We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

6,600
Open access books available

177,000
International authors and editors

195M
Downloads

154
Countries delivered to

TOP 1%
Our authors are among the most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Carbon Nanotubes in Electrochemical Sensors

M. Mazloum-Ardakani and M.A. Sheikh-Mohseni
Department of Chemistry, Faculty of Science, Yazd University
I.R. Iran

1. Introduction

Nanoscale materials, defined as having at least one dimension less than 100 nm, have received steadily growing interest due to their unique properties and application potential. Typical examples include zero-dimensional nanoparticles, one-dimensional nanowires, and two-dimensional graphenes. Because of the quantum confinement of electrons in one or more dimensions, novel electrical, optical, and magnetic properties can be achieved in nanostructures. Nowadays carbon nanotubes (CNTs) are among the most promising nanomaterials. Depending on the chirality along the graphene sheet, either semiconducting or metallic electronic states are created.

There are numerous studies on carbon nanotubes applications. For example, CNTs has been widely used in structure of different sensors. Various advantages of CNTs as sensor materials have been shown for analysis of diversified chemicals of food quality, clinical and environmental interest. High thermal conductivity, remarkable mechanical properties, chemically stability and high surface to volume ratio of CNTs is very appealing for sensing applications.

Electrochemical sensors (ECS) have been proven as an inexpensive and simple analytical method with remarkable detection sensitivity, reproducibility, and ease of miniaturization rather than other instrumental analysis methods. Since CNTs possess interesting electrochemical properties, contributed by the activity of edge-plane-like graphite sites at the CNT ends, it can be used for construction of electrochemical sensors (CNT-ECS). CNT-ECS exhibit low detection limit, high sensitivity and fast response due to the signal enhancement provided by high surface area, low overvoltage, and rapid electrode kinetics. Because of importance of electrochemical sensors and CNTs, this chapter is focused on advantages and applications of CNTs in electrochemical sensors. At first, CNTs are introduced and different electrochemical sensors are defined based on the type of output signal.

Afterwards, different methods are investigated and classified for preparation of electrochemical sensors based on CNTs. These strategies have been applied for the immobilization of CNTs on electrochemical transducers. The one common way is coating the electrode surface with a CNT suspension and in another approach the CNT is mixed with mineral oil to fabricate paste electrode. Some other methods, such as self-assembly and polymerization, are used less frequently.

Finally, the advantages and applications of CNTs are investigated in different ECSs (potentiometry and voltammetry). In potentiometric sensors, CNTs similar to other nanostructure materials have been proposed as alternative solid-state transducers that can
improve the detection limit and selectivity coefficient of the sensor. On the other hand, there are many electroanalytical methods using voltammetric and amperometric techniques with CNT-modified electrodes in the recent literature. In the case of electrocatalysis sensors the electrocatalytic activity of the electrode was improved by using CNTs.

2. Electrochemical sensors

A chemical sensor is a small device that can be used for direct measurement of the analyte in the sample matrix. Ideally, such a device is capable of responding continuously and reversibly and does not perturb the sample. By combining the sample handling and measurement steps, sensors eliminate the need for sample collection and preparation. Chemical sensors consist of a transduction element covered by a chemical or biological recognition layer. This layer interacts with the target analyte, and the chemical changes resulting from this interaction are translated by the transduction element into electrical signals. Electrochemical sensors represent an important subclass of chemical sensors in which an electrode is used as the transduction element. Such devices hold a leading position among sensors presently available, have reached the commercial stage, and have found a vast range of important applications in the fields of clinical, industrial, environmental, and agricultural analyses.

There are different methods for classification of electrochemical sensors. One of them is based on output signal from electrochemical sensor. In this manner electrochemical sensors classified to two major classes: potentiometric and voltammetric sensors.

2.1 Potentiometric sensors

Potentiometric sensors or so-called ion-selective electrodes (ISEs) have been the subject of continuous research efforts. This group of chemical sensors is characterized as simple in preparation, robust in operation and moderately selective in analytical performance. Some kinds of ISEs become routine devices in analytical laboratories (Mazloum-Ardakani et al., 2006).

Ideally, potentiometric sensors detect the ion activity in the sample. This makes it a unique class of chemical sensors that may be very useful in bioavailability or speciation studies. The Nernst Equation is normally used to describe the ideal response of such a cell:

$$\text{EMF} = K + \frac{RT}{zF} \ln a_I$$  \hspace{1cm} (1)

where EMF is the electromotive force (the observed potential at zero current), K is a constant potential contribution that often includes the liquid-junction potential at the reference electrode, \(a_I\) is the sample activity for the ion \(I\) with charge \(z\), and \(R\), \(T\), and \(F\) are the gas constant, absolute temperature, and Faraday constant, respectively (Wang, 2006). Note that the ion activity effectively describes the so-called free, or uncomplexed, concentration of the analyte, which is often the relevant driving force in chemical or biochemical reactions. This quantity may be orders of magnitude smaller than the total analyte concentration if a complexing agent is present in the sample.

