

IONIC LIQUID FUNCTIONALIZED GRAPHENE OXIDE DECORATED BY GOLD NANOPARTICLES FOR ELECTROCHEMICAL DETECTION OF PIRIMICARB PESTICIDES

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Abstract:

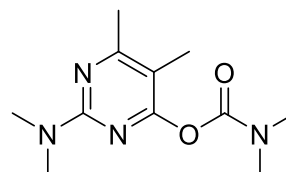
Monitoring pesticide contaminants in diverse environmental systems has become a significant concern. A non-enzymatic electrochemical sensor for pirimicarb pesticide detection has been produced by functionalization of the screen-printed carbon electrodes (SPCE) with graphene oxide, ionic liquid, and gold nanoparticles (GO/IL/AuNps/SPCE). Cyclic voltammetry and electrochemical impedance spectroscopy techniques were applied for the electrochemical characterization of the modified electrode in the presence of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as a redox probe. The system showed an exponential response in a concentration range from 50 pM to 500 nM of pirimicarb with a sensitivity of $5.74 \times 10^{-3} \mu\text{A pM}^{-1} \text{mm}^{-2}$, and the Limit of detection (LOD) is 10.30 pM.

Keywords: pirimicarb; ionic liquid; gold nanoparticles; SPCE, graphene oxide.

1. INTRODUCTION

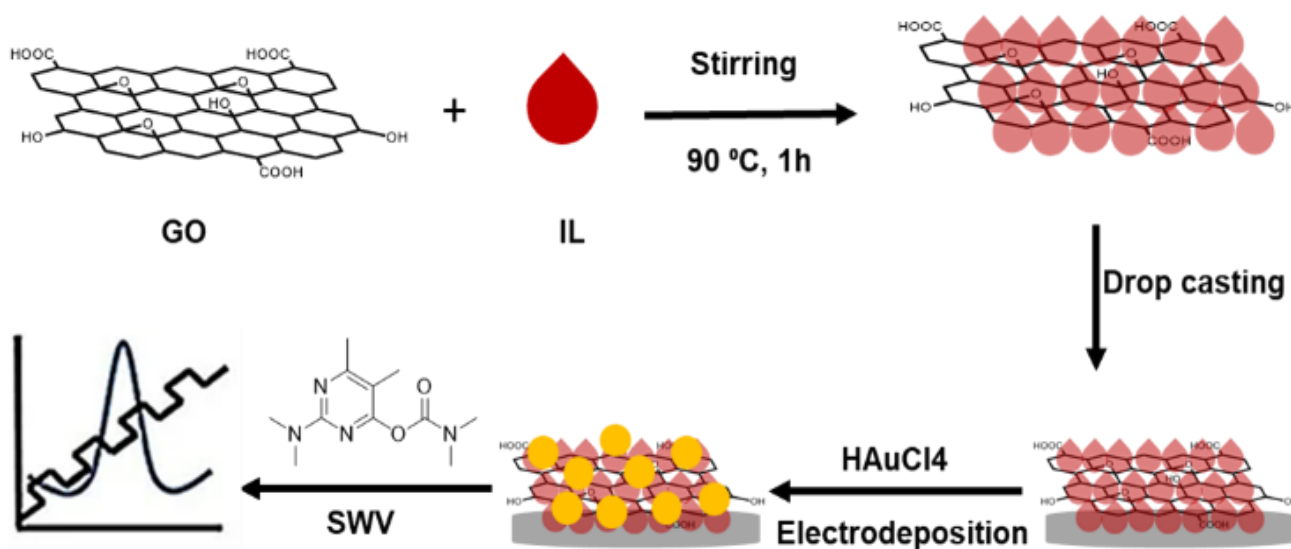
Pesticides are widely used in agricultural production for the control of insects, fungi, bacteria, weeds, rodents, and other pests [1]. The positive benefits of using pesticides in agriculture in terms of improving productivity have led to widespread acceptance of pesticides on a global scale [2,3]. The global consumption of pesticides was nearly 4.2 million metric tons in 2019, an increase of more than 80 percent when compared to 1990 [4]. The pesticide residues are not completely degraded in natural ways. Therefore, pesticides accumulate in all parts of the environment including soil, water, and air, and finally, they find their way to the food chain [5]. Consequently, they can be harmful to the environment and human health. Thus, the monitoring of their concentration periodically in the soil, surface/groundwater, and food products is considered a priority for researchers in this field [6].

