DEVELOPMENT OF A NON-ENZYMATIC BIOSENSOR BASED ON ZnO/Pd NANOPARTICLES FOR GLUCOSE DETECTION

PHÁT TRIỂN CẢM BIẾN SINH HỌC KHÔNG ENZYME TRÊN CƠ SỞ VẬT LIỆU HẠT NANO ZnO/Pd NHẰM PHÁT HIỆN NỒNG ĐỘ GLUCOSE

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DOI: http://doi.org/10.57001/huih5804.2025.184

ABSTRACT

In this study, a ZnO/Pd nanocomposite material was synthesized via a hydrothermal method for application in non-enzymatic glucose biosensors. The morphology and crystalline structure of the synthesized material were characterized using field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy (EDS). The resulting ZnO/Pd nanocomposite was subsequently employed in the fabrication of a non-enzymatic glucose biosensor, which exhibited a high sensitivity of 1.8μA·mM^{-1} and a detection limit of 1.0mM. These results highlight the promising potential of ZnO/Pd nanocomposites in the development of non-enzymatic glucose sensors in particular, and biosensors in general.

Keywords**:** *Biosensor; nanocomposite; electrochemical sensor; ZnO/Pd; non-enzymatic.*

TÓM TẮT

Trong nghiên cứu này, hạt nanocomposite ZnO/Pd đã được tổng hợp bằng phương pháp thuỷ nhiệt nhằm ứng dụng cho cảm biến sinh học glucose không enzyme. Hình thái bề mặt và cấu trúc vật liệu đã được đặc trưng bằng kính hiển vi điện tử quét phát xạ trường, phổ nhiễu xạ tia X, phổ tán sắc năng lượng tia X. Vật liệu sau khi được tổng hợp đã được ứng dụng cho chế tạo cảm biến glucose không sử dụng enzyme với độ nhạy là 1,8μA.mM^{-1}, giới hạn phát hiện là 1,0mM. Những kết quả đạt được đã chỉ ra tiềm năng ứng dụng của hạt nanocomposite ZnO/Pd trong việc phát triển cảm biến sinh học glucose không enzyme nói riêng và các cảm biến sinh học nói chung.

Từ khóa: *Cảm biến sinh học, glucose, nanocomposite, cảm biến điện hoá, ZnO/Pd, không enzyme.*

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Received: 23/02/2025
Revised: 20/5/2025
Accepted: 28/5/2025

1. INTRODUCTION

Acurate glucose detection plays a crucial role in biotechnology, clinical diagnostics and the food industry [1-3]. Although the traditional enzymatic glucose sensors exhibit high selectivity, they are still constrained by several limitations. To be more specific, enzymes are not only high cost but also highly sensitive to changes by environmental factors such as temperature, pH, humidity, and so on [4, 5]. To overcome these limitations, non-enzymatic glucose sensors have emerged as a viable alternative to the enzymatic glucose sensors [5] due to their high sensitivity and the ease of fabricating and integrating them into detection devices [6, 7].

Among metal oxide materials, Zinc oxide (ZnO) has attracted significant attention from researchers for biosensors application due to its high surface area, excellent electrical conductivity, non- toxicity [8], combined with its high isoelectric point (IEP ~9.5) [9, 10], cost- effective and outstanding chemical stability. A key advantage is that high-IEP material enhance adsorption bio-receptor such as DNA, proteins and enzymes through interactions, opens up numerous new opportunities for biological applications. Therefore, ZnO-based biosensor have been studied and widely applied in the detection of numerous substances, including glucose [11], cholesterol [12], and even in cancer cell diagnostics**.**

However, ZnO - based biosensor has been applied for the different fields, but their performance remains low. Thus, a several research groups have used a noble metal such as gold (Au), platinum (Pt) [12], silver (Ag) [13], palladium [14] combined with ZnO to enhance sensor's performance. Among these, Pd exhibits good

electrochemical catalytic activity, high biocompatibility. For example, the research group of Qingshan et al [11] have been studied electrochemical based on Pd doped ZnO nanorods (NRs) for glucose detection. They pointed out that the sensor exhibits a low detection limit (0.3 μM) and high sensitivity (0.64μA/μMcm^2).

