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Review

An Overview of Pesticide Monitoring at Environmental Samples Using Carbon Nanotubes-Based Electrochemical Sensors

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Abstract: Carbon nanotubes have received enormous attention in the development of electrochemical sensors by promoting electron transfer reactions, decreasing the work overpotential within great surface areas. The growing concerns about environmental health emphasized the necessity of continuous monitoring of pollutants. Pesticides have been successfully used to control agricultural and public health pests; however, intense use can cause a number of damages for biodiversity and human health. In this sense, carbon nanotubes-based electrochemical sensors have been proposed for pesticide monitoring combining different electrode modification strategies and electroanalytical techniques. In this paper, we provide a review of the recent advances in the use of carbon nanotubes for the construction of electrochemical sensors dedicated to the environmental monitoring of pesticides. Future directions, perspectives, and challenges are also commented.

Keywords: carbon nanotubes; electroanalysis; environmental samples; organophosphates; carbamates; pesticides

1. Introduction

Truly, the credit for the discovery of carbon nanotubes (CNTs) should be given to Radushkevich and Lukyanovich in 1952 [1]. Posteriorly, Oberlin observed the single (or double) walled carbon nanotubes in 1976 [1]. However, Iijima's report in 1991, after a random event during the test method for C_{60} synthesis [2], took the credit for such a discovery. It can be considered a milestone in nanomaterial synthesis, and, since then, CNTs have received great attention, followed by exponential growth in the number of published papers related to this topic. Due to the combination of outstanding physical (ultrahigh both fracture strength [3] and elastic modules [4] and high electrical conductivity [5]) and chemical features (inertness, although CNTs chemical functionalization is possible [6,7]) CNTs are a unique material. Therefore CNTs are one of the most commonly used building blocks of nanoscience and nanotechnology [8–10].

The structure of CNTs can be conceived of as one or more rolled-up graphene sheets [11]. As a result, a meshwork of sp^2 carbon atoms arranged in a cylindrical geometry is obtained with a high aspect ratio (1D nanomaterial) [12]. In general, two configurations are used to classify CNTs based on the number of layers comprising each tube. The single-walled carbon nanotubes (SWCNTs) are composed by a single

layer of graphene with diameters typically around 1 nm [13], and the multi-walled carbon nanotubes (MWCNTs) are formed by several concentric cylinders inserted into each other with a layer spacing of 0.3–0.4 nm and have diameters of tens of nanometers [14]. The lengths of CNTs are usually in the micrometer range [15].

The integration of CNTs in electrochemical sensing applications is very attractive due to their large surface areas [16] and wide useful potential ranges, commonly from −1.0 to +1.0 V [17–19] which support various redox reactions [20,21]. Additionally, the superficial incorporation of organic [22,23] and inorganic molecules [24,25], metallic nanoparticles [26], biomolecules [27–29], and the nanocomposites of conducting polymers and CNTs [30,31] can increase the field of applications of CNTs in electroanalytical issues.

Although CNTs present all the aforementioned properties, there is no reason that MWCNTs with a diameter larger than 10 nm should behave electrochemically differently from graphite [32]. In most cases, the presence of structural defects and edge planes are responsible for improvements in sensitivity and the electrocatalytic effects of CNTs on sensing applications [33,34]. Additionally, the observation of a heterogeneous electron-transfer rate constant (k°) coupled with $[Fe(CN)_6]^{3-/4-}$ for electrochemically activated CNTs showed that the increases in the density of defects are responsible for a huge value of k° [35].

The effect of the functionalization of CNTs also can be observed in electroanalytical applications. The sidewall oxidation is a classical route to produce CNTs with structural defects, yielding a polar soluble product suitable for processing into thin films or other applications [36]. Wei and co-authors [37] tested the O_2-plasma oxidized multi-walled carbon nanotubes (poMWCNTs) for Cd(II) and Pb(II) electrochemical detection and found that the current increased by four times in comparison with non-treated-MWCNTs. The authors attribute such improvement to oxygen-containing groups and structural defects on the carbon meshwork produced by plasma MWCNTs functionalization.

Carbon nanotubes are widely used in the development of electrochemical sensors for the detection of drugs, dyes, ions, phenols, and pesticides [38–44]. In the course of this review, we will present an overview of the recent advances in the preparation of electrochemical sensors based on carbon nanotubes for the determination of pesticides in environmental samples.

2. Environmental Relevance of Pesticides Monitoring

Pesticides are organic compounds, which are developed to control agricultural and public health pests. Although they have increased crop yield and reduced postharvest losses, intensification of agricultural practices can lead to an accumulation of pesticide residues that can impose a serious risk to human health and the environment worldwide [45–47]. The use of pesticides often results in a loss of biodiversity due to their high toxicity to birds, plants, and animals [48]. Additionally, these compounds are widely distributed in the environment and have been detected in water, soil, sewage sludge, sediment, and the aquatic biota [49–54]. In human beings, they may increase the risk of psychiatric [55] and endocrine-disrupting disorders [56] and promote renal, neurological, hepatic, and reproductive problems, even in low levels [57–59]. For these reasons, the monitoring of such compounds in the environment is an urgent demand.

The chemical classification of pesticides includes organophosphates [60], neonicotinoids [61], pyrethroids, *N*-methyl carbamates [62], and organochlorines [63]. In fact, the pesticides most widely employed are of the organophosphates and carbamates class. Pesticides can be also classified according to their application; to kill insects (insecticide), weeds (herbicide), fungi (fungicide), nematodes (nematicide), and others. Several methods have been reported in the literature for the detection of pesticides such as fluorescence spectrophotometry [64], gas chromatography with flame ionization detection [65,66], gas chromatography with mass spectrometry detection [67,68], high performance liquid chromatography with fluorescence detection [69,70], and high performance liquid chromatography coupled to mass spectrometry [71,72]. However, in all these cases, the methods require skilled labour, sophisticated instrumentation, and are expensive to run and maintain. Therefore, there is a need to develop a simple, sensitive, selective, cheap, and portable sensing platform for pesticide determination. Unlike the

spectroscopic and chromatographic methods, electrochemical assays using modified electrodes offer ultrasensitive, portable, and ease of use systems combined with low-cost voltammetric instrumentation.

