Praseodymium ferrite nano-particles based modified electrode and its application in determination of dopamine

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ABSTRACT

The present works report the graphite based electrochemical sensor modified by nano-sized praseodymium ferrite (np-PrFeO₃) materials for the detection of dopamine. The combustion technique was used to synthesize these nanomaterials of np-PrFeO₃ using praseodymium oxide and ferric nitrate as precursor materials. The nanomaterials were characterized by field emission scanning electron microscopy and transmission electron microscopy techniques. The crystallite sizes of synthesized nanoparticles (nps) were in the range from 40-45 nm with cubic crystal system. Cyclic voltammetry and Differential pulse voltammetry techniques were used to study the electrochemical property and were observed to be superior to earlier reports. The limit of detection of dopamine at PrFeO₃/GP electrode was 600 nM with 5 to 200 µM for linearity range. The phosphate buffer solution of pH 6.0 was used for all experimental work with maintaining the scan rate 100mVs⁻¹ and 50mVs⁻¹ for cyclic voltammetry and Differential pulse voltammetry, respectively.

Keywords: Dopamine; Sensor; Cyclic Voltammetry; Differential pulse voltammetry; np-PrFeO₃.

1. INTRODUCTION

Dopamine [Fig 1, DA], a biologically available important molecule recognized for its “inhibitory neurotransmitter”, and generated in the mid-brain “Dargic Neurons” connected to the brain such as memory, propulsion, understanding and cognitive behavior. Being a hormone, it not often activates the development of the central and peripheral nervous system throughout physical activity [1, 2] however it is also accountable for the emotional and endocrine process. Small DA concentrations can result in to burning mouth syndrome [3], unstable leg syndrome [4], senile dementia, fibromyalgia [5, 6], and uncommon depression [7]. Reduced DA in the cerebral zone could lead to Parkinson’s disorder [8] whereas higher DA level may affect sympathetic nervous system and trigger unusual blood pressure and heart rate census. It becomes evident to identify biomolecules such as DA in bio-fluids that can serve a significant part in regulating drug efficacy.

Several analytical techniques have been used for the identification of DA in bio-fluids and dosage forms, such as “titemetry” [9], high-performance liquid chromatography [10-12], spectrophotometry [13], chemiluminescence [14], gas-chromatography-mass spectrometry [15] and ultraviolet spectrophotometry” [16]. Nevertheless, these techniques are less suitable for clinical practices, because of their cumbersome extraction method. On the other hand, electrochemical techniques have gained considerable interest due to their high selectivity, reasonable expense, simple processing and less laborious design [17,18] for the identification of DA in bio-fluids.

The nano materials with porous morphology and larger surface area have been extensively employed as electrode material for the identification of pharmaceutically important compounds in biological fluids and dosage formulations [19-22]. A number of different type of electrodes including (MWCNTs) modified carbon paste electrode [23], MWCNTs “graphene oxide nanocomposite-modified glassy carbon electrode” (GCE) [24], activated graphene-Nafion modified GCE [25], carbon paste electrode modified with 4-porphyrin [26], and “tyrosine glassy carbon electrode modified with a nano-composite” [27] were established for identification of DA.

Alothman et al. reported “functionalized MWCNTs-modified GCE for the simultaneous estimation of DA & paracetamol (PCM) [28]. Keeley et al. developed a thin pyrolytic carbon films based sensor for simultaneous electrochemical detection of DA and PCM [29].

To the best of author’s knowledge, there is no report is available on the detection of DA using praseodymium ferrite nanoparticles (npPrFeO₃/GP) electrode. Herein, we report an economical and efficient electrode designated as np-PrFeO₃ modified with graphite for the identification of DA. The electrode material was synthesized and characterized using several analytical techniques “Field Emission Scanning Electron Microscope” (FESEM), “transmission electron microscopy” (TEM) etc. The electrochemical activity of the modified electrode (np-PrFeO₃/GP) was investigated for the detection of DA.

