Sensors and Actuators B 224 (2016) 780–788

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Surface interaction of copper phthalocyanine modified single walled carbon nanotubes with pesticides

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A R T I C L E I N F O

Article history:
Received 20 February 2015
Received in revised form 9 October 2015
Accepted 28 October 2015
Available online 31 October 2015

Keywords:
Copper(II) phthalocyanine
Single-walled carbon nanotubes
TIRE
Pesticides

A B S T R A C T

Hybrid materials were produced by mixing tetrakis(hexadecylthio) substituted copper(II) phthalocyanine ($CuPcR_4$) with acidified single-walled carbon nanotubes (SWCNTs) and they were characterised by UV–vis absorption spectroscopy, scanning electron microscopy and atomic force microscopy. Thin films of pristine $CuPcR_4$ and $CuPcR_4$/SWCNT were prepared by spin coating onto gold-coated glass slides and applied as active layers to detect pentachlorophenol (PCP), 2-chlorophenol, diuron and simazine in water utilising total internal reflection ellipsometry (TIRE) as an optical detection method. Different concentrations of pesticides in water ranging from 1 to 25 μg/L have been examined in the current work. It is revealed that the shifts in $\Delta(\lambda)$ spectra of $CuPcR_4$/SWCNT films were evidently larger than those produced by the pristine $CuPcR_4$ films, indicating largely improved films' sensitivity of the hybrid films. The sensitivity has been calculated according to the phase shift in the $\Delta(\lambda)$ spectra. The higher sensitivity was found to be 0.00396/(μg/L) towards PCP in case of $CuPcR_4$/SWCNT sensor. The lower detection limit has been calculated to be 840 ng/L.

1. Introduction

The worldwide use of pesticides and herbicides for agricultural purposes is classified as a global environmental pollution problem. Herbicides used in agriculture can easily take way to surface or ground water, possibly causing adverse ecotoxicological effects on aquatic life and changing drinking water quality [1]. Chlorophenols represent a major group of pollutants of environmental concern. Due to their widespread toxic properties, some chlorinated phenols, such as pentachlorophenol (PCP), 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol (2,4,6 TCP) have been considered as priority pollutants. The monitoring of pesticides and herbicides at comparatively low concentrations, especially in drinking and natural waters is a complicated and expensive task. The European Union has limited the maximum allowable concentration for a single pesticide to 0.1 μg/L [2], and their presence in different foods and drinks is limited by legislation. Different analytical procedures based on liquid chromatography–mass spectrometry (LC–MS) [3–5], LC–tandem mass spectrometry (LC–MS/MS) [6], high performance liquid chromatography (HPLC) [7], and gas chromatography–mass spectrometry (GC–MS) [8] have been reported to provide efficient determination of these pesticides, according to the present legislation. However these methods are time consuming, and expensive to run despite the sensitivity and specificity associated with them. Furthermore they are not suitable for application in online detection. Ellipsometry can be used in total internal reflection (TIRE) mode and in combination with the surface plasmon resonance phenomenon for sensing aspects [9–11]. There has been extensive work in applying TIRE as a technique for the detection of biomolecules [12,13]. It was established that TIRE is a more suitable technique than surface plasmon resonance (SPR) method for the registration of low molecular weight toxins such as simazine, atrazine and T2 mycotoxin [14]. TIRE technique has attracted substantial attention because of its fast response, simple instrumentation, being non-destructive method and its ability of performing measurements in non-transparent media [15].

A range of sensitive materials has been employed to construct chemical sensors; these include several types of transition metal oxides [16], conducting polymers [17] as well as organic complexes

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http://dx.doi.org/10.1016/j.snb.2015.10.105
0925-4005/

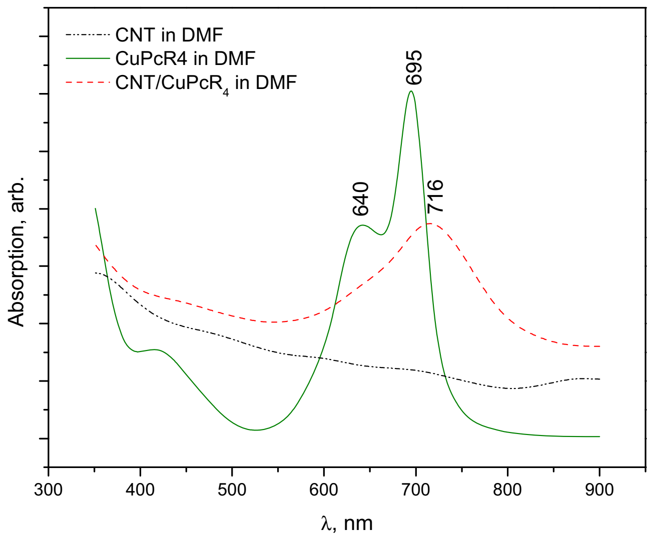

Fig. 1. Optical absorption spectra of pristine SWCNT (dashed line), $CuPcR_4$ (solid line) and SWCNT/$CuPcR_4$ hybrid (dotted line) in DMF.

like phthalocyanines [18,19]. Phthalocyanines (Pcs) in general and their metallo-derivatives (MPcs) in particular, hold a great promise for the development of many non-linear optical devices because of their activity as basis for optical limiting [20], fast response time, unique electronic adsorption properties and the extensively delocalised π–π electron skeleton.

