Chemia Naissensis, Vol 1, Issue 1, 130-149

Carbon nanotube-based electrochemical sensors for pesticide determination in aqueous solutions: a review

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ABSTRACT

Excellent mechanical, electrical and magnetic properties of carbon nanotubes (CNT) make CNTs a promising material for the development of electrochemical sensors. Pesticides are very important for an increase in crop yields. However, the intensive use of pesticides can lead to the accumulation of their remains, thus creating a severe problem and risk to human and environmental health. Those are the reasons why the monitoring of pesticides in the environment is extremely important. For that purpose, electrochemical sensors based on carbon nanotubes were designed, and their main aim is pesticide monitoring at environmental samples. A review of the recent studies of environmental monitoring of pesticides using electrochemical sensors based on carbon nanotubes is presented.

Keywords: *electrochemical sensors, pesticides, carbon nanotubes*

Introduction

Carbon nanotubes (CNTs) are officially mentioned in 1991 when Sumio Iijima discovered the existence of multi-walled CNTs (MWCNTs) as a byproduct in the synthesis of phularen (Iijima, 1991). Two years later, two groups of scientists, one led by Iijima et al. (Iijima and Ichihashi, 1993) and the other by Bethune (Bethune et al., 1993), experimentally came to the discovery of single-walled CNTs (SWCNTs).

Single-walled carbon nanotubes (Fig. 1) can be considered as long, trained layers of graphene. Their diameter is nanometer dimensions (typically between 0.7 and 1.4 nm), and the length is several thousand times greater than the diameter (Cvetićanin, 2013). Several concentric cylinders inserted into each other with a layer spacing of 0.3–0.4 nm are created multi-walled carbon nanotubes (Fig. 1) (Andrews et al., 2002).

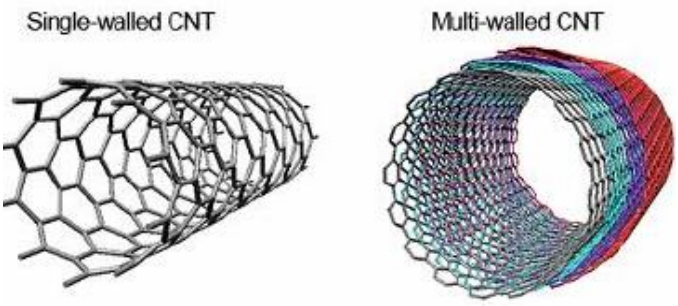


Figure 1. Single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT)

There are three main techniques for synthesis MWCNTs and SWCNTs: arc-discharge, laser-ablation, and catalytic growth. SWCNTs have higher specific stiffness and strength than MWCNTs (Batra and Sears, 2007). Due to excellent physical and elastic characteristics, high electrical conductivity (Demczyk et al., 2002; Hong and Myung, 2007; Peng et al., 2008) CNTs are a unique material.

The advantages of carbon nanotubes compared to other materials are small size, high strength, high electrical and thermal conductivity, specific shape. Due to all these properties, carbon nanotubes can be used in electroanalytical applications. The superficial incorporation of metallic nanoparticles (Yang et al., 2015), organic (Eguílaz et al., 2016) and inorganic molecules (Husmann and Zarbin, 2016) is very important because it can increase the field of electroanalytical applications. Carbon nanotubes are raw materials for the development of electrochemical sensors to detect dyes, ions, phenols, drugs, and pesticides (Govindhan et al., 2015; Wang et al., 2014; Zhang et al., 2009).

The recent advances in the creation of electrochemical sensors on the basis of carbon nanotubes for the determination of pesticides in real samples are described here.

Pesticides

Pesticides are products of natural or chemical origin whose application is protection plants against weeds, diseases, harmful insects, mites and other harmful organisms. Although the use of pesticides leads to an increase in crop yields, the intensive use of pesticides can lead to the accumulation of their remains, thus creating a serious problem and risk to human and environmental health (Damalas and Eleftherohorinos, 2011). Also, these compounds are widely distributed in the environment, and their existence in water, soil, sewage sludge, sediment has been discovered (Domínguez et al., 2016). In the human body, they may increase the risk of numerous disorders, even in low concentrations. Those are the reasons why the monitoring of pesticides in the environment is extremely important.

Classification of pesticides

Pesticides can be classified in several ways and, one of the ways is classification according to purpose, which includes acaricides, algicides, bactericides, fumigants,

fungicides, herbicides, insecticides, rodenticides, *etc.* Pesticides can be also classified according to the way of entering the organism: abdominal (digestive), contact, fumigant. According to the chemical composition, all pesticides can be divided into three groups: inorganic compounds, organic compounds, and pesticides of natural origin.

Pesticides of inorganic origin are compounds of mercury, fluorine, barium, sulfur, copper, as well as chlorates and borates. Pesticides of natural origin (for example pyrethrins, antibiotics or phytocides) are compounds which are the result of biosynthesis of living organisms (plants, bacteria, and fungi). The largest group of pesticides are organic compounds, and they include organochloric, organophosphorus compounds, derivatives of carbon, thio- and dithiocarboxylic acids, nitro derivatives of phenol, phthalimides, mineral oils, etc. (Gruzdyev, 1988).

There are several methods for the detection of pesticides. Some of them are fluorescence spectrophotometry, gas chromatography with mass spectrometry detection, high-performance liquid chromatography (HPLC) with fluorescence detection and HPLC coupled to mass spectrometry (Chen et al., 2015; Lemos et al., 2016; López et al., 2016; Mol et al., 2016). Unlike the expensive spectroscopic and chromatographic methods, electrochemical methods are cheap, sensitive, selective and simple methods for the determination of pesticides.

Electrochemical sensors based on carbon nanotube for determination of pesticides

Here, we present a general overview of the recent researches on the topic of environmental monitoring of pesticides using sensors based on a carbon nanotube, glassy carbon electrode (GCE) and carbon paste electrode (CPE) (Tables 1 and 2). As can be seen, different electrodes for the detection of various pesticides were used. Electrochemical sensors can be designed with pristine carbon nanotubes or carbon nanotubes which are modified by other compounds.

