of their improved tissue penetration, QDs emitting near-infrared light are very helpful in these applications.

Creating QDs that emit near-infrared (NIR) light to facilitate deep tissue imaging is known as "deep tissue imaging." This is important because tissue penetration may limit the use of classic imaging techniques when researching biological processes in vivo.

Utilizing QDs' photostability and brightness for single-molecule tracking and super-resolution imaging methods is known as single-molecule tracking. This makes it possible to see details at the molecular level inside of cells. By precisely localizing individual QDs and overcoming the diffraction limit, STORM techniques can enable super-resolution imaging.

By creating QDs with certain targeting ligands, as it is possible to deliver them to particular organelles inside of cells, enabling accurate subcellular structure imaging.

Creating QDs as specifically designed for the selective imaging of mitochondria is a crucial step towards comprehending cellular bioenergetics and different biological processes.

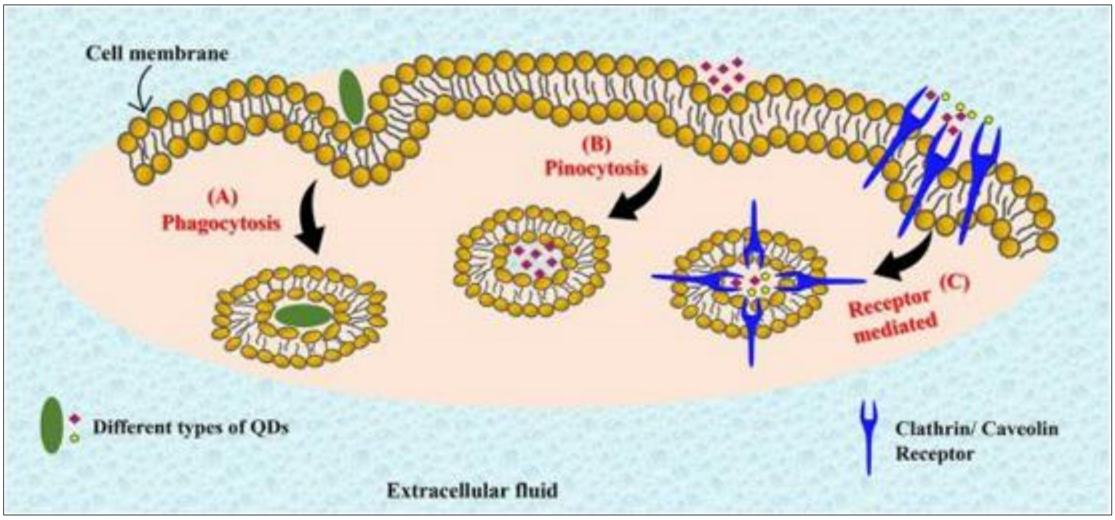

Figure 3 Mechanism of quantum dots in targeting ligands

Three-dimensional (3D) cellular imaging using quantum dots (QDs) offers a more thorough view of the cellular architecture and interactions found in intricate tissues.

Creating QDs with pH-responsive fluorescence to visualize changes in pH inside of individual cell compartments. This is especially helpful for researching acidic vesicles and intracellular organelles.

Developing QDs that respond to specific cellular signals, such as changes in reactive oxygen species (ROS) levels or enzyme activity, to provide real-time information on cellular processes.

Self-illuminating QDs, prepared systems can be created by mixing QDs with bioluminescent proteins or luciferases. This reduces the possibility of phototoxicity by doing away with the requirement for external excitation sources.

Using QDs to real-time monitoring of cellular signaling networks, vesicle trafficking, and membrane dynamics, among other dynamic cellular processes.

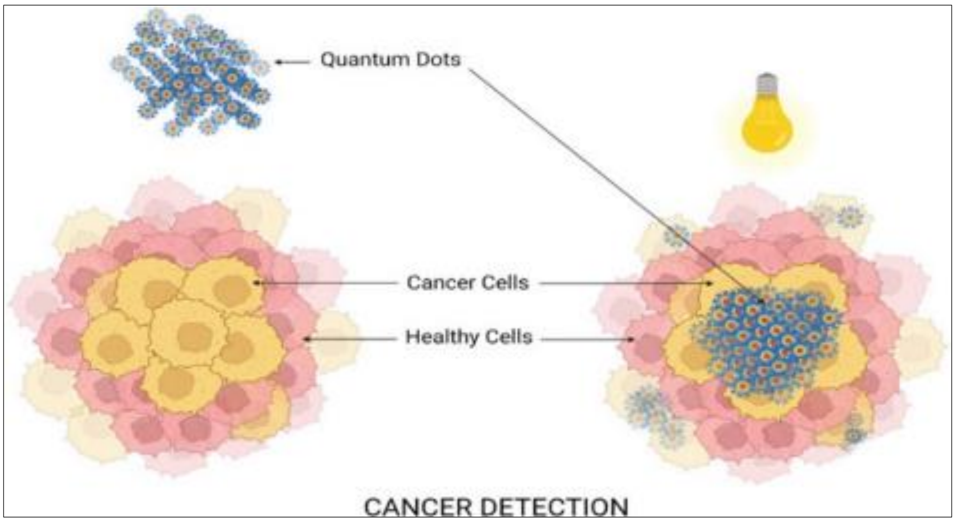

Figure 4 Detection of cancer cells in the body with the use of quantum dots

Combining machine learning techniques with quantum dot-based imaging data allows for automated and improved biological sample analysis, which will improve diagnostics and discovery processes. These novel approaches showcase the versatility and potential of quantum dots in advancing biological imaging capabilities, providing researchers with powerful tools for studying complex biological systems at various scales. As the field continues to evolve, new innovations are likely to emerge, further expanding the applications of quantum dots in biological imaging [28].

