Lecture Notes in Nanoscale Science and Technology 11

Stefano Bellucci *Editor*

Physical Properties of Ceramic and Carbon Nanoscale Structures

The INFN Lectures, Vol. II

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In Memory of the Late Giorgio Bellucci
(1931–2009)

Preface

This is the second volume in a series of books on selected topics in Nanoscale Science and Technology based on lectures given at the well-known INFN schools of the same name. The aim of this collection is to provide a reference corpus of suitable, introductory material to relevant subfields, as they mature over time, by gathering the significantly expanded and edited versions of tutorial lectures, given over the years by internationally known experts.

The Nanotechnology group at INFN – LNF organizes since 2000 a series of international meetings in the area of nanotechnology. The conferences in 2006 and 2008 were devoted to recent developments in nanoscience and its manifold technological applications. They included of a number of tutorial/keynote lectures, which are reflected in this volume, besides research talks presenting frontier nanoscience research developments and innovative nanotechnologies in the areas of biology, medicine, aerospace, optoelectronics, energy, materials and characterizations, low-dimensional nanostructures and devices. Selected papers, based on conference talks and related discussions, were published on dedicated issues of international journals.

Special poster and equipment session were devoted to the exhibit by various firms of their institutional activities in selected areas of application where nanoscience can have a deep impact. There was also the possibility for sample testing by the participants. *Tutorial lectures were delivered at the School, addressing general and basic questions about nanotechnology, such as what they are, how does one go about them, what purposes can they serve.* In tutorial sessions the nature of nanotechnology, the instruments of current use in its characterizations and the possible applicative uses were *described at an introductory level.*

The Conferences covered a large range of topics of current interest in nanoscience and nanotechnology, including aerospace, defence, national security, biology, medicine, electronics. This broad focus is reflected in the decision to publish different areas of application of these technologies in different volumes. The present set of notes results in particular from the participation and dedication of prestigious lecturers, such as Andrzej Huczko, Nicola Pugno Alexander Malesevic, Stefano Bellucci. All lectures were subsequently carefully edited and reworked, taking into account the extensive follow-up discussions at the Conferences.

A tutorial lecture by *Andrzej Huczko* and collaborators (Warsaw University, Poland) shows how different carbon and ceramic nanostructures (nanotubes,

nanowires, nanofibres, nanorods, and nanoencapsulates) have a great potential for improving our understanding of the fundamental concepts of the roles of both dimensionality and size on physical properties, as well as for many potential applications. *Stefano Bellucci* and *Pasquale Onorato* (INFN-LNF, Italy) engaged in an extensive review of the transport properties in carbon nanotubes, encompassing a description of the electronic structure from graphene to single-wall nanotubes, the quantum transport in such systems, as well as the description of experimental evidence of superconductivity in carbon nanotubes and the corresponding theoretical interpretation. *Nicola Pugno* (Turin Polytechnic University, Italy), in the first of his contributions, goes about new laws to design futuristic self-cleaning, super-adhesive and releasable hierarchical smart materials, as well as large invisible cables, based on carbon nanotube technology. He also reviewed the mechanical strength of nanotubes and megacables, with an eye to the challenging project of the carbon nanotube-based space elevator megacable. In this second contribution, he outlined the role on the fracture strength of thermodynamically unavoidable atomistic defects with different size and shape, both numerically (with *ad hoc* hierarchical simulations) and theoretically (with quantized fracture theories), for nanotubes and nanotube bundles. Focusing on graphitic allotropes, the chapter by *Stefano Bellucci* and *Alexander Malesevic* tries to give a taste of the widespread implications carbon nanostructures have on research and applications, starting from an historical overview, followed by a discussion of the structure of carbon nanotubes and graphene, over viewing several different synthesis techniques and illustrating the physical properties of these innovative materials, before summarizing their broad range of applications.

In concluding this effort, I wish to thank all lecturers, and especially those who contributed to the present second volume in this series, as well as speakers and participants to the n&n 2006 and n&n 2008 Conferences, for having contributed to create a pleasant and productive atmosphere, fostering the settling of pervasive collaborative spirit and pedagogical drive. I am confident that this first set of lectures, in turn, will provide an opportunity for those who are just now beginning to get involved with nanoscience and nanotechnology, allowing them to get contacts and prime, up-to-date information from the experts. I also wish to acknowledge the enduring dedication and caring support of my wife Gloria and our great daughters Costanza, Eleonora, Annalisa, Erica and Maristella, which allowed me to put this volume together.

