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# Carbon Nanotubes – Imprinted Polymers: Hybrid Materials for Analytical Applications

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## 1. Introduction

Molecular imprinting is a recent new and rapidly evolving technique which allows the creation of synthetic receptors (MIPs) consisting of highly cross-linked porous-rich polymers with recognition properties comparable to the biological systems related to the presence of specific recognition sites complementary in shape, size and functional groups to a target molecule. It is a facile concept, which involves the construction of sites of specific recognition, commonly within synthetic polymers. The template of choice is entrapped within a pre-polymerization complex, consisting of functional monomers with good functionality, which chemically interacts with the template. Polymerization in the presence of crosslinker serves to freeze these template-monomer interactions and subsequent removal of the template results in the formation of a molecularly imprinted polymer matrix. Due to the advantages of MIPs such as low cost, stability, and easy preparation compared with natural molecular recognition products (e.g. antibody), Molecular imprinting is a well-developed tool in the analytical field, mainly for separating and quantifying very different substances, including drugs and bio-active molecules contained in relatively complex matrices. Despite the application of MIPs as sensor matrices or separation materials, they suffer from basic limitations associated with the limited concentration of imprinted sites, and the bulk volume of the polymer matrices that requires long diffusion paths of the imprinted host molecules. These limitations lead to inefficient sensing or separation processes. MIP nanomaterials are proposed as a pain reliever for headache by improving the accessibility and the homogeneity of the binding sites. In particular, with high strength, the extremely large surface area and unique chemical properties, Carbon nanotubes (CNTs) could serve as the reinforcing element or core in fabricating core-shell structural MIPs.

Since their discovery in 1991, CNTs have attracted great attention because of their unique properties (high electrical conductivity, chemical stability, mechanical strength, large specific surface area, and high thermal stability) indicating potential for various applications.

CNTs represent a new carbon material that has been widely recognized as the quintessential nanomaterial and, because the hexagonal arrays of carbon atoms of the CNTs surface have a strong interaction with other molecules or atoms, CNTs show a great analytical potential as a solid-phase extraction adsorbent. Additionally, CNTs' surfaces can be modified by introducing various organic functional groups, thus providing a strongly physisorbing surface area, adjustable surface charge, and a source of protons for chemical ionization. It has been demonstrated that the surfaces of CNTs can be easily modified in numerous ways, either by covalent or non-covalent functionalization. All the facts mentioned before reveal that carbon nanotubes, and specially multiwalled carbon nanotubes, have great analytical potential as an effective solid-phase extraction adsorbent for chelates or ion pairs of metal ions, organic compounds, and organometallic compounds.

Based on these considerations, it could be summarized that MIPs-CNTs composites represent useful innovative materials for analytical determination of target analytes in complex matrices.

## **2. Molecularly Imprinted Polymers (MIPs): highly selective materials**

Molecular imprinting is a very useful technique to incorporate specific substrate recognition sites into polymers (Puoci et al., 2010). In particular, by this polymer synthesis technique, the formation of macromolecular networks characterized by specific recognition sites for a desired target molecule, named template could be obtained (Byrne & Salian, 2008). The specific binding properties of MIP must be attributed to specific interactions between the template and the functional groups in the polymeric network, thus the choice of the functional monomers is of primary importance to obtain performing imprinted materials (Puoci et al., 2007; Cirillo et al., 2010, 2011a)

In the synthesis of these macromolecular system, many parameters involved can affect the information associated with the binding sites, such as functional monomers/polymers, crosslinkers and solvents/porogens. Thus, both the feasibility of imprinting and the proper preparation conditions need exploration for the preparation of efficient imprinted materials (Liu Z. et al., 2010). It is important to state that MIP can be obtained in different formats, depending on the preparation method followed. To date, the most common polymerizations for preparing MIPs involve conventional solution, suspension, precipitation, multi-step swelling and emulsion core-shell. There are also other methods, such as aerosol or surface rearrangement of latex particles, but they are not used routinely (Puoci et al., 2011).

MIPs are stable polymers with molecular recognition abilities and resistant to a wide range of conditions (pH, organic solvents, temperature, pressure), and were used for several different applications, such as chromatographic stationary phases (Hishiya et al., 2003), enantiomeric separation (Adbo & Nicholls, 2001), solid-phase extraction (SPE) (El-Sheikh et al., 2010), and catalysis (Anderson et al., 2005); they were also used as receptors (Haupt, 2003), antibodies (Svitel et al., 2001), enzyme mimics (Nicholls et al., 1996), affinity and sensing materials (Syu et al., 2006), and, in recent years, pharmaceutical applications, such as drug discovery, drug purification, or drug delivery (Mosbach, 2006; Yu Y. et al., 2002; Caldorera-Moore & Peppas, 2009; Hilt & Byrne, 2004).

MIPs can be synthesized following three different imprinting approaches named covalent, non-covalent and semi-covalent procedure, according to the kind of interaction between a template and functional groups during the synthesis and recognition phases (Caro et al., 2002).

In the non-covalent procedure (Figure 1), non-covalent interactions (hydrogen bonding, p-p interactions, Van der Waals forces, etc.) are involved in both the synthesis and the recognition step (Joshi et al., 1998). This method is still the most widely used method to prepare MIP because of the advantages that it offers from the point of view of synthesis. The covalent protocol requires the formation of covalent bonds between the template and the functional monomer prior to polymerization, as well as between template and functional group in the imprinted cavities during the re-binding process (Ikegami et al., 2004). Finally, the semi-covalent approach is a hybrid of the two previous methods. Specifically, covalent bonds are established between the template and the functional monomers before polymerization, while, once the template has been removed from the polymer matrix, the subsequent re-binding of the analyte to the MIP exploits non-covalent interactions (Curcio et al., 2010).

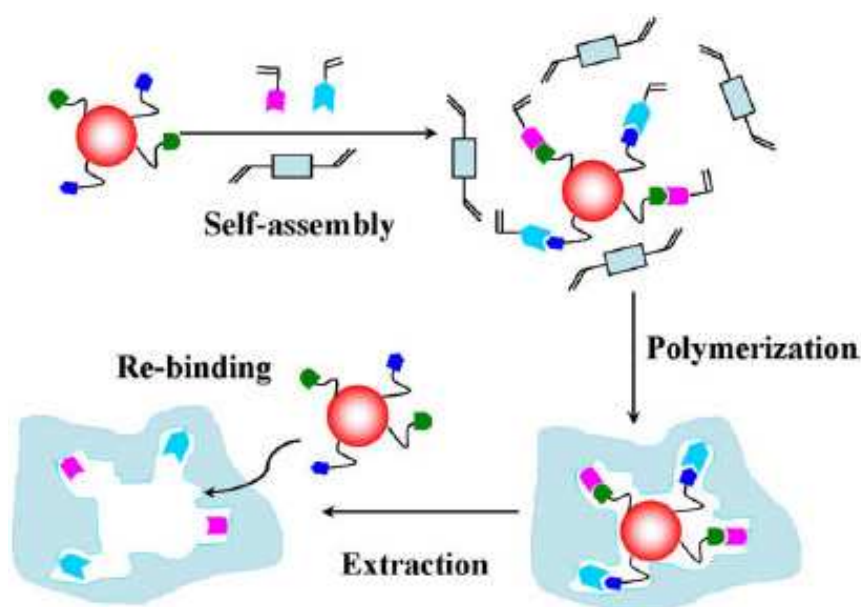


Fig. 1. Schematic representation of Non-Covalent Molecular Imprinting Process. Adapted from Liu Z. et al., 2010.

The binding sites obtained by molecular imprinting show different characteristics, depending on the type of imprinted approach. The average affinity of binding site prepared using bonding by non-covalent forces is generally weaker than those prepared using covalent methods because electrostatic, hydrogen bonding,  $\pi$ - $\pi$  and hydrophobic interactions, between the template and the functional monomers, are used exclusively in forming the molecular assemblies (Hwang & Lee, 2002). However, when covalent bonds are established between the template and the functional monomer prior to polymerization, this gives rise to better defined and more homogeneous binding sites than the non-covalent approach, since the template-functional monomer interactions are far more stable and defined during the imprinting process.