Table 1. Electrochemical sensors based on modified GCE for determination various pesticides

Electrode	Pesticide	Limit of detection (mol/L)	Linear range (mol/L)	Reference
FMWCNTs/GCE	Carbendazim	5.2×10^{-11}	5.2×10^{-11} - 2.6×10^{-4}	Sundari et al., 2010
Fullerene/MWCNT/ Nafion/GCE	Carbendazim	1.7×10^{-8}	2.0×10^{-8} - 3.5×10^{-7}	Teadoum et al., 2016
MWCNT/Pd-Ir with MB	Carbofuran	1.7×10^{-12}	4×10^{-11} - 4×10^{-9}	Li et al., 2016
MWCNTs/TiO_2NPs	Diazinon	3×10^{-9}	11×10^{-9} - 8.36×10^{-6}	Ghodsi and Rafati, 2017
β–CDs/MWCNTs/GCE	Dichlorophen	1.4×10^{-8}	5.0×10^{-8} - 2.9×10^{-6}	Sipa et al., 2018
MWCNTs/GCE	Fenitrothion and Bifenox	8×10^{-8}	2×10^{-7} - 6×10^{-5}	Salehzadeh et al., 2016
β-CD-rGO/GCE	Paichongding	1.1×10^{-6}	1×10^{-6} - 1×10^{-5} 1×10^{-5} - 5.5×10^{-5}	Zhang M. et al., 2016
AuNPs/CNT/GCE	Parathion	1.0×10^{-7}	5.0×10^{-7} - 6.0×10^{-5}	Zhang Y. et al., 2009
GCE/MWCNTs	Propham	3.65×10^{-7}	2×10^{-6} - 4.78×10^{-5}	Leniart et al., 2016
IL-MWCNT/GCE	Pyrimethanil	1.6×10^{-8}	1×10^{-7} - 1×10^{-4}	Yang et al., 2015
C_{60}–MWCNTs/GCE	Vinclozolin	9.1×10^{-8}	2.5×10^{-6} - 8.8×10^{-6}	Rather et al., 2012

Table 2. Electrochemical sensors based on carbon paste electrode (CPE) for determination various pesticides

Electrode	Pesticide	Limit of detection (mol/L)	Linear range (mol/L)	Reference
ZXCPE	Carbamyl	3×10^{-7}	$1\times10^{-6} – 1\times10^{-4}$	Salih et al., 2017
MIP/CPE	Dicloran	4.8×10^{-10}	1×10^{-6} - 1×10^{-9}	Shahtaheria et al., 2017
MWCNPE	Methiocarb	2.0×10^{-6}	6.7×10^{-6} - 2.6×10^{-4}	Inam and Bilgin, 2013

Sensors based on carbon nanotubes

There are many pieces of research based on carbon nanotubes using as bare electrode, such as CPE or modified GCE.

Carbon paste electrode is a composite electrode constructed using carbon materials such as graphite, carbon nanotubes (CNPE) or products from the combination of at least two materials. CNPE is a mixture of carbon nanotubes and a hydrophobic organic liquid (mineral oil, paraffin oil, or silicone oil) placed on a plastic or glass tube of a specific diameter (Apetrei et al., 2011).

Inam and Bilgin (2013) detected the insecticide methiocarb using a multi-walled carbon nanotube paste electrode by square-wave voltammetry (SWV). The preparation of the used electrode (CNPE) was performed by mixing the carbon nanotube powder with mineral oil (0.15:0.85 w/w ratio). Methiocarb electrochemical characterization in 0.1 mol/L H_2SO_4 presented an irreversible anodic peak at + 1.3 V vs. Ag/AgCl. The results showed a linear dynamic range between 6.7 x 10^{-6} and 2.6 x 10^{-4} mol/L and a detection limit of 2.0 x 10^{-6} mol/L, with recoveries of (98.5±0.3)% in river water samples, respectively.

A rigid and flat surface is a characteristic of a glassy carbon electrode (GCE). Before any experiment, the surface of the electrode should be cleaned by polishing with alumina, followed by sonification in ethanol and ultrapure water. After purification, the electrode can be modified by homogenous reagent dispersion prepared in ultrapure water or an organic solvent (acetonitrile, ethanol). An aliquot of dispersion is added to the surface of the electrode

(μL) and left to dry at room temperature. As a result, a homogeneous film on the surface of the electrode is obtained (Li et al., 2013).

Sundari et al. (2010) detected the pesticide carbendazim using a GCE modified with functionalized multi-walled carbon (FMWCNTs/GCE) by differential pulse adsorptive stripping voltammetry. The sensor showed a linear concentration range between 5.2 x 10^{-11} and 2.6 x 10^{-4} mol/L, with recovery percentages between 84.5% and 93.7% in water samples.

Hamid et al. (2016) investigated the electrochemical behavior of fenitrothion (FT) and bifenox (BF) using a GCE modified with multi-walled carbon nanotube by square wave voltammetry (SWV). Fig. 2 shows the SEM image of the surface GCE modified with MWCNTs (MWCNTs/GCE). Typical square wave voltammograms for a solution containing FT and BF (pH 5.0) are shown in Fig. 3. Quantification determination of FT and BF based on the cathodic peaks C_0 and C_0' is not possible. Anodic peak A_1 (at -0.061 V vs. Ag/AgCl) is related to the oxidation of FT_{red} resulting from the reduction of FT. Anodic peak A_2 (at 0.063 V vs. Ag/AgCl) is related to the oxidation of BF_{red} resulting from the reduction of BF. The detection limit for both FT and BF was found to be 0.08 μM and linear response over the range 0.2-60 μM. The method revealed recovery percentages of FT and BF in the range of 96.6-104% in river water samples.

