CHEMCOMM
Communication
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Synthesis of a new polyaniline/nanotube composite: "*in-situ*" polymerisation and charge transfer through site-selective interaction

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Received (in Cambridge, UK) 4th May 2001, Accepted 25th June 2001
First published as an Advance Article on the web 11th July 2001

A new polyaniline/multi-wall carbon nanotube (PANI/MWNT) composite has been successfully synthesized by an "*in-situ*" polymerisation process; Raman studies indicate a site-selective interaction between the quinoid ring of the polymer and the MWNTs opening the way for charge transfer processes; transport measurements clearly reveal drastic changes in the electronic behaviour confirming the formation of a true composite material with enhanced electronic properties.

Carbon nanotubes have unique electronic[1] and mechanical[2] properties and are of great interest for the fabrication of new classes of advanced materials. Here, composites based on polymers and nanotubes especially offer the possibility of obtaining materials with superior characteristics.[3] Polyaniline (PANI), a particular conducting polymer[4] with a high application potential,[5] is a promising candidate for the synthesis of such nanotube composites suitable for improved structural or functional applications. In this article we report, for the first time, the synthesis of this new material by an "*in-situ*" polymerisation process.

The composites were synthesized by polymerisation of aniline with MWNTs. The MWNTs are prepared in an arc discharge experiment by sublimation of pure graphite rods under an helium atmosphere of 660 mbar, using a current of 100 A and a voltage of 25 V. After the experiment, MWNTs were collected from the inner core of the formed cathodic deposit. A solution of HCl 1 M, containing MWNTs, was sonicated at room temperature to disperse the carbon nanotubes. The aniline monomer, in HCl 1 M, was added to the MWNTs suspension. A solution of HCl 1 M containing the oxidant $(NH_4)_2S_2O_8$ was slowly added with a constant sonication at a temperature of about −3 °C. After a few minutes, the dark suspension became green indicating good polymerisation of aniline, and then was sonicated in an ice bath for 2 h. The composite is obtained by filtering and rinsing the suspension with HCl 1 M followed by drying of the remaining powder under vacuum at room temperature for 24 h. In this process, the PANI exists in its primary doped form called the "emeraldine salt"[4] in which coexist two structures: the polaronic form and the bipolaronic structure[6] (Fig. 1).

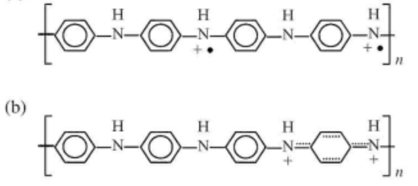

Fig. 1 Schematic structure of the emeraldine salt: (a) the polaronic form, (b) the bipolaronic structure.

Different composites were synthesised by this process, using 10, 20, 30 and 50 wt% of MWNTs (in weight of monomer). In order to compare with the *in-situ* polymerised material, additionally, an "*ex-situ*" polymerised composite has been prepared by only mixing the doped PANI with 30 wt% of MWNTs by two hours of sonication.

The structural characteristics of the composites and its constituents have been analysed by X-ray powder diffraction measurements and is shown in Fig. 2. While the diffractogram of the pure MWNTs exhibits the typical peaks at 3.42, 2.13, 2.05, 1.71 and 1.23 Å corresponding to the graphite (002), (100), (101), (004) and (110) reflections, respectively, the one of PANI shows the highly pronounced oscillation structure characteristic of the doped form (emeraldine salt) with an oxidation degree of 0.5.[7] On the other hand, the diffractograms of the composites (10 and 30 wt%) display the typical peaks of the emeraldine salt as well as the strong peaks of MWNTs which are superposed and whose heights increase proportionally to their weight percentage. Therefore, it is clear that, from a structural point of view, no additional order has been introduced. This observation has also been confirmed by microscopy studies.†

