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Highly sensitive and selective non enzymatic electrochemical glucose sensors based on Graphene Oxide-Molecular Imprinted Polymer

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ABSTRACT

Graphene Oxide-Molecular Imprinted Polymer (GO-MIP) based electrochemical sensor was developed for the first time towards enzyme less determination of glucose. This GO-MIP was obtained from a series of fictionalization, polymerization and template molecule introduction/removal during the synthesizing process. The proposed GO-MIP based electrode showed excellent electrocatalytic activity towards glucose oxidation at optimized conditions and possessing detection limit of 0.1 nM with a response time of ~2 min. The current response of GO-MIP based glucose sensor was linearly related to the concentration of glucose. The results obtained from the real time usability of electrodes in human blood matches well with commercially available glucose monitors. Further, the reusability of the material is checked up to eight cycles and interference of glucose with ascorbic acid (AA), uric acid (UA) and dopamine (DA) were also studied. The obtained results endorse the promising application of GO-MIP towards superior glucose sensing with long term stability.

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1. Introduction

Diabetes mellitus is an alarming public health problem affecting ~150 million people globally and this metabolic disorder is due to the deficiency in insulin production or poor response of the cells to insulin. This condition often results in disabilities like blindness, nerve degeneration, kidney failure and sometimes leads to death when glucose levels are not kept under control. The diagnosis and management of normal glucose level (4.4–6.6 mM) in the human body necessitate specific monitoring [1–2]. Hence, the development of fast, sensitive, selective, and reliable methods for glucose monitoring become significant in the areas of clinical diagnostics, food industry as well as biotechnology. The first enzyme-based sensor for glucose detection reported by Clark and Lyons (U.S. Patent 33,539,455, 1970) laid a platform for several other researchers to develop electrochemical glucose biosensors owing to their extraordinary sensitivity, stability and selectivity. However, the above said enzyme based biosensors suffer from limitations such as instability, low sensitivity due to indirect electron transfer, enzyme immobilization procedures, higher cost and complicated purification steps [3–4]. The instability in enzyme based sensors is caused by the intrinsic enzyme features whose activity can easily be affected by temperature, pH value, humidity and toxic chemicals. In addition, the tedious fabrication process in effective immobilization of enzymes on the electrode adds shortcoming to enzymatic sensors [5].

Consequently, to overcome the above said circumstances direct electrocatalytic detection of glucose – nonenzymatic detection has received considerable attention owing to their direct-electron-transfer-shuttle-free detecting style. The molecular imprinting based material is considered as a promising technology as it holds space for specific receptor detection [6–7]. The MIPs has greater stability, low production cost, ease of preparation and in addition it will do the functions of enzymes, the creation of three-dimensional cavities of a specific size and shape for biomolecules recognition. These MIPs possesses a special place for the specific biomolecules detection along with a few other applications in drug release, molecular recognition, catalysis and antibody mimics [8]. Graphene with two-dimensional structures, exceptional electronic and chemical properties has attracted tremendous attention in electrochemical sensing. The large specific surface area offered by unique structures of graphene serves as a suitable support for immobilization biomolecules in sensor design [9–10]. The direct electron transfer between the electrode surface and active site of biomolecules without any intermediary molecules in carbon based structures not only intensify the sensitivity but also provides nonenzymatic sensing. In addition to rapid electron transport kinetics, the high thermal conductivity, excellent mechanical flexibility and good biocompatibility make the graphene as a potential material for nonenzymatic electrochemical biosensing [11–12]. Several carbon-based structures like Cu_2O nanocubes/graphene electrode, CO_3O_4-graphene electrode, Pt-Graphene Oxide electrode and NiO-graphene hybrid based electrode etc. are studied for glucose sensing with fewer works on MIP-Graphene Oxide based nonenzymatic glucose sensing [13–16].

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In this present study, we report a novel strategy of GO-MIP material for non-enzymatic detection of the glucose molecule. The morphology, composition and electrochemical behavior of GO-MIP composite polymeric materials were investigated using diverse physiochemical characterization methods. The prepared GO-MIP based working electrode showed excellent catalytic activity against glucose, which substantiates the potentials of MIP in the electrochemical sensor design.

2. Materials and methods

2.1. Materials

Graphite powder was obtained from Sigma-Aldrich and used for the preparation of Graphene Oxide (GO). *N*, *N*′-dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP), methacrylic acid (MAA), ethylene glycol dimethyl acrylate (EGDMA) were all purchased from Avra Synthesis Pvt. Ltd. with 98% purity. Glycidyl Methacrylate (GMA) was obtained from Sigma-Aldrich Chemicals (97% purity). Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich Chemicals (99% purity). Dimethyl Sulfoxide (DMSO) was procured from Merck Chemicals (97% purity).

2.2. Methods

The prepared materials were analyzed for structural properties using X-ray diffraction (XRD) studies conducted with a PANalytical X'Pert Pro X-ray diffractometer with a CuKα radiation source (λ = 0.15406 nM) in the 2θ range between 5° and 90° with a step size of 0.02. Raman spectroscopy measurements were taken using a confocal WiTech Raman spectrometer with a Nd:YAG laser (532 nM), and functional group analysis was conducted using Fourier transform infrared spectroscopy (FTIR) with a PerkinElmer spectrometer in the range of 500 to 4000 cm^{-1} using the KBr pellet method. The morphology of the samples was using high-resolution transmission electron microscopy (HR-TEM) with a Tecnai G2 20 operated at 200 keV. Electrochemical measurements were carried out using a CH Instruments electrochemical instrument with a three-electrode system comprising glassy carbon electrodes (GCE, 3 mM diameter) as working electrodes, a Pt wire as a counter electrode, and Ag/AgCl (3 M KCl solution) as a reference electrode in 0.1 M PBS.

