



Pt-CuO nanoparticles decorated reduced graphene oxide for the fabrication of highly sensitive non-enzymatic disposable glucose sensor



Keerthy Dhara^a, John Stanley^b, Ramachandran T^a, Bipin G. Nair^b, Satheesh Babu T.G.^{a,*}

^a Department of Sciences, Amrita School of Engineering, Amrita Vishwa Vidyapeetham, Amritanagar, Coimbatore 641112, India

^b Amrita School of Biotechnology, Amrita Vishwa Vidyapeetham, Amritapuri, Clappana P.O., Kollam 690525, India

ARTICLE INFO

Article history:

Received 6 November 2013

Received in revised form 6 January 2014

Accepted 12 January 2014

Available online 21 January 2014

Keywords:

Non-enzymatic glucose sensor

Reduced graphene oxide

Copper oxide nanoflower

Platinum nanocubes

Hummer's method

ABSTRACT

Platinum nanocubes and copper oxide nanoflowers decorated reduced graphene oxide (rGO) obtained by one step chemical process. X-ray crystallographic analysis confirms that CuO in monoclinic form and Pt in cubic crystal form. Pt-CuO/rGO nanocomposite dispersed in N,N-dimethylformamide (DMF) was drop casted onto the working electrode of an indigenously fabricated screen printed three electrode system. Oxidation of glucose on the Pt-CuO/rGO nanocomposite modified screen printed electrode (SPE) was occurred at +0.35 V. The sensor showed a limit of detection 0.01 μM ($S/N=3$) and very high sensitivity of 3577 $\mu\text{A mM}^{-1} \text{cm}^{-2}$ with linear response upto 12 mM. The sensor was highly selective to glucose in the presence of commonly interfering species like ascorbic acid (AA), dopamine (DA), uric acid (UA) and acetaminophen. The sensor was employed for the testing of glucose in blood serum and the results obtained were comparable with other standard test methods.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Diabetic mellitus, considered as the second major public health problem worldwide, is a metabolic disorder due to the deficiency of insulin resulting in elevated blood glucose levels. Long term complications of diabetes include retinopathy with potential loss of vision; nephropathy leading to renal failure and cardiovascular diseases. Hence there is a great demand for a fast, reliable and low cost point of care monitoring of blood glucose level [1–3].

Development of glucose sensors became one of the hot areas of research after the pioneering work by Clarks and Lyons in 1962 [4,5]. Due to their excellent selectivity and high sensitivity towards the oxidation of glucose, glucose oxidase (GOx) based sensors gained immense popularity [6–8]. However enzyme based sensors suffer from draw backs including instability to changes in the pH, temperature, etc., and the need for complicated enzyme immobilization procedures [9,10] and higher cost associated with enzyme isolation and purification. To address these limitations, an alternative approach based on the direct electro-oxidation without the use of enzyme, 'non-enzymatic' has been tried [11]. Choosing the right catalyst for direct electrochemical activity is the key step in the fabrication of non-enzymatic glucose sensors.

The direct electrooxidation of glucose on different noble metal substrates such as platinum [12], gold [13], palladium [14] and alloys of Pt, Pd, Pb and Rh [15–17] has been explored for the development of non-enzymatic glucose sensor. However, these electrodes suffer from low sensitivity, poor selectivity and are prone to loss of activity due to absorbed intermediates and poisoning by chloride ions [18]. Metals such as copper, nickel, zinc and manganese have attracted the attention of researchers due to their low cost, good electrocatalytic activity and the possibility of promoting electron transfer reactions at lower overpotential [19,20]. Due to narrow band gap and easy to tune nano architecture, a wide variety of copper oxide based materials have been investigated for their glucose sensing capabilities. Copper oxide in different morphologies, such as nanoporous [21], nanoparticles [22], nanospheres [23], nanowires, nanoflowers [24], nanorods [25] and ball-in ball microspheres [26] have been explored. In order to improve the performance of these sensor, the role of carbon nanotubes (CNT) as support matrices for metal and metal oxide nanoparticle composite [27–31] has been investigated.

