A single step, fast and facile fabrication of the disposable cost-effective reduced graphene oxide sensor for sensitive and selective determination of dopamine

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Abstract

A disposable graphite pencil electrode is developed for dopamine sensing.
A sensitive method is established by single step reduction of graphene oxide on graphite pencil electrode (rGO-GPE) surface.
The developed electrode is more sensitive or comparable to prior graphene-based electrode.
The sensor is more cost effective with rapid fabrication and selective behavior towards dopamine. The reduced graphene oxide layers on the electrode surface effectively increased the electroactive surface area.
The linear range is obtained from 0.4 to 30 µM (R^2 = 0.998). The detection limit is achieved 0.095 µM.
The developed sensor behavior is unaffected with high concentration of ascorbic acid while well-defined peak of dopamine is obtained in the presence of uric acid. This could be attributed to attractive behavior of the sensor surface towards dopamine compared to ascorbic acid.
The ease of renewal surface made the developed electrode fouls free.
Key words: Dopamine, graphene, GPE, disposable

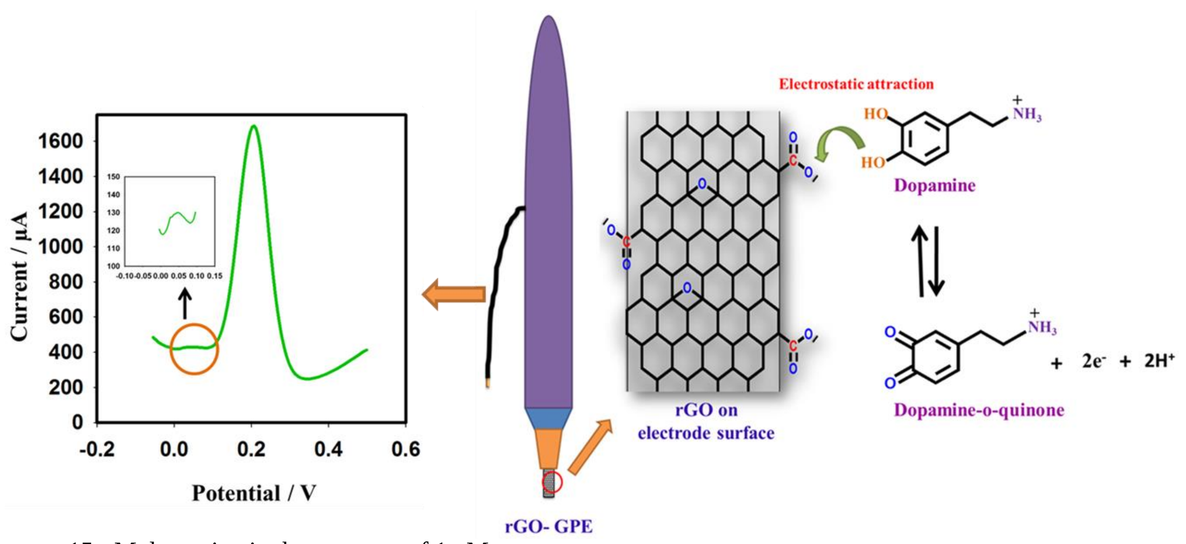
Introduction

- Dopamine is a neurotransmitter, belongs to the catecholamine family and plays a vital role in the CNS, regulates the heart beat, blood pressure, renal and digestive system.
- The abnormal metabolism or change in concentration of dopamine causes number of serious problems such as Parkinson's disease, schizophrenia, restless legs syndrome, and attention deficit hyperactivity disorder.
- The common methods developed for the dopamine detection are based on fluorescence, UV, HPLC, LC-electrospray MS, and electrochemical methods.
- The major problem with the electrochemical methods is the interferences from the uric acid and the ascorbic acid due to their close oxidation potential of dopamine.
- Graphene considered as a unique material due to excellent conductance, extremely low resistance and wide theoretical surface area (2630 m^2g^{-1}).
- In this work we first time used rGO-GPE for the detection of dopamine. It has been observed the rGO-GPE is much more sensitive for dopamine compared to the previously reported graphene based electrodes in which only graphene was used.

Methods and Materials

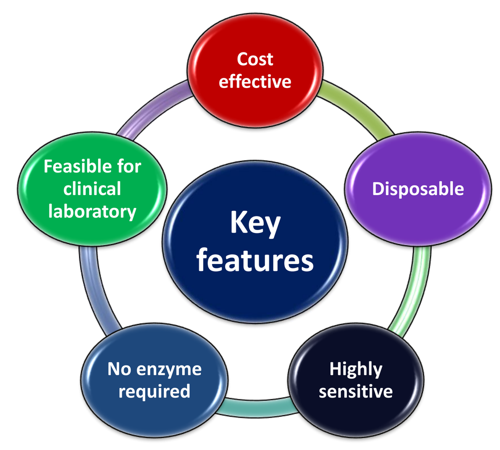
- Phenylalanine and alanine were purchased from Fluka (United States of America). Dopamine, L-tyrosine, Fructose, Glucose, ascorbic acid, L-methionine, uric acid, potassium chloride and sodium chloride were received from Sigma-Aldrich (United States of America).
- The electrochemical work station (Auto Lab, Netherland) was used for all electrochemical measurements. The weight and the pH control was done by GR-2000 and Accumet® XL50 pH meter, respectively. The FTIR and Raman spectra were recorded by NICOLET 6700 FT-IR and HORIBA Scientific LabRAM HR Evolution, respectively. The FE-SEM images of various pencil electrodes were collected by TESCAN LYRA 3instrument.