2.3. Synthesis of Graphene Oxide and functionalization

Graphene Oxide (GO) was synthesized by Modified HumMer's Method. This prepared GO was acid functionalized using a mixture of H_2SO_4 and HNO_3 in the ratio of 3:1 and ultrasonicated for 3 h. The resulting carboxyl functionalized Graphene Oxide (GO — COOH) was again neutralized by dilute hydrochloric acid, purified by frequent rinsing until the product was well-dispersed in deionized water.

2.4. Synthesis of GO-GMA

The f-GO contain many carboxyl groups present on its surface which could be esterified to attach methacrylate groups on the surface of GO. In order to obtain this, 0.58 g of GO was mixed with 1.6 g of *N*, *N*′-dicyclohexylcarbodiimide (DCC), 0.2 g dimethylaminopyridine (DMAP) in 65 ml of dimethyl sulfoxide (DMSO) at room temperature. Then, 0.55 g of Glycidyl Methacrylate (GMA) was added slowly to the mixture and stirred at 50 °C for 24 h. An equimolar amount of HCl was added to the solution (HCl neutralizes the DMAP) and the neutralized GO-GMA was then precipitated through isopropyl alcohol. The GO-GMA powder obtained was re-dispersed in water and precipitated with isopropyl alcohol. Finally, the products collected by repeated washing and filtration.

2.5. Synthesis of GO-Molecularly Imprinted Polymer (MIP)

GO-GMA-MIP with glucose as a template molecule was prepared by selectively polymerizing MIP's onto the vinyl group functionalized group of GO-GMA. To obtain this, 0.09 g of GO-GMA was added to 50 ml of methanol. To this mixture, 0.28 mM of glucose, 1 mM of methacrylic acid (MAA), 5 mM of ethylene glycol dimethyl acrylate (EGDMA) and 20 mg of azobisisobutyronitrile (AIBN) were added and stirred for 30 min at 60 °C for 24 h. The resulting product was collected and washed thoroughly several times with ethanol.

2.6. Synthesis of GO-Non-Imprinted Polymer (GO-NIP)

Preparation of GO-NIP was carried out by the above said polymerization procedure and the reaction was done without using cholesterol molecule. The whole reaction proceeds at 75 °C and the resultant NIPs are washing a number of times using ethanol solutions and allowed for drying.

2.7. Fabrication of electrode for sensing

Prior to modification, the working electrode was polished with 1.0, 0.3, and 0.5 μm alumina powders and was sonicated in ethanol and deionized water for 20 min. Then, 5 mg of GO-MIP were dispersed by sonication in 0.5 ml Nafion solution (0.5%). The dispersion was then coated by drop casting on a glassy carbon electrode and dried at room temperature. Similarly, GO-NIP based GCE was prepared for comparative study. Electrochemical measurements were carried out using a CH instrument by three electrode assembly using 0.1 M phosphate buffer solution (PBS) at the room temperature.

3. Results and discussions

The FTIR spectra of GO-COOH, GO-GMA, Glucose loaded GO-MIP, GO-MIP and GO-NIP is shown in the Fig. 1. The peaks present at 1623,

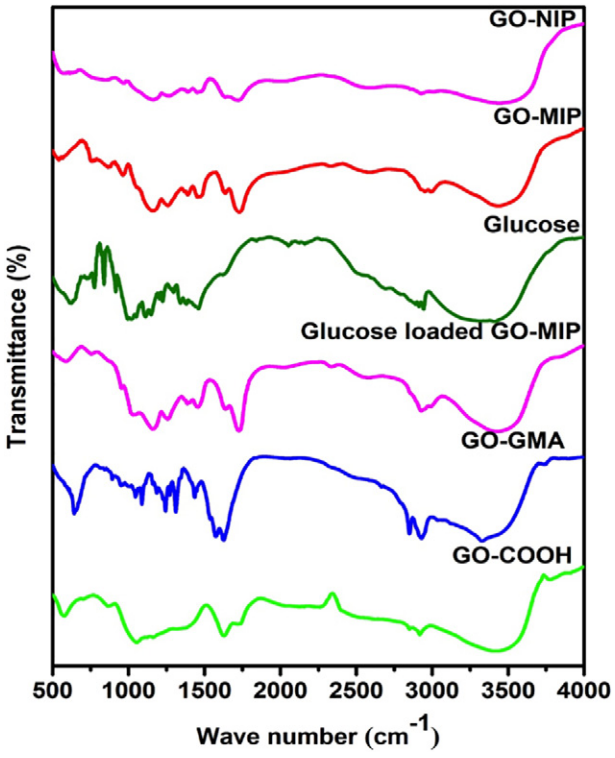

Fig. 1. FTIR spectra of GO-COOH, GO-GMA, Glucose loaded GO-MIP, Glucose, GO-MIP and GO-NIP.

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