Detection of Dimethoate Pesticide using Layer by Layer Deposition of PDAC/GO on Ag electrode

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Abstract*— Dimethoate (DMT) is an organophosphate pesticide (OP), which is widely used against insects and mites and their control in agriculture. As other OPs, DMT is also an inhibitor of acetylcholinesterase, which is responsible for the disabling of cholinesterase required for the functioning of the central nervous system. This pesticide can invade living cells of the human body through contact or ingestion. We report an electrochemical sensor based on a layer by layer deposition of PDAC/GO on silver electrodes. The sensor fabrication, physical characterization i.e. Raman spectroscopy and scanning electron microscopy of PDAC/GO based films, and its electrochemical characterization are discussed. The detection of DMT by analyzing electrochemical measurements including cyclic voltammetry and impedance spectroscopy shows that functionalization using layer by layer deposition improves electrochemical response and presents a basis for detection of DMT. The highest response is observed in the case of only one PDAC/GO layer which is attributed to the properly balanced interaction between DMT and PDAC/GO layer, and the increase of electrical resistivity of the PDAC/GO layer with its thickness.

***Keywords*—Pesticide detection, electrochemical sensor, cyclic voltammetry, impedance spectroscopy, graphene oxide**

I. INTRODUCTION

The development of a proficient detection system to identify pesticides is crucial in the current environmental circumstances. Nowadays we are 7.2 billion people thus the use of pesticides also continues to increase to satisfy the food needs of this vast human population [1]. Over 98 percent of sprayed pesticides in the fields reach places which are not the target species [2]. Dimethoate (DMT) is an organophosphate pesticide (OPs) which is widely used against various mites and insects due to their powerful insecticidal capability [3]. Despite their insecticidal efficiency to insects, these pesticides are as well neurotoxic to other living cells [4]. OPs and the products of their chemical transformations present potential hazards due to the high mammalian toxicity. They contaminate air, water, soil, and food, with high toxicity not only to insects but also to people and other animals [5]. DMT toxicity occurs by blocking acetyl-cholinesterase (AChE), an enzyme needed for the nervous system in insects, humans, and animals. Therefore, the development of pesticide detection systems facilitating the assessment and analysis of hazards is a necessity. Modern techniques for rapid analysis and online detection of the parameters that define the quality of water allow efficient monitoring of pollution in both the natural ecosystems and in wastewaters [6]. Chromatographic techniques conventionally used for detection of OPs and the products of their transformation in the environment have slow response, require complex equipment, are time-consuming, and expensive [5]. Hence, as an alternative to these techniques, new sensors for OPs are highly attractive due to their capability to provide strong electrocatalytic activity, sensor stability, high sensitivity, low surface fouling, in addition to being environmentally friendly.

Till date there is research that has been carried out to detect pesticides including various techniques with a variety of materials such as high-performance liquid chromatography (HPLC) [7], traditional gas chromatography GC-ion mobility spectrometric analysis [8], or using nanomaterials such as graphitized MWNTs [9] and GO encapsulated $CuFeS_2$ [10]. Significant research with carbon nanomaterials in numerous numbers of fields is persisting in the last few decades. In particular, graphene oxide and its combination with different materials have raised high interest in many novel applications including electrochemical sensing [11][12]. The high surface area and electrochemicalstability are the reasons to exhibit catalytic activity and are comparatively cheap [13]-[15].

Electrochemical sensors based on GO can be divided into biomolecules and non-biomolecules based. Graphene oxide is used for detection of pesticides in the role of electrode functionalization as in three electrode or two electrode systems where working electrodes or interdigitated electrode (IDE) are modified by adding the GO composites [15]-[17]. In biosensors, the principle is basically to modify the working electrodes additionally by baroreceptors such as AChE [18].

In this work, we investigate graphene oxide (GO) and poly(diallydimethylammonium chloride) (PDAC) deposited on silver electrodes and the polymeric substrate layer by layer. The detection of DMT pesticide was carried out by electrochemical methods *i.e.* cyclic voltammetry and impedance spectroscopy. GO and PDAC are deposited on top of silver electrodes layer by layer with dip coating. GO and PDAC acting as anionic and cationic solutions, respectively, are integrated by stacks on silver electrodes. PDAC is an inert polymer even under hydrazine treatment

[19] and it is chosen since it helps in protecting the integrity ,of the film. This study explores the pesticide detection capabilities of GO with the integration of polymer, which is yet to be investigated in detail. The sensitivity, swiftness, simple equipment requirements, and low-cost in comparison to other methods are key characteristics of this investigation.

