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Synthesis and characterization of new polyaniline/nanotube composites

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Abstract

New polyaniline/nanotube (PANI/NT) composites have been synthesized by “in situ” polymerization processes using both multi-wall carbon nanotubes (MWNTs) and single-wall carbon nanotubes (SWNTs) in concentrations ranging from 2 to 50 wt.%. Although no structural changes are observed using MWNTs above a concentration of 20 wt.%, the in situ synthesis results in electronic interactions between nanotubes and the quinoid ring of PANI leading to enhanced electronic properties and thus to the formation of a genuine PANI/MWNT composite material. On the other hand, using SWNTs favors the formation of inhomogeneous mixtures rather than of a homogeneous composite materials, independent of the SWNT concentration. X-ray diffraction, Raman and transport measurements show the different behavior of both classes of nanotubes in PANI/NT materials. The difficulties in the formation of a true PANI/SWNT composite are related to the far more complex structure of the SWNT material itself, i.e. to the presence of entangled bundles of SWNTs, amorphous carbon and even catalytic metal particles.

Keywords: Carbon nanotubes; Conducting polymers; Composite materials

1. Introduction

With their unique electronic [1] and mechanical [2] properties, carbon nanotubes are from great interest for the fabrication of new classes of advanced materials. Here, especially composites based on polymers and nanotubes offer the possibility to obtain materials with superior properties [3]. Polyaniline, a particular conducting polymer [4] with a high application potential [5], is a promising candidate to synthesize such nanotube composites with improved structural or functional characteristics.

We report the synthesis of new polyaniline/nanotube (PANI/NT) material by an “in situ” polymerization process using either multi-wall carbon nanotubes (MWNT) or single-wall carbon nanotubes (SWNT) materials in various concentrations. In the case of MWNTs, this process leads to the formation of a genuine composite material with enhanced electronic properties. It will be shown that the use of MWNT material leads to the formation of a genuine composite material with enhanced electronic properties while SWNT material only results in the synthesis of inhomogeneous mixtures. Due to the more complex structure of the SWNT materials, an effective self-assembling process can not take place here.

2. Experimental

Production of nanotube materials: By electric arc-discharge following the methods of Iijima [6] and Journet et al. [7] for MWNTs and SWNTS, respectively. MWNTs: Materials contain straight MWNTs as well as hollow graphitic nanoparticles. SWNTs: Materials contain high densities of entangled bundles of SWNTs as well as catalytic nanoparticles embedded in an amorphous carbon matrix. Synthesis of composites: The produced NT materials are suspended in HCl 1 M and sonicated to better disperse them. The aniline monomer, in HCl 1 M, is added to the NT suspensions. A solution of HCl 1 M containing the oxidant $(NH_4)_2S_2O_8$ is slowly added with a constant sonication at a temperature of about -3 °C. A good degree of polymerization is achieved if the dark suspension becomes green

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after a few minutes which then is sonicated in an ice bath for 2 h. The PANI/NT material is obtained by filtering and rinsing the suspension with HCl 1 M followed by drying of the remaining powder under vacuum for 24 h. Different PANI/NT materials were synthesized using 10, 20, 30, 50 wt.% of MWNT material as well as 2, 5, 10, 20, 30, 50 wt.% of SWNT material (weight percent with respect to aniline monomer). Characterization of the obtained materials were performed using X-ray diffraction, Raman spectroscopy and four-point transport measurements between 300 and 1.25 K.

3. Results and discussion

The structural characteristics of the PANI/MWNT materials have been analyzed by X-ray powder diffraction and are shown in Fig. 1. At low angles, the diffractograms of the PANI/MWNT materials show the highly pronounced oscillating structure of the primary doped PANI (emeraldine salt) with oxidation degree of 0.5 [8] and at higher angles superimposed the typical MWNT peaks whose heights increase proportionally to their weight percentages. Therefore, it is clear that, from a structural point of view, no additional order has been introduced.