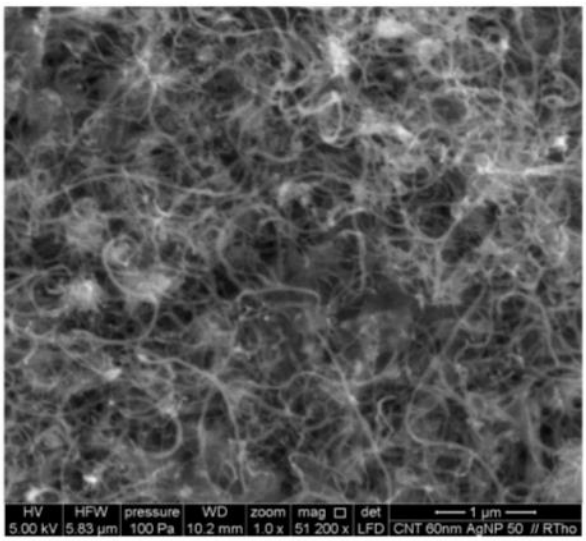


Figure 2. SEM image of MWCNTs/GCE (Hamid et al., 2016)

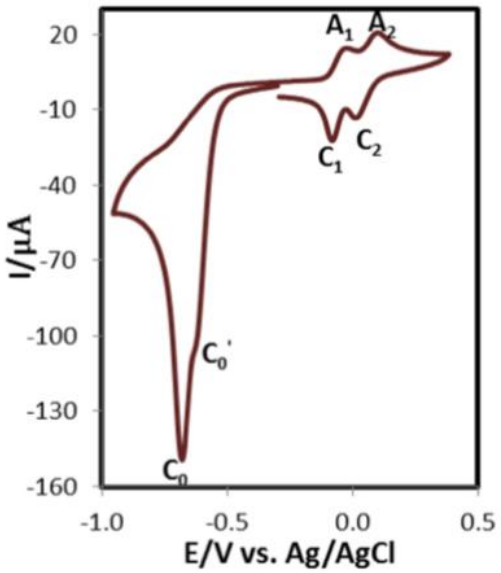


Figure 3. Cyclic voltammogram of 1.0 mM FT and 1.0 mM BF in aqueous solution containing acetate buffer (pH = 5.0, 0.2 M) and 20% ethanol (v/v) at the glassy carbon electrode. Starting potential −0.3 V, first switching potential −0.9 V and second switching potential 0.35V vs. Ag/AgCl. Scan rate 100 mV/s (Hamid et al., 2016)

Leniart et al. (2016) studied electrochemical oxidation of herbicide propham on a glassy carbon electrode modified with multi-walled carbon nanotubes (GCE/MWCNTs) by square wave adsorptive stripping voltammetry (SWAdSV). The best signal at +1.49 V vs. Ag/AgCl was recorded in 0.5 mol/L sulphuric acid. A limit of detection (LOD) and a limit of quantification (LOQ) were 3.65×10^{-7} and 1.09×10^{-6} mol/L, respectively. The determination of propham was performed using the developed method in spiked Bzura River water samples. Fig. 4 presents SWAdS voltammograms for the determination of propham in water samples using the standard addition method: 0) blank, (1) river water sample spiked with propham, (2) as (1) $+5.00\times10^{-6}$ mol/L, (3) as (1) $+9.09\times10^{-6}$ mol/L, (4) as (1) $+1.54\times10^{-5}$ mol/L, (5) as (1) $+2.00\times10^{-5}$ mol/L.

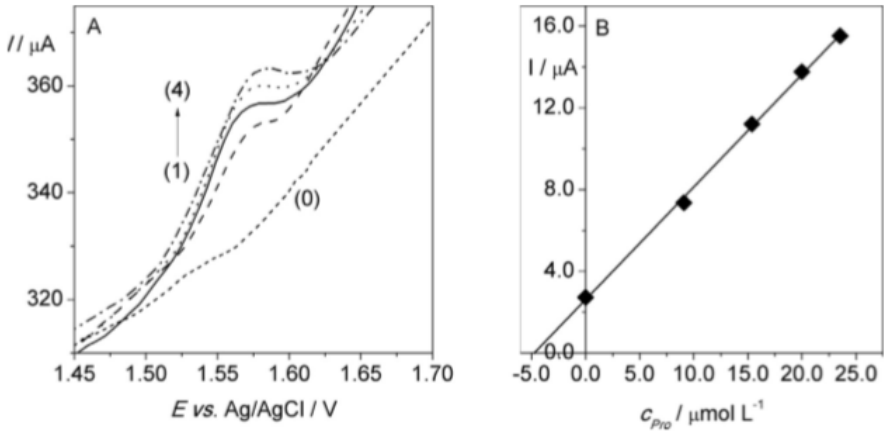


Figure 4. SWAdS voltammograms for the determination of propham in water samples using the standard addition method (Leniart et al., 2016)

Sensor based on GCE modified with MWCNTs/ TiO_2 nanoparticles

Ghodsi and Rafati (2017) developed a voltammetric sensor for diazinon pesticide determination based on glassy carbon electrode (GCE) surface modified with multi-walled carbon nanotubes covered by TiO_2 nanoparticles (MWCNTs/TiO_2NPs). The voltammetric probes were carried out by cyclic voltammetry (CV), linear sweep voltammetry (LSV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV). Prepared MWCNTs/TiO_2NPs was characterized with scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX) techniques (Fig. 5). The sensors showed a linear range between 11-8360 nM, a limit of detection 3 nM and a limit of quantification 10 nM. The developed sensor showed good sensitivity and was successfully examined for diazinon determination in real water samples. The sensor showed the highest sensitivity when SWV technique was applied (Fig. 6). Therefore next diazinon determination in real samples was obtained using SWV technique.

