

## Modulation of electrical properties in single-walled carbon nanotube/conducting polymer composites

E. Tamburri<sup>a,b</sup>, S. Orlanducci<sup>a,b</sup>, M.L. Terranova<sup>a,b</sup>, F. Valentini<sup>a</sup>, G. Palleschi<sup>a</sup>,  
A. Curulli<sup>c</sup>, F. Brunetti<sup>b,d</sup>, D. Passeri<sup>e</sup>, A. Alippi<sup>e</sup>, M. Rossi<sup>b,e,\*</sup>

<sup>a</sup> Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma “Tor Vergata”, Via della Ricerca Scientifica, 00133 Roma, Italy

<sup>b</sup> MINASlab, Università di Roma “Tor Vergata”, Via della Ricerca Scientifica, 00133 Roma, Italy

<sup>c</sup> CNR ISMN Istituto per lo Studio dei Materiali Nanostrutturati Sezione Roma 2, Via del Castro Laurenziano 7, 00161 Roma, Italy

<sup>d</sup> Dipartimento di Ingegneria Elettronica and INFN, Università di Roma “Tor Vergata”, Via del Politecnico 1, 00133 Roma, Italy

<sup>e</sup> Dipartimento di Energetica, Università di Roma “La Sapienza”, Via A. Scarpa 14, 00161 Roma, Italy

Received 11 August 2004; accepted 16 December 2004

### Abstract

The preparation and electrical characterization of a new class of composite layers formed by dispersing single-walled carbon nanotubes (SWNT) in 1,8-diaminonaphthalene polymer, the poly(1,8-DAN), are described.

The material was grown on the surface of Pt plates by electropolymerization of 1,8-diaminonaphthalene (1,8-DAN) monomer in the presence of nanotubes. This synthesis method allows the simultaneous deposition of both the host polymer matrix and the filler nanotubes. A series of composite films were prepared using untreated nanotubes as well as nanotubes treated with KOH, HNO<sub>3</sub> and HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> solutions. The structural features of the nanotubes and of the films produced have been investigated using Raman spectroscopy. Insight into the nature of nanotube dispersion and nanotube-polymer association was gained by AFM and STM analysis and by FE-SEM inspection after removing the outermost portion of composite films.

The charge transport in composite films is found to be strongly enhanced by the nanotube insertion. Depending on the SWNTs processing, currents up to 30 mA, higher by a factor of about 140 than those of the pure poly(1,8-DAN) films, were measured with an applied voltage of 250 mV.

© 2005 Elsevier Ltd. All rights reserved.

**Keywords:** Carbon nanotubes; Chemical treatment; Electrochemical treatment; Raman spectroscopy; Electrical properties

### 1. Introduction

Conducting polymeric materials possess great design flexibility together with a number of characteristics that are desirable for a number of specific applications in the fields of catalysis, conversion and storage of energy, chemical and biochemical sensing, microelectronics

and optoelectronics [1]. However, experiments have also indicated some general limitations of these materials with respect to the fabrication of devices. Conversely, significant progress has been made by preparing hybrid inorganic–organic materials in which suitable polymers are coupled with the carbon nanotubes [2–4].

Preparation techniques which utilize the mixing of polymers and nanotube dispersions are now widely used as a simple way to produce composite materials [5–9]. Progress in establishing innovative production routes could benefit the design of complex new structures which could serve different needs (see for example Ref.

\* Corresponding author. Address: Dipartimento di Energetica, Università di Roma “La Sapienza”, Via A. Scarpa 14, 00161 Roma, Italy. Tel.: +39 6 49766341; fax: +39 6 44240183.

E-mail address: [marcorossi@uniroma1.it](mailto:marcorossi@uniroma1.it) (M. Rossi).

[10]). In the case of electron-conducting polymers, a breakthrough has been the preparation of composite films via electropolymerization of the corresponding monomers in the presence of nanotubes [11–15].

In this context we felt it worthwhile to examine the feasibility of an electrochemical route for the synthesis of poly(1,8-DAN)/SWNT films using dispersions of single-walled carbon nanotubes in 1,8-diaminonaphthalene aqueous solution. Poly(1,8-DAN) belongs to a class of non-conventional conducting polymers, those obtained from the aromatic amines, that are currently stimulating the interest of the scientific community [16,17]. Following this approach, a series of poly(1,8-DAN) layers containing dispersions of SWNTs that had been subjected to different chemical treatments, have been deposited onto a platinum working electrode, and their properties investigated.

## 2. Experimental

The SWNT samples used in this work, supplied by CARBOLEX (AP-grade), were treated following three different chemical routes.

In the first treatment, 200 mg of pristine nanotube sample were dispersed by ultrasound in 200 ml of a 10 M KOH aqueous solution for 15 min. After 1 h the supernatant was removed and the resulting black solid phase was washed with distilled water until neutrality was reached. Then, the sample was dried in an oven at 50 °C.

In the second treatment, the same procedure previously described was carried out on 200 mg of pristine nanotubes suspended in 200 ml of a 2 M HNO<sub>3</sub> aqueous solution.

The third nanotube sample was obtained by dispersing 200 mg of the pristine nanotubes in 200 ml of a mixture of concentrated HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> in a 1:3 volume ratio for 30 min. To reach neutrality, they were washed with distilled water and finally dried at 50 °C.

All these three treatments were performed at room temperature using analytical grade reactants.

The polymer/SWNT composite films were grown using an electrochemical method in which SWNT and polymer are simultaneously deposited onto a platinum foil working electrode (Aldrich, thickness 0.025 mm, purity 99.9%, area 1 cm<sup>2</sup>) using a three-electrode, single compartment electrochemical cell. An Ag/AgCl saturated KCl and a platinum electrode were used as reference and counter electrode, respectively. The anodic polymerization of the 1,8-DAN monomer was carried out at the platinum foil working electrode, using cyclic voltammetry: the potential range was varied from –0.4 V up to +0.5 V with a scan rate of 50 mV s<sup>-1</sup>. All the poly(1,8-DAN)/SWNT composite films were produced by sweeping continuously for 20 cycles. The

polymerization medium was an aqueous electrolyte solution consisting of 1 mM of 1,8-diaminonaphthalene (1,8-DAN) (Aldrich) and 0.1 M HClO<sub>4</sub>. In the solution, fixed amounts (10 mg) of the three differently treated SWNT samples were dispersed. All the dispersions were de-oxygenated using a nitrogen flux.

