

Review

Synthetic Approaches, Modification Strategies and the Application of Quantum Dots in the Sensing of Priority Pollutants

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) and nitro-aromatic compounds (NACs) are two classifications of environmental pollutants that have become a source of health concerns. As a result, there have been several efforts towards the development of analytical methods that are efficient and affordable that can sense these pollutants. In recent decades, a wide range of techniques has been developed for the detection of pollutants present in the environment. Among these different techniques, the use of semiconductor nanomaterials, also known as quantum dots, has continued to gain more attention in sensing because of the optical properties that make them useful in the identification and differentiation of pollutants in water bodies. Reported studies have shown great improvement in the sensing of these pollutants. This review article starts with an introduction on two types of organic pollutants, namely polycyclic aromatic hydrocarbons and nitro-aromatic explosives. This is then followed by different quantum dots used in sensing applications. Then, a detailed discussion on different groups of quantum dots, such as carbon-based quantum dots, binary and ternary quantum dots and quantum dot composites, and their application in the sensing of organic pollutants is presented. Different studies on the comparison of water-soluble quantum dots and organic-soluble quantum dots of a fluorescence sensing mechanism are reviewed. Then, different approaches on the improvement of their sensitivity and selectivity in addition to challenges associated with some of these approaches are also discussed. The review is concluded by looking at different mechanisms in the sensing of polycyclic aromatic hydrocarbons and nitro-aromatic compounds.

Keywords: detection; sensors; polycyclic aromatic hydrocarbons; nitro-aromatic explosives



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1. Introduction

The contamination of water sources has become a global concern due to the increasing production of different chemical products, particularly organic species [1]. Organic pollutants occur in the form of sediments of different groups, such as polycyclic aromatic hydrocarbons (PAHs) and explosive residues [2,3]. These pollutants are introduced into water bodies through two major ways: industrial activities and human activities. The regular detection of these pollutants continues to be paramount because there is clear evidence of the health implications caused by the consumption of water contaminated by these species. Therefore, the U.S. Environmental Protection Agency (EPA) has decided to include them in the priority list of pollutants [1]. Priority pollutants are pollutants that have been identified to be very toxic, even at low levels or concentrations. Furthermore, these pollutants have been identified as potential causes of cancer. Some of the PAHs that occur in mixtures have been shown to exhibit higher toxicity than individual species [2]. One of the major challenges with monitoring these pollutants is that they can occur at very low levels. Despite their occurrence in low concentrations, continuous exposure to them can result in adverse effects. This shows a necessity for the development of sensitive and selective methods for detecting these species [4,5].

Techniques such as Raman scattering, infrared absorption spectroscopy, high-performance liquid chromatography (HPLC), gas chromatography–mass spectrometry (GC), quartz crystal microbalance, ion mobility spectroscopy (IMS) and metal detectors have been reported for the analysis of PAHs and explosive residues [6]. Though these methods have been successfully used to analyze PAHs, nitro-aromatic compounds and other organic contaminants in water, there are major drawbacks associated with many of them. These include relatively expensive instrumentation, highly skilled personnel necessary for their operation and difficult sample pre-treatment [7] to mention a few. These demerits have led to the search for other detection methods. One of the promising alternatives for the monitoring of organic pollutants in water is the group of techniques called optical methods, which include photoluminescence spectrometry and absorption spectrometry. The optical methods are characterized by a change in the emission intensity, peak position, and absorption of the fluorescent probe due to the interaction between the fluorescent probe and the target analyte. Optical detection techniques have been applied for the sensing of several organic pollutants, such as nitro-aromatic compounds (explosives), PAHs, pesticides and so on, with good sensitivity and selectivity being reported [8,9]. The widely used fluorescent probes are molecularly imprinted polymers (MIP), surface-enhanced Raman scattering (SERS)-based nanoparticles, non-conjugated polymers, etc. SERS methods have been widely employed in the detection of PAHs and NACs; however, their use in sensing is limited because of the weak interaction between PAHs' rings and the surfaces of SERS-based nanoparticles [10,11]. Polyurethanes (PUs) are a very versatile class of non-conjugated polymers with tunable properties, and have been used extensively in the sensing of explosives [5]. However, polyurethanes are insoluble in water; therefore, the reaction usually occurs in organic media, leading to further pollution of the environment [12]. Recently, small nanomaterials known as quantum dots have emerged as promising materials due to their superior optical properties, which can enhance the sensitivity and selective determination of PAHs and nitro-aromatic pollutants [4,13]. In this review, the sensing of organic pollutants, namely polycyclic aromatic hydrocarbons and nitro-aromatic explosives, using different types of quantum dots was discussed. Different studies on the comparison of water-soluble quantum dots and organic soluble quantum dots on fluorescence sensing mechanism were also presented. Furthermore, different approaches on the improvement of their sensitivity and selectivity as well as challenges associated with some of these approaches were also discussed.

2. Quantum Dots in Sensing Applications

An attractive and promising approach for the sensing of environmental pollutants involves using an optical method, which offers many advantages over other standard detection techniques, including cost-effectiveness, good portability and high sensitivity as well as selectivity [14]. Among different materials used in sensing organic pollutants, QDs have appeared to be the most promising materials because of their unique properties. Quantum dots (QDs) are zero-dimensional nanostructured materials with excellent optoelectronic properties [14]. Zero-dimensional nanostructured materials exist in different groups, such as semiconductor quantum dots, carbon quantum dots and graphene quantum dots. These materials are characterized by optoelectronic properties such as broad excitation spectra, narrow bandwidth emission spectra, high resistance to photo-bleaching and good stability as well as biocompatibility [15,16].

