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Surfactant-free assembling of functionalized single-walled carbon nanotube buckypapers

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Abstract

The electrical and textural properties of single-walled carbon nanotube buckypapers were tunned through chemical functionalization processes. Single-walled carbon nanotubes (SWCNTs) were covalently functionalized with three different chemical groups: Carboxylic acids (-COOH), benzylamine (-Ph-CH_2-NH_2), and perfluorooctylaniline (-Ph-$(CF_2)_7$-CF_3). Functionalized SWCNTs were dispersed in water or dimethylformamide (DMF) by sonication treatments without the addition of surfactants or polymers. Carbon nanotube sheets (buckypapers) were prepared by vacuum filtration of the functionalized SWCNT dispersions. The electrical conductivity, textural properties, and processability of the functionalized buckypapers were studied in terms of SWCNT purity, functionalization, and assembling conditions. Carboxylated buckypapers demonstrated very low specific surface areas (< 1 m^2/g) and roughness factor (R_a= 14 nm), while aminated and fluorinated buckypapers exhibited roughness factors of around 70 nm and specific surface areas of 160-180 m^2/g. Electrical conductivity for carboxylated buckypapers was higher than for as-grown SWCNTs, but for aminated and fluorinated SWCNTs it was lower than for as-grown SWCNTs. This could be interpreted as a chemical inhibition of metallic SWCNTs due to the specificity of the diazonium salts reaction used to prepare the aminated and fluorinated SWCNTs.

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The utilization of high purity as-grown SWCNTs positively influenced the mechanical characteristics and the electrical conductivity of functionalized buckypapers.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are very attractive materials due to their exceptional geometry and properties at the nanoscale. SWCNTs exhibit high electrical conductivity and superior mechanical performance, and offer multiple options for the synthesis of supramolecular complexes through molecular physical interactions or covalent functionalization. The preparation of SWCNT-based films and fibers has been up to date the most successful way to transfer SWCNTs properties from the nano- to the microscale level [1, 2].

Carbon nanotube sheets (buckypapers) are usually prepared from nanotube dispersions in polymer or surfactant solutions. Sonication and centrifugation treatments of SWCNTs in surfactant solutions improve SWCNT purity [3] and dispersion quality [4]. Residual surfactant or polymer molecules, preferentially adsorbed on SWCNT crossings [5], change some of their properties [6]. This could affect the buckypaper assembling process and final characteristics. Transparent thin films of SWCNTs can be made by vacuum filtration [7], air-spraying [8], rod-coating [9], and other techniques. New SWCNT-polymer composite thin films integrate transparency, flexibility, and conductivity [10], three very valuable features for electronic applications.

In pure SWCNT networks, electrical conductivity is controlled by the contact resistance at intertube junctions, and mechanical properties depend on weak interactions (van der Waals forces) between nanotubes. For SWCNT-polymer composites, conductivity and mechanical properties are usually discussed as percolation phenomena. Besides

conductivity and mechanical properties, textural characteristics of SWCNT films are important for some applications in energy storage and chemical catalysis [11].

SWCNTs can be dispersed in water without surfactants or polymers by chemical functionalization. The reaction of SWCNTs with nitric or sulfuric acid is a classical strategy to incorporate carboxylic acid groups that can behave as reactive units [12]. Carboxylic groups covalently attached to SWCNTs increase their hydrophilic behavior, and contribute to the stabilization of SWCNT suspensions.

Another extremely interesting route to covalently functionalize SWCNTs is the reaction with diazonium salts [13]. By using different aromatic amines, a number of functional groups can be grafted onto nanotubes sidewalls. Diazonium reactions are usually preceded by a stage of SWCNT sonication in specific solvents, and the reaction takes place with the suspended nanotubes. When diazonium salts are generated *in situ*, N,N'-dimethylformamide (DMF) works well as the solvent [14].

Buckypaper properties are determined by the nanotubes purity, dispersion, and functionalization. In this article, functionalized SWCNT buckypapers were prepared by vacuum filtration without surfactants. Three different covalent functional groups were anchored to SWCNTs: Carboxylic acids (-COOH), benzylamine (-Ph-CH_2-NH_2), and perfluorooctylbenzene (-Ph-$(CF_2)_7$-CF_3). Carboxylic groups were inserted by treatment with nitric acid, while the primary amine group and the perfluorinated aliphatic chain were both successfully grafted to SWCNTs by the diazonium salts route. These functionalization reactions on SWCNTs were studied in terms of the electrical conductivity and textural properties of the resulting buckypapers. We propose that different experimental procedures based on SWCNT covalent functionalization could be applied to modulate the properties of self-assembled SWCNT substrates for energy storage, catalysis, and sensors fabrication.

2. Experimental

2.1. Materials and analytical techniques

SWCNTs were produced by the electric arc discharge technique with Ni/Y catalysts (4/1 atomic %). SWCNTs relative purity was checked by near infrared (NIR) absorption spectroscopy [15] using a Bruker VERTEX 70 spectrometer. In order to study the role of the as-grown SWCNTs purity in buckypaper assemblage, different batches of as-grown SWCNTs were utilized with nominal NIR purity of 45-50% and 25-30%.

X-ray diffraction (XRD) measurements were performed at room temperature on a Bruker AXS D8 Advance diffractometer using CuKα radiation. Raman spectra were obtained in a HORIBA Jobin Ybon spectrometer, model HR 800 UV working with a 532 nm laser. Nitrogen adsorption analysis at -196°C for surface area determination was carried out in a Micromeritics ASAP 2020 equipment. Thermogravimetric analysis (TGA) in a carbon dioxide atmosphere up to 1300°C was carried out in a Setaram balance, model Setsys Evolution. Metal content was determined by induced coupled plasma spectroscopy using an ICP-OES JY 2000 ULTRACE equipment.

