Reduced Graphene Oxide Based Electrochemical Nonenzymatic Human Serum Glucose Sensor

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Abstract

Present work proposes green synthesis of reduced graphene oxide using lemon peel extract(vitamin-c) and its application as an electrochemical nonenzymatic human serum glucose sensor. Improved modified Hummer's method was preferred for the preparation of graphene oxide. X-ray diffraction (XRD), Ultraviolet-visible absorption spectroscopy (UV-Vis) and X-ray photon spectroscopy (XPS) analysis revealed the successful reduction of Graphene oxide (GO) using lemon peel extract. Field emission scanning electron microscopy (FESEM), Fourier transform infra-red spectroscopy (FTIR) and Raman spectroscopy supports the formation of reduced graphene oxide (rGO) nanosheets. The proposed glucose sensor exhibits high sensitivity of 1402 $\mu\text{A}\cdot\text{cm}^{-2}\cdot\text{mM}^{-1}$ (S/N=3) along with correlation coefficient of 0.9887 and low detection limit of 0.011 μM . The sensor has detected glucose with RSD of 1.99% in human blood serum. The measured values are well agreed with the values obtained using professional glucose sensor used in hospitals.

Keywords: Green synthesis; Lemon peel extract; Reduced graphene oxide; Glucose sensor.

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1. Introduction

Graphene named as a 'wonder material' due to its extraordinary properties is the thinnest and strongest material having high electrical and thermal conductivity. Graphene oxide (GO) is obtained from graphite oxide using various methods like mechanical exfoliation, chemical synthesis, chemical vapour deposition (CVD)^[1] etc. CVD is popular among them for large-scale production. In chemical synthesis toxic materials such as hydrazine hydrate or sodium borohydride are used as a reducing agent. These reducing agents may harm biological application.^[2] Due to ecologically unfriendly approach and hazardous chemicals used in thermal, chemical and electrochemical methods roused us to ponder some different technique for synthesis of reduced graphene oxide (rGO). Green synthesis using phytoextracts and bacteria are some other methods of synthesis of GO. Bacterial synthesis is carried out under ambient conditions and requires expertise. In the present study, GO is synthesized using improved modified Hummer's method. Green synthesis route is adopted to obtain rGO by using phytochemicals present in lemon peel. Lemon is a citrus fruit containing rich source of natural vitamin C and exceptional anti-oxidant as

well as antibacterial activity.^[3] Lemon peels are by-products of lemon and research shows that they are an excellent source of bioactive compounds.^[4] During the production of fruit juice and other citrus products, the peel accumulates in the bulk. Fruit peels are usually discarded as wastes; however, they are very rich sources of Vitamin C, fiber, and many nutrients, including phenolics and flavonoids which are also good antioxidant agents and contain many phytochemicals.^[5,6] A lemon peel is used as an eco-friendly and biologically safe reducing and capping agent in the synthesis of rGO. There several extractions methods are adopted in pharmaceutical industries like, Soxhlet extraction, drying, cold maceration etc. The cold maceration method is preferred to extract lemon peel due to its simplicity and effectiveness to preserve the properties of phytochemicals unaltered. Functionalized graphene with some metallic oxide shows extraordinary sensing properties.^[7] Furthermore, a green reduction is simple, eco-friendly and cost-effective. It has high electrical conductivity due to large amount of sp^2 carbon atoms. Moreover, rGO is an extremely encouraging material as a biosensor due to its remarkable specific area ($\sim 2600\text{ m}^2/\text{gm}$) and high electrical conductivity(103.3 Scm^{-1}).^[8-10] It has diversified applications in various areas such as Batteries,^[11] Biomedical,^[12] Supercapacitors,^[13] printable graphene electronics^[14] gas sensor^[15] and biosensors.^[16] Glucose biosensors have extensive industrial, environmental and

