

Synthesis and Characterisation of Carbon Nanocomposites

M. Z. Krolow, C. A. Hartwig, G. C. Link, C. W. Raubach,
J. S. F. Pereira, R. S. Picoloto, M. R. F. Gonçalves,
N. L. V. Carreño and M. F. Mesko

Abstract Carbon nanocomposites have received more attention in the last years in view of their special properties such as low density, high specific surface area, and thermal and mechanical stability. Taking into account the importance of these materials, many studies aimed at improving the synthesis process have been conducted. However, the presence of impurities could affect significantly the properties of these materials, and the characterisation of these compounds is an important challenge to assure the quality of the new carbon nanocomposites. Thus, in this work are presented the characteristics of carbon nanocomposites, the improvements and developments in the synthesis process, as well as the most used characterisation techniques of these compounds.

M. Z. Krolow · G. C. Link · M. R. F. Gonçalves · N. L. V. Carreño
Centro de Desenvolvimento Tecnológico, Universidade Federal de Pelotas, Pelotas-RS,
96010-900, Brazil

C. A. Hartwig · M. F. Mesko (✉)
Centro de Ciências Químicas, Farmacêuticas e de Alimentos, Universidade Federal de
Pelotas, Pelotas-RS, 96010-900, Brazil
e-mail: marciamesko@yahoo.com.br

C. W. Raubach
LIEC, Departamento de Química, Universidade Federal de São Carlos, São Carlos-SP,
13565-905, Brazil

J. S. F. Pereira · R. S. Picoloto
Departamento de Química, Universidade Federal de Santa Maria, Santa Maria-RS, Brazil

1 General Aspects of Carbon Nanocompounds

Nanomaterials (NMs) are defined as materials that have structural features with at least one dimension of 100 nm or less; they include nanofilms and nanocoatings (one dimension), nanotubes and nanowires (two dimensions) and nanoparticles (three dimensions) [1]. Nanomaterials may present itself in different sizes and shapes, and also differ in composition and origin. Depending on the interaction between the nanoparticles, the NMs can be found as single particles, aggregates, powders or dispersed in a matrix, over colloids, suspensions and emulsions, nanolayers and films, and coated or stabilised as fullerenes and their derivatives [2].

Carbon-based nanomaterials, including fullerenes, single- and multi-walled carbon nanotubes and carbon nanoparticles, are currently one of the most attractive nanomaterials from an applications perspective [3]. Since their discovery in 1991 by Sumio Iijima, carbon nanotubes have been intensively studied [4]. Their extraordinary electronic and mechanic properties point towards a great variety of potential future applications, including polymer composites [5], electronics [6] and drug delivery [3, 7–9].

Carbon nanotubes (CNTs), one of most researched carbon-based materials, have a unique atomic structure, very high aspect ratio and extraordinary mechanical properties (strength and flexibility), making them ideal reinforcing fibers in nanocomposites [10]. The effective utilisation of carbon nanotubes in composite applications depends strongly on the ability to disperse the nanotubes homogeneously throughout the matrix, without destroying the integrity of the nanotubes. To take advantage of the superior mechanical properties of the carbon nanotubes, they have been used as fillers in epoxy resins [11] and in the production of polymer nanocomposites [12, 13]. On the other hand, the cost of production of carbon nanofibers (CNFs) is significantly less than CNTs, and could be advantageous when compared to CNTs in some applications. The dimensions of CNFs are between 50 and 200 nm [14], which are similar to those of single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [15]. The main characteristic that distinguishes CNFs from CNTs resides in graphene plane alignment. If the graphene plane and fiber axis do not align, the structure is defined as a CNF, but when both are parallel, the structure is considered a CNT [16].

Other carbon compounds extensively studied are the carbon-containing nanoparticles, usually called carbon nanocomposites [17–21]. These materials have received great attention due to properties such as low density, high specific surface area and uniform pore size, and thermal and mechanical stability [22]. It is important to note that the differential application of this type of material is in the properties of the particles that are associated, such as magnetic, catalytic, energy and absorptive, among others [22, 23]. An image of typical nanocomposite metal/carbon obtained by means of transmission electron microscopy (TEM) can be observed in Fig. 1 [24].

Nanocomposites consisting of metal and carbon are generally produced using techniques that involve heat treatment, during which some of the carbon may or

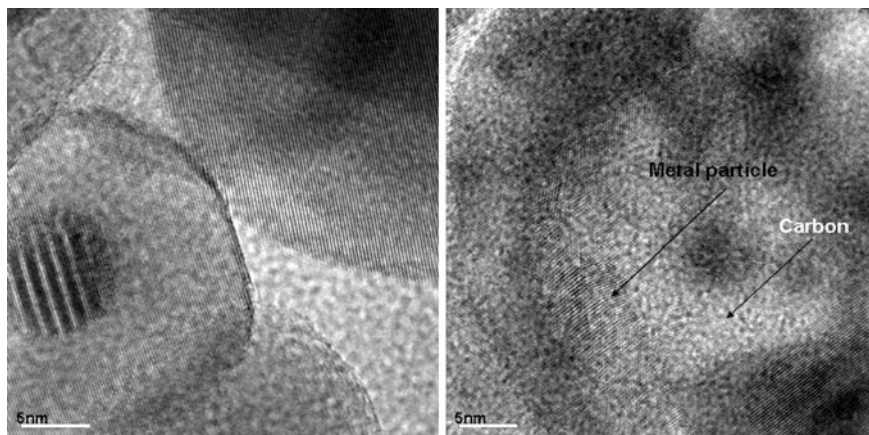


Fig. 1 TEM images of Ni/C catalyst before catalytic test. Copyright (2011), with permission from Elsevier

may not be eliminated. It is also at this stage that the metal nanoparticles are formed, and the material's crystallinity is increased. Nanoparticles often have spherical shapes with diameters between 10 and 20 nm as well as high crystallinity. These nanoparticles are very stable because they are embedded in the carbon matrix. Depending on the type of treatment they have undergone, the nanoparticles surface area can be quite variable, with values ranging from 50 m²/g to 1000 m²/g. Also, depending on the method of synthesis used or application for the product, the metal content can also vary greatly [24–29].

