



CURRENT DEVELOPMENT CARBON MATERIAL BASED ELECTROCHEMICAL AND BIO SENSORS REVIEW

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ABSTRACT

Carbon- nanomaterials based electrochemical and biosensor have been taken a great attention as robust materials for drug, pesticides and heavy metal sensing. The materials are like graphene, reduced graphene oxide, single wall and multiwall carbon nanotubes due to their excellent modifiable sidewalls, biocompatibility, high stability, high surface area, electrical and thermal conductivities as well as high mechanical strength. Currently, carbon nanomaterials based electrochemical and biosensor have great attention in the development of different types of sensor due to the carbonic materials green preparation methods, and low cost. The aim of this review is focus on summary including properties, fabrication method, and analytical performances of some carbonic materials for pesticides, drugs and heavy metals sensing application.

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INTRODUCTION

Environmental pollution is a serious problem in today's world due to industrialization in developed and developing countries. Different country uses industrial products like heavy metals, herbicides and pesticides. Currently these herbicides and pesticides are used in agricultural activities in order to increase agricultural products by controlling herbs and insects respectively (1). These compounds exhibit high acute toxicity, with the majority being hazardous to both human health and the environment (2). The determination of the level of these toxic compounds are very important required to ensure that environment and human health. The analytical methods like gas chromatography (GC), high-performance liquid chromatography (HPLC), capillary electrophoresis and mass spectrometry are commonly used for determination of pesticides will not be compromised by the usage of pesticides (3, 4, and 5). These methods are very accurate and sensitive techniques however, these techniques have several disadvantages; expensive instrumentation, high consumption of toxic organic reagents, require long analysis time, Necessity of highly trained personnel and not portable (6).

The alternative electrochemical and biosensors, they are portable, high sensitivity, Strong selectivity, use friendly and have a fast response (7). Currently many researchers have a great interest to modify the surface of working electrode with different nanomaterials. Chemically modified electrodes are attractive in minimize interference and improve sensitivity of sensing interface and it has capability to accumulate target anayte from dilute solution. Among of these materials metal oxide nanomaterials use widely in electeochemical and bio sensor. NidhiChauhan, and Chandra ShekharPundir, (2012) reported that metal oxide NPs have the ability to enhance electrode conductivity and facilitate electron transfer, thus improving analytical selectivity and sensitivity. As report shows Fe₃O₄NPs has vital property of as electrochemical biosensors is the ability to provide a favorable microenvironment in which biomolecules (such as proteins) may exchange electrons directly with an electrode (2). Currently, it's been a rapid development in environmental monitoring, industrial product controlling and medical technology mainly in fabricating robust and more effective types of chemical sensor and biosensor which are capable in detecting and measuring chemical samples or biological

species. Carbon based nanomaterials mainly graphene, carbon nanotubes carbon nanofibers and reduced graphene oxides attract researcher attention due to extra ordinary properties of carbon. There are some review papers on type's carbon materials but they didn't explain preparation methods of nanomaterials, fabrication methods and application for electrochemical and biosensor. The aim of this paper is to describes the physical and chemical properties, fabrication methods and application of carbon nanomaterials for electrochemical and biosensor.

Fabrication of Carbon nanomaterial based Electrochemical and Bio Sensor

Electrochemical sensors and biosensors are interesting current research area for analyzing pesticides, drugs, heavy metals etc. due to their high sensitivity, low cost, portability and short response time. Bahadir and Sezgintürk, (2015) reported about definition and use of biosensor that biosensors are practical and economical tools, which play important roles in the analysis of specific compounds in biological assays. The biological molecules which immobilized on working electrode make interaction with analyte.

Graphene based Sensor: Jan Tkac. (2014) reported synthesized methods graphene-based materials. Among of these methods reduction is mostly performed thermally, chemically or electrochemically and reduced graphene oxide (rGO) obtained should be distinguished from "pure" synthesized graphene. Figure 1 shows different methods for preparation of graphene and reduced graphene oxide.

