



Electrochemical sensors and biosensors for determination of catecholamine neurotransmitters: A review

José A. Ribeiro*, Paula M.V. Fernandes, Carlos M. Pereira, F. Silva

Faculdade de Ciências da Universidade do Porto, Departamento de Química e Bioquímica, Centro de Investigação em Química (CIQUP) Rua do Campo Alegre 687 Porto 4169-007 Portugal

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ABSTRACT

This work describes the state of the art of electrochemical devices for the detection of an important class of neurotransmitters: the catecholamines. This class of biogenic amines includes dopamine, noradrenaline (also called norepinephrine) and adrenaline (also called epinephrine).

Researchers have focused on the role of catecholamine molecules within the human body because they are involved in many important biological functions and are commonly associated with several diseases, such as Alzheimer's and Parkinson. Furthermore, the release of catecholamines as a consequence of induced stimulus is an important indicator of reward-related behaviors, such as food, drink, sex and drug addiction. Thus, the development of simple, fast and sensitive electroanalytical methodologies for the determination of catecholamines is currently needed in clinical and biomedical fields, as they have the potential to serve as clinically relevant biomarkers for specific disease states or to monitor treatment efficacy.

Currently, three main strategies have used by researchers to detect catecholamine molecules, namely: the use electrochemical materials in combination with, for example, HPLC or FIA, the incorporation of new materials/layers on the sensor surfaces (Tables 1–7) and *in vivo* detection, mainly by using FSCV at CFMEs (Section 10). The developed methodologies were able not only to accurately detect catecholamines at relevant concentration levels, but to do so in the presence of co-existing interferences in samples detected (ascorbate, for example).

This review examines the progress made in electrochemical sensors for the selective detection of catecholamines in the last 15 years, with special focus on highly innovative features introduced by nanotechnology. As the literature is rather extensive, we try to simplify this work by summarizing and grouping electrochemical sensors according to the manner their substrates were chemically modified. We also discuss the current and future of electrochemical sensors for catecholamines in terms of the analytical performance of the devices and emerging applications.

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Abbreviations: 5-HT, Serotonin (or 5-hydroxytryptamine); AA, Ascorbic acid; AC, Acetaminophen; Adr, Adrenaline (or epinephrine); BDD, Boron-doped diamond; BPPG, Basal plane pyrolytic graphite; CD, Cyclodextrin; CFE, Carbon fiber electrode; CFME, Carbon fiber microelectrode; CNTs, Carbon nanotubes; COMT, Catechol-O-methyltransferase; CPE, Carbon paste electrode; CV, Cyclic voltammetry; Cys, Cysteine; DA, Dopamine; DOPA, Dihydroxyphenylalanine; DOPAC, 3,4-Dihydroxyphenylacetic acid; EPPG, Edge plane pyrolytic graphite; Fc, Ferrocene; GC, Glassy carbon; Glu, Glucose; Gly, Glycine; GO, Graphene oxide; GR, Graphene; HOPG, Highly oriented pyrolytic graphite; HVA, Homovanillic acid; ITO, Indium thin oxide; LOD, Limit of detection; MAO, Monoamine oxidase; ME, Microelectrode; MIP, Molecular imprinted polymer; MWCNTs, Multi-walled carbon nanotubes; NA, Noradrenaline (or norepinephrine); NPs, Nanoparticles; NT, Neurotransmitter; PANI, Poly(aniline); PE, Paste electrode; PEDOT, Poly(3,4-ethylenedioxythiophene); PG, Pyrolytic graphite; Ppy, Poly(pyrrole); PVA, Poly(vinyl alcohol); PVC, Polyvinyl chloride; rGO, Reduced graphene oxide; RTIL, Room temperature ionic liquid; SAM, Self-assembled monolayer; SPE, Screen-printed electrode; SWCNTs, Single wall carbon nanotubes; Tyr, Tyrosine; TRP, Tryptophan; UA, Uric acid; VMA, Vanillylmandelic acid

* Corresponding author.

E-mail addresses: jadribeiro@gmail.com (J.A. Ribeiro), cmpereir@fc.up.pt (C.M. Pereira).

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1. Catecholamines

In the mammalian brain, neuronal networks process vast amounts of information received from the subject's environment from various senses such as sight, hearing, and touch, which are then combined with signals from throughout the body.

The brain uses neurons to carry information throughout the brain using trains of electrical impulses. At the interconnection between neurons, called synapses, these electrical signals are converted in a sophisticated non-linear manner into chemical signals. Synaptic vesicles fuse with the cell membrane releasing their contents, the NTs, by exocytosis. The released NT diffuses both, within and outside of the synapse, where it acts on specialist receptors which can be on the releasing neuron (as part of a feedback control), in the next neuron in the chain (to pass the message on) or perhaps most importantly in surrounding neurons (to give a neuromodulatory action and allow integration of responses between neurons). For DA, this last action is the most important in terms of its function [1,2].

Catecholamines are neurotransmitters (NTs) and/or hormones in the peripheral and in the central nervous system [3,4]. They excite, inhibit or otherwise influence the activity of cells. This class of specialized chemical messengers is composed by dopamine (DA, represented in Fig. 1A), noradrenaline (NA, also called norepinephrine, Fig. 1B) and adrenaline (Adr, also called epinephrine, Fig. 1C).

In terms of biosynthesis, all the catecholamines (so named because they share the catechol moiety) are derived from a common precursor, the amino acid tyrosine (Tyr) [3,4]. The first step in catecholamine synthesis is catalysed by tyrosine hydroxylase to form dihydroxyphenylalanine (DOPA), which gives origin to DA after the action of DOPA decarboxylase (see Fig. 2).

DA serves as a NT in several important pathways in the central nervous system and has also an important biological activity in the

peripheral nervous system. DA has also been associated with the reward system, the circuitry in the brain responsible for the motivation to seek out stimuli as well as the emotions of feeling satisfied and satiated in one's environment. It is thought that this system is activated by natural rewards such as food, drink and sex, as well as by addictive drugs [1]. For example, cocaine and other addictive drugs act by stimulating the release of DA from specific brain areas [3,4].

NA synthesis requires dopamine β -hydroxylase which catalyses the production of NA from DA. NA is a NT in the brain as well as in postganglionic sympathetic neurons where it influences sleep and wakefulness, attention and feeding behavior.

Adr is formed by the action of phenylethanolamine-*N*-methyltransferase over NA. Adr is a hormone released from the adrenal gland and it stimulates catecholamine receptors in a variety of organs [3,4]. It plays an important role during the times of physical or mental stress [5] and has been used as a common emergency healthcare medicine. Endogenous catecholamine levels have been measured in resting individuals and have been shown to be approximately 150–800 ng/L for NA and 10–50 ng/L for Adr and DA [6].

The effects of DA are mediated through interaction with five different receptors, usually referred to as D1-like (D1, D5) and D2-like (D2, D3, D4) [3,4]. DA receptors are found primarily in brain (in the substantia nigra/ventral tegmental area of the brain), although they also exist in kidney. The effects of NA and Adr are mediated through nine distinct receptors, named adrenergic receptors, grouped into three families (α 1, α 2, β), each containing three subtypes encoded by separate genes. As NA and Adr are important messengers in both, the peripheral sympathetic nervous system and the brain, adrenergic receptors are widely distributed in peripheral tissues as well as existing in high concentrations in the brain [3,4].

All three catecholamines are removed by reuptake into nerve terminals or surrounding glial cells by a Na^+ -dependent transporter [3,4]. The two major enzymes involved in the catabolism of catecholamines are monoamine oxidase (MAO) and catechol *O*-methyltransferase (COMT). MAO and COMT are widely distributed throughout the body. As can be seen in Fig. 2, homovanillic acid (HVA) is the major metabolite of DA. There are also several pathways for the NA (see Fig. 3) and Adr degradation and the vanillylmandelic acid (VMA) is the major metabolite [3,4].

The relationship between these amine compounds and human pathologies has been known for more than 150 years [7]. Currently, in fact, it is known that they are involved in several physiological mechanisms and are related to some of the most prevalent human pathologies, such neurological disorders as Parkinson's disease, Alzheimer, schizophrenia and hyperactivity [7].

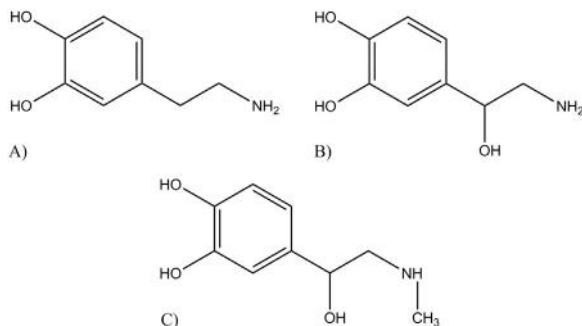


Fig. 1. Molecular structure of dopamine (A), noradrenaline (B) and adrenaline (C).

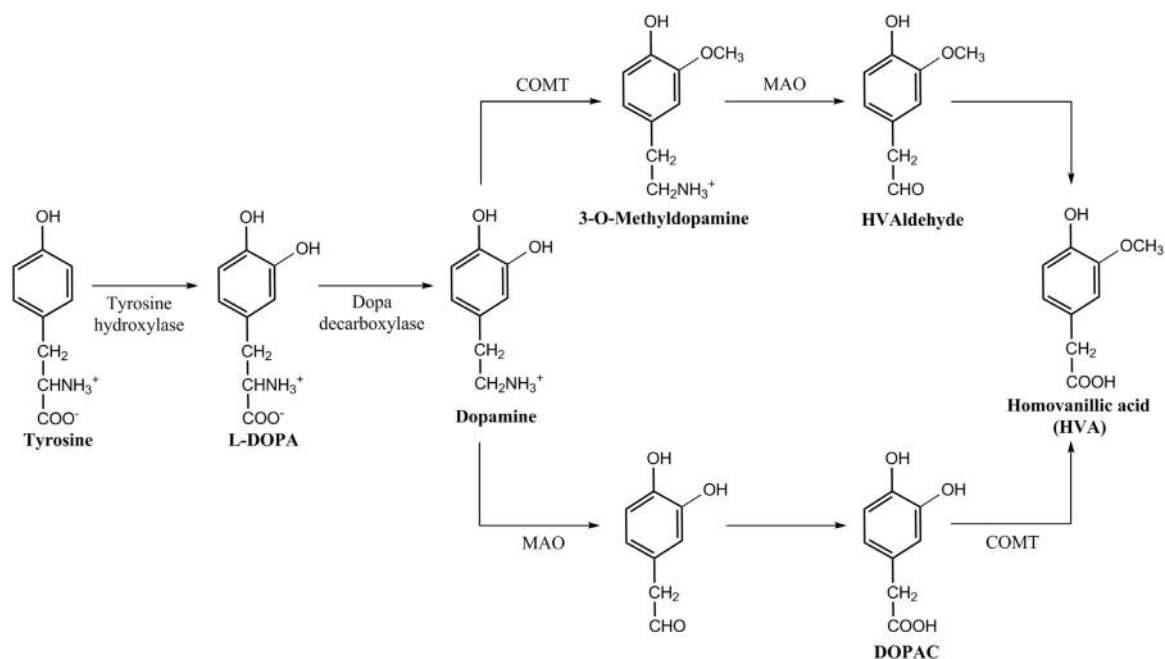


Fig. 2. Synthesis and metabolism of DA. L-DOPA: L-dihydroxyphenylalanine; MAO: monoamine oxidase; COMT: catechol-O-methyltransferase; DOPAC: 3,4-dihydroxyphenylacetic acid; HVA: homovanillic acid.

