Chapter

Recent Advances in Quantum Dots-Based Biosensors

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Abstract

Biosensors can be developed using quantum dots (QDs). An inorganic nucleus with organic molecules attached to its surface is referred to as a QD, and they are a type of new fluorescent nanomaterial. QDs possess unique excellent optical properties and chemical properties, including broad excitation spectra, adjustable particle sizes, confined emission spectra, emission of multiple fluorescence colors, superior signal brightness, and extended fluorescence lifetime. QDs have abundant functional groups, which make it easy to form hybrid nanomaterials that perform analytically well. With functionalized sensing systems, we can detect metal ions, biomarkers, and antibiotics sensitively and selectively through the hybridization of QDs with nanomaterials. In this chapter, we first introduce the research trends in the application of QDs and then discuss their surface modification for biological applications.

Keywords: biosensors, quantum dots, biological applications, fluorescent nanomaterial

1. Introduction

Semiconductor nanocrystals or quantum dots (QDs) are a type of novel fluorescent nanomaterial consisting of inorganic nuclei with organic molecules in the nanoscale range of 1–10 nm and are typically composed of atoms from groups II–VI (e.g. CdTe, CdSe) and III–V (e.g. InP, InAs) of the periodic table [1]. Their optoelectronic properties change as a function of both shape and size. Colors like orange and red are emitted by larger QDs with diameters of 5–6 nm. QDs with shorter wavelengths (2–3 nm) produce colors such as blue and green [2]. Depending on the exact composition of the QD, the specific colors vary. It is fairly common for these QD cores to be capped with an inorganic layer to boost their quantum yield, which enhances their signal-to-noise ratio [3]. As a result of the size and composition of QDs, they can emit various wavelengths, ranging from ultraviolet (UV) to visible to near-infrared (NIR). [4]. The properties of QDs are intermediate between those of bulk semiconductors and those of discrete atoms or molecules. A hydrophilic material (e.g. mercaptopropionic acid (MPA) or cysteamine) must be added to QD surfaces in order to increase their water solubility [5]. Surface conjugations with synthetic polymers such as polyethylene glycol (PEG) are often useful for preventing aggregation of these nanoparticles [6].

With their unique electronic properties and tunable emission spectrum, quantum dots have attracted considerable interest owing to their resistance to photobleaching, broad excitation wavelength, and high quantum yield [7, 8]. Various applications and

devices benefit from the unique characteristics of QDs, including solar cells, fluorescent probes, optical switches, and light sources [9, 10].

The quantum dots can be divided into core-shell QDs, doped QDs, and nuclear QDs in terms of structure. Quantum dots can also be easily modified by encapsulating the surface with amphiphilic ligands, salinizing, and exchanging ligands, further expanding their sensor applications [11–14].

Biosensors can be developed using quantum dots (QDs) [15, 16]. Molecular QDs provide researchers with the ability to study cell processes at the molecule level and may be helpful in diagnosing and treating diseases such as cancer [17]. It is possible to use quantum dots as active sensors in high-resolution cellular imaging, by changing their fluorescence properties as they react with the analyte, or by conjugating antibodies to the surface of the dots to act as passive label probes. Due to the presence of highly toxic heavy metal elements such as cadmium in QDs, these materials cannot be used in biomedical applications [18]. Environmental pollution and toxicity have been a concern in the use of nanomaterials for biomedical applications, and the development of a nontoxic and biocompatible nanomaterial is becoming increasingly important. Incorporating QDs into hybrid nanomaterials has proven easy due to their abundant functional groups [19]. Hybridizing QDs with other materials can provide enhanced thermal and chemical stability, high quantum efficiency, longer excited state lifetimes, and minimized toxicity [20].

The biosensor is a micro-analytical system. As part of the development and application of analytical sensors, biosensing incorporates molecular biological recognition entities [21]. Biosensors are sensing systems that leverage biological recognition to confer molecular specificity to analytes. In the chapter, we first introduce the research trends in the application of QDs and then discuss their surface modification for biological applications.

2. Overview of QDs-based biosensors

Biosensors have been developed using QDs as promising tools. In **Table 1**, we summarize the selected methods for detecting different targets using various QDs.

Pourghobadi et al. prepared TGA-capped CdTe QDs for the visual determination of the trace levels of dopamine. The fluorescence intensity of the samples was investigated as a result of interaction between TGA-CdTe QDs and dopamine. Fluorescence intensity decreases dramatically with an increase in dopamine concentration. Taking into account this trend, we developed a straightforward method for the detection of dopamine that is sensitive to fluorescence [22].

According to Wang et al., hydrophilic QDs can be used as molecular probes to detect trace amounts of propafenone. Electrostatic attraction and hydrogen bonds allowed propafenone to combine with CdTe QDs modified with thioglycolic acid in the weak acid. Fluorescence, UV-vis absorption, RRS, spectra, and spectral analysis have been used to study the interaction of CdTe QDs with propafenone. With the RRS method, ppb (ng mL^{-1}) levels of propafenone in serum samples can be detected in less than 30 min [23].

