



# Oxygen-containing functionalities on the surface of multi-walled carbon nanotubes quantitatively determined by fluorescent labeling

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## ABSTRACT

Control over the type and concentration of functional groups on carbon nanotubes (CNTs) require the use of reliable and sensitive analytical methods to detect, identify and quantify the functionalities on the material. Here we report the results of the selective quantification of aldehyde (together with ketone), carboxylic, and alcohol groups on arc-produced multiwalled carbon nanotubes (MWCNTs) using fluorescent labeling of surface species (FLOSS), combined with surface area and thermogravimetric analysis. The high sensitivity of the fluorescence spectroscopy combined with the selectivity of the chemistry of covalent attachment, allowed us to determine that as-produced MWCNTs contain ~1.1 at.% carboxylic groups, ~2.0 at.% aldehydes (and ketones) and <2.0 at.% hydroxyls. Surprisingly, and contrary to the behavior of single walled carbon nanotubes, these concentrations do not appear to increase for acid purified MWCNTs but rather decrease to 0.4 at.% for carboxylic groups; 1.6 at.% for aldehydes (and ketones) and <3.0 at.% for hydroxyls. Possible explanations for the observation that the acid purified MWCNTs have a lower level of the functionalities compared to the as-produced material are discussed.

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## 1. Introduction

### 1.1. Multi-walled carbon nanotubes and their properties

Carbon nanotubes have been of great interest since their discovery [1]. Depending on the synthesis conditions either single walled or multi-walled nanotubes can be produced. Multi-walled carbon nanotubes (MWCNTs), being orders of magnitude less expensive than single walled carbon nanotubes (SWCNTs), have already found large scale applications as fillers in the production of polymer composites [2,3]. High tensile strength, together with the metallic behavior of MWCNTs, make them very attractive for use where light and robust conductive materials are needed [1–3]. The fact that the production methods of MWCNTs do not necessarily require the use of metal catalysts can be beneficial since the problem of metal impurities in as-produced MWCNTs can be easily eliminated [1,4]. Interconnects in nanoelectronics and single molecule sensor devices are among the many other promising applications of MWCNTs [1,2].

### 1.2. Role of the functional groups on multi-walled carbon nanotubes

The surface of MWCNTs can be functionalized either unintentionally or intentionally [5–7]. In the first case, oxygen containing functionalities, such as carbonyls, carboxyls, and hydroxyls are usually introduced during the purification of as-produced material from the carbon impurities that are also generated in the synthesis. This is a result of the use of aggressive oxidants, for example concentrated acids, in the purification process [5]. In the case of the intentional functionalization, the oxidation of MWCNTs is intended to improve debundling of the individual MWCNTs and to increase their solubility in the polymer matrix. The chemistry of the functional groups, if known, also can be exploited for further derivatization reactions if necessary [5–7].

### 1.3. Methods to detect, identify, and quantify functional groups on multi-walled carbon nanotubes

A wide array of conventional techniques have been applied to characterize carbon nanotubes (CNTs) [8–11]. Among the most frequently used methods are FTIR [10], Raman [11], and X-ray photoelectron spectroscopy (XPS) [8]. Even though first two techniques have been tremendously successful in detection and identification of the surface functionalities on many materials, the necessity of additional independent methods to calibrate the analytical

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**Table 1**  
FLOSS results (atomic percent and surface coverage) of various oxygen containing functional groups on MWCNTs.

MWCNTs (specific surface area)	Functional groups					
	—COOH (carboxylic)		—COH (aldehyde, ketone)		—OH (alcohol)	
	groups/cm <sup>2</sup>	at.%	groups/cm <sup>2</sup>	at.%	groups/cm <sup>2</sup>	at.%
As-received (37 m <sup>2</sup> /g)	$4.3 \times 10^{13} \pm 0.1 \times 10^{13}$	1.10 ± 0.03	$7.45 \times 10^{13} \pm 0.45 \times 10^{13}$	1.94 ± 0.12	$<6.8 \times 10^{13}$	<1.8
HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> treated (46 m <sup>2</sup> /g)	$1.4 \times 10^{13} \pm 0.1 \times 10^{13}$	0.36 ± 0.03	$6.05 \times 10^{13} \pm 0.25 \times 10^{13}$	1.57 ± 0.06	$<1.2 \times 10^{14}$	<3.1
Dye	Panacyl bromide		Dansyl hydrazine		5-DTAF	