2. MATERIALS AND METHODS

2.1. Chemical and reagents.

Praseodymium oxide (Pr₂O₃), ferric nitrate (Fe(NO₃)₃·9H₂O), nitric acid (HNO₃), paraffin oil, ethanolamine (HOCH₂CH₂NH₂) and sugar (glucose, C₆H₁₂O₆) etc. were obtained from Merck (India) and graphite flakes and dopamine (C₈H₁₁NO₂) were

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2.2. Synthesis of lanthanide orthoferrites nanoparticles (np).
Praseodymium oxide (Pr$_2$O$_3$) (1.0 mM) was dissolved in 50 mL of aq. nitric acid (3.5 mM) and warmed until a brownish clear solution was obtained. After that ferric nitrite (1.0 mM), ethanolamine (1.7 mM) and sugar (2.5 mM) were added in the above solution and the mixture obtained was placed on hot plate at 150 °C until evaporated to dryness. A black fluffy mass obtained was calcined in muffle furnace at 800 °C for 6 h to get npPr$_2$O$_3$ orthoferrite nanocomposite.

2.3. Preparation of electrode.
Preparation of the electrode was carried out by mixing the graphite powder and praseodymium ferrites in the ratio 4:1 thoroughly in “mortar and pastel”. Also few drops paraffin oil was added to get a uniform paste of the mixture. The paste was then filled in a capillary glass tube (2 mm i.d.) and packed firmly by pressing with metal rod. A Pt wire was introduced from the rear-side of the capillary tube for electrical connection. Similarly, bare GP electrode was fabricated using the same procedure. The surface of electrode was cleaned by using 0.3 mM and 0.05 mM Al$_2$O$_3$ slurries successively. Lastly, the electrodes were rinsed with ethanol and dried under N$_2$ gas prior to investigation.

2.4. Apparatus and measurements.
FESEM model (Hitachi SU-8010) and TEM model (FEG 5032/21 Tecnai G2 30 S-TWIN (serial No. 9921621/D934) Model No. 943205032211 made in Czech Republic) were used for the morphology and size of synthesized nanomaterials. All electrochemical investigations were performed using “three electrode systems by Autolab Potentiostate/Galvanostate 101” (Netherlands). In this three electrode system the Ag/AgCl electrode, Pt electrode and PrFeO$_3$/GP electrodes were used as a reference, counter and the working electrode, respectively. The electrochemical study was carried out in phosphate buffer (0.1M, pH 6.0) at 25±2 °C with a scan rate 100 mV s$^{-1}$ for CV & 50 mV s$^{-1}$ for DPV in the voltage range from 0.0 to 0.6V and 0.15 to 0.4 V, respectively for CV & DPV experiments.

3. RESULTS
3.1. FESEM and TEM analysis of PrFeO$_3$ nanoparticles.
FESEM analysis was carried out for surface studies of synthesized praseodymium ferrite nanoparticles (np-PrFeO$_3$). Fig 1a demonstrated a “uniform cubic structural morphology” with a fine size distribution of the materials. Fig 1b presented a TEM analysis that also supported the FESEM results.

![Figure 1](image)

**Figure 1.** (a) FESEM image and (b) TEM image of PrFeO$_3$ nanoparticles

3.2. Electrochemical studies of PrFeO$_3$/GP electrode.
Firstly, the electrochemical measurements of newly prepared PrFeO$_3$/GP electrode and the bare GP electrode were performed by applying the standard redox system [Fe(CN)$_6$]$_{3-}$/[Fe(CN)$_6$]$_{4-}$ as reference. The comparative CV plots of 3 mM K$_3$[Fe(CN)$_6$] solution at bare GP, PrFeO$_3$/GP electrodes are represented in Fig. 2.

Certain factors, such as “particle size, surface defects, electrochemical band gap, structure, optical band gap & capping ligand” carry essential functions in the voltammetric study of semiconductor substances [31-35]. Nanomaterials are extremely relevant for electro-chemical research for such purposes. Fig. 2 represents CV plots for bare GP and PrFeO$_3$/GP obtained at 100 mV sec$^{-1}$ scan rates using phosphate buffer (pH 6.0). The peak potential separation (∆Ep) at PrFeO$_3$/GP was observed 250 mV and at bare GP electrode it was 429mV. As shown by “Velasco equation”, the lower value of ∆Ep implies the quicker electronic movement through the electrode surface and anlyte.