It should also be mentioned that, as a control in each polymerization, a non-imprinted polymer (NIP) is also synthesised in the same way as the MIP but in absence of the template. To evaluate the imprinting effect, the selectivities of the NIP and MIP are then compared.

### 3. Carbon nanotubes: fascinating nano-objects

In the last decade, the dramatic development of nanotechnology in material science and engineering has led to the study and the development of innovative nanostructured materials (Xu T. et al., 2007; Niemeyer, 2001; Cui & Gao, 2003; Whitesides, 2003): certain materials with delicate structures of “small” sizes, falling in the 1–100 nm range, and specific properties and functions related to the “size effect” (Safarik & Safarikova, 2002; Laval et al., 1999). In particular, extensive researches have been focused on medicine and biomedical engineering for the investigation of the interactions between nanomaterials and biological systems (Foldvari & Bagonluri, 2008; Bianco et al., 2005; Desai, 2000). Potential products of bionanotechnology in the pharmaceutical and biomedical industry are referred as nanomedicines, including materials to be employed as clinical bio-analytical diagnostics (Bianco et al., 2005; Pantarotto et al., 2003), carriers to improve controlled and targeted drug release (Leary et al., 2006; Sinha & Yeow, 2005) and additives to improve solubility and bioavailability of poorly soluble drugs (Ajayan et al., 1993), novel tissue engineered scaffolds and devices (Bauer et al., 2004; Mazzola, 2003; Kikuchi et al., 2004).

Within the realm of bionanotechnology, carbon nanotubes (CNTs), a major class of carbon-based tubular nanostructures have been denoted great interest in the scientific community (Ke & Qiao, 2007; Klingeler & Sim, 2011).

The walls of CNTs are made up of a hexagonal lattice of carbon atoms analogous to the atomic planes of graphite (Dresselhaus et al., 2004). CNTs can be imaginatively produced by rolling up a graphene sheet (a single layer of graphite) forming a single-walled CNTs (SWCNTs), or by rolling up many graphene layers to form concentric cylinders (multi-walled CNTs; MWCNTs). The ends of CNT may be closed with half-spheres of fullerenes. MWNTs are comprised of two up to several to tens of concentric carbon cylinders and thus generally have a larger outer diameter (2.5–100 nm) than SWNTs (0.6–2.4 nm) (Joselevich, 2004) (Figure 2).

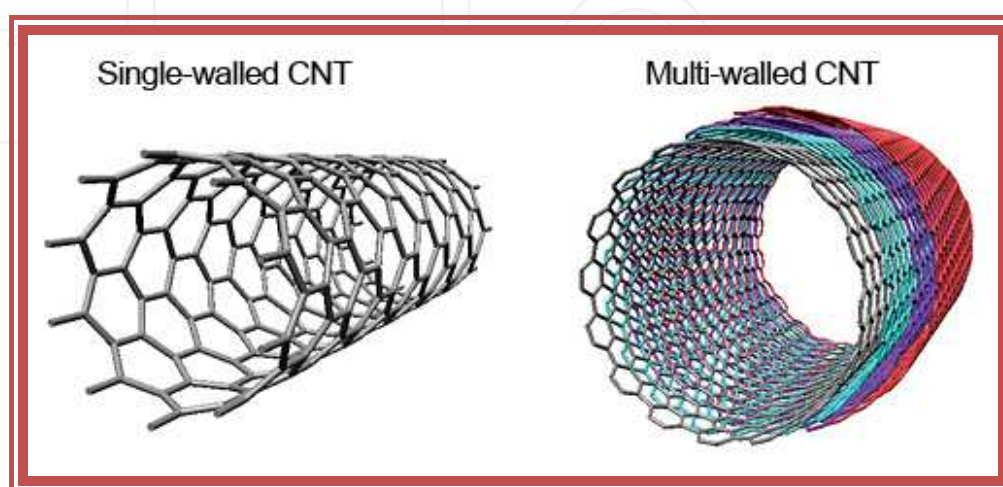


Fig. 2. Schematic representation of SWNTs and MWNTs.



Although there have been many interesting and successful attempts to grow CNTs by various methods (Klingeler et al., 2008; Vyalikh et al., 2008), the three most widely used techniques are: arc discharge, laser ablation, and chemical vapor deposition (CVD) (Ando et al., 2004).

The arc-discharge method is the one by which CNTs were first produced and recognized. In a model system, a dc arc voltage is applied between two graphite rods in the presence of an appropriate ambient gas. This method is useful for the production of both CNTs and fullerenes. In particular, when pure graphite rods are used, fullerenes are deposited in the form of soot in the chamber (Saito et al., 1992). However, a small part of the evaporated anode is deposited on the cathode, which includes CNTs (Iijima, 1991). As described by Ando et al., 2004, these CNTs represent MWNTs. They are found not only on the top surface of the cathode deposit (Ando, 1993) but also deep inside the deposit (Ando & Iijima, 1993). Large-scale synthesis of MWNTs by arc discharge has been achieved (Ebbesen & Ajayan, 1992; Colbert et al., 1994) in He gas. The same methodology could be applied to the synthesis of SWNTs if a graphite rod containing metal catalysts (Fe, Co, etc.) is used as the anode with a pure graphite cathode (Iijima & Ichihashi, 1993; Bethune et al., 1993). By using a dc pulsed arc discharge inside a furnace, homogeneous conditions in arc discharge are achieved and high-quality DWNTs are synthesized by a method called high-temperature pulsed arc discharge (Sugai et al., 1999, 2000, 2003; Shimada et al., 2004).

The laser ablation, based on the high energy density of lasers (typically a YAG or CO<sub>2</sub> laser) which is suitable for materials with a high boiling temperature such as carbon, was developed for fullerene and CNT production by Smalley's group (Guo T. et al., 1992; Thess et al., 1996). The laser has sufficiently high energy density not to cleave the target into graphite particles but to vaporize it at the molecular level converting the graphite vapor into amorphous carbon as the starting material of SWNTs (Puretzky et al., 2000; Sen et al., 2000; Kokai et al., 2000). The annealing conditions of the amorphous carbon in the laser ablation method are more homogeneous than those of the arc-discharge method, in which the electrodes and the convection flow disturb the homogeneity of the temperature and flow rate (Zhao X. et al., 2003; Kanai et al., 2001).

Chemical Vapor Deposition (CVD) is a simple and economic technique for synthesizing CNTs at low temperature and ambient pressure. Usually, a carbon feedstock is thermally decomposed in the presence of a metal catalyst (Cirillo et al., 2011b). The generated carbon dissolves in the catalyst particles and, after saturation, is deposited in the shape of CNTs.

To be distinguished from the many kinds of CVD used for various purposes, the method is also known as thermal or catalytic. Compared with arc-discharge and laser methods, CVD is more versatile because it offers better control over growth parameters. Furthermore, it harnesses a variety of hydrocarbons in any state (solid, liquid, or gas), enables the use of various substrates, and allows CNTs growth in a variety of forms, such as powder, thin or thick films, aligned or entangled, straight or coiled, or even a desired architecture of nanotubes at predefined sites on a patterned substrate. MWNTs were grown from benzene, ethylene, methane, and many other hydrocarbons (Endo et al., 1993; José-Yacamán et al., 1993; Satiskumar et al., 1999; Hernadi et al., 1996). SWNTs were first produced by Dai et al. from disproportionation of CO, and SWNTs were also produced from benzene, acetylene, ethylene, and methane using various catalysts. (Cheng et al., 1998; Satishkumar et al., 1998; Hafner et al., 1998; Kong J. et al., 1998; Flahaut et al., 1999). Due to lower synthesis

temperatures CVD grown CNTs exhibit a lower crystallinity than tubes produced using the two alternative methods mentioned above.