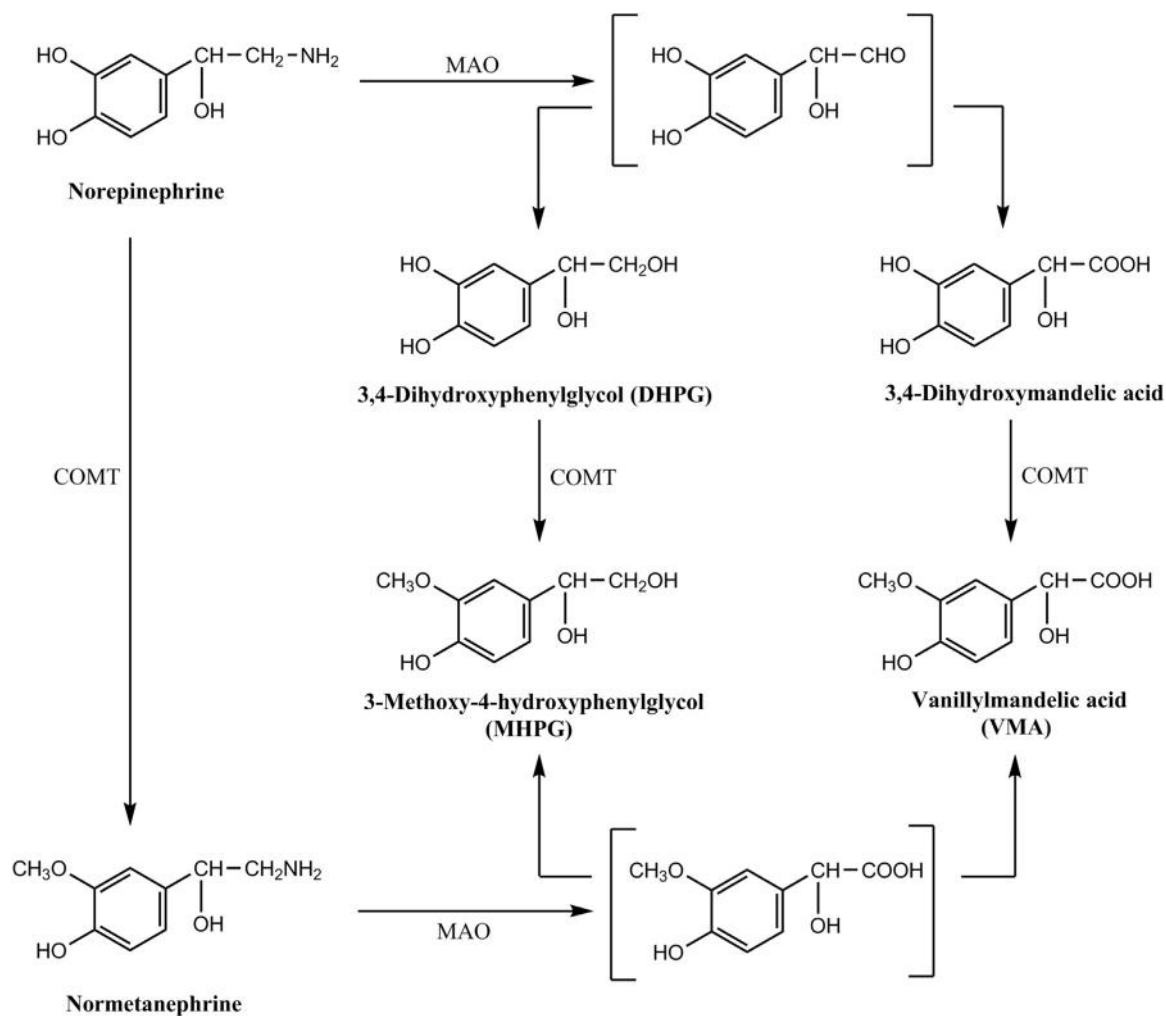


Fig. 3. Pathways of NA degradation. Unstable glycol aldehydes are shown in brackets. MAO: monoamine oxidase; COMT: catechol-O-methyltransferase; VMA: vanillylmandelic acid.

Actually, many researchers are interested in the function and measurement of catecholamine NTs as they have the potential to serve as clinically relevant biomarkers for specific disease states or to monitor treatment efficacy. NTs are present throughout the body and measurements of catecholamine concentration levels can be performed in various biological fluids, including serum, plasma, platelets, cerebral spinal fluid, saliva and urine [8]. For example, researchers concluded that the measurement of urinary catecholamines and their metabolites might be a biomarker for evaluating the status of the dopaminergic nigrostriatal system of the brain in Parkinsonism. Similarly, compared with controls, depressed patients had significantly higher levels of urinary NA along with ADR and their metabolites [8].

2. The electrochemistry of catecholamines

A wide range of analytical approaches, from spectrophotometry [9–11], Fourier transform infrared (FTIR) [12], Raman [13], chromatography [14–16], fluorescence [17,18], flow injection [19] to capillary electrophoresis [20] has been reported for catecholamine detection. Although these methods can offer good selectivity and low limits of detection (LODs), they often require complex pre-treatment steps and expensive instrumentations. On the other hand, electrochemical sensors provide an inexpensive and easily operable analytical tool for the sensitive, rapid and selective determination of catecholamines, while remaining inexpensive. Additionally, these sensors are capable of being incorporated into robust, portable, or miniaturized devices for targeted applications in clinical and diagnostic fields as biomarkers of several diseases, such as Alzheimer's disease and Parkinson's disease.

One of the first electrochemical studies involving catecholamines was reported by Ralph Adams and his team [21] at the University of Kansas in 1967, where the oxidation mechanism of some NTs, including DA, NA and ADR, was studied as a function of pH. The authors concluded that catecholamines present different electrochemical behavior depending on the pH and identified the intermediates formed in the electrochemical and chemical oxidation steps of these neurochemicals [21]. Ralph Adams was also credited with being the first to implant a carbon microelectrode into the brain of a rat with the objective of measuring the *in vivo* concentration of catecholamine NTs and their metabolites in the extracellular fluid [22,23]. The oxidation mechanism of catecholamines in physiological media (pH 7.4) is shown in Fig. 4 where each catecholamine reacted to form the corresponding ortho-quinone followed by the loss of two electrons.

The brain is a challenging environment for chemical sensing because low concentrations of analytes must be detected in the presence of interferences. Many other electrochemically detectable substances coexist with the catecholamines in the organism, such as catecholamine metabolites, other NTs (such as serotonin), uric acid (UA) and ascorbic acid (AA), among others. The ascorbate anion is a particularly interesting neurochemical.

Ascorbate (vitamin C) is a vital antioxidant molecule in the brain. Levels of ascorbate in the brain range from 200 to 400 μM in cerebrospinal fluid and from 2 to 10 mM in the brain, making it

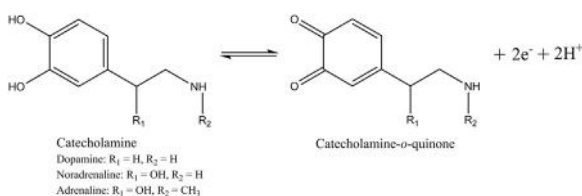


Fig. 4. Oxidation mechanism of catecholamines.

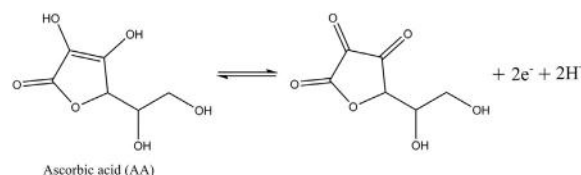


Fig. 5. Oxidation mechanism of ascorbic acid (AA).

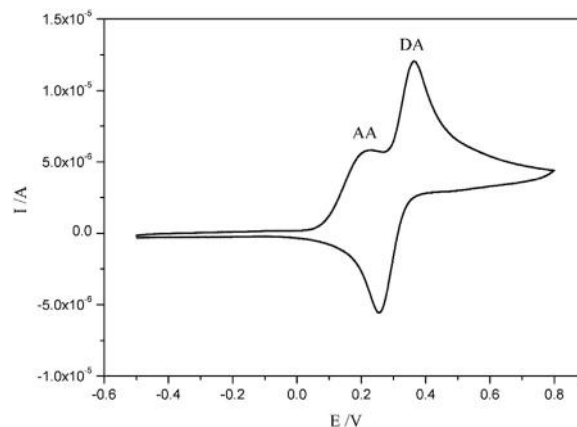


Fig. 6. CV obtained at bare Au electrode in the presence of 0.8 mM equimolar concentrations of DA and AA at pH 4.

one of the most prevalent molecules in the brain [23,24]. The oxidation reaction of AA is represented in Fig. 5.

AA is easily oxidized at the potentials close to those required for the oxidation of catecholamines at bare electrodes, as shown in the voltammogram of equimolar concentration of DA and AA at a bare Au electrode depicted in Fig. 6. Since AA usually co-exists with catecholamines in large excess, its oxidation currents dominates the electrochemical signal. Moreover, the oxidized catecholamine can catalyze the oxidation of AA, which results in the generation of a single, broad peak for both analytes [25,26]. The detection of catecholamines in the presence of ascorbate (and urate) is one of the early selectivity challenges in the determination of these NTs, which led to the development of various strategies for detection of catecholamines tabulated in Tables 1–7.

Another critical problem associated with the detection of catecholamines is the passivation of the electrode surface due the polymerization of the oxidation products of catecholamines [25,27]. The oxidized catecholamine can undergo subsequent chemical and electrochemical reactions producing a melanin-type polymer film on the electrode surface. This phenomenon is shown

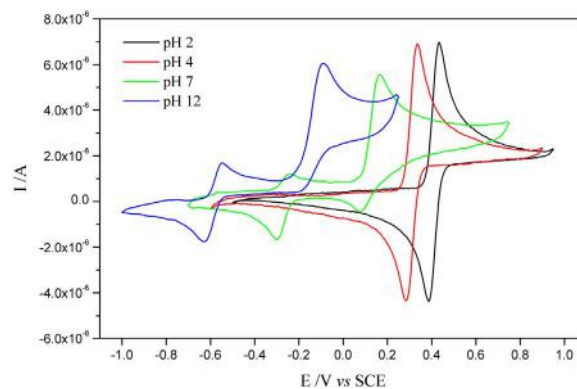
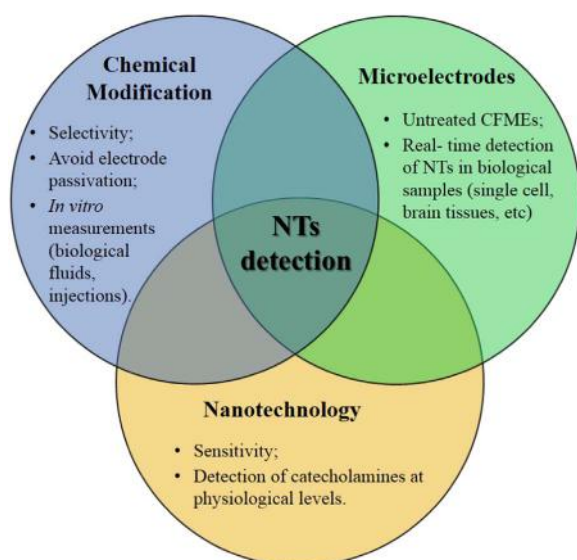


Fig. 7. CVs obtained at bare Au electrode in the presence of 0.5 mM of DA at pH 2 (black), pH 4 (red), pH 7 (green) and pH 12 (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 1. Main research strategies adopted by investigators over the years for the detection of catecholamine NTs.

in Fig. 7 for DA. In this figure, the voltammograms recorded at pH 2 and pH 4 show a reversible oxidation of DA while an alteration to the oxidation mechanism of DA can be observed in the CVs obtained at pH 7 and pH 12 due to the formation of a dopamine polymer at the electrode surface, resulting in rather poor selectivity and reproducibility (electrode poisoning or fouling).

To overcome some of the problems associated with the electroanalytical detection of catecholamines, chemical modification of the electrode surfaces was reported to alter the electrode kinetics of target species and/or the interfering species, so that the target species is oxidized at a potential less affected by that required to electrolyze the interfering species (Tables 1–7). The electrode surface treatment was also used to inhibit the polymerization of phenolic oxidation products and avoid electrode passivation (Tables 1–7).

Since the early works in the 60s of the last century, numerous works have emerged in the literature reporting the fabrication of electrochemical sensors for catecholamines determination. Based on work we have reviewed, three main strategies, summarized in Scheme 1, have been exploited by scientists to develop the analytical devices. Most of the pioneer studies were mainly based on simple/elementary modification of conventional electrode surfaces by thin films (SAMs, polymers coatings, etc.) to avoid surface passivation and to minimize interfering signals from co-existing species in biological samples (mainly AA). At same time, miniaturized electrodes, mainly untreated CFMEs, were developed and began to succeed as an important tool in biomedical research for real-time detection of catecholamines *in vivo* and *in vitro* in biological systems (single cells, slices of brain tissues, free moving/anesthetized rats, etc.). More recently, the innovative features of nanomaterials give rise to a new class electrochemical sensors and biosensors with improved analytical sensitivity. The incorporation of nanomaterials (metal NPs, CNTs, GR, among others) on sensor devices allowed the determination of catecholamines NTs at physiological levels. Most of the performance of the electrochemical sensors was evaluated *in vitro*, mainly in biological fluids and injection samples.

Electroanalytical approaches and progress achieved for the selective detection of DA was reviewed, in 2010, by Compton et al. [28] and more recently, in 2013, by Jackowska and Krysinski [29]. However, none of these papers included the electrochemical determination NA and Adr. Also in 2013, the use of carbon

nanomaterials for the electroanalytical detection for the biogenic amines, including DA, Adr and NA, was reviewed by Yang et al. [30]. Although the work focused on carbon-based materials is very elucidative and complete in this specific area, the use of other electrochemical strategies for the detection of biogenic amines was not discussed.

In this work we attempt to provide more information on electrochemical devices applied to the detection of the important NTs including DA, NA and Adr. However, considering the wide and diverse range of chemically modified electrodes hitherto developed, we have limited this review to reported significant contributions to the field since 2000. Accordingly, the following sections were organized based on different electrochemical approaches involving similar electrode chemical modification to catecholamine detection.