2.1.1 Lower detection limit

In general, the lower detection limit (LOD) is defined as the concentration of the analyte at which the signal is increased relative to the background level by three times the standard deviation of the noise (Currie, 1995). According to IUPAC recommendations, the definition
of the LOD in potentiometry is unique (Guilbault et al., 1976). The potentiometric response or the EMF is a linear function of the logarithm of the activity of the free (uncomplexed) ions $a_i$ in solution. Its slope is described by the Nernst Equation (1) as $59.2/z_i$ mV decade$^{-1}$ at 25°C (Fig. 1). Below the LOD, it has a constant value, which is ideally defined by the response of the sensor to another (interfering) ion J. The potentiometric lower LOD is defined as the cross section of the two linear parts of the response function (Fig. 1). However, typical noise during potentiometric measurements may be as low as 0.06–0.08 mV. The LOD according to the general definition used in analytical chemistry (three times the standard deviation of this noise) is therefore orders of magnitude lower than that given by the definition for potentiometry (Midgley, 1979).

2.1.2 Improvement of the lower detection limit
In most cases described so far, the lower detection limit of solvent polymeric membrane-based ion-selective electrodes (ISEs) lies in the micromolar range (Sokalski et al., 1999). In their usual design, the electric contact between the sensing membrane and the inner reference electrode is accomplished with an electrolyte solution of the ion to be measured (the primary ion). It has been established that this setup may cause severe biases because the primary ion activities near the membrane can be bigger by orders of magnitude than in the bulk of the sample (Bakker & Pretsch, 2002). This artifact, caused by zero-current ion fluxes induces less than optimal lower detection limits of the ISEs. The reason for the enhanced primary ion activity in the stagnant layer near the membrane induces by concentration gradients in the membrane. Such gradients in the membrane arise either because of an increase of the concentration of the primary ions on the inner membrane side or because of a decrease on the outer membrane side. The first mechanism is due to a coextraction of the primary ion together with its counter ion from the inner solution into the membrane, while the second one is a consequence of the partial replacement of primary ions by interfering ions from the sample on the outer membrane side (Sokalski et al., 1999).

![Fig. 1. The traditional definition of the lower LOD of potentiometric sensors is defined as the cross-section of both extrapolated linear portions of the calibration curve (DL).](image)

www.intechopen.com
There are various ways for improvement of LOD for potentiometric sensors (Mazloum-Ardakani et al., 2008). The basic of them is elimination of ion flux from inner solution. Some of these remedies have been brought below.

It was shown that ISEs with low detection limits can be fabricated for alkali metals by adding an ion-exchange resin to the inner solution of the membrane (Qin et al., 2000). In another way low detection limit ISEs can be obtained by applying a small current across the ion-selective membrane. Such constant-current (galvanostatic) systems were shown to yield detection limits down to the picomolar range (Pergel et al., 2001). In other work, it was recognized that rotating electrodes can be very useful in potentiometry if concentration polarizations near the membrane are relevant. The measuring range and detection limit of potentiometric sensors was shifted to lower concentrations with increasing rotational speeds (Ye & Meyerhoff, 2001).

2.1.3 Solid contact ion selective electrodes
In another important way the using of solid-contact (coated wire) electrodes prevent the ion release from the inner side of the membrane, compared to the traditional liquid-contact electrodes. Therefore the LOD and linear response range improved in this case. However, the original coated wire electrodes suffer from potential instabilities which have been mainly attributed to the lack of a well-defined redox couple and also the formation of a thin aqueous layer at the membrane–metal interface. Numerous works has been done to improve the stability of solid state electrode, which include the modification of electrode and the utilization of ion-to-electron transducers. In the last years different research teams have focused their investigations on different materials that are able to convert effectively the ionic signal through the ion-selective membrane into an electronic signal (ion to electron transducer) (Bobacka et al., 2008).

