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SCIENCE DIRECT
Diamond & Related Materials 15 (2006) 95 – 99
DIAMOND AND RELATED MATERIALS
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Selective interaction of single-walled carbon nanotubes with conducting dendrimer

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Received 15 December 2004; accepted 6 July 2005
Available online 1 August 2005

Abstract

We report on the transport properties of a system composed of single-wall carbon nanotubes (SWNTs) noncovalently linked to a new electrically conducting dendrimer poly(amidoamine) modified with a substituted naphthalenediimide (PAMAMC). SEM images show how the adsorption of the conducting dendrimer on SWNTs leads to the unroping of the bundles. The adsorption of PAMAMC molecules on SWNTs has been also investigated by electrical transport measurements. The electrical conductance of SWNTs drastically increases upon adsorption of conducting dendrimer. UV – Vis spectroscopy indicates that there was a modification in the electronic structure of the dendrimer as consequence of nanotube introduction while the appearance of new bands on the Raman spectra may suggest that metallic nanotubes are selectively functionalized.

Keywords: Nanotubes; Electrical properties; Composites

The assembly of complex nanostructures designed for specific functions is of increasing interest for a broad variety of applications. On this regard, conducting polymers [1] were combined with carbon nanotubes [2–4] in novel photovoltaic devices. Electronic devices made from carbon nanotubes [5,6], such as field-effect transistor (FET) devices [7–11], are much smaller and more versatile than those obtained on conventional microelectronic chips.

Semiconducting SWNTs generally show unipolar p-type behaviour [12,13]. By doping with potassium, the unipolar p-type behaviour can be switched to unipolar n-type behaviour. This approach has been used to build single tube p-n diodes [14] and complementary logic gates. n-type doping was realized by simply spin casting polyethylene imine on top of a SWNT [15,16]. These favourable intrinsic electrical characteristics and the easy ability to tune them make SWNT devices potentially attractive for a range of applications but two issues are widely recognized as impeding the development of these devices: separation according to electronic properties and manipulation into addressable arrays.

For this purpose, in this paper an innovative functionalization method of SWNTs has been proposed: an electrically conducting dendrimer based on commercial poly(amidoamine) (PAMAM) peripherally modified with a substituted naphthalene diimide. We felt that a three-dimensional structure would be more suitable to afford the pathway for conductivity and allow the formation of noncovalent links with SWNTs through stacks of π-conjugated molecules.

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doi:10.1016/j.diamond.2005.07.003

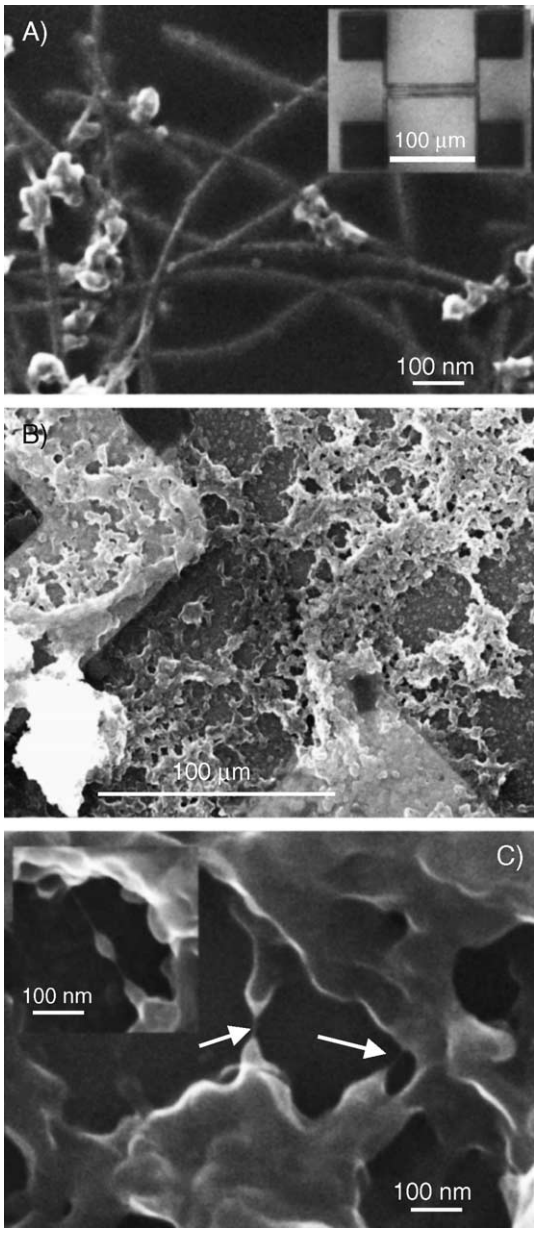

Fig. 1. SEM images of A) the specimen of pristine SWNT cross-linked bundles (the inset shows SEM micrograph of the device geometry), B) SWNTs dispersed in PAMAMC between the electrical contacts and C) SWNTs dispersed in PAMAMC (the arrows indicate the tubes; the inset shows SEM micrograph of PAMAMC coating SWNTs).