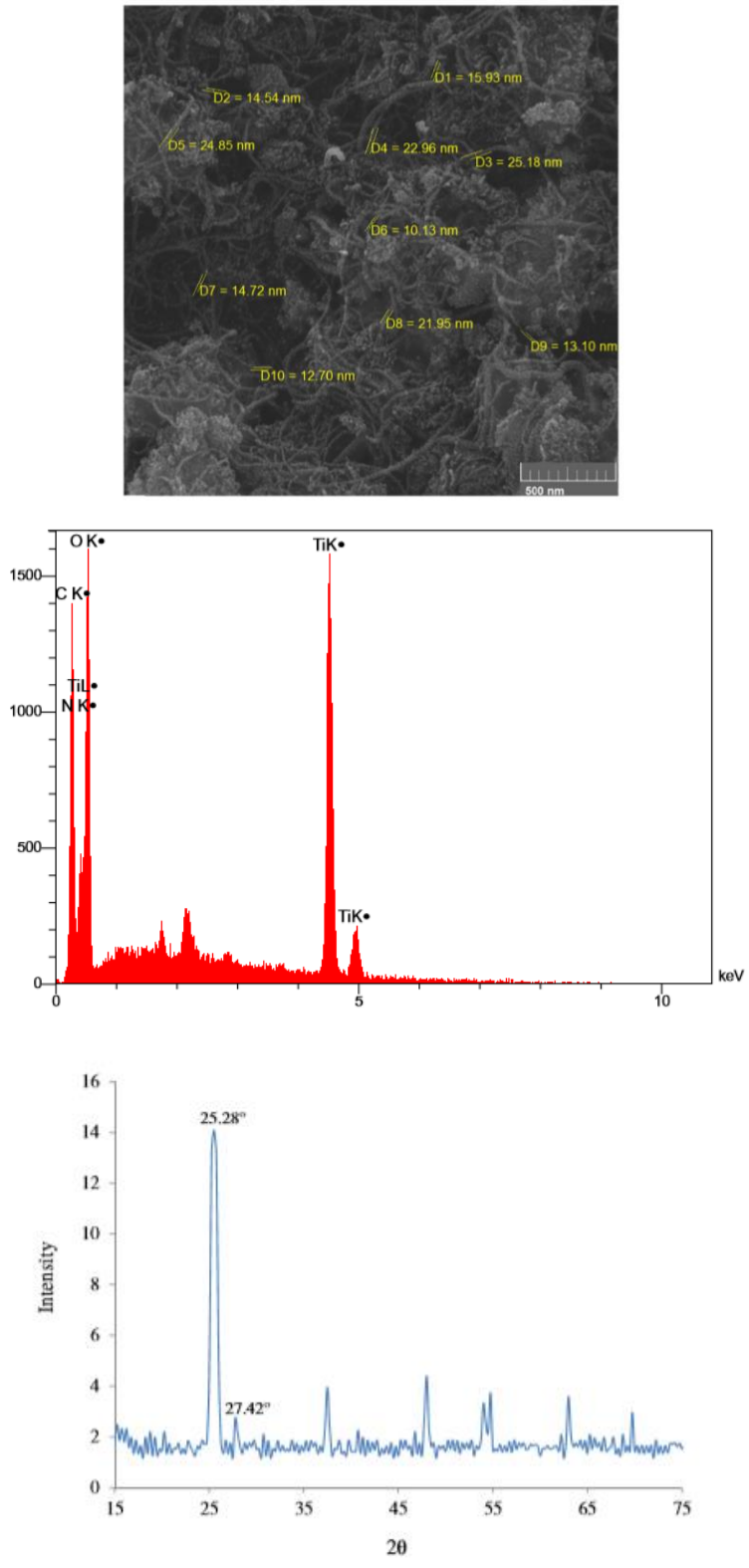


Figure 5. a) SEM image; b) EDX analysis;

c) XRD pattern of MWCNTs/TiO_2NPs nanocomposite on GCE surface (Ghodsi and Rafati, 2017)

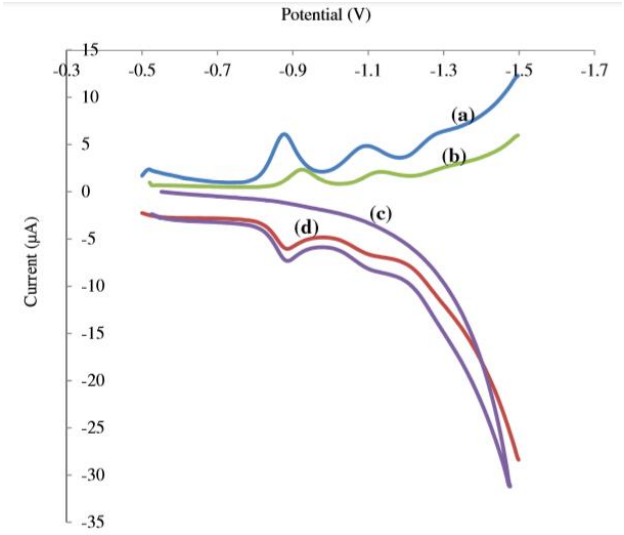
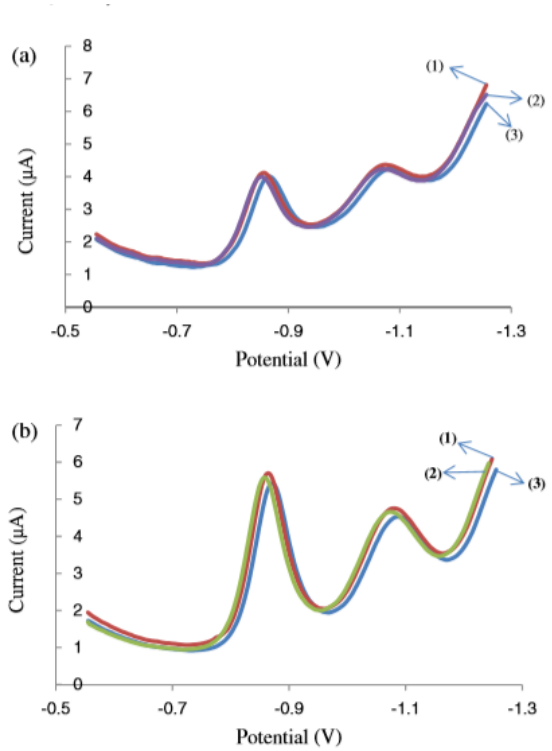


Figure 6. (a) SWV, (b) DPV, (c) CV and (d) LSV response of the developed sensor to 2 μM diazinon (Ghodsi and Rafati, 2017)

Fig. 7 represents a) SWV voltammograms of 1) a sample from well water spiked with 1 μM of diazinon, 2) a sample from tap water spiked with 1 μM of diazinon and 3) phosphate buffer containing 1 μM of diazinon obtained by GCE/MWCNTs/TiO_2NPs. Fig. 7 b) and c) represent the same SWVs with 2 μM and 3 μM of diazinon, respectively.



