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Screen-Printed Carbon Electrode Modified GNPs/ZnO for Electrochemical Sensing

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Abstract

Screen-printed carbon electrodes (SPCEs) modified with graphene nanoplatelets (GNPs) and zinc oxide (ZnO) are widely used in electrochemical sensors due to their enhanced electrochemical properties and biocompatibility. Screen-printed carbon electrodes modified with Graphene nanoplatelets (GNPs) /Zinc oxide (ZnO) nanocomposite are described. Thus, in this study, GNPs/ZnO nanocomposite was synthesized, characterized, and applied to an electrochemical sensor. The formation of GNPs/ZnO nanocomposite was characterized by UV-Vis spectroscopy and scanning electron microscopy. Moreover, SPCE-GNPs/ZnO nanocomposite were characterized using cyclic voltammetry to optimize the concentration of nanocomposite. Then, the analytical performance of the sensor was studied by measuring methylparaben as an organic compound using differential pulse voltammetry (DPV) as a preliminary study before using it for biosensing. The result showed a significant improvement in electrocatalytic activity and reproducibility. The ratio of GNPs/ZnO nanocomposite with a concentration of 1 mg/mL produced the highest current response. Moreover, the detection of methylparaben showed high sensitivity with a limit of detection (LOD) around 9.7 µM, indicating high selectivity and good reproducibility of SPCE-GNPs/ZnO. Hence, the proposed sensor of SPCE-GNPs/ZnO displayed good performance, sensitivity, and reproducibility.

Keywords: SPCE, GNPs/ZnO nanocomposite, electrochemical

I. INTRODUCTION

Screen printing technology is an electrode printing technology that uses materials such as carbon, metals, and nanomaterials on several substrates, including paper, plastic, and ceramics [1]. Screen printing can be fabricated in large quantities based on carbon electrodes that are reproducible, low-cost, and disposable. Recently, screen-printed carbon electrodes have been used in various electrochemical fields. The most applications are in chemical and biochemical sensors, energy conversion and storage, and microelectronics [2], [3].

SPCE performance can be improved by chemical modification—the purpose of modification is to increase the electron transfer rate and electrode selectivity. The modifier selection significantly affects the performance of the electrode. One of the modifiers that can be used to improve the electron transfer rate on SPCE is graphene/ZnO nanoparticles [4], [5]. Graphene Nanoplatelets (GNPs) are stacks of multiple graphene layers with some lateral dimensions in the nanoscale. Adding GNPs to SPCEs enhances the electrode's electrocatalytic properties, increases the surface area, and improves electron transfer kinetics.

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GNPs can also immobilize biomolecules like enzymes or antibodies, essential for biosensing applications. In the application, graphene tends to re-stacking due to strong van der Waals and phi-bond interaction. Re-stacking can cause graphene to lose most of its surface area. It is necessary to incorporate metal or metal oxide into graphene layers to prevent re-stacking [6].

In nanotechnology, metal oxide nanostructures are the greatest nanostructures among other nanomaterials because they have a large surface area, low toxicity, are environmentally friendly, have good chemical stability, and are biocompatible. ZnO is a metal oxide with semiconductor properties, a wide bandgap of 3.37 eV, and excitation binding energy of 60 meV [7]. In addition, ZnO is non-toxic, with high surface area and electron transfer. ZnO is a transducer material that converts biochemical reactions into measurable electrical signals. It can enhance the specificity and sensitivity of the biosensor due to its unique electrical properties and ability to bind with specific biomolecules. Therefore, ZnO is widely used in various fields, such as electronics, optoelectronics, and biosensors [7], [8].

Figure 1 exhibited the electrochemical reaction involving methylparaben on the GNPs/ZnO electrode. In the schematic described, the carbon/ZnO electrode is the working electrode in this setup. Methylparaben, an organic compound, can undergo oxidation or reduction reactions at the electrode surface. During the oxidation

process, the carbon/ZnO electrode can oxidize methylparaben molecules, releasing electrons. This process is facilitated by the ZnO component of the electrode, which acts as a catalyst for the oxidation reaction. On the other hand, during the reduction process, the carbon/ZnO electrode can accept electrons from the environment and reduce methylparaben molecules. This reduction reaction can also occur in the presence of an external power source, such as a battery.