Carbon nanotubes (CNTs), on the other hand, have been found to be extremely sensitive to their local chemical environment. This chemical sensitivity, due to their extraordinary one-dimensional carbon nanostructure, has made them ideal building blocks for chemical detection [21]. However, the poor solubility and dispersity of CNTs in conventional solvents has restricted their use as active layers processed by simple methods like spin coating. Acid-treatment as well as other modifications has shown to assist in overcoming the disadvantage of poor dispersity of CNTs [22,23]. The other downside is that CNTs are optically inert and almost are unsuitable to use as optically active layers utilising techniques such as SPR and TIRE. Further surface modification of CNTs through hybridisation with MPcs enhances their optical performance as well as gas sensing activity. This arises from the mutual π interaction between CNTs and MPc resulting in more detection efficiency compared to the individual CNTs or MPcs species [24].

This work reports the use of single-walled carbon nanotubes (SWCNT) hybridised with tetra-substituted copper phthalocyanine ($CuPcR_4$) as an optical active layer to detect pentachlorophenol (PCP), 2-chlorophenol, diuron and simazine in water using TIRE technique. The morphology and optical properties of the $CuPcR_4$/SWCNT hybrid films are also discussed.

2. Experimental

2.1. Materials

Synthesis of 2(3), 9(10), 16(17), 23(24)-tetrakis(hexadecylthio) phthalocyaninato copper(II) ($CuPcR_4$) has been described in

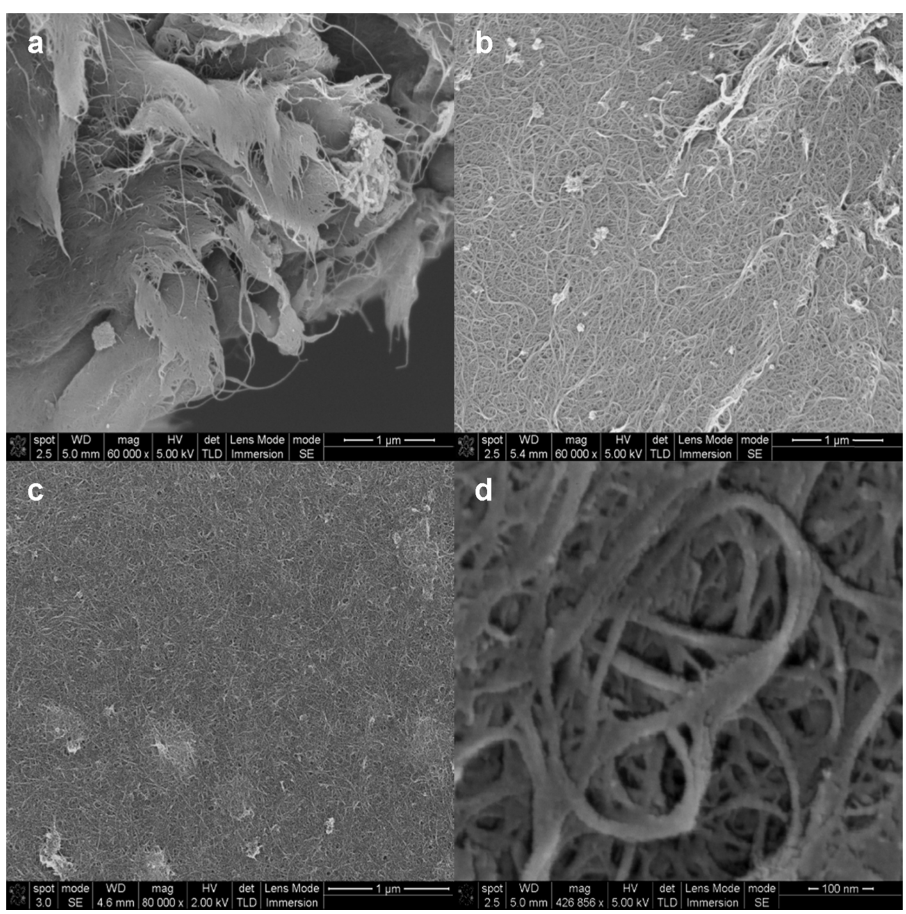

Fig. 2. SEM images of (a) pristine SWCNT, (b) acidified SWCNT and (c) SWCNT/$CuPcR_4$ hybrid in thin film forms. SWCNT/$CuPcR_4$ SEM image in 100 nm resolution is presented (d).