A facile synthesis of GO/CuO-blended nanofiber sensor electrode for efficient enzyme-free amperometric determination of glucose

Medha Gijare¹, Sharmila Chaudhari², Satish Ekar¹ and Anil Garje³*

Abstract
The development of biosensors with innovative nanomaterials is crucial to enhance the sensing performance of as-prepared biosensors. In the present research work, we prepared copper (II) oxide (CuO) and graphene oxide (GO) composite nanofibers using the hydrothermal synthesis route. The structural and morphological properties of as-prepared GO/CuO nanofibers were analyzed using an X-ray diffractometer, field-emission scanning, energy dispersive X-ray analysis, Fourier transmission infrared spectroscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. The results indicated GO/CuO nanofibers exhibit nanosized diameters and lengths in the order of micrometers. These GO/CuO nanofibers were employed to prepare non-enzymatic biosensors (GO/CuO nanofibers/FTO (fluorine-doped tin oxide)) modified electrodes for enhanced glucose detection. The sensing performance of the biosensors was evaluated using linear sweep voltammetry (LSV) and chronoamperometry in phosphate buffer solution (PBS). GO/CuO/FTO biosensor achieved high sensitivity of 1274.8 μA mM⁻¹ cm⁻² having a linear detection range from 0.1 to 10 mM with the lower detection limit (0.13 μM). Further, the prepared biosensor showed good reproducibility, repeatability, excellent selectivity, and long-time stability. Moreover, the technique used for the preparation of the GO/CuO composite is simple, rapid, cost-effective, and eco-friendly. These electrodes are employed for the detection of glucose in blood serum with RSD ~ 1.58%.

Keywords: Graphene oxide, Enzyme free, Glucose, Biosensor

Introduction
Diabetes is a widespread disease affecting millions of populations and predicted to be the major cause of death as it can damage neural systems in humans. It is essential for diabetic patients to frequently monitor and maintain glucose levels. Hence, an effective diagnosis of diabetes and a reliable glucose monitoring system are necessary. Extensive majors have been taken to control diabetes through several monitoring systems. Glucose biosensors have a great contribution in monitoring glucose levels of diabetic patients (Makaram et al., 2014; Bruen et al., 2017; Gopalan et al. 2017; Gopalan et al. 2016; Sai-Anand et al. 2014). Enzymatic electrochemical sensors suggest good selectivity and sensitivity but due to complex mobility, lack of stability and reproducibility limit their performance (Gopalan et al. 2013, Haldorai et al. 2016). These limitations are overcome by the development of enzyme-free glucose sensor devices through direct oxidation of glucose in the form oxidized layer (Sai-Anand et al. 2019). Glucose oxidase is usually practiced as an enzyme in most of the glucose biosensors. Amperometry is another widely used technique for glucose detection (Peter and Heineman, 1996, Thévenot et al., 2001). Glucose oxidase performs a major
role in the oxidation of β-d-glucose to d-glucono-δ-lactone. Hydrogen peroxide (H₂O₂) is formed as a byproduct in a catalytic reaction and oxygen as an electron acceptor. A simple technique, less analysis time, cost effective, and low detection capability are some advantages of using amperometry (Thunkhamrak et al., 2020). Regardless of excellent sensitivity and low detection limit in few nanocomposites, an enzymatic glucose sensor limits the application of sensors due to high production cost (G. Gnana kumar et al., 2017). Nowadays, graphene has attracted researchers due to the larger specific superficial area, purity, high conductivity, and low cost (Liu et al., 2019). It has diversified applications in various areas such as batteries (Ji et al., 2016), biomedical (Mallick et al., 2018), supercapacitors (Hota et al. 2020), printable graphene electronics (Hu Etal. 2016) gas sensors (Nakate et al. 2020), and biosensors (Bai et al. 2020). In chemical synthesis, graphene oxide (GO) is reduced to eliminate oxygen-containing functionalities using hazardous chemicals like hydrazine as a reducing agent. The process of chemical reduction contains crucial and lengthy steps of chemical reactions, tiresome washing cycles, and drying of residue. Moreover, the use of poisonous and explosive reducing agents in the redox process makes it non-eco-friendly. Hence, functionalized GO using eco-friendly reduction methods is necessary in biosensing applications. Copper oxide (CuO) can be used to functionalize GO as a catalyst because of its electrochemical catalytic property (Khan et al. 2021). In an electrolysis process, Cu (II) oxidizes Cu (III) by gaining electrons in the redox reaction. During the oxidation process, glucose gets converted into gluconolactone (Zhang et al. 2020; Wang et al. 2014). Hence, an efficient electron transfer in glucose oxidation can be predicted through excellent support of GO to CuO. In the present work, an enzyme-less amperometric glucose biosensor using graphene oxide (GO) and copper oxide (CuO) nanocomposites was successfully prepared using a fluorine-doped tin oxide (FTO) substrate. The prepared sensor electrode exhibits exclusive properties such as large superficial area, good catalytic activity, and excellent electrical conductivity. Moreover, the electrode provides improved sensitivity, low detection limit, and excellent recovery in human serum compared to previously reported literature. Furthermore, the preparation and detection procedures are simple, fast, less time consuming, and cost effective.