This study modified SPCE by GNPs/ZnO nanocomposites, which were used for applications in electrochemical sensors. The modification aims to improve the electrocatalytic properties of the electrodes, producing an electrochemical sensor that is more sensitive to detecting organic compounds. The preliminary study of the developed sensor was used to directly detect methylparaben, one of the most preventive compounds in pharmaceutical, food, and cosmetic products.

II. METHOD

A. Materials & Apparatus

Graphene nanoplatelets, zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) (99.5 – 101.0%), Kalium chloride (KCl), Potassium ferricyanide (K_3FeCN_6), Potassium ferrocyanide (K_4FeCN_6), phosphate buffer were purchased from Merck, chitosan with medium molar weight was purchased from Sigma-Aldrich (Germany), Silver paste, Ag/AgCl paste, dielectric paste, and carbon paste for fabricated SPCE were purchased from SunChemical® and methylparaben from Brataco (Indonesia).

The electrochemical measurements were performed with PGSTAT302 potentiostat-galvanostat using a three-electrode configuration. Screen-printed carbon electrodes were fabricated with a screen-printing machine. The morphology of ZnO nanoparticles and GNPs/ZnO nanocomposite was observed by a scanning electron microscope (SEM) (JEOL JSM IT300) with an accelerating voltage of 20 kV. The absorption was obtained by UV-Vis spectroscopy (Agilent Technologies-8453).

B. Fabrication of SPCE

Screen-printed carbon electrodes were fabricated with three different pastes for each electrode. The schematic structure of SPCE is shown in Figure 2. The electrodes were deposited onto a polytetrafluoroethylene (PTFE) substrate. (a) Electrode pad layers were deposited using Ag paste at 140 ^{0}C for 30 minutes; this layer serves as the conducting path of the electrode to contact with reference, auxiliary, and working electrodes, (b) carbon paste was deposited as working and auxiliary electrode, (c) Ag/AgCl layer as reference electrode, and (d) encapsulation layer was deposited to prevent cross-talk among electrodes. Each electrode was cured in an oven at a suitable temperature based on mesh size, modified inks, and screen printing parameters, including pressure and ink distribution. The general dimension of the strip is 3.4 × 1.0 × 0.05 cm. Working (4 mm in diameter) and counter/ auxiliary electrodes are made of carbon. The fabricated SPCE was characterized by cyclic

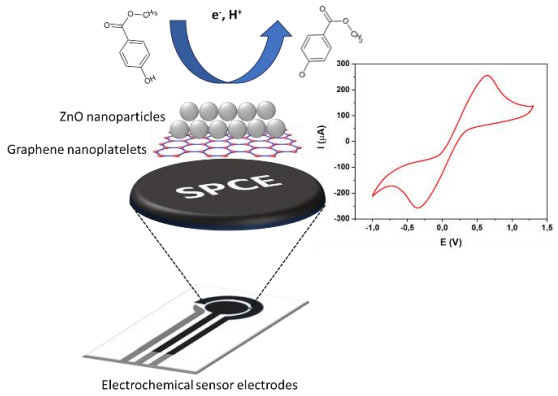

Figure 1. The schematic of electrochemical detection of organic compounds such as methylparaben.

voltammetry at 0.01M K_3FeCN_6/K_4FeCN_6 solution, and the result was compared by SPCE commercial (Metrohm DropSens).

C. Synthesis of GNPs/ZnO nanocomposite

GNPs/ZnO nanocomposite was prepared using commercial GNPs and synthesized ZnO nanoparticles based on the following procedure in previous work [9]. GNPs and ZnO nanoparticles were mixed in ethanol and stirred using a magnetic stirrer for four hours. The solution was centrifuged, and the precipitation was washed using ultra-pure water and then dried in an oven at 80^0 C. The morphology of nanocomposite products was characterized using SEM.

