Electrochemical Sensor based on Reduced Graphene Oxide/PDAC for Dimethoate Pesticide Detection

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Abstract—**Extensive use of pesticides and their accumulation in the environment requires swift actions in terms of their removal, detection, and quantification. Currently, golden standard methods used for quantification of pesticides require expensive instrumentation and are not suitable for quick measurements outside of properly equipped laboratory. Here we investigate the detection of dimethoate (DMT) using PDAC/reduced graphene oxide (rGO)-modified Ag electrodes. The sensor performance depends on the temperature used for the reduction of graphene oxide (GO) in PDAC/GO bi-layer on Ag electrode. Using this combination of nanomaterials, we show the quantification of DMT with either voltammetry or impedance spectroscopies. The former approach relies on direct electrochemical transformations of DMT which are observed at relatively high anodic potential around 0.3 V *vs.* saturated calomel electrode. Impedance spectroscopy shows complex behavior with increasing DMT concentration, but seems to be rather sensitive to low DMT concentrations. These results present a possible direction to the development of highly efficient electrochemical sensors for pesticide detection.**

Keywords— environmental sensing, organophosphorus pesticide, dimethoate; electrochemical detection; reduced graphene oxide; cyclic voltammetry; impedance spectroscopy

I. INTRODUCTION (*HEADING 1*)

Intense usage of pesticides in agriculture is becoming a high concern and a serious public health hazard throughout the world. Their long lasting in the environment is also a big concern due to their toxic nature towards mammals. These pesticides are used against the mites and pests. However, pesticides still reach over 98% places which are not the target species [1]. The usage of pesticides continues driven by the rapid increase of the world's population and the demand for satisfying the food needs [2]. Of various kinds of pesticides, the organophosphorus pesticides (OPPs) have been widely used in agriculture for variety of purposes [3]. Studies show that the residues of OPPs in plants cause a great amount of harm to the humans [4-7]. OPPs and the products of their chemical transformations present potential hazards due to a high mammalian toxicity. In consideration to the human health concern, the Codex Alimentarius Commission of the United Nation's Food and Agriculture Organization and the World Health Organization have established maximal residue limit (MRL) for pesticides over a variety of foods [8]. Dimethoate (DMT) is a commonly used OPP with many target species [9]. The toxic nature of this pesticide, like in the case of other OPPs, is based on acting on the nervous system by blocking acetyl-cholinesterase (AChE), an enzyme needed for the nervous system of insects, resulting in their eradication [10, 11]. However, this effect is also operative in humans and animals. Therefore, pesticide detection systems that can monitor and analyze pesticides are of uttermost importance for human health and environment protection. Thus, the development of pesticide detection systems facilitating the assessment and analysis of these hazards is a necessity.

The traditional analytical methods used to analyze pesticides are gas chromatography (GC), liquid chromatography (LC) and their combinations like gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-mass spectrometry (LS-MS), high performance liquid chromatography (HLPC) [12] [15]. The quantitative analysis with high sensitivity and selectivity is provided by these techniques but they are time consuming, complex equipment is required, and are also rather expensive. The development of alternative techniques is attractive if strong sensor stability and high sensitivity can be achieved. Carbon based nanomaterials with their unique physical and chemical properties gained a huge attention in numerous fields of science and have shown significance in various applications. Among many different types of carbon materials, graphene oxide (GO), alone or in combinations with different materials, has shown great capabilities in different applications including electrochemical sensing [16-18].

In our previous work we demonstrated that direct electrochemical detection of DMT is possible using layer-by-layer deposited poly(diallydimethylammonium chloride) (PDAC) and GO on silver [19]. The sensors were prepared by layer-by-layer dip coating method, where the silver electrodes on kapton sheet are stacked by layers of GO/PDAC. GO was acting as anionic solution where, PDAC was acting as cationic solution. The highest sensitivity was obtained for only one PDAC/GO bi-layer. In this paper, we further elaborate this work and investigate electrochemical sensors based on PDAC/reduced GO (rGO). rGO was obtained by thermal reduction of GO at elevated temperatures upon formation of PDAC/GO layers. The methods involved for DMT detection include cyclic voltammetry and impedance spectroscopy.