Among several pesticides used in agricultural production, carbamates are extensively used in crops worldwide due to their broad spectrum of biological activity [7]. Pirimicarb, 2-(dimethylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate (scheme 1) is a carbamate pesticide. It has a highly toxic effect and reversibly inhibits the active site of the enzyme acetylcholinesterase [8,9]. Accordingly, there is an ongoing need to investigate and develop new sensors capable of monitoring and quantifying their environmental presence with low detection limits.



Scheme 1: Chemical structure of pirimicarb.

The current standard detection methods for pirimicarb pesticides heavily rely on chromatographic techniques [10] as they are accurate, reliable, and sensitive, yet they have some drawbacks like being costly methods, complicated sample preparation, considerable analysis time, and need for expert operators. In contrast, electrochemical detection technologies offer advantages over conventional approaches, including ease of use, high sensitivity, low cost, and portability for on-site application [11]. Pesticide detection has been accomplished utilizing a variety of electrochemical techniques, using either enzymatic or non-enzymatic approaches [12,13]. The enzymatic approach requires an enzyme to functionalize the electrode surface [13].



Scheme 2. Schematic illustration of the fabrication of the sensor based on GO/IL/AuNps/SPCE.

This method has various disadvantages like undesired interaction of the enzyme with the surrounding media, challenging enzyme immobilization, and enzyme degradation [14]. Non-enzymatic pesticide detection methods, particularly the direct method, can assist to address various disadvantages associated with enzymatic detection methods [15]. In this context, a boron-doped diamond working electrode was used to accomplish direct electrochemical detection of the pesticide pirimicarb [7]. To the best of our knowledge, this is the only report that described the direct detection of pirimicarb.

Herein we designed a non-enzymatic sensor by combining different materials and using their synergetic effect for the direct detection of pirimicarb.

GO-based nanomaterials have received the attention of researchers in the nanotechnology field due to the synergistic effect of different functional groups making them interesting in many applications e.g., electronics, photocatalysts, batteries, supercapacitors, adsorbents, medicine, and sensors [16-19].

Noble metallic nanoparticles, such as AuNPs, AgNPs, and PtNPs, offer high stability, easy chemical synthesis, tuneable surface functionalization, high conductivity, and high catalytic activity. Therefore, they are widely used in fabricating electrodes for sensing applications in different domains [20].

As for Ionic liquids (ILs), they are organic salts that exhibit low melting temperature, and due to their excellent physicochemical properties, such as high ionic conductivity, wide electrochemical windows, negligible vapor pressure, chemical, and thermal stability, antifouling, biocompatibility make them attractive for fabricating electrochemical/biosensors [21].

In the present study, a non-enzymatic electrochemical sensor using graphene oxide/ionic liquid/ gold nanoparticles composite (GO/IL/AuNps/SPCE) was developed and characterized electrochemically using cyclic voltammetry and electrochemical impedance spectroscopy, then use it for the electrochemical detection of pirimicarb.

2. DESCRIPTION OF THE WORK

2.1 General methods and materials

All chemicals were purchased from Sigma Aldrich and used as received without further purification. The composite has been prepared according to the modified procedure [22, 23]. Briefly, 4.5 mL graphene oxide suspended in water (0.5 mg/mL) was mixed with an aqueous solution of 5.5 mL of 1-Butyl-3-methylimidazolium hexafluorophosphate (ionic liquid, IL). Then, the mixture was subjected to magnetic stirrer and heated in an oil bath to 90 °C for 1 hour. After cooling down, 5 μ L of the resulting composite was drop-casted on the SPCE and dried at room temperature and atmospheric pressure for approximately 24 h. After then, the gold nanoparticles were deposited on the surface of the modified electrode using 0.1 M KNO₃ solution containing 1.0 mM of H[AuCl₄]. A cyclic voltammetric mode with the potential range of 1 V to -1 V was performed for electrodeposition. The modified electrode was rinsed with distilled water (DW) to remove physically adsorbed species before use.

