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# A Promising Electrochemical Sensor Platform for the Detection of Dopamine Using CuO-NiO/rGO Composite

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**Dopamine plays a significant role in the proper functioning of the central nervous system. Hence, the ability to sense levels of dopamine is pivotal in diagnosis and treatment procedures. For sensing dopamine, a mixed metal oxide nanocomposite (NC) of copper oxide-nickel oxide/reduced graphene oxide (CuO-NiO/rGO) is fabricated by the sol–gel method, and it is used to modify the glassy carbon electrode. The structural and morphological characterizations are done by X-ray diffraction (XRD), Energy dispersive X-ray (EDAX), Raman, and Scanning electron microscopy (SEM). XRD results exhibit monoclinic CuO, cubic NiO, and hexagonal rGO structures. The Raman studies confirm the D and G bands for rGO. Different electrochemical techniques are used to examine the efficacy of nanocomposite in detecting dopamine. The CuO-NiO metal oxide NC response compared with the CuO-NiO/rGO NC shows a better response by rGO containing nanocomposite.**

**Further, the chronoamperometric method is employed, and the diffusion coefficient is calculated as $1.04 \times 10^{-6}$ $cm^2$ $s^{-1}$. The differential pulse voltammetry is carried out to measure the nanocomposite's sensitivity and detection limit (LOD). The catalyst exhibits a sensitivity of 7.2 µA $cm^{-2}$ $mM^{-1}$ and a LOD of 0.006 µM. The composite can be used as a flexible skin patch sensor to predict abnormal dopamine levels such as Parkinson's disease.**

## 1. Introduction

The detection of various hormones and chemical substances produced in the human body through appropriate biomaterials has significantly revolutionized the medical field, enabling the prompt detection and treatment of diseases. Studies on the identification techniques mainly focus on exploring more specific, non-invasive, accessible, and readily available materials for accurate and rapid identification of various biological compounds. The need for novel materials for diagnosis is increasing rapidly.[1]

Dopamine, a neurotransmitter, and a hormone are produced from the precursor L-DOPA in the brain and kidneys. This hormone comes under the amine families. Our nervous system uses it to send messages between nerve cells.[2] Hence, they are also known as a chemical messenger. The change in dopamine level in our body disturbs the signal transmission across the brain, leading to many disorders.[3,4] Neurodegenerative diseases like Parkinson's, attention deficits hyperactivity disorder (ADHD), and Schizophrenia result from diversified dopamine levels in the body. Therefore, monitoring dopamine levels is significant for the detection and curing of diseases. The approaches used for detecting dopamine are lengthy, tedious, and require expensive analytical reagents.[5–8]

Present methods for dopamine detection chiefly supported colorimetry, fluorescence, and liquid chromatography. However, the realistic performance of these methods is repeatedly obstructed fatally by causes, for instance, overlapping signals, lengthy function time, and interference from other biomolecules.[9] Electrochemical techniques for dopamine sensing have been extensively developed, especially due to the electroactive nature of dopamine molecules and the benefits of high sensitivity and speed.[10–12] This study focuses on the detection of dopamine using novel metal oxide nanocomposites using the electrochemical method. Owing to their catalytic properties, those nanomaterials are utilized in explicit fields as batteries (cathode materials) and electrochemical (biosensing) applications.[13]

Transition metal oxide (TMO) based copper and nickel oxides (CuO and NiO) are distinguished as tremendous dynamic electrodes amid these TMO. The nanocomposites have the advantage of high conductivity and outstanding electrocatalytic

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properties.[14] The new features of mixed metal oxide composites can be attributed to the independent properties of each metal oxide or to interactions between metal–metal and metal–oxygen–metal that increase the performance of the nano-structured system. Surface contact between oxide composites improves charge transfer, separation efficiency, and charge carrier life periods. As a result, mixed metal oxides are being investigated as potential sources for high surface area composites containing controlled nano-structured material.[15] The physicochemical properties of the produced mixed NiO/CuO composites can differ significantly from those of the separate metal oxides.

