

Optical absorption response of chemically modified single-walled carbon nanotubes upon ultracentrifugation in various dispersants

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Abstract

Arc discharge single-walled carbon nanotubes (SWCNTs) were modified through different oxidative treatments and functionalization reactions. The modified SWCNT powders were dispersed in four different aqueous media and purified by ultracentrifugation. Extinction coefficients of the modified SWCNTs depended on the SWCNT type but did not depend on the dispersion medium. According to visible/near infrared spectroscopy, the purity of all the modified SWCNT dispersions substantially improved after ultracentrifugation; however, the spectrum profile, the degree of purity and the centrifugation yield were influenced by the SWCNT type, the surface functional groups and the dispersion medium. Semi-quantitative purity indexes calculated from optical absorption spectra were supported by transmission electron microscopy observations. Contents in metal impurities were analyzed by energy dispersive X-ray spectroscopy. SWCNT samples processed by oxidative acid treatments and ultracentrifugation showed metal contents of lower than 0.5wt%.

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1. Introduction

Single-walled carbon nanotubes (SWCNTs) are synthesized by catalytic processes involving either the energy intensive evaporation of solid carbon precursors (arc discharge, laser evaporation, thermal plasma) or the pyrolysis of gas precursors (CVD methods). The characteristics of pristine SWCNT powder materials strongly depend on their synthesis procedure. In particular, arc-discharge SWCNTs show a high degree of structural perfection, giving rise to well-defined spectroscopic signals. However, these SWCNTs contain relatively high amounts of impurities (catalytic metal particles, graphite particles, amorphous carbon), and purification processes are commonly required for specific applications.

Typical purification strategies for arc-discharge SWCNTs include several air oxidation, acid treatment and centrifugation stages. While acid treatments are necessary for the elimination of metal catalysts, centrifugation has been proven as a powerful technique for the removal of carbonaceous impurities. We have previously demonstrated the complete elimination of graphite particles and the reduction of the amorphous carbon levels by centrifugation in a surfactant [1, 2]. Dispersions of increasing SWCNT relative purity can be obtained by repeated centrifugation cycles [3]. Researchers from Flinders University in Australia have systematically studied the enormous possibilities of high speed centrifugation for the preparation of dispersions of purified arc-discharge SWCNTs in aqueous solutions of sodium dodecylbenzene sulfonate (SDBS) [4]. Additionally, it has been reported that a high degree of SWCNT separation from their bundles can be expected after ultracentrifugation [5].

As a general rule, SWCNT purification through centrifugation depends on the SWCNT dispersion degree and relative stability in the liquid medium. This is influenced by the solvent, surfactant type, dispersion conditions, ultrasound treatments and centrifugation conditions (speed, time and temperature). Ideally, the best dispersion is achieved when all the SWCNTs are individualized and isolated. Different aqueous solutions including ionic, non-ionic, biological and polymeric surfactants have been probed as the liquid media for SWCNT dispersion [6-8]. Among them, SDBS has been widely used in the past and it is still considered as a quite efficient medium for dispersing SWCNTs [7]. According to the group at Flinders University [4], the most favorable conditions for the ultracentrifugation of arc-discharge SWCNTs in SDBS are: i) speed of around 120,000 xg, ii) time of 1-2 hours, and iii) temperature of 25°C. However, the purification of chemically functionalized SWCNTs by ultracentrifugation has not been studied so far.

The utilization of ultracentrifugation for processing chemically modified SWCNTs is not trivial, as functional groups on SWCNT surfaces may affect their stability in liquid dispersions.

The preparation of covalently functionalized SWCNT dispersions is a crucial step towards some SWCNT applications in materials science and biomedicine, as functional groups are the interaction bridges with other molecules or active centers [9-11]. In addition, the appropriate choice of the centrifugation medium will be positive for a given application: high conductivity ionic solutions for electrochemistry, cell benign environments for biomedicine, or compatibility agents (such as block copolymers) for materials science. Covalent functionalization reactions are more easily performed on pristine SWCNTs, before they are dispersed in the liquid. Therefore, it is important to ascertain if chemically modified SWCNTs can be processed by ultracentrifugation to obtain stable purified dispersions, which is a topic that has not been fully addressed in the literature so far.

Optical absorption spectroscopy in the visible-near infrared (NIR) region is considered the most precise technique for the evaluation of SWCNT purity in a liquid dispersion [12]. Other important SWCNT features can be studied from absorption spectra, including the influence of covalent functionalization on the electronic properties [6]. On the other hand, exfoliation of aggregates and bundles of a given SWCNT powder material during ultrasound treatments in a liquid dispersion medium can be monitored through absorption spectroscopy, and the maximum achievable exfoliation coincides with the maximum absorbance [13].

In the present article, we study the ultracentrifugation processing of chemically modified arc-discharge SWCNTs. Six modified SWCNT materials were prepared and dispersed in four aqueous media, and their optical absorption spectra were measured before and after centrifugation. Purification of SWCNT dispersions during ultracentrifugation was analyzed in terms of yields and changes in the relative intensities of the SWCNT characteristic absorption bands. The results were supported by electron microscopy, and a complementary analysis of the metal residue was carried out by electron energy dispersive spectroscopy. This work aims to open a simple approach for the preparation of chemically functionalized SWCNTs with a high purity and finely dispersed in selected aqueous media that will be beneficial for subsequent SWCNT applications. At once, the optical response of chemically modified SWCNTs before and after ultracentrifugation is discussed.

2. Experimental

2.1. SWCNT materials

Single-walled carbon nanotubes (SWCNTs, AP-SWNT grade) were purchased from Carbon Solutions Inc., Riverside, California. This SWCNT powder material is synthesized by the electric arc reactor method using Ni/Y catalyst and contains ~ 30 wt.% metal residue. The average diameter of the SWCNTs has been calculated to be in the range of 1.4-1.6 nm from optical absorption and Raman spectroscopy data [4]. The average SWCNT length ranges from ~ 400 to 800 nm, according to atomic force microscopy measurements, even though many SWCNTs in centrifuged samples are shorter than 400 nm [4].

The effect of surface chemistry was studied on six different modified samples, which were prepared from the AP-SWNT material. The nomenclature for the samples is summarized in Table 1, together with a brief description of the preparation protocol and mass yields (Y_p).

The AP/A material was prepared by thermal oxidation in an air flow saturated with water vapor. Approximately 100 mg of the AP material was weighed inside a ceramic boat and it was treated at 388°C for 2h in a horizontal quartz reactor. The air flow was passed through a water bubbler before entering the reactor. The weight loss during the thermal treatment was of 48.5%.

The AP/HCl sample was obtained by air oxidation followed by an acid treatment in HCl. In a typical experiment, ~ 500 mg of the AP material was put into a Petri dish and heated at 350°C for 2h in a Carbolite oven. The weight loss during the air oxidation treatment was of 10%. The resulting material was refluxed in 3M HCl for 2h, which led to an additional weight loss of 46%; thus the accumulated yield for the AP/HCl powder material was of 48.6% from the initial AP weight (51.4% weight loss). The AP/SN material was prepared from the AP/HCl by 2h reflux in a 3M 1:3 HNO₃:H₂SO₄ mixture. A partial yield of 114 wt% was obtained after the HNO₃:H₂SO₄ mixture treatment, which results in an accumulated yield of 55.4% from the initial AP weight. The weight increase during the HNO₃:H₂SO₄ treatment is associated to the insertion of oxygen functional groups. Another material, hereafter called the AP/N sample, was directly prepared from the AP material by reflux in 1.5M HNO₃ for 2h. The yield in the preparation of the AP/N material was of 89.4 wt.%, indicating that the weight of the removed metal was partially counteracted by the insertion of oxygen functional groups.