When considering the whole of CNTs applications, the solubilization of pristine CNTs in aqueous solvents remains an obstacle to realizing their potential, due to the rather hydrophobic character of the graphene sidewalls. To successfully disperse CNTs the dispersing medium should be capable of both wetting the hydrophobic tube surfaces and modifying the tube surfaces to decrease tube aggregation. Four basic approaches have been used to obtain a dispersion: surfactant-assisted dispersion (Ham et al., 2005; Islam et al., 2003; Moore et al., 2003; Yurekli et al., 2004; Vaisman et al., 2006), solvent dispersion (Fu & Sun, 2003; Ausman et al., 2000; Kim D.S. et al., 2005), functionalization of CNT sidewalls (Dyke & Tour 2004; Fernando et al., 2004; Peng et al., 2003), and biomolecular dispersion (Gigliotti et al., 2006).

#### 4. Chemical sensing

Before exploring the use of CNTs in chemical and electrochemical sensing it should be pointed out that the term sensor refers to a device that responds to a physical or chemical stimulus by producing a signal, usually an electrical one (Hillberg et al., 2005), while a biosensor is a sensor that uses biological selectivity to limit perception to the specific molecule of interest. A typical biosensor consists of two main components: the chemosensory materials (receptors) that can selectively bind target analytes and the efficient transducer that can transform the binding events into a readable signal output related to the analyte concentration in the sample (Eggins, 2002). The efficiency of chemosensors is largely dependent on the selectivity and sensitivity of the used sensory materials to a target species. In the traditional approaches a biological or biologically derived sensing element acting as a receptor is immobilized on the surface of a physical transducer to provide selective binding of analytes (Orellana & Moreno-Bondi, 2005; Jiang & Ju, 2007). As a sensing element, it is possible to use either biological macromolecules (e.g. antibodies, enzymes, receptors and ion channel proteins, nucleic acids, aptamers and peptide nucleic acids) or biological systems (e.g. ex vivo tissue, microorganisms, isolated whole cells and organelles). However, the small surface area and non-tunable surface properties of transducers greatly limit the efficiency of chemosensors, especially for the detection of ultratrace analytes. Recently, nanomaterials have found a wide range of applications as a material foundation of chemosensors, and have exhibited various degrees of success in the improvement of detection sensitivity and selectivity (Gao D. et al., 2007; Xie et al., 2006; Banholzer et al., 2008) due to their unique electrical, optical, catalytic or magnetic properties (Chen J.R. et al., 2004) and large surface-to-volume ratio (Xie et al., 2008).

##### 4.1 CNTs in chemical sensing

Among nanomaterials, carbon surfaces represent very attractive materials for electrochemical studies, such as biosensor applications, due to their different allotropes (graphite, diamond and fullerenes/nanotubes). Carbon electrodes are well polarizable. However, their electrical conductivity strongly depends on the thermal treatment, microtexture, hybridization and content of heteroatoms. Additionally, the amphoteric character of carbon allows use of the rich electrochemical properties of this element from donor to acceptor state. Application of recently developed carbon materials include,

environment-friendly and energy-saving automotive parts, high-purity components in semiconductor manufacturing equipment for highly integrated chips, internal walls of vacuum vessels in the nuclear fusion reactors expected to be an energy source in the 21st century, and negative electrodes of lithium ion secondary batteries, of which demand is rapidly increasing with the popularization of mobile electronic instruments (Kazua, 1999). During the last years a great interest has been focused on the application of carbons (Flavel et al., 2009; Ma G.P. et al., 2009) as electrode materials because of their accessibility, easy processability and relatively low cost. They are chemically stable in different solutions (from strongly acidic to basic) and able to show performance in a wide range of temperatures. Already well-established chemical and physical methods of activation allow for the production of materials with a developed surface area and a controlled distribution of pores that determine the electrode/electrolyte interface for electrochemical applications.

The possibility of using the activated carbon without binding substances (e.g. fibrous fabrics or felts) gives an additional advantage from the construction point of view. Unique properties of ultra-microelectrodes (UMEs) make them very attractive in electroanalytical measurements which require high spatial and temporal resolution (Wightman, 1988). At ultra-microelectrodes, at typical slow scan rates of voltammetry, signal to noise ratios (S/N) can increase up to one decade due to efficient mass transportation to the electrode resulting from edge effects. In addition, because of the small dimensions and low IR drop, fast scan voltammetric measurements (Garreau et al., 1990; Hsueh et al., 1993) and measurements in highly resistive media are possible at UMEs (Howell & Wightman, 1984) while high spatial resolution and minimal tissue damage (Musallam et al., 2007). can be achieved in vivo analysis. Microelectrodes are useful for measurements for changes in easily oxidized neurotransmitter concentrations in extracellular brain fluid (Kawagoe et al., 1993) as they provide a way to observe the rapid chemical changes associated with the release of neurotransmitters from neurons and their subsequent removal from the extracellular fluid (Atesa & Sarac, 2009).

The nanodimensions of CNTs guarantee a very large active surface area and are especially suited for the conception of miniaturized sensors. In addition to the high porosity and reactivity, this makes them ideal candidates for the storage of neutral species as well as electron donors, when used as electrodes in electrochemical reactions, for which they may also be called “nanoelectrodes” (Basabe-Desmonts et al., 2007; Daniel et al., 2007; Guo et al., 2004). Hence, it is not surprising that gas sensors made from individual nanotubes show good sensitivities at room temperature (J. Kong et al., 2001; Vasanth Kumar et al., 2010, 2011) in comparison to commercially available classical semiconductor sensors, which in general operate above 200°C. However, a necessary prerequisite is that the molecules to be detected must have a distinct electron donating or accepting ability, which is fulfilled, for example, by ammonia (NH<sub>3</sub>) as a donor and nitrogen dioxide (NO<sub>2</sub>) as an acceptor. The adsorption of these molecules on the nanotubes is associated with a partial charge transfer, which alters the charge-carrier concentration or, alternatively, the adsorbed molecules may affect the potential barriers present at the tube-electrode contacts. In any event, the resulting change in the electrical resistance of the nanotube is utilized as a sensor signal. However, for the detection of molecules that are only weakly adsorbed (e.g., carbon monoxide and hydrogen), the change in resistance is often too small. A possible method to overcome this drawback is accomplished by the modification of the nanotube sidewalls with nanoparticles made of a suitable metal. For instance, sensitive hydrogen sensors operating at room



temperature can be obtained via the deposition of palladium nanoparticles either by direct evaporation (Kong J. et al., 2000) or through electrodeposition (Geng et al., 2004; Teles et al., 2008). Electrodeposition offers the specific advantage of site-selectivity, since the metal decoration is restricted to the current-carrying tubes, so that the remaining substrate surface is unaffected. An example is a semiconducting SWCNT with electrodeposited Pd particles upon exposure to hydrogen. The operation mechanism is largely analogous to that of a palladium gate field-effect transistor realized within classical silicon technology (Lundstroem et al., 1975). Specifically, molecular hydrogen is split on the surface of a Pd particle into atomic hydrogen, which diffuses to the Pd/SWCNT interface. At this interface, a dipole layer is formed, which acts like a microscopic gate electrode that locally changes the charge-carrier concentration. It should be mentioned that the recovery of this type of room-temperature-operated hydrogen sensor requires a supply of oxygen to remove the hydrogen atoms in the form of water (Balasubramanian & Burghard, 2005). Carbon nanotubes exhibit high electron transfer rates for different redox couples in various media (Balasubramanian et al., 2004) which has stimulated an increasing amount of research into CNT based amperometric sensors for the detection of specific analytes in solution. The length scales of CNTs are similar to that of typical biological molecules, which gives CNTs an edge over other materials in functioning as effective electrodes in bioelectrochemical sensing (Guisseppi-Elie et al., 2002). In particular, their high aspect ratio and their diameter in the nanometer range make CNTs particularly well suited for direct electrochemical communication with the redox site of a protein, without requiring any mediator. When properly arranged, a nano-tube should have the capability to act as a 1D channel that guides electrons towards the redox center. These materials can be used to preconcentrate analytes and for the magnetic separation and molecular identification of biomolecules, and organic and inorganic species (AguilarArteaga et al., 2010).