Sensor characterization was performed using screen-printed carbon electrodes (SPCE) with a carbon counter electrode, a graphite working electrode, and an Ag/AgCl reference electrode. All measurements were carried out using PalmSens4

portable potentiostat (Palmsens BV, GA Houten, Netherlands).

2.2 Electrochemical characterization of the modified electrodes.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are powerful and effective methods to study the interfacial characteristics of different modified electrodes.

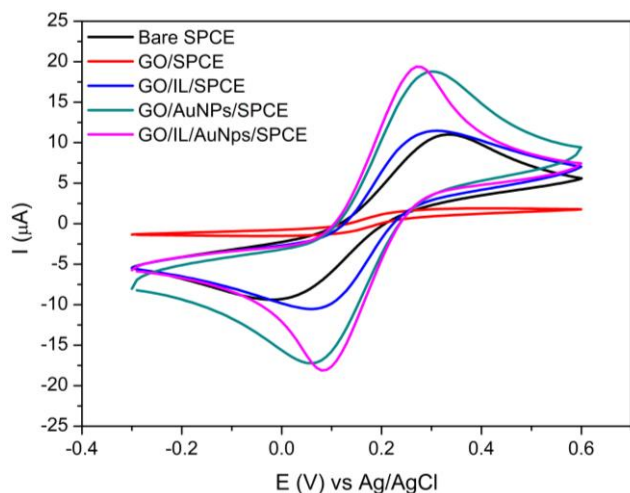


Figure.1. Cyclic voltammograms of 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl obtained with a bare SPCE, GO/SPCE; GO/IL/SPCE; GO/AuNPs/SPCE and GO/IL/AuNPs/SPCE at scan rate 100 mVs^{-1} .

The electrochemical behavior of the stepwise fabrication process was studied in 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl as presented in Figure 1. It is evident that as the electrode composition changes, the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox peak current and potential are altered.

On the one hand, well-defined redox peaks of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ at bare electrode have been observed. On the other hand, the anodic peak of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ current ($I_{\text{pa}} = 1.8 \mu\text{A}$) decreased dramatically and the anodic peak potential shifted to a higher value ($E_{\text{pa}} = 0.373 \text{ V}$) when it was modified by GO, this behavior may be due to the negatively charged GO immobilized on the electrode having a repulsive force with $[\text{Fe}(\text{CN})_6]^{3-/4-}$ [16]. GO/AuNPs exhibited a negative shift in the anodic potential of the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ ($E_{\text{pa}} = 0.306 \text{ V}$) and increase the anodic peak current ($I_{\text{pa}} = 18.7 \mu\text{A}$) compared with the bare SPCE ($E_{\text{pa}} = 0.334 \text{ V}$, $I_{\text{pa}} = 10.9 \mu\text{A}$). However, the highest anodic peak current, lower anodic peak potential, and smaller peak-to-peak separation of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ were obtained on the GO/IL/AuNPs/SPCE ($I_{\text{pa}} = 19.5$, $E_{\text{pa}} = 0.273 \text{ V}$) compared to other electrodes. The obtained results reflect the synergetic effect of GO, IL, and AuNPs in increasing the surface area of the electrode and thus accelerating the electron transfer.

The electrochemical impedance spectroscopy (EIS) in the frequency range between 0.1 Hz to 10 kHz. The result shows an enhancement in the conductivity of the electrodes when modified with GO and ionic liquid which suggests that the addition of ionic liquid diminishes the resistivity of the electrode, giving it a lower value of charge transfer resistance as shown in figure 2.

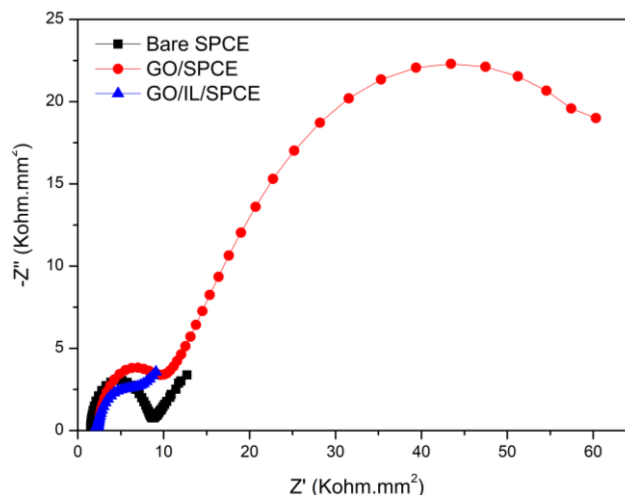


Figure.2. EIS of SPCE, GO/SPCE; GO/IL/SPCE; GO/AuNPs/SPCE and GO/IL/AuNPs/SPCE in 5.0 Mm $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl .

