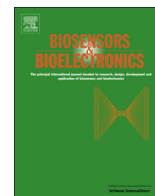




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# A facile graphene oxide based sensor for electrochemical detection of neonicotinoids

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## ABSTRACT

The increasing use of neonicotinoids in systematic seed treatment to crops is a serious cause of pollution of water resources and environment. Consequently, food sources can get eventually contaminated. To this end, it is desirable to develop suitable and effective platforms in order to obtain low-cost and sensitive sensors for neonicotinoids detection. In this work, graphene oxide modified electrodes were used as highly efficient electrochemical sensors for detection of two common insecticides – thiamethoxam and imidacloprid. The proposed sensor responded linearly in the concentration range of 10–200  $\mu\text{mol L}^{-1}$  for both analytes and the detection limits were determined as low as 8.3  $\mu\text{mol L}^{-1}$  and 7.9  $\mu\text{mol L}^{-1}$  for thiamethoxam and imidacloprid, respectively. Analytical performance was also evaluated on spiked water and honey samples.

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## 1. Introduction

Neonicotinoids were developed in the 1980s and they have represented the fastest growing class of insecticides introduced onto the market since 1990s (Jeschke and Nauen, 2008). All neonicotinoids bind selectively and with high affinity to the nicotinic acetylcholine receptors in the central nervous system of insects, thus disrupting neural transmission (Goulson, 2013; Jeschke et al., 2011). They are commonly applied to a broad variety of crops as seed dressings to control disease organisms, insects or other pests. Although seed treatment with neonicotinoids has important benefits regarding production, their use poses serious chemical contamination risks both for the environment and for food resources. In particular, the insecticides are taken-up systematically by the growing plant, transported along the tissues and thus can be presented in all plant parts, e.g. pollen or nectar that bees and other pollinating insects collect and consume (Godfray et al., 2014). Currently, the question concerning the contribution of neonicotinoids to the declining number of pollinators has led to controversy between the experts across United States and Europe (Goulson, 2013; Rundlöf et al., 2015; Wright et al., 2015). Moreover, neonicotinoids such as imidacloprid and thiamethoxam, have

shown high environmental persistence and susceptibility to transport into aquatic ecosystems through run-off and drainage of agricultural areas (Armbrust and Peeler, 2002).

Among others, electrochemical methods such as cyclic voltammetry (Kumaravel and Chandrasekaran, 2012), different pulse polarography or voltammetry (Guzvany et al., 2005; Papp et al., 2009) and square-wave voltammetry (Guiberteau et al., 2001) can be employed for simple, fast and inexpensive detection of neonicotinoids. So far, mercury-based electrodes, carbon paste electrodes, bismuth film electrodes and diverse composite modified glassy carbon electrodes have been described in the literature (Guzsvany et al., 2012).

Graphene-related materials, such as graphene oxide (GO) or reduced graphene oxide (rGO) present useful properties for their use in nanotechnology-based devices (Wu et al., 2007; Pumera, 2011). Graphene oxide, as one of the most used graphene derivatives, can be considered as individual sheets decorated with oxygen functional groups (hydroxyl, epoxy, carbonyl, carboxy etc.) on both the basal planes and edges (Mkhoyan et al., 2009). GO is usually prepared by the chemical treatment of graphite through oxidation with subsequent dispersion in water or suitable organic solvent (Dreyer et al., 2010; Georgakilas et al., 2015). Graphene oxide can be further reduced chemically or electrochemically into rGO with small number of defects and residual oxygen groups. From the electrochemical point of view, GO showing much lower

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electrical conductivity compare to rGO (Gao et al., 2009) due to the disrupted  $sp^2$ -hybridized carbon network (Ambrosi et al., 2014; Pumbera, 2010). Nevertheless, large specific area and strong hydrophilic nature of GO show great potential in the removal of aqueous pollutants, e.g. metal ions (Gong et al., 2014). The presence of oxygen groups also enables a high dispersibility of GO in a wide range of solvents, including water (Dreyer et al., 2010; Paredes et al., 2008), with a long-term stability. Therefore, stable GO dispersions can be deposited on various substrates in order to create conductive thin films by the mean of common methods such as drop-coating or spin-coating (Chen et al., 2012). In addition, reactive oxygen groups can be also favorably used for further chemical functionalization (Dreyer et al., 2010). The above mentioned properties together with high surface-to-volume ratio render GO suitable platform for development of enhanced electrochemical (bio)sensors (Gong et al., 2014; Han et al., 2013; Wu et al., 2013).

Herein, glassy carbon electrodes modified with graphene oxide prepared by Brodie method were used for the electrochemical sensing of two insecticides, namely thiamethoxam and imidacloprid. Electrochemical characteristics modified electrodes have been studied by the mean of cyclic voltammetry, electrochemical impedance spectroscopy, and square wave voltammetry. The results revealed that GO modified electrodes exhibit better and enhanced performance over the unmodified electrodes towards both analytes. Furthermore, modified electrodes were used for recovery test of spiked samples, i.e. river water and honey, in order to evaluate their overall analytical performance.

## 2. Materials and methods

### 2.1. Chemicals

Thiamethoxam, imidacloprid, boric acid, phosphoric acid, acetic acid, sodium hydroxide, potassium hexacyanoferrate (III), potassium hexacyanoferrate (II) trihydrate and graphite (Aldrich-282,863) were purchased from Sigma-Aldrich. All chemicals were of analytical grade and used without further purification. All solutions were prepared with deionized water.

