Microchemical Journal 155 (2020) 104755

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Review Article

Mn-Doped ZnS Quantum dots–An Effective Nanoscale Sensor

Jyoti Patel[a], Bhawana Jain[a], Ajaya K. Singh[a,*], Md. Abu Bin Hasan Susan[b], Lellouche Jean-Paul[c]

[a] Department of Chemistry, Govt. V. Y. T. PG. Autonomous College, Durg, Chhattisgarh 491001, India
[b] Department of Chemistry, University of Dhaka, Dhaka 1000, Bangladesh
[c] Department of Chemistry & Institute of Nanotechnology & Advanced Materials, Bar-Ilan University, Ramat Gan, Israel

ARTICLE INFO

Keywords:
Quantum dots
Mn-doped ZnS quantum dots
Chemosensing
Biosensing

ABSTRACT

Quantum dots (QDs), due *inter alia* to their colourtunable symmetry, narrow emission, broad absorption, stability, and solution processibility have received an upsurge of interest in the last decade as potential materials for diverse applications. Doped QDs, in particular, have gained significant attention as a new class of luminescent materials since dopants influence the optical behaviour of QDs. Therefore, doped ZnS QDs possess conspicuous properties like longer dopant emission lifetime and lower toxicity. The dopant emission lifetimes of transition-metal ions are longer than the energy-gap and defect-related luminescence of the host as well as the biological background fluorescence to offer immense prospect for removal of background fluorescence for sensing applications. Probes based on phosphorescence or fluorescence enhancement of QDs is crucial for the development of the detection capability. This current review highlights the optical property and various sensing strategies of Mn-doped ZnS QDs that make them exceptional probes for applications in sensing. The review not only intends to present an all-encompassing study of the well-documented usages of QDs, but is also rather addressing the current promising improvements, concepts, and excellent applications in research of doped QDs for chemo- and biosensing. Over 200 publications are overviewed and considered here in the perspective of leading applications in sensing dealing with for instance, fluorescence, phosphorescence, chemiluminescence, electrochemiluminescence and biosensing features.

1. Introduction

Within a steadily increasing database, diverse nanomaterials and nanodevices evoked fascination for promising applications due to their properties and performances prominently different from their counterparts based on bulk solids and molecules. In nanoscience and nanotechnology, it is a substantial issue to understand the mechanism of action of nanomaterials and their tunability to tailor properties as the unique properties of nanoscale materials depend upon their shape, size, and structure [1]. Semiconductor nanomaterials also called quantum dots (QDs), as expected, occupy a unique place in the recent literature with an outstanding track record with high potential, dramatic consequences, and frequently controversial experimental evidence. QDs have excellent properties as robust fluorescent materials, such as, broad absorption spectra along with narrow and symmetric emission spectra and good photo-stability [2–4]. The surface properties also have substantial influences due to high surface-to-volume ratios of these fluorescent QDs [5]. When the spatial dimensions are reduced in a nanometre range, a widening of band gap is caused [6]. QDs are fluorescent nanoscale materials having a radius comparable to that of Bohr excitonic radius of the material [7]. These small nanocrystals can cater the requirements of modern applications, such as biolabels [8,9], sensors [10,11], lasers [12,13], light-emitting diodes [14,15], and in medicines [16]. Moreover, QDs are good components in optical gain devices, regenerative solar cells, and electroluminescent devices [17]. Recently, they have found applications in photocatalysis [18], organic dye removal [19], solar paints [20], cancer targeting and drug delivery [21]. Semiconducting QDs are particles having their physical dimensions between 1 and 10 nm and are composed of groups II–VI or III–V atoms [22]. Furthermore the thermal and photo-stability of QDs can be easily enhanced using various strategies, like organic ligand modification strategies [23–25].

Zinc sulfide (ZnS), one of the significant II–VI semiconducting and crystalline material in QD applications and research [26], with 3.68 eV optical energy-gap for the zinc blende and 3.80 eV for the hexagonal wurtzite phase in the bulk form and high refractive index [27,28]. It also has large exciton binding energy (~40 meV) useful for applications in solar cells, flat panel display, lasers, sensors, imaging, and photocatalytic dye degradation, etc. [29–32]. Preparation of ZnS QDs using various capping agents has been reported, which revealed a strong

* Corresponding author.
E-mail address: ajayaksingh_au@yahoo.co.in (A.K. Singh).

https://doi.org/10.1016/j.microc.2020.104755
Received 10 January 2020; Received in revised form 19 February 2020; Accepted 19 February 2020
Available online 21 February 2020
0026-265X/

confinement effect [33]. Compared to other II–VI compound semiconductors, ZnS is more stable, nontoxic, ecologically safe, and is an excellent host for doping [34]. Therefore, it is potentially applied in both biological detection [35] and waste water treatments [18,19].

Doping a suitable element is generally an effective means for tuning the energy levels, surface states, as well as the magnetic, optical, electrical along with the structural properties of the semiconductors [36–38]. Dopants play critical role in semiconductor-based devices and thus has motivated the research on the properties and applications of semiconductor nanomaterials with the doping of intentional impurities [39]. In fact, deliberate addition of dopants or impurities for controlling the behaviours of materials works as the spirit for many technologies. The influence of dopants on semiconductor nanocrystals, a few nanometres value in scale with exceptional and size-specific optical, magnetic, and electronic behaviour are therefore critical [40]. This works by efficiently transferring the energy, from the absorbed photons to the impurities, rapidly confining the excitation and suppressing the unwanted reaction at the nanomaterials surface [41]. ZnS doped with Mn and Cu are the two largely studied doped QDs [42] and commonly proposed as suitable fluorescent and phosphorescent probes [43].

QDs as sensors, for biological and chemical detections have drawn significant interest over the past decade [44,45] due to the distinctive properties displayed by various nanoscale materials in combination with the molecular recognition moiety [46,47]. The QDs modification with biomolecules [48] and metal ions [49,50] has been an intriguing domain in sensor/biosensor applications [51,52], such as ions [53,54], biomacromolecules [55,56], and small molecules [57,58]. As compared to fluorescence, the phosphorescence of doped-QDs exhibit extended average life, with a suitable time delay to avoid scattering of light and fluorescence emission [59]. In addition, the large surfaces of QDs remain favourable for the attachment of various ligands. When the large-surface QDs are introduced, some of the small molecules, ions, and biomacromolecules go through physical or chemical reactions. This causes a change in the composition or charges on the QDs shell to allow exceptional control of few more properties [60]. Studies associated with the interactions among the QDs and metal ions revealed that capping agents at the surface intensely affects the luminescence reaction of QDs to various metal cations [61,62]. The scheme of detections depending on the interactions between QDs and metal ions is reported extensively. However the sensing technique largely depends on the fact that metal ions quench the phosphorescence or fluorescence emissions of the QDs [63,64].

Fluorescence quenching-based probes generally encounter huge background intrusions resulting in high detection limits, whereas probe depending on the signal enhancement suffer small interferences. Thus, probes on the basis of phosphorescence or fluorescence enhancement of QDs are extremely important for the development of relating detection capabilities [65].

Doped QDs remained the subject matter of quite a few exceptional reviews and book chapters [66–68] largely focussing on the preparation strategies and features of doped QDs. In this review, we aim at bringing light to the photophysical characteristics of Mn-doped ZnS QDs that make them exceptional probe due to their diverse approach in chemo or biosensing and give emphasis on the current promising developments in research for sensing applications.

2. Preparation of functionalized Mn-doped zinc sulphide quantum dots

Mn-doped ZnS QDs have drawn considerable interest in recent years, due to their remarkable physical, chemical, and optical properties [69]. Mn-doped ZnS QDs have been synthesized following various methods [70,71] which include: metal organic vapour chemical deposition, wet chemical methods, laser assisted thermal and catalytic evaporation [72].

The II–VI semiconductor lattices possess lower photon energy (for eg. ZnS) [73,74] and the energy gap of $^4T_1$–$^6A_1$ is large. Thus, doping allows the $^4T_1$–$^6A_1$ transition with high efficiency as the Mn ions work as recombination centre for the excited electron–hole pair resulting in characteristic luminescence at higher wavelength regions. Due to Mn^{2+} doping on Zn, there occurs development of a characteristic emission band at approximately 590 nm (Fig. 1), due to the prominent $^4T_1$–$^6A_1$ *d–d* transition of Mn^{2+} ions on Zn^{2+} sites (where S^{2-} ions coordinated the Mn^{2+} ones) [75–77]. When compared with the usual CdSe or ZnS QDs, Mn-doped ZnS QDs exhibited, both extended luminescent lifetimes (of the order of few ms) as well as longer Stokes shift between excitation and emission wavelengths, properties characteristics to phosphorescent emission [78]. Thus, it is likely to achieve time-resolved measurements with simple discrimination between the luminescence emission of Mn:ZnS QDs from the background fluorescence of the sample (where luminescent lifetime is shorter).

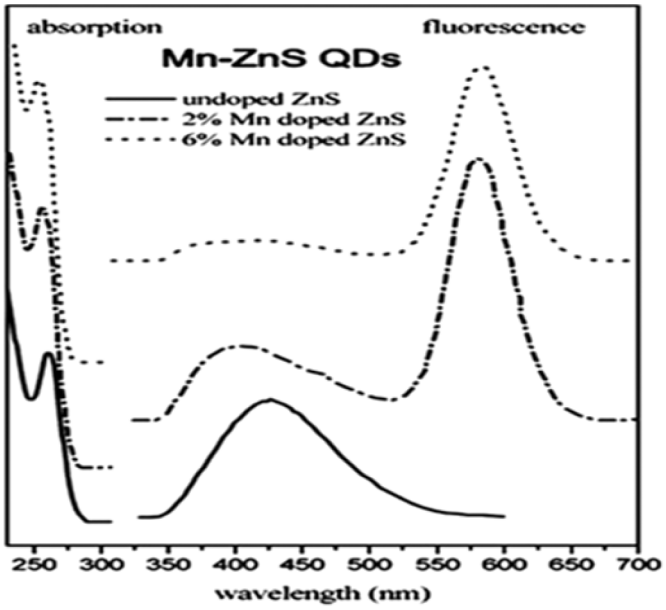

Fig. 1. Luminescence emission spectra of undoped and Mn-doped ZnS QDs. Reprinted with permission from ref. [73]. Copyright 2005 American Chemical Society.

Moreover, compared to the traditional CdSe or CdS QDs, the lack of Cd^{2+} in Mn-doped ZnS QDs reduces the toxicity of these nanoscale materials. Consequently, there has been a raised concern over the use of toxic heavy-metal containing QDs in living cells, humans and animals as the long-term impact is unknown [79]. Mn-doped ZnS QDs have therefore, proved themselves to be highly developed luminescent nanoscale materials and labelling agents for sensing and biological imaging [80].

3. Design principles for construction of chemo-sensors based on Mn-doped zinc sulphide quantum dots

In the field of chemical probes, the recognition and sensing of biologically and environmentally important metal ions has emerged as an important goal. Various analytical methods like fluorescence, phosphorescence, chemiluminescence, and electrochemiluminescence sensing of inorganic ions, small molecules, and macromolecules, etc. using Mn-doped ZnS QDs are highlighted here.

3.1. Mn-doped ZnS QDs as fluorescence-based chemo-sensors

The exploration of fluorescent sensors is a topic of considerable interest. Optical sensors based on the changes of spectral absorbance or fluorescence resulting from the interaction between metal ions and

Table 1
Use of Mn-doped ZnS QDs for Fluorescent Sensing of Small Molecules.

Analyte	Capping agent	Matrix	Detection limit	Wavelength of Detection	Effect on Luminescence	Ref.
Folic acid	3-Mercaptopropionic acid	Water	1.1×10^{-7} mol L^{-1}	596 nm	Fluorescence quenching	[58]
2,4,6-TNT	Amine	Water	1×10^{-9} mol L^{-1}	420 nm,600nm	Fluorescence quenching	[83]
Bilirubin	L-cysteine	Urine, serum	1.8×10^{-6} mol L^{-1}	410 nm,470 nm,590 nm	Fluorescence quenching	[84]
Halobenzoquinone	Cysteine, threonine, tyrosine and tryptophan	Real drinking water samples	–	590nm	Fluorescence quenching	[85]
Folic acid	3- Mercaptopropionic acid	bovine serum	6.0×10^{-9} mol L^{-1}	490 nm,595nm	Fluorescence enhancement (for Mn dopant)	[86]
L-tryptophan	Mono-6-SH-β- cyclodextrin	Water	3.0×10^{-9} mol L^{-1}	430 nm,598nm	Fluorescence enhancement	[87]
Glutathione	Dopamine	Deionised Water	—-	592 nm	Fluorescence enhancement	[88]
Creatinine	Thioglycolic acid	human serum, urine samples	7.25×10^{-9} mol L^{-1}	582nm	Fluorescence enhancement	[89]

indicators has been found to be a simple and quick approach. Fluorescent probes own many appealing properties like high sensitivity, less cost, easy detection, and remote control. Fluorescence-based probes are mostly important because of their intrinsic sensitivity and selectivity [81,82].

3.1.1. Detection of small molecules

3.1.1.1. Detection by turn-off mode. A novel fluorescence turn-off nanosensor was designed by Moritz et al. for sensing of folic acid using 3-mercaptopropionic acid (MPA)-capped Mn-doped ZnS QDs in aqueous medium [58]. The QDs displayed high fluorescence sensitivity owing to higher affinity of the carboxylate groups and nitrogen atoms present in folic acid for the Zn on the surface of the QDs. A static quenching mechanism was demonstrated through the formation of non-specific QDs by Perrin model along with fluorescence luminescence lifetime of the doped ZnS QDs. Tu et al. employed amine-capped Mn-doped ZnS nanocrystals for fluorescence sensing of 2,4,6-trinitrotoluene (TNT) through quenching of the Mn^{2+}luminescence [83]. Due to transfer of electrons from the ZnS conductive band to the TNTs lowest unoccupied molecular orbital, the aminated layer bounded anions of TNT quench the Mn^{2+}luminescence. The ion-doped sensor shows a high quantum yield and can distinguish various nitro compounds.

Another turn-off sensor is designed by Abha et al. using *L*-cysteine (*L*-cys)-modified ZnS QDs doped with Mn for bilirubin detection [84]. The luminescence quenching due to reductive photo-induced electron transfer where bilirubin worked as electron donor while QDs acted as electron acceptor was utilized for detection. To ascertain the practical efficacy of the sensor, the validation was done by detection in real samples like spiked human serum and urine with good recovery percentages. Jiao et al. designed a sensor on the basis of halobenzoquinones (HBQs)-mediated assembly of doped ZnS QDs modified with amino acids [85]. The QDs were functionalized with four different amino acids, cysteine, threonine, tyrosine, and tryptophan and discrimination of three various HBQs, *i.e.,*dichloro,dibromo and trichlorobenzoquinone were done. A charge-transfer complex formed between the aromatic rings and the amine groups of HBQs causing amassing of QDs, thus led to declining fluorescence. The amino acid-functional QDs displayed different assembly behavior with varying targets, which could be utilized to distinguish HBQs.

3.1.1.2. Detection by turn-on mode. A dual-emission ratiometric fluorescent sensor by Cu^{2+}-Mn^{2+} codoped ZnS QDs for quantitative detection of folic acid in bovine serum was designed by Wang et al. The two separated dopant emission peaks (490 and 595 nm) observed were utilized in the fluorescent sensing. By addition of folic acid, the Cu^{2+} dopant emission quenched while the Mn^{2+} dopant emission was enhanced. The sensing scheme was based on the transfer of electrons between folic acid and QDs [86]. Wei et al. synthesised the doped ZnS QDs modified with mono-6-SH-*β*-cyclodextrin and developed a ratiometric fluorescence method for detecting *L*-tryptophan [87]. A highly selective ratiometric emission response (400/598 nm) was observed for *L*-tryptophan as compared to other amino acids. The *β*-cyclodextrin coated QDs, retained the ability of molecular recognition, which helps identifying *L*-tryptophan.

An effective fluorescent probe made of dopamine-conjugated CdS:Mn/ZnS core/shell QDs was developed by Banerjee et al. and used for the sensing of glutathione (GSH) by controlling the electron transfer path of the doped QDs [88]. By modifying the surface of QDs with dopamine molecules, the fluorescence OFF condition of QDs was observed which was restored by reducing GSH when disulfide bonds were cleaved, freeing up QDs from dopamine. A novel, “turn-on” sensor for enzymeless probing of creatinine in human serum and urine samples employing thioglycolic acid-capped ZnS:Mn-doped ZnS QDs was developed by Wang et al. [89]. The emission spectrum showed a considerable increase in intensity in the presence of creatinine due to surface trap passivation of QDs through the binding of creatinine with QDs surface, resulting in the development of new radiative electron–hole recombination centers. The detailed application of Mn-doped ZnS QDs for fluorescence sensing of small molecules is summarised in Table 1.

3.1.2. Detection of inorganic ions

3.1.2.1. Detection by turn-off mode. Rofouei et al. reported a new fluorescence sensor for Ce^{3+}-ions using the fluorescence quenching of glycine dithiocarbamate (GDTC)-functional Mn-doped ZnS QDs [90]. The interaction between the QDs and the Ce^{3+}-ions quenches the fluorescence of QDs as per the Stern-Volmer equation and there exists a collisional quenching process. Rajabi et al. designed a fluorescent sensor for optical recognition of hazardous sulfide ion based on the fluorescence quenching of doped ZnS QDs [91]. The sulfide ion was detected with good sensitivity. Shang et al. synthesised *N*-acetyl-*L*-cysteine functional Mn-doped ZnS QDs for determining Zn^{2+} ions [92]. Modification of sulfur suppresses the radiative recombination process and the bright fluorescence was then quenched. The emission was restored by adding Zn^{2+}owing to the development of ZnS passivation layer surrounding the QDs. Thus, a fluorescent assay for Zn^{2+} was developed. Zhang et al. successfully prepared mercaptoacetic acid (MAA)-capped Mn-doped ZnS QDs exhibiting strong fluorescence peak at 590 nm [93]. The sulfide anion (S^{2-}) caused the fluorescence quenching and the intensity decrease was proportional to the S^{2-}concentration. When S^{2-} ions got adsorbed over surface of QDs, the S^{2-} vacancy reduced, thus quenching of fluorescence was observed.

Zhang et al. prepared the doped ZnS QDs coated with ZnS shell and created QDs-IDA (iminodiacetic acid) conjugate by modifying the surface with IDA, which improved the water-solubility as well as the luminescence quantum yield of QDs [94]. The conjugate in buffer solution selectively reacts to Ag (I) ion and quenches the fluorescence of QDs-IDA due to formation of complex between the IDA and Ag (I) ion, facilitating photoinduced electron transfer. Wang et al. developed a novel and efficient 6-mercaptonicotinic acid-*L*-cys-Mn-doped ZnS fluorometric assay for Cu^{2+}ions detection [95]. The modification

endows the QDs with good fluorescence property accessing them for Cu^{2+} ions through Cu^{2+}-S interactions. The fluorescence is quenched by Cu^{2+} owing to electron transfer-induced fluorescence quenching mechanism. On 325 nm excitation, strong red emissions at 593 nm along with a blue one at 412 nm were observed. The red fluorescence is strongly quenched as the concentration of Cu^{2+} is increased, whereas the blue one remains unaffected. Fu et al. synthesized a new composite combining Mn-doped ZnS QDs and ZIF-8 (Zeolitic imidazolate based metal-organic framework) [96]. ZIF-8 might possibly be used as a framework for QDs loading, which inturn endowed exceptional fluorescence property for the composite. The obtained composite could be used as a probe for Co^{2+} and dichromate detection.