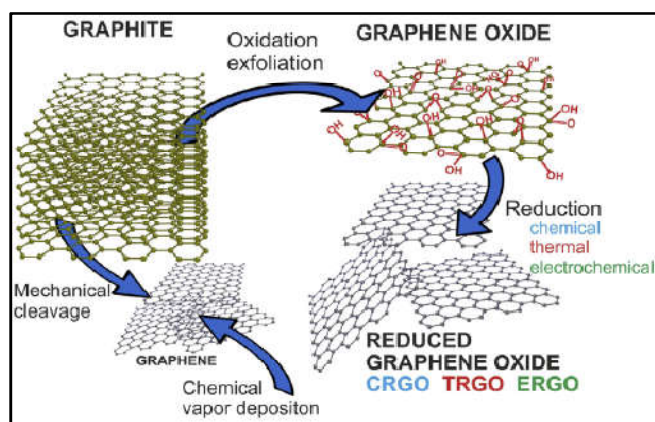
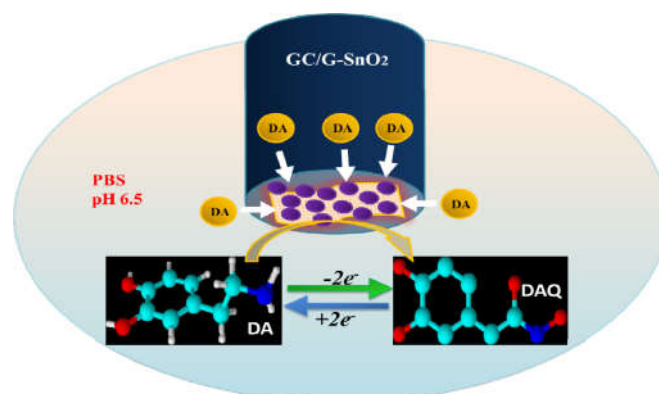


Figure 1. A schematic illustration of possible ways for preparation of graphene and rGO (9)

Graphene is an allotrope of carbon, whose structure is one-atom-thick planar sheets of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. Chao *et al* (2012) reported graphene-modified electrode for selective determination of uric acid under coexistence of dopamine and ascorbic acid was successfully determined with good peak separation. The fabricated electrode showed linearity range, correlation coefficient and limit of detection for uric acid were 2.00×10^{-6} to 1.20×10^{-4} mol/L, 0.9975 and 6.00×10^{-7} mol/L respectively. And they reported that Graphene possesses outstanding characteristics such as having a large specific surface area, excellent conductivity, and strong mechanical strength. It has been used to prepare a new generation of electrodes for electrochemical studies. Graphene synthesizing methods reported by Kasinathan and MohdZawawi (2015), as reported in the report chemical reduction of graphene oxide

technique has attracted great interest than other methods due to its conveniences in the large-scale production of high-quality graphene, environmentally compassionate, time-saving, and low-cost as well as be competent to operate under mild condition. Graphene material makes great roles in electrochemical sensor and biosensor application. Currently many researchers have attention on graphene based electrochemical and bio sensor. As reported Nurzulaikha *et al* (2015), electrochemical behavior of graphene modified SnO₂/GCE has higher electron communication than that of SnO₂/GCE and bare electrodes in dopamine solution due to the large surface area, high conductivity, and catalytic activity. Figure 2 shows good Synergistic effects aroused between graphene and SnO₂ nanoparticles improved the conductive area and facilitated the electron transfer between DA and the modified electrode surface. Differential pulse voltammetry (DPV) showed a limit of detection (LoD) of 1 μM (S/N = 3) in the presence of ascorbic acid (11). The modification of bare electrode surface area with different nanomaterials improves selectivity and sensitivity to detect very lower concentration of analyte which can't detect with bare electrode. Among of these nanomaterials, the graphene sheet at nano scale makes a great role in fabrication of electrochemical and biosensor for detection of analyte at very low concentration due to its high conductivity, high surface area, easy to fabricate and its low cost.



Schematic representation of electrocatalysis of DA at GC/G-SnO₂-modified electrode (11)

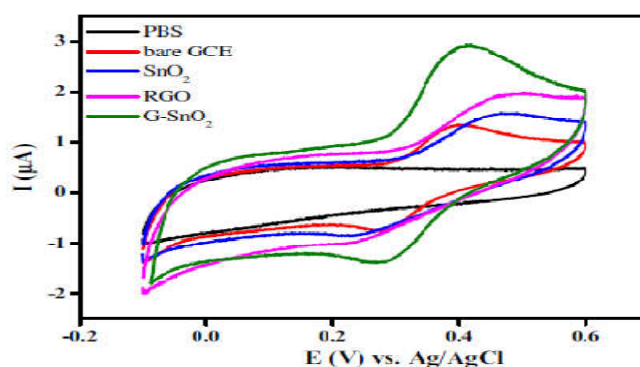


Figure 2. Cyclic voltammetry (CV) of modified GCE in 0.1 M PBS (pH 6.5) containing 50 μM DA at scan rate of 50 mV/s (11)