The application of CNTs as absorption and/or transducing materials was shown in several different works. Recently, a critical review dealing with the adsorption mechanism of analytes of different nature on carbon nanotubes was published (Cruz et al., 2010; Fontanals et al., 2007; See et al., 2010; Petrovic et al., 2010; Zeng J. et al., 2009; Augusto et al., 2010; Lucena et al., 2011;). The authors stated that this procedure cannot be explained by a single mechanism but through a combination of mechanisms. Indeed, the introduction of functional groups on the surface can facilitate the selective interaction with a given family of compounds. However, this fact has not yet been exploited for the analysis of urine samples. MWCNTs are proposed as a sorbent in an off-line SPE method for the determination of antidepressants using LC and UV detection (Bakker & Qin, 2006). MWCNTs have been applied as adsorbents for preconcentration of sulfonylurea herbicides (Lemos et al., 2008; Zhou Q. et al., 2006a, 2007), bisphenol A, 4-n-nonylphenol, 4-tert-octylphenol (Cai et al., 2003a), dichlorodiphenyltrichloroethane and its metabolites (Zhou Q. et al., 2006b); atrazine, simazine (Zhou Q. et al., 2006c), and trihalomethanes (Lu et al., 2005) in environmental water samples, barbiturates determination in pork (Zhao H. et al., 2007), for simultaneous determination of 10 sulfonamides in eggs and pork (Fang et al., 2006), for trapping volatile organic compounds in a purge-and trap GC system (Li Q. et al., 2004), to extract diethylphthalate, di-n-propyl-phthalate, di-iso-butyl-phthalate, and di-cyclohexylphthalate from aqueous solutions (Cai et al., 2003b).

Direct electron transfer has been achieved with various types of CNT electrodes for cytochrome c (Wang J. et al., 2002), horseradish peroxidase (Zhao Y. et al., 2002), myoglobin

(Zhao G.C. et al., 2003), as well as glucose oxidase (Guiseppe-Elie et al., 2003). It is noteworthy that in the latter case, the redox-active center is deeply embedded within the protein. In some cases, an oxidative pretreatment that introduces negatively charged surface groups on the CNTs was necessary to achieve high electron transfer rates. In a strategy to optimize the accessibility of the redox center, aligned CNT arrays have been fabricated using self-assembly techniques, followed by the covalent attachment of microperoxidase to the tube ends (Gooding et al., 2003). On this basis, various types of amperometric biosensors have been fabricated (Rubianes et al., 2003; Wang J. & Musameh, 2003; Wang J. et al., 2003). A glucose sensor, for example, is obtained by immobilizing glucose oxidase onto SWCNTs deposited on a glassy carbon surface (Davis et al., 2003). Hrapovic et al., 2004 combined platinum nanoparticles with carbon nanotubes and developed a new approach for the electrochemical detection of glucose (Aponte et al., 2006). Effective deposition of Pt nanoparticles on SWCNT was achieved by using a negatively charged polymer, Nafion, to dissolve and disperse SWCNT. Pt nanoparticles can easily be deposited on the Nafion-modified CNT due to charge interactions. Compared to the sensors containing only Pt or CNT, the integration of Pt and CNT lead to improved sensitivity and detection limit.

Zhang and Gorski used carbon nanotubes and redox mediators dispersed into a polymeric matrix for NADH detection and found a reduction of the overpotential (by 0.3 V), a higher sensitivity, and faster response times (Zhang M. & Gorski, 2005). Wang J. & Musameh, 2004 reported on the use of carbon nanotubemodified glassy carbon electrodes in order to accelerate the electrooxidation of insulin, which resulted in a lowering of the required detection potential and a 14 nM detection limit as studied by flow injection analysis. Wang K. et al., 2005 proposed a potentiometric sensor for ascorbic acid on the basis of cobalt phthalocyanine nanoparticles directly coated on a glassy carbon electrode by drop coating. The authors explained the selective and rapid response to ascorbic acid on the basis of the redox potential, with cobalt acting as the mediator.

Kerman et al., 2004 also described the label-free electrochemical detection of DNA based on the direct attachment of adenine probes to the sidewall and end of functionalized MWCNTs. The MWCNTs were attached onto the carbon paste electrode surface modified with thymine probes by hybridization between adenine and thymine. The combination of sidewall and end functionalization of MWNT showed enhancement of the guanine oxidation signal in the direct measurement compared to the ones from only end-modified MWCNT.

The attachment of numerous enzymes on a single carbon nanotube label provided for enormous signal enhancement. Wang J. et al., 2004 reported on a novel method to dramatically amplify enzyme-based DNA sensing by using carbon nanotubes. In the new sensing scheme, the DNA duplex acted as connectors between microbeads and CNTs. The CNT loaded with enzymes linked to the magnetic microbeads through the interaction of complementary oligonucleotides. Without the recognition event, the CNT cannot attach to the particles and is removed during the magnetic separation. The CNTs function as carriers for enzyme tags, and the enzyme reaction products were also accumulated in the CNTs. The coupling of enzyme-tagged CNTs provided a better detection limit than single-enzyme labels and a conventional glassy carbon transducer.

#### 4.2 MIPs in chemical sensing

In the sensors and biosensors technology, often there is the overriding complication that it is unusual, in “real” samples, for there to be a single species present. More commonly an

analyte of interest is accompanied by a number of different species, all present at different concentrations and all adding to the complexity of the analytical problem.

All over the world, billions of dollars are spent annually on chemical/biological detections related to medical diagnosis, environmental monitoring, public security and food safety because lab analysis using expensive equipment is usually cumbersome and time-consuming. Therefore, there has been a pressing societal need for the development of chemo/biosensors for the detection of various analytes in solution and atmosphere, which are both less expensive and simpler to construct and operate. Although considerable progress was made in the past several decades, the chemo/biosensor field remains underdeveloped and at a low level of commercialization because of the lack of alternative strategies and multidisciplinary approaches (Guan et al., 2008).

The standard approach to the analytical analysis of complex matrices is the separation of the different components. Typically, therefore, before a sensor can be used to perceive and quantify one component in a mixed solution, the various components of the complex mixture must be separated, usually by a chromatographic process, so that some form of non-selective sensor, e.g. UV absorbance measurements, can be used to detect and quantify each individual component. In order to improve the performance of chemical sensors, an improvement of their selectivity is required, so that a particular chemical species can be detected and assayed without the need for a possibly lengthy separation stage. In this direction, a technological approach is the development of the biosensor (Updike & Hicks, 1967).

Molecular imprinting is one of the most efficient strategies that offer a synthetic route to artificial recognition systems by a template polymerization technique (Ye & Mosbach, 2001; Spivak, 2005; Zhang H.Q. et al., 2006). While most research in this direction is targeted to the design of chromatographic stationary phases, their use in electrochemical sensors is expanding for electroactive analytes. In convincing work, the group of Mandler explored sol-gel polymers imprinted with the organophosphate pesticide parathion and performed gasphase and liquid-phase partitioning experiments as well as cyclic voltammetric studies (Marx et al., 2004). Imprinted films showed a more than 10-fold increased equilibrium binding over nonimprinted polymers and discriminated well against a range of other structurally similar organophosphates.

