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Preparation and Characterization of Chitosan/Reduced Graphene Oxide Film as a Sensing Material

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ABSTRACT

Sensing materials are crucial in a wide range of fields, including environmental monitoring, healthcare, security, and industrial applications. By leveraging their specific properties, sensing materials enable the development of innovative sensing devices and systems for improved detection, monitoring, and control of various parameters in our environment. This study aimed to prepare the chitosan/reduced graphene oxide film as sensing materials using a simple casting method. The reduced graphene oxide (rGO) was mixed with chitosan (CS), consisting of a concentration ratio of 200, 250, 300, 350, and 400 ppm. Three characterizations were used to describe the formed CS/rGO films, namely, Fourier transform infrared (FTIR), X-ray diffraction (XRD), and cyclic voltammetry (CV). FTIR and XRD analysis results were successfully performed, which showed that the process of loading of rGO and the film fabrication occurred in the physical interaction. The CV test also showed that the CS/rGO modified electrode has high sensitivity in PBH pH 7 and can be applied as a sensing material.

Keywords: Chitosan, reduced Graphene Oxide, Sensing Material, Shrimp Shell

ABSTRAK

Material penginderaan sangat penting dalam berbagai bidang, termasuk pemantauan lingkungan, perawatan kesehatan, keamanan, dan aplikasi industri. Dengan memanfaatkan sifat spesifiknya, bahan penginderaan memungkinkan pengembangan perangkat dan sistem penginderaan inovatif untuk deteksi, pemantauan, dan kontrol yang lebih baik dari berbagai parameter di lingkungan kita. Tujuan dari penelitian ini adalah untuk menyiapkan film kitosan/grafena oksida tereduksi sebagai bahan penginderaan menggunakan metode simple casting. Grafena oksida tereduksi (rGO) dicampur dengan kitosan (CS) terdiri dari rasio konsentrasi pada 200, 250, 300, 350, dan 400 ppm. Tiga karakterisasi yang digunakan untuk menunjukkan terbentuknya film CS/rGO adalah Fourier Transform-Infrared (FTIR), X-Ray Diffraction (XRD), dan Cyclic Voltammetry (CV). Hasil analisis FTIR dan XRD menunjukkan bahwa proses pemuatan rGO dan pembuatan film berhasil dilakukan dan hanya terjadi interaksi fisik. Uji CV juga menunjukkan bahwa elektroda termodifikasi CS/rGO memiliki sensitivitas tinggi pada PBH pH 7 dan dapat diaplikasikan sebagai material penginderaan.

Kata Kunci: Kitosan, Grafena Oksida Tereduksi, Kitosan, Material Penginderaan, Kulit Udang

1. Introduction

Sensing materials, also known as smart materials or intelligent materials, are substances that can detect and respond to changes in their environment [1]. These materials have the ability to sense various physical, chemical, or biological stimuli and convert them into measurable signals or responses [2]. The development and utilization of sensing materials have contributed to advancements in various fields, including electronics, healthcare, aerospace, agriculture, and environmental monitoring. These materials are essential for developing smart systems that can perceive and react to their environment more intelligently and adaptively [3]. One of the materials that can be applied as a sensing material is chitosan [4].

Chitosan (CS) is a biopolymer derived from chitin, primarily found in shrimps, crabs, and lobsters [5]. Shrimp shell (SS) is a type of waste generated from the shrimp processing industry or when we cook shrimp at home. Shrimp shell waste (SSW) contains fiber and chitin, which can be a source of organic matter that has the potential to be utilized [6]. SSW is usually only used as animal feed and organic fertilizer [7]. However, SSW must be utilized with regard to the proper processing process to safely and efficiently use the waste. In addition, it is also necessary to consider environmental and sanitation aspects in SSW processing to avoid negative impacts on the surrounding environment [8]. Therefore, further research is needed to explore its potential use in various industries to create added value from existing resources.