Tetracycline was detected in milk using MoS_2 QDs and CdTe QDs developed by Liang et al. As a first step, MoS_2 QDs emit blue light at 433 nm, while CdTe QDs produce yellow light at 573 nm under 365 nm excitation. We used MoS_2 QDs and CdTe QDs to construct a fluorescent sensor with dual signals at 433 nm and 573 nm. MoS_2/CdTe-based sensors show a lower fluorescence intensity as tetracycline concentration

QD type	Sensor model	Target	Linear range	Real sample type	Ref.
Ni-doped CdTe	Fluorescence	Pyrazinamide	2–100 μM	Plasma samples	4
CdTe	Fluorescence	Dopamine	0.5–10 μM	Biological fluids	22
CdTe	Fluorescence	Propafenone	0.003–7.0 μg mL^{-1}	Human serum	23
MoS_2/CdTe	Fluorescence	Tetracycline	0.1–1 μM	Milk samples	24
CdTe–Con A	Fluorescence	Lipopolysaccharide and Serratia marcescens	10–90 fg/mL	—	25
CdSe	Fluorescence	Urea	1–120 mM		26
CdTe	Fluorescence	Salbutamol	6.27×10^{-8} to 2.09×10^{-7} M	Pig urine samples	27
Pd-doped CdTe	Fluorescence	Diazinon	2.3–100 μM	Environmental water samples	36
CdS@MOF	Electrochemiluminescence	Carcinoembryonic antigen	—	Human serum samples	39
CdTeS @ SiO2	ImageJ software	Folic acid	5–80 μM	Serum samples	29
α-FeOOH@ CdS/Ag	Electrochemiluminescence	17β-estradiol	0.01–10 pg. mL^{-1}		35
ZnCdS QDs@MIP	Fluorescence	Ascorbic acid	1–500 μM	Vitamin C tablets	48
MoS_2/GQD	Electrochemical	Caffeic acid	0.38–100 μM	Red wine samples	52
CdTe	Photoinduced electron transfer	Double-strand DNA	0.0874 μg mL^{-1} and 20 μg mL^{-1}	Synthetic samples	55
Polymer CdTe/CdS	Fluorescence	Glucose	0.2–5 mM	Human body fluids	61

Table 1.
Summary of the QDs-based biosensors.

is increased, and 573 nm is quenched more apparent than 433 nm as tetracycline concentrations are increased [24].

Conjugated CdTe QDs with TGA caps were successfully prepared as a novel biosensor for detecting LPS at concentrations of fg/mL. CdTe QDs showed high crystalline lattice planes with an average size of 4–5 nm in the high-resolution transmission electron photograph. The electrostatic attraction force between positively charged Con A species and negatively charged CdTe QD surfaces was responsible for the adsorption of Con A onto CdTe QD surfaces [25].

The MPA-CdSe QDs were used to detect urea in a case study based on a fluorescence-based "turn-on" probe. MPA-CdSe QDs are sensitive to pH change, and this property makes them useful for detecting urea sensitively and selectively in the presence of urease. By releasing ammonia ions as the enzymatic reaction occurs, the pH of the solution changes, and the fluorescence intensity of the system increases along with the concentration of urea [26].

Researchers conducted experiments to improve the quantum yield of CdTe QDs in 2021 (59.673%). A pH value of 140°C and heating for 40 minutes have been suggested for producing high photoluminescence from CdTe QDs. Salbutamol effectively reduces the fluorescence intensity of CdTe QDs. Fluorescence quenching was linearly related to Salbutamol concentration. Using CdTe QDs as a new fluorescent probe, Salbutamol was successfully measured in pig urine [27].

The main obstacles to their extensive application in biomedicine are their poor biodistribution, low in vivo stability, and high cytotoxicity.

Cd and Se elements in QDs are mostly responsible for their cytotoxicity. The surface conjugations with synthetic polymers such as polyethylene glycol (PEG) are often useful for preventing aggregation of these nanoparticles.

It remains a significant concern about the toxicity of these NPs, despite all the advances in the synthesis of QDs with different coatings. Further research is needed in this area. Researchers are currently working on modifying the surface of QDs to enhance their capacity to capture specific and efficient heavy metals and reduce their release into the environment.

3. Surface modification for biological applications

To maintain the electronic properties and optical of the core material, one must choose the correct passivating agent when considering real-life applications. Surface ligands play a crucial role in the biological applications of quantum dots. The surface of quantum dots can be easily modified with, metal ions doped, metal-organic frameworks (MOFs), molecularly imprinted polymer (MIP), aptamers, multiwalled carbon nanotubes (MWCNTs), graphene quantum dots and carbon quantum dots, silanization, polymer, and transition metal oxide, which further expands the application of quantum dots in the sensor field.

3.1 Silica

To encapsulate QDs, silica nanoparticles have attracted considerable attention due to outstanding biocompatibility, high surface-to-volume ratio, ease of functionalization, and low cost. As labels for signal amplification to detect S. aureus, Ag_2S QDs loaded onto dendritic mesoporous silica nanospheres (DMSNs) were employed by Wang et al. as electrochemical immuno-biosensors.

As signal-amplifying labels, quantum dots and DMSNs have several advantages. A first step in enriching Ag_2S QDs was achieved by taking advantage of high surface area and the extensive pore channels of DMSNs. Each Ag_2S/DMSNs signal amplification label loaded with a tremendous amount of Ag_2S QDs increased the amount of Ag_2S QDs on each S. aureus cell. This resulted in a lower detection limit and a wider detection range for the electrochemical immuno-biosensor. When an electrochemical immuno-biosensor is activated, differential pulse voltammetry can be used to identify S. aureus. From Ab-Ag_2S/DMSNs, Ag (I) ions are liberated by leaching with HNO_3 [28].

