Electrochimica Acta 127 (2014) 86–94

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Differential pulse striping voltammetric determination of molluscicide niclosamide using three different carbon nanomaterials modified electrodes

Yuanyuan Yao[a,b], Long Zhang[a,b], Xuemin Duan[a], Jingkun Xu[a,*], Weiqiang Zhou[a], Yangping Wen[a,b,*,1]

[a] Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, PR China
[b] College of Science, Jiangxi Agricultural University, Nanchang 330045, PR China

ARTICLE INFO

Article history:
Received 22 October 2013
Received in revised form 4 January 2014
Accepted 4 February 2014
Available online 17 February 2014

Keywords:
Carbon nanotube
Graphene oxide
Niclosamide
Anodic stripping voltammetry
Electrochemical sensor

ABSTRACT

Three different carbon nanomaterials modified electrodes based on single(multi)-walled carbon nanotubes (S(M)WCNTs) and electrochemically reduced graphene oxide (ER-GO) modified glassy carbon electrodes (GCE) were fabricated and used to investigate the electrochemical behavior of niclosamide (NA) by cyclic voltammetry and differential pulse anodic stripping voltammetry. Experimental parameters, such as the preconcentration time, scan rate, and the pH value of buffer solution were optimized. A possible working mechanism for the electrochemical detection of NA was also proposed. The electrochemical performances of these three carbon nanomaterials modified electrodes were compared with one another. Among three modified electrodes, ER-GO/GCE displayed lowest peak potential, highest sensitivity, best repeatability, reproducibility and peak shape as well as higher peak current response. Additionally, ER-GO/GCE exhibited better linearity than S(M)WCNTs/GCE over ranges from 0.020 to 23.1 μM with the detection limit of 6.6 nM (*S*/*N* = 3), and also successfully employed for real sample analysis with NA tablets. Satisfactory results indicated that ER-GO/GCE can provide a promising candidate for the trace analysis of NA in agriculture.

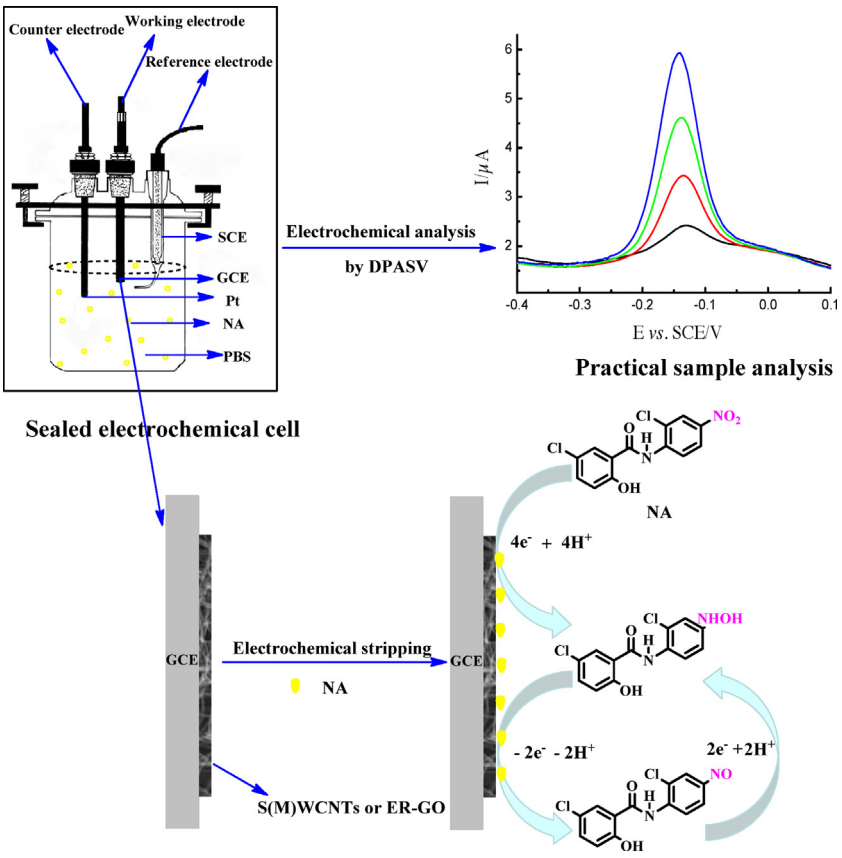
1. Introduction

Pesticide residues, as one of the main international standards of agricultural products quality, have caused serious damage of agricultural ecological safety, especially the damage of agricultural soil and water ecosystem, and also harm to human health and life quality through the food chain due to their toxicity and bioaccumulation property [1]. Hence, looking for effective methods to analysis of pesticide residues is essential [2]. Various methods have been exploited for the determination of pesticide residues in the last few years. Techniques such as colorimetry, gas and liquid chromatography (GC and LC) [2], gas and liquid chromatography-mass spectrometer (GC-MS and LC-MS) [3], high performance liquid chromatography (HPLC) [4], and UV–Vis spectroscopy [4,5] have been used for the determination of pesticide residues. These methods are generally high-sensitive, but often require a tedious sample purification steps to remove potentially interfering chemicals in matrices. In contrast, electrochemical techniques have been proposed as efficient alternatives for the determination of pesticide residues owing to their advantages of time-saving, simple operation, sensitivity, selectivity, low-cost and on-field detection, and increasing attention has been drawn to the detection of the trace amount of pesticide residues.