Multiple numbers of research have been reported so far, claiming better detection and sensitivity. Here, a metal oxide composite comprising CuO-NiO with rGO (rGO intensifies the sensitivity of dopamine detection by increasing the electron transfer kinetics and the electrocatalytic properties of the composite) has been utilized to recognize dopamine using the electrochemical method.[16] Graphene-based materials are extensively exploited in the scientific and engineering communities due to their unique structure and properties. Such outstanding results have been achieved by employing innovative graphene oxide (GO)-based non-enzymatic electrochemical sensors. GO is known as a two-dimensional nanomaterial with hexagonal carbon due to the covalent C single bond O bonds in graphene structure.[17] In addition to the potential uses of graphene, the incorporation of nanomaterials with graphene aid in reducing the accumulation of graphene sheets. The nanomaterials function by reducing the strong van der Waals interactions within the graphene sheets.[18]

Various research in the last decade suggests different techniques for the rapid and extensive synthesis of graphene. It was found that the localization of electrons in graphene can be achieved by the $sp^2$ hybridization using nanoparticles.[19] Similarly, incorporating graphene in metal oxide nanomaterials improved properties.[20] The glucose sensor in which $Ni(OH)_2$ nanoplates are dispersed in the graphene nanosheets showed better performance.[21] Graphene with polymer has shown good performance in the detection of dopamine.[22] Graphene-based biosensor for sensing proteins has also been studied.[23]

The main challenge faced in biosensing is the sensitivity of the catalyst to the analyte, Durability, Reproducibility, and Repeatability. The present work discusses the potential solution to these problems using electrochemistry in a competitive immunoassay for quantifying dopamine. A mixed metal oxide nanocomposite of CuO-NiO/rGO has been proposed for the detection of dopamine. The availability of localized electrons from the metal oxides and the large surface area of the reduced graphene sheets are pivotal in enhancing the sensing mechanism.[24]

## 2. Experimental Section

All the chemicals used to synthesize the nanocomposites (graphene, copper acetate [98%], copper nitrate [99.99%], nickel nitrate [99.99%], sodium borohydride [98%], sodium hydroxide [97%]) and the chemicals used in the study—dopamine, disodium hydrogen phosphate, and potassium dihydrogen phosphate (99.99%) were of analytical grade, procured from Sigma Aldrich. Deionized water was used as the solvent for preparing standard solutions. Since dopamine got easily oxidized, prior to each experiment, the dopamine solution was freshly prepared.

### 2.1. Synthesis of Mixed Metal Oxide Nanocomposite

The sol–gel route was used for synthesizing CuO-NiO nanocomposite. The precursor solution was prepared by adding 0.5 M of $Cu(CH_3COO)_2{\bullet}2H_2O$ and 0.5 M of $Ni(NO_3)_2{\bullet}6H_2O$ separately to 1 M of NaOH solution, and two different solutions were obtained. The two solutions were mixed, and the solution was blended for 2 h at room temperature (RT) and dried in a hot air oven at 120 °C for 10 h. The nanocomposite was further calcinated at 400 °C for 2 h.[25]

### 2.2. Synthesis of Mixed Metal Oxide Nanocomposite with rGO

The CuO-NiO/rGO nanocomposite was prepared by the sol–gel technique. The precursor solution was prepared 0.5 M of $Cu(CH_3COO)_2{\bullet}2H_2O$, 0.5 M of $Ni(NO_3)_2{\bullet}6H_2O$ and rGO in 200 mL of double distilled water and sonicated to obtain a homogeneous mixture. $NaBH_4$ (reducing agent) was added in drops to the prepared solution with continuous stirring. The final mixture was stirred at 100 °C and centrifuged after cooling. After decanting, the final product was collected and dried in a hot air oven at 120 °C for 10 h. Then nanocomposite was powdered and calcinated at 400 °C for 2 h.[25]