2.2 Carbon nanotubes in potentiometric sensors
Electroactive conducting polymers have been the most commonly used as ion to electron transducer in solid contact potentiometric sensors due to their ability to generate a high redox capacitance that confers a high stability to the recorded signal (Michalska, 2006). However, carbon materials including three-dimensionally ordered macroporous carbon, SWCNT and MWCNT have been used to facilitate the ion to electron transfer in solid-state ISE (Lai et al., 2007; Parra et al., 2009). Carbon-based materials are outstanding transducers, insensitive to oxygen and light, and very hydrophobic, which make them more advantageous compared to the conducting polymers in some applications. Furthermore, carbon nanotubes did not show any evidence of the formation of a water layer between the ion selective membrane and the transducer that see in the case of conducting polymer (Lai et al., 2007). The transduction mechanism of carbon nanotubes in solid-contact ions elective electrode has been studied by Crespo et al. (2009), and they proposed an asymmetric capacitor model to illustrate why carbon nanotubes can act as ion to electron transducer in solid-state ISEs. The nanostructured characteristics of CNTs that are associated to their high surface to volume ratio, together with the inert character of the carbon structures, seem to be the intrinsic reasons for their outstanding transducing properties. Specifically, SWCNT display some distinctive characteristics. All the atoms in SWCNT are located at the surface; therefore, the current flows at the surface and small variations of the local chemical environment can be detected. For this reason, SWCNT are also a suitable material for ultrasmall sensors.
From a practical point of view, ensemble of carbon nanotubes are easy to handle and can easily be deposited on different electrode surfaces. There are different strategies for utilization of CNTs in construction of solid contact ion selective electrodes. We classified these methods in two categories. These classes are carbon paste-CNT (CPE-CNT) and other solid electrode (except carbon paste)/CNT/polymeric membrane (SE/CNT/PM). The other solid electrodes may be glassy carbon and gold electrodes.

2.2.1 Carbon paste-CNT ion selective electrodes (CPE-CNT-ISE)

Due to advantages of carbon paste electrodes (CPEs) such as renewability, stable response, low ohmic resistance, and no need for internal solution, they have recently attracted attention to use as electrochemical sensors (Wang, 2006). To date, most CPE-based potentiometric sensors reported are based on incorporation of a selective agent into the carbon paste. The base of carbon pastes is usually a mixture of powdered graphite and mineral oil binder. Nowadays, carbon nanotubes have been used in carbon paste electrodes for preparation of different electrochemical sensors because of their special properties. For construction of CPE-CNT-ISE four or five components is needed: powdered graphite, paraffin, CNT, ionophore and a suitable salt as additive (if necessary). General procedure for preparation of CPE/CNT-ISE is as flowing: the components with appropriate weight mixed well usually with a mortar and pestle until a uniformly wet paste was obtained. Often different amount of components was used and several carbon paste electrodes prepared because the weight of components must be optimized. Sometimes the ionophore may be dissolved in a suitable solvent and then mixed with other component of carbon paste. This is doing for better homogenizing of components of the paste.

After construction of carbon paste, the paste was then packed into the end of an appropriate tube (usually: 3-5 mm internal diameter and 3-10cm long). This tube may be glassy or plastic. A copper wire was inserted into the opposite end to establish electrical contact. When necessary, a new surface was obtained by pushing an excess of paste out of the tube, which was then polished with paper. The electrode was finally conditioned by soaking in a solution of primary ion. The time of conditioning and the concentration of primary ion solution must be optimized.

In some of cases the room-temperature ionic liquids was used instead of paraffin for binder agent in carbon paste or it was used as fifth or sixth components of carbon paste. Incorporation of mineral oil gives CPEs some disadvantages. Mineral oil is not component-fixed since it is derived from refining of petroleum and processing of crude oil. As a result, contaminants or matrix components may unpredictably influence detection and analysis. In addition, the mechanical stability of CPEs rests somewhere between that of membrane electrodes and solid electrodes. Therefore ionic liquids have been used in carbon paste electrodes. These sensors are, in turn, called carbon ionic liquid electrodes (CILEs) (Safavi et al., 2007). Ionic liquids are a good choice as binders in carbon paste electrodes due to their chemical stability, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity and good electrochemical and thermal stability (Maleki et al., 2006).

Using CNT in the composition of the carbon paste (for preparation of potentiometric sensors) not only improves the conductivity of the sensor, but also increases the transduction of the chemical signal to electrical signal. By increasing the conductivity, the dynamic working range and response time of the sensor improve. If the transduction property of the sensor increases, the potential response of the sensor improves to Nernstian values. Also, a wider linear response range and higher sensitivity was reached when the...
CNTs were present in the composition of the electrode. However, with increasing the amount of the CNTs higher than a certain value in the composition of the carbon paste long response time and lower sensitivity for the potentiometric sensor obtained. It is probably due to the high surface area formed on the electrode surface that may offer special opportunities for the capturing ions on the electrode surface (Faridbod et al., 2010).