II. MATERIALS AND METHODS

A. Materials and Chemicals

GO aqueous solution was purchased from Graphene Supermarket (SKU-HCGO-W-175) and it has a concentration of 5 g/L. Flake size is in the range 0.5 – 5 µm and with single layer ratio of at least 60%. PDAC (20 wt.%) was purchased from Sigma Aldrich (CAS-No. 6062-79-32). DMT (CAS No. 60-51-5) was purchased from Sigma-Aldrich.

B. Electrode preparation

The silver electrodes of 17 mm length are painted on Kapton substrate of which 2 mm is left for the external 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 (1 wt. %). The shape of the deposited layer was controlled by putting a mask and making the deposition on the desired area. The PDAC/GO bilayer is deposited by alternating dip coating the silver electrode/Kapton for 5 minutes in GO (diluted to from 5 g/L to 1 g/L in distilled water) and PDAC. Between alternating depositions, the samples were cleaned with HCl diluted solution and drying with nitrogen. In this work we opted to form one bi-layer PDAC/GO, based on previously obtained results [19]. After the film deposition, the electrode with PDAC/GO is left overnight. The GO in a bi-layer deposited onto the electrodes was later reduced by thermal treatment. This is done by placing the electrodes on a hotplate device in air atmosphere. The thermal treatment is performed at three different temperatures (100, 150, and 200 °C). Partial conversion of GO to rGO was visually observed by the change of the coloration of GO from yellow-brown color to black.

C. Physical characterization

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 an 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.

D. Electrochemical measurements

Electrochemical measurements were performed 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 carried out 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.

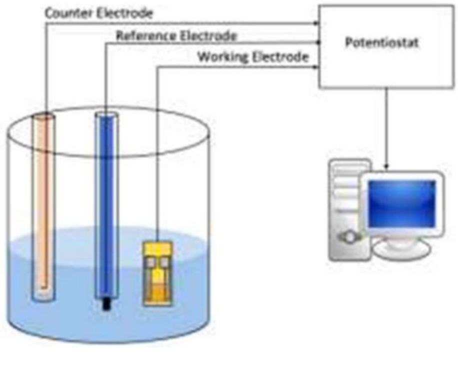

Fig. 1. a) Schematic of electrochemical setup using saturated calomel electrode), as reference, a wide Pt foil as a counter electrode, GO on Ag/Kapton as a working electrodes and 1 mol dm−3 KNO3 as a supporting electrolyte

III. REUSLTS AND DISCUSSION

A. Raman characterization

The Raman spectra of PDAC/GO layers reduced at different temperatures show typical features of a highly disordered material [19-22] with D (disorder) and G (graphitic) bands, located around 1350 and 1580 cm^{-1}, respectively, being the most pronounced features of the spectra (Figure 2). Also, the overtone bands, i.e. 2D region, are clearly visible. These bands are found at around 2670 cm^{-1} and 2930 cm^{-1}. Following Ref. [23] the first band is denoted as 2D (G') while the second one is denoted either as 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 significant amount of defects [23]. There are variations of relative intensities of observed bands (certain increase of G-to-D band intensity and decrease of 2D region with increasing temperature), but the overall conclusion is that thermal treatment did not change the disorder in rGO significantly. However, we expect that conductivity of rGO is changed with respect to that of parental GO (which is very poor conductor). This conclusion is in line with previous results considering conductivity changes of electrochemically reduced GO, showing that significant increase of conductivity is expected upon very mild reduction, [24] and color change upon thermal treatment. We note that Raman spectroscopy showed homogeneous distribution of PDAC/rGO over silver electrodes.

B. Electrochemical measurements

Before the electrochemical experiments with DMT were conducted, an extensive cycling of working electrode is performed to stabilize the voltammetric response. The potential window in which experiments are performed is chosen to prevent extensive surface oxidation of Ag (from anodic side) and further electrochemical reduction of rGO (from cathode side). In this way, any electrochemical response observed upon the addition of DMT can be ascribed solely to the interaction and electrochemical conversion of DMT with/on PDAC/rGO-modified Ag electrode. Cyclic voltammograms presented in Figure 3 depict the response of PDAC/rGO- modified Ag electrodes without DMT and upon two successive additions of DMT, at three different temperatures considered to reduce GO. From the results it is observed that the temperature opted to reduce GO certainly plays a role on electrochemistry of DMT on the bi-layer rGO/PDAC. Irrespective of the temperatures considered for the thermal annealing of GO, a direct electrochemical oxidation of DMT is observed.