3.1.2.2. Detection by turn-on mode. A novel approach for Cd^{2+} ions determination based on the fluorescence enhancement of core–shell CdS:Mn/ZnS QDs was reported by Banerjee et al. [97]. The idea was to alter the surface of QDs with a metal ion-selective ligand through zero length coupling process. The sensing was based on electron transfer scheme between the ligand and QDs and on exposure to Cd^{2+}, subsequent blocking of the electron transfer pathways occurred. The strategy can also be used for detecting potentially harmful metal ions. A new ratiometric probe for Cu^{2+} detection was developed by He et al. based on dually-emitting MPA-ZnS:Mn QD showing sharp peaks at 430 and 590 nm [98]. With the increase in Cu^{2+} ions concentration, the ratio for dual emission intensity (I_{430}/I_{590}) of QDs steadily improved. Based on this output, a highly sensitive probe was established for Cu^{2+} ions sensing, signifying its probable applications.

Jing et al. presented a fluorescence sensor array recognizing nine different metal ions on the basis of amino acids-modulating QDs [99]. They synthesized two different QDs, 3-MPA and alpha-thioglycerol-capped ZnS QDs doped with Mn embellished with two varying amino acids (glutamine and arginine). Amino acids can bind QDs as well as form complexes with metal ions with their amine, carboxyl, or hydroxyl groups thus conveying differential detection of ions. Consequently, the fluorescence signals for metal ions either enhance or decline. Moreover, the six-receptor sensor assortment was applied to differentiate the mixtures of metal ions with different oxidation states, the quantisation of pure metal ions and nine metal ions spiked in tap water. Table 2 highlights the applications of Mn-doped ZnS QDs for fluorescent sensing of inorganic ions.

Quenching mechanism is usually divided into static and dynamic quenching. The static quenching initiates from the lightless complexes of the quencher and fluorescent material in the ground state, whereas in dynamic quenching, the quenching agent and fluorescent material interact in excited state, resulting in the intensity decrease. The mechanism of dynamic quenching can be analyzed quantitatively by Stern-Volmer's equation [90] (Eq. (1)).

$$F_0/F = 1 + K_{SV}\,Cq \quad (1)$$

Table 3
Fluorescence Quenching Constants of Mn-doped ZnS QDs by Various Analytes.

Analyte	K_{sv} (M^{-1})	Ref.
Folic acid	2.24×10^3	[58]
2,4,6-TNT	5.5×10^3	[83]
Ce^{3+}	9.2×10^4	[90]
S^{2-}	4.5×10^4	[91]
Zn^{2+}	4.2×10^4	[92]
S^{2-}	1.6×10^4	[93]
Ag^{+}	5.8×10^5	[94]
Cu^{2+}	1.9×10^6	[95]
Co^{2+}, $Cr_2O_7^{2-}$	4.311×10^4, 2.742×10^4	[96]

where F_0 and F are the fluorescence intensity of the ZnS QDs in absence and presence of a quencher, Cq is the quencher concentration, and K_{SV} is the dynamic quenching constant or Stern-Volmer's constant. The values of Stern-Volmer's constant for fluorescence quenching by various analytes are given in Table 3.

3.1.3. Detection of macrobiomolecule

Nano-bio-systems play a vital role in improvement of the multimodal/multidimensional sensing devices to recognize novel functionalities by considering the inner level molecular interactions. To study the protein structure and dynamics, the intrinsic fluorescence (IF) of proteins work as an efficient tool. The recognition of protein and discrimination resolution was significantly improved by Li et al. exploring the IF as the fourth channel optical input along with triple-channel optical output of QDs (phosphorescence from Mn^{2+} dopant, fluorescence from host ZnS and Rayleigh scattering from QDs) [100]. To recover the IF difference and their interaction with ZnS QDs, plasma modification of proteins was explored for multidimensional optosensing device. Thus, a sensor device for specific and extremely discriminative recognition of proteins in urine samples, human serum and cancer cells was established.

3.1.3.1. Detection by turn-off mode. A fluorescent probe for tyrosinase (TYR) determination was developed by Zhang et al. based on dopamine-functionalized Mn-doped ZnS QDs [101]. TYR causes oxidation of dopamine to dopaquinone and a photoinduced electron transfer process occurs between the two resulting in fluorescence quenching. It was applied for detection of TYR in serum samples of chicken.

3.1.3.2. Detection by turn-on mode. Shao et al. presented an antithrombin (AT) assay by fluorescence anisotropy (FA) in heparin medium on the basis of polyethyleneimine-capped ZnS QDs [102]. The QDs showed a low background for FA value supporting the assay of large molecules. The FA value increased upon addition of AT molecules

Table 2
Use of Mn-doped ZnS QDs for Fluorescent Sensing of Inorganic Ions.

Analyte	Capping agent	Matrix	Detection limit	Wavelength of Detection	Effect on Luminescence	Ref.
Ce^{3+}	Glycine Dithiocarbamate	Water	2.29×10^{-7} mol L^{-1}	415 nm,575 nm	Fluorescence quenching	[90]
S^{2-}	2-Mercaptoethanol	Water	1.2×10^{-6} to 2.6×10^{-5} mol L^{-1}	424 nm,594 nm	Fluorescence quenching	[91]
Zn^{2+}	N-acetyl-L-Cysteine	Tap Water	6.7×10^{-7} mol L^{-1}	598 nm	Fluorescence quenching	[92]
S^{2-}	Mercaptoacetic acid	Lake Water	1.5×10^{-7} mol L^{-1}	590 nm	Fluorescence quenching	[93]
Ag^{+}	Iminodiacetic acid	Water	2.6×10^{-7} mol L^{-1}	258 nm,285 nm	Fluorescence quenching	[94]
Cu^{2+}	L-cysteine & 6-mercaptonicotinic acid	Environmental water samples	1.2×10^{-9} mol L^{-1}	593 nm,412 nm	Fluorescence quenching	[95]
Co^{2+}, $Cr_2O_7^{2-}$	ZIF-8	Human serum albumin and tap water	2.7×10^{-7} mol $L^{-1}$and 2.2×10^{-7} mol L^{-1}	592 nm	Fluorescence quenching	[96]
Cd^{2+}	Azacrown ether	Water	—	592 nm	Fluorescence enhancement	[97]
Cu^{2+}	Mercaptopropionic acid	Water	14×10^{-9} mol L^{-1}	430 nm,590 nm	Fluorescence enhancement	[98]

to the heparin-QDs system resulting various linear range of detection for AT. Chang et al. developed a fluorescent biosensor on the basis of mercaptophenylboronicacid (MBA)-capped doped ZnS QDs for the glycoprotein-transferrin (TRF) determination [103]. TRF bounds to MBA via boronate affinity. In the presence of TRF, there occurs efficient fluorescence enhancement due to obstructed transfer of electrons from QDs to boronic acid. The probe can detect TRF in serum and potentially be employed for sensing trace glycoproteins in complex biomedical samples. The same group designed another turn-on sensor based on 3-acrylaminophenyl-boronic acid-capped ZnS QDs for glycoproteins detection [104]. In the absence of glycoproteins, the fluorescent emission was weak owing to the transfer of electron from QDs to boron at the surface. When glycoprotein was added a noticeable fluorescence enhancement was observed because of the inhibition of electron transfer process as the boron moieties covalently bind the glycans of the glycoprotein.

3.1.4. Detection by molecularly imprinted polymers

Molecular imprinting technology, one of the significant approaches is widely studied and used for producing biomimetic receptors. By applying techniques of molecular imprinting over surface functionalized doped QDs, molecularly imprinted polymers (MIPs) having binding sites at surface showing good optical properties became possible. The technology is based on a polymer matrix assembled over an imprint, held by selected functional monomers [105–107]. The engineered selectivity for binding to an analyte of interest is the key aspect of MIP [108]. The MIP-QDs complex work as a fluorescent probes, which allows simple and cost-efficient selective probing of analyte in biological samples [109].

3.1.4.1. Detection by turn-off mode. Zhao et al. prepared QDs based MIP composite nanospheres by ultrasonication-assisted encapsulation method depending on the interaction involving hydrophobic and van der Waals forces [110]. These QDs-MIP nanospheres were efficiently used for the fluorescent sensing of diazinon on the basis of luminescence quenching by template analyte rebinding in the polymer matrix into the recognition cavities. Thus, a novel strategy was presented to fabricate inorganic organic MIP nanocomposites desirable for applications in biomedical or chemical sensing. Tan et al. developed a novel method and produced mixed organic–inorganic imprinted doped QDs composite for detection of bovine haemoglobin [111]. Amine-capped ZnS QDs were used as support, while methacrylic acid and acryl amide worked as functional monomer and γ-methacryloxypropyltrimethoxysilane as a grafting agent. For surface graft imprinting at QDs surface, bovine haemoglobin was used as the template. Vazquez et al. successfully synthesised MIP-coated doped ZnS QDs by precipitation polymerization method involving ultrasound irradiation [112]. MIP was prepared with cocaine as template molecule, 2,2′-azobisisobutyronitrile as initiator, ethylenedimethacrylate as monomer while divinylbenzene as cross-linking agent. The fluorescence of QDs was quenched by cocaine and its metabolite for instance, benzoylecgonine and ecgonine methyl ester which was not observed with other drugs of abuse such as cannabis abuse or heroin. Thus, the probe recognizes only cocaine and metabolites. Vazquez et al. also designed a second fluorescent probe for cocaine determination in compound samples such as serum and oral fluids. The matrix effect was found to be crucial dealing with QDs-based sensor for complex samples. Specific approaches like solid phase extraction and centrifugation methods and easy pre-treatments methods have been explored as a substitute for complicated and costly instrumentation of cocaine. The QDs material possibly served as an interphase for the development of strategies for point-of-care screening works [113].

A molecularly imprinted membranes (MIMs) for fluorescent recognition of bisphenol A, was demonstrated by Zhang et al. [114]. To fabricate QD-entrapped MIMs, acrylamide and *N,N′*-methylenediacrylamide hydrogel membranes were incorporated over mercaptopropyltriethoxysilane-capped QDs. After being activated by electron transfer between the QDs and bisphenol A, the fluorescence of entrapped QDs quenches. Thus, trace levels of bisphenol A can be detected. Ren et al. [115] synthesised an acrylamide-based MIP-coated QDs as sensor for detection of insecticide chlorpyrifos (CPF). CPF loading over MIP causes the quenching of fluorescence. Hu et al. prepared fluorescent magnetic molecularly imprinted polymers (FMMIPs) with ZnS QDs as a luminescent core, *N*-nitrosodiphenylamine (NDPhA) as a template, (3-aminopropyl)triethoxysilane (APTES) as a monomer and tetraethylorthosilicate as cross-linking agent [116]. The fluorescence quenching with increasing concentration of NDPhA was further used for its sensing and applied to tap water and seawater samples with good recoveries. Hu et al. also developed a fluorescent MIP nanosensor by a free-radical polymerization method, with QDs as a core, sulfapyridine (SPD) as template, methacrylic acid as monomer and ethylene glycol dimethacrylate as cross-linking agent [117]. These MIPs could sense SPD through quenching of fluorescence. Liu et al. developed a strategy to produce MIP-embellished doped ZnS QDs for sensing of acrylamide in food sample [118]. The fluorescent graphene oxide-based imprinted polymer with propionamide as template, ethylene glycol dimethacrylate as cross-linking agent and methacrylic acid as the monomer was synthesized with QDs as its fluorescence source. On loading acrylamide, fluorescence quenching occurred.

Xu et al. developed a novel method for synthesizing MIPs-based QDs with magnetic Fe_3O_4 nanopaticles for the sensing of dibutyl phthalate [119]. The polymer holds specific molecular recognition properties of MIPs, magnetic separation, as well as the fluorescence characteristics of QDs. Chmangui et al. synthesized MIPs with 5,7-dimethoxycoumarin (DMC) as template molecule and methacrylic acid as monomer, attached over the surface of QDs and designed a fluorescent probe for aflatoxins (AFs) determination in non-dairy beverages [120]. The probe was selective for AFs (AFB1, AFB2, AFG1, and AFG2) with a detection limit close to the maximum total AFs levels in foodstuffs permitted by European authorities *i.e.,* 0.1 to12 μg kg^{-1} for AFB1, and 4 to 15 μg kg^{-1} for overall AFs (AFB1, AFB2, AFG1 and AFG2) in foodstuffs. Thus the method could be applied for AFs assessment in several non-dairy beverage samples.

Ren et al. prepared an MIP probe with acrylamide as monomer, ethylene glycol dimethacrylate as cross linking agent for selective detection of cyphenothrin [121]. On addition of cyphenothrin, there occurs a charge transfer from QDs to cyphenothrin causing fluorescence quenching. With similar mechanism, Ren et al. fabricated another probe for nicosulfuron using MIP coated *L*-cys-modified Mn-doped ZnS QDs [122]. The probe is synthesized by sol gel process with APTES as monomer, and tetraethoxysilane as cross-linker working for fluorescence quenching mechanism. The reason behind quenching is the charge transfer from QDs to the template nicosulfuron. Abbasifar et al. proposed a new sensor for atropine detection utilizing the fluorescence quenching effect of polydopamine (PDA)-coated molecularly imprinted QDs [123]. The QDs were prepared using $Na_2S_2O_3$ as precursor, *L*-cys as capping agent and dopamine as monomer producing efficient recognition sites. The MIP shell shields the QDs from interferring molecules thus a selectivity for target molecule was developed.

There are also sensor design made from a hybrid QD/mesoporous silica/MIP (QD/MS/MIP). Zhang et al. prepared the novel composite material using (3-isocyanatopropyl)triethoxysilane as monomer, tetraethoxysilane as cross-linking agent, and applied it for sensing of tetracycline (TC) [124]. A new complex formation take place between QD/MS/MIP and TC due to transfer of energy from QDs to the complex causing fluorescence quenching. Another hybrid probe was designed by Wang et al. for recognition of serotonin (5-hydroxy tryptamine, 5-HT) based on Mn:ZnS QDs/SiO_2/MIP [125]. Complex formation take place between both amino groups of Mn:ZnS QDs/SiO_2/MIP and hydroxyl groups of 5-HT causing transfer of energy from QDs to complex resulting in quenching of QDs fluorescence. Geng et al. demonstrated an

alternative approach for synthesis and validation of doped ZnS QDs embedded in molecularly imprinted mesoporous silica microspheres, which could sense sparfloxacin [126]. A new functional monomer was synthesized by the thiol-ene click chemistry reaction of 3-(methacryloyloxy) propyltrimethoxysilane and 3-mercaptopropionic acid. Sparfloxacin was used as the template and QDs for signal transduction. The method has rapid response time with good selectivity for structural analogues and could be used for the recognition of target antibiotic in various complex samples.

3.1.4.2. Detection by turn-on mode. Sadeghi et al. synthesised MIP-coated ZnS QDs capped with the florfenicol (FF) MIP by sol–gel surface imprinting approach [127]. The functional monomer was APTES while tetraethoxysilane was used as the cross-linker. The fluorescence intensity got improved with growing concentration of FF as compared to the non-imprinted coated QDs. A fluorescent MIP for selective recognition of α-fetoprotein, a tumor biomarker, was demonstrated by Tan et al. [128]. They used amino-modified QDs as support, γ-methacryloxypropyl trimethoxysilane as grafting agent and 4-vinylphenylboronic acid and methyl methacrylate as the monomers and a graft imprint was created over QDs. The MIP QDs rapidly detected α-fetoprotein and has a wide scope for various other glycoproteins.

3.2. Mn-doped ZnS QDs as phosphorescence-based chemo-sensors

In ZnS QDs doped with Mn^{2+}, the detection of transition ($^4T_1(4\ G) - {}^6A_1(6S)$) in room-temperature phosphorescence (RTP) has become a hotspot and this has been extensively studied for development of probes with great success [129,130]. The use of phosphorescent QDs helps avoiding the interferences from the biological matrices since the long-lived phosphorescence possess an appropriate delaytime [131,132]. As phosphorescence is less frequent phenomena than fluorescence, the selectivity is also enhanced [133]. Reportedly, the QDs show a potential phosphorescence emission (~590 nm) [134], as a result the transfer of energy from the ZnS to Mn^{2+} and consecutive transition to the ground state($^6A_1$) from the triplet state ($^4T_1$) of Mn^{2+} involved in the ZnS host lattice [135]. It is merely the prime stage, when phosphorescent QDs are employed in optical sensing, still proven to be very probable [136,52]. For the biosensors, any intricate sample pre-treatment is not essential [137,138].

3.2.1. Detection of small molecules

3.2.1.1. Detection by turn-off mode. Bian et al. successfully prepared doped ZnS QD probes surface capped with *L*-cys and *N*-acetyl-*L*-cys (NAC) [139]. The QDs have been effectively employed to trace the *L*-Ascorbic Acid (AA) content in human urine samples as the RTP of the QDs were efficiently quenched by AA (Fig. 3).This could perhaps be used for RTP sensing of soluble analytes in biological samples and have potential in biomedical or clinical analysis.

A RTP turn-off sensor for recognition of clenbuterol (CB) based on melamine (MA)-enhanced RTP of MPA-capped QDs was explained by Gong et al. [140]. As both MA and CB have good hydrogen-bonding ability, hydrogen-bonding interaction might be present there [141]. The RTP intensity of QDs was increased by MA in acidic state, moreover quenched by CB as a result of aggregation. Miao et al. synthesized MPA-capped ZnS QDs/cetyltrimethylammonium bromide (CTAB) nanohybrids by electrostatic self-assembly, which augmented the RTP of the QDs [142]. They further studied the RTP changes and their function for rutin recognition. As both are negatively charged, due to the competition between rutin and the QDs, the rutin/CTAB hybrids are more stable. With the increase of rutin concentration, CTAB escapes from the QD surface, thus the RTP intensity of nanohybrids reduces. This improves the detection ability of QDs for rutin and other flavonoids.

A system was developed by Zhang et al. for heparin detection in aqueous solutions [143]. The system consisted of 3-MPA capped ZnS QDs/polybrene (hexadimethrinebromide) hybrids as nanosensor in which the RTP intensity was enhanced on adding polybrene due to electrostatic self-assembly. With increasing heparin, RTP intensity got reduced as heparin was actively bounded to polybrene facilitating it to deprive from the surface of QD. A simple and rapid scheme for quercetin recognition based on RTP of 3-MPA capped ZnS QDs was proposed by Zhang et al. [65]. In the system, Al^{3+} interacts with the carboxyl groups of QDs causing aggregation and augmentation of phosphorescence signals. Quercetin addition led to the development of a stable complex with Al^{3+} causing dissociation of Al^{3+} from QDs surface resulting in a significant revival of RTP intensity of the QDs-Al^{3+} system. The change in the RTP was proportional with the amount of quercetin added.

A simple route for the detection of 2,4,5-trichlorophenol (2,4,5-TCP) by synthesizing MIP-capped ZnS QDs was reported by Wei et al. [144]. RTP of QDs was quenched by 2,4,5-TCP in a concentration-dependent manner explained by a Stern–Volmer equation. Another multifunctional molecularly imprinted phosphorescent probe for 2,4,6-TCP determination was reported by Wei et al. made of a magnetite (Fe_3O_4) core embellished with a MIP-QDs [145]. The composite material displayed strong phosphorescence due to the presence of QDs and good magnetism. Moreover high selectivity was observed and could effectively be applied for 2,4,6-TCP determination in spiked river water and waste water. A possible mechanism about the acetone effect on RTP of QDs was described by Gonzalez et al. by synthesizing *L*-cys capped ZnS QDs showing a strong RTP in aqueous medium [138]. Further it was useful for the analytical control of acetone in urine and water samples measuring the quenching rate of QDs phosphorescence with high selectivity.

Zou et al. synthesized magnetic Fe_3O_4 nanoparticles and QDs nanocomposites (MNPs/QD NCs) coalescing the chemosensory property of QDs with the magnetic response of Fe_3O_4 nanoparticles [146]. It was used for the RTP sensing and magnetic separation of captured ultratrace 2,4,6-trinitrotoluene (TNT). The nanocomposites exhibited a good response for TNT detection through the quenching of $^4T_1$–$^6A_1$ emission. The proposed method is suitable for sensing ultratrace TNT and differentiating various nitro compounds as well as in degradation of organics contaminated water. He et al. detected a type of quinolone, enoxacin in biological fluids based on the RTP method of doped ZnS QDs without using deoxidants or any inducers for the detection [131]. The method was applied to observe the concentration of enoxacin in urine with time after the oral medication in healthy volunteer.