Elemental analysis was performed using a Thermo Flash 1112 analyzer. For a typical C, H, and N determination, samples are burnt in pure oxygen at 950°C in the presence of V_2O_5. Combustion products pass through an oxidant bed of CuO at 950°C to be converted into NO_x, CO_2, and H_2O. Then, a reductor bed of Cu metal at 500°C transforms NO_x into N_2. The gases are separated in a polar chromatographic column, and quantified by thermal conductivity. For oxygen content analysis, samples are heated to 1080°C, and the pyrolisis products are reduced to CO in a carbon black bed.

Atomic force microscopy (AFM) was performed in a Veeco Nanoscope V equipment in the tapping mode. A phosphorous (n)doped Si tip was utilized with a resonance frequency of around 300 KHz and a force constant of 40 N/m. Electrical conductivity was measured using a Keithley 4200-SCS equipment in a four point probe configuration. The four tip probes were separated by distances of 1.3 mm and aligned on the buckypapers diameter.

2.2. Preparation of carboxylated buckypapers

As-grown SWCNTs were purified following an experimental procedure inspired in Ref. [16]. Fig. 1 shows a schematic chart of a typical SWCNT purification process. 500 mg of SWCNTs were refluxed in 75 mL of 7M HNO_3 at 150°C for time intervals ranging between 1-6 h, preferentially between 2-4 h. The resulting mixture was separated into two centrifugation tubes, bath sonicated for 30 min, and centrifuged (Hermle LaborTechnik, Z383) at 3500 rpm (6000g) for 15 min. The supernatants were decanted off, and each sediment was redispersed in 50 mL of deionized water by 30 min bath sonication. Dispersions were centrifuged at 3500 rpm maintaining pH at 1-2 [17] by the addition of small amounts of HCl. Centrifugation at 3500 rpm was repeated twice more to maximize the removal of amorphous carbon impurities [17]. The yield of the centrifugation processes at 3500 rpm was of ~ 50 wt%.

The resulting sediments were redispersed in deionized water, bath sonicated for 3 h, and centrifuged at 13000 rpm (23000g) for 1h. The supernatant (Supernatant 1, Fig. 1), enriched in SWCNTs, was carefully decanted and stored. The sediment was redispersed in water, bath sonicated for 30 min, centrifuged at 13000 rpm, and decanted. This was repeated twice to obtain supernatants 2 and 3 (Fig. 1). The final sediment (SED 1) was discarded. Supernatants 2 and 3 were mixed, sonicated for 30 min, and centrifuged at

13000 rpm 1h to obtain Supernatant 4 and SED2. Supernatants 1 and 4 were mixed, sonicated, and centrifuged at 13000 rpm to obtain SED3 and the purified SWCNT-COOH dispersion. As-prepared SWCNT-COOH dispersions were observed to be stable for at least several weeks.

Carboxylated buckypapers were prepared from purified SWCNT-COOH dispersions by slow vacuum filtering through 1.2 μm polycarbonate membranes with diameter of 4.7 cm. The buckypapers were dried at ambient temperature before being separated from the polycarbonate membranes. SWCNT-COOH buckypapers had a diameter of approximately 4 cm, thickness of 0.05 mm, and mass of 30-50 mg. The purified material yield was of ~ 15 wt%.

2.3. Preparation of aminated and fluorinated buckypapers

SWCNT-Ph-CH_2-NH_2 and SWCNT-Ph-$(CF_2)_7$-CF_3 were both synthesized through the diazonium salts route (Fig. 2). The aromatic amines used in the reaction were chosen with the aim of obtaining different grafted functionalities and thus buckypapers with different chemical nature. A terminal amine grafting was obtained using 4-aminobenzylamine while a hydrophobic inert chain was grafted via 4-(perfluorooctyl)aniline. Both arylamines were purchased from Sigma-Aldrich and used as received.

In a typical experiment, 30 mg of as-grown SWCNTs were dipped into 25 mL of DMF, and sonicated in an ultrasonic bath (45 kHz) for 1h. Then, the mixture was sonicated in an ultrasonic tip (Hielscher DRH-P400S; 400 W maximum power; 24 kHz maximum frequency) for 30 min at 60% amplitude and 50% cycle time. The resulting suspension was observed to be homogeneous and stable. Separately, the arylamine was dissolved in 25 mL of acetonitrile and degassed with argon for a few minutes. The influence of

stoichiometry on the reaction yields and the buckypapers characteristics was studied utilizing two different amounts of the aromatic amine: 0.9 and 9.8 mmol, approximately standing for 0.4 and 4 equivalents per mol of carbon. The SWCNTs and the arylamine liquid fractions were blended in a vial under constant magnetic stirring, keeping the system temperature at 60ºC. Then, 100 μL of isoamyl nitrite were added to the mixture and the vial was sealed, leaving a small slit to prevent overpressure due to nitrogen evolution. The reaction underwent overnight at 60ºC and the products were vacuum filtered in a 0.1 μm pore size (47 mm diameter) PTFE membrane. The filtered material was washed with DMF until the liquid fell colourless, and afterwards rinsed with anhidrous diethyl ether to remove DMF. The buckypaper was obtained when the functionalized material was carefully peeled from the membrane. The peeled sheet was finally dried in a vacuum oven at room temperature.