3. Environmental Monitoring of Pesticides Using Electrochemical Sensors Based on Carbon Nanotubes

In Table 1, the most relevant works related to pesticide electrochemical monitoring using carbon nanotubes-based electrochemical sensors reported in recent years are summarized. From that, we have a general overview of the current scenario related to this research topic, and, as can be seen, a number of works have been reported using different electrode architectures for the detection of various target analytes. Electrochemical sensors designed with pristine carbon nanotubes or combinations of carbon nanotubes with other modifiers can be found amongst these. There are modified electrodes consisting of CNTs and ionic liquids (ILs), porphyrin, phthalocyanines, metallic nanoparticles, and others. Thus, we discussed the technical issues and the main analytical features, as well as the future challenges of these reports in specific subsections, which were classified according to the type of electrode modifier.

3.1. Carbon Nanotubes Sensors

Carbon nanotubes are one of the most used nanostructures. In the literature different electrode architectures based on carbon nanotubes using as bare electrodes, mainly carbon paste electrodes and glassy carbon electrodes as support, are reported. Carbon paste electrode (CPE) is a composite electrode constructed using carbon materials such as graphite (classical carbon paste electrodes), carbon nanotubes (carbon nanotube paste electrodes, CNPE), or derivates from the combination of two or more materials. CNPE consists of a homogeneous mixture of carbon nanotubes and a hydrophobic organic liquid (mineral oil, paraffin oil, or silicone oil) placed on a glass or plastic tube of diameter and depth defined [73,74]. Inam et al. [75] detected the methiocarb insecticide by square-wave voltammetry (SWV) using a multi-walled carbon nanotube paste electrode. The preparation of CNPE was performed by mixing the carbon nanotube powder with mineral oil in the 0.15:0.85 w/w ratio. After it was homogenized, the paste was inserted in a plastic syringe (3-mm diameter) using a copper wire as an electrical contact connected to the system. Electrochemical characterization of methiocarb in 0.1 mol·L^{-1} H_2SO_4 presented an irreversible anodic peak at +1.3 V vs. Ag/AgCl (3.0 mol·L^{-1} NaCl), which was used for its quantification. They obtained a linear dynamic range between 6.7×10^{-6} and 2.6×10^{-4} mol·L^{-1} and a detection limit of 2.0×10^{-6} mol·L^{-1}. The sensor was applied for methiocarb determination in soil and river water samples, and the results obtained were very satisfactory, with recoveries of (99 $\pm$ 1)% and (98.5 $\pm$ 0.3)%, respectively.

Some studies about the combined use of carbon nanotubes-based sensors and the square-wave stripping voltammetry method showed a considerable increase in the recorded analytical signals. Mercan et al. [76] performed the determination of cyromazine insecticide using a multi-walled carbon nanotube paste electrode by square-wave adsorptive stripping voltammetry. The analytical curve obtained was linear between 2.5×10^{-6} and 5.0×10^{-4} mol·L^{-1}, with a detection limit of 7.2×10^{-7} mol·L^{-1}. The method was applied with success in the direct determination of cyromazine in spiked natural water samples, with recoveries of (102 $\pm$ 2)% and (101 $\pm$ 2)% for river and tap water samples.

Table 1. Electrochemical sensors based on carbon nanotubes for the detection of pesticides.