### 2.3. Fabrication of Modified Electrode and Electrochemical Study

The CuO-NiO and CuO-NiO/rGO nanocomposites were separately dispersed in distilled water and Nafion (proton conductor). The catalytic ink obtained was drop-casted on glassy carbon electrodes (GCE) and dried at RT.[26] The electrochemical cell consists of three electrodes. The working electrode was a glassy carbon disc held in a Teflon coating. The reference electrode was saturated with calomel solution, and the counter electrode was a high surface area graphite rod. For the electrochemical detection of dopamine, 0.05 M phosphate buffer solution (PBS) was prepared with di-sodium hydrogen phosphate ($Na_2HPO_4$) and potassium di-hydrogen phosphate ($KH_2PO_4$). The pH of the PBS buffer solution was 7. Cyclic voltammetry was carried out to examine the dopamine detection. A scan rate of 50 Mv $S^{-1}$ was used for the initial analysis. To find out effect of scanrate, a range of 50–250 mV $s^{-1}$ was used for analysis. Different concentrations of dopamine were added to the phosphate buffer solution, and the electrochemical behavior of the catalyst was analyzed (**Figure 1**).

## 3. Results and Discussions

Dopamine has a benzene ring structure to which two hydroxyl side groups are attached along with an amine group to the ring. Dopamine comes under a bronsted base, i.e., it can accept hydrogen from a donor. Dopamine is highly redox-active and can be easily quantified in electrochemistry, unlike other biomolecules that require enzymes and redox couples to get

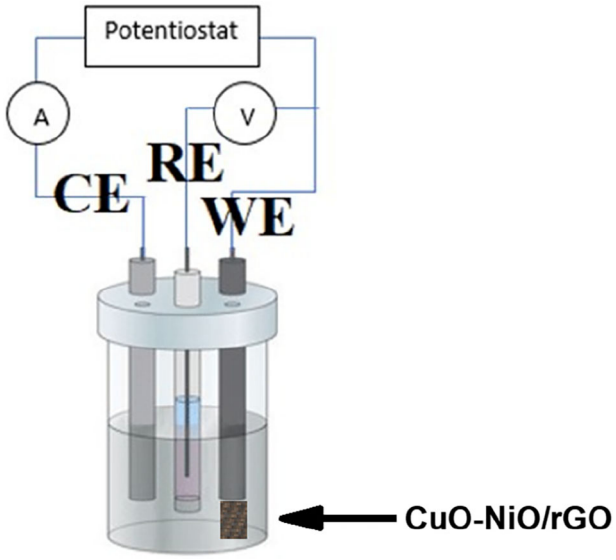


**Figure 1.** Schematic of electrochemical cell.

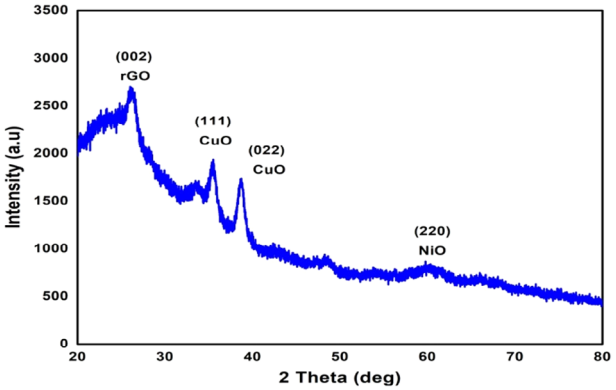


**Figure 2.** XRD pattern of CuO-NiO/rGO nanocomposite.

activated.[1] Though dopamine is present in very low quantities, the high surface area of the rGO incorporated in the CuO-NiO nanocomposite facilitates the easy detection of dopamine. Dopamine gets oxidized to dopamine quinine and gets reduced quickly by receiving hydrogen. The metal oxide-based nanoparticles of CuO and NiO help in catalyzing the redox reactions as they contain a free hydroxyl group at their surface. This backs up the process of transferring electrons between the catalyst and the dopamine. The hydroxyl group binds with the amine group of dopamine for the electron transfer process.[27]

### 3.1. X-Ray Diffraction of CuO-NiO/rGO Nanocomposite

The X-ray diffraction (XRD) pattern of CuO-NiO/rGO nanocomposite is exemplified in **Figure 2**. The results of the XRD analysis revealed the phases of monoclinic CuO, Cubic NiO, and hexagonal rGO. The pattern acquired from the study has a good confirmation with the customary JCPDS card no. 080–1268 (CuO), 47–1049 (NiO) and 75–1621(rGO). The peak at 26.2° corresponding to the diffraction plane (0 0 2) is due to the incorporation of graphene in the CuO-NiO/rGO. There were no impurity peaks