Frascati, Italy
May 2010

Stefano Bellucci

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Contents

Formation and Characterization of Carbon and Ceramic Nanostructures

Andrzej Huczko, Michał Bystrzejewski, Hubert Lange, and Piotr Baranowski

Abstract Different carbon and ceramic nanostructures (nanotubes, nanowires, nanofibres, nanorods, and nanoencapsulates) have great potential for improving our understanding of the fundamental concepts of the roles of both dimensionality and size on physical properties, as well as for many potential applications. Carbon nanotubes (CNTs) were produced in carbon arc plasma using different starting carbons, as the anode material. Low-graphitized carbons (including carbon black) proved to be much more efficient comparing to the regular graphite material. The optical emission and absorption spectroscopy was used for spectral diagnostics of the carbon arc. Carbon arc was also used to produce carbon onions containing magnetic nanocrystallites (Fe and magnetic alloys) in the core. The process was optimized and the procedure to isolate encapsulates was elaborated. Carbon nanocapsules containing Fe were also obtained via combustion synthesis from mixtures NaN_3-C_6Cl_6-Ferrocene. This technique also proved to be very efficient to produce silicon carbide nanowires from Teflon (PTFE) and different reductants ($CaSi_2$, Si). The protocol to isolate and efficiently purify the final product (up to 98 wt%) was proposed.

Synthesis of Carbon Nanotubes in Carbon Arc

We have studied the CNTs synthesis by using the arc discharge technique as well non-equilibrium plasmas, e.g., [1–12]. The aim of those studies was also the plasma diagnostics based mainly on optical emission spectroscopy (OES), e.g. [13–18].

In this work we summarize our recent research in which the influence of carbon electrode structure on effectiveness of single-walled carbon nanotubes (SWCNTs) formation in the carbon arc discharge under the presence of catalysts

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was investigated. This study was undertaken after Zhao et al. [19] had shown that using the arc discharge with Fe-doped graphite anode generated in Ar-H_2 atmosphere one can obtain macroscopically oriented web-like product which appeared to be very rich in high quality SWCNTs. The authors showed also that the as–obtained bulk product can be easily purified from catalyst by a liquid-phase process on a macroscale [20]. In fact, Fe and other transition metals, e.g. Co, has already been used for SWCNTs synthesis via arc discharge method for a long time [21, 22]. However, we did not succeed while trying to reproduce this process. Since all the experimental conditions were nearly the same, including the origin of the electrodes (Toyo Tanso Comp.), the only reasonable explanation of the high process yield seemed to be related to different properties of the electrode materials. Indeed, it was established that the electrodes were of different batches and different preparation receipts. Thus, the diversity could be related to the electrodes structure in a nanometric scale. To elucidate the mentioned mysterious effect a number of tests were performed with different anode materials and gas atmospheres. The experiments and results are discussed below.

Along with CNTs synthesis, we extended our research by using optical emission (OES) and absorption (OAS) spectroscopy for the diagnostics of carbon arc.

Experimental

The experimental system has been described in details elsewhere [23]. The most important feature of our arc reactor is a possibility of automatic control of the arc gap within 1 and 2 mm and its position on the optical axis of a system for plasma spectroscopy measurements. The pressure was also controlled in the reactor chamber during the synthesis. Different types of Fe-doped (ca. 1 at.% Fe) electrodes were tested in the process of SWCNTs synthesis which was carried out in Ar, Kr, Xe, Ne and N_2-H_2 (40 vol%) gas mixtures. First, all the starting electrodes differed with degree of graphitization, namely with the size of primary particles. The XRD patterns of the electrode materials are shown in Fig. 1. Well- and medium-graphitized