2 Synthesis of Carbon Nanocomposites

The synthesis of nanomaterials has been widely studied, mainly in regard to carbon nanotubes in view of the desire to obtain CNTs with high quality and at low cost. However, in recent years, many carbon compounds containing nanoparticles also have been studied and, as mentioned before, in many cases these compounds could present some advantages in several industrial applications. In this way, many studies on the synthesis process have been performed with the goal of obtaining compounds with good characteristics using techniques that take less time and require less-toxic reagents.

Carbon-based nanocomposites containing nanoparticles can be synthesised in several ways. The supports for the carbon nanoparticles can be produced, for example, using silica matrices [30–32], also through deposition, the CVD method, on the carbon mold [22]. Then, to remove the silica, the material is subjected to a solution containing hydrofluoric acid. In such cases, which produce a carbon matrix in the first step, the nanoparticles are usually introduced into the pores of

the matrix by wet impregnation and the composites are subjected to heat treatment. On the other hand, the carbon matrix and the nanoparticles can be produced in situ by, for example, the polymeric precursor method, used for both types of matrices, silica-based and carbon-based [24, 26, 33].

A system of nanomaterials that has received great attention lately is the so-called core-shell system, which consists of nanoparticles that form a core, the surface of which is coated with a thin layer of another material. Usually, this system has a core of a metal or oxide and a shell made of a carbonaceous or polymeric material, or even other oxides or metals. In these systems, the shell provides a layer that protects the core against oxidation, as in the case of nanocrystals of Fe (core)/iron oxide (shell) or Fe (core)/Au (shell), or to provide reactive capacity that does not represent the core alone [27, 34].

There are several types of synthetic routes for the synthesis of nanocomposites, among which are impregnations, the polymeric precursor, CVD, ball milling and sol-gel synthesis [24, 27, 35–37]. More than one method can be combined in different stages of the formation of nanocomposites, such as solvothermal and hydrothermal co-precipitation, or they can be combined with the reduction of metal through the use of a reducing agent [38, 39].

The method of wet impregnation can be used when one of the components of the composite, such as a silica matrix, for example, is already available. Normally, this procedure is performed in a solvent in which the separation of the particles is easy, such as a low molecular weight alcohol. Seo and co-workers [27] impregnated cations of Fe and Co into silica powder of high surface area. Later, they were reduced to a metallic state, at high temperature and atmosphere of H_2 . The procedure was followed by deposition of a thin carbon layer, from methane decomposition on the FeCo nanoalloy, by CVD method, methane decomposed on the FeCo nanoalloy. To make the compounds water-soluble, a non-covalent functionalisation step was applied using phospholipid-poly (ethylene glycol). The materials showed excellent magnetic activity and high stability, with applicability as a contrast agent [27].

The polymeric precursor method is widely used when to form a matrix containing well-dispersed nanoparticles, based on the Pechini [40] procedure. This method, involves the complexation of metal cations with a complexing agent such as citric acid and subsequent polymerisation by polyesterification reactions, using, for example, ethylene glycol as the polymerising agent. Carreño and colleagues developed a catalyst metal/carbon via the polymeric precursor route. After the synthesis of polymer resin, the material was calcined at high temperatures under inert N_2 atmosphere. In breach of the organic chains, the reducing atmosphere of CO formed was able to reduce the metals to the metallic state, thus forming composite metal nanoparticles in an amorphous carbon matrix in which nanoparticles of easily oxidised metals such as nickel and cobalt remained protected from oxidation [24, 41].

High-energy milling is a generic term that can be used to describe various grinding processes, such as mechanical alloying, mechanical milling or mechanochemical process, depending on the precursor powders used in the mix. In all cases, the activation process is mechanical. In this case, not only the mechanical friction is

important, but also the main reaction mechanism that is related to collision between the balls and powder processed. The grinding process is usually performed using a solvent such as isopropyl alcohol. This method is widely applied in the development of nanostructured metals and alloys and of ceramics [40, 42–44].

The sol–gel method of synthesis is very attractive for the synthesis of nanostructures containing more than one component, since the slow reaction kinetics allow good structural engineering of the final product. Another advantage is that the reactions are conducted at low temperatures or at room temperature. The sol–gel process involves inorganic precursors that undergo various chemical reactions, resulting in the formation of a three-dimensional molecular network. One of the most common routes is via hydrolysis and condensation of metal alkoxides to form larger metal oxide molecules that polymerize to form the coating. The sol–gel procedure allows coating of substrates with complex shapes on the nanometer to micrometer scale, which some commonly used coating procedures cannot achieve. The substrates include colloidal particles, organic/inorganic crystals, or even fibers and nanotubes [45–47].

The sol–gel method is also widely used for the synthesis of silica matrices. The silicon alkoxides are the most commonly used to create a sol–gel matrix such as the SiO_2/C prepared by Gushikem and colleagues [36], or even to enclose a network of nanoparticles in the xerogel [48].

Nanocomposites containing carbon nanotubes have been explored later. The addition of these nanotubes to various matrices, such as metal, for example, can improve the mechanical properties, like stiffness, wear and fatigue, and electrical properties in comparison to matrices without nanotubes [49]. Some years ago, it was observed the low wetting of the nanotubes in a metal matrix in the case of composites synthesised by hot pressing [50, 51]. Alternatively, powder coating processes can be employed with great success, making the distribution of carbon nanotubes more homogeneous. The chemical coating of carbon nanotubes by loads of metal nanoparticles has been widely used [52]. In this whole context, it is easy to see the importance of analytical control of these loads present in the nanotubes, as well as the proportions of metal/nanotube nanocomposites for the formation of technologically relevant materials, since small variations in these parameters can make big changes in the properties of the final product.