Reference buckypapers were prepared from as-grown SWCNT dispersions in DMF. The experimental process was analogous to that for the preparation of aminated and fluorinated buckypapers, but without the addition of the functionalization reactants.

3. Results and discussion

3.1. Purity

Buckypapers functionalized with carboxylic acids were prepared by vacuum filtration of purified SWCNT-COOH suspensions. The purification procedure described in Fig.1 removed most of the metallic particles present in the as-grown SWCNTs. The purified SWCNT-COOH material was produced with a relative NIR purity of higher than 70%.

Graphitic impurities in as-grown SWCNTs are clearly detected by XRD analysis (Fig. 3.a). Graphite particles give a sharp peak in the diffractograms at $2\theta = 26.6°$, while a

secondary band at 2θ = 26.2° could be due to graphitic onions [18]. Most of the graphitic impurities remain in the sediment after high speed centrifugation, while supernatants are enriched in SWCNTs [16]. Diffraction patterns for the sediments produced during the purification process (Fig. 3.c) showed a clear increase in the graphite and graphitic onions intensities compared to the as-grown SWCNTs. The graphitic bands substantially decreased in the diffractogram for the purified SWCNT-COOH material.

Fig. 3.b depicts the XRD profile for a purified SWCNT sample that was further treated in an inert atmosphere at 700°C. This material showed low intensity graphitic bands, and a prominent signal at 2θ = 6.2° due to SWCNT bundles [19]. Small secondary bands at 2θ = 10, 16, 21° were also detected, corresponding to the SWCNT bundles form factor [19]. It is noteworthy that the SWCNT diffraction bands did not appear for the purified SWCNT-COOH material if it was not treated at 700°C. The high temperature treatment produced the evolution of functional groups, the elimination of surface defects, and the SWCNT aggregation into big crystalline ropes that could be detected by XRD. The diffraction pattern in Fig. 3.b is nearly identical to that reported in [18] for an analog material.

Metal content in purified SWCNT-COOH was of 0.33wt% Ni and 0.22wt% Y, as determined from ICP analysis. The amount of metal impurities was substantially reduced by the nitric acid treatment, but it further decreased during high speed centrifugation cycles (Table 1). The intensity of the Ni XRD signal at 2θ = 44.6° accordingly decreased after the purification treatment (Fig. 3).

Buckypapers were easily obtained from purified SWCNT-COOH solutions when as-grown SWCNTs with NIR relative purity of 45-50% were utilized. However, only buckypaper fragments were usually obtained from low purity SWCNT materials such as

SED 3 solutions or as-grown SWCNTs of 25-30% NIR purity. Almost identical observations were done during the preparation of functionalized buckypapers through the diazonium salts route. In this case, buckypapers were also easily obtained from as-grown SWCNT suspensions in DMF when the initial relative purity was of 45-50%. The preparation of buckypapers using as-grown SWCNTs with NIR purity of 25-30% was difficult or even not possible.

3.2. Functionalization

The treatment with 7M HNO_3 produced a high level of covalent functionalization on SWCNTs. Oxygen content reached nearly 23wt% after the nitric acid reflux, and it further increased to higher than 30wt% after the high speed centrifugation cycles. The following oxygen sequence can be observed in Table 1: SED 1 < SED 2 < SED 3 < Purified-SWCNT. This indicates that SWCNTs were efficiently functionalized, and became stable in water dispersion. The minimum number of surface carboxylic groups was determined from TGA, assuming that most of them thermally evolve between 150 and 300ºC [20]:

$$N_{-COOH}\left[\frac{mmol}{g}\right] = \frac{10\{Wt\%(150℃) - Wt\%(300℃)\}}{45\left[\frac{mg}{mmol_{-COOH}}\right]}$$

The results of this calculation (Table 1) demonstrate the efficient functionalization of purified SWCNTs with –COOH groups.

The incorporation of covalently bonded oxygen strongly influences the Raman spectrum of SWCNTs (Fig. 4). As-grown and purified SWCNTs showed similar G band average intensities (Table 1), but the G/D intensity ratio decreased after the purification process (from 49 to 12). The high degree of functionalization implies a change in the SWCNT resonant conditions that leads to the increment of the Raman D band intensity.

Nitric acid treated SWCNTs before the high speed centrifugation cycles showed much lower intensity and G/D ratio (G/D = 5) than as-grown or purified SWCNTs. Intensities and G/D values for SED 1, SED 2, SED 3, and purified SWCNTs (Table 1) correspond to increasing levels of purity and covalent functionalization.

The functionalization degree of buckypapers prepared through the diazonium salts route was studied by elemental analysis (Table 2). Carbon, hydrogen, and nitrogen were determined directly, and fluorine can be evaluated by difference. Since as-grown SWCNTs were utilized for diazonium reactions, the final products contained residual metal catalysts, and only small amounts of oxygen.

Buckypapers can be prepared just by dispersion and vacuum filtration of as-grown SWCNTs in DMF. Good quality SWCNTs with minimum NIR purity of higher than 45-50% were required for the assembling of complete consistent sheets. Elemental analysis revealed that nitrogen content in buckypapers of as-grown SWCNTs was in the range of 1-2wt%. This indicates that residual DMF remained physically adsorbed on the SWCNTs even after rinsing with diethyl ether, and could help the buckypapers assembling process.

