Optical Detection of Herbicides in Water using Dye-Modified Single Walled Carbon Nanotubes

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Abstract—**Hybrid materials were produced by mixing $CuPcR_4$ with acidified single-walled carbon nanotubes (SWCNTs) and characterised by UV-Vis absorption spectroscopy, scanning electron microscopy and atomic force microscopy. Thin films of pristine $CuPcR_4$ and SWCNT/$CuPcR_4$ 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 utilizing Total Internal Reflection Ellipsometry (TIRE) as an optical detection method. Different concentrations in water ranging from 0.5 to 20 µg/L have been examined in the current work. It is revealed that the shifts in $\Delta(\lambda)$ spectra of SWCNT/$CuPcR_4$ films were evidently larger than those produced by the pristine $CuPcR_4$ films, indicating largely improved films' sensitivity of the hybrid films.**

Keywords-phthalocyanine; carbon nanotubes; TIRE; PCP; 2PC; diuron; simazine.

I. 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 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]. This work reports the use of single-walled carbon nanotubes (SWCNT) hybridized 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 SWCNT/$CuPcR_4$ hybrid films are also discussed.

II. EXPERIMENTAL

The experimental set-up for TIRE measurements was built on M2000V (J.A. Woollam Co., Inc.) spectroscopic ellipsometer, operating in the 370-1000 nm wavelength range. Further details of TIRE method and the experimental set-up are found in previous publications [14,16]. The samples for TIRE study were prepared by the evaporation of 3-5 nm of chromium on microscopic glass slides followed by the evaporation of 25-30 nm gold layer.

Synthesis of 2(3),9(10),16(17),23(24)-tetrakis(hexadecylthio) phthalocyaninato copper (II) ($CuPcR_4$) has been described in our previous work [17]. All other materials were purchased from commercial suppliers. SWCNTs were first acidified and cut into short and uncapped nanotubes according to a multi-step procedure developed by Smalley and co-workers [18]. This was carried out by refluxing the nanotubes in 2.6 M HNO_3 for 48 h followed by stirring in a mixture of concentrated H_2SO_4 and HNO_3 (3:1, v:v) at 40 °C for 12 h. The mixture was centrifuged and washed thoroughly in deionised water and dried at 70 °C for 12 hours. The acidified SWCNTs (0.5 mg) were added to a solution of $CuPcR_4$ (1.5 mg/mL) in chloroform and ultrasonicated for 15 min. Thin films were produced by spin-casting the obtained solution onto gold-coated slides using a photoresist spinner (Microsystem model 4000) at 2000 rpm. Similarly, thin films were produced from a solution of pristine $CuPcR_4$ in chloroform (2 mg/ml) for comparison. Pentachlorophenol (PCP), 2-chlorophenol, diuron and simazin solution in deionized water in the concentration range 0.5-20 µg/L was used in this study. After detection, deionized water was injected into the cell to remove adsorbed molecules from film surface.

III. RESULTS AND DISCUSSION

A. UV-Vis. Absorption Spectra

Fig. 1 shows the UV-visible absorption spectra of solutions of SWCNTs, $CuPcR_4$ and SWCNT/$CuPcR_4$ hybrid in chloroform. $CuPcR_4$ exhibits typical electronic absorption spectrum with strong absorption region in the wavelength range 640-695 nm (Q-band) arising from electron transitions from the highest occupied molecular orbital (HOMO) a_{1u} to the lowest unoccupied molecular orbital (LUMO) e_g [19]. The maximum of the Q-band in the absorption spectrum of the SWCNT/$CuPcR_4$ hybrid is broadened and red-shifted by ~21 nm in comparison with $CuPcR_4$ spectrum. It can also be seen that the Q-band splitting has disappeared in the hybrid absorption spectrum, which indicates dominant monomer absorption. These changes are suggested to take place due to the strong π-π interaction between carbon nanotubes and phthalocyanine molecules, where phthalocyanines are usually considered as electron donors, while carbon nanotubes as acceptors [20]. This interaction has been frequently ascribed to the reduced aggregation in the MPc/CNT composites [21,22].