The electrochemical experiments were performed using an AUTOLAB PGSTAT 12 apparatus. The *I/V* characterizations of the films deposited onto Pt foils were performed at room temperature by using a 4155B Agilent Semiconductor Analyser. The samples were placed in a chamber kept at  $P = 10^{-2}$  mbar. Electrical contacts were made both to the film surfaces and to the metal electrode substrates. Contacts on the film surfaces were obtained by deposition of Ag pads. For all the samples the contacts showed a perfect ohmic behaviour.

The films' structural analysis was performed by use of Raman spectroscopy. The Raman spectra of untreated and treated nanotube samples as well as of the composite films were recorded at room temperature in the back-scattering configuration using an Ar-ion laser beam (wavelength: 514.5 nm; laser power: 10 mW; spectral resolution: 3 cm<sup>-1</sup>).

The morphology of the films was investigated using a Field Emission type Scanning Electron Microscope (FE-SEM Hitachi S-4000) and a Scanning Probe Microscope (SPM NT-MDT Solver Pro) for Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) investigations.

AFM images were realized in semi-contact mode, using commercial silicon cantilevers. STM images were obtained in constant current mode using Pt/Ir tips, previously tested on an HOPG standard sample in order to verify their suitability for topographic performances. The STM measurements were performed at a tunnelling current of 1.0 nA and at bias of +0.1 V relative to the tip. Both STM and AFM characterizations were performed in air and at room temperature.

## 3. Results and discussion

### 3.1. Electropolymerization of 1,8-DAN

The result of the electrochemical oxidation of the 1,8-DAN at the Pt electrode can be observed in Fig. 1(a), which shows the voltammograms recorded during some of the first cycles. At the beginning of the process, the occurrence of an irreversible anodic oxidation is indicated by the broad peaks in the potential region (0.2–0.5) V vs. Ag/AgCl. This result agrees with literature data [17,18], which attribute the anodic irreversible peak to the oxidation of an amino group. The mechanism of the monomer oxidation occurring under our experimental conditions would thus be similar to that reported in

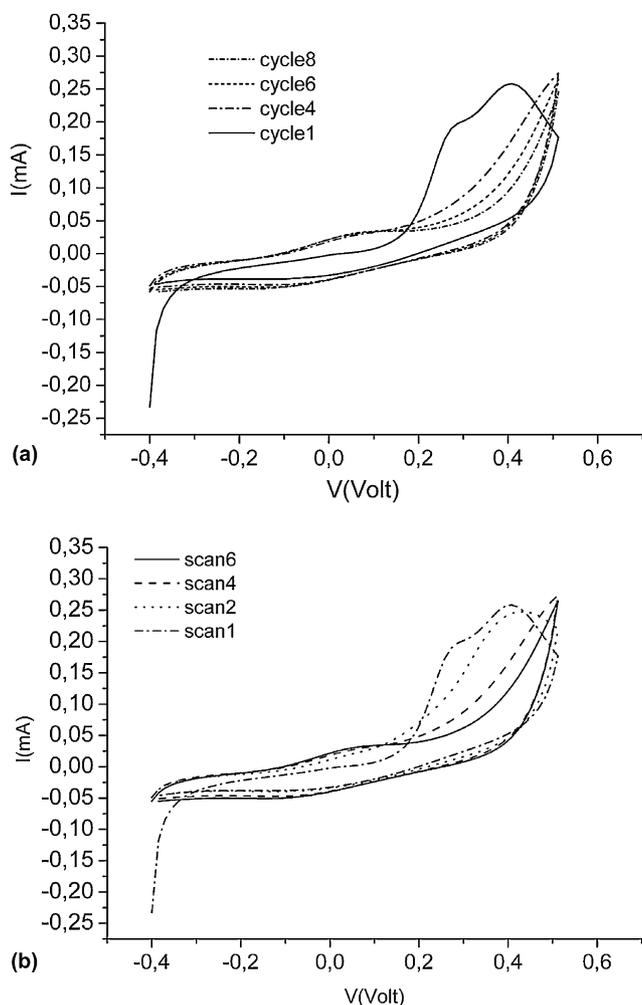


Fig. 1. Cyclic voltammograms for polymerization of 1,8-DAN at platinum electrode (sweep rate of 50 mV/s) from 0.1 M HClO<sub>4</sub> solution containing: (a) 1 mM 1,8-DAN; (b) 1 mM 1,8-DAN and 10 mg of SWNTs.

Refs. [19,20]. During successive cycles, we observed a slight decrease of the voltammetric peak related to the monomer oxidation and the appearance of new reduction-oxidation waves in the potential region ranging from  $-0.2$  V up to  $+0.2$  V. These voltammetric peaks reflect the electroactivity of poly(1,8-DAN) which is being formed on the electrode surface [18]. It is interesting to note that the features of the cyclic voltammograms registered during the synthesis of the polymer/SWNT systems were similar to those of the pure polymer (Fig. 1(b)). This means that the introduction of nanotubes into the polymer matrix does not alter the fundamental electrochemical properties of the polymer.

### 3.2. Morphological and structural characterization

Fig. 2 presents a 3D view from an AFM scan of the surface of a polymer/SWNT composite film. Images obtained from many different regions of several

polymer/SWNT composite films show similar topographical features characterized by the coalescence of polymer globules. The length of such elongated structures ranges between 400 and 600 nm; the transverse dimension between 100 and 200 nm. It is to be noted that a surface morphology characterized by nodular structures is typical of other conducting polymers [21–23]. Many researchers have found a correlation between polymer film surface morphology and polymer conductivity. In particular a nodular structure has been associated with highly doped conducting films in which the nodules represent dopant-rich, highly conductive areas [23]. In our composite films we find the same nodular structures indicating that the polymer growth process has not been affected significantly by the insertion of nanotubes.