Sivaprasad *et al.* (2014) reported preparation, characterization, and application of a polyaniline (PAN) and graphene composite modified glassy carbon electrode (PAN/Gr/GCE) for the voltammetric determination of doripenem (DPM) and meropenem metabolites (MPM) in human urine and serum

samples. Figure 3 shows good fabrication of PAN/Gr/GCE by polymerization of aniline monomer on graphene modified glass carbon electrode. In the reported work graphene considered an excellent support material due to its high surface area to volume ratio, remarkable mechanical stiffness and excellent electrical conductivity, which is very beneficial in designing electrochemical sensors. Fig.4 shows fabricated PAN/Gr/GCE electrode for determination of doripenem and meropenem metabolites with linear dependence of current versus concentration was reached in a wide concentration range from 2.5×10^{-7} M to 3.5×10^{-4} M using cyclic voltammetry and differential pulse voltammetric methods and detection limits 3.6×10^{-9} M and 1.75×10^{-9} M for DPM and MPM respectively (50).

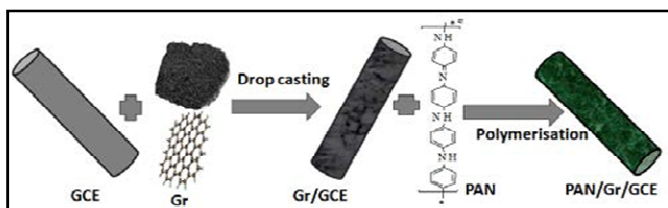


Figure 3. Schematic diagram of electrode modification process with Polyaniline (PAN) and graphene (Gr) composites, scan rate 50 mV/S, potential applied 0-1.5V (50)

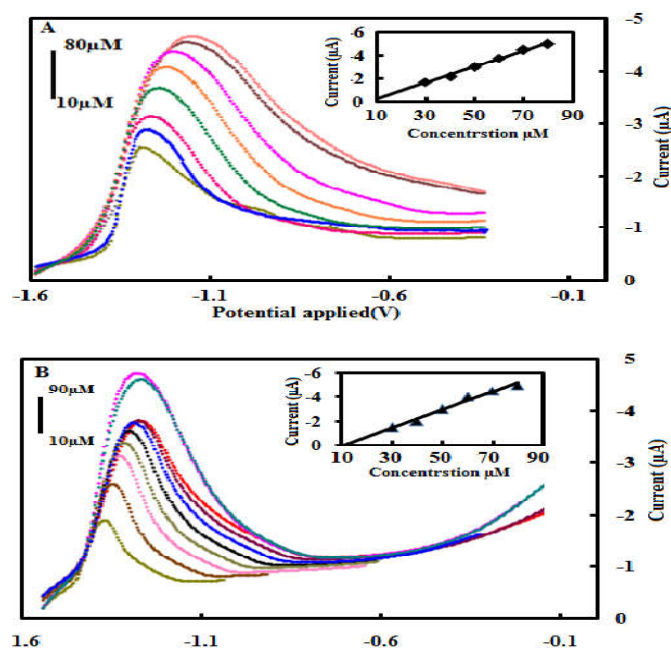


Figure 4. DPV responses of DPM (A) and MPM (B) at PAN/Gr/GCE in PBS buffer solution with increasing concentrations of 10-90 μ M (50)