3. Electrochemical sensors based on polymer films

3.1. The importance of Nafion®

One of the major breakthroughs in the development of selective electrochemical techniques was carbon electrodes coated with a polymeric material, Nafion®, in the 1880s [31]. Nafion® consists of a tetrafluoroethylene main chain with perfluoroether side chains terminated with a sulfonic acid group whose ionization yields an anionic Nafion® membrane [31]. The incorporation of Nafion® polymeric membrane in electrochemical devices has several advantages. For example, Nafion® coated sensors increase the selectivity in the determination of catecholamines (pK_a : 8.4–8.9) that exist as cationic species in physiological pH and proven to be very effective in minimizing the effect of some endogenous interferents (ascorbate, urate, etc.) [32,33]. These sensors were also used to avoid electrode passivation and to enhance the surface biocompatibility during *in vivo* and *in vitro* experiments [32,33].

As shown in Table 1, several studies have been reported in the literature using electrodes modified with Nafion® for the determination of catecholamines at physiological pH, in the presence of endogenous interferents (mainly AA and UA). The use of Nafion® coating together with other polymers or incorporating nanomaterials with electrocatalytic properties (metal NPs or CNTs, for example) to increase the selectivity and sensitivity of the determination was also reported in the literature.

However, there were several limitations commonly associated with ion-exchange membranes coated electrodes such as difficulties in the control of film thickness, poor reproducibility arisen from the solvent evaporation method, slow response due to low diffusion coefficients of analytes through the film coating and problems related to memory effects caused by the strong affinity between cations and the membranes. In addition, electrodes modified with ion-exchange membranes cannot be used to simultaneously determine catecholamines and AA (or UA) at physiological pH since the membrane is selective to cations.

Following the introduction of Nafion®, a large variety of new polymers has emerged with many applications in electroanalytical chemistry aiming to overcoming some of the abovementioned limitations.

3.2. The large variety of polymers

The unique electrochemical properties of polymers have attracted considerable interest in the development of electrochemical sensors for catecholamines. Table 2 summarises examples of work in which conducting and non-conducting polymer modified electrodes were applied to the determination of the amine NTs.

Table 1List of works reported in literature for the determination of catecholamines using electrodes modified with Nafion[®].

| Catecholamine | Interferents | Electrode | Modifying agent | LOD ^a /μM | Refs. |
|---------------|-----------------------|------------------|---|--------------------------|---------|
| DA | NR/AA, UA | GC | Nafion [®] | 0.08/1 | [34,35] |
| DA | AA | CPE | Carbon-PVC/Nafion [®] composite | NR | [36] |
| DA | AA, UA, glu | Carbon SPE | Pre-treated graphite/Nafion [®] composite | 0.023 | [37] |
| DA | AA | CPE | Clinoptilolite/Nafion [®] | 0.01 | [38] |
| NA | AA | Au | C60-[dimethyl-(β-cyclodextrin)] ₂ /Nafion [®] | 0.08 | [39] |
| DA | AA | GC | Adr film/Nafion [®] | NR | [40] |
| DA, NA, Adr | AA | GC | Nordihydroguaiaretic acid/Nafion [®] | NR | [41] |
| Adr | AA | GC | MnO ₂ /Nafion [®] | 0.005 | [42] |
| DA, 5-HT | AA, UA | GC | Nafion [®] /nanostructured Pt | 0.01, NR | [43] |
| DA | AA | Au/Si substrates | Dendritic Au rod surface with Nafion [®] layer | 0.1 | [44] |
| DA | AA, UA | GC | CNTs-Nafion [®] film | 0.0025 | [45] |
| DA | AA | GC | Fc functionalized CNTs/Nafion [®] | 0.3 | [46] |
| DA, 5-HT | AA, UA, DOPAC, others | GC | Ni(OH) ₂ NPs-MWCNTs composite/Nafion [®] | <u>0.015</u> , 0.003 | [47] |
| DA | AA, UA | GC | CuO-MWCNTs-Nafion [®] nanocomposite | 0.4 | [48] |
| DA | AA, UA | ITO coated PET | Nafion [®] -MWCNTs composite ink | 0.2 | [49] |
| DA | AA | Au | Poly(anilineboronic acid)-ssDNA-SWCNT nanocomposite/Nafion [®] | 0.000016 | [50] |
| DA, UA, TRP | Tyr, cys, glu | F-doped SnO | Ruthenium red dye-MWCNTs-Nafion [®] | <u>0.15</u> , 0.14, 0.14 | [51] |

PVC: polyvinyl chloride; CD: cyclodextrin; Fc: ferrocene; TRP: tryptophan; NR: not reported.

^a In case of simultaneous determination the LOD value corresponding to the catecholamine is underlined.**Table 2**

List of works reported in literature for the determination of catecholamines using electrodes modified with polymers.

| Catecholamine | Interferents | Electrode | Modifying agent | LOD ^a /μM | Refs. |
|--------------------------------------|-------------------------------------|-----------|---|---------------------------------|---------|
| DA/Adr/DA | AA, UA/AA, UA/AA | Au, GC | Dopamine polymer | 0.2/0.3/0.04 | [63–65] |
| NA, UA | Metal ions, starch, lactose, others | GC | Poly(5-HT) | <u>0.6</u> , 0.5 | [66] |
| DA, Adr | AA, glu, gly, others | GC | Poly(serine) | 0.3, 0.1 | [67] |
| NA | AA | GC | Poly(isonicotinic acid) | 0.006 | [68] |
| DA, AA, UA | | Au, Pt ME | PEDOT | <u>0.1</u> , 0.2, 0.05 | [69] |
| DA | AA, UA | Pt | PEDOT/poly(DA) hybrid film | 0.65 | [70] |
| DA, AA, UA | AA, UA | GC | Poly(eriochrome black T) | <u>0.02</u> , 10, 1.0 | [71] |
| DA, Adr | AA | GC | Poly(luminol) | NR | [72] |
| DA, Adr/Adr | AA, UA | GC | Poly(cafeic acid) | 0.2, 0.1/ <u>0.2</u> , 7.0, 0.6 | [73,74] |
| NA, AA, UA | | GC | Poly(calconcarboxylic acid) | <u>0.1</u> , 0.5, 0.5 | [75] |
| DA, AA | | GC | Poly(malachite green) | <u>0.03</u> , 0.16/NR | [76,77] |
| DA, AA, UA | | GC | PVA | <u>1.4</u> , 7.6, 0.6, | [78] |
| DA | AA | GC | Poly(N,N-dimethylaniline) | 0.2 | [79] |
| DA | AA | GC | Poly(hippuric acid) | 0.01 | [80] |
| NA | AA, UA | GC | Ulathrin polymer of 2-amino-1,3,4-thiadiazole | 0.0017 | [81] |
| DA/DA, Glu | AA/AA, DOPAC | GC | Melanin-type polymer | 0.05/ <u>0.05</u> , 143 | [82,83] |
| DA, AA | | CPE | Ppy/ferrocyanide | <u>0.151</u> , 0.134 | [84] |
| DA | AA | GC | Poly(1-naphthylamine) | NR | [85] |
| DA, AA, UA | Metal ions, cys, glu, others | GC | Poly(4-aminobutyric acid) | <u>1.0</u> , 5.0, 0.5 | [86] |
| DA | AA | GC | Ni(II) complex polymer | 0.15 | [87] |
| Adr, AP | | GC | Poly(curcumin) | <u>0.05</u> , 0.1 | [88] |
| DA | AA, NO ₂ ⁻ | GC | Poly(benzophenone-4) | NR | [89] |
| DA, 5-HT, AA | | GC | Poly(phenosafranine) | <u>0.02</u> , 0.02, 0.01 | [90] |
| DA | AA, UA | Au | Ni hexacyanoferrate/poly(1-naphthol) hybrid film | 0.021 | [91] |
| DA, AA | | GC | Poly(acriflavine) | 1.5 | [92] |
| DA | AA | GC | Poly(p-aminobenzene sulfonic acid) | 0.02 | [93] |
| NA, 5-HT | AA, UA | GC | Eriochrome Cyanine R polymer film | <u>1.5</u> , 0.05 | [94] |
| DA | AA | CFME | Poly(1,2-phenylenediamine) | 0.01 | [95] |
| DA | | GC | Lithium tetracyanoethylenide/poly(1-lysine) | 0.0005 | [96] |
| Adr, AA, UA | | GC | PBCACP | <u>0.03</u> , 0.4, 0.009 | [97] |
| DA | AA, UA, Adr, NA, DOPAC | GC | Poly(tyramine) and poly(pyrrole-1-propionic acid) | 0.1 | [98] |
| Adr, AA, UA | | GC | Oxerodized poly(p-aminophenol) | <u>0.0065</u> , 1, 0.018 | [99] |
| DA | AA, UA | GC | Poly(4-(2-pyridylazo)-resorcinol) | 0.2 | [100] |
| DA | AA, UA | CPE | Poly(solochrome dark blue) | 0.8 | [101] |
| DA | AA | GC | Poly(p-toluene sulfonic acid) | 0.6 | [102] |
| DA, UA, NO ₂ ⁻ | AA, cys, valine, metal ions, others | GC | Thiazole-based copolymer film | <u>0.2</u> , 0.25, 0.5 | [103] |
| DA | AA | GC | Poly(sulfosalicylic acid) | 0.005 | [104] |
| DA | AA, UA | GC | Poly(chromotrope 2B) | 0.3 | [105] |
| DA, AA, UA | | GC | Oracet blue | <u>0.02</u> , 1.3, 0.4 | [106] |
| DA, UA, NO ₂ ⁻ | Glu, cys, AA, others | GC | Poly(2-mercaptobenzothiazole) | <u>0.05</u> , 0.1, 0.30 | [107] |

PEDOT: poly(3,4-ethylenedioxythiophene); PVA: poly(vinyl alcohol); Ppy: poly(pyrrole); AP: p-acetoaminophenol; PBCACP: poly(3,3'-bis[N,N-bis(carboxymethyl)amino-methyl]-o-cresolsulfonaphthalein); NR: not reported.

^a In case of simultaneous determination the LOD value corresponding to the catecholamine is underlined.

The most frequently selected procedure used for the deposition of polymer films was by electropolymerization under galvanostatic, potentiostatic, or most commonly potentiodynamic conditions. Electropolymerization of polymers has several advantages, including the easy preparation of uniform films with well controlled thickness on the electrode surfaces [52,53], offers high physical and chemical stability due to the strong adhesion of the films to the active surface of the electrodes, and polymers are considered a very effective substrate for biomaterial immobilization [52,53]. For example, cyclodextrins were incorporated into poly(3-methylthiophene) [54] and carboxymethylated polymeric matrices [55] to increase the selectivity of the electrochemical sensors for DA determination in the presence of AA.

The use of electropolymerized layers for the detection of catecholamines is based on the diffusion of the analyte to the electrode surface and several studies demonstrated the efficiency of the polymeric films of organic acids for the determination of the NTs in the presence of AA, as the interference of ascorbate is eliminated by electrostatic repulsion.

It is important to note the application of molecularly imprinted polymer (MIP) materials to the electrochemical sensors field. Electrosynthesized MIPs were prepared on different electrodes surfaces using poly(pyrrole) (Ppy) [56,57], Ppy-phenylboronic acid [58], poly [59,59], bis(2,2'-bithienyl)methane derivatives [60] and poly(o-aminophenol) [61,62] for the selective determination of catecholamines against structural analogs and coexisting interferences in biological samples.

4. Electrochemical sensors based on SAMs

The heterogeneous structure of polymers usually show a wide variation of molecular weights, making it difficult to control the functions and properties of the modifying layer at the molecular level [108]. One alternative that has been widely exploited in recent decades is the formation of SAMs on oxide-free metals, especially gold (Au) surfaces. In electroanalytical chemistry, Au polycrystalline electrodes modified by SAMs functionalized with a mercapto group (SH) provide a powerful method for the preparation of interfaces with high chemical stability. Furthermore, the monolayers show a high degree of orientation and packing, molecular organization and coverage of the Au surfaces [109,110].

SAMs can also be the base for the design and construction of complex structures for use in electrochemical sensors devices. The simple functionalization of the SAMs or the use of mixtures of

SAMs allows the immobilization of NPs, cells, proteins, DNA and other biomolecules, providing a powerful tool for the determination of organic species of biological, clinical and environmental interest [111].

Malem and Madler were the first to highlight the use of SAMs of mercaptocarboxylic acids for the development of an electrochemical sensor for the determination of DA in the presence of AA [112]. The double function of the negatively charged terminal carboxylic acid groups of the SAMs were used to define the structure and stability of the molecular packing in the electrodes and inhibit the activity of AA by electrostatic repulsion.

The use of Au surfaces modified with SAMs, mainly composed of mercaptocarboxylic acids or aminoacids, for the determination of catecholamines in the presence of several biological endogenous interferents are summarized in Table 3.

In the same manner, carbon electrodes modified by covalent binding of amino acids [113–116] were used for the determination of DA, which in addition to catalysing the oxidation of the biogenic amines, eliminate the interference of AA by electrostatic interaction. Recently, 4-pentenoic acid was used as a photochemical modifying agent for the fabrication of a carboxyl-terminated monolayer on a BDD electrode [117], which was used for the detection of DA in the presence of AA.

