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Development of Tunable Nanocomposites Made from Carbon Nanotubes for Electrochemical Applications

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1. Introduction

The advent of the nanotechnology field has brought about novel devices and materials at the nanometer scale triggered by the demand of miniaturizing electronic, optical, actuating and sensing systems. In this nanotechnology era, the concept of nanocomposite has been brought to light though it has been present in nature and used from historical times. A nanocomposite can be defined as a material made of more than one solid phase where at least one of the constituent parts has a nanometer scale dimension. Building blocks with dimensions in the nanosize range make possible to design and create new materials with unprecedented versatility and improvement in their physical and chemical properties. The promise of nanocomposites lies in their multifunctionality for different applications and the possibility of unique combinations of properties unachievable with conventional materials.

As mentioned before, the concept of enhancing properties and improving characteristics of materials through the creation of multiple phase nanocomposites is not recent. Mother Nature has a lot of examples of nanocomposites such as the structure of seashells and the bones. The idea has also been practiced since civilization started and humanity began producing more efficient materials for functional purposes. The Maya blue pigment, an ancient nanostructured material which was found to be very resistive to acids or (bio)corrosion phenomena, is a composite of organic and inorganic constituents, primarily leave dyes combined with a natural clay (Jose-Yacaman et al., 1996).

Nanocomposites comprise a wide scope ranging from metal/ceramic nanocomposites, polymer-based nanocomposites to natural or biomimetic nanobiocomposites. They still share tremendous challenges, especially in the control over the distribution in size and dispersion of the nanosize constituents and in the tailoring and understanding of the role of the interfaces (Ajayan et al., 2003; Harris, 2004; Moniruzzaman et al., 2006; Spitalsky et al., 2010).

Among the broad world of nanocomposites, the conducting ones attract special attention because of their special applications in electronics and electrochemistry (Grossiord et al.,

2006; Céspedes et al., 1996; Xiao & Li., 2008; Li et al., 2008; Li et al., 2009; Rajesh et al., 2009; Navratil & Barek, 2009). Nanocomposite for electrode applications are formed by at least one conducting and one insulating phase. In this context, carbon nanotubes arise as ideal conducting phase due to their unique chemical and physical properties. At this moment carbon nanotube composites comprise a very dynamical emerging field and it turns out very difficult to cover the entire spectrum of such topic (Ajayan et al., 2003; Rubianes & Rivas, 2003; Wang & Musameh, 2003; Barrera et al., 2005, Harris, 2004; Moniruzzaman et al., 2006; Spitalsky et al., 2010; Li et al. 2008; Xiao & Li, 2008). Therefore in this chapter we will focus on conducting nanocomposites based on carbon nanotubes/insulating polymers and special attention will be stressed on CNT epoxy composites as robust, easy-processing and cheap platforms for electrochemical applications (Céspedes et al., 1996; Pumera et al., 2006; Pacios et al, 2008; Olivé-Monllau et al., 2010). We will introduce an electrochemical characterization approach based mainly on impedance spectroscopy which can allow us to find the optimized CNT composition for electroanalytical purposes and which can be extended to other electrochemical applications. Additionally, we will briefly describe basic concepts and provide generic examples that can give important insights in this field.

2. Basic considerations on the structure and properties of carbon nanotubes

Carbon nanotubes have captured the interest as nanoscale materials due to their structure (as a model of a 1D system) and their impressive list of superlative and outstanding properties such as high Young´s modulus and strength, unique richness in electrical properties, high thermal conductivity, chemical and electrochemical anisotropy and biocompatibility.

The graphene layers have become the starting point to explain the structure of carbon nanotubes. The way the graphene sheet is wrapped up can be described by a pair of indices (n,m) that define the chiral vector, $\vec{C} = n\vec{a}_1 + m\vec{a}_2$, in which $\vec{a}_1$ and $\vec{a}_2$ are the basis vectors of the hexagonal graphene lattice (Fig. 1). Three different types of nanotube structures can be generated by rolling up the graphene layer: zigzag ($m=0$), armchair ($n=m$) and chiral nanotubes (the rest of vectors) (Saito et al., 1998; Louie, 2001). Although CNT are closely related to 2D graphene, the tube curvature and the quantum confinement in the circumferential direction of the nanotube bring about the unique properties that make CNT different from graphene. One of these unusual properties is the electronic conductivity which strongly depends on the chirality and CNT diameter. CNTs can exhibit singular electronic band structures and can show metallic and semiconduncting behavior. As a general rule, n,m tubes with n-m being an integer multiple of 3 are metallic while the remaining tubes are semiconducting. The band gap of semiconducting tubes can be approximated by the relation $E_g = 0.8eV / d$, with d being the diameter of the nanotube (Wildoer et al., 1998). Therefore the bigger the diameter, the more metallic behavior is found. Moreover, carbon nanotubes can behave like quantum wires due to the confinement effects on the tube circumferences. They can exhibit a ballistic flow of electrons with electron mean-free paths of several micrometers, and are capable of conducting very large current densities (Javey et al., 2004). For instance, carbon nanotubes have been shown to withstand current densities up to 10^9 A/cm^2, a current density which is about 2-3 orders of magnitude larger than in metals such as Al or Cu.

So far we have considered CNTs formed by a single graphene wall (SWNT) with diameters ranging generally from 0.4 nm up to 1.5 nm and with an important diversity in electronic

conductivity, from semiconducting to metallic behavior. However CNTs can also be made by multiple graphene layers disposed in different arrangements. Such structures, known as multi-walled carbon nanotubes (MWCNTs), have typically diameters in the range of 2-100 nm and metallic behavior. MWCNTs can appear as several concentric tubes fitted one inside the other (hollow MWCNTs) or with the graphene planes forming an angle with respect to the axis of the tube (herringbone or bamboo MWCNTs), see schemes in Fig. 1. The bamboo-like tubes differ from the herringbone ones in that some of the graphene layers are periodically closed along the length of the tube forming compartments. The main difference between the hollow morphology and the herringbone and bamboo ones lies on the high density of terminating edge planes that contain the last two morphological variations of MWCNTs.

The bonding in CNT is basically sp^2, however the circular curvature, apart form yielding quantum confinement and quantized conductance, also causes σ-π rehybridization, an effect that is stronger as the CNT diameter decreases (Han, 2005; Srivastava, 2005). In such case three σ bonds are slightly out of plane and for compensation the π orbitals are more delocalized outside the tube (Fig. 1). The electron cloud distortion induced by the curvature, which yields a rich π-electron conjugation outside the tube, can make CNT more electrochemically active and electrically and thermally more conductive. Moreover, the latter fact together with the combination of size, structure, topology and light weight confer nanotubes remarkable mechanical properties such as high stability, high strength and stiffness together with low density and elastic deformability. That is a big difference with respect to graphite or graphene in which the sp^2 hybrid orbital form three in-plane σ bonds with an out-of-plane π orbital.

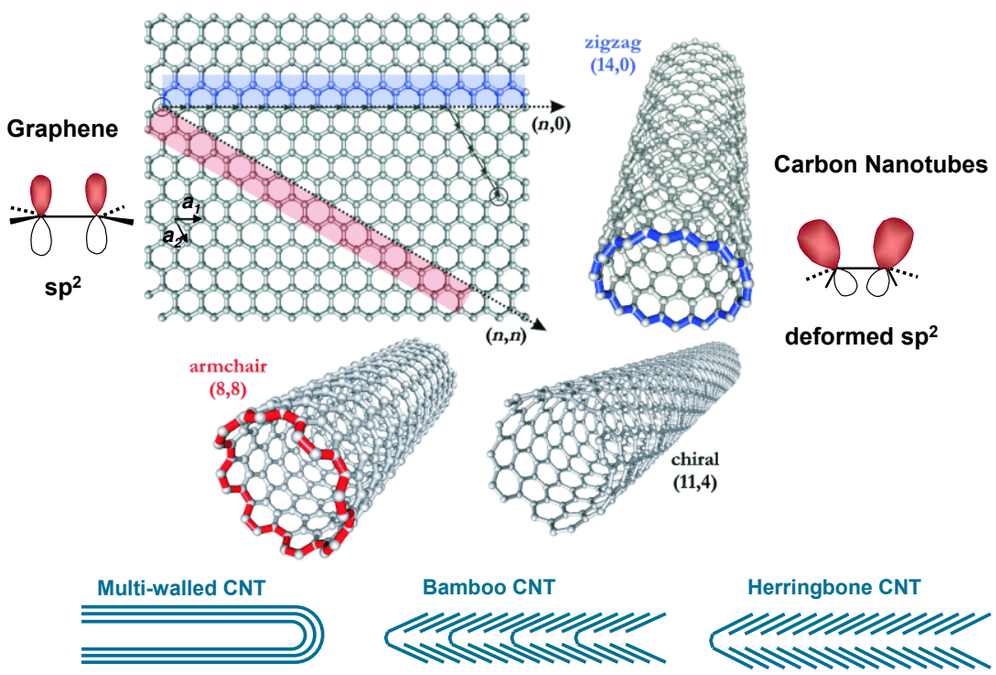


Fig. 1. Roll-up of a graphene sheet leading to three different types of SWNTs together with their bonding structures. Different structures of multi-walled CNT. Adapted from Ref. (Balasubramanian, 2005).

CNTs provide a high specific surface system which together with the σ-π rehybridization and the presence of structural defects facilitate different chemical processes such as (bio)chemical derivatization, intercalation, molecular adsorption, doping, charge transfer, etc (Han, 2005; Niyogi, 2002; Chen, 2003; Hirsch, 2002; Burghard, 2005; Tasis, 2006). These characteristics are being considerably exploited for different applications such as biochemical and chemical sensing, energy storage or separation techniques. A good understanding of the chemical properties of CNTs is mandatory for enhancing the efficiency of practical devices and also for comprehending related fundamental processes such as their electrochemical properties.