**Methodology**

Natural graphite powder (S.Aldrich, 99.99%), potassium permanganate (K₂MnO₄, 99%), hydrogen peroxide (H₂O₂, 30%), sulfuric acid (H₂SO₄, 99.99%), hydrochloric acid (HCl, 30%), phosphoric acid (H₃PO₄, 85%), copper oxide (CuO, 99.9%), 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. Deionized (DI) water was purchased from Sharad Agencies, India. The phosphate buffer solution (PBS) was prepared in the laboratory using the standard method. All the chemicals are of analytical research (AR) grade and used without further purification.

**Synthesis of graphene oxide**

Graphene oxide was synthesized using an earlier reported method (Marcano et al., 2010). Graphite powder and NaNO₃ in 2:1 proportion were mixed with concentrated H₂SO₄ and H₃PO₄ in the ratio of 9:1 (wt %). Fifteen grams of KMnO₄ was slowly added while stirring followed by the addition of the required amount of H₂O₂. If the mixture turns into bright yellow color, this represents a great oxidation level of GO. In order to eradicate SO₄²⁻ ions, the solution was repeatedly washed and the brownish black precipitate was collected.

**Synthesis of GO/CuO nanocomposites**

Initially, 0.5 g GO and 0.2 g CuO were dissolved in DI and the solution was constantly stirred for half an hour by raising its temperature to 100 °C. Fifty milliliters of NaOH solution was slowly added to it. The temperature of the solution was retained for 10 min and allowed to cool. The GO/CuO composite was collected after evaporation.

**Preparation of GO/CuO nanocomposite electrode**

Ten milligrams of the GO/CuO nanocomposite was dispersed in 5 ml of DI water and 5 μl of PVA using bath sonication for half an hour. Then, 10 μl of the suspension was drop casted on the previously cleaned FTO substrate. The working area of the electrode was 1 cm². The electrode was annealed at 250 °C.

**Mechanism of GO/CuO/FTO glucose sensing**

A new decorum for the synthesis of the GO/CuO nanocomposite by in situ hydrothermal reduction of GO and CuO nanobelt formation is developed as shown in Fig. 1. With the existence of NaOH, DI water assists in the growth of Cu (OH)₂ nanograins morphology on the GO surface. The epitaxial growth process caused the formation of CuO nanobelts. The augmented temperature of the above reaction mixture leads to the formation of a fiber-like GO/CuO nanostructure. A glucose sensing performance of the GO/CuO/FTO-modified electrode was studied in the presence of phosphate buffer solution (PBS:7.4 pH).

Normally, when glucose disperses in PBS, it creates d-gluconolactone and hydrogen peroxide (H₂O₂). It further generates D-gluconate with H⁺ ions due to
electrooxidation of glucose at grain boundaries of CuO. Hence, gluconolactone is the key product accountable for oxidation that hydrolyzes gluconic acid. H+ ions lessen the pre-absorbed oxygen by discharging electrons which decrease the barrier potential between successive grains and lifts the electrical conductivity (Wu et al., 2010).

\[
\begin{align*}
\text{CuO} + H_2O & \rightarrow Cu(OH)_2 + e^- \\
\text{Cu}^{3+} + \text{glucose} + e^- & \rightarrow \text{gluconolactone} + \text{Cu}^{2+} \\
\text{gluconolactone} & \rightarrow \text{hydrolysis} \rightarrow \text{gluconic acid}
\end{align*}
\]