Other strategies used for detection of the NTs were based on the immobilization of biomolecules with electrocatalytic properties, such as quercetin [118], peroxidase enzyme [119], and metal-complexes [120,121], on SAM-modified electrodes in order to increase the sensitivity and selectivity of the detection. Moreover, thiolated cyclodextrins [122] and calixarenes [123] Au modified electrodes were used for the selective detection of DA due to the specific recognition of the ligands present at the electrode surface.

Although electrochemical sensors based on monolayers show good selectivity and sensibility, they are mainly based on electrostatic interactions and, therefore, pre-concentration of the catecholamine needs to be done before measurements, which can be regarded as a limitation from the analytical point of view.

5. DNA biosensors for catecholamine detection

During the last decades, there was an emerging focus on the use of nucleic acids as a tool for recognition and motoring of many compounds of analytical interest [139]. DNA is a biomacromolecule with a double helix structure with high charge density, has conductive properties, can be easily doped with electrocatalytic

Table 3

List of works reported in literature for the determination of catecholamines using electrodes modified with SAMs.

| Catecholamine | Interferents | Electrode | Modifying agent | LOD (or Sensitivity) ^a /μM (or μA μM ⁻¹) | Refs. |
|---------------|--------------|-----------|---|---|-----------|
| DA/Adr | AA | Au | L-cysteine | 0.02/0.01 | [124,125] |
| Adr | AA | Au | Homocysteine | 0.1 | [126] |
| DA | AA | Au | N-acetylcysteine | 0.8 | [127] |
| DA | AA | Au | 3,3'-dithiodipropionic acid | (0.098) | [128] |
| Adr | AA | Au | HMTMBH | 0.29 | [129] |
| DA | AA | Au | 3-mercaptopropylphosphonic acid | 0.15 | [130] |
| Adr | AA | Au | 3-amino-5-mercaptopropyl-1,2,4-triazole | 0.01 | [131] |
| Adr, UA | | Au | 2-(2,3-dihydroxy phenyl)-1,3-dithiane | 0.51, 9.0 | [132] |
| DA | AA | Au | N,N'-[1,1'-dithio(phenyl)]bis(salicylaldehyde) | 0.03 | [133] |
| DA | AA | Au | Mercaptopropionic acid | NR | [134] |
| DA | AA | Au ME | 3-mercaptopropionic acid (FIA) | 0.074 | [135] |
| DA, AA | | Au | In-situ functionalized 4-aminothiophenol | 1.2, 2.4 | [136] |
| Adr, UA | | Au | 4-nitrothiophenol/4-mercaptopropionic acid binary SAM | 0.037, 0.5 | [137] |
| DA, AA | | Au | 2,2'-dithiobisethaneamine and 6,6'-dithiobisethaneamine | 0.5, 0.3 | [138] |

HMTMBH: 2-Hydroxy-N'-1-[(E)-1-(3-methyl-2-thienyl)methylidene]benzohydrazide; NR: not reported.

^a In case of simultaneous determination the LOD/Sensitivity value corresponding to the catecholamine is underlined. When LOD is not reported the Sensitivity is shown in brackets.

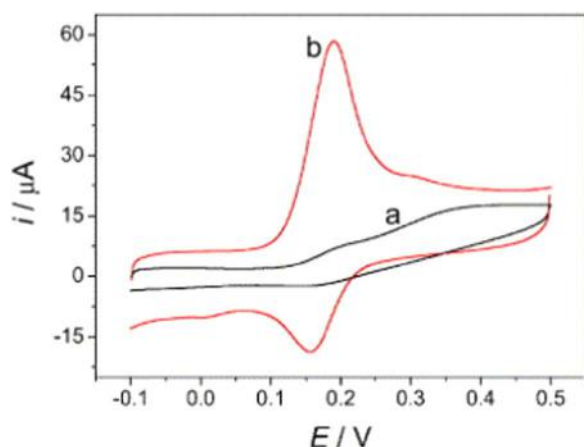


Fig. 8. Cyclic voltammograms of 20 μM NA at 50 mV/s at bare GC electrode (a); Au NPs/DNA/GC electrode (b). Figure from reference [152].

materials and has an enormous capacity to complex with a wide variety of small molecules [140,141]. For these reasons, electrochemical DNA sensors have been widely used to study the interaction of drugs with DNA [142,143], DNA hybridization [144] and detection of molecules of chemical and biological interest [139,145,146].

Lin et al. had made an important contribution to the development of DNA biosensors for the detection of catecholamines. In their electrochemical studies, DNA [147] and RNA [148] were respectively electrodeposited on carbon electrodes for the determination of DA in the presence of AA. Furthermore, the same research group also used conducting polymers [149–151] as a basis for incorporation of DNA for the simultaneous determination of DA and 5-HT [149], DA and Adr [150] and DA and UA [151]. Most significantly, Lin et al. [152], reported the application of multilayer films containing DNA doped with Au-NPs to the selective determination of NA in the presence of AA. Fig. 8 shows the CVs of NA on the Au NPs/DNA/GC electrode (Fig. 8b) and at the corresponding bare GC electrode (Fig. 8a). NA only shows a broad small anodic peak (0.40 V) at GC electrode but a sharp anodic peak (0.19 V) with an increase of about 10 times in the peak current was obtained at the modified electrode. The DNA layer provided a specific template for the electrocatalytic Au NPs deposition and also a selective surface matrix for NA accumulation, resulting in a strong catalytic activity towards the oxidation of the catecholamine. The layer-by-layer electrode successfully distinguishes the voltammetric signal of AA and NA, which are indistinguishable at the bare electrode. A LOD of 5 nM NA was obtained by using DPV technique.

Recently, a DNA-octadecylamine Langmuir–Blodgett film was attached to the surface of a GC electrode to prepare a novel voltammetric sensor for Adr, in the presence of AA and UA [153]. The combination of the features of DNA and carbon nanomaterials was also employed for the sensitive detection of catecholamines. An Au electrode modified with a bio-composite film containing a multi-walled carbon nanotube (MWCNT)-chitosan/poly(amidoamine) nanocomposite that was then attached with DNA was used as a biosensor to determine DA and UA in the presence of AA [154]. Furthermore, a DNA and graphene (GR) bi-layer modified carbon ionic liquid electrode (CILE) was fabricated for the determination of DA, in the presence of excess AA [155]. The presence of DNA and GR on the CILE surface largely enhanced the electron transfer rate with accumulation effect. The proposed method was further applied to the DA determination in injection solution and human urine samples.

6. Nanotechnology applied to the electrochemical sensing of catecholamines

The development of new synthetic methods in nanotechnology over the last decades allowed the production of uniform nanostructures with size between 1 and 100 nm, with different shapes (spheres, rods, wires, cubes, etc.) and different composition (organic, metallic or semiconducting oxide) [156]. Some of these nanomaterials, such as nanocrystals, nanowires, metal NPs and CNTs have found applications in several different areas, such as catalysts in materials science, as controlled release drug systems in medicine, in optical and electronic devices, batteries, capacitors, among other applications [156–159].

Recent reviews have highlighted the unique physicochemical properties of NPs [160–162], CNTs [30,163–165] and GR [30,166,167] to the design of a new generation of electrochemical sensors with controlled and optimized properties for the detection of many molecules of chemical and biological interest. Some of the features that these nanomaterials give to the electrochemical sensors include high active surface area (due to high surface-to-volume ratio), high electrocatalytic activity, improved signal-to-noise ratio, improved selectivity and fast mass transport. Enhanced convergent mass transport rather than linear diffusion to nanoelectrodes facilitates the study of faster electrochemical processes. The use of nanomaterials also provides control over the local microenvironment which is highly advantageous for incorporating sensitive or biological material (enzymes, proteins, etc.) into the electrochemical system.

6.1. Application of NPs in electrochemical sensors for catecholamines

In recent years, NPs of noble metals and metal oxide NPs have received considerable attention in electroanalysis because of their unique physical and chemical properties. The main advantage of the use of NPs is that the superstructures give rise to porous, high-surface area electrodes and, thus, improves the electrochemical catalytic oxidation of catecholamines.

In general, there were several reports on the immobilization of Au NPs on carbon and Au electrodes previously modified with SH-terminated monolayers (covalent immobilization) [168–174] or monolayers containing positively charged amine polar head groups (electrostatic interaction) [175,176]. The modified electrodes were then applied as electrochemical sensors for the determination of catecholamines, in the presence of several interferents (mainly AA). For example, the catalytic properties of Au NPs immobilized on a mixed SAMs (dithiothreitol + dodecanethiol) Au electrode were used for Adr detection under physiological conditions [177]. Interestingly, a well-defined redox wave of Adr was observed at the nano-Au electrode due to the excellent catalytic activity of nano-sized Au particles, which increased the voltammetric peak current and decreased the overpotential needed for the redox reaction to become kinetically viable. A LOD of 6.0×10^{-8} M was achieved using CV technique.

Besides the immobilization of NPs with the help of organized layers, other methodologies have been used for attaching NPs on an electrode surface including the use of polymers, as described in works summarized in Table 4. Several of these studies demonstrate that NPs were capable of resolving overlapped catecholamine, AA and UA peaks into three well-defined peaks.

Although Au NP superstructures were extensively used, other metal and metal oxide NPs (Cu, Pd and CuO, etc.) were also used in the development of new electrochemical devices to catecholamines sensing (see Table 4). The NPs were prepared mainly through reduction reaction in an aqueous solution, by metal vapor synthesis routes or by electrochemical depositions on inert bases.

Recently, in 2012, Oztekin et al. [178] reported the application

Table 4

List of works reported in literature for the determination of catecholamines using electrodes modified with of metal and metal oxide NPs.

| Catecholamine | Interferents | Electrode | Modifying agent | LOD ^a /μM | Refs. |
|--------------------|--|-----------------|---|------------------------------|-----------|
| DA, 5-HT/DA | AA/AA, UA | ITO | Au NPs | 0.0005, 0.0003/34.50 | [185,186] |
| DA, AA | | ITO | Au NPs and Au nanoplates | NR | [187] |
| Adr, NA, DA | AA | CG, ITO | Pd NPs | NR | [188] |
| DA | | CPE | Carbon NPs | NR | [189] |
| DA | AA | CPE | CuO NPs | 0.055 | [190] |
| DA, AA, UA | | GC | MgO nanostructures | 0.05, 0.2, 0.04 | [191] |
| NA, AC, folic acid | | CPE | ZrO ₂ NPs | 0.0895, 0.912, 9.86 | [192] |
| DA, UA, AA | | GC | LaFeO ₃ NPs | 0.030 | [193] |
| DA | AA, UA | CPE | Mesoporous silica NPs | 0.1 | [194] |
| DA, AA | | CPE | Cobalt phthalocyanine NPs | 1.0, 1.7 | [195] |
| DA | | PE | Cu-iron hexacyanoferrate nanodispersion | 0.05 | [196] |
| DA | UA, metal ions, AA, others | GC | Ni-doped V ₂ O ₅ NPs | 0.028 | [197] |
| DA | AA | Au | Magnetic Fe ₃ O ₄ NPs | 0.030 | [198] |
| NA | AA, DA, metal ions, others | GC | Carbon-coated Ni magnetic NPs | 0.060 | [199] |
| DA | AA | GC | Au NPs-decorated MoS ₂ nanocomposite | 0.080 | [200] |
| DA, AA, UA | | CPE | Pd NPs-loaded carbon nanofibers nanocomposites | 0.2, 15, 0.7 | [201] |
| DA | AA, UA, AC | ITO | Phenylsulphonated carbon NPs/functionalized silicate particles | 0.1 | [202] |
| NA, tyr, nicotine | DA, Adr, AA, UA, others | PE | ZnO nanorods and acrylic acid derivative mediator | 0.039, NR, NR | [203] |
| DA, AA | | GC | Poly(4-aminothiophenol-β-CD)/Au NPs | NR | [204] |
| DA, UA, G, AA | | GC | Poly(safranin T)/Au NPs/DNA/Au NPs | 0.0002, 0.008, 0.0005, 0.004 | [205] |
| DA | AA, UA | Au | PEDOT/Au NPs (in the presence of SDS) | 0.00039 | [206] |
| DA, AA, UA, TRP | Metal ions, levodopa, others | GC | Overoxidized poly(imidazole)/Au NPs | 0.08, 2.0, 0.5, 0.7 | [207] |
| DA | AA, UA, Adr, others | Pt | Doped Ppy/Ag NPs | 0.0005 | [208] |
| DA, UA | AA | GC | Overoxidized PPy/Cu NPs | 0.00085, 0.00018 | [209] |
| NA, AC, tyr | DA, Adr, Glu, others | GC | Poly(trisamine)/Au NPs | 0.07, 0.1, 0.9 | [210] |
| DA, AA, UA | Glu, cys, metals ions, others | GC | Cu NPs-poly(sulfonazo III) composite film | 0.01, 0.15, 0.10 | [211] |
| DA | | BDD | PAH/(PSS/PAH) _n /(Au NPs/PAH) _m /Au NPs | 0.6 | [212] |
| DA | | ITO | (PAH/iron phthalocyanine/Ag NPs) _n | 0.86 | [213] |
| DA | AA | ITO | Carbon NPs/poly(diallyldimethylammonium chloride) | 0.05 | [214] |
| DA, AA | Glu, UA, cys, CH ₃ OH, others | Quartz, Si, ITO | Poly(ethylenimine)/P ₂ W ₁₆ V ₂ -Au-Pd alloy NPs | 0.83, 0.43 | [215] |
| DA | AA, Adr, cys, glu, NA, others | Au | MBA/Fc-capped Au NPs-streptavidin conjugates | 0.2 | [216] |
| DA | | GC | Pt NPs-hydroxyl-terminated PAMAM dendrimers composites | 0.0001 | [217] |

G: guanine; A: adenine; AC: acetaminophen; PEDOT: poly(3,4-ethylenedioxythiophene); SDS: sodium dodecyl sulfate; TRP: tryptophan; PPy: poly(pyrrole); PAH: poly(allylamine hydrochloride); PSS: poly(sodium 4-styrene-sulfonate); MBA: 4-mercaptophenylboronic acid; Fc: ferrocene; PAMAM: poly(amido amine); NR: not reported.