Table 1 shows different parameters of one carbon paste-CNT potentiometric sensor in comparison of some other potentiometric sensor without CNT. As can be seen detection limit, linear range and slope is improved in the case of carbon paste-CNT rather than other electrodes.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Slope (mV/decade⁻¹)</th>
<th>Detection limit (mol L⁻¹)</th>
<th>Linear range (mol L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE-CNT</td>
<td>29.3</td>
<td>2.5×10⁻⁹</td>
<td>5.0×10⁻⁹ to 1.0×10⁻⁴</td>
</tr>
<tr>
<td>Khani et al., 2010</td>
<td>32.6</td>
<td>8.9×10⁻⁷</td>
<td>1.0×10⁻⁶ to 1.0×10⁻¹</td>
</tr>
<tr>
<td>Mahajan et al., 2009</td>
<td>34</td>
<td>1.0×10⁻⁸</td>
<td>1.0×10⁻⁸ to 1.0×10⁻³</td>
</tr>
<tr>
<td>Yu et al., 2007</td>
<td>58.8</td>
<td>1.5×10⁻⁷</td>
<td>3.2×10⁻⁷ to 3.2×10⁻⁴</td>
</tr>
<tr>
<td>Abu-Shawish, 2009</td>
<td>29.6</td>
<td>6.5×10⁻⁷</td>
<td>1.0×10⁻⁶ to 1.0×10⁻¹</td>
</tr>
<tr>
<td>Ion et al., 2009</td>
<td>28.7</td>
<td>4.5×10⁻⁷</td>
<td>5×10⁻⁶ to 1×10⁻²</td>
</tr>
<tr>
<td>Lu et al., 2003</td>
<td>30.2</td>
<td>5.0×10⁻⁸</td>
<td>1.0×10⁻⁷ to 1.0×10⁻²</td>
</tr>
<tr>
<td>Rofouei et al., 2009</td>
<td>30.0</td>
<td>4.4×10⁻⁸</td>
<td>7.0×10⁻⁸ to 1.0×10⁻¹</td>
</tr>
<tr>
<td>Gupta et al., 2007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bakhtiarzadeh &amp; Ghani, 2008</td>
<td>30.0</td>
<td>5.0×10⁻⁸</td>
<td>1.0×10⁻⁷ to 1.0×10⁻²</td>
</tr>
</tbody>
</table>

Table 1. Different parameters of some Hg (II)-potentiometric sensors.

2.2.2 Solid electrode (except carbon paste)/CNT/polymeric membrane ion selective electrodes

Solid electrodes with extended anodic potential windows have attracted considerable analytical interest. Of the many different solid materials that can be used as working electrodes, the most often used are carbon, platinum and gold. Silver, nickel, and copper can also be used for specific applications. In this book the carbon paste electrode not considered in solid electrode and discussed in previous section.

Among solid electrodes the glassy carbon electrode (GCE) has been very popular because of its excellent mechanical and electrical properties, wide potential window, chemical inertness (solvent resistance), and relatively reproducible performance. The material is prepared by means of a careful controlled heating program of a premodeled polymeric (phenol formaldehyde) resin body in an inert atmosphere (Adams, 1969). The carbonization process proceeds very slowly over the 300-1200 °C to ensure the elimination of oxygen, nitrogen, and hydrogen. The structure of glassy carbon involves thin, tangled ribbons of cross-linked graphite-like sheets. Because of its high density and small pore size, no impregnating procedure is required. However, surface pretreatment is usually employed to create active and reproducible glassy carbon electrodes and to enhance their analytical performance. Such pretreatment is usually achieved by polishing (to a shiny “mirror-like” appearance) with successively smaller alumina particles (down to 0.05µm). The electrode should then be rinsed with deionized water before use. Additional activation steps, such as electrochemical, chemical, heat, or laser treatments, have also been used to enhance the
The improved electron transfer capability has been attributed to the removal of surface contaminants, exposure of fresh carbon edges, and an increase in the density of surface oxygen groups (that act as interfacial surface mediators) (Wang, 2006). Because of special properties of GCE it has been used very as transducer for construction of solid contact ion selective electrodes. There are different ways for utilization and deposition of CNT on solid electrodes. In one method, a solution of CNT was prepared by introducing appropriate amount of CNT into DMF (usually in concentration of 1 mg/ml) and sonication of this solution. Then suitable amount of DMF-CNT solution (about 5 µl) was placed directly onto the GCE surface and dried at room temperature to form a CNT film at the GCE surface. This method can be carried out in some more details as flowing: CNTs were deposited by spraying an aqueous dispersion containing $10^{-2}$ w.t. % of the CNTs and 1% w.t. of sodium dodecyl sulphate (SDS), thereby coating the GC with a layer of CNTs. Before deposit, the dispersion was homogenized using a sonicator. The CNTs were deposited in successive steps. The dispersion of CNTs was sprayed; the layer of CNTs was then dried, thoroughly washed with water, and dried again. The process was repeated several times.