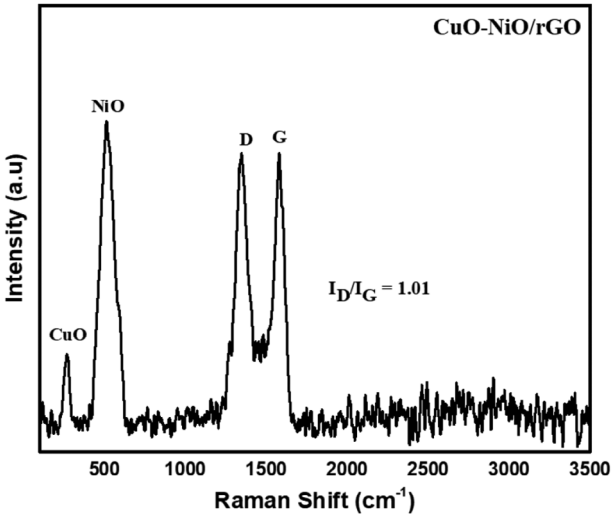


**Figure 3.** Raman spectrum of the prepared CuO-NiO/rGO nanocomposite.

in the XRD diffractogram; this validates the high purity of the synthesized nanocomposite.[28,29]

### 3.2. Raman Studies

Raman peaks are at 265, 514, 1348, and 1579 cm$^{-1}$. The peaks at 1348 and 1579 cm$^{-1}$ correspond to the D and G peaks of rGO ($sp^2$ bonding) (**Figure 3**). The intensity ratio of the D and G peaks ($I_D/I_G$) of rGO is 1.01. The other peaks at 265 and 514 cm$^{-1}$ are due to the $A_g$ mode of CuO and the 1LO mode of NiO.[16]

### 3.3. Morphological Analysis

The scanning electron microscopy (SEM) photograph obtained with the CuO-NiO/rGO nanocomposite is demonstrated in **Figures 4**a,b. The formation of rod-like structures can be seen. The rGO is formed as two-dimensional sheets on the CuO-NiO nanocomposite. The EDAX spectrum obtained with prepared CuO-NiO/rGO nanocomposite is reported in Figure 4c. The chemical composition Figure 4c of the prepared sample from the EDAX analysis is indicated as Cu (2.79%), Ni (1.82%), Carbon (76.10%), and O (19.28%). The EDAX found that the elements were present and validated the effective composite of CuO-NiO/rGO.[16]

### 3.4. Electrochemical Analysis of Dopamine on Synthesized Nanocomposite

A cyclic voltammetry (CV) study was carried out for the bare GCE and the metal oxide modified GCE with and without dopamine (0.05 M PBS buffer solution) to understand the effect of modified GCE. **Figure 5a** shows no visible redox peaks for the bare carbon electrode in the presence of 100 μM of dopamine with a 50 mV s$^{-1}$ scan rate. Whereas the modified electrode had a