II. MATERIAL AND METHODS

A. PDAC/GO film deposition

GO aqueous solution was purchased from Graphene Supermarket (SKU-HCGO-W-175) and it has a concentration of 5 g/L, flake size: 0.5 – 5 μm and thickness of 1 atomic layer (at least 60%). PDAC (20 wt.%) was purchased from Sigma Aldrich (CAS-No. 6062-79-32). The silver electrodes of 17 mm length are tinted on Kapton substrate and 2 mm of which is left for the electrical contact. Then the Kapton sheet with silver paint is thermally heated in an oven at a temperature of 120 °C for 2 hours. Next, prior to layer-by-layer deposition, Kapton substrates are plasma-cleaned and immediately dipped in a beaker of diluted PDAC in distilled water to 1%. The bilayer of PDAC/GO is deposited by alternating dip coating the silver electrode/Kapton for 5 mins in GO (diluted to 1% in distilled water.) and PDAC. Cleaning with HCl diluted solution and drying with nitrogen, between alternating depositions was maintained. Finally, the film was dried with nitrogen. In this work we have opted to form 1, 2, 4, and 8 bilayers of PDAC/GO. After the film deposition the electrode with PDAC/GO bilayers is left overnight and used for the electrochemical analysis for pesticide detection. The desired shape of the deposited layer was controlled by putting a mask and making the deposition on the desired area.

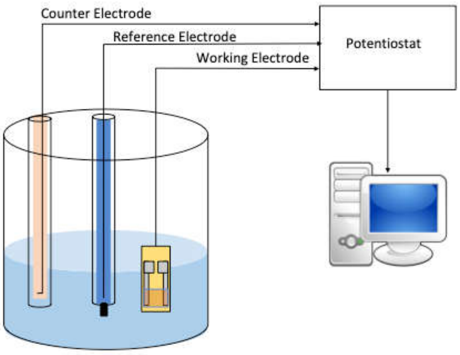

Figure 1: Schematic of electrochemical setup using saturated calomel electrode (SCE), as reference, a wide Pt foil as a counter electrode, GO on Ag/Kapton as a working electrodes and 1 mol dm^{-3} KNO_3 as a supporting electrolyte.

B. Physical Characterization

Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX) characterization was done using a Phenom ProX electron microscope. Raman spectra, excited with diode-pumped solid state high brightness laser (excitation wavelength 532 nm), were collected on a DXR Raman microscope (Thermo Scientific, USA) equipped with an Olympus optical microscope and a CCD detector. The laser beam was focused on the sample using objective magnification 10×. The scattered light was analyzed by the spectrograph with a 900 lines mm^{-1} grating. Laser power on the sample was kept at 1 mW to prevent thermal degradation of the samples.

C. Electrochemical measurements

Electrochemical measurements were done in an all-glass one compartment electrochemical cell, figure 1. As working electrodes, modified Ag electrodes were used, while saturated calomel electrode (SCE) and a wide Pt foil were used as a reference and counter electrode, respectively. As a supporting electrolyte 1 mol dm^{-3} KNO_3 was used. Experiments were done using Gamry Interface 1010TM Potentiostat/Galvanostat/ZRA. Measurements were performed in quiescent solution. Cyclic voltammetry was investigated in the potential range −0.30 to +0.40 V *vs.* SCE. Electrochemical impedance spectroscopy was performed in potentiostatic mode (at −0.1 and +0.3 V *vs.* SCE), in the frequency range 1 Hz to 100 KHz, with 7 points per decade. AC voltage amplitude was 5 mV. DMT (CAS No. 60-51-5) was purchased from Sigma-Aldrich

III. RESULTS AND DISCUSSION

A. Raman and SEM analysis of PDAC/GO

The Raman spectra of as-received GO shows typical features of a highly disordered graphitic material [20] with D (disorder) and G (graphite) band, located around 1350 and 1580 cm^{-1}, respectively, being the most pronounced features of the spectra. Also, the overtone bands, *i.e.* 2D region, are also clearly visible. The higher order bands are found at around 2670 cm^{-1} and 2930 cm^{-1}. Following [21], the first band is denoted as 2D (G’) while the second one is attributed to either D+D’ or D+G. These bands are considered to be defect-activated and dependent on the number of layers in graphite/graphene. Moreover, their appearance is also associated with wrinkled graphene layers which contain a significant amount of defects [21]. This is important as Fig. 2 shows that after modification of Ag electrode there is no change of the Raman spectra (the bands of PDAC are not visible because of very low concentration) when compared to that of GO.

