

Electroactive polymer-carbon nanotube composites: smart organic materials for optoelectronic applications

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Resum

Los nanotubos de Carbono combinados con polímeros conductores intrínsecos contribuirán en un futuro al progreso en nanoelectrónica y al desarrollo de nuevos y mejores dispositivos electrónicos y optoelectrónicos. Este artículo resume nuestro trabajo en materiales compuestos polianilina-nanotubos de carbono altamente funcionales y procesables, y muestra la estrecha relación existente entre las interacciones polímero-nanotubo y la funcionalidad y comportamiento en el procesado de los materiales obtenidos.

Paraules clau: nanotubos de carbon · polímeros conjugados · nanocomposites

Abstract

Carbon nanotubes combined with intrinsically conducting polymers may contribute to further progress in nanoelectronics and to the development of improved electronic and optoelectronic devices. This article summarizes our work on highly functional and processable polyaniline-carbon nanotube composite materials. It also demonstrates the close relation between functionality and processing behavior and describes nanotube-polymer interactions.

Keywords: carbon nanotubes · conjugated polymers · nanocomposite materials

1. Introduction

Organic electronics, a growing field of research, can improve the semiconducting, conducting, and light-emitting properties of organic materials through novel synthesis and self-assembly concepts. Performance improvements, coupled with the use of traditional casting/printing/stamping techniques to process these “electroactive” materials on large areas of materials such as plastic or paper, mean that they could be used in optoelectronic applications, including low-cost information displays on flexible plastic for e-newspapers, and low cost memory and logic for smart cards. These types of novel products will contribute to meeting society’s demands for access to instant information, data handling, and communication. Today, two classes of materials are of paramount interest in the field of research into the optoelectronic applications of organic electronics: electroactive polymers [1] and carbon nanotubes [2].

Electroactive polymers (or intrinsically conducting polymers) are polymers that possess the electrical, electronic, magnetic and optical properties of a metal and the mechanical properties (flexibility, toughness and processing) of a conventional poly-

mer. Their properties are intrinsic to “doped” forms of polymers. In the doped state, the backbone of a conducting polymer consists of a truly conjugated and delocalized p electron system that provides semiconducting, conducting and other electroactive properties. Doping may be carried out chemically or electrochemically and always involves dopant counterions which stabilize the doped state.

The concept of doping is illustrated in Figure 1, which shows a non-redox doping process in polyaniline (PANI), using protonic acids. During this doping process the number of electrons associated with the polymer backbone does not change. However, the energy levels are rearranged and a stable polysemiquinone radical cation (a polaron) is produced, leading the polymer into a highly conducting regime. The highly conducting form of polyaniline, which corresponds to a salt, can be reversibly dedoped into its non-conducting base form. Moreover, the whole process is accompanied by very beautiful and reversible changes in color. Some other typical intrinsically conducting polymers are polypyrrole, polythiophene, poly-3,4-ethylenedioxythiophene (PEDOT) and poly-(para-phenylene). Just over 10 years after the discovery of intrinsically conducting polymers [3], the first organic light-emitting devices (OLEDs) [4] have been developed. This represents a tremendous boost for the further development of various types of electronic and optoelectronic devices made out of electroactive polymers [5]. The key to further progress lies in improving charge carrier mobility and processing. Here, novel nanoscale concepts such as na-

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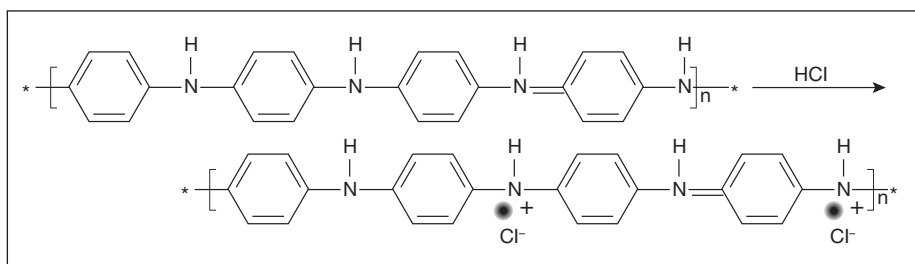


Figure 1. Non-redox doping process in polyaniline (PANI), resulting in transformation from its insulating state into a conducting state.