On the other hand, Raman spectroscopy (Fig. 3) reveals that the electronic behaviour of the composites varies significantly from the one of its constituents. The Raman spectrum of the PANI shows the typical bands of the doped polymer in good agreement with a previous paper.[8] The spectra of pure nanotubes exhibit the three usual bands of MWNTs: the D-line at 1350 cm^{-1} (amorphous carbon and disorder induced line), the G-line at 1580 cm^{-1} (in-plane stretching E_{2g} mode) and a shoulder around 1600 cm^{-1} assigned to the D′-line (disorder line).[9] While the spectrum of the 10 wt% composite (not shown) is still identical to that of PANI, from 20 wt% on, the composite spectra clearly display different characteristics. Here, it is worth noting the remarkable decrease of the intensity of the PANI 1485 cm^{-1} band with respect to the 1161 cm^{-1} band. This band at 1485 cm^{-1} has been assigned to an in-plane deformation of

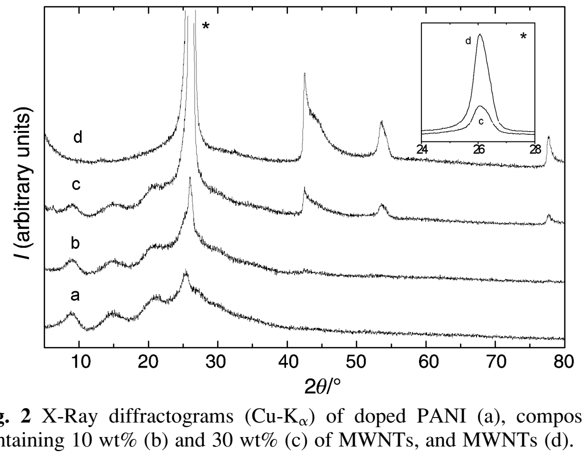

Fig. 2 X-Ray diffractograms (Cu-K_α) of doped PANI (a), composites containing 10 wt% (b) and 30 wt% (c) of MWNTs, and MWNTs (d).

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† Electronic supplementary information (ESI) available: electron micrographs of PANI/MWNT composites. See http://www.rsc.org/suppdata/cc/b1/b104009j/

DOI: 10.1039/b104009j

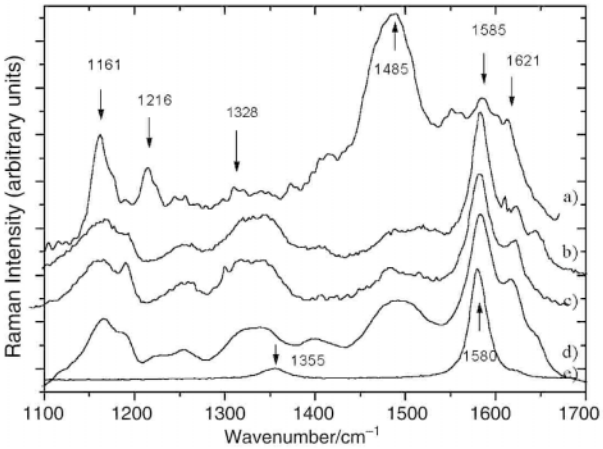

Fig. 3 Raman spectra (λ_{exc} = 514.5 nm) of doped polyaniline (a), composite using 20 (b), 30 (c) and 50 wt% (d) of MWNTs, and pure MWNTs (e).

the C–C bond of the quinoid ring of the doped PANI.[8] 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* polymerisation. This interaction then may facilitate charge-transfer processes between the two components of the system and thus influence the transport properties of the composite.

Consequently, the transport behaviour (4 point-measurements between 300 and 1.25 K) has been studied on the MWNTs, the PANI, the *in-situ* polymerised composites (10, 20, 30 and 50 wt%) as well as on the *ex-situ* 30 wt% composite (Fig. 4). PANI shows a typical room temperature resistivity of 0.3 Ω cm.[10] It increases by 7 orders of magnitude following a $T^{-1/4}$-hopping law upon cooling to 1.7 K. The MWNTs resistivity is 2 Ω cm at room temperature and increases up to 15 Ω cm at low temperature.