On the other side, Raman spectroscopy (Fig. 2) reveals that the electronic behavior of the composites in the concentration range between 20 and 50 wt.% varies significantly from the one of its constituents. Here, a remarkable decrease of the intensity of the PANI 1485 cm^{-1} band with respect to the 1161 cm^{-1} band can be noticed. This band at 1485 cm^{-1} has been assigned to an in-plane deformation of the C–C bond of the quinoid ring of the doped PANI [9]. Therefore, this pronounced decrease gives evidence that a site-selective interaction between the quinoid ring of the doped polymer and the nanotubes occurs as a consequence of the in situ polymerization. This clearly influences the transport properties as can be seen in Fig. 3.

Here, for highly filled PANI/MWNTs obtained by in situ polymerization, the following remarkable facts are to be noted. (i) The room temperature resistivity is decreased by one order of magnitude as compared to pure PANI (even for the 10 wt.% sample). (ii) The low temperature resistivity is much smaller than both the PANI and the MWNTs ones. (iii) The conductivity of PANI and of MWNT has increased during the in situ polymerization process (compared to ex situ produced material). This suggests that the in situ polymerization above a certain concentration threshold clearly favors a charge transfer between PANI and MWNTs resulting in an overall material which is more conducting than the starting components. Saturation is reached for MWNT concentrations higher than 30 wt.%. Altogether, a true PANI/MWNT composite with enhanced electronic properties has been successfully synthesized.

Better understanding of the favorable interaction between PANI and NTs was expected by the use of the intrinsic simpler nanotubes, namely SWNTs. However, the use of SWNT materials already implies first changes in the synthesis conditions of PANI/SWNT materials: SWNT concen-

