



Development of molecular imprinted polymers based strategies for the determination of Dopamine

Shabi Abbas Zaidi

Department of Chemistry, Kwangwoon University, 20 Kwangwoon-ro, Nowon-Gu, Seoul 01897, Republic of Korea



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ABSTRACT

Dopamine (DA) is a valuable neurotransmitter of enormous biological significance and it is widely distributed in the mammalian central nervous system (CNS). DA has been known to play a critical role in the functioning of central nervous system (CNS), renal, and hormonal systems. It has been discovered that the lack of DA is associated with many clinical conditions including debilitating ailment, Schizophrenia, and Parkinson's disease. Many reliable methods have been reported for the accurate determination of DA, however, interferences from co-existing molecules such as ascorbic acid (AA), and Uric acid (UA) are inevitable. To overcome it, molecular imprinted polymer (MIP) is considered one of the best strategy owing to its pre-determined selectivity for an imprinted template. A considerable amount of research has been done on MIP based approach for DA determination. Furthermore, various types of ways including the utilization of conducting monomers, graphene, carbon nanotubes (CNTs), gold nanoparticles (AuNPs), and so on have been incorporated to enhance the signal response. In this review, we have not included the vast literature available for dopamine, instead, we have summarized the recent developments of MIP based strategies for the determination of DA using articles encompassing 2010 to till now as well as outlined the current challenges and developmental needs of MIP strategies.

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1. Introduction

Dopamine (3, 4-dihydroxyphenyl) ethylamine, DA) is considered an important neurotransmitter and significant member of catecholamine family. It plays many valuable roles in the functioning of the central nervous system (CNS), hormonal, and renal

systems [1]. Its normal concentration range is approximately 10^{-7} – 10^{-3} M. The variation in the concentration level of DA is directly correlated to a variety and progression of certain neurological disorders including Alzheimer, Schizophrenia, Parkinson, and drug addiction. For example, the DA concentration varies from 1.22 ng/mL to almost complete depletion in Parkinson disease, whereas the low concentration range between 1.89–189 ng/mL in serum is a biomarker of Alzheimer and Schizophrenia disorders. It has been also reported that extremely low DA level (0.007–0.015 ng/mL) in cerebrospinal fluid (CSF) might be a pos-

E-mail address: shabizaidi79@gmail.com

sible sign of pure autonomic failure and multiple system atrophy. Moreover, it is known to regulate the cardiovascular functions, human metabolism, and behavior and movement among others. For these reasons, the accurate and reliable determination of DA is an important concern in disease diagnosis, hence, there are a plethora of techniques available for the detection of DA [2–4]. For example, gas chromatography-mass spectrometry (GC–MS), high performance liquid chromatography-mass spectrometry (HPLC–MS), HPLC-fluorescence, surface plasma resonance, fluorescence, and electrochemical sensors have been employed for DA detection with extremely low detection limits despite that some of these methods pose inherent limitations such as expensive instrument, time-consumption, complicated sample pretreatment and low portability [5,6]. Among other techniques, electrochemical detection method possesses numerous advantages including rapid response, cost-effectiveness, high sensitivity, simple operation and convenient portability and it has been employed to fabricate numerous nanosensors [7–14]. Hence, it is one of the most attractive and potential technique for the trace DA detection. This technique is amenable to DA since it is an electrochemically active molecule [15,16].

Generally, the performances of the various methods are adversely affected by interferences from other active biomolecules such as ascorbic acid (AA) and uric acid (UA) which coexist in biological fluids in 2–3 folds higher concentration level. Moreover, in the electrochemical analysis, the electrochemical oxidation peak potential for DA usually overlaps the peak for AA. Hence, the selectivity has been becoming a long-standing target of researchers. In order to exploit the potential of electrochemical methods, various modifications of electrode materials are carried out for enhanced selectivity and sensitivity. Among many strategies in this regard, the introduction of molecular imprinting polymers (MIPs) has been proved a major approach for excellent selectivity for the determination of DA in the presence of some common interferences [17,18]. The molecular imprinting technique is considered one of the most useful preparation strategies to obtain highly selective polymeric materials called molecular imprinted polymers (MIPs). The MIP is a template-directed polymerization method in which a cocktail solution containing a template (target) molecule, a monomer, and a cross-linker is dissolved in an appropriate solvent resulting into highly cross-linked polymer due to the new bonds created between the template and cross-linked polymer during the curing process. The polymerization step is followed by template removal step, leaving the permanent nano-sized cavities of the original template which correspond to shape, size and orientation of template molecules [19–21].