B. Morphology

Fig. 2 shows SEM images of pristine SWCNTs, acid-treated SWCNTs and SWCNT/$CuPcR_4$ hybrid deposited as thin film from chloroform solution onto silicon substrate. Pristine CNTs typically tend to bundle together (Fig. 2a) and to aggregate due to Van der Waals attraction between individual tubes [23] as well as the high length to diameter ratio; this makes them hard to disperse in common organic solvents. Chemical modification has been performed to achieve enhanced interaction between SWCNTs and $CuPcR_4$ molecules leading to the formation of a composite with much improved solubility in chloroform.

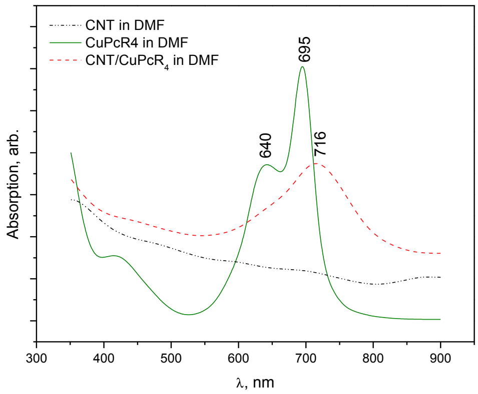

Figure 1. Optical absorption spectra of pristine SWCNT (dashed line), $CuPcR_4$ (solid line) and SWCNT/$CuPcR_4$ hybrid (dotted line) in chloroform.

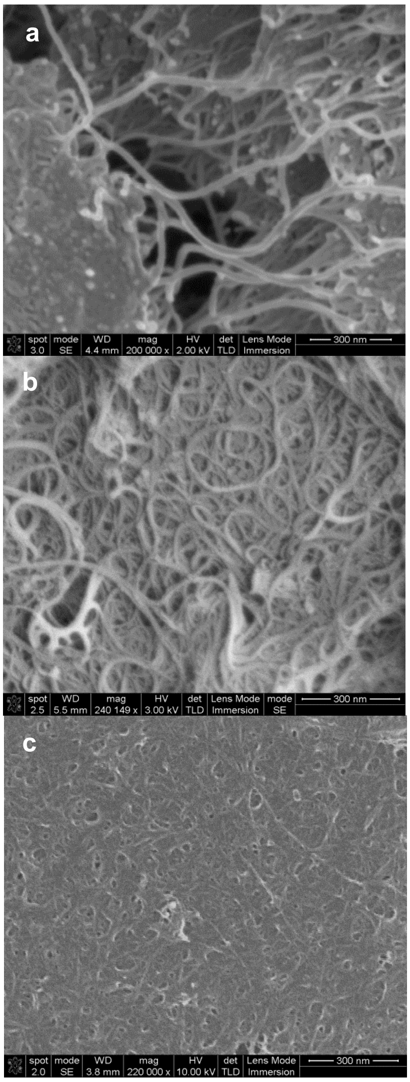

Figure 2. SEM images of (a) pristine SWCNT in powder form, (b) acidified SWCNT in thin film form and (c) SWCNT/$CuPcR_4$ hybrid in thin film form.

The obtained solution is conveniently used for thin film deposition using spin-coating technique. Fig. 2b shows that the intrinsic quality of SWCNTs structure is still preserved after the acid treatment. However, after mixing with phthalocyanine (Fig. 2c), the composite dispersion was significantly improved to form a uniformly suspended solution in chloroform; hence smoother films were obtained to perform optical investigation, using TIRE experiments.