Structural and optical characterization
For structural characterization, an XRD analysis for the synthesized GO and GO/CuO powder was done with Bruker D8-Advanced Diffractometer using Cu Ka radiation (\(\lambda = 0.154 \text{ nm}\)) from the range of 5 to 85° with a scanning rate of 2°/min. Surface morphology and elemental composition of GO and GO/CuO samples were characterized FESEM: FEI Nova NanoSEM 450, Raman analysis was done using a micro-Raman spectrometer (Jobin-Yvon HR 800 UV) using a He–Ne (633 nm) laser excitation source. XPS analysis of GO and CuO was carried out by Multifunctional XPS (PHI ulvac probe III Scanning Microprobe). For the FTIR study, FTIR-6100 spectrometer (JASCO) in the transmission (T) mode in the wavenumber range 4000–400 cm\(^{-1}\) was taken.

Electrochemical measurement
Wonatech potentiostat was used for voltammetric and amperometric measurements for glucose detection with a three-electrode system which comprises GO/CuO/FTO as a working electrode along with platinum as counter and Ag/AgCl as reference electrode. The electrocatalytic performance of the electrode was studied using linear sweep voltammetry (LSV) and chronoamperometry.

Results and discussion
XRD analysis
XRD pattern of GO and GO/CuO nanocomposite is presented in Fig. 2.

The reflection peak which occurred at (002) at 11.92° shows the occurrence of oxygen functionalities on the GO surface with an interlayer basal space of 0.79 nm (Tong et al. 2011). The peak (100) at 42.56° suggested the static disorder of GO. In the case of the GO/CuO nanocomposite, the reflection peak (002) at 24.04° showed a shift with basal spacing of 0.37 nm. The fall in basal space suggested that GO was converted to rGO (Dhara et al. 2015). All peaks of CuO are in good

Fig. 1 Glucose sensing mechanism of GO/CuO/FTO electrode

Fig. 2 XRD pattern of a GO and b GO/CuO
agreement with the JCPDS file: 48-1548, which confirms a high degree of purity and crystallinity of CuO.

**FESEM and EDS analysis**

The surface morphology of prepared GO and GO/CuO nanocomposites was characterized by FESEM as shown in Fig. 3.

Graphene oxide showed a thin wrinkled paper-like structure. In the GO/CuO nanocomposite, high-density nanofibers of sizes in the range of 70–200 nm and several nanometers in length were distributed on the graphene layer. The formation of GO/CuO can be explained as follows.

Due to the increase in temperature during the synthesis, quick evaporation of water molecules caused a contraction of CuO nanoparticles and GO sheets. GO was thermally reduced to modified graphene. The graphene 2D material has a strong hydrophobic center and...
hydrophilic surrounding (Georgakilas et al. 2016). It was noted that the active GO surface lowers the internal energy.

Furthermore, CuO has a monoclinic nature and excellent thermal conductivity. Therefore, CuO nanoparticles together with GO formed a fiber-like structure. The distribution of chemical elements present in the composite was examined using the energy dispersive spectrum (EDS) as shown in Fig. 4.

**FTIR analysis**

FTIR spectra for GO and GO/CuO nanocomposite is as shown in Fig. 5.

The bending and stretching modes of O-H groups were represented as broad spectra present around 3203 cm\(^{-1}\) and the peak at 1734 cm\(^{-1}\) showed C=O stretching vibrations on the surface of GO. The C-O stretching vibrations were assigned to the peak at 1054 cm\(^{-1}\) (Xu Zhu et al. 2012). This surface functional group exhibited the probable bonding of CuO on the GO surface. The peaks at low frequencies below 1000 cm\(^{-1}\) in GO/CuO spectra could be ascribed to Cu-O-Cu and Cu-O-C vibrations (Q Chen et al. 2012). This demonstrated the chemical composition of GO/CuO where GO was partially reduced in presence of cuprous ions.

**Raman spectroscopy**

Raman analysis of the GO-CuO nanocomposite is presented in Fig. 6.