In this study, we successfully fabricated a non-enzymatic glucose sensor based on ZnO/Pd nanoparticles. The nanomaterials were synthesized via hydrothermal method and subsequently characterized using field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS) and X-Ray diffraction (XRD). Afterward, the ZnO/Pd nanomaterials were drop-coated onto the working area of the glassy carbon electrode (GCEs) to fabricate the sensing electrodes. Electrochemical characterization was examined using cyclic voltammetry (CV) and chronoamperometry (CA). The obtained results demonstrated the potential of the ZnO/Pd nanocomposite in the development of the non-enzymatic glucose sensors.

2. MATERIALS AND METHODS

2.1. ZnO/Pd synthesis

ZnO/Pd nanoparticles were synthesized via a simple hydrothermal method using Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), sodium hydroxide (NaOH) and palladium chloride ($PdCl_2$) as precursors. Initially, 0.087g of $Zn(CH_3COO)_2{\cdot}2H_2O$ and 0.5g of NaOH were dissolved in 100ml of deionized water and stirred to ensure homogeneity. After that, the mixture was magnetically stirred for 30 minutes. Subsequently, 2.5ml of 0.0014M $PdCl_2$ aqueous solution prepared with a small amount of HCl to aid solubility, was added dropwise to the precursor solution. The final mixture was then transferred into a Teflon-lined stainless-steel autoclave and heated at 180°C for 4 hours. After the reaction, the autoclave was allowed to cool naturally to room temperature under ambient conditions. The resulting gray-colored precipitate was collected by filtration, washed thoroughly with deionized water and absolute ethanol, and then dried at 80°C for 12 hours.

2.2. Methodology

Field-emission scanning electron microscopy was used to examine the surface morphology of ZnO/Pd. The crystalline structure was evaluated though an X-Ray diffraction with Cu-Kα radiation (= 1.5418Å). The elemental composition and purity of ZnO/Pd was investigated by utilizing an energy dispersive X-ray spectroscopy. To investigate the electrochemical properties of the non-enzymatic glucose sensor, cyclic voltammetry (CV) measurements were conducted in 0.1M NaOH solution within a potential range of -0.8V to 1V at a scan rate of 100mV/s.

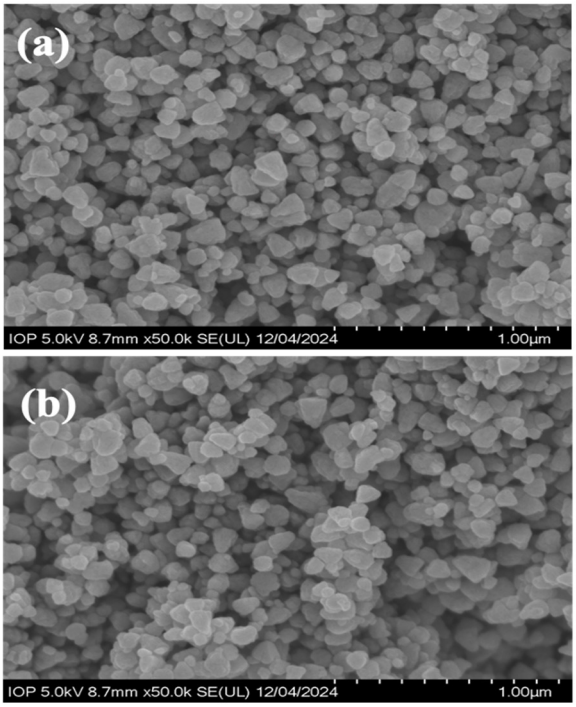
2.3. Preparation of the modified electrodes

The preparation of a glassy carbon electrodes (GCE) was carried out as follows: the GCEs were first cleaned in a hydrogen peroxide solution at 70 °C for 15 minutes and then thoroughly rinsed with deionized water. Next, the GCEs were purified using cyclic voltammetry (CV) method in 0.05M H_2SO_4 solutions, with a potential range of -1 to 2V and a scan rate of 50mV/s at room temperature for 7 minutes. Following purification, 2mg ZnO/Pd was dispersed in 1ml of acetone and ultrasonic treated for 2 hours at room temperature. The resulting suspension was then drop-cast onto the surface of the GCE and allowed to dry naturally at room temperature.