Nitrogen content for SWCNT-Ph-CH_2NH_2 ranged from 1.9 to 2.5wt% (Table 2), indicating that SWCNTs were efficiently functionalized with the terminal amino group. The increase in the arylamine reactant amount from 0.4 to 4 equivalents produced an increase from 1.9 to 2.5wt% of nitrogen in the product. It was not possible to assemble buckypapers using SWCNTs with NIR purity of 25-30% and 0.4 equivalents of the arylamine reactant, but the sheet assemblage improved using those SWCNTs with 4 equivalents of the arylamine. A complete buckypaper was obtained using good quality as-grown SWCNTs and 0.4 equivalents of the arylamine.

SWCNT-Ph-$(CF_2)_7$-CF_3 buckypapers were obtained using SWCNTs of 45-50% NIR purity and 0.4 equivalents of the arylamine. As for the carboxylated and the aminated SWCNTs, it was not possible to assemble fluorinated buckypapers with SWCNTs of 25-30% initial NIR purity. When 4 equivalents of the arylamine were utilized for the fluorination reaction, a slurry was formed that prevented the product filtration.

Chemical functionalization affects SWCNT self assembling in different ways. For the preparation of carboxylated buckypapers from water dispersions, functionalization was required to achieve stable dispersions of purified SWCNTs. In the case of buckypapers prepared through the diazonium salts route, functionalization did not substantially improve the assembling of buckypapers from as-grown SWCNT-DMF dispersions.

3.3. Texture

Buckypapers prepared by vacuum filtration of SWCNT dispersions are flexible and easy to manipulate (Fig. 5). Carboxylated buckypapers are highly hydrophilic and can be impregnated with small amounts of water solutions or electrolytes, but are not resistant to immersion in water. Buckypapers prepared from DMF dispersions, and functionalized through the diazonium salts route, looked like the carboxylated sheets, but their texture at the microscale resulted to be completely different. The final texture of the buckypapers mainly depends on the preparation procedure. This could be applied to the design of catalytic substrates or electrodes with controlled porosity.

Fig. 6 shows the AFM characterization for a carboxylated buckypaper, as well as for an aminated one. The carboxylated buckypaper presents a low roughness factor (R_a = 14 nm), corresponding to a very low porosity material; its BET specific surface area from nitrogen adsorption analysis was of lower than 1 m^2/g. The intensive reflux in nitric acid and the subsequent high speed centrifugation processing result in a highly agglomerated

SWCNT material. The aminated buckypaper showed a roughness factor of 69 nm, and a specific surface area of 168 m^2/g, revealing significant texture differences with the carboxylated buckypaper. Aminated and fluorinated buckypapers presented almost identical microtextural features. Since experimental BET surface areas for as-grown SWCNT powders typically range between 250 and 300 m^2/g, it can be concluded that chemical functionalization of buckypapers induced a reduction in SWCNT porosity.

The very low roughness of carboxylated buckypapers allowed the AFM visualization of SWCNT bundles on the buckypaper surface. Fig. 7 shows a phase image of thin SWCNT-COOH bundles of 3-5 nm. The SWCNT network forms a regular height peak-valley topography on the buckypaper surface.

3.4. Electrical conductivity

Electrical conductivity was measured for a series of buckypapers with different purity and surface functional groups (Table 3). As-grown SWCNT buckypapers demonstrated sheet resistances (R_s) in the range of 45-55 Ω/□. The R_s for good quality SWCNTs (45-50% NIR purity) was lower than for SWCNTs of 25-30% NIR purity. This purity effect was observed for as-grown SWCNT buckypapers, as well as for SWCNTs after chemical functionalization.

Sheet resistances for purified SWCNT-COOH buckypapers ranged between 30-50 Ω/□. Conductivity was 2-4 times higher than for as-grown SWCNT buckypapers. This moderate increase in the SWCNT bulk electrical conductivity should be understood as a combined effect of purification and covalent oxygen functionalization. The electrical conductivity measured for SWCNT-COOH buckypapers was lower than that reported in Ref. [16].

Amine functionalized buckypapers presented sheet resistances in the range of 60-650 Ω/□. The electrical conductivity for aminated SWCNTs was lower than for as-grown SWCNT, especially when SWCNTs were reacted with a great excess of the arylamine (4 equivalents). Also, substantial changes in the electrical conductivity were measured for fluorinated SWCNTs compared to as-grown SWCNTs. Sheet resistances increased to 650-1700 Ω/□. The conductivity for fluorine functionalized buckypapers was lower than for the aminated SWCNTs. Sidewall functionalization through the diazonium salts route produced a decrease in the buckypapers electrical conductivity. The conductivity variation was dependent on the choice of the functional group bonded.

According to some theoretical studies, covalent sidewall functionalization of metallic or semiconductiong SWCNTs originates a localized electronic state near the nanotube Fermi level [21, 22]. This impurity state produces a drastic drop in the electrical conductivity of metallic SWCNTs [22]. Since sidewall functionalization through the diazonium salts route is selective towards metallic SWCNTs [23, 24], the conductivity decrease measured for aminated and fluorinated buckypapers could be interpreted as a chemical inhibition of the metallic SWCNTs contribution. The modification of the SWCNT electronic properties through chemical bonding could be applied to the design of chemical sensors based on buckypapers.

4. Conclusions

Covalently functionalized buckypapers were prepared by vacuum filtration of SWCNT dispersions that did not contain surfactants or polymers. It was observed that flexibility and mechanical resistance of the buckypapers depend on the SWCNTs purity and dispersion conditions. Carboxylated buckypapers can be prepared from stable water suspensions of SWCNTs previously purified by nitric acid treatment and centrifugation.