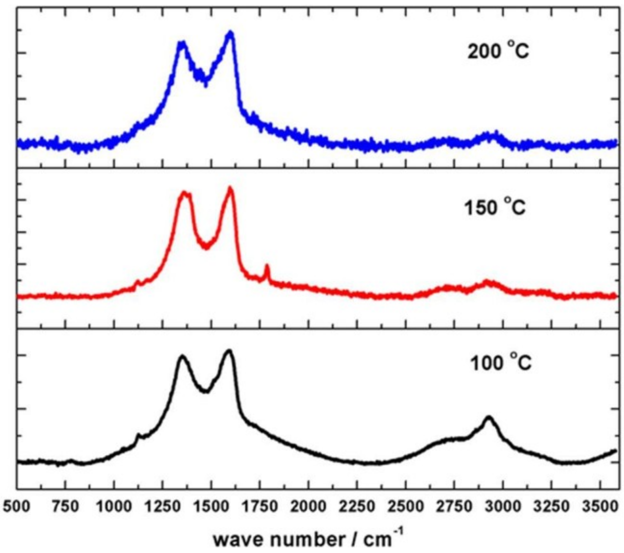

Fig. 2. Raman spectra of PDAC/rGO-modified Ag electrode prepared at different temperatures (as indicated in the figure).

Cyclic voltammograms in the absence of DMT show similar features for all three temperature of GO reduction. In the low potential region only capacitive response is seen, while close to anodic vertex potential surface oxidation of Ag starts. Upon addition of DMT in all three cases one can see one prominent anodic peaks observed in anodic scan, corresponding to oxidative transformations of DMT. Upon reversal of potential scan two reduction peaks can be seen which are associated with reduction of DMT oxidation of its products and possibly reduction of DMT. We believe that it is not very likely that DMT is reversibly converted to its oxo-analogue in anodic scan, and more radical transformation like fragmentation of DMT can be expected. Hence, it is more likely that in the cathodic scan some fragments of oxidized DMT get reduced. This can be supported by asymmetry in charge under anodic and cathodic peaks, where more charge is seen in cathodic scan. However, it is clear that the current response is dependent on the concentration of DMT, providing the basis for its quantification using prepared sensors. Still, we note that the best behavior in terms of current response to the increased concentration of DMT is seen for the case of PDAC/rGO prepared at 150 °C. For this temperature, we see a clear increase of anodic and cathodic current peaks with the increase of DMT concentration.