Graphene oxide (GO) nanosheets impregnated with silver nanoparticles (Ag NPs) were fabricated by the in situ reduction of adsorbed Ag + by hydroquinone in a citrate buffer solution. Paper-like Ag NP/GO composite materials were fabricated owing to convenient structure characterisation and antibacterial tests. Antibacterial activity was tested using *Escherichia coli* and *Staphylococcus aureus* as model strains of Gram negative and Gram positive bacteria, respectively. The as-prepared composites exhibit stronger antibacterial activity against both. The Ag NP/GO composites performed efficiently in bringing down the count of *E. coli* from 106 cfu/mL to zero with 45 mg/L GO in water. The micron-scale GO nanosheets (lateral size) enable them to be easily deposited on porous ceramic membranes during water filtration, making them a promising biocidal material for water disinfection. GO nanosheets can be viewed in the Fig. 2 [53].

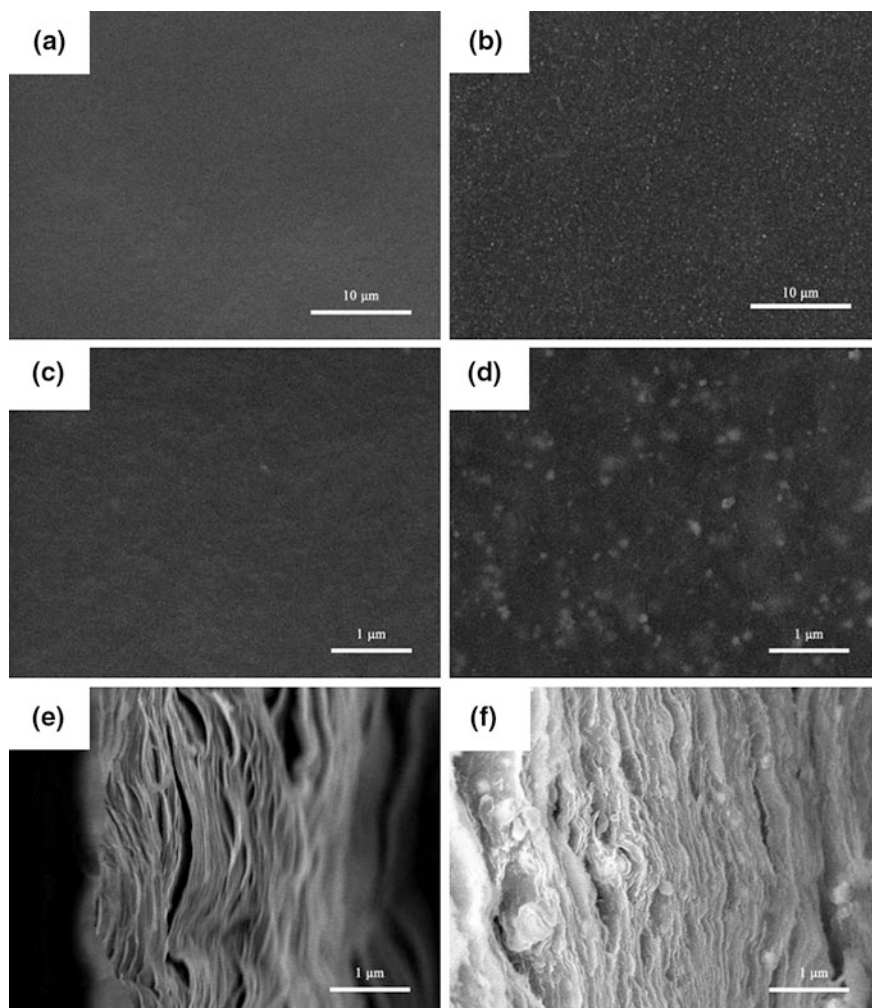


Fig. 2 *Top view FESEM images of (a and c) GO paper and (b and d) Ag NP/GO composite paper. Side-view FESEM images of the cross sections of (e) GO paper and (f) Ag NP/GO composite paper. Copyright (2011), with permission from Elsevier*

In other work, the authors synthesised one-dimensional rod-like nickel nanostructure fabricated through a simple, efficient and one-pot solvothermal approach with hydrazine hydrate and trimethylamine as reducing and morphology-directing agents. Magnetisation studies showed that the nanorod presents a distinct enhanced coercive force as a reflection of the 1 D nanostructure. Because of the high coercive force, we believe that the as-obtained Ni nanorod is suitable material for potential applications in magnetic storage devices and catalysis [54].

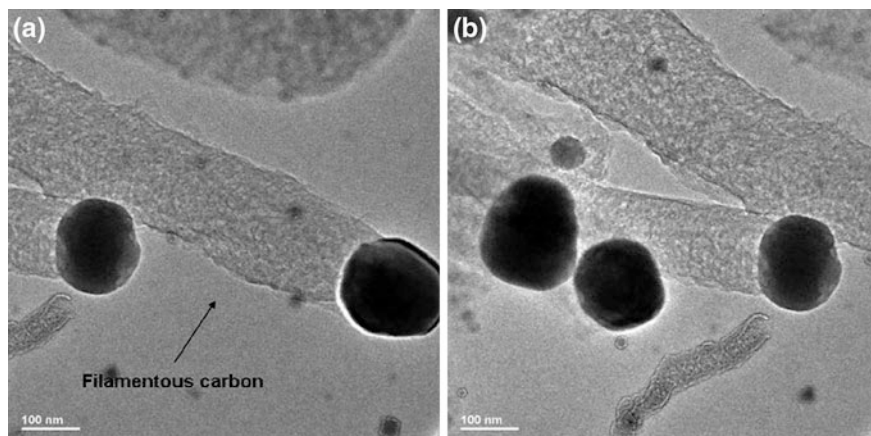


Fig. 3 TEM images of Ni/C catalyst after catalytic test at 500 °C. Copyright (2009), with permission from Elsevier

3 Applications of Carbon Nanocomposites

3.1 Catalytic Applications

Materials of various matrices containing various transition metals have been widely applied as catalysts [55, 56]. In the field of catalysts based on carbon, Tavasoli and coauthors [37] reported the synthesis of Co/CNT by sequential impregnation method, in order to investigate the interesting catalytic properties of this composite display. They varied the cobalt loadings from 15 to 40 wt %. The authors assessed the physicochemical characteristics and catalytic performance for Fischer–Tropsch synthesis and compared the results with an alumina-supported cobalt catalyst. The results showed that the hydrocarbon yield obtained by the CNT-supported cobalt catalyst is surprisingly much larger than those obtained from cobalt on other inorganic supports, and moreover the CNT caused a slight decrease in the reaction product distribution to lower molecular weight hydrocarbons.