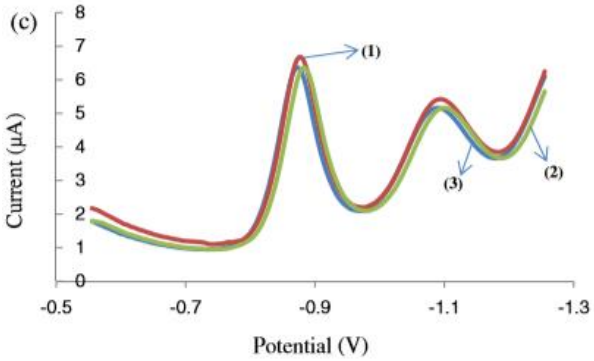


Figure 7. SW voltammograms of 1) a sample from well water spiked with 1 μM of diazinon, 2) a sample from tap water spiked with 1 μM of diazinon and 3) phosphate buffer containing 1 μM of diazinon obtained by GCE/MWCNTs/TiO_2NPs. Panels b and c show same SWVs with 2 μM and 3 μM of diazinon respectively (Ghodsi and Rafati, 2017)

Sensor based on low silica X zeolite modified carbon paste electrode

The team of scientists worked on the development of an electrochemical sensor for the detection of carbamyl pesticides, which is based on low silica X (LSX) zeolite modified carbon paste electrode. For characterization of synthesized LSX zeolite was used XRD analysis. Fig. 8. shows intense diffractions peaks at 2θ values equal to 6.12°, 13.96°, 24.31°, 26.69° and 30.97° which corresponds to the characteristic peaks of zeolite X.

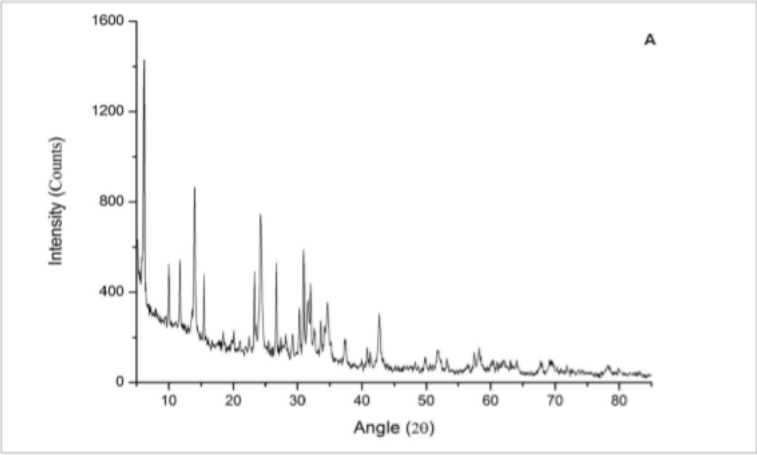


Figure 8. X-ray diffraction patterns of Low Silica X Zeolite (LSXZ) (Salih et al., 2017)

The electrochemical behavior of the ZXCPE in potassium hexacyanoferrate III/II solution was investigated by cyclic voltammetry (CV). Fig. 9. represents the responses obtained by CV between -0.2 and +0.7 V (vs. SCE) at CPE and ZXCPE in 0.1 M KCl

solution containing 1 mM $[Fe(CN)_6]^{3-/4-}$ (1:1) at 50 mV/s. At CPE (curve b), the values of current Ipa = 18 μA, Ipc = - 19 μA were recorded, while the modified electrode of ZXCPE showed an evident increase in current value (Ipa = 26 μA, Ipc = - 26 μA). This implies that the electron transfer rate at ZXCPE is improved (Salih et al., 2017).

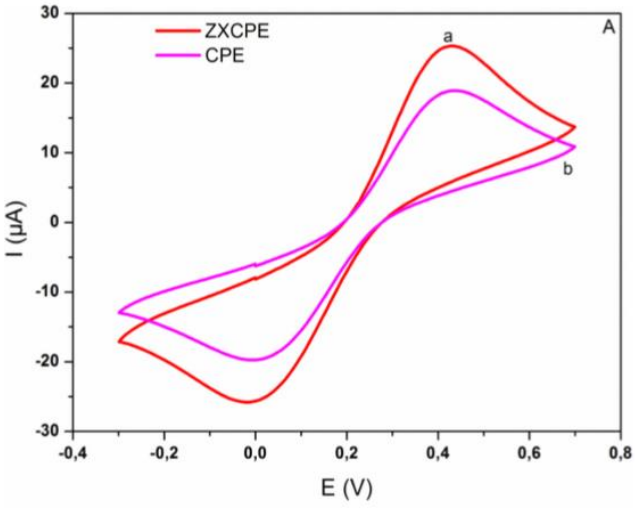


Figure 9. Cyclic voltammograms of ZXCPE and CPE in 1 mM $[Fe(CN)_6]^{3-/4-}$/0.1 M KCl at 50 mv/s (Salih et al., 2017)

Sensors based on metallic nanoparticles and carbon nanotubes

Metallic nanoparticles are important, because, in combined use with carbon nanotubes, they improve the electrochemical characteristic of electrodes, more precisely higher analytical sensitivities and lower detection limits.