Aminated and fluorinated SWCNTs were obtained through diazonium salts reactions in DMF, and were then directly filtered to get the buckypapers. Texture and porosity of the buckypapers were strongly influenced by the preparation method; while carboxylated buckypapers demonstrated very low specific surface areas and roughness factors, aminated and fluorinated buckypapers were rough and porous. The electrical conductivity of purified SWCNT-COOH buckypapers was 2-4 times higher than that of as-grown SWCNTs, but it decreased for the aminated and fluorinated buckypapers. SWCNT purity positively influences the buckypapers electrical conductivity. Chemical functionalization produces a decrease in the bulk conductivity of materials containing both metallic and semiconducting SWCNTs.

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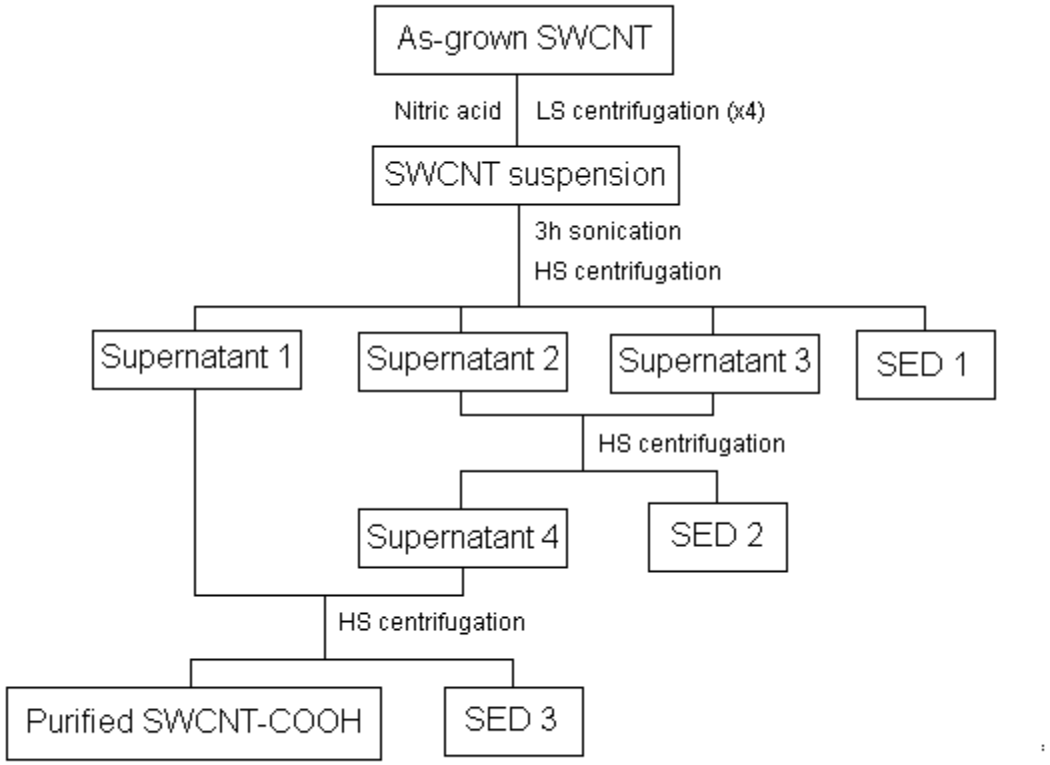


Figure 1. Scheme of the experimental procedure for the preparation of purified SWCNT-COOH. (LS = Low Speed; HS = High Speed centrifugation).

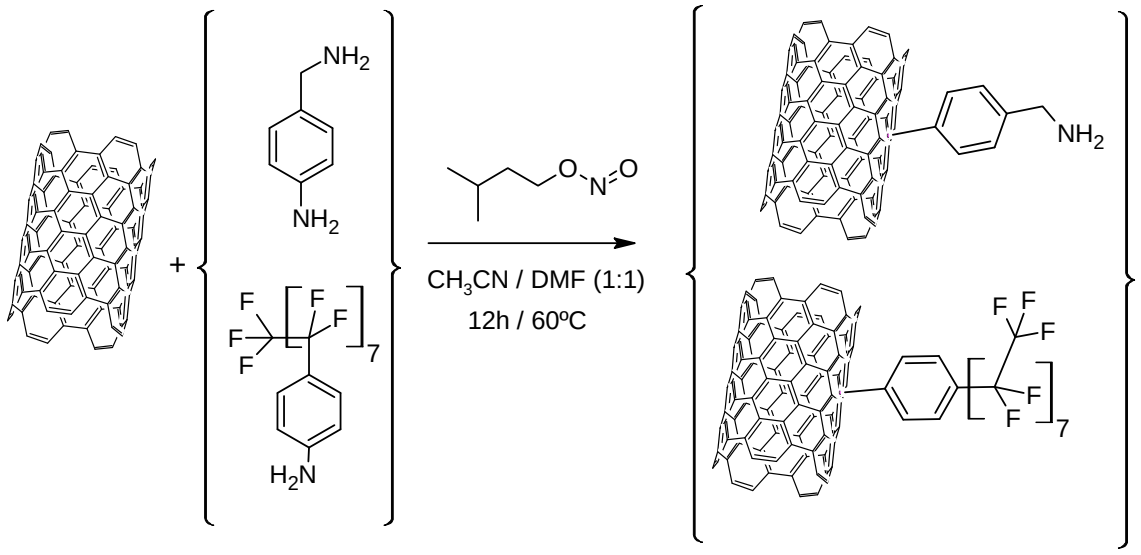


Figure 2. Scheme of the diazonium salts reaction for the preparation of the aminated and fluorinated SWCNTs.