Yang et al. developed a fluorescent probe for the visual detection of folic acid based on silica-coated CdTe QDs nanoparticles. The emission intensity of CdTeS QDs@SiO_2 decreased when folic acid was present, and folic acid itself showed fluorescence emission peaks. A gradient color change of nanoparticles was observed with increasing folic acid concentration [29].

For a sensitive NIR immunosensor, Han et al. immobilized CdTe/CdS QDs and antibodies on amino-functionalized SiO_2 [30]. Another case involved the modification of Au@SiO_2 by CdS QDs [31]. ECL signals were greatly enhanced due to the combination of SPR of Au cores and chemical enhancement from coreactants. SiO_2 with quantum dots appears to be a better choice for increasing loading.

CdTe/SiO_2 nanoparticles were compared by Shen et al. for their amplification effects (SiO_2@CdTe and CdTe@SiO_2). This resulted in much stronger ECL emission from CdTe@SiO_2 and lower cytotoxicity than SiO_2@CdTe, suggesting that bioanalysis of CdTe@SiO_2 may prove useful for clinical diagnosis. Compared with solid SiO_2, mesoporous SiO_2 provided higher loading sites and surface area [32].

In their study, Dong et al. experimented with mesoporous SiO_2 as a substitute for solid SiO_2. Their results showed that the ECL intensity and stability were much greater on mesoporous SiO_2 [33].

3.2 Transition metal oxide

QDs-based biosensors can also be assembled using transition metal oxides with variable valence states. ECL reaction could be corrected by using transition metal elements as catalysts. In situ activated CdS QDs/TiO_2 nanocomposites were used by Dai et al. to develop an enhanced PSA aptamer sensor. As a result of the TiO_2 nanotubes' degradation of H_2O_2 reactants, the CdS QDs were significantly more sensitive to the ECL reaction [34].

Miao et al. immobilized the CdS QDs onto the 3D urchin-like α-FeOOH, realizing ultrasensitive quantitation of 17β-estradiol. In contrast, the Fenton-like process produced more $SO^{4\bullet-}$ radicals through the conversion cycle of Fe^{3+} and Fe^{2+}, which supported ECL responses through electron transfer [35].

3.3 Metal ions doped

In recent years, transition metal ions have been investigated as quantum dots because they are not only more efficient than undoped quantum dots, but they also have additional advantages such as chemical stability, longer excited state lifetimes, reduced toxicity, high quantum efficiency, and larger Stokes shift to avoid self-absorption. The doping of transition metal ions with various impurities such as Sm^{3+}, Mn^{2+}, Zn^{2+}, Ag^{+}, Gd^{3+}, Tb^{3+}, Cu^{2+}, Er^{3+}, Eu^{3+}, and Co^{2+} into II–VI QDs has been reported to date. Biological studies can be improved by using QDs doped with cadmium, since they have less toxic cadmium content than their undoped counterparts.

Safari et al. investigated the possibility of using Ni:CdTe d-dots as nanoprobes for the detection of pyrazinamide (PZA) in plasma samples by hydrothermal method with 3-mercaptopropionic acid as the capping reagent **Figure 1**. It has been demonstrated that Ni-doped CdTe QDs have enhanced biocompatibility, photostability, and decreased cytotoxicity when compared to undoped CdTe QDs. For the rapid determination of PZA in plasma samples, a simple, inexpensive, sensitive, and selective method was developed based on fluorescence quenching of Ni:CdTe. Since PZA binds to the surface of Ni-doped CdTe quantum dots, it effectively quenches the emission of the quantum dots [4].

Najafi et al. reported Pd: CdTe QDs by hydrothermal method using palladium ions as a dopant. A linear quenching of fluorescence intensity occurs in the presence of Diazinon. Diazinon was detected in environmental waters using this novel nanoprobe at very high levels of sensitivity and selectivity, as shown in **Figure 2**. Also, the cytotoxicity assay of Pd: CdTe QDs was successfully conducted, which indicates its tremendous potential in biotechnology and medicine [36].