We examine this result in greater detail by combining spectroscopic and electron transport of SWNTs and SWNTs modified with the conducting dendrimer. Electrical transport measurements and Raman spectroscopy are used to characterize the deposited material. It is proposed that the enrichment of metallic nanotubes may proceed by functionalization of metallic nanotubes with conducting PAMAM (PAMAMC). We seek to develop these chemical methods as means of selectively manipulating a heterogeneous mixture of nanotubes in solution.

The transport properties were measured in a thin-film transistor geometry (inset of Fig. 1A). Source-drain electrodes were fabricated using e-beam lithography technique on a 250 nm-thick thermal silicon oxide on a Si wafer. The electrodes consisted of a 40 nm bottom layer of Al coated with 40 nm thick layer of Au. The device geometry was varied with the source-drain channel length, L_{sd} , ranging from 8 to 16 μm and the channel width, W, ranging from 50 to 100 μm.

SWNTs were obtained from CarboLex, Inc. and consisted of ≈50–70 vol.% carbon as SWNTs; noticeable amount of SWNT bundles of 30–50 nm in diameter was found.

Conducting PAMAM was a laboratory preparation synthesized by reaction between the amino terminal groups of a generation three PAMAM and the hydrochloride salt of monoimide monoanhydride in *N*,*N*-dimethylformamide (DMF): details for the synthesis and reaction with PAMAM end groups are reported in references [17,18]. Noncovalent interactions between PAMAMC and SWNTs have been achieved by sonication in DMF followed by centrifugation to remove undissolved tubes.

Two types of FET devices were prepared. In the first type of device, SWNTs were deposited from DMF solution onto SiO_2/Si wafer with previously patterned electrical contacts. The second type of device was fabricated by depositing SWNTs dispersed in modified PAMAM onto the electrodes. In both types, a network of nanotubes connects the source and drain contacts, and the network serves as the channel of a field-effect transistor (Fig. 1B). We measured the source-drain current (I_{sd}) as a function of the gate voltage (V_g) under gate voltage sweep for both types.

Micrographs of the SWNTs and SWNTs modified with PAMAMC were obtained with a scanning electron microscope JEOL 6500. Raman spectroscopy was performed on powdered samples after DMF removal by vacuum distillation in order to study nanotubes typical peaks before and after interaction with PAMAMC. The instrument was a Bruker RF100 provided of NdYAG laser (λ=1064 nm; 1.17 eV).

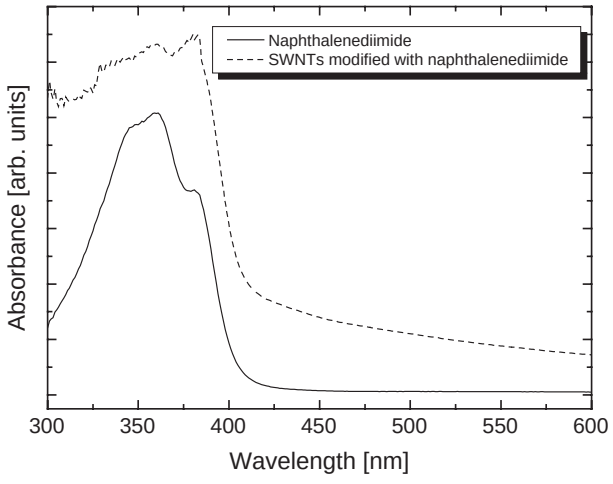

Fig. 2. UV–Vis spectra of naphthalenediimide and SWNTs dispersed in naphthalenediimide.

