Development of electrochemical sensor for dopamine using PEDOT-rGO-CuNPs modified electrode

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Abstracta

Designing of electrode materials for sensing of biological compounds has been attracting researchers for many decades. In this work, the nanocomposite electrode material, Copper nanoparticles (CuNPs) decorated Poly(3,4-ethylenedioxythiophene)-reduced Graphene Oxide (PEDOT-rGO), was developed to modify the Glassy carbon electrode (GCE) for the determination of the electrochemical characteristics of dopamine on a). The composite was characterised by common analytical techniques. The TEM image of the composite showed the deposition of CuNPs on PEDOT-rGO. Cyclic voltammetric studies were carried out on PEDOT-rGO-CuNPs at pH 6.0. Differential Pulse Voltammetry (DPV) was used to study the relationship between response current and dopamine concentration. The linear range of dopamine concentration was obtained as 3×10^{-8} to 6.4×10^{-5} M and lower limit of detection 5×10^{-9} M. The composite, PEDOT-rGO-CuNPs, was verified excellent for the detection of dopamine.

Keywords: *Dopamine; CuNPs; Electrochemical sensors; PEDOT; rGO; composite*

1. Introduction

Dopamine plays a critical role in the way our brain controls our movements and is thought to be a crucial part of the basal ganglia motor loop [1, 2]. Thus, shortage of dopamine, particularly the death of dopamine neurons in the nigrostriatal pathway, is the cause of Parkinson's disease, in which a person loses the ability to execute smooth and controlled movements [3]. So, its quantitative determination in a living body is crucial, therefore, dopamine sensor is a device of importance in the analytical task. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most commonly employed conducting polymer in many fields because of its excellent electrochemical and optical properties [4, 5]. This polymer can be simply obtained by anodic oxidation of the relevant monomer, even in aqueous solutions, in the presence of various anionic counter-ions [6]. Graphene oxide (GO) is of great interest due to its low cost, easy access and widespread ability to convert back to graphene. GO is viewed as the precursor to produce graphene (reduced GO) by chemical and thermal reduction. Furthermore, in recent years, many GO derivatives, such as GO-based composites, GO-based coating and thin films, as well as GO-based nanoparticles, emerged as functional materials for various applications [7-8]. The aim of this work is to study the electrochemical behaviour and the direct electrochemical determination of dopamine by developing a composite composed of CuNPs decorated on PEDOT-rGO. Advantages of the modified glassy carbon electrode and electrochemical techniques led to a development of a sensor for dopamine with features of low cost, sensitivity selectivity and reproducibility of the method.

2. Experimental

Dopamine was purchased from Alfa Aesar 3,4-ethylenedioxythiophene (EDOT) from Sigma Aldrich (India). Copper sulphate, sodium sulphate, di-potassium hydrogen phosphate and potassium dihydrogen phosphate from Merck (India) were used as received.

2.1. Fabrication of PEDOT-rGO-CuNPs

PEDOT-GO was deposited on the GCE. GO doped PEDOT film was deposited by electro-polymerisation method on the GC electrode by potential cycling from -0.2 to 1.2V vs Ag/AgCl at a scan rate of 50mV/s. Solution containing 10 mM of EDOT and 1 $mgml^{-1}$ of GO was used. The electrochemical reduction of PEDOT-GO was carried by amperometric method by applying -0.9V for 600s in the presence of pH 7.4. For the further deposition of Cu nanoparticles, the PEDOT-rGO nanocomposite modified electrode was deposited solution containing 10 mM of $CuSO_4$ and 100 mM of Na_2SO_4 and electrodeposition was carried out at a potential of -1.0V (vs. Ag/AgCl) for 200 s [9].

3. Results and Discussions

3.1. Surface Study

The scanning electron microscopy (SEM) image of PEDOT-GO and PEDOT-rGO modified electrode was discussed earlier [10]. Cu nanoparticles on the PEDOT-rGO surface was studied by SEM and AFM. The SEM image of Cu NPS -PEDOT-rGO showed random distribution CuNPs on the surface (Fig. 1a). The surface roughness parameters, indicated as mean roughness (Ra), root mean square of Z data (Rq) and mean difference (Rz) in the five highest peaks and five lowest valleys were 3.2, 28 and 34. The surface roughness of PEDOT-rGO- CuNPS is shown in Fig. 1b. The GO was electrochemically reduced and its surface exhibited higher roughness as shown in AFM. Porous morphology was observed for PEDOT-rGO-CuNPs electrode which confirms incorporation of CuNPs in the modified electrode.