3. RESULTS AND DISCUSSION

3.1. Characterization of ZnO/Pd NPs

As shown in Figure 1 (a), the FE-SEM image of ZnO nanomaterial exhibits a nanoparticle structure with the average particle size ranging of 50 nm to 100nm. Figure 1 (b) presents the FE-SEM image of ZnO/Pd nanocomposite material. It can be observed that the particles size distribution and morphology closely resemble those of pure ZnO. However, in this case, the presence of Pd is not clearly visualized due to the low Pd concentration.



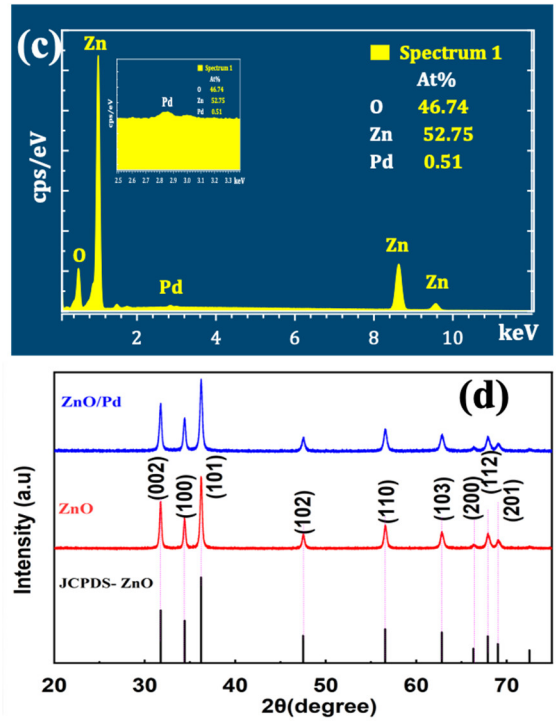


Figure 1. FE-SEM images of (a) ZnO, (b) ZnO/Pd nanoparticles, (c) EDS spectra and (d) XRD pattern of ZnO/Pd nanoparticles

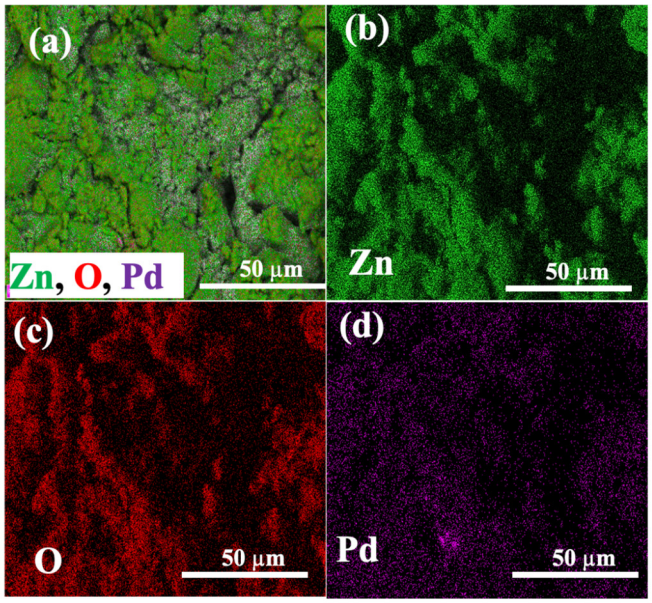


Figure 2. EDX mapping images of (a) ZnO/Pd, (b) Zn, (c) O, (d) Pd

In this work, energy dispersive X-Ray spectroscopy (EDX) was used to examine the elemental composition of ZnO/Pd sample. As indicated in Figure 1 (c), the presence of Zn, O, and Pd peaks confirms the successful synthesis of the ZnO/Pd nanoparticles.

To investigate the crystalline phases of the analytical sample, XRD measurement was carried out, as shown in Figure 1 (d). As observed in figure, the diffraction peaks at 2θ = 31.744°, 34.402°, 36.228°, 47.507°, 56.550°, 62.815°, 66.321°, 67.985°, and 69.020° correspond to the crystal planes (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively. These diffraction patterns are consistent with the hexagonal wurtzite ZnO structure (JCPDS No: 36-1451).

To further analyze the spatial elemental distribution, EDX mapping was used, as shown in Figure 2 (a-d). It can be seen that elements are homogeneously distributed in the experimental sample. This suggests that Pd is uniformly distributed over the surface of the ZnO nanoparticles.