Based on the correlation of prepared electrodes to bare GP electrode, np-PrFeO$_3$/GP electrode can be assumed to be better for electron transport over GP. CV analysis for DA indicates that the peak oxidation currents at the PrFeO3/GP electrode were observed to be 3.506 and that is approximately 1.5 times greater than bare GP.

![Figure 2](image)

**Figure 2.** “Cyclic Voltammogram obtained for 3.0 mM Fe(CN)$_6^{3-}$ at PrFeO$_3$/GP and bare GP electrodes at 100 mVs$^{-1}$ scan rate with phosphate buffer solution of pH 6.0”.

3.3. Effect of the scan rate and pH on the oxidation of DA
The effect of scanning rate for electro-catalytic oxidation of DA was examined by varying the scan rates from 5 mVs$^{-1}$ to 600 mVs$^{-1}$ in CV technique. The results obtained indicated a linear increase in the peak current with an increase of scan rate. Fig. 3b displays diffusion regulated at the electrode surface during the oxidation phase. The pH of supporting electrolyte serves as a critical part in electrochemical molecular oxidation. To investigate the effect of pH on DA oxidation, pH of 0.1 M phosphate buffer solution varies in the range between 4.0 and 7.0.

![Figure 3](image)

**Figure 3.** (a) pH study with making variation from pH 4 to 7 and (b) Current in µA during scan rate study with making variation from 5 to 600 mVs$^{-1}$ using 100 µM concentration of dopamine
It was observed that when the pH was increased from 4.0 to 6.0, the peak currents of DA also get increased and then decreased with a further increase in pH value. As the highest peak current value at npPrFeO/GP was observed with pH 6.0, the buffer with pH 6.0 was taken as standard for all other studies. Fig. 3a displays the oxidation behavior at different pH.

3.4. Electrocatalytic oxidation of DA at PrFeO/GP electrode.

The electro-catalytic activity of modified electrodes was determined by CV and DPV techniques. The CV and DPV plots for the np-PrFeO/Gp electrode and bare GP electrode are displayed in Fig. 4.

The results obtained from the above study indicated that the oxidation peak potential at bare GP electrode and PrFeO/GP electrode were 305 mV for DA.

3.5. Comparison of present study with literature

A comparison of the current electrode with the literature reported electrode is present in Table 1. It may be concluded that the newly developed npPrFeO/GP electrode is superior to the previously reported electrode for the detection of DA in sensitivity i.e. linearity range and lower detection limit.

4. CONCLUSIONS

In this work, we have synthesized a nanocomposite of Lanthanide ferrite using the combustion technique and praseodymium oxide and ferric nitrate as precursor material. Further, the nanocomposite was characterized using various analytical techniques viz. FESEM, TEM etc. The crystallite sizes of synthesized nanoparticles were in the range from 40-45 nm with cubic crystal system. CV and DPV techniques were used for electrochemical behavior of synthesized materials. The detection limit of DA at PrFeO/GP electrode was 600 nM with 5 to 200 µM for linearity range. The phosphate buffer solution of pH 6.0 was used for all experimental work with maintaining the scan rate 100mVs⁻¹ and 50mVs⁻¹ respectively. The modified electrode displayed excellent sensitivity in detection of DA. The method developed can be used for the detection of related pharmaceutical both in dosage and in biological fluids.

3.6. Repeatability, stability and reproducibility of electrodes.

To test the stability of the modified electrode (PrFeO/GP), it was stored at 30°C ± 1°C for a month. It was observed after storing for a month the electrode is capable of providing 95% retention sensitivity which further indicates the stability of electrode. The electrode behaviors were recorded for ten successive tests, and consistent output was observed which suggests strong repeatability of the method. Also a set of four electrodes were designed using a similar fabrication method to test reproducibility. The results of all four electrodes were identical, indicating strong reproducibility. Fig. 5 indicates the repeatability study with the four electrodes.

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