Graphene one atom thick two dimensional array of carbon atoms packed in a dense honeycomb crystal structure attracted tremendous attention due to its excellent electrical and mechanical properties [32], large surface area, high stability and low cost [33,34]. They have also been employed for the development of electrochemical super capacitor [35], photovoltaic cells [36], biosensors [37,38] and field effect transistors [39]. Graphene decorated with metals oxides of copper [40], nickel [41] and metal nanoparticles

* Corresponding author. Tel.: +91 944236863; fax: +91 422 2656274.

E-mail addresses: tgsatheesh@gmail.com, tg.satheesh@cb.amrita.edu (S.B. T.G.).

such as platinum and gold [42], and alloy nanoparticles like nickel-platinum [43] have been employed for the direct electrooxidation of glucose. So far there is no report on graphene decorated with copper oxide and platinum nanoparticles for the amperometric sensing of glucose.

This paper reports the one step synthesis of copper oxide nanoflowers and platinum nanocubes decorated graphene and its application in the amperometric sensing of glucose. The sensor showed very high sensitivity ($3577 \mu\text{A mM}^{-1} \text{cm}^{-2}$) and the oxidation of glucose occurs at a low potential (+0.35 V). Graphene with large surface area is an excellent platform for accommodating large number of catalytic sites. One step fabrication process coupled with high sensitivity and selectivity together with affordable cost for developing markets makes this sensor highly suitable for point of care glucose monitoring. Through the well known mechanism [44], copper oxide catalyzes glucose oxidation and platinum nanoparticles act as a co-catalyst to enhance the electron transfer during the oxidation of glucose.

2. Materials and methods

2.1. Chemicals and reagents

Graphite powder (<20 μm), β -D-(+)-glucose, L-ascorbic acid (AA), dopamine (DA), acetaminophen and hexachloroplatinate hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) were purchased from Aldrich. Copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) was purchased from Finar chemicals (India). All other chemicals were of analytical grade and used as received without further purification. Medical grade conductor paste (carbon ink-BQ242, Ag/AgCl-5874, silver ink-5064) and the thinner for the respective inks were purchased from Du Pont Company Pte Ltd., Singapore. De-ionised water from Elix-10 system (Millipore, Germany) was used for all the experiments.

2.2. Characterization and instrumentation

Absorption spectra in the range of 200–800 nm was recorded with UV-vis spectrophotometer (Pharmaspec 1700, Shimadzu). Fourier transform infrared spectra (FTIR) were recorded in the transmission mode on a Thermo Nicolet, iS10 FTIR spectrometer using the KBr pellet and ATR mode for the range 400–4000 cm^{-1} . X-ray photoelectron spectroscopic (XPS) analysis was carried out using KRATOS Axis Ultra (Kratos Analytical, United Kingdom). A monochromated Al $K\alpha$ radiation (1486.6 eV) was focused on a sample surface area of 0.7 mm \times 0.3 mm. The survey scans were obtained by employing three passing sweeps of 15 eV and a step size of 0.1 eV. Raman spectra were recorded on a LabRAM HR UV-VIS-NIR Raman microscope from HORIBA Jobin-Yvon (633 nm laser source).

All electrochemical measurements were carried out using electrochemical analyzer CHI608D (CH Instruments, TX, USA). A three electrode system consisting of an Ag/AgCl reference electrode, carbon working and counter electrodes was screen printed onto a polyethylene terephthalate (PET) substrate.

High resolution scanning electron micrograph (HRSEM) was recorded using FEI quanta FEG 200-HRSEM. High resolution transmission electron microscopic (HRTEM) analysis was carried out using the JEOL JEM 2100 TEM.

Small angle X-ray diffraction (SA-XRD) measurements were performed at room temperature (25 $^\circ\text{C}$) on a Rigaku Miniflex II X-ray diffractometer, using $K\beta$ foil filtered Cu $K\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) with a scintillator detector (40 kV, 15 mA). The step time was 1 s at $0.04^\circ/\text{step}$ in a 2θ range of 5–90 $^\circ$.