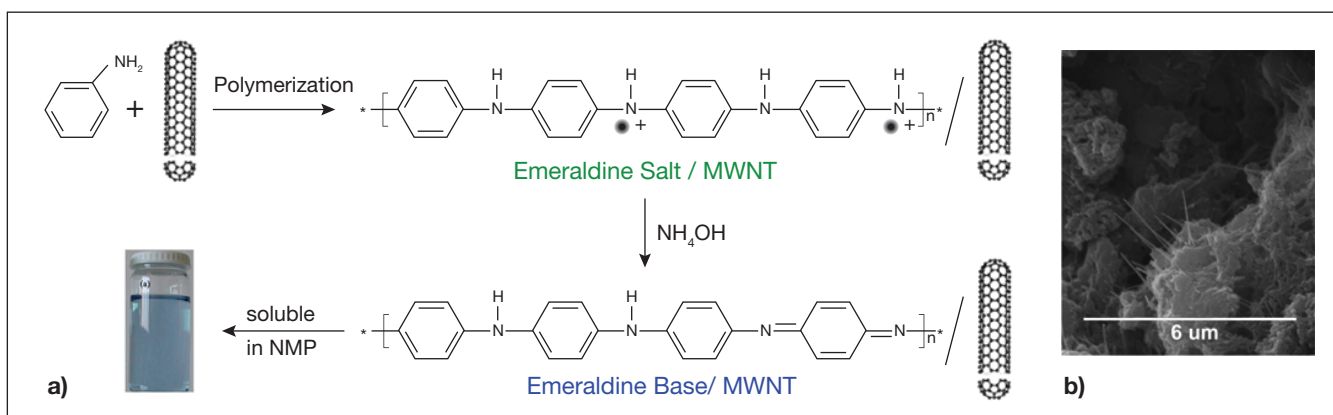


Figure 2. (a) Synthesis of PANI-MWNT composite. In-situ polymerization yields the green emeraldine salt-MWNT composite which is subsequently transformed into the blue, soluble emeraldine base-MWNT composite. (b) SEM image of the emeraldine base-MWNT solid powder.

nostructuring and novel nanomaterials will enable further improvements to be made in the field of organic optoelectronic applications.

Carbon nanotubes (CNTs)—highly attractive nanobuilding blocks—are now being used in this field [6]. CNTs are nanoscale objects consisting of one or several graphene sheets that are seamlessly closed to form single-wall or multi-wall carbon nanotubes (SWNTs or MWNTs respectively). With their unique structural, mechanical, thermal, electronic and optical properties, [2] they offer a broad range of applications in various fields of science and technology, [7] such as nanoelectronics (from conducting wires to semiconducting logic switches), field-emitting devices (flat panel displays, movable X-ray scanners) and nanoelectromechanical systems (NEMS, including nanoactuators as well as chemical and biochemical sensors). Furthermore, carbon nanotubes blended into common plastic materials yield highly reinforced, supertough and/or conducting composites, i.e. new classes of advanced materials. Carbon nanotubes can also be considered natural partners for intrinsically conducting polymers. Their dimensions and electronic structure combine well with the chain structure and the delocalized electron system of these electroactive polymers. Their mutual interactions may lead to highly favorable synergetic effects between both constituents, which might contribute to further improvements in organic electronic devices.

With these considerations in mind, we carried out intensive research on novel composite materials, based on carbon nanotubes and electroactive polymers. We focused on two key issues: enhanced functionality and the processing properties of the obtained materials. These issues are directly linked to favorable interactions between the carbon nanotubes and the poly-

mer chains. Thus, they are also closely related to the synthesis approach and self-assembling processes. We will outline this approach in the following description of our research on polyaniline (PANI)-carbon nanotube (CNT) composites.