2.1. Semiconductor Quantum Dots

Semiconductor QDs are generally divided into different groups, such as binary and ternary QDs. These QDs are prepared through two approaches, namely organic and aqueous. Studies have shown that organic-soluble QDs have a higher affinity for organic pollutants than water-soluble QDs do [17]. However, there are environmental concerns with organic-soluble quantum dots, and so the focus is being shifted to water-soluble QDs [18]. These QDs have been recently used as chemical sensors for aromatic compounds

in fluorescence and electrochemical methods. These quantum dots exist in different classes, such as binary and ternary. Binary QDs may consist of different periodic table elements such as ZnSe, ZnS, CdTe, CdS, AgS, etc. [19–22]. Among these compositions, cadmium-based sensors have been mostly reported for the application of sensing aromatic compounds. In 2019, Cao et al. synthesized cucurbit-modified CdTe QDs for the fluorescence sensing of p-nitroaniline. In 2010, Yang et al. detected PAHs using TiO₂-nanotube-modified CdTe QDs. The detection of PAHs was observed via the intensity enhancement, which occurs as a result of fluorescence resonance energy transfer between PAHs and TiO₂-nanotube-modified CdTe QDs [23]. In 2016, Qian et al. functionalized CdTe with an amino acid for the determination of trace TNT explosive. L-cysteine served as a stabilizer, which enhanced the interaction between the functional groups of TNT and the QDs' surface [24]. However, this type of chemical sensor is being limited by the intrinsic toxicity of cadmium. Recently, binary cadmium-free QDs have been used as chemical sensors for nitro-aromatic explosives. In 2021, Sharma et al., synthesized blue, fluorescent, zinc selenide QDs for the recognition of nitro-aromatic compounds. The sensing was performed via fluorescence techniques. The quenching of mercaptopropionic-acid-capped QDs has been shown to occur via the inner filter effect (IFE) [25]. The IFE mechanism can be observed through spectral overlapping between the absorption spectrum of 2,4,6 TNP and the excitation spectrum of ZnSe (Figure 1).

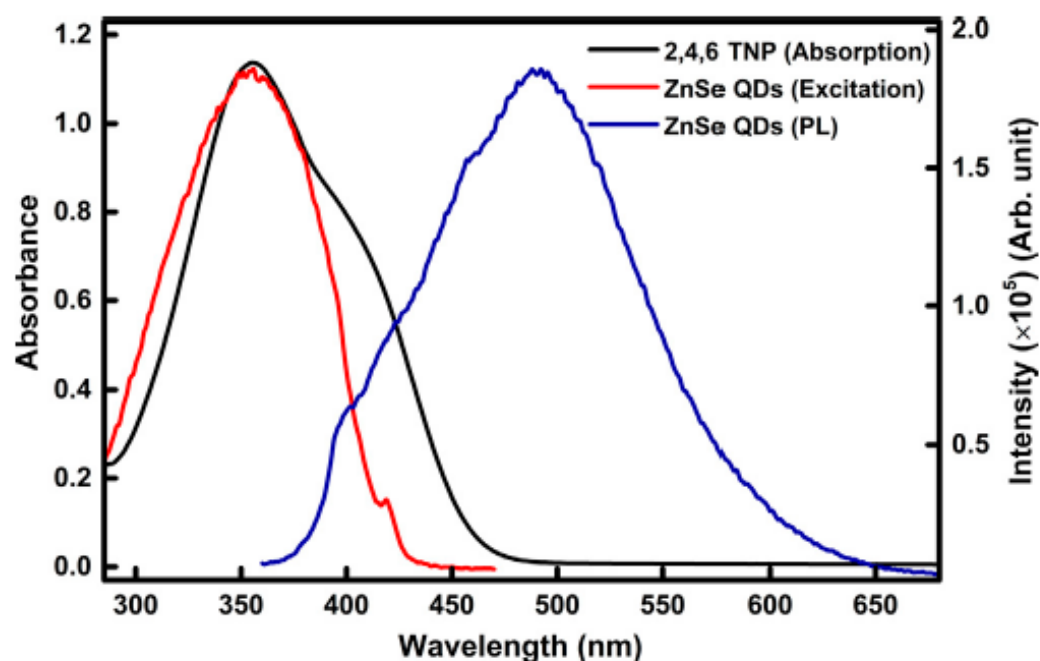


Figure 1. Spectral overlapping of the absorption spectrum of 2,4,6 TNP with PL and the PL excitation spectra of ZnSe QDs [25].

Ternary QDs exist in different groups, such as CdSeTe, CdZnSe, CuInX₂ (X = S, Se and Te) AgInX₂ (X = S, Se and Te), etc. However, current research is being focused on cadmium-free ternary QDs because of their low toxicity [16,26]. Ternary QDs can be synthesized in two ways, namely an organic route and an aqueous route (which can be further divided into two approaches: direct synthesis and ligand exchange). However, there have been challenges in synthesizing ternary QDs due to the uncontrolled reactivity of the cationic precursors of In³⁺ and Ag⁺ or Cu⁺, which can lead to the formation of undesired products such as indium sulfides. Different studies on their synthesis have shown that this challenge can be overcome by (1) the use of dual stabilizers and (2) the use of a single precursor (that can produce both In and Cu or Ag) [27]. Furthermore, the reactivity of the cationic precursors in an organic medium can be balanced through the use of either single stabilizer or dual stabilizers [28]. Their optical properties are said to be