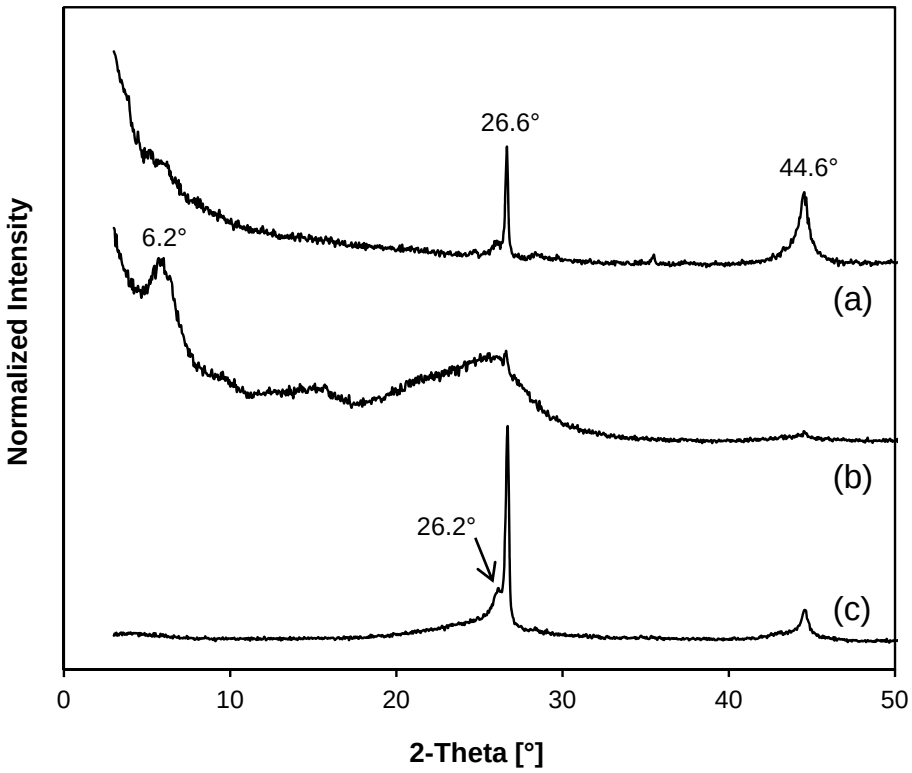


Figure 3. XRD profiles normalized to the maximum intensity for: a) As-grown SWCNTs, b) purified SWCNTs further treated at 700°C, c) SED 1.

Table 1. TGA residue, oxygen content, number of surface carboxylic groups, Raman G band intensity, and Raman G/D band intensities ratio for various samples.

	TGA residue [Wt.%]	Oxygen [Wt.%]	-COOH [mmol/g]	Raman I_G	Raman G/D
As-grown SWCNT	34.7	1.7	0.15	1915	49
HNO_3-treated SWCNT[a]	7.1	22.6	1.41	450	5
Purified SWCNT-COOH	1.8	30.4	1.93	1914	12
SED 3	5.5	28.1	1.78	1355	10
SED 2	6.7	23.0	1.47	928	14
SED 1	7.2	21.0	1.11	277	4

[a]This sample corresponds to the material called "SWCNT suspension" in Fig.1.

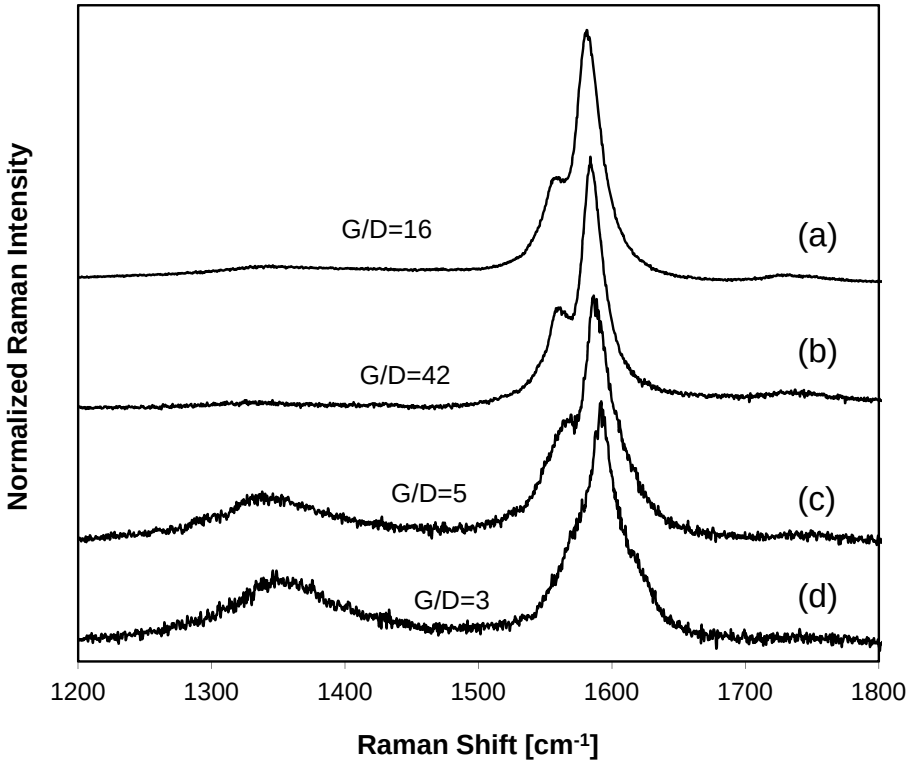


Figure 4. Raman spectra and G/D intensity ratios for: a) Purified SWCNT-COOH, b) as-grown SWCNTs, c) HNO_3 treated SWCNTs, d) SED 1.