Reduced Graphene Oxide base Sensor: Recently reduced graphene oxide (RGO) has received greater attention of researchers in different fields due to its unique physicochemical properties like, high surface area, easy to functionalize with other materials and it owns high conductivity (18). Palanisamy *et al* (2012) reported that synthesized reduced graphene oxide by Hummer method the nano sheets were wrinkled and they are uniform in size. The reported work was reduced graphene oxide (RGO)/zinc oxide (ZnO) composite on glassy carbon electrode (GCE) by simple and green electrochemical approach. The modified electrode immobilized by Glucose oxidase (GOx) for glucose sensing. The fabricated biosensor showed good performance over an acceptable linear range from 0.02 to 6.24 mM with a detection

limit of 0.02 mM. Reduced graphene oxides has branched networks which uses to connect and anchor other nanomaterials likes semi-conductors or metal oxide nanomaterials (18) due to this excellent properties, reduced graphene oxides receive a great attention of researcher in the area of modification surface area of working electrodes. The conducting polymers and reduced graphene oxides anchor metal oxide nanomaterials on the surface of solid working electrode. Using these materials as electron transfer catalyst and for anchoring other materials may increase electro transfer communication between modified working electrode and analyte. Nguyen *et al* (2015) reported reduced graphene oxide/PANI modified GCE electrodes for H_2O_2 sensing application. Figure 5 shows electrochemical behavior of shows that net oxidation peak current of H_2O_2 obtained at GCE/RGO-g-PANI (2.35 mA) was approximately 8 and 7 times higher than those of bare GCE (0.30 mA) and GCE/PANI (0.35 mA), respectively (17).

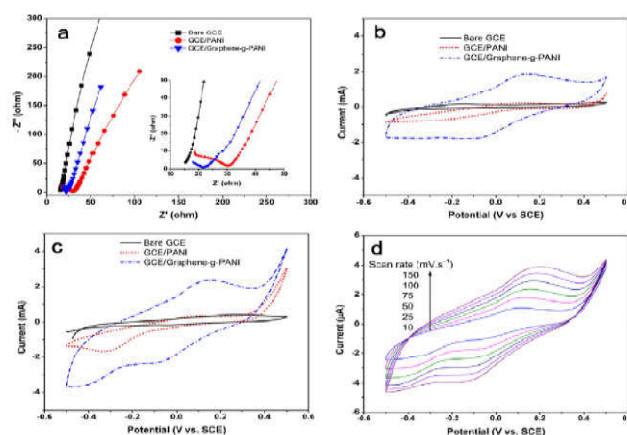


Figure 5. (a) Electrochemical impedance spectra of bare glassy carbon electrode (GCE), GCE/PANI and GCE/RGO-g-PANI electrodes in 0.1MPBS at pH 6.0 containing 2.5mM $[Fe(CN)_6]^{3-4-}$; cyclic voltammograms of bare GCE and GCE/PANI and GCE/RGO-g-PANI electrodes in 0.1 M PBS at pH 6.0 in the (b) absence and (c) presence of 10 μ M H_2O_2 at a scan rate of 10 $mV s^{-1}$; (d) cyclic voltammograms of the GCE/RGO-g-PANI composite in 0.1 M PBS at pH 8.0 in the presence of 10 μ M H_2O_2 at different scan rates (17)

Carbon Nanotubes based Sensor: Carbon nanotubes (CNTs) are one-dimensional (1D) carbon allotrope. Depending on the atomic arrangement of the carbon atoms making up the nanotube (chirality), the electronic properties can be metallic or semiconducting in nature, making them widely used in several applications due to their unique electrical, mechanical, optical, thermal and other properties (12). Carbon nanotubes consist of two types of nanotubes, which are single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Figure 6 shows that SWCNTs is made up of one layer of graphite cylinder sheet but MWCNTs is made up of by are concentric graphite tubules with multiple layers of graphite sheets. Kasinathan and MohdZawawi (2015), reported various techniques of synthesizing CNTs such as CVD (28-30), arc discharge method (31,32), microwave-induced method (33), hydrothermal method(34), remote plasma enhanced chemical vapour deposition (RPE CVD) (35,36), catalytic chemical vapour deposition CCVD (37), induction thermal plasma (38), meso-scale simulation (39), water assisted ethanol pyrolysis (40), formation via microwave (MW) assisted solid state metathesis reaction (SSM) (41), electric field induced needle-pulsed plasma (42)

and thermo catalytic decomposition of methane (43). Single chirality SWCNT-samples can be produce by purification of mixed chirality samples via density-gradient centrifugation (44, 45), ion exchange (46) or gel chromatography (47).