Zhang et al. (2009) developed a voltammetric sensor for parathion pesticide determination based on glassy carbon electrode (GCE) surface modified with AuNPs/CNT. Firstly, modification of the GCE surface was performed with 5 μL of a 0.5% m/m Nafion aqueous dispersion containing CNTs. After that, the AuNPs were electrodeposited on the CNTs/GCE in 0.2 mol/L H_2SO_4 solution containing 5 mmol/L $HAuCl_4$. Electrodeposition is performed by cyclic voltammetry between −0.2 V and +1.0 V (vs. SCE). The analytical curve shows linearity in the range 5.0×10^{-7}-6.0×10^{-5} mol/L and a LOD of 1.0×10^{-7} mol/L, with recovery percentages between of 104.3% in water samples. In Fig. 10. are shown the SEM images obtained for the CNTs (Fig. 10a), AuNPs deposited on GCE (Fig. 10b) and AuNPs deposited on CNTs/GCE (Fig. 10c).

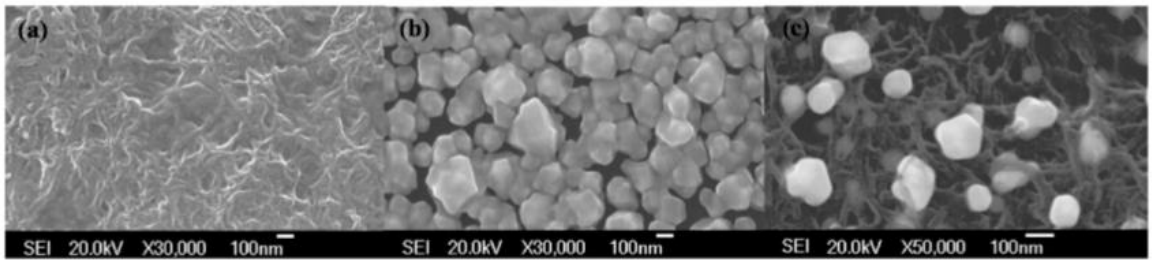


Figure 10. a) SEM image of the CNTs, b) Au nanoparticles on GCE, c) Au nanoparticles combined with CNTs on GCE (Zhang et al., 2009)

Sensors based on β-cyclodextrin and carbon nanotubes

Sipa et al. (2018) successfully developed an electrochemical sensor based on a glassy carbon electrode modified with β–cyclodextrins and multi-walled carbon nanotubes (β–CDs/MWCNTs/GCE) for detection of the pesticide dichlorophen (Dcp). The voltammetric measurements carried out by square-wave adsorptive stripping voltammetric (SWAdSV) and in phosphate buffer (PBS) (pH=6.5) as a supporting electrolyte (Fig. 11). The results showed a linear concentration range from 5.0×10^{-8} mol/L to 2.9×10^{-6} mol/L and a limit of detection 1.4×10^{-8} mol/L. The determination of Dcp in river water was performed using this sensor.

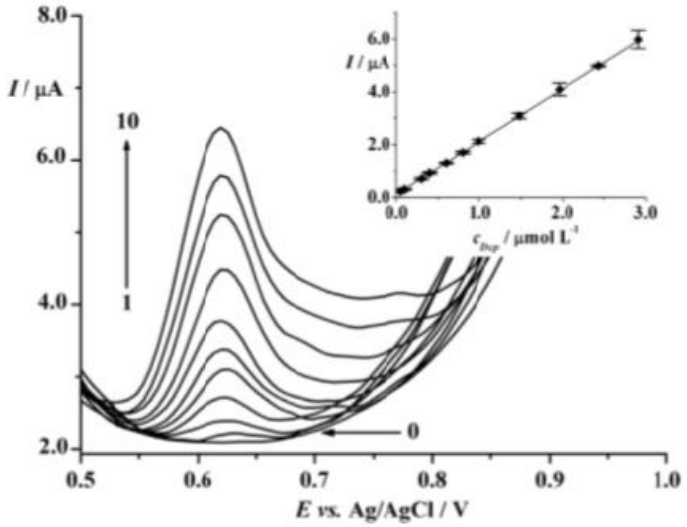


Figure 11. SWAdSV responses at β–CDs/MWCNTs/GCE in PBS (pH 6.5) containing different concentrations of Dcp: (0) supporting electrolyte, (1) 5.0×10^{-8}, (2) 1.0×10^{-7}, (3) 3.0×10^{-7}, (4) 6.0×10^{-7}, (5) 8.0×10^{-7}, (6) 1.0×10^{-6}, (7) 1.5×10^{-6}, (8) 2.0×10^{-6}, (9) $2.4 \times$

10^{-6}, and (10) 2.9×10^{-6} mol/L. The inset show the corresponding calibration graph of Dcp. The error bars were constructed as confidence level (p) of 95% (n = 4) (Sipa et al., 2018)

Sensors based on molecularly imprinted polymer and carbon nanotubes

High selective sensor based on a molecularly imprinted polymer (MIP) and carbon nanotubes modified carbon paste electrode for detection of dicloran pesticide were designed by Shahtaheria et al. (2017). Beside a MIP, a non-imprinted polymer (NIP) was also synthesized and applied in the carbon paste electrode. The MIP-CP electrode was very selective for dicloran and showed very high recognition ability in comparison to NIP-CP. There was a significant difference between the ability of MIP and NIP to adsorb dicloran. Fig. 12 presents the square wave voltammograms related to the determination of the defined concentration of dicloran by MIP-CP, NIP-CP, and bare CP.