D. Optimization of nanocomposite concentrations and analytical performance of sensor

The optimization of nanocomposite concentration was carried out at concentrations of 0.5, 1.0, and 1.5 mg/mL of nanocomposite. The nanocomposite powder was dispersed in ethanol and sonicated for 30 minutes. Subsequently, 2.5 – 5.0 µL solution was drop cast onto the surface working electrode, and then the electrode was dried in an oven for 30 minutes. Each electrode was analyzed by cyclic voltammetry at a potential range of -1 to 1.2 V, scan rate 100 mVs^{-1} with K_3FeCN_6/K_4FeCN_6 and 0.1 M KCl solution. The performance of electrodes was analyzed by differential pulse voltammetry (DPV) at

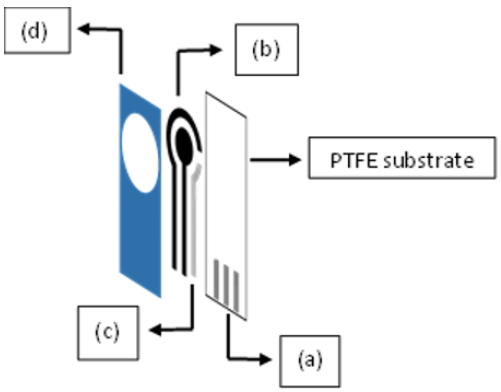

Figure 2. The schematic structure of fabricated SPCE consists of (a) an electrode pad, (b) a working and auxiliary electrode, (c) a reference electrode, and (d) an encapsulation layer.

a potential range of 0.1 to 1.2 V, with the scan rate of 100 mV/s in methylparaben and phosphate buffer solution at pH 7.

III. Results and Discussion

A. Voltammetry characterization of SPCE

The ferri/ferrocyanide redox couple was used for comparing the voltammetric behavior of fabricated SPCE and SPCE commercials. Potassium hexacyanoferrate (II) and potassium hexacyanoferrate (III) are chosen as models because they can characterize electrochemical systems in aqueous and organic solutions [10]. As shown in Figure 3, typical voltammetric profiles result from the following electrochemical process:

$$Fe(CN)_6^{3-}{}_{(aq)} + e \rightleftharpoons Fe(CN)_6^{4-}{}_{(aq)} \quad (E_0 = +0.356\,V) \quad (1)$$

The peak separations of the anodic and cathodic peak currents of fabricated SPCE are 0.2758 V, whereas the commercial SPCE is 0.2807 V. The substrate, paste, dimensions, and fabrication process can cause a difference in peak separation. The difference in the paste may include information regarding particle size, components, etc. At the same time, the fabrication process consists of the curing temperature. In this study, PTFE substrate must be used in the low-curing temperature; meanwhile, ceramics alumina substrate, as in commercial SPCE can be used for the high-curing temperature. The difference can affect a significant limiting factor in charge transfer [10]-[12]. The cathodic and anodic current ratios for fabricated SPCE and commercial SPCE are close to 1, showing a reversible properties of K_3FeCN_6/K_4FeCN_6. Hence, the fabricated SPCE can be used for further experiments.

B. Characterization of GNPs/ZnO nanocomposite and SPCE-GNPs/ZnO

Dispersion of ZnO nanoparticles was characterized using UV-Vis spectrophotometry. By measuring the absorbance at different wavelengths, the UV-Vis spectrophotometer can provide information about the dispersion of ZnO nanoparticles. The absorbance spectrum can reveal the presence of any aggregation or agglomeration of nanoparticles, as well as the size and shape of the nanoparticles. The UV-Vis spectra (Figure 4 (a)) showed a sharp peak with high intensity at wavelength 366.50 nm, indicating that the ZnO nanoparticle on the nanometer scale and particle size distribution is narrow. The SEM image in Figure 4(b) shows that the morphology of ZnO nanoparticles is spherical and confirms that the particle distribution is narrow size with range of 33-70 nm [13]-[15]. After the hybridization of GNPs and ZnO, the nanocomposite of GNPs/ZnO was characterized by scanning electron microscopy (SEM) as shown in Figure 4 (c). The hybridization of GNPs and ZnO offers the opportunity to combine the unique properties of both materials, resulting in enhanced or synergistic effects.

There are some critical aspects of the hybridization of GNPs and ZnO nanoparticles, such as enhanced electrical properties. GNPs possess excellent electrical conductivity due to their graphene structure, while ZnO is a semiconductor material. By combining GNPs and ZnO, the electrical conductivity of the composite can be improved, making it is suitable for applications in

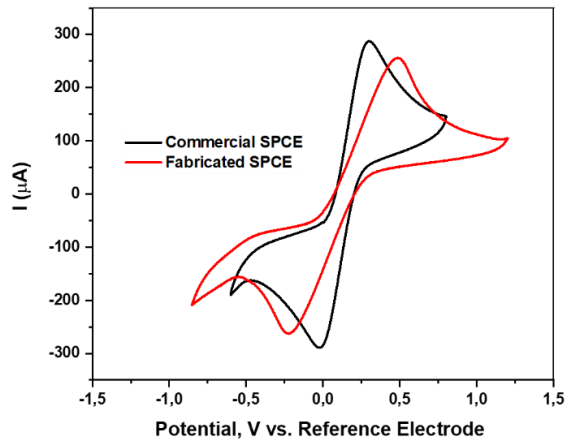

Figure 3. Voltammogram of fabricated SPCE vs. commercial SPCE.