Although graphite, fullerene and carbon nanotubes are built from the same basic element, the chemical reactivity is substantially different among them. The chemical reactivity is higher for a CNT than for a graphene layer but lower if compared with fullerene (Niyogi, 2002). Such behavior can be closely related to the surface curvature of the carbon structure (Niyogi, 2002; Han, 2005; Chen, 2003; Burghard, 2005) and the higher strain that is generated by such spherical geometry. A higher surface reactivity with decreasing nanotube diameter is thus expected (Chen, 2003).

The reactivity of different graphitic carbon allotropes is also characterized by having chemical anisotropy. Taking as a reference, for instance, the layered structure of Highly Oriented Pyrolytic Graphite (HOPG), it is known the its basal plane is more inert than the highly reactive edges (edge HOPG) which contain unsatisfied valences or dangling bonds prone to reaction with oxygen or water (McCreery, 2008). Such anisotropy is also observed in adsorption processes. The same anisotropy in the chemical reactivity can be considered on CNT, since the walls behave differently than the ends which can be either capped or just finishing in terminal edges (Balasubramanian, 2005; Burghard, 2005; Hirsch, 2002; Katz, 2004). The chemical reactivity is increased at the capped ends (due to the presence for instance of pentagons) or at the edges of an open nanotube, which become the more reactive sites of the CNT irrespective of its diameter. Such anisotropy in the chemical reactivity will also have strong implications from the point of view of electrochemistry.

Although, the CNT ends exhibit a higher chemical reactivity than the walls, the presence of local defects on the walls constitute also efficient reactive sites. For instance, when CNTs are subjected to oxidative acid treatment, the local generation of carboxylic, cetones, alcohols and ester groups leads to active sites that can be profited for (bio)molecular anchoring (Hirsch, 2002; Katz, 2004; Tasis, 2006; Esplandiu, 2009a). Such acid treatments also open the CNT capped ends, bringing about an increase of oxygen rich terminal groups. Such defects together with the reactivity associated with the generated strain from the curvature are very important for the attachment of a wide diversity of molecules (complexing agents, fluorescent and electroactive groups, (bio)catalysts, or biomolecules, (proteins, carbohydrates, nucleic acids, etc). Chemical modification turns out to be one of the key issues for the development of selective electrochemical (bio)sensors for (bio)recognition or catalyst materials to be used in energy-storage devices. Moreover, chemical modification also aids to overcome one of the drawbacks for CNT applications which is the difficulty of dispersing them in solvents, especially in aqueous media.

In general, the electrochemical performance of carbon materials is basically determined by the electronic properties (specially their band structure in terms of density of states), and given its interfacial character, by the surface structure and surface chemistry (i.e. surface terminal functional groups or adsorption processes) (McCreery, 2008). Such features will

affect the electrode kinetics, potential limits, background currents and the interaction with molecules in solution.

We have mentioned the chemical anisotropy characteristic of graphitic materials, which is also present in their electronic properties. For instance, it is well known that in the layered structure of HOPG, the electronic conductivity in the plane parallel to the graphene layers (basal plane) is about four orders of magnitude lower than in the perpendicular one (edge plane) (McCreery, 1990). The basal plane of HOPG is atomically ordered, with higher electronic resistance and chemically more inert than edge plane HOPG. Such anisotropy also influences the electrochemical behavior inducing an electrochemical anisotropy as well. It has been demonstrated that in graphite, the basal plane exhibits slow electron transfer kinetics whereas the reactive edge sites can increase the electron transfer rate in almost five orders of magnitude. The same electrochemical anisotropy can also be expected in CNTs. The open ends of carbon nanotubes have been likened to the edge planes of HOPG whereas the tube walls are suggested to have similar electrochemical properties to those of basal HOPG (Moore, 2004; Banks, 2005).

Electrochemical experiments with carbon nanotube electrodes showed enhanced electron transfer reactivity (increased redox currents and reduced peak separations in the voltammetry which enables lower detection limits and enhanced sensitivity) for a variety of systems as compared to other electrode materials (Wang, 2005; Gooding, 2005; Banks, 2006). These features have impelled some research groups to label CNTs as unique electrocatalytical materials. However this issue has open a big debate since all these claims have been concluded from analyzing CNT systems that were little characterized in terms of CNT purity (amorphous carbon, metal catalyst, etc.). Indeed metal impurities from the CNT growth procedure can produce electrocatalytical effects and might bring about misinterpretations. So far there is no an absolute assessment of the relative contribution of metal catalyst and the CNT itself in the electrochemical process. Caution has to be taken in attributing enhanced electrocatalytical properties of CNTs on different redox systems as compared to other graphitic carbon electrodes. It is quite probable that CNTs themselves exhibit electrocatalytic effects but in the same way as what was found on edge pyrolytic graphite systems (Moore, 2004). CNT defects such as edge-plane like sites (like the ones at the open ends of nanotubes) can have an important role in such electrocatalytic behavior. However, the possible electrochemical enhancement at the defect sites should not induce us to completely disregard the electrochemical behavior of the sidewalls. Although they can be considered less electrochemically active some groups have already shown important electrochemical performance from the sidewall sites (Dumitrescu et al., 2009).

Moreover, it has also been suggested that a thin layer diffusion within the CNT porous layer can also contribute to explain the electron kinetics observed with CNTs specially when the CNT electrode is composed of CNT multilayers (Streeter et al., 2008).

From the discussion above one can conceive that the electrochemical behavior of CNTs is rather complex for an unequivocally assessment. There are many concerns that have to be taken into account which arise from the different growth techniques, the quality of the CNTs, the chemical processing steps employed, incomplete characterization, CNT electrode configuration, etc (Dumitrescu et al, 2009). However unique advantages of the CNTs are coming from their nanometer size which can be manipulated to design novel electrode architectures (Gooding, 2005; Esplandiu, 2009a) or for signal amplification purposes (Wang, 2005; Merkoci, 2006; Kim, 2007). Related with the latter issue, CNT systems exhibit a high effective surface area which is beneficial not only for enhancing electrochemical currents of

diffusing electroactive species but also for allowing the load of high density electrochemical active (bio)molecules which can improve electrochemical signals. Another example related with the fact that CNTs are versatile materials for the design of unusual electrode configurations can be provided by the CNT modified electrodes with the nanotubes disposed in an upright configuration, which due to the nanometer size they can establish excellent wiring to the redox center of metalloproteins or enzymes favoring the direct electron transfer process (Yu, 2003; Patolsky, 2004; Liu, 2005; Esplandiu, 2009b).

3. CNT-polymer nanocomposite electrodes

3.1 General considerations and fabrication methods

As mentioned before, the nanometer dimensions of CNTs, their remarkable high specific surface area, high aspect ratio, low-weight and their additional extraordinary physical and chemical properties make them ideal fillers for polymer matrices and thus for imparting new functionalities to polymer nanocomposites. The use of carbon nanotubes has attracted a great deal of attention not only to develop better structural-reinforced materials thanks to the advantageous CNT mechanical properties (high stiffness, tensile strength) but also for conferring remarkable conductivity to polymer matrices (Ajayan et al., 2003; Wang & Musameh, 2003; Barrera et al., 2005, Harris, 2004; Moniruzzaman et al., 2006; Coleman, 2006; Spitalsky et al., 2010; Li et al. 2008; Xiao & Li, 2008; Martone et al., 2010).

However the fabrication of high performance CNT composites still results challenging and several important requirements should be fulfilled for an effective improvement of CNT-based composite properties. One of the crucial ones is to get a very homogenous dispersion of CNTs in the solvent or host matrix and an optimized concentration of the CNT load (Barrera et al., 2005; Olek, 2006; Grossiord et al., 2006; Sahoo et al. 2010; Grady, 2010). High CNT purification, good interfacial bonding or good adhesion between nanotubes and polymers are also necessary conditions for improving mechanical/electrical properties of the composites. Moreover, alignment of the CNTs in composites which provides enhanced anisotropic characteristics has also been observed to improve in some cases the mechanical properties of the composites (Olek, 2006).

CNTs are difficult to disperse and dissolve in any organic and aqueous medium due to the strong Van der Waals interactions which drive their aggregation. Dispersion can be achieved by mechanical and chemical methods. The mechanical techniques involve physically separating the tubes from each other by mechanical agitation (shear mixing, ultrasonication, magnetic stirring, etc). The chemical methods often use surfactants or chemical treatment of the tube surface which enhance the interactions between the filler and the matrix.

Several processing methods are available for fabricating the CNT/polymer composites based on the nature of the polymer being used (Grossiord et al., 2006; Olek, 2006; Spitalsky et al., 2010; Sahoo et al., 2010; Sánchez et al. 2009). The most common method is based on the mixing of the CNTs and a polymer in a suitable solvent before evaporating the solvent to form the composite films. For thermoplastic polymers which are insoluble in any solvent the melting processing is the common alternative (e.g. melting of thermoplastic polymers to form a viscous liquid and then mixing with CNTs). For thermosetting polymers such as epoxy, the CNTs are mixed with monomers (usually liquid) and then they are thermally cured with crosslinking/catalyzing agents. Other approaches are the layer by layer assembly of polymers on CNTs (normally with oppositely charged polyelectrolytes), in situ

polymerization on the CNT surface, coagulation of CNT/polymer by phase inversion such as in the case of polysulfone/CNT composites, etc.

