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Au nanoparticles decorated reduced graphene oxide for the fabrication of disposable nonenzymatic hydrogen peroxide sensor

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ABSTRACT

A simple approach is followed for the fabrication of disposable nonenzymatic hydrogen peroxide (H_2O_2) sensor using gold nanoparticles decorated reduced graphene oxide (Au/rGO) nanocomposite. Au/rGO nanocomposite was prepared by one pot reduction of graphene oxide and Au(III) ions. The composite was characterized using various spectroscopic and microscopic techniques. The Au/rGO nanocomposite suspension was cast on the indigenously fabricated screen printed electrode (SPE). Voltammetric studies on the modified electrode showed that the Au/rGO nanocomposite modified SPE have enhanced catalytic activity towards H_2O_2. The sensor exhibited linear relationship in the range from 20 μM to 10 mM with a sensitivity of 1238 μA mM^{-1} cm^{-2} and a limit of detection 0.1 μM. The sensor also showed excellent selectivity in presence of other electroactive species such as ascorbic acid, dopamine, glucose and uric acid.

1. Introduction

Fast and reliable determination of hydrogen peroxide (H_2O_2) has gained considerable interest due to its wide variety of applications including environmental [1], clinical [2], pharmaceutical [3], fuel cells [4], paper industry [5], food industry [6], textiles industry [7], and chemical synthesis [8]. In living organisms, H_2O_2 is associated with many different intracellular pathways and biological processes, which can be related to several diseases including diabetes, cancer, aging and atherosclerosis [9]. H_2O_2 is also a byproduct of some of the classical biochemical reactions catalyzed by enzymes such as glucose oxidase (GOx), cholesterol oxidase (ChoOx), glutamate oxidase (GlOx), oxalate oxidase (OxaOx), lactate oxidase (LOx), and etc. Hence H_2O_2 determination has a great significance in both industrial and academic purposes.

Different analytical methods have been reported for the detection and measurement of H_2O_2 that are based on titrimetry [10], chemiluminescence [11], spectrophotometric [12], and fluorescence [13]. However, accuracy in measurements and detection at low level has been a challenging task in the aforementioned analytical techniques. Moreover, the above mentioned analytical methods for H_2O_2 detection also displayed a few other drawbacks such as lack of selectivity, long analysis time and use of expensive reagents [14]. Since H_2O_2 is an electroactive molecule, electrochemical detection is found to be an alternative method and which has attracted much attention due to its fast analysis, sensitive, selective, cost effective and simple fabrication process.

Numerous enzyme modified electrodes are used for detecting relatively low concentrations of H_2O_2 [15]. However, the most common and serious problem with enzyme based H_2O_2 sensors is their stringent operating conditions, high cost, insufficient stability and loss of activity originating from the intrinsic nature of the enzymes [16]. Therefore, much attention has been focused on exploring the electrocatalysis of H_2O_2 without using the enzyme. In that aspect, chemically modified electrodes have received increasing interest owing to their advantages such as higher sensitivity, selectivity, excellent stability, less prone for surface fouling, lower over potentials for electron transfer process compared to the conventional electrodes [17,18].

The role of metal nanoparticles is highly imperative. Various metal nanoparticles such as platinum (Pt) [19], gold (Au) [20], silver (Ag) [21], palladium (Pd) [22], copper (Cu) [23] and nickel (Ni) [24] have drawn more attention in fabrication of enzyme-free/nonenzymatic H_2O_2 sensors, due to their unique physical and chemical properties [25]. Redox mediators such as thionine [26] and Prussian blue [27] modified metal nanoparticles were successfully employed for the detection of hydrogen peroxide. Among them, gold nanoparticles have been widely used for electrochemical sensing, due to the ease of preparation, simple surface functionalization [28,29], chemical stability [30] and very low charge transfer resistance [31].

Metal nanoparticles modified conducting carbon matrix such as carbon nanotubes, graphite and graphene could increase the electrochemically active surface area, which helps to enhance the electron transfer rate between the electrode and analyte molecule [32]. Due to the combination of two nanomaterials, more rapid and highly sensitive current response towards the detection molecule is expected [33]. Graphene is well known for its high conductivity, large surface area, extended

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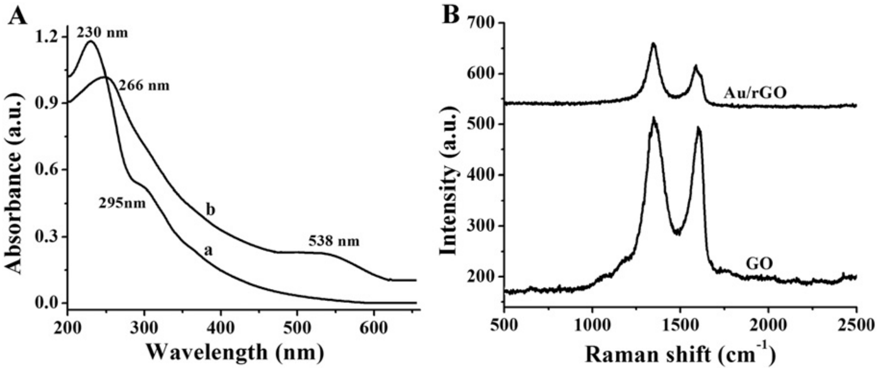

Fig. 1. (A) UV–visible spectra of GO and Au/rGO nanocomposite and (B) Raman spectra of GO and Au/rGO nanocomposite.

charge carrier mobility, excellent mechanical and thermal properties [34,35], which promise its application in various fields [36]. Graphene modified electrodes were successfully employed to study and determine some biological and organic molecules including DNA [37], proteins [38], gas [39], biomolecules [40] and heavy metals [41].

