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Review Article

Recent Advances in Fluorescence Detection of Catecholamines

Ahmad Moslehipour *

Farabi Research Center, Jam, Bushehr, Iran

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Abstract:

This study presents an overview on the recent advances in fluorescence methods for detection of catecholamines. In the past few decades, development of fluorescence probe has appeared as an important research area, which attracted a remarkable amount of attention due to its considerable sensitivity, simplicity, and selectivity. In this study, detection of catecholamines based on fluorescent metal nanoparticles, fluorescent semiconductor nanoparticles, fluorescent dyes, conjugated polymers, graphene, carbon nanotube sensors, biosensors, chemiluminescence as well as combination of Fluorescence methods with electrophorese, chromatography, electrochemical techniques, and Raman spectroscopy were evaluated.

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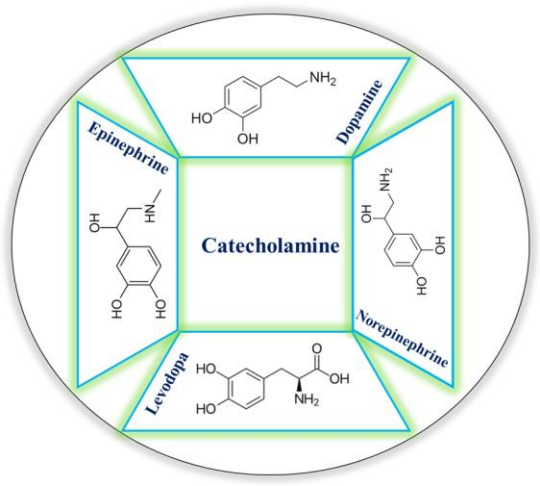
Keywords: Catecholamine; Fluorescence spectroscopy; Nanotechnology.

Graphical Abstract:



Biography:

Ahmad Moslehipour received his B.Sc. degree in applied chemistry in **2013** from University of Kurdistan, Iran and his M.Sc. degree in Analytical Chemistry in **2015** from Sharif University of Technology, Iran. He is a researcher in Farabi research Center, Jam, Bushehr, Iran. His research encompasses the synthesis of nanoparticles, quantum dots, analytical chemistry and fluorescence spectroscopy.

1. Introduction

Catecholamines, such as dopamine (DA), levodopa (L-dopa), noradrenaline (NA, also called norepinephrine), and adrenaline (Adr, also called epinephrine), function as neurotransmitters or hormones at central and peripheral levels. Neurotransmitters as messengers of neurologic data, are endogenous molecules transferring an electrical impulse from a nerve cell to another nerve or tissues and regulate many biological processes in central nervous, hormonal, and cardiovascular systems [1-3]. Dopamine (DA) is also found in non-neuronal tissues such as the kidney, where it contributes in the

*Corresponding author: Ahmad Moslehipour, Email: Ahmad.chem@yahoo.com

regulation of sodium balance. L-DOPA (L-3, 4-dihydroxyphenylalanine or levodopa) plays vital roles in biochemistry and medicinal chemistry. It can be converted to dopamine by dopadecarboxylase to increase the dopamine level in brain and can also cross the blood-brain barrier, whereas the dopamine itself is not capable of [4-6]. Epinephrine [EP], a hormone produced by the adrenal medulla, which acts as a neurotransmitter involved in regulating visceral functions. Norepinephrine (NE) is a catecholamine that reaches much higher concentrations during the conditions of stress or danger [7, 8].

Participation of the catecholamines in several controlling systems and metabolic procedures supports their significant use as biomarkers for the identification and treatment of several disorders. For example, nonstandard catecholamines concentrations in biological fluids (e.g., urine, blood plasma, and extracellular fluid of the central nervous system) can be indicator of Huntington's and Parkinson's diseases [9]. Therefore, sensitive and selective detection of catecholamines concentrations is very important.

Many different methods have been reported for the determination of catecholamines such as chromato-gramphic techniques [10, 11] capillary electrophoresis (CE) [12, 13], electrochemical detection [14-16], and fluorescent or colorimetric probes [17-24]. However, these methods have some limitations. For instance, the chromatographic methods are time-consuming, labor intensive, and expensive with complicated procedures. On the other hand, selectivity of the electrochemical catecholamines sensors may be troubled by the presence of other molecules with the similar redox potentials [25]. Therefore, there are increased demands for new experimental approaches.

Among the aforementioned techniques, the fluorescence methods may be convenient to overcome other methods' disadvantages since they are fast, simple and selective. In this regard, many fluorescence-based sensing methods have been reported for various catecholamines [26]. The purpose of this review was to discuss the considerable progress in catecholamines-fluorescence sensing for the last 11 years. In addition, several fluorescence methods and effective parameters were compared.

2. Detection of Catecholamines Based on Fluorescent Metal Nanoparticles

Metal nanoparticles have considerable effect on the development of new fluorescent approaches for detection of catecholamines. Many articles have reported the detection of catecholamines based on the interaction of the metal nanoparticle and the complexes [27-29]. Tang *et al.* [30] developed a sensitive fluorescence nanosensor for dopamine based on formate bridged Tb (III) complex and silver nanoparticles. HCOO- acted as a co-ligand of Tb (III) and also as a linker to bridge between the Tb(III) complex and AgNPs as well as favored to combine with primary amine of DA compared with epinephrine (Figure 1). The formate-bridged action strengthened AgNPs-based surface enhanced fluorescence of Tb^{3+}-DA complex and improved the selectivity of DA.