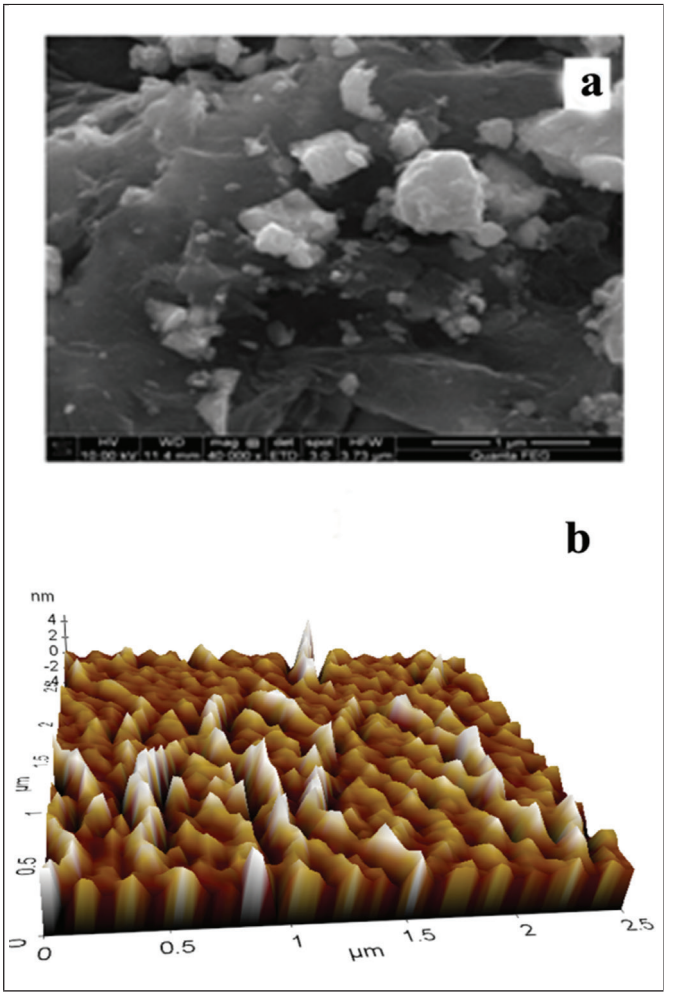


Fig.1. SEM images of a) PEDOT-rGO-CuNPs and AFM images of b) PEDOT-rGO-CuNPs.

3.2. Fourier Transform Infrared (FT-IR)

The following FT-IR peaks indicate the presence of characteristic functional group in PEDOT-GO (Fig.2a). The peak at 3401 cm^{-1} is due to –O-H stretching vibration. The peak at 1645cm^{-1} corresponds the –C=O stretching vibration, 1084 cm-1 corresponding to the –C-O- stretching vibration, peaks at 988 and 863 cm^{-1} attribute due to –C-S bending vibration in the PEDOT-GO presented in (curve a). Similar peaks at 3435 cm^{-1} for –O-H stretching vibration, peaks at 1035 and 1394 cm^{-1} are corresponding to –C-O, -C-H bending vibrations, respectively. The absence of peak at 1645 cm^{-1} suggests that GO is reduced to rGO (Fig. 2b). The presence CuNPs are absorption band at 624 and 689 cm^{-1}suggests CuNPs asymmetric stretching bond was observed (Fig. 2c).

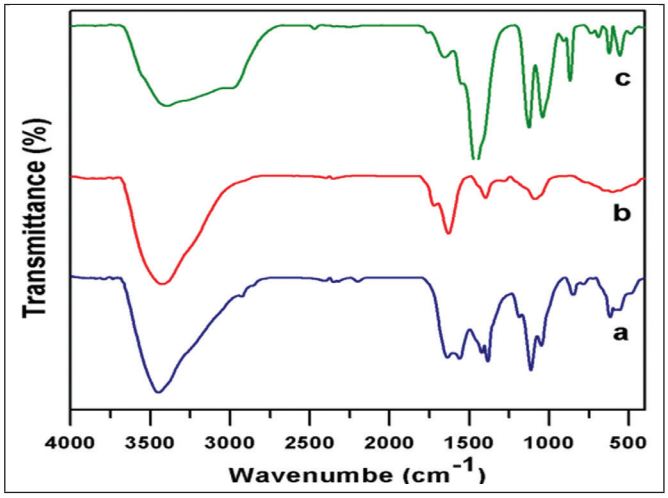


Fig. 2. FT-IR spectrum of a) PEDOT-GO, b) PEDOT-rGO and c) PEDOT-rGO-CuNPs. SEM images of a) PEDOT-GO, b) PEDOT-rGO and c) PEDOT-rGO-CuNPs.