As mentioned in the introduction, we will mainly focus on the fabrication and properties of rigid CNT-polymer composite electrodes based on an epoxy matrix. Epoxy resins are a family of polymers widely used for their excellent chemical properties, their good adhesion to other materials and their excellent insulating characteristics (Céspedes et al., 1996). Furthermore, epoxy CNT composites are easily prepared, inexpensive, widely available, ease of machining and malleable before curing and exhibit the advantage of generating a fresh surface by only polishing every time that is needed for successive experiments. CNTs have atomically smooth and quite inert surfaces and as such there is a lack of interfacial bonding or adhesion between the CNT and the polymer chain that limits the composite performance. Chemical modification can provide optimum surface sites that enhance the interaction with the host matrix. Accordingly, our typical procedure consisted in CNT treatment with concentrated HNO_3 acid to increase the CNT purity and to generate oxygen functionalities which provide better interaction or adhesion with the polymeric resin. After acid treatment, the CNTs were dispersed in the resin and hardener agents by mechanical agitation and allowed to cure during 24 h at 80ºC. Electrode surface was then polished with different sandpapers of decreasing grain size (Pacios et al., 2009; Olivé-Monllau et al., 2009). Figure 2 shows a schematic approach of the composite electrode preparation.

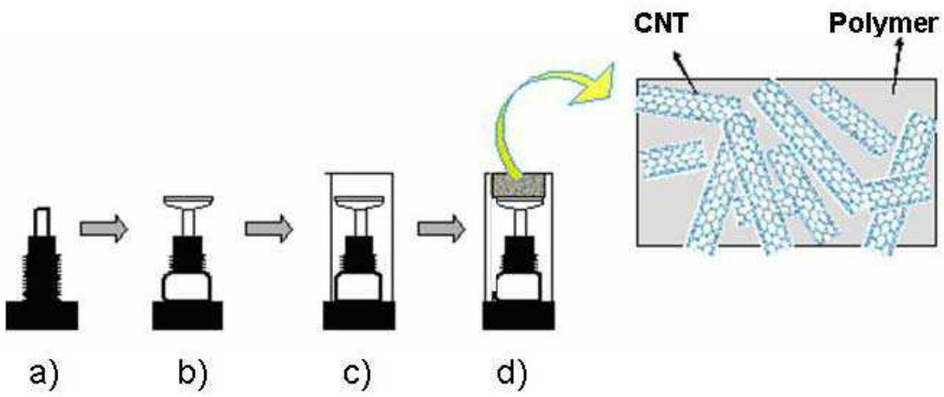


Fig. 2. Electrode assembly. Composite electrodes were prepared by using a PVC tube body small copper disk soldered at the end of an electrical connector. The composite was prepared by first mixing manually the epoxy resin and the hardener in a 20:3 ratio (w:w), respectively. Then different weight proportions of CNT were added to the epoxy mixture. The carbon paste was well mixed during one hour and put in the cavity of the PVC body and thermally cured. A) Electrical connector; B) copper disk fixture; C) mount of PVC body; D) introduction of carbon-epoxy paste.

3.2 Electrical properties of composites: percolation curves

Many studies have been performed to incorporate and adjust the CNT amount in polymer matrices to tailor electrical properties according to the different purposes since many applications (electromagnetic interference shielding, antistatic coatings, etc.) normally require specific levels of conductivity (Mylvaganam & Zhang, 2007). Following our main interest, that is the use of CNT composites for electrochemical applications, one has to

assure, as a first step, the amount of CNT necessary in the matrix for a good electrical conductivity. One way to get a wide overview of the electrical properties of the nanocomposites is by performing percolation curves. Systems composed of polymeric matrix and conductive filler experience the percolation transition which refers to the critical concentration of the filler at which the electrical properties of the composite are significantly changed (Céspedes et al., 1996; Martin et al., 2004; Olek, 2006; Singh et al., 2009; Faiella et al., 2009; Olivé-Monllau et al., 2009; Kara et al., 2010). The CNT composite becomes conductive above a critical value which is called percolation threshold and defines the insulator – conductor transition. At this point the first conductive network is formed through the matrix. For reaching the electrical percolation threshold and therefore be electrically conductive, it is not necessary a direct physical connection or overlapping of the CNTs. Nanotubes can just be close enough to allow for a hopping/tunneling electron effect.

The electrical percolation threshold depends on many factors including the size and the shape of the filler, the matrix properties, preparation method, filler properties, dispersion of the filler in the matrix, interaction between compounds, etc. One of the interesting features of CNT composites is that they can reach percolation thresholds at a very low weight fraction of nanotubes due to their high aspect ratio (Sandler, J.K.W. et al., 2003). Numerous studies have been performed on the evaluation of the electrical percolation threshold of CNT/polymer systems (Martin et al., 2004; Olek, 2006; Singh et al., 2009; Faiella et al., 2009; Kara et al., 2010). Depending on the functionalization, exfoliation and dispersion of CNTs, composite processing and properties of the components, different values of percolation thresholds were obtained ranging from 0.005 up to 5 wt%.

As a matter of illustration, let´s concentrate on the percolation curves for CNT epoxy composite in comparison with the one corresponding to graphite epoxy composite (fig. 3) (Olivé-Monllau et al., 2009). The figure shows the variation of resistivity as a function of the percentage of carbon nanotubes or graphite. In the case of CNT composite, the percolation threshold is achieved around 1% of CNT content whereas in the case of the graphite composite the percolation threshold was about 12%. Below that critical value the carbon composites behave as insulators and above that point the resistivity of the composites is very low and their variations are almost negligible. It is worth noting the smaller percolation threshold of the CNT composite as compared to its graphite analog.

Another way to characterize the electrical properties of the carbon composites is by using conductive Atomic Force Microscopy (C-AFM) (O'Hare et al., 2002; Pacios et al., 2008). This technique consists in the use of a conductive tip operating in standard contact mode with the sample. As a voltage is applied between tip and sample, a current is generated, the intensity of which will depend on the sample nature. Thus, a map of current distribution along the sample is measured simultaneously with the surface topography. The C-AFM mapping images allowed us to observe the conductive microzones where the electrochemical charge transfer can take place (light regions), and the non conductive insulating microzones where such processes are suppressed (dark regions). As seen in Fig. 4 the composite with 20% of MWCNT loading showed slightly more conductive areas than in the case of the composite with 10% of MWCNT loading, as expected. Moreover, from the topographic AFM images one can estimate a value of roughness (R). Indeed, as the MWCNT loading of the composite increases, the roughness of the surface also increases. Such increase in the conducting areas and in the surface roughness with the CNT load also greatly influence the double-layer capacitance values as will be discussed later on with the electrochemical characterization.

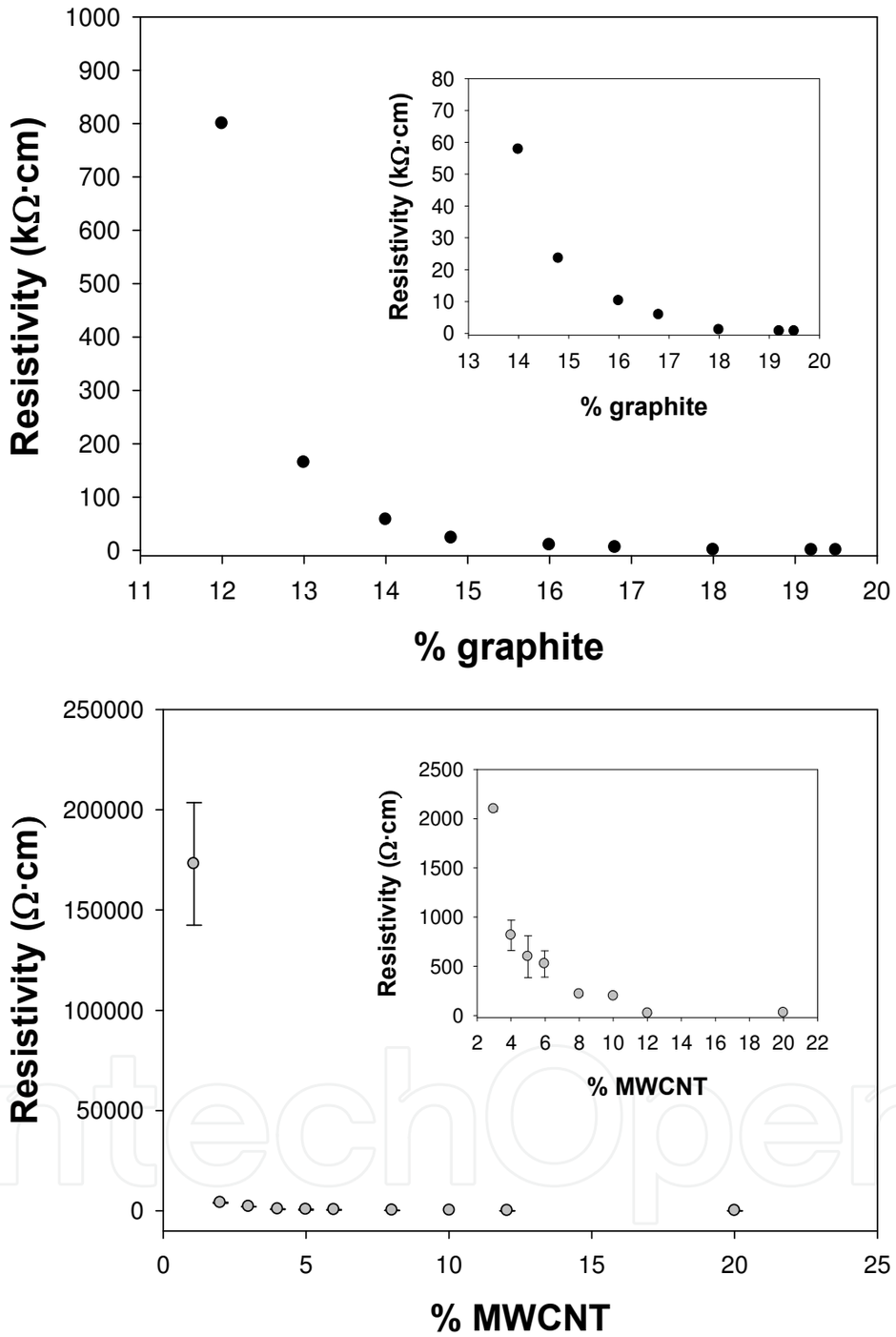


Fig. 3. Percolation curve obtained for graphite and CNT epoxy composites. The trend follows the percolation theory. The insets show the results in a zoom scale. Graphite composite percolation curve was adapted from Ref. (Olivé-Monllau et al., 2009) and the carbon nanotube composite curve was reproduced from Ref. (Olivé-Monllau et al., 2010) with permission. Copyright, 2010, Elsevier.