After deposition of CNTs on GCE surface (GCE/CNT), suitable amount (10-100 µl) of polymer membrane solution deposit onto the electrode by drop casting. The electrode maintain under dry ambient conditions for appropriate time for example for one day (GCE/CNT/polymeric membrane). The membrane solution has been prepared by four components: a suitable polymer (e.g. poly vinyl chloride (PVC)), plasticizer (e.g. di butyl phthalate (DBP)), ionophore and additive (if it is necessary). The type and the amount of these components must be optimizing to potentiometric sensor show best response. The conditioning of the prepared sensor is necessary before use (Mazloum-Ardakani et al., 2005).

The layer of CNTs on the solid electrode (GC or gold electrode) functions as a transducer providing a high degree of stability in the potentiometric signal, converting the ionic current in the polymeric membrane to the electronic current that flows through the solid electrode conducting rod. This fabrication of solid-contact ISEs based on CNT requires the additional step to produce the intermediate layer, which makes this type of electrode more complicated to prepare than coated wire electrode. Recently, a facile method has been reported to fabricate single piece solid-contact electrode by adding CNTs into the polymeric membrane solution directly and sonication of it (Zhu et al., 2009). Then this solution subsequently, is drop cast on the solid electrode disk and the solvent is evaporated overnight at room temperature. With the aid of polymeric dispersants CNTs facilitating the ion- to-electron transfer can be well-dispersed in different polymer matrices, which lead to a general approach to prepare all solid-state ion-selective sensors by simple one-step drop casting method.

For combination of properties of conducting polymers and carbon nanotubes a composite of them can be used as ion-to-electron transducer in solid contact ion selective electrodes. In one of the reported methods, negatively charged carbon nanotubes were used as dopants in the electrochemical synthesis of the one conducting polymer. This conducting polymer doped with CNT (CP/CNT) electropolymerized on a solid electrode (CP/CNT/GCE) as transducer and the sensing polymeric membrane applied at CP/CNT/GCE (Mousavi et al., 2009).

2.3 Voltammetric sensors

In voltammetry a time-dependent potential is applied to an electrochemical cell, and the current flowing through the cell is measured as a function of that potential. A plot of current
as a function of applied potential is called a voltammogram, providing quantitative and qualitative information about the species involved in the oxidation or reduction reaction. Direct voltammetry of more substance at bare electrodes takes place in high over potential and at nearly potential close to other (Mazloum-Ardakani et al., 2010a). In addition, the direct oxidation results electrode surface contamination (fouling) due to the adsorption of oxidized products. These cases result poor sensitivity, poor selectivity and unstable analytical signals. To avoid the above obstacles in electroanalytical methods, modified electrodes have been developed (Kalimuthu & John, 2009). Chemically modified electrodes represent a modern approach to electrode systems. These electrodes rely on the placement of a reagent onto the surface, to impart the behavior of that reagent to the modified surface. The modification of electrode surfaces can solve many electroanalytical problems, and may form the basis for new analytical applications and different sensing devices. There are four principle enhancement techniques for voltammetric sensors and modified electrodes, namely selective preconcentration, permselectivity, selective recognition and electrocatalysis. Among different voltammetric sensors, in this section we discussed only the voltammetric sensors based on electrocatalysis.

2.3.1 Electrocatalysis voltammetric sensors

Often the desired redox reaction at the bare electrode involves slow electron transfer kinetics and therefore occurs at an appreciable rate only at potentials substantially higher than its thermodynamic redox potential. Such reactions can be catalyzed by attaching to the surface a suitable electron transfer mediator. Electrocatalytic reactions play a central role in electrochemistry and a vital role in sensing and energy-related applications. The function of the mediator is to facilitate the charge transfer between the analyte and the electrode. In most cases the mediated reaction sequence (e.g., for an oxidation process) can be described as below:

\[
\text{M}_{\text{red}} \rightarrow \text{M}_{\text{ox}} + \text{ne}
\]

\[
\text{M}_{\text{ox}} + \text{A}_{\text{red}} \rightarrow \text{M}_{\text{red}} + \text{A}_{\text{ox}}
\]

where M represents the mediator (or modifier) on the electrode surface and A is analyte (Bard & Faulkner, 2001). Hence, the electron transfer takes place between the electrode and mediator and not directly between the electrode and the analyte. The active form of the catalyst is electrochemically regenerated. The net results of this electron shuttling are a lowering of the overvoltage of analyte oxidation to the formal potential of the mediator and an increase in current density.

