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Ruthenium Nanoparticles Functionalized Chemically Reduced Graphene for Analytical Detection of Hydrogen Peroxide

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ABSTRACT

A novel method for analytical detection of H_2O_2 based on ruthenium nanoparticles (RuNPs) functionalized chemically reduced graphene (CRGR) nanocomposite is developed. The RuNPs/CRGR nanocomposite was characterized employing different techniques, such as transmitted electron microscope (TEM), cyclic voltammetry (CV) and chronoamperometry (CA). The RuNPs/CRGR nanocomposite sensor exhibits higher catalytic effect to H_2O_2 by greatly enhancing the reduction peak current and completely eliminating the interference of other species as compared with a bare electrode. A fast amperometric response was observed by the RuNPs/CRGR electrode with a linear range from 10 to 170 µM and lower detection limit of 0.16±0.01 µM as compared to some other reports. The high reproducibility, specificity as well as long time stability obtained with the proposed sensor indicated that the present method is an effective for H_2O_2 determination.

Introduction

Recent activities in electroanalytical chemistry have focused on the design and development of nanomaterials based biosensors. Particularly, noble metals have potential applications in the construction of electrochemical sensors and biosensors due to their own fascinating surface structure, good electrocatalytic activity, strong stability and limited aggregation [1,2]. Therefore, modification of electrochemical interface with nanosized metal or metal oxide nanostructures is one of the recent approaches used extensively in the development of sensing platforms [3]. In this context, various nanostructured metals have been recently used in this propose, such as Pt, Pd, Ag, Au and Ni [4-10]. Of these, Ru has also been employed for modification of different electrode surfaces because of its good electrochemical and photochemical catalysis and excellent charge storage property, including nano-ruthenium oxide/riboflavin (RuOx/RF), 3D platinum ruthenium (PtRu) bimetallic nanoparticles, and nafion/ruthenium oxide were constructed and utilized to biological determination [11-13].

Graphene is a first example of truly two-dimensional (2D) crystal materials with an atomic scale thickness, has a short history but is rising in materials science [14,15]. In view of its unique physical and chemical properties, such as high mechanical strength [16], natural 2D template effect [17] and large specific surface area [18]. Thus, graphene has been proposed as a preferred substrate for the immobilization of different nanomaterials. Recently, graphene supported metal nanocomposites as a new class of hybrid materials combining the advantages of both graphene substrate and active metal nanoparticle components have shown extensive applications in many advanced fields, such as memory electronic, optoelectronic transistors [19,20], catalysis [21], energy storage [22,23], and electrochemical sensors and biosensors [24-26].

Hydrogen peroxide (H_2O_2) has received a great practical importance in analytical application because it is not only a product of the reactions catalyzed by many highly selective oxidases but also an essential component in food, pharmaceutical, environmental and many other fields [27]. In this propose, different analytical techniques have been employed for the determination of H_2O_2, such as photometry [28], chemiluminescence [29] and fluorescence [30]. Among them, electrochemical technique has been the most widely used due to lower detection limits, short response time and high sensitivity. Although some studies have showed successful results in this direction [4-9], there have been no reports concerning the uses of RuNPs nanocomposite chemically reduced graphene (CRGR) for the electrochemical applications and analytical determinations of H_2O_2 so far.

In this report, a novel analytical strategy based on RuNPs/CRGR nanocomposite was developed for the detection of H_2O_2. The RuNPs/CRGR nanocomposite is characterized by scanning electron microscopy (SEM), cyclic voltammetry (CV) and chronoamperometry (CA). The experimental parameters affecting the response of the nanocomposite sensor were optimized in terms of pH and applied potential.