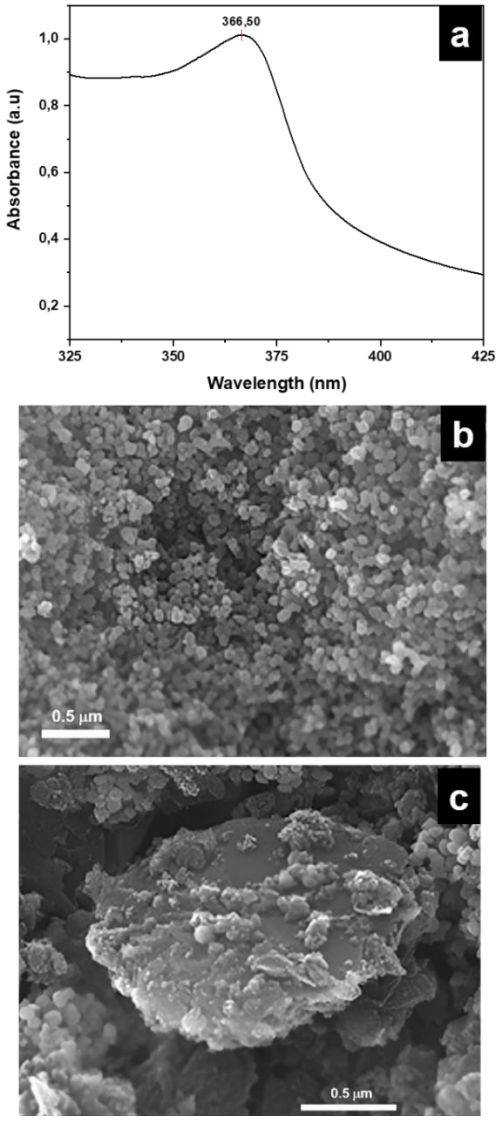

Figure 4. (a) UV-Vis spectra and (b) SEM image of ZnO nanoparticles, and (c) SEM image of GNPs/ZnO nanocomposite.

electronics, sensors, or energy devices. GNPs have a large surface area, providing a high contact area for ZnO nanoparticles. This increased surface area allows for more interactions between the two materials, leading to improved properties such as enhanced catalytic activity or increased surface reactivity. The combination of GNPs and ZnO can result in synergistic effects, where the properties of the composite are greater than the sum of its components. This can include improved conductivity, enhanced optical properties, or increased stability, depending on the specific application and composition of the hybrid material.

Figure 5 shows the SEM images of GNPs/ZnO. The flake layer is GNPs, and ZnO nanoparticle was embedded onto the GNPs surface sheet. The ZnO nanoparticles are supported by the GNPs, increasing the surface area and resulting in improved properties. The ZnO nanoparticles reduce the van Deer walls force among graphene sheets; thus, the graphene did not undergo aggregation [16], [17]. By utilizing GNPs as a support, the surface area available for ZnO nanoparticles is increased. This increased surface area allows more ZnO nanoparticles to be present, leading to a higher concentration of active sites. As a result, the properties of the composite material, such as catalytic activity, electrical conductivity, or sensing capabilities, can be improved [18], [19].

C. Analytical performance of electrodes and optimization concentrations of nanocomposite

The behavior of bare SPCE and modified SPCE was investigated using cyclic voltammetry in a potential range from -1.2 V to 1.2 V at a scan rate of 100 mV/s in 0.01 M phosphate buffer containing 0.1 M KCl (pH 7.0). Cyclic voltammetry has been chosen as a convenient and