dependent on the optimization of different parameters, including (i) the type of stabilizers, (ii) refluxing time, (iii) type or amount of dopants [29] and (iv) the type of synthetic method [30]. Apart from being environmentally friendly, these fluorescent probes exhibit two major outstanding properties: direct bandgaps and absorption coefficients as large as 10^{-5} cm^{-1} [16,31]. However, these semiconductors suffer from surface defects, which are undesirable in sensing applications since they result in self-quenching. This challenge can be addressed by coating the core semiconductor with another semiconductor referred to as the shell [32]. While QDs have great potential as fluorescent probes in the sensing of organic molecules, the affinity of their surfaces for the target molecules must be improved. Recently, a few studies on the improvement of their affinity for aromatic compounds have been reported. In 2021, Maluleke et al. reported the synthesis of graphene oxide (GO)-modified CuInS/ZnS QDs for the sensing of PAHs. The addition of different concentrations of PAHs to the GO-modified QDs has shown enhancement of photoluminescence (PL) intensity. This enhancement was ascribed to the π - π stacking between the chemical sensor and the PAHs [33].

2.2. Carbon Quantum Dots

Carbon quantum dots are generally carbon-based nanoparticles that exhibit optoelectronic properties due to the quantum confinement effect [34]. Carbon quantum dots (CQDs) have attracted much attention in many applications because of their advantages, such as water solubility, fluorescence, low toxicity, cheap scale-up production, abundance and ease of modification [35]. CQDs can be prepared from different carbon sources, such as food waste [36], waste biomass sources [37], corncobs [38] and weak organic acids [39]. Carbon dots are typically prepared via chemical methods and physical methods. Chemical methods include electrochemical synthesis, combustion/thermal/hydrothermal/acidic oxidation, supported synthesis, microwave/ultrasonic and solution chemistry methods. Physical methods include arc discharge, laser ablation/passivation and plasma treatment [40,41]. These materials have been investigated for the fluorescence sensing of aromatic compounds due to their fluorescence properties. However, they have not been investigated for PAHs such as phenanthrene, naphthalene, pyrene, anthracene, etc. Recently, Hu et al. synthesized CQDs for the fluorescence sensing of para-nitrophenol. The sensor and the phenol interacted through the IFE mechanism. This mechanism was proven via spectral overlap [42]. In 2015, Cheng et al. also prepared CQDs for the fluorescence sensing of 2,4,6-trinitrophenol. The quenching of the CQDs by the phenol was suspected to be due to the IFE [43]. Fan et al. reported the fluorescence detection of 2,4,6-trinitrophenol (TNP) using manganese (Mn)-doped CDs. The probe showed fluorescence quenching with an increasing concentration of TNP and high selectivity in the midst of other nitroaromatic compounds [41].

2.3. Graphene Quantum Dots

Graphene quantum dots are zero-dimensional (0D) nanomaterials that are prepared by converting 2D graphene. The particles of these materials are non-quasi-spherical, which is the feature that makes them different from CQDs [44]. These QDs can be synthesized from different sources, such as coal [45], natural graphite [46], rice husk biomass [47], etc. Recently, GQDs have also emerged as fluorescent probes because of their advantages, such as a large surface area, biocompatibility, lower toxicity and ease of surface modification [48]. These QDs are prepared via two types of methods, namely the “top-down” approach and the “bottom-up” approach. The “top-down” approach involves breaking down large-scale macroscopic carbon-based materials such as natural graphite, carbon fibers, graphene oxide, and metal-organic frameworks and so on. The “bottom-up” method involves the growing of GQDs from different sources, such as plant extracts [49,50], rice husks [47], wood charcoal [51], rice grains [52], coffee grounds [53], etc. Chen et al. explored the synthesis of GQDs through a “bottom-up” route using starch as the precursor [54]. Though these QDs have been mostly investigated for the fluorescence sensing of PAHs and NACs,

there are few reports on their use in sensing PAHs. Furthermore, these materials' sensitivity and selectivity have been shown to depend on size and shape, surface modification and heteroatom doping [55]. Kaur et al. explored the fluorescence detection of trinitrophenol (TNP) based on nitrogen-doped GQDs [56]. The doping with nitrogen atoms enhanced the interaction between the QDs and the phenol. Fluorescence quenching was observed owing to the transfer of energy from N-GQDs, which act as a donor to TNP, which is electron-deficient due to nitro-groups (Figure 2). Chen et al. also did a similar study using creatinine-capped nitrogen-doped GQDs (Figure 3) [57]. Recently, Nsibandé et al. synthesized ferric-ion-modified GQDs for the recognition of pyrene in an aqueous medium. The ferric ions have been reported to turn off the fluorescence intensity of the QDs, while pyrene turned on the intensity [58].