Different derivatives of hydroquinone (Mazloum-Ardakani et al., 2010b) and transition metal complexes (Amini et al., 2001; Janda et al., 1996; Shahrokhian et al., 2004) are well known as electron mediators or modifiers in the electrocatalytic determination of some important compounds by voltammetric sensors. These modifiers have a high electron transfer rate constant. Usually, modifier in the absence of analyte exhibits a well-behaved redox reaction in cyclic voltammetry technique. But in the presence of analyte the anodic peak current in cyclic voltammogram increased drastically and the cathodic peak eliminated at suitable potential scan rate (low scan rates). This mechanism is called electrocatalysis or EC (Bard & Faulkner, 2001). Different electrochemical techniques such as cyclic voltammetry, chronocoulometry and hydrodynamic voltammetry can be used for investigation of electrocatalysis. These techniques will provide the means to determine different kinetic parameters such as rate of electron transfer between electrode and modifier,
rate of chemical reaction between modifier and analyte and transfer coefficient (α) for oxidation of modifier and analyte (Mazloum-Ardakani et al., 2009). Since differential pulse voltammetry has high current sensitivity and good resolution, it has been used for quantitative analysis by electrocatalysis voltammetric sensors. For obtaining the calibration curve differential pulse voltammetry apply for different concentrations of analyte. Then the peak current of differential pulse voltammograms plot versus concentrations of analyte. The most important merit of figures for one voltammetric sensor are linear range of calibration curve and detection limit. These can affect by different parameters. For example, even the factors that increase the current sensitivity can improve the detection limit of the sensor (Beitollahi et al., 2009).

Utilization of even substrate with modifier that improves the electrocatalysis of analyte will increase the sensitivity and thus the detection limit and other factors of the sensor will be better. Nanomaterials can be used in structure of the voltammetric sensors for this purpose. There are different methods for modification of the electrode and utilization of nanomaterials (e.g. carbon nanotubes) in voltammetric sensors. In the next section we classified these methods and explain them in details.

2.4 Carbon nanotubes in electrocatalysis voltammetric sensors
Carbon nanotubes represent an increasingly important group of nanomaterials with unique geometric, mechanical, electronic, and chemical properties (Baughman, 2002). The unique properties of carbon nanotubes make them also extremely attractive for the tasks of surface modification in voltammetric sensors. More recent studies have demonstrated that carbon nanotubes-modified electrodes can promote the electrochemical reactivity of important analytes and impart resistance against surface fouling in electrocatalysis voltammetric sensors (Wang & Musameh, 2003). The electrocatalytic activity of carbon nanotubes has been attributed to the presence of edge plane defects at their end caps (Banks et al., 2004).

Modification of the electrode and utilization of carbon nanotubes for preparation of electrocatalysis voltammetric sensors can be divided into two major groups: modification of the bulk (such as carbon paste and carbon ceramic electrodes) and modification of the surface of the electrode (such as adsorption and preparation of polymer film). The most usual methods for using of carbon nanotubes in electrocatalysis voltammetric sensors have been discussed as flowing: modification of the bulk of carbon paste and carbon ceramic by both modifier and carbon nanotubes; modification of the surface of other solid state electrodes (except carbon paste and carbon ceramic e.g. glassy carbon) by drop casting of a solution of carbon nanotube at electrode surface and then modification with modifier; modification of the surface of glassy carbon electrode by a polymer and carbon nanotubes simultaneously.

2.4.1 Carbon nanotubes in bulk modification
There are tow methods for bulk modification of electrodes in electrocatalysis voltammetric sensors. In one of them carbon paste has been used as matrix for incorporating carbon nanotubes and modifier. General procedure for preparation of carbon paste electrode was described in section 2.2.1. In electrocatalysis voltammetric sensors three component has been used: carbon powder, paraffin and modifier. The amount of modifier is 0.5-10% w/w of total weight commonly. The subtle electronic properties of carbon nanotubes suggest that they have the ability to promote electron transfer when used as the electrode material in electrochemical reactions.
These properties provide a new manner of electrode surface modification for designing new voltammetric sensors and novel electrocatalytic materials (Beitollahi et al., 2008). Therefore carbon nanotubes incorporate as a forth component in carbon paste to improve the electrocatalytic properties of the electrocatalysis voltammetric sensors. The effect of carbon nanotubes on the response of a one electrocatalysis voltammetric sensor has been described below as an example.