To date molecularly imprinted polymers have been successfully used with most types of transduction platforms and a range of methods have been used to bring about close integration of the platform with the polymer (Adhikari & Majumdar 2004). By using MIP it is possible to overcome the commonly founded limitations in the traditional biosensor approach (Orellana & Moreno-Bondi, 2005; Jiang & Ju, 2007), based on the use of biological macromolecules (e.g. antibodies, enzymes, receptors and ion channel proteins, nucleic acids, aptamers and peptide nucleic acids) or biological systems (e.g. ex vivo tissue, microorganisms, isolated whole cells and organelles) as sensing element. In the last years, indeed, although biological receptors have specific molecular affinity and have been widely used in diagnostic bioassays and chemo/biosensors, great affords have been made in synthesizing artificial recognition receptors to overcome the limit in the efficiency of chemosensors, especially for the detection of ultratrace analytes due to the small surface area and non-tunable surface properties of transducers. Another limitation of traditional biosensors is that often natural receptors for many detected analytes do not exist;

furthermore, they are produced via complex protocols with a high cost and require specific handling conditions because of their poor stability (Whitcombe et al., 2000; Wulff, 2002; Haupt & Mosbach, 2000; Ye & Haupt, 2004).

During the past ten years, the literatures on the development of MIP-based sensors, in particularly electrochemical (Riskin et al., 2008;) and optical (McDonagh et al., 2008; Basabe-Desmonts et al., 2007; Li J. et al., 2007a; Feng et al., 2008) sensors, have been dramatically growing (Nilsson et al., 2007; Ramanavicius et al., 2006). It was found that the manufacture of composites consisting of molecularly imprinted conducting polymers results in obtaining materials that exhibit both predetermined selective molecular recognition and electrical conductivity (Deore et al., 2000). This type of materials, mostly frequented based on overoxidized polypyrrole, is of special interest for use in the field of sensor technology (Shiigi et al., 2003).

MIP-based electrochemical sensors were first reported in the early 1990s by Mosbach's group (Andersson et al., 1990), and to date, remarkable progress in MIP-based electrochemical sensors have been achieved in the use and the performance of conductometric/potentiometric MIP nanomaterials (Zhou Y.X. et al., 2003), which were used to detect many different analytes (Augisto et al., 2010) such as barbituric acid (Mirsky et al., 1999), amino acid derivatives (Panasyuk et al., 1999), morphine (Kriz et al., 1995), atrazine (Kim Y. et al., 2007), benzyltriphenylphosphonium chloride (Kriz & Mosbach, 1995), thiophenol (Kröger et al., 1999), glutamic acid (Ouyang et al., 2007), folic acid (Prasad et al., 2010a; Prasad et al., 2010c), tolazoline (Zhang Z. et al., 2010a), tryptophan (Prasad et al., 2010d; Kong Y. et al., 2010), clindamycin (Zhang J. et al., 2010), 2,4-dichlorophenoxy acetic acid (Xie et al., 2010), histamine (Bongaers et al., 2010), caffeine (Alizadeh et al., 2010; Vinjamuri et al., 2008), theophylline (Kan et al., 2010) uracil and 5-fluorouracil (Prasad et al., 2009), salicylic acid (Kang et al., 2009), uric acid (Patel et al., 2009), resveratrol (Xiang & Li, 2009), hydroquinone (Kan et al., 2009; Kan et al., 2008a), bisphenol (Kolarz & Jakubiak, 2008), and dopamine (Kan et al., 2008b).

Despite the application of MIPs as sensor matrices or separation materials, they suffer from basic limitations associated with the limited concentration of imprinted sites, and the bulk volume of the polymer matrices that requires long diffusion paths of the imprinted host molecules. These limitations lead to inefficient sensing or separation processes (Shi et al., 2007). In order to increase the efficiency of MISPE, a method is increasing the surface area of polymer. Higher surface area can contain more functional groups, thus the interaction between polymer and bioactive compounds will be increased accordingly (Tian et al., 2011). A useful approach is the fabrication of robust multilayer structures by the photo-crosslinking of the layers (Sun et al., 1998, 2000). This process transformed the electrostatic interlayer stabilizing interactions into covalent bonds. This achievement, together with the stated limitations of MIPs, suggested that the surface imprinting of LbL nanostructured films might be a viable technique to fabricate effective MIP matrices.

## 5. CNTs-MIPs composites: innovative materials for analytical determinations

Among the different applications of CNTs in nanotechnology, polymer composites, consisting of additives and polymer matrices, including thermoplastics, thermosets and elastomers, are considered to be an important group of relatively inexpensive materials for many engineering applications (Ma et al., 2010; Yang et al., 2007). The technology implications are significant to



many fields, from semiconductor device manufacturing to emerging areas of nanobiotechnology, nanofluidics, and chemistry where the ability to mold structures with molecular dimensions might open up new pathways to molecular recognition, drug discovery, catalysis, and molecule specific chemio-biosensing (Hua et al., 2004).

The main approaches for the fabrication of these materials can be divided into “grafting to” and “grafting from” approaches (Liu M. et al., 2009; Baskaran et al., 2004).

The “grafting to” approach involves pre-formed polymer chains reacting with the surface of either pristine or pre-functionalized carbon nanotubes. (See Figure 3). The main approaches exploited in this functionalization strategy are radical or carbanion additions as well as cycloaddition reactions to the CNT double bonds. Since the curvature of the carbon nanostructures imparts a significant strain upon the  $sp^2$  hybridized carbon atoms that make up their framework, the energy barrier required to convert these atoms to  $sp^3$  hybridization is lower than that of the flat graphene sheets, making them susceptible to various addition reactions. Therefore, to exploit this chemistry, it is only necessary to produce a polymer centered transient in the presence of CNT material. Alternatively, defect sites on the surface of oxidized CNTs, as openended nanostructures with terminal carboxylic acid groups, allow covalent linkages of oligomer or polymer chains. The “grafting to” method onto CNT defect sites means that the readymade polymers with reactive end groups can react with the functional groups on the nanotube surfaces. An advantage of the “grafting to” method is that preformed commercial polymers of controlled molecular weight and polydispersity can be used. The main limitation of the technique is that initial binding of polymer chains sterically hinders diffusion of additional macromolecules to the CNT surface, leading to a low grafting density. Also, only polymers containing reactive functional groups can be used.

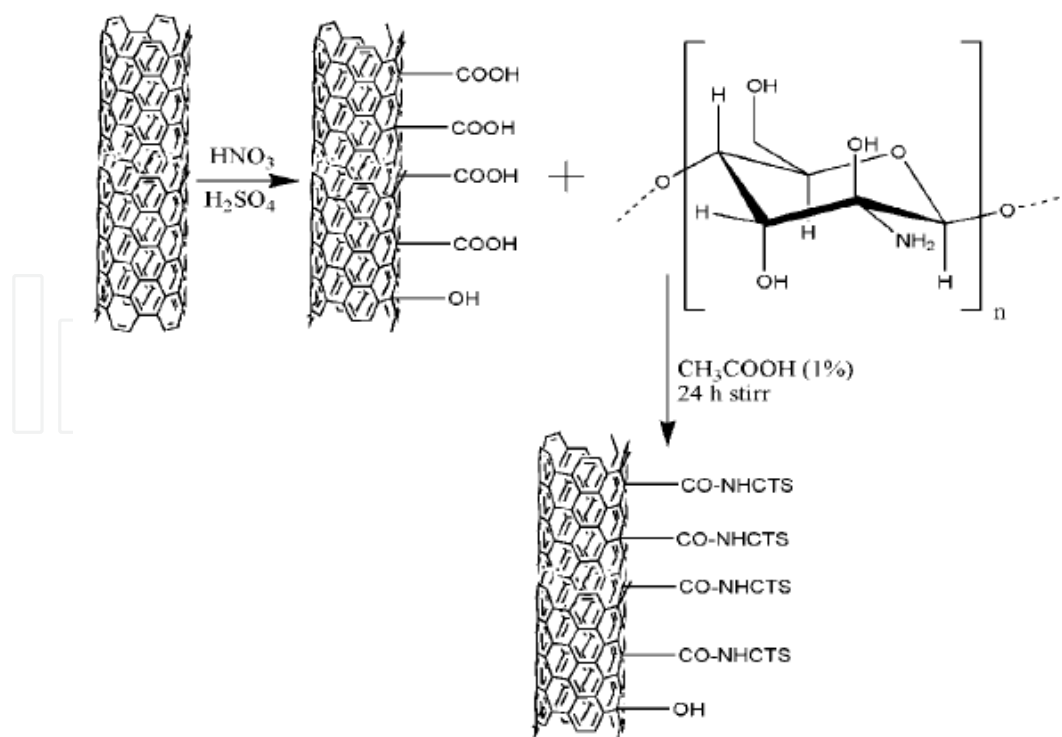


Fig. 3. Synthesis of CNTs-polymer composites by “Grafting to” approach as reported by Venkatesan & Kim, 2010.