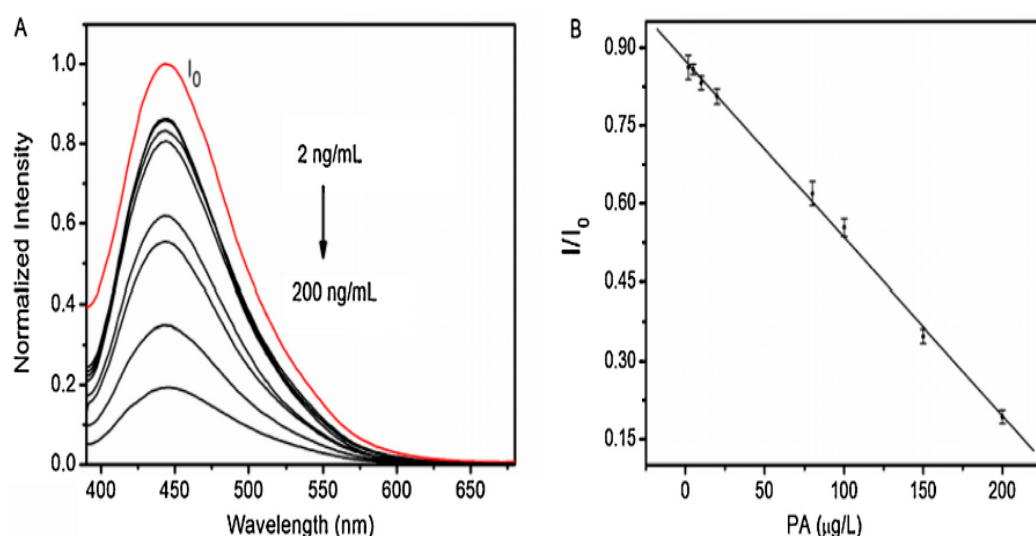


Figure 2. (A) Fluorescence emission spectra of BSA/creatinine/N-GQDs–chitosan solid film in the presence of PA at 0 (red line I_0), 2, 5, 10, 20, 80, 100, 150 and 200 ng/mL (from top to bottom). (B) Stern–Volmer curve. I and I_0 were the fluorescence intensities of BSA/creatinine/N-GQDs–chitosan fluorescent solid film at 360 nm in the presence and absence of PA, respectively [57].

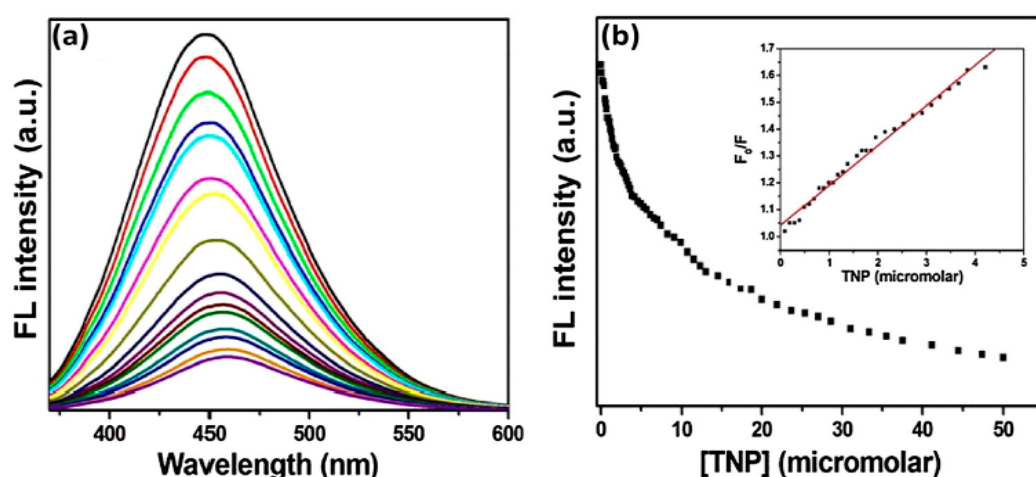


Figure 3. (a) FL behavior of N-GQDs in the presence of various TNP concentrations (from top to bottom (0–50 M)). (b) FL emission curve of N-GQDs with increased concentration of TNP (inset: Stern–Volmer plot for the quenching process) [59].

3. Effect of Surface Chemistry on Sensitivity and Selectivity

The versatile surface chemistry of semiconductor QDs provides a platform for modification through different strategies. This has enabled researchers to anchor and tailor various receptors for specific target analytes, thereby enhancing their sensitivity. QDs can therefore work as signal transducers and receptors in composite materials. It is expected that changes in the surface charge or ligand components of the QDs would affect the efficiency of the core electron–hole recombination and consequently the luminescence efficiency. Therefore, a chemical sensing system based on QDs can be developed by using fluorescence changes, which are induced by either the direct physical adsorption or chelating of ions and small molecules on the surface of the QDs activated by the exchanged ligand [60,61].

Reports have shown that the selectivity and sensitivity of sensors can be enhanced through surface modification, which can be done by functionalizing the material or conjugating it to a material that has an affinity for the pollutants of interest [62]. The effective detection and differentiation of pollutants can be done by conjugating QDs to different molecules such as graphene derivatives, polymers, proteins, enzymes, nucleic acids, etc. [27]. Peveler et al. studied the multi-channel detection and differentiation of explosives [63]. The functionalization of QDs' surfaces has been reported to affect the recognition properties, which have an effect on the sensitivity and selectivity [63]. Recently, Aswathy et al. exploited the quenching efficiency of sulfur-containing amino acids such as L-cysteine and L-methionine. The modified QDs were found to be selective and more sensitive towards picric acid. The energy transfer between the QDs and the TNP is ascribed to the acid–base reaction. From Figure 4, it was observed that L-cysteine-capped ZnS-Mn²⁺ QDs gave a higher quenching efficiency than those that were L-methionine-capped. However, the cause of this difference was not explained. These results could mean that the quenching efficiency is dependent on the structure of the functionality or the surface chemistry of the amino acids [64].