Analyte	Electrode	Linear Range ($mol \cdot L^{-1}$)	Limit of Detection ($mol \cdot L^{-1}$)	Reference
Amitrole	FeTAPc-MWCNT/BPPGE	–	5.0×10^{-10}	Siswana et al. 2008 [77]
Amitrole and diuron	FeTAPc-SWCNT/GCE	5.0×10^{-5}–1.0×10^{-4}	2.1×10^{-7} and 2.6×10^{-7}	Mugadza et al. 2010 [78]
Bentazone	PANI-β-CD/fMWCNT/GCE	1.0×10^{-5}–8.0×10^{-5}	1.6×10^{-6}	Rahemi et al. 2013 [79]
6-benzylaminopurine	MIP-MWNT@SnS_2/GCE	1.0×10^{-10}–1.0×10^{-2}	5.0×10^{-11}	Gan et al. 2016
Carbaryl	MWCNT/CoPc/GC	3.3×10^{-7}–6.6×10^{-6}	5.5×10^{-9}	Moraes et al. 2009 [80]
Carbendazim	FMWCNTs/GCE	5.2×10^{-11}–2.6×10^{-4}	5.2×10^{-11}	Sundari et al. 2010 [81]
Carbendazim	fullerene/MWCNT/Nafion/GCE	2.0×10^{-8}–3.5×10^{-7}	1.7×10^{-8}	Teadoum et al. 2016 [82]
Carbendazim	GO–MWNTs/GC	1.0×10^{-8}–4.0×10^{-6}	5.0×10^{-9}	Luo et al. 2013 [83]
Carbendazim	MWCNT/GCE	2.6×10^{-5}–3.1×10^{-6}	5.5×10^{-8}	Ribeiro et al. 2011 [84]
Carbendazim	MWNT-PMRE	2.0×10^{-7}–1.0×10^{-5}	9.0×10^{-9}	Li et al. 2009 [85]
Cyromazine	MWCNTPE	2.5×10^{-6}–5.0×10^{-4}	7.2×10^{-7}	Mercan et al. 2011 [76]
Cypermethrin	P3MT/MWCNT/GCE	3.6×10^{-8}–6.0×10^{-7}	3.6×10^{-12}	Sundari et al. 2011 [86]
Deltamethrin	P3MT/MWCNT/GCE	3.8×10^{-8}–4.9×10^{-7}	3.8×10^{-12}	Sundari et al. 2011 [86]
Dicofol	P3MT/MWCNT/GCE	1.4×10^{-7}–6.7×10^{-7}	1.4×10^{-11}	Sundari et al. 2011 [86]
Diuron and fenuron	GO–MWCNTs/GCE	9.0×10^{-6}–3.8×10^{-4} and 9.0×10^{-7}–4.7×10^{-5}	1.5×10^{-6} and 3.5×10^{-7}	Mani et al. 2015 [87]
2,4-dichlorophenoxyacetic acid	FePy-MWCNT/CPE	9.9×10^{-6}–1.4×10^{-4}	2.1×10^{-6}	Wong et al. 2013
Fenvalerate	P3MT/MWCNT/GCE	1.4×10^{-7}–5.9×10^{-7}	1.4×10^{-11}	Sundari et al. 2011 [86]
Isoproturon	P3MT/MWCNT/GCE	3.4×10^{-7}–1.2×10^{-6}	3.4×10^{-11}	Sundari et al. 2011 [86]
Lindane	MIP-MWCNT/Cu	1.0×10^{-10}–1.0×10^{-3}	1.0×10^{-10}	Anirudhan et al. 2015
MCPA and 4-chloro-2-methylphenol	PANI-β-CD/fMWCNT/GCE	1.0×10^{-5}–5.0×10^{-5}	1.1×10^{-6} and 1.9×10^{-6}	Rahemi et al. 2015 [88]
MCPA	PANI-β-CD/fMWCNT/GCE	1.0×10^{-5}–1.0×10^{-4}	9.9×10^{-7}	Rahemi et al. 2012 [89]
Methiocarb	CNT/PE	6.7×10^{-6}–2.6×10^{-4}	2.0×10^{-6}	Inam et al. 2013 [75]
Methyl-parathion	BMIMPF6–SWNT/GCE	2.0×10^{-9}–4.0×10^{-6}	1.0×10^{-9}	Fan et al. 2008 [90]
Methyl-parathion	Au/CNTs/GCE	3.8×10^{-7}–5.3×10^{-5}	1.9×10^{-7}	Zhang et al. 2009 [42]
Methyl-parathion	Pd/MWCNTs/GC	3.4×10^{-7}–4.8×10^{-5}	1.7×10^{-7}	Huang et al. 2010 [91]
Pentachlorophenol	QDs-MWCNT/GCE	8.0×10^{-8}–4.0×10^{-6}	2.0×10^{-9}	Feng et al. 2015 [92]
Pyrimethanil	IL-MWCNT/GCE	1.0×10^{-7}–1.0×10^{-4}	1.6×10^{-8}	Yang et al. 2015 [93]
Triclosan	MWCNT/GCE	1.7×10^{-7}–6.0×10^{-6}	5.7×10^{-8}	Yang et al. 2009 [94]
Vinclozolin	C_{60}–MWCNTs/GCE	2.5×10^{-6}–8.8×10^{-6}	9.1×10^{-8}	Rather et al. 2012 [95]
Voltage	P3MT/MWCNT/GCE	3.4×10^{-7}–1.2×10^{-6}	3.4×10^{-11}	Sundari et al. 2011 [86]

Au: gold; β-CD: β-cyclodextrin; $BMIMPF_6$: 1-butyl-3-methylimidazolium hexafluorophosphate; BPPGCE: basal plane pyrolytic graphite electrode; CNT: carbon nanotube; CoPc: cobalt phthalocyanine; C_{60}: fullerene; FePy: 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphyrin iron(III); FeTAPc: iron(II) tetraaminophthalocyanine; FMWCNTs: functionalized multi-walled carbon nanotubes; GO: graphene oxide; IL: ionic liquid; MIP: molecular imprinted polymer; MWCNT and MWNTs: multi-walled carbon nanotubes; MWCNTPE: multi-walled carbon nanotubes paste electrode; PANI: polyaniline; Pd: palladium; PMRE: polymeric methyl red film; P3MT: poly(3-methyl thiophene); QDs: quantum dots; SWCNT: single-walled carbon nanotube.

Glassy carbon electrode (GCE) is an electrode with a rigid and flat surface with a honeycomb aspect. Experimentally, the electrode surface should be cleaned by simple polishing with alumina (0.05, 0.5, and/or 1.0 μm) on a polishing cloth, followed by brief sonication in ethanol and ultrapure water before any electrochemical measurement or modification procedure. After this step, GCE can be modified by a homogeneous dispersion of reagents prepared in ultrapure water or organic solvent (e.g. dimethylformamide, acetonitrile, or ethanol). An aliquot of the dispersion is added on the electrode surface using the nanomaterials (μL) and then left to dry at room temperature, obtaining a homogeneous film over the electrode surface [96,97]. Sundari et al. [81] detected carbendazim using a GCE modified with functionalized multi-walled carbon (FMWCNTs/GCE). A peak current increase of fifteen times was obtained from the GCE modification with FMWCNTs. The sensor showed a wide linear concentration range of 5.2×10^{-11} to 2.6×10^{-4} mol·L^{-1} by using differential pulse adsorptive stripping voltammetry. The determination of the pesticide in soil and water samples was achieved with recovery percentages between 84.5% and 93.7%, demonstrating the good applicability of the proposed sensor.