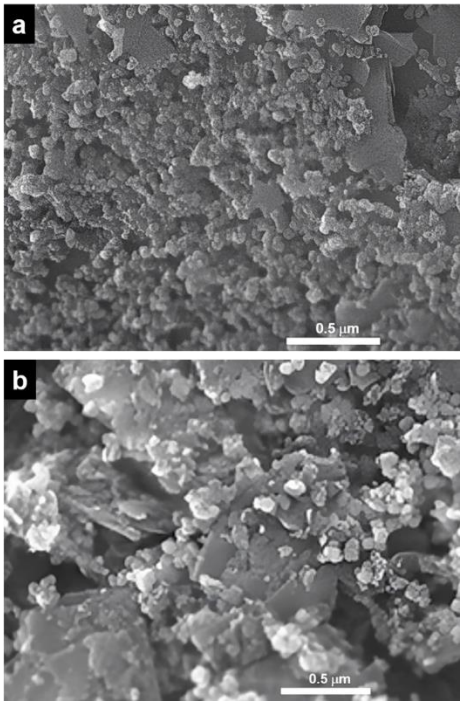

Figure 5. SEM images of (a) bare SPCE and (b) SPCE-GNPs/ZnO.

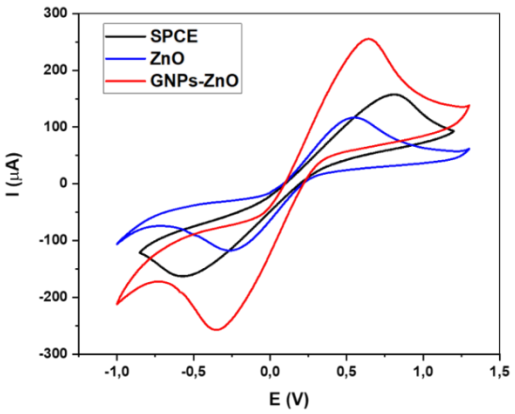

Figure 6. Voltammogram curve of bare SPCE (black line), SPCE-ZnO (blue line), and SPCE-GNPs/ZnO (red line).

effective technique to investigate the surface characteristics of electrodes [20].

As shown in Figure 6, the current response of $K_3[Fe(CN)_6]$ at bare SPCE is higher than SPCE-ZnO. Factors influencing the response, since ZnO nanoparticles tended to agglomerate when the modified electrode was dried after drop casting the ZnO nanoparticles on the surface electrode. Subsequently, reducing the surface area of the electrode then reducing the electrochemical response [21], [22]. The increasing current response is observed after modification of SPCE with GNPs/ZnO nanocomposite. it indicated that the presence of ZnO nanoparticles introduces electrochemical activity or redox processes, potentially due to the inherent properties of ZnO, such as its semiconductor behavior or catalytic activity.

On the other hand, when GNPs/ZnO composites are formed on the SPCE surface (SPCE-GNPs/ZnO, represented by the red line), the voltammogram curve exhibits further changes compared to the SPCE-ZnO curve. The presence of graphene nanoplatelets (GNPs) in the composite can enhance electrical conductivity and increase surface area, leading to improved electrochemical performance. The red line indicates that the SPCE-GNPs/ZnO composite may show a higher current response or additional redox peaks than the bare SPCE (red line) and SPCE-ZnO (blue line), indicating the synergistic effects of the hybrid material. In addition, the increasing current is also associated with increasing electrical conductivity and the surface-to-volume ratio of the electrode, which suggests that GNPs/ZnO nanocomposite is an effective modification in electrodes [20], [23]. The difference between current response and peak-to-peak separation can be seen in Table 1.

The optimization concentration of the nanocomposite was investigated by cyclic voltammetry in 0.01 M K_3FeCN_6/K_4FeCN_6 (K3/K4) solution

TABLE 1
THE ELECTROCHEMICAL RESPONSE OF BARE ELECTRODES AND MODIFIED ELECTRODES

Electrodes	E_{pa}	E_{pc}	I_{pa}	I_{pc}
Bare SPCE	0.757	0.527	100.97	65.74
SPCE-ZnO	0.615	0.303	213.1	173.54
SPCE-GNPs/ZnO	0.520	0.225	102.26	86.89

containing 0.1 M KCl. In cyclic voltammetry, the redox couple K3/K4, specifically potassium ferricyanide ($K_3[Fe(CN)_6]$) and ferrocyanide ($K_4[Fe(CN)_6]$), is commonly studied due to its reversible one-electron transfer process. The amounts of nanocomposite on the surface electrode could affect the current response of electrodes due to the catalytic properties of GNPs/ZnO nanocomposite enhancing the electron transfer [24], [25]. This can be controlled by using different concentrations of GNPs/ZnO (0.5, 1, and 1.5 mg/mL) with the same volume (2.5 µL) on the SPCE surface.

