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Review Article

Quantum Dots For Imaging and Drug Delivery in Cancer Therapy

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ABSTRACT

One of the main causes of mortality globally is cancer. It is hard to diagnose and treat cancer because every case can be different. In contrast to earlier diagnostic methods, improvements in nanomedicine have enabled tumor identification and rapid cellular-level analysis of tumor cells. Quantum dots (QDs), sometimes referred to as nanoscale semiconductor crystals, are nanoparticles with distinct optical and electrical characteristics, such as intense and brilliant fluorescence. QDs, with their customizable optical characteristics, have attracted a lot of attention because the majority of traditional organic label colors lack the potential for near-infrared (>650 nm) emission. Due to their remarkable optical characteristics and quantum confinement, these nanoscale particles have become indispensable tools in bioimaging and cancer drug delivery. The same light wavelength can excite a variety of QD types, and their narrow emission bands can be detected simultaneously for many assays. QD excretion, along with photography, has demonstrated amazing applicability in bioimaging, novel medication development, targeted gene delivery, biosensing, photodynamic therapy, and diagnosis. In addition to its value in drug delivery in cancer treatment, the current review sought to highlight the relevance of QD in imaging

INTRODUCTION

A collection of illnesses known as cancer is distinguished by the quick proliferation of aberrant cells throughout the body. The majority of cancer cases are caused by mutations or alterations in the expression of tumor suppressor genes, DNA repair genes, and proto-oncogenes. In addition to signs of an unhealthy lifestyle (tobacco use, bad diet), genetic (hormones, mutations, immune conditions) and environmental (radiation, chemicals, pollutants) variables are responsible for the majority of cancers. In addition, aging raises the risk of developing cancer considerably [2]. The use of tumor-specific antibody conjugates for active tumor targeting in novel anticancer therapies has attracted a lot of attention in the fields of oncology, pharmacology, and nanomedicine. This method will enable to enhance therapeutic effectiveness and lower systemic

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toxicity [3]. Nanotechnology has revolutionized the pharmaceutical and medical sectors with its revolutionary potential, paving the way for early diagnosis and medication delivery. Quantum dots (QDs), nanoscale zero-dimensional crystals that have a wide range of optical, spectral, magnetic, and electrochemical characteristics, are at the forefront of this nanotechnological revolution. QDs have received a lot of attention among the numerous nanomaterials as a crucial instrument in bioimaging and cancer drug delivery. [4] Ekimov and Onushenko first described quantum dots (QDs), sometimes referred to as nanoscale semiconductor crystals, in a glass matrix in 1981, and the first application for biological imaging was published in 1998. The field of QDs has been steadily expanding ever since, with applications in areas such as photodetectors, biomedical imaging, computing, light-emitting diode (LED) manufacturing, photovoltaic devices, solar cells, and more. [5] QDs have exceptional optical characteristics that make them promising candidates for use as luminescent nano-probes and carriers in biological applications. Drug QD nano-carriers can be loaded with drugs by dissolving, dispersing, adsorbing, and coupling, among other methods. The carriers next alter the physical and chemical properties of drugs (such as saturation solubility, dissolution rate, crystal form, particle surface hydrophobicity and hydrophilicity), as well as their biological behavior and physical response, thereby affecting how drugs are absorbed, distributed, metabolized, and excreted [6].

Structure of QDs:

Quantum dots are composed of tiny metal particles that are around a thousand times smaller than a hair. These particles are shaped into different shapes and covered in various biomaterials. Quantum dots fluoresce in UV light, and their size determines the shade they produce. For example, QD (2 nm) had red fluorescence, whereas QD (2 nm) fluoresced clearly in green. The majority of fluorescent quantum dots are made of chemicals ranging from group II to VI and III to V, such as Cd, Hg, Se, Ag, Ln, P, Pb, Te, and Zn. The frequency that quantum dots produce becomes more constrained as their size decreases. They have a defined discharge frequency, so their spectra do not show a variety of fluorescence radiations [7]. The structure of quantum dots includes a core, shell, and sometimes a surface coating, which gives them a high degree of stability in photo and chemical behaviors, surface activation, and photo luminescence quantum yield [2].