Wang et al. reported a novel MIP-based RTP optosensor by molecular imprinting method by using the MIP layer over the QDs surface to provide RTP source [52]. The new RTP sensing scheme was applied for detection of trace pentachlorophenol in water where the RTP quenching occurs due to a charge transfer from QDs to pentachlorophenol species. An ultrasound-assisted technique was proposed by Ren et al. for the rapid synthesis of phosphorescent adenosine-triphosphate (ATP)-capped ZnS QDs [147]. This allowed the sensing of arginine and methylated arginine base on Mg^{2+}–ATP–arginine ternary arrangement together with QDs phosphorescence. Wu et al. reported a novel RTP quenching scheme by doped ZnS QDs which was then applied for detecting raceanisodamine hydrochloride and atropine sulfate in organic fluids attained by the quenching of the RTP intensity of QDs [148]. The effect demonstrated a high selectivity for these drugs.

Zou et al. synthesized *L*-cys capped ZnS QDs modifying the properties of QDs by alteration of the functional groups and installing detection receptors at the surface with that of phosphorescence [149]. It was employed for RTP sensing and for Rayleigh scattering (RS) chemodosimetry for ultratrace imaging of TNT in water. The interdots amassed with TNT due to the development of Meisenheimer complexes (MHCs) ascribed to the acid-base pairing relations between *L*-cys and TNT, hydrogen bonding, and electrostatic interaction among *L*-cys intermolecules. Even though the MHCs could quench the fluorescence of QDs, the light scattering was greatly affected by the aggregation of

interdots. Thus, on excitation of QDs wavelength dominant RS enhancement was seen at defect-related luminescence, employed in chemodosimetry for TNT imaging. The method could also be used for distinguishing various nitro compounds. A simple protocol for RTP determination of protease by cytochrome-C (Cyt C)-capped ZnS QDs was proposed by Wu et al. [150]. The QDs were synthesized with Cyt C as ligand, which is an electron transfer protein. The method removed the postsynthetic conjugation of protein and analyte reactions in turn-on form. Due to the enzymatic digestion of Cyt C and elimination of the electron-transfer quencher element from the QDs, the primarily "locked" RTP of QDs could be activated with protease. The probe could also proficiently distinguishing active and inactive serine proteases.

A simple and precise RTP method was proposed by Demirhan et al. using *L*-cys-capped ZnS QDs as a probe for sensing of melamine in dairy products [151]. The method was based on the phosphorescence quenching by different melamine concentrations in the range of 50–500 ng/mL. Ma et al. prepared N-acetyl-*L*-cysteine (NAC)-modified ZnS QDs and proposed a novel RTP method for the determination of hydrochlorothiazide (HCT), as the RTP was effectively quenched by HCT [152]. The dynamic quenching mechanism was demonstrated by both the Stern-Volmer model and phosphorescence lifetimes of QDs. A RTP sensor for dopamine based on ZnS QDs was developed by Diestra et al. [153]. Upon addition of dopamine, the orange emission band of QDs is strongly quenched. The oxidized dopamine quinone works as electron acceptor. The developed nanosensor displayed a high sensitivity to determine dopamine in biological fluids at very low levels. Zhang et al. presented an optical scheme based on MIPs-capped Mn-doped ZnS QDs for determining a mycotoxin Patulin (PAT) in apple juice [154]. Molecular imprinting sol–gel method was applied for the synthesis using 6-hydroxynicotinic acid (6-HNA) as template. The sensor permitted selective binding and recognizing of the target PAT with various analogues (2-hydroxynicotinic acid, coumalic acid and 5-hydroxymethyl-2- furaldehyde) and different mycotoxins (aflatoxin B1, ochratoxin A and deoxynivalenol). Thus a phosphorescent method was proposed for the detection of PAT.

3.2.1.2. Detection by turn-on mode. A simple scheme for urea-sensing system was developed by Bi and co-workers, composed of phosphorescent ZnS QDs doped with Mn and urease (Fig. 2). The QDs worked for pH-induced biochemical reactions. The RTP of QDs steadily increased with urea concentration. With the increasing urea concentration, there occurred a decrease in the rate of change of pH value; however the increased OH reduced the departing rate of ligands from the QDs surface, lowering the non radiative transition, so continue to enhance lightening [155].

A RTP turn-on probe for the determinationof tiopronin in biological fluids was described by Gong et al. on the basis of homocysteine-capped ZnS QDs [156]. The RTP intensity was firstly quenched by Cu^{2+}, and then quickly recovered by tiopronin. The sensor operates in a turn-on form and provides high sensitivity. Jin et al. explored MPA-Mn-doped ZnS QDs-$KMnO_4$ hybrid system and devised a redox scheme based "off-on" RTP control [157]. It was used for detecting glutathione (GSH) in food, wine and other organic samples with detection limit of 9.7×10^{-8} mol L^{-1}. $KMnO_4$ quenches the RTP of QDs which was revived by GSH. The probable scheme may be that $KMnO_4$ oxidizes SO_4^{2-} on QDs surface which get reduced to S^{2-} on adding GSH. A novel ascorbic acid (AA)-induced phosphorescence enhancement of sodium tripolyphosphate-capped Mn-doped ZnS QDs was reported by Wang et al. and used for determination of AA in biological fluids [158]. The chelating capacity permits AA to remove the Zn and Mn from the QD surface producing holes, which were entrapped by Mn^{2+}. At the same time the reducing property allows AA to reduce Mn^{3+} to Mn^{2+}, thus increasing the excitation and orange emission of the QDs.

A RTP turn-on analysis of heparin was demonstrated by Yan et al. by polyethyleneimine (PEI)-capped doped ZnS QDs [159]. The method covered the complete therapeutic dosage concentration range in post-operation, cardiovascular surgery and long-term therapy and was employed for the determination of heparin even in 100-fold diluted serum sample. Both particle size and ligand loading quantities were greatly affected by the chain length of PEI ultimately influencing the sensitivity and detection window. Li et al. designed a poly(dialyldimethylammonium chloride) (PDAD) ZnS QDs nanohybrid as RTP sensor for hyaluronic acid (HA) detection [160]. Addition of HA causes rigorous electrostatic interaction with PDAD-Mn-doped ZnS QDs, causing aggregation between QDs and HA thus enhancing RTP proportionally with HA concentrations. The method efficiently avoids the background fluorescence interferences. Thus, it easily detects HA in biological samples and can be used for HA detection in sodium hyaluronate eye drops and human serum. The detailed applications of Mn-doped ZnS QDs for phosphorescence sensing of small molecules are summarised in Table 4.

3.2.2. Detection of inorganic ions

3.2.2.1. Detection by turn-off mode. A new mercury ions sensor was

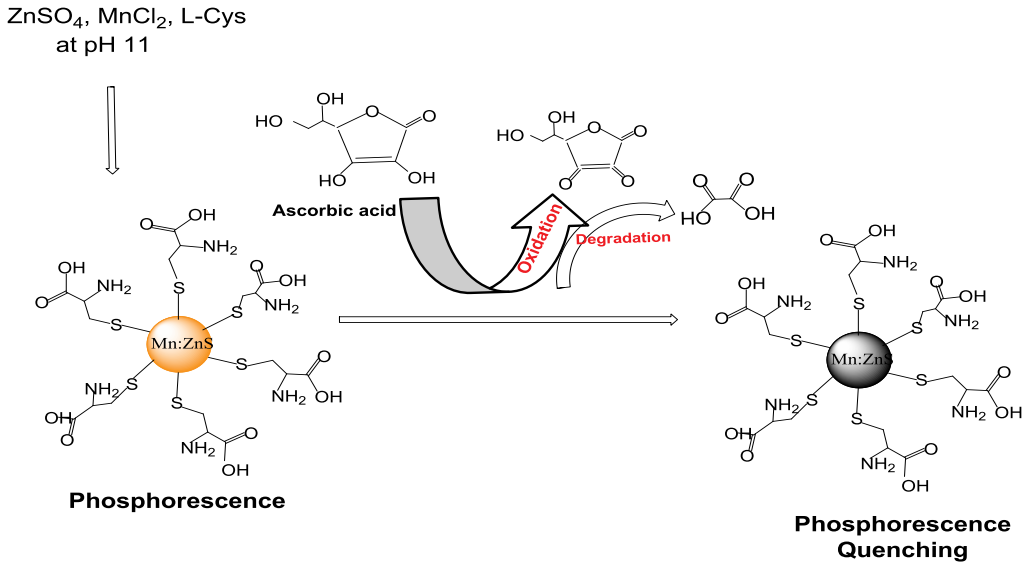

Fig. 2. Mechanism for the working of Mn-doped ZnS QDs for phosphorescent sensing of Ascorbic Acid [139].

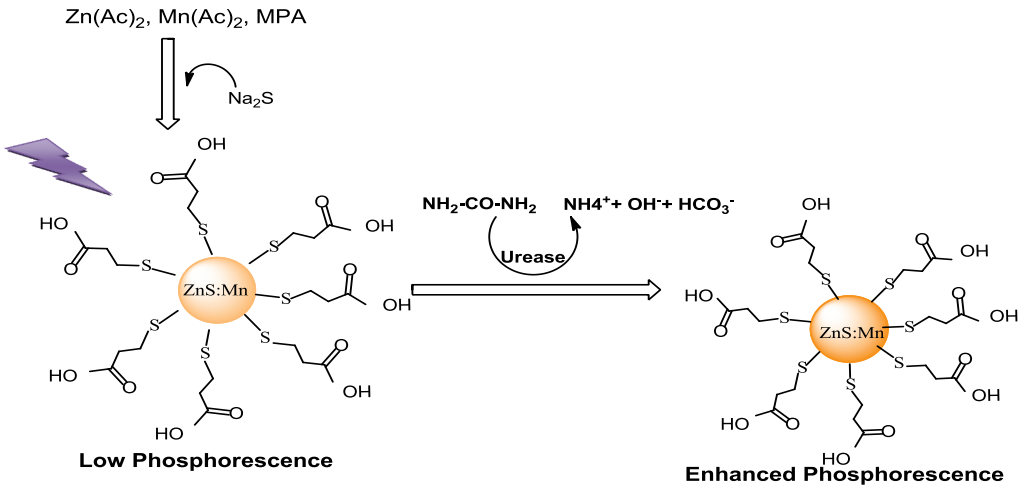

Fig. 3. Mechanism of Mn-doped ZnS QDs for sensing of Urea [155].

designed by Xie et al. by synthesizing CTAB-capped Mn-doped ZnS QDs and label-free thymine (T)-rich aptamers [161]. RTP of the QDs was linearly quenched by the formed T–Hg^{2+}–T dsDNA through electron transfer and aggregation effect. Chen et al. successfully fabricated GSH-capped ZnS QDs based novel RTP probe for Pb^{2+} [162]. GSH as capping agent improved the selectivity of sensor due to its exceptional binding with Pb^{2+} [163]. The RTP of GSH-Mn-ZnS QDs was quenched by Pb^{2+}, thus developing a RTP sensor. Further, a rapid and sensitive probe was also fabricated by Chen et al. for determination of selenite [164]. It worked on the RTP quenching of QDs by addition of selenite in the presence of glutathione, which was due to HSe^- ions, the resulting product of glutathione and selenite reaction. The method was used successfully for selenite determination in sodium selenite pills and vitamin E vaccines. Jin et al. developed 3-MPA capped Mn-doped ZnS QDs-Fenton hybrid structure for sensing of Fe^{2+} in biological fluids and environmental sample [165]. The hydroxyl radicals generated by the Fenton reaction quenched the phosphorescence of QDs at low concentration level. However, Fe^{2+} or H_2O_2 separately at same concentration cannot quench the phosphorescence. Thus, based on the Fenton reaction, Fe^{2+}can be detected indirectly. The quenching effect due to Fe^{2+} was because of the electron transfer from conduction band of the QDs to the unoccupied band of hydroxyl radicals.

A time-resolved phosphorescence (TRP) method was developed by Jing et al. for detection of Fe^{2+} ions, using cysteine-bridged MPA-capped ZnS QDs [166]. Cysteine improved the phosphorescence of the QDs as well as the quenching efficiency due to Fe^{2+} ions. The TRP mode removed the interference due to short-lived fluorescent and background scattering of the biological fluids. Employing TRP mode increases the precision for the sensing of analyte in biological samples and the recovery values of spiked Fe^{2+}in biological fluids are also higher than that with steady state phosphorescence mode. A phosphorescent sensor for $Cr^{3+}$was developed by Zhao et al. It was found that Cr^{3+} could selectively quench the RTP from denatured bovine serum albumin (dBSA)-capped ZnS QDs [167]. The phosphorescence quenching was attributed to the electron transfer from QDs to Cr^{3+}. Deng et al. synthesized *L*-cys-modified ZnS QDs doped with Mn by low cost materials emitting intense phosphorescence even in deoxygenated condition and used it for the detecting permanganate anions (MnO_4^-) [168]. Due to the oxidation of *L*-cys and the enhanced surface defects of QDs, the RTP of QDs get quenched strongly by MnO_4^-. Bian et al. prepared *N*-acetyl-*L*-cys-capped ZnS QDs doped with Mn for detecting Co^{2+} ion [169]. With the enhancing concentration of Co^{2+} ion, RTP intensity dramatically quenched. The method can be applied for detecting Co^{2+} in pond and tap water samples.

Zou et al. described a “two-step” method for alginate-capped ZnS QDs with ultra-broad Stokes shift and extended lifetime [170]. The Zn^{2+} and Mn^{2+}-uncoordinated carboxy at the surface of QD probe strongly quench the $^4T_1$-$^6A_1$ emission of $Mn^{2+}$by inner filter effect, which is due to coordination and formation of a complex with Cu^{2+}. The method could be used for Cu^{2+}detection from water treatment plants, showing exceptional detection with good sensitivity. Thus, an effective method with RTP as a signal output for Cu^{2+} sensing was developed. Gan et al. proposed a rapid and selective method for RTP detection of sulfide by MPA-capped Mn-doped ZnS QDs and Pb^{2+} sensing scheme [171]. The QDs exibited effective phosphorescence quenching to $Pb^{2+}$and phosphorescence recovery was observed on adding sulfide to the system. Thus, a phosphorescence "off-on" sensor was developed for rapid, on-line screening of sulfide in water. Gan et al. also proposed a simple RTP method with MPA-capped QDs designed for selective recognition of Pb^{2+} [172]. Pb^{2+}effectively quenched the phosphorescence of QDs. The mechanism behind quenching involves both energy and charge transfers during interaction of QDs at excited-state with Pb^{2+}causing the QDs loose the excitation energy, thus dynamic quenching occurs. Qin et al. designed a simple RTP probe for phosphate detection based on Ce^{3+} modulated MPA-capped QDs [173]. The sensor makes use of the phosphorescence emission of QDs and lanthanides-phosphates affinity. Ce^{3+} interacts electrostatically with carboxyl groups over QDs surface, causing aggregation of QDs, thus altering the RTP signals. The added phosphates have high affinity for Ce^{3+}causing desorption of Ce^{3+} from QDs surface recovering the RTP of the QDs.

3.2.2.2. Detection by turn-on mode. A silica-coated S^{2-} enhanced Mn-doped ZnS QDs was fabricated by Ren et al. with a silica shell over the QDs surface for imaging of intracellular Zn^{2+}ions [174]. The probe showed negligible cytotoxicity, fine linearity for calibration plot against Zn^{2+}ions concentration as well as excellent selectivity for Zn^{2+} in a turn-on form. By monitoring the growth of Mn-doped ZnS QDs *in situ*, Wu et al. selectively detected H_2S, an endogenously formed signalling molecule [175]. Doping Mn^{2+} prevented the background fluorescence of the biological surroundings whereas the host material ZnS ascertained the selectivity as only sulfide is capable of precipitating Mn^{2+} and $Zn^{2+}$from any aqueous solution. A combination of enzyme inhibition activity and phosphorescence property of QDs was utilized for determination of paraoxon, an organophosphorus pesticide (OP) by Ban et al. where Mn:ZnS QDs act as sensor for hydrogen peroxide (H_2O_2) determination (Fig. 4) [176]. When paraoxon was present, the serine hydroxyl group of the enzyme acetylcholinesterase (AChE) gets phophorylated forming a stable complex thus inhibiting the enzyme activity. This inturn causes a decrease in H_2O_2 production leading to lesser phosphorescence quenching.

Pang et al. developed Eu^{3+}-mediated on-off-on phosphorescent

Table 4
Use of Mn-doped ZnS QDs for Phosphorescence Sensing of Small molecules.

Analyte	Capping agent	Matrix	Detection limit	Wavelength of Detection	Effect on Luminescence	Ref.
L-Ascorbic acid	N-acetyl-L-cysteine, L-cysteine	Urine	7.2×10^{-7} mol $L^{-1}$to 1.3×10^{-6} mol L^{-1}	583 nm, 580nm	Phosphorescence quenching	[139]
Clenbuterol	MPA	Biological fluids	3.2 ng mol L^{-1}	590nm	Phosphorescence quenching	[140]
Rutin	3-MPA	Biological fluids	0.037 mgL^{-1}	590nm	Phosphorescence quenching	[142]
Heparin	3-MPA	Biological fluids	1.6×10^{-7} mol L^{-1}	590nm	Phosphorescence quenching	[143]
Quercetin	3-MPA	Urine, Serum	0.047 mg L^{-1}	590nm	Phosphorescence quenching	[65]
2,4,5-trichloro-phenol	MIP	Water	–	596nm	Phosphorescence quenching	[144]
2,4,6-trichloro-phenol	MIP	River water, waste water	3.5×10^{-10} mol L^{-1}	594 nm	Phosphorescence quenching	[145]
Acetone	L-cysteine	Natural water,Urine	0.2 mgL^{-1}	595nm	Phosphorescence quenching	[138]
TNT	MEA	Water	1.25×10^{-8} mol L^{-1}	465 nm, 515nm	Phosphorescence quenching	[146]
Enoxacin	L-cysteine	Serum	5.86×10^{-8} mol L^{-1}	590nm	Phosphorescence quenching	[131]
Pentachloro-phenol	MIP	River water	8.6×10^{-8} mol L^{-1}	600nm	Phosphorescence quenching	[52]
Arginine	ATP	Urine	2.3×10^{-7} mol L^{-1}	595 nm	Phosphorescence quenching	[147]
Raceanisidamine hydrochloride, Atropine Sulphate	L-cysteine	Human serum, Urine	1.1×10^{-7} mol L^{-1}, 9.0×10^{-8} mol L^{-1}	590 nm	Phosphorescence quenching	[148]
TNT	L-cysteine	Pond water	8.0×10^{-10} mol L^{-1}	580nm	Phosphorescence quenching	[149]
Protease	Cytochrome-C	Trypsin	2.0×10^{-9} mol L^{-1}	580nm	Phosphorescence quenching	[150]
Melamine	L-cysteine	Dairy products	5.95 ng/mL	590 nm	Phosphorescence quenching	[151]
Hydrochloro-thiazide	*N*-acetyl-*L*-cysteine	—	1.25×10^{-6} mol L^{-1}	590nm	Phosphorescence quenching	[152]
Dopamine	*L*-cysteine	Urine samples	7.8×10^{-9} mol L^{-1}	598nm	Phosphorescence quenching	[153]
Patulin	3-aminopropyltriethoxysilane	Apple juice	3.2×10^{-7} mol L^{-1}	585 nm	Phosphorescence quenching	[154]
Urea	MPA	Urine	1.4×10^{-5} mol L^{-1}	590nm	Phosphorescence Enhancement	[155]
Tiopronin	Homocysteine	Biological fluids	0.18 ng mol L^{-1}	590nm	Phosphorescence Enhancement	[156]
Glutathione	3-MPA	Food, Wine, biological samples	9.7×10^{-8} mol L^{-1}	588 nm	Phosphorescence enhancement	[157]
Ascorbic Acid	Sodium Tripolyphosphate	Urine, Plasma	9.0×10^{-9} mol L^{-1}	425 nm, 595nm	Phosphorescence enhancement	[158]
Heparin	Polyethyleneimine	Human serum	0.6×10^{-7} mol $L^{-1}$to 1.5×10^{-7} mol L^{-1}	585nm	Phosphorescence enhancement	[159]
Hyaluronic acid	MPA	Sodium hyaluronate eye drops, human serum	0.03 mg mL^{-1}	590 nm	Phosphorescence enhancement	[160]

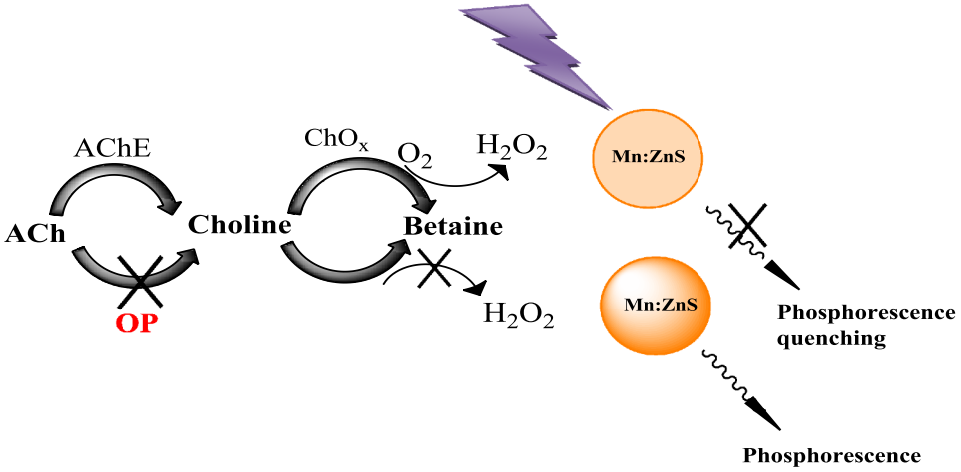

Fig. 4. Mechanism of the use of Mn-doped ZnS QDs for phosphorescent sensing of organophosphorus pesticide [176].