3.2. Cyclic voltammetry

In this work, cyclic voltammetry was used to determine none-enzyme glucose sensor characterization in a NaOH solution 0.1M with and without the presence 2.5mM of glucose, scan rate of 100 mV/s within the potential range of -0.5V to + 0.7V. As shown in Figure 3 (a), the current response of bare GCEs in NaOH solution with and without the presence of glucose, remained unchanged due to the lack of catalytic activity in the glucose oxidation reaction.

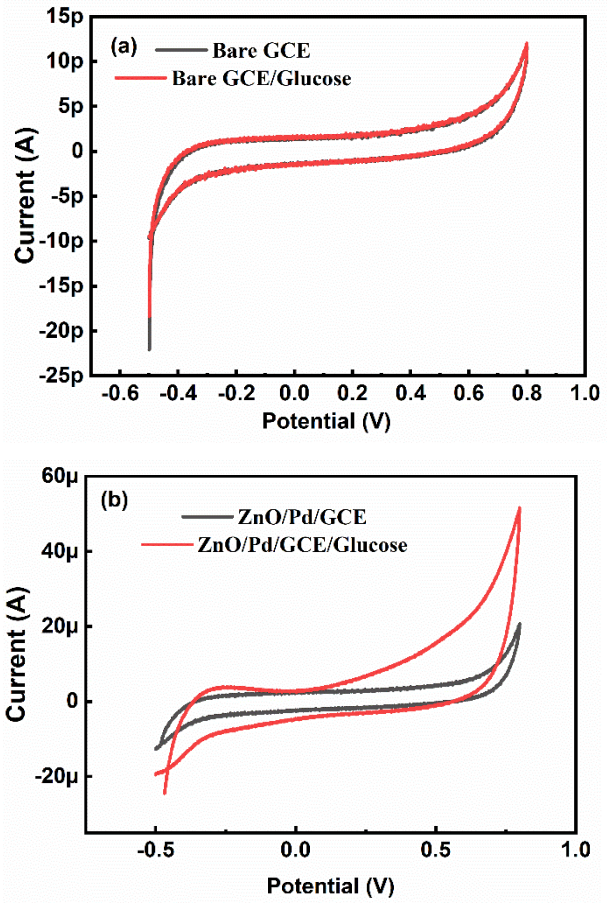


Figure 3. Cyclic voltammograms of (a) bare GCE and (b) ZnO/Pd/GCE recorded in 0.1M NaOH with and without 2.5mM glucose at 100mV/s

In the case of ZnO/Pd/GCE, the redox peaks are observed within this potential range in absence of glucose. The current response of ZnO/Pd/GCE are enhanced when 2.5mM glucose concentration is added, thanks to ZnO/Pd catalyzing the glucose oxidation process, and improving electron transfer capability (Figure 3 (b)).

The CV response of the ZnO/Pd/GCEs was examined in 0.1M NaOH solution with the presence of difference glucose concentration (1.0mM, 1.5mM, 2.0mM, 2.5mM), at scan rate of 100mV/s. As observed in Figure 4 (a), the current density gradually increases when the concentration of glucose increases from 1.0mM to 2.5mM.

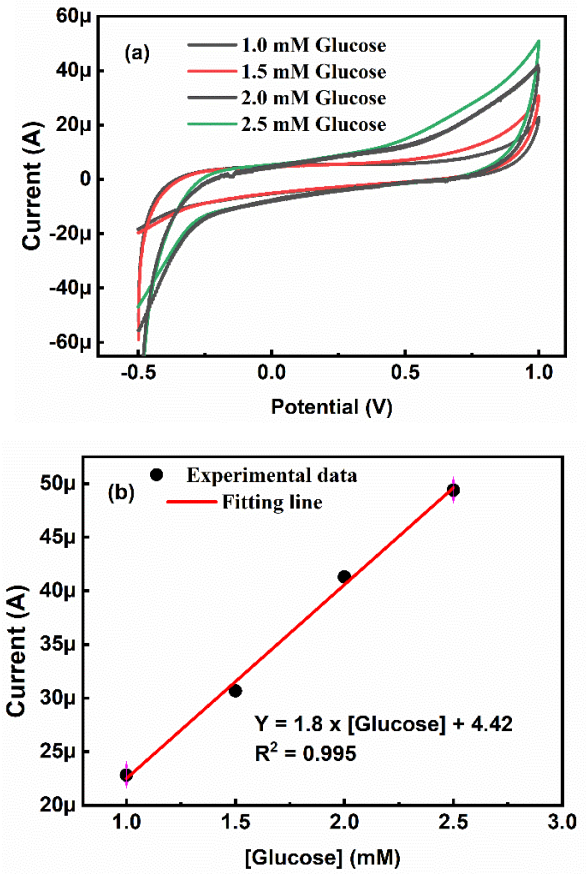


Figure 4. (a) Cyclic voltammogram of non-enzymatic glucose sensor with different glucose concentrations from 1mM to 2.5mM at scan rate of 100mV/s, (b) calibration curve of the non-enzymatic glucose sensor