Other studies related to glassy carbon electrodes modified with carbon nanotubes have been reported for the detection of different pesticides [84,94]. The detection of analytes in low concentrations is the major challenge for many research groups. The combination of carbon nanotubes and graphene has allowed excellent analytical performance for the detection of pesticides in real samples to be reached [83,87]. Mani et al. [87] modified a GCE surface with graphene oxide and multi-walled carbon nanotubes (GO–MWCNT) for the sensitive detection of diuron and fenuron herbicides. GO–MWCNT film-modified GCE exhibited excellent electrocatalytic effects on the oxidation process of diuron and fenuron in terms of lower overpotential and highly enhanced peak currents. In Figure 1A is shown the electrochemical profile recorded for 1.0 mmol·L^{-1} diuron in 0.1 mol·L^{-1} phosphate buffer solution (pH 5) using as the working electrode: (1) bare GCE; (2) GO/GCE; (3) MWCNTs/GCE; and (4) GO–MWCNTs/GCE. The GO–MWCNTs/GCE sensor exhibited greatly enhanced anodic peak at the potential of +0.80 V, promoting a 2.25-fold increase in the peak current and a 80 mV decrease in overpotential compared to the MWCNTs/GCE sensor (electrocatalytic profile). In Figure 1B are presented the SEM images of GO showing a characteristic wrinkled, scrolled, and folded intrinsic thin sheet-like morphology (1) and the incorporation of a tubular network of MWCNTs onto the surface of the GO sheets (GO-MWCNT) (2). A TEM image recorded for GO demonstrated a sheet-like morphology with sheet thicknesses between 1 and 2 nm (3), and a GO–MWCNT composite with MWCNTs firmly attached on both sides of the GO sheets (4). The analytical curves presented linear ranges from 9.0×10^{-6} to 3.8×10^{-4} mol·L^{-1} and from 9.0×10^{-6} to 4.7×10^{-5} mol·L^{-1} for diuron and fenuron, respectively. The determination of these pesticides in lake water and irrigation ditch water samples was performed with recoveries from 95.1% to 104.3%. In this case, the water samples were filtered to remove the solid impurities and diluted in the ratio of 1:50 with 0.1 mol·L^{-1} phosphate buffer (pH 5) solution.

The modification of the GCE surface with carbon nanotubes trapped into electrochemically prepared polymeric matrices was an approach explored by Li et al. [85] and Sundari et al. [86]. In the work of Li et al. [85], it was designed as a GCE modified with MWCNT-polymeric methyl red film for the determination of carbendazim and using linear-sweep voltammetry; a detection limit of 9.0 nmoL^{-1} and satisfactory recoveries for water samples were achieved (between 90.3% and 94.7%). Sundari et al. [86] evaluated the electrochemical response of various pesticides (cypermethrin, deltamethrin, dicofol, fenvalerate isoproturon, and voltage) using a GCE modified with MWCNTs and poly(3-methyl thiophene (P3MT) film, which is a conducting polymer. As can be seen in Table 1, wide linear concentration ranges and low detection limits were reported using differential pulse adsorptive stripping voltammetry.

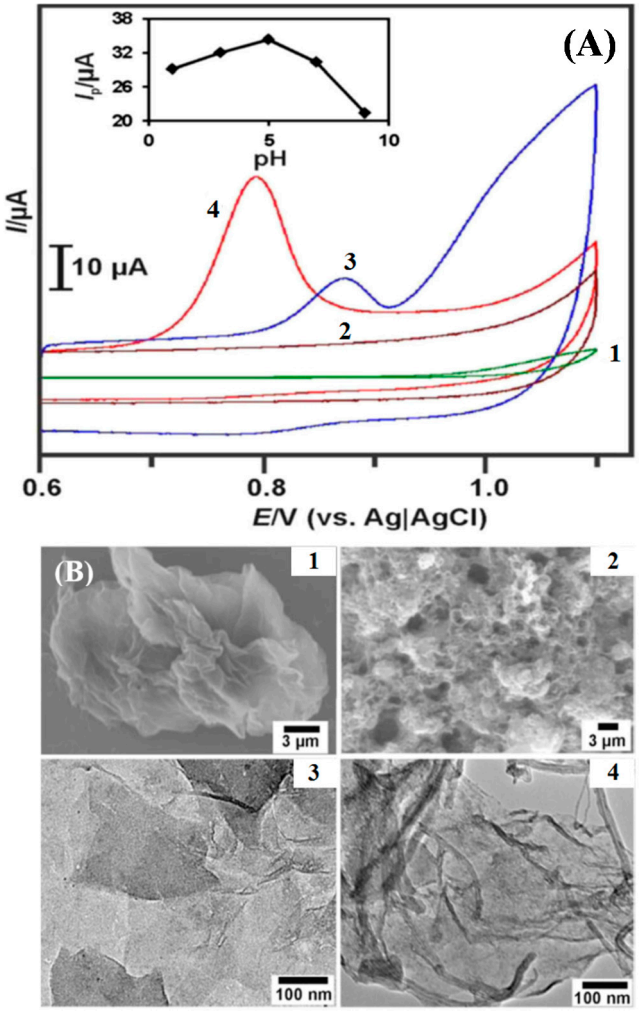

Figure 1. (**A**) Cyclic voltammograms (CVs) obtained at bare (1) GCE, (2) GO/GCE, (3) MWCNTs/GCE, and (4) GO–MWCNT/GCE for 1.0 mmol·L^{-1} diuron in 0.1 mol·L^{-1} phosphate buffer (pH 5) solution at a scan rate of 50 mV s^{-1}. Inset: plot of I_p versus pH from CVs obtained at GO–MWCNTs/GCE. (**B**) SEM images of GO (1) and GO–MWCNTs (2). TEM images of GO (3) and GO–MWCNTs (4). (Reproduced with permission of Springer from [87]).