Key features of study



15 µM dopamine in the presence of 1mM ascorbic

Scheme 1 Electrochemical reaction of dopamine on the surface of the rGO-GPE



Scheme 2 Key features of Dopamine fabricated sensor

Results

❖ Raman and IR spectra of GO

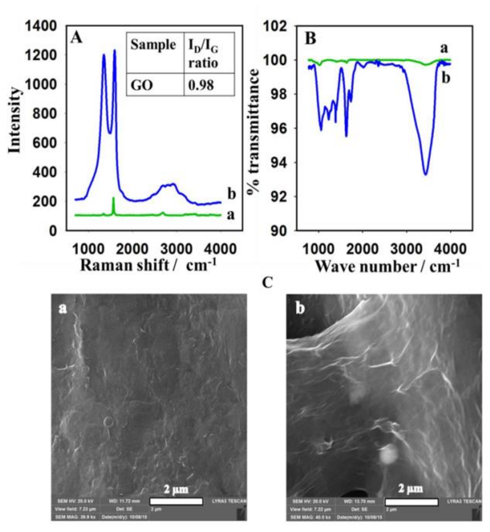


Fig. 1 (A) Raman (B) FTIR spectra of (a) G (b) GO. (C) SEM images of bare (a) or rGO-GPE (b) at 2 µm magnification.

❖ Effect of pH

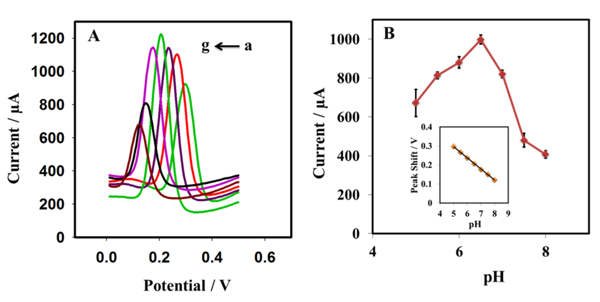


Fig.4 (A) SWVs in 0.1 M PBS solution containing 50 µM dopamine at various pH values at rGO-GPE. (B) Graph indicated the peak current and peak shift with pH change.

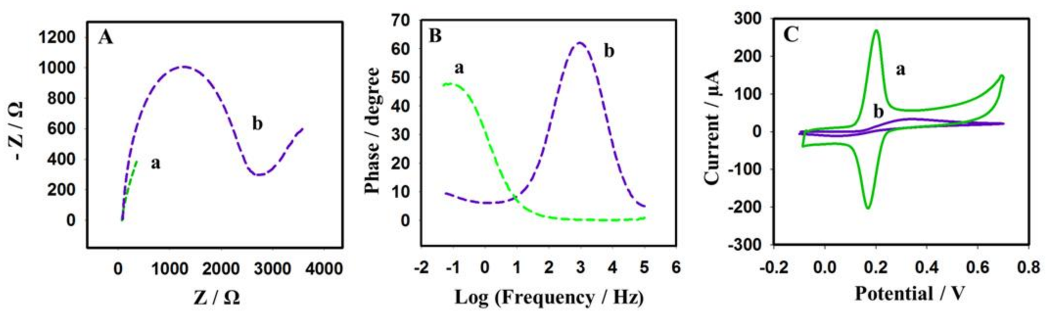


Fig. 2 (A) Nyquist (B) bode phase plots of 5 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ on (a) rGO, and (b) bare GPE. (C) CVs of (a) rGO and (b) bare GPE were recorded at 0.1 V/s in a 1 mM dopamine 0.1 M PBS.