The fundamental vibrations of GO and GO/CuO were observed in the sequence of 1200 to 1700 cm\(^{-1}\). The D (disorder bands) and G (tangential bands) were formed at breathing mode A\(_{1g}\) symmetry and first-order scattering of E\(_{2g}\) photons by Sp\(^2\) carbon (C-C bond) respectively (AC Ferrari et al. 2006). A broad 2D band of GO with a higher wavenumber was located at 2918 cm\(^{-1}\) confirming the multilayered nature of GO. The 2D band of GO/CuO predicted the reduction of GO to rGO caused GO/CuO to stack. The ID/IG ratio of GO/CuO was slightly decreased specifying that there were some structural changes that occurred during thermal reduction.

**XPS analysis**

XPS spectrum of GO and GO/CuO nanocomposite is presented in Fig. 7. The peaks centered at C, O, and
CuO are core-level regions associated with C1s, O1s, and Cu2p peaks respectively.

**Deconvoluted spectrum of GO/CuO**
A deconvoluted spectrum of GO/CuO is shown in Fig. 8.

Carbon in the nanocomposite was identified by the high-resolution spectrum of C1s. The major peak at 283.5 eV exhibited sp² (C-C, C=C) bonding and the shoulder peaks revealed C=O and O-C=O bonding. The chemical bonding states of C-OH and C-O-C were located at characteristic peaks 286.8 eV. The presence of CuO and Cu2O was confirmed using high-resolution O1s spectra. The characteristic peaks observed at 530.2 eV belong to Cu-O, -C=O bonding in GO/CuO. The peak shown at 532.9 eV was assigned to oxygen present in GO. The XPS spectrum of Cu 2p showed a peak at 932.5 eV for Cu 2p 3/2 and confirmed the presence of CuO as a catalyst. A binding energy peak at 952.2 eV was allocated to Cu 2p 1/2 (Wu J et al. 2018).

**Electrochemical measurements**
Linear sweep voltammogram to study the electrocatalytic activity of the modified electrodes is represented in Fig. 9.

The electrodes were scanned at 100 mv/s in presence of 5 mM D (+) glucose. There was no signal response detected for bare FTO (curve a). GO/FTO (curve b) and CuO/FTO (curve c) showed a small increase in background current due to the large superficial area of GO and electrocatalytic capability for glucose oxidation of CuO respectively. A well-defined glucose oxidation peak was observed for GO/CuO/FTO (curve d) in the presence of 5 mM glucose at + 0.6 V. This indicates that the GO/CuO/FTO composite electrode is necessary to obtain high sensitivity and better electrocatalytic activity.

During the oxidation process, CuO was oxidized to CuOOH and glucose to gluconolactone by Cu (III) (Wei H et al. 2009).

Further, the electrochemical effect on GO/CuO/FTO with a variable scan rate was examined using LSV as shown in Fig. 10. The electrode was scanned from 10 to 300 mv/s (a to h) in PBS electrolyte in the presence of 5 mM D (+) glucose. The oxidation occurred at + 0.6 V for each scan and the oxidation peak current was increased with an increase in scan rate. This revealed that electrochemical reaction takes place on GO/CuO nanocomposite demonstrating its ability towards enzyme sensing (Wang et al. 2012). Hence, further electrochemical and amperometric measurements were carried out at the optimized potential of + 0.6 V vs. Ag/AgCl.

**Amperometric measurements**
The amperometric response of the GO/CuO/FTO electrode was measured and presented in Fig. 11a. The proposed electrode revealed that the electron transport between PBS solution and electrode in the redox process is enhanced due to the high electrical conductivity and electrocatalytic activity of the GO/CuO nanocomposite (Hsu et al. 2012). The calibration curve in Fig.11b displayed two linear ranges corresponding to low glucose concentration (0.1–1 mM) and high concentration (1–10 mM).

The corresponding linear regression equations were $I_p = 424.95c + 569.22$ with $R^2 = 0.9984$ ($N = 9$) and $I_p = 27.666c + 826$ with $R^2 = 0.9963$ ($N = 9$) respectively. For low glucose concentration the sensitivity was 1274.8 μA mM⁻¹ cm⁻² (S/N = 3) whereas for high concentration was 830 μA mM⁻¹ cm⁻² along with a low detection limit of 0.13 μM. A comparative study of performance of various glucose biosensors is displayed in Table 1.

