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Development of Electrochemical Sensor Based on Graphene Oxide Electrode Modified by Silver-Doped ZnO Nanorods for Detection of Carbamate Pesticide in Food

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A facile approach was used to develop a novel electrochemical sensor based on graphene oxide (GO)/ glassy carbon electrode (GCE) modified by silver (Ag)-doped ZnO nanorods for the determination of carbamate pesticides (CP). The electrochemical deposition technique was used to fabricate the proposed electrode, and scanning electron microscopy and energy dispersive X-ray spectroscopy were carried out to characterize the electrode surface morphology and determine the elements present in the sample, which confirmed the successful formation of Ag-doped ZnO nanorods. The electrochemical properties were considered by differential pulse voltammetry (DPV) and cyclic voltammetry. Due to the good conductivity and strong catalytic activity of Ag-doped ZnO nanorods, the developed sensor revealed a limit of detection as low as 0.34 nML^{-1} by DPV, indicating a good stability, acceptable reproducibility and selectivity and great potential in determination of CP compounds in foodstuffs.

Keywords: Graphene oxide electrode; Ag-doped ZnO nanorods; Differential pulse voltammetry; Carbamate pesticide; Cyclic voltammetry

1. INTRODUCTION

To affirm increase in crop production by the reduction of pests and elimination of diseases, certain neurotoxin compounds termed as pesticides are employed in a large scale [1]. Food and environment regulation bodies have ratified control schemes as the concern of the hazard of pesticide residue in food and environment contamination have increased [2]. In accordance to these criteria and to ensure safe public health, the official laboratories have to check large quantities of samples in an efficient manner [3]. Therefore, analytical systems that are quick, cost-effective, highly sensitive with large quantity of sample input and on-site facility are required to identify the risk of pesticide contamination in food products like fruits, vegetables, etc [4]. Gas Chromatography or high performance liquid chromatography are the commonly remarkable methods to determine the pesticide residue in real life samples [5-7]. The common demerits of these methods are that they are prolonged, complex and expensive procedures [8, 9]. Therefore, a demand exists for a simple, quick, and cost-effective method to determine pesticide residue. In recent times, a number of studies about class specific determination of carbamate pesticides such as magnetic graphene solid-phase extraction, fluorescent, electrochemical biosensor, microfluidic chips, voltammetry techniques [10-13] have been done. Even though these methods were simple and not time-consuming, they were in need of complementary equipment which had prevented them from being used for quick on-site analysis. Also, the biosensors were in need of further development like better reproducibility and stability to detect the pesticide residues in real life samples. The electrochemical impedance spectroscopy (EIS) is an engaging energy conversion technique that allows direct analyte detection by the study of electrical properties of the sensing device interface [14-16]. The EIS measurements associate the examination of impedimetric transformations at the interface of the electrode when a biological or chemical element comes in contact with the electrode interface that acts as a bio-receptor. To be specific, EIS brings together the examination of resistive and capacitive attributes of the electrode interface on the basis of slight amplitude disruption of the system from a steady state. This clearly means EIS is a non-destructive testing method. This work addressed a sensor fabricated with graphene oxide modified with Ag-doped ZnO nano rods and the assembling of an electrochemical sensor to detect the carbamate pesticide, for the first time. The samples were characterized using cyclic voltammetry, square wave voltammetry, and electrochemical impedance spectroscopy.

2. MATERIALS AND METHOD

Graphene colloid was obtained later by reducing the aqueous graphene oxide (GO) by using N, N-Dimethylformamide (DMF, 99.8%) in the presence of hydrazine monohydrate. First, 25 ml of the GO suspension (~5 mg GO/mL) was added to 120 ml of DMF and sonicated for an hour to uniformly dispersed GO in DMF solution. To this, 2 ml of hydrazine monohydrate was added. Then they were placed in a water bath of 80 ± 5 °C for 8 h. The reaction mixture precipitated into black solids. Then, to obtain a graphene colloidal suspension in DMF, the acquired graphene was thinned down by using DMF 6 times (resulting concentration ~0.25 mg/mL), and sonicated for an hour to stabilize and homogenize the graphene distribution in the DMF solution.