Carreño et al. [24] synthesised nickel-carbon nanocomposites for use as catalysts for ethanol steam reforming. The authors proposed the use of castor oil as a carbon precursor in the synthesis. The results showed that nickel/carbon catalysts have a high activity for ethanol steam reforming. The authors concluded that catalytic activity was increased at high reaction temperatures, which may be associated with the formation of filamentous carbon. Images of nickel/carbon catalyst after their performance are displayed in Fig. 3.

It is important to note that this work shows an economical and environmentally friendly alternative to preparing catalysts from renewable resources, like castor oil, that are a low-cost, biomass-derived feedstock. This oil is obtained from extracting of the plant *Ricinus communis*, of the family *Euphorbiaceae* that grows in large quantities in most tropical and sub-tropical countries, such as Brazil [57].

3.2 *Sensors Applications*

Because of their excellent electrochemical properties, such as rapid electron kinetics, semi- and superconducting electron transport, high tensile strength composites, and hollow core suitable for storing guest molecules, CNTs have attracted attention as an electrode material for electrochemical sensors. Associating CNTs and conducting polymer with synergistic effect it's possible improve the electrical and mechanical properties of polymers in order to develop high performance sensor [4, 58].

Very recently, a sensor for determination of creatinine was produced. The biosensor was produced from a mixture of creatinine amidohydrolase, creatine amidino-hydrolase and sarcosine oxidase coimmobilised via N-ethyl-N0-(3-dimethylaminopropyl) carbodiimide and N-hydroxy succinimide onto nano-composite films of carboxylated-NTC/polyaniline electrodeposited on the surface of a platinum electrode. The sensor could detect creatinine in levels as low as 0.1 μM . The results showed that the use of a NTC/polyaniline composite to construct a creatinine biosensor led to improved analytical performance of the sensor, which required low power and possessed fast response times, high sensitivity and storage stability. The authors also suggested, based on the results, that this composite could be used to improve the performance of various other types of biosensors [59].

3.3 *Magnetic Applications*

Li et al. [38] studied uniform nitrogen-enriched, carbon-encapsulated nickel nanospheres obtained by a novel solvothermal method. The spheres as-prepared presented a core-shell structure with a nickel core surrounded by 10 nm thickness nitrogen-enriched carbon shell. Samples showed ferromagnetic behavior, due to the metallic nickel core. The introduction of the nitrogen element resulted in the surface modification of the encapsulating metal nanospheres, and this material, according to the authors, may play an important role in biomedical or other applications.

Sunny et al. [60] developed a simple and low-cost technique for obtaining highly stable, carbon-coated, nickel nanostructures at relatively low reaction temperatures. The nickel nanoparticles were obtained by a sodium borohydride reduction technique and coated with oleic acid. The samples were subjected to calcination at 873 K, in high purity nitrogen flow. This method obtained face-centered, cubic nickel nanoparticles with 5 nm thick carbon layers. The large saturation magnetisation combined with high stability make the nanoparticles suitable for use in functionalised drug targeting, as solid lubricants and electromagnetic shield materials (Fig. 4).

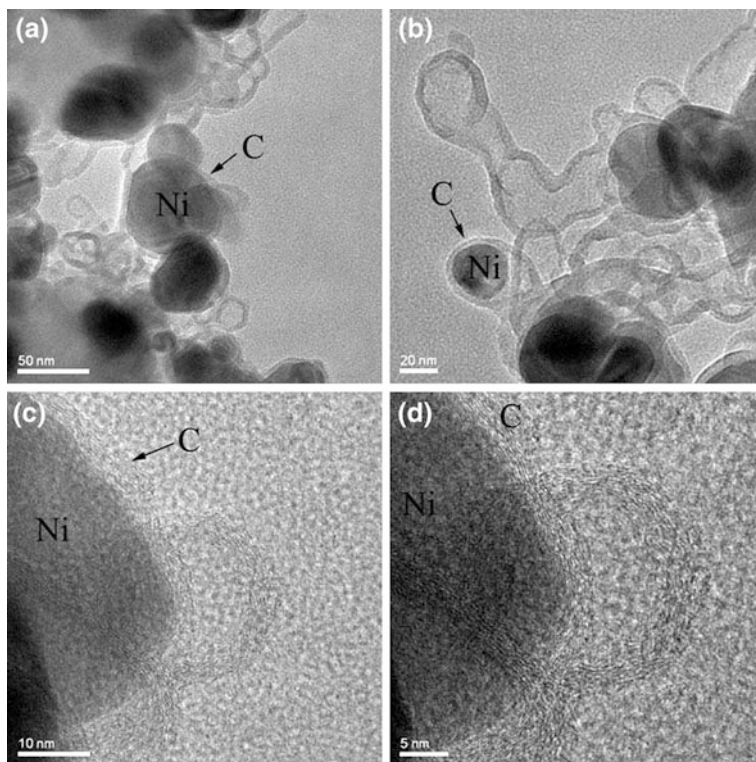


Fig. 4 TEM image (a–b) and HRTEM image (c–d) of Ni@C. Copyright (2009), with permission from Elsevier

Sunny et al. [39] still studied magnetic nickel/carbon hybrid nanostructures like a novel material with microwave absorbing properties. It was found that hybrid nanostructures are an effective microwave absorber with reflection loss less than -10 dB in the S and X-bands. The space charge polarization from the nickel carbon interface and intrinsic magnetic loss of the hybrid magnetic metal carbon nanostructures cause enhanced microwave absorbing properties

Powdered activated carbon (AC) has been the standard adsorbent for the reclamation of residential and industrial wastewaters for the recent decades [61, 62]. Associating these properties with magnetic properties, magnetic activated carbon (MAC) has been used to remove organic and inorganic pollutants [63, 64]. One recent example of these studies is the comparison between AC and MAC with regard to imidacloprid adsorption. MAC powder was formed from an iron oxide/AC composite. In conclusion, the authors observed less surface area and micropore volume for the magnetic powder; however, it was concluded that MAC powder can be successfully applied for the removal of environmental pollutants [65].