The “grafting from” approach involves the polymerization of monomers from surface-derived initiators on CNTs. These initiators are covalently attached using the various functionalization reactions developed for small molecules, including acid-defect group chemistry and side-wall functionalization of CNTs. (See Figure 4). The advantage of “grafting from” approach is that the polymer growth is not limited by steric hindrance, allowing high molecular weight polymers to be efficiently grafted. In addition, nanotube-polymer composites with quite high grafting density can be prepared. However, this method requires strict control of the amounts of initiator and substrate as well as accurate control of conditions required for the polymerization reaction. Moreover, the continuous  $\pi$ -electronic properties of CNTs would be destructed by the acid oxidation, even worse, CNTs may be destroyed to several hundred nanometers in length. As a result, compared with the “grafting from”, the “grafting to” has much less alteration of the structure of CNTs (Yan & Yang, 2009; Mylvaganam & Zhang, 2004; Zhang M.N. et al., 2004).

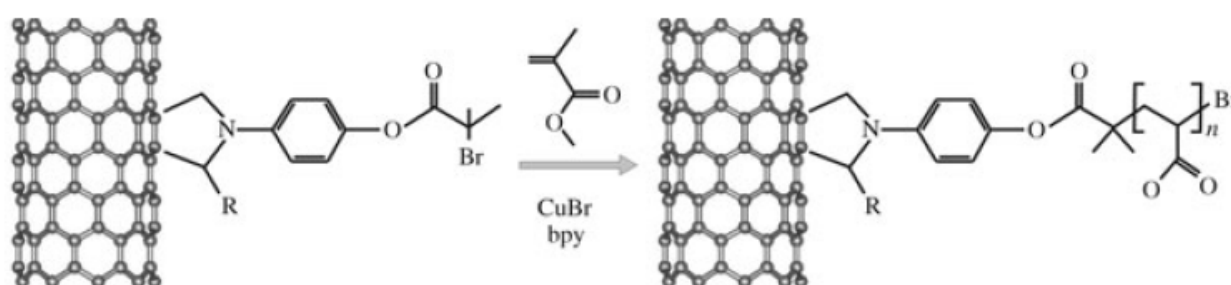


Fig. 4. Synthesis of CNTs-polymer composites by “Grafting from” approach as reported by Balasubramanian & Burghard, 2005.

Many techniques including esterification (Gao C. et al., 2007; Sano et al., 2001; Kahn et al., 2002; Huang W. et al., 2003; Lin et al., 2003), “click” chemistry (Li H.M. et al., 2005), layer-by-layer self-assembly (Kong H. et al., 2005; He & Bayachou, 2005; Qin et al., 2005; Artyukhin et al., 2004), pyrene moiety adsorption (Bahun et al., 2006; Martin et al., 2004; Qu et al., 2002; Petrov et al., 2003; Gomez et al., 2003), radical coupling (Liu Y.Q. et al., 2005; Lou et al., 2004), anionic coupling (Huang H.M. et al., 2004), radical polymerization (Qin et al., 2004a; Shaffer & Koziol, 2002), supercritical  $\text{CO}_2$ -solubilized polymerization or coating (Wang J.W. et al., 2006; Dai et al., 2004),  $\gamma$ -ray irradiation (Xu H.X. et al., 2006), cathodic electrochemical grafting (Petrov et al., 2004), polycondensation (Zeng H.L. et al., 2006a; Gao C. et al., 2005; Nogales et al., 2004), reversible addition fragmentation chain-transfer (RAFT) polymerization (Xu G.Y. et al., 2006; You et al., 2006; Cui H. et al., 2004; Hong et al., 2005, 2006), anionic polymerization (Chen S.M. et al., 2006; Liu I.C. et al., 2004), ring-opening polymerization (Zeng H.L. et al., 2006b; Qu et al., 2005; Buffa et al., 2005; Gao J.B. et al., 2005) and atom transfer radical polymerization (ATRP) (Kong H. et al., 2004; Qin et al., 2004b; Yao et al., 2003) have been employed to functionalize CNTs with polymers.

CNTs exhibit a high aspect ratio and high conductivity, which makes CNTs excellent candidates for conducting composites (Sahoo et al., 2010) (Figure 5).

The observation of an enhancement of electrical conductivity by several orders of magnitude of CNTs in polymer matrices without compromising other performance aspects of the polymers such as their low weight, optical clarity, low melt viscosities, etc., has

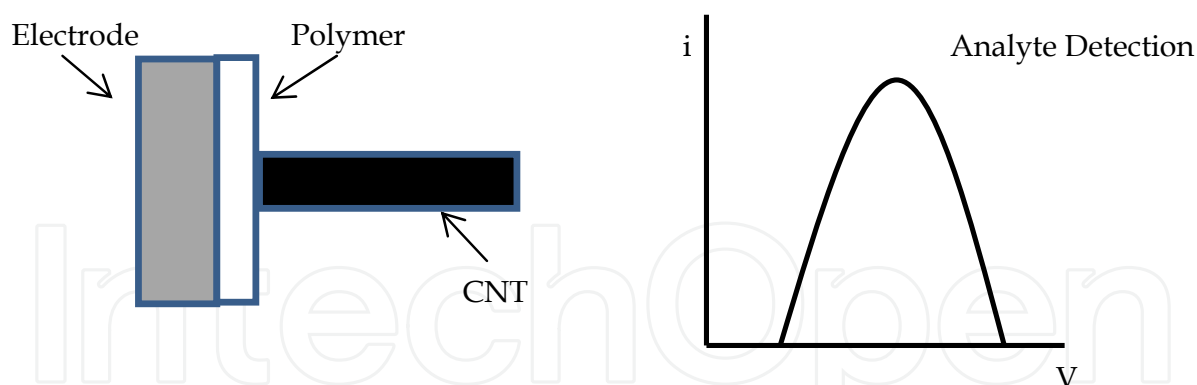


Fig. 5. Schematic representation of electrochemical detection by CNTs composite electrode. Adapted from Teles & Fonseca, 2008.

triggered an enormous activity worldwide in this scientific area (Spitalsky et al., 2010). Nanotube-filled polymers could potentially, among the others, be used for transparent conductive coatings, electrostatic dissipation, electrostatic painting and electromagnetic interference shielding applications (Bauhofer & Kovacs, 2009; Breuer & Sundararaj, 2004; Moniruzzaman & Winey, 2006; Winey et al., 2007). The electrical conductivity in CNTs-polymer nanocomposites depends on dispersion (Sandler et al., 2003; Li J. et al., 2007b; Song & Youn, 2005), alignment (Choi et al., 2003; Fangming et al., 2003), aspect ratio (Bai & Allaoui, 2003; Bryning et al., 2005), degree of surface modification (Georgakilas et al., 2002) of CNTs, polymer types (Ramasubramaniam et al., 2003) and composite processing methods (Li J. et al., 2007b). Based on their characteristic, CNTs-polymer composites can behave as conductors, semiconductors or insulators (Maruccio et al., 2004).

