



Rudimentary simple method for the decoration of graphene oxide with silver nanoparticles: Their application for the amperometric detection of glucose in the human blood samples



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ABSTRACT

Graphene oxide decorated with silver nanoparticles (GO-Ag) was prepared by anodic dissolution of silver in the aqueous dispersion of GO. The composites were characterized by XRD, XPS, TEM, AFM, and Raman spectroscopy. The electrooxidation of glucose on GO-Ag modified electrodes have been tested by cyclic voltammetry and chronoamperometry. The detail mechanism of redox processes on the GO-Ag electrodes has been studied. A few μg loading of silver has demonstrated to give current in μA for the mM concentration of glucose. A linear relationship between peak height in the voltammograms and glucose concentration in the range 1–14 mM has been proposed for amperometric detection of glucose. From the results, the detection limit for glucose sensing is estimated to be as small as $4 \mu\text{M}$. The selectivity for glucose in presence of interfering molecules viz. ascorbic and uric acids is tested. Proof-of concept is presented by carrying out the measurements in real human blood samples.

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1. Introduction

Glucose estimation in blood samples has been exceedingly important with an advent of alarming rate of *Diabetes mellitus* affected patients (~ 150 million people), world-wide [1]. Self-monitoring of the blood glucose level is one of the key-factors in controlling this disease. In this context, the devices based on glucose oxidase (GO_x) modified electrodes have been extremely popular for last several decades [2]. Unfortunately, GO_x , being protein is vulnerable to denature at high temperature, low humidity and change in pH. In this scenario, non-enzymatic glucose sensors are highly desirable and thus deserves significant attention. Glucose is known to get electrochemically oxidized over various metal oxide electrodes, viz. CuO , NiO , Ag/CuO and Co_3O_4 [3–6], which leads to a detectable amperometric signal. Being poor conductor most of these oxides possess limitation to develop good electrochemical sensors. One of the ways to overcome this limitation is to disperse them on the conducting support which would not only prevent them to agglomerate but also would provide conducting pathway. Among various materials, crystalline carbons viz. carbon nanotubes and graphene would be the most appropriate choice for this purpose.

Between these two, lots of studies are available in the literature, about the use of CNT-Cu [7], CNT-Pt [8] and MWCNT-Ni [9] composites for glucose sensing applications. However, the literature regarding silver graphene based materials are relatively rare and lot of room for further development is available. With this background, we have undertaken the detail investigation regarding development of GO-silver nanoparticle composite based material for the amperometric detection of glucose. Following properties of individual Ag and GO and their likely synergistic interaction has motivated us to choose this combination.

In case of Ag, its oxides are formed in situ at sufficiently positive potentials [10,11]. AgO so-formed, chemically reacts quantitatively with glucose to yield Ag_2O , which shows distinct anodic peak in a reverse cycle; proportional to the glucose concentration. Moreover, kinetics of formation of silver oxides is very facile [12] which is advantageous in minimizing the response time. Furthermore, Ag_2O has inherent good electrical properties (*ca.* 20 S cm^{-1}) due to the oxygen vacancies at room temperature, which would be advantageous to minimize the current losses and help in improving the sensitivity.

Graphene and its analogues i.e. graphene oxide and reduced graphene oxide have several desirable properties such as high surface area, electronic conductivity and, chemical stability in the oxidative environment. GO provides chemical and mechanical stable matrix for the metal nanoparticles. Thus, most of the surface

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area of the nanoparticles available for the reaction which otherwise would have occupied by capping agents. Moreover, GO and r-GO are demonstrated to undergo charge transfer with various metals and semiconductor nanoparticles. This synergistic property of metal nanoparticles with GO make them promising combination in the electrocatalysis [13].

In the current work, we demonstrate preparation of GO-Ag composite with rudimentary simple electrochemical approach which we have already successfully tested before for MWCNTs-Ag composites [14]. GO-Ag electrode showed excellent selectivity and rapid detection for glucose with good sensitivity, indicating potential use of GO-Ag in fabricating enzyme-free glucose sensor.

2. Experimental

2.1. Preparation of Graphene Oxide (GO)

GO samples were prepared by Hummers method [15] with a slight modification [16]. In brief, graphite powder (0.5 g), sodium nitrate (0.5 g) and sulfuric acid (23 ml) were mixed in an ice-bath under a continuous stirring. Potassium permanganate (3.0 g) was slowly added into the reaction mixture at 20 °C. Flask was then transferred to water bath (35 ± 5 °C) and solution was stirred for an hour to get thick pasty product. 100 ml water was added and temperature of the bath was raised to 90 ± 5 °C under constant stirring for another 15 min. The solution was diluted by adding 500 ml water and 3 ml H₂O₂ (30%) which led to color change from dark brown to yellow. The mixture was filtered and washed several times with hot water to eliminate the acid residue. The resultant solid was dried under vacuum and stored in a desiccator for subsequent use.