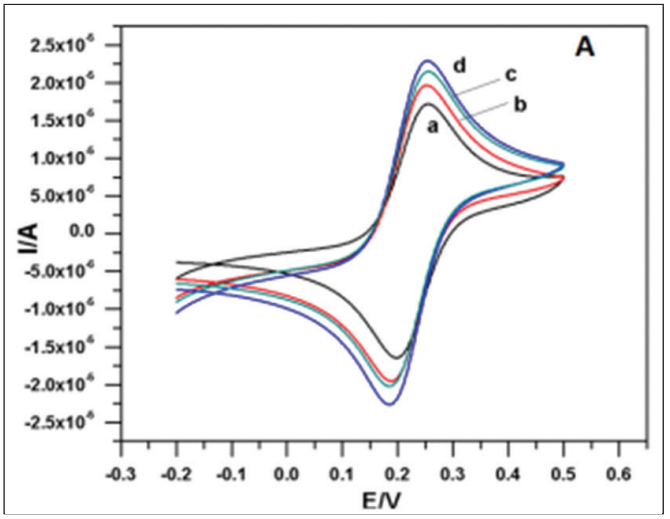
3.3. Electrochemical studies of PEDOT-rGO-CuNPs

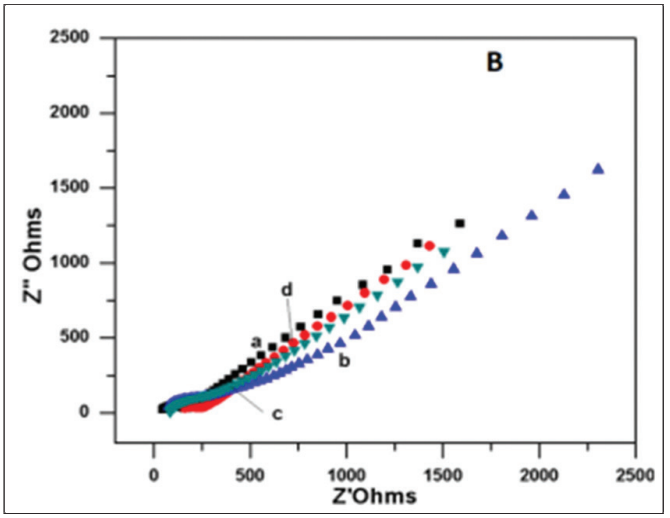
The cyclic voltammograms (CV) of 1mM $[Fe(CN)_6]^{3-/4-}$ on the bare GC electrode (curve a), PEDOT-GO (curve b), PEDOT-rGO (curve c) and PEDOT-rGO- CuNPs (curve d) modified electrodes were recorded in 0.1M of KCl at a scan rate of 50 mVs^{-1} (Fig. 3A). Modification of the PEDOT-GO (curve b), PEDOT-rGO (curve c) GC electrode led to an increase in the peak current when compared to the bare GC electrode. This could be attributed to high surface coverage and electrocatalysis. Now, the modification of PEDOT-rGO-CuNPs onto the GC electrode significantly increased the redox peak current compared to the other modified electrodes. This is due to the conducting surface on the electrode.