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Materials

Graphite, rhuthenium chloide ($RuCl_3$), H_2O_2, ascorbic acid (AA), uric acid (UA), dopamine (DA), glucose (Glu), acetaminophen (AP), tryptophan (TR), sodium dihydrogen phosphate and disodium hydrogen phosphate were purchased from Sigma-Aldrich (USA). Graphene (GR) was synthesized by Hummers method [31]. RuNPs were prepared through borohydride reduction of $RuCl_3$. Other chemicals were used of extra-pure quality. All solutions were prepared with doubly

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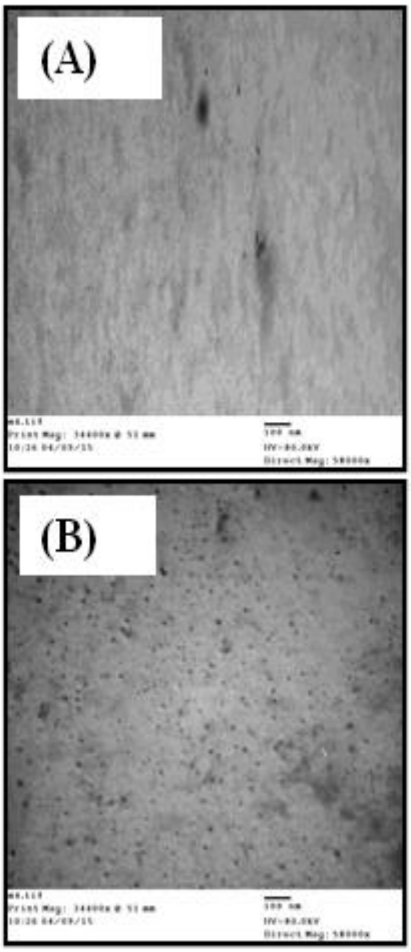

Fig 1. TEM images of (A) CRGR and (B) RuNPs/CRGR.

distilled water obtained from a Milli-Q water purifying system (18 MΩ cm).

Instruments

Cyclic voltammograms, and chronoamperograms were recorded using a EG&G 273A Potentiostat/Galvanostat (USA). SEM images were obtained using a Cambridge Stereoscan 240. RuNPs/CRGR/GCE, CRGR/GCE and bare GCE, with an electrode area of 0.07 cm^2, were used as working electrodes. Reference and counter electrodes were Ag/AgCl and platinum wire, respectively.

Reduction of GR

Chemical reduction of graphene (CRGR) was carried out according to the following procedure; a 0.5 g of GR was added into a flask containing 200 mL deionized water and ultrasonicated for 12 h to get a yellow-brown solution. The solution was then heated to 80 ˚C, followed by the addition of 5.0 g $NaBH_4$. Then, the black solid was washed after 2 h with ethanol and distilled water for several times and vacuum dried at 60 ˚C for 12 h.

Sensor preparation

RuNPs/CRGR nanocomposite sensor was prepared by mixing a 1.0 mg of CRGR with 1.0 mL of RuNPs at constant stirring for about 12 h. Then, GCE was polished with 0.05 µm alumina slurries on a polishing cloth to a mirror finish and ultrasonically cleaned for a minute in distilled water. Thereafter, a 1.0 mg/mL of RuNPs/CRGR nanocomposite solution was drop casting onto a polished GCE and dried in a condensed system for about 12 h. Then, the RuNPs/CRGR/GCE was rinsed thoroughly with doubly distilled water and stored until used.