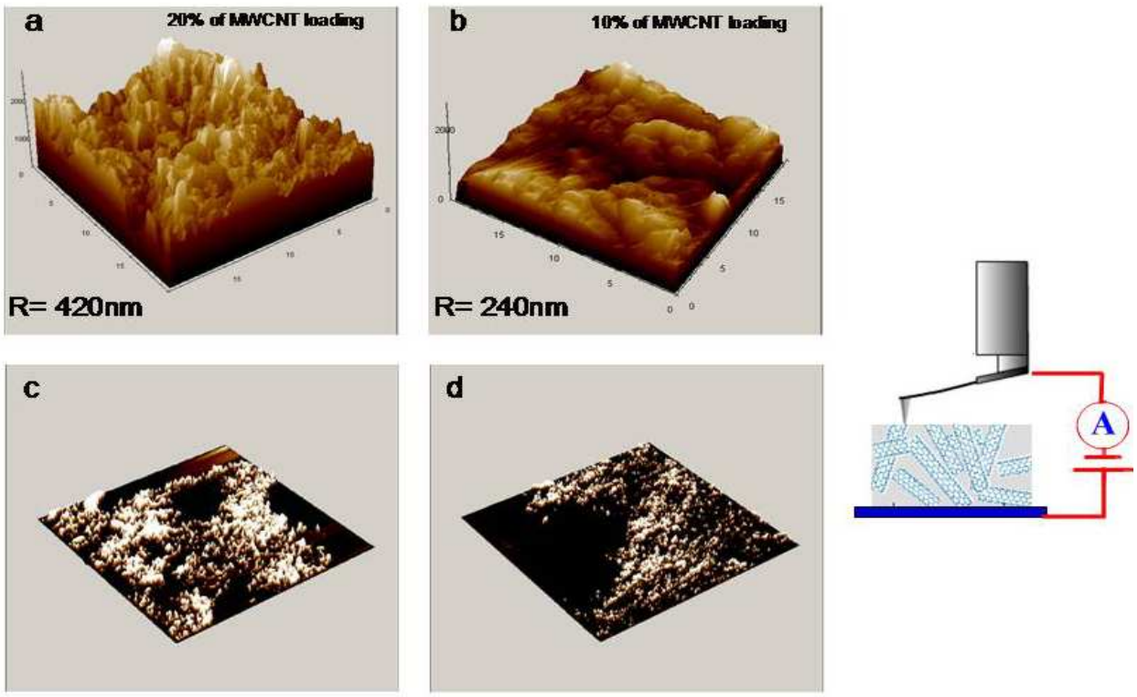


Fig. 4. Topographical AFM images with their corresponding conductivity mappings for 20% of CNT loading (a,c) and 10% of CNT loading (b,d). The x-axis, y-axis and z-axis units are μm, μm and nm respectively. Scheme of a C-AFM set-up. Adapted from Ref. (Olivé-Monllau et al., 2010) with permission. Copyright, 2010, Elsevier.

3.3 Electrochemical properties

Carbon composites for electrochemical applications were introduced by Adams in the fifties by using carbon paste electrodes (Adams, 1958), a mixture of a polycrystalline graphite powder with water-immiscible insulating organic liquid (Nujol, hexadecane, etc.). After that, other polymer alternatives were used such as epoxy, Nafion or conducting polymers (Navarro-Laboulais et al., 1994; Céspedes et al, 1996; Zhao & O' Hare, 2008; Olivé-Monllau et al., 2009; McCreery, 2008; Navratil & Barek, 2009). Since then the electrochemical properties of different carbon composite electrodes were studied in detail covering a wide range of issues from electroanalysis, pharmaceuticals, biological, redox processes and mechanistic electrochemistry. However with the advent of CNTs, the use of composite electrodes has been boosted. CNT composite electrodes are a suitable material for ion intercalation, catalyst entrapment/deposition for applications in electromechanical systems (artificial muscles or motors), energy applications (lithium batteries, supercapacitors, solar cells, (bio)fuel cells, etc.) and for (bio)chemical sensing (diagnostic medicine, genetics, drug, food and environmental sensing). Many groups have reported the use of CNT (bio)composites based on Teflon, epoxy, chitosan, poplystyrene or polysulfone for a wide variety of electroanalytical assays (Wang, 2005; Pumera et al., 2006; Xiao et al., 2008; Yogeswaran & Chen, 2008; Pacios et al., 2008; Sánchez et al., 2009; Kara et al., 2010; Olivé-Monllau et al., 2010).

In general carbon composite materials present improvements in the electrochemical response over conventional solid carbon electrodes such as the typical glassy carbon

electrodes or other metal electrodes (McCreery, 2008). First, the composites exhibit the interesting advantage of easy surface renewal without extensive polishing. Second, the graphitic particles or nanotubes exhibit randomly exposed edges and are usually quite electrochemically reactive. Third, the background current (I_c) responsible of the noise in the electrochemical signal is considerable small. Such background current is related with the double layer charging capacitance of the electrode which is mainly determined by the active area, that is, the fractional area of carbon exposed to the solution (A_{act}). The active area is much smaller than the geometric area (A_{geom}) of the electrode since the remaining part is coated with the host polymer. On the other side the faradaic current (I_f) related to the electrochemical electron transfer process is more proportional to the geometric area of the electrode if the active areas are not so far away from each other. That makes that the electrochemical signal(I_f)/noise (I_c) ratio be proportional to A_{geom}/A_{act} and hence bigger than in the case of conventional metal electrodes of the same geometric area. Fourth, such nanocomposite electrodes can behave, under certain conditions, as an array of microelectrode with all the advantages that they comprise for electroanalytical applications (fig.5) (Arrigan, 2004). Apart from exhibiting low noise current which leads to lower limits of detection than macroelectrodes, they can exhibit increased electrochemical signal and fast

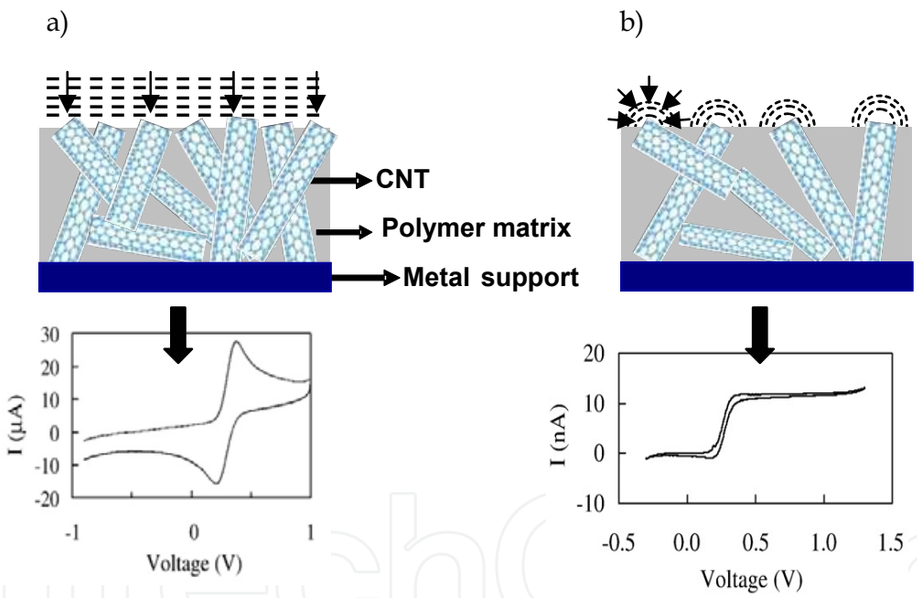


Fig. 5. Schematics showing the diffusion profile of the electroactive species for different composites and their corresponding cyclic voltammogram (CV) response. In case a) the active exposed areas of the electrodes are closer, so the diffusion layer of the different electrochemical active spots overlap generating a linear diffusion of the electroactive species and the CV response is in a peak-shaped profile. In case b) the composite behaves as a microelectrode array, the electrochemical active spot of the electrode are sufficiently far away that the diffusion profiles are hemispherical and very dependent on the perimeter of the active surface. That brings about an enhanced and fast mass transport of the electroactive species and consequently fast response and higher faradaic signal with respect to the background noise. The CV profile changes to a sigmoidal shape in which a steady state current is rapidly reached.

response due to the enhanced mass transport to the interfacial reaction zone. As the electrochemically active zones electrode dimension becomes smaller than the diffusion length, relative to the time scale of the measurement, the flux of reactant to the electrode is enhanced because it becomes dominated by hemispherical diffusion causing the electrode to approach a steady state limiting current. Both of these factors, the low background current and the enhanced mass transport lead to enhanced signal/background ratios, high sensitivity, fast electrode response and low detection limits. Fifth, carbon composites retain the wide potential window of carbon materials compared with conventional metals. Sixth, a composite permits addition of a variety of reagents to the host material, including electrocatalysts, enzymes, chemical recognition agents, to confer selectivity (Fig.6). Seventh, the host polymer provides big robustness to the electroactive material, a feature that can only be limited in presence of certain organic solvents.