Table 5
Use of Mn^{2+}-doped ZnS QDs for Phosphorescence Sensing of Inorganic ions.

Analyte	Capping agent	Matrix	Detection limit	Wavelength of Detection	Effect on Luminescence	Ref.
Hg^{+}	CTAB	Tap and river water samples	1.5×10^{-9} mol L^{-1}	595nm	Phosphorescence quenching	[161]
Pb^{2+}	Glutathione	Real water samples	0.450 μgL^{-1}	590nm	Phosphorescence quenching	[162]
Selenite	–	Sodium selenite tablets and injections	8.5×10^{-8} mol L^{-1}	–	Phosphorescence quenching	[164]
Fe^{2+}	3MPA	Environmental samples and biological fluids	3.0×10^{-9} mol L^{-1}	588 nm	Phosphorescence quenching	[165]
Fe^{2+}	Cysteine bridged, MPA capped	Serum	1.9×10^{-10} mol L^{-1}	602 nm	Phosphorescence quenching	[166]
Cr^{3+}	Bovine serum albumin	Water sample	3.0×10^{-9} mol L^{-1}	585 nm	Phosphorescence quenching	[167]
MnO_4^{-}	*L*-cysteine	water	2.4×10^{-7} mol L^{-1}	585 nm	Phosphorescence quenching	[168]
Co^{2+}	*N*-acetyl-*L*-cysteine	Real water samples	6.0×10^{-8} mol L^{-1}	583nm	Phosphorescence quenching	[169]
Cu^{2+}	Alginate	Tail water	6.0×10^{-9} mol L^{-1}	590 nm	Phosphorescence quenching	[170]
Pb^{2+}	MPA	water samples	6.89×10^{-8} mol L^{-1}	580 nm	Phosphorescence quenching	[171]
Pb^{2+}	MPA	lake and tap-water	3.69×10^{-8} mol L^{-1}	580nm	Phosphorescence quenching	[172]
PO_4^{3-}	MPA	River and lake water	2.71×10^{-3} mol L^{-1}	590 nm	Phosphorescence quenching	[173]
Zn^{2+}	3MPA	Human hepatocellular liver carcinoma cell line	8.0×10^{-10} mol L^{-1}	595nm	Phosphorescence enhancement	[174]
H_2S	Bovine serum albumin	Biological samples	3.0×10^{-4} mol L^{-1}	585 nm	Phosphorescence enhancement	[175]
S^{2-}	MPA	water samples	6.89×10^{-8} mol L^{-1}	580 nm	Phosphorescence enhancement	[171]
Para-oxon	Glutathione	Vegetable samples	1×10^{-13} mol L^{-1}	580 nm	Phosphorescence enhancement	[176]
$P_2O_7^{4-}$	*N*-acetyl-*L*-cys-teine	Urine samples	145×10^{-11} mol L^{-1}	594 nm	Phosphorescence enhancement quenched by Eu^{3+}	[177]

sensor with extended decay lifetime for detecting pyrophosphate ions (PPi) [177]. The Eu^{3+} induced electron transfer and aggregation of QDs lead to phosphorescence quenching. On adding PPi, the QDs aggregation is redispersed and stronger interaction between $Eu^{3+}$and PPi removes Eu^{3+} from the QDs surface, causing phosphorescence enhancement. The long-lived phosphorescence (1920 μs) of QDs removed interferences due to short-lived fluorescence by time resolved measurements in biological samples. Table 5 highlights the applications of Mn^{2+}-doped ZnS QDs for phosphorescence sensing of inorganic ions.

3.2.3. Detection of macrobiomolecules

The photoluminescence sensor array has highly sensitive response for protein analytes. However, applying this technology for detection of proteins, experiences interferences from autofluorescence emission and scattering of light in real biological sample. To address this issue, Ching et al. proposed a time-resolved phosphorescent (TRP) probe based on ZnS QDs capped by different ligands for the analysis of proteins [178]. The sensing platform assisted as a convenient approach for the detection of proteins in complex samples. The work has also enhanced the discrimination efficiency of the sensor arrays for complicated biological or diagnostic application.

3.2.3.1. Detection by turn-off mode. Enzyme attachment over the surface of nanomaterials reduces the unfolding of proteins and disorderness improving enzyme stability thus providing wide possibilities in biosensor applications. Moreover, the multipoint attachment of enzyme over the surface of nanoparticles efficiently improves the enzyme-substrate interaction by evading the amassing of free enzymes improving their activity [179–181]. Wu et al. reported the glucose oxidase (GOD) conjugated ZnS QDs doped with Mn with 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC)/N-hydroxysuccinimide (NHS) as coupling reagents for phosphorescent sensing of glucose [137]. It worked on quenching of RTP due to H_2O_2 produced from GOD-catalyzed glucose oxidation. The biosensor was assessed for thermal stability, enzyme activity, and glucose sensing in real serum samples. QDs and GOD were associated, to create sensors for glucose detection through coupling agent [182], which depended on the fact that H_2O_2 can quench QDs. Utilizing the RTP of QDs, a method was given by Miao et al. for rapid and sensitive sensing of glucose without any complicated conjugation between QDs and GOD [183]. The scheme depends on the quenching of H_2O_2 on MPA-capped QDs known as photoinduced electron transfer. GOD decomposes glucose, releasing H_2O_2 which inturn gets electrons from QDs through photoinduced

Table 6
Use of Mn-doped ZnS QDs for Phosphorescence Sensing of Macrobiomolecules.

Analyte	Capping agent	Matrix	Detection limit	Wavelength of Detection	Effect on Luminescence	Ref.
Glucose	MPA	Serum samples	3.0×10^{-6} mol L^{-1}	595 nm	Phosphorescence quenching	[137]
Glucose	3-MPA	Urine, serum samples	2.9×10^{-6} mol L^{-1}	595 nm	Phosphorescence quenching	[183]
Trypsin	Bovine serum albumin	Biomolecules	4.0×10^{-8} mol L^{-1},3.0×10^{-9} mol L^{-1}	590 nm	Phosphorescence quenching	[184]
L-Tyrosine	4-morpholineethane sulfonic acid	Human urine	2.2×10^{-7} mol L^{-1}	590 nm	Phosphorescence quenching	[185]
Diprophyllin	MPA	DPP injections	8.93×10^{-10}mol L^{-1}	590 nm	Phosphorescence quenching	[186]
Glutamic acid	*L*-cysteine	Food stuff, Chicken and beef cubes, chicken soup	6.79 ng mL^{-1}	590 nm	Phosphorescence quenching	[187]
Phosphopeptides	MPA	Urine, serum samples	0.9 ng mL^{-1}	590 nm	Phosphorescence Enhancement	[188]
Protamine	3-MPA	Human serum samples	0.14 μg mL^{-1}	590 nm	Phosphorescence Enhancement	[189]
Histidine	*N*-acetyl-*L*-cysteine	Human urine samples	7.4×10^{-7} mol L^{-1}	589 nm	Phosphorescence enhancement	[191]
Domoic acid	Polyethyleneimine	Shellfish tissue sample	6.7×10^{-8} mol L^{-1}	590 nm	Phosphorescence enhancement	[192]
Lysozyme	Bovine serum albumin	Biomolecules	4.0×10^{-8} mol L^{-1},3.0×10^{-9} mol L^{-1}	590 nm	Phosphorescenceenhancement	[184]
Thrombin	Thrombin-binding aptamers	Plasma, serum	1.3×10^{-11} mol L^{-1}	581 nm	Phosphorescence enhancement	[193]
Alkaline phospha-tase	MPA	Human serum	6.5×10^{-8} mol L^{-1}	590 nm	Phosphorescence enhancement	[194]

electron transfer. A protein-templated preparation of ZnS QDs doped using bovine serum albumin (BSA) was reported by Wu et al. [184]. A double-channel sensing scheme was developed for proteins by combining the phosphorescence emission and resonant light scattering (RLS) of the QDs and BSA phosphorescent recognition of trypsin and RLS detection of lysozyme. The proposed probe employs single type of QDs but can sense two varied proteins. By taking advantage of the role of ligands on the emission of QDs and the digestion of proteins by protease, the phosphorescent channel was explored for trypsin biosensing through phosphorescence quenching.

Deng et al. successfully synthesised 4-morpholineethanesulfonic acid-modified ZnS QDs doped with Mn and used it for the recognition of *L*-tyrosine (*L*-Tyr) in urine samples [185]. Due to the transfer of electron from QDs to *L*-Tyr, even at low concentration levels *L*-Tyr efficiently quenched the phosphorescence of QDs. The probe offers good selectivity and can determine *L*-Tyr in urine samples. A novel strategy was developed by Zheng et al. applying the phosphorescence of MPA-capped ZnS QDs for detection of diprophyllin (DPP) [186]. With the increase of diprophyllin, the phosphorescence intensity quenches because of electron transfer from photo-excited QDs to electron acceptor DPP. Thus a label-free, sensitive and selective RTP method was given for the detection of DPP in real samples. Kara et al. presented a simple scheme with *L*-cys-capped ZnS QDs for the sensing of glutamic acid (GLU), 2-aminopentanedioic acid or 2-aminoglutaric acid in foodstuffs [187]. The process was based on the RTP quenching of QDs on interaction with GLU. The given technique is free from the interferences from common cations or autofluorescence.

3.2.3.2. Detection by turn-on mode. A RTP sensor based on zirconium (IV)-modulated MPA capped Mn-doped ZnS QDs for phosphopeptides was developed by Gong et al. considering the advantages of the RTP properties of doped QDs and Zr^{4+}phosphopeptide affinity pair [188]. Zr^{4+}effectively quenched the RTP of QDs. The higher affinity of phosphopeptides towards Zr^{4+}facilitated the dissociation of the ion from the QDs surface, thus giving rise to a stable complex in the solution with phosphopeptides recovering the RTP of QDs. The method was significant clinically and could analyze protein-peptide phosphorylation. A simple process for the RTP determination of protamine was proposed by Zhang et al. [189]. A highly positive cationic peptide, protamine forms MPA-capped ZnS QD/protamine complex by electrostatic interaction with QDs, which causes the aggregation and enhancement of the RTP of QDs. It was found that the phosphorescence of the QDs enhanced apparently with the increased concentration of protamine. When analytes were added to QDs, the non radiative relaxation centres of surface became passivated by binding with analyte. Thus, surface trap sites either were filled or actively come near the band edges. Thus, a photoluminescence-activation effect got induced that enhanced the RTP of QDs [190].

Bian et al. reported a turn-on phosphorescence probe with Co^{2+}-adsorbed *N*-acetyl-*L*-cys (NAC) capped ZnS QDs for histidine detection [191]. The quenching of QDs by $Co^{2+}$was due to the adsorption of Co^{2+} on QDs surface and was recovered by binding of Co^{2+} with histidine. Thus a phosphorescence turn on sensor for selective determination of histidine in biological samples was developed. An improved MIP-based probe was constructed by Dan et al. combining RTP of QDs with two fragment imprinting [192]. Polyethyleneimine-capped Mn-doped ZnS was entrenched in MIPs, providing the binding sites causing interaction with the carboxyl groups of templates. The analytes rebinding with fragment cavities altered the aggregation of QDs in QDs-MIPs resulting in phosphorescence enhancement. Thus, an enhanced probe for domoic acid (DA) recognition was proposed. Zhang et al. presented a phosphorescent sensor for thrombin that works through thrombin-aptamer recognition [193]. A competent phosphorescence energy transfer donor-acceptor pair was prepared with thrombin-binding aptamers-labelled Mn-doped ZnS QDs (TBA QDs) as donor and the carbon nanodots (CNDs) as acceptor. The π-π stacking action of

CNDs and aptamers causes the phosphorescence quenching of TBA QD donors. With the addition of thrombin to the TBA-QDs-CNDs system, quadruplex-thrombin complex forms, and the phosphorescence is "turned on" releasing the energy acceptor CNDs from the energy donors. Thus, the thrombin biosensor worked based on restored phosphorescence, Thus, a phosphorescence energy transfer based biosensor was established combining the photophysical properties of QDs as well as the superquenching ability of CNDs. Li et al. prepared a phosphorescence sensor for alkaline phosphatase (ALP) detection using adenosine 5′-monophosphate (AMP), a natural biomolecule as a substrate [194]. A QDs/Eu^{3+}nanocomposite was prepared which quenched the phosphorescence of Mn-doped ZnS QDs owing to photo-induced electron transfer. On adding AMP to ALP, ALP hydrolyses AMP to adenosine and phosphate ions. These phosphate ions have higher affinity for Eu^{3+}causing its desorption from QDs, thus restoring the RTP of QDs. The detailed applications of Mn-doped ZnS QDs for phosphorescence sensing of macrobiomolecules are summarised in Table 6.

The interaction between the quencher and excited state of the phosphorescent material causes the declining in intensity as well as lifetime of the phosphorescence molecule resulting in dynamic quenching. Amazingly, the phosphorescence lifetime of remains unchanged in static quenching condition. The dynamic quenching can also be described by Stern-Volmer equation [166]

$$P_0/P = 1 + K_{SV}\,Cq \quad (2)$$

where P_0 and P are the phosphorescence intensity of the Mn-ZnS QDs in lack and presence of a quencher, Cq is the quencher concentration, and K_{SV} is the Stern-Volmer's constant. The values of Stern-Volmer's constant for phosphorescence quenching by various analytes are given in Table 7.

3.2.4. Detection of DNA

In diagnosis of genetic diseases, highly sensitive detection of DNA is crucial. Common approaches are often based on arduous, semi-quantitative amplification of target DNA to get good detection sensitivity. Besides, most detection systems entail separation of hybridized and unhybridized DNA strands immobilized on a solid substrate, intricated by solution–surface binding kinetics. The mechanism of working behind these emissions tunable QD probes is the quenching of the phosphorescence intensity. In first step, quencher gets adsorbed over the QDs surface, lowering the phosphorescence intensity. On introducing a receptor, quencher gets removed with recovery of the phosphorescence intensity.

Ertas et al. synthesised *L*-cys-modified Mn-doped ZnS QDs/Idarubicin(IDA) nanohybrids, useful for DNA detection to investigate IDA/ds-DNA interaction [195]. For the phosphorescence signal of QDs, IDA was a quencher there by forming QDs–IDA complexes. As the DNA is added, IDA interacts with it, desorbs from surface of QDs and the RTP gets enhanced due to released QDs. So, a novel sensitive method for ds-DNA recognition was proposed. Bi et al. constructed an MPA-functional Mn-doped ZnS QDs/ethidium bromide (EB) nanohybrid as successful probe for DNA [196]. EB quenches the phosphorescence of QDs owing to photo induced electron transfer, thereby development of nanohybrids stores RTP. In the interim, EB may possibly be inserted to DNA or separate from the QDs surface thus releasing the phosphorescence. Thus, RTP sensor for rapid and sensitive DNA detection was developed.

A nanohybrid was prepared by Li et al. using methylene blue (MB) and 3-MPA-modified ZnS QDs doped with Mn, which could detect trace DNA through electrostatic interaction [197]. The RTP of QDs was quenched by MB through photoinduced electron transfer. On adding DNA, MB binds with it by insertion, desorbs from the QDs surfaces thus restoring the RTP. A feasible method for sensing of trace DNA in biofluid was thereby set up. A self-assembly of nanohybrids for the DNA detection using octa (3-aminopropyl) octasilsequioxane octahydrochloride (OA-POSS) and 3-MPA-modified ZnS QDs was reported by He et al. [136]. The key advancement involved OA-POSS containing eight quaternary ammonium groups at corners which acted as linking agents for MPA-QDs by electrostatic self-assembly. These linkers aid MPA-QDs to form QD/OA-POSS nanohybrids possessing 7.5 times higher RTP intensity compared to MPA-QDs. DNA consists of negatively charged phosphate groups, which compete with negatively charged MPA-QDs forming a stable complex with OA-POSS [198]. This causes a decrease in the phosphorescence signals, with the increasing DNA concentration. This was the basis in the novel method for the determination of DNA. Yu et al. proposed a novel RTP prober for DNA in spiked urine samples using QDs/methyl violet (MV)nanohybrids [199]. MV as electron acceptor gets adsorb over QDs and quenches the RTP by electron-transfer. DNA addition restores the phosphorescence signals due to its binding with DNA and the exclusion of MV from QDs. Miao et al. constructed MPA-modified ZnS QDs/doxorubicin (DXR) nanohybrids and used it as probe for DNA [200]. DXR quenches the RTP of QDs by photoinduced electron transfer, moreover the nanohybrids restored the RTP. On adding DNA, it was inserted in DXR. Consequently, DXR gets desorbed from the QD surface releasing the phosphorescence of QDs. Thus the method helps in detection of DNA in body fluid.

A riboflavin (RF)-modified MPA functionalized ZnS QDs doped with Mn was developed by Gong et al. for DNA detection [201]. The RTP was stored by RF via photo induced electron transfer forming a QDs/RF nanohybrid through electrostatic attraction. RF binds with DNA by electrostatic interaction and intercalation. RF gets separated from the QD releasing the RTP of the QDs. Thus an RTP sensor was developed for DNA detection in biological fluids. Kara et al. developed a new “turn off-on” probe with *L*-cys-modified ZnS QDs for assessing the mechanism

Table 7
Phosphorescence Quenching Constants of Mn-doped ZnS QDs by Various Analytes.