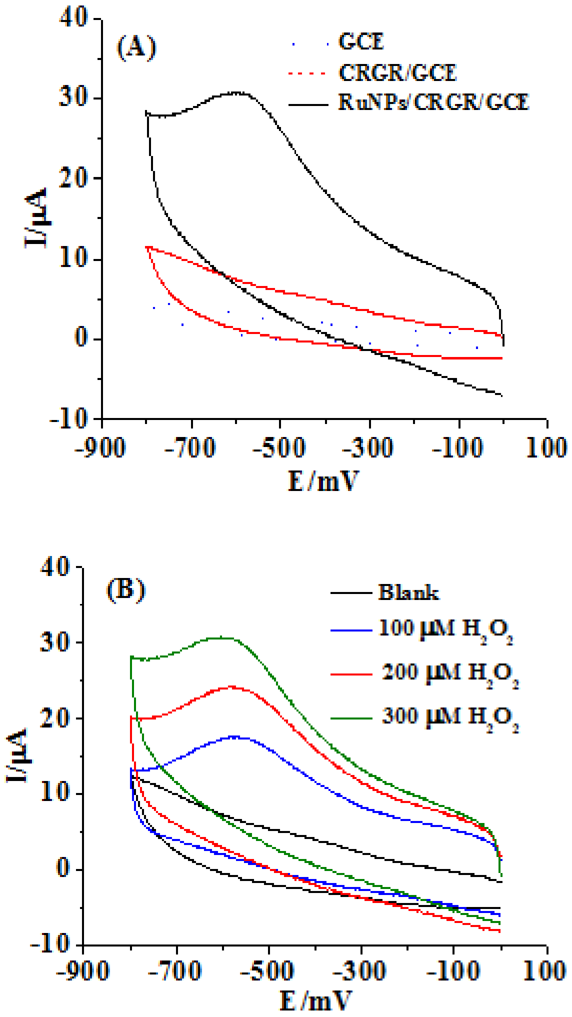

Fig 2. (A) CVs recorded for bare (dotted line), CRGR (dashed line) and RuNPs/CRGR (solid line) electrodes in PBS of pH 7.0 containing 300 µM H_2O_2. (B) CVs recorded for RuNPs/CRGR electrode in PBS (blank), 100, 200 and 300 µM of H_2O_2.

Results and discussion

Characterization of RuNPs/CRGR nanocomposite

Figure 1A and 1B showed the representative TEM images of the CRGR and RuNPs/CRRG, respectively. As obvious, TEM image of CRGR shows a smooth surface while CRGR covered uniformly and wholly the GC surface. However, the morphology of RuNPs/CRGR was very different than that obtained with CRGR which shows a high-yield and ultrafine RuNPs are homogeneously dispersed onto CRGR. This might be due to the incorporation of RuNPs into CRGR structure with an average size of RuNPs in the nanocomposite was estimated to be 17 nm.

Electrochemical behavior of the RuNPs/CRGR nanocomposite sensor

In order to investigate the electrocatalytic reduction of H_2O_2, a comparison between responses of H_2O_2 reduction on the RuNPs/CRGR nanocomposite (solid line), CRGR (dashed line) and bare (dotted line) electrodes with a 300 µM H_2O_2 was recorded (Fig. 2A). As shown, a sharp reduction peak for H_2O_2 was obtained with the RuNPs/CRGR electrode, however no peak can be shown in case of bare or CRGR electrodes. The higher and excellent catalytic response of the RuNPs/CRGR sensor to H_2O_2 might be due to the nanometal of RuNPs that was successfully composite with CRGR.

On an attempt to study the reliability of the RuNPs/CRGR sensor for the electrochemical detection of H_2O_2, the responses of the RuNPs/CRGR nanocomposite were recorded at different concentrations of H_2O_2 as shown in Figure 2B. As the concentration of H_2O_2 in the solution increased the reduction peak current remarkably increased. This indicated that the proposed sensor is potentially suitable for H_2O_2 detection.

Optimization of H_2O_2 detection

Experimental parameters that can affect the response of H_2O_2 sensor was carried out in terms of pH and applied potential. The effect of solution pH on the electrocatalytic reduction of H_2O_2 with the RuNPs/CRGR electrode were investigated in the range from 4 to 8 (Fig. 3A). The reduction peak current of H_2O_2 increased with the increasing pH from 4.0 to 7.0, while increasing pH more up to 8 the catalytic response did not increase further. Thus, pH 7.0 was selected as the optimum solution pH for H_2O_2 detection.