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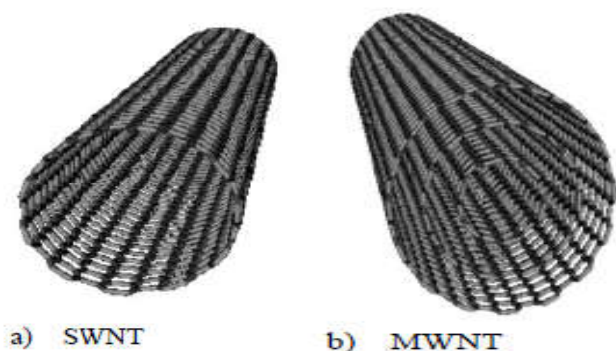


Figure 6. Types of Carbon Nanotubes (a) SWNT (b) MWNT (12)

Carbon nanotubes have great role currently in the area of fabrication electrochemical and bio sensors by modifying the surface of working electrode. Zeid Abdullah Allothmana et al (2010) reported some traditional methods like polychromotrope 2B modified GC electrode [10], Nafion/carbon-coated iron nanoparticles–chitosan composite film modified electrode and Pt/Au hybrid film modified electrode and AP (e.g., l-cysteine film modified GC electrode, carbon-coated nickel magnetic nanoparticles modified GC electrodes, and 4-amino-2-mercaptopyrimidine self-assembled monolayer modified gold electrode have disadvantage; most of these methods face oxidation of biomolecule at electrode, fouling of electrode (due to adsorption of the oxidation products), unstable analytical signal, require high over potential, high detection limit, slow response and most of all are complex. The current use of carbon nanotubes (CNTs) modified electrodes has gained great attention in the area of the

electrochemical techniques for electronic and optoelectronic devices, biomedical, pharmaceutical, cosmetic, automotive, aeronautic and aerospace industries, catalytic, and analytical chemistry (17, 18) due to their modifiable sidewalls (19), biocompatibility (2) for electrochemical biosensor, high stability, thermal behavior (21) which reduce short circuit between modified electrode as sensor and analyte, high surface area (22) which increases the electron transfer communication. Allothmana *et al* (2010) reported the lower detection limits 0.8 for dopamine(DA) and $0.6\mu\text{molL}^{-1}$ for acetaminophen(AP), by using multiwall carbon nanotubes modified glassy carbon electrode with good stability, reproducibility (1.3% (DA) and 2.3% (AP)), repeatability (1.9%) and high recovery in pharmaceutical preparation (1.7% (DA) and 2.7% (AP)), and human serum (1.7% (DA) and 1.9% (AP)). Simultaneous electrochemical determination of dopamine and acetaminophen using multiwall carbon nanotubes modified glassy carbon electrode Sensors shown in Figure 7.

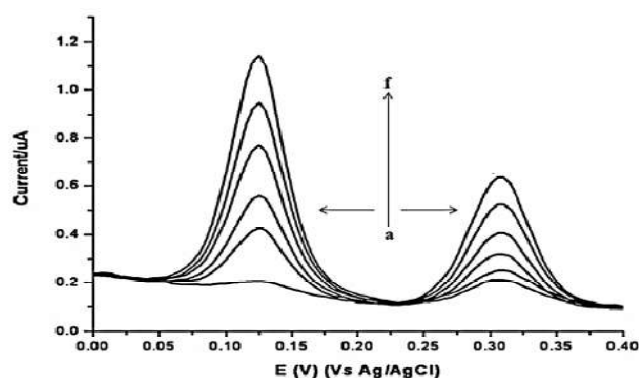


Figure 7. DPVs for the mixture containing DA and AP with different concentrations at f- MWCNTs modified electrode, DA concentrations: (a) $2\mu\text{mol L}^{-1}$, (b) $10\mu\text{mol L}^{-1}$, (c) $50\mu\text{mol L}^{-1}$, (d) $120\mu\text{mol L}^{-1}$, (e) $150\mu\text{mol L}^{-1}$, (f) $200\mu\text{mol L}^{-1}$; AP concentrations: (a) $10\mu\text{mol L}^{-1}$, (b) $40\mu\text{mol L}^{-1}$, (c) $80\mu\text{mol L}^{-1}$, (d) $140\mu\text{mol L}^{-1}$, (e) $200\mu\text{mol L}^{-1}$, (f) $250\mu\text{mol L}^{-1}$; scan rate: 30mVs^{-1} , pH 8.0 (18)