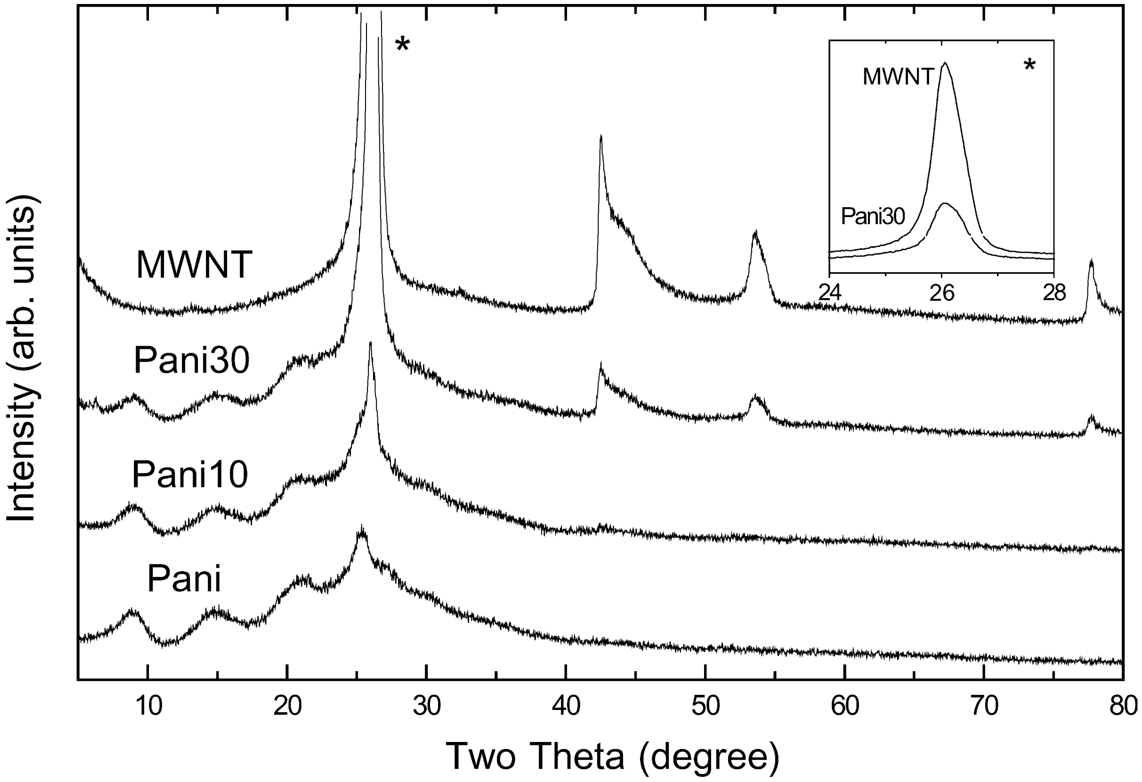

Fig. 1. X-ray diffractograms of PANI, PANI/MWNT 10, 30 wt.% and MWNTs.

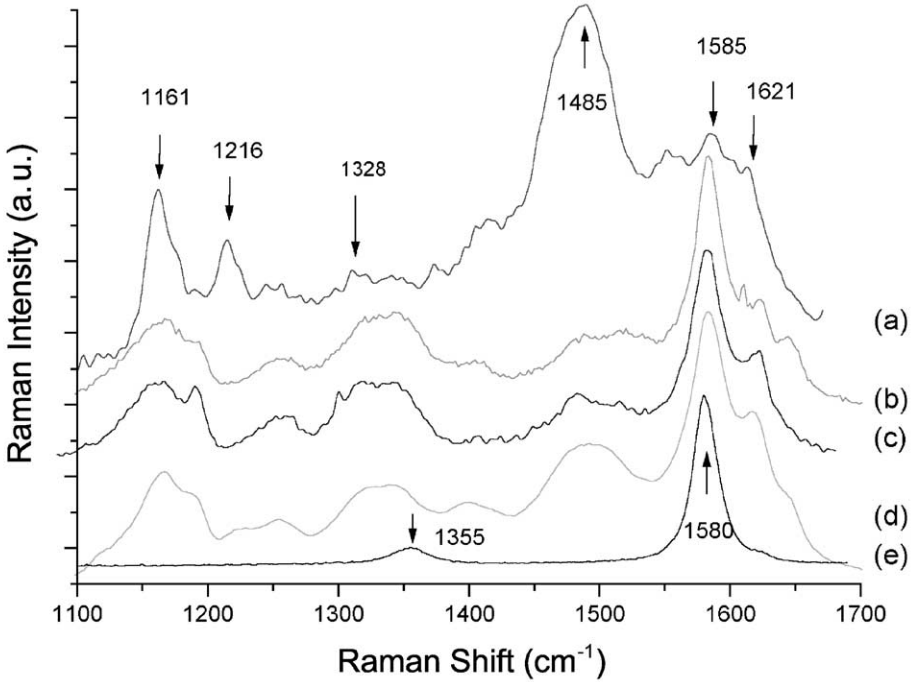

Fig. 2. Raman spectra of (a) PANI, (b–d) PANI/MWNT 20, 30, 50 wt.% and (e) MWNTs.

trations higher than 5 wt.% do not favor anymore the polymerization process and the formation of agglomerates of SWNT material is observed. Here, especially the presence of amorphous carbon sterically hinders a successful polymerization. Therefore, for the following syntheses, the amount of amorphous carbon first was reduced by the pre-oxidation of the starting SWNT material at 350 °C in air for 1 h [10]. Only the use of this pre-treated material then