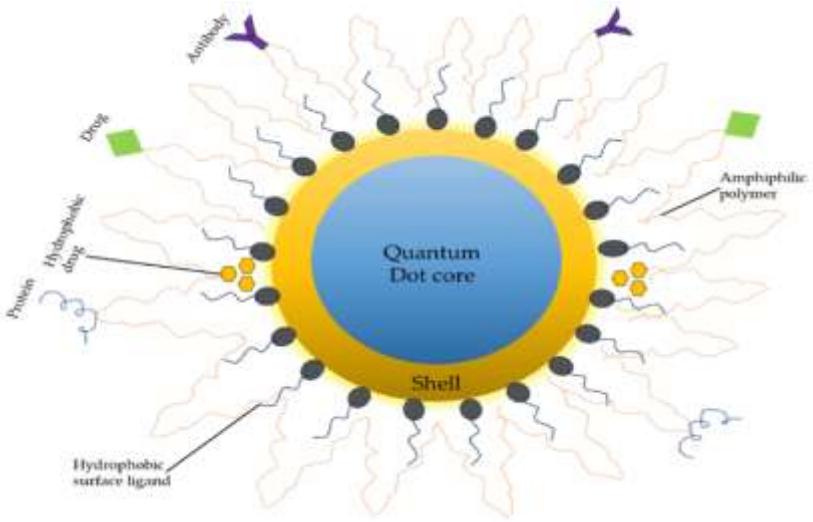

Fig.1: Basic Structure of QDs With Shell, Core & Ligand.

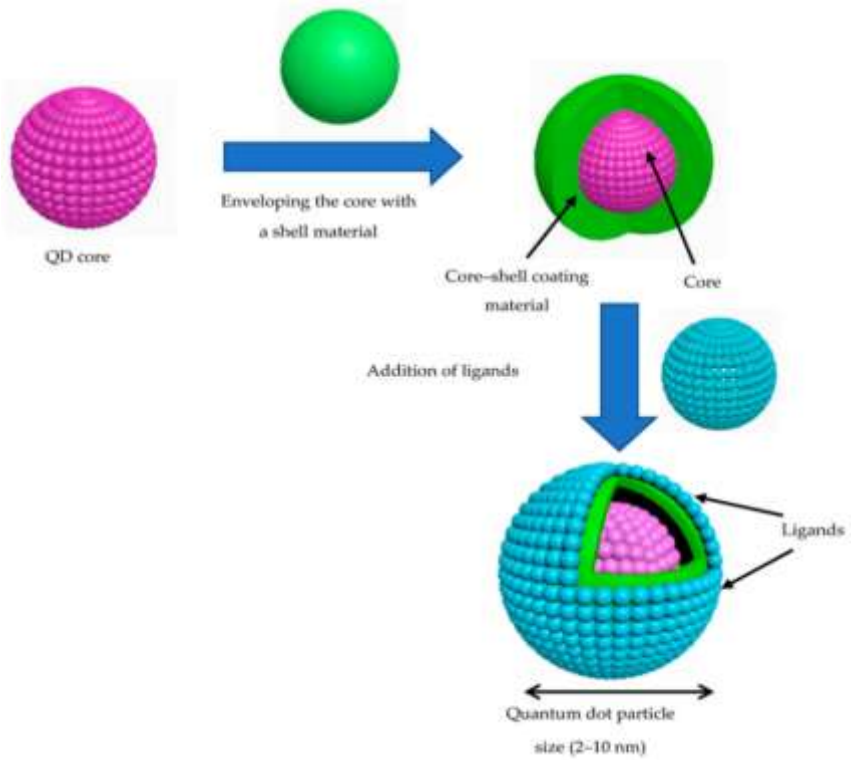

Fig.2: Formation of Quantum Dot Particle.