As shown in Figure 7, the peak current for 1 mg/mL GNPs/ZnO was obtained to be the highest. The further concentrations of nanocomposite in lower and higher than 1 mg/mL cause a gradual decrease in peak current. The lower concentrations may be related to not being distributed well. In comparison, the higher concentrations are connected to an increase in the thickness of the nanocomposite layer due to decreasing the surface-ratio-to-volume of the surface working electrode [25], [26]. Hence, GNPs/ZnO nanocomposite with a 1 mg/mL concentration was selected as the optimum concentration for the modified electrode.

D. The use of GNPs/ZnO nanocomposite-based sensor for methylparaben detection.

The primary concern is in the application of nanostructured electrodes for electrochemical sensors. One of the applications of GNPs/ZnO nanocomposite-based sensors is the detection of organic compounds, specifically methylparaben. The study of the detection of methylparaben was investigated by the Differential pulse voltammetry method at a potential range of 0.1 to 1.2 with a scan rate of 100 mV/s in 1 mM methylparaben. Differential Pulse Voltammetry (DPV) has been chosen as a voltammetry technique because the DPV method gives a sensitivity response than CV [24], [25].

Figure 8 indicates that the shifting peak current in DPV between a bare SPCE and an SPCE-GNPs/ZnO electrode can be influenced by several factors, such as enhanced electrocatalytic activity. The incorporation of graphene nanoplatelets (GNPs) and zinc oxide (ZnO) on the SPCE surface can enhance its electrocatalytic activity. This increased activity can lead to higher peak currents for the analyte species than the bare SPCE electrode. The shifting peak current observed between

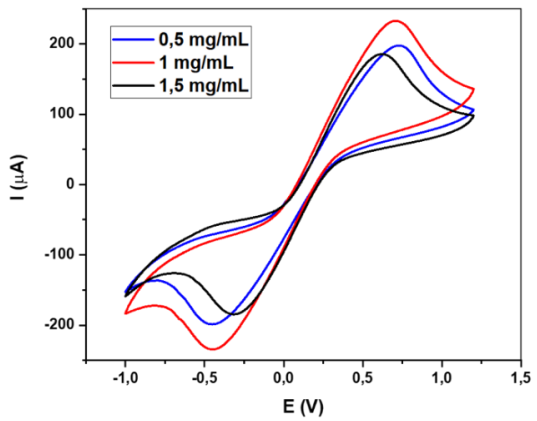

Figure 7. The current response of K3/K4 in different concentrations of GNPs/ZnO nanocomposite.

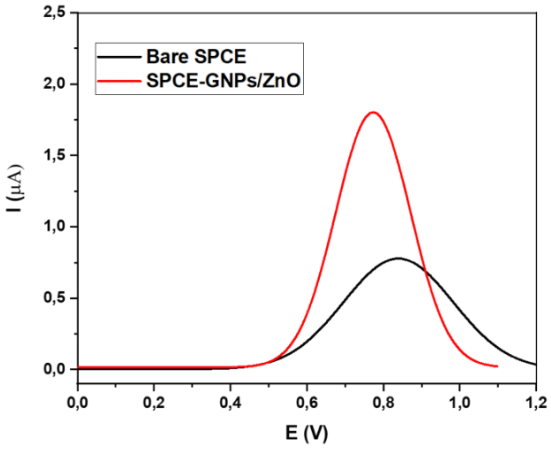

Figure 8. DPV voltammogram of 1 mM methylparaben at bare SPCE (black line) and SPCE-GNPs/ZnO (red line).

the two electrodes can be attributed to the difference in their catalytic properties. Improved electron transfer kinetics: GNPs and ZnO on the SPCE electrode can facilitate faster electron transfer between the electrode surface and the analyte species. This improved electron transfer kinetics can result in higher peak currents and a shifting peak current between the bare SPCE and SPCE-GNP/ZnO electrodes. Surface area effect: Incorporating GNPs and ZnO on the SPCE electrode surface increases its effective surface area. This increased surface area provides more active sites for the analyte species to interact with, leading to higher peak currents. The shifting peak current observed between the two electrodes can be due to the difference in their surface areas and the corresponding availability of active sites. Synergistic effect: Combining GNPs and ZnO on the SPCE electrode can create a synergistic effect that enhances the electrochemical response. This synergistic effect can lead to higher peak currents and a shifting peak current between the bare SPCE and SPCE-GNP/ZnO electrodes [24].