^a In case of simultaneous determination the LOD value corresponding to the catecholamine is underlined.

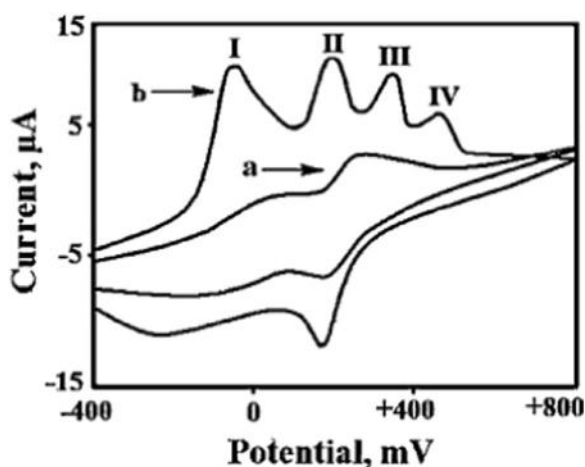


Fig. 9. CVs of 1.0 μM DA in the presence of 100 μM of interfering substances (AA, UA and p-acetamidophenol) in PBS, pH 2.0, performed by bare GC (a) and Cu NPs/GC (b) electrodes. Potential sweep rate was 100 mV/s vs Ag/AgCl/KCl_{sat}; redox peaks of (I) AA, (II) DA, (III) p-acetamidophenol, and (IV) UA. Figure from reference [178].

of a Cu NP-modified GC electrode for the selective determination of DA in the presence of AA, UA and p-acetamidophenol. As shown in Fig. 9, the modification of the electrode surface with Cu NPs (Fig. 9b) resolved the problem related to the merging of voltammetric peaks observed at the bare electrode surface (Fig. 9a). Well-defined voltammetric peaks at potentials around −48, +205,

+372 and +485 mV were observed for AA (I), DA (II), p-acetamidophenol (III) and UA (IV), respectively, at the Cu NPs/GC electrode. In addition, Cu NPs considerably increased the electro-oxidation rate of DA and interferents and the lowest LOD obtained was found to be 0.05 nM. The electrochemical sensor based on Cu NPs was successfully applied for the determination of DA concentration in human serum samples.

There were several works reports on the combined of NPs and MIPs to specifically and selectively interact with catecholamines. For example, Au [179] and Pd [180] NPs were incorporated in biocompatible porous sol-gel MIP-material for the selective detection of DA and NA, respectively, in the presence of other catecholamines and biological interferents. Recently, Xue et al. [181] reported the direct synthesis of functionalized Au NPs and their use as novel functional monomer to fabricate a conductive MIP film on Au electrode. DA was used as template molecule and *p*-aminobenzenethiol as a cross-linker. The modified electrode was employed for the sensitive (LOD of 7.8 nM) and selective detection of DA in the presence of AA and UA.

Several research groups demonstrated the incorporation of enzymes on an electrode surface to improve their catalytic activity. Detection systems containing NPs and enzymes together were applied to the sensitive determination of catecholamines. Electrode surfaces modified with peroxidase immobilized on PEGylated polyurethane NPs [182] and laccase immobilized on phytic acid functionalized silica NPs [183] were used for the detection of DA. In addition, Pt NPs dispersed in an ionic liquid and laccase was used as biosensor for the determination of Adr [184].

6.2. CNT based electrochemical sensors for catecholamines

Notably, CNTs and GR offer many advantages over other nanomaterials due to their excellent electrical and thermal conductivity and high mechanical strength that exceed those of any existing materials.

The first paper that demonstrated the use of CNTs for the detection of catecholamines was published by Britto et al. [218] in 1996. The CNT modified paste electrode increased the sensitivity for the determination of DA and showed nearly ideal, reversible kinetics, which is unusual for DA at carbon electrodes. After this pioneer study, a vast number of scientific publications was published over the last few years, demonstrating the significant developments that have taken place in the field of CNT-based electrochemical sensors.

Work reported by Macpherson et al. [219] has particularly highlighted the unique characteristics of CNTs as an electrode material for developing high performance electrochemical sensors for DA. Pristine SWCNTs were grown in a two dimensional network arrangement on an inert support that behaved as a macroscopic electrode with an unprecedented low background currents. The feature was found to be dependent on the area of SWCNTs. This has in turn facilitated the CV measurements of DA oxidation of 100 nM (solid black line) and 500 nM (dashed line) (Fig. 10a). For comparison, the CV response for 100 nM (solid black line), 1 μ M (dashed line), and 10 μ M (dotted line) DA at a GC electrode is shown in Fig. 10b). The GC electrode shows quasi-reversible electron transfer characteristics but this is only evident at concentrations greater than 1 μ M. In contrast, although the CVs for DA electrolysis at the pristine SWCNTs are electrochemically sluggish, a concentration of 100 nM can easily be measured. These CVs highlighted the promising nature of native SWCNTs in electroanalysis.

The electrode performance was found to be depend on the synthesis method of the nanotubes, modification of CNTs surface, the method of electrode attachment and the addition of electron mediators [30]. Therefore, CNT paste electrodes, CNTs directly deposited or grown on electrodes, polymer coatings containing CNTs and electrodes modified by combination of electrocatalyst nanomaterials/(bio)molecules were fabricated for the sensitive and selective determination of catecholamines. Reports on the use

of CNT modified electrodes for the determination of catecholamines, in the presence of several endogenous biological interferents, are summarized in Table 5. Recently, several types of magnetic CNTs have been synthesized by decorating CNTs with different magnetic nanoparticles in order to provide additional advantages (enhanced sensitivity, high signal-to-noise ratio, shorter time of analysis, etc.) to the electrochemical detection systems.

CNTs were functionalised to increase their sensitivity of catecholamines detection. For example, $-\text{COOH}$ groups [220,221], $-\text{OH}$ groups [221,222], boronic acid [223], benzofuran derivative [224] and poly(diallyldimethylammonium chloride) [225] were covalently attached to the sidewalls of CNTs, while surfactants, polymers, aromatic compounds or other biomolecules were non-covalently attached [226–228] before they were used in catecholamine NTs determination. The functionalised CNT surface cannot only preserve their original properties but also bring in new properties and therefore broaden the applications of CNTs in electroanalysis [30].

Recently, the immobilization of enzymes, such as laccase [229,230] and tyrosinase [231–234], by entrapment in the CNT matrix was used as a promising strategy for the sensitive and selective amperometric detection of catecholamines. Tyrosinase is an interesting enzyme for biosensing applications because it can reduce interfering effects of compounds in biological systems as the enzyme is only sensitive to phenolic compounds.

According to Prasad et al. [235,236], CNTs play a pivotal role in achieving conducting property, a high surface-to-volume ratio and maximum film porosity in MIP technology. The research group fabricated a dual-template imprinted polymer-modified carbon ceramic electrode, containing dispersed MWCNTs for the simultaneous analysis of AA and DA in the presence of several co-existing biological interferents [235]. The oxidation peak potentials for both analytes (≈ 300 mV) was large enough to allow selective and sensitive analysis of one in the presence of other, without any cross reactivity, interferences and false-positives. The LODs obtained were found to be as low as 13 nM for AA and 1.4 nM for DA. Furthermore, the research group also explored the relative advantages of using covalently made MWCNTs bearing terminal monomeric unit [236] toward the development of a MIP-modified pencil graphite electrode for the selective determination of Adr.

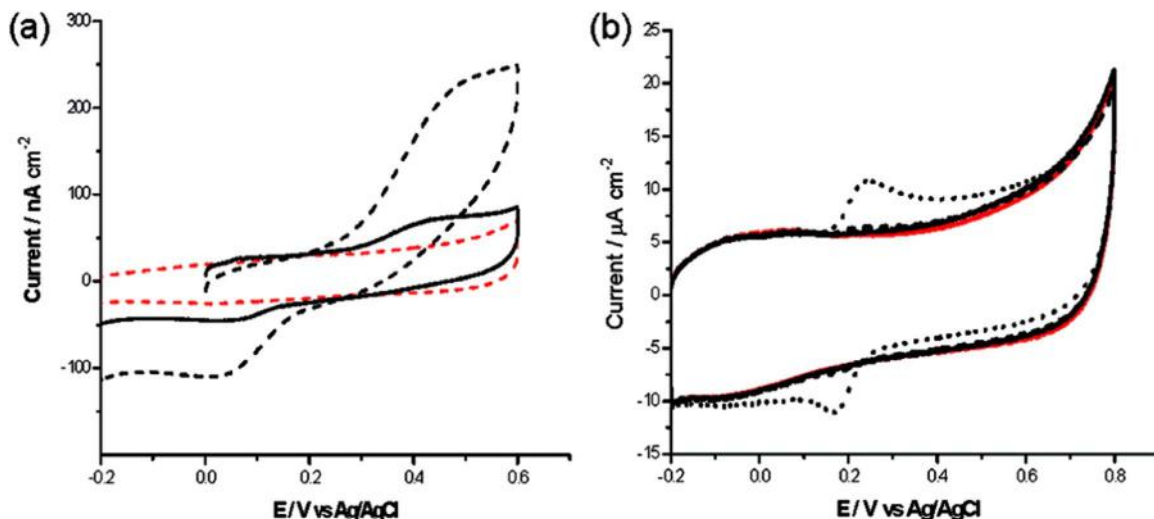


Fig. 10. CVs for the oxidation of DA (in 0.1 M NaCl, 0.1 M acetic acid buffer, pH 5) at a scan rate of 100 mV/s: (a) a SWCNTs network electrode at concentrations of 100 nM (solid line) and 500 nM (dashed line); (b) a GC electrode at concentrations of 100 nM (solid line), 1 μ M (dashed line), and 10 μ M (dotted line). In both cases, the red line represents the background response without DA. Figure from reference [219]. Reprinted (adapted) with permission from P. Bertoncello, J.P. Edgeworth, J.V. Macpherson, P.R. Unwin, Trace level cyclic voltammetry facilitated by single-walled carbon nanotube network electrodes, *J. Am. Chem. Soc.*, 129 (36), 10982–10983. Copyright (2007) American Chemical Society.