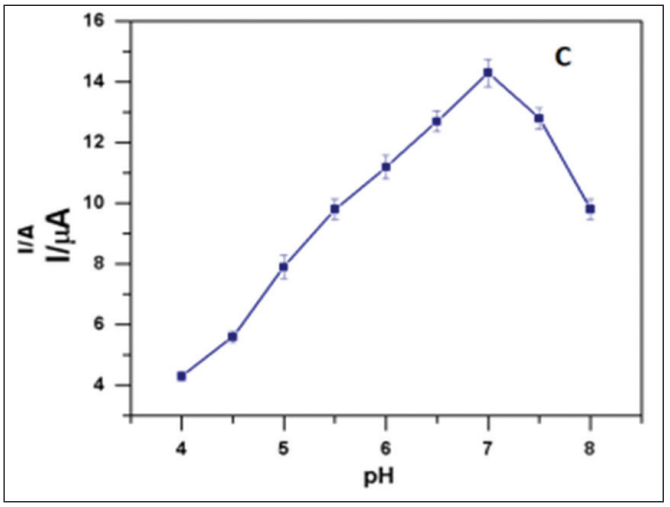
Performance of the modified electrode was further studied by Electrochemical Impedance Spectroscopy (EIS), which provides useful information on the modification of the electrode surface. The charge transfer resistance is indicated by semicircle portion. The charge transfer process of the CuNP-PEDOT-rGO modified GC electrode was recorded by monitoring charge transfer resistance (R_{ct}) at the electrode/electrolyte interface. Therefore, the modified electrode agreed with the Randles equivalent circuit of $R_s(Q_{dl}(R_{ct}W))$. In this circuit, R_s is the solution resistance, Q_{dl} is the capacitance, R_{ct} is the charge transfer resistance of the modified electrode PEDOT–GO–PPO and W is the Warburg element. Fig. 3B displays the EIS of bare GC (curve a), PEDOT-GO (curve b), PEDOT-rGO (curve c) and CuNP-PEDOT-rGO (curve d) modified electrodes at the polarization potential 25 mV and frequency of 1-1,00,000 Hz. The Nyquist diagrams for bare, PEDOT-GO, PEDOT-rGO and PEDOT-rGO-CuNPs arrived at the R_{ct} values of 359, 143, 105 and 65 Ω, respectively. Comparatively, the R_{ct} value of PEDOT-rGO-CuNPs (curve d) is the lowest one. These results demonstrate that the large conducting surface is present in PEDOT-rGO-CuNPs, which can lead to good conducting reaction pathways between the electrode/electrolyte interactions and provides a good platform for sensing application.

The major parameter to set for response of the sensor is pH. To set this, 0.1mM of dopamine was mixed with the buffer solution. The pH is a highly affecting parameter for the sensor. There is a close relationship between the response current and pH. Fig.3C shows effect of pH on the response current of the PEDOT-rGO-CuNPs sensor. Response current for the sensor at the pH 4 - 8 was studied for 0.1mM of dopamine. The activity of the sensor decreased below and above pH 7.0. However, the change of response current with increase of pH with decrease of conductivity of the sensor was observed. The sensor PEDOT-rGO-CuNPs got good response current. The optimum pH of the sensor was 7.0 to detect dopamine using this nanocompsite. Fig. 3D shows the cyclic voltammograms of 0.1mM dopamine on plain bare GC (curve a), PEDOT-GO (curve b), PEDOT-rGO (curve c) and PEDOT-rGO-CuNPs (curve d) at pH 7.0. There was a characteristic reversible redox peak observed in the curve a. When the modified electrode employed, the redox peaks became quasi reversible and increase in the oxidation and reduction peak currents were observed. This indicates that the modified GCE catalyzes the oxidation and reduction of dopamine. In all the cases, dopamine and *o*-dopaquinone redox reaction was observed. Comparatively, the highest

redox currents for dopamine were observed only at PEDOT-rGO-CuNPs-GCE electrode. Dopamine showed 2e-process. This confirms the effective incorporation of CuNPs onto the PEDOT-rGO matrix and better sensing capability of the modified electrode.







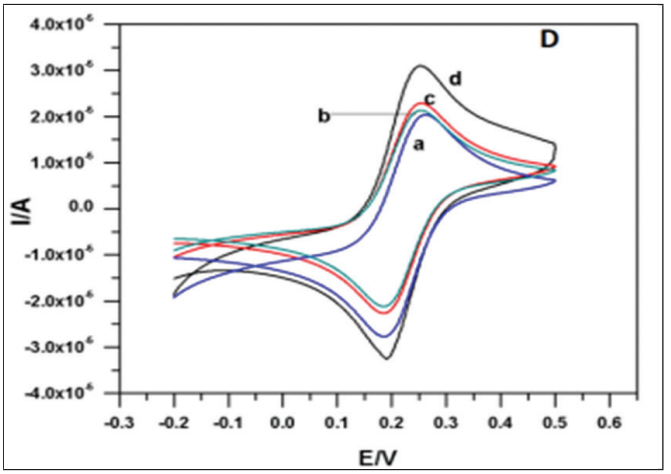


Fig. 3A. Cyclic Voltammetric studies in the presence of 1 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl. B) EIS of (a) GCE (b) PEDOT-GO,(c) PEDOT-rGO and (d) PEDOT-rGO-CuNPsv measured in presence of 1 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl. C) Effect of pH by response current study for the PEDOT-rGO-CuNPs. D) CVs obtained for dopamine of 0.01mM at the (a) bare GC, (b) PEDOT-GO (c) PEDOT-rGO and (d) PEDOT-rGO-CuNPs in PB solution (pH 7.0) at a scan rate of 50 mVs^{-1}.