3.2. Phthalocyanine/Carbon Nanotubes Sensors

Metal phthalocyanines and porphyrins are compounds with excellent electrical properties. Their efficient capabilities of electronic transfer, which are achieved with the π-electron system present in their structure, and their capacity to accommodate different metal ions such as Ni^{2+}, Fe^{3+}, Cu^{2+}, and Mg^{2+} become these promising materials. Many studies reported the use of metal phthalocyanines and porphyrins and MWCNT as modifiers on surface electrode [78,80,98]. Siswana et al. [77] carried out the electrocatalytic detection of amitrole using a pyrolytic graphite electrode modified with multi-walled carbon nanotubes and iron (II) tetra-aminophthalocyanine (MPc). The MPc complex was electropolymerized onto a multi-walled carbon nanotube-modified electrode, allowing an enhancement in the electrocatalytic detection of amitrole. The results obtained showed a low detection limit (0.5 nmol·L^{-1}) and excellent sensitivity of 8.8 ± 0.4 μA/nmol·L^{-1}. The proposed sensor showed no interference from other pesticides present in aqueous solutions. Mugadza et al. [78] reported the simultaneous detection of amitrole and diuron using GCE modified with iron(II) tetraaminophthalocyanine (FeTAPc)-single-walled carbon nanotube (SWCNT). These chemical species promoted the electrocatalytic oxidations of amitrole and diuron, and the linear concentration ranges for amitrole and diuron were from 5.0×10^{-5}

to 1.0×10^{-4} mol·L^{-1}, and detection limits of 2.1×10^{-7} mol·L^{-1} and 2.6×10^{-7} mol·L^{-1} were obtained, respectively. Figure 2 illustrates the reaction between SWCNT and MPc that occurred in the amine groups.

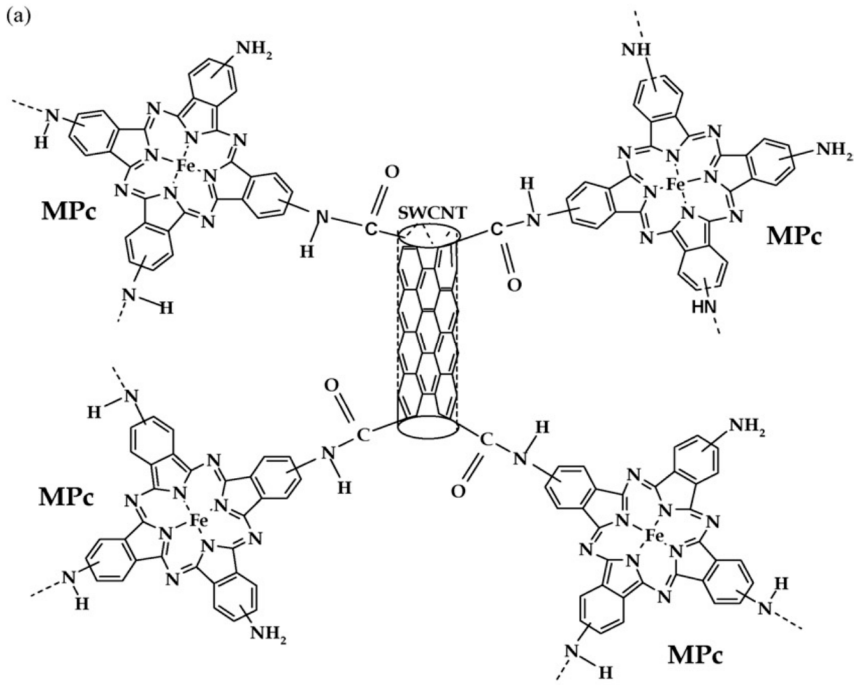

Figure 2. Representation of dendrimers formed between a SWCNT and FeTAPc. (Reproduced with permission of Elsevier from [78]).

3.3. Molecularly Imprinted Polymers/Carbon Nanotubes Sensors

Molecularly imprinted polymers (MIP) are a type of material that have biomimetic recognition of analytes similar to selective enzyme-substrate systems and/or antigen-antibody interactions. MIP is generally prepared through polymerization or electropolymerization that occurs in the presence of the template molecule to be printed. As result, a polymeric skeleton is formed around the analyte, containing complementary functional groups [99,100]. In an exciting example of an MIP approach applied to the selective sensing of pesticides, Yaqub et al. [101] reported the preparation of artificial receptors via in situ MIP synthesis directly on gold electrodes of quartz crystal microbalance (QCM, a piezoelectric transducer) for the selective determination of atrazine. Using the obtained sensing material, atrazine was detected at ppb (parts per billion) levels with good selectivity toward its main metabolites. Gan et al. [102] proposed a sensor based on MIP and MWCNT on GCE for the determination of 6-benzylaminopurine (BAP). The experimental procedure for the preparation of the electrode was based on a mixture of multi-walled carbon nanotubes@SnS_2 (MWCNT@SnS_2) and molecularly imprinted chitosan (CHIT) on the surface of GCE (core/shell-structured). In Figure 3 is illustrated the possible mechanism of molecular imprinting at the surface of MWCNT@SnS_2. The proposed sensor showed a highly improved sensitivity and high selectivity from the use of the imprinted CHIT, which served as the selective recognition sites. Under the optimal conditions, the analytical curve was linear in the concentration from 1.0×10^{-9} to 1.0×10^{-2} mol·L^{-1}, with a detection limit of 5.0×10^{-11} mol·L^{-1}. The determination of BAP in vegetable and fruit samples was carried on by the standard addition method. The results obtained showed good precision in the electrochemical analysis, with relative standard deviation (RSD) less than 3% (n = 6). The designed sensor was shown to be rapid, sensitive, and cost-effective for BAP determination.