**Selectivity, stability, and reproducibility**
The selectivity and stability of the GO/CuO/FTO sensor electrode are presented in Fig. 12.

The biological range of glucose concentration in human serum is 3–8 mM, which is quite greater compared to other interfering substances like ascorbic acid, dopamine, etc. Hence, the electrode amperometric responses were examined with 1 mM D (+) glucose with the abovementioned interfering species (0.1 mM) in PBS (7.4) solution. It was observed that the glucose sensing ability of the proposed sensor was unaffected by the interfering substances. The reproducibility of the sensor was studied using 10 similar sensors. The current response was observed for 1 mM glucose concentration for each sensor. RSD of 2.7% confirms the significant reproducibility. The aging effect (stability) of the samples was also tested periodically for 30 days with of 1 mM glucose concentration and an RSD of 2.64% was
achieved. This demonstrates that the GO/CuO/FTO electrode has good repeatability, reproducibility, and stability as a glucose biosensor.

Determination of glucose concentration in human serum
The blood glucose level in human serum samples was determined using the proposed glucose biosensor. The human serum samples were received from a standard pathology laboratory. The samples were diluted (100 folds) using the standard dilution method before analysis. The results obtained using the GO/CuO/FTO sensor were compared with the certified values received from the pathology laboratory (Table 2). The average recovery rate was 99.17% along with an RSD of 1.58% which assured the reliability and applicability of the GO/CuO/FTO sensor to determine the glucose concentration in a real sample.

Fig. 8 Deconvoluted spectrum of GO/CuO a C1s, b O1s, and c Cu2p

Fig. 9 LSV of a FTO, b GO/FTO, c CuO/FTO, and d GO/CuO/FTO at 100 mv/s scan rate

Fig. 10 LSV of GO/CuO/FTO electrode with variable scan rate
**Table 1** Comparison of the enzyme-free GO-based glucose sensor with its composites

| Electrode            | Method of detection | Potential (V) | Sensitivity (μA mM\(^{-1}\) cm\(^{-2}\)) | Linear range (mM) | LOD (μM) | Ref.                  |
|----------------------|---------------------|---------------|------------------------------------------|-------------------|---------|----------------------|
| GO/CuO/FTO           | Amp                 | 0.6           | 830, 1274.8                              | 0.1–1             | 0.13    | Present work         |
| PDDA/Ch/GOx/PtAuNPs/ | Amp                 | 0.5           | 110, 62.3                                | 0.5–2             | 0.2     | Sridara et al. (2020) |
| Cu/CuO/CSs on GCE    | Amp                 | 0.65          | 63.8, 22.6                               | 0.01–0.69         | 0.005   | Yin et al. (2016)    |
| Au/GO on GCE         | Amp                 | 0             | 5.20, 4.56                               | 0.1–2             | 0.025   | Shu et al. (2015)    |
| GR–CuO NPs           | Amp                 | 0.6           | 1065                                     | 1 μM–8 mM         | 1       | Hsu et al. (2012)    |
| GOx/CdS/Gr/GCE       | CV                  | –             | 1.76                                     | 2–16              | 0.7     | Wang et al., 2011    |
| GO–CuONPs            | Amp                 | 0.7           | 162.52                                   | 2.79 μM–2.03 mM   | 0.69    | Song et al., 2013   |

The prepared GO/CuO/FTO enzyme-free glucose biosensor exhibit good linearity, high sensitivity, low detection limit, and fast response time of 5 s.
Table 2 Analysis of the glucose sensing performance of GO/CuO/FTO electrode

| Sample | Certified method (mM) | Proposed method (mM) | RSD (%) | Recovery rate (%) |
|--------|-----------------------|----------------------|---------|------------------|
| 1      | 4.5                   | 4.59                 | 2       | 102              |
| 2      | 6.11                  | 6.00                 | 1.81    | 98.19            |
| 3      | 5.22                  | 5.3                  | 1.5     | 101.5            |
| 4      | 5                     | 4.75                 | 1       | 95               |

Conclusion

The GO/CuO/FTO electrode was successfully prepared using the hydrothermal method and employed as a glucose biosensor. The developed sensor has numerous advantages, such as a simple, eco-friendly method, quick detection with LOD 0.13 μM, fast analysis, high sensitivity of 1274.8 μA mM⁻¹ cm⁻² (S/N = 3), good selectivity, excellent reproducibility, and good stability. The RSD of 1.58% obtained in human serum samples supports the reliability of the developed biosensor.