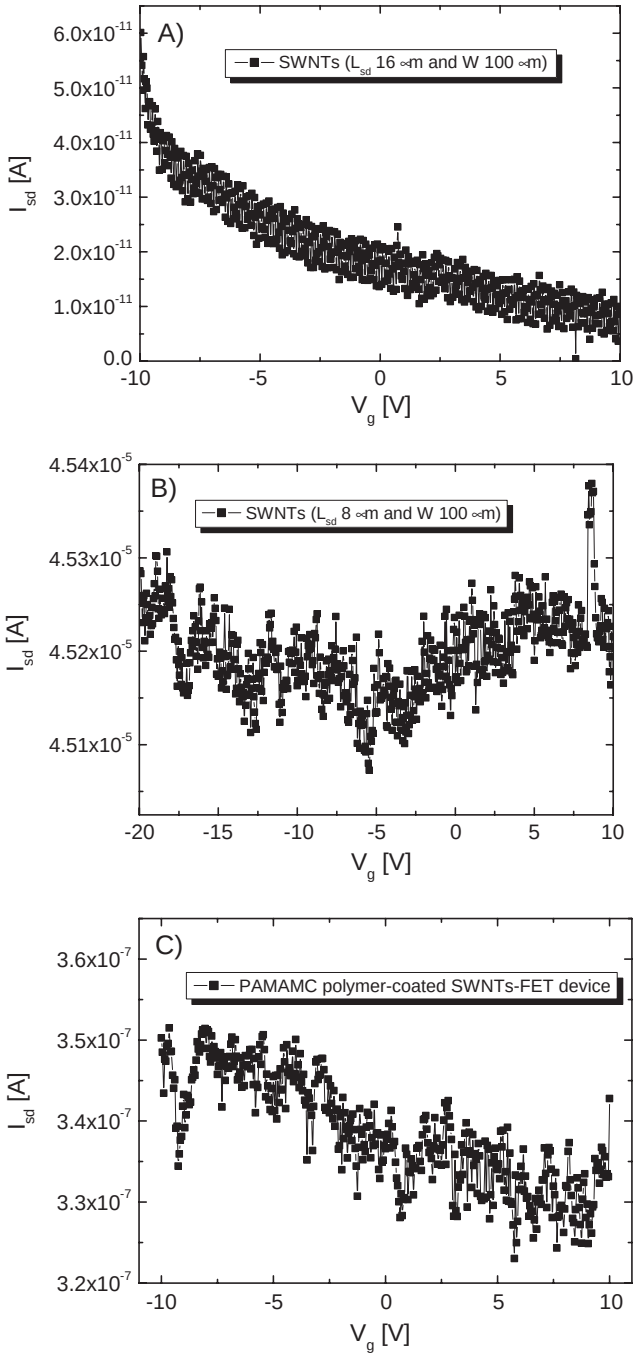

Fig. 3. A) I_{sd} vs V_g at V_d=0.5 V for SWNTs-FET with a channel width of 100 μm and a channel length of 16 μm; B) I_{sd} vs V_g at V_d=0.5 V for SWNTs-FET with a channel width of 100 μm and a channel length of 8 μm C) I_{sd} vs V_g at V_d=0.5 V for PAMAMC/SWNTs-FET device with a channel width of 100 μm and a channel length of 16 μm.

The SEM study of pristine SWNT network reveals a large number of cross-linked nanotube bundles (Fig. 1A). SEM micrographs (Fig. 1C) put in evidence locally that the addition of the dendrimer to carbon nanotubes leads to the unroping of SWNTs.

Since the conducting dendrimer has been obtained by peripheral modification by a substituted naphthalenediimide, UV–Vis spectroscopy was then used to verify the occurrence of interactions dispersing SWNTs in naphthalenediimide (Fig. 2). Naphthalenediimide spectrum (Fig. 2) shows two peaks at 360 and 380 nm respectively. Passing from naphthalenediimide to the composite containing nanotubes, no new signal appears but a difference in their intensity is evident. This finding suggests a slight modification in the electronic structure of the dendrimer as a consequence of nanotube introduction and, accordingly, a weak interaction as a noncovalent bond.

Fig. 3A plots the transistor characteristics for the SWNT network with device dimensions of L_{sd} 16 μm and W 100 μm. From I_{sd} vs V_g measurements with drain voltage, V_d, fixed at 0.5 V, we found that the ensemble of SWNTs in each device appeared p-type, exhibiting an overall electrical conductance decrease by a factor 4–5 when the gate voltage was swept from −10 to 10 V. The nonelectrical depletion of FET device at positive gate voltage was due to conduction of small percentages of metallic nanotubes in the ensemble.

The data from the device fabricated using SWNTs networks with L_{sd} 8 μm and W 100 μm are plotted in Fig. 3B. The drastic switching clearly differed from the first device with the lack of gate dependence. The high off-state current is consistent with the behavior of a narrow band gap semiconductor. Fuhrer et al. [19] have shown that the