### 2.2. Synthesis of graphene oxide

Graphene oxide (GO) was prepared according to the Brodie method (Brodie, 1855). Briefly, 10 g of graphite (Aldrich, 282,863), 200 mL distilled water and 85 g of  $\text{NaClO}_3$  were mixed in a round flask placed into an ice bath. A total of 60 mL of fuming  $\text{HNO}_3$  was added from a dropping funnel in 210 min during periodic stirring. The thick slurry was then left aging for 18 h at room temperature. The loss of large quantities of nitrous fumes was prevented by a distillation column and the addition of an extra volume of acid (40 mL) after aging. Then it was slowly heated to 60 °C by a basket heater ( $< 1.5 \text{ }^\circ\text{C min}^{-1}$ ) and kept at 60 °C for 8 h. The solid GO sample was washed with  $5 \times 200 \text{ mL}$  of 3 M HCl solution and  $7 \times 1 \text{ L}$  of distilled water to remove acidic and saline impurities until the electrical conductivity of the supernatant was below  $10 \text{ } \mu\text{S cm}^{-1}$ . Finally, the suspension was filtered and dried at 60 °C to yield a brown graphite oxide with an elemental composition of  $\text{C}_2\text{O}_{0.75}\text{H}_{0.24}$  and a water content of 10.0 wt% at 24 °C and 46% relative humidity. For preparation of the suspension, 10 mg of powder were placed in 5 mL of distilled  $\text{H}_2\text{O}$  pre-adjusted at  $\text{pH}=12.5$  by NaOH (1 M). The sample was sonicated (20 min, Branson 2510, 100 W, 45 kHz) and left under mild agitation (48 h). Then, the vial was left to stand still for 1 h and a 4 mL from the supernatant was removed in order to isolate a fine dispersion of graphene oxide.

### 2.3. Characterization methods

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI VersaProbe II (Physical Electronics) spectrometer using an Al  $K_{\alpha}$  source (15 kV, 50 W). All spectra were measured in a vacuum of  $1.4 \times 10^{-7} \text{ Pa}$  and at room temperature. The XPS spectra were evaluated with MultiPak (Ulvac - PHI, Inc.) software. All binding energy (BE) values were referenced to the C1s peak at 284.80 eV.

Samples for transmission electron microscopy (TEM) were prepared by casting a droplet of a dilute aqueous suspension of GO on copper grids coated by Formvar carbon film. Micrographs were obtained by a JEOL, JEM-2100 instrument operating at 200 kV.

### 2.4. Modification of electrodes

Glassy carbon electrodes (GCE, 3 mm in diameter, 2Theta Czech Republic) were polished on wet silicon carbide paper using alumina 1 and  $0.05 \text{ } \mu\text{m}$   $\text{Al}_2\text{O}_3$  powder sequentially and then washed in ethanol followed by distilled water. The GCEs were afterwards modified with graphene oxide by drop-coating:  $10 \text{ } \mu\text{L}$  of water dispersion was coated onto the GCE surface and allowed to dry at room temperature.

### 2.5. Electrochemical measurements

All electrochemical experiments were performed using a PGSTAT128N potentiostat (Metrohm Autolab B.V.) monitored by NOVA software. A conventional three-electrode cell configuration was employed. Modified GCEs were used as working electrodes, with a saturated Ag/AgCl (2Theta, Czech Republic) and a platinum wire as reference and counter electrode, respectively. All experiments were performed at room temperature.

## 3. Results and discussion

### 3.1. Characterization of graphene oxide

Graphene oxide (GO) was characterized by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) prior further electrochemical and analytical studies. C1s XPS spectra of GO showed considerable degree of oxidation represented by different oxygen functional groups in its structure. The deconvolution of C1s spectrum of GO (Fig. 1) revealed the presence of following carbon bonds: C-C (284.8 eV), C-O-C (286.6 eV), C=O (287.6 eV), O-C=O (289.5 eV) and C-O (285.7 eV).

The morphology of GO was studied also by TEM as shown in Fig. 2. Clearly, graphene oxide consists of sheets with large lateral sizes of several micrometers. On the other hand, it appears that the sheets are oligo-lamellar (few layers of GO), as suggested by their "transparency" to electrons, and as we have previously shown with AFM and dynamic light scattering (Liaros et al., 2013).

### 3.2. Electrochemical properties of GO modified electrodes

The effect of scan rate on the electrochemical behavior of GO modified electrode in  $0.1 \text{ mol L}^{-1}$  KCl containing  $5 \text{ mmol L}^{-1}$   $[\text{Fe}(\text{CN})_6]^{4-/-3-}$  was studied by cyclic voltammetry (see Fig. 3). As it can be seen, the peak currents increase linearly with the square route of scan rate in the range of  $10\text{--}300 \text{ mV s}^{-1}$  thus indicating that the electrochemical process at the electrode surface is diffusion controlled. The linear regression equation can be expressed as  $I_a = 6.4x + 5.2$  with  $R^2 = 0.997$  and  $I_c = -6.4x - 6.4$  with  $R^2 = 0.996$ , respectively.

The electron transfer properties were further characterized by

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