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biomedical applications. In clinical medicine, these biosensors are used to monitor patients, blood glucose level to diagnose and treat diabetes. Diabetes is a metabolic disease that causes an abnormal blood sugar level, which consequently activates several metabolic pathways related to inflammation and apoptosis events.^[17] This disease has no cure thus far. Hence, patients with diabetes consistently need to monitor their blood glucose levels to avoid complications. Thus, developing a fast, sensitive and reliable biosensor to detect glucose is necessary. Electrochemical biosensors, especially those containing glucose oxidase (GOx), are the preferred devices for determining blood glucose due to their simplicity, selectivity, sensitivity and direct point care assays.^[18] However, challenges in the use of enzyme-based glucose biosensors remain because of the low efficiency of enzyme immobilisation on a solid electrode. To overcome this problem, many researchers have utilised nanomaterials with different structures and developed non-enzymatic glucose sensors.^[19] In the present case, reduced graphene oxide (rGO) is modified using Fluorine-doped Tin Oxide (FTO) substrates. rGO/FTO modified electrode was used as an enzyme-free biosensor to detect glucose concentration in an efficient way using Linear sweep voltammetry and cyclic voltammetry. An important part of this study was to evaluate sensitivity, selectivity, reproducibility, and stability with a low detection limit. Moreover, the green reduction method employed for the preparation of rGO is an inexpensive and eco-friendly way. The fabricated glucose biosensor was also used in an investigation of glucose level in the existence of obstructing substances in real human blood serum.

2. Materials and Methods

Graphite powder (98%), Potassium permanganate (KMnO_4 , 99%), Hydrogen peroxide (H_2O_2 , 30%), sulphuric acid (H_2SO_4 , 99.99%), Hydrochloric acid (HCL, 30%), Phosphoric acid (H_3PO_4 , 85%), Polyvinyl alcohol (PVA, 99%), Fluorine-doped Tin Oxide (FTO) substrates, D (+) glucose, dopamine, L-ascorbic acid, D (-) fructose, lactose were purchased from Qualigens fine chemicals, India. Deionised (DI) water was purchased from Sharad agencies, India. Phosphate buffer solution (PBS) was prepared in the laboratory using the standard method, and Lemons were purchased from a local market. All the chemicals are of AR grade and used without further purification.

2.1 Preparation of GO

Synthesis of GO was carried out by using modified Hummer's method.^[20] The graphite powder was added to H_2SO_4 and H_3PO_4 (9:1 proportion) and stirred for 1 h at 100 °C. Potassium permanganate was added during stirring process. For oxidation purpose, H_2O_2 was added into the mixture resulting in yellow color. Repeatedly washing with 5% HCl and DI water along with centrifuge (4000 rpm) causes complete removal of SO_4^{2-} . After drying at 60 °C for nearly 24 h the resultant product (rGO) was collected.^[21]

2.2 Preparation of Phytoextracts

Fresh lemon were purchased from local market and cleaned using DI water. The lemon peels were blended with domestic blender and kept in DI water for cold maceration overnight. The mixture was then stirred for half an hour at 50 °C followed by filtration. The stock was stored at 4 °C for further use.

2.3 Reduction of GO using aqueous peel extract of lemon

50 mg GO (0.1 mg/ml) was dispersed in DI via sonication for 45 min. An aqueous peel extract of lemon (10 ml) was added to the aqueous GO solution. This mixture was refluxed for 6 h at 90 °C until it changes to brown-black color. The supernatant was centrifuged at 4000 revolutions per minute and dried at 100 °C in vacuum oven.^[22]

2.4 Preparation of rGO/FTO modified electrode

10mg of rGO powder was dispersed in 5 ml DI water and 5 μl PVA using bath sonication for 30 minutes. 10 μl of the suspension was drop casted on previously cleaned FTO substrate. Working area of the electrode was 1 cm^2 . The electrode was annealed at 250 °C and used for further electrochemical measurements.