CNTs-polymer composites were successfully synthesized and employed for different applications, both in biomedical and engineering fields. One of the most representative example is a study regarding an ammonia gas sensors based on single-walled carbon nanotubes functionalized with covalently attached poly(m-aminobenzenesulfonic acid). The sensor was operated as a chemiresistor, with the carbon nanotubes forming a random network between interdigitated electrodes, and improved response and recovery times were observed (on the order of 15 min) (Bekyarova et al., 2004). In another work, a carbon nanotube/poly(ethylene-co-vinyl acetate) composite electrode was developed for amperometric detection in Capillary Electrophoresis (Frost et al., 2010). The new electrode also generated improved S/N, decreased fouling, and resulted in better long-term stability (Chen Z. et al., 2009). Zhou D. et al., 2008 describes a novel sieving matrix composed of both a quasi-interpenetrating polymer network (IPN) and PDMA functionalized MWNTs. Atom transfer radical polymerization was used to graft PDMA on MWNTs. The functionalized MWNTs were compatible with the quasi-IPN network. The rigid structure of MWNTs increased the stability and sieving ability of the matrix. Results showed that this novel matrix was advantageous in terms of resolution, speed, and reproducibility. Carbon nanotubes have been used to improve the efficiency of  $\text{Ru}(\text{bpy})_3^{2+}$  modified polyacrylamide electrode because of their high conductivity (Xing & Yin, 2009). Carbon nanotubes modified with polypyrrole-silica nanocomposites seem very promising for electrochemical DNA sensor design (Ramanacius et al., 2006). MWCNTs were also grafted with poly(acrylamide) (PAAM) and with poly(N,Ndimethylacrylamide) (PDMA) at same grafting percentage by using  $\text{N}_2$  plasma technique and used in the removal of  $\text{Pb}^{2+}$  from aqueous solution under

ambient conditions (Shao et al., 2010). Authors found that the grafted PAAM and PDMA improved MWCNT adsorption capacity in the removal of  $\text{Pb}^{2+}$  from large volumes of aqueous solutions. Furthermore, MWCNTgPAAM had much higher adsorption capacity than MWCNT-g-PDMA, which was attributed to higher amide group content in acrylamide than that in *N,N*-dimethylacrylamide.

A particular kind of CNTs-polymer composites is represented by CNTs-MIPs composites, in which the polymer part is a molecularly imprinted polymer (Chang et al., 2011; Walcarius et al., 2005). CNTs impart electrical conductivity to MIPs, while molecular imprinting on these one-dimensional nanostructures will endow the nanotubes with molecular recognition functions, further expanding their application fields (Guan et al., 2008). Several examples of using these materials are reported in literature for biomedical, pharmaceutical and environmental applications (Figure 6).

In pharmaceutical fields, in Zhang Z. et al., 2010b, a novel sensitive and selective imprinted electrochemical sensor was constructed for the direct detection of L-histidine by combination of a molecular imprinting film and MWNTs. The sensor was fabricated onto an indium tin oxide electrode via stepwise modification of MWNTs and a thin film of MIPs via sol-gel technology. The introduced MWNTs exhibited noticeable enhancement on the sensitivity of the MIPs sensor, meanwhile, the molecularly imprinted film displayed high sensitivity and excellent selectivity for the target molecule. H. Y. Lee & Kim, 2009 reports of the synthesis of CNTs-MIP composite to be potentially applied to probe materials in biosensor system for theophylline recognition based on CNT field effect. Hydroxyl-

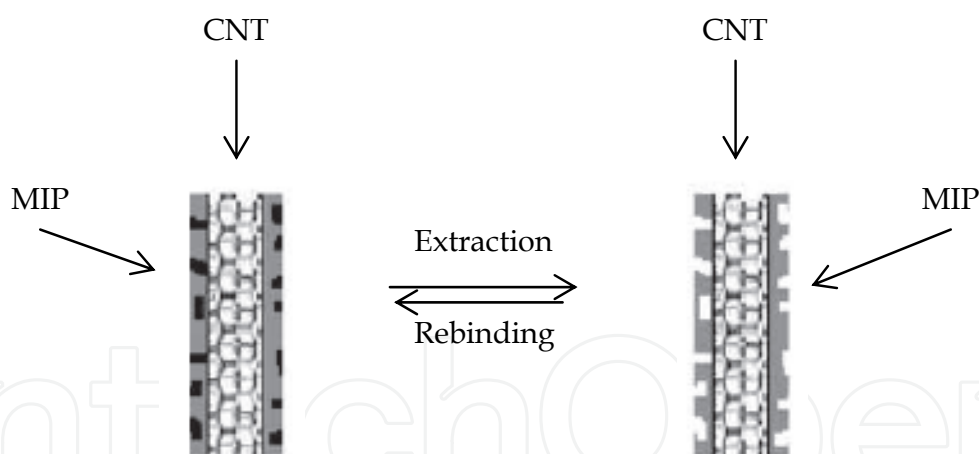


Fig. 6. Schematic representation of CNTs-MIPs recognition process. Adapted from Z. Zhang et al., 2010d.

functionalized CNT was modified by silanisation with 3-chloropropyl trimethoxysilane. The iniferter groups were then introduced by reacting the CNT-bound chloropropyl groups with sodium *N,N*-diethyldithiocarbamate. UV light-initiated copolymerization of ethylene glycol dimethacrylate (crosslinking agent) and methacrylic acid (functional monomer) resulted in grafting of MIP on CNT for theophylline as a model template. The theophylline-imprinted polymer on CNT showed higher binding capacity for theophylline than non-imprinted polymer on CNT and selectivity for theophylline over caffeine and theobromine (similar structure molecules). Another theophylline sensor

based on CNTs-MIPs composites is shown in Lee E. et al., 2008. In this study acrylated Tween 20 was used as a linking molecule of MIPs to CNT. MIPs were formed for theophylline as a model template on the surface of CNT with methacrylic acid (functional monomer) and ethylene glycol dimethacrylate (crosslinking agent) using a photografting polymerization technique. The adsorbed layer of 2,2-dimethoxy-2-phenylacetophenone initiated a radical polymerization near the surface by UV-light irradiation. The theophylline-imprinted polymer on CNT showed higher binding capacity for theophylline than non-imprinted polymer (NIP) on CNT and selectivity for theophylline over caffeine (similar structure molecules).

In another work (Prasad et al., 2010a), MIP-carbon composite is prepared via in situ free radical polymerization of a synthetic monomer and subsequent crosslinkage with ethylene glycol dimethacrylate, in the presence of carbon powder and folic acid as template. The detection of folic acid with the MIP fiber sensor was found to be specific and quantitative in aqueous, blood serum and pharmaceutical samples, without any problem of nonspecific false positive contribution and crossreactivity.

An insulin imprinted polymer (Prasad et al., 2010b) was synthesized over the surface of vinyl group functionalized MWCNTs using phosphatidylcholine containing functional monomer and crosslinker. Phosphatidylcholine is a major component of all biological membrane; its incorporation in polymer backbone assures water compatibility, biocompatibility and specificity to molecularly imprinted nanomaterials, without any crossreactivity or interferences from biological sample matrices. An electrochemical sensor fabricated by modifying multiwalled carbon nanotubes molecularly imprinted polymer onto the pencil graphite electrode, was used for trace level detection of insulin in aqueous, blood serum, and pharmaceutical samples by differential pulse anodic stripping voltammetry.

A sensitive molecularly imprinted electrochemical sensor has been developed in Huang J. et al., 2011a for the selective detection of tyramine by combination of MWCNTs-gold nanoparticle composites and chitosan. Chitosan acts as a bridge for the imprinted layer and the nanocomposites. The molecularly imprinted polymer (MIP) was synthesized using tyramine as the template molecule, silicic acid tetrachlyl ester and triethoxyphenylsilane as the functional monomers. The molecularly imprinted film displayed excellent selectivity towards tyramine. A thymidine sensor (Zhang Z.H. et al., 2010) was developed by casting thin film of molecularly imprinted sol-gel polymers with specific binding sites for thymidine on carbon electrode by electrochemical deposition. The excellent performance of the imprinted sol-gel/MWCNTs electrode towards thymidine can be ascribed to the MWCNTs functional layer with electrochemical catalytic activities and the porous imprinted film with plentiful selective binding sites. Under the optimized analytical conditions, the peak current was linear to thymidine concentration from 2 to 22  $\mu\text{mol L}^{-1}$  with the detection limit of  $1.6 \times 10^{-9} \text{ mol L}^{-1}$ .