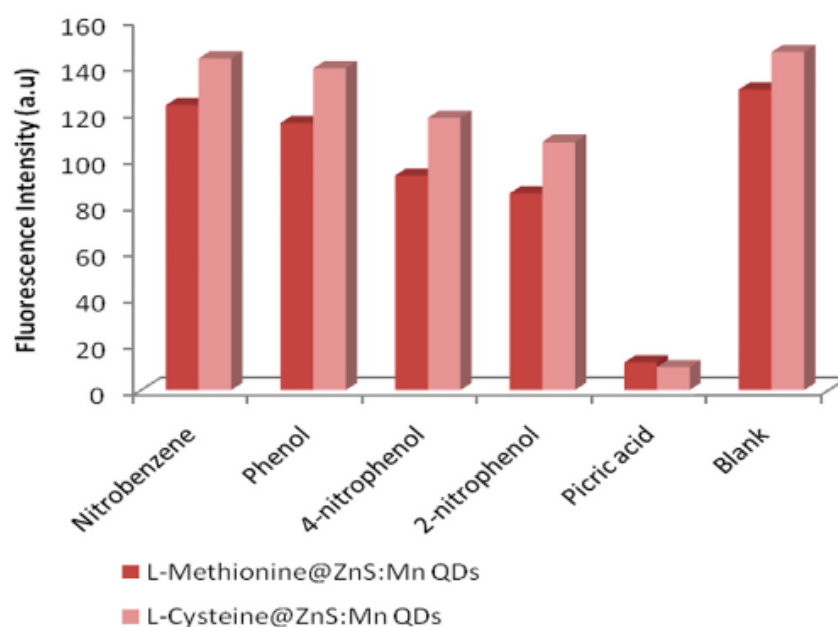
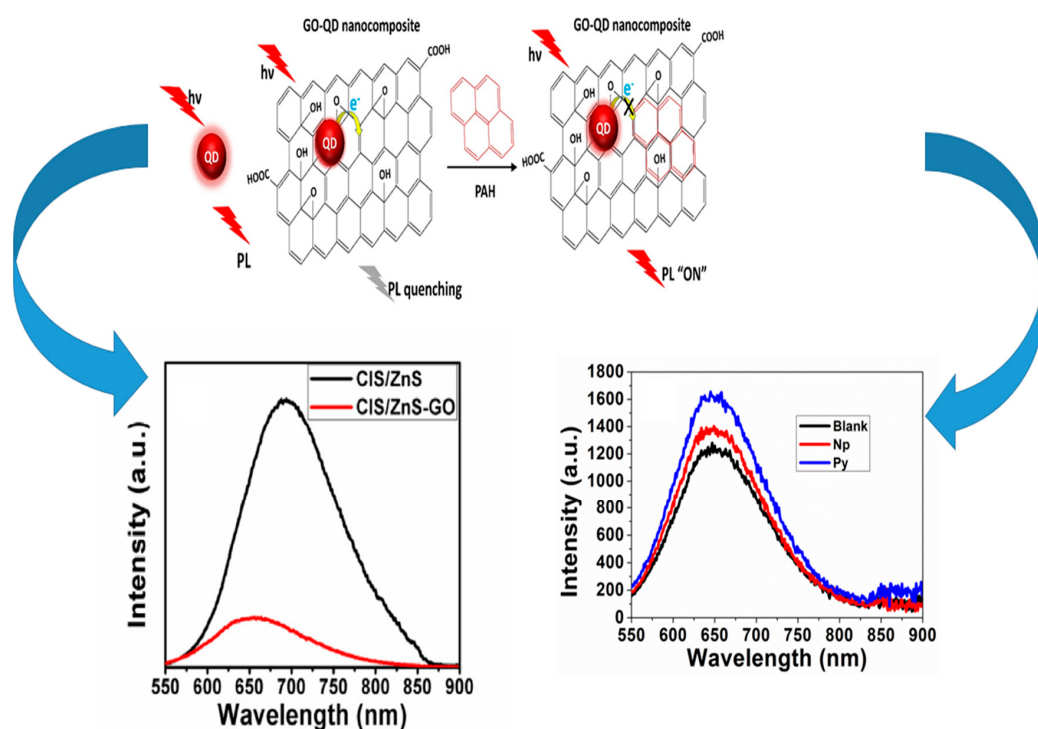


Figure 4. Effect of various aromatic compounds on the fluorescent intensity of L-cysteine/L-methionine-capped ZnS-Mn²⁺ QDs (concentration of picric acid is 2×10^{-7} M and other aromatics are 2×10^{-5} M).

Surface-modified QDs have been extensively employed as fluorescent probes for the detection of organic pollutants. This detection takes place through two basic photo-physical mechanisms: fluorescence resonance energy transfer (FRET) and quenching. The concentration of the nitroaromatic substrates on QDs' surfaces through donor–acceptor complexes