Inspection of the composite film by FE-SEM after lightly abrading the surface yielded an image of the distribution and mode of organization of nanotubes inside the host matrix. The FE-SEM images of Fig. 3 reveal the inner morphology of a polymer/SWNT deposit produced using SWNT treated with the HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture. Fig. 3(a) reveals the presence of a random network of interconnected bundles, packed underneath the outermost polymer sheet. This kind of fibre-like organization is found to extend over the whole film area. The bundles present homogeneous structures with diameters in the range 100–300 nm and seem to be enveloped by a uniform polymer skin, as shown in more detail in Fig. 3(b) and (c). In some case we evidenced the formation of large and inhomogeneous polymer/nanotube aggregates on the film surface (Fig. 3(d)).

Fig. 4 is a STM image of the same polymer/SWNT system showing a boundary region between nanotubes and polymer. In Fig. 4(a) and (b) one can clearly observe an array of aligned bundles, each of about 10 nm diameter, in close contact with polymer globules. Fig. 4(c) provides a top-view of the same region and shows the presence of a polymeric deposit. However, no exact information about the relative location of the two materials can be extracted from this 3-dimensional image. The apparent depression in which the polymer seems to be located can be rationalized by considering the lower conductivity of the poly(1,8-DAN) with respect to that of nanotubes, taking into account the physics aspects of the STM analysis. The STM images also indicate that the nanotubes have not been damaged during the polymerization process.

From the combined STM and FE-SEM analysis of a series of samples it is argued that deposition of poly(1,8-DAN) occurs either in the form of large aggregates or in the form of coatings uniformly wrapping the nanotube bundles. The capacity of the polymer to produce two different kinds of deposits seems to be influenced by the degree of dispersion of nanotubes in the starting solution used for polymerization. Relatively thin bundles, such as that of Fig. 4, are likely to act as nucleation

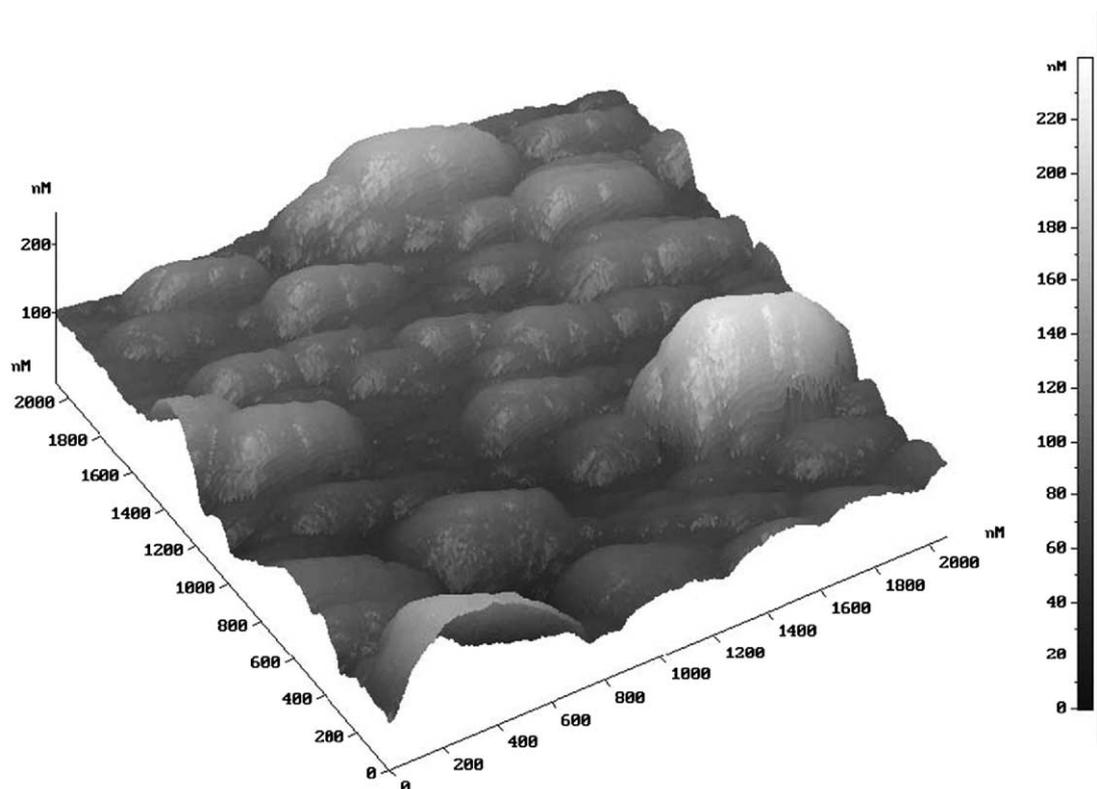


Fig. 2. AFM image of a typical surface morphology of SWNT/polymer films.

centers for the polymerization process, allowing the aggregation of the polymer into large shapeless nodules which encompass the whole bundle array. But if a noticeable amount of oligomers can occasionally be adsorbed onto the walls, as in the case of larger SWNT bundles, polymerization seems to proceed on the surface and results in polymer growth and deposition around the bundle. Such a mode of polymer condensation is consistent with the inner morphology depicted in Fig. 3(b) and (c).