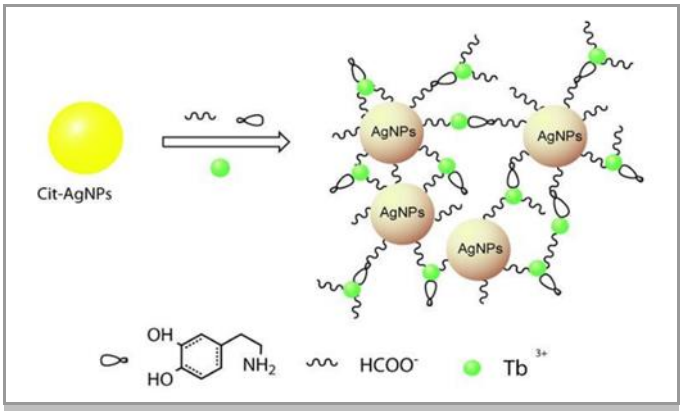


Figure 1. Schematic illustration of the formate-bridged AgNPs and Tb (III) nanosensor for DA. Reprinted from [30].

In another work, a simple fluorescent sensing method based on the dual signal amplifications of silver nanoprisms and acetate on Tb^{3+} luminescence was developed for dopamine detection. By rational design of anisotropic silver nanoprisms, a large surface enhanced fluorescence (SEF) effect was obtained. The use of acetate co-ligand further amplified the fluorescence signal and improved the selectivity of the composite sensor [31]. Liu *et al.* [29] reported a fluorescence approach for detection of catecholamines using the magnetite nanoparticles (Fe_3O_4 NPs) in the presence of Amplex UltraRed (AUR) and H_2O_2. Fe_3O_4 NPs catalyze H_2O_2-mediated oxidation of AUR. After connection of catecholamines to Fe_3O_4, the resulting complexes induce decreased activity of the Fe_3O_4 NPs, mediated through the coordination between Fe^{3+} on the NP surface and the catechol moiety of catecholamines (Figure 2). Accordingly, Fe_3O_4 NPs-catalyzed H_2O_2-mediated oxidation of AUR is inhibited by catecholamines [29].

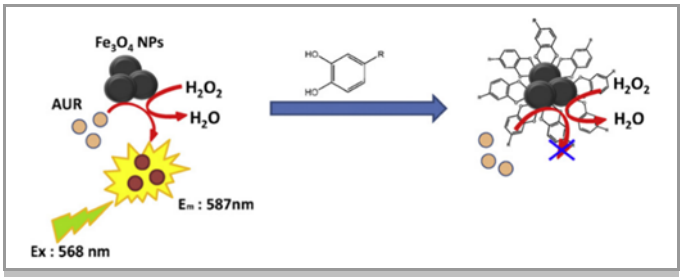


Figure 2. Mechanism of the Fe_3O_4 NP-H_2O_2-AUR probe for sensing catecholamines. Reprinted from [29].

A DNA-mediated silver nanostructure can be used in the facile detection of dopamine by the fluorescence enhancement resulting from specific binding of

intercalating dye with the DNA that is released by dopamine from the nanoparticle [32]. BSA-stabilized Au nanoclusters (BSA-AuNCs) can form a fluorometric dual channel sensor for the measurement of dopamine. upon addition of dopamine, the AuNCs show a remarkable decline of the emission intensity as a result of the photo-induced electron transfer mechanism from the electrostatically attached dopamine to the BSA-AuNCs [33]. Aswathy *et al.* [34] applied Cu^{2+} modified BSA stabilized gold nanoclusters (BSA-Au NCs) as a turn-on method for dopamine sensing. The fluorescence intensity of BSA-Au NCs was initially quenched by the Cu^{2+} ion, and then the addition of dopamine molecule causes the retrieval fluorescence by binding with the metal ion and eliminating it from the surface of BSA-Au NCs. Mono-6-amino-β-cyclodextrin (NH2-β-CD) functionalized gold nanoclusters (β-CD-AuNC) is a valuable technic for dopamine detection. The NH2-β-CD molecules conjugate onto the surface of 11-mercaptoundecanoic acid capped AuNCs (11-MUA-AuNC) via a carbodiimide coupling reaction. Dopamine can be captured by the β-CD cavities to form an inclusion complex in which the oxidized dopamine can quench the emission of the β-CD-AuNC sensor by electron transfer [35]. In addition, there is a facile aptamer-based sensing strategy for dopamine through the fluorescence resonance energy transfer (FRET) between rhodamine B (RB) and gold nanoparticles (AuNPs). Dopamine-binding aptamers (DBA) can protect AuNPs from salt-induced aggregation, resulting in the fluorescence quenching of RB via FRET [36]. Calix[4]resorcinarene polyhydrazide (CPH) capped nanoparticles (CPH-AuNps) can be used as a selective and sensitive fluorescent probe for L-Dopa [37].