The other two samples (AP/NH₂ and AP/F) were synthesized by the in-situ generated aryl diazonium salts route. The synthesis details have been previously published [9, 14]. Briefly, 100 mg of AP SWCNTs were tip sonicated in approximately 25 mL of N,N-Dimethylformamide (DMF). Separately, the reactive amine (4-amino benzylamine for AP/NH₂ or 4-heptadecafluorooctyl aniline for AP/F) was dissolved into 25 mL of acetonitrile and added to the SWCNT dispersion. The mixture was heated to 60°C under constant magnetic stirring, and then approximately 1 mL of isoamyl nitrite was added. The reaction mixture was left overnight at 60°C, vacuum filtered through a 0.1 μm Teflon membrane, washed with DMF and rinsed with diethyl ether or methanol. Yields in the preparation of AP/NH₂ and AP/F materials were of 109 and 111 wt.% respectively. The weight increase during the reactions accounts for the insertion of surface functional groups.

2.2. Preparation of SWCNT dispersions

Various aqueous media were utilized for the dispersion of the SWCNT materials. The dispersants were water-soluble solids that were representative of four different categories (Table 2). Sodium dodecylbenzenesulfonate (SDBS) is an anionic surfactant that has been previously utilized in the purification of SWCNTs by ultracentrifugation [4]. Hexadecyltrimethylammonium bromide (CTAB) is a cationic surfactant. Pluronic® F68, a commercial product registered by BASF, is an ‘ABA’-type triblock copolymer containing polyethyleneoxide (PEO) and polypropyleneoxide (PPO) blocks with a sequence EO₇₆-PO₂₉-EO₇₆ (M_w = 8,400 g/mol, 80% PEO). The PEO block is strongly hydrophilic, while the less hydrophilic PPO block preferentially adsorbs on the SWCNTs. Gum Arabic is a branched polysaccharide that was chosen as representative of natural stabilizers. All the dispersants were purchased from Sigma-Aldrich and were dissolved at concentrations of 0.5 or 1% wt/vol in water (Table 2).

All the pristine and modified SWCNT powders were dispersed in the four aqueous media following identical protocols. The dispersant (11 mL) was added to 11 mg of the SWCNT sample. The mixture was bath sonicated for approximately 5 min and tip sonicated (Hielscher UP400S at 24 kHz, 0.5 cycles, 60% amplitude) in an ice bath for 1h. A small amount of the dispersion was separated for the determination of the extinction coefficient. The rest of the dispersion was centrifuged at 120,000 xg for 1h in a Beckman Coulter L-100 XP ultracentrifuge provided with a SW55Ti 3671 rotor and

Beckman centrifugation tubes ref. 326819. The supernatant was carefully decanted and the sediment was discarded.

2.3. Characterization techniques

Visible-NIR spectra of the dispersions were measured in 2 mL quartz cuvettes using Shimadzu UV-2401PC and Bruker VERTEX 70 spectrometers. The dispersant solutions were utilized to appropriately dilute the SWCNT dispersions and for the blank measurements. In order to determine the SWCNT concentration after centrifugation, the extinction coefficients of all the SWCNT materials were measured before centrifugation in the four different dispersant media. Extinction coefficients (ϵ) were calculated applying the Lambert-Beer law: $A_\lambda = \epsilon l C$, where A_λ is the absorbance at a given wavelength excitation (λ), C is the SWCNT dispersion concentration (mg mL^{-1}) and l is the optical pathway, which is given by the length of the quartz cuvette (1 cm). Extinction coefficients were calculated at 850 nm, as it corresponds to a spectral region that is weakly influenced by possible changes in the relative intensity of SWCNT characteristic bands and absorption backgrounds.

In the present article, improvements in the SWCNT relative purity upon centrifugation are systematically analyzed by means of the purity index. Purity indexes were calculated from spectral data in the window of $7750\text{-}11750\text{ cm}^{-1}$, where the S_{22} band transition can be found for all the SWCNT samples studied [12]. The dispersions were diluted in the liquid media utilized for their preparation until absorbance was between 0.2-1 units, most preferably between 0.3-0.6 units, in the acquisition spectral window. The total area below the S_{22} curve is called A_t , while the baseline subtracted peak area is called A_s . According to Itkis et al. [12], SWCNT purity should be a function of the ratio A_s/A_t , which is hereafter called the purity index.

The characterization of the modified SWCNT powder materials was performed by infrared (IR) spectroscopy and thermogravimetric analysis (TGA). IR spectra were measured in the Bruker VERTEX 70 spectrometer on pellets ($d = 13\text{ mm}$, $t = 1\text{ mm}$) containing spectroscopic-grade KBr and approximately 0.5 mg of the SWCNT samples. TGA experiments were performed in a Setaram Setsys Evolution balance. Experiments for the calculation of functionalization degrees were performed in a nitrogen flow and consisted on heating ramps of $5^\circ\text{C}/\text{min}$ up to 1000°C . On the contrary, metal contents were calculated after combustion of the samples in an air flow at 1000°C . The TGA residue after complete oxidation of the SWCNT samples mainly consists of metal

oxides. The initial metal content was calculated assuming an oxygen content of 25 Wt.% in the TGA residue [15]. This typical value has been previously calculated comparing nickel and yttrium contents in the AP SWCNT powder material (determined by plasma spectroscopy) with the weight of the corresponding TGA residue ($\text{NiO} + \text{Y}_2\text{O}_3$).

Even though the purity index is an excellent parameter for the assessment of SWCNT relative purity, other factors including chemical treatments could have some influence on the SWCNT absorption spectra. Therefore, the purity evaluation resulting from absorption spectroscopy was checked by transmission electron microscopy (TEM, JEOL-200FXII). TEM is the most appropriate analytical technique for a qualitative purity evaluation as it allows the observation of all the carbonaceous impurities, metal particles and the SWCNT structure. A disadvantage of the TEM technique is that SWCNT dispersions have to be filtered to eliminate most of the dispersant, and SWCNTs strongly agglomerate during the filtration-sedimentation process. For TEM sample preparation, a small amount of the filtered samples was sonicated in ethanol and placed onto C/Cu 200 mesh Lacey microscopy grids. However, dispersion in ethanol does not recover the original SWCNT disaggregation in the aqueous media.

Finally, purity evaluation of the SWCNT samples was completed with the metal content determination, which was carried out by energy dispersive X-ray spectroscopy (EDX, Hitachi S3400N).

3. Results and discussion

3.1. Characterization of the modified SWCNT powder samples

Metal content in the pristine and modified SWCNT powders was analyzed by EDX and TGA (Table 3). Thermal treatments in an air atmosphere produced the elimination of a part of the carbon materials, which led to an increase in the metal content. The amount of metal impurities decreased for the three samples that were treated with oxidant acid processes (AP/HCl, AP/SN and AP/N). In particular, the metal content reduction was remarkable (from 24.9 to 2.6 wt.%) in the case of AP/SN, as it was prepared by several subsequent stages of oxidation and acid treatment. Metal contents of the samples that were functionalized through diazonium routes (AP/NH₂ and AP/F) were not expected to change substantially during chemical processing, since no acid treatments were used. Therefore, the decrease in the relative metal content that was detected from the AP (24.9

wt%) sample to the AP/NH₂ (22.3 wt%) and the AP/F (15.2 wt%) samples could be associated to the weight of amine or fluoride moieties. From EDX elemental analysis (Table 3), it can be concluded that both nickel and yttrium impurities show an analogous evolution with chemical processing.

Functionalization degrees (θ) of chemically modified SWCNT materials were calculated from TGA experiments in an inert flow (Figure 1, Table 4), making the following assumptions: i) weight losses between 120 and 800°C were directly assigned to the evolution of functional groups, ii) only one type of functional group was considered for each SWCNT sample, iii) metal contents determined by TGA in an air flow (Table 3) were taken into account for the calculation of total carbon atoms, and iv) weight loss in the AP sample was subtracted to the other samples for the calculation of their respective functionalization degree. The highest functionalization degrees were obtained for the oxidized materials prepared by both air oxidation ($\theta_{AP/A} = 1/25$) and liquid phase oxidation ($\theta_{AP/SN} = 1/10$, $\theta_{AP/N} = 1/29$). The θ value for the AP/SN material is particularly high. Interestingly, the AP/HCl material also demonstrated a substantially high functionalization degree ($\theta_{AP/HCl} = 1/190$), even though many oxygen bearing groups evolved as CO₂ during the acid treatment with HCl. Stable groups (carbonyl, quinone) can probably convert into C-OH, while labile groups including carboxylate, lactone and anhydride are leached as carbonic acid [16]. The materials prepared through diazonium reactions (AP/NH₂ and AP/F) showed lower functionalization degrees than the oxidized materials. The difference between the AP/NH₂ ($\theta = 1/88$) and AP/F ($\theta = 1/342$) materials could be explained by the large volume occupied by the perfluorinated moiety or the lower reactivity of its corresponding diazonium compound.