response still impede the quantitative, as opposed to qualitative, use of Raman and FTIR spectroscopy to determine the concentrations of the functional groups [9,10,12]. Another drawback of using FTIR or Raman alone is that not all functional groups can be detected by either of the methods. For example, Raman while sensitive to the presence of defects in CNTs, via the intensity of the D (1300–1400 cm<sup>-1</sup>) band, has not identified oxygen functionality directly on these materials. On the other hand, XPS, combined with derivatization labeling reactions, has been used in identification and quantification of surface functionalities [13,14]. However, the sensitivity of FTIR ( $\sim 10^{14}$  groups/cm<sup>2</sup>) [15] and XPS ( $\sim 10^{13}$  groups/cm<sup>2</sup>) [16] is less than that of fluorescence methods ( $\sim 10^9$  groups/cm<sup>2</sup>) [17].

It is worth mentioning here a recently described approach to identify and quantify oxygen functionalities on SWCNTs based on the combined results from water adsorption–desorption and temperature-programmed desorption (TPD) experiments [12]. However, the lack of selectivity of the probing method brings some uncertainty to the identification and relative content determination in this technique [12].

#### 1.4. Fluorescence detection techniques and their advantages

Fluorescence techniques in combination with labeling reactions have been used to quantify functional groups on polymers [16] and biological moieties [18,19]. The high selectivity of the detection, provided by the specificity of the covalent bonding, together with excellent sensitivity ( $\sim 10^9$  groups/cm<sup>2</sup>) [17], favor fluorescence-based detection in the identification and quantification of functional groups on the surfaces of different materials at concentrations below the detection limits of conventional techniques. Recently, fluorescence labeling of surface species (FLOSS) was successfully used to label and quantify oxygen containing functionalities on self-assembled monolayers [20], activated carbon fibers [21], graphitic nanofibers [22], and single-walled carbon nanotubes (SWCNTs) [23,24]. In the case of SWCNTs, FLOSS routinely detected and quantified oxygen containing functionalities with concentrations below 1 at.% [24], suggesting the possible applicability of the method to other carbon materials, similar to SWCNTs. Here we report the results of FLOSS on MWCNTs, with the goal of understanding the nature and quantity of oxygen functional groups present on the as-produced material, and how this would evolve following purification processes.

## 2. Materials and methods

Solid non-catalytic MWCNTs (arc-produced, #MRGC) were purchased from MER Corp. (Tucson, AZ). According to the manufacturer, the material did not contain any metal impurities, since it was produced without usage of any catalyst, a result confirmed by thermogravimetric analysis (TGA) (Fig. S1).

MWCNTs were purified from carbon impurities via the treatment with a mixture of concentrated nitric and sulfuric acids as described elsewhere [25,26] (see SI for details). The specific surface areas of the samples were determined from nitrogen adsorption

isotherms (ASAP 2020 analyzer, Micromeritics Instrument Corporation) using the BET method (Table 1) [27]. All fluorescence spectra were taken with a Fluoromax-2 instrument (Jobin Yvon) at right angle geometry using 10 mm rectangular quartz cuvettes. Transmission electron microscopy (TEM) was done on a Jeol JEM 2100 instrument at an acceleration voltage of 200 kV.

Dyes were chosen based on their verified high specific reactivity with certain functional groups [16,18,19]. Dansyl hydrazine (5-dimethylaminonaphthalene-1-sulfonyl hydrazine) (DH), panacyl bromide (4-(9-anthroyloxy)phenacyl bromide) (PB) and 5-(4,6-dichlorotriazinyl)aminofluorescein (5-DTAF) were purchased from Molecular Probes (Eugene, OR) and used to label carbonyl, carboxyl, and hydroxyl groups on MWCNTs, respectively (Scheme 1). The concentrations of the functional groups on MWCNTs were determined using the depletion strategy described elsewhere [24]. Briefly, concentrations of functional groups were found from the difference of the fluorescence intensity of the fluorophore solutions before and after the reactions with known masses of MWCNTs samples [24].