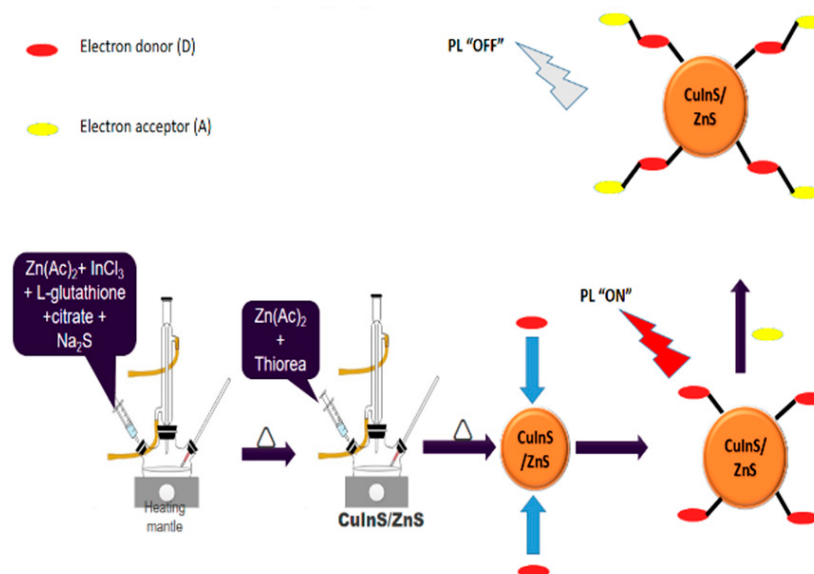
leads to the quenching of QDs' luminescence. In 2012, Freeman et al. reported the use of chemically modified CdSe/ZnS to detect nitro-aromatic explosives such as trinitrotoluene (TNT) and trinitrotriazine (RDX). They observed that the luminescence of the mercapto (MPA)-functionalized CdSe/ZnS could not be quenched by nitro-aromatic compounds, and this observation has been attributed to a lack of donor units. In order to optimize the quenching efficiency, MPA-functionalized QDs were covalently linked to different electron donors, such as tyramine, dopamine, 5-hydroxydopamine and 6-hydroxydopamine. The fluorescence quenching of the QDs modified with these capping ligands followed the order tyramine < dopamine < 5-hydroxydopamine < 6-hydroxydopamine. This order demonstrated that the quenching efficiency is dependent on the donating properties of the capping ligands. Another aspect to consider when modifying QDs is the pH of the medium. Freeman et al. demonstrated that the luminescence of the electron-donor-modified QDs decreases as the pH of the medium increases [65]. Another study on the detection of PAHs by semiconductor QDs was carried out by Baslak et al. in 2014. In their study, different PAHs—2-hydroxy-1-naphthaldehyde (2H-1N), 9,10-phenanthraquinone (PQ), 9-anthracenecarboxaldehyde(9-AC) and quinolone (Q)—showed different quenching effects, and this has been attributed to the molecular structure or functional groups of the PAHs [66]. The interaction of the surface-modified QDs, PAHs and NACs is schematically illustrated in Schemes 1 and 2.



Scheme 1. Fluorescence detection of different polycyclic aromatic hydrocarbons by surface-modified QDs [33].

Surface modification is also believed to improve the lifetime of a sensor. Mitra et al. (2016) explored the effect of lifetime on the sensing of organic pollutants such as bisphenol A, 1-naphthol, phenol and picric acid (Figure 5) [67]. Apart from the functionalization and conjugation, reaction parameters were said to cause an effect on the sensing of the pollutants. Liu et al. (2016) investigated the effect of pH in the reaction between AgInZnS and Cu ion [68]. Furthermore, the sensitivity of the sensors is also dependent on the types of functional groups of the sensors in addition to the functionalization approaches [69,70]. Different results on sensitivity of different sensors towards PAHs and NACs are shown in Table 1. Apart from surface functional groups, the sensitivity of fluorescent probes has been shown to be dependent on the type of synthetic method. Recently, Nsibande et al.

prepared QDs using GO and citric acid via the “top-down” approach and “bottom-up” approach, respectively. The as-prepared materials successfully detected pyrene in an aqueous medium. The QDs prepared via the “bottom-up” route gave a better limit of detection (LOD) as compared to the result obtained by the QDs synthesized through the “top-down” route. Furthermore, the two types of QDs exhibited different optical properties, and this can be observed from their emission spectra (Figure 5) [58]. QD-based sensors can also be modified through doping with a metal or non-metal. Surface doping with a metal has been reported to enhance the electrochemical properties of QD sensors; however, there have been few reports on the doping of fluorescent probes and electrochemical sensors [56,58,71,72].



Scheme 2. Fluorescence detection of different nitroaromatic compounds by surface-modified QDs.

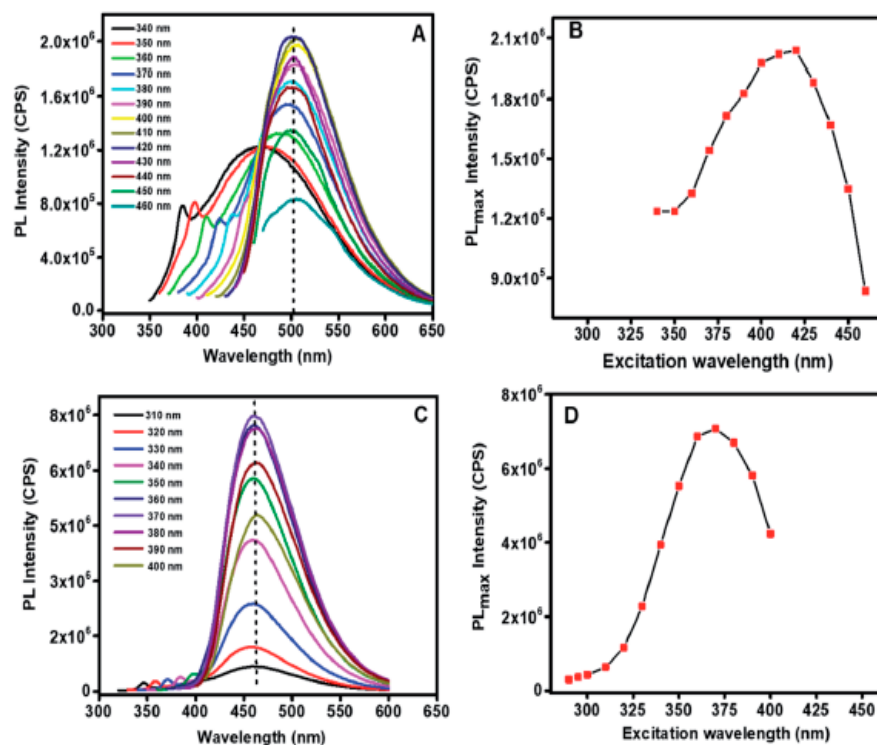


Figure 5. The effect of excitation wavelength on the emission spectra of (A) GO-QDs and (C) CA-QDs. (B,D) the effect of excitation wavelength on the maximum PL intensity (PL_{max}) in each case.