2.3. Synthesis of Pt-CuO/rGO nanocomposite

Graphite oxide was prepared by following the Hummer's method [45] which involves the oxidation of graphite flakes using KMnO_4 in acidic medium. Graphene oxide (GO) was obtained by exfoliating 100 mg of graphite oxide in 200 mL of distilled water (0.5 mg/mL) by sonication. To this dispersion, 5.81 mL of 1 M of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.275 mL of 0.0772 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were added which found to be optimum in terms of the sensing properties of the composite. After 20 min stirring, 50 mL of 0.79 M sodium borohydride was added drop wise to the reaction mixture and stirred at room temperature for several hours. The precipitate was filtered and washed with distilled water several times to remove the unreacted contents. The product obtained was dried at 70 $^\circ\text{C}$. Finally the nanocomposite was annealed at 300 $^\circ\text{C}$ for 4 h to convert Cu in the nanocomposite to CuO. The nanocomposite obtained was termed as Pt-CuO/rGO.

2.4. Fabrication of sensor electrode (Pt-CuO/rGO/SPE)

The screen printed electrodes (SPE) consist of three electrodes (working, pseudo reference and auxiliary) were fabricated by traditional screen printing technique. The SPE was activated by 20 cycles in the potential range of –0.2 to +1.8 V at a scan rate of 0.1 V/s in 1 M sulphuric acid. 10 mg of Pt-CuO/rGO nanocomposite was dispersed in 2 mL of DMF using ultrasonication. 10 μL of the suspension was drop cast on an activated screen printed electrode (2 mm dia) and dried.

2.5. Electrochemical studies

The electrocatalytic behavior of the sensor electrode was studied using linear sweep voltammetry (LSV) at a potential window of –0.2 to +1.0 V at various scan rates in 0.1 M NaOH with and without glucose. The steady state current response (amperometry) was obtained at a constant potential of +0.6 V with reference to pseudo reference electrode Ag/AgCl. Electrochemical impedance spectroscopic (EIS) analysis was carried out in 0.1 M NaOH solution at its open circuit potentials, in the frequency range of 0.01 Hz to 1 MHz with potential amplitude of 5 mV.

3. Results and discussions

3.1. Characterization of Pt-CuO/rGO nanocomposite

Fig. 1A represents the UV-Visible spectrum of GO (curve a) and Pt-CuO/rGO nanocomposite (curve b). The peak at 230 nm in GO is attributed to the π - π excitation and the peak seen at 295 nm is the n- π excitation of carboxylic moieties (C=O) (curve a). The peak at 295 nm in GO disappeared in Pt-CuO/rGO due to the reduction of C=O and the peak at 230 nm red shifted to 270 nm due to the extension of conjugation (curve b).

In the FTIR spectra (Fig. 1B), the peak at 1725 cm^{-1} (curve a) due to the stretching mode of carboxylic moieties (C=O group) presents in GO disappears in Pt-CuO/rGO (curve b) indicates the reduction of GO to rGO. Further, the C=C stretch of GO at 1628 cm^{-1} was shifted to 1637 cm^{-1} in Pt-CuO/rGO. The intensity of the peak at 3407 cm^{-1} (O-H stretch) was decreased due to the reduction of GO to rGO. The peak observed at 3436 cm^{-1} in Pt-CuO/rGO nanocomposite is due to the presence of CuO. Further, the characteristic peak of CuO at 532 cm^{-1} is shifted to 542 cm^{-1} in the nanocomposite [46].

Fig. 1C depicts the Raman spectrum of GO (curve a) and Pt-CuO/rGO (curve b). The predominant peaks obtained at 1344 and 1591 cm^{-1} are the D and G bands respectively. The frequency of D and G bands in GO and Pt-CuO/rGO are found to be same and the ratio of intensity D/G is also same [GO (1.04), Pt-CuO/rGO (1.03 s)]

Download English Version:

<https://daneshyari.com/en/article/7147091>

Download Persian Version:

<https://daneshyari.com/article/7147091>

[Daneshyari.com](https://daneshyari.com)