In this work, gold nanoparticles decorated reduced graphene oxide nanocomposite (Au/rGO) was synthesized by single step method and it is applied for the nonenzymatic electrochemical detection of H_2O_2 in neutral medium. The performance of the sensor in terms of linearity, sensitivity, stability, response time and selectivity were evaluated and discussed.

2. Materials and methods

2.1. Chemicals

Graphite powder (<20 μm), ascorbic acid (AA), uric acid (UA), acetaminophen, dopamine hydrochloride (DA) and β-D (+) glucose were supplied by Aldrich. Medical grade conductor paste (carbon ink-BQ242, Ag/AgCl-5874, silver ink-5064) and the thinner for the respective inks were purchased from DuPont Company Pte Ltd., Singapore. Chloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$), hydrogen peroxide (H_2O_2), sodium chloride (NaCl), and potassium chloride (KCl) were purchased from Finar chemicals, India. Di-sodium hydrogen phosphate anhydrous (Na_2HPO_4) and potassium dihydrogen orthophosphate (KH_2PO_4) were procured from Loba chemie, India. All other reagents were of analytical grade and used as received. Deionized water (15 M Ω cm) from Elix-10 system (Millipore, Germany) was used for all the experiments.

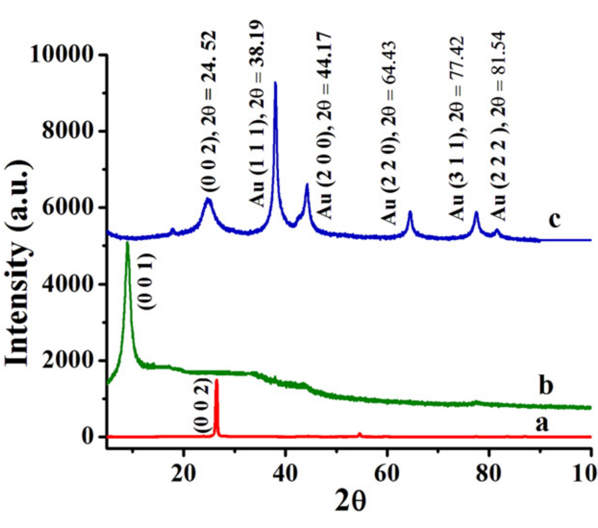

Fig. 2. XRD patterns of (a) graphite, (b) GO and (c) Au/rGO nanocomposite.

2.2. Synthesis of Au/rGO nanocomposite

Graphene oxide (GO) was synthesized from graphite powder using acid mediated oxidation process based on modified Hummer's method [42]. Single step chemical reduction route was followed to prepare Au/rGO nanocomposite. GO in water (200 mL, 0.5 mg mL^{-1}) was ultrasonicated for two hours and then mixed with 100 mM $HAuCl_4.3H_2O$ (0.3 mL) solution under stirring. After 30 min, 0.5 M sodium borohydride (20 mL) was added drop wise to the reaction mixture and stirred at room temperature for ten hours. The obtained product was re-suspended in water and centrifuged. This process was repeated several times to remove the unreacted reactants. The product was dried at 70 °C.

2.3. Characterization

All the electrochemical experiments were carried out using electrochemical analyzer CHI608D (CH Instruments, TX and USA). Small-angle X-ray diffraction (SA-XRD) measurements were performed at room temperature (25 °C) on a Rigaku Miniflex 600 model X-ray diffractometer, using Kβ foil filtered Cu Kα radiation (λ = 1.541 Å) with a NaI scintillator detector. The step time was 1 s at 0.02°/step in a 2θ range of 5–90°. Raman spectra were recorded on a LabRAM HR UV–vis–NIR Raman microscope from HORIBA Jobin-Yvon (514 nm laser source). UV–visible spectra in the range of 200–800 nm were recorded with UV–vis spectrophotometer (Pharmaspec 1700, Shimadzu). Morphology was analyzed using field emission scanning electron microscopy (FESEM) FEI QUANTA FEG 250 and high resolution transmission electron microscope (HRTEM) JEOL JEM 2100 TEM.

2.4. Fabrication of modified screen printed electrodes

A disposable three electrode array was printed by screen printing. The SPEs were activated by cycling the potential between −0.2 to +1.8 V at a scan rate of 100 mV s^{-1} for 20 times in 1 M sulphuric acid. The sensor electrodes were fabricated by casting 10 μL of suspension of the nanocomposite (5 mg mL^{-1}) on the working electrode (2 mm dia). The modified SPE was represented as Au/rGO/SPE.