Table 2. Elemental analysis for buckypapers prepared by vacuum filtration of DMF suspensions.

Buckypaper	Initial purity[a]	Atomic content				Buckypaper quality[c]
		C [wt%]	H [wt%]	N [wt%]	Difference [wt%]	
SWCNT	25-30%	70.12	0.76	1.34	27.75	++
SWCNT	45-50%	75.10	1.03	1.79	22.94	+++
SWCNT-Ph-CH_2-NH_2	25-30%	70.72	0.84	1.89	26.55	+
SWCNT-Ph-CH_2-NH_2[b]	25-30%	71.30	1.23	2.50	24.97	++
SWCNT-Ph-CH_2-NH_2	45-50%	76.40	1.10	2.39	20.11	+++
SWCNT-Ph-$(CF_2)_7$-CF_3	25-30%	67.90	0.76	1.25	30.09	+
SWCNT-Ph-$(CF_2)_7$-CF_3	45-50%	68.16	0.79	0.93	30.12	++

[a]NIR relative purity [15] of the as-grown SWCNTs utilized in each case.
[b]It was prepared with 4 equivalents of the arylamine, instead of 0.4 equivalents used for the others.
[c]Evaluated by direct inspection.

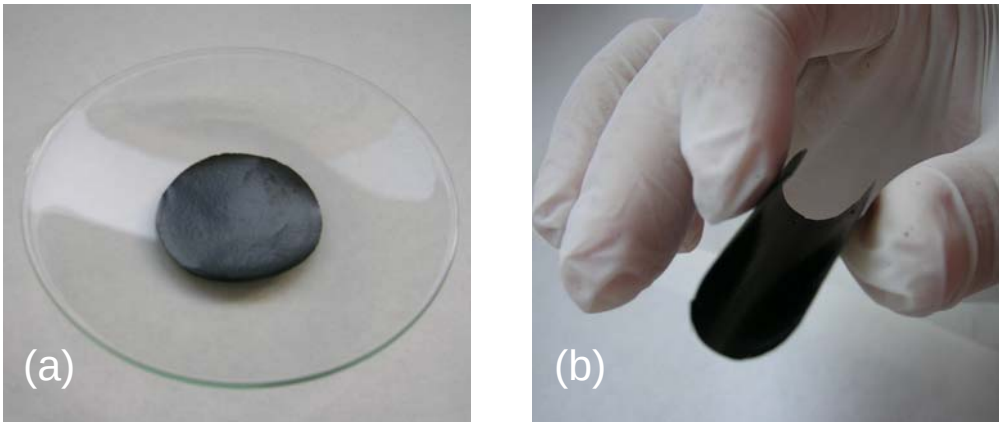
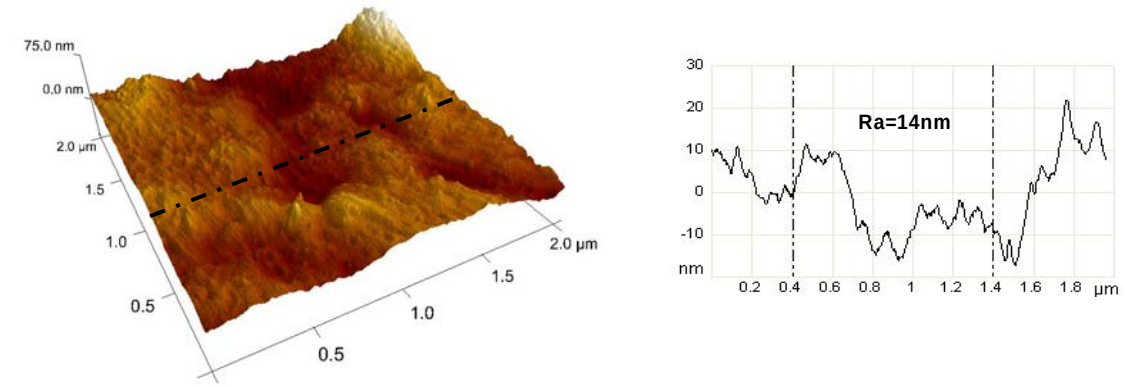
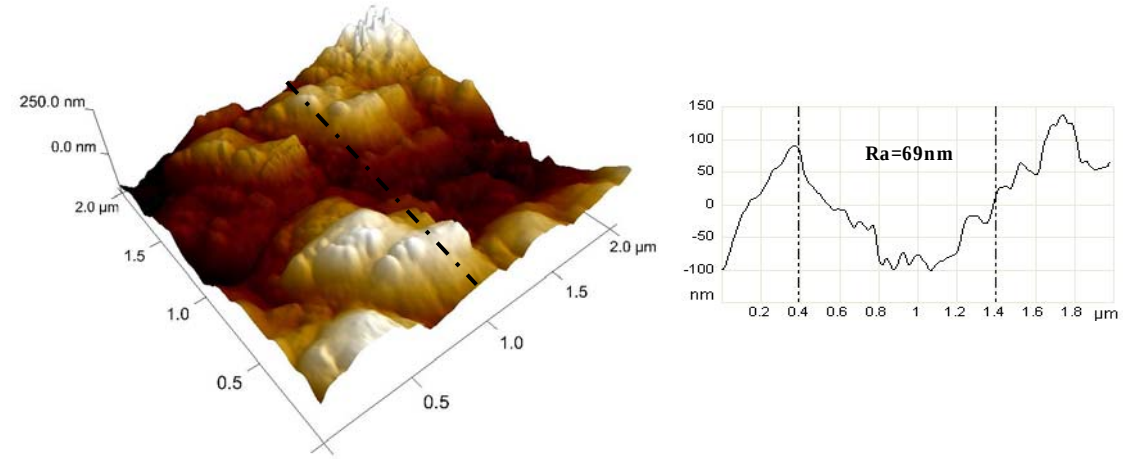


