Characterization and Modification of Chitosan-reduced Graphene Oxide Composite Films for Electrochemical Sensor

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Abstract: Chitosan-reduced graphene oxide composite film was succesfully fabricated by electrodeposition method for electrochemical sensor. In this regard, we have prepared chitosan-reduced graphene oxide composites using a simple methodology, where chitosan-reduced graphene oxide composite can coat on the surface of screen-printed copper electrode via a simple electrodeposition method. In this work, the characterization of the composite film was intensively investigated by XRD and FT-IR method. The results of the XRD represented reduced graphene oxide structure in 2θ, appeared at 26.61° with interlayer spacing was about 3.347Å. The characterization of FT-IR confirmed the successful rGO presence in matrix polymer of chitosan.

1 INTRODUCTION

Electrochemical analysis is a quantitative or qualitative analysis method based on the electrical properties of a solution of the analyzed substance in an electrochemical cell (Hendayana, 1994).

The electrochemical method is the most common method in various fields of application, in particular electrochemical sensors and biosensors developed for pharmaceutical, food, agriculture and environmental analysis because they have many advantages, such as high sensitivity, cheap and easy to operate the tool and quick response (Beitollahi et al., 2009), (Gajdar et al., 2016) dan (Mazloum-Ardakani et al., 2011).

There are several advantages of electrochemical sensors because electrodes can sense material present in a sample without damaging the system with low detection limits and high specificity. The active sensing material on the electrode must act as a catalyst and catalyze the chemical and biochemical compound reaction in order to obtain a signal for production. The combination of biosensors and electrochemical sensors leads to a new type of sensor called electrochemical biosensors, which applies electrochemical methods to the construction and work of biosensors (Kumar & Zou, 2005).

An electrochemical cell generally consists of three types of electrodes, namely the working electrode, the reference electrode, and the counter electrode. The material used for the manufacture of electrochemical cells must be able to be used over a wide temperature range, stable form, resistant to solutions, organic solvents and reagents, durable, and most importantly is made of transparent material, so that the solution and the electrodes can be observed (Sawyer, 1995). Ideal working electrodes are electrodes that have a reproducible surface area and low background current.

(Vyskocil & Barek, 2009) have been determinated of metronidazole based on electrochemical sensors has many advantages ranging from high sensitivity, low cost and easy to use and is widely used in different fields, especially in analytical chemistry.

The growing importance of polymer-coated nanomaterials from biological polymer sources has brought chitosan to the fore, especially because of its biological properties, which have been used in many engineering and biological fields (Jayakumar et al., 2010)

Chitosan is a biopolymer that has recognized properties such as biodegradability and biocompatibility (Muzzarelli, 2010). Due to its biocompatibility, hydrophilicity, non-toxicity, good mechanical stability, cost-effectiveness and availability of reactive functional groups for chemical modifications, chitosan has also been brought into sharp focus as a suitable matrix (Kaur et al., 2019).

Over the past few years, chitosan-based sensor materials have been widely developed, including in conduction polymers, metal nanoparticles, and oxidizing agents (Yang et al., 2010).

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Polymer composites have now developed into one of the largest groups in material science and offer significant potential for the production of advanced materials in a wide variety of applications (G. Singh et al., 2012). Once nanofillers are distributed on a molecular scale within a polymer matrix, chemical bonding interacts with the matrix. These chemical functionalities have been found to be a practicable and effective way to improve the dispersion of graphene materials and the interfacial bonding between graphene and the polymer matrix (Verdejo et al., 2008). GO has been reported to be well dispersed in the chitosan matrix on a molecular scale because of interactions between the chitosan matrix and the GO sheets (Yang et al., 2010).

In recent years, many electrochemical techniques have used electrocatalysts, one of which is graphene. Graphene is a hexagonal lattice that has a single atom and has many researchers' attention because of its new mechanical and electronic features (Ramanathan et al., 2008). Graphene has unique electrical, mechanical, and optical properties that researchers around the world use to create advanced electronic materials including transparent conductors and ultrafast transistors (R. Singh et al., 2019). Due to its extraordinary properties, this novel nanomaterial has great potential in electrochemical sensor.