We made one electrochemical sensor based on carbon paste electrode modified with 3,4-dihydroxybenzaldehyde-2,4-dinitrophenylhydrazone incorporating carbon nanotubes, which makes the modified electrode highly sensitive for simultaneous electrochemical detection of norepinephrine, acetaminophen and tryptophan (Mazloum-Ardakani et al., 2011). Fig. 2 depicts the cyclic voltammetry responses for the electrochemical oxidation of 0.3 mM norepinephrine at unmodified carbon paste (curve b), modified carbon paste with only modifier (curve e), modified carbon paste with only carbon nanotubes (curve d) and modified carbon paste with both modifier and carbon nanotube (curve f). As it is seen, the peak potential of the norepinephrine at carbon paste modified with carbon nanotube is lower than unmodified carbon paste which indicates the catalysis effect of carbon nanotube. However, modified carbon paste with modifier and carbon nanotube (curve f) shows much higher anodic peak current for the oxidation of norepinephrine compared to modified

Fig. 2. Cyclic voltammograms of (a) unmodified carbon paste and (c) modified carbon paste with modifier in 0.1 M phosphate buffer solution (pH 7.0); (b) as (a) +0.3 mM norepinephrine; (d) as (b) at the surface of modified carbon paste with only carbon nanotubes; (e) as (b) at the surface of modified carbon paste with modifier; (f) as (b) at the surface of modified carbon paste with modifier and carbon nanotube. All scan rates are 10 mVs⁻¹
carbon paste with only modifier (curve e), indicating that the combination of carbon nanotube and the modifier has significantly improved the performance of the electrode toward norepinephrine oxidation. Also the linear range and detection limit of carbon paste based electrocatalysis voltammetric sensor will be improved by using of carbon nanotubes. For example the detection limit and linear range of a carbon paste sensor without carbon nanotubes for determination of dopamine reported as $1.0 \times 10^{-6}$ M and $2.0 \times 10^{-6}$ to $1.5 \times 10^{-3}$ M, respectively (Safavi et al., 2006). However these are $8.7 \times 10^{-8}$ and $1.0 \times 10^{-7}$ to $9.0 \times 10^{-4}$ at our reported carbon paste sensor based on carbon nanotubes (Mazloum-Ardakani et al., 2009).

Another way for bulk modification of electrode is using of carbon ceramic as matrix which can hold modifier and carbon nanotubes simultaneously. The carbon ceramic electrodes prepared by sol–gel techniques are interesting materials in the fields of electrochemical sensors and biosensors owing to their renewability, polishesibility, chemical stability, physical rigidity, porosity, and permeability in electroanalysis (Lin & Brown, 1997).

The advantages and utilization of carbon nanotubes in carbon ceramic based sensors is similar to carbon paste sensors. The general procedure for construction of modified carbon ceramic sensors with carbon nanotubes is as flowing (Tsionsky et al., 1994).

The mixture solution of methyltrimethoxysilane, methanol and hydrochloric acid (each of them with appropriate concentration) has been stirred to ensure uniform mixing, after which suitable amount of graphite powder (e.g. 1.0 g in 1 mL of solution) and carbon nanotubes (e.g. 0.01 g in 1 mL of solution) has been added and the mixture shaken for about 5 min. The mixture has been added to Teflon or glassy tube with about 3 mm inner diameter. Then it is dried for about 48 h at room temperature.

### 2.4.2 Carbon nanotubes in surface modification

One common way for modification of the surface of electrode with carbon nanotube was described in section 2.2.2. Suitable amount of a solution of carbon nanotube in a solvent (e.g. 5 µl of carbon nanotube in DMF with concentration of 1 mg/ml) was placed directly onto the solid electrode (e.g. glassy carbon) surface and dried at room temperature to form a carbon nanotube film at the electrode surface. After that, usually the electrochemical deposition has been applied for immobilization of modifier at the glassy carbon electrode. This procedure is as flowing.

Electrochemical activation of the glassy carbon electrode has been performed by continuous potential cycling from about -1.1 to 1.6 V at sweep rate of 100 mVs$^{-1}$ in sodium bicarbonate solution (e.g. 0.1 M) until a stable voltammogram obtain. After rinsing with doubly distilled water, the activated electrode was modified subsequently as follows. It was placed in a buffer solution containing modifier (in concentration of 0.1 to 1 mM) and was modified by cycling the potential around the redox peak of modifier for several cycles or several minutes (Mazloum-Ardakani et al., 2007). Finally, the electrode was rinsed thoroughly with water and the GCE/CNT/mod is prepared.

In another way for modification of the surface of the electrode the carbon nanotube dispersed in conducting polymer film at the surface. Recently, conducting polymer/CNTs composites have received significant interest because the incorporation of CNTs into conducting polymers can lead to new composite materials possessing the properties of each component with a synergistic effect that would be useful in particular application (Chen et
Polypyrrole and polyaniline can be used for fabrication of CNT/PPy and CNT/PANI nanocomposite electrodes due to the ease in the preparation through copolymerization by a chemical or electrochemical approach and the resulting nanocomposites exhibit high conductivity and stability (Guo et al., 2005). The SEM image of three different composite of CNT/conducting polymer has been shown in fig. 3. This figure indicates the difference between conducting polymer film and composite of CNT/polymer. The SEM images of the PPy-CNT, PANI-CNT and PEDOT-CNT composites show commonly a three-dimensional (3D) network composed of interconnected fibrils with similar diameters. The diameter of the as-received CNTs was in the range of 10–30 nm, while the fibrils in the composites were of 30–60 nm in width. This difference indicates that the conducting polymer formed a uniform coating on the surface of individual CNTs. It can then be concluded that the 3D network was formed with the CNTs serving as the backbone, thus greatly enhancing the mechanical properties of the composite film (Peng et al., 2007).