Synthesis of QDs:

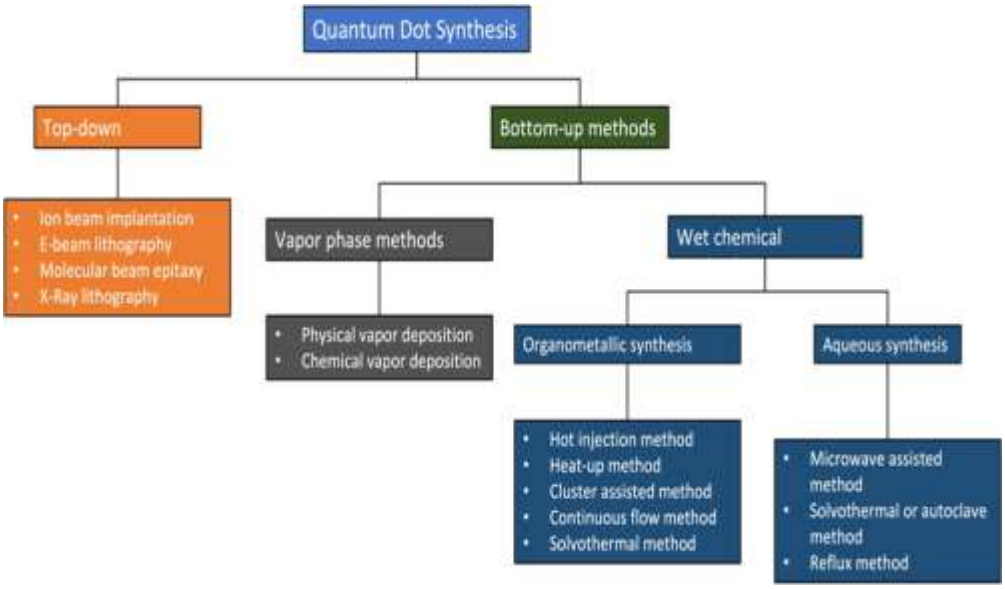

Fig.3: Quantum Dots Synthesis Flow Chart.

QDs Synthesis:

1. Top-down approach

The top-down method involves creating QDs by ablating bulk semiconductor materials. This covers techniques like reactive ion etching, electron beam lithography, and focused ion beam. These procedures create QDs with a diameter of about 30 nm. But these methods have drawbacks, such as the incorporation of pollutants during synthesis [2].

2. Bottom-Up Methods for GQDs Synthesis

Using advanced bottom-up methods that begin with tiny aromatic precursors or other carbon sources, which are also produced by the breakdown of bulk materials, GQDs with regulated morphology and well-distributed sizes have been synthesized.

3. Other Synthesis

Hydrothermal synthesis can also be used to create QDs. This is a method of single-pot synthesis whereby inorganic salts are crystallized from aqueous solution by controlling temperature and pressure. Due to the pressure confinement inside the autoclave, the temperature may be increased to very high levels in this method. This causes partial chemical breakdown and encourages molecular interactions, which leads to the synthesis of QD [2].

The usage of quantum dots (QDs) in the treatment of cancer.

The use of nanotechnology for cancer therapy, known as Nano-Oncology, has seen significant development during the previous ten years. The engineering of nanomaterials for cancer therapy and diagnosis has demonstrated the possibility of transforming the cancer treatment by creating novel theranostic nanoparticles for simultaneous imaging and therapy [13]. QDs can be used in a variety of cancer therapy-related studies, such as identifying molecular targets, sentinel lymph node mapping, drug delivery and tracking, surgical oncology, fluorescence resonance energy transfer and photodynamic therapy, personalized and predictive medicine, and multifunctional design and development [9].

***Imagining:**

In identifying the right cancer treatment, imaging is a crucial clinical method [15]. Molecular imaging of cancer using nanotechnology is a potential platform. Due to their distinct optical and electronic properties, quantum dots (QDs) are being extensively investigated as a novel probe for biomedical imaging, both in vitro and in vivo. The physicochemical properties of QDs, including their size, shape, composition, and surface characteristics, have been thoroughly studied in an effort to address the challenges that QDs present for biomedical imaging [12]. Within a photodynamic method for therapy, CNTs have shown a significant potential for imaging in both in vivo (utilizing mice) and in vitro [14]. QDs, a novel type of inorganic nano-fluorescent probe, have demonstrated remarkable benefits in multi-color fluorescence imaging and detection over extended periods of time. The advancement of QD labeling facilitates the study of nano-drugs at the cellular and live animal level. The creation of therapeutic multifunctional nanomedicines and fluorescence imaging technology of quantum dots is anticipated to be used in the diagnosis and treatment of cancer [6].