The Raman analysis of nanotube samples and of the pure and composite polymer films has been performed in the 1100–1800  $\text{cm}^{-1}$  spectral region, where one can observe the peaks produced by the tangential modes of carbon nanotubes as well as the peaks ascribable to different forms of poly(1,8-DAN). In Fig. 5(a)–(d) the Raman spectra in the region of tangential modes of graphite are presented for untreated SWNT (Fig. 5(a)) and for SWNT treated with KOH (Fig. 5(b)),  $\text{HNO}_3$  (Fig. 5(c)) and  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture (Fig. 5(d)), respectively. The spectrum of Fig. 5(a) shows the G-band occurring at 1607  $\text{cm}^{-1}$ , probably derived from the Raman-allowed optical mode  $E_{2g}$  of nanographite [24] or of 2D graphite [25]. The spectrum also shows the D-band occurring at 1332  $\text{cm}^{-1}$  and this is attributed to defects in the graphitic systems [26]. The two Lorentzians at 1569 and 1594  $\text{cm}^{-1}$  are, respectively, assigned to

the  $\omega_G^-$  and  $\omega_G^+$  modes of nanotubes; these bands are due to the vibrations along the circumferential direction and to the vibrations along the direction of the nanotube axis [25]. In the Raman spectra of the treated samples (Fig. 5(b)–(d)) an enhancement of the D-band is noted. This effect is particularly evident in the spectrum of the SWNT treated with sulphuric/nitric acid mixture and indicates the formation of structural defects on the surface of tubes. The spectrum of SWNT in KOH reveals a sharp decrement in the intensity of the  $\omega_G^-$ -band, which is consistent with the introduction of  $-\text{OH}$  groups into the nanotube structure and therefore with an increased density of  $\text{sp}^3$ -point defects on the surface of carbon atoms [27].

In our experiments evidence of the functionalization by hydrophilic groups ( $-\text{OH}$ ,  $-\text{COOH}$ ) of SWNT when they are treated with KOH or sulphuric/nitric acid mixture [28] comes from the FT-IR spectra, taken from similarly treated samples [29] and moreover from the observation that such SWNT give stable dispersions in aqueous solution.

As previously noted, not remarkable differences from pristine nanotubes are detected in the Raman spectra of the SWNT after the room temperature treatment in  $\text{HNO}_3$  [30]. The intensity of the  $\omega_G^-$ -band suggests that the treatment was not effective in oxidizing the material. On the other hand SWNT do not give stable dispersions

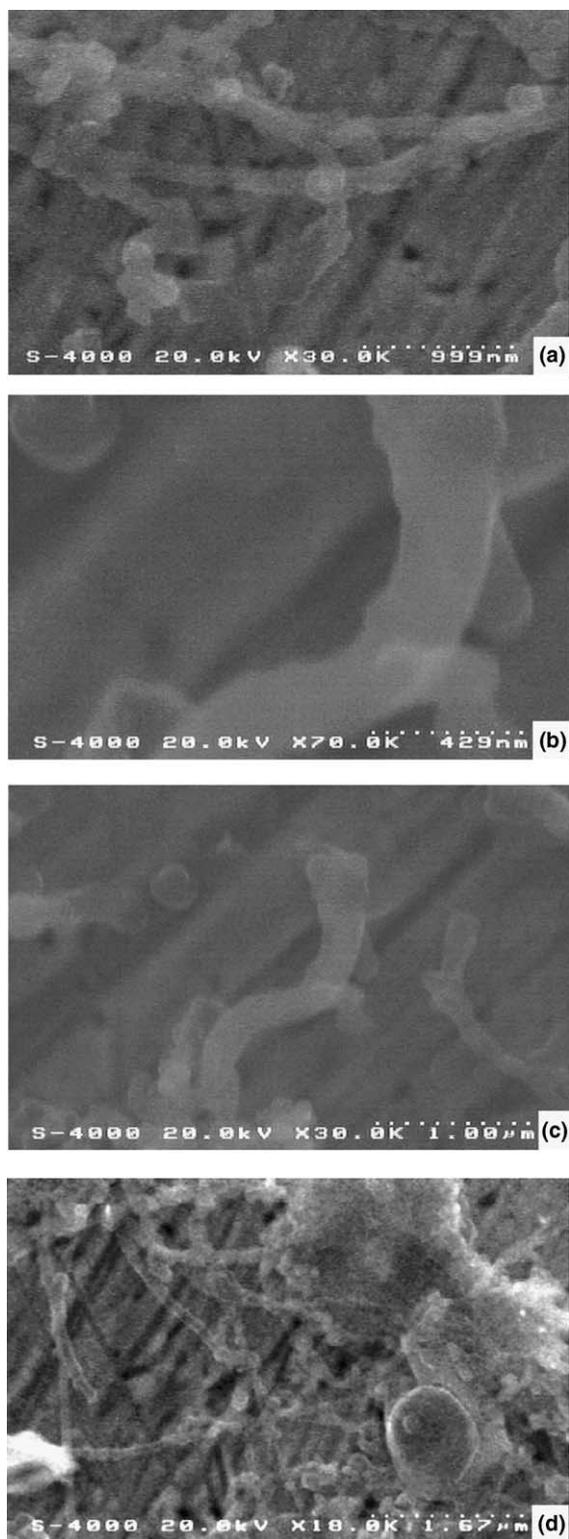


Fig. 3. FE-SEM images taken from a composite SWNT/polymer film after slight scratching of the top surface and showing: (a) shape and distribution of SWNT bundles and typical scratches of the Pt substrate; (b,c) details of SWNT bundles coated with polymer; (d) polymer aggregation in globular micro-islands.

in aqueous solution confirming the absence of significant amount of  $-OH$  or  $-COOH$  polar groups. It is to be

noted that other authors found functional groups only when the nanotubes were treated with concentrated  $HNO_3$  solution at high temperature [31].

However the SWNT treated with  $HNO_3$  showed an increment of the D-band/G-band intensity ratio. This effect can be related to the intercalation and subsequent exfoliation (by  $HNO_3$ ) of the graphitic layers that are present as impurity in the pristine samples.