ZhiwenXu *et al.* (2019) reported an electrochemical which fabricated Fe_3O_4 /multiwalled carbon nanotube/laser scribed graphene composites functionalized with chitosan modified electrode for sensing of cadmium and lead. Figure 8 shows sensitive electrochemical sensor for simultaneous voltammetric sensing of cadmium and lead. The fabricated electrochemical sensor was a highly active, sensitive, facile and low-cost for determination of cadmium (Cd^{2+}) and lead (Pb^{2+}) simultaneously using square wave anodic stripping voltammetry (SWASV) with working concentration linear range from 1 to $200\mu\text{g L}^{-1}$ and detection limit of 0.1 and $0.07\mu\text{g L}^{-1}$ for Cd^{2+} and Pb^{2+} (S/N = 3), respectively (25). The hybrid materials increase the surface area of working electrode which may increase interaction between working electrode and analyte. Among of these hybrid materials the multiwalled carbon nanotubes have excellent properties for sensor application like fast electron transfer rate, chemical stability, capability to accumulate metal ions and increased surface area. Ivanova *et al* (2011) reported a simple and reliable amperometric acetylcholinesterase biosensor in which single-walled carbon nanotubes and Cophtalocyanine modified screen-printed carbon electrodes as working electrode with working concentration range 5–50 ppb of paraoxon and 2–50 ppb of malaaxon and detection limits of 3 and 2 ppb.