(a) In vitro tumor imaging:

Tumors In Vitro with QDs are used in imaging, and recent studies have demonstrated that they can create fluorescent in vitro images of tumor cells. QDs are superior to traditional fluorescence organic dyes due to their distinct characteristics [2]. The in-vitro approach allows for the regulated and unnatural handling of organs, tissues, cells, and biomolecules [10]. Using quantum dots, many research produced in vitro fluorescent pictures of human cancerous cells taken from melanoma, ovarian, breast, pancreatic, glioblastoma, ovarian epidermoid, lung, hepatocellular, and adenocarcinoma cancers. [7] Tissue staining, cell imaging, and biomolecular tracking in cells are the

main categories indicated by in vitro fluorescent imaging [10]. The toxicity of cadmium-containing QDs remained a significant problem when using QDs for biological imaging and cell research. However, the potential toxicity of cadmium is no longer an issue for in vitro and in vivo imaging experiments thanks to recent advancements in the surface modification of QDs and cadmium-free QDs [11]. In their study, Zhang et al. demonstrated that anti-type-1 insulin-like growth factor receptor (IGF1R) quantum dots are a viable substitute for targeting and imaging breast cancer cells. In that work, it was essential to find that MCF-7 breast cancer cells had an upregulated IGF1R using Quantum dots-hostile to IGFR1 form [7].

(b) tumor imaging in vivo:

Because of their superb fluorescence signals and multiplexing capabilities, QDs are a promising tool for cancer bioimaging, particularly in vivo. Researchers have published numerous instances of employing QDs to image malignancies in vivo [2].

In vivo investigations refer to the depiction and study of biomolecules and biological systems in the whole organism, and they often involve conducting experiments in the animal's vast system. As opposed to in vitro imaging, in vivo QD imaging faces a number of difficulties due to the rise in complexity brought about by multicellular organisms and increasing size. There are four primary categories of QDs in vivo imaging applications: QDs biodistribution, vascular imaging, QDs tracking, and tumor imaging [10]. Fluorescent imaging has been widely used to detect tumors in vivo using aggressive tumor targeting methods and passive enhanced permeation and retention (EPR) effect. For example, Hong et al. created six-armed PEG modified Ag2S (6PEG-Ag2S) QDs as a biocompatible NIR-II imaging contrast agent with high SBR that is free of heavy metals and may be used for passive tumor targeting for organ registration, tumor identification, and tumor angiography [16].

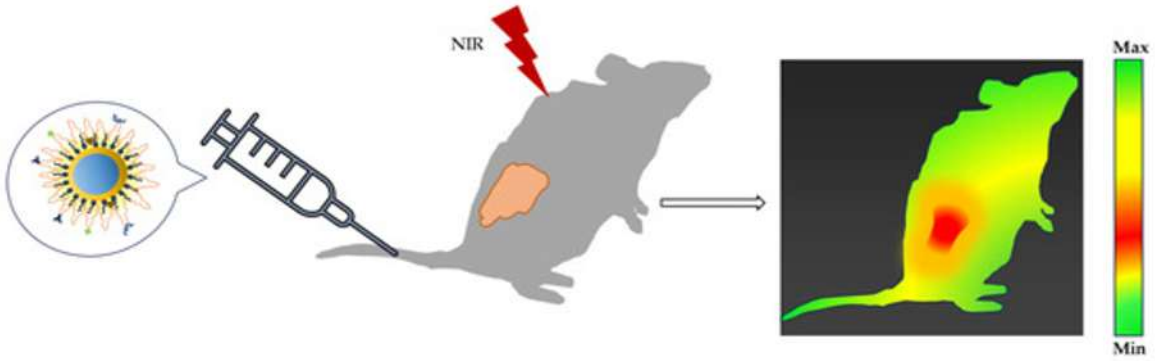

Figure 4: A schematic representation of QD administered into a tumor-bearing mouse for in vivo tumor research is shown.

For targeted imaging and cancer treatment, Zhu et al. created, for example, near-infrared (NIR) fluorescent silver selenide (Ag2Se) QDs labeled with Cetuximab. In contrast to using Ag2Se QDs alone, the multifunctional nanoprobe was said to show fluorescent contrast at the tumor site, and the fluorescence was still easily seen there 24 hours after injection. This nanoprobe, according to their findings, considerably slowed tumor development, and the survival rate of bare mice with orthotopic tongue cancer increased from 0% to 57.1%. According to reports, this platform was able to effectively target orthotopic tongue cancer [2].