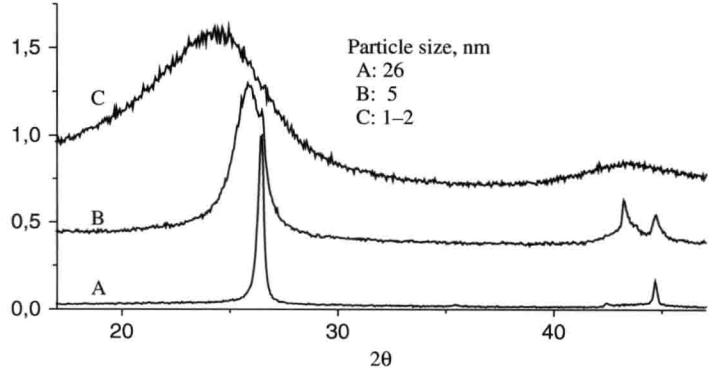

Fig. 1 XRD patterns of starting carbon electrodes

and amorphous electrodes, A, B and C, respectively, doped with Fe, Ni or Co catalysts were sublimated in the arc. The electrodes C were home made from industrial carbon black (IRB) mixed with a tar pitch and catalysts. The electrodes were baked at 1,300 K.

Both A and B electrodes were Toyo Tanso Comp. (Japan) products. The profile of XRD curve B in Fig. 1 points to a fact that this electrodes is composed of a mixture of low as well highly graphitized carbon. The arc discharge current varied between 10 and 50 A and pressure in the reactor chamber was kept constant at about 300 mb.

The morphology and characteristics of the carbon products were investigated using SEM, TEM and Raman spectroscopy techniques.

The plasma diagnostics was performed by a combined optical emission and absorption spectroscopy. Both techniques were applied to 0–0 bands of d $^3\Pi_g$–a $^3\Pi_u$ and B $^2\Sigma^+$–X $^2\Sigma^+$ spectra of C_2 and CN radicals, respectively. The absorption spectroscopy was also used for the detection of iron atoms.

Since our OES method has been frequently used and described in details elsewhere [15–17, 24], here we highlight only the most important points of the OAS method, which we began to use recently. The aim of OAS was to detect CN, C_2 radicals and Fe atoms in the arc plasma periphery, i.e. in the so-called dark plasma zone. To the best of our knowledge such measurements related to carbon arc plasma under condition of carbon nanostructures formation have never been performed so far. Shortly, the method is based on a calculation of respective absorption spectra assuming different temperatures and optical depths. The latter ones were expressed by column densities.

The spectral absorption is define as $A_\nu = 1 - \exp(-\kappa_\nu l)$, where $\kappa_\nu = \sum \kappa_\nu^J$ is the spectral absorption coefficient at a given frequency ν, which is a function of temperature and column density of the absorbing species. The summation obviously covers contribution from all the rotational line of components situated in the vicinity of a given frequency ν. The calculations were performed taking into account collision and Doppler broadening by the use of the Voigt profile. The as-calculated absorption spectra were convoluted with the Gaussian apparatus function of 0.023 nm in width at the half-maximum. An examples of a simulated CN absorption spectrum, assuming temperature equal to 3,500 K and column density 10^{15} cm^{-2}, along with an experimental spectrum are shown in Fig. 2, *left* and *right*, respectively.

The absorption was recorded on the background of a continuum spectrum emitted by a Xe arc lamp. Because of a light modulation caused by interference at the protected window located in front of a CCD detector, both experimental and calculated spectra had to be smoothed within the 0.052 nm spectral window. The as-filtered spectra are represented by thick lines in Fig. 2. The absorption at maximum 0–0 band served as a measure of CN column density. Examples of absorption growth curves, including 1–1 band head, for two temperatures 2,000 and 4,000 K are shown in Fig. 3.

Let us note that the absorption at the 0–0 band head does not vary much with temperature and therefore can be used for CN(v = 0) column density determination

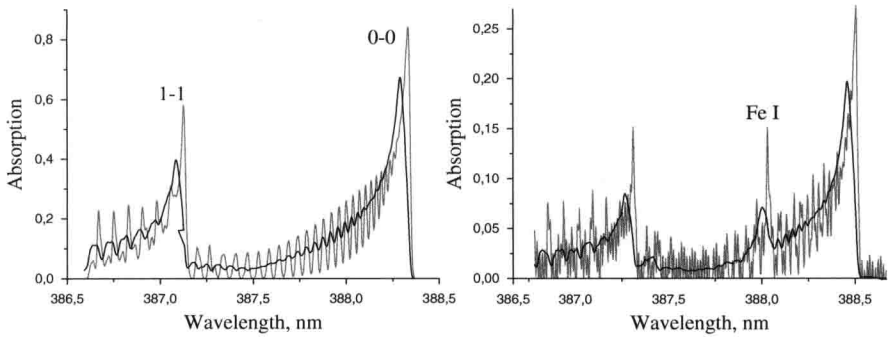

Fig. 2 Calculated (T = 3,500 K, nl = 10^{15} cm^{-2}) and experimental spectra of CN(B $^2\Sigma^+$ X $^2\Sigma^+$)

with a high precision. On the other hand a significant variation of the absorption at 1–1 band head can be used for temperature determination through the ratio of the absorption at 1–1 to 0–0 band heads. This ratio, however, changes also with the column density. Therefore temperature can be derived on the basis of the ratio only in the case of a sufficiently weak absorption. The same procedure for detection of C_2 by OAS was applied in [25].