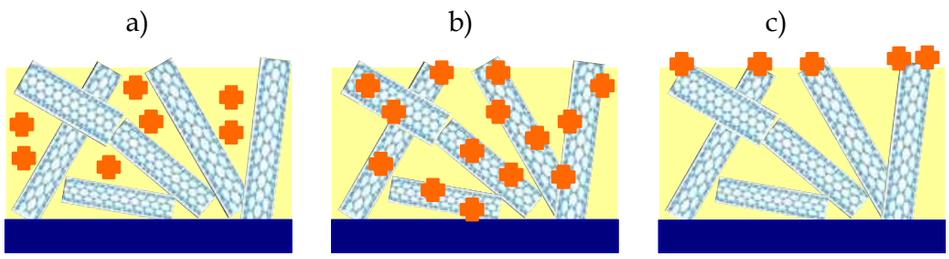


Fig. 6. Different strategies for (bio)chemical modification of the composite matrix that can confer selectivity for (bio)sensing or increase electrocatalytic effects. Composites can be modified with a wide variety of species (catalyst nanoparticles, redox mediators, enzymes, proteins, biomolecular receptors or ligands, etc.) in bulk or at the surface. In case a) the modifiers are introduced when preparing the carbon + polymer mixture and remain embedded or trapped in the composite. In case b) the carbon material is previously covalently or non-covalently functionalized with the species and then mixed with the polymer. In case c) the (bio)species are immobilized on the surface of the already prepared composite.

Carbon nanotube composites apart from sharing the electrochemical advantages of the carbon composites outlined before, they have added features coming from their nanoscale size, structure and high aspect ratio. Such distinct characteristics can contribute to innovative electrochemical applications and to establish the differences with respect to other carbon materials (McCreery, 2008; Esplandiu, 2009a). For instance, novel composite electrode architectures can be accomplished and tailored according to electrochemical applications, a field that is still far from being fully exploited, and which can also provide important insights for a more fundamental understanding of CNT electrochemistry. Thus, the high aspect ratio of carbon nanotubes can be used to form controllable CNT microelectrode array composites in similar direction than the CNT composites proposed by Meyyappan and coworkers (Fig. 7) (Koehne et al., 2004). Taking advantage of the electrochemical anisotropy of the CNTs, one could tailor the tubes in an upright configuration with the more electrochemical reactive sites or tube endings facing to the analytes. That could greatly improve the sensitivity and detection limits to the range of few molecules. At the same time the CNT edges can promote (bio)functionalization in a easier way than other forms of carbon and act as molecular wires where electroactive biomolecules can be plugged at their ends facilitating the direct electron transfer. Alternatively, and

following the continuous search of ultrasensitive electrochemical detectors, CNT composites can be used as specific biorecognition indicators profiting from their high surface area available for loading electroactive markers which can amplify biorecognition events. On the other hand, the design of 3D CNT ensembles with high surface area and mesoporous character can yield large double layer capacitances, or provide suitable electrode frameworks for ion intercalation or catalyst entrapment/deposition, all being important for the development of electromechanical systems or electrochemical energy storage systems (Esplandiu, 2009a).

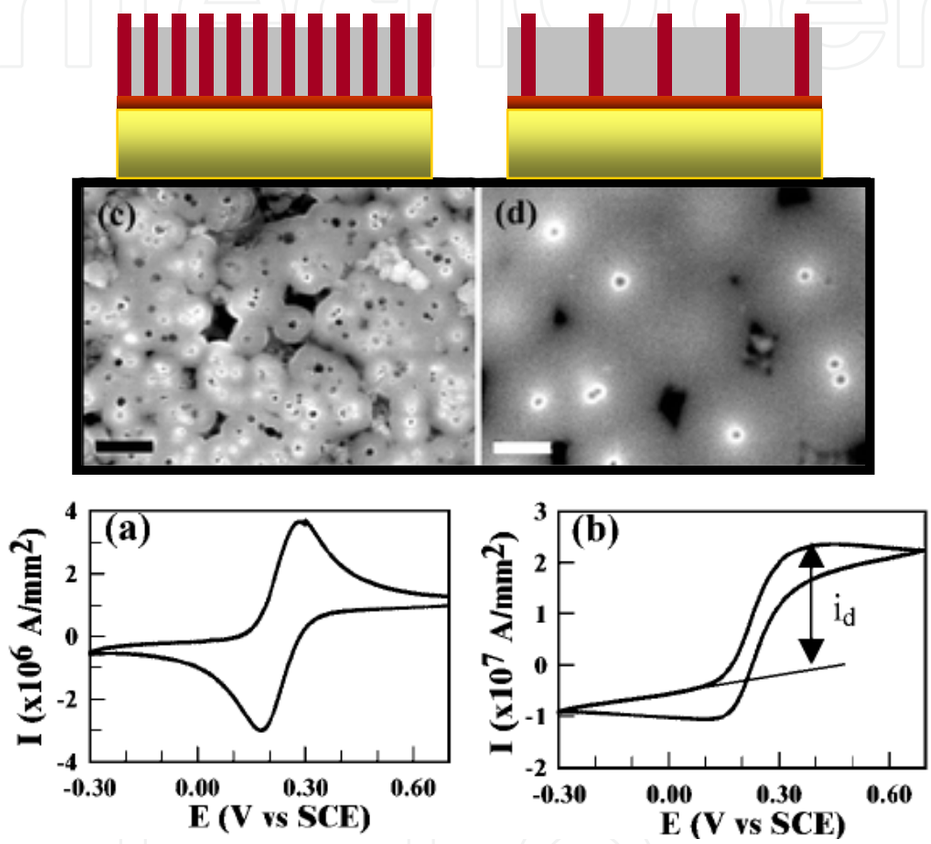


Fig. 7. CNT nanocomposite formed from vertically aligned CNTs grown by plasma CVD deposition and then encapsulated in a dielectric (SiO_2). After that, a planarization was performed by using chemical mechanical polishing which allowed the ends of the carbon nanotubes to be exposed to the solution. The figure shows two composite schemes, with higher and lower density of vertically aligned CNTs. a) and b) shows the CV measurements in presence of a redox couple with the high-density MWCNT nanoelectrode array (2. 10^9 electrodes/cm^2) and low density one (with ca. 7.10^7 electrodes/cm^2) respectively. C) and d) show the scanning electron images for the high and low density arrays. Adapted from Ref. (Koehne et al., 2004).

However, CNT composites still exhibit difficulties that can limit the desired electrochemical performance, some of them mentioned in sections before like difficulties in the dispersion and adhesion with the polymer host together with the lack of homogeneity of the different commercial CNT lots, different amounts of catalyst or amorphous carbon impurities in the

nanotubes as well as big dispersion in their diameter/length. These variations are difficult to quantify and make mandatory not only an electrical characterization but also an electrochemical characterization of the composite before being used in the desired application together with the optimization of the CNT load in the composite. Many electrochemical groups have done the optimization of the composite proportions under the criteria of maximizing the particle loading without losing its physical and mechanical stability (Céspedes et al., 1996; Pumera et al., 2004; Pacios et al., 2008). The type of carbon nanotubes can affect the maximum attainable carbon loading and the goal of those approaches was to achieve the maximum conductivity value. However and taking into account the low reproducibility of the composite electrochemical performance due to the mentioned limitations, it is important not only to consider the conductivity of the composite material (which can be extracted from the electrical characterization through the percolation curves) but also the reproducibility regarding their electrochemical properties.

For instance, from the electroanalytical point of view, the requirements to achieve a good electrode performance are high sensitivity, rapid response time and low limit of detection. These features are related with some physical parameter such as material resistivity, heterogeneous electron transfer and double layer capacitance of the composite electrode. Accordingly, it is important to perform the electrochemical characterization of such parameter for each electrode composition to determine the optimum CNT composite which can bring about the best electroanalytical properties (Olivé-Monllau et al., 2010).

Electrochemical impedance spectroscopy (EIS) can be used to characterize each resulting conductive composite. This technique provides, in an easy way, information about the electron transfer rate, double-layer capacitance, contact resistance and resistance of the solution (Pacios et al., 2008; Esplandiu et al., 2009b; Olivé-Monllau et al., 2010). Thereby, we can determine the composite that exhibits a high electron transfer rate, the lowest double layer capacitance and ohmic resistance to guarantee a high signal/noise ratio, high sensitivity and low detection limits. These results can also be contrasted with voltammetric measurements. For illustration of the electrochemical characterization of CNT composites for electroanalytical purposes, we will continue with the CNT epoxy system characterized by electrical means in the section before.

3.3.1 Electrochemical impedance spectroscopy measurements

Impedance spectroscopy is a technique which is used to characterize electrode processes and complex interfaces. This method studies the system response to the application of a periodic small-amplitude AC signal (around 10 mV). An AC potential is applied ($E(t) = E_o \cos(\omega + t)$) and a AC current is obtained $I(t) = I_0 \cos(\omega t - \varphi)$ (Fig. 8 a). From the relation of both signals the impedance (Z) is obtained ($Z = E(t)/I(t)$). The measurements are carried out at different frequencies and thus the name impedance spectroscopy. In our case it was about (0.1Hz to 100 kHz). Impedance methods allows characterizing the double layer interface at the electrodes and the physicochemical processes of widely differing time constants, sampling electron transfer at high frequency and mass transfer at low frequency. Impedance results are commonly fitted to equivalent electrical circuits of resistors and capacitors, such as the circuit shown in Fig 8 b, which is often used to interpret simple electrochemical systems. There are many ways to plot impedance data. Since the function impedance is an AC signal, one can express it in terms of complex number ($Z = Z_{real} + j\, Z_{imag}$) and plot the Z_{real} vs Z_{imag}. Such kind of plot is called Nyquist plot as the one shown in Fig. 8 c, and provides visual insight into the system dynamics at the electrochemical interface. Normally

such plot exhibits a kind of semicircle profile plus a linear region (the points at which the impedance data cut the real impedance axis represent resistances). In the typical plot of Fig. 8 b R_{ct} is the charge-transfer resistance, which is inversely proportional to the rate of electron transfer (a rough estimation of R_{ct} is related to the width of the semicircle); C_d is the double-layer capacitance, R_s is the electrolyte resistance and, Z_w is the Warburg impedance, which arises from mass-transfer limitations and can be used to measure effective diffusion coefficients. If in an electrochemical system the electron transfer rate is the limiting step, the charge resistance is quite large and the impedance spectrum is dominated by the semicircle feature. Then it is said that the electrochemical process is kinetically controlled. On the other side, if the electron transfer is fast and the diffusion of the electroactive species is the limiting factor, the linear part dominates the impedance spectra and it is said that the process is diffusion controlled.

