



Paste electrode based on the thermally reduced graphene oxide in ambient air – Its characterization and analytical application for analysis of 4-chloro-3,5-dimethylphenol

Mariola Brycht^{a,*}, Andrzej Leniart^{a,1}, Janez Zavašnik^{b,c}, Agnieszka Nosal–Wiercińska^d, Krzysztof Wasinski^e, Paulina Pórolniczak^e, Sławomira Skrzypek^{a,1}, Kurt Kalcher^f

^a University of Lodz, Faculty of Chemistry, Department of Inorganic and Analytical Chemistry, Tamka 12, 91-403 Lodz, Poland

^b Centre for Electron Microscopy and Microanalysis, Jožef Stefan Institute, Jamova Cesta 39, SI-1000 Ljubljana, Slovenia

^c Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Strasse 1, 40237 Düsseldorf, Germany

^d Maria Skłodowska–Curie University, Faculty of Chemistry, M. Skłodowska–Curie Sq. 3, 20-031 Lublin, Poland

^e Institute of Non–Ferrous Metals Division in Poznań, Central Laboratory of Batteries and Cells, Forteczna 12, 61-362 Poznań, Poland

^f Karl–Franzens University, Institute of Chemistry – Analytical Chemistry, Universitätsplatz 1, A–8010 Graz, Austria

ARTICLE INFO

Article history:

Received 7 April 2018

Received in revised form

29 May 2018

Accepted 4 June 2018

Available online 5 June 2018

Keywords:

Graphene

Reduced graphene oxide

Paste electrode

4-chloro-3,5-dimethylphenol

Square-wave voltammetry

ABSTRACT

In this study, thermally reduced graphene oxide (TRGO) was synthesized *via* thermal reduction of graphene oxide in air and used to construct a thermally reduced graphene oxide paste electrode (TRGOPE). The TRGO was characterized under a structural and morphological point of view. A wide range of complementary instrumental techniques, such as Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) spectroscopy, transmission electron microscopy (TEM), selected area electron diffraction (SAED), and atomic force microscopy (AFM), were applied. A novel electrochemical sensor based on TRGO in air was constructed, and an electrochemical characteristics of the TRGOPE were investigated using electrochemical techniques, such as electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Compared to a conventional carbon paste electrode (CPE), a significantly improved electrochemical response of TRGOPE toward a ferrocyanide/ferricyanide redox couple was found due to the excellent conductivity of graphene. The TRGOPE was further successfully applied for the determination of an antiseptic and disinfectant agent, 4-chloro-3,5-dimethylphenol (PCMX). TRGOPE showed an excellent electrocatalytic oxidation activity toward PCMX with higher current response, improved sensitivity toward determination of PCMX as well as much lower limits of detection (LOD) than a CPE allowing highly sensitive voltammetric determination of PCMX. Under optimized experimental conditions, the square-wave voltammetric (SWV) signal of PCMX at a potential of *ca.* +0.7 V increased linearly with the increase of the PCMX concentration in the linear dynamic range (LDR) from 0.1 to 4.5 $\mu\text{mol L}^{-1}$ with an LOD of 20.8 nmol L^{-1} , a sensitivity of 5.0 $\mu\text{A L } \mu\text{mol}^{-1}$, and a precision expressed as an intra-day and inter-day precision ($n = 10$) of 1.4% and 2.0%, respectively, with 0.1 $\mu\text{mol L}^{-1}$ of PCMX. Furthermore, the applicability of the TRGOPE for PCMX analysis in water samples (river and tap waters) was successfully demonstrated with satisfactory results.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Voltammetry is a useful, simple and straightforward analytical technique commonly used to determine electrochemical properties

and perform quantitative analyses of electrochemically active compounds. The advantages of the voltammetry over other analytical techniques, such as chromatography, spectroscopy, and spectrometry, include short analysis time, lower apparatus cost, simplicity of use, relatively high sensitivity with a very large useful linear concentration range, the ability of miniaturization, applicability for real-time detection, and less sensitivity to matrix effects [1]. Above-mentioned assets make voltammetric techniques convenient and promising tools in the analysis of electrochemically

* Corresponding author.

E-mail address: mariola.brycht@chemia.uni.lodz.pl (M. Brycht).

¹ ISE Member.

active compounds, and one of them, namely square-wave voltammetry (SWV), is considered as a very fast (seconds), highly sensitive technique in which discrimination and elimination against charging background current can be obtained [2,3]. Extremely important in many electrochemical techniques is the type of electrodes used in them. Therefore, in recent times, great efforts have been taken in order to develop improved and cutting-edge electrodes. Presently, carbon-based paste electrodes are promising electrochemical sensors and they represent one of the most frequently used types of working electrodes in voltammetry [4–6]. The conventional carbon paste electrodes (CPEs) as a mixture of an electrically conducting graphite powder and an insulating liquid [4] are nowadays classified as bare or unmodified CPEs [5]. CPEs provide many advantages, such as fairly inert electrochemistry, quick and very effective renewability, wide applicable potential window, low residual background current, very simple fabrication, and high stability [6]. In addition, CPEs can be simply modified with various types of modifiers [4,7] in order to obtain novel sensors which are characterized by lower detection limit, higher sensitivity and lower overpotential than unmodified conventional CPEs. The most often used CPEs modification type is carried out by means of a partial substitution of graphite powder with other materials, however, complete replacement of graphite with other carbonaceous materials, such as for example glassy carbon, carbon nanotubes or graphene, can also be made.