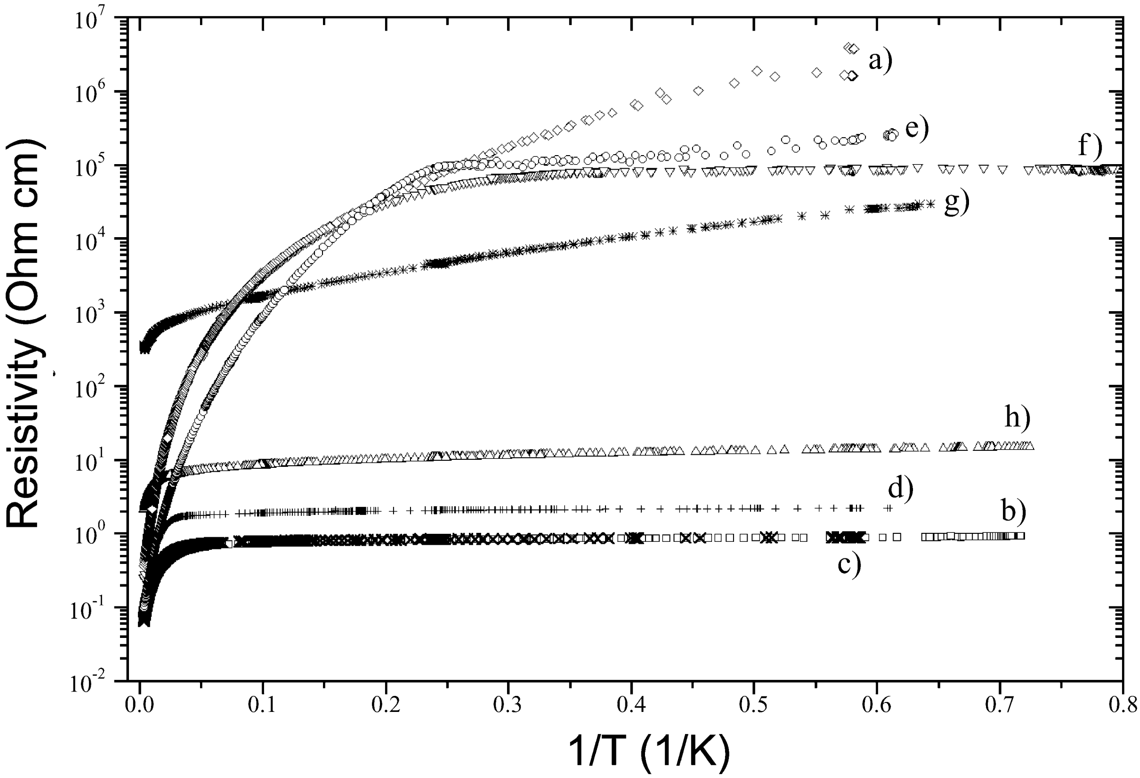

Fig. 3. Temperature dependence of resistivity in PANI/MWNT. (a) PANI, (b–e) in situ PANI/MWNT 50, 30, 20, 10 wt.%, (f) ex situ PANI/MWNT 30 wt.%, (g) ex situ PMMA 30 wt.%, (h) MWNTs.