#### 2.1. Labeling and quantification of carboxylic groups

Solutions of panacyl bromide (PB) gave a linear dependence of the fluorescence vs. concentration in the range of 4–67 nM and were used to calibrate the fluorescence signal from the dye in further depletion experiments (Fig. 1). The peak at about 403 nm is the Raman scattering of the CH<sub>3</sub> stretching mode ( $\sim 2933$  cm<sup>-1</sup>) of the solvent (acetone).

To label carboxyl groups on MWCNTs, two samples of as-produced and two samples of the acid treated MWCNTs ( $\sim 50$  mg each) were reacted in separate beakers with solutions of PB of known concentrations (see SI for the details). Upon the completion of the reaction, supernatants from each of the beakers were collected together with the supernatants after the successive (4 times at least) washings of the samples with the neat solvent (acetone) to remove the physisorbed PB from MWCNTs. Fluorescence spectra of the recovered supernatant solutions were taken to determine the concentration of PB that remained non-reacted (Figs. 2 and 3).

#### 2.2. Labeling and quantification of carbonyl groups

Carbonyl (aldehyde, together with ketone) groups were labeled with dansyl hydrazine and quantified in a manner similar to the strategy explained above (Figs. S2–S4).

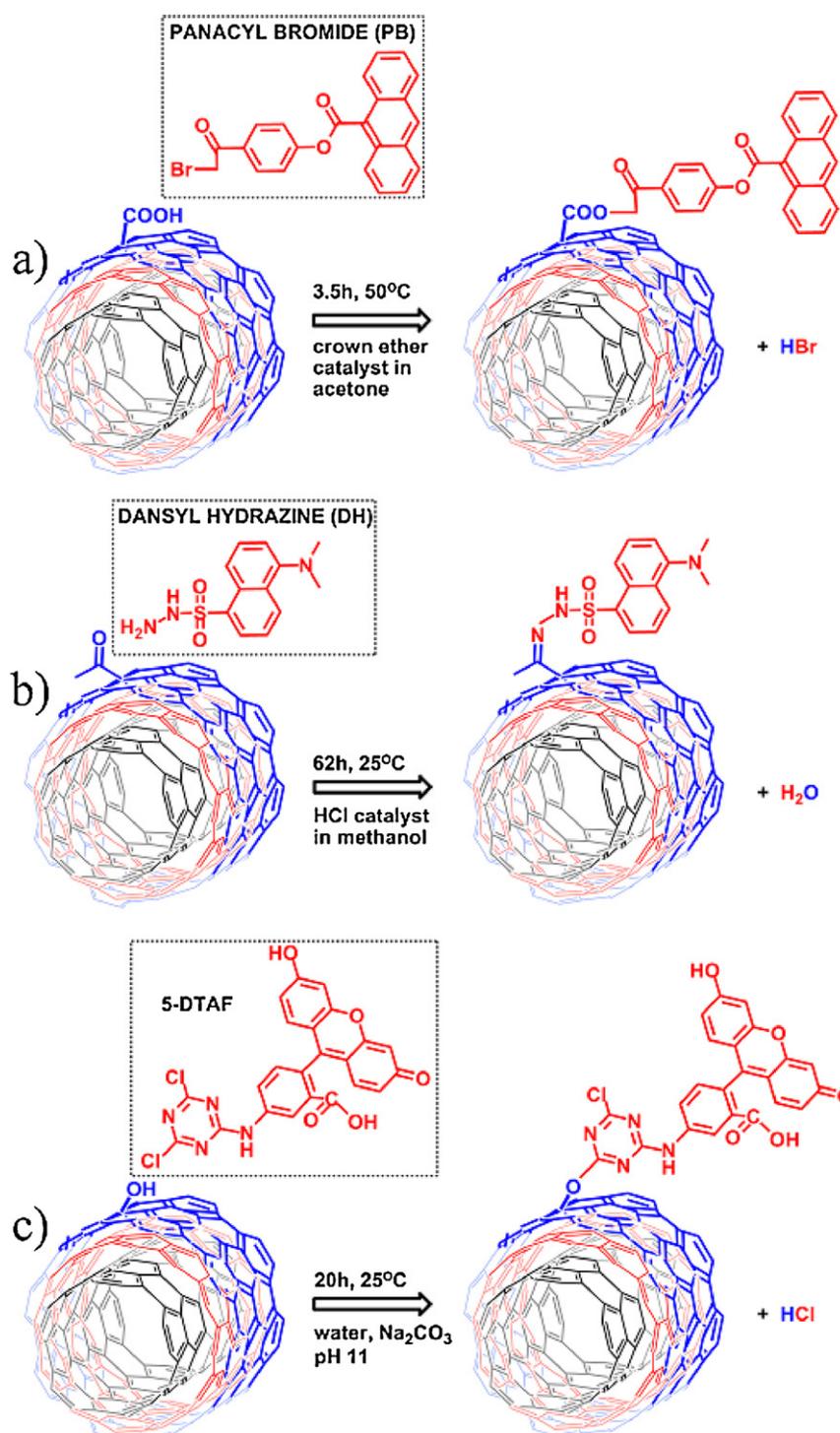
#### 2.3. Labeling and quantification of alcohol groups