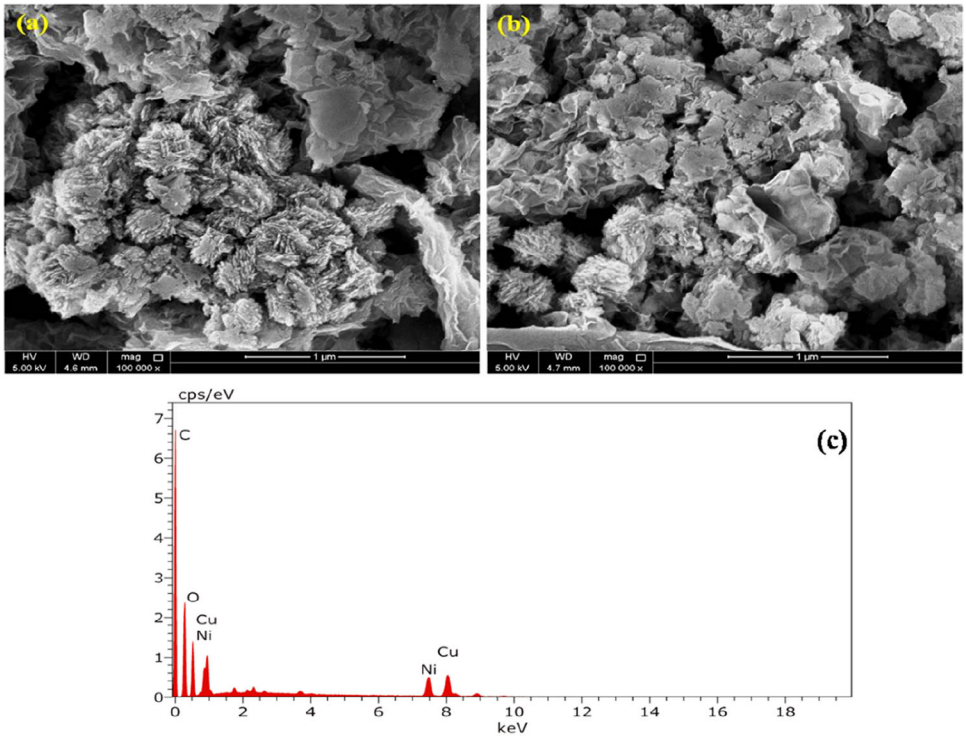


**Figure 4.** a, b) FE-SEM and (c) EDS images of the prepared nanocomposite.

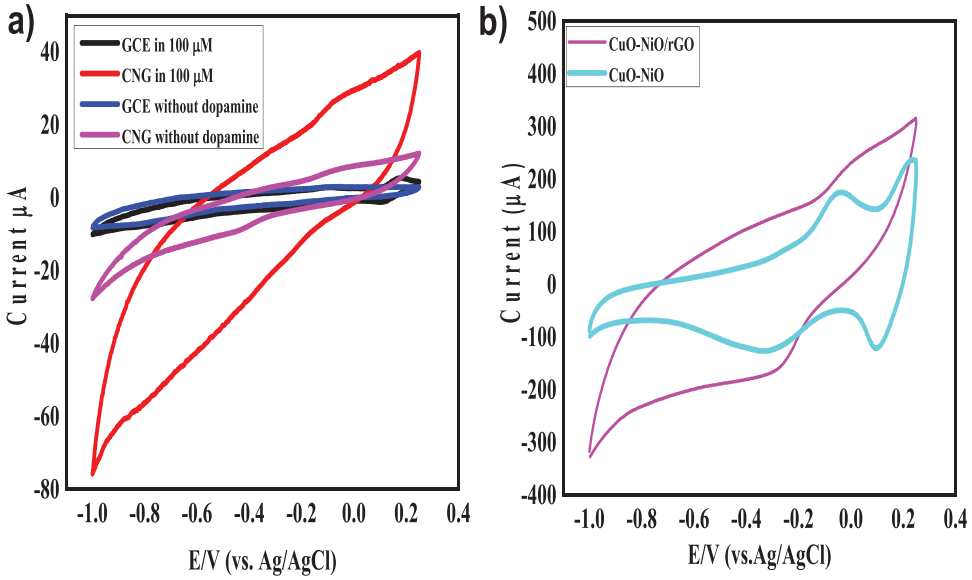


**Figure 5.** a) Response of bare and modified CuO-NiO/rGO (CNG) with GCE electrodes in the presence and absence of dopamine at 50 mV $s^{-1}$ scan rate and b) dopamine (500 µM) detection of CuO-NiO nanocomposite with and without rGO at 50 mV $s^{-1}$ scan rate.

good response to the addition of 100 µM of dopamine, confirming the sensitivity of the modified electrode to dopamine and the area covered by the response curve was less than the conduction of the modified curve. Figure 5a portrayed oxidation at lower potential and prominent redox peaks visible in the analysis using the modified electrode, which implies good electrocatalytic behavior of the metal oxide nanocomposite.[30] The electrocatalytic response of CuO-NiO and the rGO incorporated CuO-NiO nanocomposite with a 50 mV $s^{-1}$ scan rate was also observed. Figure 5b depicts enhanced conductivity and redox characteristics in the modified electrode containing the rGO.[31]