Surface chemistry characterization of the SWCNT powders was accomplished by IR spectroscopy (Figure 2). The spectrum of the AP material was dominated by the band of adsorbed water at 1628 cm⁻¹, which is associated to residual moisture. The other peaks in the AP spectrum correspond to the carbon skeleton or to the presence of a few oxygen groups, except the peaks at 1390 and 667 cm⁻¹, which are artifacts due to the measurement equipment. Curiously, no substantial changes were observed in the IR spectrum after the thermal oxidation of the AP material at 350°C for 2 hours in an air atmosphere. However, changes became visible after the subsequent acid treatment with HCl. In fact, bands at 1710, 1581, 1166 and 1128 cm⁻¹ appeared in the AP/HCl spectrum that can be assigned to carbonyl, alcohol or phenolic groups [17]. The treatment with H₂SO₄/HNO₃ (AP/SN material) led to an increase in the relative

intensity of carboxylic acid bands at 1724 and 1180 cm^{-1} [17, 18]. A similar spectrum was obtained after direct treatment of the AP material with nitric acid (AP/N); however, the relative intensity of carboxylic acid bands at 1719 and 1189 cm^{-1} was lower than in the case of AP/SN. This fact is in agreement with previously reported data indicating that treatments with mixed sulfuric/nitric acids show higher specificity than just nitric acid towards the production of surface carboxylic acids [19].

Some new spectral signals are observed in the IR spectrum of the AP/NH₂ and AP/F samples, which were both functionalized through the diazonium salts route. The AP/NH₂ sample clearly shows bands at 1510 and 827 cm^{-1} , which could be respectively associated to C=C-C and C-H stretching in para-disubstituted benzene rings [20]. The band at 1654 cm^{-1} could be assigned to the N-H stretching in primary amines [20]. In the AP/F material, other peaks that could be assigned to long chain polyhalogenated hydrocarbons appear at 1240 and 1211 cm^{-1} [20], while signals at 1517 and 863 cm^{-1} (para-disubstituted benzene rings) show very weak intensity. This fact seems to confirm that functionalization degree, in terms of moieties per carbon atom, for the AP/F material was lower than for AP/NH₂.

3.2. Extinction coefficients of the chemically modified SWCNT dispersions

Extinction coefficients (ϵ) at 850 nm were determined for all the dispersions of chemically modified SWCNTs in the four different aqueous media (Table 5). Extinction coefficients had to be determined in order to allow an estimate of the SWCNT concentration after centrifugation, and some additional conclusions regarding the optical response of chemically modified SWCNTs can be drawn from the ϵ values. Dispersions were initially prepared with a concentration of 1 mg/mL, which is the same starting concentration utilized in the ultracentrifugation experiments. However, absorbances at 1 mg/mL are outside the measurement range and the dispersions had to be first of all diluted to 0.1 mg/mL, which was the highest concentration included in the calibrations. It has been reported that important deviations from the exact extinction coefficients may occur when initial SWCNT concentrations are too high [21]. However, errors in our case have been estimated to be of < 4%. In fact, the extinction coefficient of an AP SWCNT dispersion in SDBS resulted to be 22.3 $\text{mL mg}^{-1} \text{cm}^{-1}$ at 850 nm, which is in good agreement with the value of 23.5 $\text{mL mg}^{-1} \text{cm}^{-1}$ at 891 nm published by the Australian group from Flinders University [4]. Extinction coefficients were quite similar

in the four different media while they showed wide variations depending on the SWCNT chemical processing.

It has to be taken into account that metal contents were quite different for each modified SWCNT material. This fact has a significant influence, since ϵ values were calculated on the basis of the initial sample mass. For example, the metal content of AP/A powders (~ 43 wt%) was much higher than that of the original AP material (~ 25 wt%), contributing to the ϵ decrease from 22.3 to 4.7 mL mg⁻¹ cm⁻¹. However, other factors can influence the ϵ variation, including the number of oxygen functional groups, the presence of defects at the SWCNT surfaces, or a decrease in the solid dispersability.

The AP/HCl, AP/SN and AP/N materials, with similar metal contents (~ 8 , 3 and 7 wt% respectively), showed extinction coefficients in the range of 15-20 mL mg⁻¹ cm⁻¹. These ϵ values were lower than that for the AP material, whose metal content was quite higher (~ 25 wt%). The three AP/HCl, AP/SN and AP/N materials suffered structural damage during oxidative acid treatments, causing changes in their electronic properties, hence the decrease in the ϵ values. Moreover, the amount of oxygen functional groups, which were responsible for the structural damage, does not appear to be decisive. In fact, many oxygen functional groups were eliminated from the AP/HCl material during the treatment in HCl, while the AP/SN and AP/N materials reached much higher functionalization degrees.

The AP, AP/NH₂ and AP/F materials had comparable metal contents, while AP/NH₂ and AP/F showed substantially lower ϵ values than AP SWNTs. It can be concluded that extinction coefficients of the chemically modified SWCNT materials are influenced by the SWCNT structural integrity, type of the functional group, dispersability and content in metal impurities.

3.3. Yield of the centrifugation process

It has been stated above that the first objective of the present work was the purification of chemically modified SWCNTs through ultracentrifugation in different liquid media. Therefore, the most important parameter to be obtained was the final dispersion purity, which will be discussed later. Another parameter of practical interest is the centrifugation yield, which was evaluated from measurements of absorbance at 850 nm and applying the previously determined extinction coefficients. The calculated yields (Y_c) are listed in Table 6. The total yield (Y_t) of the process starting with AP SWCNTs and including the chemical treatment step was also calculated (Table 6).

The highest centrifugation yields were achieved with SDBS as the dispersion medium. The other three liquid media showed different results depending on the SWCNT material. The lowest yields were obtained for the materials functionalized through the diazonium salts method (AP/NH₂ and AP/F). Low yields were usually associated to dispersions showing low stability or to materials with a poor dispersability. Some errors in the calculated yields must be assumed due to the difficult reproducibility of the supernatant/sediment separation.

It can be concluded that SDBS stabilized SWCNT dispersions better than the other liquid media, resulting in higher centrifugation yields. However, it is possible to process chemically modified SWCNTs through ultracentrifugation in other aqueous media, even though yields can substantially decrease. The only requirement for a successful centrifugation is to start from dispersions with a minimum quality and stability.

3.4. Purity evaluation from visible/NIR spectroscopy

Figure 3 shows normalized visible/NIR spectra of AP SWCNT dispersions before centrifugation and after centrifugation at 120,000 xg for 1h in SDBS, CTAB, Plu and GA. Figure 3 spectra correspond to dispersions which were diluted until their optical thickness was of approximately 0.4 absorbance units at 850 nm. Electronic transitions in metallic SWCNTs are observed between 600 and 800 nm (M₁₁ transitions) and transitions in semiconducting SWCNTs appear at 900-1200 nm (S₂₂) and 400-600 nm (S₃₃). The absolute absorbance intensity always decreases during centrifugation as a result of sedimentation; however, the relative intensity (SWCNT signal to background ratio) of all the characteristic bands clearly increased after centrifugation, and the variation can be mostly assigned to an improvement in the relative purity. Since the relative intensity of both the metallic and semiconducting SWCNT bands increased during centrifugation, it is clear that the process was not selective with respect to the electronic character. Moreover, spectrum profiles were nearly identical in the four liquid media, suggesting that SWCNT chirality and diameter distributions are preserved during ultracentrifugation. Band positions are at approximately the same wavelengths in the four liquid media.

Figure 4 compares absorbance spectra of the different chemically modified SWCNTs after centrifugation in SDBS at 120,000 xg for 1h. It can be observed that chemical treatments altered the SWCNT optical properties and the shape of the absorption spectrum. Red-shifts were observed for SWCNTs treated with oxidative acid processes.