Several individuals such as (Muralidharan et al., 2016) have investigated reduced chitosan graphene oxide film, stating that it is clear from studies on mechanical properties that the tensile strength and module of chitosan composites have improved drastically with the incorporation of rGO as a filler reinforcement. The added graphene increases the chitosan voltage strength from 39.7 MPa to 69.5 MPa.

Based on the description above, the researchers were interested in conducting a study of chitosan-graphene oxide reduced modification for electrochemical sensor.

2 EXPERIMENTAL

2.1 Materials

Chitosan and reduced graphene oxide (RGO) was obtained from Sigma Aldrich, Co., 3050 Spruce Street St. Louis, MO 63103 USA 314-771-5765 with 82% deacetylation degree and molecular weight of 190,000-310,000 Da using the viscometer method. All chemicals have a standard analytical level and are used when received. Solvents and electrolyte solutions are prepared using double distilled water (DD) without further purification.

2.2 Fabrication of Chitosan/rGO Composite Flm Modified Screen-printed Copper Electrode

To achieve a mirror-like coating on the electrode, the bare screen-printed copper electrode surface (diameter = 5 mm) was washed by polishing with 0.05 µm alumina, and then ultrasonically with distilled water.

Chitosan solution was prepared by dissolving 1 g of chitosan powder in 100 mL of 1.0% (v/v) acetic acid solution. Then, the chitosan solution was stirred for 24 h and refrigerated at 4°C (Baccarin et al., 2017). Reduced graphene oxide (rGO) has been prepared in different concentration (50, 100, 150, 200 and 500 ppm) and has been distributed into 100 mL of double distilled water.

2.3 Characterization Method

Electrodes were characterized using Potentiostat/Galvanostat Electrochemical Workstation Corrtest with model CS-350. X-ray diffraction (XRD) were observed with a Shimadzu XRD-6100 to analyze the crystallinity of graphene oxide reduction. The Fourier Transform Infrared (FT IR) spectra were performed using Shimadzu Pestige 21 for chitosan and chitosan / rGO.

3 RESULTS

3.1 Preparation of Chitosan-Reduced Graphene Oxide (rGO) Electrodes

Preparation of chitosan/rGO electrodes was carried out in several stages, namely stiring, sonication and fabrication. Chitosan was made with a concentration of 1% using 1% acetic acid solvent, while reduced graphene oxide (rGO) under the Sigma Aldrich brand was dissolved using aquabides and made with several variations of 50, 100, 150, 200 and 250 ppm.

The reduced graphene oxide (rGO) has been added to the chitosan solution for 2 h under stirring at room temperature and sonicated to ensure homogeneous solution for 30 min. Fabrication of reduced chitosan-graphene oxide sensors was carried out using the electrodeposition method. The electrodes are then applied to the electrochemical cell as a working electrode.

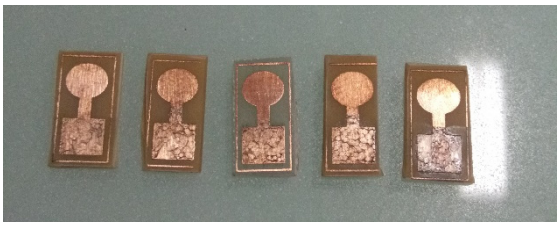

Figure 1: Chitosan/rGO Composite Film.

3.2 Characterization of Graphite and rGO by X-ray Diffraction (XRD)

The composite film structure was further investigated with X-ray diffraction (XRD). The typical peaks of graphite (Fig.2b) observed at 26.53° with a d- spacing 3.3571 Å (Fig.2b). This is in accordance with previous literature (Sandhya et al., 2018). The sharp peak produced by graphite shows high crystallinity. In Fig.1a, the XRD patterns of rGO shows the sharp peak disappeared and move to higher 2θ angles at 26.61° with a d-spacing of 3.347 Å (Ali Umar et al., 2013).

Due to the covalently bound oxygen atoms and the displacement of sp3 hybridized carbon atoms above and below the original graphene film, rGO films are thicker than graphite films (Hassan et al., 2009). It has been confirmed from the XRD patterns that the rGO has been completely reduced.