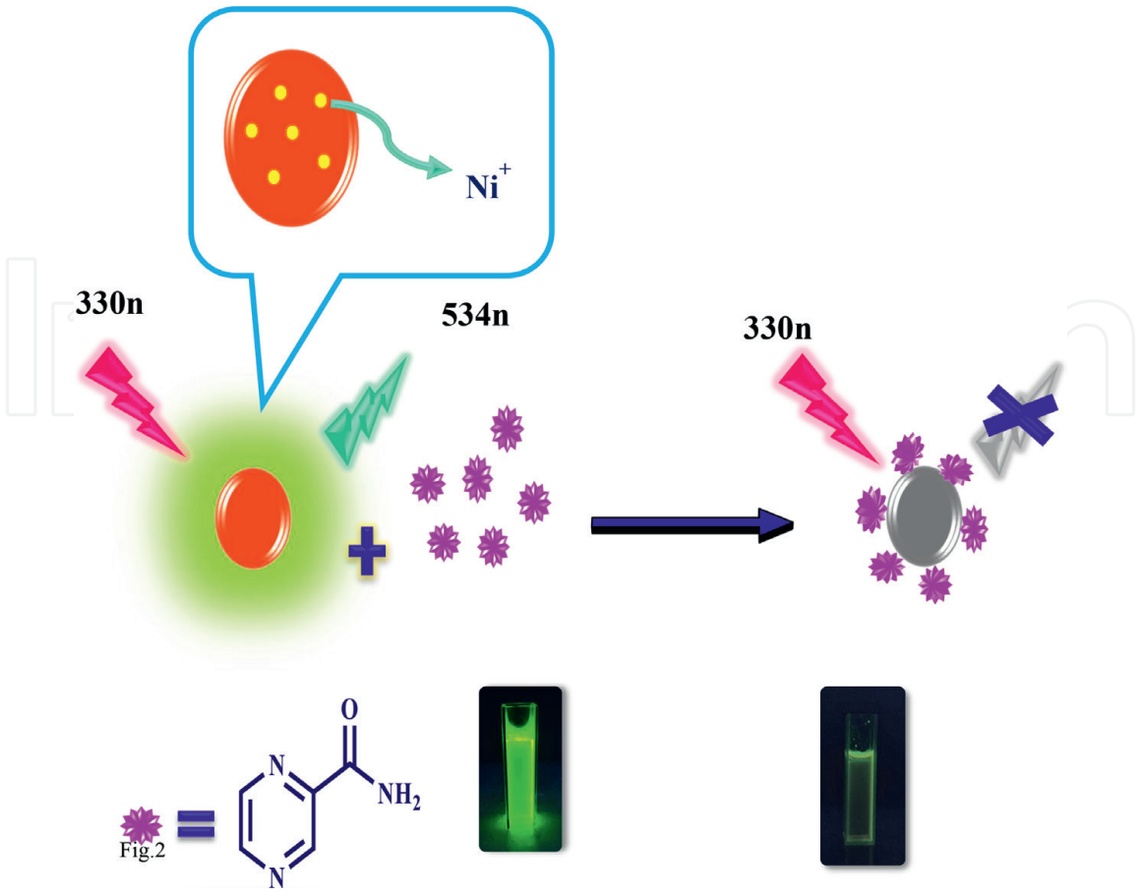

Figure 1.
Schematic illustration of PZA detection mechanism using Ni-doped CdTe [4].

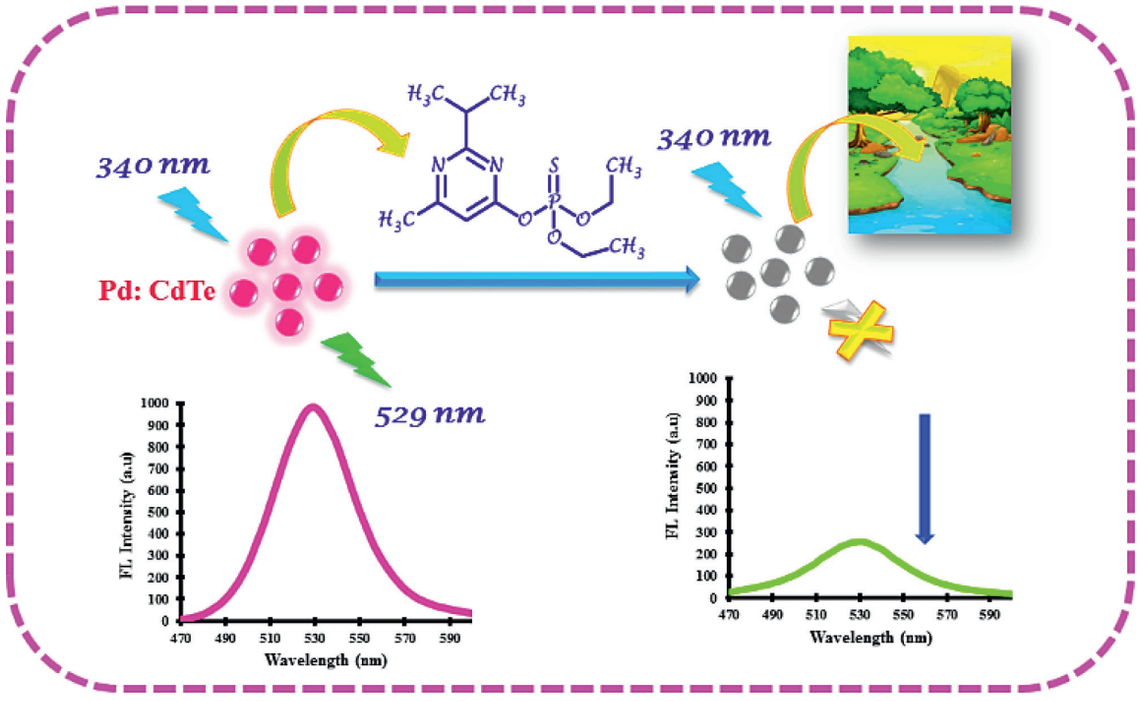

Figure 2.
The schematic illustration for Pd: CdTe QDs sensor for the detection of DZN [36].

3.4 Metal-organic frameworks

With their nice monodisperse structure and large surface area, metal-organic frameworks (MOFs) represent advanced hierarchical nanostructures that have been regarded as suitable QD loading hosts for amplification and stabilization of signals [37].