The effect of applied potential on the amperometric response of H_2O_2 was also studied and presented in Figure 3B. As can be seen, the current response of H_2O_2 increased as the applied potential shifted from −0.4 V to more negative value. The maximum current response was observed at −0.6 V, applying more negative potential did not significantly increase the current response. Hence, −0.6 V was selected as the optimum applied potential for H_2O_2 detection.

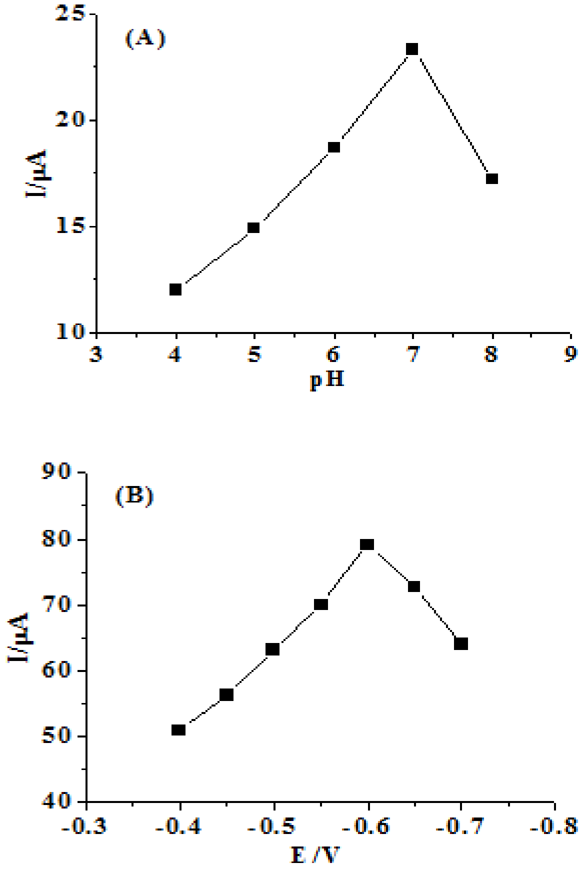

Fig 3. Optimization of H_2O_2 detection with the RuNPs/CRGR electrode: (A) pH and (B) Applied potential.

Sensitivity of the RuNPs/CRGR nanocomposite sensor response of H_2O_2 sensor

In order to investigate the validity of the RuNPs/CRGR nanocomposite for H_2O_2 determination, the amperometric successive additions of H_2O_2 at different concentrations was recorded (Fig. 4A). The nanocomosite sensor showed an excellent and fast amperometric response through the addition of H_2O_2 with a dynamic linear range from 10−170 µM (Fig. 4B). The sensitivity of H_2O_2 sensor was 1.1±0.1 µA μM^{-1}, with a response time of 5.88±0.23 s μM^{-1}. The linear regression equation was expressed as: Ip (µA) = 7.81 (±0.51) + 0.45 (±0.01) $[H_2O_2]$ (µM), with the correlation coefficient of 0.993. The relative standard deviation (RSD) was estimated to be 1.5% with low detection limit of 0.16±0.01 µM. The obtained detection limit was lower than other reported H_2O_2 sensors [4-8], indicating the higher sensitivity of the proposed sensor to H_2O_2 which can be effective for analytical determination of H_2O_2 in practical applications.

