



Immobilization of ruthenium phthalocyanine on silica-coated multi-wall partially oriented carbon nanotubes: Electrochemical detection of fenitrothion pesticide

Thiago C. Canevari^{a,*}, Thiago M. Prado^b, Fernando H. Cincotto^b, Sergio A.S. Machado^b

^a Engineering School, Mackenzie Presbyterian University, 01302-907 São Paulo, SP, Brazil

^b Institute of Chemistry, State University of São Paulo, P.O. Box 780, 13560-970 São Carlos, SP, Brazil

ARTICLE INFO

Article history:

Received 10 July 2015

Received in revised form 7 December 2015

Accepted 9 December 2015

Available online 10 December 2015

Keywords:

Composites

Nanostructures

Sol-gel chemistry

Electrochemical measurements

Catalytic properties

ABSTRACT

This paper reports on the determination of the pesticide fenitrothion using a glassy carbon electrode modified with silica-coated, multi-walled, partially oriented carbon nanotubes, SiO₂/MWCNTs, containing ruthenium phthalocyanine (RuPc) synthesized *in situ*. The hybrid SiO₂/MWCNTs/RuPc material was characterized by UV–vis absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM) and differential pulse voltammetry. The modified electrode showed well-defined peaks in the presence of fenitrothion in acetate buffer, pH 4.5, with a sensitivity of 0.0822 μA μM⁻¹ mm⁻² and a detection limit of 0.45 ppm. Notably, the modified SiO₂/MWCNTs/RuPc electrodes with did not suffer from significant influences in the presence of other organophosphorus pesticides during the determination of the fenitrothion pesticide. Moreover, this modified electrode showed excellent performance in the determination of fenitrothion in orange juice.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Pesticides are a class of chemical compounds widely used to combat insects and pests in agriculture and are occasionally employed for the residential pest combat. Despite the fact that only a small quantity of the applied pesticides, less than 0.5%, are actually absorbed by plants, they have a direct influence on the development of ecosystems [1]. It is very important to highlight that most pesticides are water soluble and highly toxic and therefore may indirectly contaminate aquatic organisms and humans.

Among the different classes of existing pesticides [2] organophosphate pesticides (OP) receive a considerable amount of attention as they are commonly used for combating pests in different types of crops and are known to be extremely harmful to the nervous system of humans. It has been reported that the toxicity of organophosphorus pesticides in humans is related to the P=O bonds forming adducts with molecules and metabolites [3].

Fenitrothion, (O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate, is an organophosphate pesticide widely used to combat pests in many countries worldwide [4,5]. Fenitrothion is considered highly toxic and is part of what is known as the 'Red List' of pesticides according to the UK Environmental Agency [6]. Therefore, the quantification of fenitrothion pesticide in the environment and particularly in food is extremely important to help avoid associated health problems for humans.

Different analytical techniques [7–10] that require highly skilled labor and the pre-treatment of samples are sometimes used to quantify fenitrothion. Alternatively, electroanalytical techniques are used, as they do not always require sample pre-treatment processes as the pesticide analysis is performed using different types of modified electrodes [11–13].

Based on this contextual background, the development of hybrid materials for use in electrochemical sensors has generated a significant amount of interest due to the possibilities which may be realized from combined elements compared to separate materials [14,15]. Among the hybrid materials which have generated significant interest in this regard are materials based on the combination of silica base and carbon allotropes (carbon nanotubes and graphene species), as the resultant hybrid may offer enhanced properties such as robustness, high chemical and

* Corresponding author. Fax: +55 16 3521 3109.

E-mail address: tcanevari@gmail.com (T.C. Canevari).

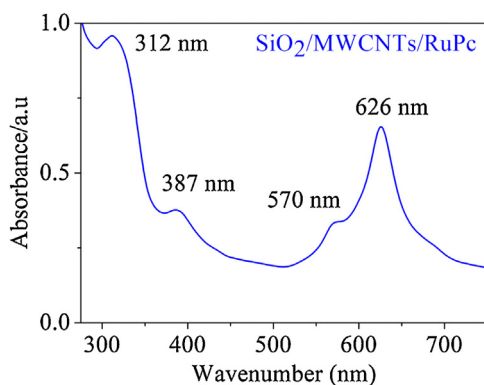


Fig. 1. UV–vis absorption spectrum of SiO₂/MWCNTs/RuPc hybrid material in nujol (mineral oil).

mechanical stability, high reactivity due to varied functionality and unique properties related nanoscale structure. The different functional groups offered by these hybrids could facilitate interaction with other species with a view to improving the sensitivity and selectivity of electrochemical sensors.

Metal phthalocyanines (MPc) are macrocyclic compounds with π structure which are employed for practical use in several areas [16–21]. In particular, MPc have been used in the development of electrochemical sensors due to their excellent redox properties [22–25]. One MPc that has attracted significant research interest is phthalocyanine ruthenium (RuPc), due to its excellent catalytic properties [26].

With this in mind, this manuscript reports on the development of an electrochemical sensor with a view to the quantification of fenitrothion in orange juice. The sensor design was based on the initial synthesis of hybrid silica and multi-walled partially oriented carbon nanotubes (SiO₂/MWCNTs), which in-turn facilitated the *in situ* synthesis of phthalocyanine ruthenium.

