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Nanostructured Sensors Based on Carbon Nanotubes for Electrochemical Analysis of Cadmium in Food Samples

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ABSTRACT

Food samples are facing enormous challenges from contaminants of heavy metal ions that are released into the environment by long-term industrial and agricultural activities. One of the most hazardous environmental pollutants is cadmium ions (Cd(II), Cd^{2+}) because of their high toxicity and long-term stability. Heavy metal ions tend to enter into human body by the food chain and cause liver damage, nervous system diseases, as well as kidney. Since the trace of Cd^{2+} excess to its limit is very hazardous a sensitive determination method for cadmium ions is very important. One of the methods for monitoring cadmium heavy metal ions is electrochemical technique. The techniques based on modified electrodes can act as efficient method for sensitive analysis of Cd^{2+} in real samples. Among the different modifiers, carbon nanotubes (CNTs) have been used broadly over the last two decades for various potential applications in electrode modification systems. CNTs due to the tubular structures are one of the most valuable modifiers because of their distinct features for instance inertness, porous structure, low density, and affinity for pollutants. In the present work, modified electrochemical sensors based on CNTs were reported to show their potential as active materials for sensitive detection of Cd^{2+} in food complicated samples.

INTRODUCTION

Increase in the world population, agricultural events, urbanization, unpremeditated industrialization, and extreme chemical usage have increased environmental pollution by presenting toxic contaminants. There are numerous sources through which impurities, especially heavy metals are brought in, for example, heavy metals are released into the environment through food samples, photographic constituents, petrochemical products, battery manufacturing industries, fertilizer production, printing, metallurgical, leather tanning, etc. Therefore, such industries pose a substantial to for people and environment [1-5]. Contamination of heavy metal ions contains cadmium, zinc, chromium, nickel, mercury, arsenic, lead, and copper. The metal ions are extremely non-biodegradable and toxic, besides, causing severe health problems in humans and animal species. Many researches have been reported by heavy metal ions about toxic impact on human health for instance severe lungs, mood swings, gastrointestinal tract damage, violent behavior, insomnia, auto-immune illnesses, and high blood pressure [6-9].

Nanotechnology has an effective role in environmental fields. Recently, much research has been reported about the potential applications of nanostructures for the analysis of heavy metal ions in food and other samples [10]. Several nanostructured materials have been used by the research community, among others, carbon nanotubes (CNTs) are presently highly recommended and applied for monitoring of heavy metal ions. Advantages of CNTs include chemical inertness, large surface area, porous structure, strong affinity towards pollutants, and light mass density. The capability for modification of the surface electrodes with different functional groups provides another edge to the nanostructured tubular compounds as one of the best modifiers with an easily modifiable surface [11-13]. Numerous functional groups such as amine, carboxyl, hydroxyl, and ligands can be used with ease on the surface of CNTs through functionalization to make the structures specific and selective for certain pollutants. Also, several specific forms of pollutants can be analyzed in real samples by chemically modified carbon nanotube electrodes [14-17].

With the knowledge of the extent of damage produced by heavy metal ions such as Cd^{2+}, it becomes imperative

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to monitor the presence of the ion in food samples. Several techniques for instance inductively coupled plasma mass spectrometry [18], inductively coupled plasma optical emission spectrometry [19], atomic absorption spectroscopy [20], and electrochemistry [21] have been applied for the analysis of Cd^{2+}. Despite being highly selective and sensitive, these dedicated instrumental methods suffer from some limitations such as complex sample preparation steps, expensive instruments, etc. [22,23]. However, electrochemical techniques have been shown to less complex procedures and equipment, high sensitivity, and miniaturization, which is suitable for the production of sensors in the detection of Cd^{2+} [24,25]. The present study reports an overview of nanostructured modified electrodes based on CNTs for analysis of cadmium ions in food samples by electrochemical techniques.

Cadmium

Cadmium is considered one of the most toxic heavy metal ions and is usually found in pesticides, plastics, combustion of fossil fuels, fertilizers, etc. Both short-term and long-term exposure to the heavy metal ion above the tolerance levels is detrimental to human health and leads to serious diseases such as several types of cancers [26]. The presence of Cd^{2+} causes the DNA repair proteins to be inhibited and DNA lesions are happen. Therefore, renal dysfunction, osteoporosis, and numerous neurodegenerative disorders such as Parkinson's disease, Alzheimer's disease, and amyotrophic lateral sclerosis [27-30] are observed. Cadmium ions are categorized as a carcinogen by the International Agency for Research on Cancer (IARC), especially creating cancer in the kidneys. World Health Organization (WHO) has reported the allowable limit of cadmium ions in drinking water is 3.0 μg/L [31]. Meanwhile, the potential sources of cadmium ions in drinking water contamination are the industrial wastewater discharge to the environment. Also, other industrial sources of cadmium ions contamination include electroplating, metal plating, cooling tower blow down, coating operations, etc. Moreover, cadmium ions are applied in solar cells, batteries, and pigments. Furthermore, impurities in the zinc of galvanized pipes and some metal fittings is considered as one main source of non-industrial sourced cadmium ions contamination in drinking water [32-35].