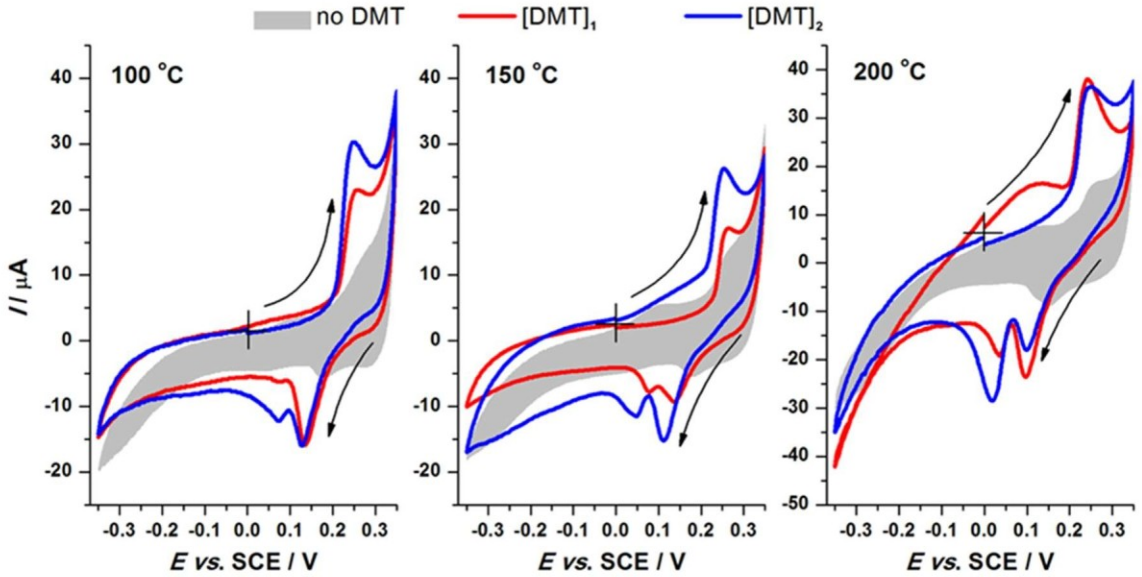

Fig. 3. Cyclic voltammograms of PDAC/rGO electrodes prepared at different temperatures (indicated in the figure). Shaded CV curves give electrode responses in the absence of DMT. Scan is started at 0 V vs. SCE (indicated by cross) and proceeded in anodic direction (indicated by arrows).

Figure 4 present cyclic voltagramms of PDAC/rGO prepared at 150 °C with successive additions of DMT. It is clear that current response (both anodic A1 peak and cathodic C1 peak) shows monotonous increase upon addition of DMT but linearity of peak current *vs*. DMT concentration is not obtained in the entire range of concentrations (Fig. 5 inset).

If the current of A1 peak or C1 peak is used to construct calibration curve for DMT detection similar sensitivities are obtained with good linearity in DMT concentration range 3×10^{-4} to 9×10^{-4} mol dm^{-3} ($R^2 > 0.92$). However, we propose that a better analytical signal is obtained when the difference between A1 (anodic, positive) and C1 (cathodic, negative) peak current is taken for construction of the calibration curve (see Figure 4, inset).

In addition to cyclic voltammetry, we have also performed EIS measurements of PDAC/rGO-modified Ag electrode at two different potentials, −0.1 and 0.3 V vs. SCE. Figure 5 show Nyquist plots with respect to the successive addition of DMT (the same concentrations as in the Figure 4). It is clearly observed that the addition of DMT induces changes to the spectra, yet the changes are not monotonous with increase in the concentration of DMT. EIS spectra recorded at lower potential indicate high resistances and no clear charge transfer. This agrees with the fact that DMT electrochemistry observed only at higher potentials and leads to the conclusion that DMT affects interfacial region and dominantly changes double layer capacitance in the low potential range. This is in line with the increase of capacitive response below −0.1 V vs. SCE observed in voltammetric experiments when DMT concentration is increased. In the high-potential region there are Faradaic processes associated with DMT electrochemistry which result with significantly altered EIS spectra recorded at +0.3 V when DMT is added to the solution. We note that non-monotonous change of the EIS spectra coincides with the concentration range where voltammetric response deviates from linearity and exclude the possibility of experimental error. We suspect that this behavior is due to the differences in the integrations of DMT with PDAC/rGO layer and silver surface when concentration of DMT increases. It is obvious that small additions of DMT affect surface processes on Ag at high anodic potentials (Figure 3, shaded cyclic voltammograms vs. cyclic voltammograms in the presence of DMT) and the overall response in EIS experiments is the results of both altered Ag surface oxidation/reduction and Faradaic processes associated with direct electrochemistry of DMT. Finally, we note that EIS seems to be much more sensitive to small concentrations of DMT while voltammetry seems as a reliable method for detection of higher concentrations of DMT.

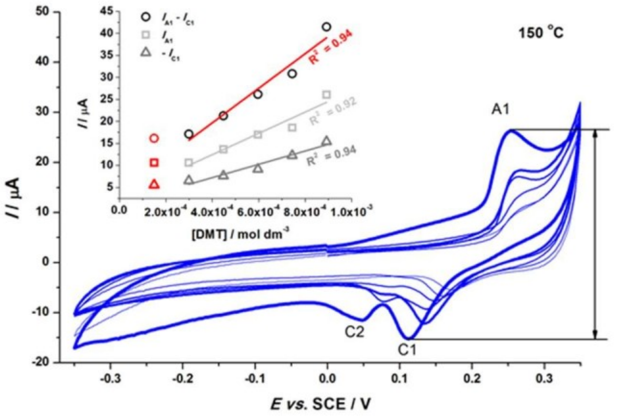

Fig. 4. Cyclic voltammograms of PDAC/rGO-modified Ag electrode prepared at 150 °C upon successive additions of DMT (thicker line indicates higher concentration). Inset gives three different calibration curves constructed using current peaks corresponding to A1, C1, or their combination.