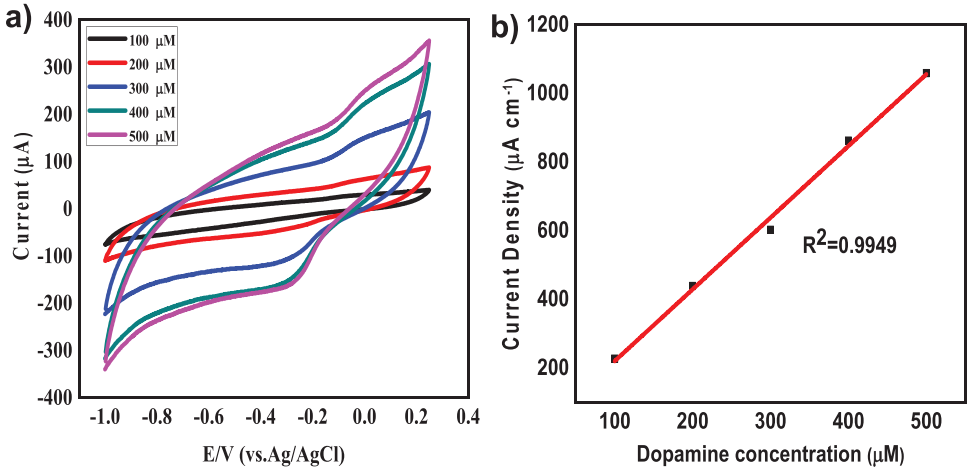


**Figure 6.** a)The linear increase in the anodic and cathodic peak current with the increasing concentration demonstrates the sensitivity of the metal oxide nanocomposite in detecting dopamine.[32] b) Linear response of CuO-NiO/rGO nanocomposite with increasing dopamine concentration.

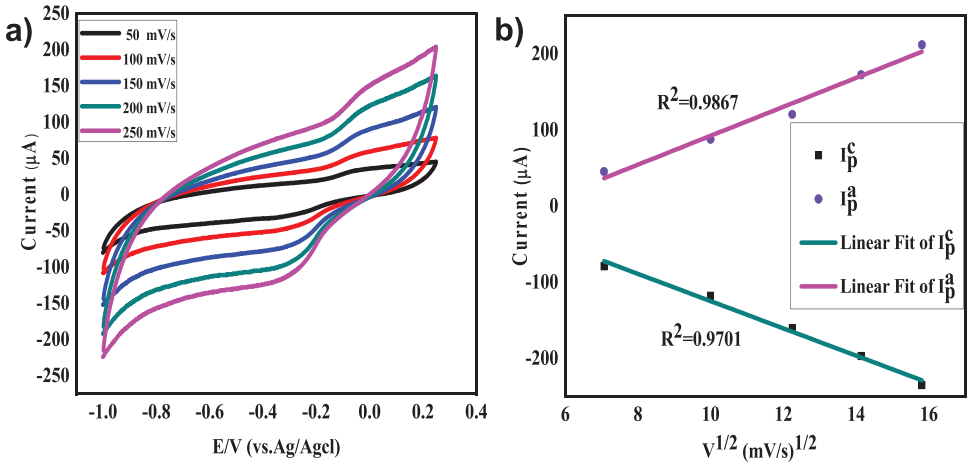


**Figure 7.** a) Electrochemical response of CuO-NiO/rGO with increasing scan rate in 100 µM of dopamine and b) linear regression response of the cathodic and anodic peak currents with a calibration plot.

### 3.5. Effect of Concentration

The redox peak current of the modified electrode is monitored for increasing dopamine concentration with −0.28 V reduction potential (**Figure 6**a). The linear intensification of the peak current with concentration confirms the reversible nature of the electron transfer process. The high sensitivity obtained while detecting the dopamine by CuO-NiO/rGO nanocomposite (Figure 6b) results from surface chemical reactions occurring at low ionization potential. Thus, the electrons transfer in the redox reaction is enhanced, resulting in high redox current values.

### 3.6. Effect of Scan Rate

The electrochemical behavior of the modified electrode is determined via the cyclic voltammetry Figure 7a. The oxidation peak is obtained at 0.18 V; also, the oxidation peak keeps its position irrespective of the change in scan rate. In contrast, current get increased for higher scan rates. It shows that the metal oxide nanocomposite indicates good catalytic behavior for detecting dopamine.[33] In the analysis optimum scan rate was found to be 250 mV $s^{-1}$.