3.4 Biomedical Applications

Magnetic drug delivery, as proposed by Widder et al. [66], is a method by which a magnetically susceptible material coated with a drug-laden matrix is injected and then an externally placed magnet is used to guide the drug matrix to the target site. Several types of ferromagnetic materials have been used as matrices for application in drug delivery systems, as well as the magnetic separation of biomolecules. Composites of ferromagnetic material and activated carbon can be used for such purpose. The ferromagnetic material such as iron provides the magnetic properties, while activated carbon works as a drug-adsorption matrix. One of the methods [35] to prepare the magnetic target carrier is by a high-impact ball milling process in which fine Fe particles are welded to activated carbon by utilising the so-called mechanochemical effect. However, the major disadvantage is that it is easily separated into Fe and activated carbon while being transferred in veins. The first particles used for drug delivery were based on colloidal magnetite coated with cross linked albumin. These microspheres were used by Widder and coworkers [67] to encapsulate doxorubicin, and were captured magnetically in Yoshida sarcoma tumors implanted in rat tails. Since these first publications, several studies on biomedical applications were realised.

Most recently, in the same field of ferromagnetic metal/carbon composites, Rudge and coworkers studied a method to prepare composites of carbon/iron by a milling technique originally developed for making composite powders [68]. The authors obtained particles with size predominantly between 0.5 and 5.0 μm , which absorbed and desorbed doxorubicin, a potent chemotherapeutic with a narrow therapeutic index. Chemical analysis showed the particles to be composed primarily of carbon, iron and oxygen, with traces of phosphorous, hydrogen, nitrogen and sulfur, and parts per million of trace metals. This study demonstrates the importance of analytical investigation of systems used in biomedical applications.

Five years later, a carbon composite rich in fcc-Co and enclosed by carbon matrix was used as potential magnetic carrier [28]. The particles, which were made of cobalt and carbon, had high surface area for drug adsorption and sufficient magnetic susceptibility for targeting the composite through the use of an external magnet. Before using the cobalt, the authors attempted to use iron to synthesize the material for ion exchange, but the Fe^{2+} oxidized to Fe^{3+} during the ion exchange. Therefore, cobalt which also shows strong magnetic properties was selected. The Co-C composite formed was a spherical 250-300 μm size particle. The spherical particles were ground to a fine powder.

In the biomedical field, the CNTs also have received great attention. Many applications for CNTs have been proposed, including biosensors, drug and vaccine delivery vehicles and novel biomaterials [69]. CNTs can be used as nanofillers in existing polymeric materials to both dramatically improve mechanical properties and create highly anisotropic nanocomposites [70, 71]. They can also be used to create electrically conductive polymers and tissue engineering constructs with the capacity to provide controlled electrical stimulation [72, 73].

An example of the utility of CNTs in biomedicine is their relatively large length-to-diameter aspect ratio (which can exceed 106, with an average length of 1 mm and diameter of ~ 1 nm) with a very large surface area, which makes CNTs attractive for high sensitivity molecular detection and recognition. Consequently, a large fraction of the CNT surface can be modified with functional groups of various complexities, which would modulate CNTs' *in vivo* and *in vitro* behavior [74].

As CNTs are intrinsically not water soluble, modification through chemical functionalisation using suitable dispersants and surfactants can enhance solubility to the range of g/mL4 and is essential for their controlled dispersion. For example, constituent polar molecules can render CNTs soluble, whereas nonpolar moieties make CNTs immiscible. Such processes have proved especially important in that nonsolubilised CNTs have been found to cause cell death in culture [75–77].

Each CNT could be intrinsically different due to limitations on the fabrication of structurally identical CNTs with minimal impurities [55]. Subtle variations in local and overall charge, catalyst residue (typically Fe, Co, and Ni), and length of individual nanotubes are three representative issues that preclude precise use of CNTs in the biomedical sciences.

4 Characterisation of Carbon Nanocomposites

With the advent of nanotechnology for developing new materials with a wide variety of special properties, there is a need for greater control of the characteristics of these compounds and also the impurities that could be present, as these new materials have been used for very different applications in almost all fields of technology. The principal techniques for analysis of the composition and structure of nanocomposites are scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray (EDX) spectroscopy [38]. The EDX technique has been widely used to identify metals and/or contaminants in nanocomposites. Sunny et al. used this technique to verify the presence or absence of contaminants in carbon nanotubes. SEM is used to investigate the morphology of nanocomposites. Using the SEM technique, it is possible to observe the surface defects of the material [38, 39, 60–63].

Another technique that is widely used for characterisation of nanocomposites is XPS [64, 65]. This technique can be applied to detect the presence of the elements in the material surface. Maldonado et al. used the XPS technique to evaluate the compositional and structural properties of carbon nanotubes doped with N₂ [66]. XPS spectroscopy was used to investigate fluorine's interaction with the surfaces of nanocompounds. In this study, a MWCNT, SWCNT and a fiber were fluorinated in F₂- and ClF₃ atmosphere at room temperature [35].

Taking into account that metal impurities can affect the physical, chemical and surface properties of carbon nanocomposites and could complicate or prevent their use for industrial applications, it is important to control this type of contamination [78–81]. In addition, it is important to emphasise that there are many applications

of carbon nanocomposites in medicine and related areas, and impurities in these materials could cause many risks to human health [82, 83]. Since the presence of metallic impurities can increase the potential risk of using carbon nanocomposites, it is necessary to develop methods to identify metallic elements in low concentrations in these materials [78, 84].