In the Raman spectrum of pure poly(1,8-DAN) films obtained by electropolymerization of 1,8-diaminonaphthalene (Fig. 6(a)), there are five peaks centered at 1270, 1320, 1390, 1591 and 1625  $cm^{-1}$ , respectively, which have been assigned on the basis of literature data [32]. Here the quinoid band at 1625  $cm^{-1}$  and a broad band at about 1300  $cm^{-1}$ , corresponding to the stretching of the aromatic ring, are ascribed to the totally oxidized form of poly(1,8-DAN). The band at 1580  $cm^{-1}$  and the double peak at 1300–1365  $cm^{-1}$ , typical of the naphthalene ring, are conversely ascribed to the totally reduced form of poly(1,8-DAN). In our case the shift of the 1365  $cm^{-1}$  peak towards higher energies can be due to the overlap with a 1415  $cm^{-1}$  signal produced by the stretching of  $C=N$  bonds. Moreover, visible in the spectrum is a peak centered at 1270  $cm^{-1}$ , which is assigned to the stretching of  $C-H$  bonds. Overall the Raman analysis of pure poly(1,8-DAN) films suggests the presence of a partially oxidized form of the polymer.

The Raman spectra of the composite films exhibit the same bands registered in the spectrum of pure polymer films, even if the signals due to the oxidized form of the poly(1,8-DAN) are more evident. As an example, we report in Fig. 6(b) the spectrum of the composite film obtained using  $HNO_3/H_2SO_4$ -treated SWNT. There is a broad band at 1415  $cm^{-1}$  produced by the  $C=N$  stretching in quinoid structures [20]. It is to be noted that the Raman spectra of polymer/SWNT composite films do not show peaks clearly ascribable to the nanotubes. This is due to the fact that both the radial breathing modes and the tangential modes of nanotubes give peaks which coincide with those from the poly(1,8-DAN), which are of much greater intensity.

### 3.3. Electrical properties

The charge transport properties of the polymer/SWNT composites have been investigated by performing I-V measurements. All the investigated films showed an ohmic behaviour. Fig. 7 shows the  $I/V$  curve for the poly(1,8-DAN)/ $HNO_3$ - $H_2SO_4$  treated SWNT system. Fig. 8 reports the values of current intensity registered at 250 mV for a pure poly(1,8-DAN) polymer film and for a series of polymer/SWNT composite films produced using nanotubes submitted to the various treatments. Comparison of the electrical properties of the various systems is made possible by considering that the films have similar thicknesses, as indicated by the fact that

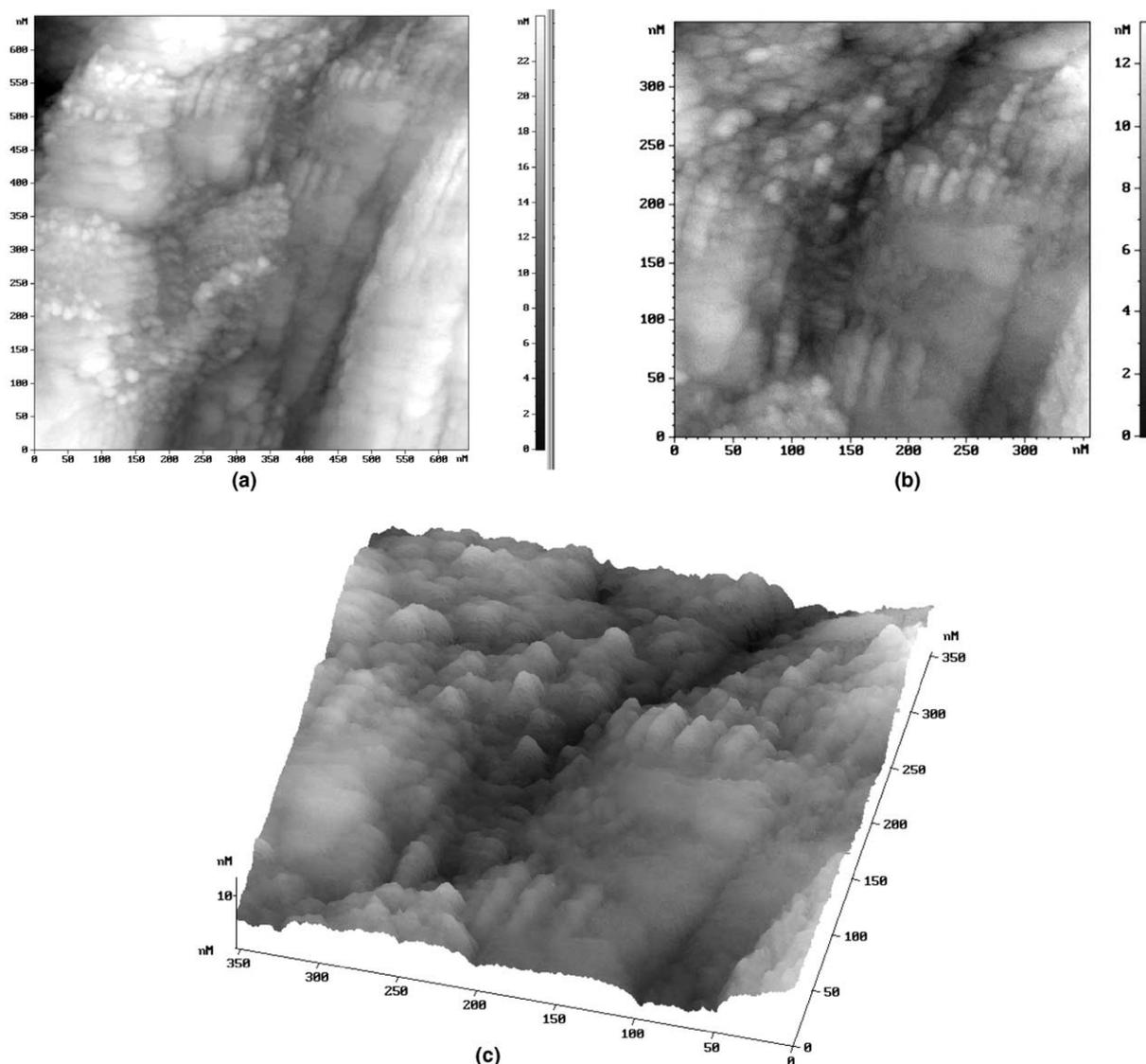


Fig. 4. Imaging by STM of SWNT bundles embedded in the polymeric matrix: (a) large scale image of an array of bundles contacting polymer micro-islands; (b) higher resolution of the same area; (c) top view micrograph showing the material microstructure on a 3-dimensional scale.