Niclosamide (2′,5-dicloro-4′-nitrosalicylanilide, NA, its molecule structure is shown in Scheme 1), one of the most effective and commercially available molluscicide in schistosomiasis control programs, was recommended by the World Health Organization for the use of effective against aquatic snails and all the species of tapeworm infections [5–8]. Despite its wide applications in agriculture, veterinary, and public health, NA is selectively toxic to target snails and nontarget aquatic organisms [8–10], and caused problems to terrestrial and aquatic plants by long-time administration [9,10]. Therefore, a great challenge remains to develop a sensitive and selective method for the determination of NA, especially monitoring of NA concentration levels in pharmaceutical, environment or food control. Among electrochemical

* Corresponding authors.
E-mail addresses: xujingkun@tsinghua.org.cn (J. Xu), wenyangping1980@gmail.com (Y. Wen).
[1] Tel.: +86 791 83813048; fax: +86 791 83813538.

http://dx.doi.org/10.1016/j.electacta.2014.02.013
0013-4686/



Scheme 1. The working mechanism and practical sample analysis of NA.

techniques, differential pulse voltammetry is considered as one of the most sensitivity method for the trace detection of pesticide residues. However, this method has rarely been reported for the determination of NA using different materials modified electrodes. Alemu et al. [11,12] studied the electrochemical behavior and voltammetric determination of NA by a glassy carbon electrode (GCE). Ghalkhani et al. [13] reported the electrocatalytic reduction of NA based on carbon nanoparticle/chitosan modified electrode. Mehretie et al. [14] explored the electrochemical investigation of NA at poly(3,4-ethylenedioxythiophene) modified GCE. However, numerous studies have reported, carbon nanomaterials such as carbon nanotubes (CNTs) and graphene are good candidates as ideal electrode modified materials for the fabrication and application of electrochemical sensors and biosensors. Hence, differential pulse voltammetry for the highly sensitive determination of NA with carbon nanomaterials modified electrodes need to be explored.

CNTs and graphene, two different sp^2 carbon nanostructures, have become the hottest research in novel carbon nanomaterials today, especially as sensing electrode materials, were used widely for various potential applications in many fields [15,16]. According to the literature statistic of different novel carbon nanomaterials and their sensing application, CNTs and graphene are one of the most popular novel carbon nanomaterials. Moreover, the researches on the application of CNTs and graphene in chemo/biosensors generally increased year by year. CNTs, a one-dimensional carbon material, can be thought of as graphitic sheets with a hexagonal lattice that have been wrapped up into a seamless cylinder [17], and can be divided into multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) according to the layer number of graphitic sheets. Due to their high electrical conductivity and electrocatalytic activity, chemical and physical stabilities, unique structure with internal tube cavity, large specific surface area, and hydrophobicity, CNTs are considered as one of the best sensing materials for electrochemical and biochemical applications [18–21]. Graphene, a two-dimensional carbon material in a hexagonal configuration with one-atom-thick sp^2-bonded carbon sheet, has attracted tremendous attention due to its unique physical and chemical properties, such as high surface area, chemical stability, excellent conductivity, and mechanical strength [22–25]. Many methods have been developed to produce graphene. However, most of graphene used in electrochemistry is produced by the reduction of graphene oxide (GO) [22,26]. Electrochemical methods are considered as one promising green strategy for graphene synthesis [22,24]. Electrochemically reduced graphene oxide (ER-GO) is a simple, inexpensive, efficient, and environmentally friendly electrochemical method to obtain graphene [24,27].

Up to now, application of CNTs and graphene for the electroanalytical detection of NA has not been reported. In this contribution, three carbon nanomaterials modified electrodes with S(M)WCNTs and ER-GO were successfully constructed for the highly sensitive determination of NA using differential pulse anodic stripping voltammetry (DPASV). The electrochemical response and mechanism of NA based on these modified electrodes were studied. Finally, the as-fabricated sensing electrode was employed for determination of NA in tablets sample.

2. Experimental

2.1. Chemicals

NA was obtained from Sigma-Aldrich. SWCNTs (1.0 wt%) and MWCNTs (4.39 wt%) suspension were purchased from Chengdu