The techniques employed for the determination of metal impurities include atomic spectrometry, for which the samples are most commonly prepared as aqueous solutions. This poses a problem for the determination of impurities in carbon nanocomposites, since these materials are difficult to dissolve due to their structure [85, 86].

Some authors describe different sample preparation methods for carbon nanotubes, including dry ashing, microwave-induced combustion (MIC) or microwave-assisted wet digestion using a mixture of nitric and perchloric acid or with hydrogen peroxide for subsequent determination of Al, Cu, Cr, Fe, Mn, Mo, Ni, Zn and halogens by inductively coupled plasma optical emission spectrometry (ICP OES), by inductively coupled plasma mass spectroscopy (ICP-MS) and by ion chromatography (IC) [87–89]. Additionally, the authors purposed the use of direct solid sampling electrothermal atomic absorption spectroscopy (DSS-ET AAS) for the determination of Al, Cd, Co, Cr, Cu, Mg, Mn and Pb in SWCNTs and MWCNTs [87]. However, for the determination of metals in carbon nanocomposites, there are no applications in literature, so methods should be developed to improve the quality control of these kinds of materials.

5 Conclusion

The increase in the applications of carbon compounds, especially in industry and medicine, requires the development of suitable synthesis processes and also analytical methods for quality control of these compounds. The techniques used to determine the presence of metals in carbon compounds and the sample preparation technique for quantification of such metals should be selected based on factors such as the time required for analysis, simplicity of the procedure, reagent consumption, sample mass, waste generation and low range limits of detection. Regardless of the chosen methodology, studies in the literature point to the need for the determination of metal contaminants in carbon compounds, since some elements that have been found in relatively high levels can interfere with human health or affect the properties of materials intended for industrial applications.

Acknowledgments The authors are thankful for the financial support of Brazilian research financing institutions: CAPES, CNPq and FAPESP

References

1. Tiede, K., Boxall, A.B.A., Tear, S.P., Lewis, J., David, H., Hasselov, M.: Food additives and contaminants part a-chemistry analysis control exposure and risk. *Assessment* **25**(7), 795–821 (2008)
2. Jiang, J.K., Oberdorster, G., Biswas, P.: *J. Nanopart. Res.* **11**(1), 77–89 (2009)
3. Huczko, A.: *Appl. Phys. Mater. Sci. Process.* **74**(5), 617–638 (2002)
4. Iijima, S.: *Nature* **354**(6348), 56–58 (1991)
5. Miyagawa, H., Misra, M., Mohanty, A.K.: *J. Nanosci. Nanotechnol.* **5**(10), 1593–1615 (2005)
6. Jeong, W., Kessler, M.R.: *Chem. Mater.* **20**(22), 7060–7068 (2008)
7. Bianco, A., Kostarelos, K., Prato, M.: *Curr. Opin. Chem. Biol.* **9**(6), 674–679 (2005)
8. Maynard, A.D., Aitken, R.J., Butz, T., Colvin, V., Donaldson, K., Oberdorster, G., Philbert, M.A., Ryan, J., Seaton, A., Stone, V., Tinkle, S.S., Tran, L., Walker, N.J., Warheit, D.B.: *Nature* **444**(7117), 267–269 (2006)
9. Oberdorster, G., Oberdorster, E., Oberdorster, J.: *Environ. Health Perspect.* **113**(7), 823–839 (2005)
10. Wang, Z.L., Poncheral, P., de Heer, W.A.: in *Nanostructures Systems* (1999), 14–18
11. Ajayan, P.M., Stephan, O., Colliex, C., Trauth, D.: *Science* **265**(5176), 1212–1214 (1994)
12. Bower, C., Rosen, R., Jin, L., Han, J., Zhou, O.: *Appl. Phys. Lett.* **74**(22), 3317–3319 (1999)
13. Jin, L., Bower, C., Zhou, O.: *Appl. Phys. Lett.* **73**(9), 1197–1199 (1998)
14. Ku, B.K., Emery, M.S., Maynard, A.D., Stolzenburg, M.R., McMurphy, P.H.: *Nanotechnology* **17**(14), 3613–3621 (2006)
15. Wang, H., Xu, Z., Eres, G.: *Appl. Phys. Lett.* **88**(21), 213111 (2006)
16. International Standard Organization: In ISO/TS 27687:2008. Switzerland, Geneva (2008)
17. Gorria, P., Sevilla, M., Blanco, J.A., Fuertes, A.B.: *Carbon* **44**(10), 1954–1957 (2006)
18. Jin, J., Li, R., Wang, H.L., Chen, H.N., Liang, K., Ma, J.T.: *Chem. Commun.* **4**, 386–388 (2007)
19. Lu, A.H., Schmidt, W., Matoussevitch, N., Bonnemann, H., Spliethoff, B., Tesche, B., Bill, E., Kiefer, W., Schuth, F.: *Angewandte Chemie Int Ed.* **43**(33), 4303–4306 (2004)
20. Park, I.S., Choi, M., Kim, T.W., Ryoo, R.: *J. Mater. Chem.* **16**(33), 3409–3416 (2006)
21. Yang, N., Zhu, S.M., Zhang, D., Xu, S.: *Mater. Lett.* **62**(4–5), 645–647 (2008)
22. Zlotea, C., Chevalier-Cesar, C., Leonel, E., Leroy, E., Cuevas, F., Dibandjo, P., Vix-Guterl, C., Martens, T., Latroche, M.: *Faraday Discuss.* **151**, 117–131 (2011)
23. Tarasov, K., Beaunier, P., Che, M., Marceau, E., Li, Y.L.: *J. Nanopart. Res.* **13**(5), 1873–1887 (2011)
24. Carreno, N.L.V., Garcia, I.T.S., Raubach, C.W., Krolow, M., Santos, C.C.G., Probst, L.F.D., Fajardo, H.V.: *J. Power Sources* **188**(2), 527–531 (2009)
25. Ao, Y., Xu, J., Fu, D., Shen, X., Yuan, C.: *Sep. Purif. Technol.* **61**(3), 436–441 (2008)
26. Carreno, N.L.V., Garcia, I.T.S., Leite, E.R., Longo, E., Lucena, P.R., Carreno, L., Barreto, L.S., Santos, R.: *Mater. Lett.* **61**(16), 3341–3344 (2007)
27. Seo, W.S., Lee, J.H., Sun, X.M., Suzuki, Y., Mann, D., Liu, Z., Terashima, M., Yang, P.C., McConnell, M.V., Nishimura, D.G., Dai, H.J.: *Nat. Mater.* **5**(12), 971–976 (2006)
28. Sharma, A., Nakagawa, H., Miura, K.: *Carbon* **44**(10), 2089–2091 (2006)
29. Zhai, Y., Dou, Y., Liu, X., Park, S.S., Ha, C.-S., Zhao, D.: *Carbon* **49**(2), 545–555 (2010)
30. Ehrburger-Dolle, F., Morfin, I., Geissler, E., Bley, F., Livet, F., Vix-Guterl, C., Saadallah, S., Parmentier, J., Reda, M., Patarin, J., Iliescu, M., Werckmann, J.: *Langmuir* **19**(10), 4303–4308 (2003)
31. Ryoo, R., Joo, S.H., Jun, S.: *J. Phys. Chem. B* **103**(37), 7743–7746 (1999)
32. Vix-Guterl, C., Boulard, S., Parmentier, J., Werckmann, J., Patarin, J.: *Chem. Lett.* **10**, 1062–1063 (2002)
33. Leite, E.R., Carreno, N.L.V., Longo, E., Pontes, F.M., Barison, A., Ferreira, A.G., Maniette, Y., Varela, J.A.: *Chem. Mater.* **14**(9), 3722–3729 (2002)