As shown in Figure 8, SPCE-GNPs/ZnO have a higher current response and lower potential oxidation than bare SPCE indicating better sensitivity and selectivity due to the synergistic effect of GNPs and ZnO enhances electrocatalytic electron transfer [25].

The reproducibility of SPCE-GNPs/ZnO was measured using three different electrodes in 1 mM methylparaben. As shown in Figure 9(a) and (b), the RSD for SPCE-GNPs/ZnO was obtained to be 4.54 %, and the peak of potential anodic was stable at an average of 0.7754 V. The modified electrode shows acceptable reproducibility, as the RSD value is less than 10 % [27]. It shows that the measurements obtained using different SPCE-GNPs/ZnO electrodes in 1 mM methylparaben are relatively consistent and reliable. These results demonstrate that the SPCE-GNPs/ZnO electrode is reproducible and can directly detect organic compounds (especially methylparaben) without a mediator.

The sensitivity and linearity performance of SPCE-GNPs/ZnO were evaluated by differential pulse voltammetry at a different concentration under optimization conditions. This study reveals the developed sensor's working linear range and detection limit. The calibration curve of methylparaben was

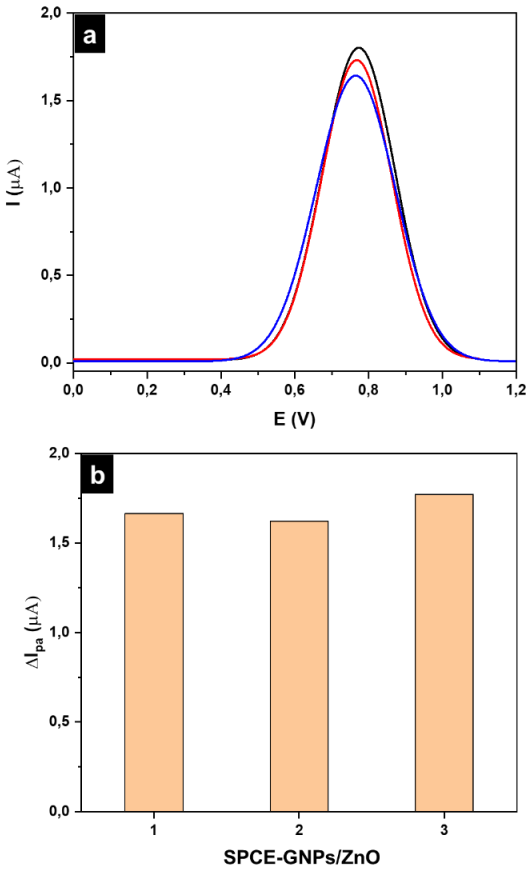

Figure 9. (a) DPV voltammogram of 1 mM methylparaben, (b) Current peak response of 1 mM methylparaben at SPCE-GNPs/ZnO.

obtained by plotting current values against the concentration. As shown in Figure 10, the peak oxidation current of methylparaben increases with increasing concentration, and the peak current of oxidized methylparaben has a good linear relationship from 10 – 1000 µM. Above 1000 µM, the peak current becomes constant or saturated, which indicates the saturation of the recognition site in the sensing layer.

The limit of detection was calculated according to linear regression $y = 0.15375 + 0.00168\,x$ (R^2 = 0.993) from the calibration curve and the equations of LOD = 3 $\delta b/b$ with δb being the standard deviation, and S is the slope of linear calibration plot. Hence, the calculated limit of detection is 9.7 µM.

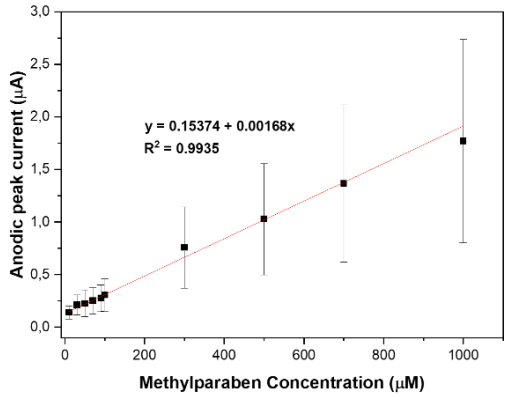

Figure 10. Anodic peak current vs. concentration of methylparaben ranging from 100 – 1000 µM in PBS pH 7 at SPCE-GNPs/ZnO.