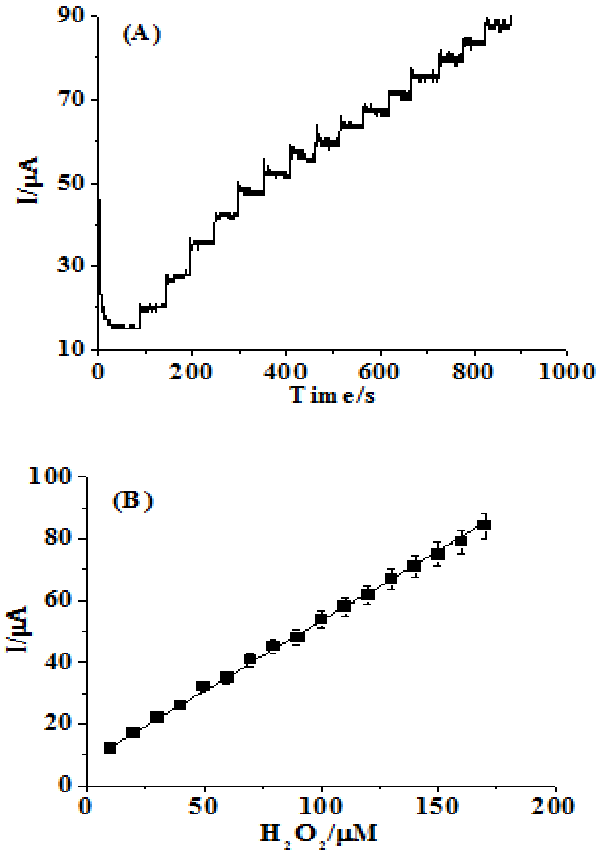

Fig 4. Amperometric response of the RuNPs/CRGR electrode in PBS (pH 7.0) after multiple additions of H_2O_2. (B) Plot shows the corresponding calibration curve.

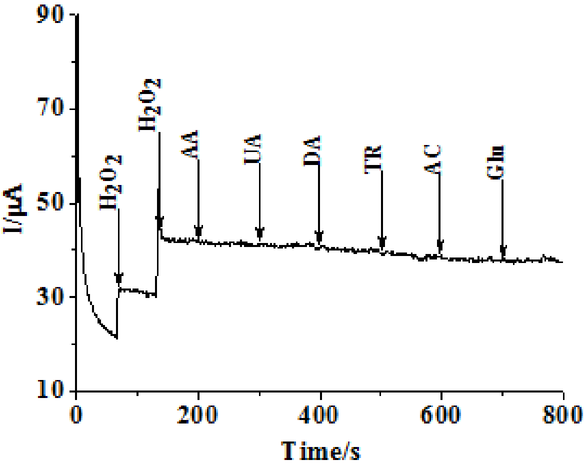

Fig 5. Amperogram of the addition of 10 µM H_2O_2 and 1.0 mM of other interfering species.

Selectivity of the RuNPs/CRGR sensor

The selectivity of RuNPs/CRGR nanocomposite sensor to H_2O_2 detection with other biological interfering substances, such as AA, UA, DA, TR, AC and Glu was investigated. Figure 5 shows the amperometric response of 10 µM H_2O_2 and 1.0 mM of other interferences. The result indicated that, these substances did not show any interfering effect during detection of H_2O_2 demonstrating that the present sensor has completely eliminated the diffusion of interfering substances.

Stability of the RuNPs/CRGR sensor

The stability of the sensor towards H_2O_2 detection was also examined for one month during that the sensor retained about 95% of its initial response to H_2O_2. In this context, the repeatability of the sensor was investigated for 5 electrodes prepared according to our method. The results indicated that, there was no significant different in their catalytic responses to H_2O_2 elucidating a good repeatability of the sensor. These results confirmed that the RuNPs/CRGR sensor has long time stability and good repeatability without significant change in its response to H_2O_2 detection.

Conclusion

A new method based on RuNPs/CRGR nanocomposite for the fabrication of H_2O_2 sensor was developed. The nanocomposite sensor displays intensive electrocatalytic activity towards the reduction of H_2O_2 by enhancing the cathodic peak current and completely eliminating the interference of other species. The RuNPs/CRGR sensor showed an excellent amperometric response to H_2O_2 reduction with linear range from 10−170 µM and detection limit of 0.16 µM. Moreover, the sensor showed good reproducibility as well as anti-interfering ability and long term stability.

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