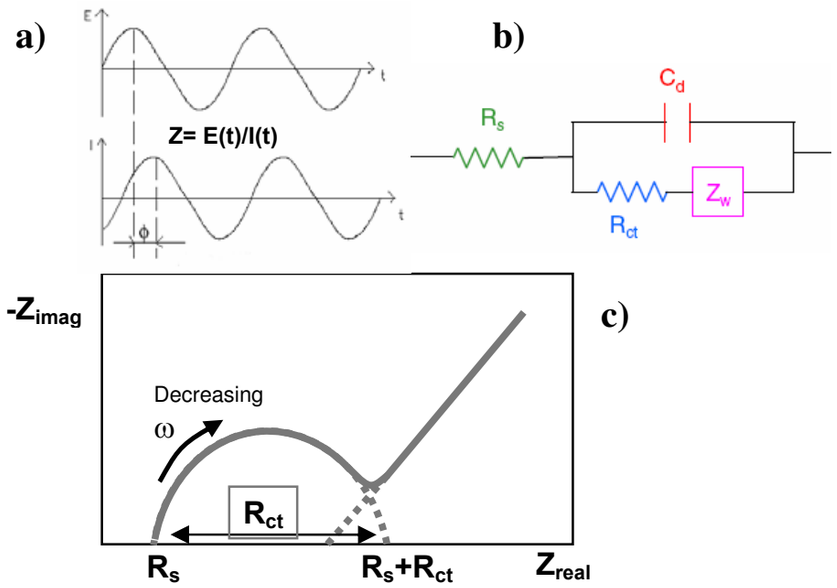


Fig. 8. Impedance function and typical equivalent circuit at the electrochemical interface. Representations of the impedance data (Nyquist plot).

Thus the impedance spectra can give us a broad overview of the different processes taking place at the electrochemical interface (capacitive, resistive, diffusion effects) and which one is dominating more at specific range of frequencies.

By means of electrochemical impedance spectroscopy we could obtain general trends in the electrochemical parameters of our CNT epoxy composites such as the solution resistance or the ohmic resistance ((R_Ω) which comprises the resistance of the solution (Rs) plus any contact resistance (Rc)), charge transfer resistance (R_{ct}) and the double-layer capacitance (C_{dl}) for composites with different MWCNT loading. Such electrochemical characterization was performed in presence of benchmark redox species such as $Fe(CN)_6^{3-/4-}$ which is very sensitive to the electrode surface characteristics. These parameters were obtained by fitting the impedance spectra to a simple equivalent circuit (inset Fig. 9). This circuit was sufficiently suitable to interpret the R_Ω, C_{dl} and R_{ct} values in terms of the interfacial phenomena that occur at the electrochemical cell (Olivé-Monllau et al., 2010).

We studied different compositions of MWCNT-epoxy composite electrodes by varying the MWCNT loading from 3% to 20%. Fig. 9 shows, on one hand, the impedance response of composites with low resistivity (from 20% to 10% of MWCNT loading) (Olivé-Monllau et al. 2010). In such cases the impedance behavior is dominated by a small diameter semicircle representing kinetic-controlled electrode process, though in some cases the diffusion-controlled process starts to be discerned at low frequencies (inset of the figure). On the other hand, the impedance plot for composites with higher resistivity (from 7% to 3% of MWCNT loading) appears to be dominated by a big diameter semicircle and only the kinetic-controlled electrode process is present in the recorded frequency range.

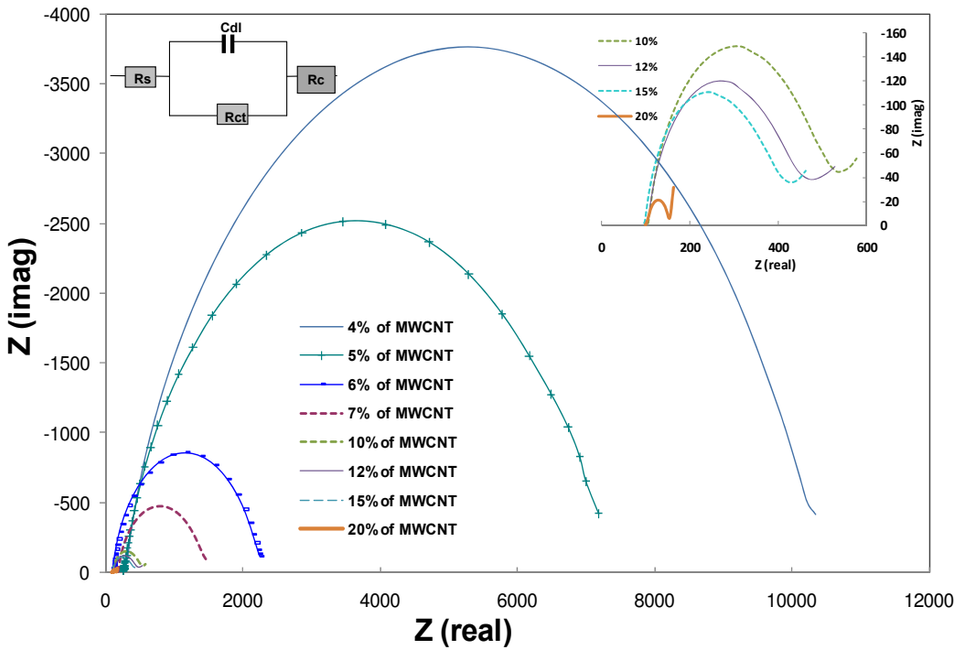


Fig. 9. Impedance spectra for different MWCNT loading electrodes in the presence of $Fe(CN)_6^{3-/4-}$. The insets in the figure show the equivalent circuit used for the impedance spectra fitting and a zoom of the low impedance composite electrodes. Reproduced from Ref. (Olivé-Monllau et al., 2010) with permission. Copyright, 2010, Elsevier.

The ohmic resistance parameter consists of the solution resistance (which is dependent on the ionic concentration, the type of ions and also the electrode area) in series with the contact or the ohmic composite resistance. The latter resistance is the one that has a direct relation with the dry resistance taken for the percolation plot of Fig. 1. Since the solution and contact resistance appear in series, they cannot be independently resolved in the impedance data. Fig. 10 A shows the variations of the ohmic resistance as a function of the carbon nanotube composition. At low carbon loads (< 6% of MWCNT loading), the ohmic resistance is dominated by the contact or composite resistance whereas at higher carbon loads (≥ 6% of MWCNT loading), the ohmic resistance is more dominated by the solution resistance reaching an averaged value of about 100 ohms. This behavior is in agreement with the obtained results in the percolation curve. Low bulk resistance is suitable for electroanalytical materials since it favorably affect the response time and sensitivity of the electrode.

The quantitative values of R_{ct} are depicted in Fig. 10B (Olivé-Monllau et al., 2010). The R_{ct} parameter is inversely proportional to the heterogeneous charge transfer rate and also affects the sensitivity and response time of the electrode. From Fig. 10 B, it is clearly observed the decrease of R_{ct} with the increasing of CNT load. This parameter normalized by the electrochemical active area should be constant for conventional metal electrode interfaces. However in the case of CNT materials that might not be expected. As mentioned before, it is quite accepted that CNTs exhibit electrochemical anisotropy with higher electrode kinetics on edges and lower electron transfer rates on the walls. That makes the electrode kinetics of CNT electrodes to be very dependent on the carbon nanotubes nature and structure. Indeed, we have normalized R_{ct} with respect to the electrochemical active area (see section next section for electroactive area evaluation) and listed its variation with the CNT composition in Table 1. Again a decrease of the R_{ct} parameter with CNT proportion has been obtained which probably speaks of the strong relation between electrochemical reactivity and the surface characteristics of the conducting material. As the carbon load increases, the probability of having more electroactive sites increases and hence the electrode kinetics.

Therefore, composites with low charge transfer resistances are appropriated to be used in electrochemical measurements. According to the results, composites between 20% and 9% of MWCNT loading presented lower charge transfer resistance values. The use of composites in such range of proportions will guarantee fast electron exchange (Olivé-Monllau et al., 2010). However and in spite of the enhanced kinetics, high load of conducting material can increase the background current and smear the faradaic signal response, especially when the electroactive species are present in low concentration.

Therefore it is important to consider the remaining impedance parameter represented by the double layer capacitance which is directly related to the charging or background current. This parameter exhibits increased values with electrodes comprising high surface area of conducting material. In general composites contain only a fraction of conductive area exposed to the solution with the remainder occupied by the insulating polymer. The electrode capacitance, which is determined nearly exclusively by the exposed carbon becomes low, and in turn decreases the background current. That enhances the signal to noise ratio and consequently decreases the analyte detection limits.

Fig. 10C depicts the decrease of the double-layer capacitance values with the decrease of the MWCNT loadings. Note the remarkable lower values of the capacitance double layer between 3% and 11% of MWCNT loading. Higher carbon loads, not only increase the conducting areas but also the surface roughness and porosity of the composites and consequently the background current increments remarkably.

According to the impedance results and taking into account the properties required by an electrode for electroanalytical purposes, such as rapid response time, low limit of detection and high sensitivity, the interval between 9% of MWCNT loading and 11% of MWCNT loading seems to be optimal to fulfill all these requirements. It is important to stress that the fabricated composites in such interval present similar electrochemical performance. The benefit of using composites in such range is that small variations in the composite composition (due to, for example, limitations in the CNT dispersion, purification, etc.) produce a small change in the electrochemical composite behavior. Indeed, under these conditions the electrochemical reproducibility is increased (Olivé-Monllau et al., 2010).