Analyte	$K_{sv}(M^{-1})$	Reference
L-Ascorbic acid by NAC-Mn/ZnS & Cys-Mn/ ZnS	9.3×10^4 & 5.12×10^3	[139]
Clenbuterol	1.86×10^8	[140]
Rutin	6.18×10^4	[142]
Heparin	1.58×10^8	[143]
Quercetin	4.34×10^4	[65]
2,4,5-trichlorophenol by MIP & NIP	2.51×10^4 & 1.18×10^4	[144]
2,4,6-trichlorophenol by MIP & NIP	1.32×10^5& 1.49×10^4	[145]
TNT	8.27×10^8	[146]
Pentachlorophenol MIP & NIP	3.5×10^4 & 1.4×10^4	[52]
Arginine	1.71×10^8	[147]
Raceanisodamine Hydrochloride & Atropine Sulfate	8.6×10^4 & 4.13×10^5	[148]
TNT	6.96×10^8	[149]
Protease	1.42×10^6	[150]
Melamine	1.5×10^5	[151]
Hydrochlorothiazide	7.8×10^3	[152]
Dopamine	1.1×10^8	[153]
Patulin by MIP & NIP	4.84×10^4 & 2.38×10^4	[154]
Pb^{2+}	1.2×10^4	[162]
Fe^{2+}	5.53×10^5	[165]
Fe^{2+}	1.88×10^6	[166]
Cr^{3+}	5.02×10^6	[167]
MnO_4^-	8.4×10^3	[168]
Co^{2+}	2.42×10^6	[169]
Cu^{2+}	3.68×10^5	[170]
S^{2-}	1.12×10^6	[171]
Pb^{2+}	3.45×10^6	[172]
PO_4^{3-}	7.84×10^7	[173]
Glucose	9.7×10^5	[137]
Glucose	4.2×10^5	[183]
Trypsin & Lysozyme	8.01×10^8 & 2.06×10^{10}	[184]
L-Tyrosine	9.1×10^3	[185]
Diprophyllin	3.1×10^6	[186]
Glutamic Acid	1.9×10^5	[187]

of acrylamide (ACR)-DNA interactions [202]. The RTP signal quenching was due to photo induced electron transfer mechanism, as ACR was absorbed over QDs surface by electrostatic interaction. On addition of DNA, ACR get removed from the QDs surface causing the phosphorescence emission to "turn-on" mode. The absorbance value of DNA also declined with ACR addition causing a slight red shift. The results showed that ACR and DNA interacted by groove binding mode via electrostatic forces and the information would also be helpful to recognize the binding of DNA to other potential cancer molecules.

3.3. Mn-doped ZnS QDs as chemiluminescence-based chemo-sensors

Chemiluminescence (CL) has been a significant and powerful analytical tool in various fields [203,204]. It has intrigued a widespread attention due to its broad linear range, relative high sensitivity, easy instrumentation, and zero background interference [205]. Still, the advancement of CL remained constrained to few reaction systems as the intensities of many reactions are not strong sufficient for sensing commands. With the introduction of nanoscale materials, the application of the CL method was diversified [206]. Sensitized CL is a fast approach to make use of the reactions having low quantum yields for analytical functions. The energy produced is transmitted to a sensitizer, generally an organic fluorophore having a high quantum effficiency, which can intensify it. A species that could interact with fluorophore either enhance or quench the CL emission. Concerning the semiconductor QDs sensitized CL, only a few reports are there [207,208]. Xiao et al. applied novel Mn-doped ZnS semiconductor QDs as sensitizers in Hydrogen peroxide-periodate (H_2O_2—$NaIO_4$) CL system [209], for detecting phenols and established the mechanism of reaction [210]. Effects of the synthesised QDs on H_2O_2—$NaIO_4$ system were studied, analysing the factors influencing QDs behaviour. In fact, hydrogen peroxide reacts with periodate directly producing $\bullet O_2^-$ radicals which generate $(O_2)_2$* excited molecules, transferring energy to QDs having higher efficiency fluorescence. QDs then emit a stronger light.

Zhou et al. prepared *L*-cys-modified ZnS@Si QDs as sensitizers enhancing the CL signals emitted from NaClO—H_2O_2 interaction. [211] The CL enhancement was due to the sensitizers (QDs) catalyzing the decomposition of H_2O_2, generating intermediates superoxide anion (O_2^{*-}) and hydroxyl radical (*OH). The resulted *OH reacted to O_2^{*-} forming $^1O_2$ and $(^1O_2)_2$* an oxygen excimer species, which quickly returns to its lower state transferring its energy to sensitizer by an electron-transfer. Thus, the sensitizer in the excited state returns to lower state enhancing the CL-signals. MIP-coated ZnS QDs doped with Mn were synthesized by Liu et al. for the detection of 4-nitrophenol (4-NP) by fluorescence quenching, which is due to electron transfer between QDs and 4-NP [206]. Further, MIP-QDs were applied to the system for improving the selectivity of the method and probable mechanism was given to describe the CL intensity quenching and reaction process. The oxidation of sulfite in acidic medium by Ce(IV) or $KMnO_4$ is a significant CL reaction, having fairly weak CL emission. Azizi et al. reported that the oxidation of sulfite in acidic medium by Ce(IV) produces a strong CL signal in the presence of ZnS QDs doped with Mn as sensitizers and atropine as enhancer allowing advancement of detection systems [212]. Thus, a rapid, sensitive, and novel CL analysis system was developed for atropine measurement in pharmaceutical formulation.

3.4. Mn-doped ZnS QDs as electrochemiluminescence-based chemo-sensors

Electrogenerated chemiluminescence (ECL) is a type of light emission, produced as a result of the electron-transmission reactions involving electrogenerated species. ECL is drawing interests owing to its wide linear range, higher sensitivity, uncomplicated instrumentation and cost effectiveness [213]. As ECL reactions involve electrochemical as well as chemical reactions, it is probable to find new co-reactants by means of chemically modified electrode. High ECL efficient, low ECL background and easy accessibility are desirable for immunoassay and DNA analysis [214].

Due to convenient ECL merits and distinctive quantum size dependent electrochemical properties, QD ECL has become highly intriguing [215]. Relevance of QDs to ECL are mostly dependent on cathodic ECL, with co-reactants being there [216,217]. Other features, like electrocatalytic behaviour of QDs, however not concerned great attention. Study of anodic ECL revealed that $QD^{+\bullet}$ cation radical forms as a result of the electro-oxidation of QDs directly [218,219]. Wang et al. synthesized ZnS QDs with Mn doping and explored the ECL phenomena in glassy carbon electrode tailored with a ZnS:Mn^{2+} QDs film in aqueous solution having H_2O_2 as coreactant [220]. A novel ECL signal peak at ca. −1.50 V *vs.*a saturated carbon electrode on the QDs-adapted glassy carbon electrode at pH 9, was observed owing to the excited state of Mn^{2+} at Zn^{2+}site, which is not present in pure ZnS QDs having potential of −2.0 V. The work would develop the ECL research of doped QDs and support the application of semiconductors in biological and environmental analysis.

4. Design principles for construction of bio-sensors based on Mn-doped zinc sulphide quantum dots

QDs have come out as an attractive entrant for applications in biomolecular sensing [221,222] and cellular imaging [223,224]. The surface plasmon resonance (SPR)-based metal-enhanced fluorescence (MEF) effect of metallic nanostructures has been found to be very significant [225]. The SPR of metallic nanostructures, particularly the Ag nanoparticles enhances the electromagnetic field of the surrounding leading to the increase of photoluminescence and shortening in the lifetime of nearby fluorophores [226,227]. A number of MEF materials so far developed have been targeted for the enhancement of the fluorescence from organic fluorophores [228,229]. Very few has been developed for inorganic fluorescent species, like QDs [230,231], while for biomolecular sensing it is still in the rudimentary stage.

Ag nanoparticle (AgNP) enhanced time-resolved fluorescence (TR-FL) probe was developed by Zhu et al. [232]. It worked on the MEF principle using the Mn-doped ZnS QDs bond with aptamers hybridized with quencher BHQ-2 labelling strands, for the recognition of vascular endothelial growth factor-165 ($VEGF_{165}$), a biomarker of cancer in cancer angiogenesis [233]. Aptamers may be small oligonucleotides with single strand or peptides produced by SELEX method (systematic evolution of ligands by exponential enrichment) [234] having high affinity, stability, and specificity thus considered as alternative reagents to antibodies [235]. Upon interaction with targets, aptamers transform from long metastable structure to a distinctive stable folded structure [236]. The aptamers modified with QDs and the BHQ-2 quencher-labelling strands are attached with streptavidin(SA)-modified AgNPs thus forming a sensor, which showed lower fluorescence intensity in the duplex state due to FRET between the QDs and quenchers. On addition of $VEGF_{165}$, the quencher-strands are displaced, disrupting the FRET. Thus, the QDs signals within the immediacy of AgNPs got restored.

A novel approach for the nanofabrication of Mn-doped core/shell ZnS/ZnS QDs was presented by Geszke et al. [237]. After the growth of the shell, fluorescence emission enhanced considerably. The surface MPA molecules support the conjugation of QDs with targeting folic acid molecules. The capturing of QDs by FR^+T47D breast cancer cells was explained by two photon confocal microscopy. The stability and lesser toxicity of the QDs are utilized here for biomedical applications. Cao et al. prepared ZnS QDs doped with Mn inserted in SiO_2 spheres by reverse microemulsion method and used it as a fluorescent probe for imaging HeLa cells [238]. The core/shell nanocomposites were homogeneous, identical sized and most of nanoparticles holding one QD in the center of the sphere. With the increase of the hydrolysis time of tetraethyl orthosilicate, the thickness of SiO_2 shell increased from 7 to 18 nm. Even at higher concentrations, no significant cytotoxicity was observed in the samples against the HeLa cells after 24 h incubation.

The red fluorescence of the cytoplasm, establishes its relevance in biolabelling.

The techniques of fluorescence imaging have been successfully applied to *in vivo* imaging of biological cells and tissues. For targeted cancer imaging, Cd-free luminescent QDs with a cancer marked ligand had proved to exhibit promising biocompatibility with very low cytotoxicity. A fluorescent, 3-MPA-stabilized ZnS QDs doped with Mn was synthesized by Yu et al. by nucleation doping strategy showing strong orange fluorescence and low-cytotoxicity to HeLa cells [239]. Both folic acid and 2,2′-(ethylenedioxy)-bis-(ethylamine) are covalently bound over the surface of Mn-doped ZnS nanoparticles probed by FTIR detection. The *in vitro* cytotoxicity assessment use HeLa cell. The biodistribution of fluorescent Mn-doped ZnS-folic acid probe in tumor mouse was explored by determining the Zn concentration in the tissues. The tumor cells targeting fluorescent probe in nude mouse tumor shows orange fluorescence on exposure to a 365 nm lamp. Thus, fluorescent probes reveal its promising application for *in vivo* imaging and marking tumor. A nanoparticulate system with multifunctional properties like specific targeting, imaging, and drug delivery was prepared by Bwatanglang et al. [240]. In this case, ZnS QDs doped with Mn ions are encapsulated using chitosan which act as a stabilizer and active binding site for conjugation of other biomolecules. For specific targeting of the nanocarrier, folic acid was used as targeting agent. Consequently, the composite formed emits orange-red fluorescence around 600 nm. MTT assay revealed that up to 500 μg/mL concentration, the composites do not show any toxicity for (MCF-7 and MDA-MB-231) breast cancer cell lines and the noncancer breast cell line MCF-10. Using Mn-doped ZnS QDs as fluorescence markers, by confocal laser scanning microscopy the cellular uptake of the nanocomposites were assessed, which showed that the chitosan-shelled QDs with folic acid improved the binding affinity and the internalization of the nanocarrier toward folate receptor-overexpressed cells. Thus owing to the nontoxic nature, the system could successfully be used for theranostic applications.

A novel approach for the identification of glycoproteins was described by Sang et al. [241]. A novel channel, fluorescence polarization (FP) was introduced, into a "single probe with three signalling channels". FP, RTP and light scattering were the three signalling channels and poly(acrylic acid)- Mn:ZnS QD conjugated with aminophenylboronic-acid was the single probe. For the evaluation of discriminating capability, ten different glycoproteins were involved. The incorporation of the signalling prototype with various receptive principles was established as a potential approach to improve the discrimination capacity of the sensor array. Diaz-Diestra et al. explained the adaptability of the doped QDs in production of reactive oxygen species and for detecting cells [242]. By substitution of Mn-doped ZnS in CdSe/ZnS system, it eliminated the Cd-based cores. It was also found that for tyrosinase (Tyr) enzyme, Mn-doped ZnS QDs act as immobilizing agents showing no deactivation which catalyses oxidation of H_2O_2 and its reduction on biosensor surface. The observations were explained by catalase-cycled kinetic mechanism. Quantum yield of singlet oxygen were observed to be 0.62 and 0.54 in buffer and water respectively, when QDs were employed as photosensitizer due to chemical trapping energy transfer mechanism. QDs were also well tolerated by HeLa Cells. Thus the QDs act as luminescent nanoprobes for bioimaging.

Swift et al. used *E. coli* and studied the subcellular localization, penetration requirements, stress responses induction as well as fate of Mn-doped ZnS nanocrystals [243]. It was synthesised in "green" conditions with very low ZnS-binding protein, incapable to pierce the sheet of unmodified *E. coli* but translocated into the cells cytoplasm modified by chemical treatment. The method depended on dose and showed bacterial transformation. Cells with lower doses of nanocrystals did not show any considerable activation of the unfolded protein but on high doses, it showed oxidative stress. Finally, it was suggested that protein-capped low cytotoxic inorganic core QDs implausibly caused any damage to microbial ecosystem. A biocompatible *L*-cys capped ZnS QDs doped with Mn was prepared by Pandey et al. by room temperature nucleation strategy and the efficiency of the capping agent, *L*-cysteine was studied for intracellular imaging [244]. The QDs were found non-toxic even at 1500 μg/mL concentrations having extensive applications in intracellular imaging. For the first time, Sung et al. demonstrated a sensitive and selective phosphorescence probe for cancer-associated human NAD(P)H:quinone oxidoreductase isozyme 1 (NQO1) based on phosphorescence energy transfer [245]. With ZnS QDs doped with Mn ions as donors and trimethylquinone propionic acids working as acceptors, a RTP NQO1 probe was developed. The phosphorescence is quenched owing to transfer of energy from QDs to covalently bonded quinines and was restored by the removal of the quinone quencher by NQO1. The cytotoxicity assay showed a low cellular toxicity. Thus, it could detect cancer cells expressing NQO1. Cortes et al. prepared dihydrolipoic acid-capped Mn-doped ZnS QDs possessing strong phosphorescent signal, which is now bioconjugated with anti-IgG antibody and used for developing a phosphorescence immunoassay for Prostate Specific Antigen (PSA) [246]. Elemental mass spectrometry coupled with asymmetric flow field flow fractionation techniques facilitated the exact determination of the bioconjugation reaction efficiency. The assay was also applied to cellular media of prostate cancer cells for PSA quantification. Zhang et al. developed a dopamine-functionalized ZnS QDs probe doped with Mn for intracellular imaging of A549 cells [104]. The probe revealed low cytotoxic nature in MTT assay. Thus could be applied for tracking of TYR related diseases and clinical diagnosis.

5. Future perspective

Despite the preface of new promising nanoparticles into the class of QDs, attributing advanced property and reduced cytotoxicity,extended dopant emission are likely to efficiently reduce background fluorescence and light scattering interference. Due to extended phosphorescence life times, ZnS QDs doped with Mn could successfully be used for time resolved optical detection like FRETsensing. FRET-based biosensors could be a key for point-of-care diagnostics, where FRET would find a good place including tracking of the target molecules, studying of changes in biochemical pathways and cell structures. Novel constructive attachment onto the surface of QDs, with proper fluorophores or highly absorptive nanoscale materials such as carbon ribbons, carbon nanotubes, graphene oxide, AuNPs and nanorods, magnetic nanoparticles, and other metal and metal-oxide nanoparticles, could produce a new research dimension in a multidisciplinary science. Mn/ZnS QDs require to be further engineered to acquire, for instance, any magnetic property (thus MRI sensitivity), to allow real-time tracking diagnosis using computer tomography (CT) scan and/or magnetic resonance imaging (MRI) scan before performing the surgery, which is still at a very early stage. Mn/ZnS QDs were renowned as a biological labeling agent and were a potential candidate for the *in vivo* bioimaging application. For *in vivo* bio-labelling function, along with luminescent property, it is desired to integrate additional properties such as paramagnetism and radio-opacity.

Taken together, these research achievements and economic trends provide an overall strong and optimistic foundation for the future of Mn-doped ZnS QDs which could open up new avenues of research in semiconductor physics with exciting applications ranging from optoelectronics to nanoseparation.

6. Conclusion and outlook

In this review, current progresses of the fundamental PL properties, optimization of synthesis and the luminescence performance of Mn-doped ZnS semiconductor nanocrystals were briefly reviewed. In summary, recent studies that focused on applications of Mn-doped QDs demonstrate that the QDs have an outstanding potential for chemo/biosensing and bioimaging. The QDs also possess an excellent potential for medical research, diagnostics, and innovative methods. Various

approaches in sensing as well as the benefits and/or shortcomings of surface modifications of the QDs have been considered for fabricating desirable QDs structures for specific applications. In principle, the attachment of a suitable functional group or capping agent on a QD is intended to improve the physical, chemical, and biological properties of the resulting structure.

Declaration of Competing Interest

Authors declare no conflict of interest.

Acknowledgments

Mrs. Jyoti Patel is thankful to DST, New Delhi, India for research fellowship grant (Women Scientist Scheme-A No. SR/WOS-A/CS-82/2018). Dr. Bhawana Jain is thankful to UGC, Delhi, India for research project grant (Post Doctoral Fellow, No. F.15–1/2013–14/PDFWM-2013–14-GE-CHH-18784 (SA-II)).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.microc.2020.104755.