2.5 Mechanism of reduction of GO by lemon peel phytoextract

Fig. 1 exhibits mechanism of reduction of GO by lemon peel phytoextract. The reduction of GO by the phytoextract may invent from the oxidized products such as flavonoids, polyphenols, tannis, terpenoids, saponins, *etc.* present in lemon fruit peel.^[23] These phytochemicals usually have a large binding affinity towards O_2 functional groups to create their respective oxides and water molecules as its by-product. Flavonoid compounds show excellent antioxidation properties due to their ability to reduce to the phenolic hydroxyl group. The phenolic hydroxyl group may react with the oxygen-containing groups decorated on GO sheets by releasing water molecules. GO contains reactive species namely, hydroxyl, epoxide, and carbonyl species.^[24] When aqueous GO and lemon peel phytoextract was mixed, sonicated, and refluxed at 95 °C, acidic polyphenols in phytoextract may react with epoxide fraction through nucleophilic reaction. It results in opening up carbon-oxygen bond. Similar nucleophilic attacks of polyphenols with the eradication of water molecules might be experienced by carbonyl and hydroxyl groups. The process results in the conversion of GO to rGO, along with the production of black-colored graphene and its stable compounds.

The epitaxial growth process resulted in the formation of crumpled rGO nanosheets. A glucose sensing performance of rGO/FTO modified electrode was studied in presence of phosphate buffer solution (PBS: 7.4 pH). Normally, when glucose disperses in PBS, it creates D-gluconolactone and hydrogen peroxide (H_2O_2). It further generates D-gluconate with H^+ ions due to electro oxidation of glucose. Hence gluconolactone is the main product responsible for oxidation

Fig. 1 Mechanism of green reduction of GO and rGO/FTO electrode for glucose sensing.

that hydrolyses gluconic acid. H^+ ions reduce the pre-absorbed oxygen by releasing electrons which reduces barrier potential between consecutive grains and boosts the electrical conductivity.^[25] The probable chemical reaction may occur as,

$$\text{glucose} + O_2 \rightarrow H_2O_2 + \text{gluconic acid} \quad (1)$$

2.6 Structural and optical Characterization

X-Ray Diffraction (XRD) pattern of graphite powder, GO and rGO were taken using Phillips, Holland instrument ($CuK\alpha$, $1.542 \text{ \AA}$, $5-85^\circ$). The surface morphology and elemental composition of GO and rGO was done using field emission scanning electron microscope (FESEM: FEI Nova NanoSEM 450), Raman analysis was done by using raman spectrometer (Jobin-Yvon HR 800 UV) along with He-Ne (633 nm) laser source. The surface composition GO and rGO were analysed by multifunctional X-ray photoelectron spectroscopy (XPS) (ULVAC, PHI500 Versa Probe III with $1486.6 \text{ eV K}_{\alpha} \text{ Al}$ X-ray source). Fourier Transform Infrared Spectroscopy (FTIR) study was done with FTIR-6100 spectrometer (JASCO) in the transmission (T) mode in the wave number range $4000-500 \text{ cm}^{-1}$.

2.7 Experimental set up for electrochemical measurements

Wonatech potentiostat was used in voltametric measurements for glucose detection along with three-electrode system, rGO/FTO, platinum and Ag/AgCl as a working, counter and reference electrode respectively. These three electrodes were placed inside the beaker containing fixed volume of PBS as electrolyte. 150 W Xenon lamp with illumination intensity of 100 mW/cm^2 was used to study I-V characteristics. The electrocatalytic performance of the electrode was studied using Linear Sweep Voltammetry (LSV) and Cyclic Voltammetry (CV).

3. Results and Discussion

3.1 XRD analysis

Fig. 2 illustrates XRD spectra of graphite, GO and rGO. The peak observed at 26.8° (002) with a d-spacing value $\sim 0.335 \text{ nm}$ (JCPDS file 75-1621) corresponds to the characteristic peak of hexagonal graphite. For GO, the characteristic peak at around 9.18° ($d \sim 0.79 \text{ nm}$) which may be ascribed to the existence of oxygen-rich groups on both sides of the sheets and water molecules trapped between the sheets.^[26] In case of rGO spectrum, a broad peak at 27.24° along with $d \sim 0.328 \text{ nm}$ confirms the complete formation of rGO.^[27]

Fig. 2 XRD spectrum of graphite, GO and rGO.