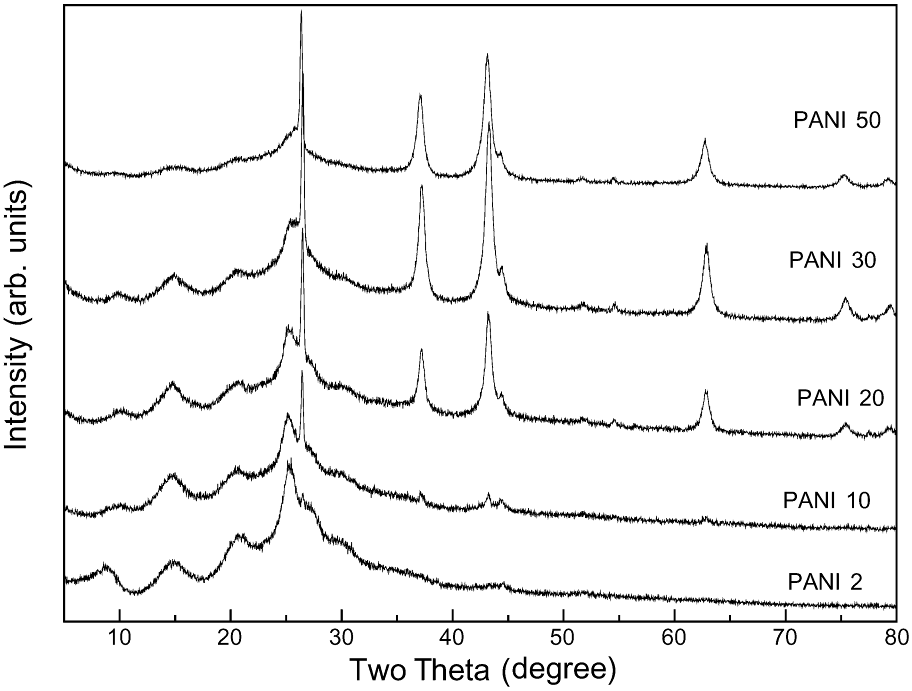

Fig. 4. X-ray diffractograms of PANI/SWNT 2, 10, 20, 30, 50 wt.%.

allowed the synthesis of PANI/SWNT material for concentrations higher than 5 wt.% of SWNTs.

X-ray diffraction (Fig. 4) on the obtained PANI/SWNT materials reveals: (i) existence of highly pronounced oscillating PANI structure at low angles (polymerization has taken place successfully even at high SWNT concentrations); (ii) superposition of typical SWNT peaks on PANI structure; (iii) additional peaks belonging to metal nanoparticles which appear due to elimination of amorphous carbon. Like in the case of MWNTs, from a structural point

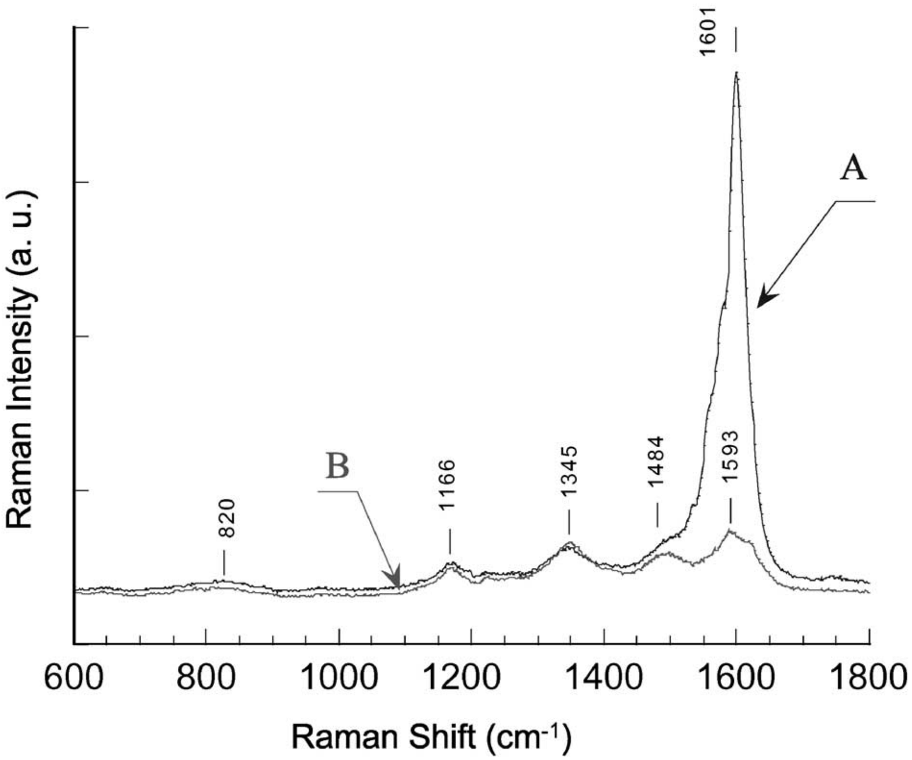

Fig. 5. Raman spectra of PANI/SWNT 50 wt.%. Spectra A and B are taken on two different zones of the sample.