2.3 Electrochemical detection of pirimicarb using GO/IL/AuNPs/SPCE electrode.

In order to investigate the efficacy of the GO/IL/AuNPs/SPCE electrode for the detection of pirimicarb, the square-wave voltammetry (SWV) technique has been applied.

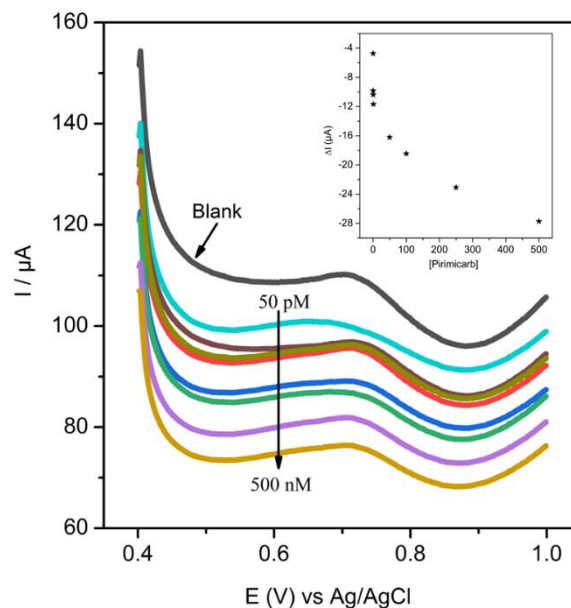


Figure.3. SWV of GO/IL/AuNPs/SPCE electrode with the variation of the concentration from 50 pM to 500 nM in 0.1 M PBS (pH = 7). Inset; plot of ΔI versus the concentration of pirimicarb.

The square wave voltammetry was carried out between 0.4 V and 1.0 V, and 30 Hz. As shown in Figure 3. The SWV shows a decreasing anodic current with increasing the concentration of the pirimicarb in the range between 50 pM to 500 nM, which is probably caused by the adsorption of the pirimicarb on the surface of the electrode, and thus affects the electroactive sites of the electrode. The detection limit was found to be 10.30 pM according to (S/N=3).

3. SUMMARY

In summary, a simple electrochemical sensor based on (GO/IL/AuNps/SPCE) composites was fabricated in order to use it in the detection of pirimicarb. The obtained results from the cyclic voltammetry and electrochemical impedance spectroscopy confirm that the modified electrode has a higher surface area and low resistivity comparable to the SPCE bare electrode. An exponential calibration curve was obtained for a pirimicarb in the range from 50 pM to 500 nM and a low detection limit (10.3 pM) with $5.74 \times 10^{-3} \mu\text{A pM}^{-1} \text{mm}^{-2}$.

An unexpected behavior has been observed during the detection of pirimicarb using the SWV technique, where the anodic current of pirimicarb decreased with the increasing concentration which is contrasted with its behavior in reported studies. In [7], the direct electrochemical oxidation of pirimicarb using a boron-doped diamond electrode resulted in an increase with an anodic oxidation peak by increasing the concentration. The adsorption of the pirimicarb on the electrode surface seems to decrease the effective electrode area and thus cause a decrease in the anodic current. Therefore, further investigations are required to understand the sensing mechanism, i.e., the behavior of the pirimicarb on the surface of the modified electrodes and/or the electrode behavior itself.

Now we are working on the enhancement of the designed electrode (GO/IL/AuNps/SPCE) performance. The suggested sensor will be fabricated using different ratios of GO and IL, as well as we will immobilize the gold nanoparticles on the electrode surface using the drop-casting method instead of the electrodeposition approach.

Briefly, in this study, we have designed an electrode with promising sensing behavior for molecules with environmental interest, which encourage us to carry out further studies to find the optimal sensing conditions.

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