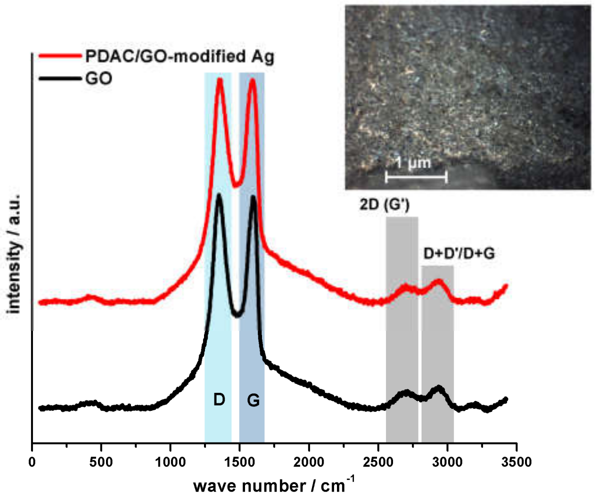

Figure 2. Raman spectra of GO (dispersion dried on a glass substrate) and the spectra of PDAC/GO-modified Ag electrode (8 layers). The inset shows the optical micrograph of the electrode where the Raman spectrum was taken.

Considering that the 2D region matches the one of pure GO, it can be concluded that there is no extra exfoliation or restacking of GO layers during the electrode modification with PDAC/GO layers. On the other hand, as the D and G bands are also unchanged during the deposition process, we conclude that the defect concentration is not altered during the electrodes' modification and that the physical structure of GO is preserved during this process. We note that Raman spectroscopy showed a homogeneous distribution of GO over the silver electrode and that the presence of GO on the electrodes was confirmed for 1, 4, and 8 layers of PDAC/GO.

SEM analysis (Fig. 3) was not able to detect GO sheets due to rather low concentration and its high transparency, but the EDX analysis confirmed the presence of carbon and oxygen (roughly 30 at.% and 15 at.% respectively, for the electrode with 8 PDAC/GO layers), besides Ag. This is in line with the results of Raman spectroscopy showing distinct signal of GO (Fig. 2). Yet again, this is a clear confirmation of an effective functionalization of silver electrode by PDAC/GO layers. We also note that the presence of carbon and oxygen was confirmed after the electrochemical measurements suggesting that deposited layers are stable under operating conditions.

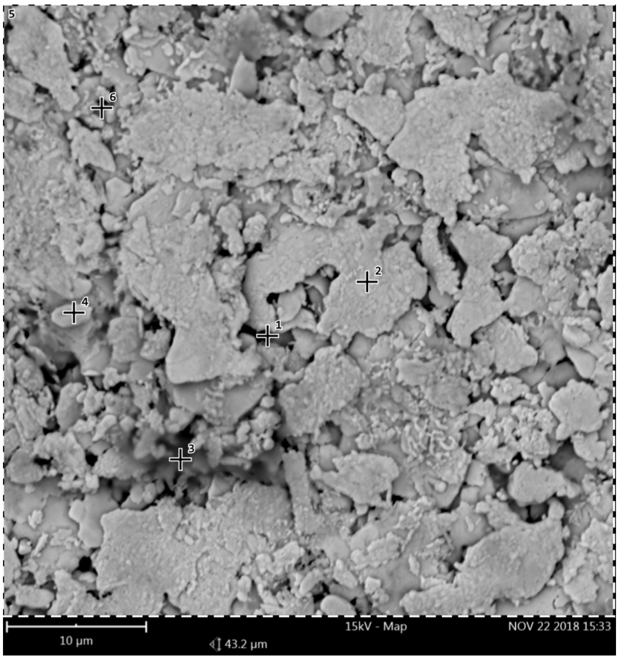

Figure 3. SEM micrograph PDAC/GO-modified Ag electrode

B. *Detection of DMT*

Before the electrochemical experiments we performed extensive cycling of the working electrode potential during which a significant alteration of electrochemical response was observed (Fig.4). It is important to note that these processes are not seen on the bare electrode. Also, the electrochemical window in which the experiments were performed was carefully chosen in order to avoid both extensive surface oxidation of silver and irreversible reduction of graphene oxide. Namely, surface oxidation processes of Ag commence above anodic vertex potential in cyclic voltammetry experiments, while GO is irreversibly reduced in nearly pH neutral solutions below −0.7 V *vs.* SCE [22]. Hence, a peculiar evolution of the voltammetry response can be associated with specific interactions between Ag substrate and PDAC/GO layer. After approx. 15 potentiodynamic cycles, the voltammetric response was stabilized, and such electrodes were used for DMT detection.