Figure 5. Buckypaper obtained by direct filtration of an aqueous solution of purified SWCNT-COOH.



(a)



(b)

Figure 6. AFM topography and roughness factor (R_a) for: a) SWCNT-COOH, and b) SWCNT-CH_2-NH_2 buckypapers.

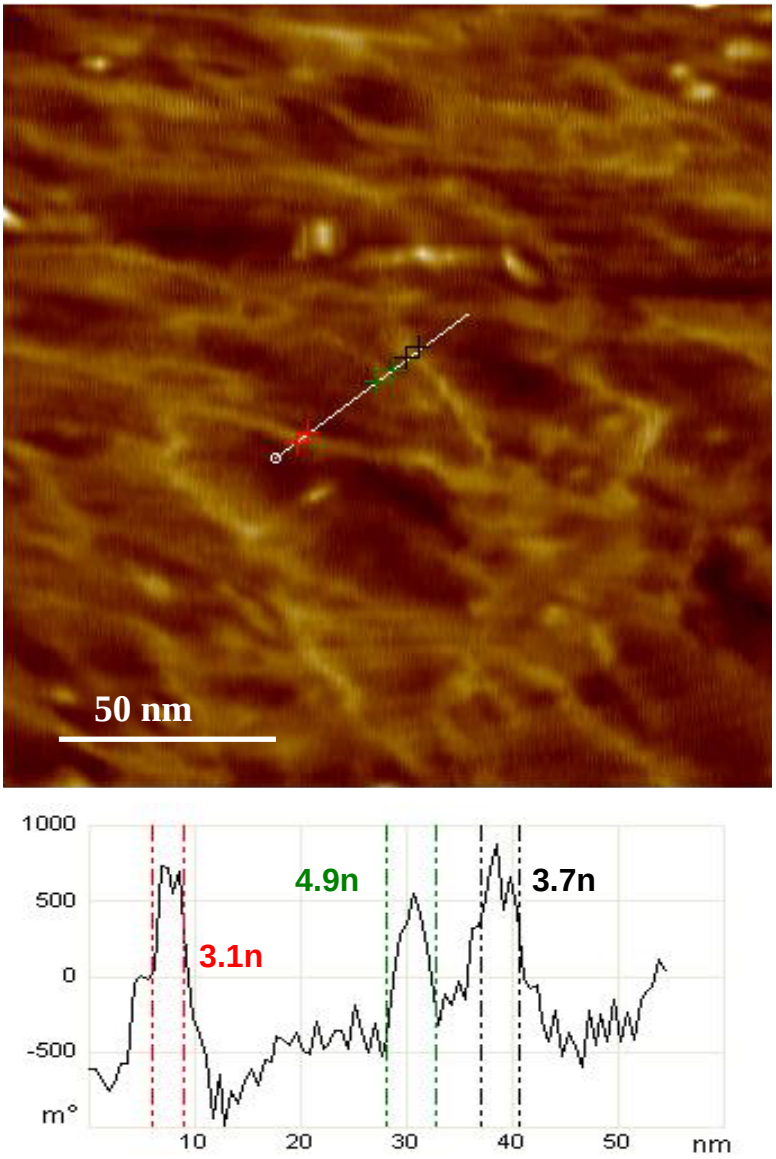


Figure 7. AFM detail of a SWCNT-COOH buckypaper surface, showing small nanotube bundles.

Table 3. Electrical conductivity (σ) and sheet resistance (R_s) for various buckypapers.

Buckypaper	Initial purity[a]	Thickness [cm]	σ [S/cm]	R_s [Ω/□]
Purified SWCNT-COOH[b]	45-50%	0.003	10.8	30.8
Purified SWCNT-COOH[c]	45-50%	0.003	6.90	49.2
SWCNT (DMF)	25-30%	0.011	1.69	53.7
SWCNT (DMF)	45-50%	0.007	3.04	47.0
SWCNT-Ph-CH_2-NH_2	25-30%	0.008	0.30	413
SWCNT-Ph-CH_2-NH_2[d]	25-30%	0.009	0.17	646
SWCNT-Ph-CH_2-NH_2	45-50%	0.007	2.17	66.8
SWCNT-Ph-$(CF_2)_7$-CF_3	25-30%	0.007	0.08	1686
SWCNT-Ph-$(CF_2)_7$-CF_3	45-50%	0.009	0.16	698

[a]NIR relative purity [15] of the as-grown SWCNTs utilized in each case.
[b]2h of nitric acid reflux.
[c]4h of nitric acid reflux.
[d]It was prepared with 4 equivalents of the arylamine, instead of the 0.4 equivalents used for the others.