The calibration plot of the square root of scan rate and the peak current indicates the surface-confined electrochemical redox process of the modified electrodes (Figure 7b). The linear response of the oxidation and reduction peaks with the increasing scan rate and concentration confirms the diffusion-controlled electron transfer process.[34]

### 3.7. Chronoamperometric Study

The amperometric response is calculated at 0.18 V and a step potential is submitted to the working electrode, and the current response at different times is plotted. The exponential decrease in the current for different concentrations was obtained in **Figure 8**a. The linear relation between the current and the square root of time is depicted in Figure 8b. The slope of the Cottrell

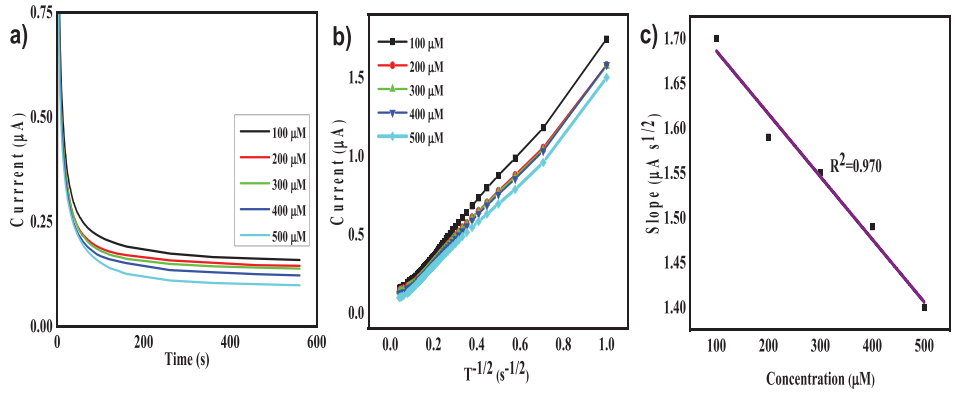


**Figure 8.** Chronoamperometric of the modified electrode in different dopamine concentrations (a) linear plot of current versus time. b) Corresponding current versus $T^{-1/2}$. c) Plot of corresponding slopes versus dopamine concentration.

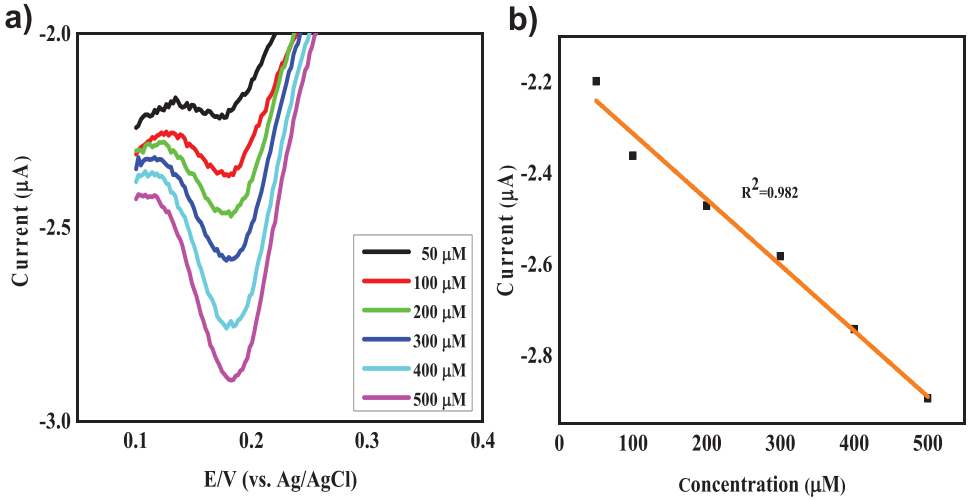


**Figure 9.** Differential pulse voltammetry of the modified electrode in different dopamine concentrations. a) Linear plot of peak current and dopamine concentration. b) Linear regression response of different dopamine concentrations.