This effect has been previously assigned to sample agglomeration [22] or to modifications in the SWCNT band-gaps [23]. The magnitude of the shift was in the order of: AP/HCl > AP/SN > AP/N > AP/A. Surprisingly, the material showing the largest red-shift had the lowest functionalization degree. Spectra for the materials modified through the diazonium method (AP/NH₂ and AP/F) did not show substantial spectral shifts with respect to the AP SWCNTs, indicating that no charge transfer occurred between the functional group and the nanotube in these cases [24].

Relative intensities of the SWCNT characteristic absorption bands were quantified through the calculation of purity indexes. Figure 5 compares the NIR purity indexes for the different chemically modified materials after centrifugation (120,000 xg, 1h) in the four liquid media. Purity indexes of the dispersions in SDBS before centrifugation are also included for comparison. The values for the other three media (CTAB, Plu and GA) before centrifugation are not included in Figure 5 since they were almost identical to those in SDBS. The purity index of the AP/A material before centrifugation was nearly twice that of AP SWCNTs. Therefore, the thermal oxidation in air caused a decrease in the relative amounts of amorphous carbon impurities. In fact, selective elimination of amorphous carbon through controlled air oxidation has been demonstrated for the same AP material [25]. Purity indexes of acid treated materials (AP/HCl, AP/SN and AP/N) were slightly higher than that of AP SWCNTs. This effect can be associated to the elimination of metal particles or to the destruction of certain amorphous carbon impurities. On the contrary, purity indexes of the AP/NH₂ and AP/F materials before centrifugation were lower than for AP SWCNTs. The decrease in the relative intensity of SWCNT bands can be associated to the functionalization through diazonium salts, in agreement with previous observations for laser-grown SWCNTs [26].

Ultracentrifugation at 120,000 xg for 1h was validated as a purification method for dispersions of chemically modified SWCNTs in different aqueous media (Figure 5). Purity indexes after centrifugation improved by 2-3 times, depending on the centrifugation medium and the SWCNT type. The lowest purity indexes were obtained in GA solutions, and there was not a clear sequence among the other three media. A maximum NIR purity index of nearly 0.32 was reached for the AP/A material dispersed in Plu. The AP and AP/HCl materials showed purity indexes of higher than 0.3 in CTAB; the AP/SN, AP/N and AP/NH₂ materials reached maximum values in the range of 0.25-0.3; and the AP/F material only surpassed 0.2 after centrifugation in a Plu

solution. Few changes can be expected in the purity indexes through the variation of centrifugation conditions. In fact, small improvements were observed upon increasing centrifugation times and rates at the expense of drastically decreasing the yields.

Even though NIR purity indexes are mostly associated to the SWCNT mass fraction in the dispersion, other factors could modify the relative intensity of SWCNT characteristic absorption bands, including the functionalization degree, the type of the functional group or the SWCNT structural damage. Moreover, it has been observed that spectral backgrounds are influenced by chemical functionalization, aggregation and the SWCNT length distribution [27]. In order to confirm the visible/NIR results in terms of the real SWCNT purity, a series of dispersions after centrifugation were filtered and studied by TEM.

3.5. TEM characterization and metal content

TEM images at a magnification of 2,000x (Figure 6) offer a general view of SWCNT samples. Clearly, the ultracentrifugation process was successful in the purification of the chemically modified materials. Relatively homogeneous samples can be observed, mostly containing SWCNT bundles. In some cases (AP, AP/A, AP/NH₂ and AP/F), metal particles are still present among SWCNT bundles. In addition, surfactant aggregates with different sizes can be observed, while amorphous carbon and graphite-like impurities were drastically reduced. It must be noted that SWCNT agglomeration in the TEM images is much greater than in the original dispersions. During filtration, SWCNTs aggregated into large size bundles and fell on the filtration membrane together with the other solid impurities and the adsorbed surfactant. Dispersion in ethanol was not able to completely disaggregate the materials.

Image 6.c, corresponding to sample AP/HCl, consists of a dense network of SWCNT bundles without impurities. Therefore, the treatment including air oxidation and HCl reflux seems to be particularly suitable for the purification of arc discharge SWCNTs, in agreement with previous works [22]. Curiously, the purity index of the AP/HCl material after centrifugation in SDBS was slightly lower than those for the AP and AP/A materials.

Figure 7 includes TEM images at 30,000x, in which SWCNT bundles can be observed in some detail. The centrifuged AP material contained bundles of unaltered SWCNTs. In the AP/A material, individual SWCNTs were less clearly observed, indicating that a layer of SDBS surfactant remained adsorbed on the bundles. Apparently, the presence

of oxygen functional groups in the AP/A material contributed to an increase in surfactant adsorption. The image of AP/HCl (Figure 7.c) shows again bundles in which individual SWCNTs can be clearly observed, since elimination of oxygen bearing groups during the HCl treatment led to a decrease in the SDBS adsorption strength. However, certain globular structures are observed on AP/HCl bundles that could be associated to SDBS adsorbed on SWCNT wall defects. Images of the AP/SN and AP/N materials show even larger amounts of globular aggregates on SWCNT bundles. Ultracentrifugation purification of the AP/N material seems to be more difficult than for the other acid treated materials, since some amorphous carbon can still be seen with the nanotubes (Figure 6.e and 7.e). SWCNT bundles in the AP/NH₂ and AP/F materials (Figure 7.f and 7.g) are covered by a thick surfactant layer that was not removed by filtration and washing. This layer could be formed by the functional groups, particularly in the case of the big heptadecafluorooctyl moieties, together with large surfactant agglomerations strongly adsorbed on the functional groups. Metal particles and some carbon impurities are also observed in the AP/NH₂ and AP/F images.

Removal of metal impurities is an important topic in SWCNT purification, particularly for some applications including biomedical materials, biomolecular carriers or mechanical reinforcement in nanocomposites. Figure 8 shows the metal content analysis by EDX for the SWCNT materials before and after ultracentrifugation at 120,000 xg for 1h in SDBS. For all the pristine and chemically modified materials, ultracentrifugation eliminated substantial amounts of the residual metal catalysts. Metal removal during ultracentrifugation was greater than 95% for the acid treated samples, nearly 90% for the AP SWCNTs and 50-65% for samples AP/A, AP/NH₂ and AP/F. Metal contents in the acid treated samples after centrifugation were lower than 0.5 wt%.

Determination of the metal content in final products allows a better assessment of the purification process efficiency. The purification recovery factor (PRF) can be calculated as [28]: $PRF = (P_{prod} / P_{AP}) \cdot Y$, where P_{prod} and P_{AP} are the purity index of the product and the starting AP material respectively, and Y is the total yield of the process (Y_T) corrected for the metal content. The PRF provides an estimate of the fraction of SWCNTs which survive the purification process by taking into account the change of the purity index, yield and the change of the metal content. Figure 8 includes PRF values for the purification of functionalized SWCNTs by centrifugation in SDBS at 120,000 xg for 1h. Values of ~ 70 mass % and 60-70 mass % are reached for purified AP and acid treated SWCNTs respectively, while values of ~ 30 mass % were

calculated for samples previously functionalized by the diazonium salts method. Taking into account the final purity levels, PRF values indicate a high efficiency in the purification of pristine and acid treated SWCNTs; however, efficiencies were somewhat lower for the processing of the other materials.

4. Conclusions

Arc discharge SWCNT powders were chemically modified by six different protocols, dispersed in four different aqueous media, and purified by ultracentrifugation, reaching high levels of purity through the preferential removal of carbon impurities and metal catalyst particles. It can be concluded that, if the modified SWCNT material can be reasonably well dispersed in the aqueous medium, then the ultracentrifugation process always leads to substantially purified supernatant dispersions. However, the resultant degree of purity and the centrifugation yield depend on the chemical processing, the type of functional groups and the dispersion medium.

Extinction coefficients of the chemically modified SWCNT materials are influenced by the chemical functionalization, the material agglomeration and the metal content. On the contrary, extinction coefficients were nearly identical for a given SWCNT material in the four liquid media utilized.

