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Highly selective and sensitive electrochemical detection of dopamine with hydrothermally prepared β-MnO_2 nanostructures

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ABSTRACT

We report the electrochemical detection of dopamine (DA) with β-MnO_2 nanostructures prepared by simple hydrothermal methodology with varying reaction conditions. The prepared nanostructures were subjected to all physicochemical properties to study their structure and morphology. Docking study was carried out to seek out the binding prospects of dopamine molecule with β-MnO_2 surface and the binding affinity values were pointed out for all potential bindings. Further, the chronoamperometric (CA) analysis was performed to analyse the detection efficiency of dopamine in the presence of common interferences like uric acid (UA) and ascorbic acid (AA). The highly sensitive and selective β-MnO_2 electrodes show a linear detection property from 0.03 to 65 μM with a limit of detection (LOD) of 8.2 nM.This could be ascribed to the purity of β-MnO_2 and its unique one-dimensional morphology. Thus, the electrode can be used as a reliable sensor for the detection of dopamine in biological diagnosis.

1. Introduction

Dopamine (DA) present in the central nervous system, ventral and many other parts of our body mainly functions as the neurotransmitter. The electric signals from the neuron to other parts of the body are transmitted by these neurotransmitters. Neurotransmitters are classified as biogenic amines, amino acid, peptides and gaseous neurotransmitter based on the functional groups present in them [1]. DA is a biogenic amine neurotransmitter due to the presence of amino group in it. DA works as a transmitter for internal and external electrical impulses from one part of the body to another, a chemical messenger of the neural system, a regulator for attention, cognition, pleasure and so on. Increased level of DA in the body causes depression and drug addiction, whereas it's diminutive level causes diseases like Parkinson's disease, schizophrenia, attention deficit hyperactivity disorder [1,2]. These important insights gain the researcher's attention in developing reliable sensing strategy towards DA.

The DA detection has been reported with distinct working principles namely Calorimetry [3,4], Fluorescence [5,6] SERS [7] and Electrochemiluminescence [8]. However, there are certain limits of these methods such as interference with other molecules, expensive and time-consuming procedures and non-portability which reduces their commercial use. Comparatively electrochemical methods like amperometry and voltammetry techniques provide highly sensitive and selective platforms with inexpensive and portable setups [9–17]. However, less number of redox sites on the bare electrode limits the sensitive and selective detection of dopamine due to the fouling effect [18]. Therefore, Nanomaterials modified surfaces can be used to overcome these problems. Recently, many research works are focused on the development of suitable electrode platforms based on metal nanoparticles, metal oxide nanoparticles, carbon-based materials and conducting polymers for DA sensing. Among these materials, metal oxides attract the researchers due to their high stability with tunable electronic properties. There are some reports with the $CoTiO_3$-TiO_2 [9], Fe_2O_3 [10], ZnO [11], Al_2O_3 [12], Co_3O_4 [13], NiO [14], MgO [15], SnO_2 [16] and $LaMnO_3$ [17] nanostructures used for DA detection with improved sensitivity and selectivity. We have carried out electrochemical detection of DA using MnO_2 due to its uniqueness like low cost of preparation, abundancy in nature, environmental friendly and manifold structures (α, β, γ, δ, etc.). There are few literatures dealing with the sensitive detection of dopamine with composites of the MnO_2 nanostructure. However, composite chosen are high cost, toxic and non-environmental friendly. For instance Dejiang Rao k. k. et al. prepared nanocomposites using carbon nanotubes (CNT), graphene oxide and gold nanoparticles along with MnO_2, which are coming under as above said group. Tian Gan, et al., reported dopamine sensing using the composite of polypyrole with MnO_2. Similarly, Beibei Yang et al., used platinum and graphene with MnO_2 for the electrochemical detection of

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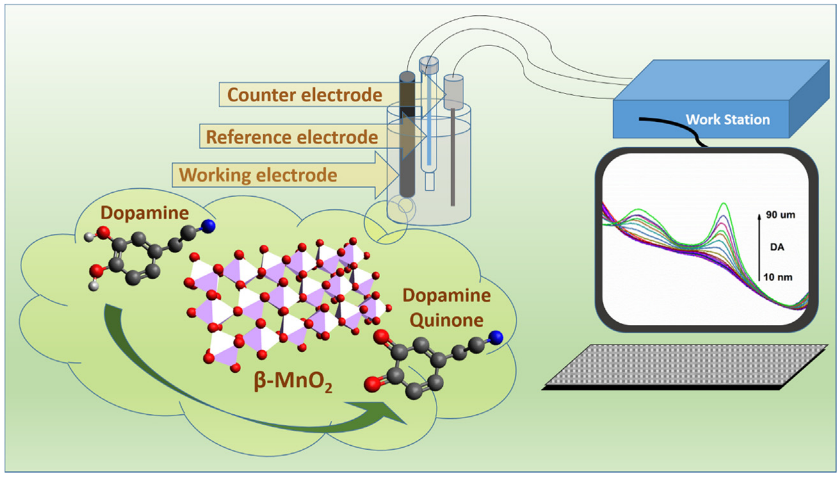