SS contains protein (20-40%), calcium carbonate (20-50%), chitin (15-40%), and lipids (0-14%) [9]. Chitin (Ch) is chemically a polymer of β-(1,4)-2-acetamide-2-dioxy-D-glucose, which mammals cannot digest. Ch is insoluble in water, so its use is limited. However, hydrolyzed chitin using strong bases (deacetylation process) to CS β-(1,4)-2-amino-2-dioxy-D-glucose will have better chemistry [10]. CS has gained significant attention in various fields due to its versatile properties, including its potential as a preservative, cosmetics, water treatments to remove heavy metals, gauze, and a sensing material [11]. CS possesses several characteristics that make it suitable for sensing applications [12]. CS has functional groups such as hydroxyl groups (OH) and amine groups (NH_2), which are important groups in reacting with other analytes [13]. Besides that, CS possesses several characteristics that make it suitable for sensing applications, i.e., biocompatibility, film-forming ability, and chemical modifications [14]. Overall, CS is a promising sensing material for various applications due to its special qualities and adaptability. Its potential is still being explored, and work is being done to improve its performance across different sensing systems. However, CS has weaknesses in terms of weak mechanical strength, excessive swelling, unstable, and low electrical conductivity [4], so other materials need to be added to improve these properties in sensing material. One of the materials that can be added is reduced graphene oxide.

Due to its unique properties, reduced graphene oxide (rGO) or graphene is a highly prospective material for sensing applications. The rGO has several characteristics that make it suitable for sensing applications. It has a large surface area, outstanding electrical conductance, strong chemical durability, fast response time, selectivity, and versatility [15]. These properties make rGO a versatile and attractive material for various sensing applications, including environmental monitoring, healthcare diagnostics, gas sensing, and biosensing [16]. Ongoing research and development in this field continue to explore and optimize the potential of rGO-based sensors for practical applications.

Therefore, incorporating the three materials is expected to combine each component's advantages and positively impact its implementation as a sensing material. It is necessary to create sensing material from CS/rGO film. The formed film was characterized, and its potential as a sensing material was studied using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Cyclic Voltammetry (CV).

2. Method

The materials used in this study include chitosan (CS) with a deacetylation degree of 87.5%, glacial acetic acid (CH_3COOH), reduced graphene oxide (rGO), Phosphate Buffer Solution (PBS), and distilled water purchased from Merck (Darmstadt, Germany). The first step in this study was to prepare the CS/rGO film. The preparation of CS/rGO was carried out by a simple casting method. As much as 50 mL of chitosan solution and 50 mL of rGO solution were placed into 250 mL of a beaker glass, stirred for 3 hours, and sonicated at room temperature. After that, the mix was poured into the mold until a CS/rGO film was formed [17]. Each sample was marked as indicated in Table 1.

Table 1. Name and variation of treatments for each sample.

Sample	CS with rGO concentration ratio (ppm)
A	200
B	250
C	300
D	350
E	400

Fourier-Transform Infrared Spectroscopy (FTIR) was performed for CS/rGO films. The FTIR testing showed how the functional groups of the CS/rGO film interacted with infrared to show vibrations in the form of bands and provided information on the composition of the bonds that occurred to the carbon unit atoms in the film. The FTIR analysis was carried out using Agilent Technologies Alpha at room temperature. The functional group of the CS/rGO film was identified using an FTIR spectrophotometer at a wavenumber range of 450 to 4000 cm^{-1}. The identified functional groups were compared with the absorption peaks in the literature.