GQDs/UiO-66 NC were prepared by Abdolmohammad-Zadeh et al. resulting from terephthalic acid (TA) oxidation with H_2O_2 resulting from cholesterol oxidation with ChOx. As a result of the H_2O_2 oxidation of TA, a highly fluorescent product was produced, enabling a direct correlation between the intensity of fluorescence and the amount of cholesterol in solution [38].

The bi-coreactants, TEOA@AuNPs and CdS QDs@MOF, were prepared by Wei et al. to synergistically enhance the ECL signal. A TEOA@AuNPs nanocarrier was used to carry CEA aptamers via Au-S bonds in addition to acting as coreactants. After CEA's aptamer was bound to $Ru(bpy)_3^{2+}$, the ECL signal was also weakened because of increased impedance between $Ru(bpy)_3^{2+}$ and the bi-coreactants. An ECL biosensor for CEA analysis has been successfully constructed using the ECL system [39].

According to Yan et al., a fluorescent aptasensor was constructed by encapsulating CHAs in MOF-5-NH_2 and self-cycling CHAs (scCHAs). Patulin (PAT) in apple juice can be detected sensitively using a dual amplification strategy. As a result of the 17 s CS and 17 s AP hairpins, the 17 s AP includes an aptamer domain, which allows cyclic amplification without the addition of an extra aptamer. Further, hybridization strength between hairpins and aptamer domains was optimized to obtain the strongest signal change following PAT binding to aptamer domains [40].

Using a direct encapsulation method, Cui et al. prepared CdS QDs@MOF-5 composites for ultrasensitive cTnI detection [41].

CdSe nanocomposites were synthesized in situ using MIL-101. The as-prepared composites showed high ECL activity and sensing selectivity because of MIL-101's highly selective adsorption and efficient accumulation abilities [42].

For diverse sensing applications, MIL-53(Al)@CdS, MIL-53(Fe)@CdS, and MIL-53(Al)@CdTe are among the QD-loaded composites described in this study [43, 44].

Some MOFs can also serve as catalysts in the ECL process, in addition to their loading capacity. CdTe QDs were loaded on both the internal framework and external surface of NH_2 MIL-88(Fe) by Zhou et al. for signal amplification [45]. CdTe@IRMOF-3@CdTe composites were used as ECL labels in a sandwich immunosensor developed by Zhuo et al. As a coreactant accelerator, 2-amino terephthalic acid (2-NH_2-BDC) acted as an organic ligand of IRMOF-3 in the ECL process to increase the intensity and sensitivity of the ECL process [46].

According to Du et al., CdS@TiO_2 emits a highly transcendent ECL, whereas curcumin-Au NPs incorporated in ZIF-8 led to an intense reduction in ECL from CdS@TiO_2. ECL-RET acceptors have also been developed from Ag nanoclusters (Ag NCs [47].

4. Molecularly imprinted polymer

In the presence of template molecules, molecularly imprinted polymers (MIPs) are synthesized through polymerization reactions between functional monomers and crosslinking monomers. These polymers are widely used for many applications, including artificial antibodies, drug delivery, and chemical sensors catalysis. Due to

its unique ability to recognize target analytes and chemical stability, MIP has become a research hotspot in chemical sensors. According to Yang et al., ascorbic acid can be quantitatively measured with a ternary QD-based MIP ratiometric fluorescence sensor based on ternary QDs. Under a single excitation wavelength of 380 nm, the sensor exhibited well-resolved emission peaks at 530 and 705 nm, respectively, corresponding to ZnCdS QDs@MIP and CdTeS QDs@SiO_2. CdTe QDs were embedded in the SiO_2 shell to serve as the reference signal, and ZnCdS QDs were encapsulated in the MIP to serve as the response signal [48].

Qi et al. fabricated MIP using L-arginine, which is a part of microcystin, as the segment template for the adsorption and determination of microcystin. After studying a series of structural analogs of MC-LR, we selected L-leucine as the segment template to prepare MIP. Sol-gel polymerization was used to fabricate the MIP@CQDs@SiO_2 fluorescence sensor using 4-aminopropyltriethoxysilane as the monomer and tetraethylorthosilicate as the crosslinker. Polymer layers with specific recognition sites were capable of selectively adsorbing MC-LR molecules, causing CQDs to show fluorescence quenching behavior via electron transfer [49].

Chmangui et al. synthesized a composite material based on the molecularly imprinted technique by using DMC as a dummy template. 5,7-dimethoxycoumarin (DMC) contains coumarin moiety which assists with the specific recognition and imprinting of cavities within the prepared MIP layer. This moiety is identical to that found in AFs. A sensitive and selective detection of total AFs in non-dairy beverages is therefore expected through the anchorage with Mn-doped ZnS QDs. The prepared Mn-doped ZnS QDs were first deposited on a DMC dummy template, which was then coated with polyethyleneglycol (PEG). An efficient fluorescent screening method for non-dairy beverage analysis was found to be reliable with MIP-Mn-doped ZnS QDs composites [50].

5. Graphene quantum dots and carbon quantum dots

As a result of their electronic transport properties, chemical, and exceptional physical, graphene quantum dots (GQDs) and carbon quantum dots (CQDs) are being investigated for the development of next-generation biosensors. An explosion of reports have been published in recent years on biotransducer designs and biosensing applications utilizing these nanomaterials for facilitation, improvement, or otherwise developing novel approaches to analyte detection and monitoring.