plots are used in the determination of the diffusion coefficient of dopamine at the electrode surface due to the electrocatalytic reduction [35] and is estimated using the Cottrell equation,

$$i = nFACD^{1/2}\prod^{-1/2} t^{-1/2}, \quad (1)$$

Here, $m$ ($n$FACD$^{½}\prod^{-½}$) is the slope of the linear plot in Figure 8c, $n$ is the number of electrons that are required for the reduction, F is the Faraday constant, $A$ is the area of the modified electrode, $C$ is the bulk concentration of the analyte in the solution, and $D$ is the diffusion constant. The diffusion coefficient value estimated for the CuO-NiO/rGO modified electrode for dopamine detection is $1.04 \times 10^{-6}$ cm$^2$ s$^{-1}$.

### 3.8. Differential Pulse Voltammetry

Differential pulse voltammetry was utilized to study the peak currents at different analyte concentrations to get more sensitivity. This technique eliminates the non-faradaic currents, so it is possible to obtain well-defined peaks for all the concentrations (**Figure 9**). The oxidation peak is attained at +0.18 V. The peak currents increase linearly with an increase in dopamine concentration (0.050–200 μM). The sensitivity of the modified GCE is estimated to be 7.2 μA cm$^{-2}$ mM$^{-1}$. The LOD is computed to be 0.06 μM via on $3F/S$. ($F$: standard deviation of the blank signals [$n$ = 3] and $S$: the slope of the calibration plot). Compared to previously reported non-enzymatic dopamine recognition, CuO-NiO/rGO electro-catalyst modified electrode has the smallest LOD in **Table 1**.

To assess the durability of the sensor and discover the electrode's storage capacity, the sensor performance of the composite with modified GCE was checked weekly. In contrast, the electrode was accumulated at a lower temperature, ≈4 °C, when not in use. It was observed that the electrode maintained 95.6% of its primary current even after uninterrupted use for 2 months, indicating excellent durability. For the reproducibility studies, six entity electrodes were traced in PBS (pH 7.0) towards 10 μM dopamine and the relative standard deviation (RSD) was 3.25%. Five repetitive measurements were executed at one customized electrode and the RSD was 3.52%. Accordingly, the sensor has an acceptable range of repeatability and reproducibility.

**Table 1.** Comparison of analytical parameters for dopamine sensors based on CuO-NiO/rGO.

| Modified electrodes | Liner dynamic range [μM] | The lower detection limit [μM] | Ref. |
|---|---|---|---|
| Graphene/GCE | 4–100 | 2.64 | [31] |
| $Cu_2O$/graphene/GCE | 0.1–10 | 0.01 | [36] |
| Graphene/$MoS_2$/CNTs | 0.1–100 | 0.05 | [37] |
| Graphene | 4–100 | 2.64 | [38] |
| Chitosan/Graphene | 1.0–24 | 1.0 | [39] |
| SWCNT | 1–10 | 0.790 | [40] |
| Gold and graphene nanocomposite/GCE | 0.1–10 | 0.04 | [41] |
| Gold-$\beta$-cyclodextrin-graphene/glassy carbon electrode | 0.5–150 | 0.15 | [42] |
| CuO-NiO/rGO with modified glassy carbon electrode | 0.05–200 | 0.006 | Present study |

## 4. Conclusion

Dopamine is a neurotransmitter produced in the brain. Dysfunction of the dopamine system has been implicated in different nervous system diseases like Parkinson's, attention deficits hyperactivity disorder (ADHD), and Schizophrenia. In this work, the. potential of electrochemistry for quantifying dopamine was investigated. The prepared mixed metal oxide nanocomposite, CuO-NiO/rGO showed substantial biosensing properties. This highly sensitive immunoassay has a detection range that can detect as little as 0.06 μM. Furthermore, this nanocomposite exhibits high reproducibility and rapid results and offers a simple protocol that can produce reliable, quantitative results for our end-users. The prospecting work will be spotlighted on the production of CuO-NiO/rGO integrated stretchable sensor devices for dopamine sensing and used to detect Parkinson's disease.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Data available on request from the authors.

## Keywords

amperometric studies, mixed metal oxide nanocomposite, proton conductor, voltammetry

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