2. Synthesis and processing

First, we produced straight and well-graphitized multi-wall carbon nanotubes (MWNTs) in our own electric arc-discharge system. Pure graphite anodes were evaporated under 66kPa of helium by applying 60 A and 25 V. The obtained nanotubes had micrometer lengths and diameters of 20-40 nm.

For the synthesis of PANI-MWNT composites, we applied an in-situ approach for the first time, i.e. we carried out the polymerization of aniline in the presence of MWNTs (Figure 2a) [8,9]. An aniline monomer solution in HCl 1M was added to MWNTs suspended in HCl 1M and the oxidant $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (ammonium peroxydisulfate, APS) was added to initiate the polymerization process. This rapidly resulted in a dark green suspension. After several washing and filtering cycles we obtained PANI powder in its primary doped form, i.e. emeraldine salt (ES). In a next step, we transformed ES into its soluble emeraldine base (EB) form [9]. We dedoped both ES and the ES-MWNT composite with 3 wt% of aqueous ammonium hydroxide (NH_4OH). After several washing and filtering cycles, EB and EB-MWNT composite were obtained as powders. Assuming that no MWNTs got lost in the washing and filtering cycles, and taking into account the process yields, we estimated the content of MWNTs in the final EB-MWNT composite at about 50 wt%. SEM microscopy showed that the MWNTs were embed-

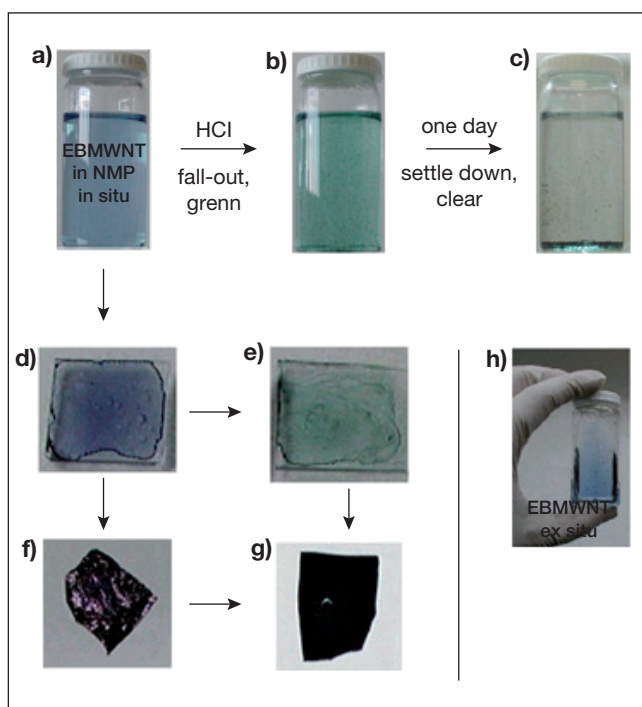


Figure 3. Processing properties of EB-MWNT. (a) Solution in NMP. Addition of HCl results in (b) fall out and (c) settling of the solid material. The solution becomes clear. (d) Casted film from EB-MWNT blue solution onto glass. (e) Exposure of blue EB-MWNT film from (d) to HCl vapor results in a green ES-MWNT film. (f) Free-standing film obtained from (d). (g) Free-standing film obtained from (e) which can also be obtained from a free-standing EB-MWNT film (f) after exposure to HCl vapor. (h) Ex-situ polymerization results in agglomerates and non-stable solutions.

ded in the polymer matrix (Figure 2b). The MWNTs were completely covered by EB throughout the material and could only be seen sticking out at the edges of the polymer blocks.

Like pure EB itself, EB-MWNT containing about 50 wt% of MWNTs was completely dispersed in *n*-methylpyrrolidinone (NMP), resulting in a stable, blue solution. No black MWNTs (or agglomerates thereof) could be seen. Attempts to transform the EB-MWNT solution into an ES-MWNT solution by adding a few drops of HCl immediately led to the fall-out of small agglomerates. After a day, the solution was completely colorless and all the agglomerates had settled to the bottom of the flask.