Table 1. Effect of different materials on the limit of detection of polycyclic aromatic hydrocarbons and nitro-aromatic compounds.

Semiconductor Sensor	Modifier	Detection Technique	LOD (mol L ⁻¹)	Detection Range (mol L ⁻¹)	Pollutant/Analyte	References
GO-CdSeTeS/ZnS	L-cysteine	Fluorescence	2.26×10^{-9} μ M	$0.1\text{--}0.5 \times 10^{-6}$	PAHs	[4]
GO-CdSeTe/ZnSe/ZnS	L-cysteine	Fluorescence	0.19 mg/L	$0.1\text{--}0.5 \times 10^{-6}$	PAHs	[60]
CuInS ₂	BSA	Fluorescence	28 nmol/L	$5.0 \times 10^{-8}\text{--}3 \times 10^{-6}$	Nitro-aromatics	[61]
CdTe	L-cysteine					[41]
Fluorescence	1.1 nM	Nitroaromatics				[73]
CdS	lysozyme	Fluorescence	0.1	$5 \times 10^{-7}\text{--}1.5 \times 10^{-5}$	Nitro-aromatics	[48]
CdTe(S)	polyacrylamide	Fluorescence	2.1 nmol/L	$0\text{--}7.0 \times 10^{-9}$	Nitro-aromatics	[74]
CdTe	(TGA)/CD	Fluorescence	0.085 μ M	$5 \times 10^{-7}\text{--}7.5 \times 10^{-5}$	PAHs	[40]
CdSe	oleylamine	Fluorescence	2.1×10^{-8} mol/L		Nitro-aromatics	[75]
CdSe/ZnS	1,4-dihydro-nicotinamide adenine dinucleotide (NADH)	Fluorescence	0.1 nM		RDX	[76]
CQDs	-NH ₂		0.4 μ M	$1.0 \times 10^{-7}\text{--}1.58 \times 10^{-5}$		[75]
CdSe	PAMAM-G4 dendrimer		27 nM	$5.5 \times 10^{-8}\text{--}5.5 \times 10^{-7}$		[76]
CQDs	-NH ₂		2.13×10^{-7}	$0\text{--}1.0 \times 10^{-6}$		[77]
GQDs	Sulfur		9.3×10^{-8}	$1.0 \times 10^{-7}\text{--}9.9 \times 10^{-5}$		

4. Nanocomposite as Sensors

A nanocomposite can be defined as a material that is composed of two or more nanomaterials, with enhanced chemical properties and physical properties. The purpose of a composite is to achieve a synergy effect in the sensing process. Nanocomposites present an alternative approach to overcome the current limitations of individual nanomaterials [78].

4.1. Mesoporous-Silica-Coated-QD Composites

The phrase “mesoporous materials” refers to solids based on either ordered or disordered networks with a broad or narrow distribution of pores within the range of 20 to 50 nm, which is good for the incorporation of QDs. These materials have the potential to be used in surface modification for both fluorescence sensing and electrochemical sensing [79,80]. The porous structure of mesoporous silica is known for its large surface area and volume. These properties make it easy for the QDs to be embedded into the mesoporous silica for the formation of a nanocomposite with enhanced properties of QDs. There have been few reports on the development of mesoporous-silica-coated QDs for the detection of pollutants. For instance, a chiral nematic mesoporous-silica-encapsulated CdS film was used for the detection of trace TNT [81].

4.2. QD–GO Composites/Hybrids

Graphene and its derivatives have attracted much attention in different areas of research because of their good physical and chemical properties [82]. Graphene oxide (GO) can be best described as a single-layer planar hexagonal array of carbon atoms to which different functional groups such as carboxylic acid, hydroxyl and epoxy are attached [83]. These carbon-based materials are emerging as the most promising platform for the preparation of nanocomposites for different sensing of NACs and PAHs [84].

Graphene, graphene oxide (GO) and reduced graphene oxide (rGO) can be easily combined with semiconductor QDs to form composites with enhanced sensitivity and selectivity towards the detection of organic pollutants [85]. Graphene, GO and their composites have been widely used for wastewater treatment because of their high adsorption capacity. The π -electron system of graphene and its derivative make them suitable modifiers of QDs for the fluorescence detection of π -electron-rich organic pollutants. Mitra et al. (2016) explored rGO-based sensors for the fluorescence detection of both PAH analytes and NACs. The results of their study showed an enhancement of PL intensity of the sensor by the pollutants (Figure 6) [67]. In 2016 and 2017 Adegoke et al. investigated the selectivity and sensitivity of a QD–GO composite for the detection of PAHs [4,60]. Their study showed that PAHs could be detected by a QD–GO composite through an enhancement mechanism. Recently, Liu et al. synthesized CuInS₂ quantum dot (QD) and graphene oxide (GO) nanocomposites as a fluorescent sensor for the detection of kanamycin [82].