the currents measured during the pure polymer and the composite synthesis were the same. As one can observe, the pure poly(1,8-DAN) film exhibits a rather low value of current ( $220 \mu\text{A}$ : point A of Fig. 8). The intrinsic conductivity of the polymer is due to the presence of positive charges, namely polarons and bipolarons, delocalized along the conjugated chain and likely stabilized by the perchlorate anions present in the synthesis solution. These anions would act as an anionic dopant and the polymer can thus be considered a p-type semiconductor. A different behaviour is found for the polymer/SWNT systems, which, in any case, exhibit a higher conductivity than the pure polymer. Moreover it is clear that, even if both chemically treated and untreated SWNT are found to enhance the charge transport, the electrical properties of the composites show significant variations depending on the treatments to

which the SWNT were submitted. Starting from a value of 4 mA (point B of Fig. 8) for the films containing non-treated nanotubes, current values measured at 250 mV were:

- 10 mA for films containing SWNT treated with  $\text{HNO}_3$  (point C of Fig. 8);
- 20 mA for films containing SWNTs treated with KOH (point D of Fig. 8);
- 30 mA for films containing SWNT treated with the sulphuric/nitric acid mixture (point E of Fig. 8).

This indicates that the incorporation of nanotubes inside the polymeric matrix leads to an increase in charge transport by a factor ranging between 20 and 140, depending on the chemical processing of the SWNT.

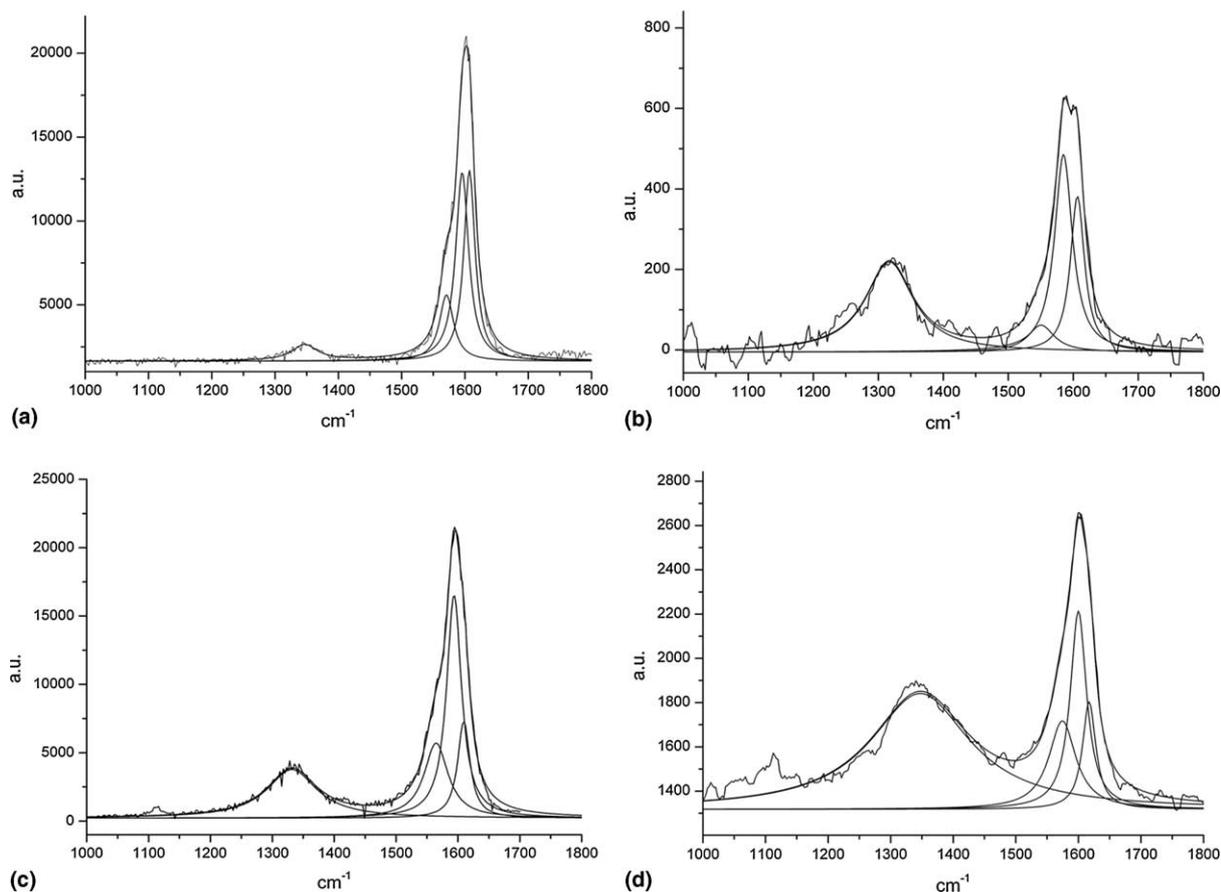


Fig. 5. Raman spectra in the region of the tangential modes of graphite taken from different samples of nanotubes: (a) untreated SWNT; (b) SWNT treated by KOH; (c) SWNT treated by HNO<sub>3</sub>; (d) SWNT treated by the HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture. The spectral data have been derived by curve fitting of the spectra to Lorentzian lines after background subtraction.