Imaging of the blood vessels:

QDs have proven to have excellent micron-level spatial resolution and high penetration depth, making them useful for imaging tumor blood vessels in vivo. In the meantime, the outstanding optical characteristics of NIR-II (Near Infrared-II) QDs can be used to perform real-time, high-resolution angiography in order to investigate the mechanism of angiogenesis and provide hemodynamic data. This is essential in the real-time diagnosis and intervention therapy of cancer, as well as in the non-invasive, accurate identification of benign and malignant tumors in situ and the early diagnosis of malignant solid tumors [16].

- QDs for Drug Delivery:

Many teams have concentrated on integrating therapeutic and diagnostic skills into a single, nanoparticle-based agent. Because they may serve as the primary nanocarrier or as the fluorescent markers in a more complicated design [5], QDs are excellent candidates for theranostic platforms. QDs are only one instance of the many nanoparticles that have been extensively studied for use in medication delivery. Reports indicate that the antitumor efficacy is improved while the systemic adverse effect is decreased, which is due to the effective nanoparticle entrapment of anti-cancer drugs and the regulated distribution in tissues and cells [2]. Important characteristics for effective targeted delivery are demonstrated by nanoparticle drug carriers, including a sufficiently long blood circulation, protection of the cargo from degradation, a high drug loading capacity, a regulated drug release profile, and the integration of several targeting ligands on their surface. In addition, fluorescence can be used with QD probes to track drug delivery in vivo and monitor the biodistribution of carriers and intracellular uptake [10].

Table 1. Using QDs for targeted drug delivery in vitro and in vivo [2].

QDs Used In Vitro	Drug	Cell Line
Iron oxide carbon QDs encapsulated in chitosan	Curcumin	MCF-7cells
Transferrin (TF) – conjugated Carbon QDs	Doxorubicin	MCF-7cells
Graphene oxide QDs conjugated with glucosamine and boric acid	Doxorubicin	MCF-7cells
Magnesium nitride (Mg/N) doped carbon QDs (CQDs)	Epirubicin (EPI)	4T1 and MCF-7cells
Nitrogen-doped Graphene QDs (N-GQDs)	Methotrexate (MTX)	MCF-7 human breast cancer cells
PEGylated molybdenum disulfide QDs	Doxorubicin	U251cells
Zinc oxide adipic dihydrazide heparin	Paclitaxel	A549cells
Cadmium-sulfide-modified chitosan	Sesamol	MCF-7cells
PEGylated Silver graphene QDs (Ag-GQDs)	Doxorubicin	HeLa and DU145 cells
QDs used in vivo		
Graphene QDs	Doxorubicin	MCF-7cells
Silver sulfide (Ag2S) QDs conjugated with chitosan	Doxorubicin	HeLa cells
Manganese doped zinc sulfide (Mn-ZnS) QDs conjugated with folic acid (FA)	5-fluorouracil (5-FU)	4T1 breast cancer cells
PEGylated silver sulfide Ag2S QDs	Doxorubicin	MDA-MB-231 human breast tumour cells
Graphene QD (GQD)-modified magnetic chitosan	Doxorubicin	Hepatocellular carcinoma
Red-emissive carbon QDs	Doxorubicin	HeLa cells
Black phosphorus QDs (BPQDs) encapsulated in platelet-osteosarcoma hybrid membrane	Doxorubicin	Osteosarcoma
Nitrogen-doped carbon QDs conjugated with folic acid	Doxorubicin	4T1 and MCF-7 cells

PEGylated molybdenum disulfide (MoS2) QDs conjugated with arginylglycylaspartic acid (RGD)peptide	Doxorubicin	HepG2 cells

Table 2. The main results of the QDs used for drug delivery in different malignancies [4].

