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Electrodeposition of copper nanoparticles using pectin scaffold at graphene nanosheets for electrochemical sensing of glucose and hydrogen peroxide

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ABSTRACT

A simple electrodeposition approach has been described for the preparation of copper nanoparticles (CuNPs) using biopolymer pectin as a scaffold and graphene as a support. The formation of graphene/pectin-CuNPs was confirmed by scanning electron microscopy, UV-Visible spectroscopy and X-ray diffraction studies. The graphene/pectin-CuNPs film modified electrode was prepared and its electrocatalytic applications to the oxidation of glucose and reduction of H_2O_2 have been explored. An amperometric glucose sensor was fabricated which exhibited excellent sensor performance in terms of wide linear range (10 μM–5.5 mM), low detection limit (2.1 μM) and high sensitivity (0.0457 $\mu A \mu M^{-1} cm^{-2}$). Likewise, an amperometric sensor has been fabricated for the determination of H_2O_2 which displayed linear range of 1 μM–1 mM, detection limit of 0.35 μM and sensitivity of 0.391 $\mu A \mu M^{-1} cm^{-2}$. The sensor displayed appreciable repeatability, reproducibity and stability. Furthermore, practical feasibility of the sensor has been demonstrated in human serum and contact lens cleaning solution to determine glucose and H_2O_2, respectively. The main advantages of sensor include simple and green fabrication approach, roughed and stable electrode matrix, high sensitivity and stability, fast in sensing and highly reproducible.

1. Introduction

The development of sensitive glucose biosensors for the accurate and reliable determination of blood glucose level is of great significance to control diabetics [1–3]. Numerous enzymatic glucose biosensors have been reported based on glucose oxidase (GOx) immobilized at various modified electrodes [3–8]. However, enzyme electrodes often suffer from serious drawbacks, such as, instability of immobilized enzyme, lack of long term stability, enzyme leaching and poor electrical communication to the highly buried active sites of enzyme [1]. Also, activity of the GOx has been affected by pH, temperature and immobilization methods [9]. Nonenzymatic glucose sensors are attractive alternative approach for the detection of glucose to avoid enzyme related issues [10] and therefore, many efforts have been focused on the fabrication of non-enzymatic glucose sensor using different electrode modifiers [11–13]. Electrodes modified with nanomaterials are widely used for the construction of glucose sensors attributed to their extraordinary physiochemical properties such as, large surface-to-volume ratio, high conductivity, and excellent electrocatalytic ability [12,14]. In recent times, numerous copper nanoparticles (CuNPs) based electrodes are reported for the determination of glucose [9,10,15–17]. However, most of the methods reported in the literature are based on chemical methods which require the use of reduction agents [18], thermal condition [19], microemulsions [20], and micelles [19] etc., These methods also involved with tedious procedures and the as-prepared CuNPs has the possibility of easily oxidized to copper oxide during the course of preparation in the aforementioned methods [21]. On the other hand, green agents such as biopolymers stabilized preparation methods have the ability to overcome the difficulties encountered by the

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chemical synthesis methods. Therefore, herein, we established a simple green method to synthesis biopolymer stabilized CuNPs using pectin as a scaffold. The method involves simple and efficient electrodeposition methods without using any reducing agent and complex methods. Pectin (polygalacturonic acid) is a naturally occurring polysaccharide occurring at the cell walls of the plants and highly biodegradable [22,23]. The use of carbon based materials such as carbon nanotubes and graphene as supports is well established approach to improve the stability and conductivity of the nanoparticles, which also aid to overcome surface fouling issues [24,25]. Therefore, we deposited pectin stabilized CuNPs at graphene, where graphene prepared on the electrode surface through electrochemical reduction method. The as-prepared graphene/pectin-CuNPs has been well characterized by analytical, spectral and electrochemical methods. The graphene/pectin-CuNPs film exhibited excellent electrocatalytic ability to the oxidation of glucose and displayed excellent sensor performance with the reported glucose sensors in terms of wide linear range, high sensitivity and selectivity, fast response time, high stability and appreciable practicality. Additionally, the graphene/pectin-CuNPs film also exhibited excellent electrocatalytic ability to the reduction of hydrogen peroxide (H_2O_2) and therefore we also developed a nonenzymatic H_2O_2 sensor. H_2O_2 is a vital constituent of plant tissues, which regulates the plant metabolism, acclamatory processes and gene expression [26,27]. In addition, it possesses good antibacterial and antiseptic properties and extensively used in industries as an oxidizing agent, antibacterial agent and bleaching agent [28,29]. Therefore, an accurate and reliable method for the determination of H_2O_2 is highly important for clinical and industrial analysis [15,30–32].