Using fluorescent ssDNA probes coupled with CQD sensors, Loo et al. reported complementary DNA strand detection. Fluorescence resonance energy transfer (FRET) is quenched in this scheme thanks to the p-p stacking from DNA base pairs and CQD-conjugated p-systems. Due to electrostatic repulsion, the fluorescence of the ssDNA probe was restored when it hybridized with the target [51].

In order to fabricate a polyphenol index biosensor, Vasilescu et al. developed a molybdenum disulfide (MoS_2)/GQD biotransducer on which they drop-casted laccase. It was reported that the caffeic acid sensor had a linear range of 380 nanomolar to 100 millimolar with a low level of detection of 320 nanomolar. A notable finding of their voltammetric studies was that laccase's response was similar with each electrode formulation, although the MoS_2/GQD electrode contributed to a higher electron transfer efficiency [52].

6. Aptamers

In nucleic acids, aptamers are short, single-stranded sequences that bind specific molecules selectively and strongly. To create them, ligands undergo systematic transformations and exponential evolutions. Several applications rely on aptamers, including cancer cell imaging, biomedicine, therapeutics, gene therapy, biosensing, or targeted drug delivery, despite their high binding affinity, long-term stability, ease of modification, low immunogenicity, and low cost.

An ATmega328P prototype biosensor for the detection of E. coli in water samples using aptamer I and II-conjugated SPIONs and CdTe QDs has been developed by Pandit et al. We then conjugated E. coli-specific aptamers I and II to both types of nanoparticles. In terms of microbial detection, conjugated SPIONs and CdTe-MPA QDs display high quantum yields and significant magnetic and fluorescent properties. It is an effective tool to detect microbes using a conjugated SPION followed by a CdTe-MPA QD that has a high quantum yield, as well as significant magnetic and fluorescent properties. Bioconjugation of *E. coli*-specific aptamer I and II with SPIONs as well as QDs studied using various methods demonstrated selective separation and subsequently, detection of *E. coli*. The ATmega 328P prototype biosensor was further used to capture and detect E.coli using CdTe MPA QDs conjugated with aptamer II. Up to 100 cfu can be detected by the biosensor, demonstrating its sensitivity. We can detect on the spot, it is easy to use and less time-consuming. The ATmega328P prototype biosensor is capable of detecting E. coli in water if it is combined with cadmium-based QDs. As a result of the technology's rational extension and exploration, other pathogenic microorganisms can be detected in a wide variety of food samples. Additionally, the system meets the need for a portable, miniaturized pathogen detection device that can be deployed in the field [53].

Using SPCE/C60/MWCNTs-PEI/PQdot/GLA/APT aptasensors, Jamei et al. analyzed thrombin protein. By modifying SPCE electrodes with C60/MWCNTs-PEI/PQ dot nanocomposites, sensitive electrochemical aptasensors could be manufactured, as shown in **Figure 3**. In addition to their suitable stability, their high number of surface amine groups, their surface-to-volume ratio, their fast electron transfer kinetics, and their high electrical conductivity, these C60/MWCNTs-PEI/PQ dot nanocomposites possess unique characteristics. This nanocomposite's high surface-to-volume ratio and high number of surface amine groups increased the number of thrombin binding sites. A sensitive aptasensor was first developed using polymer quantum dots, which exhibit unique characteristics and are easy to synthesize [55].

A QDs-based biosensor was reported by Liu et al. using Pr^{3+}–rutin complexes as both quenchers and receptors. Using the Pr^{3+}–rutin complex, we were able to detect QDs in a favorable "off" state by efficiently quenching their fluorescence. Our approach relies on the electrostatic association of the cationic Pr^{3+}–rutin complex on the surface of QDs. The static association reduces the fluorescence intensity of QDs due to ultrafast photoinduced electron transfer. In addition, Pr3 + −rutin complexes also serve as receptors for dsDNA. As a result of adding herring sperm DNA, Pr^{3+}–rutin complexes were removed from QD surfaces and the QDs' fluorescence was restored [54].

The FRET method was employed by RezanejadeBardajee et al. in order to detect complementary DNA (as a positive control) and RNA from the COVID-19 virus by high-sensitivity detection of CdTe-ZnS QDs bioconjugates. A ligand exchange process replaces thiolated DNA (capture DNA) with surface-bound TGA molecules to form