The selectivity of the study was assessed using the oxidative current response of methylparaben (MP) in the presence of potential interfering substances. A few select interfering compounds were chosen, including 4-hydroxy benzoic acid (HBA) due to its similar structure to MP. Additionally, salicylic acid (SA) and ascorbic acid (AA) were included as they are commonly used in healthcare products.

An interference study was conducted on solutions containing binary mixtures of the target analyte methylparaben (MP) and various interference substances at a 1:1 concentration ratio (mol/mol). As shown in Figure 11, no significant interference peaks were observed. Furthermore, salicylic acid and ascorbic acid did not exhibit any interference, and the oxidation current peaks were very close to the oxidation current peaks of MP. Therefore, the interference substances did not affect the measurement of MP. This result suggests that the sensor demonstrated specific recognition and selectivity for MP. However, a slight decrease in peak current response was observed in hydroquinone B (HBA) in solution due to the smaller size of HBA than MP. Moreover, the molecular structures of MP and HBA are similar, thus creating intense competition between the two molecules to occupy cavities in the sensitive layer matrix. This result implies that the imprinted cavities were explicitly formed to detect MP selectively.

IV. Conclusion

In conclusion, this investigation presents a study that highlights the synthesis, characterization, and utilization of a nanocomposite consisting of Graphene nanoplatelets (GNPs) and Zinc oxide (ZnO) to modify screen-printed carbon electrodes (SPCEs) in the realm of electrochemical sensors. The GNPs/ZnO nanocomposite formation was effectively characterized by means of UV-Vis spectroscopy and scanning electron microscopy.

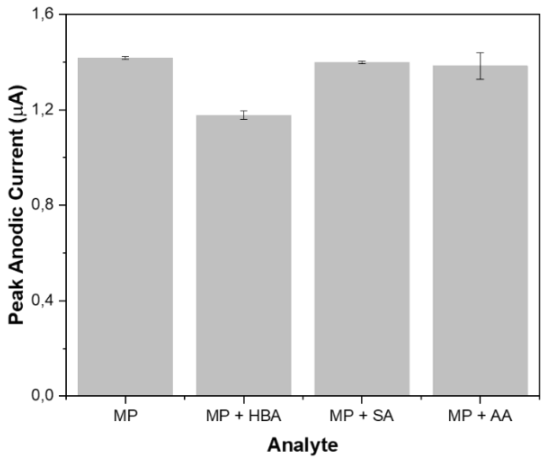

Figure 11. The peak current of selectivity test on SPCE-GNPs/ZnO with analyte a combination of methylparaben (MP), hydroxy benzoic acid (HBA), salicylic acid (SA), and ascorbic acid (AA).

Cyclic voltammetry was employed to optimize the concentration of the nanocomposite on SPCEs, ultimately revealing that a concentration of 1 mg/mL of GNPs/ZnO nanocomposite showcased the highest current response. The sensor's performance was evaluated by detecting methylparaben, an organic compound, utilizing differential pulse voltammetry (DPV). These findings indicate a significant enhancement in electrocatalytic activity and reproducibility, coupled with heightened sensitivity, selectivity, and a low limit of detection (LOD) of approximately 9.7 µM for detecting methylparaben. Overall, the proposed SPCE-GNPs/ZnO sensor demonstrates exceptional performance, sensitivity, and reproducibility, laying the groundwork for potential applications in the field of biosensing. This research contributes to the advancement of electrochemical sensors by employing modified screen-printed carbon electrodes adorned with the GNPs/ZnO nanocomposite, which provides heightened electrochemical properties and biocompatibility for the precise and dependable detection of organic compounds.

DECLARATIONS

Conflict of Interest

The authors declare no conflicts of interest that could potentially influence the research, data analysis, interpretation, or presentation of the findings in this paper.

CRediT Authorship Contribution

Atik Dwi Oktaviani: Investigation, Data Curation, Writing - Original Draft, Visualization;
Robeth Viktoria Manurung: Writing – Review, Editing, Conceptualization, Methodology, Investigation, and Supervision.

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