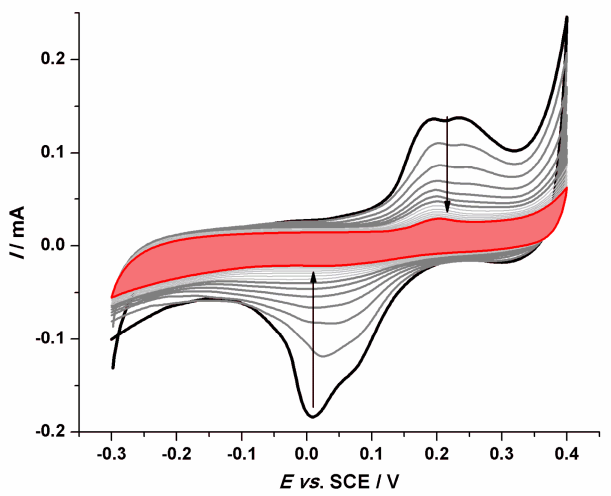

Figure 4. Consecutive voltammograms of PDAC/GO-modified Ag electrode (8 layers). First cyclic voltammogram – solid black line, stable cyclic voltammogram – shaded.

Fig. 5A shows the response of PDAC/GO-modified Ag electrode without pesticide (only supporting electrolyte) and with two different concentrations of DMT.

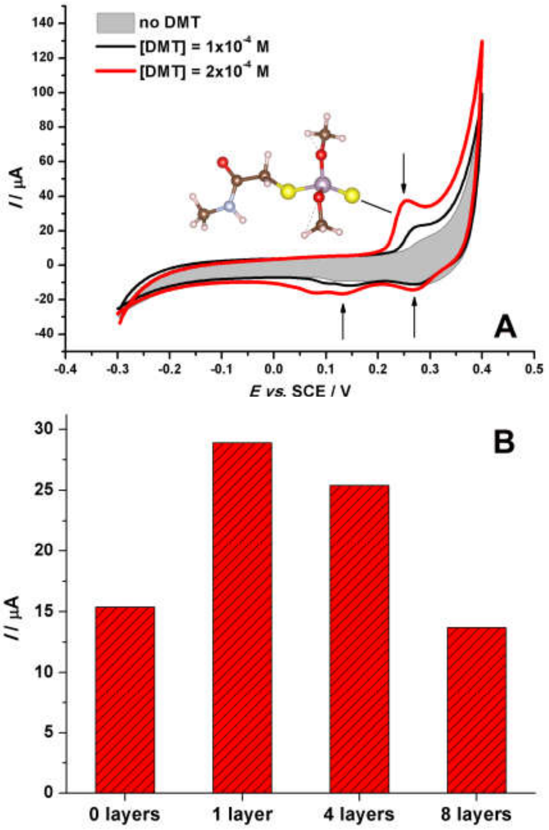

Figure 5. A: cyclic voltammograms of PDAC/GO-modified Ag electrode (1 layer) with 2 different concentrations of DMT (background cyclic voltammogram is shaded). Voltammetry peak of DMT oxidation is denoted. The inset represents the molecular structure of DMT. B: Background-corrected current response upon addition of 2×10^{-4} M DMT given as a function of number of layers.

Based on the observed response it is clear that the anodic peak between 0.2 and 0.3 V *vs.* SCE can be ascribed to direct electrochemical oxidation of DMT. This peak is followed by two cathodic peaks observed between 0 and 0.3 V *vs.* SCE.

Such a clear voltammetric response presents a basis for DMT detection based on its electrochemical transformations. Also, we have analyzed the effect of the number of layers on the voltammetry response of PDAC/GO-modified Ag electrode (Fig. 5B) and concluded that the highest sensitivity is observed for one PDAC/GO layer. Based on these results it can be concluded that two factors determine the overall electrochemical response. The first one is the specific interaction of PDAC/GO layers with DMT. We suspect that there is adsorption of DMT on GO in line with previous literature results [24] which is essential to concentrate DMT on the electrode before charge-transfer occurs. The other factor is the layer conductivity which is low (both GO and PDAC are poor conductors) and hinders charge-transfer. Based on the results in Fig. 5B we conclude that in the case of one PDAC/GO layer these opposing factors are properly balanced.