❖ Electrode active surface area study

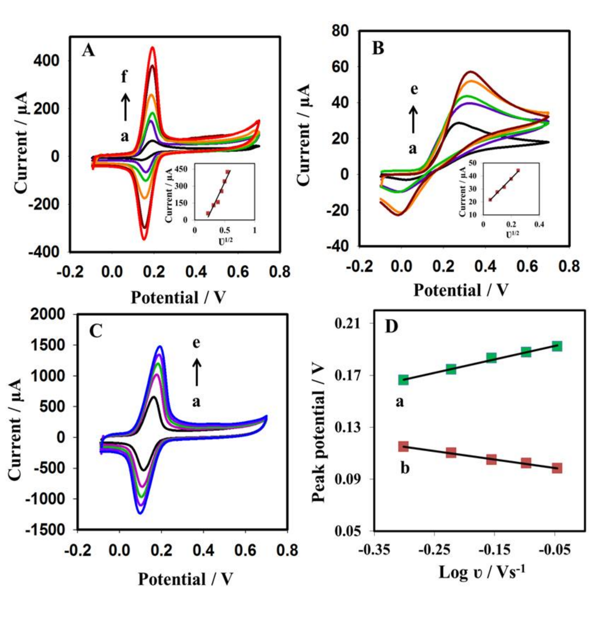


Fig. 3 (A) CVs of 1mM dopamine using (A) rGO or (B) bare GPE at scan rates of 50-300 mV/s. (C) CVs at higher scan rate (500-900 mV/s). (D) The linear relationship between Log υ vs. (a) anodic and (b) cathodic peak potentials

❖ Calibration Curve

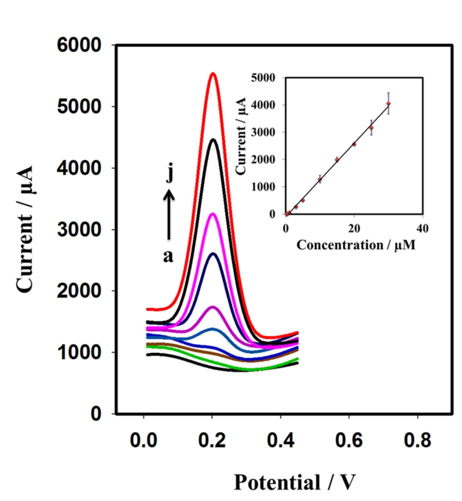


Fig. 5. SWVs at various concentrations of dopamine from 0.4 µM to 30 µM.

Results (contd.)

Table 1 Comparison of the developed sensor with other graphene based sensors.

Electrode	Technique	LOQ (µM)	LOD(µM)	Ref.
GR–CS/GCE	DPV	5		[1]
GR-GCE	DPV	4	2.64	[2]
GR-modified GCE	CV	2.50	0.5	[3]
GR–SnO2/CILE	DPV	0.5	0.13	[4]
PPy/graphene/GCE	CV	0.5	0.1	[5]
GNS/paste electrode	DPV	4	0.6	[6]
PAM/rGO/GCE	CV	0.3	0.1	[7]
PGR/GCE	Amperometry	5	2	[8]
3D-rGO/GCE	DPV	5	0.17	[9]
Pt/RGO/GCE	DPV	10	0.25	[10]
mp-GR/GCE	DPV	4	0.15	[11]
Au/Gr-AuAg	SWV	0.3	0.205	[12]
Au/Gr-Au	SWV	100	30.3	[12]
rGO-GPE	SWV	0.4	0.095	This work

Table 2 Detection of dopamine in human urine sample

Sr#	Found (µM)	Added (µM)	Recovered (µM)	%cent recovery
1	0	5	4.82	96.4
2	0	10	10.64	106.4
3	0	15	15.27	101.8

Discussion

- The characteristic Raman and FTIR spectra obtained of synthesized GO. FE-SEM images indicated formation of rGO on GPE surface (Fig.1).
- The impedance study also indicated the sharp decrease in charge transfer resistance. The sharp reversible peak for 1 mM dopamine observed on modified surface (Fig.2).
- The huge increase in electroactive surface area for dopamine was observed from 0.063 to 0.631 cm^2·electroactive surface area (Fig.3). The value of ks calculated by using equation 1 was 5.81 s^{-1}. The ks value is larger compared reported values 0.25 s^{-1} [13] and 0.77 s^{-1} [14] for dopamine

$$\log k_s = \alpha \log (1-\alpha) + (1-\alpha) \log \alpha - \log (RT/nF\upsilon) - \alpha (1-\alpha)nF\Delta E_p/2.3RT \qquad 1$$

- The pH of the sensing medium has shown significant effect on the dopamine response and maximum was found at 6.5 pH. The slope peak shift Vs. PH was -58.6 mV/pH and it was almost equal to the theoretical value -59 mV/pH (Fig. 4).

$$E \text{ vs. } Ag/AgCl = 58.97 - 58.6[pH] \qquad 2$$

- The developed sensor was found linear from 0.4 to 30 µM with LOD 0.095 µM (Fig. 5).
- The developed sensor found better or comparable with other graphene based sensors (Table 1)
- The rGO-GPE was successfully applied for sensing of dopamine in human urine sample (Table 2)

Conclusions

- Highly cost effective
- Disposable is due to fast modification time
- Graphene layers efficiently improved the electroactive surface area and facilitate the fast charge transfer
- The sensor found linear for dopamine from 0.4 to 30 µM.
- The modified surface was found attractive towards dopamine molecules over ascorbic acid
- The LOD and RSD for dopamine was 0.095 µM and 4.1%, respectively
- The fouling effect of dopamine could be avoided by single use
- It could safe lot of time which is required for surface cleaning .

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