There is a colorimetric and fluorometric probe based on gold nanoparticles (AuNPs) and aptamers specifically targeting dopamine. Aptamers modified with the fluorophore used as a dopamine's sensor based on the color change of AuNPs and the fluorescence recovery of fluorophore conjugated on the aptamers in the presence of dopamine [38]. Concentration of the norepinephrine in dopaminergic cells can be readily detected using the bio-barcode assay, which is based on the magnetic Dynabeads containing antibodies and nanoparticles that are loaded both with DNA barcords and with antibodies that can sandwich the target protein captured by the Dynabead-bound antibodies [39]. Also, a colorimetric and fluorometric probe has been developed for the determination of norepinephrine based on formation of brown silver nanoparticles in the presence of norepinephrine [40].

A fluorescent technique for the detection of dopamine (DA) has developed based on **the** surface-enhanced Tb(III)/ La(III) co-luminescence using silver nanoflowers (AgNFs). Tb(III)/La(III)-DA complexes mainly bind to the sharp tips of AgNFs and thus shorten the distance between the complexes, which gives rise to obvious surface-enhanced Tb(III)/La(III) co luminescence effect [41]. There is a dual-signal detection of dopamine based on label-free luminescent NaGdF4:Tb nanoparticles. In the presence of dopamine, the NaGdF4:Tb nanoparticles **revealed** luminescence quenching under the excitation of 272 nm, while they provide enhanced luminescence under 297 nm excitation, recognizing both turn off and turn on detection of dopamine [42].

3. Detection of catecholamines based on fluorescent semiconductor nanoparticles.

Quantum Dots (QDs), owning to their tunable absorb and emit wavelengths, excellent resistant to photobleaching, large shift and high extinction coefficients, have shown great applications in biological labeling, biomolecules detection, drug delivery, biological imaging, and medical diagnoses [43-46]. Qu *et al*. [47] reported an approach for label-free detection of dopamine based on carbon nanoparticles (CNPs). In addition, Xiangzhao *et al.* [48] constructed a fluorescent nanoprobe for dopamine and glutathione by CdTe quantum dots (QDs) and dopamine-quinone (formed by oxidation of dopamine). Dopamine captures on the surface of quantum dots via dual interactions and quenches the photoluminescence of the modified QDs by an electron transfer process (Figure 3). Glutathione can chemically decrease the dopamine-quinone on the QDs, and this results in recovered photoluminescence.

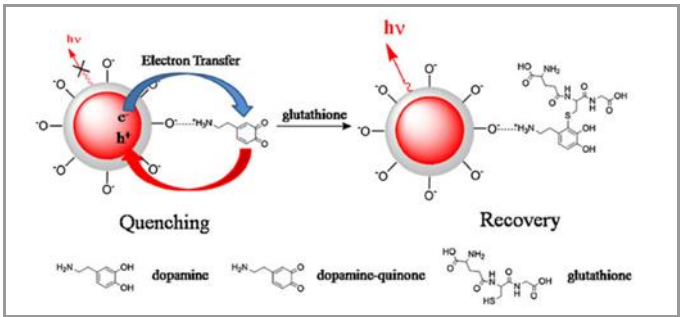


Figure 3. Illustration of the mechanism of nanosensor for the detection of dopamine and glutathione based on the quenching and recovery of the photoluminescence of QDs. Reprinted from [48].

Zhu *et al.* [49] developed a novel fluorescent biosensor based on dopamine aptamer labeled carbon dots and nano-graphite. In this method, aptamer-carbon dots were in charge of energy donor (fluorophor) and nano-graphite served as an energy acceptor. In the absence of dopamine, aptamer-carbon dots were adsorbed on the surface of nano-graphite,

which led to the fluorescence quenching of aptamer-carbon dots. When it was in presence, dopamine combined with the surface of carbon dots and the fluorescence intensity of aptamer- carbon dots recovers.

Simultaneous detection of multiple analytes has attracted considerable interest. In a paper, anchoring molecularly imprinted polymers (MIPs) on the surfaces of two different color quantum dots (QDs) can provide a simultaneous detection method for norepinephrine (NE) and epinephrine (E). NE-QDs@MIP using the NE as template and E-QDs@MIP using E as template synthesized on the surfaces of CdTe@SiO_2 and CdTe/CdS/ZnS/SiO_2 QDs, respectively. The mixture of NE-QDs@MIP and E-QDs@MIP could be excited at the same excitation wavelength and the simultaneous measurement of NE and E recognized by monitoring the two different color fluorescence signals without spectral overlap [50].

CdSe@Ag_2Se core–shell fluorescent quantum dots are the sensitive electrochemical sensor for methyldopa by casting of an aliquot of thioglycolic acid capped CdSe@Ag_2Se on a glassy carbon electrode surface [51]. Thioglycolic acid (TGA)-capped cadmium telluride (CdTe) quantum dots are the simple and cost effective nano-biosensor based for the detection of dopamine in alkaline media [52]. Carbon dots and 3‑mercapropionic acid-coated cadmium telluride quantum dots (CdTe QDs) can be used as a ratiometric fluorescence nanoprobe for the detection of epinephrine (EP) and norepinephrine (NE). Under single-wavelength excitation (370nm), the hybrid nanoprobe shows dual emission peaks at 460 nm and 610 nm belongs to carbon dots and CdTe QDs, respectively. CdTe QDs emission quenches by EP or NE via electron transfer from QDs to the oxidation products of catecholamines, while the fluorescence intensity of CDs stays constant, which constructs a ratiometric fluorescence assay for the catecholamines detection [53].