The glassy carbon electrode (GCE) was cleaned as the following process: a) the GCE surface was soft polished with 1, 0.3 and 0.05 µm of alumina for 20 minutes, b) the tip of GCEs was ultra-sonicated in ethanol and distilled water for 20 min, respectively. The sterile substrates were placed in an oven at 80 °C before moving forward. The GO films were developed by air brushing the synthesized graphene colloidal suspension on the GCE substrate. The air brush was in conjunction with an argon tank with a valve to control gas pressure. The air-brush was held 10 cm away from the surface of the GCE substrate and the streams of graphene suspension were kept at 90^0 to the substrate. The surface was then put on a hot plate at 120 °C.

In a typical electrochemical process, 0.1M zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and 0.05M silver nitrate ($AgNO_3$) were added to DI water and subjected to 45 min vigorous stirring. 0.1M hexamethylenetetramine (HMTA) is dissolved in 30 ml DI water and then was added to the previous solution. The resultant was subjected to 30 min stirring. A few drops of ammonium hydroxide (NH_4OH) were added to adjust the pH to 10. A homogenous mixture was made by stirring it for 20 min. The aqueous solution (30 mM) was put into a galvanic cell. The anode, platinum electrode, and the cathode, GO/GCE electrodes, were placed inside the solution. Vertically aligned Ag-doped ZnO nanorods were produced with 0.5 mA/cm^2 current density, 60 min growth time and 80 °C growth temperature. DI water and nitrogen gas were used to wash and dry the sample respectively after growing the nanostructures. The samples were characterized by Field Emission Scanning Electron Microscopy (FE-SEM, FEI Sirion 200) attached with energy dispersive X-ray spectroscopy (EDX) for elemental analysis.

Cyclic voltammetry (CV) measurements were taken from -0.6 to +0.6 V against a reference electrode with 0.05 V/s scan rate in 1 mM ferri/ferrocyanide redox couple solution ($[Fe(CN)_6]^{4-/3-}$, 1:1) in 0.1 M pH 7 phosphate buffered (PB), used as a background electrolyte at ambient temperature. To measure the amount of pesticide, 20 μL of carbamate pesticide (CP) compound was added in the electrode working area and left for 30 min. The biosensor was washed with ample quantity of bi-distilled water before measuring the impedance.

3. RESULTS AND DISCUSSION

FESEM was used to characterize and examine the synthesized GO/GCE and Ag-doped ZnO/GO/GCE electrodes. Figure 1a exhibits the image of graphene oxide on GCE. As graphene oxide is the stacked layers of graphite, we can see the white lines indicating its folded structure.

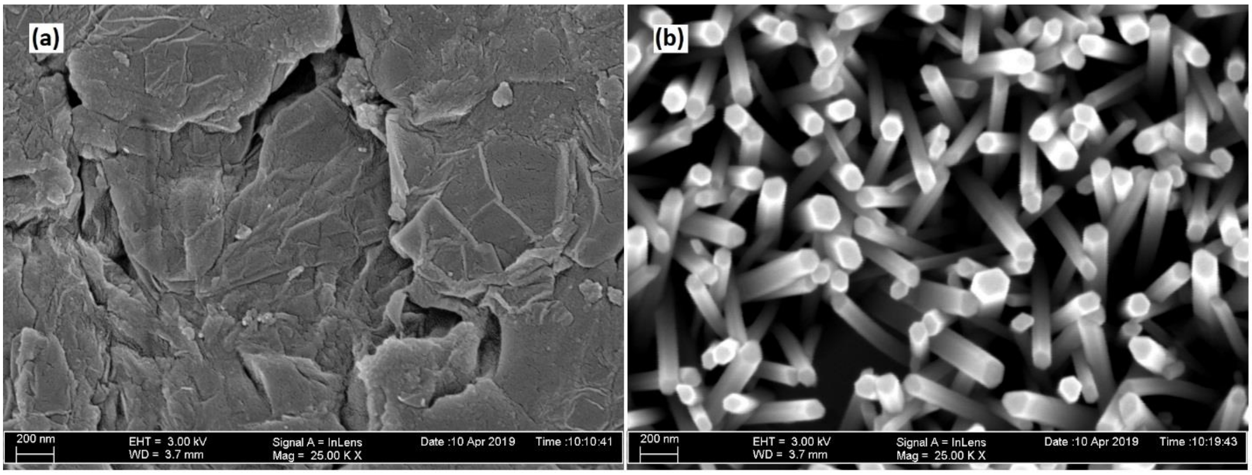

Figure 1. FESEM images of (a) GO/GCE and (b) Ag-doped ZnO/GO/GCE electrode at 80 °C growth temperature and 0.5 mA/cm^2 current density.