Curiously, when applying an ex-situ synthesis in which MWNTs were added directly to ES and then transformed to EB, the resulting EB-MWNT material did not disperse as well as it did in the in-situ material. Agglomerates form and fall out with time (Figure 3).

Blue colored films were obtained by casting NMP solutions of EB-MWNT and EB onto glass substrates, followed by vacuum drying at 70°C for 24 h. Subsequent immersion of these films in distilled water resulted in free-standing blue films of EB and EB-MWNT, which could easily be transformed into the corresponding green films of ES and ES-MWNT by exposure to HCl vapor for a few seconds (Figure 3). These observations clearly show the importance of in-situ polymerization in further processing of the EB-MWNT composite material obtained.

3. Results and discussion

Directly after synthesis, we took a UV-Vis spectrum of EB and EB-MWNT solutions in NMP (Figure 4a). The maximum at 320 nm corresponded to the $p-p^*$ transition centered on the benzenoid unit of EB. The maximum at 624 nm corresponded to the quinoid exciton band. However, it was striking that the EB-MWNT solution showed a new and very strong band with its maximum at 283 nm. This band was related to the $p-p^*$ transition centered on the quinoid unit. It would seem that the presence of MWNTs led to the enhanced response of the quinoid-related rings. The rest of the features were identical to pure EB. This led us to assume that this is a two-phase system: free EB, and a new phase of EB whose conformation is more planar, a fact that is related to the presence of MWNTs. Thermogravimetric analysis (TGA) (Figure 4b) clearly confirmed the existence of an additional MWNT-related EB phase, which started to decompose at temperatures about 150 °C higher than the backbone of pure EB.

In addition, infra-red spectroscopy (Figure 4c) revealed significant changes in the EB-MWNT composite, most of which were directly related to a relative increase in the vibration strength of C-C bonds of the quinoid versus benzenoid groups (range 1585-1380 cm^{-1}), as well as changes related to ring-

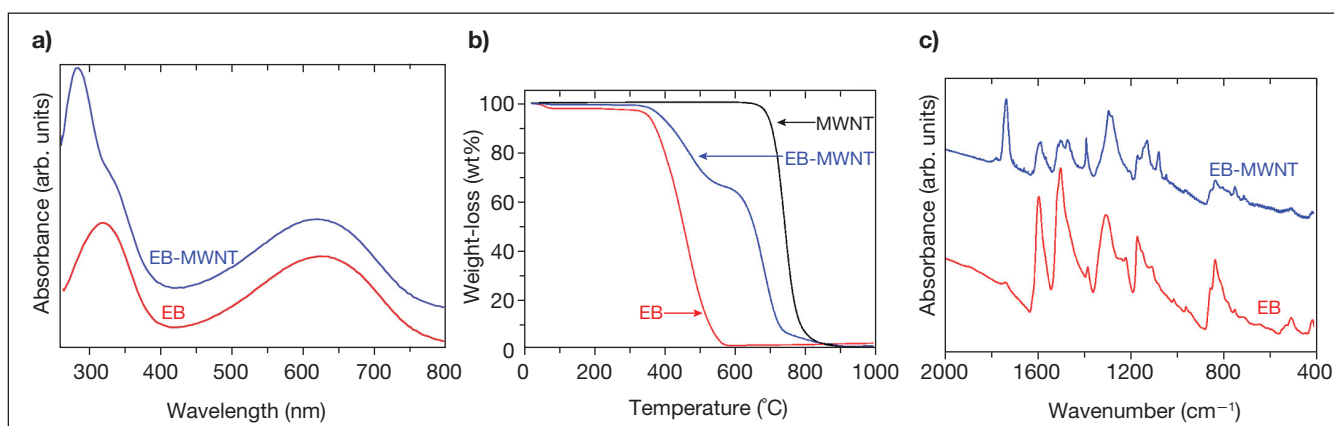


Figure 4. Characterization of EB and the EB-MWNT composite. (a) UV-Vis spectra of solutions; (b) TGA powder material and (c) FTIR spectra of pressed pellets. Figures adapted from our own work published in [9].