IV. SUMMARY AND CONCLUSION

PDAC/rGO-modified Ag electrodes were prepared by layer-by-layer dip coating of Ag with PDAC and GO and successive thermal treatment at three different temperatures – 100, 150 and 200 °C. Raman spectroscopy confirmed functionalization of Ag surface. In preliminary voltammetric test, direct electrochemistry of DMT on prepared electrodes was confirmed while the best behavior in terms of current response (anodic and cathodic) vs. DMT concentration was observed for the electrode prepared at 150 °C. For this electrode more detailed analysis confirmed linear voltammetric responses in the concentration range 3×10−4 to 9×10−4 mol dm−3 (R2 > 0.94). As a strategy to increase sensitivity of voltammetric detection, it was proposed to use the combination of anodic and cathodic current response as analytical signal. EIS measurements also confirm that PDAC/rGO-modified Ag electrode is very sensitive to the presence of DMT, with a note that changes in EIS spectra are not monotonous with respect to DMT concentration. Presented results could be used as guidance for the development of novel electrochemical sensor for pesticides, based on their direct electrochemistry. In this way, complicated and expensive instrumentation can be avoided, while very quick detection is possible even outside a fully equipped laboratory.

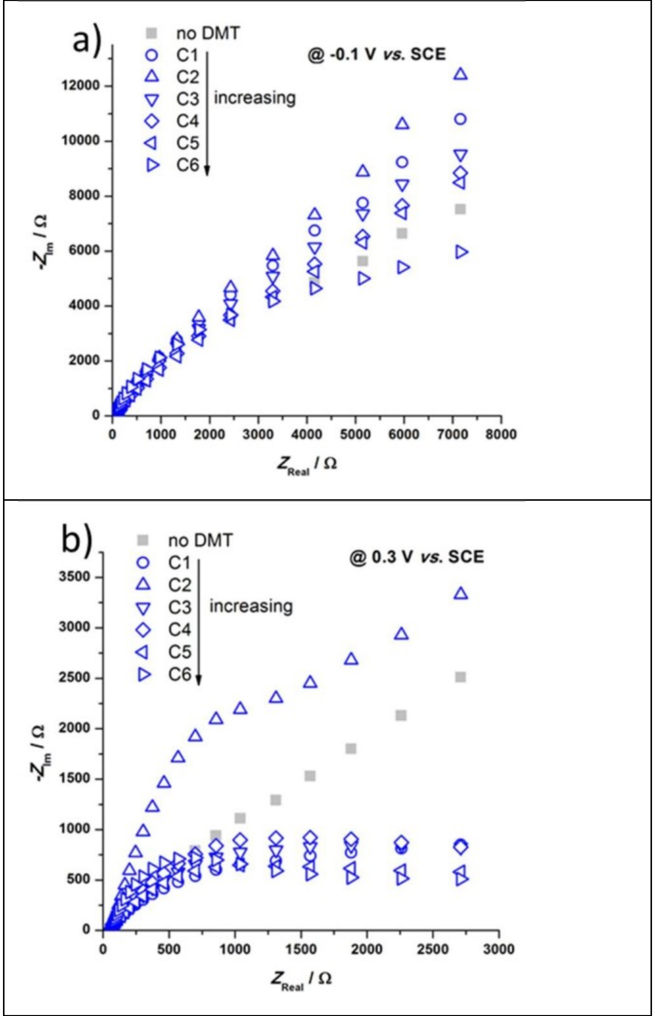

Fig. 5. EIS spectra (Nyquist plots) for PDAC/rGO-modified Ag electrode upon successive additions of DMT (same concentrations as in Figure 4). Spectra are provided for a) E = −0.1 V and b) E = 0.3 V vs. SCE. EIS spectra in the absence of DMT are given by filled squares.

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