3.2 UV-Vis spectra analysis

Fig. 3 represents UV-Visible spectra of GO and rGO. GO showed two characteristic peaks at 225 and 303 nm that can be correlated to the electronic transition from π - π^* and n - π^* orbitals, respectively.^[28] The absorption peak at 228 nm is red shifted to 281 nm indicates that electronic conjugation within the reduced graphene oxide sheet is revived upon reduction of graphene oxide.^[29,30]

Fig. 3 UV-Visible spectra of GO and rGO.

3.3 FESEM and EDS analysis

Figs. 4(a) and (b) exhibits FESEM and EDS of GO and rGO. FESEM of GO shows wrinkled sheet like structure while for rGO, agglomeration of nanosheets along with irregular arrangement of stacked crumpled sheets was observed. This may be attributed to the nucleophilic reaction of flavonoids and polyphenols with the eradication of water molecules from carbonyl and hydroxyl groups during rGO synthesis.

3.4 FTIR analysis

FTIR spectra for GO and rGO is displayed in Fig. 5. The spectrum of GO exhibits a broad band at 3100-3500 cm^{-1} region due to the surface O-H stretching vibrations or due to the absorbed water molecules.^[31] In addition to these, bands correspond to epoxide ring vibrations, C=O stretching vibrations and C=C stretching vibrations are visible at 1054 cm^{-1} , 1734 cm^{-1} and 1633 cm^{-1} respectively. A petite band ranging from 3200 to 3400 cm^{-1} (O-H stretching vibration) is observed in rGO as shown in Fig. 5. It can be implicated that rGO thus contains less amount of O-H group. A reduction in intensity of absorption of O₂ functional groups is observed in rGO supports the reduction of GO using lemon peel extract.

Fig. 4 FESEM and EDS of (a) GO and (b) rGO.

Fig. 5 FTIR spectrum of GO and rGO.

Fig. 6 Raman spectrum of GO and rGO.

3.5 Raman spectroscopy

Raman spectrum of GO and rGO is showcased in Fig. 6. The Raman spectrum of graphene is usually characterized by two specific modes of vibrations G and D. G band represents the first-order scattering of the E_{2g} phonon of hexagonal sp^2

carbon atoms and the D band is due to the breathing mode of k-point phonons of A_{1g} symmetry.^[32] The blue shift of G band is due to the reduction of O_2 functional group during green reduction of GO. A decrease in I_D/I_G ratio suggests an increase in the size of sp^2 domains and ordered crystal structure of rGO.^[33] Presence of 2D band at 2697 cm^{-1} strongly supports reduction of GO.^[34]

3.6 XPS analysis

C1s spectra of rGO shows the reduction of GO using aqueous lemon peel extract and validates the removal of O_2 functional group (Fig. 7). For GO sample, the C 1s bands can be deconvoluted into three bands attributed to C-C, C=O and C(O)OH bonds at 284.8, 286.5 and 288.5 eV, respectively.^[35] The C 1s XPS spectrum of rGO shows a significant intensity decrease of C=O and C(O)OH bands in comparison to that of GO, indicating effective deoxygenation of GO after the reduction. However, after being reduced, the peak intensity of oxygen with functionalities was decreased sharply as shown in figure indicating effective deoxygenation of GO after the reduction. This finding proved the reduction of GO. For rGO sample, the peaks of C-C, C=O and C(O)OH bands locate at 284.5, 285.4 and 283.7 eV, respectively. Thus, there are the shifts in binding energy values of these bands of rGO. These shifts may due to the change in chemical environment of carbon atoms after reduction.^[36] In addition, after reduction process, the surface C/O atomic ratio increases from 2.12 to 5.57. These results show that the removal of oxygen containing groups of GO using aqueous peel extract of lemon as reduction reagent was relatively successful.