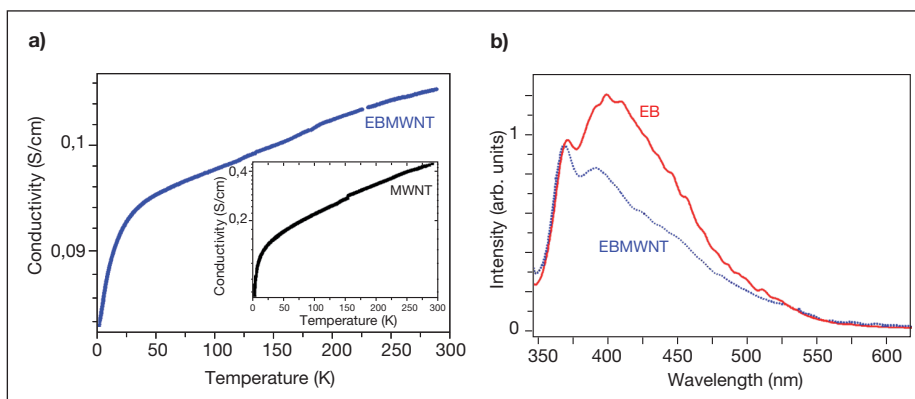


Figure 5. Characterization of EB and the EB-MWNT composite. (a) Temperature-dependent electrical conductivity (4-point configuration) of pressed pellet. (b) Photoluminescence of corresponding solutions. Figures adapted from our own work published in [10].

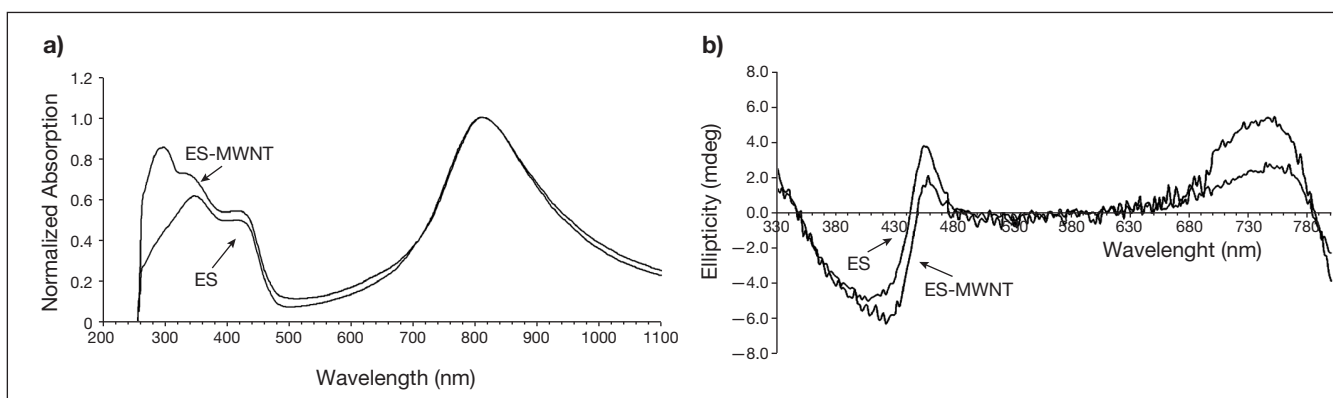


Figure 6. HCSA-doped ES and ES-MWNT in NMP. (a) UV-Vis spectra. (b) Circular dichroism spectra. Figures adapted from our own work published in [11].

deformations of the quinoid and benzenoid groups (range $1105\text{--}950\text{ cm}^{-1}$).