References

[1] S. Raj, J.H. Yun, G.R. Adilbish, K. Ch, I.H. Lee, M.S. Lee, Y.T. Yu, Formation of core@multi-shell CdSe@CdZnS–ZnS quantum dot heterostructure films by pulse electrophoresis deposition, Superlattices Microstruct. 83 (2015) 618–626.
[2] P. Zrazhevskiy, M. Sena, X. Gao, Designing multifunctional quantum dots for bioimaging, detection and drug delivery, Chem. Soc. Rev. 39 (2010) 4326–4354.
[3] A.M. Smith, S. Nie, Semiconductor nanocrystals: structure, properties, and band gap engineering, Acc. Chem. Res. 43 (2010) 190–200.
[4] V. Pandey, V.K. Tripathi, K.K. Singh, T. Bhatia, N.K. Upadhyay, B. Goyal, G. Pandey, I. Hwang, P. Tandon, Nitrogen donor ligand for capping zns quantum dots: a quantum chemical and toxicological insight, RSC Adv. 9 (2019) 28510–28524.
[5] R.K. Chandrakar, R.N. Baghel, V.K. Chandra, B.P. Chandra, Synthesis, characterization and photoluminescence studies of Mn doped ZnS nanoparticles, Superlattices Microstruct. 86 (2015) 256–269.
[6] L. Brus, Electronic wave functions in semiconductor clusters: experiment and theory, J. Phys. Chem. 90 (1986) 2555–2560.
[7] S.A. Ziaudeen, R.R. Gaddam, P.K. Pallapothu, M.K. Sugumar, J. Rangarajan, Supra gap excitation properties of differently confined PbS-nano structured materials studied with opto-impedance spectroscopy, J. Nanophotonics 7 (2013) 073075.
[8] M. Bruchez, M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, Semiconductor nanocrystals as fluorescent biological labels, Science 281 (1998) 2013–2016.
[9] W.C. Chan, S. Nie, Quantum dot bioconjugates for ultrasensitive nonisotopic detection, Science 281 (1998) 2016–2018.
[10] X. Chen, Y. Liu, Q. Ma, Recent advances in quantum dot-based electrochemiluminescence sensors, J. Mater. Chem. C 6 (2018) 942–959.
[11] L. Shi, V. De Paoli, N. Rosenzweig, Z. Rosenzweig, Synthesis and application of quantum dots FRET-based protease sensors, J. Am.Chem. Soc. 128 (2006) 10378–10379.
[12] J.A. Lott, N.N. Ledentsov, V.M. Ustinov, A.Y. Egorov, A.E. Zhukov, P.S. Kop'ev, D. Bimberg, Verical cavity lasers based on vertically coupled quantum dots, Electron. Lett. 33 (1997) 1150–1151.
[13] D.L. Huffaker, G. Park, Z. Zou, O.B. Shchekin, D.G. Deppe, 1.3 Mm room-temperature gas-based quantum-dot laser, Appl. Phys. Lett. 73 (1998) 2564–2566.
[14] H.S. Jang, H. Yang, S.W. Kim, J.Y. Han, S.G. Lee, D.Y. Jeon, White light-emitting diodes with excellent color rendering based on organically capped cdse quantum dots and Sr_3SiO_5: $Ce^{3\pm}$, $Li^{\pm}$ phosphors, Adv. Mater. 20 (2008) 2696–2702.
[15] Q. Sun, Y.A. Wang, L.S. Li, D. Wang, T. Zhu, J. Xu, Y. Li, Bright, multicoloured light-emitting diodes based on quantum dots, Nat. Photon. 1 (2007) 717–722.
[16] Y.P. Kim, Y.H. Oh, E. Oh, S. Ko, M.K. Han, H.S. Kim, Energy transfer based multiplexed assay of proteases by using gold nanoparticle and quantum dot conjugates on a surface, Anal. Chem. 80 (2008) 4634–4641.
[17] D.V. Talapin, J.S. Lee, M.V. Kovalenko, E.V. Shevchenko, Prospects of colloidal nanocrystals for electronic and optoelectronic applications, Chem. Rev. 110 (2010) 389–458.
[18] H.R. Rajabi, H. Arjmand, H. Kazemdehdashti, M.J. Farsi, A comparison investigation on photocatalytic activity performance and adsorption efficiency for the removal of cationic dye: quantum dots vs. magnetic nanoparticles, Environ. Chem. Eng. 4 (2016) 2830–2840.
[19] H.R. Rajabi, F. Karimia, H. Kazemdehdashti, L. Kavoshi, Fast sonochemically-assisted synthesis of pure and doped zinc sulfide quantum dots and their applicability in organic dye removal from aqueous media, J. Photochem. Photobiol. 181 (2018) 98–105.
[20] G. Shen, Z. Du, Z. Pan, J. Du, X. Zhong, Solar paint from TiO_2 particles supported quantum dots for photoanodes in quantum dot − sensitized solar cells, ACS Omega 3 (2018) 1102–1109.
[21] J. Pardo, Z. Peng, R.M. Leblanc, Cancer targeting and drug delivery using carbon-based quantum dots and nanotubes, Molecules 23 (2018) 378–398.
[22] H.R. Rajabi, M. Shamsipur, A.A. Khosravi, O. Khani, M.H. Yousefi, Selective spectrofluorimetric determination of sulfide ion using manganese doped ZnS quantum dots as luminescent probe, Spectrochim. Acta Mol. Biomol. Spectrosc. 107 (2013) 256–262.
[23] E. Nam, C. Lee, S.J. Kim, H.K. Chung, H. Chae, Stability and dispersion improvement of quantum-dot films by hydrosilylation between quantum-dot ligands and a siloxane matrix, Opt. Express 27 (2019) 20037–20046.
[24] S. Choi, J. Moon, H. Cho, B.H. Kwon, N.S. Cho, H. Lee, Partially pyridine-functionalized quantum dots for efficient red, green, and blue light-emitting diodes, J. Mater. Chem. C 7 (2019) 3429–3435.
[25] D.R. Larson, W.R. Zipfel, R.M. Williams, S.W. Clark, M.P. Bruchez, F.W. Wise, W.W. Webb, Water-soluble quantum dots for multiphoton fluorescence imaging in vivo, Science 300 (2003) 1434–1436.
[26] R. Chen, D.J. Lockwood, Developments in luminescence and display materials over the last 100 years as reflected in electrochemical society publications, J. Electrochem. Soc. 149 (2002) S69–S78.
[27] F. Wei, G. Li, Z. Zhang, Hydrothermal synthesis of spindle-like ZnS hollow nanostructures, Mater. Res. Bull. 40 (2005) 1402–1407.
[28] Y.C. Zhang, G.Y. Wang, X.Y. Hu, Q.F. Shi, T. Qiao, Y. Yang, Phase-Controlled synthesis of ZnS nanocrystallites by mild solvothermal decomposition of an air-stable single-source molecular precursor phase-controlled synthesis of ZnS nanocrystallites by mild solvothermal decomposition of an air-stable single-source molecular precursor, J. Cryst. Growth 284 (2005) 554–560.
[29] S. Kayal, M.A. Halder, ZnS quantum dot-based super selective fluorescent chemosensor for soluble ppb-level total arsenic [As(III) + As(V)] in aqueous media: direct assay utilizing aggregation-enhanced emission (AEE) for analytical application, Analyst 144 (2019) 3710–3715.
[30] X. Fang, T. Zhai, U.K. Gautam, L. Li, L. Wu, Y. Bando, D. Golberg, ZnS nanostructures: from synthesis to applications, Prog. Mater. Sci. 56 (2011) 175–187.
[31] X. Fang, Y. Bando, U.K. Gautam, T. Zhai, H. Zeng, X. Xu, M. Liao, D. Golberg, ZnO and ZnS nanostructures: ultraviolet-light emitters, lasers and sensors, Crit. Rev. Solid State Mater. Sci. 34 (2009) 190–223.
[32] X. Lu, J. Yang, Y. Fu, Q. Liu, B.C. Lu, Z. Su, White light emission from Mn^{2+} Doped ZnS nanocrystals through the surface chelating of 8-Hydroxyquinoline-5-Sulfonic acid, Nanotechnology 21 (2010) 115702.
[33] A. Rahdar, Study of different capping agents effect on the structuraland optical properties of Mn doped ZnS nanostructures, World Appl. Program 3 (2013) 56–60.
[34] W.Q. Peng, S.C. Qu, G.W. Cong, X.Q. Zhang, Z.G. Wang, Optical and magnetic properties of ZnS nanoparticles doped with Mn, J. Cryst. Growth 282 (2005) 179–185.
[35] S. Bhowal, A. Ghosh, S.P. Chowdhuri, R. Mondal, B.B. Das, A novel metallogel based approach to synthesize (Mn, Cu) doped ZnS quantum dots and labeling of MCF-7 cancer cells, Dalton Trans. 47 (2018) 6557–6569.
[36] Z. Chen, D. Li, W. Zhang, Y. Shao, T. Chen, M. Sun, X. Fu, Photocatalytic degradation of dyes by $ZnIn_2S_4$ microspheres under visible light irradiation, J. Phys. Chem. C 113 (2009) 4433–4440.
[37] X. Wang, S. Shen, S. Jin, J. Yang, M. Li, X. Wang, H. Hana, C. Li, Effects of Zn^{2+} and Pb^{2+} dopants on the activity of Ga_2O_3-based photocatalysts for water splitting, Phys. Chem. Chem. Phys. 15 (2013) 19380–19386.
[38] Y. Jia, S. Shen, D. Wang, X. Wang, J. Shi, F. Zhang, H. Han, C. Li, Composite $Sr_2TiO_4/SrTiO_3$(La,Cr) heterojunction based photocatalyst for hydrogen production under visible light irradiation, J. Mater. Chem. A 1 (2013) 7905–7912.
[39] D.J. Norris, A.L. Efros, S.C. Erwin, Doped nanocrystals, Science 319 (2008) 1776–1779.
[40] A.P. Alivisatos, Semiconductor clusters, nanocrystals and quantum dots, Science 271 (1996) 933–937.
[41] N. Pradhan, D. Goorskey, J. Thessing, X.G. Peng, An alternative of CdSe nanocrystal emitters: pure and tunable impurity emissions in ZnSe nanocrystals, J. Am. Chem. Soc. 127 (2005) 17586–17587.
[42] L. Tan, C. Kang, S. Xu, Y. Tang, Selective room temperature phosphorescence sensing of target prote in using Mn-doped ZnSQDs-embedded molecularly imprinted polymer, Biosens. Bioelectron. 48 (2013) 216–223.
[43] A.A. Bol, A. Meijerink, Doped semiconductor nanoparticles – A new class of luminescent materials, J. Lumin. 87–89 (2000) 315–318.
[44] R. Gill, M. Zayats, I. Willner, Semiconductor quantum dots for bioanalysis, Angew. Chem. Int. Ed. 47 (2008) 7602–7625.
[45] Qi, H.; Teng, M.; Liu, M.; Liu, S.; Li, J.; Yu, H.; Teng, C.; Huang, Z.; Liu, H.; Shao, Q.; Umar, A.; Ding, T.; Gao, Q.; Guo, Z.Biomass-derived nitrogen-doped carbon quantum qots: highly selective fluorescent probe for detecting Fe3+ ions and tetracyclines. J. Colloid. Interf. Sci.2018.
[46] S.A. Nsibande, P.B.C. Forbes, Development of a quantum dot molecularly imprinted polymer sensor for fluorescence detection of atrazine, Luminescence (2019) 1–9.
[47] Y. Song, Y. Li, Z. Liu, L. Liu, X. Wang, X. Su, Q.A. Ma, Novel ultrasensitive carboxymethyl chitosan-quantum dot-based fluorescence "Turn on-off" nanosensor for lysozyme detection, Biosens. Bioelectron. 61 (2014) 9–13.
[48] A. Hoppe, T. Denneberg, J. Jeppsson, B. Kagedal, Urinary excretion of amino acids in normal and cystinuric dogs, Br. Vet. J. 149 (1993) 253–268.
[49] B. Han, J. Yuan, E. Wang, Sensitive and selective sensor for biothiols in the cell based on the recovered fluorescence of the CdTe quantum dots − Hg(II) system, Anal. Chem. 81 (2009) 5569–5573.

[50] B. Dong, L. Cao, G. Su, W. Liu, H. Qu, D. Jiang, Synthesis and characterization of the water soluble silica coated ZnS:Mn nanoparticles as fluorescent sensor for Cu (2+) ions, J. Colloid Interface Sci. 339 (2009) 78–82.

[51] Z. Cai, G. Chen, X. Huang, M. Ma, Determination of lysozyme at the nanogram level in chicken egg white using resonance Rayleigh-Scattering method with Cd-doped ZnSe quantum dots as probe, Sens. Actuators B Chem. 157 (2011) 368–373.

[52] H.F. Wang, Y. He, T.R. Ji, X.P. Yan, Surface molecular imprinting on Mn-doped ZnS quantum dots for room-temperature phosphorescence optosensing of pentachlorophenol in water, Anal. Chem. 81 (2009) 1615–1621.

[53] F. Wei, H. Yu, M. Hu, G. Xu, Z. Cai, J. Yang, L. Li, Q. Hu, Manganese modified CdTe/CdS quantum dots as a highly selective probe to detect trace copper element in beer samples, Anal. Methods 4 (2012) 1438–1444.

[54] Y.H. Zhang, H.S. Zhang, X.F. Guo, H. Wang, L-Cysteine-Coated CdSe/CdS core-shell quantum dots as selective fluorescence probe for copper(II) determination, Microchem. J. 89 (2008) 142–147.

[55] S.C. Jaricot, M. Darbandi, E. Kucur, T. Nann, Silica coated quantum dots: a new tool for electrochemical and optical glucose detection, Microchim Acta 160 (2008) 375–383.

[56] J. Qian, H. Dai, X. Pan, S. Liu, Simultaneous detection of dual proteins using quantum dots coated silica nanoparticles as labels, Biosens. Bioelectron. 28 (2011) 314–319.

[57] H. Zhang, B. Jiang, Y. Xiang, Y. Zhang, Y. Chai, R. Yuan, Aptamer/Quantum dot-based simultaneous electrochemical detection of multiple small molecules, Anal. Chim. Acta 688 (2011) 99–103.

[58] M. Geszke-Moritz, G. Clavier, J. Lulek, R. Schneider, Copper- or Manganese-doped ZnS quantum dots as fluorescent probes for detecting folic acid in aqueous media, J. Lumin. 132 (2012) 987–991.

[59] J. Traviesa-Alvarez, J. Costa-Fernandez, R. Pereiro, A. Sanz-Medel, Direct screening of tetracyclines in water and bovine milk using room-temperature phosphorescence detection, Anal. Chim. Acta 589 (2007) 51–58.

[60] W.E. Mahmoud, Functionalized ME-Capped CdSe quantum dots based luminescence probe for detection of Ba^{2+} ions, Sens. Actuat. B 164 (2012) 76–81.

[61] Y.H. Chan, J. Chen, Q. Liu, S.E. Wark, D.H. Son, J.D. Batteas, Ultrasensitive Copper (II) detection using plasmon-enhanced and photo-brightened luminescence of CdSe quantum dots, Anal. Chem. 82 (2010) 3671–3678.

[62] T.W. Sung, Y.L. Lo, Highly sensitive and selective sensor based on silica-coated CdSe/ZnS nanoparticles for Cu ion detection, Sens. Actuat. B 165 (2012) 119–125.

[63] R.Z. Zhang, W. Chen, Nitrogen-Doped carbon quantum dots: facile synthesis and application as a "Turn-Off" fluorescent probe for detection of Hg^{2+} ions, Biosens. Bioelectron. 55 (2014) 83–90.

[64] K. Zhang, J.K. Guo, J.J. Nie, B.Y. Du, D.J. Xu, Ultrasensitive and selective detection of Cu^{2+} in aqueous solution with fluorescence enhanced cdse quantum dots, Sens. Actuat. B 190 (2014) 279–287.

[65] Z. Zhang, Y. Miao, L. Lian, G. Yan, Detection of quercetin based on Al(3+)-amplified phosphorescence signals of manganese-doped ZnS quantum dots, Anal. Biochem. 489 (2015) 17–24.

[66] J.D. Bryan, D.R. Gamelin, Doped semiconductor nanocrystals: synthesis, characterization, physical properties and applications, Prog. Inorg. Chem. 54 (2005) 47–126.

[67] H. Hu, W. Zhang, Synthesis and properties of transition metals and rare-earth metals-doped ZnS nanoparticles, Opt. Mater. 28 (2006) 536–550.

[68] N. Pradhan, D.D. Sarma, Advances in light-emitting doped semiconductor nanocrystals, J. Phys. Chem. Lett. 2 (2011) 2818–2826.

[69] E. Sotelo-Gonzalez, L. Roces, S. Garcia-Granda, M.T. Fernandez-Arguelles, J.M. Costa-Fernandez, A. Sanz-Medel, Influence of Mn concentration on Mn-doped ZnS quantum dotsynthesis: evaluation of the structural and photoluminescent properties, Nanoscale 5 (2013) 9156–9161.

[70] Q. Xiao, C. Xiao, Synthesis and photoluminescence of water-soluble Mn^{2+}-Doped ZnS quantum dots, Appl. Surf. Sci. 254 (2008) 6432–6435.

[71] A.K. Kole, C.S. Tiwary, P. Kumbhakar, Room temperature synthesis of Mn doped ZnS D-Dots and observation of tunable dual emission: effects of doping concentration, temperature, and ultraviolet light illumination, J. Appl. Phys. 113 (2013) 11430801–11430811.

[72] C.W. Cheng, G.Y. Xu, H.Q. Zhang, J.M. Cao, P.P. Jiao, X.X. Wang, Low-temperature synthesis and optical properties of Wurtzite ZnS nanowires, Mater. Lett. 60 (2006) 3561–3564.

[73] S. Sapra, A. Prakash, A. Ghangrekar, N. Periasamy, D.D. Sarma, Emission properties of manganese-doped ZnS nanocrystals, J. Phys. Chem. B 109 (2005) 1663–1668.

[74] T.J. Norman, D. Magana, T. Wilson, C. Burns, J.Z. Zhang, D. Cao, F. Bridges, Optical and surface structural properties of Mn^{2+}-Doped ZnSe nanoparticles, J. Phys. Chem. B 107 (2003) 6309–6317.

[75] R. Beaulac, P.I. Archer, X. Liu, S. Lee, G.M. Salley, M. Dobrowolska, J.K. Furdyna, D.R. Gamelin, Spin-Polarizable excitonic luminescence in colloidal Mn^{2+}-Doped CdSe quantum dots, Nano Lett. 8 (2008) 1197–1201.

[76] R. Beaulac, P.I. Archer, D.R. Gamelin, Luminescence in colloidal Mn^{2+} doped semiconductor nanocrystals, J. Solid State Chem. 181 (2008) 1582–1589.

[77] M. Wang, L. Sun, X. Fu, C. Liao, C. Yan, Synthesis and optical properties of ZnS:Cu (II) nanoparticles, Solid State Commun. 115 (2000) 493–496.

[78] A. Segura-Carretero, A. Salinas-Castillo, A.A. Fernández-Gutiérrez, Review of heavy-atom-induced room-temperature phosphorescence: a straightforward phosphorimetric method, Crit. Rev. Anal. Chem. 35 (2005) 3–14.

[79] A.M. Smith, H. Duan, A.M. Mohs, S. Nie, Bioconjugated quantum dots for in vivo molecular and cellular imaging, Adv. Drug Deliv. Rev. 60 (2008) 1226–1240.

[80] M.L. Desai, B. Deshmukh, N. Lenka, V. Haran, S. Jha, H. Basu, R.K. Singhal, P.K. Sharma, S.K. Kailasa, K.H. Kim, Influence of doping ion, capping agent and pH on the fluorescenceproperties of zinc sulfide quantum dots: sensing of Cu^{2+} and Hg^{2+} ions and their biocompatibility with cancer and fungal cells, Spectrochim. Acta. A Mol. Biomol. Spectrosc. 210 (2019) 212–221.

[81] R.H. Yang, K.A. Li, K.M. Wang, F.L. Zhao, N. Li, F. Liu, Porphyrin assembly on B-Cyclodextrin for selective sensing and detection of a zinc ion based on the dual emission fluorescence ratio, Anal. Chem. 75 (2003) 612–621.

[82] R.H. Yang, Y. Zhang, K.A. Li, F. Liu, W.H. Chan, Fluorescent ratioable recognition of Cu^{2+} in water using a pyrene-attached macrocycle/γ-cyclodextrin complex, Anal. Chim. Acta 525 (2004) 97–103.

[83] R. Tu, B. Liu, Z. Wang, D. Gao, F. Wang, Q. Fang, Z. Zhang, Amine-Capped ZnS − mn nanocrystals for fluorescence detection of trace TNT explosive, Anal. Chem. 80 (2008) 3458–3465.

[84] K. Abha, J. Nebu, J.S. Anjali Devi, R.S. Aparna, R.R. Anjana, A.O. Aswathy, S. George, Photoluminescence sensing of bilirubin in human serumusing L-Cysteine tailored manganese doped zinc sulphide quantum dots, sens, Actuators-B-Chem. 282 (2019) 300–308.

[85] Z. Jiao, P. Zhang, H. Chen, J. Li, Z. Zhong, H. Fan, F. Cheng, Halobenzoquinone-Mediated assembly of amino acid modifiedmn-doped ZnS quantum dots for halobenzoquinones detection indrinking water, Anal. Chim. Acta 1026 (2018) 147–154.

[86] Y. Wang, M. Yang, Y. Ren, J. Fan, Cu-Mn codoped ZnS quantum dots base-dratiometric fluorescent sensor for folic acid, Anal. Chim. Acta 1040 (2018) 136–142.

[87] Y. Wei, H. Hao, J. Zhang, X. Hao, C. Dong, Sensitive and selective detection of L-Tryptophan using mn–ZnS Qds as the ratiometric emission probe, Anal. Methods 6 (2014) 3227–3230.

[88] S. Banerjee, S. Kar, J. Manuel Perez, S. Santra, Quantum dot-based off/on probe for detection of glutathione, J. Phys. Chem. C 113 (2009) 9659–9663.

[89] N. Tajarrod, M.K. Rofouei, M. Masteri-Farahani, R. Zadmard, Quantum dots-based fluorescence sensor for sensitive and enzymeless detection of creatinine, Anal. Methods 8 (2016) 5911–5920.

[90] M.K. Rofouei, N. Tajarrod, M. Masteri-Farahani, R.A. Zadmard, New fluorescence sensor for Cerium(III) ion using glycine dithiocarbamate capped manganese doped ZnS quantum dots, J. Fluoresc. 6 (2015) 1855–1866.

[91] H.R. Rajabi, M. Shamsipur, A.A. Khosravi, O. Khani, M.H. Yousefi, Selective spectrofluorimetric determination of sulfide ion using manganese doped ZnS quantum dots as luminescent probe, Spectrochim. Acta Mol. Biomol. Spectrosc. 107 (2013) 256–262.