The X-Ray diffraction (XRD) analysis was used to determine the crystalline structure of the loading process of rGO to CS film using the Shimadzu XRD-6100 diffractometer. The Cu-Kα radiation used was λ=0.154 nm to observe the sample diffraction pattern from 2θ of 5° to 30° with a scan speed of 2 min^{-1} with a voltage of 40 kV and a current of 200 mA**.**

The electrochemical properties of reduced chitosan-graphene oxide-based electrodes were tested using cyclic voltammetry (CV). This measurement uses an Edaq potentiostat consisting of three electrodes: the working electrode, the reference electron, and the counter electrode. The chitosan-rGO composite, on top of the platinum substrate, acts as the working electrode, the calomel electrode as the reference electrode, and the platinum electrode as the supporting electrode. The sensitivity of CS/rGO film on a platinum substrate in Phosphate Buffer Solution (PBS) as electrolyte solution using an Ossila. Also, the potential rate used was -600 mV/s to +600 mV/s.

3. Results and Discussion

3.1. Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

The results of the FTIR study demonstrated in Figure 1 indicate that the five characteristic bands frequently observed in natural CS were the band at 3200-3600 cm^{-1}, which suggested the existence of OH groups, the band at 3100-3500 cm^{-1}, which displayed NH_2 bonds, the band at 1600-1700 cm^{-1}, which provided C=O bonds, the band at 1500-1600 cm^{-1}, which suggested N-H bonds, and the band at 1300-1400 cm^{-1}, that specified C-N bonds [18]. As seen in line b in Figure 1, these five bands were also observed in the CS/rGO film spectrum, as shown in line b, but in slightly different peak intensities. All the bands' intensities appeared to be smaller in the CS/rGO film. In the CS/rGO film, the intensity of all the bands observed was lower. In addition, the band at 1401.5 cm^{-1} showed C=C bond of CS/rGO film, which indicated the presence of rGO. This is due to the interaction of rGO as a filler to the CS polymer matrix. Furthermore, the chemical structure of CS in the composite film hardly changed with increasing amounts of rGO, so these results indicated a physical interaction, but this rarely occurs in terms of chemical reactions between CS and rGO.

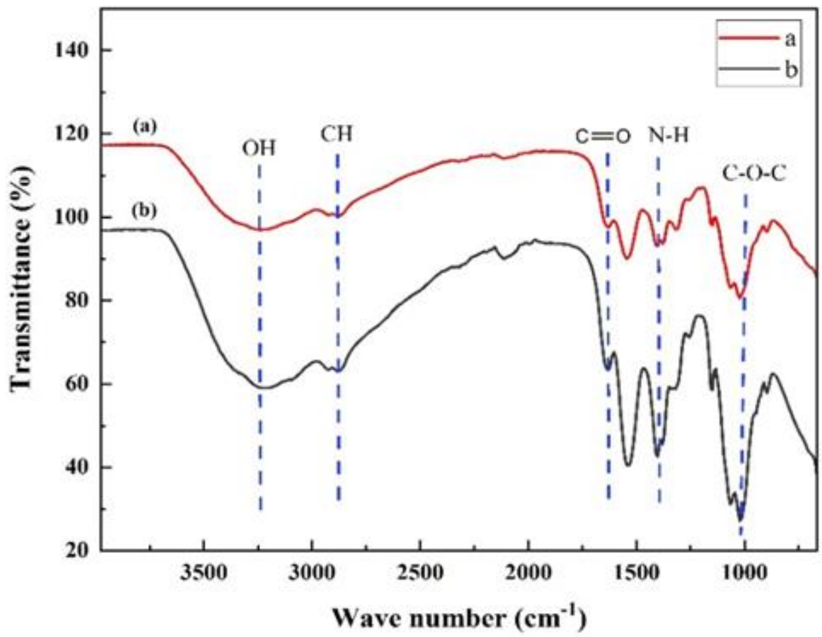

Figure 1. FTIR spectra of CS and CS/rGO film-based electrode.