Yields drastically decrease as ultracentrifugation speed and time increase. Optimal parameters for the purification of chemically modified SWCNTs are similar to those previously found for unmodified SWCNTs (120,000 xg, 1-2h) [4]. Some purity improvements could be achieved increasing centrifugation speed and time. However, small increments in the relative intensity of SWCNT visible-NIR characteristic bands imply important reductions in the yield.

Whenever the elimination of metal impurities is of capital importance, the best results will be obtained by ultracentrifugation of SWCNTs previously treated with oxidant processes and acids. Metal contents can be decreased below 0.5 wt% by that means.

The highest centrifugation yields were obtained with the anionic surfactant SDBS. Different aqueous media showed somewhat different purification results depending on the chemical modifications or functional groups of the SWCNT materials.

Acknowledgements

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Table 1. Nomenclature, summary of the preparation procedure, majority surface functional group and yield in the preparation (Y_p) of the different SWCNT powder materials.

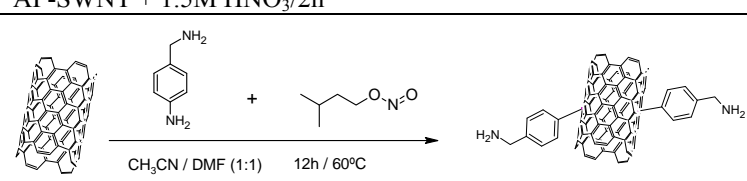
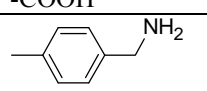
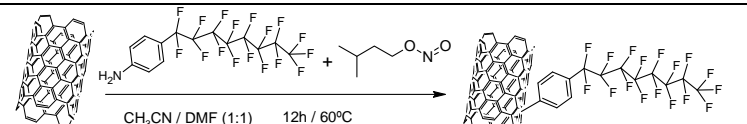
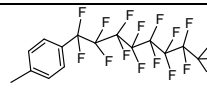
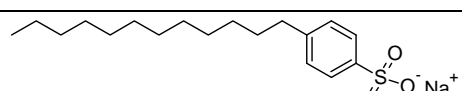
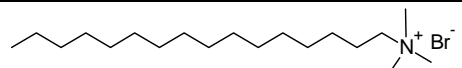
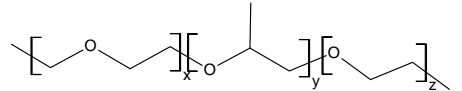
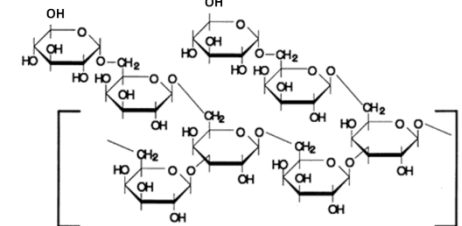
Abbreviation	Description	Functional group	Y_p [Wt.%]
AP	AP-SWNT from Carbon Solutions		100
AP/A	AP-SWNT + 388°C/2h/air/water	-C=O	51.5
AP/HCl	AP-SWNT + 350°C/2h/air + 3M HCl/2h	-C-OH	48.6
AP/SN	AP/HCl + 3M 3:1 H ₂ SO ₄ :HNO ₃ /2h	-COOH	55.4
AP/N	AP-SWNT + 1.5M HNO ₃ /2h	-COOH	89.4
AP/NH ₂			109
AP/F			111

Table 2. Name, structure, description and concentration of the four dispersants utilized in the present work.

Abbreviation	Name	Structure ^a	Category	C [Wt./vol.%]
SDBS	Sodium dodecylbenzenesulfonate		Anionic surfactant	0.5
CTAB	Hexadecyltrimethylammonium bromide		Cationic surfactant	0.5
Plu	Pluronic [®] F-68		Block copolymer	1
GA	Gum Arabic from acacia tree		Natural gum (branched polysaccharide)	0.5

^aPossible structure occurring in Gum Arabic

Table 3. Metal content of the SWCNT powder samples from EDX and TGA (air).

<i>Sample</i>	<i>Nickel [mass %]</i>	<i>Yttrium [mass %]</i>	<i>TGA residue [mass %]^a</i>	<i>TGA total metal [mass %]^a</i>
<i>AP</i>	22.6	5.9	33.2	24.9
<i>AP/A</i>	32.2	9.5	56.8	42.6
<i>AP/HCl</i>	9.3	1.4	10.2	7.7
<i>AP/SN</i>	6.5	1.1	3.4	2.6
<i>AP/N</i>	7.9	2.5	9.9	7.4
<i>AP/NH₂</i>	21.9	5.3	29.7	22.3
<i>AP/F</i>	14.4	4.1	20.3	15.2

^aThe TGA residue after complete oxidation of the SWCNT samples mainly consists of metal oxides. The initial metal content was calculated assuming an oxygen content of 25 Wt.% in the TGA residue [15].

Table 4. Functionalization degree (θ) of the SWCNT powder samples calculated from TGA data (inert).

<i>Sample</i>	<i>TGA residue at 800°C [mass %]</i>	<i>TGA weight loss between 120-800°C [mass %]</i>	<i>Evolved functional group</i>	<i>θ (1 group per X carbon atoms)</i>
<i>AP</i>	96.5	3.0 ^a	---	---
<i>AP/A</i>	80.2	15.5	C=O (28 g/mol)	1/25
<i>AP/HCl</i>	94.5	4.3	C-OH (29 g/mol)	1/190
<i>AP/SN</i>	68.9	29.2	COOH (45 g/mol)	1/10
<i>AP/N</i>	76.3	13.5		1/29
<i>AP/NH₂</i>	89.9	9.1	C ₆ H ₅ -CH ₂ -NH ₂ (107 g/mol)	1/88
<i>AP/F</i>	82.9	15.3	C ₆ H ₅ -C ₈ F ₁₇ (524 g/mol)	1/342

^aWeight loss in the AP sample was subtracted to the others for the calculation of their respective functionalization degree.

Table 5. Extinction coefficients (ϵ) at 850 nm of pristine and functionalized SWCNT dispersions in different surfactants.

<i>Sample</i>	ϵ [$mL\ mg^{-1}\ cm^{-1}$]			
	<i>SDBS</i>	<i>CTAB</i>	<i>Plu</i>	<i>GA</i>
<i>AP</i>	22.3	22.3	23.3	18.7
<i>AP/A</i>	4.7	5.8	4.4	5.3
<i>AP/HCl</i>	16.0	18.2	15.5	17.6
<i>AP/SN</i>	22.9	18.9	15.7	22.6
<i>AP/N</i>	17.6	14.2	13.3	16.3
<i>AP/NH₂</i>	7.9	7.8	6.3	9.5
<i>AP/F</i>	5.2	7.7	4.4	6.1

Table 6. Centrifugation yields (Y_c) and total yields (Y_t) for the preparation of the purified SWCNT materials after centrifugation (120,000 xg, 1h) in different surfactants.

<i>Sample</i>	<i>SDBS</i>	<i>CTAB</i>	<i>Plu</i>	<i>GA</i>
<i>AP</i>	18	9.5	5.3	2.3
<i>AP/A</i>	31	28	14	17
<i>AP/HCl</i>	33	14	4.5	22
<i>AP/SN</i>	32	20	24	16
<i>AP/N</i>	22	8.5	13	13
<i>AP/NH₂</i>	6.5	4.4	0.4	0.6
<i>AP/F</i>	13	2.8	4.6	4.7
Y_t [mass %] ^b				
<i>AP</i>	18	9.5	5.3	2.3
<i>AP/A</i>	16	14	7.2	8.8
<i>AP/HCl</i>	16	6.8	2.2	11
<i>AP/SN</i>	18	11	13	8.9
<i>AP/N</i>	20	7.6	12	12
<i>AP/NH₂</i>	7.1	4.8	0.4	0.7
<i>AP/F</i>	14	3.1	5.1	5.2

^a Y_c was calculated from absorbance data at 850 nm.

^b Y_t is expressed as a mass % of the starting AP material and was calculated from Y_c and Y_p data (Table 1).