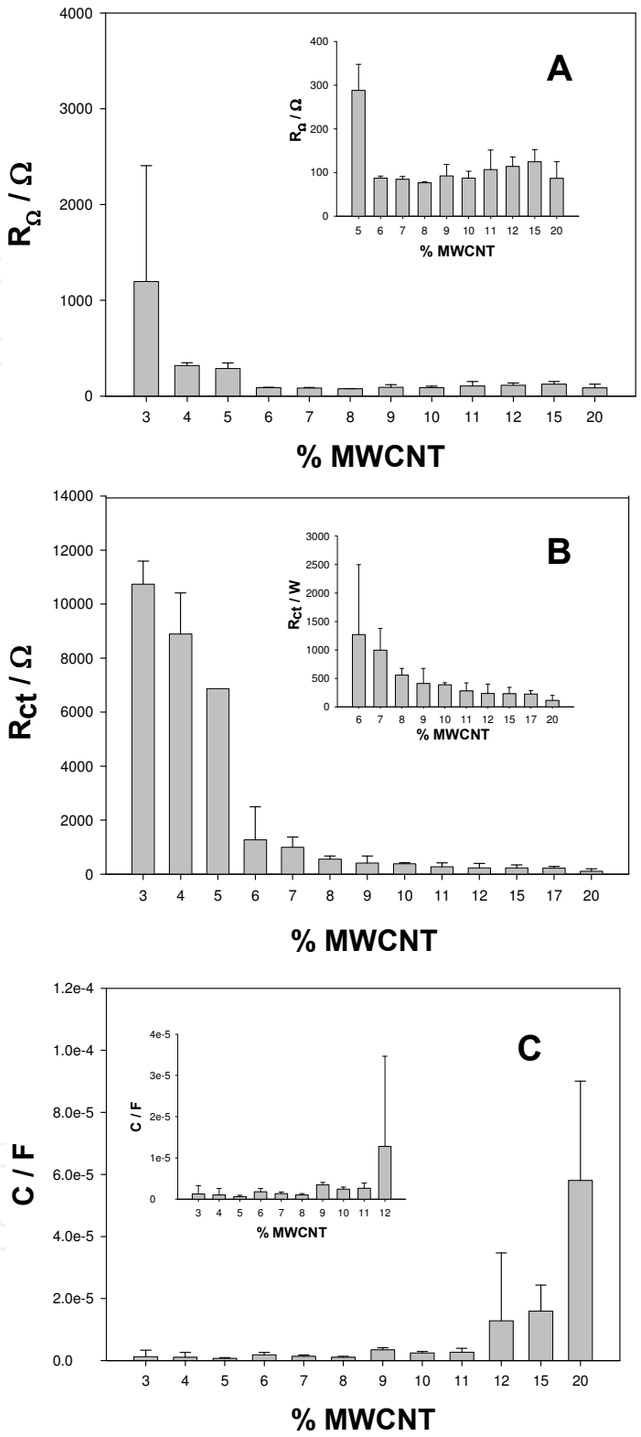


Fig. 10. A) Values of the ohmic resistance, B) charge transfer resistance and C) double layer capacitances extracted from the fitting of the impedance spectra together with their standard deviation for the different CNT loading electrodes. The insets show the values at the lower scale for each evaluated physical parameter. Readapted from Ref. (Olivé-Monllau et al., 2010) with permission. Copyright, 2010, Elsevier.

3.3.2 Cyclic voltammetry characterization

We can also perform cyclic voltammetry in order to and compare the results obtained with the impedance technique. Cyclic voltammograms were taken for the different composite composition electrodes in presence of the benchmark $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$redox couple (Olivé-Monllau et al. 2010). First of all, it is important to point out the abrupt change in the current/potential shape between 5% and 6% of the MWCNT proportion. At 5% MWCNT proportion, the current potential profile has a more sigmoidal shape as can be appreciated in more detail in the inset of Fig.11, which can be ascribed to an electrochemical behavior more related with a microelectrode array. Beyond 6% of MWCNT proportion, the composite electrodes exhibit the typical peak-shaped profile corresponding to more massive electrodes with planar diffusion characteristics. Different parameters were extracted from the cyclic

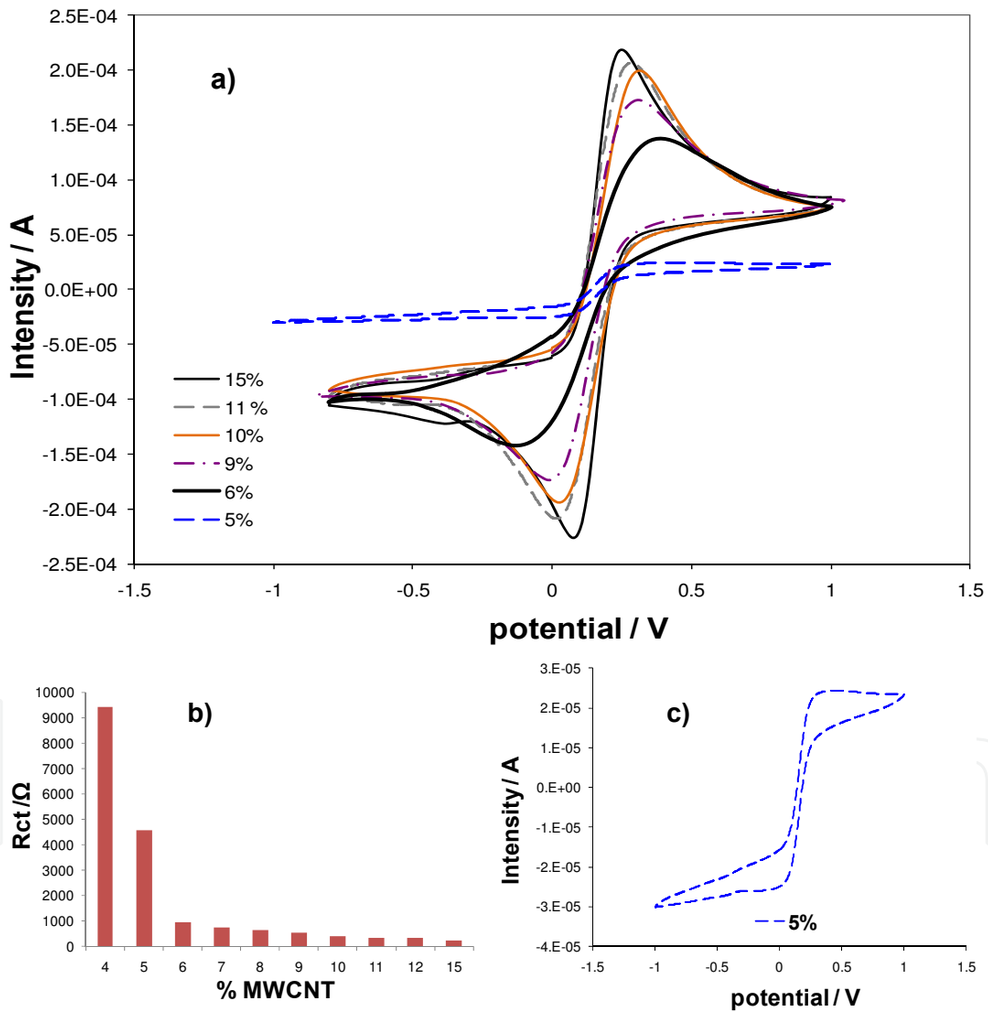


Fig. 11. a) Cyclic voltammograms for the different CNT composites in presence of the ferrocyanide/ferrycianide couple and compensated from any ohmic resistance. B) Trend of the charge transfer resistance for different composite compositions. C) A zoom of the cyclic voltammogram obtained by a composite with 5 % of CNT loading. Reproduced from Ref. (Olivé-Monllau et al., 2010) with permission. Copyright, 2010

voltammograms such as the peak separation potential (ΔE) and peak current (Ip) as shown in table 1. One can observe an increase of the peak current with the MWCNT loading, due to an increase of the electroactive area, together with a decrease of peak separation related to an enhancement of the electron transfer rate. The relative electroactive area (Table 1) was estimated from the peak-shaped voltammograms (up to a proportion of 5%) by quantifying the peak current with the use of this relationship, $I_p=3.10^5 \cdot n^{3/2}(\alpha D_{red}\upsilon)^{1/2}AC^*_{red}$ (Pacios et al, 2008; Olivé-Monllau et al., 2010), which is appropriate for electron transfer-controlled processes. In this equation α represents the transfer coefficient which was considered to be approximately 0.5, D_{red}= 6.32 x 10^{-6} $cm^2 \cdot s^{-1}$ corresponds to the diffusion coefficient of the reduced species, υ =0.01 $V \cdot s^{-1}$ represents the scan rate, A is the electroactive area and C^*_{red} = 0.01M is the bulk concentration of the electroactive species. We also evaluated the exchange current (i_o) from Tafel plots (log current vs. potential), a parameter which provides information about the reversibility of the process (Sánchez et al., 2009; Olivé-Monllau et al., 2010). From the value of the exchange current we can also evaluate the charge transfer resistance through the relation ($i_o=RT/nFR_{ct}$). The trend observed for this parameter resembles very closely the results obtained from the impedance measurements. From the comparison of the R_{ct} values extracted from voltammetry with the ones obtained by impedance measurements (Table 1), it can be observed that their values agree quite well for higher MWCNT loads (greater than 7%). By normalizing R_{ct} with respect to the electroactive area, one can observe that this parameter is also decreasing with the increase of the active area, similar to what was observed in the impedance section. That again indicates the influence of the electrochemical anisotropy of carbon nanotubes which can be more noticeable as the MWCNT loading is increased.