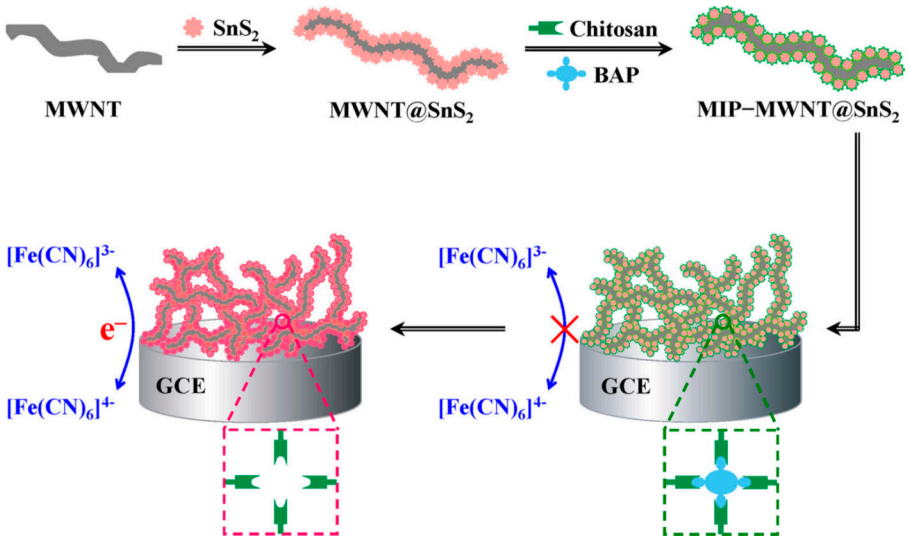

Figure 3. Schematic illustration of the molecular imprinting mechanism on molecularly imprinted polymers (MIP) and MWCNT@SnS_2/GCE. (Reproduced with permission of Springer from [102]).

3.4. Ionic Liquid/Carbon Nanotubes Sensors

Ionic liquids (ILs) are important compounds that have unique physical and chemical properties such as high conductivity, high viscosity, low toxicity, chemical and thermal stability, and non-volatility. An IL is a salt in liquid state formed by positively (cation) and negatively (anion) charged ions. The modification on an electrode surface with IL and MWCNT has provided a synergism that allowed the development of several analytical methods for the determination of pesticides [90,103]. Yang et al. [93] reported a rapid, simple, and sensitive electroanalytical method for the determination of pyrimethanil (PMT) using a GCE modified with multi-walled carbon nanotubes and 1-butyl-3-methylimidazolium hexafluorophosphate. The employed modifiers allowed an enhancement of the oxidation peak current of PMT, demonstrating their excellent electrochemical properties. In Figure 4a is shown the electrochemical behaviours of 5.0×10^{-5} mol·L^{-1} PMT on different electrodes. An oxidation peak and an absence of reduction peaks, featuring an irreversible system, can be seen. The much higher current obtained using MWCNTs–IL/GCE in comparison with that obtained using a GCE can be observed in Figure 5a. The improved current response can be attributed to the synergistic effect of MWCNTs and IL that allowed the electron transfer rate to be enhanced. The morphology of MWCNTs and MWCNTs-IL was characterized by TEM. First, from Figure 4b, MWCNTs is highly entangled, with a diameter of several tens of nanometers. The TEM image obtained for MWCNTs-IL (Figure 4c) shows MWCNTs to be much unfolded and a little widened after IL was added, indicating that IL could untangle MWCNTs and increased the effective surface area of MWCNTs. In our recent work, similar behaviour was diagnosed, and the unfolding MWCNTs effect caused by IL can be explained by the 'cation–π' interactions between the imidazolium cation of the IL and the π-electrons of the MWCNTs functionalized surface, as schematized in Figure 5 [104]. Under the optimum conditions, the sensor exhibited a linear concentration range for PMT from 1.0×10^{-7} to 1.0×10^{-4} mol·L^{-1}. Apart from showing good reproducibility, stability, and no-interference, the sensor was employed with success in the detection of PMT in real samples (fruit and water samples) using a standard addition method, with recoveries ranging from 96% to 110%.

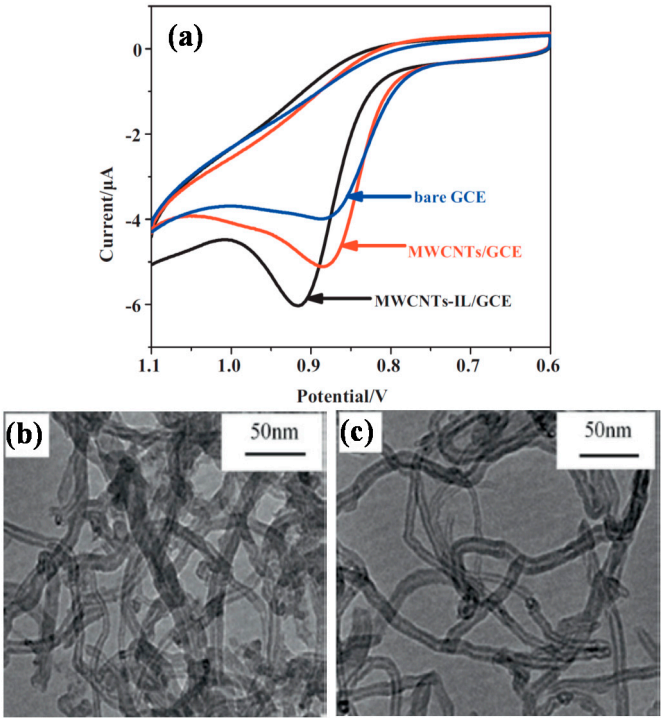

Figure 4. (**a**) CVs for 5.0×10^{-5} mol·L^{-1} PMT on different electrodes in PBS (pH 6.0). TEM images of (**b**) MWCNTs and (**c**) MWCNTs-IL. (Reproduced with permission of Elsevier from [93]).

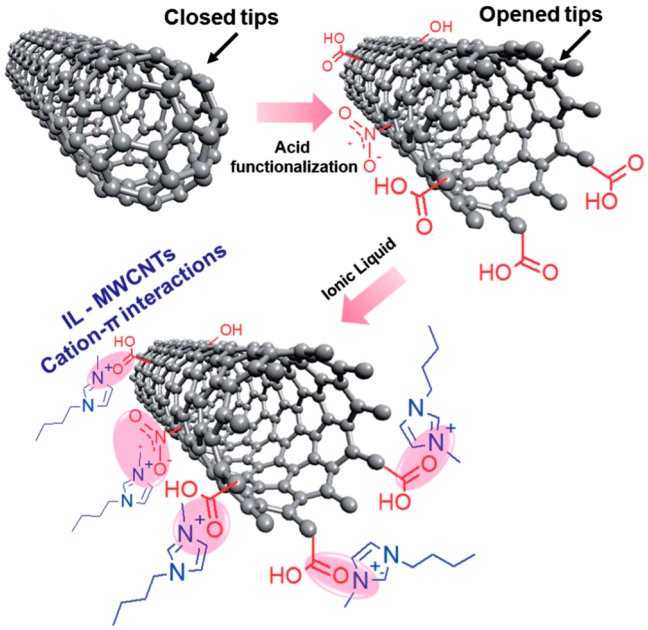

Figure 5. Illustration of the "cation–π" interaction between IL and MWCNTs after functionalisation. Note: in this illustration, for simplicity, a single-walled carbon nanotube (SWCNT) was used in place of the MWCNT. (Reproduced with permission of Royal Society of Chemistry from [104]).