Alcohol groups were labeled with 5-DTAF and quantified similar to the strategy, explained above (Figs. S5 and S6).

#### 2.4. Control experiments

##### 2.4.1. Dye physisorption control experiments

In order to avoid a contribution to the total depletion from the dye which could possibly physisorb to the walls of the glass beaker



**Scheme 1.** Fluorescent dyes and the labeling reactions (a) carboxylic groups with panacyl bromide, (b) carbonyl groups with dansyl hydrazine, (c) alcohol groups with 5-DTAF.

during the reaction, depletion in each experiment was determined with reference to the experiment without MWCNTs in solution, which was treated the same way as the solutions with MWCNTs. In addition, a series of control experiments with deactivated dyes were done to determine how much of the dye physisorbs to MWCNTs, using a strategy described elsewhere [24] (Figs. S7–S9).

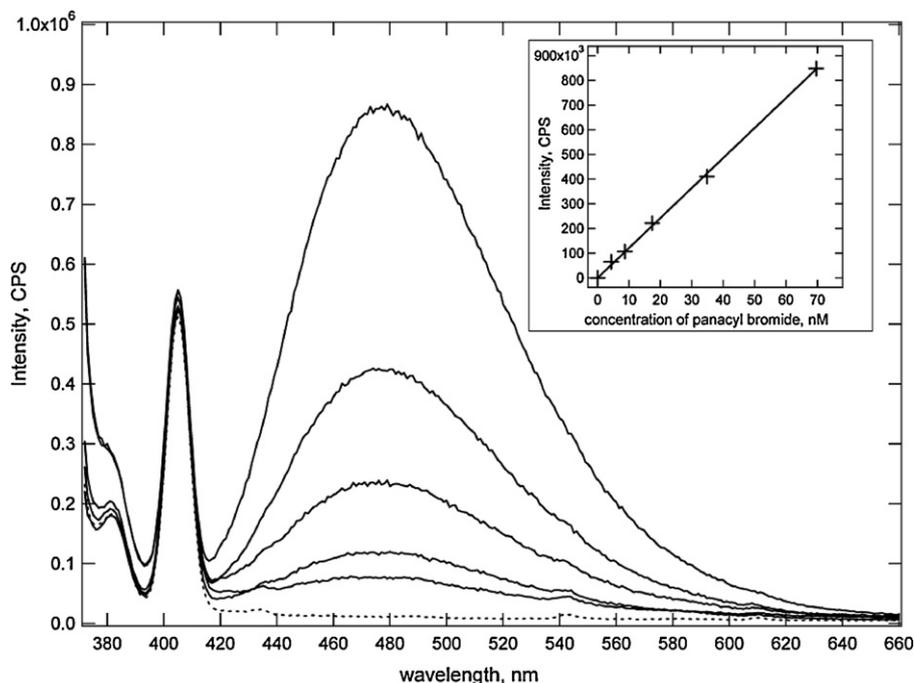
#### 2.4.2. Reaction time control experiments

It was checked if the chosen reaction times were long enough to label the majority of the accessible functional groups. For this purpose, after the first labeling run was complete, the reacted

samples were subject to contact with fresh portions of the labeling solutions. After the second labeling run a small additional depletion, compared to the first run, was observed for PB and DH, suggesting that the reaction times were sufficient (Figs. S10 and S11).