Table 5

List of works reported in literature for the determination of catecholamines using electrodes modified with CNTs.

| Catecholamine | Interferents | Electrode | Modifying agent | LOD/ (or Sensitivity) ^a /μM (or μA μM ⁻¹) | Refs. |
|------------------------------|------------------------------|--------------------|---|--|-----------|
| DA | AA | Grafite SPE | MWCNTs | 0.015 | [237] |
| Adr, NA/Adr | AA, UA, DA/AA, UA, DA, NA | PG | MWCNTs | 0.00015, 0.00009/0.00015 | [238,239] |
| DA | AA, UA | GC | Electrochemically pretreated SWCNTs | 0.015 | [240] |
| DA | AA | GC | Boron-doped CNTs | 0.0014 | [241] |
| DA | AA | GC | MWCNTs doped cobalt phthalocyanine | 0.256 | [242] |
| DA, paracetamol | AA, UA | GC | MWCNTs decorated with Co NPs | 0.015, 0.001 | [243] |
| NA | AC, folic acid | PE | Molybdenum(VI) complex CNTs | 0.043 | [244] |
| DA, UA | AA | GC | SWCNTs/cetylpyridinium bromide multi-layer films | 0.6, 7.0 | [245] |
| DA | AA, UA | PE | MWCNTs/poly(glycine) | 0.012 | [246] |
| Adr, AA | AC, TRP | GC | MWCNTs/imidazole derivative | 0.38, 0.96 | [247] |
| DA, AA, UA | | GC | Functionalized MWCNTs-poly(neutral red) film | (0.146, 0.028, 0.084) | [248] |
| DA, 5-HT | AA, UA | PE | MWCNTs/poly(<i>N</i> -acetylaniline)/β-CD | NR | [249] |
| DA | AA | GC | Multilayer films of PDDA/MWCNTs | NR | [250] |
| DA, UA/NA, UA, AA | AA/NR | GC/Carbon SPE | Poly(acrylic acid)/MWCNTs | 0.02, 0.11/0.131, 0.458, 498 | [251,252] |
| DA, AA, Adr | | GC | MWCNTs-poly(methylene blue) film | 67, 200, 69.9 | [253] |
| DA, NA, Adr, 5-HT, L-dopa/DA | AA, UA/AA | Au ME/CPE | PEDOT-CNTs nanocomposite | NR/0.02 | [254,255] |
| Adr | AA, UA | Au | PPy-Au NPs-SWCNTs composite | 0.002 | [256] |
| DA | Glu, AA, UA, gly | Au | Poly(ethyleneimine)-MWCNTs-Au NPs composite | 0.00656 | [257] |
| Adr | AA, UA | GC | Surfactant doped PPy-MWCNTs composite | 0.04 | [258] |
| DA | AA | GC | PANI/MWCNTs with incorporated β-CD | 0.012 | [259] |
| DA, 5-HT/DA | AA | GC/PE | CNTs-ionic liquid composite | 0.06, 0.008/0.01 | [260,261] |
| NA | Sugars, aminoacids, others | PE | ZnO-CNTs-ionic liquid nanocomposite | 0.02 | [262] |
| DA | AA, UA | GC | Fc-SWCNTs adducts | 0.05 | [263] |
| Adr | NA | PE | Quinazoline derivative-MWCNTs composite | 0.0094 | [264] |
| DA | AA | GC | Per-6-amino-β-CD-COOH functionalized SWCNTs | 0.5 | [265] |
| Adr | | GC | Brilliant cresyl blue-MWCNTs-dihexadecyl phosphate | 0.01 | [266] |
| DA, AA | | PE | Thionine-Nafion [®] supported on MWCNTs | 0.08, 0.08 | [267] |
| Adr, UA, folic acid/DA, UA | Metal ions, AA, others/ NR | PE | EBNBH-CNTs nanocomposite | 0.216, 8.8, 11.0/0.087, 15 | [268,269] |
| DA, AA, UA | Glu, aminoacids, Adr, others | PG | MWCNTs-1,4-naphthoquinone nanocomposite | 0.003, 1.9, 0.1 | [270] |
| DA | AA, UA, metal ions, glu | GC | Co(II) complex-MWCNTs composite | 1.76 | [271] |
| DA, AA | | PE | Ag NPs-CNTs nanocomposite | 0.3, 12 | [272] |
| Adr, piroxicam | AA, UA, aminoacids | GC | Ni hydroxide NPs-MWCNTs composite | 0.29, 0.11 | [273] |
| DA, AA, UA | | GC | N-doped CNTs functionalized with Fe ₃ O ₄ NPs composite | 0.05, 0.24, 0.047 | [274] |
| DA | AA, UA, citric acid, others | GC | NiFe ₂ O ₄ MPs decorated with MWCNTs | 0.02 | [275] |
| DA | UA | Au SPE | Protein coated MPs/-COOH-SWCNTs | 0.71 | [276] |
| DA | AA, UA | Au, Pt, carbon SPE | DA binding to streptavidin-coated MPs-SWCNTs wiring | 0.002 | [277] |
| DA | | Band electrodes | Sparse networks of pristine SWCNTs (FIA) | 0.000005 | [278] |

AC: acetaminophen; TRP: tryptophan; CD: cyclodextrin; PDDA: poly(diallyldimethylammonium chloride); PEDOT: poly(3,4-ethylenedioxythiophene); PPy: poly(pyrrole); EBNBH: 2,2'-[1,2-ethanediylbis(nitriloethylidene)]-bis-hydroquinone; PANI: poly(aniline); Fc: ferrocene; MPs: magnetic particles; NR: not reported.

^a In case of simultaneous determination the LOD value corresponding to the catecholamine is underlined. When LOD is not reported the Sensitivity is shown in brackets.

This system responded a highly sensitive and selective response for Adr, prevalent in aqueous and real samples at ultratrace level (linear range: 0.49–32 nM, LOD: 0.11 nM), without any cross-reactivity and matrix effects.

6.3. GR based electrochemical detection of catecholamines

Since the discovery of GR in 2004, this nanomaterial has stimulated tremendous interest in its highly diverse applications to bioscience and biotechnologies, including the development of high performance electrochemical devices.

In 2009, Alwarappan et al. [279] reported the analytical detection of DA at GR/SWCNT incorporated electrochemical sensors. The corresponding DA CV obtained at the GR and SWCNTs modified electrodes is shown in Fig. 11a) and b), respectively. The results revealed that the GR electrode exhibited redox peaks with a less positive ΔE_p (-107 ± 6 mV) and a higher magnitude of redox

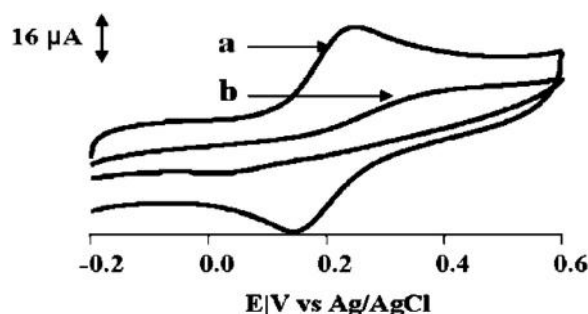


Fig. 11. CVs of 2.5 mM DA obtained at GR (a) and SWCNTs (b) modified electrodes, in PBS pH 7.4. Figure from reference [279]. Reprinted (adapted) with permission from S. Alwarappan, A. Erdem, C. Liu, C.-Z. Li, Probing the electrochemical properties of graphene nanosheets for biosensing applications, J. Phys. Chem. C, 113 (20), 8853–8857. Copyright (2009) American Chemical Society.

current ($1.0 \pm 0.2 \mu\text{A mm}^{-2}$) than those obtained by using the SWCNTs ($\Delta E_p = -109 \pm 8 \text{ mV}$; $I_p = 0.42 \pm 0.2 \mu\text{A mm}^{-2}$). Thus, the authors concluded that GR exhibited a superior biosensing performance than SWCNTs toward DA detection due to the greater sp^2 character, conductivity and density of surface negative charge of GR.

Meanwhile, also in 2009, Wang et al. [280] conducted a parallel experiment using GR and MWCNTs for the selective sensing of DA, in the presence of AA. The GR modified surface exhibited high selectivity for sensing DA within the linear range used ($5\text{--}200 \mu\text{M}$) and a better performance than the MWCNTs modified surface. Taking into account the results obtained, the authors concluded that GR was a better candidate as advanced electrode material to fabricate sensing interfaces for electroanalysis.

The “top-down” fabrication of GR is based on graphite exfoliation by physical, electrochemical and chemical procedures. Chemical vapor deposition is one of the most prospective “bottom-up”

methods for the mass production of GR besides the chemical or thermal reduction of graphene oxide (GO). Recently, the fabrication procedures of GR and its derivatives and the advances of GR-based electrochemical sensors and biosensors was excellently reviewed [166,167]. Interestingly, some of the oxygen functional groups on GO can also be reduced and regenerated electrochemically, resulting in reduced graphene oxide (rGO) with better electrical properties, a high density of defects and edge-like planes. Such combined features facilitate fast electron transfer and enabled recently the application of rGO in electrochemical sensing and biosensing [166,167].

Both GR and rGO were widely used as electrode materials for sensing catecholamines. Some of the related publications are resumed Table 6. The electrochemical sensors for catecholamines were mostly performed by applying GR dispersed in an organic solvent or simply growing on the electrode surface. Alternatively, multilayer GR nanosheets (or their hybrids) were also directly

Table 6

List of works reported in literature for the determination of catecholamines using electrodes modified with GR or GR derivatives.

| Catecholamine | Interferents | Electrode | Modifying agent | LOD ^a /μM | Refs. |
|--------------------------------------|---|--------------------|--|-------------------------------|---------------|
| DA | AA | GC/GC, graphite/PE | GR | 0.04/2.64/0.4 | [280,310,311] |
| DA, AA, UA | | SPE | GR-ionic liquid composite | 0.12, 0.95, 0.20 | [312] |
| NA | AA, UA | Pd | GR | 0.06744 | [313] |
| DA, AA/DA | UA/AA, glu, others | Graphite/PE | GR nanosheets | 0.25, 0.45/0.6 | [314,315] |
| DA, UA | AA, metal ions, glu, AC, others | GC | Multi-nanopore GR | 1.5, 2.0 | [316] |
| DA, AA, UA | | GR slice | 3D GR | 5.0, 5.0, 5.0 | [317] |
| DA | AA | ITO | GR foam | 0.002 | [318] |
| DA | AA, UA | Carbon SPE | Oxidized GR nanoribbons | 4.0 | [319] |
| DA, AA, UA/DA, AA, UA | NR/glu | GC | Nitrogen doped GR | 0.12, 0.95, 0.20/0.93, NR, NR | [320,321] |
| DA | AA, UA | GC | Multilayer GR nanoflake films on Si substrates | 0.17 | [322] |
| DA | AA | GC | Covalent immobilization of GO film | 0.27 | [323] |
| DA/DA, AA, UA | AA, UA/Inorganic ions | GC | Chemically rGO/Electrochemically rGO | NR/0.5, 0.5, 0.3 | [324,325] |
| DA | AA | GC | β-CD-GR sheet nanocomposite | 0.005 | [326] |
| DA | AA, UA, Adr, cys, others | GC | GR/quercetin | 0.01 | [327] |
| DA | AA | GC | GR/PVP | 0.0002 | [328] |
| DA, AA, NO ₂ [−] | | GC | GR/poly(CD)/MWCNTs | 0.05, 1.65, 1.65 | [329] |
| DA | AA, UA, metal ions, glu, others | PE | Poly(methylene blue)-GR-ionic liquid composite film | 0.0056 | [330] |
| DA, UA | AA, glu, nitrite | GC | Poly(acrylamide)-rGO nanocomposites film | 0.1, 0.5 | [331] |
| DA | AA, tyramine, others | GC | GR-PANI/DA aptamer | 0.00000198 | [332] |
| DA, AA, UA | | GC | Chitosan-GR composite | 1.0, 50, 2.0 | [333] |
| DA, UA | | GC | GR/chitosan multilayer films | 0.05, 0.1 | [334] |
| DA, UA | AA, glu, metal ions, others | GC | Chitosan/silica sol-gel composites with rGO and Au NPs | 0.3, 0.7 | [335] |
| DA, UA | | GC | Au NPs-β-CD-chitosan-GR nanocomposite | 0.08, 0.04 | [336] |
| DA | AA, UA | Carbon SPE | GR/PANI/polystyrene nanofibers | 0.00005 | [337] |
| DA | AA, UA | GC | rGO-highly dispersed Ppy composite | 0.0004 | [338] |
| DA, AA, UA, G, A | Metal ions, citric acid, glu, others | GC | Overoxidized poly(imidazole)/GO composite film | 0.63, 18, 0.59, 0.48, 1.28 | [339] |
| DA | | GC | Au NPs decorated Ppy/rGO hybrid sheets | 0.00001829 | [340] |
| DA | KCl, NaCl, citric acid, glu, AA | GC | PDDA/PSS functionalized rGO/PAMAM dendrimer encapsulated Au NPs multilayers film | 0.02 | [341] |
| DA | AA, UA | GC | Oligo(phenylene ethynylene)s-rGO nanocomposite | 0.005 | [342] |
| DA, AA, UA | | GC | Au NPs-β-CD-GR composite | 0.15, 10, 0.21 | [343] |
| DA, AA | | GC | Zeolite A-Cu NPs-rGO composite | 0.041, 11 | [344] |
| DA, AA, UA | | GC | Amino-group functionalized Fe ₃ O ₄ NPs-GR sheets | 0.126, 0.074, 0.056 | [345] |
| DA, AA, UA | Glu, urea, aminoacids, metal ions | GC | Graphitic carbon nitride nanosheets-GO composite | 1.172, 0.096, 0.228 | [346] |
| DA, AA, UA | | GC | Nanohybrid of cobalt tetraphenylporphyrin-rGO | 0.03, 1.2, 0.15 | [347] |
| DA, AA, UA | | GC | GR-Ni hydroxide composite | 0.12, 30, 0.46 | [348] |
| DA, TRP, AA, UA | Citric acid, NaH ₂ PO ₄ , glu, others | GC | Hemin-GO-CNTs complexes | 0.017, 0.017, 0.17, 0.017 | [349] |
| DA | AA | GC | rGO-MWCNTs-phosphotungstic acid composite | 1.14 | [350] |
| DA | AA, UA, metal ions, cys, others | GC | rGO-carbon dots composite | 0.0015 | [351] |

AC: acetaminophen; PVP: poly(vinylpyrrolidone); CD: cyclodextrin; PANI: poly(aniline); G: guanine; A: adenine; PDDA: poly(diallyldimethylammonium chloride); PSS: polysodium 4-styrenesulfonate; PAMAM: polyamidoamine; TRP: tryptophan; NR: not reported.