Sr. no.	Types of QDs	Drug	Targeted Diseases	Inference
1.	CDs	Epirubicin and Temo zolomide	Brain Tumour	• Triple conjugated system showed profound cytotoxicity in tumour cells with minimal effects on normal cells. • Conjugating with transferrin improved the cytotoxicity and cellular uptake of conjugated QDs.
2.	GQDs	Imatinib	Blood Cancer	• Higher IC50 values were observed for drug-loaded GQDs. • Drug-loaded GQDs induced mild apoptosis.
3.	CQDs	5-fluorouracil	Breast Cancer	• The nanoconjugate exhibited higher cytotoxicity than the free drug. • Better release profile in acidic environments.
4.	CQDs	Curcumin	Breast Cancer	• Viable cancerous cell count was lowered, and late apoptosis was boosted in MCF-7 breast cancer cell lines upon treatment. • Controlled drug release by curcumin CQDs. • The nano composite showed pH-dependent drug release owing to chitosan's pH sensitivity.
5.	CQDs	Camptothecin	Breast Cancer	• Sustained drug release was observed for upto100h, followed by a rapid release phase. • Dose-dependent cytotoxicity observed. • pH-responsive drug release observed.
6.	CQDs	Doxorubicin	Breast Cancer	• Elevated drug release was observed at acidic pH. • Higher apoptotic effect of transferrin (Tf) DOX CQDs than free DOX. •DOX Tf CQDs better internalised than free drugs and DOX CQDs • Real-time drug release tracking through CQDs.
7.	CQDs	Gemcitabine	Breast Cancer	• Elevated drug release in acidic pH compared to physiological pH. • IC50 value of drug-loaded QDs is 2 times less than the free drug. • Drug-loaded QDs were localised in the tumour region, sparing the healthy normal cells.
8.	Ag QDs	Methotrexate	Cervical Cancer	• IC50 values of drug-loaded targeted QDs were found to be comparable to those of free drug in cancer cell inhibition. • No significant cytotoxicity was observed after 24 h.
9.	CDs	Doxorubicin	Cervical and kidney cancer	• The β-cyclodextrin decorated CDs showed acidic pH-dependent drug release. • Selective targeting of cancer cells achieved upon decoration with β-cyclodextrin.
10.	CDs	Doxorubicin	Cervical cancer and liver cancer	• Showed3timeshigherfluorescence intensity of DOX CDs cubosomes at 24h. • Significantly lower cell viability by DOX CDs cubosomes. • In vivo DOX CDs cubosomes exhibited the lowest average tumour volume.

				• Reduced cardiotoxicity and hepatotoxicity of DOX CDs cubosomes.
11.	Ag QDs	Doxorubicin	Lung Cancer	• FA conjugation augmented the cytotoxic action of the DOX-MUA-QDs. • FA-MUA-DOX QDs obstructed the colony-forming ability of A549 effectively at concentrations near their cytotoxic thresholds. • DNA damage in the cells treated by FA-MUA-DOX QDs was genotoxic to the A549 cells.
12.	CDs	Doxorubicin	Liver cancer	• Increased drug release at pH 5.2. • Sustained release from CDs (72 h), whereas free DOX released completely in 10 h. • DOX-PEI CDs had stronger fluorescence in tumours and improved drug delivery compared to free DOX. • The DOX-PEI CDs animal group had better survival than the free DOX group, indicating a superior safety profile for the nanoconjugate.
13.	BPQDs	Doxorubicin	Osteosarcoma	• Prominent aggregation of DOX in the tumour tissue from the BPQDs. • The stability of BPQDs is augmented through OPM encapsulation. • NIR light irradiation triggered DOX release. • In vivo studies showed notable tumour reduction.
14.	GQDs	Doxorubicin	Colorectal cancer	• EpCAM aptamer conjugated nanoparticles encapsulated DOX, ZIF-8, and GQDs facilitated triple delivery for the treatment of colorectal cancer. • Drug release from the nano conjugate was favoured at acidic pH 5.4 with a burst release prior to gradual release.
15.	GQDs	Gemcitabine	Pancreatic cancer	• Conjugation of GQDs with human serum albumin nanoparticles demonstrated sustained drug release and improved stability. • HA targeted CD44 receptors for enhanced delivery to resistant cells.
16.	Ag QDs	Etoposide+ methotrexate	Skin Cancer	• Ferromagnetic QD nanocomposites showed sustained release for 30h. • Reduced cell viability in a concentration-dependent manner.
17.	CdSe QDs	Methotrexate	Throat cancer	• Higher cytotoxicity by drug conjugate than free MTX with 4 times more efficacy.
18.	GQDs	Doxorubicin/ Curcumin	Colorectal and breast cancer	• Enhanced tumour penetration due to MiRGD peptide • Better release profile in an acidic environment, indicating its selective targeting. • Higher drug accumulation at the tumour site than that of free drugs.
19.	CDs	Doxorubicin	Adenoid Cystic Carcinoma	• DOX-CDs biocompatible and non-toxic to normal cells. • DOX-CDs-induced apoptosis inhibited tumour growth and prolonged the survival of the mice.
20.	Ag-In-Zn QDs	Compound C-2028	Lung and prostate cancer	• Strong cytotoxic action against cancer cells with low IC80 values.