[92] Y. Shang, L. Qi, F.Y. Wu, Functionalized manganese-doped zinc sulfide quantum dot-based fluorescent probe for zinc ion, Microchim. Acta 177 (2012) 333–339.

[93] B.H. Zhang, F.Y. Wu, Y.M. Wu, X.S. Zhan, Fluorescent method for the determination of sulfide anion with ZnS:Mn quantum dots, J. Fluoresc. 20 (2010) 243–250.

[94] B.H. Zhang, L. Qi, F.Y. Wu, Functionalized manganese-doped zinc sulfide core/shell quantum dots as selective fluorescent chemodosimeters for silver ion, Microchim. Acta 170 (2010) 147–153.

[95] J. Wang, J. Yu, X. Wang, L. Wang, B. Li, D. Shen, Q. Kang, L. Chen, Functional ZnS:Mn(II) quantum dot modified with L-cysteine and 6-mercaptonicotinic acid as a fluorometric probe for Copper(II), Microchim. Acta 185 (2018) 420.

[96] X. Fu, H. Li, R. Lv, D. Hong, B. Yang, W. Gu, X. Liu, Synthesis of Mndoped ZnS quantum dots/ZIF-8 composite and its applications as a fluorescent probe for sensing coand dichromate, J. Solid State Chem. 264 (2018) 35–41.

[97] S. Banerjee, S. Kar, S.A. Santra, Simple strategy for quantum dot assisted selective detection of cadmium ions, Chem. Commun. 26 (2008) 3037–3039.

[98] L. He, Z. Bao, K. Zhang, D. Yang, B. Sheng, R. Huang, T. Zhao, X. Liang, X. Yang, A. Yang, C. Zhang, P. Cui, J.A. Zapien, H. Zhou, Ratiometric determination of copper(II) using dually emitting Mn(II)-doped ZnS quantum dots as a fluorescent probe, MicroChim. Acta (2018) 1–9.

[99] W. Jing, Y. Lu, G. Yang, F. Wang, L. He, Y. Liu, Fluorescence sensor arraybased on amino acids-modulating quantum dots for the discrimination of metal ions, Anal. Chim. Acta 985 (2017) 175–182.

[100] C. Li, P. Wu, X. Hou, Plasma assisted quadrupole-channel optosensing of proteins and cells with Mn-doped ZnS quantum dots, Nanoscale 8 (2016) 4291–4298.

[101] F. Zhang, L. Xu, Q. Zhao, Y. Sun, X. Wang, P. Ma, D. Song, Dopamine-Modified Mn-doped ZnS quantum dots fluorescence probefor the sensitive detection of tyrosinase in serum samples and living cells imaging, Sens. Actuators B- Chem. 256 (2018) 1069–1077.

[102] M. Shao, H.F. Wang, Heparin-Mediated fluorescence anisotropy assay of antithrombin based on polyethyleneimine capped mn-doped ZnS quantum dots, Analyst 138 (2013) 4618–4623.

[103] L. Chang, X. He, L. Chen, Y. Zhang, Mercaptophenylboronic acid-capped Mn-doped ZnS quantum dots for highly selective and sensitive fluorescence detection of glycoproteins, Sens. Actuators B- Chem. 243 (2017) 72–77.

[104] L. Chang, H. Wu, X. He, L. Chen, Y. Zhang, A highly sensitive fluorescentturn-on biosensor for glycoproteins based on boronic acid functional polymer capped Mn-doped ZnS quantum dots, Anal. Chim. Acta 995 (2017) 91–98.

[105] S.A Zaidi, Recent developments in molecular imprinted polymer nanofibers and their applications, Anal. Methods 7 (2015) 7406–7415.

[106] J.E. Lofgreen, I.L. Moudrakovski, G.A. Ozin, Molecularly imprinted mesoporous organosilica, ACS Nano 5 (2011) 2277–2287.

[107] F.G. Tamayo, E. Turiel, A. Martín-Esteban, Molecularly imprinted polymers for solid-phase extraction and solid-phase microextraction: recent developments and future trends, J. Chromatogr. A 1152 (2007) 32–40.

[108] L. Tan, W.M. Li, H. Li, Y.W. Tang, Development of surface imprinted core–shell nanoparticles and their application in a solid-phase dispersion extraction matrix for methyl parathion, J. Chromatogr. A 1336 (2014) 59–66.

[109] H. Ahmadpour, S.M.M. Hosseini, Molecularly imprinted modified cdses/ZnS core-shell quantumdots embedded glass slide for highly selective and sensitive solid-phase optosensing of trace amount of lidocaine in biologicalsamples, Anal. Methods 11 (2019) 851–859.

[110] Y. Zhao, Y. Ma, H. Li, L. Wang, Composite Qds@ MIP nanospheres for specific recognition and direct fluorescent quantification of pesticides in aqueous media, Anal. Chem. 84 (2012) 386–395.

[111] L. Tan, C. Huang, R. Peng, Y. Tang, W. Li, Development of hybrid organic–inorganic surface imprinted Mn-doped ZnS Qds and their application as a sensing material for target proteins, Biosens. Bioelectron. 61 (2014) 506–511.

[112] M.P. Vazquez, J.S. Gonzalez, E.P. Vazquez, M.J. Tabernero, A.M. Bermejo, P.B. Barrera, A.M. Pineiro, Synthesis and characterization of novel molecularly imprinted polymer–coated Mn-doped ZnS quantum dots for specific fluorescent recognition of cocaine, Biosens. Bioelectron. 75 (2016) 213–221.

[113] M.P. Vazquez, C.B. Sanchez, A.F. Río, J.S. Gonzalez, A.M. Bermejo, P.B. Barrera, A.M. Pineiro, Development and application of molecularly imprinted polymer–Mn-doped ZnS quantum dotfluorescent optosensing for cocaine screening in oral fluid and serum, Talanta 181 (2018) 232–238.

[114] X. Zhang, S. Yang, W. Zhao, L. Sun, A. Luo, Mn-Doped ZnS Qds entrapped in molecularly imprinted membranes for detection of trace bisphenol A, Anal. Methods 7 (2015) 8212–8219.

[115] X. Ren, H. Liu, L. Chen, Fluorescent detection of chlorpyrifos using Mn (II)-Doped ZnS quantum dots coated with a molecularly imprinted polymer, Microchim. Acta 182 (2015) 193–200.

[116] Y. Hu, J. Liu, J. Li, T. Chen, M. Wu, Dual-Functional imprinted magnetic nanoprobes for fluorescent detection of N-Nitrosodiphenylamine, Anal. Methods 10 (2018) 2384–2389.

[117] Y. Hu, X. Li, J. Liu, M. Wu, M. Li, X. Zang, One-Pot synthesis of a fluorescent molecularly imprinted nanosensor for highly selective detection of sulfapyridine in water, Anal. Methods 10 (2018) 884–890.

[118] Y. Liu, X. Hu, L. Bai, Y. Jiang, J. Qiu, M. Meng, Z. Liu, L. Ni, A molecularly imprinted polymer placed on the surface of grapheme oxide and doped with Mn(II)-doped ZnS quantum dots for selective fluorometric determination of acrylamide, Microchim. Acta 185 (2018) 48.

[119] W. Xu, T. Li, W. Huang, Y. Luan, Y. Yang, S. Li, W. Yang, A magnetic fluorescence molecularly imprintedpolymer sensor with selectivity for dibutyl phthalate via Mn doped ZnS quantum dots, RSC Adv. 7 (2017) 51632–51639.

[120] A. Chmangui, M.R. Driss, S. Touil, P. Bermejo-Barrera, S. Bouabdallah, A. Moreda-Pineiro, Aflatoxins screening in non-dairy beverages by Mn-doped ZnS quantum dots-molecularly imprinted polymer fluorescent probe, Talanta 199 (2019) 65–71.

[121] X. Ren, L. Chen, Quantum dots coated with molecularly imprinted polymeras fluorescence probe for detection of cyphenothrin.biosens, Bioelectron 64 (2015) 182–188.

[122] X. Ren, L. Chen, Preparation of molecularly imprinted polymer coated quantum dots to detect nicosulfuron in water samples, Anal. Bioanal. Chem. 407 (2015) 8087–8095.

[123] J. Abbasifar, A. Samadi-Maybodi, Selective determination of atropine using poly dopamine-coated molecularly imprinted Mn-doped ZnS quantum dots, J. Fluoresc. 26 (2016) 1645–1652.

[124] L. Zhang, L. Chen, A new fluorescence probe based on hybrid mesoporous silica/quantumdot/molecularly imprinted polymer for detection of tetracycline, ACS Appl. Mater. Interfaces 8 (2016) 16248–16256.

[125] Z. Wang, Y. Zhang, B. Zhang, X. Lu, Mn^{2+} doped ZnS QDs modified fluorescence sensor based on molecularlyimprinted polymer/sol-gel chemistry for detection of serotonin, Talanta 190 (2018) 1–8.

[126] Y. Geng, M. Guo, J. Tan, S. Huang, Y. Tang, L. Tan, Y. Liang, The fabrication of highly ordered fluorescent molecularly imprinted mesoporousmicrospheres for the selective sensing of sparfloxacin in biological samples, Sens. Actuators B- Chem. 281 (2019) 821–829.

[127] S. Sadeghi, M. Jahani, F. Belador, The development of a new optical sensor based on the Mn doped ZnS quantum dots modified with the molecularly imprinted polymers for sensitive recognition of florfenicol, Spectrochim. Acta A Mol. Biomol. Spectrosc. 159 (2016) 83–89.

[128] L. Tan, K. Chen, C. Huang, R. Peng, X. Luo, R. Yang, Y. Cheng, Y.A. Tang, Fluorescent turn-on detection scheme for A-Fetoprotein using quantum dots placed in a boronate-modified molecularly imprinted polymer with high affinity for glycoproteins, Microchim. Acta 182 (2015) 2615–2622.

[129] W.S. Zou, D. Sheng, X. Ge, J.Q. Qiao, H.Z. Lian, Room-Temperature phosphorescence chemosensor and Rayleigh scattering chemodosimeter dual-recognition probe for 2,4,6-Trinitrotoluene based on manganese-doped ZnS quantum dots, Anal. Chem. 83 (2010) 30–37.

[130] P. Wu, L.N. Miao, H.F. Wang, X.G. Shao, X.P.A. Yan, Multidimensional sensing device for the discrimination of proteins based on manganese-doped ZnS quantum dots.angew, Chem. Int. Ed. 50 (2011) 8118–8121.

[131] Y. He, H.F. Wang, X.P. Yan, Exploring mn-doped ZnS quantum dots for the room-temperature phosphorescence detection of enoxacin in biological fluids, Anal. Chem. 80 (2008) 3832–3837.

[132] J.M. Costa-Fernandez, R. Pereiro, A. Sanz-Medel, The use of luminescent quantum dots for optical sensing, Trends Anal. Chem. 25 (2006) 207–218.

[133] J.M. Traviesa-Alvarez, I. Sanchez-Barragan, J.M. Costa-Fernandez, R. Pereiro, A. Sanz-Medel, Room temperature phosphorescence optosensing of benzo[a] pyrene in water using halogenated molecularly imprinted polymers, Analyst 132 (2007) 218–223.

[134] R. Thakar, Y.C. Chen, P.T. Snee, Efficient emission from core/(doped) shell nanoparticles: applications for chemical sensing, Nano Lett. 7 (2007) 3429–3432.

[135] J.H. Chung, C.S. Ah, D.J. Jang, Formation and distinctive decay times of Surface- and Lattice-Bound Mn^{2+} impurity luminescence in ZnS nanoparticles, J. Phys. Chem. B 105 (2001) 4128–4132.

[136] Y. He, H.F. Wang, X.P. Yan, Self-Assembly of Mn-doped ZnS quantum dots/octa (3-aminopropyl)octasilsequioxane octahydrochloride nanohybrids for optosensing DNA, Chem. Eur. J. 15 (2009) 5436–5440.

[137] P. Wu, Y. He, F.H. Wang, X.P. Yan, Conjugation of glucose oxidase onto Mn-doped ZnS quantum dots for phosphorescent sensing of glucose in biological fluids, Anal. Chem. 82 (2010) 1427–1433.

[138] E. Sotelo-Gonzalez, M.T. Fernandez-Arguelles, J.M. Costa-Fernandez, A. Sanz-Medel, Mn-Doped ZnS quantum dots for the determination of acetone by phosphorescence attenuation, Anal. Chim. Acta 712 (2012) 120–126.

[139] W. Bian, J. Ma, W. Guo, D. Lu, M. Fan, Y. Wei, Y. Li, S. Shuang, M.M. Choi, Phosphorescence detection of L-Ascorbic acid with surface-attached N-Acetyl-L-Cysteine and L-Cysteine Mn doped ZnS quantum dots, Talanta 116 (2013) 794–800.

[140] Y. Gong, Z. Fan, Melamine-Modulated mercaptopropionic acid-capped manganese doped zinc sulfide quantum dots as a room-temperature phosphorescence sensor for detecting clenbuterol in biological fluids, Sens. Actuator B 202 (2014) 638–644.

[141] X. Zhang, H. Zhao, Y. Xue, Z. Wu, Y. Zhang, Y. He, X. Li, Z. Yuan, Colorimetric sensing of clenbuterol using gold nanoparticles in the presence of melamine, Biosens. Bioelectron. 34 (2012) 112–117.

[142] Y. Miao, Z. Zhang, Y. Gong, Q. Zhang, G. Yan, Self-Assembly of manganese doped zinc sulfide quantum dots/CTAB nanohybrids for detection of Rutin, Biosens. Bioelectron. 52 (2014) 271–276.

[143] Z. Zhang, Y. Miao, Q. Zhang, L. Lian, G. Yan, Selective room temperature phosphorescence detection of heparin based on manganese-doped zinc sulfide quantum dots/polybrene self-assembled nanosensor, Biosens. Bioelectron. 68 (2015) 556–562.

[144] X. Wei, Z. Zhou, J. Dai, T. Hao, H. Li, Y. Xu, L. Gao, J. Pan, C. Li, Y. Yan, Composites of surface imprinting polymer capped Mn-doped ZnS quantum dots for room-temperature phosphorescence probing of 2,4,5-Trichlorophenol, J. Lumin. 155 (2014) 298–304.

[145] X. Wei, M. Yu, C. Li, X. Gong, F. Qin, Z. Wang, Magnetic nanoparticles coated with a molecularly imprinted polymerdoped with manganese-doped ZnSquantum dots for the determination of 2,4,6-Trichlorophenol, Microchim. Acta 185 (2018) 208.

[146] W.S. Zou, J. Yang, T.T. Yang, X. Hua, H.Z. Lian, Magnetic-Room temperature phosphorescent multifunctional nanocomposites as chemosensor for detection and photo-driven enzyme mimetics for degradation of 2,4,6-Trinitrotoluene, J. Mater. Chem. 22 (2012) 4720–4727.

[147] H.B. Ren, X.P. Yan, Ultrasonic assisted synthesis of adenosine triphosphate capped manganese-doped ZnS quantum dots for selective room temperature phosphorescence detection of arginine and methylated arginine in urine based on supramolecular Mg^{2+}–adenosine triphosphate–arginine ternary system, Talanta 97 (2012) 16–22.

[148] H. Wu, Z. Fan, Mn-Doped ZnS quantum dots for the room-temperature phosphorescence detection of raceanisodamine hydrochloride and atropine sulfate in biological fluids, Spectrochim. Acta Mol. Biomol. Spectrosc. 90 (2012) 131–134.

[149] W.S. Zou, D. Sheng, X. Ge, J.Q. Qiao, H.Z. Lian, Room-Temperature phosphorescence chemosensor and rayleigh scattering chemodosimeter dual-recognition probe for 2,4,6-Trinitrotoluene based on manganese-doped ZnS quantum dots, Anal. Chem. 83 (2011) 30–37.

[150] P. Wu, T. Zhao, J. Zhang, L. Wu, X. Hou, Analyte-Activable probe for protease based on cytochrome C-Capped mn: zZnS quantum dots, Anal. Chem. 86 (2014) 10078–10083.

[151] B.E. Demirhan, B. Demirhan, H.E. Kara, Room-Temperature phosphorescence determination of melamine in dairy products using L-Cysteine-Capped Mn-doped zinc sulfide (ZnS) quantum dots, J. Dairy Sci. 98 (2015) 2992–3000.

[152] J. Ma, F. Wang, M. Fan, T. Wang, W. Bian, S. Shuang, Phosphorescence detection of hydrochlorothiazide using Mn-doped ZnS quantum dots, Anal. Methods 5 (2013) 6094–6099.

[153] D.D. Diestra, B. Thapa, J.B. Huarac, B.R. Weiner, G. Morell, L-Cysteine capped ZnS:mn quantum dots for room-temperature detection of dopamine with high sensitivity and selectivity, Biosens. Bioelectron. 87 (2017) 693–700.

[154] W. Zhang, Y. Han, X. Chen, X. Luo, J. Wang, T. Yue, Z. Li, Surface molecularly imprinted polymer capped mn-doped ZnS quantum dots as a phosphorescent nanosensor for detecting patulin in apple juice, Food Chem. 232 (2017) 145–154.

[155] L. Bi, X.T. Dong, Y.H. Yu, Room-Temperature phosphorescence sensor based on manganese doped zinc sulfide quantum dots for detection of urea, J. Lumin. 153 (2014) 356–360.

[156] Y. Gong, Z. Fan, Label-Free room-temperature phosphorescence turn-on detection of tiopronin based on Cu-modulated homocysteine-capped manganese doped zinc sulfide quantum dots, J. Lumin. 160 (2015) 299–304.

[157] Q. Jin, Y. Li, J. Huo, X. Zhao, The “Off–On” phosphorescent switch of Mn-doped ZnS quantum dots for detection of glutathione in food, wine and biological samples, Sens. Actuator B 227 (2016) 108–116.

[158] H.F. Wang, Y. Li, Y.Y. Wu, Y. He, X.P. Yan, Ascorbic acid induced enhancement of room temperature phosphorescence of sodium tripolyphosphate-capped Mn-doped ZnS quantum dots: mechanism and bioprobe applications, Chem. Eur. J. 16 (2010) 12988–12994.

[159] H. Yan, H.F. Wang, Turn-On room temperature phosphorescence assay of heparin with tunable sensitivity and detection window based on target-induced self-assembly of polyethyleneimine-capped Mn-doped ZnS quantum dots, Anal. Chem. 83 (2011) 8589–8595.