3.7 Electrochemical nonenzymatic detection

Figs. 8 (a-b) represents cyclic voltammograms in PBS (7.4 pH) electrolyte solution to study the electrocatalytic activity of the modified electrodes. No faradaic peak was observed on the bare FTO in presence of glucose. A very low oxidation current was exhibited on bare GO/FTO at +0.7 V. A well defined glucose oxidation peak was observed for bare

Fig. 7 C1s spectrum of GO and rGO.

Fig. 8 (a) Cyclic Voltammogram of various electrodes at 100 mv/s scan rate and (b) LSV: effect of variable scan rate on rGO/FTO electrode.

rGO/FTO in presence of 1mM glucose compared to bare rGO/FTO. The oxidation current of rGO/FTO is greater ($\sim 340 \mu\text{A}$) than GO/FTO at +0.7 V. This indicates that rGO is necessary to obtain high sensitivity and better electrocatalytic activity.

The rGO/FTO electrode was scanned from 10 to 300 mv/s in PBS (7.4 pH) solution containing 1 mM D (+) glucose as shown in Fig. 8b. The applied potential was between -0.5 V and +1.2 V, while oxidation occurred at +0.7 V and peak current was increased with an increase in scan rate. The sensor electrode exhibited the maximum current flow and clear oxidation at +0.7 V. This indicates that electrochemical reaction takes place on rGO/FTO nanocomposite electrode demonstrating its ability towards enzyme sensing. The cyclic

voltammogram of rGO/FTO electrode exhibited a linear increase in current density with the increase in glucose concentration as shown in Fig. 9a. The time taken to obtain a stable response was $\sim 5\text{s}$.

The possible mechanism of oxidation of glucose is as follows: During, electrooxidation of glucose in PBS, D-gluconolactone and hydrogen peroxide (H_2O_2) generated D-gluconate with H^+ ions. The gluconolactone hydrolysed gluconic acid and H^+ ions reduced the pre-absorbed oxygen by releasing electrons. This revealed that the electron transport between PBS solution and electrode in the redox process was enhanced due to the high electrical conductivity and electrocatalytic activity of the rGO.

Fig. 9 (a) Cyclic Voltammogram of rGO/FTO with variable glucose concentration at 100 mv/s scan rate and (b) Calibration curve.

Table 1. Comparison of the enzyme free glucose sensor based on rGO and its composites.

Electrode	Detection Potential (V)	Sensitivity ($\mu\text{A}/\text{mM cm}^2$)	Detection range (mM)	Detection limit (μM)	Ref.
rGO	+0.7	1402	0.1 - 10	0.011	This work
Nafion/GOx/rGO-6/ZnONRs /Au/PET	- 0.8 to +0.8	2.26	11.5	37.5	[37]
Ni NPs/ATP/RGO	0.0 to -1.5	1414.4	1-710 μM	0.37	[38]
NiCo ₂ O ₄ anowrinkle-rGO	-	548.9	0.005-8.6	2	[39]
AuPtNP /rGO	-	48	0–2.4	5	[40]
rGO/NiO	-	-	1 to 15	19.35	[41]
CuO (NP)/rGO	-	4760 (± 3.2)	-	0.091 (± 0.003)	[42]
CuNWs/rGO/ITO	+0.6V	9.3	0-5	-	[43]

Fig. 9b represents oxidative current response of rGO/FTO electrode with variable glucose concentration (0.1-10mM). The calibration curve gives linear regression equation as $I_p = 58.171c + 797.17$, $R^2 = 0.9887$ ($N=8$). The sensitivity of sensor electrode is calculated from slope of calibration curve. The sensor offered a sensitivity of $1402 \mu\text{A. mM}^{-1}\text{cm}^{-2}$ ($S/N=3$). Similarly, inset:b shows oxidative current response of rGO/FTO electrode with lower glucose concentration (0.1-0.5mM). It gives the linear regression equation as $I_p = 163.73c + 759.26$, $R^2 = 0.9983$ ($N=3$) along with a low detection limit of $0.011 \mu\text{M}$. The performance analysis of the proposed sensor (rGO/FTO) in this work is compared with other enzymatic and non-enzymatic glucose sensors reported earlier are displayed in Table 1.