The distance between all the lines are not similar to each other which explained that graphene oxide does not have specific lateral size. The average lateral size can be measured but it cannot represent the specific size distribution as graphene is meant to have non-uniform size. As shown in Figure 1b, the morphology of the synthesized Ag-doped ZnO nanomaterials are very high-density rod-shaped structures. These structures are made of high aspect ratio of Ag-doped ZnO nanorods. It can be seen that the typical length and width of these Ag-doped ZnO nanorods are approximately 2 μm and 100 nm, respectively.

Thus, as reported, the synthesis of dense homogenous ZnO structures with a high aspect ratio is effective when done by electrochemical method, which holds good for electrochemical sensor applications that have high sensitivity and selectivity.

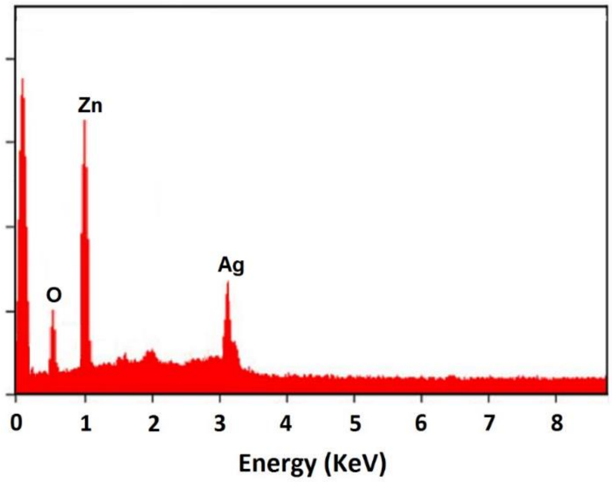

Figure 2. EDX analysis of Ag-doped ZnO nanorods grown on GO/GCE electrode using electrochemical method at 0.5 mA/cm^2 current density and 80 °C growth temperature.

Energy dispersive X-ray spectroscopy (EDX) attached with FESEM was used in order to determine the elements present and the purity of synthesized rod-shaped Ag-doped ZnO nanostructures. Fig 2 clearly shows that the synthesized nanorods consist only of Zn, Ag, and O, proving that Ag-doped ZnO nanostructures do not have any impurities or contaminations.

CV and EIS techniques were commonly used as an appropriate tool to track the individual steps of the development of a biosensor [17].

It was observed that no oxidation or reduction peaks were recorded for the GCE and Ag-doped ZnO/GO/GCE electrodes in the absent and present of CP in the electrolyte solution. Addition of CP to the electrochemical cell lead to increase the background current for both of GCE and Ag-doped ZnO/GO/GCE. Figure 3b shows the well-defined redox peaks for Ag-doped ZnO/GO/GCE electrode which can be related to the oxidation and reduction in absent of CP in the electrolyte, respectively. When CP compound was added to the electrolyte, recorded CVs showed a sharp oxidation peak at 0.35 V for Ag-doped ZnO/GO/GCE. Figure 3b demonstrates that the addition of CP had led to an increase in the oxidation peak of Ag-doped ZnO/GO/GCE. It can be considered as the catalyzed oxidation of CP. High current of oxidation peak refers to the higher sensitivity response for the determination of CP. Electrochemical reversibility and the high electron transfer rate of Ag-doped ZnO nanorods demonstrate the potential for these nanostructures to be used as mediators for electron transferring between analytes and electrode surface in electro-catalysis activities.