A different MWNTs-MIPs composites was prepared by using dopamine as a template molecule by the selective copolymerization of methacrylic acid and trimethylolpropane trimethacrylate in the presence of the template and vinyl group functionalized MWNT surface (Kan et al., 2008b). In this work, for grafting MIPs on MWNTs, the vinyl group was first introduced on the surface of MWNTs, which directed the selective polymerization of functional monomers and cross linkers in the presence of DA on the MWNTs surface. The thickness of the MIPs can be adjusted by changing the concentration



of prepolymerization monomers. The resulting MWNTs-MIPs possessed a faster adsorption dynamics, higher selectivity for the template. The modified electrode fabricated by modifying the MWNTs-MIPs on the glassy carbon electrode can recognize dopamine with a linear range from  $5.0 \times 10^{-7}$  to  $2.0 \times 10^{-4}$  mol/L.

A sensor for the detection of Uric acid was proposed in (Yu J.C.C. & Lai, 2006) by polymerization of polymethacrylic acid on the surface of vinyl-functionalized CNTs in the presence of the template. The MIP adsorbs more Uric acid than NIP and the imprinting efficiency was found to be about 4.41. The MIP modified MWCNTs can be deposited on the MWCNTs electrode surface and used for the electrochemical detection for the template. The differences of adsorption amounts between MIP and NIP electrodes were determined by CVs with different adsorption times. The adsorption reached saturation after 5min of adsorption and the result was close to the rebinding experiments. The sensitivities of the MIP and NIP modified electrodes were about  $11.03$  and  $5.39 \text{ mM}^{-1} \text{ cm}^{-2}$ , respectively, and the difference mainly came from the affinity cavities which were created by the imprinted template.

A novel protein molecularly imprinted membrane (PMIM) was synthesized in Zhang M. et al., 2010 on the surface of MWNTs through a surface molecular imprinting technique by using bovine serum albumin as the template molecule, acrylamide as the functional monomer, N,N'-methylenebisacrylamide as the crosslinker. The selectivity adsorption experiments showed that the PMIM/MWNTs also had higher adsorption capacities for BSA than for such molecules, as HSA, HB, pepsin and HRP. The PMIM/MWNTs displayed a 2.6 fold increase in affinity to BSA compared to the nPMIM/MWNTs. The PMIM/MWNTs, on the other hand, did not exhibit any significant change in affinity to other molecules compared to the nPMIM/MWNTs.

An estrone sensor was developed in Gao R. et al., 2011 by using a semicovalent imprinting strategy, which employed a thermally reversible covalent bond at the surface of silica coated CNTs. The synthesis of the nanocomposites involves silica shell deposition on the surface of CNTs, MIPs functionalized onto the silica surface, and final extraction of estrone by thermal reaction and generation of the recognition site. Authors state that the core-shell CNTs@MIPs nanocomposites developed in this work can also be applied as a selective coating for electrochemical or quartz crystal microbalance sensors to monitor for estrone residue in environmental water

MIP-CNTs nanocomposites are also proposed as innovative drug delivery devices (Yin et al., 2010). MIP nanotubes were fabricated by atom transfer radical polymerization (ATRP) and applied in enantioselective drug delivery and controlled release. Authors found that S-propranolol imprinted nanotubes provided differential release of enantiomers, whereby the release of the more therapeutically active S-propranolol (eutomer) is greatly promoted whilst the release of the less active R-enantiomer (distomer) is retarded.

In environmental field, a recent work (Zhang Z. et al., 2010c) a novel MIPs with core-shell structure is fabricated by using MWNTs as the core material. Prior to polymerization, the silicon-oxygen group was grafted onto the MWNTs surface, then silicon-oxygen groups grafted onto the MWNTs surface could copolymerize directly with functional monomers and crosslinkers in the presence of the template molecules by hydrolysis and condensation, which can lead to the formation of MIPs on the surface of MWNTs. The imprinted material,



which showed a good selective recognition to Sudan IV with  $Q_{\max}$  of  $63.2 \text{ mmol g}^{-1}$ , was applied as sorbents for the enrichment and determination of trace Sudan IV in real samples by online SPE-HPLC.

CNTs were used successfully to enhance the binding capacity of a molecularly imprinted polypyrrole modified stainless steel frit for determination of ochratoxin A in red wines (Yu J.C.C. & Lai, 2007; Wei et al., 2007). In a different work (Li Y. et al., 2010), a molecularly imprinted polymer-graphene oxide hybrid material was synthesized by reversible addition and fragmentation chain transfer (RAFT) polymerization for the selective detection of 2,4-dichlorophenol in aqueous solution with an appreciable selectivity over structurally related compounds.

Diaz-Diaz et al., 2011 describes an electrochemical sensors based on a catalytic 2,4,6-trichlorophenol molecularly imprinted microgel that mimics the dehalogenative function of the natural enzyme chloroperoxidase for p-halophenols. Two strategies were explored: a carbon paste modified with the polymer and the drop-coating of screen-printed electrodes with powder suspensions of the polymer and carbon nanotubes. With this last design, 2,4,6-trichlorophenol concentrations above 25 mM could be detected.

In similar studies, an electrochemical imprinted sensor for sensitive and convenient determination of Bisphenol A (Huang J. et al., 2011b) and clindamycin (Zhang Z. et al., 2010a) were developed. In both the cases, MWCNTs and gold nanoparticles were introduced for the enhancement of electronic transmission and sensitivity, while thin film of molecularly imprinted sol-gel polymers with specific binding sites for the templates were cast on gold electrode by electrochemical deposition. The resulting composites displayed excellent selectivity towards.

A simple method was developed (Gao R. et al., 2010) to synthesize core-shell molecularly imprinted polymers for the extraction of triclosan with fast kinetics, high capacity and favorable selectivity by combining a surface molecular imprinting technique with a sol-gel process based on carbon nanotubes coated with silica.

By a surface imprinting technique, in Zhang H. et al., 2011, a composite imprinted material, on the basis of a MWCNTs-incorporated layer using melamine as a template, methacrylic acid as a functional monomer, and ethylene glycol dimethacrylate as a cross-linker, was synthesized. In this work, the poly(acrylic-acid)-functionalized CNTs were synthesized to increase the diameter of CNTs. Then, the vinyl group was introduced to the surface of poly(acrylic-acid)-functionalized CNTs by an amidation. Using Melamine as a template molecule, imprinted CNT composite material was fabricated by a thermal polymerization. Applied as a sorbent, the imprinted materials were used for the determination of Melamine in the spiked sample by online SPE combined with HPLC.

By the same approach, Ga(III)-imprinted-CNTs sorbent was prepared in Zhang Z. et al., 2010d by using Ga(III) ion-8hydroxyquinoline complex as a template molecule. The imprinted sorbent was applied successfully for extraction of Ga(III) ion from fly ash lixivium followed by FAAS detection. Authors state that compared with the others literature methods for Ga determination, their method is sufficiently accurate and precise to be used for Ga(III) ion analysis in fly ash samples, and performed better characteristics such as selectivity and cleanliness of the extracts.

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Materials are important to mankind because of the benefits that can be derived from the manipulation of their properties, for example electrical conductivity, dielectric constant, magnetization, optical transmittance, strength and toughness. Materials science is a broad field and can be considered to be an interdisciplinary area. Included within it are the studies of the structure and properties of any material, the creation of new types of materials, and the manipulation of a material's properties to suit the needs of a specific application. The contributors of the chapters in this book have various areas of expertise. therefore this book is interdisciplinary and is written for readers with backgrounds in physical science. The book consists of fourteen chapters that have been divided into four sections. Section one includes five chapters on advanced materials and processing. Section two includes two chapters on bio-materials which deal with the preparation and modification of new types of bio-materials. Section three consists of three chapters on nanomaterials, specifically the study of carbon nanotubes, nano-machining, and nanoparticles. Section four includes four chapters on optical materials.

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