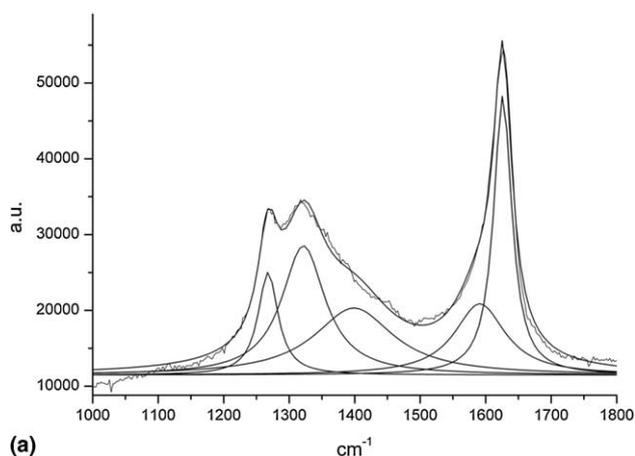
The strong dependence of the film conductivity on the chemical treatments of nanotubes deserves some comment. The introduction of nanotubes into a polymeric matrix and the production of arrays of interconnected bundles are expected to create pathways for charge transport. This effect is clearly evident in the case of non-conducting polymers [33], where the incorporation of nanotubes allows the production of a final conducting composite material. In the present experiments, considering that a conducting polymer is used as the host matrix, the SWNT are expected to act as bridges efficiently connecting conductive domains of poly(1,8-DAN) and thus facilitating the total charge transport. This situation can be accounted for by the nanometer-scale structures that are revealed in FE-SEM and STM images. It is also to be noted that indeed under our experimental conditions the insertion of nanotubes inside the polymer matrix is influenced by the presence of hydrophilic groups, such as the –OH and –COOH groups introduced at the tube surfaces by the chemical treatments. The polarity introduced by these functionalizations facilitates the dispersion of nanotubes within the matrix. The opening of conducting channels therefore appears to be more efficient in the case of more effective oxida-

tion processes, such as those induced by KOH and HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> solutions. With the use of these reactants, the current at a given voltage was increased by factors of 5 and 7.5, respectively, with respect to that measured when using untreated nanotubes. Conversely, when the chemical processes are less efficient in producing –OH and –COOH groups, it is verified that the current increased only a factor of about 2.5 relative to that of untreated nanotubes.

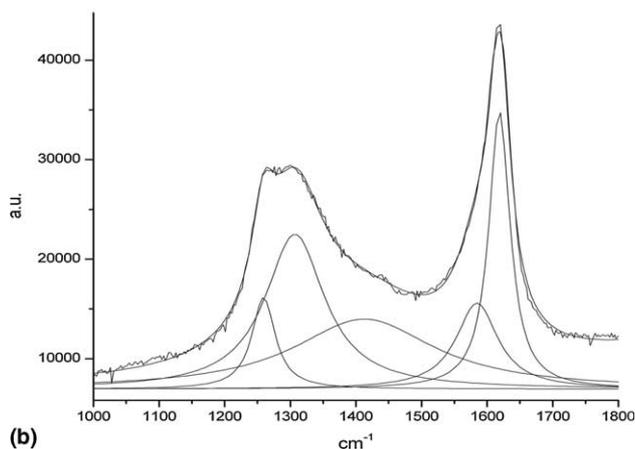
Concerning the conductivity of pure SWNT, no significant differences are found between treated and untreated material. Experiments performed using multifinger electrodes, with the same quantity of nanotubes (50 μg) indicate for both treated and untreated nanotubes resistance values in the range 300–2000 Ω, typical values for metal-like nanostructured materials.

#### 4. Conclusions

In the present study we synthesized poly(1,8-DAN)/SWNT composites, by using monomer precursors that undergo polymerization in the presence of a solution



(a)



(b)

Fig. 6. Raman spectra of: (a) pure poly(1,8-DAN) film; (b) composite poly(1,8-DAN)/SWNT film ( $\text{HNO}_3/\text{H}_2\text{SO}_4$  treated nanotubes).

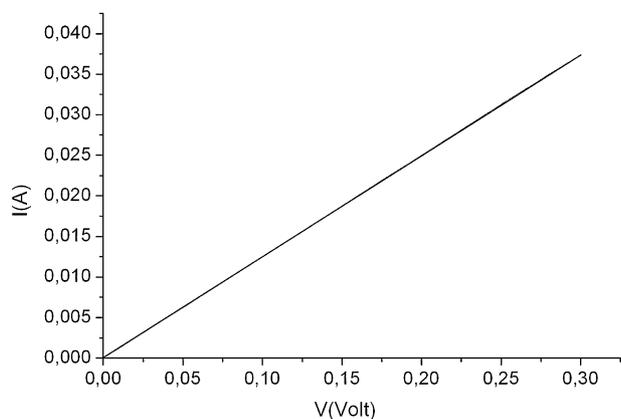


Fig. 7.  $I/V$  curve of a poly(1,8-DAN)/SWNT film ( $\text{HNO}_3/\text{H}_2\text{SO}_4$  treated nanotubes).

containing nanotubes. Following this electrochemical synthesis route, it is possible to generate polymer-based composites in which the nanotubes are not simply mixed up or blended with the polymer, but are also in intimate contact with the polymer through specific chemical interactions.

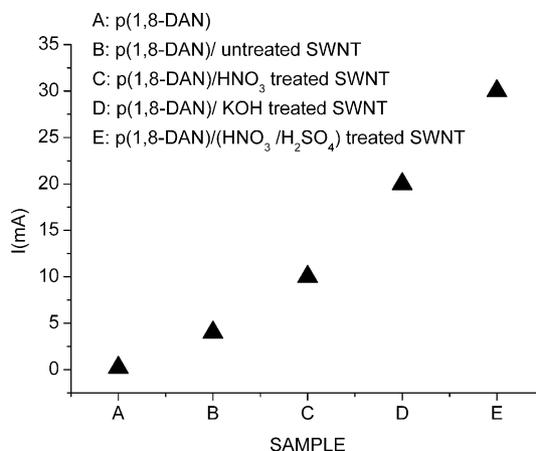


Fig. 8. Values of current intensity measured at 250 mV for series of films submitted to different treatments: (a) pure polymer film; (b) polymer film containing untreated nanotubes; (c) polymer film containing nanotubes treated by  $\text{HNO}_3$ ; (d) polymer film containing nanotubes treated by KOH; (e) polymer film containing nanotubes treated by the  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture.