34. Figuerola, A., Di Corato, R., Manna, L., Pellegrino, T.: *Pharmacol. Res.* **62**(2), 126–143 (2010)
35. Benjamin, J.S.V., Volin, T.E.: *Met. Trans.* **5**, 1929–1934 (1974)
36. Rahim, A., Barros, S.B.A., Arenas, L.T., Gushikem, Y.: *Electrochim. Acta* **56**(3), 1256–1261 (2011)
37. Tavasoli, A., Sadagiani, K., Khorashe, F., Seifkordi, A.A., Rohaniab, A.A., Nakhaeipour, A.: *Fuel Process. Technol.* **89**(5), 491–498 (2008)
38. Li, X.L., Tian, X.L., Zhang, D.W., Chen, X.Y., Liu, D.J.: *Materials science and engineering B-advanced functional. Solid-State Mater* **151**(3), 220–223 (2008)
39. Sunny, V., Kumar, D.S., Mohanan, P., Anantharaman, M.R.: *Mater. Lett.* **64**(10), 1130–1132 (2010)
40. Cava, S., Beninca, R., Tebcherani, S.M., Souza, I.A., Paskocimas, C.A., Longo, E., Varela, J.A.: *J. Sol–Gel. Sci. Technol.* **43**(1), 131–136 (2007)
41. Carreno, N.L.V., Leite, E.R., Longo, E., Lisboa, P.N., Valentini, A., Probst, L.F.D., Schreiner, W.H.: *J. Nanosci. Nanotechnol.* **2**(5), 491–494 (2002)
42. Carreno, N.L.V., Maciel, A.P., Leite, E.R., Lisboa, P.N., Longo, E., Valentini, A., Probst, L.F.D., Paiva-Santos, C.O., Schreiner, W.H.: *Sensors and Actuators B-Chemical* **86**(2–3), 185–192 (2002)
43. Koch, C.C.: *Nanostruct. Mater.* **9**(1–8), 13–22 (1997)
44. Subrt, J., Perez-Maqueda, L.A., Criado, J.M., Real, C., Bohacek, J., Vecernikova, E.: *J. Am. Ceram. Soc.* **83**(2), 294–298 (2000)
45. Benvenutti, E.V., Moro, C.C.M., Costa, T.M.H., Gallas, M.R.: *Quím. Nova* **32** (7), 1926–1933 (2009)
46. Chen, Q., Boothroyd, C., Soutar, A.M., Zeng, X.T.: *J. Sol-Gel. Sci. Technol.* **53**(1), 115–120 (2010)
47. Ocana, M., Hsu, W.P., Matijevic, E.: *Langmuir* **7**(12), 2911–2916 (1991)
48. Laranjo, M., Kist, T., Benvenutti, E., Gallas, M., Costa, T.: *J. Nanopart. Res.* **13**(10), 4987–4995 (2011)
49. Daoush, W.M.: *Powder Metall. Met. Ceram.* **47**(9–10), 531–537 (2008)
50. Caturla, F., Molina, F., MolinaSabio, M., RodriguezReinoso, F., Esteban, A.: *J. Electrochem. Soc.* **142**(12), 4084–4090 (1995)
51. Dujardin, E., Ebbesen, T.W., Hiura, H., Tanigaki, K.: *Science* **265**(5180), 1850–1852 (1994)
52. Moustafa, S.F., Daoush, W.M.: *J. Mater. Process. Technol.* **181**(1–3), 59–63 (2007)
53. Bao, Q., Zhang, D., Qi, P.: *J. Colloid Interface Sci.* **360**(2), 463–470 (2011)
54. Alagiri, M., Muthamizhchelvan, C., Ponnusamy, S.: *Mater. Lett.* **65** (11), 1565–1568
55. Steen, V., Prinsloo, E.F.F.: *Catalysis Today* **71** (3–4), 327–334 (2002)
56. Tavasoli, A., Sadaghiani, K., Nakhaeipour, A., Ahangari, M.: *Iran. J. Chem. Chem. Eng. Int. Engl Ed* **26**(1), 9–16 (2007)
57. Ogunniyi, D.S.: *Bioresour. Technol.* **97**(9), 1086–1091 (2006)
58. Wei, C.Y., Srivastava, D., Cho, K.J.: *Nano Lett.* **2**(6), 647–650 (2002)
59. Yadav, S., Kumar, A., Pundir, C.S.: *Anal. Biochem.* **419** (2), 277–283
60. Sunny, V., Sakthi Kumar, D., Yoshida, Y., Makarewicz, M., TabiÄ, W., Anantharaman, M. R.: *Carbon* **48** (5), 1643–1651 (2010)
61. Hamadi, N.K., Swaminathan, S., Chen, X.D.: *J. Hazard. Mater.* **112**(1–2), 133–141 (2004)
62. Misirli, T., Bicer, I.O., Mahramanlioglu, M.: *Fresenius Environ. Bull.* **13**(10), 1010–1015 (2004)
63. Oliveira, L.C.A., Rios, R., Fabris, J.D., Garg, V., Sapag, K., Lago, R.M.: *Carbon* **40**(12), 2177–2183 (2002)
64. Xing, W., Zhuo, S.P., Gao, X.L.: *Mater. Lett.* **63**(13–14), 1177–1179 (2009)
65. Zahoor, M., Mahramanlioglu, M.: *Chem. Biochem. Eng. Q.* **25**(1), 55–63 (2011)
66. Widder, K.J., Senyei, A.E., Scarpelli, D.G.: *Proc. Soc. Exp. Biol. Med.* **58**, 141–146. (1978)
67. Widder, K.J., Morris, R.M., Poore, G.A., Howard, D.P., Senyei, A.E.: *Eur. J. Cancer Clin Oncol.* **19**(1), 135–139 (1983)