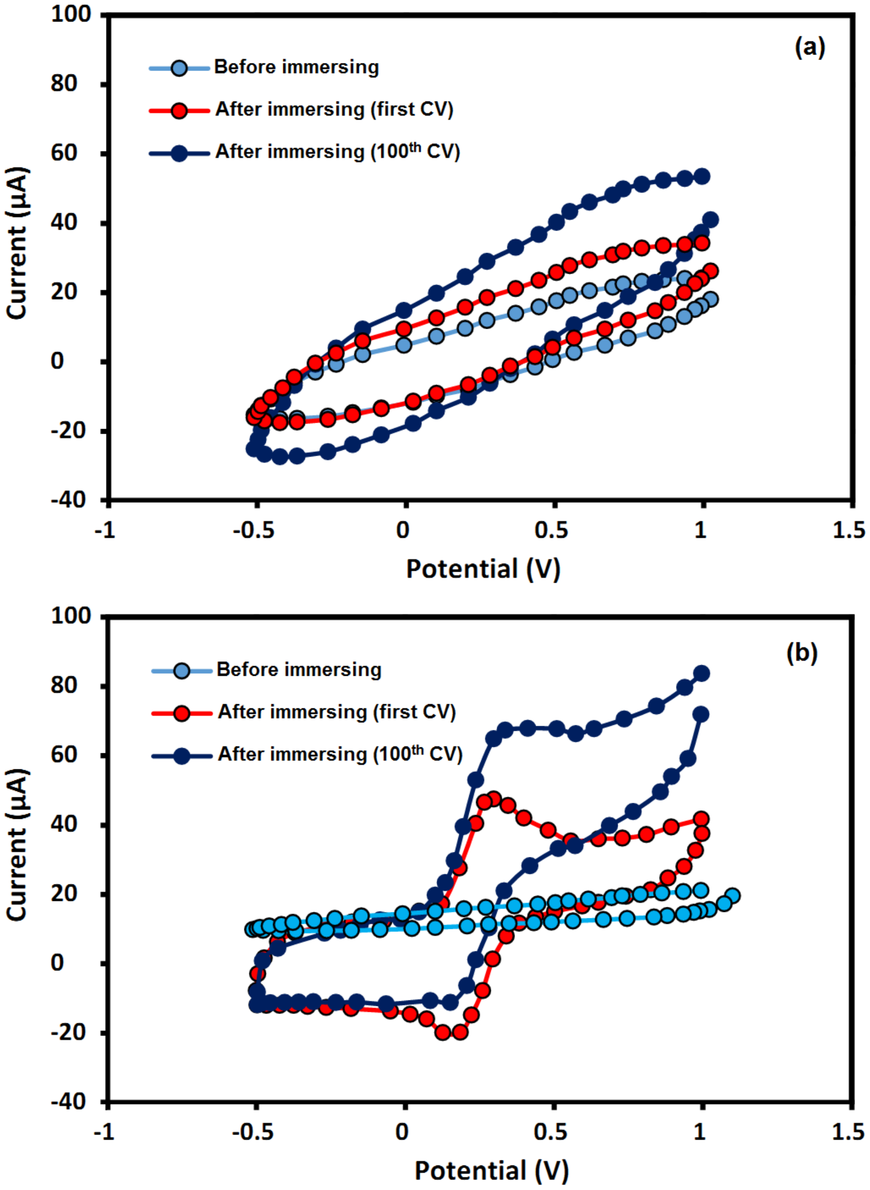

Figure 3. Recorded CVs of (a) GCE and (b) Ag-doped ZnO/GO/GCE before immersing, after immersing electrodes in first and 100th cycles in 0.1 M phosphate buffer solution pH 7.0 and the scan rate of 50 mV s^{-1}.

Furthermore, Figure 3 shows the typical cyclic voltammograms obtained after electrode-modifying process. The voltammograms of the Ag-doped ZnO/GO/GCE electrode showed precise peaks of cathode and anode because of the changeable inter-conversion of $[Fe(CN)_6]^{3-/4-}$. A dramatic increase in the diffusion of the redox probe next to the electrode surface was seen leading to a critical increase in both peaks. This occurred as a result of Ag-doped ZnO nano rods that had developed on the GO/GCE electrode.

