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Electrochemical sensing of glucose by reduced graphene oxide-zinc ferrospinels

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ABSTRACT

We have developed $ZnFe_2O_4$ magnetic nanoparticles/reduced graphene oxide nanosheets modified glassy carbon ($ZnFe_2O_4$/rGO/GCE) electrode as a novel system for the electrochemical glucose sensing. Via a facile in situ hydrothermal route, the reduction of GO and the formation of $ZnFe_2O_4$ nanoparticles occurred simultaneously. This enables the $ZnFe_2O_4$ nanoparticles dispersed on the reduced graphene sheet. Characterization of nanocomposite by X-ray diffraction (XRD) and transmission electron microscopy (TEM) clearly demonstrate the successful attachment of $ZnFe_2O_4$ nanoparticles to graphene sheets. Electrochemical studies revealed that the $ZnFe_2O_4$/rGO/GCE possess excellent electrocatalytic activities toward the oxidation of glucose and the performance of sensor is enhanced by integration of graphene nanosheets with $ZnFe_2O_4$ nanoparticles.

1. Introduction

Reduced graphene oxide (rGO) is an excellent electron-transporting material in the photocatalytic process. It is a single layer of two-dimensional sp^2 hybridized carbon nanosheet with great thermal conductivity, large surface area, excellent electron mobility, high transparency and mechanical strength flexibility [1]. Recently integration of graphene nanosheets with metal nanoparticles to form graphene-metal hybrids has been intensively developed in various applications such as catalysis, surface enhanced raman scattering, targeted drug delivery and removal of organic pollutants [2–4]. Graphene acts as a separator to prevent the particles aggregating and the synergetic effects between graphene and the second components improves hybrids functionalities [5,6]. Spinel ferrites (MFe_2O_4) are important class of magnetic materials where oxygen forms a face cubic centered (fcc) close packing, and M^{2+} and Fe^{3+} occupy either tetrahedral or octahedral interstitial sites [7]. Among the magnetic nanoparticles, nanosized zinc ferrite ($ZnFe_2O_4$) particles are occupying an important place for their unusual properties such as narrow bandgaps, excellent visible-light response, good photochemical stability and favorable magnetism [8,9]. Although the enzymatic glucose sensors have obtained the majority of glucose sensors in the market due to being fast and reversible but they still suffer from the lack of stability attribute to the intrinsic nature of enzymes and it remains the main problem in this type of sensors [10,11]. It is necessary to utilize sensors which are stable at high temperatures and under aggressive environment. In this article, we reported a new type of flexible electrochemical sensor based on $ZnFe_2O_4$/rGO hybrids as an enzymeless glucose sensor. We have fabricated $ZnFe_2O_4$/rGO nanoparticles on glassy carbon electrode (GCE) substrate using different graphene content. The electrochemical oxidation behaviour of glucose was investigated and the modified electrode exhibited a wide linear range and a low detection limit towards glucose as well as possess excellent stability and reproducibility. The successful dispersion of magnetic $ZnFe_2O_4$ nanoparticles on graphene nanosheets has enabled the construction of a high sensitive sensor due to the low electronic noise from thermal effect.

2. Materials and methods

2.1. Chemicals and reagents

$Zn(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, ethanol (C_2H_5OH, 99.7% purity), D-(+)-glucose, uric acid (UA), ascorbic acid (AA), sucrose and fructose were obtained from Aldrich. All other reagents were of analytical grade and were used as received. Deionized water

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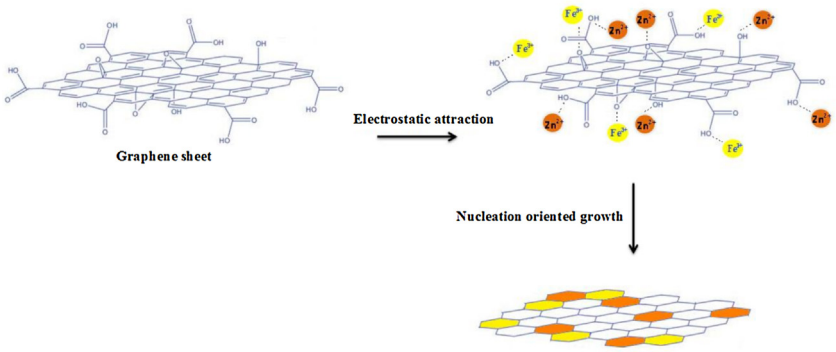

Scheme 1. The synthesis process of the $ZnFe_2O_4$/rGO nanocomposite.

was used for all experiments which were carried out at room temperature.