The main aim of this method is to develop a biopolymer assisted electrochemical synthetical method for the preparation of CuNPs and for the development of glucose and H_2O_2 sensor. The described method has advantages over previous methods to prepare high stable, uniform and electrochemically active CuNPs. The preparation is fast, green, simple electrode fabrication procedure and highly reproducible.

2. Experimental

2.1. Reagents and apparatus

Graphite (powder, <20 μm), LM-pectin (DE 35%, pectin (from citrus peel), copper nitrate (purum, ≥98%, ≤26% Cu basis), glucose and H_2O_2 were purchased from Sigma-Aldrich and used as received. The supporting electrolyte used for all the electrochemical studies was 0.1 M phosphate buffer solution, prepared using NaH_2PO_4 and Na_2HPO_4, while the pH were adjusted to get desired pH using either using H_2SO_4 or NaOH. Prior to each experiment, all the solutions were deoxygenated with pre-purified nitrogen gas for 15 min unless otherwise specified. Blood sample used in this study were collected from healthy man (26-year-old male). The blood sample was taken from cubital vein and transferred to a test tube and stored at −20 °C before analysis. The collected blood sample was allowed to clot; subsequently the clot was removed through centrifugation for 20 min at the speed of 2000 × g. The serum separated as a supernatant was collected and stored at the temperature of −20 °C. Contact lens cleaning solution containing 3% H_2O_2 was purchased from a local drug store in Taipei, Taiwan to demonstrate practicality osf the sensor.

The electrochemical measurements were carried out using CHI 611A electrochemical work station. Electrochemical studies were performed in a conventional three electrode cell using BAS glassy carbon electrode (GCE) as a working electrode (area 0.071 cm^2), Ag|AgCl (saturated KCl) as a reference electrode and Pt wire as a counter electrode. Amperometric measurements were performed with analytical rotator AFMSRX (PINE instruments, USA) with a rotating disc electrode (RDE) having working area of 0.24 cm^2. Scanning electron microscope (SEM) studies were performed using Hitachi S-3000H scanning electron microscope. Ultra violet visible (UV-Vis) spectroscopy studies were performed by U-3300 spectrophotometer. X-ray diffraction (XRD) and Attenuated total reflectance-FT-IR (ATR–FTIR) spectroscopy studies were carried out using XPERT-PRO (PANalytical B.V., The Netherlands) diffractometer (Cu Kα radiation, k = 1.54 Å) and Perkin-Elmer IR spectrometer respectively.

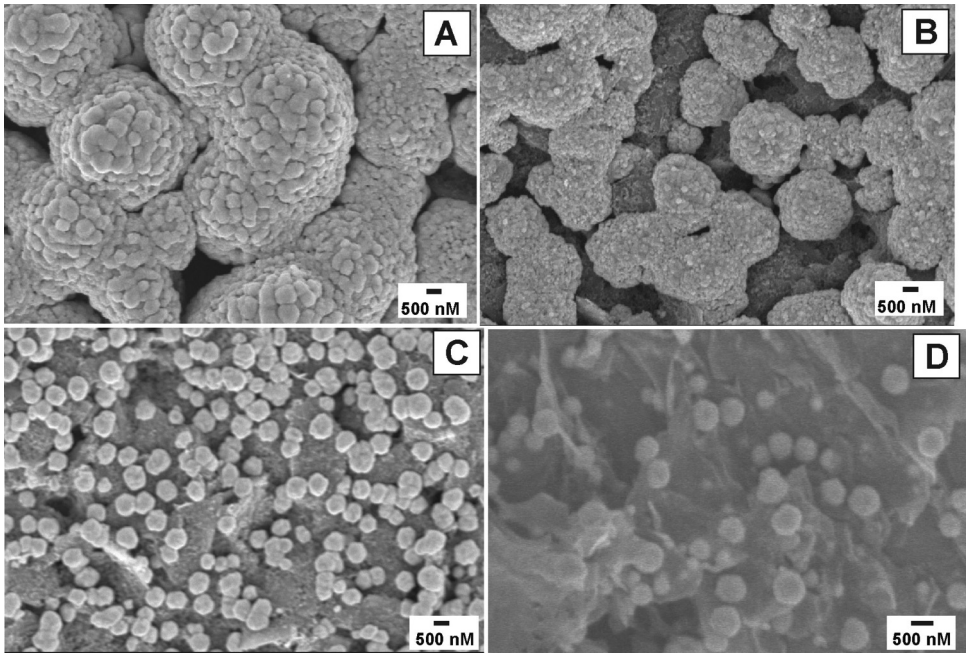

Fig. 1. SEM images of pectin-CuNPs at the potential of –1.20 V (A), – 0.80 V (B) and – 0.60 V (C). SEM image of graphene/pectin-CuNPs.