산화타이타늄-셀룰로오스 복합재 제조 및 바이오센서 응용 TiO₂-celluose nanocomposites: Fabrication and bio-sensor application

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1. Introduction

Inorganic-organic nanocomposite materials form an attractive new class of functional hybrid material demonstrating improved optical, thermal and mechanical properties due to synergistic results developed from the physical or chemical interactions between the inorganic and organic materials [1]. These hybrid materials offer the advantages of flexibility, light-weight, low cost and low impact resistance and have wide applications such as sensors, solar cells, displays, etc.

Titanium dioxide (TiO₂) is a wide band gap semiconductor which has recently attracted enormous interests due to its wide range of chemical and physical properties including chemical stability, electrical conductivity, photocatalytic activity, and photosensitivity [2]. It is applicable in solar cell, photocatalysis, photoelectrochemical cell, chemical sensor, and electronic device [3]. In this study, flexible and biodegradable TiO₂-Cellulose hybrid nanocomposite (TCHN) was fabricated and applied to a glucose sensor.

2. Experimental

Cellulose solution was first prepared by cotton pulp (MVE, DPW 7450) dissolving in LiCl/DMAc solvent at 155 °C with mechanical stirring followed by solvent exchange technique [4]. Then, TiO₂ nanoparticle was mixed with 15 mL of DMAc and sonicated in an ultrasonic bath for 1 h to get a homogeneous mixture. These stock solutions with various weight ratios of TiO₂ were added to 50 g of

1.5 wt% cellulose solution. The mixture was mechanically stirred for 2 h. The obtained mixture was spin coated onto a glass substrate and cured with isopropyl alcohol and DI water to get TiO2-cellulose films. Glucose oxidase (GO_x) was immobilized into TCHN by physical adsorption method. Firstly, GOx solution was prepared by dissolving 0.025 g of GOx (EC 232-601-0, type X-S: Aspergillus niger, 155000 units/g, Sigma-Aldrich) per 10 ml of 0.1M phosphate buffer solution (pH 7.2). Secondly, TCHN samples were immersed into pH buffer and GOx solution for 16 h, at room temperature. To measure electrical property, a cell was constructed which consists of gold wire (ϕ 0.3 mm, 5 cm length) as one electrode and GOx immobilized TCHN as another electrode. Glucose (99.5%, EC 200-075-1 from Sigma Life Science) solution prepared in DI water with varying concentration (1~20 mM) was used as an electrolyte. The slope of current vs. potential (I-V) curve was used as a measure of enzyme activity.

3. Results and Discussion

Figure 1 shows SEM images of TCHN with 30 wt% of TiO₂.



Fig.1. SEM (a) surface and (b) cross sectional images of TCHN with 30 wt% TiO

Cross sectional and surface morphology display well dispersed TiO_2 nanoparticles into cellulose film. Larger portion of bright nanoparticles were displayed with increasing TiO_2 concentration.



Fig.2. I-V characteristics showing effect of wt% of TiO_2 on enzyme activity of TCHN glucose sensor at 6 mM

To study the effect of wt% of TiO₂ on sensitivity of TCHN glucose sensor, the I-V characteristics of samples were measured at 6 mM glucose solution and shown in fig. 2. It is observed that current level increased up to 12.45 μ A with increasing wt% of TiO₂ into cellulose at 3V applied potential. This can be attributed to increase crystalline of TiO₂ blended to the cellulose surface.



Fig. 3. Sensitivity of glucose biosensor as a function of glucose concentration for 30 wt% TiO_2

To determine the detection range of proposed sensor, calibration curve was plotted by drawing sensitivity as a function of glucose concentration and shown in fig. 3. The linear response obtained in this study was in the range of $1 \sim 10$ mM which covers clinical range of $3.5 \sim 6.5$ mM glucose.

The detection mechanism of this proposed biosensor is believed to be the fact that GOx-glucose reaction results in releasing trapped electrons to the conduction band of TiO_2 which in turn increases the

conductivity of the biosensor [5].

4. Conclusion

A feasibility study is carried out employing TiO₂cellulose hybrid materials. GOx was found attached with TiO₂. Current level of this conductometric biosensor enhanced with increasing weight ratio of TiO₂ into cellulose. Sensors were found highly sensitive at lower concentration (\leq 10 mM). The improved sensitivity and linear response is obtained by tailoring the material properties like surface area, structure and conductance of the film.

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