The transport properties of the highly filled composites obtained by *in-situ* polymerisation exhibit the following remarkable facts. i) The room temperature resistivity is decreased by one order of magnitude as compared to PANI. ii) The low temperature resistivity is much smaller than both that of PANI as well as MWNTs (1.1 Ω cm for both the 50 and the 30 wt%, 2 Ω cm for the 20 wt% composites). iii) The temperature dependence of the resistivity is weaker than that of PANI. Regarding point iii), we can propose the following explanation. In this composite system, both the matrix and the filler (MWNTs) are conducting. At high temperatures, the conductivity is dominated by the polymer. Decreasing the temperature, the matrix becomes more and more resistive. On the other hand, the filler network which shows a very weak temperature dependence becomes more conducting than the matrix at low temperature. This means that the low temperature conductivity is due to the MWNTs. Actually this consideration is supported by the *ex-situ* polymerised 30 wt% composite (curve f) for which the low temperature resistivity shows the characteristic plateau due to MWNTs conduction.

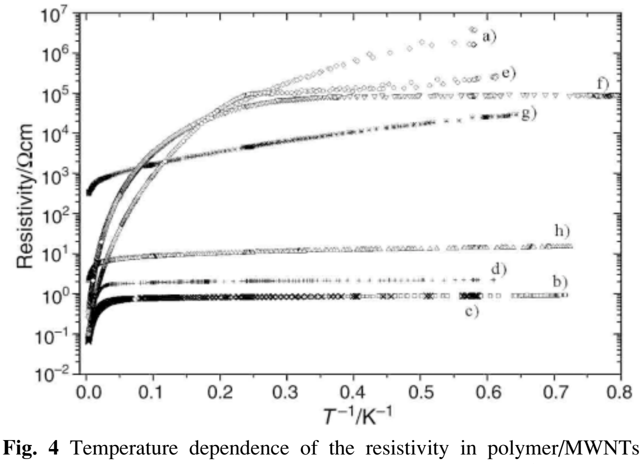

Fig. 4 Temperature dependence of the resistivity in polymer/MWNTs composite: PANI (a), *in-situ* PANI/MWNTs composites with 50 (b), 30 (c), 20 (d) and 10 wt% (e) of MWNTs, the *ex-situ* 30 wt% PANI/MWNTs composite (f), the *ex-situ* 30 wt% PMMA/MWNTs composite (g) and MWNTs (h).

Looking in more detail at the *in-situ* polymerised samples (curves b to d), the points i) and ii) further show that both the conductivity of PANI and of MWNTs has increased during the *in-situ* polymerisation process. This behaviour indicates that the electrical contacts between the MWNTs and the PANI grains have been improved. In accordance with the Raman observations, this suggests that *in-situ* polymerisation favours the charge transfer between PANI and MWNTs resulting in an overall material which is more conducting than the starting components. On the other hand, the apparent saturation of the resistivity decrease as well as of the increase of Raman intensity at 1485 cm^{-1} between the 30 and 50 wt% samples may be related to both the problems of achieving a homogeneous dispersion of large quantities of MWNTs in a matrix and the use of a microprobe in Raman spectroscopy. For the sake of comparison, additionally, a poly(methyl methacrylate) PMMA/MWNTs composite was prepared by mixing the insulating PMMA polymer with 30 wt% of MWNTs. In contrast to the PANI composites, the electronic behaviour of this material is completely different, especially in what concerns the temperature dependence of the resistivity, which is much stronger. Therefore, this observation further underlines the existence of a particular behaviour in case of the PANI/MWNTs composites. Further enhancement of the observed effects may be expected by using purified MWNTs, provided that the conducting path would include polyhedral particles as well.

Summarising, we have demonstrated the synthesis of a new PANI/MWNTs composite with enhanced electronic properties. Here, Raman and transport measurements show that the synthesis by an *in-situ* process leads to effective site-selective interactions between the quinoid ring of the PANI and the MWNTs facilitating charge-transfer processes between the two components. More detailed studies on the electronic behaviour along with the exploitation of the mechanical properties are currently carried out.

This work was supported by the EC RTN contract NANOCOMP (HPRN-CT-2000-00037).

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