C. Total internal reflection ellipsometry

The adsorption of PCP onto the surface of CuPcR$_4$ and SWCNT/CuPcR$_4$ thin films in water solutions has been studied using TIRE method. CuPcR$_4$ and SWCNT/CuPcR$_4$ hybrid films were spun onto gold-coated glass substrates as described in the experimental section. The typical TIRE spectra of Cr/Au films were reported earlier [17]. The spectrum of $\Psi(\lambda)$, demonstrating the amplitude ratio of A_p/A_s, resembles very much the conventional surface plasmon resonance (SPR) curve, while the spectrum of $\Delta(\lambda)$ is associated with the phase shift between p- and s-components of polarized light. The latter changes sharply from 270° down to -90° near the plasmon resonance. According to Arwin's modelling [11], the position of the sharp drop in $\Delta(\lambda)$ spectrum is about 10 times more sensitive to analytes adsorption than $\Psi(\lambda)$ spectrum. Fig. 3 represents the spectra of $\Psi(\lambda)$ and $\Delta(\lambda)$ of CuPcR$_4$ and SWCNT/CuPcR$_4$ hybrid thin films before and after exposure to PCP, 2PC, diuron and simazine in two concentrations (2 and 20 µg/l). The initial response time of the sensors was fraction of a minute but the spectra were measured 5 minutes after injection of contaminated water or pure water to achieve the equilibrium response or recovery, respectively. During exposure to contaminated water, it was difficult to detect shifts in $\Psi(\lambda)$ because of the shape of the curve, however, significantly larger shifts have been observed in $\Delta(\lambda)$ spectra. These are typical features of TIRE method as reported earlier [14,15,24]. The spectra of $\Delta(\lambda)$ were further enlarged and shown above Fig. 3a and Fig. 3b to provide better assessment. It can clearly be seen that the adsorption of the analytes on hybrid film has resulted in larger shifts than on pure CuPcR$_4$. Carbon nanotubes in general are characterised with uniform surface with delocalised π-electrons of high density, which enhances their adsorption properties, especially for analytes with oxygen-containing aromatic molecules [25]. Complete recovery of $\Delta(\lambda)$ spectra are observed after flushing the cell with deionised water in the case of PCP and 2PC interaction as previously established for films of metal phthalocyanines with other types of substituents [26]. However, when exposed to simazine and diuron-contaminated water, films did not show complete recovery after flushing with water.

Theoretical fitting to experimental Ψ and Δ spectra was carried out by applying a 4-layer model consisting of water solution, active layer, Au layer and BK7 glass. The optical parameters (film thickness *d*, refractive index *n* and extinction coefficient *k*) at λ=633 nm of the organic and the hybrid films before and after exposure to contaminated water were determined and summarised in Table I.

TABLE I. CHANGES IN THE OPTICAL PARAMETERS CAUSED BY THE ADSORPTION OF ANALYTES.

		CuPcR$_4$			**SWCNT/CuPcR$_4$**		
		n	***k***	***d,nm***	***n***	***k***	***d,nm***
Initial film		1.56	0.32	37.4	1.41	0.28	54.9
Exposd films	PCP	1.59	0.31	38.1	1.47	0.29	56.5
	2PC	1.59	0.32	37.9	1.45	0.30	55.8
	Diuron	1.57	0.33	37.6	1.43	0.29	55
	Simazine	1.56	0.33	37.7	1.45	0.27	55.1