2.2. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized from graphite flakes (purchased from Sigma Aldrich) according to the modified Hummer method [12,13]. In brief, 5 g of graphite flakes and 2.5 g of $NaNO_3$ were mixed together followed by the addition of 108 ml concentrated H_2SO_4 and 12 ml H_3PO_4. After 10 min stirring in an ice bath, 15 g of $KMnO_4$ were slowly added to keep the temperature of the mixture below 5 °C to prevent overheating and explosion. The mixture was stirred at 35 °C for 12 h and the resulting solution was diluted by adding 400 ml of water under vigorous stirring. To ensure the completion of reaction with $KMnO_4$, 15 ml of H_2O_2 was added to the mixture. The reaction product was centrifuged and washed with deionized water and 5% HCl solution repeatedly. Finally, the product was dried at 60 °C.

2.3. Synthesis of magnetic $ZnFe_2O_4$/rGO composite

The $ZnFe_2O_4$/rGO nanocomposite with different graphene content (10, 20, 30 wt%) were synthesized. The method for the synthesis of $ZnFe_2O_4$/rGO nanocomposite with 30 wt% graphene oxide content is as follows: 96 mg of GO was dispersed into 72 ml of absolute ethanol with sonication for 1 h. Then 0.357 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.9696 g of $Fe(NO_3)_3 \cdot 9H_2O$ were added to 24 ml of absolute ethanol with stirring for 30 min at room temperature. The above two systems were then mixed together, and stirred for 30 min, yielding a stable dark green homogeneous emulsion. The resulting mixture was transferred into a 200 ml Teflon-lined stainless autoclave and heated to 180 °C for 12 h under autogenously pressure. The reaction mixture was allowed to cool to room temperature and the precipitate was filtered, washed with distilled water five times, and dried in a vacuum oven at 60 °C for 12 h. The product was labeled as $ZnFe_2O_4$/rGO (30 wt%). For comparison, the same method was used to synthesize pure $ZnFe_2O_4$ without rGO. The synthesis process of the nanocomposite is shown in Scheme 1.

2.4. Characterization

X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were used to analyze and investigate the synthesized nanocomposite structure. The surface morphological studies have been investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Hitachi SU 8000 model instrument). The cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry measurements have been recorded using AUTOLAB model PGSTAT conducted on a three-electrode cell at room temperature in 0.1 M phosphate buffer solution of pH 7.4. The surface polish of bare glassy carbon electrode (3 mm diameter) was carried out with 1.0 and 0.3 μm alumina slurry to eliminate the effect of traces on the rate of electron transfer. After figure-8 motions polish of glassy carbon electrode, the surface was rinsed with distilled water and followed by sonication in distilled water for a few minutes to ensure complete removal of the alumina particles. The treated GCE surface was deposited by nanocomposite with different graphene oxide content for electrochemical measurements.

3. Results and discussion

3.1. Characterization of $ZnFe_2O_4$ and $ZnFe_2O_4$/rGO nanocomposite

The morphology of the pure $ZnFe_2O_4$ NPs, reduced graphene oxide and the resulting $ZnFe_2O_4$/rGO (30 wt%) nanocomposite were characterized by TEM (Fig. 1). The images revealed the pure $ZnFe_2O_4$ NPs with diameters ranging from 20 to 90 nm and reduced graphene oxide with curled and corrugated structure as shown in Fig. 1a and b respectively. Graphene oxide as a supporting substrate can minimize the metallic NPs agglomeration. The reduced graphene oxide has the unique 2D structure which enables it to be a great electron-transporting material (Fig. 1d). Densely distribution of the $ZnFe_2O_4$ NPs on the graphene sheets can be seen in Fig. 1f which illustrated the electrostatic adsorption of the positive Zn and Fe on the graphene oxide sheets by the oxygen-containing functional groups. The structures of GO, rGO and zinc ferrite/graphene composites were characterized using the XRD analysis (Fig. 2). The diffraction pattern of GO showed a strong peak at around $2\theta = 10.2°$, originated from its (001) reflection which is consistent with the lamellar structure of GO. This peak had disappeared in rGO, indicating the oxygen groups have been removed and GO has been reduced to rGO nanosheets [14]. It has been observed that the two stronger peaks corresponding to (220) and (311) reflections at $2\theta \approx 30°$ and 35.5°. These peaks merged into a peak (400) which is the reflection of the cubic $ZnFe_2O_4$ phase $2\theta \approx 38.18°$ [15]. The Bragg planes of (422) and (440) were corresponded to the tetrahedral structure of $ZnFe_2O_4$ nanoparticles ($2\theta \approx 51–60°$). Moreover there is no visible sign of (001) in diffraction peak of $ZnFe_2O_4$/rGO which due to growth of magnetic nanoparticles within GO interlayers and exfoliation of graphene oxide [16]. GO, $ZnFe_2O_4$ NPs and $ZnFe_2O_4$/rGO nanocomposite were further examined by FT-IR spectrum. The peaks (curve a) at 3410 cm^{-1} and 1743 cm^{-1} are corresponded to the stretching vibrations of O—H and C=O respectively, while the vibration of carboxyl groups are found at 1620 cm^{-1} and 1278 cm^{-1} [17]. The distinct adsorption bands at 550 cm^{-1} (curve b), can be assigned to the tetrahedral position.