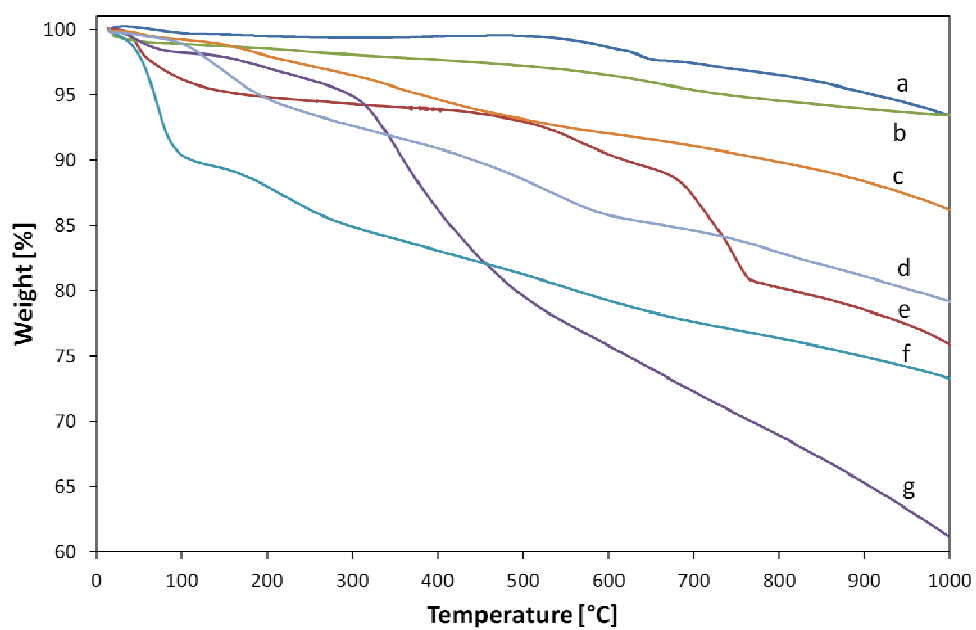


Figure 1. TGA (N₂, 5°C/min) of the SWCNT powder samples: a) AP, b) AP/HCl, c) AP/NH₂, d) AP/F, e) AP/A, f) AP/N, and g) AP/SN

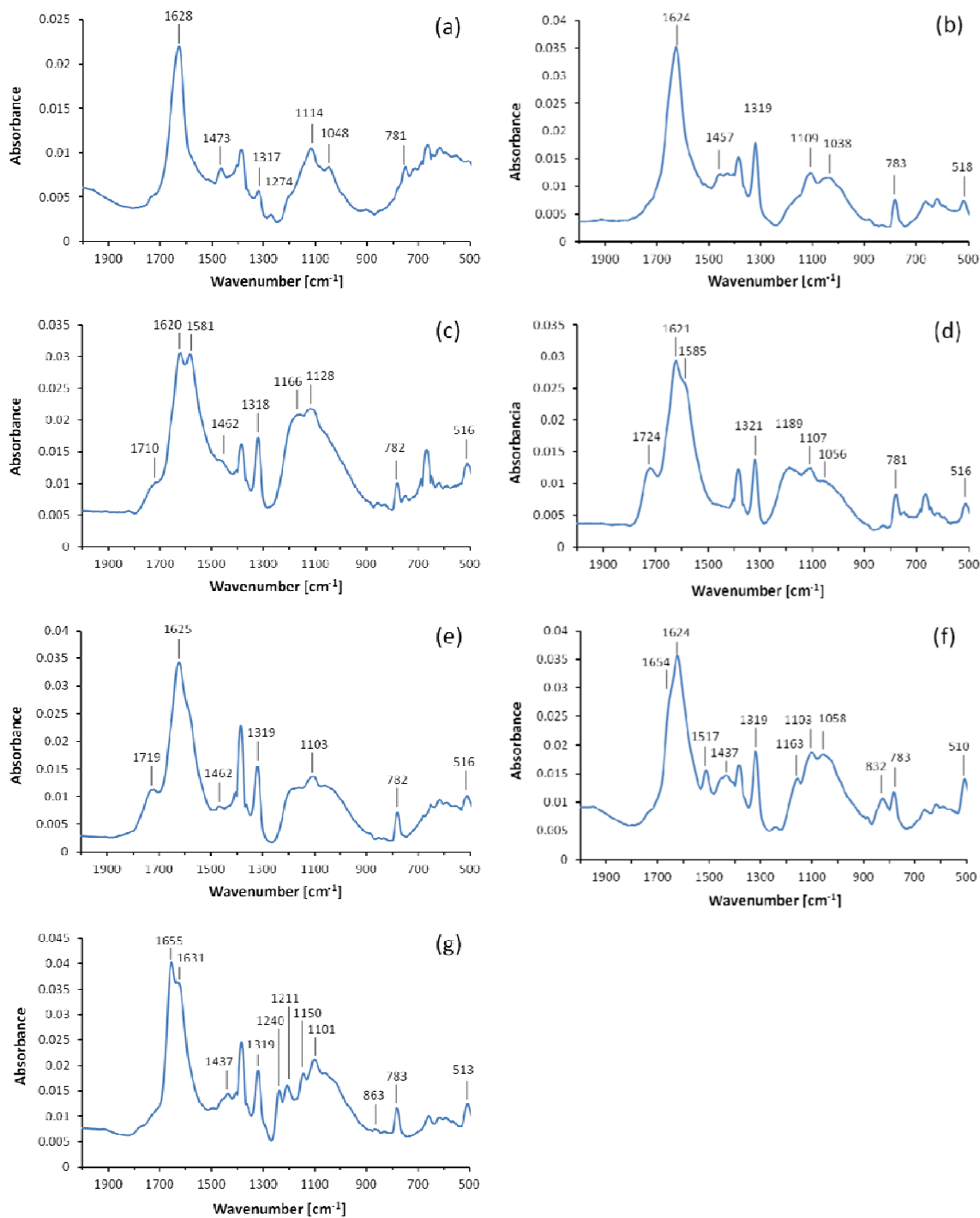


Figure 2. MIR spectra of the SWCNT powder samples: a) AP, b) AP treated at 350°C for 2h in air, c) AP/HCl, d) AP/SN, e) AP/N, f) AP/NH₂, and g) AP/F.

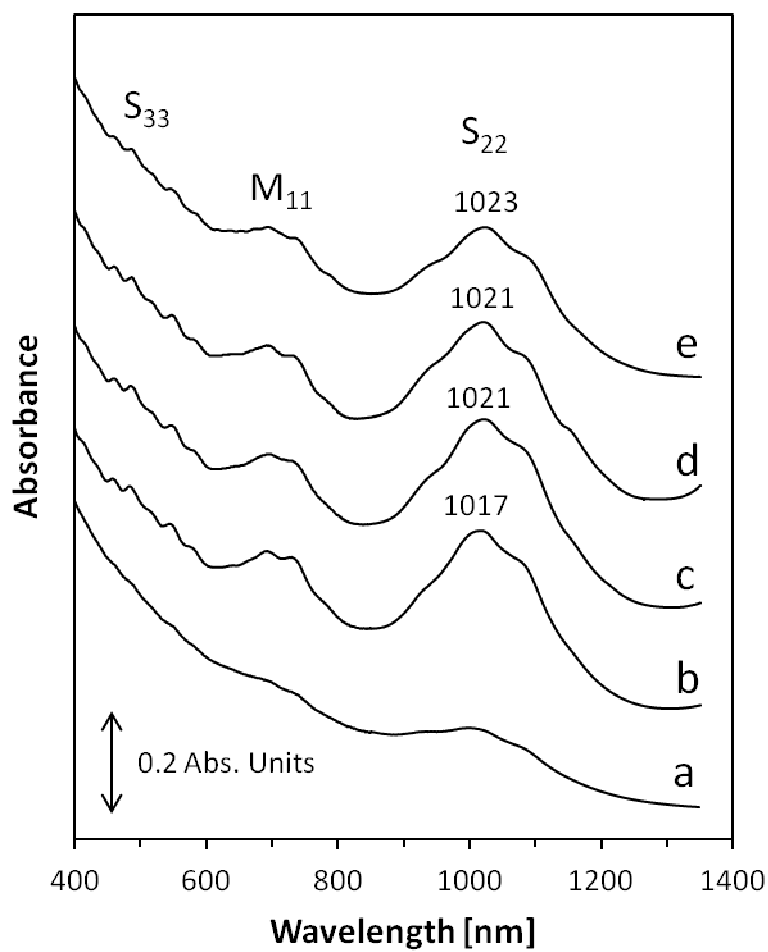


Figure 3. Vis/NIR spectra of AP SWCNT dispersions in a) SDBS before centrifugation, and b) SDBS, c) CTAB, d) Plu, and e) GA after centrifugation at 120,000 xg for 1h (spectra normalized at 850 nm). For spectral measurements, SWCNT concentrations were adjusted into a range of approximately 0.4 absorbance units at 850 nm.

