



# Hydrophilic graphene surface prepared by electrochemically reduced micellar graphene oxide as a platform for electrochemical sensor

Nontapol Akkarachainon<sup>a</sup>, Pranee Rattanawaleedirojn<sup>b</sup>, Orawon Chailapakul<sup>a,c,\*</sup>,  
Nadnudda Rodthongkum<sup>b,\*\*</sup>

<sup>a</sup> *Electrochemistry and Optical Spectroscopy Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand*

<sup>b</sup> *Metallurgy and Materials Science Research Institute, Chulalongkorn University, Soi Chula 12, Phayathai Road, Pathumwan, Bangkok 10330, Thailand*

<sup>c</sup> *National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Phayathai Road, Pathumwan, Bangkok 10330, Thailand*

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## ABSTRACT

Graphene is one of the promising hydrophobic carbon-based nanomaterials used for electrode modification in electrochemical sensor. However, hydrophobicity of graphene makes it incompatible with aqueous electrolyte solution, leading to significant impediment to the electron transfer process. Here, we aim to alter graphene property to be hydrophilicity by using an electrochemically reduced micellar graphene oxide for electrode surface modification. Then, this system was applied for the simultaneous determination of toxic pesticides (e.g. carbofuran and carbendazim). Interestingly, the modified electrode offers an improved electrochemical sensitivity, verified by a drastic increase in current signal of carbofuran (4 times) and carbendazim (12 times) compared to an unmodified electrode. Under the optimal conditions, low detection limits of carbofuran and carbendazim were found to be  $10 \mu\text{g L}^{-1}$  and  $5 \mu\text{g L}^{-1}$ , respectively. Ultimately, this system was successfully applied for the sensitive and simultaneous determination of carbofuran and carbendazim residues in various agricultural products.

## 1. Introduction

With the advent of nanotechnology, various nanomaterials, such as metallic nanoparticles [1,2] and carbon based nanomaterials (*i.e.* fullerenes [3], carbon nanofibers [4], carbon nanotubes [5], carbon nanodots [6], graphene) have been used to modify the electrode surfaces. Among carbon based nanomaterials, graphene (G) [7–12] has become a promising material for electrode modification due to its outstanding properties, such as large surface area, fast electron transfer kinetics and high electrical conductivity. However, the use of pristine G always suffers from a high tendency of self-agglomeration and re-stacking via Van der Waals interaction, leading to loss of effective surface area and conductivity; thus, it is necessary to prevent the self-agglomeration of G. Alternatively, graphene oxide (GO), containing oxygen groups on the plane of carbon atom, has become an attractive material. An important property of GO is well dispersibility in water due to the high polarity of oxygen; nonetheless, GO is often classified as an electrical insulator because of the disruption from the oxygen groups. Therefore, GO is used as a precursor and reduced into pristine

G by removal of oxygen-groups, described as a reduction reaction. GO which is reduced into G is called reduced graphene oxide (RGO). There are several methods for producing of RGO [13–16] including chemical reduction, thermal reduction and electrochemical reduction. From the previous reports [17], although RGO prepared by chemical reduction is a large scale method; however, it was contaminated by the reducing agents resulting in poor-quality yields. Likewise, for thermal reduction at high temperature, it usually produces the very high surface area of RGO, but the heating process can damage the structure of RGO sheets [18]. Nevertheless, GO which is reduced by electrochemical method, denoted as an electrochemically reduced graphene oxide (ERGO) [19,20], can be created as the best quality compared to others. Unfortunately, because of the entire carbon structure of G, it is classified as a hydrophobic material [21]. Thus, the surface of graphene refuses to closely contact with an aqueous solution. In this work, we aim to alter a property of graphene surface to be hydrophilic by simply using a common surfactant for improving of the interfacial property.

Surfactants are the surface-active compounds consisting of hydrophilic heads on one side and long chain hydrophobic tails on another

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [corawon@chula.ac.th](mailto:corawon@chula.ac.th) (O. Chailapakul), [Nadnudda.R@chula.ac.th](mailto:Nadnudda.R@chula.ac.th) (N. Rodthongkum).

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side. Normally, the surfactant molecules possess an important property of reducing the interfacial tension. Previously, surfactants were used to prevent the self-agglomeration of G by intercalation between G sheets [22–24]. Furthermore, it has been previously reported that surfactant can improve the interface property between electrode and electrolyte solution [25]. Also, it was well known that micelles are formed spontaneously in aqueous solution at a sufficiently high concentration of surfactant. There are several applications that use micelles for electrode modification to improve the electrode surface properties [26,27]. Accordingly, surfactant becomes a material of interest for the development of a new electrode for an electrochemical sensor. Here, cetyltrimethylammonium bromide (CTAB), a positively charged surfactant with quaternary ammonium group, is used along with GO for the electrode surface modification.

One of the current environmental problems which our world is confronting is a contamination of natural resource by toxic chemical substances, especially for the pesticide residues. Carbofuran (CBF) and carbendazim (CBZ), generally used as an insecticide and a fungicide, are considered as one of the most hazardous pesticides. Both of them have potential to wreak widespread destruction of natural environment and potentially contaminate in various agricultural products. With inadvertent use of them, there will be inevitable contamination in air, food and water and adversely impact through the food chain [28]. Consequently, they not only devastate wildlife, but also severely harm to the human health. Previously, it was reported that CBF and CBZ are the carcinogenic substances causing chronic and acute diseases [29–31]. Thus, the development of sensitive sensor for detection of these compounds is essential to control the contamination in environment.