2. Experimental

2.1. Reagents

All of the reagents used were of high purity: Multiwalled carbon nanotubes (Aldrich), tetraethyl orthosilicate, Tetraethyl orthosilicate (TEOS) (Aldrich, 98%); ruthenium acetate (Aldrich), fenitrothion (Aldrich), malathion (Aldrich), chlorpyrifos (Aldrich), ascorbic acid (Aldrich) dimethylformamide (DMF), ethanol (Aldrich 99.9%) and HF (Synth, 47%). A 0.1 mol L⁻¹ pH 4.5 acetate buffer solution was prepared in ultrapure water. All other aqueous solutions were also prepared with ultrapure water.

2.2. Preparation of SiO₂/MWCNTs hybrid material

The hybrid SiO₂/MWCNTs material, containing 20 wt.% of carbon nanotubes was prepared according to the procedure described in Ref. [27] with some modifications. Briefly, a solution of TEOS (0.0225 mol) and ethanol 1/1 (v/v) was prepared and left to mix for 20 min, after which 2 mL of H₂O was added and the solution was stirred for a further 5 min. Then, 0.9 g of multi-walled carbon

nanotubes were added to the mixture and the solution was stirred for another 5 min. Finally, 0.5 mL of hydrofluoric acid (47%) was added and the mixture was sonicated until gel formation was observed. The fresh gel was left to rest for 10 days at room temperature to complete the sol–gel process. After this time, the formed xerogel was finely ground and the powder was washed with ethanol in a Soxhlet extractor for 1.5 h, before being subjected to heat treatment at 323.

Then, the hybrid SiO₂/MWCNTs material was subjected to acid treatment by dispersion in a 1:3 acid solution of H₂SO₄/HNO₃ followed by reflux for 12 h. This type of acid treatment promotes the formation of functional groups, namely carboxyl, hydroxyl and ester groups, which would favor the incorporation of other species on the surface of the carbon nanotubes.

2.3. In situ synthesis of ruthenium phthalocyanine on the SiO₂/MWCNTs hybrid material

The ruthenium phthalocyanine (RuPc) was synthesized *in situ* on the previously functionalized hybrid material according to the following procedure: [28] 1 g of the hybrid material (SiO₂/MWCNTs) was dispersed in 10 mL of aqueous ruthenium acetate (1×10^{-3} mol L⁻¹) and placed in a water bath set to 363 K, until complete evaporation of the solvent was achieved. This step serves to incorporate the ruthenium in the SiO₂/MWCNTs through associations with the silanol groups and even more so with carbon nanotubes, due to their higher functionality. These functional groups favor ion exchange reactions with the ruthenium acetate and form SiO₂/MWCNTs/Ru. Then, 500 mg of the newly formed SiO₂/MWCNTs/Ru was mechanically mixed with phthalonitrile in a 1:4 ratio. This mixture was placed in a glass ampoule which was submerged in a 473 K silicone bath for 2 h under slow rotation. These conditions led to the condensation of phthalonitrile and the formation of ruthenium phthalocyanine (RuPc). The newly formed ruthenium phthalocyanine, named SiO₂/MWCNTs/RuPc, was then washed with ethanol in a Soxhlet extraction system to remove any residual phthalocyanine that had not adsorbed on the material.

2.4. Preparation of the modified glassy carbon electrode

The glassy carbon electrodes (GCEs) were subjected to electrochemical treatment prior to surface modification, which consisted of several cyclic voltammetry measurements in 0.1 M H₂SO₄ over the potential range of –0.5–1 V. Then, modification of the electrodes was achieved by adsorbing a film from a dimethylformamide (DMF) solution which contained 1 mg/mL hybrid materials of SiO₂/MWCNTs or SiO₂/MWCNTs/RuPc. The films (either SiO₂/MWCNTs or SiO₂/MWCNTs/RuPc) were prepared by the addition of a 9 μ L drop of the DMF solution onto the electrode surface followed by solvent evaporation over approximately 4 h at room temperature.

2.5. Apparatus

The UV/vis spectrum of SiO₂/MWCNTs/RuPc was obtained from a JASCO spectrophotometer. The hybrid material containing ruthenium phthalocyanine in powder form was dispersed in mineral oil (Nujol) and the mixture was placed between two quartz plates.

XPS was performed in a VSW HA 100 spectrometer equipped with a hemispherical electron analyzer, using an Al anode as the X-ray source. The correction of the binding energies for charge was obtained using the reference Si 2p line from silica.

Field emission gun scanning electron microscopy (FEG-SEM) of SiO₂/MWCNTs/RuPc was performed in a FEI

Table 1
Summary of binding energy (eV) of Ru 3d_{5/2}, N 1s, C 1s, O 1s and Si 2p components of SiO₂/MWCNTs/RuPc hybrid material.

Sample	C 1s	Ru 3d _{5/2}	Si 2p	O 1s	N (nitrogen)
SiO ₂ /MWCNT/RuPc	285.0	279.3	103.5	530.2	397.5
	287	283.1	–	532.2	399.3
	289.8	–	–	533.7	402.2

Download English Version:

<https://daneshyari.com/en/article/1487360>

Download Persian Version:

<https://daneshyari.com/article/1487360>

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