Method and analysis

As it was mentioned over the years, several separation and spectroscopic techniques have been used for the analysis of Cd heavy metal ions. Although the techniques provide high sensitivity and accuracy but accompanied by certain limitations, for instance, high costs and they are time-consuming and do not allow on-site analysis. Still, attention in recent years has focused on the detection of Cd heavy metal ions with several electrochemical techniques, especially voltammetric techniques because of their benefits for instance fast, easy, low detection limit, broad linear dynamic range, and relatively inexpensive way to determine them compared to other analytical techniques. Although the previous techniques are selective and sensitive, because of the limitations they cause, electrochemical techniques are preferred for the analysis of Cd ions [36]. Electrochemical techniques, particularly voltammetry, contain methods for the analysis of one or more analytes by calculating the peak current versus potential. Among different electrochemical techniques, voltammetry is the only electrochemical technique with high sensitivity [37]. There are several voltammetric techniques such as polarography, cyclic voltammetry (CV), normal pulse voltammetry (NPV), Differential pulse voltammetry (DPV), square wave voltammetry (SWV), adsorption stripping voltammetry (AdSV), anodic stripping voltammetry (ASV), and cathodic stripping voltammetry (CSV) for analysis of heavy metal ions [38].

Electrodes

One of the main steps for electrochemical analysis of cd heavy metal ions is selecting the working electrode where carbonaceous electrodes are dominant. The carbon-based electrodes seem to further improve the potential of the electrochemical techniques. The electrodes have benefits such as wide potential window, and flexiblity, with conductive and surface properties that permit the sensitive analysis of electroactive analytes. The most common carbon-based electrodes are carbon paste electrode (CPE), graphite electrode (GE), glassy carbon electrode (GCE), and screen-printed carbon electrode (SPCE). Although, the electrodes are widely applied for the analysis of Cd heavy metal ions but for improvement in the selectivity and sensitivity the electrodes should be modified with appropriate electrode materials [39-46].

Carbon nanotubes

Carbon has the property to exist in several molecular forms that are introduced as allotropes of carbon. The allotropes are considered as different structural modifications of carbon elements. One of the allotropic forms of carbon is carbon nanotubes (CNTs) that composed of cylindrical graphite sheets rolled up in a tube-like structure [47]. CNTs are calcified in two groups involving single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs have cylindrical shapes involving a single shell of graphene while MWCNTs are composed of multiple layers of graphene sheets. Fig. 1 (a and b) presents the structures of SWCNTs and MWCNTs [48].

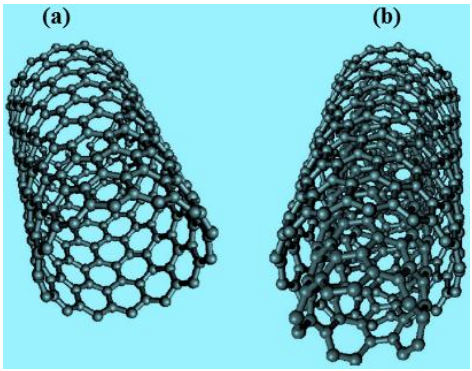


Fig. 1. Structures of (a) SWCNT and (b) MWCNT [48].

Also, the different structure of SWCNTs based on the rolling of graphene sheets is displayed in Fig. 2 [49]. The structure of the nanotubes is based on the orientation of the tube axis concerning the hexagonal lattice and is specified through its chiral vector, represented by chiral indices (n, m). The origin of the armchair (n = m) and zigzag (n = 0) nanotube structure is from the geometric arrangements of carbon atoms at the seam of the cylinders. However, nanotubes structure with two enantiomers with right and hand side helicity (n ≠ m) are chiral [39]. CNTs were introduced by Sumio Iijima in 1991 using the arc-discharge method and characterized by high-resolution transmission electron microscopy [50]. Chemical bonding in nanotubes is composed of sp^2 bonds, which are stronger than the sp^3 bonds found in alkanes and make nanotubes a unique strength [51,52].

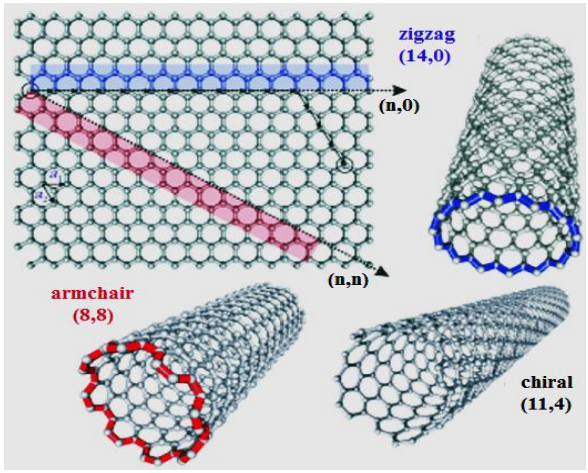


Fig. 2. Roll-up of a graphene sheet leading to the three different forms of CNTs [49].