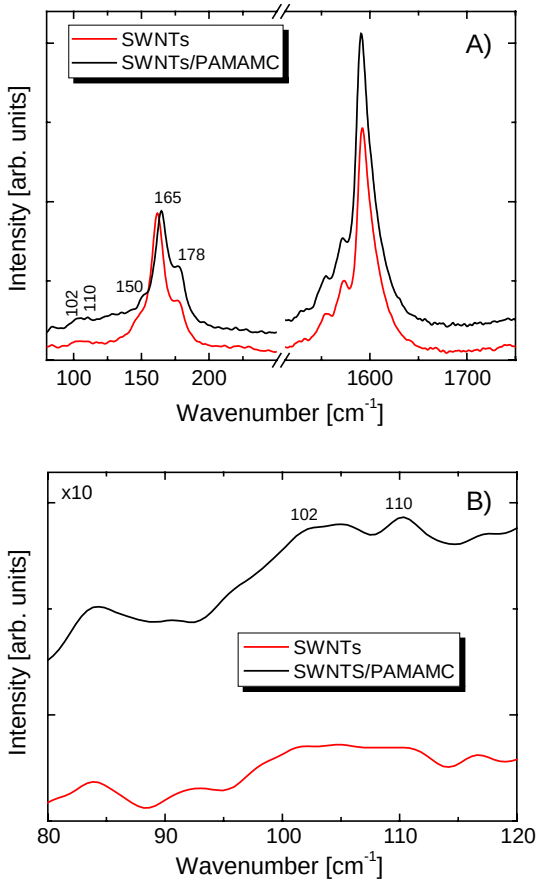

Fig. 4. A) Raman spectra of SWNTs and SWNTs modified with PAMAMC; B) Raman spectra of SWNTs and SWNTs modified with PAMAMC for wavenumbers below 120 cm^{-1} with the signal multiplied by ten.

ensemble of a metallic and a semiconducting SWNT network forms a Schottky barrier with a barrier height approximately equal to 1/2 band gap of the semiconducting SWNTs. Consequently such resistor networks are electrically conducting if the density of connected resistors exceeds a percolation threshold.

Fig. 3C shows the characteristic for the SWNT network modified with PAMAMC device with the dimensions of L_{sd} 16 μm and W 100 μm. The device shows a weak gate dependence of conductance. In this device, the on-state current is higher with respect to that observed for the same device tested with SWNTs (see Fig. 3A). According to a similar study reported on reference [20], this change could be explained by the effect of interaction of PAMAMC on the tubes. The key difference between the device reported on reference 20 and the present one is that in our case the device properties are achieved without precision assembly of the nanotubes suggesting that the random carbon nanotube networks may be a material for thin-film electronic applications.

The conduction is also accompanied by a high off-state current. The higher off-state current with respect to the SWNTs-FET could be explained by metallic tubes within a SWCNT bundle that may be preferably selected under polymer interaction, resulting in a decrease of the gate dependence.

In order to confirm this hypothesis in Fig. 4A comparison of the Raman spectra of SWNTs and SWNTs dispersed in PAMAMC is reported. The spectra are dominated by significative differences only when the radial breathing modes are considered (Fig. 4A). This low frequency bands can be attributed to the nanotube diameter [21,22]. As when the nanotubes are incorporated in the polymer the bands located at 147 and 161 cm^{-1} are shifted toward higher frequencies then the shifts observed can be explained by intercalation of polymer into the bundles as observed in Fig. 3C.

Bands belonging to this group are very sensitive to the excitation wavelength; the intensity of each band is enhanced when the photon energy of the excitation light corresponds to the transition between the van Hove singularities (E_{ii}) in the valence and conduction bands of all possible nanotubes [21,22]. Compared to the SWNTs network, there are two new weak bands at about 110 and 102 cm^{-1} for SWNTs modified with PAMAMC (Fig. 4B). These new bands related to the tubes of 2.03 and 2.2 nm diameter, are attributed by Lefrant et al. [23] to the metallic tubes whose calculated energies E_{11}^{M} of 1.23 and 1.14 eV, respectively, are not so far from the excitation energy 1.17 eV ($\lambda = 1064$ nm). This result may suggest that the conducting dendrimer deposition creates material with a selection of metallic nanotubes. An appropriate Raman evidence of the selective interaction with metallic SWNTs needs a comparative Raman study performed at different excitation laser energies situated outside and inside of metallic window when the semiconducting and metallic tubes are resonantly excited, respectively. This will remain a challenging task for our work in the next future on this new class of materials.

We therefore conclude that the high off-state current of PAMAMC coated SWNTs is not caused by continuous paths of larger diameter nanotubes (i. e. in the PAMAMC/SWNT system the laser couples preferentially to smaller tubes) but could be attributed to the selection of metallic nanotubes.

A system composed of SWNTs noncovalently linked to a new electrically conducting dendrimer has been demonstrated to interact with tubes and unrope them. This ensemble in such a FET device collectively exhibits large electrical conductance changes under electrostatic gating, owing to the interaction between SWNTs and the conducting dendrimer. The effect of sidewall functionalization on the nanotube surface conductance gives rise to important aspects for building nanotube-based electronics.

Acknowledgements

One of the authors (I.A.) gratefully acknowledges the financial support from the National Consortium of Materials Science and Technology (INSTM). This work was carried out with the financial support from the MIUR (PRIN 2003, prot. 2003093440).

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