Figure 4 (b) indicates the linear relationship between glucose concentration and current response. The sensor output signal increase linearly as the glucose concentration increases from 1.0 to 2.5mM.

The linear relationship between the current response and the glucose concentration is described by the following equation:

$$Y = 1.8 \times [Glucose] + 4.42$$

Where, Y is the current intensity measured in μA, and glucose concentration is expressed in μM.

In this case, the sensitivity of sensor was found to be 1.8μA.mM^{-1}, with a correlation coefficient (R) of 0.995.

In this work, chronoamperometry (CA) measurement was also carried out in 0.1M NaOH with a different glucose concentration (1.0 - 2.5mM) at a fixed potential of 0.4V for 100s, as shown in Figure 5.

As can be observed from the Figure 5 (a, and b), the chronoamperometric response increased with increase in glucose concentration from 1 to 2.5mM. The response time is less than 5s, indicating the rapid response of the glucose sensor.

The linear current response of ZnO/Pd/GCE increases 1 to 2.5mM with the sensitivity of 0.81μA.mM^{-1} and the obtained correlation coefficient of 0.996.

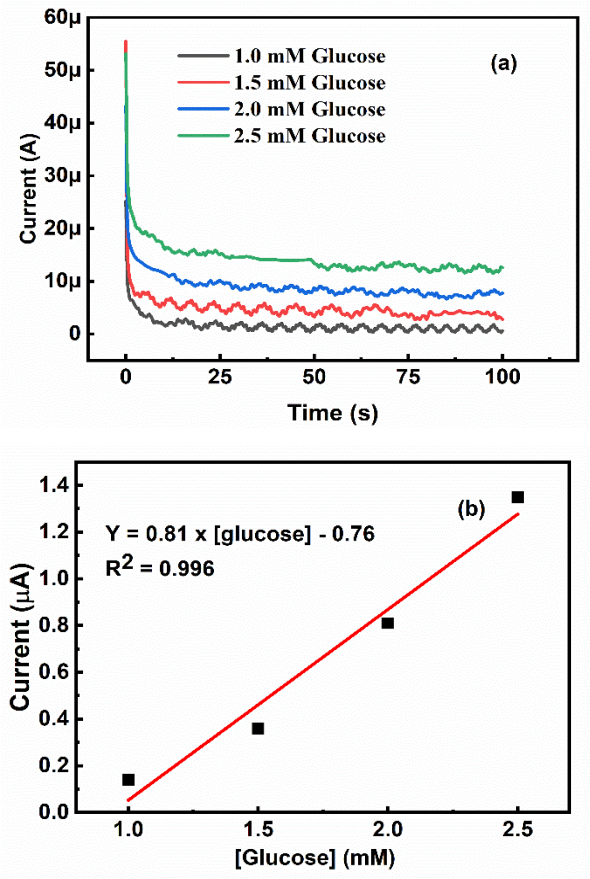


Figure 5. (a) chronoamperometric (CA) response of non-enzymatic glucose sensor in 0.1M NaOH with different glucose concentrations (1 - 2.5mM) at 0.4V for 100s, (b) calibration curve of the non-enzymatic glucose sensor

4. CONCLUSIONS

In summary, the ZnO/Pd nanoparticles were successfully synthesized via a hydrothermal method for

non-enzyme glucose sensor application. The characteristic of ZnO/Pd nanomaterial were examined by FE-SEM, XRD and EDS. The developed non-enzyme glucose sensor based on ZnO/Pd exhibited high sensivity ($1.8\mu A.mM^{-1}$) and a limit of detection as low as 1mM. The obtained results demonstate potential of ZnO/Pd nanoparticles in the development of non-enzymatic glucose biosensor for both biomedical and environmental applications.

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THÔNG TIN TÁC GIẢ

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