Beside cyclic voltammetry, we also performed EIS measurements at different potentials (Fig. 6). At two different potential, EIS spectra of PDAC/GO-modified Ag electrode are different and also respond differently to the presence of DMT. The introduction of DMT induces changes in the EIS response, and these changes are more pronounced and in line with the change of the DMT concentration in the high potential region (*i.e.* 0.3 V *vs*. SCE). There is obvious DMT oxidation at this potential (Fig. 5A), and the changes in the EIS spectra are in line with reduced charge-transfer resistance.

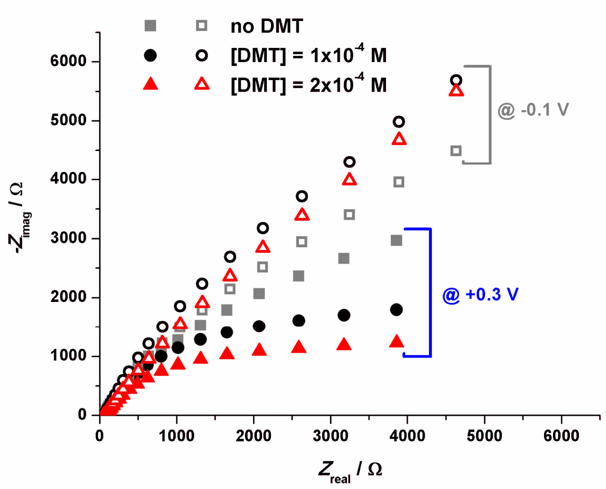

Figure 6. Impedance spectra of PDAC/GO-modified Ag electrode (1 layer) at different concentrations of DMT and two different potentials: −0.1 V vs. SCE (open symbols) and +0.3 V *vs.* SCE (full symbols).

Here we do not intend to fit these EIS spectra to any specific equivalent circuit as this would require deeper kinetic analysis of DMT oxidation, but it is clear that EIS measurements could be yet another strategy for DMT detection, besides its direct oxidation in potentiodynamic regime. However, we performed Kramers–Kronig analysis on the EIS data, folowing the the method of Boukamp [25] (Fig. 7), and confirmed that systems are linear, stable and causal. The goodness of fit was always below 10^{-4}. This result stimulates further and deeper analysis to unveil the underlying physical process in electrochemical behavior of DMT on used sensing electrodes as the presented results show very attractive possibility for direct electrochemical detection of DMT without additional functionalization of electrodes with bioreceptors.

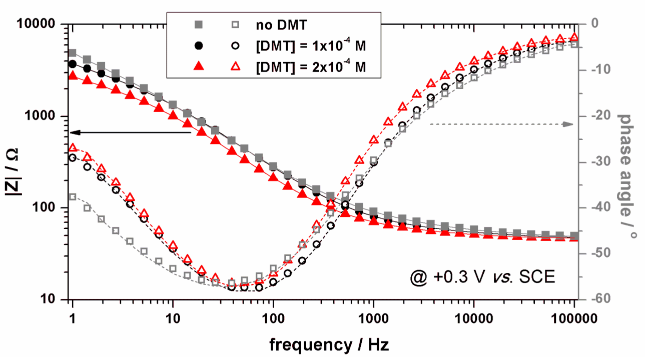

Figure 7. Kramers-Kronig fit of the EIS data for PDAC/GO-modified Ag electrode (1 layer) at different concentrations of DMT at +0.3 V *vs*. SCE. Symbols give experimental data points, while lines give the results of the fit.

IV. Conclusions

It is possible to observe direct electrochemical transformations of organophosphorous pesticide dimethoate on PDAC/GO-modified Ag electrodes. The functionalization using layer by layer deposition is very important as it improves electrochemical response and presents a basis for detection of DMT. The best behavior is observed in the case of only one PDAC/GO layer. Such behavior is ascribed to the properly balanced interactions of DMT with PDAC/GO layer and the increase of the electrical resistivity of the PDAC/GO layer with its thickness (*i.e.* the number of deposition steps).

In the present contribution, we show that DMT detection is possible either using cyclic voltammetry or EIS measurements. In the first case, DMT oxidation is seen around 0.3 V *vs*. SCE, while in the latter case EIS response is very sensitive to DMT concentration at the same electrode potential. However, it is also important to note that direct electrochemical oxidation of DMT presents a basis for the application of much more sensitive electrochemical techniques like square wave voltammetry or differential pulse voltammetry. The potential of described PDAC/GO-modified Ag electrodes in the detection of DMT can be fully exploited using these techniques.

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