### 3. Results and discussion

The results of the FLOSS on MWCNTs are summarized in Table 1. Since control experiment showed significant physisorption of 5-DTAF (label for the alcohol groups) to MWCNTs (Figs. S8 and S9),



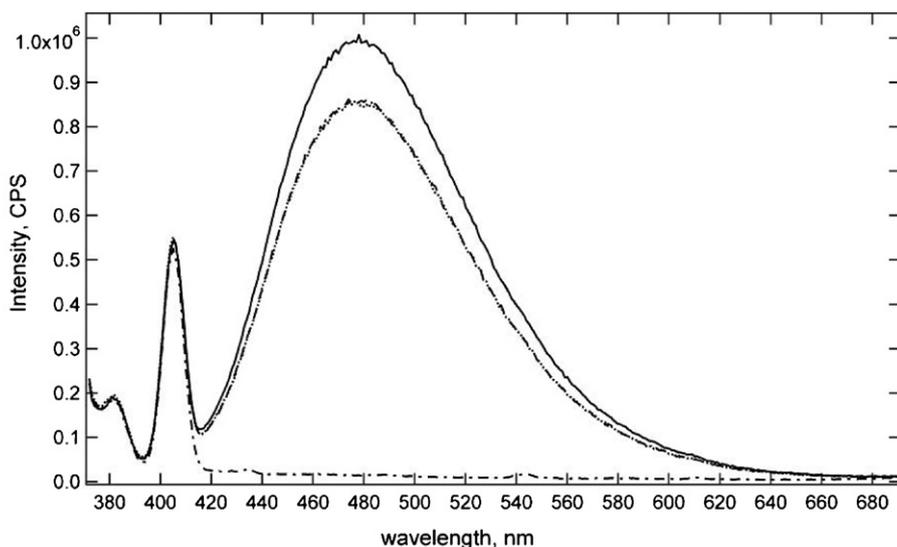
**Fig. 1.** Emission spectra of panacyl bromide (PB) of different concentrations (from top to bottom): 67 nM, 35 nM, 17 nM, 9 nM, 4 nM; neat acetone (dotted line) excited at 362 nm (inset: calibration plot of fluorescence intensity at 475 nm vs. PB concentration).

the concentration of alcohol groups, determined from the depletion experiment, has to be considered as an upper limit.

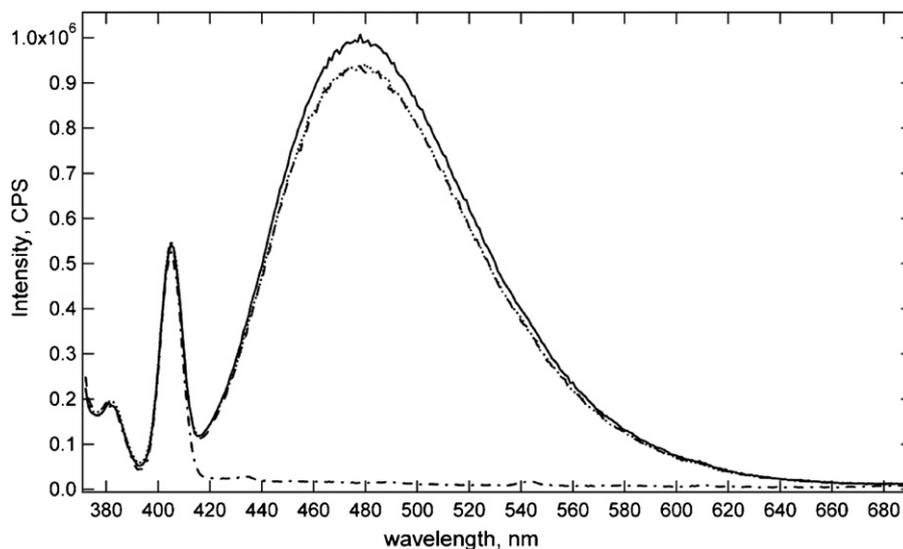
Overall analysis of the concentrations of the functionalities determined by FLOSS suggests that carbonyls are the most abundant functionalities for both as-produced and the acid treated MWCNTs, similar to SWCNTs [24]. Surprisingly, it was also found that the as-produced material contains substantially greater concentrations of oxygen functionality than the acid treated MWCNTs (Table 1). Tentative explanations to these finding can be made based on the knowledge of the composition of both materials. According to the manufacturer, the as-produced MWCNTs, used in this study, contain a substantial amount of carbonaceous impurities (up to 70%). One might reasonably expect that carbon impurities, being more disordered and richer with defects that can oxidize