[160] D. Li, J. Qin, J. Lv, J. Yang, G. Yan, “Turn on” room-temperature phosphorescentbiosensors for detection of hyaluronic acid based on manganese-doped ZnS

quantum dots, RSC Adv. 8 (2018) 2873–2879.
[161] W.Y. Xie, W.T. Huang, H.Q. Luo, N.B. Li, CTAB-Capped mn-doped ZnS quantum dots and label-free aptamer for room-temperature phosphorescence detection of mercury ions, Analyst 137 (2012) 4651–4653.
[162] J. Chen, Y. Zhu, Y. Zhang, Glutathione-Capped mn-doped ZnS quantum dots as a room-temperature phosphorescence sensor for the detection of pbions.spectrochim, Acta Mol. Biomol. Spectrosc. 164 (2016) 98–102.
[163] E.M. Ali, Y.G. Zheng, H.H. Yu, J.Y. Ying, Ultrasensitive Pb^{2+} detection by glutathione-capped quantum dots, Anal. Chem. 79 (2007) 9452–9458.
[164] J. Chen, Y. Zhu, Y. Zhang, Room-Temperature phosphorescence probe based on mn-doped ZnS quantum dots for the sensitive and selective detection of selenite, RSC Adv. 6 (2016) 62193–62199.
[165] Q. Jin, Y. Hu, Y. Sun, Y. Li, J. Huo, X. Zhao, Room-Temperature phosphorescence by Mn-doped ZnS quantum dots hybrid with fenton system for the selective detection of Fe, RSC Adv. 5 (2015) 41555–41562.
[166] W. Jing, Y. Lu, F. Wang, L. He, J. Sun, Y. Liu, Time-Resolved determination of Fe (II) ions using cysteine-bridged Mn-doped ZnS quantum dots as a phosphorimetric probe, Microchim. Acta 185 (2018) 298.
[167] T. Zhao, X. Hou, Y.N. Xie, L. Wu, P. Wu, Phosphorescent sensing of Cr^{3+} with protein-functionalized mn-doped ZnS quantum dots, Analyst 138 (2013) 6589–6594.
[168] P. Deng, L.Q. Lua, W.C. Cao, X.K. Tian, Phosphorescence detection of manganese (VII) based on Mn-doped ZnS quantum dots, Spectrochim. Acta Mol. Biomol. Spectrosc. 173 (2017) 578–583.
[169] W. Bian, J. Ma, Q. Liu, Y. Wei, Y. Li, C. Dong, S.A. Shuang, Novel phosphorescence sensor for Co^{2+} ion based on Mn-doped ZnS quantum dots, Luminescence 29 (2014) 151–157.
[170] W.S. Zou, M.Y. Deng, Y.Q. Wang, X. Zhao, W.H. Li, X.H. Huang, Alginate capped and manganese doped ZnS quantum dots as a phosphorescent probe for time-resolved detection of copper(II), MicroChim. Acta (2018) 1–9.
[171] T. Gan, N. Zhao, G. Yin, J. Liu, W. Liu, Mercaptopropionic acid-capped Mn-doped ZnS quantum dots and Pb^{2+}As sensing system for rapid and sensitive room-temperature phosphorescence detection of sulfide in water, J. Photochem. Photobiol. A Chem. 364 (2018) 88–96.
[172] Gan, T.; Zhao, N.; Yin, G.Y.; Tu, M.; Liu, J.; Liu, W.Mercaptopropionic acid-capped Mn-doped ZnS quantum dotsas a probe for selective room-temperature phosphorescencedetection of Pb2+ in water. New J. Chem., 2017,doi: 10.1039/C7NJ02625K.
[173] J. Qin, D. Li, Y. Miao, G. Yan, Detection of phosphate based on phosphorescenceof mn doped ZnS quantum dots combined with Cerium(III), RSC Adv. 7 (2017) 46657–46664.
[174] H.B. Ren, B.Y. Wu, J.T. Chen, X.P. Yan, Silica-Coated S-Enriched manganese-doped ZnS quantum dots as a photoluminescence probe for imaging intracellular Zn ions, Anal. Chem. 83 (2011) 8239–8244.
[175] P. Wu, J. Zhang, S. Wang, A. Zhu, X. Hou, Sensing during in situ growth of mn-doped ZnS Qds: a phosphorescent sensor for detection of H_2S in biological samples, Chem. Eur. J. 20 (2014) 952–956.
[176] R. Ban, J. Zhu, J. Zhang, Manganese-doped ZnS quantum dots as a phosphorescent probe for use in the bi-enzymatic determination of organophosphoruspesticides, Microchim. Acta 181 (2014) 1591–1599.
[177] J. Pang, Y. Lu, X. Gao, P. Song, F. Yang, Y. Liu, On-Off-On luminescent pyrophosphate probe based on the use of Mn-doped ZnS quantum dots and using Eu (III) as a mediator, Microchim. Acta 185 (2018) 480.
[178] N. Chang, J. Mao, Y. Lub, J. Yang, Y. Pu, S. Zhang, Y. Liu, Time-Resolved phosphorescent sensor array based on quantum dots for recognition of proteins, Sens. Actuator B-Chem. 233 (2016) 17–24.
[179] J. Kim, J.W. Grate, P. Wang, Nanostructures for enzyme stabilization, Chem. Eng. Sci. 61 (2006) 1017–1021.
[180] Y.H. Lin, F. Lu, Y. Tu, Z.F. Ren, Glucose biosensors based on carbon nanotube nanoelectrode ensembles, Nano Lett. 4 (2004) 191–195.
[181] A. Wei, X.W. Sun, J.X. Wang, Y. Lei, X.P. Cai, C.M. Li, Z.L. Dong, W. Huang, Enzymatic glucose biosensor based on zno nanorod array grown by hydrothermal decomposition, Appl. Phys. Lett. 89 (2006) 123902.
[182] L. Cao, J. Ye, L. Tong, B.A. Tang, New route to the considerable enhancement of glucose oxidase (GOx) activity: the simple assembly of a complex from cdte quantum dots and GOx, and its glucose sensing, Chem. Eur. J. 14 (2008) 9633–9640.
[183] Y. Miao, Detection of glucose with room-temperature phosphorescent quantum dots without conjugation, Sens. Biosensing Res. 5 (2015) 112–116.
[184] P. Wu, T. Zhao, Y. Tian, L. Wu, X. Hou, Protein-Directed synthesis of Mn-doped ZnS quantum dots: a dual-channel biosensor for two proteins, Chem. Eur. J. 19 (2013) 7473–7479.
[185] P. Deng, L.Q. Lu, T. Tan, Y. Jin, X.Z. Fan, W.C. Cao, X.K. Tian, Novel phosphorescent mn-doped ZnS quantum dots as a probe for the detection of L-Tyrosine in human urine, Anal. Methods 9 (2017) 287–293.
[186] J. Zheng, X. Fang, J. Qin, Z. Zhang, Y. Miao, G.A. Yan, Sensitive phosphorescence method based on MPA-Capped Mn-doped ZnS quantum dots for the detection of diprophyllin, New J. Chem. 40 (2016) 3857–3862.
[187] H.E.S. Kara, B. Demirhan, B.E. Demirhan, Mn-Doped ZnS quantum dots as a room-temperature phosphorescent probe for analysis of glutamic acid in foodstuffs, Turk. J. Chem. 40 (2016) 762–771.
[188] Y. Gong, Z. Fan, Highly selective manganese-doped zinc sulfide quantum dots based label free phosphorescent sensor for phosphopeptides in presence of zirconium (IV), Biosens. Bioelectron. 66 (2015) 533–538.
[189] Z. Zhang, Y. Miao, Q. Zhang, G. Yan, Facile and sensitive detection of protamine by enhanced room-temperature phosphorescence of mn-doped ZnS quantum dots, Anal. Biochem. 478 (2015) 90–95.
[190] Q. Ma, Z.H. Lin, N. Yang, Y. Li, X.G.A. Su, Novel carboxymethyl chitosan-quantum dot-based intracellular probe for zn ion sensing in prostate cancer cells, Acta Biomater. 10 (2014) 868–874.
[191] W. Bian, F. Wang, Y. Wei, L. Wang, Q. Liu, W. Dong, S. Shuang, M.F. Choi, Doped zinc sulfide quantum dots based phosphorescence turn-off/on probe for detecting histidine in biological fluid, Anal. Chim. Acta 856 (2015) 82–89.
[192] L. Dan, H.F. Wang, Mn-Doped ZnS quantum dot imbedded two-fragment imprinting silica for enhanced room temperature phosphorescence probing of domoic acid, Anal. Chem. 83 (2013) 4844–4848.
[193] L. Zhang, P. Cui, B. Zhang, F. Gao, Aptamer-Based turn-on detection of thrombin in biological fluids based on efficient phosphorescence energy transfer from mn-doped ZnS quantum dots to carbon nanodots, Chem. Eur. J. 19 (2013) 9242–9250.
[194] D. Li, J. Qin, Q. Xu, G. Yan, A Room-Temperature Phosphorescence Sensor for the Detection of Alkaline Phosphatase Activity Based on Mn-Doped ZnS Quantum Dots 274 (2018) 78–84.
[195] N. Ertas, H.E. Kara, S.L-Cysteine capped Mn-doped ZnS quantum dots as a room temperature phosphorescence sensor for in-vitro binding assay of idarubicin and DNA, Biosens. Bioelectron. 70 (2015) 345–350.
[196] L. Bi, Y.H. Yu, Phosphorescent quantum dots/ethidium bromide nanohybrids based on photoinduced electron transfer for DNA detection, Spectrochim. Acta Mol. Biomol. Spectrosc. 140 (2015) 479–483.
[197] Y. Li, Y.M. Miao, M.Q. Yang, Y.X. Wu, G.Q. Yan, DNA detection based on Mn-doped ZnS quantum dots/methylene blue nanohybrids, Chin. Chem. Lett. 27 (2016) 773–778.
[198] C. McCusker, J.B. Carroll, V.M. Rotello, Cationic polyhedral oligomeric silsesquioxane (POSS) units as carriers for drug delivery processes, Chem. Commun. 8 (2005) 996–998.
[199] H. Yu, Y.X. Ping, Mn-Doped ZnS quantum dots/methyl violet nanohybrids for room temperature phosphorescence sensing of DNA, Sci. China Chem. 54 (2011) 1254–1259.
[200] Y. Miao, Z. Zhang, Y. Gong, G. Yan, Phosphorescent quantum dots/doxorubicin nanohybrids based on photoinduced electron transfer for detection of DNA, Biosens. Bioelectron. 59 (2014) 300–306.
[201] Y. Gong, Z. Fan, Room-Temperature phosphorescence turn-on detection of DNA based on riboflavin-modulated manganese doped zinc sulfide quantum dots, J. Flouresc. 26 (2016) 385–393.
[202] H.E.S. Kara, Novel “Turn off-on” sensors for detection of DNA-Acrylamide interaction usingZnS quantum dots as a phosphorescent probe, Turk. J. Chem. 43 (2019) 125–136.
[203] A.M. Powe, K.A. Fletcher, N.N. St.Luce, M. Lowry, S. Neal, M.E. McCarroll, P.B. Oldham, L.B. McGown, I.M. Warner, Molecular fluorescence, phosphorescence and chemiluminescence spectrometry, Anal. Chem. 76 (2004) 4614–4634.
[204] A. Shahvar, M. Saraji, D. Shamsaei, Smartphone-Based chemiluminescence sensing for TLC imaging, Sens. Actuators B 255 (2018) 891–894.
[205] Z. Wang, J. Li, B. Liu, J. Hu, X. Yao, J. Li, Chemiluminescence of CdTe nanocrystals induced by direct chemical oxidation and its size-dependent and surfactant-sensitized effect, J. Phys. Chem. B 109 (2005) 23304–23311.
[206] J. Liu, H. Chen, Z. Lin, J. Lin, Preparation of surface imprinting polymer capped Mn-doped ZnS quantum dots and their application for chemiluminescence detection of 4-Nitrophenol in tap water, Anal. Chem. 82 (2010) 7380–7386.
[207] H. Chen, R. Li, L. Lin, G. Guo, J.M. Lin, Determination of L-Ascorbic acid in human serum by chemiluminescence based on hydrogen peroxide-sodium hydrogen carbonate-cdse/cds quantum dots system, Talanta 81 (2010) 1688–1696.
[208] X. Yu, J. Bao, Determination of norfloxacin using gold nanoparticles catalyzed Ce (IV)-sodium sulfite chemiluminescence, J. Lumin. 129 (2009) 973–978.
[209] J.X. Liu, H. Chen, L. Lin, C. Lu, J. Lin, Sensitized chemiluminescence reaction between hydrogen peroxide and periodate of different types of mn-doped ZnS quantum dots, Chinese Sci. Bull. 55 (2010) 3479–3484.
[210] J.M. Lin, M. Yamada, Oxidation reaction between periodate and polyhydroxyl compounds and its application to chemiluminescence, Anal. Chem. 71 (1999) 1760–1766.
[211] Y. Zhou, H. Chen, N. Ogawa, J.M. Lin, Chemiluminescence from NaClO–H_2O_2 and enhanced by L-Cysteine capped mn-doped ZnS quantum-dots, J. Lumin. 131 (2011) 1991–1997.
[212] S.N. Azizi, M.J. Chaichi, P. Shakeri, A. Bekhradnia, Determination of atropine using Mn-doped ZnS quantum dots as novel luminescent sensitizers, J. Lumin. 144 (2013) 34–40.
[213] M.M. Richter, Electrochemiluminescence, Chem. Rev. 104 (2004) 3003–3036.
[214] Y. Yuan, S. Han, L. Hu, S. Parveen, G. Xu, Coreactants of tris(2,2′-bipyridyl)ruthenium(II) electrogenerated chemiluminescence, Electrochim. Acta. 82 (2012) 484–492.
[215] X. Michalet, F.F. Pinaud, L.A. Bentolila, J.M. Tsay, S. Doose, J.J. Li, G. Sundaresan, A.M. Wu, S.S. Gambhir, S. Weiss, Quantum dots for live cells,in vivo imagingand diagnostics, Science 307 (2005) 538–544.
[216] H. Jiang, H.X. Ju, Electrochemiluminescence sensors for scavengers of hydroxyl radical based on its annihilation in CdSe quantum dots film/peroxide system, Anal. Chem. 79 (2007) 6690–6696.
[217] N. Myung, Z.F. Ding, A.J. Bard, Electrogenerated chemiluminescence of CdSe nanocrystals, Nano Lett. 2 (2002) 1315–1319.
[218] S. Wang, E. Harris, J. Shi, A. Chen, S. Parajuli, X. Jing, W. Miao, Electrogenerated chemiluminescence determination of C-Reactive protein with carboxyl cdse/ZnS core/shell quantum dots, Phys. Chem. Chem. Phys. 12 (2010) 10073–10080.
[219] X. Liu, H. Jiang, J.P. Lei, H.X. Ju, Anodic electrochemiluminescence of cdte quantum dots and its energy transfer for detection of catechol derivatives, Anal.

Chem. 79 (2007) 8055–8060.
[220] X.F. Wang, J.J. Xu, H.Y.A. Chen, New electrochemiluminescence emission of Mn-doped ZnS nanocrystals in aqueous solution, J. Phys. Chem. C 112 (2008) 17581–17585.
[221] C.Y. Zhang, H.C. Yeh, M.T. Kuroki, T.H. Wang, Single-Quantum-Dot-Based DNA nanosensor, Nat. Mater. 4 (2005) 826–831.
[222] Y.P. Ho, M.C. Kung, S. Yang, T.H. Wang, Multiplexed hybridization detection with multicolor colocalization of quantum dot nanoprobes, Nano Lett. 5 (2005) 1693–1697.
[223] X. Gao, L. Yang, J.A. Petros, F.F. Marshall, J.W. Simons, S. Nie, In vivo molecular and cellular imaging with quantum dots, Curr. Opin. Biotechnol. 16 (2005) 63–72.
[224] Y. Hiroshi, W. Masaki, O. Yukihiro, T. Manabu, K. Noritada, M. Yoshitaka, N. Hirofumi, B. Yoshinobu, H. Shuji, Monitoring transplanted adipose tissue-derived stem cells combined with heparin in the liver by fluorescence imaging using quantum dots, Biomaterials 33 (2012) 2177–2186.
[225] J.R. Lakowicz, Radiative decay engineering: biophysical and biomedical applications, Anal. Biochem. 298 (2001) 1–24.
[226] C.D. Geddes, J.R. Lakowicz, Metal-Enhanced fluorescence, J. Fluoresc. 12 (2002) 121–129.
[227] K. Sokolov, G. Chumanov, T.M. Cotton, Enhancement of molecular fluorescence near the surface of colloidal metal films, Anal. Chem. 70 (1998) 3898–3905.
[228] I.L. Medintz, H.T. Uyeda, E.R. Goldman, H. Mattoussi, Quantum dot bioconjugates for imaging, labelling and sensing, Nat. Mater. 4 (2005) 435–446.
[229] S. Mackowski, S. Wörmke, A.J. Maier, T.H. Brotosudarmo, H. Harutyunyan, A. Hartschuh, A.O. Govorov, H. Scheer, C. Bräuchle, Metal-Enhanced fluorescence of chlorophylls in single light-harvesting complexes, Nano Lett. 8 (2008) 558–564.
[230] A.V. Akimov, A. Mukherjee, C.L. Yu, D.E. Chang, A.S. Zibrov, P.R. Hemmer, H. Park, M.D. Lukin, Generation of single optical plasmons in metallic nanowires coupled to quantum dots, Nature 450 (2007) 402–406.
[231] Y. Fu, J. Zhang, J.R. Lakowicz, Silver-Enhanced fluorescence emission of single quantum dot nanocomposites, Chem. Commun. 3 (2009) 313–315.
[232] D. Zhu, W. Li, H.M. Wen, S. Yu, Z.Y. Miao, A. Kang, A. Zhang, Silver nanoparticles-enhanced time-resolved fluorescence sensor for $VEGF_{165}$ based on Mn-doped ZnS quantum dots, Biosens. Bioelectron. 74 (2015) 1053–1060.
[233] A.X. Zhu, D.G. Duda, D.V. Sahani, R.K. Jain, HCC and angiogenesis: possible targets and future directions, Nat. Rev. Clin. Oncol. 8 (2011) 292–301.
[234] X. Fang, W. Tan, Aptamers generated from cell-SELEX for molecular medicine: a chemical biology approach, Acc. Chem. Res. 43 (2010) 48–57.
[235] E.J. Cho, J.W. Lee, A.D. Ellington, Applications of aptamers as sensors, Annu. Rev. Anal. Chem. 2 (2009) 241–264.
[236] L.C. Bock, L.C. Griffin, J.A. Latham, E.H. Vermaas, J.J. Toole, Selection of single-stranded DNA molecules that bind and inhibit human thrombin, Nature 355 (1992) 564–566.
[237] M. Geszke, M. Murias, L. Balan, G. Medjahdi, J. Korczynski, M. Moritz, J. Lulek, R. Schneider, Folic acid-conjugated core/shell ZnS:Mn/ZnS quantum dots as targeted probes for two photon fluorescence imaging of cancer cells, Acta Biomater. 7 (2011) 1327–1338.
[238] J. Cao, H. Niu, D. Han, S. Yang, Q. Liu, T. Wang, J. Yang, Biocompatible ZnS:Mn (2+) quantum dots/SiO_2 nanocomposites as fluorescent probe for imaging hela cell, J. Mater. Sci. Mater. Med. 26 (2015) 2361–2366.
[239] Z. Yu, X. Ma, B. Yu, Y. Pan, Z. Liu, Synthesis and characterization of ZnS:Mn/ZnS core/shell nanoparticles for tumor targeting and imaging in vivo, J. Biomater. Appl. 28 (2013) 232–240.
[240] I.B. Bwatanglang, F. Mohammad, N.A. Yusof, J. Abdullah, M.Z. Hussein, N.B. Alitheen, N. Abu, Folic acid targeted mn:ZnS quantum dots for theranostic applications of cancer cell imaging and therapy, Int. J. Nanomed. 11 (2016) 413–428.
[241] L.J. Sang, H.F. Wang, Aminophenylboronic-Acid-Conjugated polyacrylic acid–Mn-doped ZnS quantum dot for highly sensitive discrimination of glycoproteins, Anal. Chem. 86 (2014) 5706–5712.
[242] D.D. Diestra, J.B. Huarac, D.P. Rincon, J.A. Gonzalez-Feliciano, C.I. Gonzalez, B.R. Weiner, G. Morell, Biocompatible ZnS:Mn quantum dots for reactive oxygengeneration and detection in aqueous media, J. Nanopart. Res. 17 (2015) 46101–46114.
[243] B.J. Swift, F. Baneyx, Microbial uptake, toxicity and fate of biofabricated ZnS:Mn nanocrystals, PLoS ONE 10 (2015) 1–14.
[244] V. Pandey, G. Pandey, V.K. Tripathi, S. Yadav, M.R. Mudiam, Nucleation temperature-controlled synthesis and invitro toxicity evaluation of L-Cysteine-Capped Mn:ZnS quantum dots for intracellular imaging, Luminescence 31 (2016) 341–347.
[245] Y.M. Sung, S.R. Gayam, P.Y. Hsieh, H.Y. Hsu, E.W.G. Diau, S.P. Wu, Quinone-Modified mn-doped ZnS quantum dots for room-temperature phosphorescence sensing of human cancer cells thatoverexpress NQO1, ACS Appl. Mater. Interfaces 7 (2015) 25961–25969.
[246] M. Garcia-Cortes, M.T. Fernandez-Arguelles, J.M. Costa-Fernandez, A. Sanz-Medel, Sensitive prostate specific antigen quantification using dihydrolipoic acid surface-functionalized phosphorescent quantum dots, Anal. Chim. Acta 987 (2017) 118–126.