^a In case of simultaneous determination the LOD value corresponding to the catecholamine is underlined.

used as a sensing electrode. In addition, several nanocomposites were prepared by incorporation of GR or its derivatives within polymeric matrixes.

The combination of GR with other nanomaterials (metal/metal oxide NPs and CNTs) was also extensively explored by researchers for the fabrication of high performance electrochemical sensor devices. Electrode surfaces modified with nanocomposites containing GR/rGO and Au nanostructures [281–285], Pt NPs [286–288], Ag NPs [289], Pd–Pt NPs [290], TiO₂ NPs [291], CuO₂ NPs [292], ZrO₂ NPs [293] or CNTs [294–296] were used as

electrochemical sensors for the detection of the biogenic amines in the presence of several endogenous interferents. These resulting nanocomposites often exhibit superior surface area and electrical conductivity, less biofouling and improved sensitivity compared to pristine GR.

Some research groups reported the modification of GR or its derivatives by chemical/physical attachment of specific functional groups for application in the electrochemical sensing of catecholamines. GC electrodes modified with sulfonated GR [297], hydrogenated GR [298] and GR (or its derivatives) functionalised

Table 7

List of other strategies reported in the literature for the determination of catecholamines.

| Catecholamine | Interferents | Electrode and modifying agent | LOD/ (or Sensitivity) ^a /μM (or μA μM ^{−1}) | Refs. |
|-----------------------------|----------------------------------|--|--|-----------|
| DA | AA | Ordered mesoporous carbon in GC | NR | [369] |
| DA, UA | AA | -COOH functionalized ordered mesoporous carbon material-ion liquid gel on GC | <u>0.0041</u> , 0.0015 | [370] |
| NA | | Mesoporous carbon SPE (enzyme catalysed reaction) | 0.0006 | [371] |
| DA, Adr | | Ordered mesoporous carbon-fullerene in GC | NR | [372] |
| DA | AA, UA, citric acid, glu, others | Fullerene-C ₆₀ coated Au electrode | 0.00026 | [373] |
| DA | AA | Gold nanofilm in Au electrode | 1.5 | [374] |
| DA | AA | Nanoporous gold modified GC | 0.017 | [375] |
| Adr, UA | AA | PG electrode modified with nanodiamond-graphite film | <u>0.003</u> , 0.003 | [376] |
| DA/DA, AA, UA | AA/NR | Exfoliated graphite electrode/Exfoliated graphite paper electrode | 0.050/ <u>0.11</u> , 2.0, 0.02 | [377,378] |
| DA, UA | AA, glu, metal ions, others | Pre-treated pencil graphite electrode | <u>0.033</u> , 0.12 | [379] |
| DA/DA, 5-HT, AA/Adr | AA, 5-HT | Different classes of carbon electrodes: GC, BDD, EPPG, BPPG and HOPG | NR/ <u>0.090</u> , 0.060, 0.200/0.17 | [380–382] |
| DA, AA, UA | Metal ions, citric acid | Modified GC electrode by electrochemical method in basic media | <u>2.67</u> , 23.38, 4.70 | [383] |
| DA, AA, UA | | Pre-treated CPE | <u>0.198</u> , 1.0316, 1.73 | [384] |
| DA, AA | | Amorphous carbon nitride electrode material | <u>0.0656</u> , 1.05 | [385] |
| DA | AA | Nano-sized Au electrode/Au nanowire (lithographic technology) | 0.128/(0.0002) | [386,387] |
| DA | AA | Redox cycling at unmodified Au microelectrode array | 0.454 | [388] |
| DA | AA | Bare ITO electrode and scan rate control | 0.001 | [389] |
| DA | AA | Tyrosinase-modified BDD electrode (carbodiimide coupling reaction) | 1.3 | [390] |
| DA | | GC electrode modified with tyrosinase immobilized on eggshell membrane | 25 | [391] |
| DA | | Membrane-based Au electrode | 0.0013 | [392] |
| DA | | GC electrode modified with electrospun CeO ₂ /Au composite nanofibers | 0.056 | [393] |
| DA | AA | Pt electrode modified with phosphotungstic acid-ZnO electrospun fibers | 0.089 | [394] |
| DA | AA, UA | Carbon nano onion-PDDA composite modified GC | 10 | [395] |
| DA | UA, TRP, gly, glu, others | Au electrode modified with MnO ₂ nanowires-chitosan | 0.04 | [396] |
| DA | Adr, NA, AA | MIP coated Si-ITO electrode | 2 | [397] |
| DA | AA | GC in the presence of the <i>p</i> -phenylenediamine as a nucleophile | 0.12 | [398] |
| NA | AA, UA | Electrooxidation of NA in the presence of morpholine nucleophile at bare Au | 0.87 | [399] |
| DA | AA | Redox ions (Fe(CN) ₆ ^{4−}) deposited on a polyelectrolyte-coated Au electrode | NR | [400] |
| DA, AA, UA | | Tetrabromo- <i>p</i> -benzoquinone modified CPE | (<u>0.0074</u> , 0.0022, 0.0024) | [401] |
| DA | | CFE modified with 2,6-AQDS, 4-carboxyphenyl and catechols | NR | [402] |
| DA | AA | 2,4,6-triphenylpyrylium ion encapsulated into Zeolite Y on GC | 0.2 | [403] |
| DA, AA, UA | | Methylene blue immobilized on a phosphorylated zirconia-silica composite | <u>1.7</u> , 8.3, 3.7 | [404] |
| DA | AA | Molecular wires monolayers of oligo(phenyleneethynylene) | 10 | [405] |
| DA, aminochrome | AA, tartaric acid, others | K ₂ UO ₂ [213] deposited electrochemically on Pd–Al electrode | <u>0.41</u> , 0.45 | [406] |
| DA, AA | | Copper dispersed sol-gel composite electrode | <u>5.8</u> , 8.6 | [407] |
| DA | AA, metal ions, UA, others | CPE modified titanium phosphate grafted on the surface of silica gel | 0.043 | [408] |
| DA | AA, UA | TiO ₂ nanotubes modified with Au, Pt and Pd NPs | 0.030 | [409] |
| DA, UA | AA, glu, metal ions, others | CPE modified poly(beryllon II)/nanowires-LaPO ₄ composite | <u>0.03</u> , 0.23 | [410] |
| NA, paracetamol, folic acid | | CPE modified with MCM-41 mesoporous material | <u>0.04</u> , 0.7, 0.06 | [411] |
| DA | Adr | MCR-ALS at Au NPs chemically modified CPE | 0.0355 | [412] |
| DA | Adr, NA, L-DOPA, others | RNA aptamer immobilized at a cysteamine-modified Au electrode | 1.0 | [413] |

NADH: nicotinamide adenine dinucleotide; PDDA: poly(diallyldimethylammonium chloride); 2,6-AQDSA: 2,6-anthraquinone disulfonic acid; MCR-ALS: multivariate curve resolution by alternating least-squares.

^a In case of simultaneous determination the LOD/Sensitivity value corresponding to the catecholamine is underlined. When LOD is not reported the Sensitivity is shown in brackets.

with ethylenediaminetetraacetic acid [299], ferulic acid [300], L-tyrosine [301], cetyltrimethylammonium [302], ionic liquid [303], porphyrin [304,305] and 3,4,9,10-perylene-tetracarboxylic acid [295,306] were applied in the detection of DA. Recently, the properties of MIP-based GR electrochemical sensors [307–309] resulted in a successful specific recognition of DA against structural analogs and coexisting interferences in biological samples.

7. Other strategies for determination of catecholamines

In this section, we discuss other methods and electrode materials used for the effective detection of catecholamines. Some of these strategies used in the construction of the electrochemical sensors are summarized in Table 7. Notably, new materials that have emerged over the last decade for biosensing applications, such as mesoporous carbon, nanodiamond and fullerene, have provided to electrochemical sensors good biocompatibility, fast response time and high sensitivity and selectivity. Nanowires, membranes and nanofibers were also applied to catecholamine sensing. Other methodologies reported rely on the modification of the electrode surfaces with (bio)molecules and nanomaterials with electrocatalytic properties in order to increase the performance of the electrochemical devices.

Among the methodologies reported for the detection of catecholamines, we also pay special attention to the following features: (1) immobilization of charge transfer mediators, such as organometallic complexes [352–357], on substrates in order to enhance the electrocatalytic determination of catecholamines; (2) sensors based on cationic [358,359] and anionic surfactants [360–362], which operates by formation of micelles with ascorbate and the catecholamine, respectively, and thereby separates them electrochemically and prevents the passivation of the working electrode by the amines; (3) electrodes modified with specific macrocyclic receptors, such as cucurbit[8]uril [363] and calix[4]arene crown-4 ether [364], aiming to increase the selectivity for the determination of DA in the presence of AA. Recently, room temperature ionic liquids (RTILs) emerged as a new class of electrode modifiers due to their single electrochemical characteristics. Some studies have reported that RTIL layers have improved the detection performance in monitoring of DA in the presence of high concentration of AA [365–368].

8. ITIES as an analytical tool for catecholamines detection

In contrast to the methodologies discussed so far, some reports have demonstrated the possibility of detecting catecholamines by voltammetry at a polarized interface between two immiscible electrolyte solutions (ITIES), where neither oxidation nor reduction of the analyte takes place. The transfer of ions across the ITIES provides the analytical signal and, thus, the problem related to the electrode surface fouling due to the polymerization of the oxidation products of catecholamines is immediately eliminated.

The first study of partition of amines, including DA and NA, between water and an organic solvent phase using electrochemical techniques was presented by Homolka et al. [414], in 1984. In 1991, Dvořák et al. [415] was also the first to report the assisted transfer of β -phenylethylammonium ions (including DA and NA) by the ionophore dibenzo-18-crown-6 (DB18C6) in a water/nitrobenzene (W/NB) system.

In 2004, Shao and co-workers [416] presented a study of ion transfer (IT) and assisted/facilitated ion transfer (FIT) reactions of the protonated dopamine (DAH^+ , $\text{pK}_a=8.8$) at the water/1,2-dichloroethane (W/DCE) interface. The electrochemical behavior of FIT of DA at the liquid/liquid interface was performed using

macrocyclic polyethers as ionophores: DB18C6, dibenzo-24-crown-8 and benzo-15-crown-5. When ionophores were added into the DCE phase, the transfer Gibbs energy of DAH^+ decreased and voltammograms were shifted to the middle of the potential window (CV between -400 and 475 mV). In case of simple IT, DAH^+ transfer occurs very close to the positive end of the potential window (CV between -325 and 225 mV). The lowest concentrations of DAH^+ detected were ~ 0.3 μM by simple IT and ~ 0.05 μM by the FIT, using DPV technique and DB18C6 as an ionophore. The authors concluded that the selectivity for DA was achieved by the use of DB18C6 as an ionophore in the FIT voltammetry of DAH^+ across the ITIES. AA does not interfere in the determination of DAH^+ as the ascorbate ion is not transferred through the interface within the potential window. Thus, the use of ITIES as analytical tool resolved one of the major problems observed in the electrochemical determination of DA at solid electrodes: the lack of selectivity between DA and the coexisting excess AA in biological samples. However, other ions present in physiological samples, such as Na^+ and K^+ , can form stable complexes with DB18C6 interfering in the determination, which can be a serious limitation for the detection of catecholamines in biological micro-environments.

Similarly, Arrigan et al. [417–419] also studied the FIT of DAH^+ by the DB18C6 across the water/DCE interface from the analytical point of view. The sensitivity [419,420], selectivity in the presence of ascorbate [417,418] and the effect of the nature of ligands [420] on the determination of DAH^+ was extensively studied by Arrigan's research group. The authors concluded that the drawback of current signal saturation observed at conventional (millimeter-sized) liquid–liquid interfaces was overcome by using the micro-fabricated porous membranes, which resulted in detection of lower concentrations of DA (0.5 μM comparing to 2 μM at large interfaces).

Recently, the interfacial transfer of DAH^+ and NAH^+ at the water/1,6-dichlorohexane (W/DCH) interface, using DB18C6 as ionophore, was reported in the literature [421,422]. The LODs obtained were 0.35 and 1.7 μM for DAH^+ and NAH^+ , respectively [422]. The authors highlighted the use of alternatives to the highly toxic solvents conventionally used as organic phase, such as NB and DCE, which is an important improvement for the application of liquid–liquid interfaces as electrochemical sensors.

9. Analytical performances of electrochemical approaches

The critical analysis of the sensitivity achieved by electrochemical methodologies used in the determination of catecholamines displayed in Tables 1–7 allows us to conclude that the desired nanomolar LOD has been obtained in a few cases only. For example, the LOD of few nanomolar (< 10 nM) needed for the detection of catecholamines under physiological conditions was achieved in only 5 studies using electrode surfaces modified with polymers (see Table 2). Nevertheless, the number of scientific works achieving low concentration levels of catecholamines increases by the incorporation of nanomaterials (metal/metal oxide NPs: 7 studies, Table 4; CNTs: 9 studies, Table 5; and GR/GR derivatives: 10 studies, Table 6) in the electrochemical sensor devices, enhancing the unique features introduced by these nanomaterials in the development of high performance electrochemical sensors and biosensors. The used of emergent materials including mesoporous carbon and fullerene also allowed the detection of trace levels of catecholamines (see Table 7).