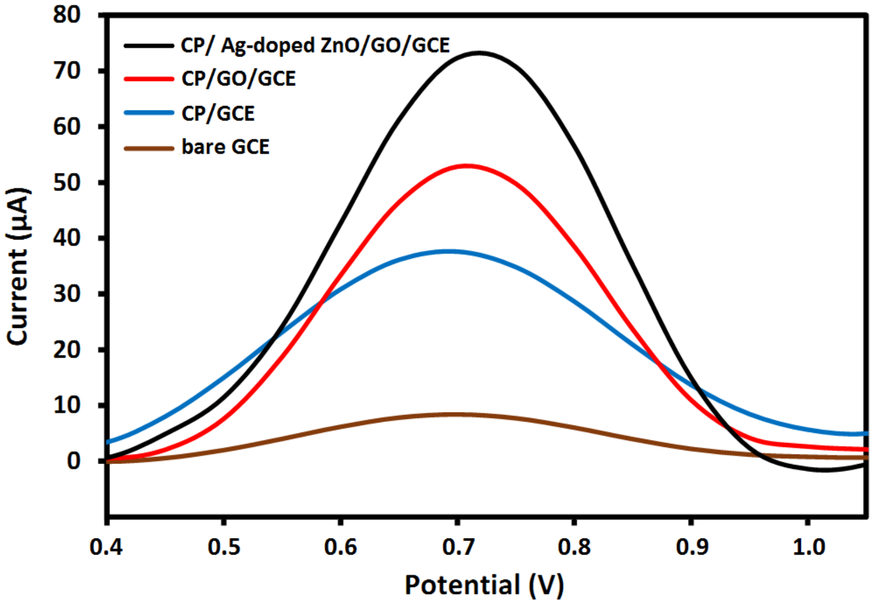

Figure 4. Typical DPV obtained after electrode-modifying process

At optimum experimental environment, the respective DPV of bare GCE, CP/GCE CP/GO/GCE and CP/ Ag-doped ZnO/GO/GCE in 0.1 M phosphate buffer solution at pH 7.0 is as seen in figure 4. When CP was not present, GCE showed no peak. A clear-cut reduction peak was seen for Ag-doped ZnO/GO/GCE when 0.1 µM CP was added to the 0.1 M phosphate buffer solution (pH 7.0). This relates to the reduction of the nitro group to the hydroxylamine group, which is coherent with previous studies [18, 19].

The chelation between the Ag-doped ZnO and phosphoric group upon the addition of CP solutions resulted in the adsorption of CP on the modified electrode surface. Substituting the Ag-doped ZnO/GO/GCE with GO/GCE as the working electrode to improve 0.1 µM CP, they likewise exhibited reduction peak in phosphate buffer solution (pH 7.0), but the reduction peak current was clearly lower than Ag-doped ZnO/GO/GCE. This outcome was credited to these explanations: (1) GO had an abundant amount of amine groups, which presented electrostatic anchoring points for CP [20]; (2) GO had great catalytic performance for CP; (3) Ag-doped ZnO had the sturdy attraction with the phosphoric group of CP and had catalytic performance for CP [21]. Significantly, collective Ag-doped ZnO nanorods with GO film modified electrode improved the electrochemical stability properties of GO, and upgraded selectivity of the modified electrode. On the basis of these merits, Ag-doped ZnO/GO/GCE displayed noteworthy improvement of the current response.

In order to measure the sensitivity and detection limit of CP sensor, differential pulse voltammetric (DPV) studies of Ag-doped ZnO/GO/GCE electrode was done in 0.1 M phosphate buffer solution at pH 7.0 and injection low concentration of CP. Fig. 5a reveals the DPV response to successive injection of 0.1 µM CP. Figure 5b displays the curves of catalytic peak currents vs. CP concentration that exhibited the linear relationship and linear response of sensor to detection of CP. The sensitivity and detection limit of sensor were estimated 0.686 µA/µM and 0.34 nM, respectively. Table 1 indicates the comparison of different techniques in detecting the CP as mentioned in the literature.