Carbon nanotubes as electrode materials

To improve the selectivity and sensitivity in the analysis of Cd heavy metal ions and to study their toxicity on both human health and the environment, electrochemical techniques should be combined with certain modifiers that facilitate the electron transfer in electrochemical reactions. Among the different modifiers, nanostructured materials are very useful compounds for surface modification of the electrodes. In recent years, the presence of nanostructures in electrochemical sensors has developed innovative and significant analytical methods for the analysis of heavy metal ions such as Cd ions. Nanostructured electrodes are promising tools for the scientific community for monitoring of toxic heavy metal ions, because of their selectivity and sensitivity, reproducibility, fast response time, low detection limit, and the possibility for simultaneous determination of heavy metal ions [53-55]. The nanomaterials due to unique properties for instance specific morphology, size, and surface chemistry are good candidates in various fields. Some of the most important chemical properties of nanomaterials are the high surface energy, high surface-to-volume ratio, unique electromagnetic properties, and unique oxidation-reduction properties [56,57].

One of the most effective nanostructures in electrochemical studies is CNTs. The nanotubes are considered excellent electron mediators due to their large surface area. Thus, CNTs are appropriate electrode surface modifiers for the enhancement of the analytical characteristics of electrodes. Usually, CNTs can be synthesized by several methods for instance pulse laser vapor, electric arc discharge, catalytic decomposition of gaseous hydrocarbons, as well as chemical vapor deposition [58-60]. Also, CNTs can be modified with different functional groups. Modification of the surface of CNTs creates a significant role in the properties of CNTs and can be performed using physical adsorption or chemical bond formation [61]. Moreover, CNTs can be composite with different chemicals to create a synergic effect as electrode materials [62-64].

Various modified electrodes based on CNTs were used for the detection of cadmium ions in food samples. Afkhami et al. reported a method for Cd(II) in rice samples. The analysis was accomplished by ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, multiwalled carbon nanotubes, silica nanoparticles (IBMS) as a potentiometric sensor [65]. Bagheri et al. analyzed Cd ions in fish samples. In the study, an electrochemical sensor based on triphenylphosphine-modified carbon nanotube (TMCN) was applied [66]. Aboufazeli et al. analyzed Cd^{2+} in different food samples with satisfactory results. In the study, an imprinted polymer coated on multiwall carbon nanotubes (IPMWCNTs) modified electrode was designed and used for sensitive detection of Cd^{2+} ions [67]. Afkhami et.al designed a nanostructured sensor based on 4-((1H-1,2,4-triazol-3-ylimino)methyl)phenol/multi-walled carbon nanotubes incorporated into the carbon ionic liquid paste (TMCIL). Then, an anodic stripping voltammetry technique was used to monitor the level of Cd^{2+} ions in different food samples [68]. Chamjangali et al. introduced a modified voltammetric sensor for Cd^{2+}. They used a MWCNT/poly(pyrocatechol violet)/bismuth film (MWCNTPB) for the detection of cadmium (II) in water samples [69]. Han et.al used different carbon-based nanomaterials for instance CNTs and anodic stripping voltammetry for the detection of heavy metal ions in foodstuff. Using the method they obtain a limit of detection of 21 nM as well as one dynamic linear range of 0.5-9.0 μM for Cd(II) ions [70]. Table 1 presents a summary of the analysis of Cd heavy metal ions using electrochemical sensors based on CNTs. The data indicated that electrochemical techniques based on CNTs modified electrodes are promising methods for sensitive and selective detection of Cd ions in complicated real samples.

Table 1
Nanostructured modified electrodes based on CNTs for the analysis of cadmium heavy metal ions in food samples.

Modifier	Linear Range (μM)	Limit of Detection (nM)	Ref.
IBMS	4.50×10^{-9}–1.00×10^{-1} (M)	2.00 (nM)	[65]
TMCN	0.10–150.00 (nM)	7.40×10^{-5} (μM)	[66]
IPMWCNTs	_	1.30 (ng mL^{-1})	[67]

TMCIL	0.20–23.00 (μg L^{-1})	0.08 (μg L^{-1})	[68]
MWCNTPB	1.00–300.00 (μg L^{-1})	0.20 (μg L^{-1})	[69]
CNTs	0.500–9.00 (μM)	21.00 (nM)	[70]

CONCLUSION

Advances in nanoscale science create new opportunities to improve more cost-effective and environmentally acceptable food treatment technology. The remarkable chemical and physical properties of carbon-based nanostructures make the materials excellent candidates for surface modification of the electrodes. The aim of the work is presentation the ability of CNTs-based electrochemical sensors for analysis of Cd heavy metal ions in food samples. The CNTs also can be used as modified and composite forms in the electrode systems. Therefore, using the modified and composite CNTs an enhancement effects of the nanostructures can be achieved. A survey of the previous literature shows there are different methods for electrode surface modification by CNTs for Cd ions analysis. The researches indicate using CNTs-based electrochemical sensors it is possible to design selective and sensitive methods for monitoring the low levels of Cd heavy metal ions in complicated food samples. Also, it is an important factor in determining the potential application of CNTs in commercial treatment plants in the future.

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