The fluorescent intensity of TGA–CdS QDs can be quenched by Co^{2+}. However, with the addition of dopamine into the solution of Co^{2+}@TGA–CdS QDs, the fluorescent intensity efficiently quenches due to the creation of Co^{2+}–dopamine complex. Thus, the concentration of dopamine can be determined by following the reduction in the emission intensity of the Co^{2+}@TGA–CdS QDs [54]. Wang *et al.* [55] reported a fluorescence method for the detection of Serotonin based on a Mn-doped ZnS quantum dots@silica Nanoparticle@molecularly imprinted polymers (QDs@SiO_2@MIPs). A complex produced between the amino group of QDs@SiO_2@MIPs and the hydroxyl group of 5-HT when 5-HT rebinding, the energy of the QDs would be transferred to the complex, which led to its emission quenching.

4. Detection of Catecholamines Based on Fluorescent Dyes.

Fluorescent dyes are the significant tools **detecting the** analytes by fluorescence spectroscopy [56-59]. A terbium-sensitized spectrofluorimetric assay has developed for determination of catecholamines using sodium dodecyl benzene sulphonate (SDBS). Kamruzzaman *et al*. [60] reported that fluorescence sensitization of terbium ions (Tb^{3+}) starts by complexation with catecholamines in the presence of SDBS. The fluorescence intensities of the Tb^{3+}–catecholamine complexes highly enhance by introducing SDBS. Also, a boronic acid compound was identified as a selective fluorescent sensor for L-DOPA. This compound not only has the ability to interact with dopamine and catechol, but also has no fluorescence emission change for similar material such as L-tyrosine [61]. Calcein blue (CB) complexed with Fe^{2+} ion can be a fluorescent sensor dopamine. The fluorescence arising from CB of the CB-Fe^{2+} complex is quenched by the Fe^{2+} ion. After adding dopamine to a solution of the CB-Fe^{2+} complex, a dopamine-Fe^{2+} complex is formed as the result of a ligand exchange reaction between CB and dopamine which causes the fluorescence from CB to be recovered [62].

Sanguansap *et al.* [63] reported two sensing elements based on **the** fluorescence sensors as a promising discriminating probe of dopamine and norepinephrine, acting as a proper guest linker between two self-recognition sensing components. 2, 3-diaminophenazine provides a simple and sensitive fluorescent probe for the measurement of dopamine. Dopamine caused autooxidation in the presence of oxygen with catalysis by Mn^{2+} and made 2,3-dihydro-1H-indole-5,6-dione. 2, 3-Diaminophenazine provided relatively strong fluorescence, which in aqueous solution caused fluorescence quenching [64]. (E)-2,2′-(5-(2-(4-(dicyanomethylene)-6-methyl-4H-pyran-2-yl)vinyl)-2-hydroxy benzylazanediyl)diacetic acid Fe(II) complex is a fluorescent reagent that can be used to detect dopamine. This complex creates using the cyanopyranyl group as the fluorophore and an Fe^{2+} complex both as the ligand exchange site and fluorescence quenching moiety [65].

Ortho-phthalaldehyde (OPA) can permeate live cells and form bright fluorogenic adducts with intracellular monoamines (e.g. setrotonin, dopamine and nor-epinephrine) and with L-DOPA, which can be imaged sensitively by fluorescence microscope [66]. Oxidation with cerium (IV) is a spectrofluorimetric method for the determination of catecholamines [67]. Wang *et al.* [68] developed a fluorescent probe for

detection of dopamine by synthesis of bis-boronic acid compounds based on 2-(4-Boronophenyl) quinoline-4carboxylic acid (PBAQA).

5. Fluorescence Methods and Electrophorese

Capillary electrophoresis (CE) has demonstrated to be a promising alternative for the catecholamines, mainly due to their high separation efficiency, short separation time, and low sample volume requirement [69-73]. Capillary zone electrophoresis method with laser-induced fluorescence detection is presented for the determination of noradrenaline and dopamine [74], serotonin [75], simultaneous analysis of DA, EP and NE in urine samples without complex pretreatment procedures [76, 77], amino acids and catecholamines [78, 79], and single-cell chemical analysis [80]. Capillary electrophoresis with laser-induced native fluorescence (LINF) detection offers the ability to characterize low levels of selected analyte classes, depending on the excitation and emission wavelengths used [81, 82]. Also, this method is used for chiral analysis of amino acids [83]. Microchip electrophoresis with electrochemical detection is a sensitive method for detection of dopamine [84, 85]. The new methods for the determination of epinephrine, norepinephrine, and dopamine by capillary electrophoresis with on-line chemiluminescence detection have been reported [86-88].