As a next step, we tested the functionality of the material. First, we performed temperature-dependent conductivity measurements (Figure 5a) on the bulk powder materials. The room temperature value for EB fell below the experimental limit (below 10^{-10} S/cm). Therefore, no temperature dependence could be measured. However, with about 0.1 S/cm , the room temperature conductivity for the EB-MWNT powder drastically increased by at least nine orders of magnitude compared to EB. Its temperature dependence resembled that of the MWNTs, indicating that conduction occurred through a percolated three-dimensional network of MWNTs. However, the room temperature value of the EB-MWNT composite did not reach the value of a pure MWNT network, which is expected to be one or two orders higher in magnitude. This indicates the existence of additional tunneling barriers between the MWNTs, formed by the EB coating around the MWNTs. As a further indication of functionality, we observed the enhanced thermal stability of the composite, which decomposes in air at temperatures $150\text{ }^{\circ}\text{C}$ higher than the backbone of pure EB. Secondly, we investigated the photophysical properties of the composite and measured its photoluminescent behavior ($\lambda_{\text{exc}}=330\text{ nm}$) [10] (Figure 5b). EB shows a broad emission maximum at about 400 nm caused by reduced benzenoid/amine groups. This is usually suppressed drastically when EB is transformed by chemical doping into a highly conducting state. However, EB-MWNT also luminesced and essentially maintained the fea-

tures of EB. Here, the reduction of the long-wave emission band was in agreement with a more planar conformation of EB on MWNTs. It is highly remarkable that the presence of 50 wt% of MWNTs in the EB-MWNT composite, which make it highly conductive, did not result in a quenching of luminescence.

More recently, we studied the optical activity properties of PANI-MWNT solutions. It is well known that the addition of chiral acids transforms EB into the corresponding emeraldine salt (ES), whose backbone then adopts a chiral structure which is responsible for its optical activity. Therefore, the starting point in our case was the stable, blue EB-MWNT solution. To this solution, we added the chiral *S*-(+)-10-camphorsulfonic acid (HCSA). In contrast to the addition of HCl, which results in precipitation of the MWNTs, the addition of HCSA resulted in a stable, green solution of the corresponding emeraldine salt (ES-MWNT). Figure 6a shows the UV-Vis spectrum of the resulting ES-MWNT composite and that of ES for comparison. The three characteristic bands at 345 , 415 , and 810 nm are associated with $p\text{-}p^*$, polaron- p^* and p -polaron band transitions of ES. The broad p -polaron band at 810 nm is typical of an arrangement of polymer chains in the “compact coil” form [11]. ES-MWNT essentially showed the same features, as well as a dominant band at 295 . As in the case of EB-MWNT, this band corresponded to the $p\text{-}p^*$ transition centered on the quinoid unit and was related to the coating of EB onto MWNTs. Furthermore, both solutions had become optically active (Figure 6b). These observations are consistent with the polymer adopting a “compact coil” conformation. The circular dich-

oism spectrum for ES-MWNT showed that the polymerization of aniline in the presence of nanotubes and doping did not inhibit the polymer's ability to become optically active. The effects of introducing optical chirality into PANI-CNT composites and its technological implications are being investigated in more detail by our group, in a joint research program with the group of Dr. Marc in het Panhuis at the University of Wollongong (Australia).

4. Conclusions

In this article we have described the formation of a highly functional and completely soluble polyaniline-multi-wall carbon nanotube composite. This composite has enhanced conductivity and improved thermal stability. It is also luminescent, optically active and can be processed from solutions into films, coatings and fibres [12]. We believe that these findings provide the basis for novel smart organic materials of great use in smart optoelectronic applications and devices.

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References

[1] MacDiarmid A.G. (2001). "Synthetic Metals": A Novel Role for Organic Polymers (Nobel Lecture), *Angew. Chem. Int. Ed.* 40:2581-2590