Traditional analytical methods are commonly used for CBF and CBZ determination, such as ultraviolet spectroscopy [32], spectrophotometry [33], gas chromatography [34], high-performance liquid chromatography [35,36] and capillary electrophoresis [37]. Unfortunately, these techniques still have some drawbacks, for example, high cost, non-portability, long analysis time and complicated sample pretreatment. Thus, electrochemical technique has become an interesting option due to its inexpensiveness, fast analysis and portability; however, the performance of conventional electrodes has not sufficed to accomplish the sensitive analyses. To unravel this problem, modification of working electrode surface to improve both analytical performance and sensitivity of electrochemical sensor is very crucial.

Herein, the modified electrodes were fabricated by using an electrochemically reduced micellar graphene oxide (ERMGO) and CTAB, and then this system was applied for the simultaneous detection of CBF and CBZ in the agricultural products. The electrode preparation was thoroughly optimized, and the analytical performances of ERMGO modified electrode were compared with ERGO modified electrode and unmodified electrode. Overall, this system offers several advantages, such as fast and easy fabrication, excellent electrochemical sensitivity, high analytical performance and extremely low cost. Indeed, this novel platform might be an alternative approach for further development of high performance electrochemical sensor in various applications.

## 2. Experimental

### 2.1. Materials

Graphene oxide (GO) was purchased from XF Nano, Inc. (Nanjing, China). Cetyltrimethylammonium bromide (CTAB), potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) and disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) were obtained from Sigma-Aldrich (St. Louis, MO, USA). All aqueous solutions were prepared in Milli-Q water (18.2 M $\Omega$  cm). Carbon graphene ink and silver/silver chloride ink were purchased from Gwent group (Torfaen, United Kingdom) for screen-printed carbon electrode preparation.

### 2.2. Apparatus

The electrochemical measurements using square-wave voltammetry (SWV) and cyclic voltammetry (CV) were performed on a 910 PSTAT mini (Metrohm Siam Company Ltd). SWV measurements of CBF and CBZ were carried out using an applied potential ranging from 0 to 1.0 V with the optimal parameters including step potential of 10 mV, amplitude of 20 mV and frequency of 10 Hz. Furthermore, electrochemical impedance spectroscopy (EIS) was performed on  $\mu$ AUTOLAB type III potentiostat (Metrohm Siam Company Ltd.) using a solution of 0.5 M KCl containing 1 mM  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  with a frequency range from 0.1 to  $10^5$  Hz and an amplitude of 0.01 V.A. JSM-6400 field emission scanning electron microscope (Japan Electron Optics Laboratory Co., Ltd., Japan) was used for electrode surface morphology characterization. Contact angle measurement was performed by using a 200-k1 goniometer (Ramehart Instrument Co).

### 2.3. Preparation of screen-printed carbon electrode (SPCE)

A three-electrode configuration of screen-printed carbon electrode pattern was designed by Adobe Illustrator. The electrodes were prepared by using an in-house screen-printing procedure. Firstly, silver/silver chloride was screened on PVC substrate as reference electrode (RE) and conducting pad, and then heated up at 55 °C until the ink was dried out. Afterwards, carbon graphene ink was screened over as working electrode (WE) and counter electrode (CE), and heated up at 55 °C till the ink was dried out [38].

### 2.4. Preparation of GO solution for electrode modification

To prepare GO solution, 1.6 mg of GO was dispersed in 1 mL of water with an ultrasonication for 2 h. After that, the dispersed GO solution was mixed with 0.1 M phosphate buffer solution pH 7 at the ratio of 1:1, denoted as GO solution. Likewise, micellar graphene oxide solution was prepared. Firstly, 0.02 g of CTAB was dissolved in 10 mL of water. Secondly, 1.6 mg of GO was sonicated in 1 mL of water for 2 h. Afterwards, the mixture of dispersed GO solution, 0.1 M phosphate buffer solution pH 7 and CTAB solution was mixed at a ratio of 10:9:1, denoted as MGO solution.

### 2.5. Fabrication of electrochemically reduced graphene oxide modified electrode

To fabricate electrochemically reduced graphene oxide modified electrode, 100  $\mu\text{L}$  of GO solution was dropped onto a SPCE, covering over 3 electrodes. Cyclic voltammetry was performed from  $-0.5$  to  $-1.7$  v (vs Ag/AgCl) at a scan rate of 100  $\text{mV s}^{-1}$  for 10 cycles. Eventually, reduced graphene oxide was deposited on the working electrode surface. This modified electrode is called ERGO modified electrode. Similarly, to fabricate electrochemically reduced micellar graphene oxide modified electrode, 100  $\mu\text{L}$  of MGO solution was dropped onto a SPCE. Then, the reducing process was carried out by cyclic voltammetry in a potential range of  $-0.5$  to  $-1.5$  V (vs Ag/AgCl) at a scan rate of 100  $\text{mV s}^{-1}$  for 10 cycles. Finally, reduced micellar graphene oxide would be deposited onto the working electrode surface. This modified electrode model is denoted as ERMGO modified electrode.

### 2.6. Real sample preparation

Three agricultural products were selected as real samples including soybeans, rice and tomatoes. They were purchased as raw products from local markets. To prepare the real samples, agricultural product specimens were infused in 50 mL of chloroform and leaved them for a day. Next, 30 mL of chloroform was collected, and removed by rotary evaporator. Then, 10 mL of ethanol was added instead and collected

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