The present data demonstrate that the electrical properties of the poly(1,8-DAN)/SWNT composites are strongly governed by the chemical state of the nanotubes, which in turn controls matrix/nanotube connectivity and phase segregation. In particular an extensive functionalization of nanotubes via the formation of large numbers of  $-\text{OH}$  and  $-\text{COOH}$  groups (as produced by the KOH and  $\text{HNO}_3/\text{H}_2\text{SO}_4$  treatments) is found to enhance the current values measured for the host poly(1,8-DAN) matrix by factors of 20 and 140, respectively. These results can be rationalized by considering that nanotubes functionalized by hydrophilic groups form stable solutions and that a uniform mixing of nanotube bundles and 1,8-diaminonaphthalene moieties is expected to occur during the process of polymerization. Moreover, the ratio of  $-\text{NH}_2$  to  $-\text{OH}$  or  $-\text{COOH}$  groups has an impact on the nanotube/polymer interaction.

The findings of the present research prove that the above described synthesis approach can be a feasible pathway for the fabrication of a very important class of materials based on nanotube/polymer systems. In particular, the investigation of the effects on the composite's properties induced by the different treatments of the nanotubes indicates that it would be possible to further maximize the electrical and electrochemical performances of the base polymer. In this context the choice of carefully tailored chemical processing turns out to be a key task in the rational design of new structures able to serve the future demands of technology. In addition, the role played by some electrolytes acting as dopants during the polymerization process has to be clarified. Systematic studies on the effect of different solvents and dopants are being performed in our laboratories, and will be analyzed in a forthcoming paper.

## Acknowledgments

The research work has been partially supported by the Italian National Program FISIR “Development of technologies and modelling for the synthesis of nano-phases and nanostructured materials”.

## References

- [1] Skotheim TA, Elsenbaumer RL, Reynolds JR, editors. Handbook of conducting polymers. 2nd ed. New York: Marcel Dekker; 1998.
- [2] Ijima S. Nature 1991;354(6348):56–8.
- [3] Ijima S, Ichihashi T. Nature 1993;363(6430):603–5.
- [4] Dresselhaus MS, Ecklund G. Science of fullerenes and carbon nanotubes. San Diego: Academic Press; 1996.
- [5] Wang J, Musameh M. Anal Chem 2003;75(9):2075–9.
- [6] Li B, Cao T, Cao W, Shi Z, Gu Z. Synth Met 2002;132(1):5–8.
- [7] Kymakis E, Alexandrou I, Amaratunga GAJ. Synth Met 2002;127(1–3):59–62.
- [8] Kymakis E, Amaratunga GAJ. Appl Phys Lett 2002;80(1):112–4.
- [9] El-Hami K, Matsushige K. Chem Phys Lett 2003;368(1–2):168–71.
- [10] Mamedov AA, Kotov NA, Prato M, Guldi DM, Wicksted JP, Hirsch A. Nat Mater 2002;1(3):190–4.
- [11] Li X, Wu B, Huang J, Zhang J, Liu Z, Li H. Carbon 2003;41(8):1670–3.
- [12] Park C, Ounaies Z, Watson KA, Crooks RE, Smith Jr J, Lowther SE, et al. Chem Phys Lett 2002;364(3–4):303–8.
- [13] Jurewicz K, Delpoux S, Bertagna V, Béguin F, Frackowiak E. Chem Phys Lett 2001;347(1–2):36–40.
- [14] Maser WK, Benito AM, Callejas MA, Seeger T, Martinez MT, Scheiber J, et al. Mater Sci Eng C 2003;23(1–2):87–91.
- [15] Feng W, Bai XD, Lian YQ, Liang J, Wang XG, Yoshino K. Carbon 2003;41(8):1551–7.
- [16] Song FY, Shiu KK. J Electroanal Chem 2001;498(1–2):161–70.
- [17] Majid S, El Rhazi M, Amine A, Curulli A, Palleschi G. Microchim Acta 2003;143(2–3):195–204.
- [18] Oyama N, Sato M, Ohsaka T. Synth Met 1989;29(1):501–6.
- [19] Lee JW, Park DS, Shim YB. J Electrochem Soc 1992;139(12):3507–13.
- [20] Li X-G, Huang M-R, Duan W, Yang Y-L. Chem Rev 2002;102(9):2925–3030.
- [21] Porter TL, Caple K, Caple G. J Vac Sci Technol A 1994;12(4):2441–5.
- [22] Silk T, Hong Q, Tamm J, Compton R. Synth Met 1998;93(1):59–64 and 65–71.
- [23] Barishi JN, Stella R, Spinks GM, Wallace GG. Electrochim Acta 2000;46(4):519–31.
- [24] Ferrari AC, Robertson J. Phys Rev B 2000;61:4095–14017.
- [25] Dresselhaus MS, Dresselhaus G, Jorio A, Souza Filho AG, Saito R. Carbon 2002;40(12):2043–61.
- [26] Tuinstra F, Koenig JL. J Chem Phys 1970;53(3):1126–30.
- [27] Pan H, Liu L, Guo Z, Dai L, Zhang F, Zhu D, et al. Nano Lett 2003;3(1):29–32.
- [28] Esumi K, Ishigami A, Nakajima A, Sawada K, Honda H. Carbon 1996;34(2):279–81.
- [29] Curulli A, Valentini F, Orlanducci S, Tamburri E, Terranova ML, Nunziante Cesaro S, et al. Proceedings of 2004 Fourth IEEE Conference on Nanotechnology 2004, Munich—Germany, in press.
- [30] Valentini F, Orlanducci S, Terranova ML, Amine A, Palleschi G. Sens Actuators B 2004;100(1–2):117–25.
- [31] An KH, Jeon KK, Moon JM, Eum SJ, Yang CW, Park GS, et al. Synth Met 2004;140(1):1–8.
- [32] Palys BJ, Bukowska J, Jackowska K. J Electroanal Chem 1997;428(1–2):19–24.
- [33] Sandler J, Shaffer MSP, Prasse T, Bauhofer W, Schulte K, Windle AH. Polymer 1999;40(21):5967–71.