Chemical modification of electrode surfaces had apparently resulted in an elimination of effects of interfering biological agents, which in turn and has made it feasible to simultaneously determine catecholamines and other relevant species such as AA,

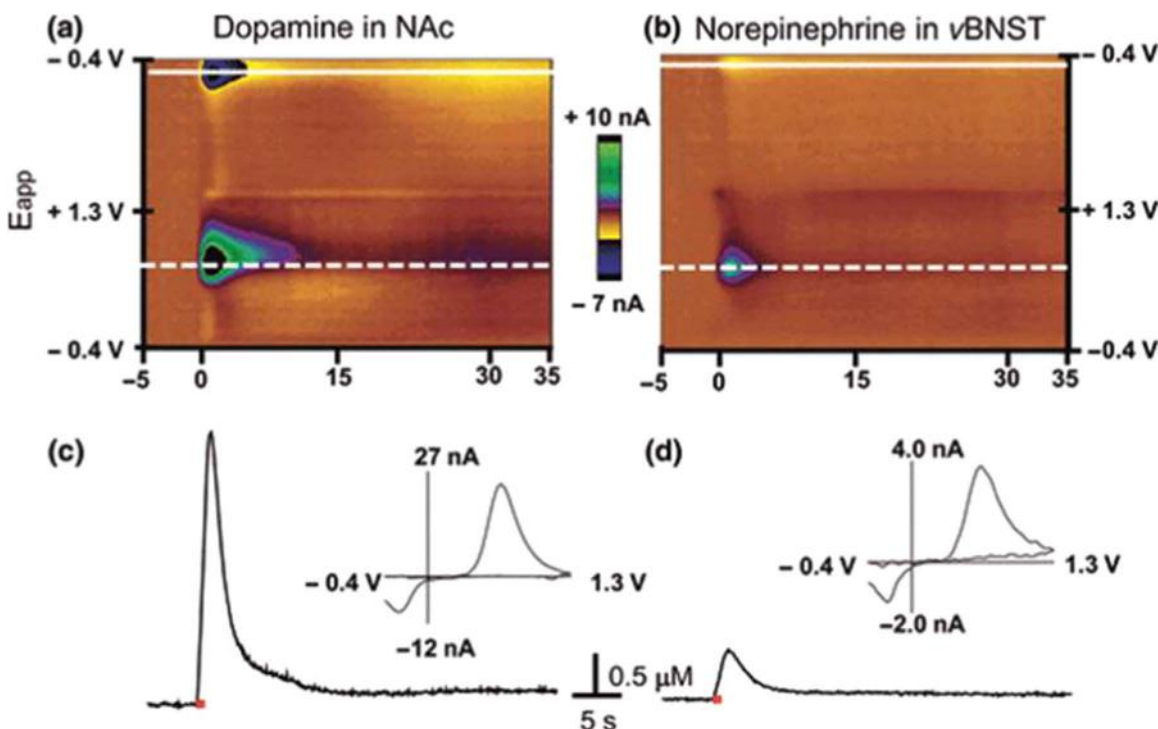


Fig. 12. Signal identification of voltammetric data recorded in the NAc and vBNST. Upper panels: color plots for the voltammetric data, with current changes encoded in false color for DA in NAc (a) and NA in the vBNST (b). The sets composed of all background-subtracted cyclic voltammograms recorded for 40 s before and after electrical stimulation of the VTA/SN and VNB (60 Hz, 60 pulses; delivered at 0 s). Catecholamine concentration changes are apparent in the color plots at the potential for their oxidation (~ 0.65 V, dotted line) and reduction (~ -0.23 V, solid line). The traces of DA in the NAc (c) and NA in the vBNST (d) evoked by the electrical stimulation measured. The traces (dotted line) were shown at the potential at which catecholamine is oxidized. Electrical stimulation is indicated with the solid red bars under the traces. Insets: background-subtracted cyclic voltammograms recorded at the maximum of the evoked release. Figure from reference [470]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 8

List of works reported in literature for the real-time determination of catecholamines in biological systems.

| Electrode and modifying agent | Application | Refs. |
|---|--|-----------|
| Hydrogenated conical-tip carbon microelectrodes | Detection of DA in anesthetized rat brain | [471] |
| Carbon nanopipette electrodes | <i>In vivo</i> detection endogenous DA release in <i>Drosophila larvae</i> | [472] |
| Boron-doped diamond microelectrodes | <i>In vivo</i> detection of DA in corpus striatum of the mouse brain | [473] |
| Diamond microelectrodes | High-speed DA detection in monkey striatum | [474] |
| ITO-glass substrate | Measure quantal exocytosis from cells in microfluidic channels | [475] |
| ITO planar microelectrode (basal pole) | Study of catecholamine exocytosis from chromaffin cell | [476] |
| Fused-silica-insulated Pt microelectrodes | Monitoring catecholamine single vesicle exocytosis from chromaffin cells | [477] |
| PEDOT: Nafion [®] coated CFMEs | DA release from nucleus accumbens of a rat | [478] |
| Microchip Au electrodes modified with MPA | Measuring DA exocytosis from PC12 cells | [479] |
| CFMEs modified with 4-sulfobenzene | DA release from mouse brain slices | [480] |
| CFME coated with tyrosinase-chitosan biopolymer-ceria/titania NPs | <i>In vivo</i> measurement of DA in the brain of anesthetized rats | [481] |
| Polyamide-coated fused-silica CFME | Long-term (from day to day over periods of months) <i>in vivo</i> DA dynamic measurements in rats and mice | [482] |
| Polyethylenimine CNT fiber microelectrodes | <i>In vivo</i> monitoring of neurochemicals | [483] |
| CNT yarn microelectrodes | Detection of DA in rat brain slices | [484] |
| CFMEs modified with SWCNTs | Simultaneous detection of DA and 5-HT in the striatum of anesthetized rat | [485] |
| Functionalized SWCNTs assembled onto disk CFMEs | Detect DA changes in the ventral nerve cord of <i>Drosophila melanogaster</i> | [486] |
| GR-modified CFME | Detection of DA in mice hippocampus tissue | [487] |
| Carbon fiber MEAs | Monitor DA release in heterogeneous regions of rat striatum | [488,489] |
| Carbon fiber MEAs (n=7) | DA release monitored different locations on single PC12 cells | [490,491] |
| Carbon-ring MEAs (n=8 to n=15) | Multisite sensing of exocytotic events from single PC12 cells | [492] |
| CFME assemblies (2–4 separately sensing elements) | Monitoring DA release in the striatum of anesthetized rats | [493] |
| Microfabrication of silicon-substrate MEAs | Heterogeneous spatial DA recording in the striatum of anesthetized rats | [494] |
| Pt MEAs (n=4) | Electrochemical imaging of fusion pore openings in chromaffin cells | [495] |
| Au MEAs | DA exocytosis from PC12 cells | [496] |
| Boron-doped nanocrystalline diamond MEAs | Catecholamine secretion from chromaffin cells | [497] |
| Ultramicroelectrode arrays (n=16, 25 or 36) | Multisite measurements of DA secretion from PC12 cells | [498,499] |

PEDOT: polyethylenedioxythiophene; MPA: mercaptopropionic acid; PC12: pheochromocytoma.

at $\sim +0.65$ V (dashed line) and their catecholamine-*o*-quinone forms are reduced at ~ -0.23 V (solid line). The current at $\sim +0.65$ V in both regions increased rapidly during an external induced electrical stimulation and afterwards decreased back to the pre-stimulation basal level (Fig. 12c and d). Data analysis allowed to conclude that the average maximum DA concentration evoked in the NAc was ~ 4 -fold higher than the maximal NA concentration in the *v*BNST evoked by the same stimulation.

Other detection methodologies, rather than the use of untreated-CFMEs, were recently introduced by scientists aiming to improve the performance of electrochemical sensors for real-time detection of catecholamines in several biological systems, namely: (1) the manufacture of microelectrodes with optimized geometry, (2) the use of electrodes with unprecedented minimal-size and (3) the utilization of emergent electrode materials (diamond, ITO, etc.) with improved electrocatalytic properties (see Table 8).

As shown in this review so far, over the past several decades researchers have investigated surface-modification techniques to enhance the selectivity, sensitivity, robustness and kinetic properties of the electrode surfaces for NTs detection. Some examples of modified microelectrodes, including selective surface coatings and/or incorporation of nanomaterials on electrode surfaces, among others, along with its applicability in real-time catecholamine detection in different neurotransmission studies are shown in Table 8.

Recent advances in microfabrication processes have enabled the development of microelectrode arrays (MEAs) with highly reproducible geometrical and electrical characteristics. These arrays are compatible with neurochemical measurements and have been utilized for a variety of *in vitro* and *in vivo* detection of catecholamines in multiple micro-environments (see Table 8). Devices with multiple sensing elements allowed the spatially resolved profiling of DA dynamics in rat brain and enable parallel *in vitro* catecholamine determination in biological cells.

11. Conclusion

This review has offered an overview of the electrochemical sensors developed for sensing catecholamine NTs during the last 15 years. Electrochemical sensors provide a powerful analytical tool for the sensitive, simple, rapid and selective determination of catecholamines, while remaining inexpensive. Additionally, these sensors are capable of being incorporated into robust, portable, or miniaturized devices, enabling tailoring the detection of catecholamines for particular applications in clinical and diagnostic fields as biomarkers of several diseases, such as Alzheimer's disease and Parkinson's disease.

From the experimental point of view, chemical modification of solid electrodes was essential to overcome some of the prevalent problems related with the electrochemical detection of catecholamines. These include (1) detection of catecholamines in the presence of the major interferent AA, that often exists at a much higher concentration than targeted catecholamines in biological samples and whose oxidation occurs at very similar potentials to that of catecholamines, making electrochemical signal separation difficult; and (2) passivation of the electrode surface caused by the polymeric melanin type of oxidation products of catecholamines.

Thus, electrode surfaces modified with conducting/non-conducting polymers or SAMs, along with the incorporation of (bio) molecules with electrocatalytic properties (enzymes, metal complexes, etc.) or specific ligands/receptors (cyclodextrins, calixarenes, etc.), provided a means to increase the sensitivity and selectivity for catecholamine detection in the presence of various interferents (mainly AA and UA). Meanwhile, other strategies have also been reported for the sensitive detection of catecholamines,

such as the use of the emerging mesoporous carbon, nanodiamond and fullerene, the use of electrodes modified with ionic liquids, detection of catecholamines in the presence of surfactants, use of membrane-coated electrodes, among others.

Voltammetry at liquid-liquid interfaces (ITIES) was recently used for the detection of catecholamines. The common detection problems of these NTs related to the electrode surface fouling and the interference of the coexisting excess AA was immediately eliminated by using biphasic systems. Moreover, although the introduction of micro-interfaces improved the LODs obtained, the application of ITIES as electrochemical sensors for detection of catecholamines in biological micro-environments awaits further improvements.

The recent discoveries in nanotechnology provided a driving force in developing new electrochemical sensors for catecholamine molecules. The incorporation of NPs, CNTs or GR/GR derivatives on an electrode surface, or the use of sophisticated nanocomposites combining different nanomaterials and/or other electrocatalyst molecules, allow to achieve higher sensitivity, selectivity, speediness, stability, reliability, accuracy and low cost sensor devices.

It is important to note that a vast number of the developed electrochemical sensors were applied to the simultaneous determination of catecholamines and AA (and/or UA, and/or other NTs), as a result of the elimination of the interference of biological agents due to the successful chemical modification of electrode surfaces. Many of the sensors developed were successfully applied to the determination of catecholamines in real-life samples including biological fluids (human urine and serum) and pharmacological samples. However, the desired nanomolar limit of detection was only obtained in few cases and was mainly achieved due to the incorporation of nanomaterials into the detection substrates.

The real-time detection of catecholamines in both *in vitro* and *in vivo* investigation experiments is of utmost importance in biomedical research field to understand the physiological role of these NTs in neurotransmission events associated to several diseases or reward-related behaviors. Although the large number of scientific papers reporting the use of modified macroelectrodes for the determination of catecholamines, which were mostly applied to the *in vitro* detection of these NTs, the real-time mapping of these NTs in biological microenvironments, ranging from single cells experiments to *in vivo* measurements in rat brain, was mainly carried out by the use of FSCV (and/or amperometry) at untreated CFMEs. The currently available methodology for miniaturization of the electrodes (ultramicroelectrodes) and the chemical modification of the sensor surfaces (selective coatings, incorporation of nanomaterials, etc.) can give rise to the development of sensor devices with improved sensitivity and selectivity and optimized kinetic properties for the real-time detection of catecholamines. Moreover, the use of sensor arrays (MEAs) provided a powerful tool for the heterogeneous spatial recording of catecholamines in the rat brain and enable parallel *in vitro* recording of catecholamines in biological cells.

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