Abbreviations
GO: Graphene oxide; CuO: Copper oxide; FTO: Fluorine-doped tin oxide; PVA: Polyvinyl alcohol; PBS: Phosphate buffer solution; LSV: Linear sweep voltammetry; LOD: Limit of detection; RSD: Relative standard deviation

Acknowledgements

Not applicable

Authors’ contributions

Medha Gijare: First author, Conceptualization, Methodology, Data curation, Writing—original draft preparation, Investigation. Sharmila Chaudhari: Supervision and review. Satish Ekar: Visualization, Investigation, Supervision. Anil Garje: Corresponding author, Writing—reviewing and editing, Validation. All authors read and approved the final manuscript.

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare that they have no competing interests.

Author details

1. Department of Physics, Baburaoji Gholap College, Savitribai Phule Pune University, Pune, Maharashtra 411027, India. 2. Department of Physics, Anantnarao Pawar College, Pirangut, Savitribai Phule Pune University, Pune, Maharashtra 412115, India. 3. Department of Physics, Sir Parashurambhau College, Savitribai Phule Pune University, Pune, Maharashtra 411030, India.

Received: 22 April 2021 Accepted: 26 July 2021

Published online: 01 September 2021

References

Amala G, Gowtham SM (2017) Recent advancements, key challenges and solutions in nonenzymatic electrochemical glucose sensors based on graphene platforms. RSC Adv. 7:36949-36976. https://doi.org/10.1039/C7RA02843H, 7, 59, 36949, 36976
Bai Y, Xu T, Zhang X. Graphene-based biosensors for detection of biomarkers. Micromachines. 2020(11):160. https://doi.org/10.3390/mi11010160
Bruen D, Delaney C, Flores L, Diamond D. Glucose sensing for diabetes monitoring: recent developments. Sensors. 2017;17:1866. https://doi.org/10.3390/s17081866
Chen Q, Zhang L, Chen G. Facile preparation of graphene-copper nanoparticle composite by in situ chemical reduction for electrochemical sensing of carbohydrates. Anal Chem. 2012;94(1):171–8. https://doi.org/10.1021/ac202772u
Dhara K, Ramachandran T, Nair BG, Satheeshbabu TG. Single step synthesis of au–CuO nanoparticles decorated reduced graphene oxide for high performance disposable nonenzymatic glucose sensor. J Electroanal Chem. 2015;743:1-9. https://doi.org/10.1016/j.jelechem.2015.02.005
Ferrari AC, Meyer JC, Scardaci V, Caisirighi C, Lazzeri M, Mauri F, et al. Raman spectrum of graphene and graphene layers. Phys Rev Lett. 2006;97:187401. https://doi.org/10.1103/PhysRevLett.97.187401
Georgakilas V, Tiwari JN, Kemp KC, Perman JA, Bourlinos AB, Kim KS, et al. Noncovalent functionalization of graphene and graphene oxide for energy materials, biosensing, catalytic, and biomedical applications. Chem Rev. 2016;116(9):5464-5419. https://doi.org/10.1021/acs.chemrev.5b00620
Gopal AI, Komath N, Sai Anand G, Lee KP. Nanodiamond based sponges with entrapped enzyme: a novel electrochemical probe for hydrogen peroxide. Biosens Bioelectron. 2013;63:46-51. https://doi.org/10.1016/j.bios.2013.02.036
Gopal AI, Muthuchamy N, Komath S, Lee KP. A novel multicomponent redox polymer nanobead based high performance non-enzymatic glucose sensor. Biosens Bioelectron. 2016;84:53-63. https://doi.org/10.1016/j.bios.2015.10.079
Gopal AI, Muthuchamy N, Lee KP. A novel bismuth oxychloride-graphene hybrid nanosheets based non-enzymatic photoelectrochemical glucose sensing platform for high performances. Biosens Bioelectron. 2017;89(P):1-10. https://doi.org/10.1016/j.bios.2016.07.017