3.4. Effect of concentration

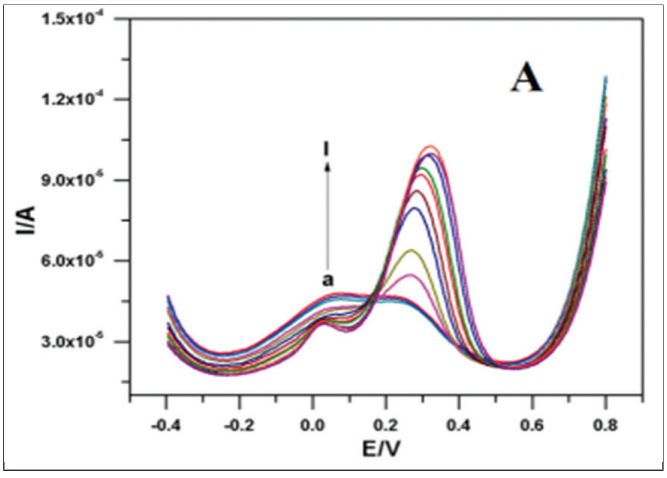
Differential pulse voltammetry was employed to determine the concentration of dopamine by using the PEDOT-rGO-CuNPs/GCE. The DPVs (Fig. 4A) were recorded for dopamine with different known concentrations under identical experimental conditions and in each voltammogram the oxidation peak current was measured. The peak currents were correlated with the dopamine concentration. The concentration of dopamine was directly proportional to the response current at pH 7.0 in a particular range and then it reached a steady state. The catalytic reaction was a first-order reaction, in the linear range and attained steady state and then it followed zero-order kinetics. The linear range of dopamine concentrations (Fig. 4B) showed a detection range 3×10^{-8} to 6.4×10^{-5} M and the lower limit of detection determined was equal to 5×10^{-9}M. The experimental results showed that the methods were simple and rapid with high accuracy. A plot of inverse of current verses substrate concentration was constructed to find out maximum current response

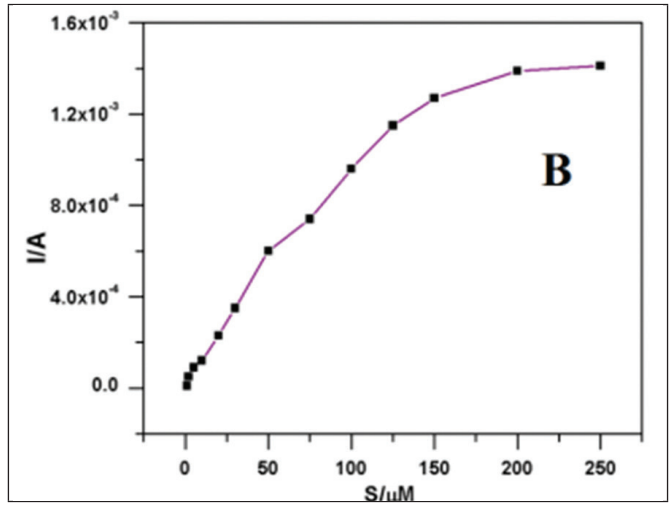
(I_{max}). The (I_{max}) was 1.24x10^{-4}µA which showed the possibility of detection of dopamine at both low and high concentrations. The modified electrode was compared with already existing sensors, and the results are shown in table.1.