3.5. Metallic Nanoparticles/Carbon Nanotubes Sensors

Metallic nanoparticles have experienced growing interest for use in electroanalytical chemistry as electrode modifiers for a set of important advantages that can be achieved, including high effective surface area and electrocatalytic activity toward the oxidation/reduction of a number of

substances [105]. The synergistic effect from the combined use of metallic nanoparticles and carbon nanotubes has been explored in recent years for the sensing of pesticides. Metallic nanoparticles and carbon nanotubes improve the electrochemical performance of bare electrodes, providing high electroactive surface area and, therefore, higher analytical sensitivities and lower detection limits. The use of gold nanoparticles (AuNPs) and palladium nanoparticles (PdNPs) combined with multi-walled carbon nanotubes for the modification of GCE surfaces was proposed by Zhang et al. [42] and Huang et al. [91]. In the work of Zhang et al. [42], for preparation of the AuNPs/CNTs modified GCE, firstly, the GCE surface was modified with 5 µL of a 0.5% m/m Nafion aqueous dispersion containing CNTs. Then, the AuNPs were electrodeposited on the CNTs/GCE by cyclic voltammetry (between −0.2 V and +1.0 V vs. SCE) in 0.2 mol·L^{-1} H_2SO_4 solution containing 5 mmol·L^{-1} $HAuCl_4$. In Figure 7 are shown the SEM images obtained for the CNTs (Figure 6a) and AuNPs deposited on GCE (Figure 6b) and on CNTs/GCE (Figure 6c). From these, it is clear that well dispersed AuNPs were obtained on the CNTs/GCE substrate using the cyclic voltammetric procedure with a diameter in the range of 80–100 nm. The authors showed that AuNPs possess electrocatalytic activity towards the reduction of parathion. Using linear sweep voltammetry under optimum experimental conditions, the obtained analytical curve was linear from 5.0 × 10^{-7} to 6.0 × 10^{-5} mol·L^{-1}, with a detection limit of 1.0 × 10^{-7} mol·L^{-1}. The developed voltammetric procedure was applied in the parathion quantification of spiked water and vegetable samples with recovery percentages ranging from 98.3% to 104.3%.

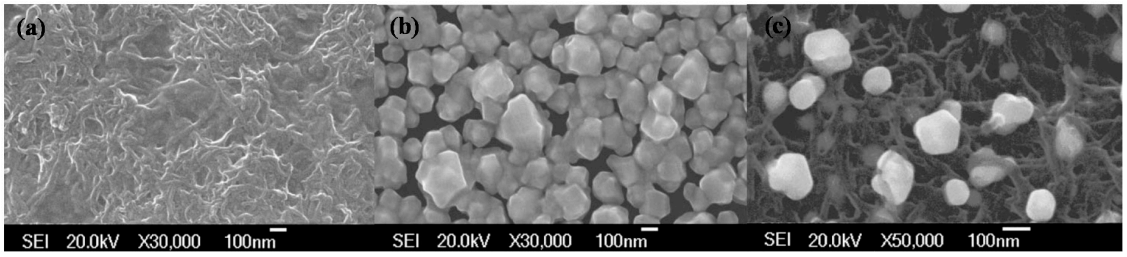

Figure 6. (**a**) FE-SEM of the CNTs; (**b**) Au nanoparticles on GCE; and (**c**) Au nanoparticles combined with CNTs on GCE. (Reproduced with permission of Springer from [42]).

In another similar research, the parathion pesticide was determined using a GCE modified with MWCNTs and PdNPs. In this case, the PdNPs were chemically synthesized via a reduction reaction in an ethylene glycol solution containing MWCNTs. Thus, a nanocomposite of the PdNPs supported on the MWCNTs surface was obtained and applied in the GCE modification procedure. The obtained Pd-MWCNTs/GCE was used to study parathion electrochemical behaviour in a function of pH and determine this compound by DPV. The obtained analytical curve was linear from 3.4 × 10^{-7} to 4.8 × 10^{-5} mol·L^{-1}, with a detection limit of 1.7 × 10^{-7} mol·L^{-1}. Thus, the use of PdNPs provides very similar analytical features to those obtained using AuNPs. However, in this case, the authors have not tested the analytical performance of the proposed sensor for the parathion quantification in environmental samples. Therefore, future real applications must be carried out.