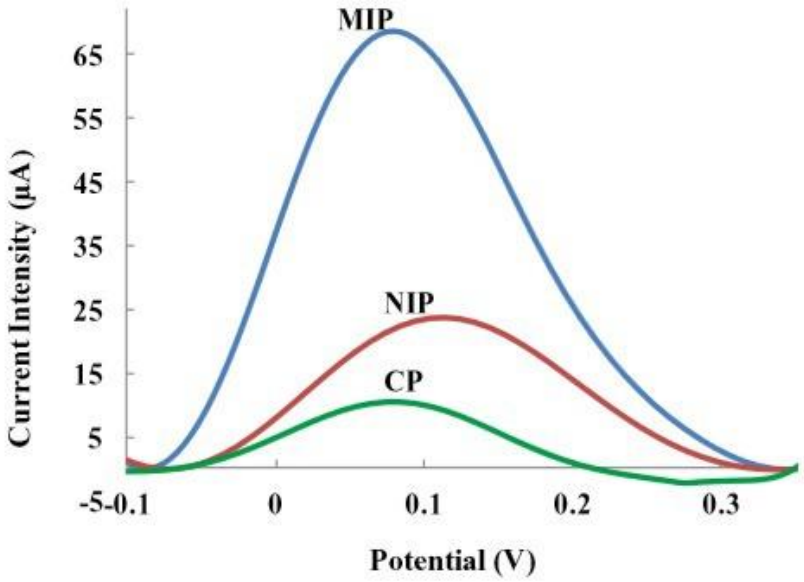


Figure 12. The voltammograms of MIP-CP, NIP-CP, and CP for the defined concentration of dicloran (5×10^{-7} mol/L) (Shahtaheria et al., 2017)

The obtained calibration curve was linear from 1×10^{-6} to 1×10^{-9} mol/L, and LOD and LOQ were 4.8×10^{-10} and 9.4×10^{-10} mol/L, respectively. The designed sensor was successfully used for the determination of dicloran in real samples, such as tap water, river water.

Conclusion

All these studies, as well as a large number of studies not mentioned in this review, have shown that pesticides from different groups can be quantified using electrochemical sensors based on carbon nanotubes. Carbon nanotubes have provided electrochemical sensors with the relatively good analytical performance required for the detection of pesticides. Either they were used alone or in combination with different types of modifiers. Some of the modifiers used are metal particles, TiO_2 nanoparticles, LSX zeolites, β-cyclodextrins, molecularly imprinted polymer, *etc*. The aim of modifying the electrode from the carbon paste and the glassy carbon electrode is to achieve a well expressed analytical signal and to shift the working potential closer to zero. Both of these effects are desirable in order to achieve high sensitivity and good selectivity.

It means that the use of carbon nanotubes as electrode modifiers, for the preparation of electrochemical sensors used to track pesticides, had a positive effect. It is undoubtedly necessary to continue research in order to overcome all the challenges for progress in this area.

An interesting approach to future research is the ability to design devices by which different analytes will be simultaneously determined at different points of the sensor. This challenge is related to the current goals, relating to the miniaturization of analytical devices, the minimal consumption of chemical reagents and the generation of waste, and the ability to carry instruments outside the laboratory. Regarding material synthesis, which will be suitable for making the sensor, currently, the preparation of composites of carbon nanotubes with other allotropic carbon modifications is a trend, such as carbon black, diamond or graphene.

Acknowledgment

This work was supported by the Serbian Ministry of Education, Science, and Technological Development through the framework of the project TR 34008.

Conflict-of-Interest Statement

Declarations of interest: none.

References

Andrews, R., Jacques, D., Qian, D., & Rantell, T. (2002). Multiwall carbon nanotubes: Synthesis and application. Accounts of Chemical Research, 35, 1008–1017.

Apetrei, C., Apetrei, I. M., Saja, J. A. D., & Rodriguez-Mendez, M. L. (2011). Carbon paste electrodes made from different carbonaceous materials: Application in the study of antioxidants. Sensors, 11, 1328–1344.

Batra, R. C., & Sears, A. (2007). Continuum models of multi-walled carbon nanotubes. International Journal of Solids and Structures, 44 (22-23), 7577-7596.

Bethune, D. S., Kiang, C. H., De Vries, M. S., Gorman, G., Savoy, R., Vazquez, J., & Beyers, R. (1993). Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls. Nature (London), 363, 605-607.

Chen, M., Zhao, Z., Lan, X., Chen, Y., Zhang, L., Ji, R., & Wang, L. (2015). Determination of carbendazim and metiram pesticides residues in reapeseed and peanut oils by fluorescence spectrophotometry. Measurement, 73, 313–317.

Cvetićanin, M. J. (2013). Functionalized materials based on carbon nanotubes. Doctoral dissertation, Belgrade.

Damalas, C. A., & Eleftherohorinos, I. G. (2011). Pesticide exposure, safety issues, and risk assessment indicators. International Journal of Environmental Research and Public Health, 8, 1402–1419.

Demczyk, B. G., Wang, Y. M., Cumings, J., Hetman, M., Han, W., Zettl, A., & Ritchie, R. O. (2002). Direct mechanical measurement of the tensile strength and elastic modulus of multi walled carbon nanotubes. Materials Science and Engineering: A, 334, 173–178.

Domínguez, I., Romero González, R., Arrebola Liébanas, F. J., Martínez Vidal, J. L., & Garrido Frenich, A. (2016). Automated and semi-automated extraction methods for GC – MS determination of pesticides in environmental samples. Trends in Environmental Analytical Chemistry, 12, 1–12.

Eguílaz, M., Gutierrez, F., González-Domínguez, J. M., Martínez, M. T., & Rivas, G. (2016). Single-walled carbon nanotubes covalently functionalized with polytyrosine: A new material for the development of NADH-based biosensors. Biosensors and Bioelectronics, 86, 308–314.

Ghodsi, J., & Rafati, A. A. (2017). A voltammetric sensor for diazinon pesticide based on electrode modified with TiO2 nanoparticles covered multi walled carbon nanotube nanocomposite. Journal of Electroanalytical Chemistry, 807, 1-9.

Govindhan, M., Lafleur, T., Adhikari, B. R., & Chen, A. (2015). Electrochemical sensor based on carbon nanotubes for the simultaneous detection of phenolic pollutants. Electroanalysis, 27, 902–909.

Gruzdyev, G. S. (1988). The chemical protection of plants. (2nd ed.). Moscow: Mir Publishers.

Hong, S., & Myung, S. (2007). Nanotube electronics: A flexible approach to mobility. Nature Nanotechnology, 2, 207–208.