Haldorai Y, Hwang SK, Gopal AI, Huh YS, Han YK, Voit W, Sai-Anand G, Lee K, P (2016) Direct electrochemistry of cytochrome c immobilized on titanium nitride/multi-walled carbon nanotube composite for amperometric nitrite biosensor. Biosens Bioelectron. 197543-552. https://doi.org/10.1016/j.bios.2015.12.054
Hota P, Mah M, Bose S, Dinda D, Ghoshal KU, Su Y, et al. Ultra-small amorphous MoS2 decorated reduced graphene oxide for supercapacitor application. J Mater Sci Technol. 2020;40:196–203. https://doi.org/10.1016/j.jmst.2019.08.032
Hsu YW, Hu TK, Sun CL, Nien YT, Pu NW, Ger MD. Synthesis of CuO/graphene nanocomposites for nonenzymatic electrochemical glucose biosensor applications. Electrochimica Acta. 2012;82:152–7. https://doi.org/10.1016/j.electacta.2012.03.094
Hu A, Li R, Bridges D, Zhou W, Bai S, Ma D, et al. Photonic nanomanufacturing of high-performance energy devices on flexible substrates. J Laser Applications. 2016;28(2):022602. https://doi.org/10.1063/1.4944449
Ji L, Praveen M, Victor A, Xingcheng X, Mataz. A graphene-based noncomposites for nonenzymatic electrochemical glucose biosensor applications. Electrochimica Acta. 2012;82:152–7. https://doi.org/10.1016/j.electacta.2012.03.094
Liu F, Wang C, Sui X, Adi M, Riaz MA, Xu M, et al. Synthesis of graphene materials, biosensing, catalytic, and biomedical applications. Chem Rev. 2016;116(9):5464-5419. https://doi.org/10.1021/acs.chemrev.5b00638
Makaram P, Owens D, Aceros J. Trends in nanomaterial-based non-invasive biosensing technology. J Mater Sci Technol. 2018(1):105103. https://doi.org/10.1016/j.jelechem.2018.12.003
Marcarino DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, et al. Improved performance disposable nonenzymatic glucose sensor. J Electroanal Chem. 2015;743:1-7. https://doi.org/10.1016/j.jelechem.2015.02.005
Mallick A, Madhapatra AS, Mitra A, Gereche J, Ningthoujam R, Chakrabarti P. Magnetic properties and bio-medical applications in hyperthermia of lithium zinc ferrite nanoparticles integrated with reduced graphene oxide. J Appl Phys. 2018;123(5):055103. https://doi.org/10.1063/1.5009833
Marchetti DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, et al. Improved synthesis of graphene oxide. ACS Nano. 2010;8(8):4806–14. https://doi.org/10.1021/nn1006368
Nakate UT, Choudhary SP, Ahmed R, Patil P, Nakate YT, Hahn YB, et al. Graphene oxide (GO) nanocomposite based room temperature gas sensor. In: Tomer V, editor.
Functional nanomaterials. Materials horizons: from nature to nanomaterials, vol. 2020. Singapore: Springer; 2020. p. 303–28. https://doi.org/10.1007/978-981-15-4810-9_12.

Peter K, Heineman WR. Laboratory techniques in electroanalytical chemistry. New York: Marcel Dekker; 1996. p. 60.

Sai-Anand G, Anantha-Iyengar KS-W, Komath S, Lee K-P. One pot synthesis of new gold nanoparticles dispersed poly (2-aminophenyl boronic acid) composites for fabricating an affinity based electrochemical detection of glucose. Sci Adv Mater. 2014;6(7):1356–64. https://doi.org/10.1166/sam.2014.1836.

Sai-Anand G, Swanesan A, Benzigar MR, Singh G, Gopalan AI, Baskar AV, et al. Recent progress on the sensing of pathogenic bacteria using advanced nanostructures. Bull Chem Soc Jpn. 2019;92(1):126–44. https://doi.org/10.1246/bcsj.20180280.

Shu H, Chang G, Su J, Cao L, Huang Q, Zhang Y, et al. Single-step electrochemical deposition of high-performance au-graphene nanocomposites for non enzymatic glucose sensing. Sensors and Actuators B: Chemicals. 2015;220:319–31. https://doi.org/10.1016/j.snb.2015.09.094.