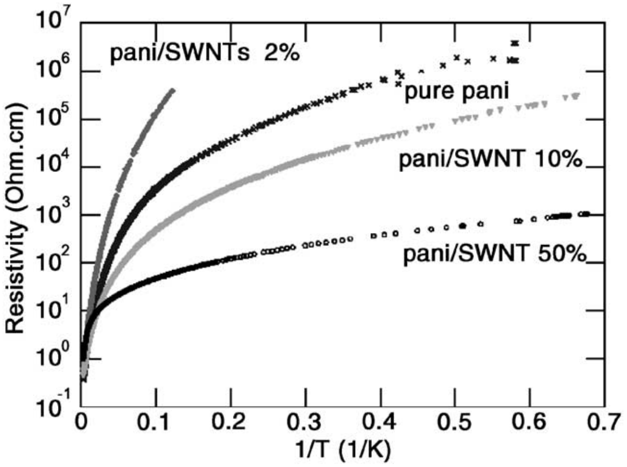

Fig. 6. Temperature dependence of resistivity in PANI/SWNT.

of view, no additional order can be observed in the formed PANI/SWNT materials.

In contrast to the PANI/MWNT material, optical microscopy studies reveal the formation of a rather inhomogeneous material. Independent of the SWNT concentration, the PANI/SWNT materials consist of irregular agglomerates in the order of a few millimeters.

Raman measurements further support this observation. Depending on the zone of the focal spot on the PANI/SWNT sample, large variation of the Raman spectra can be seen (Fig. 5). Here, the typical spectra of SWNTs material (peaks at 1600 and 1350 cm^{-1}) together with small contributions of PANI as well as the typical spectra of PANI together with (very) small contributions of SWNTs can be found in an irregular manner. It becomes clear that the SWNTs have not been dispersed homogeneously in the polymer matrix and the obtained PANI/SWNT materials behave more like inhomogeneous mixtures rather than true composite materials.

The transport measurements (Fig. 6) on the PANI/SWNT materials reveal: (i) higher SWNT concentrations lead to reduced temperature dependence and to improved low temperature conductivity values. However, it is unexpected that the 2 wt.% material is more resistive than PANI alone. (ii) All T-dependencies are hopping-like. Both points suggests that grain size effects due to the presence of agglomerates play a role. No information about specific interaction of SWNTs with PANI can be obtained.

All the measurements consistently show that using SWNTs only, inhomogeneous PANI/SWNT materials have been formed. The presence of amorphous carbon, bundles of entangled SWNTs as well as metal nanoparticles in the used SWNT material prevent a homogeneous dispersion of the SWNTs in the polymer matrix resulting in the formation of small agglomerates. In order to obtain true PANI/SWNT composite materials, the dispersion of the SWNT materials has to be drastically improved.

4. Conclusions

Using MWNT material, the formation of a genuine PANI/MWNT composite has been demonstrated. Here, the synthesis by an in situ polymerization process leads to effective site-selective interactions between the quinoid ring of the PANI and the MWNTs. This facilitates charge transfer processes between the two components and results in enhanced electronic properties.

On the other hand, the use of SWNT material under the same polymerization conditions only results in the synthesis of inhomogeneous mixtures. Here, the formation of homogeneous dispersions of SWNTs in the PANI matrix is hindered by the presence of amorphous carbon and entangled nanotubes as well as metal nanoparticles in the starting SWNT material. Therefore, effective self-assembling processes allowing site-selective interactions, like in the case of MWNT material, cannot take place. It becomes clear that the overall structure of the NT material plays a critical role in the formation of true composite materials. In general, further improvements can be envisaged by the use of purer and/or soluble NT materials [11].

Acknowledgements

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