2.2. Preparation of Graphene Oxide decorated with Silver nanoparticles.

GO-Ag composite was prepared by electrochemical deposition of silver nanoparticles on graphene oxide sheets. Dispersion of GO was prepared by sonicating GO sheets (0.1 mg ml⁻¹) in MilliQ[®] water for 30 minutes. Silver electrodes (diameter ca. 2 mm) were polished using emery paper and rinsed with DI water. The composites were prepared by electrolysis of GO dispersion with silver electrodes at of 20 V for 30 minutes. The color of solution was changed from brown to colorless, followed by grey deposit on the cathode (negative electrode) and dark brown adherent film on anode (positive electrode). The cathode deposit was separated from solution by centrifuging at 5000 rpm for 10 minutes. In order to compare the influence of graphene oxide, the control experiment was performed on silver nanoparticles (AgNps) without GO. For that, AgNps were prepared in water keeping all other parameters same without adding graphene oxide. In this experiment as the reaction progresses the solution became pale yellow in color indicating formation of silver nanoparticles.

2.3. Material Characterization

UV-visible spectra were recorded using an Agilent 8453 diode array single beam spectrophotometer. Powder X-ray diffractograms (XRD) were recorded on the dried product using a Bruker, D8-Advance, X-ray diffractometer (CuK α , 40 kV and 40 mA). Transmission electron microscopic (TEM) images were recorded on the samples using a Technai G2 20V TWIN transmission electron microscope (20–200 kV). X-ray photoelectron spectroscopy (XPS) was performed using ESCA-3000 VG Scientific Ltd. (England) spectrometer with monochromated Al K α source (1486.7 eV). AFM images were recorded using Nano Wizard[®] 3-AFM (JPK instruments) on a mica substrate. Raman spectra were

recorded at room temperature using the 633 nm line, from a He-Ne laser. The laser beam was focused onto a spot ~1 μ m in diameter, and the laser power at the sampling position was 10 mW. The Raman band of a silicon wafer at 520 cm⁻¹ was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be better than 1 cm⁻¹. For the Raman measurements, the sample solutions were taken in a standard 1 × 1 cm² cuvette or on glass slides and the Raman signal was collected at 180° scattering geometry or with a 50X LWD (long working distance) objective and detected using a CCD (Synapse, Horiba Jobin Yvon) based monochromator (LabRAM HR800, Horiba Jobin Yvon, France) together with an edge filter, covering a spectral range of 200–1800 cm⁻¹.

2.4. Electrochemical Measurements

The electrochemical measurements were performed with Bio Logic Potentiostat/galvanostat (SP-300) workstation in a typical three electrodes system; Glassy carbon as a working electrode, Hg/HgO/sat. Ca (OH)₂ as a reference electrode and Pt-wire as a counter electrode.

2.5. Preparation of GO-Ag modified electrode.

Electrochemical activity for composite was studied by drop casting the dispersion on GC electrode. For this purpose, GC electrode (3 mm diameter) was polished with alumina powder (0.5 μ m) and rinsed with MilliQ[®] water. GO-Ag deposit formed at cathode was transferred in MilliQ[®] water (1 mg/ml) and sonicated till a uniform dispersion was formed. From this an aliquot of 40 μ l was drop casted onto pre-cleaned GC and vacuum dried at room temperature. Similarly, an aliquot of 40 μ l AgNps was drop casted on the GC electrode and electrochemical measurements were performed.

2.6. Determination of blood glucose using screen printed electrodes.

To verify feasibility of sensor, GO-Ag composite was employed to estimate glucose in human blood samples. For this purpose screen printed three electrode system (Zensor TE100 SPE's) comprising of carbon as working electrode, Ag/AgCl as reference electrode and Platinum as counter electrode were used. The composite was drop-casted (5 μ l volume) on working electrode and dried at room temperature. Onto it 20 μ l of 0.1 M NaOH was added and background was recorded. Further 20 μ l blood drop was added to 20 μ l of 0.1 M NaOH and amperometric response for blood glucose was recorded at 0.6 V. All the safety protocols are followed in handling, testing and disposing of human blood samples.

3. Result and Discussion

3.1. Material Characterization of GO-Ag.

Formation of GO-Ag was confirmed by performing various structural characterizations. The morphology of the product examined by TEM, as indicated in Fig. 1a revealed a decoration of about 50 ± 5 nm diameter spherical silver nanoparticles over graphene oxide sheets. Close examination revealed that some particles are having hexagonal shape and their facets are clearly legible in the micrograph (Inset Fig. 1). This was further supported by AFM results of the composite showing graphene sheets decorated uniformly with silver nanoparticles (Fig. 1b).

Crystallographic studies of composite were carried out by XRD analysis. Fig. 1c shows a typical powder diffractogram recorded on GO-Ag sample. The observed peaks at 38.33°, 44.48°, 64.68°, and

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