				• Cytotoxicity reduced upon conjugation withβ-cyclodextrin but vice versa with folic acid conjugation.

CHALLENGES

The toxicity of QDs remains the biggest impediment to clinical translation, despite the possible immense social advantages they provide for human illness. The biochemical processes underlying cytotoxicity are now being understood. The toxicity of QDs has been linked to their charge, size, concentration, and stability, as well as the bioactivity of their outer coating [9].

Despite the enormous potential of QDs in biomedical imaging and detection, toxicological and pharmacological problems, primarily related to heavy metals and colloidal instability, impede progress toward cancer diagnosis and treatment as well as other illnesses. Nanotoxicology The development of these applications in vitro may not be hampered by these issues, but they present significant obstacles to their use in vivo for human cancer imaging [12].

(Cd Se) ZnS is the most prevalent QD makeup. It has a core of cadmium and selenium, both of which are well known to be harmful [9].

Although CdSe and CdTe semiconductor materials have been widely utilized as the core of QDs, they have been shown to exhibit cytotoxicity at low concentrations. As a result, silicon or AgInS2 core-based novel QDs that exclude Cd, Se, and Te elements have already been created, and these QDs have been shown to have minimal toxicity [11].

FUTURE PROSPECTS

Scientists in the domains of chemistry, biology, medical engineering, and pharmaceutical sciences have come together in a shared effort to establish QDs as technological advancements with features that could significantly advance in vivo and in vitro imaging as well as achieve notable advances in the field of nanomedicine research [10].

The flexibility of QDs allows for novel approaches to treating cancer. Recent research has shown that black phosphorus material functions as a "nanoknife," allowing for the exact tumor ablation described in the article. BPQDs are being investigated for use in chemotherapeutic medication delivery and may potentially be used as nanoknives as well as nanocarriers [4].

A variety of efforts should be made to create unique QDs based on their composition, sizes, surface coatings, and valences in order to reduce toxicity and optimize detection performance. Consider, however, challenges such as shell coating degradation brought about by QD [7].

In vivo theranostics [11], an approach that likely allows for the simultaneous diagnosis and treatment of stem cells in vivo, is made possible by the development of hybrid materials between QDs and other functional molecules during the evolution of QDs.

Immunomodulatory capabilities may be included in future QD-based treatments. QDs that are functionalized with immune checkpoint inhibitors or stimulatory molecules may help the immune system identify and destroy cancer cells. For a full cancer treatment, such approaches might combine with chemotherapy and radiation [4].

CONCLUSION

The use of nanoparticles in the battle against cancer has been the subject of considerable study.

Because nanoparticles have a number of traits necessary to address the drawbacks of standard cancer therapy methods, they may be used as a basis for early diagnosis and treatment. The most recent nanoparticles to show distinctive characteristics that might revolutionize cancer diagnosis and treatment are quantum dots. The characteristics of these features include their tiny tunable size, consistent photoluminescence, high surface-to-volume ratio, and possibility for biocompatibility. QDs have been widely used for tumor imaging in vitro and in vivo, and they have also been combined with therapeutic medicines for targeted drug delivery in vivo. Early tumor identification and diagnosis, bioimaging, targeted gene-drug delivery, phototherapy, and medication delivery are the main applications of QDs in cancer therapy. Due to their excellent biocompatibility, low cytotoxicity, and high capacity for cell uptake, QDs are also the preferred method of drug administration. There is no doubt that QDs have tremendous promise for use in bio-imaging, sensors, drug delivery, and other fields. To realize the true potential of QDs in clinical practice, a number of challenges must yet be overcome, including overall toxicity, body clearance, the scalability of the synthesis procedure, environmental effects, manufacturing costs, and other factors. Theranostic platforms are always being created by combining QDs with additional kinds of nanoparticles and/or biologically active compounds.

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