Song J, Xu L, Zhou C, Xing R, Dai Q, Liu D, et al. Synthesis of graphene oxide based CuO nanoparticles composite electrode for highly enhanced nonenzymatic glucose detection. ACS Appl Mater Interfaces. 2013;5:12928–34. https://doi.org/10.1021/am403598F.

Sridara T, Upan J, SaiAnand G, Tuantantanont A, Karuwan C, Jaimunee J. Non-enzymatic amperometric glucose sensor based on carbon nanodots and copper oxide nanocomposites electrodes. Sensors. 2020;20(3):808. https://doi.org/10.3390/s20030808.

Thévenot D, Toth K, Durst R, Wilson G. Electrochemical biosensors: recommended definitions and classification. Anal Lett. 2001;34(5):635–59. https://doi.org/10.1081/AL-100103209.

Thunkhamrak C, Chuntib P, Ounnunkad K, Banet P, Aubert PH, SaiAnand G, et al. Highly sensitive voltammetric immunosensor for the detection of prostate specific antigen based on silver nanoprobe assisted graphene oxide modified screen printed carbon electrode. Talanta. 2020;208:109389. https://doi.org/10.1016/j.talanta.2019.120389.

Tong X, Wang H, Wang G, Wan L, Ren Z, Bai J, et al. Controllable synthesis of graphene sheets with different numbers of layers and effect of the number of graphene layers on the specific capacity of anode material in lithium-ion batteries. J Solid-State Chemistry. 2011;184(5):982–9. https://doi.org/10.1016/j.jssc.2011.03.004.

Wang AJ, Feng JJ, Li ZH, Liao QC, Wang ZZ, Chen JR. Solvothermal synthesis of cu/Cu2O hollow microspheres for non-enzymatic amperometric glucose sensing. Cryst Eng Comm. 2012;14:289–95. https://doi.org/10.1039/C2CE05869J.

Wang K, Liu Q, Guan QM, Wu J, Li HN, Yan JJ. Enhanced direct electrochemistry of glucose oxidase and bio sensing for glucose via synergy effect of graphene and CdS nanocrystals. Biosens Bioelectron. 2011;26:2252–7. https://doi.org/10.1016/j.bios.2010.09.043.

Wang X, Liu E, Zhang X. Non-enzymatic glucose biosensor based on copper oxide-reduced graphene oxide nanocomposites synthesized from water-isopropanol solution. Electrochim Acta. 2014;130:253–60. https://doi.org/10.1016/j.electacta.2014.03.030.

Wei H, Sun JJ, Guo L, Li X, Chen GN. Highly enhanced electrocatalytic oxidation of glucose and shikimic acid at a disposable electrically heated oxide covered copper electrode. Chem Commun (Camb). 2009;20(20):2842–4. https://doi.org/10.1039/b904673a.

Wu HK, Cao WM, Li Y, Liu G, Wen Y, Yang HF, et al. In situ growth of copper nanoparticles on multiwalled carbon nanotubes and their application as non-enzymatic glucose sensor materials. Electrochim Acta. 2010;55:3734–40. https://doi.org/10.1016/j.electacta.2010.04.021.

Wu J, Wang P, Wang F, Fang Y. Investigation of the microstructures of graphene quantum dots (GQDs) by surface-enhanced raman spectroscopy. Nanomaterials. 2018;8(10):964. https://doi.org/10.3390/nanom8100964.

Xu Z, Liu Q, Zhu X, Li C, Xu M, Liang Y. Reduction of graphene oxide via ascorbic acid and its application for simultaneous detection of dopamine and ascorbic acid. Int J Electrochem Sci. 2012;7:5172–84.

Yin H, Cui Z, Wang L, Nie Q. In situ reduction of the copper/carbon spheres composite for enzymatic less glucose sensors. Sensors Actuators B: Chemicals. 2016;222:1018–23. https://doi.org/10.1016/j.snb.2015.09.097.

Zheng T, Li M, Wang Y, Wang D, Zhang P, Yang W, et al. A flexible non-enzymatic glucose sensor based on copper nanoparticles anchored on laser-induced graphene. Carbon. 2020;165:5056–13. https://doi.org/10.1016/j.carbon.2019.10.006.