68. Rudge, S.R., Kurtz, T.L., Vessely, C.R., Catterall, L.G., Williamson, D.L.: *Biomaterials* **21**(14), 1411–1420 (2000)
69. Lin, Y., Taylor, S., Li, H.P., Fernando, K.A.S., Qu, L.W., Wang, W., Gu, L.R., Zhou, B., Sun, Y.P.: *J. Mater. Chem.* **14**(4), 527–541 (2004)
70. Koerner, H., Price, G., Pearce, N.A., Alexander, M., Vaia, R.A.: *Nat. Mater.* **3**(2), 115–120 (2004)
71. Sen, R., Zhao, B., Perea, D., Itkis, M.E., Hu, H., Love, J., Bekyarova, E., Haddon, R.C.: *Nano Lett.* **4**(3), 459–464 (2004)
72. Grunlan, J.C., Mehrabi, A.R., Bannon, M.V., Bahr, J.L.: *Adv. Mater.* **16** (2), 150–153, (2004)
73. Supronowicz, P.R., Ajayan, P.M., Ullmann, K.R., Arulanandam, B.P., Metzger, D.W., Bizios, R.: *J. Biomed. Mater. Res.* **59**(3), 499–506 (2002)
74. Firme, C.P., Bandaru, P.R.: *Nanomed. Nanotechnol. Biol. Med.* **6**(2), 245–256 (2010)
75. Lu, Q., Moore, J.M., Huang, G., Mount, A.S., Rao, A.M., Larcom, L.L., Ke, P.C.: *Nano Lett.* **4**(12), 2473–2477 (2004)
76. Sayes, C.M., Liang, F., Hudson, J.L., Mendez, J., Guo, W.H., Beach, J.M., Moore, V.C., Doyle, C.D., West, J.L., Billups, W.E., Ausman, K.D., Colvin, V.L.: *Toxicol. Lett.* **161**(2), 135–142 (2006)
77. Zhang, L.W., Zeng, L.L., Barron, A.R., Monteiro-Riviere, N.A.: *Int. J. Toxicol* **26**(2), 103–113 (2007)
78. Hou, P.X., Liu, C., Cheng, H.M.: *Carbon* **46**(15), 2003–2025 (2008)
79. Ismail, A.F., Goh, P.S., Tee, J.C., Sanip, S.M., Aziz, M.: *NANO* **3**(3), 127–143 (2008)
80. Tasis, D., Tagmatarchis, N., Bianco, A., Prato, M.: *Chem. Rev.* **106**(3), 1105–1136 (2006)
81. Trojanowicz, M.: *Trac-Trends Anal. Chem.* **25**(5), 480–489 (2006)
82. Hurt, R.H., Monthieux, M., Kane, A.: *Carbon* **44**(6), 1028–1033 (2006)
83. Liu, X., Guo, L., Morris, D., Kane, A.B., Hurt, R.H.: *Carbon* **46**(3), 489–500 (2008)
84. Braun, T., Rausch, H., Biro, L.P., Konya, L., Kiricsi, I.: *J. Radioanal. Nucl. Chem.* **262**(1), 31–34 (2004)
85. Banks, C.E., Crossley, A., Salter, C., Wilkins, S.J., Compton, R.G.: *Angewandte Chemie-Int. Ed.* **45**(16), 2533–2537 (2006)
86. Pumera, M.: *Langmuir* **23**(11), 6453–6458 (2007)
87. Mello, P.A., Rodrigues, L.F., Nunes, M.A.G., Mattos, J.C.P., Muller, E.I., Dressler, V.L., Flores, E.M.M.: *J. Braz. Chem. Soc.* **22**(6), 1040–1062 (2011)
88. Mortari, S.R., Cocco, C.R., Bartz, F.R., Dressler, V.L., Flores, E.M.D.: *Anal. Chem.* **82**(10), 4298–4303 (2010)
89. Pereira, J.S.F., Antes, F.G., Diehl, L.O., Knorr, C.L., Mortari, S.R., Dressler, V.L., Flores, E.M.M.: *J. Anal. At. Spectrom.* **25**(8), 1268–1274 (2010)

NanoCarbon 2011

Selected works from the Brazilian Carbon Meeting

Avellaneda, C. (Ed.)

2013, VIII, 140 p., Hardcover

ISBN: 978-3-642-31959-4