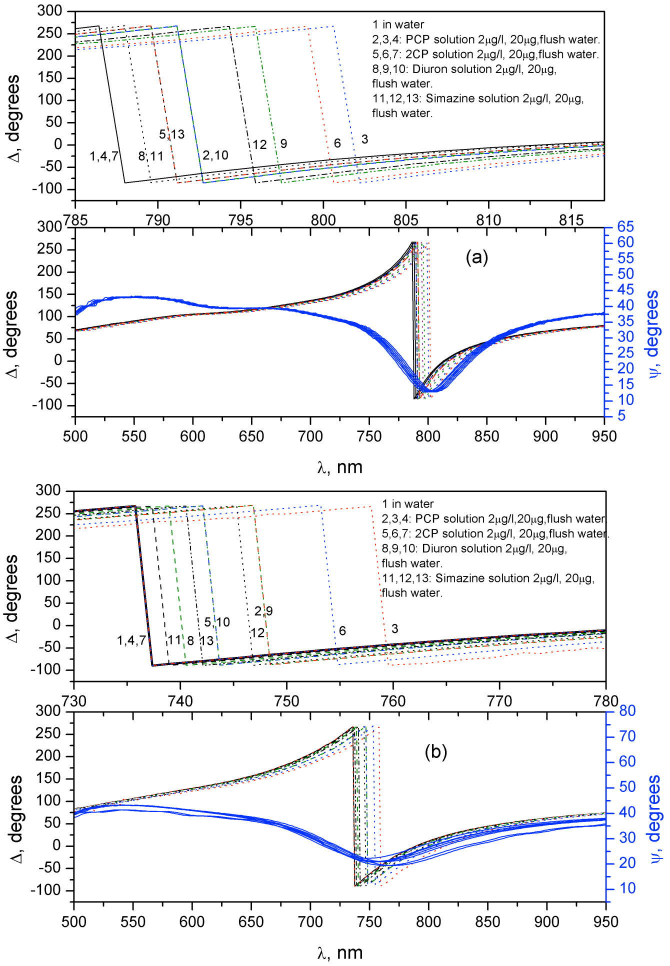

Figure 3. Ψ(λ) and Δ(λ) TIRE spectra of (a) CuPcR$_4$ coated Cr/Au and (b) SWCNT/CuPcR$_4$ hybrid films in water and after exposure to contaminated water.

The data in Table I show an increase in film thickness as well as optical parameters (*n* and *k*) for both films after exposure. The increase in films' thickness in the case of SWCNT/CuPcR$_4$ composite was more significant which is probably due to the predominant surface interaction of the analyte with SWCNT/CuPcR$_4$ films.

Fig. 4 shows the dependence of phase shift change ($\delta\Delta$) on analytes concentration in the range 0.5-20 µg/L in water for CuPcR$_4$ and SWCNT/CuPcR$_4$ layers. The minimum detection limit of PCP was 0.8 μg/L for CuPcR$_4$ layer, which is similar to that determined in our previous publication where films of octatosylamido substituted zinc phthalocyanine were used as active layers for PCP detection using TIRE technique [10]. In the case of SWCNT/CuPcR$_4$ layers the minimum detection limit of PCP was found to be 0.5 μg/L. Detection limits of 2PC, diuron and simazine were 1, 1.8 and 2 μg/L respectively when interacting with CuPcR$_4$ film, while films of SWCNT/CuPcR$_4$ hybrid show lower detection limits of 0.7, 1 and 1.3 μg/L, respectively.

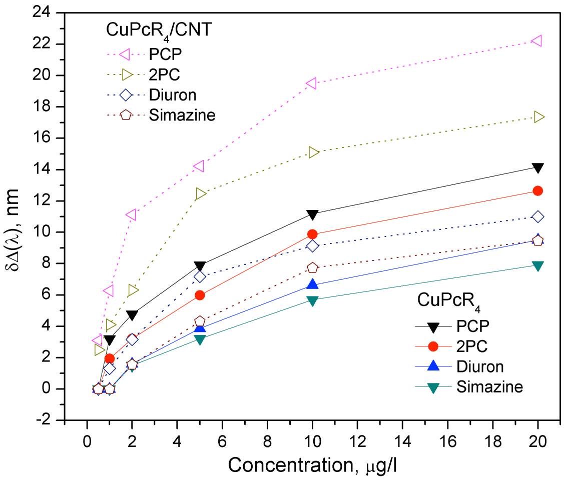

Figure 4. Dependence of phase shift changes (δΔ) in the phase shift spectra of SWCNT/CuPcR$_4$ hybrid and pristine CuPcR$_4$ films on the concentration of PCP solutions in water in range 0.5-10 μg/L

IV. CONCLUSION

Thin films of single-walled carbon nanotubes (SWCNT) hybridized with tetra-substituted copper phthalocyanine (CuPcR$_4$) have been used as optical active layers to detect pentachlorophenol (PCP), 2-chlorophenol, diuron and simazine in water using Total Internal Reflection Ellipsometry (TIRE) technique. The morphology and optical properties of the hybrid films indicate π-π interaction between SWCNT and CuPc. The interaction of the analytes solution in water with SWCNT/CuPcR$_4$ hybrid films as well as with pristine CuPcR$_4$ was studied. Changes in the phase shift (Δ(λ)) spectra of SWCNT/CuPcR$_4$ films were found to be larger than those demonstrated by the pristine CuPcR$_4$ films.

V. ACKNOWLAGEMENTS

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