6. Chromatographic Methods and Fluorescence Spectroscopy

Several analytical methods based on high performance liquid chromatography (HPLC) [89-95], solid phase extraction (SPE) [96, 97], combination of chromatography with electrochemical methods [98, 99] chemiluminescence [100-102], and thin-layer chromatographic (TLC) [103] has been developed for separation and quantification of catecholamines. High performance liquid chromatography-fluorescence detection methods are employed to measurement of catecholamines in the catfish Heteropneustes fossilis [104], human plasma [105, 106], mouse striatum [107], human urine [108-110], porcine muscle [111], rat serum [112], mouseurine [113], standard solutions [114], rat brain [115, 116], and rat plasma [117, 118].
Sakaguchi *et al.* [119] have developed a liquid chromatographic (LC) derivatization method for simple and selective determination of catecholamines and indoleamines in human urine. This method uses "fluorous interaction" in which perfluoroalkyl compounds show affinity with each other. Silva *et al.* [120] have reported an optical fibre (OF) analyzer for measuring catecholamines in biological samples with induced fluorescence. The technique included a chromatographic column for catecholamine separation and a fluorescence-based OF detection (FOF-analyzer). Iminodiacetic acid-Cu(II) functionalized Fe_3O_4@SiO_2 magneticnnanoparticles can be used as the new adsorbents for magnetic solid phase extraction (MSPE) of neurotransmitters from rabbit plasma. By doing so, the employed weak acidic extraction condition avoided the oxidation of neurotransmitters, and thus facilitated operation and ensured higher recoveries [121].

7. Electrochemical Method and Fluorescence Spectroscopy

In many works, the electrochemical behaviors of catecholamines have been studied [122-126]. The electrochemical sensors for the detection of catecholamines typically work based on the oxidation of catechol part [127-130]. The dimeric Cu(II)complex[Cu(m2-hep)(hep-H)]2 _ $2ClO_4$ along with silver nanoparticles (SNPs) have been used as modifier in the construction of a biomimetic sensor (1–SNP–GCPE) for determining certain catecholamines [131]. Kisler *et al.* [132] have developed transparent microelectrode arrays capable of simultaneous amperometric measurement of oxidizable molecules and fluorescence imaging through the electrodes. Pasquarelli *et al.* [133] presented the suitability of diamond MEAs for simultaneously detecting amperometric and fluorescence signals associated with calcium transients and catecholamine release in in vitro chromaffin cells. Liu *et al.* [134] have worked on the applications of the Fluorescent False Neurotransmitter and a suitable probe for coupled amperometry and TIRFM (total internal reflexion fluorescence microscopy) investigations of exocytotic secretion. Fajardo and co-workers [135] have demonstrated a glassy carbon electrode modified with graphene quantum dots and gold nanoparticles (GCE/GQDs/AuNPs) for norepinephrine (NE) determination using squarewave stripping voltammetry. GQDs were characterized using the UV–Vis and fluorescence spectroscopy.

8. Fluorescent Biosensors

Montesinos *et al.* [136] have reported the simultaneous on-line monitoring of catecholamine and labetalol release from bovine isolated chromaffin cells and from rat perfused adrenal glands, as well as single cell amperometry. In this method, to avoid the problems derived from the different amount of cells retained in the filters and the different responsiveness to dimethylphenyl piperazinium (DMPP) from one batch of cells to another, data are expressed as the fluorescence/amperometry ratios.

A method for the selective labeling and imaging of catecholamines in live and fixed secretory cells is demonstrated by Hettie *et al.* [137]. The technique is a turn-on fluorescence probe (NeuroSensor 521) that can exploit the high concentration of catecholamines within secretory vesicles for the selective recognition of norepinephrine and dopamine (Figure 4). The utility of the sensor is validated by selectively labeling and imaging norepinephrine in secretory vesicles. This method was confirmed in fixed cells by co-staining with an anti-PNMT (phenylethanolamine N-methyltransferase) antibody.

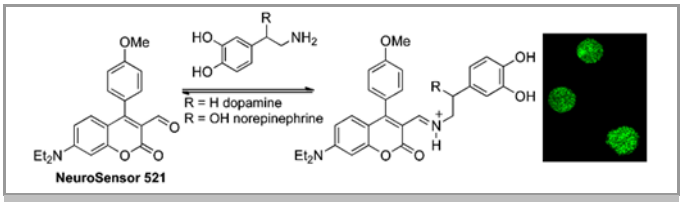


Figure 4. Schematic illustration of catecholamine recognition with NeuroSensor 521. Reprinted from [137].

Chaicham *et al.* [138] have reported an analytical procedure based on the intermolecular assembled complexes of two fluorescence probes and a suitable catecholamine acting as a guest linker by the reaction between boronic acid and aldehyde moieties of the sensors with the diol and amine units of catecholamines, respectively (Figure 5). The FRET-on/off enhanced by the catecholamines.