Husmann, S., & Zarbin, A. J. G. (2016). Design of a prussian blue analogue/carbon nanotube thin-film nanocomposite: Tailored precursor preparation, synthesis, characterization, and application. Chemistry-A European Journal, 22, 6643–6653.

Iijima, S. (1991). Helical microtubules of graphitic carbon. Nature (London), 354, 56-58.

Iijima, S., & Ichihashi, T. (1993). Single-shell carbon nanotubes of 1-nm diameter. Nature (London), 363, 603-605.

Inam, R., & Bilgin, C. (2013). Square wave voltammetric determination of methiocarb insecticide based on multiwall carbon nanotube paste electrode. Journal of Applied Electrochemistry, 43, 425–432.

Lemos, M. A. T., Matos, C. A., De Resende, M. F., Prado, R. B., Donagemma, R. A., & Netto, A. D. P. (2016). Development, validation, and application of a method for selected avermectin determination in rural waters using high performance liquid chromatography and fluorescence detection. Ecotoxicology and Environmental Safety, 133, 424–432.

Leniart, A., Brycht, M., Burnat, B., & Skrzypek S. (2016). Voltammetric determination of the herbicide propham on glassy carbon electrode modified with multi-walled carbon nanotubes. Sensors and Actuators B: Chemical, 231, 54-63.

Li, J., Kuang, D., Feng, Y., Zhang, F., Xu, Z., Liu, M., & Wang, D. (2013). Electrochemical tyrosine sensor based on a glassy carbon electrode modified with a nanohybrid made from graphene oxide and multiwalled carbon nanotubes. Microchimica Acta, 180, 49–58.

Li, S., Yin, G., Wu, X., Liu, C., & Luo, L. (2016). Supramolecular imprinted sensor for carbofuran detection based on a functionalized multiwalled carbon nanotube-supported Pd-Ir composite and methylene blue as catalyst. Electrochimica Acta, 188, 394-300.

López, A., Dualde, P., Yusà, V., & Coscollà, C. (2016). Retrospective analysis of pesticide metabolites in urine using liquid chromatography coupled to high-resolution mass spectrometry. Talanta, 160, 547–555.

Mol, H. G. J., Tienstra, M., & Zomer, P. (2016). Evaluation of gas chromatography - Electron ionization - Full scan high resolution orbitrap mass spectrometry for pesticide residue analysis. Analytica Chimica Acta, 935, 161–172.

Peng, B., Locascio, M., Zapol, P., Li, S., Mielke, S. L., Schatz, G. C., & Espinosa, H. D. (2008). Measurements of near-ultimate strength for multiwalled carbon nanotubes and irradiation-induced crosslinking improvements. Nature Nanotechnology, 3, 626–631.

Rather, J. A., & De Wael, K. (2012). C_{60}-functionalized mwcnt based sensor for sensitive detection of endocrine disruptor vinclozolin in solubilized system and wastewater. Sensors and Actuators B: Chemical, 171–172, 907–915.

Salehzadeh, H., Ebrahimi, M., Nematollahi, D., & Salarin, A. A. (2016). Electrochemical study of fenitrothion and bifenox and their simultaneous determination using multiwalled carbon nanotube modified glassy carbon electrode. Journal of Electroanalytical Chemistry, 767, 188-194.

Salih, F. E., Achiou, B., Ouammou, M., Bennazha, J., Ouarzane, A., Younssi, S. A., & Rhazi, M. E. (2017). Electrochemical sensor based on low silica X zeolite modified carbon paste for carbaryl determination. Journal of Advenced Research, 8, 669-676.

Shahtaheria, S. J., Faridbod, F., & Khadem M. (2017). Highly selective voltammetric sensor based on molecularly imprinted polymer and carbon nanotubes to determine the dicloran pesticide in biological and environmental samples. Procedia Technology, 27, 96-97.

Sipa, K., Brycht, M., Leniart, A., Urbaniak, P., Nosal-Wiercińska, A., Pałecz, B., & Skrzypek, S. (2018). β–Cyclodextrins incorporated multi-walled carbon nanotubes modified electrode for the voltammetric determination of the pesticide dichlorophen. Talanta, 176, 625-634.

Sundari, P. L. A., Palaniappan, S. P., & Manisankar, P. (2010). Enhanced sensing of carbendazim, a fungicide on functionalized multiwalled carbon nanotube modified glassy carbon electrode and its determination in real samples. Analytical Letters, 43, 1457–1470.

Teadoum, D. N., Noumbo, S. K., Arnaud, K. T., Ranil, T. T., Ze Mvondo, A. D., & Tonle, I. K. (2016). Square wave voltammetric determination of residues of carbendazim using a fullerene/multiwalled carbon nanotubes/nafion/coated glassy carbon electrode. International Journal of Electrochemistry, 2016, 7839708.

Wang, T., Zhao, D., Guo, X., Correa, J., Riehl, B. L., & Heineman, W. R. (2014). Carbon nanotube-loaded nafion film electrochemical sensor for metal ions: Europium. Analytical Chemistry, 86, 4354–4361.

Yang, J., Wang, Q., Zhang, M., Zhang, S., & Zhang, L. (2015). An electrochemical fungicide pyrimethanil sensor based on carbon nanotubes/ionic-liquid construction modified electrode. Food Chemistry, 187, 1–6.

Yang, N., Chen, X., Ren, T., Zhang, P., & Yang, D. (2015). Carbon nanotube based biosensors. Sensors and Actuators B: Chemical, 207, 690–715.

Zhang, M., Zhao, H. T., Yang, X., Dong, A. J. Zhang, H., Wang, J., Liu, G. Y., & Zhai, X. C. (2016). A simple and sensitive electrochemical sensor for new neonicotinoid insecticide Paichongding in grain samples based on β-cyclodextrin-graphene modified glassy carbon electrode. Sensors and Actuators B: Chemical, 229, 190-199.

Zhang, Y., Kang, T.-F., Wan, Y.-W., & Chen, S.-Y. (2009). Gold nanoparticles-carbon nanotubes modified sensor for electrochemical determination of organophosphate pesticides. Microchimica Acta, 165, 307–311.