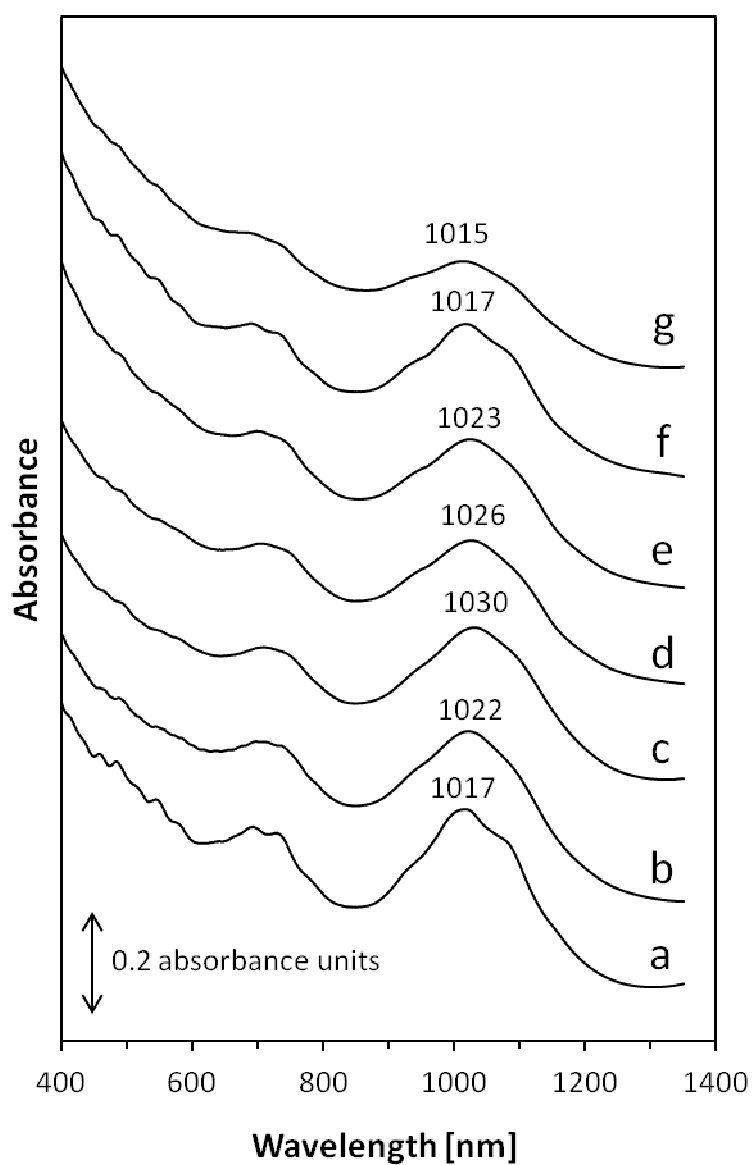


Figure 4. Vis/NIR spectra of different SWCNT dispersions after ultracentrifugation at 120,000 xg for 1h in SDBS: a) AP, b) AP/A, c) AP/HCl, d) AP/SN, e) AP/N, f) AP/NH₂, and g) AP/F (spectra normalized at 850 nm). For spectral measurements, SWCNT concentrations were adjusted into a range of approximately 0.4 absorbance units at 850 nm.

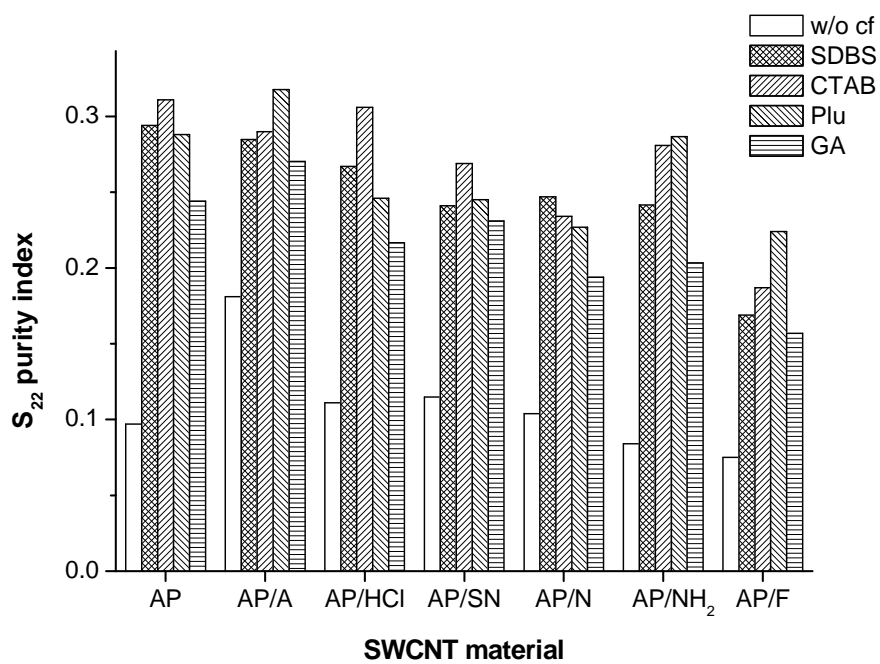


Figure 5. NIR purity index of different SWCNT dispersions before centrifugation (w/o cf) and after centrifugation at 120,000 xg for 1h in SDBS, CTAB, Plu, and GA.