Electrochemical performance of rGO/FTO sensor electrode is found to be superior in one or more parameters under consideration compared to other enzymatic and non-enzymatic glucose sensors presented in Table 1.

3.8 Selectivity, stability, and reproducibility

The proposed biosensor was examined for the commonly occurring interfering species like ascorbic acid, dopamine, fructose, and lactose in human blood serum (Fig. 10a).

Selectivity: The biological range of glucose concentration in human serum is 3-8mM, which is quite greater compared to other interfering substances like ascorbic acid, dopamine, fructose and lactose. Hence, the electrode responses were examined with 1 mM D (+) glucose with above mentioned interfering species (0.1 mM each) in PBS (7.4) solution. The glucose sensing ability of proposed sensor was unaffected by the interfering species exhibited excellent selectivity of it.

Reproducibility: The reproducibility of the sensor was studied using 20 similar sensors. The current response was observed for 1mM glucose concentration in PBS buffer (7.4 pH) for each sensor electrode using linear sweep voltammetry. The peak currents were noted and RSD was calculated mathematically. The reproducibility of the sensor was studied using 20 similar sensors electrodes. The current response was

observed for 1mM glucose concentration for each sensor. RSD of 1.7% confirms the significant reproducibility.

Stability: The stability of sensor was studied by measuring current response for 1mM glucose concentration in PBS buffer (7.4 pH) using linear sweep voltammetry for four weeks. The peak currents were noted after each week and RSD was calculated mathematically. The stability of the sensors was also tried and tested intermittently for a period of 4 weeks and yielded with RSD of 2.08% (Fig. 10b) which supports excellent stability of the proposed sensors. A repeatability of the proposed sensors was examined by measuring the current response for 5 times over 6 days and RSD of 1.57% was observed in performance as presented in Fig. 10c.

3.9 Diagnosis of glucose in human serum

The glucose concentration level in human blood samples was determined using proposed rGO based glucose biosensor. All human blood serum samples were collected from pathology laboratory of a renowned hospital. These samples were diluted (100 folds) using standard dilution method before analysis. However, the results obtained using proposed sensors were compared with the certified values received from pathology laboratory. The average recovery rate of 98% exhibits the reliability of the proposed sensor for human serum glucose biosensor application. Table 2 presents the experimental data for the human serum glucose concentration.

Table 2. Determination of glucose in human serum and its recovery.

Human Serum Samples	Glucose added (mM)	Glucose recovered (mM)	Recovery (%)	RSD (%)
1	0.2	0.195	97.5	2.5
2	0.5	0.496	99.2	0.8
3	1	0.98	98	2
4	3	2.92	97.33	2.66

Fig. 10 (a) Selectivity (b) Stability (c) reproducibility of the rGO/FTO sensor electrode.

4. Conclusion

The lemon peel phytoextract is a promising candidate for the green reduction of GO. The eco-friendly approach, cost-effectiveness, and simplicity in fabrication of rGO/FTO electrode are some highlights of this work. The proposed biosensor has good stability, excellent reproducibility, and selectivity. It shows high sensitivity of $1402 \mu\text{A} \cdot \text{cm}^{-2} \cdot \text{mM}^{-1}$ ($S/N=3$) towards glucose in human serum along with correlation coefficient (R^2) of 0.9887. The LOD of 0.011 μM makes it favorable for investigating glucose concentration in human serum samples. We believe that this work can introduce an emerging concept of rGO based functionalized nanomaterials to realize simple and reliable electrochemical glucose sensor platforms.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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