Nowadays, the most extensively investigated allotrope of carbon is a two-dimensional honeycomb lattice of sp^2 -bonded carbon atoms, graphene [8]. Significant attention of the scientific community has been paid to this material in recent years due to its unique properties, such as exceptionally high electrical and thermal conductivities, large specific surface area, chemical inertness, and considerable mechanical strength [8,9]. These extraordinary properties make graphene a suitable nanomaterial for electrochemical applications, especially in sensing and biosensing [10].

Hitherto, various ways and techniques have been introduced to synthesize reduced graphene oxide (RGO), and the use of different reduction methods has a major impact on the final structural, morphological, electrical, and physical properties of synthesized RGO [11]. However, among all reduction methods, chemical [12,13] and thermal [13] reductions of graphene oxide (GO) are the most commonly used methods. Although, the synthesis of RGO using chemical reduction of GO allows to smoothly remove the functional groups from GO [14], unfortunately, this method have also some disadvantages. Due to the removal of oxygen atoms, the chemically reduced graphene oxide (CRGO) shows strongly agglomerated, hydrophobic and crumpled structure [15]. In addition, the use of strongly reducing agents, which are usually carcinogenic, introduces several impurities within CRGO, which can strongly influence the properties of RGO (its conductivity and electrochemical activity). In comparison to the chemical reduction, the thermal reduction of GO shows many advantages [15]. First, there is no necessity for the separation of RGO from the chemical reduction by-products. Second, thermally reduced graphene oxide (TRGO) shows a wrinkled structure with high reduction level and higher electrical conductivity of RGO. Last but not least, the degree of thermal reduction can be regulated by temperature, duration of heating, as well as gaseous environment (argon, nitrogen, ultrahigh vacuum, air) [15,16].

It is well-known that phenol and its derivatives are chemical compounds regarded as major environmental and water pollutants [17]. Among all phenolic compounds, the most widespread and the largest group of phenols are chlorophenols, commonly used in large quantities in wood preservatives, leather impregnating agents, dyestuffs, pesticides, detergents, personal care formulations, stabilizers, antiseptics, disinfectants, and many other

products [18–20]. In addition, chlorinated phenols are considered as very toxic and carcinogenic. Due to their widespread use, the environmental contamination of wastewater, groundwater, and consequently, drinking water supplies with these chemicals is noted [21,22]. One of the phenolic compounds is 4-chloro-3,5-dimethylphenol, also known as chloroxylenol (PCMX, Fig. 1) which is widely used as an antibacterial agent in many antiseptic and disinfectant formulations [23]. PCMX is also used as a biocide [23,24] and as a preservative in cosmetics (creams, deodorants, antibacterial soaps, hair care products), pharmaceutical products (wound cleanser), air deodorants, and in ECG paste [24]. Although, PCMX has low mammalian toxicity [25], it is toxic to freshwater fish and aquatic invertebrates [26]. In addition, PCMX has both mutagenic and teratogenic effects, might have adverse reproductive effects, may cause skin and eye irritation or produce allergic reactions [25]. Up to now, by far the most frequently used methods for the determination of PCMX have been high-performance liquid chromatography (HPLC) with fluorescence detection (HPLC-FL) [27] and HPLC with electrochemical detection (HPLC-EC) [28], liquid chromatography with UV detection (LC-UV) [29], ultra-performance liquid chromatography with multi-wavelength photoelectric diode-array detection (UPLC-PDA) [30], and gas chromatography with tandem mass spectrometric detection (GC-MS/MS) [31]. PCMX has been also determined using micellar electrokinetic chromatography (MEKC) [32] and capillary electrophoresis with amperometric detection (CE-AD) [33]. So far, there is no report in the scientific literature concerning the electrochemical investigations of PCMX.

In this study, 4-chloro-3,5-dimethylphenol was chosen as a model analyte, and the TRGOPE was applied to investigate the electrochemical behavior of PCMX using CV and SWV for the first time in this paper.

2. Experimental

2.1. Chemicals

The chemicals used in this work were of analytical reagent grade and used without further purification. Potassium ferricyanide ($K_3[Fe(CN)_6]$, 5.0 mmol L^{-1}) and potassium ferrocyanide ($K_4[Fe(CN)_6] \times 3H_2O$, 5.0 mmol L^{-1}) were dissolved in 0.1 mol L^{-1} potassium chloride (KCl) (all from Witko, Poland). A stock solution of 1.0 mmol L^{-1} PCMX (99% purity, Sigma-Aldrich, Poland) was prepared by dissolving an appropriate amount of PCMX in acetone, and stored in a glass flask in a refrigerator when not used. Britton-Robinson buffer solution (BRBS, 0.04 mol L^{-1}) was used as supporting electrolyte and was prepared using 0.04 mol L^{-1} phosphoric acid, 0.04 mol L^{-1} acetic acid, and 0.04 mol L^{-1} boric acid. The required pH values in the pH range of 2.0–11.0 were adjusted with 0.2 mol L^{-1} sodium hydroxide. The solutions were prepared using triply distilled water. Graphite powder (Lonza KS 5–75), potassium bromide (KBr, spectrometry grade, Sigma-Aldrich,

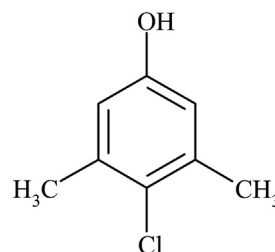


Fig. 1. Chemical structure of 4-chloro-3,5-dimethylphenol.

Download English Version:

<https://daneshyari.com/en/article/6602155>

Download Persian Version:

<https://daneshyari.com/article/6602155>

[Daneshyari.com](https://daneshyari.com)