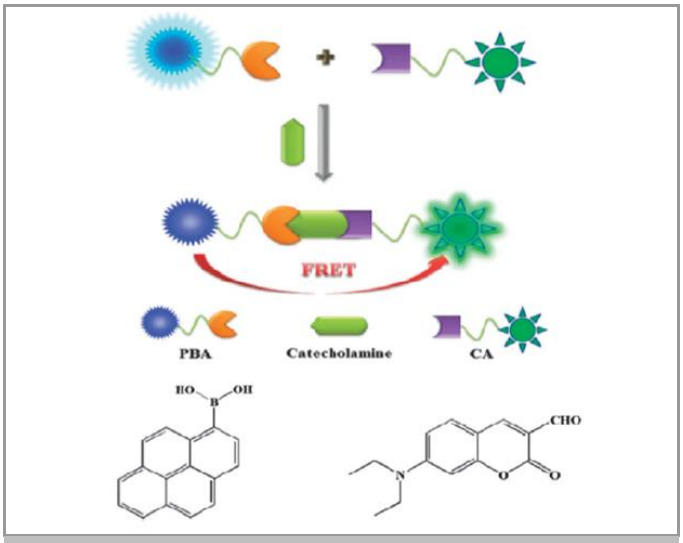


Figure 5. Conceptual design of an intermolecular assembled complex for catecholamine sensing by a FRET-on process. Reprinted from [138].

DNA-stabilized silver nanoclusters (DNA-AgNCs) are a new category of biocompatible, fluorescent nanostructures that have recently been demonstrated to offer promise as biosensors (as seen in Figure 6). Two different DNA sequences form dopamine-sensitive nanoclusters can support two distinct DNA-AgNCs. DNA-Ag nanoclusters provide a novel, low-cost method to detection of dopamine [139].

Zebrafish can be as a model for novel fluorescent tracer of dopamine neurotransmission, which can provide the selective labeling and study of retinal dopaminergic amacrine cells in vivo [140].

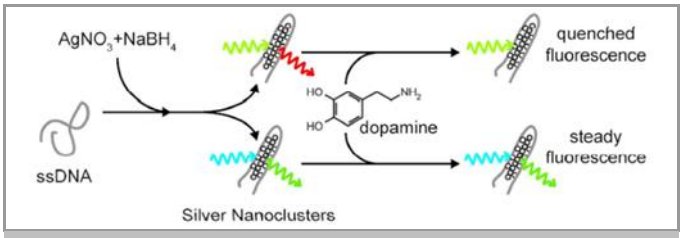


Figure 6. DNA S5 silver nanoclusters acts as ratiometric, "turn-off" dopamine sensors. Reprinted from [139].

Dopamine, in lipid bilayer and at the surface of DMPG vesicles can be evaluate through different regions of the lipid vesicle, which synthesizes using 7-nitrobenz-2-oxa-1,3-diazol-4-yl (NBD) labeled phospholipid molecules either tagged to the head group (NBDPE) or the acyl chain (NBDPG) (Figure 7). Dopamine induced quenching of NBD fluorescence in the lipid vesicles that cause change in the excited state lifetime for NBDPG [141].

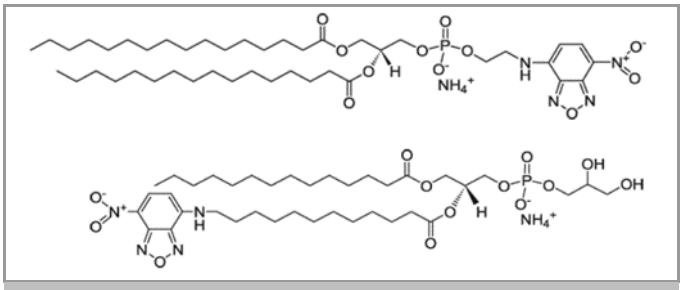


Figure 7. Molecular structures of NBDPE (top) and NBDPG (bottom). Reprinted from [141].

Combination of obtaining highly fluorescent derivatives of the analytes as a result of their interaction with benzylamine and 1,2-diphenylethylenediamine in the presence of peroxidase as a catalyst, creates a unique biosensor for the simultaneous multiplex fluorescent determination of catecholamines and their metabolites in biological liquids [142].

The chromatic vesicles are robust and easy to prepare, and the universal method could provide a viable platform for quantification of catecholamines in biological fluids. The idea of achieving fluorescence spectrum indirectly induced by specific ligand/receptor binding at a surrounding polymer matrix can be further stretched to numerous biological molecular recognition procedures [143].

9. Chemiluminescence Techniques

Chemiluminescence detection is known to be a sensitive, selective, and versatile method that can be used in combination with separation techniques such

as high performance liquid chromatography, capillary electrophoresis, and chip electrophoresis [144, 145].
The chemiluminescence emission of the KIO4–luminol system in strong alkaline solutions can enhance by tgallic acid, acetaldehyde and Mn^{2+}. Oxidation of the two reducing agents by KIO_4 catalyzes by Mn^{2+} may produce O^{2-}, $^{\bullet}OH$, and O_2, as revealed by the reactive oxygen species (ROS)-scavenging experiments. The proposed technique is applied to the determination of catecholamines in pharmaceutical injections [146]. A sensitive method based on quantum dot (QD)-enhanced capillary electrophoresis chemiluminescence (CE–CL) detection is presented by Zhao *et al.* [147] for simultaneous determination of dopamine (DA) and epinephrine (E). In this work, CdTe QD is added into the running buffer of CE to catalyze the post-column CL reaction between luminol and hydrogen peroxide, attaining higher CL emission. Xu *et al.* [148] reported a novel flow injection analysis-direct chemiluminescence (FI-CL) method for determination of dopamine based on the enhancing effect of dopamine on the chemiluminescence reaction of luminol with an Ag(III) complex in alkaline solution [148]. Introducing gold nanoparticles (AuNPs) to the running buffer further improves the sensitivity of luminol-H2O2 chemiluminescence detection for catecholamines [149]. Chemiluminescence based on enhancing effect of Si doped carbon dots (Si-CDs) and cetyltrimethylammonium bromide (CTAB) on HCO3--H2O2 [150] and alkaline Luminol - Hydrogen Peroxide System for Sequential Injection are two effective techniques for detection catecholamines [151]. The hot electron-induced cathodic electrochemiluminescence at the naturally oxide-covered tantalum electrode is applied to the ultra-trace analytical method (Figure 8). This method is an effective assay for determination of catecholamines [152].