3.2. X-Ray diffraction (XRD) analysis

According to the XRD pattern shown in Figure 2, the CS/rGO film diffraction pattern produced four peaks at 9.8°, 18.59°, 22.57°, and 37.14° with a d-spacing of 9.9 Å. The resulting peaks indicate a physical interaction between CS and rGO due to a shift of the peak at the 2θ position of rGO and a shift of the peak at the 2θ position of CS. In addition, the thickness of the film determines the d-spacing of the CS/rGO films: the thicker the film, the larger the d-spacing. Conversely, the thinner the sample layer, the smaller the d-spacing value [19]. This can also be seen from the study reported by [17], who reported that the rGO interlayer distance decreased from 3.3571 Å for graphite to 3.347 Å for rGO due to the very thin rGO [17] layer due to the high degree of exfoliation layer.

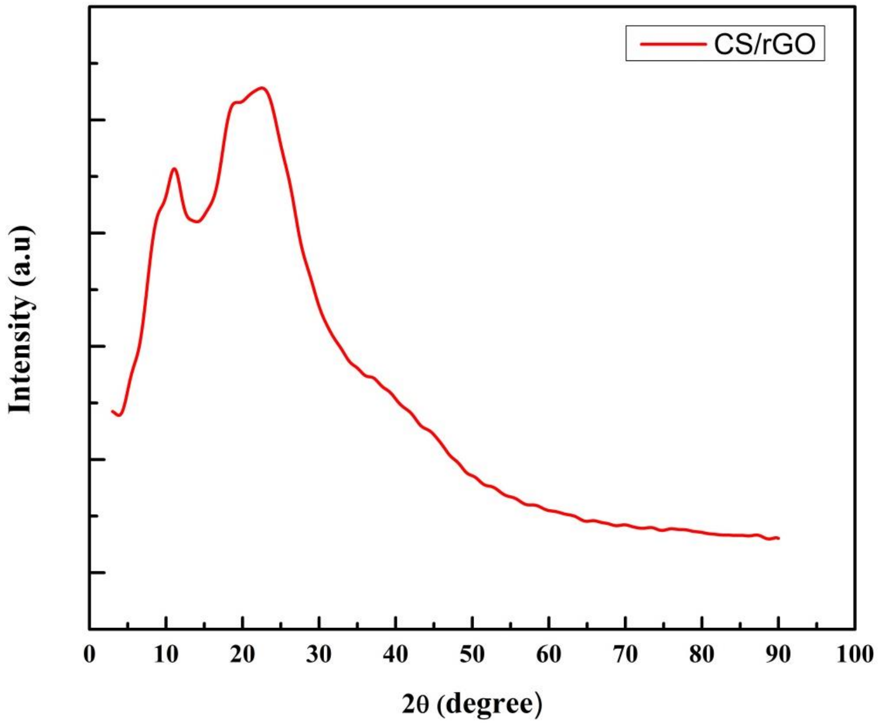

Figure 2. X-Ray diffraction pattern of CS/rGO.

3.3. Cyclic Voltammetry (CV) analysis

The sensitivity assessment of the CS/rGO film was executed using cyclic voltammetry (CV). The most favorable point of reduction current was observed in PBS with a pH of 7, achieved with CS/rGO modified electrodes containing rGO at a concentration of 250 ppm, as depicted in Figure 3(a). Consequently, this electrode was utilized as the active electrode to determine the optimal scan rate. Subsequently, a series of scan rate tests were performed at (25, 50, 75, and 100) mV/s. The outcomes of the scan rate experimentation indicated that the ideal scan rate was 75 mV/s (Figure 3(b)).