MIP offers great selectivity and considerable promise for applications in clinical analysis, medical diagnostics, environmental monitoring and drug delivery. Nevertheless, the MIPs modified sensors typically suffer from low sensitivity due to lack of conductivity and electrocatalytic activity. This drawback warrants to find an effective way of transducing selective recognition process into analytical signals. Thus, many different materials including nanomaterials and conducting polymers were utilized which could effectively enhance the sensitivity of MIP films [22–24].

Recently, there is no specific and authoritative review reported covering various aspects of fabrication of MIP based approach for DA biosensors. Thus, in this review, we intend to survey the recent development of MIP based strategies for the determination of DA using articles encompassing 2010 to date. We have focused to describe the details of many substantial articles explaining the design of sensors, and utilities of the prepared sensors so that readers might get the principles behind such devices and relevant detection strategies. Finally, we outline the current challenges and developmental needs of MIP strategies for the determination of DA from the perspective of material synthesis and their novel

applications in disease diagnosis and treatment in the near future (Table 1).

2. Classification of different methods for the fabrication of DA detection

We have classified the various strategies of MIP based DA sensors into many sections considering the valuable factors in the articles. Nevertheless, some of the factors may be overlapped in the following sections.

2.1. Functional monomer

(a) Polypyrrole (PPy) based MIPs

Polypyrrole fabricated MIP films have received much attention in the determination of DA due to following reasons.

1. It can be electro-polymerized easily and quickly.
2. It shows partial cross-linking behavior thus removing the need for cross-linking comonomer
3. Easy electrochemical template extraction and rebinding.
4. Performs well in neutral pH region
5. Electrically conductive, environmentally stable and biocompatible
6. Over-oxidation of PPy imparts the perm-selectivity behavior for electropositive groups of DA against anionic interfering species such as AA due to the formation of carbonyl and carboxylic groups into PPy backbone

Considering these excellent features of PPy, Maouche et al. fabricated a DA imprinted film on glassy carbon electrode (GCE) in an aqueous solution of pyrrole with LiClO_4 as supporting electrolyte via chronoamperometry. This was the first work showing that chronoamperometry can be successfully applied for the growth of excellent MIP film [25]. Kan et al. electropolymerized PPy in the presence of DA on multi-walled carbon nanotubes (MWCNTs) owing to their unique characteristics such as enhanced conductivity and electron facilitation, high stability, low resistance, and high surface area over GCE. In this approach, the MWCNTs were electrodeposited onto a GCE electrode followed by PPy electropolymerization in the presence of DA. The sensor displayed an excellent affinity for DA as compared to UA, AA, and EN molecules [26].

The Kan et al. group designed another approach in which MIP and silica colloidal crystal template (SCCT) technique were combined and pyrrole was electropolymerized onto the SCCT modified GCE surface in the presence of DA. After etching of silica microspheres and extraction of DA successively, three dimensional ordered macroporous (3DOM) structured MIP electrochemical sensor (3DOM-MIPs/GCE) was obtained [27].

Tsai et al. developed an excellent DA imprinted sensor using over-oxidized PPy (OPPy) on platinum microelectrode. This is the only work where OPpy-MIP microelectrode has been applied for acute *in vivo* detection of DA in the rat striatum with 3,4-dihydroxy-L-phenylalanine (L-DOPA) successfully as shown in Fig. 1. The over-oxidation of PPy film exhibited good selectivity for DA in the presence of some analogous compounds and it offered 14.5 fold selectivity for DA/AA slope in comparison with that of PPy-MIP (no over-oxidation) [28].

In a very similar approach, Qian et al. prepared PPy/CNTs-MIP by adding the 0.5 mL H_2O_2 to the CNTs/pyrrole/ FeCl_2 /DA/ H_2O mixture and the reaction was carried out for 6 h. Then, the DA molecules were extracted and the resulting hybrid solution was dripped over GCE. During electrochemical sensing, the unique PPy with plenty of cavities could bind DA through π - π stacking between aromatic rings and hydrogen bonds between amino groups of DA and

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