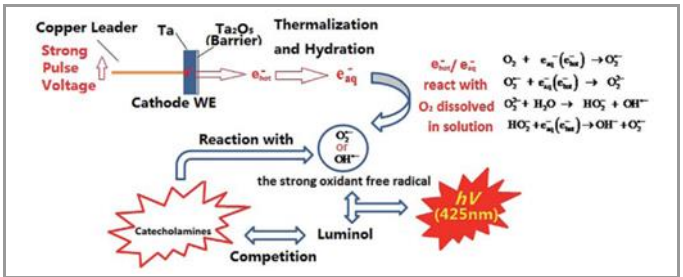


Figure 8. The possible mechanism of the quenching effect of catecholamines. Reprinted from [152].

10. Conjugated polymers

Among fluorescence sensors, more and more consideration has been paid on conjugated polymers (CPs) due to the superquenching properties that result from the conjugated polymer backbone, on which one single quencher molecule can provide a fast quenching. In a solution including radish peroxidase (HRP) and H2O2, catecholamine oxidizes, which can quench the photoluminescence (PL) intensity of poly(2,5-bis(3-sulfonatopropoxy)-1,4-phenylethynyl-enealt-1,4-poly(phenylene ethynylene)) (PPESO3). This is a water-soluble fluorescent conjugated polymer probe for catecholamines [153]. Under alkaline conditions, catecholamine is rapidly oxidized to its quinone derivative. Quinone is an active specie which is rapidly oxidized to dopachrome and spontaneously polymerized by covalent attachment and aggregation [154,155]. The resulting polymers are conjugated structures with fluorescence properties that can be simple and rapid method for detection of catecholamines [156-159].
Fluorescence polymer membrane [160], human dopamine receptor-conjugated multidimensional conducting polymer nanofiber (NF) membrane [161], Molecularly Imprinted Polymers (MIPs) [162-164], Functionalized Poly(L‑dopa)-Coated Gate Field-Effect Transistor [165], boronic acid derivatives [166], Oxidation of catecholamines [167], and fluorescent copolymer [168] are reported as fluorescence sensors for detection of catecholamines. Qian *et al.* [168] presented a method based on conjugated polymer nanoparticles with phenylboronic acid tags on the surface for fluorescence detection of dopamine in both living PC12 cells and brain of zebrafish larvae [169]. The in situ reaction between resorcinol and dopamine provides a turn-on fluorescence approach for dopamine detection [170]. A ceramic-based miniature biosensor is designed through the formation of polylevodopa, which can selectively quench the luminescence of graphene quantum dots owing to Förster resonance energy transfer (FRET) [171].
Jiang *et al.* [172] have constructed a conjugated polymer layer consisting of an oxaborole containing polymer and a glycopolymer for dopamine detection. The optimum binding affinity between the polymers promotes the selectivity to dopamine through a displacement mechanism while remaining unaffected by other structurally related analogs and saccharide products.
There is an exquisite label-free fluorescent and colorimetric dual-readout assay based on specific oxidation ability of monophenolamine substrates to catecholamines and a unique fluorogenic reaction between resorcinol and catecholamines (Figure 9). By **the** employing commercially available tyramine as the model substrate (dopamine as the product), the tyrosinase-incubated tyramine solution exhibits obvious pale yellow with intense blue fluorescence in the presence of resorcinol and O2, where the absorbance and fluorescence intensity are directly

related to the concentration of added tyrosinase [173]. The coupling of catecholamines with resorcinols based on the easily accessible conjugate 4-(2-((2,4 dihydroxybenzyl)amino)ethyl)benzene-1,2-diol is another approach for evaluation of catecholamines [174].

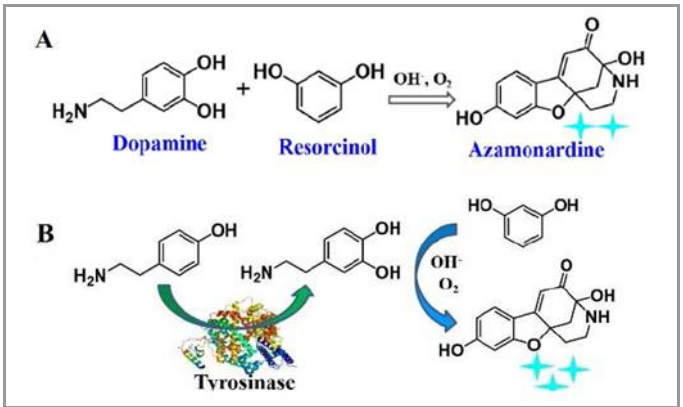


Figure 9. (A) Schematic representation of dopamine reacting with resocinol in synthesis of fluorescent azamonardine. (B) Schematic representation of tyrosinase-enabled in situ synthesis of fluorescent azamonardine. Reprinted from [173].