As an example for using of composite of CNT and conducting polymer in voltammetric sensors, we can state a reported sensor based on PANI/CNTs composite. This PANI/CNTs composite modified electrode fabricated by galvanostatic electro polymerization of aniline on MWCNTs-modified gold electrode, exhibits enhanced electrolytic behavior to the reduction of nitrite and facilitates the detection of nitrite at an applied potential of 0.0 V. A linear range from 5.0×10⁻⁶ to 1.5×10⁻² M for the detection of sodium nitrite has been observed at the PANI/MWCNTs-modified electrode with a detection limit of 1.0 µM (Guo et al., 2005).
In another example of surface modification by conducting polymer/CNT composite the films of overoxidized polypyrrole directed single-walled carbon nanotubes (SWNTs) have been electrochemically coated onto glassy carbon electrode (Li et al., 2007). For preparation of this composite, electroactive monomer pyrrole was added into the solution containing sodium dodecyl sulfate and SWNTs. Then, electropolymerization was proceeded at the surface of glassy carbon electrode and a novel kind of conducting polymer/SWNTs composite film with the orientation of SWNTs were obtained correspondingly. Finally, this obtained polypyrrole (PPy)/ SWNTs film modified electrode was oxidized at a potential of +1.8 V. This oxidized composite film modified glassy electrode exhibited excellent electrocatalytic properties for some species such as nitrite, ascorbic acid, dopamine and uric acid; and was used as a new sensor for practical applications. Compared with previous CNTs modified electrodes, in this reported work SWNTs were oriented towards the outside of modified layer, which made the film easily conductive. Moreover, this proposed film modified electrode was more stable, selective and applicable.

3. Conclusion and future directions

There are numerous studies on carbon nanotubes applications because of interesting and unique properties of them. One important application of CNTs is using of them in structure of different sensors. Since CNTs possess interesting electrochemical properties, it can be used for construction of electrochemical sensors specially potentiometric and voltammetric sensors.

In potentiometric sensors, CNTs have been proposed as alternative solid-state transducers that can improve the detection limit and selectivity coefficient of the sensor by facilitating the ion to electron transfer and elimination of the ion flux from the internal solution. Carbon paste and solid electrode/CNT/polymeric membrane are two way for utilization of CNTs in potentiometric sensors that discussed in detail.

The unique properties of carbon nanotubes make them extremely attractive for the tasks of surface modification in voltammetric sensors. CNT-modified electrodes can improve the electrocatalytic activity of the modifier for electroanalysis of important analytes and impart resistance against surface fouling in electrocatalysis voltammetric sensors. Modification of the electrode with a modifier and utilization of carbon nanotubes for preparation of electrocatalysis voltammetric sensors was divided and discussed into tow major groups: modification of the bulk and modification of the surface of the electrode.

In the future, synthesis of novel carbon nanotubes for example by functionalization of them for improving of their properties, and using of them in construction of different electrochemical sensors will open a new window to electrochemical sensors field. Also, application of CNTs in microelectrodes and nanosensors can be interesting.

So far we have discussed the one sensor and one analyte approach, however, arrays of independent electrodes can offer much more analytical information and thus hold a great potential for many practical applications. The use of multielectrode or multisensor arrays takes advantage of the partial selectivity of an individual electrode, by combining several electrodes and examining the relative responses of all the sensors together.

4. Acknowledgment

The authors would like to thank Yazd University Research Council.
5. References


www.intechopen.com


www.intechopen.com


www.intechopen.com
Carbon Nanotubes are among the strongest, toughest, and most stiff materials found on earth. Moreover, they have remarkable electrical and thermal properties, which make them suitable for many applications including nanocomposites, electronics, and chemical detection devices. This book is the effort of many scientists and researchers all over the world to bring an anthology of recent developments in the field of nanotechnology and more specifically CNTs. In this book you will find:

- Recent developments in the growth of CNTs
- Methods to modify the surfaces of CNTs and decorate their surfaces for specific applications
- Applications of CNTs in biocomposites such as in orthopedic bone cement
- Application of CNTs as chemical sensors
- CNTs for fuel cells
- Health related issues when using CNTs

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License, which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.