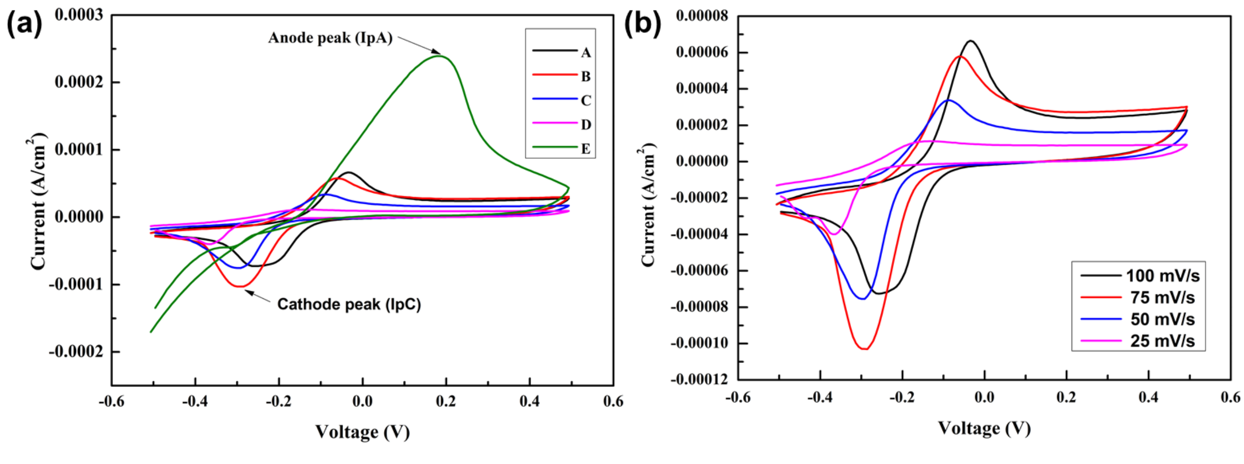

Figure 3. Voltammogram of (a) CS/rGO modified electrode with variation of rGO at scan rate 75 mV/s and (b) Scan rate variation of CS/rGO modified electrode with concentration rGO at 250 ppm.

Conversely, the linearity assessment (Figure (4)) was carried out by analyzing the reduction current peaks, resulting in a linear equation of y = 0.000753x-0.022788, with a determination coefficient (R^2) of 0.99998. This outcome underscores the substantial sensitivity of the CS/rGO-modified platinum electrode when employed as a sensing material [20].

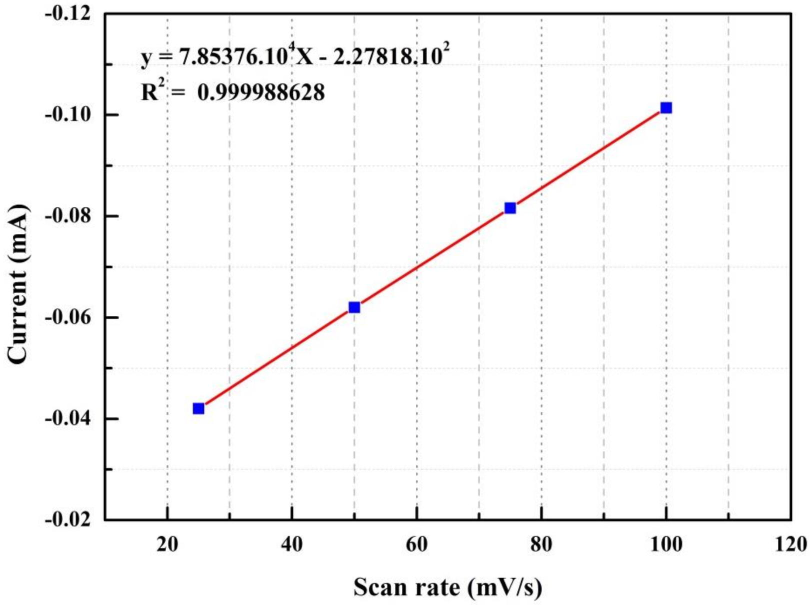

Figure 4. Regression line of CS/rGO.

4. Conclusion

In conclusion, CS/rGO films were successfully prepared. The characterization results from FTIR, XRD, and CV show that CS/rGO films can potentially be applied as the sensing material. In this study, sensitivity testing showed that the CS/rGO modified electrode with an rGO concentration of 250 ppm was the optimal electrode to be applied as a sensing material.

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