3.6. β-Cyclodextrin/Carbon Nanotubes Sensors

A sequence of papers was reported by Rahemi et al. [79,88,89] dedicated to the construction of pesticide electrochemical sensors based on β-cyclodextrin and carbon nanotubes. Cyclodextrin molecules are cyclic oligosaccharides formed of six to twelve α-D-glucopyranose monomers, which are linked by 1 and 4 carbon atoms [106]. β-cyclodextrin (β-CD) is a type of cyclodextrin molecule constituted of seven D-glucopyranose units, which possesses a hydrophilic exterior and an interior hydrophobic cavity [89]. Cyclodextrin can be explored for electroanalytical proposes using its ability for molecular recognition and selective pre-concentration of analytes on the modified electrode surface [107–109]. In the first work of Rahemi et al. [89], the chlorophenoxy herbicide MCPA

(4-chloro-2-methyl-phenoxyacetic acid) was determined by cyclic voltammetry using an electrochemical sensor based on GCE modified with MWCNTs, β-CD, and polyaniline (PANI) film. The designed molecular host–guest recognition showed an improved electrocatalytic oxidation of MCPA molecules and, therefore, improved electrochemical sensitivity. Using cyclic voltammetry, the sensor response was linear from 1.0×10^{-5} to 1.0×10^{-4} mol·L^{-1}, with a detection limit of 9.9×10^{-7} mol·L^{-1}. The developed method was successfully applied in the MCPA quantification in river water samples, with results statically similar those found by a high-performance liquid chromatographic (HPLC) method. Moreover, the authors demonstrated the excellent operation lifetime and selectivity of the proposed voltammetric sensor. This same sensor architecture was later applied for the determination of berbicide bentazone [79] and MCPA and its metabolite 4-chloro-2-methylphenol [88]. Again, linear concentration ranges and detection limits at micromolar levels were obtained, as well as excellent accuracy.

3.7. Fullerene and Quantum Dots/Carbon Nanotubes Sensors

Fullerene (C_{60})-functionalized carbon nanotubes were explored for the construction of electrochemical sensors with enhanced analytical performance for the determination of endocrine disruptor vinclozolin and carbendazim by Rather et al. [95] and Teadoum et al. [82]. In both works, a GCE was employed as a bare electrode. In the work of Rather et al. [95], the GCE surface was modified with a 0.1 mg·mL^{-1} MWCNTs:C_{60} (2:1 *w*/*w*) suspension, followed by an electrochemical treatment of the modified electrode by cyclic voltammetry between 0.0 and −2.0 V in a 0.1 mol·L^{-1} tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solution prepared in acetonitrile. In Figure 7 is shown the general scheme of electrode modification. Vinclozolin was determined by square-wave voltammetry, exploring the enhanced effect of cetyltrimethyl ammonium bromide (CTAB) surfactant. Under optimum experimental conditions, the obtained analytical curve was linear from 2.54×10^{-6} to 8.75×10^{-6} mol·L^{-1}, with detection and quantification limits of 9.1×10^{-8} mol·L^{-1} and 3.0×10^{-7} mol·L^{-1}, respectively. The sensor was applied to vinclozolin quantification of wastewater samples with satisfactory recovery percentages. Recently, Feng et al. [92] reported the construction of an electrochemical sensor for pentachlorophenol determination in fish meat based on ZnSe quantum dot decorated MWCNTs. In this case, DPV was employed as voltammetric technique, and the analytical curve and detection limit were in the order of nanomolar concentration.

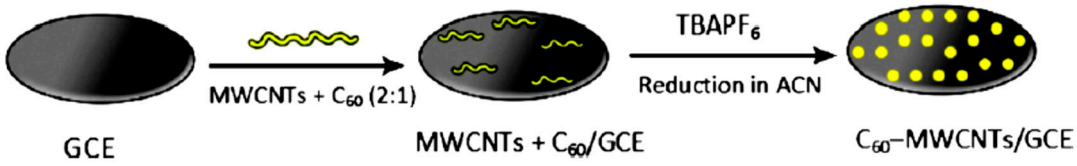

Figure 7. Scheme of fabrication of the C_{60}–MWCNTs/GCE sensor. (Reproduced with permission of Elsevier from [95]).

4. Conclusions, Challenges and Future Perspectives

A review of the literature demonstrated that carbon nanotubes provided electrochemical sensors with relatively good analytical performance in pesticide determination. Pesticides from different classes were electrochemically quantified using carbon nanotubes-based electrochemical sensors. The main electrode modification strategies consisted of the incorporation of carbon nanotubes within the composition of carbon paste electrodes and the modification of the surface of glassy carbon electrodes using the classical dropping cast method. Carbon nanotubes were used alone or in combination with different types of modifiers, including conductive polymers, phthalocyanines, porphyrins, metallic nanoparticles, ionic liquids, and graphene, among others. In general, a typical result achieved from the modification of carbon paste or glassy carbon electrodes is the very high increment of the analytical signal and the displacement of the working potential closer to zero. Both of these effects are desired to ensure high sensitivity and good analytical selectivity. The revised works

demonstrated the construction of analytical curves with good linear concentration ranges (typically two concentration decades or more) and low detection limits (at least at the micromolar level). Moreover, in most cases, a good stability of response, precision of measurement, and accuracy in the recovery of spiked environmental samples are proved. Therefore, the positive effects of the use of carbon nanotubes as electrode modifiers for the preparation of electrochemical sensors dedicated to pesticide monitoring is very well illustrated and demonstrated. From the well-established electrochemical sensing performance of carbon nanotubes-based sensors toward pesticides, a set of challenges should be investigated and overcome for the advance of this important research topic. An interesting approach for future investigations is the possibility of designing multiplexed arrays using microfluidic devices, with which different analytes could be simultaneously determined in different sensing points. This challenge is linked with a current and relevant trend in (electro)analytical chemistry, which is the miniaturization of the analytical devices, with minimization of the consumption of chemical reagents and waste generation, as well as the proposition of portable instrumentation for analysis in the field (outside of the lab doors). From an analytical point-of-view, the amperometric and voltammetric methods dedicated to the sensing of pesticides should to be subjected to more rigorous analytical tests in order to verify the selectivity and reproducibility (and improve them if necessary), long-term stability, and applicability in diversified matrice samples, once most of the electroanalytical methods are employed in an analysis of spiked water samples using bulk electrodes. The robustness of the electroanalytical methods must also be evaluated from the analysis of a great number of environmental samples. In terms of sensor architecture material, a current trend is the preparation of composites of carbon nanotubes with another allotropic carbon forms, such as carbon black, graphene, or diamond. These classes of carbon composite electrodes are very promissory for electroanalysis purposes, and future electrochemical investigations should be carried out on the sensing and biosensing of pesticides.

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