In Fig. 2 (*right*) one can also find an absorption line at 387.8 nm which corresponds to absorption by Fe I atoms in the a $^5D_2$ state. There are also some other iron absorption lines and one of them, namely at 388.62 nm, which appears not to be overlapped by any neighboring lines, was chosen for quantitative Fe I (a $^5D_3$) measurements. For such a purpose a similar absorption growth curves were constructed.

It is worth to mention here that all such calculations can be quite easy performed by using the Matlab software.

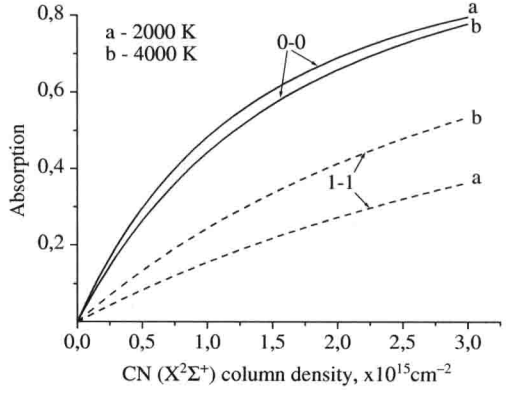

Fig. 3 Absorption growth curves at 0–0 and 1–1 CN(X $^2\Sigma^+ \rightarrow$ B $^2\Sigma^+$) band heads

Results and Discussion

Carbon Nanotubes

As it was already mentioned, the SWNTs were produced with a high yield when the electrodes with the smallest primary particles, i.e. the electrode B and C (Fig. 1) were arc sublimated [12]. Then the product was almost entirely in a web-form. Such a web was obtained in Ar-H_2 and in N_2-H_2 gas mixtures when electrodes B and C contained Fe catalyst. The photos of the web are shown in Fig. 4.

Let us note that the very fine web starts growing just at the electrode tip. It can be on the cathode as well on the anode, *left* and *right* photos in Fig. 1, respectively. The arcing in Ar-H_2 gas mixture of the electrode A, i.e. well graphitized one, and therefore having the largest primary particle, resulted only in a rubber-like soot. Examples of TEM images of the web and soot are shown in Fig. 5. Evidently the product obtained from the well-graphitized electrode A contains mostly soot and graphite nanoparticles with embedded catalyst, while the web-like product from the electrode B is rich into CNTs. Comparative SEM and TEM images of products in Fig. 4 are shown in Fig. 6. The bulk product formed from more amorphous carbon, i.e. using carbon black (C), seems to be slightly more fine and pure.

Other catalysts from the transition metal group (Co and Ni) were also tested for SWCNTs formation by Ar-H_2 arc discharge using electrodes prepared of carbon material C. It follows from the work by Zhao et al. [19] that such catalysts or their binary mixtures are not suitable for SWCNTs production by Ar-H_2 arc plasma. However, it is very likely that the authors used well graphitized electrodes. We found that although a macroscopic web was not formed, the final product appeared in a form of a fine membrane which could be peeled off from the reactor lid and contained SWCNTs shown in Fig. 7.

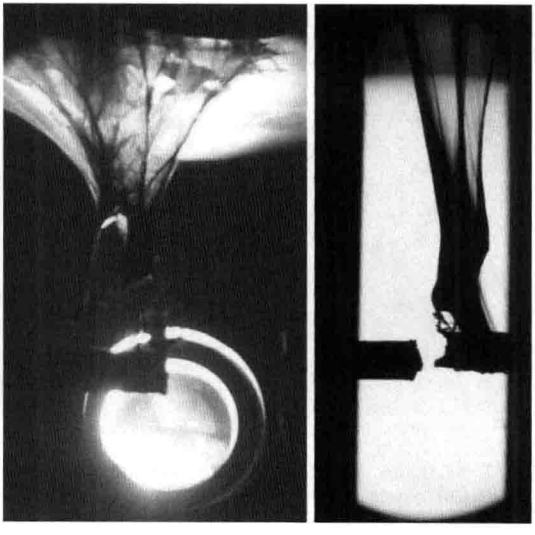

Fig. 4 Photograph of web-like products from two tests performed with electrode B (N_2-H_2 atmosphere) and C (Ar-H_2 atmosphere), respectively. Catalyst: Fe