5. Limitations of quantum dots [29- 31]:

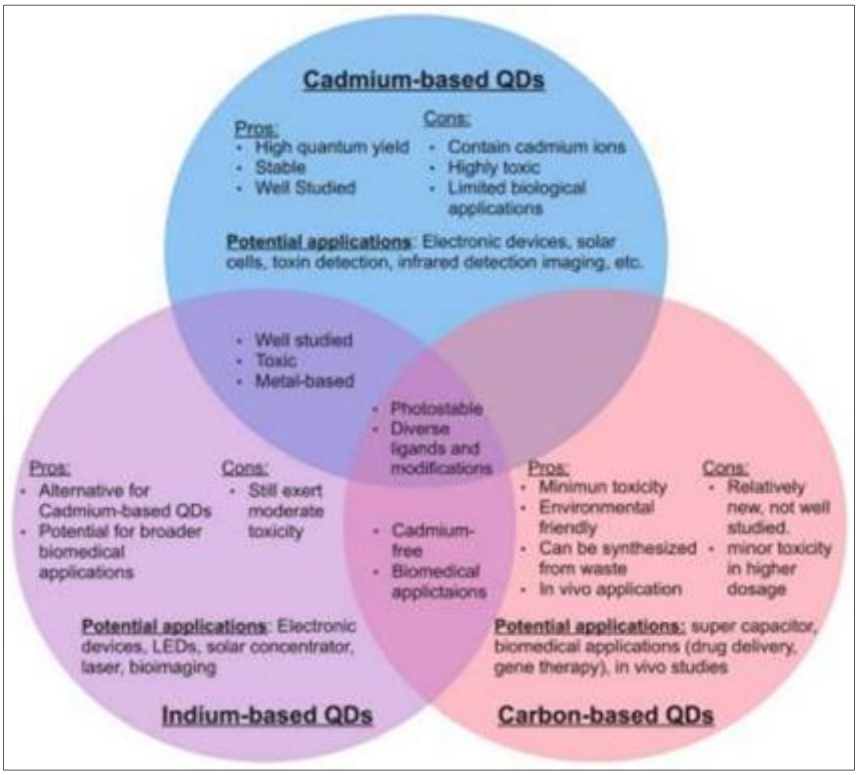

Figure 5 Advantages and disadvantages of various quantum dots

A lot of quantum dots are extremely toxic, particularly those made of cadmium selenide (CdSe). Their toxicity makes their use in biological applications questionable since it puts living things at danger and necessitates careful handling and disposal.

Structural instability is a potential problem for quantum dots. If the protective shell is broken or removed, it could affect their fluorescence and cause them to blink or lose all of it. Their dependability in tests and imaging applications may be impacted by this instability.

Quantum dots are not as able to diffuse across cellular membranes as regular fluorophores because of their larger size. This feature may reduce their usefulness in cellular applications and increase the risk of cell injury during delivery.

Under some circumstances, such as exposure to UV light or aquatic environments, quantum dots can deteriorate. Over time, this deterioration may change their optical characteristics and decrease their efficacy.

It can be difficult to consistently manage the size and optical characteristics of quantum dots. Size variations might result in different emission wavelengths, which makes using them in multiplexing applications more difficult.

Quantum dots may exhibit blinking behavior, where they intermittently switch between emitting and non-emitting states. This phenomenon can complicate data interpretation in fluorescence-based assays.

Because of their sensitivity to their surroundings, quantum dots' stability and performance may be impacted. Their features of fluorescence can be affected by variations in pH, ionic strength, or the presence of certain compounds.

Quantum dots, especially those that emit blue light, are made under difficult conditions that must be precisely controlled in order to guarantee quality and performance. This intricacy might restrict scalability and raise production costs.

6. Conclusion

Quantum dots (QDs) are nanosized semiconductor crystals with unique chemical and physical properties, enabling them to emit bright, photobleaching-resistant light. They are classified into three types: core type, core-shell, and alloyed type. Core-type QDs are composed of a single substance, while core-shell QDs have a semiconductor core surrounded by a shell. Alloyed QDs are manufactured using high-temperature or wet-chemical processes. Silicon-based QDs display unusual optical and electrical features due to quantum confinement forces. QDs have excellent optoelectronic capabilities and can produce photoluminescence quantum yields of up to 90%. They are useful for various applications, including optoelectronics and photocatalysis. There are three main types of QDs: colloidal, magnetic, and fluorescent. Colloidal synthesis is a widely used technique, while electrochemical synthesis offers customized properties. QDs are being developed to enhance biological imaging capabilities, including intracellular imaging, deep tissue imaging, single-molecule tracking, super-resolution imaging, targeting ligands, and selective imaging of mitochondria. They have revolutionized health science by providing innovative solutions for diagnosis, treatment, and research.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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