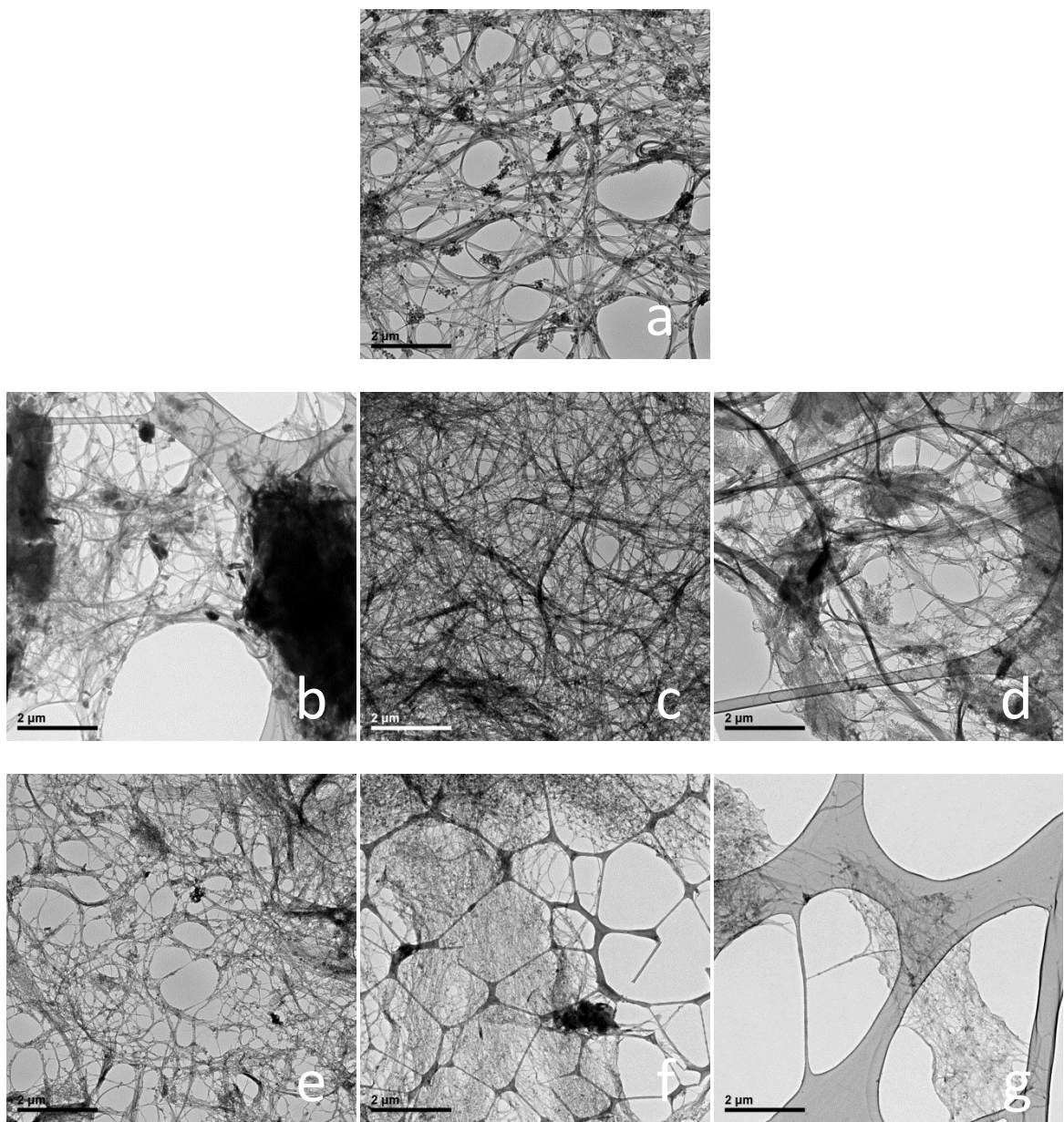


Figure 6. TEM images (magnification = 2000x) of SWCNT samples after ultracentrifugation processing in SDBS: a) AP, b) AP/A, c) AP/HCl, d) AP/SN, e) AP/N, f) AP/NH₂, and g) AP/F.

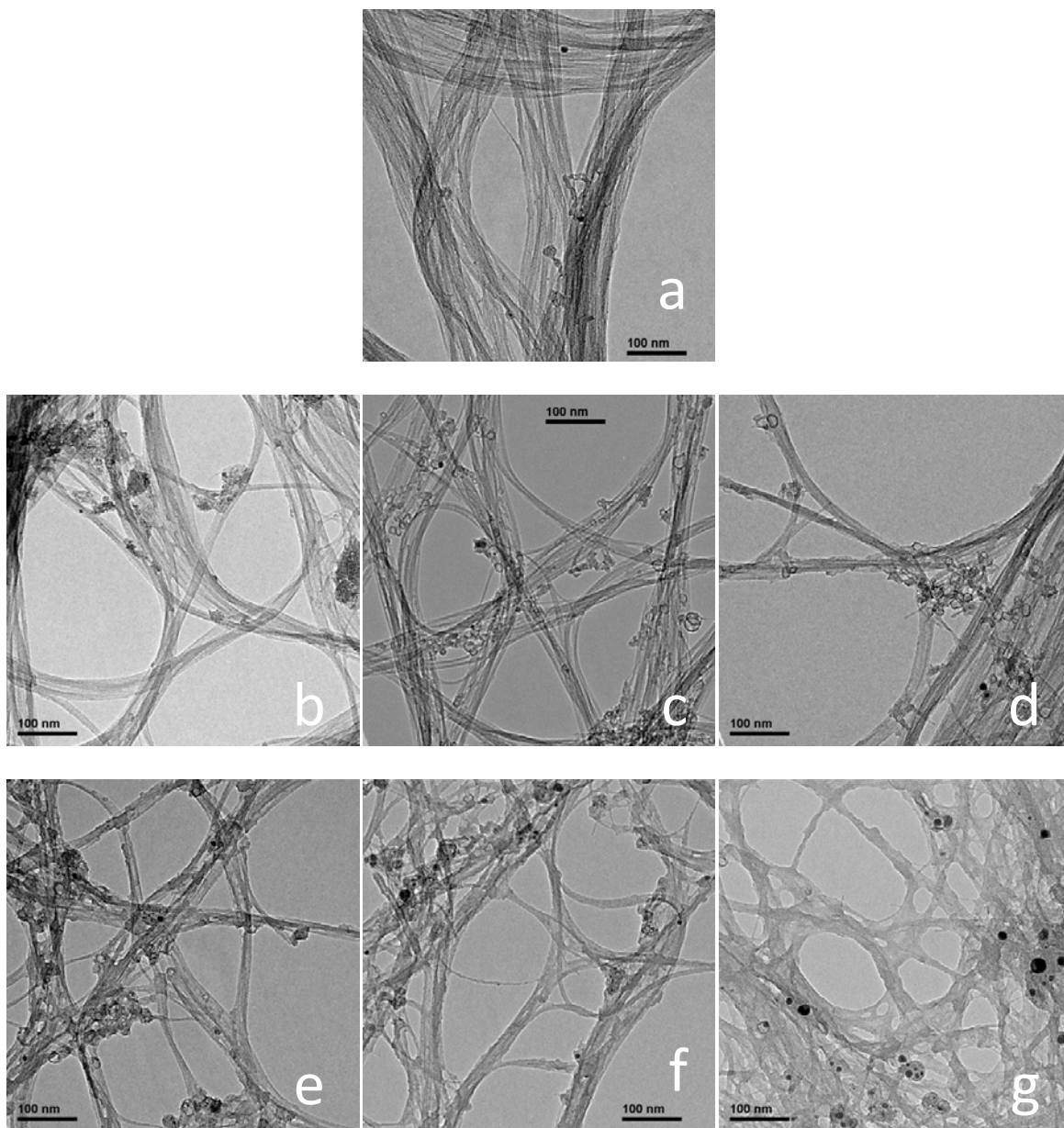


Figure 7. TEM images (magnification = 30000x) of SWCNT samples after ultracentrifugation processing in SDBS: a) AP, b) AP/A, c) AP/HCl, d) AP/SN, e) AP/N, f) AP/NH₂, and g) AP/F.

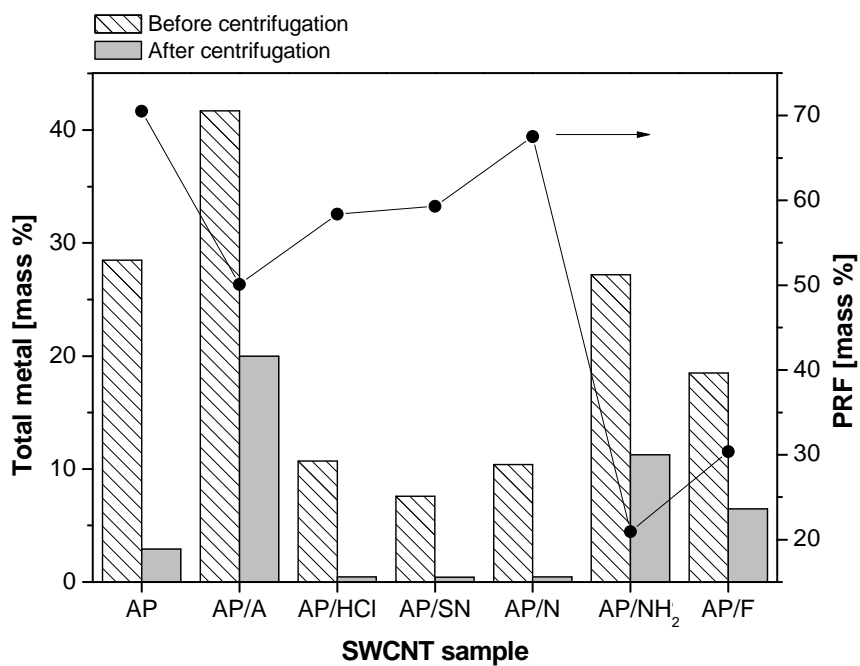


Figure 8. EDX analysis of the total metal content in the SWCNT samples before and after ultracentrifugation at 120,000 xg for 1h in SDBS, together with the calculated purification recovery factors (PRFs) after centrifugation.