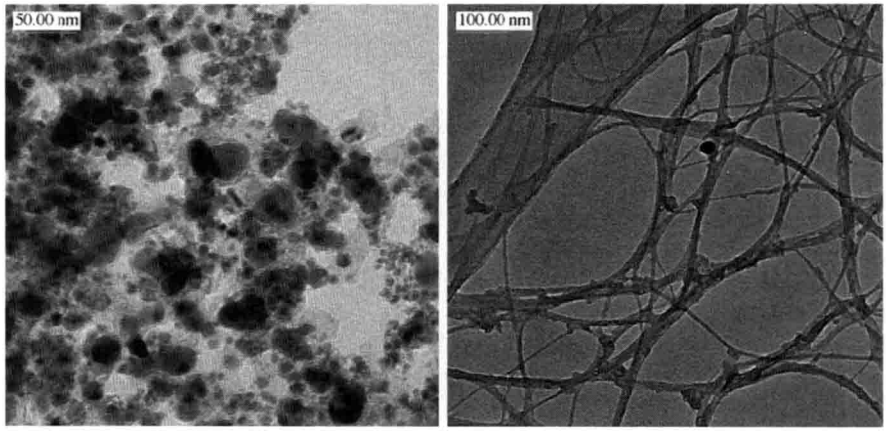

Fig. 5 TEM images of products obtained from electrode A (*left*) and B (*right*) during arc discharge in Ar–H_2 gas mixture. Arc current: 50 A and pressure: 260 kPa. Catalyst: Fe

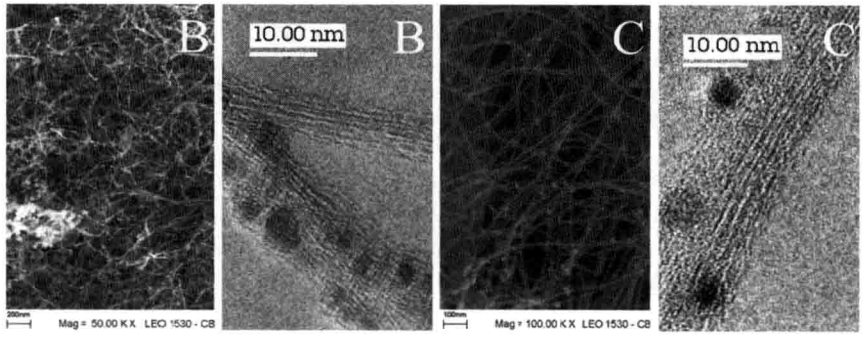

Fig. 6 SEM and TEM images of products obtained from electrodes B and C during arc discharge in Ar–H_2 gas mixture. Arc current: 50 A and pressure: 260 kPa. Catalyst: Fe

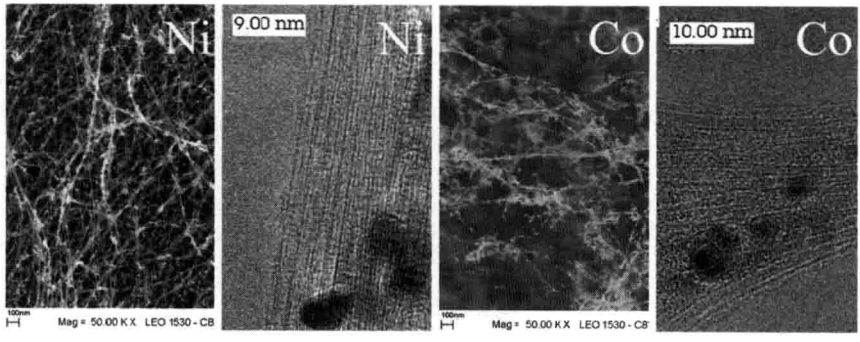

Fig. 7 SEM and TEM images of products obtained from electrode material C prepared (IRB) and Co- and Ni- catalysts