- [2] Dresselhaus M.S., Dresselhaus G., Avouris Ph. (Eds.), *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*, *Topics in Applied Physics*, Vol. 80, Springer, Berlin, Germany 2001.
- [3] Shirakawa H., Louis E.J., MacDiarmid A.G., Chiang C.K., Heeger A.J. (1977). Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, $(CH)_x$, *J. Chem. Soc. Chem. Commun.* 578-580
- [4] Burroughes J.H., Jones C.A., Friend R.H. (1988). New Semiconductor Device Physics in Polymer Diodes and Transistors, *Nature* 335:137-141
- [5] Skotheim T.A., Elsenbaumer R.L., Reynolds J.F. (Eds.), *Handbook of Conducting polymers 2nd ed.*, Marcel Dekker, New York, 1998
- [6] Iijima S. (1991). Helical microtubules of graphitic carbon, *Nature* 354:56-58
- [7] Baughman R.H., Zakhidov A.A., De Heer W.A. (2002). Carbon nanotubes — the route towards applications, *Science* 279:787-782
- [8] Cochet M., Maser W.K., Benito A.M., Callejas M.A., Martínez M.T., Benoit J.M., Schreiber J., Chauvet O. (2001). Synthesis of a new polyaniline/nanocomposite: "in-situ" polymerisation and charge transfer through site-selective interaction, *Chem. Comm.* 1450-51
- [9] Sainz R., Benito A.M., Martínez M.T., Galindo J.F., Sotres J., Baró Arturo M., Corraze B., Chauvet O., Maser W.K. (2005). Soluble Self-Aligned Carbon Nanotube/Polyaniline Composites, *Adv. Mater.* 17:278-281
- [10] Sainz R., Benito A.M., Martínez M.T., Galindo J.F., Sotres J., Baró A.M., Corraze B., Chauvet O., Dalton A.B., Baughman R.H., Maser W.K. (2005). A soluble and highly functional polyaniline carbon nanotube composite, *Nanotechnology* 16:S150-154
- [11] Panhuis M.i.h., Sainz R., Innis P., Kane-Maguire L.A.P., Benito A.M., Martínez M.T., Moulton S.E., Wallace G.G., Maser W.K. (2005). Optically Active Polymer Carbon Nanotube Composite, *J.Phys.Chem. B* 109(48):22725-29
- [12] Maser W.K., unpublished results.

About the authors

Wolfgang Maser studied Physics at the University of Bonn in Germany. After receiving his Diploma in 1990 he completed his PhD Thesis at the Max-Planck-Institute for Solid State Research in Stuttgart, Germany. In 1993, he obtained from the University of Tübingen in Germany the doctoral degree for his work on photo-physical studies of nonlinear effects in buckminsterfullerene. After postdoctoral stays at the University of Sussex (UK), Montpellier (France) and Zaragoza (Spain) his research interest focused on the production of carbon nanotubes by all three

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Raquel Sainz studied Chemistry at the Universidad de Zaragoza where she obtained her Diploma degree in 2005. From 2004 to 2007 she carried out her PhD thesis at the Instituto de Carboquímica (CSIC) under the supervision of Dr. Ana M. Benito and Dr. Wolfgang Maser. She received her PhD degree from the Universidad de Zaragoza in 2007 for her work on polyaniline nanotubes composite materials. Currently she has a

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Teresa Martínez studied chemistry at the Universidad de Zaragoza in Spain where she obtained her graduate degree in Chemistry in 1978 and her doctor's title in 1982. From 1982 to 1995 she worked in coal conversion processes and upgrading of coal liquids and oil fractions. Based on her experience in coal carbonisation and electrodes graphitisation, she undertook in 1995 her first project in the preparation of

carbon nanostructures. In 1996 she founded with Ana Benito the 'Group of Carbonaceous Nanostructures and Nanotechnology' at the Instituto de Carboquímica and initiated the R&D work on the production techniques of carbon nanotubes. Since 2005 she is Professor of CSIC. Her current research interests are in carbonaceous nanomaterials and related materials relevant for applications (energy, field effect tran-

sistor-biosensors, field-emission, nanobiology).

Ana M. Benito studied Organic Chemistry and Biochemistry at the Universidad de Zaragoza from 1982 to 1987, and received her PhD degree from the same university in 1993. She did postdoctoral research at the University of Sussex (UK) during two years (1994–1995) where she worked on synthesis of fullerenes derivatives and production of

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