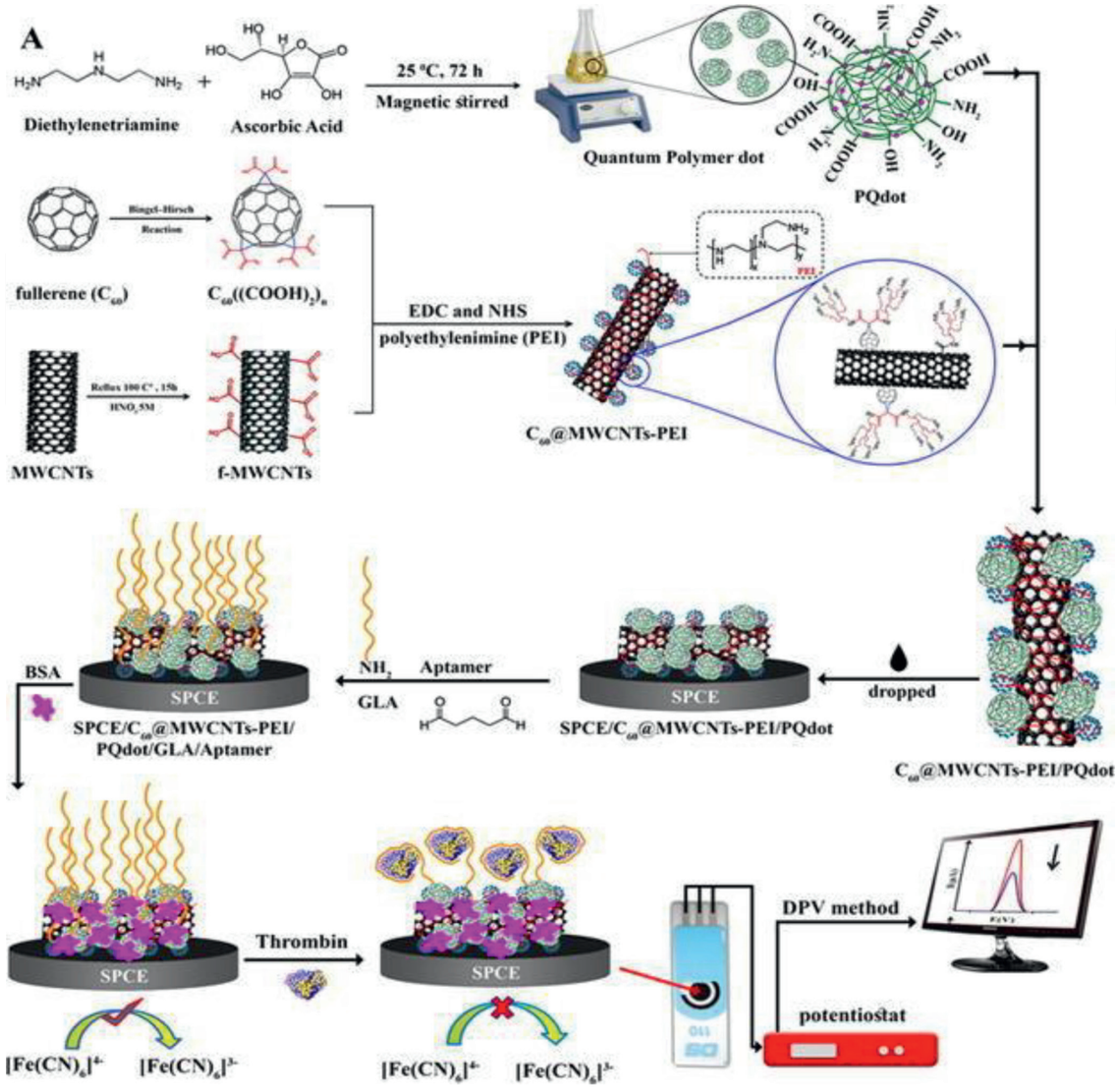

Figure 3.
Schematic of stepwise preparation electrochemical aptasensor and C60/MWCNTsPEI/PQdot [54].

DNA-conjugated quantum dots (QDs-DNA). Besides designing the BHQ_2-DNA oligonucleotide, an oligonucleotide from the viral genome was also designed for the FRET experiment. As a final application, these elements can be used for detecting viral RNAs (via FRET experiment) and for sensing target DNA sequences (via the QDs-DNA bioconjugate nanoprobe) [56].

7. Multiwalled carbon nanotubes

A number of chemically modified QDs have been developed using multiwalled carbon nanotubes (MWCNTs) because of their unique properties, such as high electrical conductivity, high mechanical strength, high thermal conductivity, and large surface area to volume. In analytical sensing, multiwalled carbon nanotubes (MWCNTs) have been shown to reduce detection limits, increase sensitivity, and prevent surface fouling.

As part of their study, Baslak et al. functionalized MWCNT surfaces with silver nanoparticles and encapsulated the silver nanoparticles with poly(glycidyl

methacrylate) (pGMA). An initiated chemical vapor deposition (CVD) method was used to coat MWCNT surfaces with pGMA. The chemical vapor deposition (CVD) method produces thin films in a dry environment. By initiating chemical vapor deposition (iCVD), complex geometries can be coated uniformly without solvent-related damages, which are typically observed in conventional wet coating. During the iCVD process, the substrate is cooled so that the species can adsorb and grow on the surface. This prevents the substrate from being damaged by high temperatures, plasma, or light sources, which can alter the substrate's properties physically or chemically. As a result, iCVD was selected as an ideal method for functionalizing and encapsulating MWCNT surfaces [57].

The authors of Vinoth et al. describe a method for integrating ZnO QDs into MWCNTs using ultrasonication to decorate the QDs on the surface of the nanotubes (MWCNT/ZnO QDs), using both electromechanical detection of glucose and photocurrents simultaneously. A chronoamperometry measurement, a differential pulse voltammetry measurement, and a cyclic voltammetry measurement were used to evaluate the performance of the enzyme-free glucose sensor. Ascorbic acid, uric acid, and dopamine all interfere with the glucose sensor based on MWCNT/ZnO QDs, while sucrose exhibits good anti-interference properties. A nanocomposites heterostructure made from MWCNT/ZnO QDs shows excellent photocurrent activity toward visible detection [58].