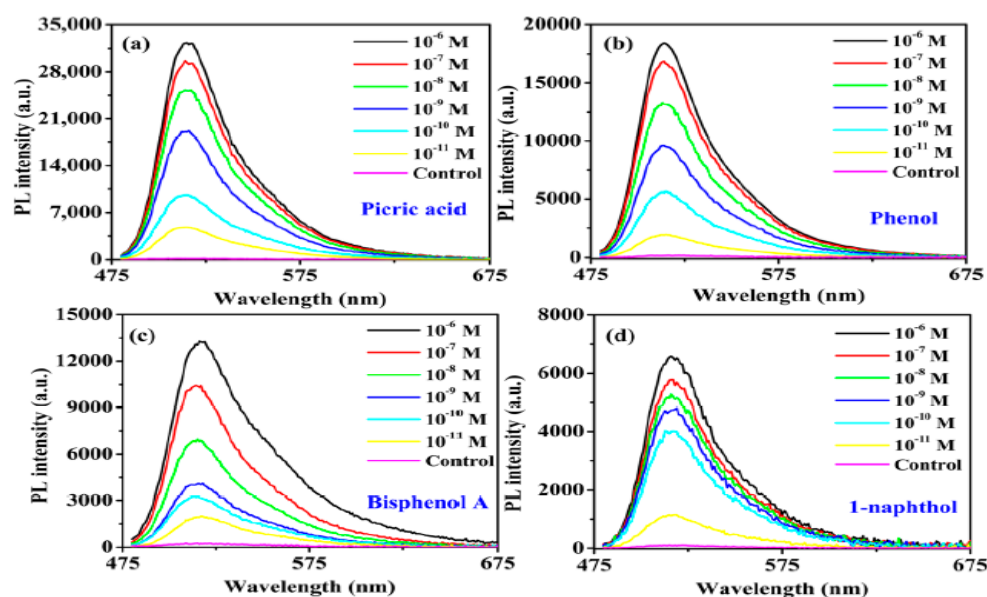


Figure 6. “Turn-On” fluorescence response of four different organic pollutants; picric acid (a), phenol (b), bisphenol A (c) and 1-naphthol (d) toward a RGPD-fl composite probe [67].

5. Detection Mechanisms

Different approaches based on surface modification with different molecules or ligands are said to cause different detection mechanisms. For instance, mechanisms of fluorescence detection are not only based on quenching but also based on mechanisms such as fluorescence turn-on, spectral shift, lifetime and anisotropy [5]. A study on the determination of 2,4,6-trinitrophenol (TNP) by Liu et al. demonstrated that the quenching mechanism for the detection of electron-deficient NACs occurs through acid–base pairing between amino functional groups and the electron-deficient rings [61]. The quenching mechanism can occur in two ways: static and collisional quenching. These are differentiated through time-resolved measurements of fluorescence lifetime. In the static quenching process, the fluorescence lifetime of the sensor remains unchanged as the concentration of the quencher is increased. In the collisional quenching, the fluorescence lifetime becomes shorter as the concentration of the quencher increased. The quenching mechanism is normally triggered by the transfer of electrons from electron donors to electron-deficient compounds [73,86]. Theoretically, it means that the fluorescence enhancement, also known as fluorescence “turn-on” is encountered for the detection of explosive residues or pollutants that are not electron-rich [79]. The detection of PAHs also occurs through fluorescence “turn-on” [40]. This type of mechanism is said to be triggered by energy transfer between the sensor and the species. Energy transfer of this nature can be due to different factors, such as hydrogen bonding and π – π interaction [58].

6. Conclusions

The continuous discharge of PAHs and NACs into the environment through man-made and natural processes suggests that there should be regular monitoring of these pollutants in water sources. Fluorescence detection has turned out to be an important technique for monitoring PAHs and NACs. Semiconductor nanocrystals have shown better sensitivity and selectivity due to their versatile surface chemistry. Reports from several studies have shown that binary quantum dots (QDs) have attracted much more attention in sensing applications and the detection of PAHs. However, these have been based on the use of heavy-metal-based QDs. Furthermore, the literature has also shown that there are challenges in detecting PAHs without substituents because many modifiers cannot react with their π – π system. As far as the environment is concerned, we suggest developing fluorescent probes or chemical sensors based on ternary QDs for monitoring PAHs and

nitro-aromatics (explosives). Ternary QDs and carbon-based QDs are emerging as the better alternative for sensing aromatic organic pollutants, due to their low toxicity. Furthermore, different modification approaches have been shown to enhance the sensitivity of the fluorescent probes. This review of different studies has also shown that organic-soluble QDs exhibit better properties for sensing applications. However, aqueous-synthesized QDs will be preferred due to environmental concerns based on the toxicity of organic-soluble ternary QDs. Conjugation of the ternary QDs with a good selection of appropriate ligands or carbon-based material conjugates has emerged as the better way for the improvement of stability and sensitivity. This is due to their excellent optical properties, such as narrow emission peaks, high quantum yield (QY), large Stokes shift and tunable emissions from short wavelengths (visible region) to longer wavelengths (near-infrared region). Nevertheless, group I-III-VI ternary quantum dots (QDs) are emerging as alternative fluorescent probes or chemical sensors for the monitoring of nitroaromatics (explosives). However, there is no report on the sensing of PAHs using these fluorescent probes. Furthermore, the proper selection of conjugate may enhance the selectivity and sensitivity of the probes. Although group I-III-VI QDs are potential environmentally friendly sensors, their surface defects are a challenge in FRET-based studies. Nevertheless, different sensing mechanisms derived from surface modification of these materials can improve their efficiency for energy transfer, which is an essential part of sensing organic pollutants.

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