Electrodes	i_o (A)	R_{ct} (Ω)	i_p (A)	A (cm^2)	ΔE (V)	R_{ct} A (Ω cm^2)	R_{ct}^{EIS} A (Ω cm^2)
4%	$2.68 \cdot 10^{-6}$	9418					
5%	$5.52 \cdot 10^{-6}$	4572					
6%	$2.70 \cdot 10^{-5}$	936	$1.61 \cdot 10^{-4}$	0.30	0.476	280.8	641.4
7%	$3.36 \cdot 10^{-5}$	751	$1.96 \cdot 10^{-4}$	0.37	0.427	277.9	468.4
8%	$4.04 \cdot 10^{-5}$	625	$2.07 \cdot 10^{-4}$	0.39	0.335	243.8	250.6
9%	$4.63 \cdot 10^{-5}$	545	$2.33 \cdot 10^{-4}$	0.43	0.299	234.3	257.6
10%	$6.09 \cdot 10^{-5}$	415	$2.40 \cdot 10^{-4}$	0.45	0.283	186.8	186.3
11%	$7.24 \cdot 10^{-5}$	348	$2.53 \cdot 10^{-4}$	0.47	0.261	163.6	178.1
12%	$7.45 \cdot 10^{-5}$	339	$2.71 \cdot 10^{-4}$	0.50	0.261	169.5	175.3
15%	$1.04 \cdot 10^{-4}$	243	$2.72 \cdot 10^{-4}$	0.51	0.169	123.9	117.9

Table 1. Cyclic voltammetry parameter for the different composite compositions, i_o corresponds to the exchange current, R_{ct} to the charge transfer resistance, I_p to peak current, A to the active area and ΔE to the peak separation potential, R_{ct} A^{-1} and R_{ct}^{EIS} A^{-1} represent the normalized R_{ct} with respect to the active area obtained by voltammetry and EIS respectively. Adapted from Ref. (Olivé-Monllau et al., 2010).

3.3.3 Electroanalytical performance

In this part we will illustrate the impact of the CNT composite loading on the electroanalytical detection. Ascorbic acid was used as an analyte for evaluating the electroanalytical characteristics. Measurements were carried out at a fixed potential of 0.6 V. The MWCNT composite response to changes in concentration of ascorbic acid was evaluated by chronoamperometric measurements. The analytical parameters as the detection limit, sensitivity and the linear range were evaluated for 10% of MWCNT composite and compared to those obtained with 20% of MWCNT loading (composition used in the vast majority of previous studies reported by our research group (Pumera et al, 2006; Pacios et al., 2008). For each composition three electrodes were evaluated. Table 2 shows the calibration plot parameters for 20% and 10% of MWCNT loading composite electrodes using ascorbic acid as analyte. The experimental results show that when the MWCNT loading decreases from 20% up to 10%, the sensitivity slightly decreases, but the linear range remarkably increases and the limit of detection (LOD) becomes one order of magnitude lower (Olivé-Monllau et al., 2010). These results suggest that MWCNT loading of 10% seems to be an optimal proportion, since it can achieve a quite good sensitivity but what is more importantly very low limits of detection and wide range of linearity. That agrees very well with the results obtained by impedance spectroscopy which showed that the range between 9-11% exhibits a good behavior of the impedance parameters for the electroanalytical purposes with low charge transfer resistance, ohmic resistance and double layer capacitance. Although a microelectrode array response was obtained at 5% of CNT loading that could be quite beneficial for electroanalytical purposes, we decided to take a range with slightly higher CNT percentage. We found that the ohmic resistance for 5% CNT composite is rather bigger than in the case of CNT composites with a CNT loading between 9-11% and that could smear the electroanalytical response.

Electrodes	Sensitivity/μA L mg^{-1} ($\%RSD^{95\%}_{n=3}$)	LOD/mg L^{-1}	Lineal Range /mg L^{-1}
20% of MWCNT	0.29 (9%)	0.40	0.40 – 330
10% of MWCNT	0.20 (7%)	0.04	0.04 – 700

Table 2. Calibration parameters for 20% and 10 % of MWCNT composite electrode extracted from chronoamperometric measurements with ascorbic acid as analyte and 0.01M KNO_3/HNO_3 as background electrolyte. Reproduced from Ref. (Olivé-Monllau et al., 2010) with permission. Copyright, 2010, Elsevier.

The results, above and in the previous sections, show that the adjustment of the CNT composition, according to the electrical and electrochemical parameters, is very important to further get improved electroanalytical features. These studies can be extended to more complex electrochemical systems such as the development of (bio)sensors. That issue comprises one of the cornerstones of CNT composite applications since a frenetic research activity has burst around the field of enzymatic and protein sensors, DNA and genosensors and immunosensors. Thus, tailoring the CNT amount of the composites together with a proper (bio)functionalization (either in bulk or at the surface) of (bio)receptors, redox mediators and catalysts one can get efficient (bio)chemical sensors that can be even integrated

in microfluidics systems. Further improvements can be achieved by a controlled geometrical rearrangement of the CNTs in the polymer matrix to get an enhanced electron transfer process. However, the applications of CNT nanocomposites are not only limited to the electroanalysis field with the development of (bio)chemical sensors. Polymer CNT nanocomposites as actuators (artificial muscles) or as novel electrochemical energy harvesting devices comprise another promising though changeling field. For energy generation and storage, CNT composites hold promise as supercapacitors, Li-ion batteries, solar cells and fuel cells due to their high specific surface area and mesoporous character. It is quite expected that for most of the latter applications and in contrast to the electrochemical (bio)sensing devices, the capacitance parameter has to be maximized to get the intended purposes. Again, the impedance studies as a function of the CNT loading can result a very useful tool for tuning the CNT proportion amount to achieve the best performance of those applications.

4. Conclusions

The advent of CNT nanocomposites has opened innovative perspectives for research, development and applications and nowadays these composite comprise a broad world difficult to embrace.

CNT composites share the advantages of other graphitic carbon composites such as high signal to noise ratio, broad potential window, easy surface renewal, (electro)chemical anisotropy with higher electroactivity at edges, easily machinable and excellent platform for (bio)chemical modification. Apart from that, the main advantage of CNT nanocomposites in electrochemistry comes from their nanometer size, structure and high aspect ratio. Such distinct features provide versatility to tailor the CNT composites in different electrode arrangements which can allow the controlled fabrication of microelectrode arrays, the exposition of the more electroactive sites, the enhancement of the electron exchange or the promotion of better ways of (bio)functionalization. Moreover, controlled and novel electrode arrangements together with a proper CNT chemical processing and complete characterization could also help to unveil the uncertainties related to the electrochemical process itself in CNTs. Another advantage of CNT composites comes from their high surface area which can be used to load high amount of (bio)recognition indicators and amplify the electrode response. Moreover, the design of 3D CNT composites with high surface area and mesoporous character can yield large double layer capacitances, or provide suitable electrode frameworks for ion intercalation or catalyst entrapment/deposition, all being of big impact for the development of electromechanical systems or electrochemical energy storage systems. Though the CNT composites exhibit many benefits for the electrochemical purposes, they also suffer from some limitations that can smear the electrochemical performance. These limitations are coming from difficulties in the dispersion and adhesion with the polymeric matrix together with a lack of homogeneity in the CNT production or different amounts of the catalyst impurities. That makes necessary a previous electrochemical characterization of the composite that can help to optimize the CNT load before being used in the desired application.

Therefore in this chapter, we have attempted to highlight CNT epoxy composites as robust, easy-processing, and cheap platforms for basically electroanalysis applications and an electrochemical procedure to evaluate the physical parameters for optimizing the nanocomposite performance according to the intended purpose. Among the electrochemical techniques, EIS provides a versatile tool to optimize the composite material. On one side, it

is possible to extract the ohmic resistance which can be related to the percolation resistivity. On the other side, other useful parameters can be extracted such as the charge transfer resistance, which is related with the heterogeneous electron transfer rate and which depends on the surface electrochemical reactivity. Moreover, EIS also allows the extraction of the electrode capacitance which can be correlated to the background current, an important parameter to minimize in order to enhance the signal/noise ratio. Consequently all these parameters are relevant for the composite response and by a proper evaluation of them as a function of the CNT amount in the composite, one can choose the proportion which fulfills the electroanalytical requirements of high sensitivity, fast response and low limits of detection. In the present work such composition ranges between 9% and 11% of MWCNT loading. Moreover, small variations in composition around this optimal range do not produce high changes in the electrochemical composite behavior. To confirm these predictions, we showed that the electroanalytical detection of ascorbic acid was easily improved using the optimal 10% of MWCNT loading electrode. We achieved at that CNT proportion remarkable lower LOD and wider lineal range than using the 20% of MWCNT loading electrode. Such optimal CNT loading values can allow us to fabricate extremely attractive and robust composite electrodes with very interesting application as amperometric (bio)sensors at low electroanalyte concentration.

The electrochemical characterization here proposed can be extended to more complex systems like (bio)chemical CNT composite sensors or CNT nanocomposites for being used as actuators or oriented energy applications.

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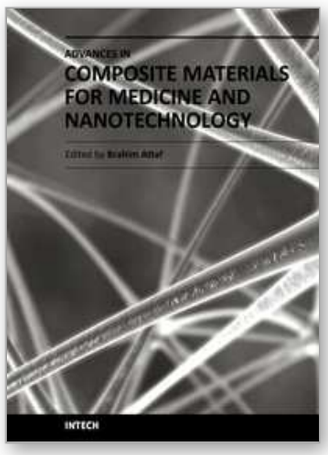
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Due to their good mechanical characteristics in terms of stiffness and strength coupled with mass-saving advantage and other attractive physico-chemical properties, composite materials are successfully used in medicine and nanotechnology fields. To this end, the chapters composing the book have been divided into the following sections: medicine, dental and pharmaceutical applications; nanocomposites for energy efficiency; characterization and fabrication, all of which provide an invaluable overview of this fascinating subject area. The book presents, in addition, some studies carried out in orthopedic and stomatological applications and others aiming to design and produce new devices using the latest advances in nanotechnology. This wide variety of theoretical, numerical and experimental results can help specialists involved in these disciplines to enhance competitiveness and innovation.

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