8. Polymer

Multifunctional polymer layers can enhance QDs' interaction with target analytes by incorporating a variety of functionalities. QDs are usually synthesized with polymers that contain organic cyclic chains such as calixarene and cyclodextrin. The use of polyethylene glycol (PEG) derivatives in the synthesis of QDs has also become increasingly popular in recent years. PEG derivatives are readily available, require simple encapsulation processes, and are readily available.

According to Yi et al., a fluorescence nanoprobe detecting parathion-methyl (MP) through host-guest recognition is the first enzyme-free fluorescent nanoprobe. It is possible to form distinct molecular recognition function on MoS2 QD surfaces by introducing this molecule on the surface of MoS_2 QDs, as shown in **Figure 4**.

With the PET process, p-NP molecules from MP hydrolysis under alkaline conditions can enter into small cavities of molecular beads and further quench their fluorescent properties, thereby providing a fluorescence sensing platform for MP. Based on the optimization of various experimental conditions, the results show that the molecular probe is excellent in terms of selectivity and sensitivity, has a wide linear range, and has been able to detect MP with a low detection limit [59].

Gupta et al. studied interactions between chitosan, the most abundant biopolymer, and luminescent CdSe QDs synthesized by cyclic voltammetry and capped with MPA. MPA-CdSe QDs were found to react dynamically with chitosan (crystal size 2.3 × 0.5 nm, zeta potential 47 × 6 mV). Based on our assessments, the number of chitosan molecules bound and the binding constant Ka by MPA-CdSe QDs are ~1.z 3 and 7.332 × 1015 L Mol-1 at 298 K, respectively. Chitosan's strong affinity for MPA-CdSe QDs is confirmed by the high Ka. Using the above calculations, chitosan-MPA CdSe QDs were found to be stable over a long period of time and to disperse in water homogeneously. Biomolecule interaction can be strongly influenced by the size, shape, and surface chemistry of QDs [60].

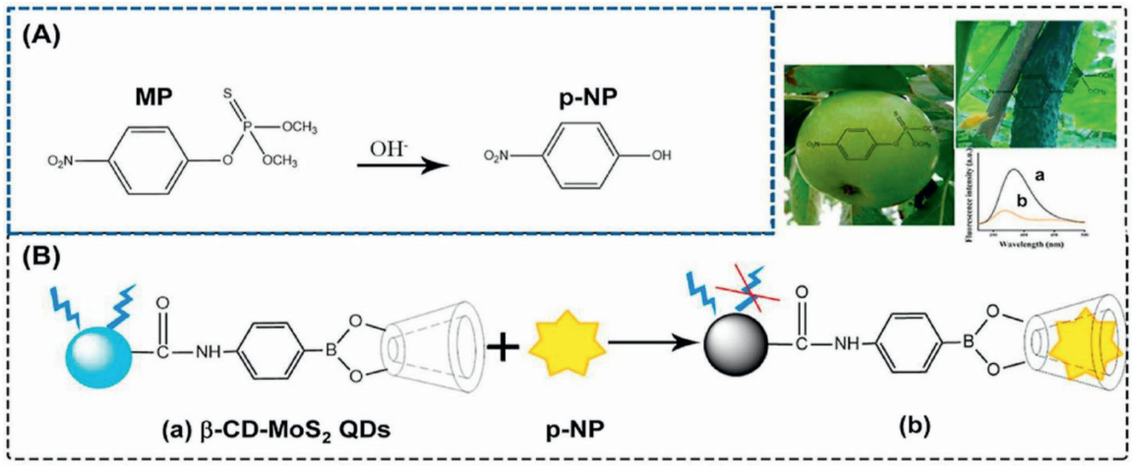

Figure 4.
Schematic illustration of parathion-methyl detection using β-CD-functionalized MoS2 QDs [59].

A ratiometric fluorescence probe developed by Yu et al. detects H_2O_2 and glucose selectively using cationic conjugated polymer (CCP) and cationic transition metal dichalcogenides (CdTe/CdS QDs). H_2O_2 causes fluorescence quenching of QDs due to FRET between CCP and QDs. In order to create new H2O2 and glucose enzymatic assays, these phenomena can be exploited. This method can be applied to other oxidases to quantify substrates such as choline, xanthine, cholesterol, and lacate, since many oxidases generate H_2O_2.

According to the proposed design, it is able to provide two advantages and advantages over conventional systems: (I) we use the signal transformation process to design a dual-emission nanoprobe with excellent properties such as high selectivity, fast response time, and resistance to outside interferences, and (II) because the QDs exhibit excellent NIR properties, we were able to directly measure glucose in whole blood [61].

9. Conclusion

A comprehensive summary of recent advances in surface modification QDs for biological applications is presented in this chapter. Surface ligands are the most important factor in obtaining useful materials from quantum dots for biological applications. The surface of quantum dots can be easily modified with, metal ions doped, metal-organic frameworks, molecularly imprinted polymer, aptamers, multi-walled carbon nanotubes, graphene and carbon quantum dots, silanization, polymer, and transition metal oxide, which further expands the application of quantum dots in the sensor field.

The surface modification QDs have shown that design of QDs to detect, with high sensitivity and selectivity, various analytes was an effective strategy. Traditional QDs have challenges such as being environmentally friendly, biocompatible, having a broad excitation spectrum, and having poor photostability, wavelength tenability dependent on size, and low quantum yield. Modification QDs help overcome these issues by being extremely energy-efficient and highly quantum yielding.

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