Schematic Diagram 1. Illustration of electrochemical detection of DA on the β-MnO_2/GCE.

dopamine [19–22]. The ultimate aim of our experiment is to prepare a low cost and environmental friendly material for the sensitive detection of dopamine. Rutile nature of β-MnO_2 provides more active sites on the surface, fast electron transport and high thermal stability [23–25], which leads to the fast and improved redox reaction of the analyte during the detection process. In this regard, we perform docking analysis to find out the binding probabilities of dopamine with β-MnO_2 nanostructure and then we prepare pure β-MnO_2 nanostructure by simple and cost-effective hydrothermal process. Further, the electrochemical detection of DA was investigated by modified MnO_2 electrode using Cyclic Voltammetric (CV), Differential Pulse Voltammetric (DPV) and Chronoamperometric (CA) analyses (Schematic diagram 1).

2. Experimental methods

2.1. Materials

$MnSO_4 \cdot H_2O$ (> 98% of purity), $(NH_4)_2S_2O_8$ (> 98.5% of purity), Cetyl trimethylammonium bromide (CTAB) (> 99% of purity), NaOH (> 99% of purity), Na_2HPO_4 (> 98% of purity), NaH_2PO_4 (> 99% of purity), Dopamine Hydrochloride (> 99% of purity), Uric Acid (> 99% of purity) and L-Ascorbic acid (> 99% of purity) were bought from HiMedia Laboratories and used without further purification. Double Distilled Water (DDW) used throughout this work.

2.2. Synthesis of β-MnO_2 nanostructures

MnO_2 nanostructures were synthesized by dissolving 20 mM $MnSO_4 \cdot 5H_2O$, 20 mM $(NH_4)_2S_2O_8$ and 0.2 g of CTAB in DDW and 1 M NaOH solution were added dropwise to adjust the pH of the solution then the solution was transfered to the Teflon-lined stainless steel autoclave. The autoclave was then placed in the hot air oven at different temperatures (140, 160 and 180 °C) for 12 h. After the completion of the reaction, the precipitate is collected separately, further centrifuged and washed with DDW and finally dried at 60 °C. The resultant products were then finely powdered by mortar and pestle and stored at ambient condition for further analyses.

2.3. Electrochemical cell construction

Here we used Glassy Carbon Electrode (GCE) modified with β-MnO_2 nanostructures as a working electrode. Before the modification process, GCE was polished with 0.2, 0.1 and 0.05 µm alumina slurries to get the pure mirror-like surface, degreased in 1:1 wt% of ethanol and water to remove the residues present on the surface. 2 µl of well dispersed β-MnO_2 nanoparticles in DDW (20 mg/ml) was drop cast on the surface of GCE and dried in ambient condition. The cell construction was done by using β-MnO_2/GCE as a working electrode, platinum coil (Pt) as a counter electrode and Ag/AgCl electrode as a reference electrode. The CV analysis was carried out in 0.1 M phosphate buffer to find out the optimum pH and scan rates. The DPV studies were performed for various concentrations of DA with the interference molecules (AA and UA) to find out the selectivity towards dopamine. Finally, the CA analysis was carried out with periodical increment in DA concentrations.

3. Results and discussion

3.1. Binding affinity calculation

The sensitive and selective detection of DA was strongly related to the hydrogen bonding between the dopamine molecules with the electrode surface [26]. In order to evaluate the binding affinity of the DA with β-MnO_2, we performed docking studies by using AutoDock Tool (1.5.1) software. The structure of β-MnO_2 and dopamine were drawn using ACD/Chemsketch software. The β-MnO_2 structure was then processed with Autodock software [27], after finding the exact grid box, the structure saved as a PDBQT file format. Similarly, the molecular structure of DA was also saved in above-described format. Then Autodock Vina was performed to find the binding affinities of the probe with β-MnO_2 molecular structure. The results were collected and then processed with Chimera (1.11.1) software and the simulated results are shown in Fig. 1 (1 − 9). It shows the nine possible binding modes of dopamine molecules with the β-MnO_2. The possible hydrogen bondings are indicated with a yellow line indexed with the distance of hydrogen from the oxygen atom. The binding parameters are further calculated and listed in Table 1.

Here model 1 possess a high binding affinity as − 4.1 with no deviation in the structure of dopamine. Remaining models exhibit lower binding affinity and also has a higher structure deviation compared to the model 1. That confirms that there is a possibility of dopamine binding with β-MnO_2 lattice. So further, we proceeded with the electrochemical detection of dopamine.

3.2. Structural analysis

XRD patterns of the samples prepared at different pH conditions are plotted in the Fig. 2(a). In which the peaks at 28.54, 37.41, 41.02, 42.82, 46.02, 56.71, 59.40, 64.93, 67.27 and 72.43° corresponding to the planes (1 1 0), (1 0 1), (2 0 0), (1 1 1), (2 1 0), (2 1 1), (2 2 0), (0 0 2), (3 1 0) and (1 2 2) are well matched with the JCPDS No. 24-735. It reveals the pyrolusite structure of MnO_2 (β-MnO_2). The sample prepared at pH 3 doesn't show any other peaks, but in the samples