Table 1. Comparison of existing electrode for neurotransmitters with PEDOT-rGO-CuNPs

Sl. No.	Modified Electrode	Linear Range (µM)	Lower Limit of Detection (µM)	Reference
1.	Au@PSi-P3HT/GCE	1 to 460 x 10^{-6}	0.63 x 10^{-6}	11
2.	AuNPs/ PM/CPE electrodes	0.2 to 11 x 10^{-6}	0.067 x 10^{-6}	12
3.	PT/Au/CNT	1.0 to 10 x 10^{-6}	0.69 x 10^{-6}	13
4.	OPEDOT–AuNPs–ERGO	4.0 to 100 x 10^{-6}	1.0 x 10^{-6}	14
5.	Ti_3C_2/G-MWCNTs/ ZnO	0.01 to 30 x 10^{-6}	3.2 x 10^{-9}	15
6.	Ag/PPy/ Cu_2O/GCE	0.01 to 250 x 10^{-6}	0.0124 x 10^{-6}	16
7.	PEDOT-rGO-CuNPs	0.03 to 64 x 10^{-6}	5 x 10^{-9}	This Work

The results of amperometric response of dopamine in presence of potential interferences such as ascorbic acid, D-glucose and L-glutamic acid with phosphate buffer at pH 7.0 are illustrated in Fig. 4C. The interfering substances were added serially to the same solution and the DPV measurements were carried out. As there was no change in the current response, the selectivity of the sensing is verified excellent.





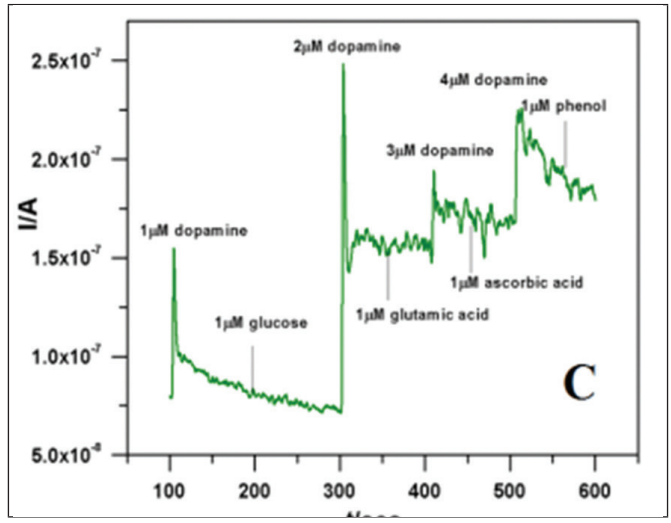


Fig. 4A. DPVs of PEDOT-rGO-CuNPs film dopamine concentrations buffer (a-l). (B) Correlation between response current and dopamine concentration at pH 7.0 and 25.0◦C. (C) Effect of interference on the response of the dopamine biosensor.

3.5. Recovery, Stability and Reproducibility

The performance of the fabricated electrochemical biosensor using PEDOT-rGO-CuNPs was compared with the results of High-Performance Liquid Chromatography (HPLC) for dopamine detection. The quantification and percentage of recovery were determined for live samples.

The recovery was determined by spiking a human urine extract sample with three different additions of dopamine. The standard of dopamine and one human urine extract sample. The results obtained from the present method and HPLC are compared in the following table.

Table.2 Determination of dopamine in human urine.

Sl. No.	Sample	Dopamine Spiked*[M]*	Dopamine Found*[M]*	Recovery *(%)*	Dopamine found by HPLC*[M]*	Recovery *(%)*
1	Human urine	1.00×10^{-6} 1.00×10^{-7}	0.99×10^{-6} 1.03×10^{-7}	99 103	0.98×10^{-6} 1.02×10^{-7}	98 102
2	Human urine	1.00×10^{-6} 1.00×10^{-7}	0.99×10^{-6} 1.01×10^{-7}	99 101	1.01×10^{-6} 1.03×10^{-7}	101 103
3	Human urine	1.00×10^{-6} 1.00×10^{-7}	1.01×10^{-6} 1.04×10^{-7}	101 104	1.02×10^{-6} 1.05×10^{-7}	102 105

4. Conclusion

PEDOT-rGO-CuNPs modified GCE electrode fabricated for sensing of dopamine. The electrode was very sensitive at pH 7.0. DPV was used to study the relationship between response current and dopamine concentration. The linear range of dopamine obtained for the concentration of dopamine was 3×10^{-8} to 6.4×10^{-5} M and the lower limit of detection 5×10^{-9} M. So, the present electrode material may be a convenient one for the fabrication of electrochemical sensor towards dopamine sensing.

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Conflict of Interest

There is no conflict of interest

Reference

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