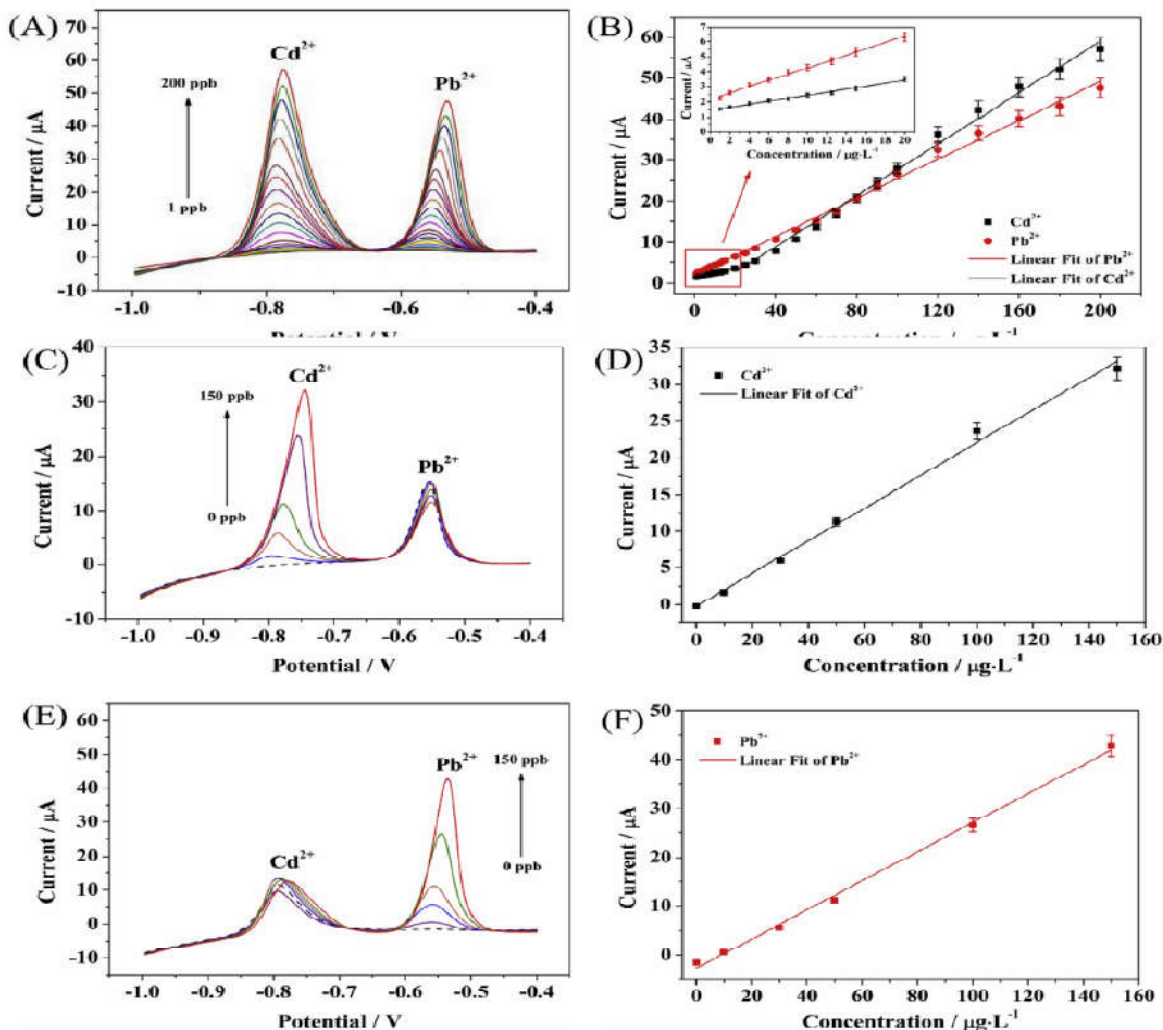


Figure 8. (A) SWASV responses of Fe₃O₄/MWCNTs/LSG/CS/GCE for different concentrations of Cd²⁺ (1, 2, 4, 6, 8, 10, 12.5, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180 and 200 μ g L⁻¹) and Pb²⁺ (1, 2, 4, 6, 8, 10, 12.5, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180 and 200 μ g L⁻¹); (B) The calibration curves for Cd²⁺ and Pb²⁺; SWASV responses for individual determination of (C) Cd²⁺ (0, 10, 30, 50, 100 and 150 μ g L⁻¹) and (E) Pb²⁺ (0, 10, 30, 50, 100 and 150 μ g L⁻¹); the corresponding calibration curves for (D) Cd²⁺ and (F) Pb²⁺ (25)

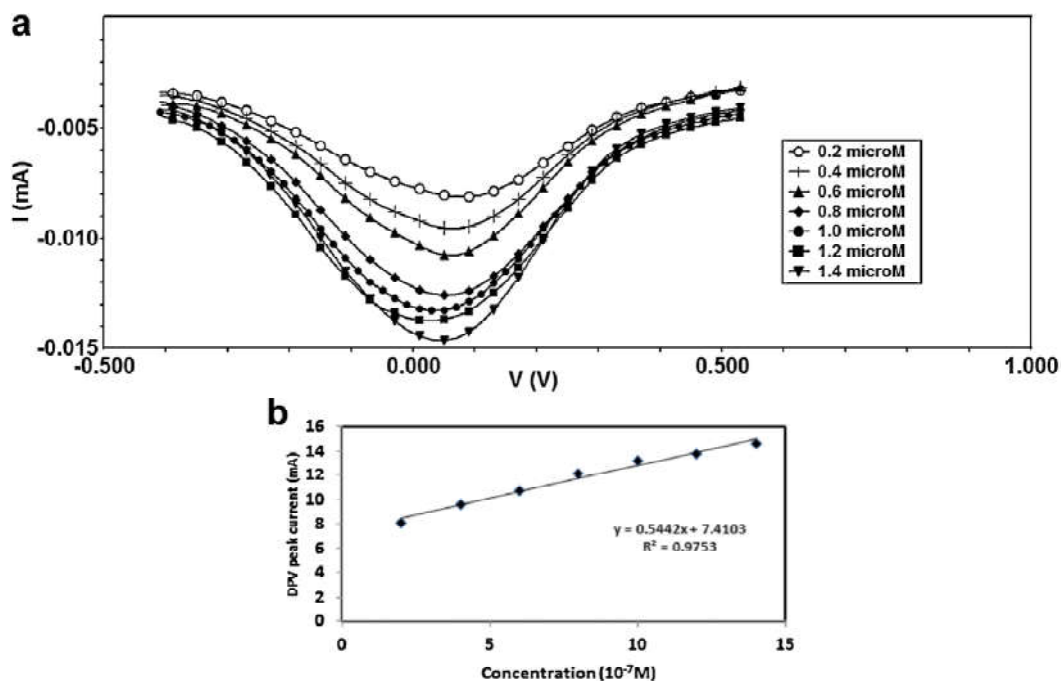


Figure 9. DPV of PANI-ES graphite electrode in phosphate buffer of pH 7 at different malathion concentrations (a) and maximum peak current versus malathion concentration (b) (27)

Some current carbon nano material based electrochemical and biosensor summarized in the following table.