The oxidation of levodopa in alkaline media, forms polylevodopa nanoparticles that are able to quench the fluorescence emission of CdTe quantum dots (QDs) via energy transfer mechanism. Moslehipour *et al*. [175] designed a ratiometric probe by making use of variations in both the emission of QDs and the intrinsic emission of polylevodopa nanoparticles (Figure 10) [175].

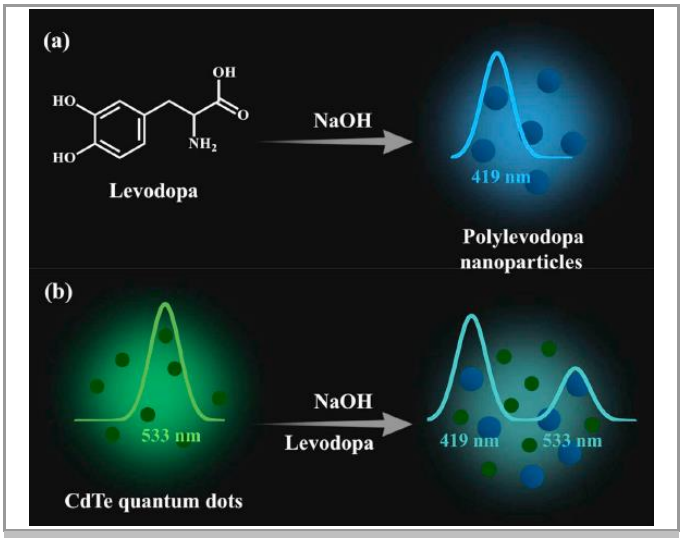


Figure 10. Schematic illustration of the oxidation of levodopa in alkaline media and quenching of QDs by produced polymeric products. Reprinted from [175].

11. Carbon Nanotube Sensors

Single-walled carbon nanotubes have stimulated much interest in their biological applications due to their remarkable electrical, structural, and physiochemical properties. For example, they have been employed as nanoelectronic biosensors with extraordinary sensitivity for the rapid detection of catecholamines [176, 177].

Kruss *et al*. [178] applied a new technique, corona phase molecular recognition (CoPhMoRe), to identify adsorbed polymer phases on fluorescent SWCNTs that allow for the effective detection of catecholamines. In this method, catecholamines increase the fluorescence of specific single-stranded DNA- and RNA wrapped SWCNTs. Near-infrared (NIR) fluorescent probe based on DNA-functionalized SWCNTs [179], nonphotobleaching fluorescent nanosensor array based on SWCNTs [180], and noncovalent interactions between single-stranded DNA (ssDNA) oligonucleotides and SWCNTs [181] are reported as sensors for direction of catecholamines.

12. Graphene

Graphene oxide (GO) holds great potential for optical biosensors because of its significant characteristics such as sp2/sp3 coexisting structure, high mechanic strength, facile surface modification, and super fluorescence quenching capacity. Nanoelectronic field-effect transistors (FETs) based on reduced graphene oxide (rGO) patterns [182], GO-based photoinduced charge transfer (PCT) label-free near-infrared (near-IR) fluorescent biosensor [183], Chemically modulation of GO photoluminescence [184], reduced graphene oxide/multiwall carbon nanotubes/gold nanoparticlesDehua [185], graphene quantum dots [186, 187], amino acids functionalized GO [188], and tremella-like ZnIn2S4/graphene composite [189] are presented as graphene sensors based on fluorescence emission for catecholamines detection.

13. Raman spectroscopy

The surface enhanced Raman spectroscopy (SERS) based sensors is a rapid and sensitive technique for the detection of neurotransmitters. Silver and gold nanoparticles at excitation wavelengths of 532 nm, 633 nm, and 785 nm are used for the detection of melatonin, serotonin, glutamate, dopamine, GABA, norepinephrine, and epinephrine [190]. Kaya *et al*. [191] have reported a sensitive method based on surface-enhanced resonance Raman scattering (SERRS) platform that allows fast and sensitive detection of dopamine (DA) without any pretreatment. The iron-nitrilotriacetic acid attached silver nanoparticle (Ag-Fe(NTA)) substrate plays a significant role in this approach. The Fe-NTA receptors can trap DA adjacent the silver core and the NTAFe-DA complex formed provides resonance enhancement with a 632.8 nm laser.

14. Conclusion

In this review, the significant progress in the fluorescence-based catecholamine sensing over the last eleven years (from 2009 to 2020), considering the sensing mechanism, procedures, and the synthesis were summerized. A stronger detection of the catecholamine's concentration is essential not only for diagnosis purposes, but also for research and development of new drugs, practical sensors, and the study of mechanisms. It is obvious that the fluorescence based techniques have some benefits over other analytical approaches, such as inexpensive instrumentation, simple processes, high sensitivity, and fast examination times. However, further improvement in fluorescent sensors seems to be necessary since the some of them act based on **the** nanoparticles that suffer from toxicity, poor water solubility, and low photostability.

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No potential conflict of interest was reported by the author.

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