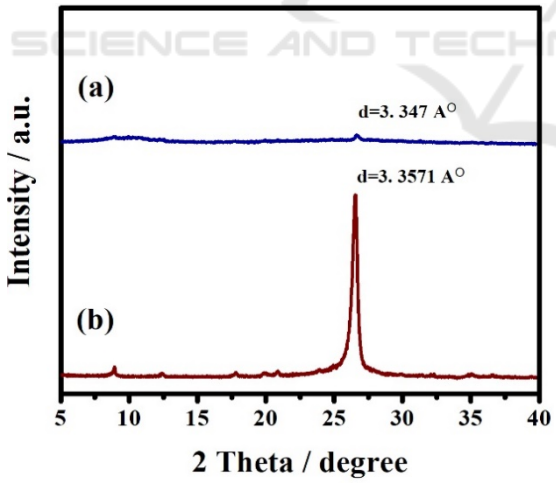

Figure 2: XRD patterns of (a) rGO and (b) graphite.

3.3 Characterization of Chitosan and Chitosan/rGO

Chitosan and rGO can be mixed well and forming a homogeneously aqueous solution, and at room temperature stable. And then, chitosan /rGO was cast into substrates, and the films formed. Fig. 3 described the chitosan and chitosan / rGO FT-IR spectra.

The chitosan spectrum (Fig.3a), the characteristic hydroxyl group of OH peaks appeared at 3410.15 cm^{-1} and the absorption spectrum acquired at 1651.07 cm^{-1} and 1558.48 cm^{-1} correspond to stretching vibration of carboxylic group C=O of -NHCO- and the N-H bending vibration of $–NH_2$ group (Yang, 2010). Characteristic of CH_3 and C-H functional groups are the bands at 1411.89 cm^{-1} and 2877.79 cm^{-1}. And chitosan/rGO film, its spectrum shows a combination of characteristics which includes the absorption peak at 3441.01 cm^{-1} (Fig.3b), assigned to extend NH_2 (amine) vibration group.

In the FT-IR peak of chitosan/rGO, The C-O stretching chitosan intensity vibration is found to have faded due to the interaction of chitosan and rGO. Meanwhile, the intensities of C=C stretching vibration peak at 1558.48 cm^{-1} and the presence of chitosan-derived N-H bonding. Deformation peak of N-H from chitosan at 1411.89 cm^{-1}. All these result confirm that rGO presence on the chitosan polymer matrix. And in the composite films, the chemical structure of chitosan barely changes with the increasing content of rGO, indicating that there was primarily physical interaction but scarcely a chemical reaction between chitosan and rGO.

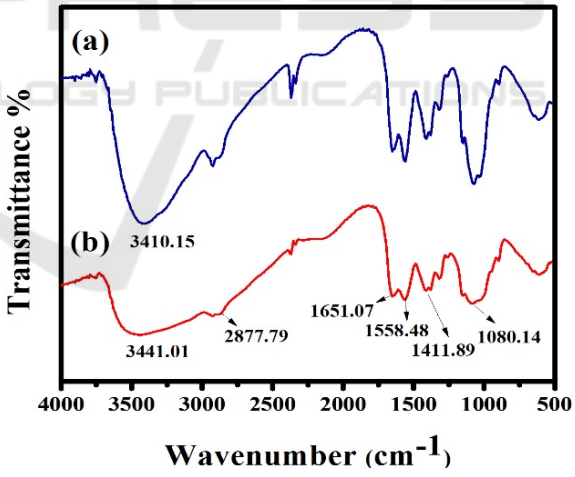

Figure 3: FT-IR spectra of (a) chitosan and (b) chitosan/rGO.

4 CONCLUSION

Fabrication of the chitosan-reduced graphene oxide (rGO) in screen-printed copper electrode modified was successfully by electrodeposition method and was used for electrochemical sensor. The characterizations of XRD confirmed the successful

formation of rGO. Furthermore, the spectra of FT-IR also indicated rGO presence on the chitosan polymer matrix composite film.

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