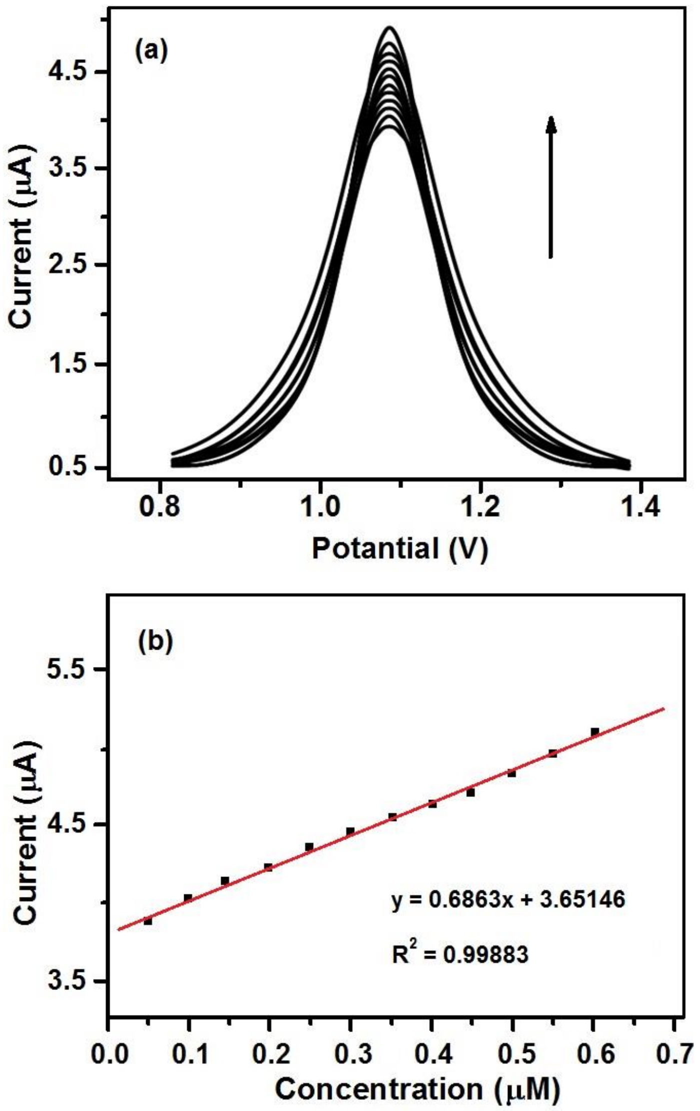

Figure 5. DPV response of Ag-doped ZnO/GO/GCE electrode to successive injection of 0.1 Mm CP in 0.1 M phosphate buffer solution at pH 7.0 and scan rate is 50 mV s^{-1}. The inset shows plot of catalytic peak currents vs. CP concentration.

Table 1. Comparison of techniques for determination of CP.

Method	Electrode	Detection limit	Ref.
Chronoamperograms	GC/PANI/MWCNT/AChE	1.4 μM L^{-1}	[22]
DPV	ZnO/Ag/MPTMS/OHP	0.07 nM	[23]
Cyclic voltammetry	Screen printed electrode	0.36 μM L^{-1}	[24]
Square-wave voltammograms	Zirconia/ordered macroporous polyaniline	0.2 nML^{-1}	[21]
DPV	NiO modified screen-printed electrode	0.024 μML^{-1}	[25]
Cyclic voltammetry	Paper-based Mitochondrial	20 nML^{-1}	[26]
DPV	MWCNTs@TiO$_2$/CMCS	0.4 μML^{-1}	[27]
DPV	Ag-doped ZnO/GO/GCE	0.34 nML^{-1}	This work

The results reveal that detection limit of Ag-doped ZnO/GO/GCE electrode for the detection of CP are comparable and better than the other techniques attained from the literature which can be ascribed to a high effective surface area and aspect ratio of Ag-doped ZnO nanorods in the surface of electrode.

4. CONCLUSIONS

A facile technique was used to develop a novel electrochemical sensor based on GO/GCE electrode modified by Ag-doped ZnO nanorods for determination of CP. The electrochemical deposition method was used to fabricate the proposed electrode, and SEM and EDX were carried out to characterize the electrode surface morphology and determined the elements present in the sample, which confirmed the successful formation of Ag-doped ZnO nanorods. The electrochemical properties were considered by DPV and CV. Due to the good conductivity and strong catalytic activity of Ag-doped ZnO nanorods, the developed sensor revealed a limit of detection as low as 0.34 nML^{-1} by DPV, indicating a good stability, acceptable reproducibility and selectivity and great potential in determination of CP compounds in agricultural products.

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