Electrode	Analyte	Linear range	LoD(S/N = 3)	Reference
f-MWCNTs/ GCE	Dopamine	3-200 μmolL^{-1}	0.8 μmolL^{-1}	18
	Acetaminophen	3-300 μmolL^{-1}	0.6 μmolL^{-1}	18
AChE-Fe ₃ O ₄ NPs/cMWCNTs/ITO	Malathion	0.1-40nM	0.1nmolL ⁻¹	2
	Chlorpyrifos	0.1-50nM	0.1nmolL ⁻¹	2
	monocrotophos	1-50nM	0.1nmolL ⁻¹	2
	Endosulfan	10-100nM	0.1nmolL ⁻¹	2
PANI-ES SWCNTs/GCE	Malathion	2.0 × 10 ⁻⁷ M to 14.0 × 10 ⁻⁷ M	2.0 × 10 ⁻⁷ M	27
PAN/Gr/GCE	doripenem	2.5 × 10 ⁻⁷ M to 1.2 × 10 ⁻⁴	3.5 × 10 ⁻⁹ M	49
	Meropenem	2.5 × 10 ⁻⁷ M to 1.2 × 10 ⁻⁴	1.75 × 10 ⁻⁹ M	49
Graphene/SnO ₂ /GCE	Dopamine	1-5 μM and 5-50 μM	1 μM	11
RGO-g-PANI/GCE	H ₂ O ₂	0.05 to 14 μM	0.37 μM	17
RGO/ZnO	Glucose	0.02-6.24mM	0.02mM	16
Fe ₃ O ₄ /MWCNTs/LSG/CS/GCE	Cd ²⁺	1to 200 $\mu\text{g L}^{-1}$	0.1 $\mu\text{g L}^{-1}$	25
	Pb ²⁺	1to 200 $\mu\text{g L}^{-1}$	0.07 $\mu\text{g L}^{-1}$	25

Ebrahima *et al* (2014) reported that composite of polyanilinenanofiber and single walled carbon nanotube modified graphite electrode as working electrode for detection of malathion with working concentration range from $2.0 \times 10^{-7}\text{M}$ to $14.0 \times 10^{-7}\text{M}$ and minimum detection limit in the linear range for the modified electrodes was $2.0 \times 10^{-7}\text{M}$ malathion (27). Figure 9b indicates the reduction peak current of the PANI-ES graphite electrode exhibits a linear dependence on malathion concentration with increasing concentration from $2.0 \times 10^{-7}\text{M}$ to $14.0 \times 10^{-7}\text{M}$. Single wall carbon nanotube uses in the area of removing environmental pollution like pesticides due to its strong adsorption of pesticides, having large surface area, sensitivity properties, high biocompatibility during biological molecule immobilization and good conductivity.

Currently these properties attract many researchers interest in fabrication of electrochemical and biosensor with carbon nanotubes. From the above table data the biological molecule AChE increases the selectivity and sensitivity for detection of malathion. The biosensor AChE-Fe₃O₄NPs/cMWCNTs/ITO has limit of detection 0.1nmolL^{-1} which can detect at very low concentration than that of non-enzymatic biosensor (electrochemical sensor) PANI-ES SWCNTs/GCE with limit of detection $2.0 \times 10^{-7}\text{M}$ for the same analyte. Since outer part of enzymes is covered by fats it may decrease the conductivity of modified bare electrode with enzymes in biosensor. The challenges may be solved by modifying the bare electrode with different nanomaterials before immobilizing enzymes on it. The fat part may enter in small holes of nanomaterials and the active part of enzyme participates directly with analyte. Therefore the enzyme part selects the analyte from the sample of matrix which shows a good selectivity of electrochemical biosensor for different detection and determination of analyte with very small concentration in application area.

Conclusion

Carbon nanomaterials and other nanomaterials have been used widely in the current development of nanomaterial based electrochemical and biosensing system. All carbon material based electrochemical and biosensor which were discussed in this paper have good sensitivity, selectivity, stability and response time. Carbon based nanomaterials are not used only for electrochemical and biosensor application but also it may be used in the area of battery, Capacitor and solar cells.

Recommendation

This paper focuses on physical and chemical properties, fabrication methods and application of carbon nanomaterials for electrochemical and biosensor. The paper describes only carbonic materials for electrochemical and biosensor. Carbon nanomaterials may be value for solar cell, battery and capacitor.

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