in ambient, would have a higher content of oxygen containing functional groups compared to the MWCNTs. For these reasons, most probably, the contribution of the functional groups on carbon impurities to the overall concentration of the functional groups on as-produced material is predominant.

Acid treatment of the material, on the other hand, changes the relative content of MWCNTs and carbon impurities, mostly destroying the latter. This leads to the decreased overall concentration of the functional groups on acid treated material compared to the as-produced, non-purified MWCNTs. Transmission electron microscopy (TEM) showed that as-received, non-purified MWCNTs contain a substantial amount of amorphous (shapeless material) together with graphitic carbon (pieces of the material with distinct edges) impurities (Fig. 4). The impurities in purified MWCNTs, on



**Fig. 2.** Emission spectra of panacyl bromide reacted with carboxyls of as-received MWCNTs: experiment without MWCNTs (solid line at the top), after reaction with 46.1 mg MWCNTs (dotted line), after reaction with 41.9 mg MWCNTs (dashed line); neat acetone (dash-dotted line at the bottom). Excitation at 362 nm.



**Fig. 3.** Emission spectra of panacyl bromide reacted with carboxyls of  $\text{HNO}_3/\text{H}_2\text{SO}_4$  purified MWCNTs: experiment without MWCNTs (solid line at the top), after reaction with 46.1 mg MWCNTs (dotted line), after reaction with 44.7 mg MWCNTs (dashed line); neat acetone (dash-dotted line at the bottom). Excitation at 362 nm.

the other hand, are mostly comprised of graphitic carbon (Fig. 5). TEM results, thus, support the suggested explanation for the lower oxygen functionalities content in the case of purified MWCNTs, compared to as-received, non-purified MWCNTs. However, to

make the suggested explanation more confirmative, further characterization of the samples needs to be done (e.g. Raman, XPS).

#### 4. Conclusions

Fluorescence labeling of surface species (FLOSS) was successfully applied to as-produced and acid purified MWCNTs to detect, identify and quantify carbonyl, alcohol, and carboxyl surface functionalities. It was found, that carbonyls are the most abundant functionalities for both materials. The lower content of the functional groups on acid treated MWCNTs compared to the as-produced MWCNTs was explained by the predominant contribution of the highly functionalized carbon impurities in the non-treated material. The acid treatment appears to preferentially remove the amorphous carbon, leaving graphitic like carbon impurities. Reproducibility of the FLOSS, accompanied with the results of series of the control experiments, demonstrated that FLOSS can be efficiently used in the surface characterization of MWCNTs.

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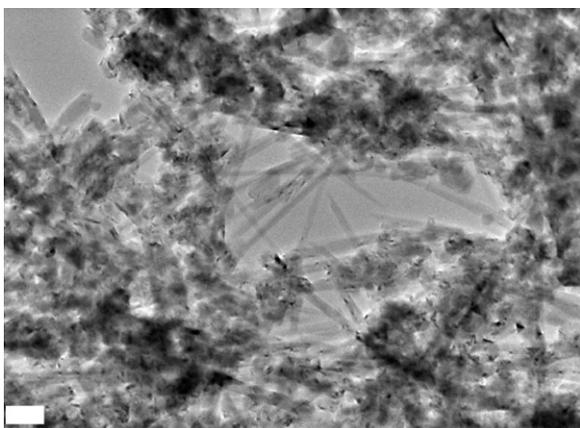
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#### Appendix A. Supplementary data

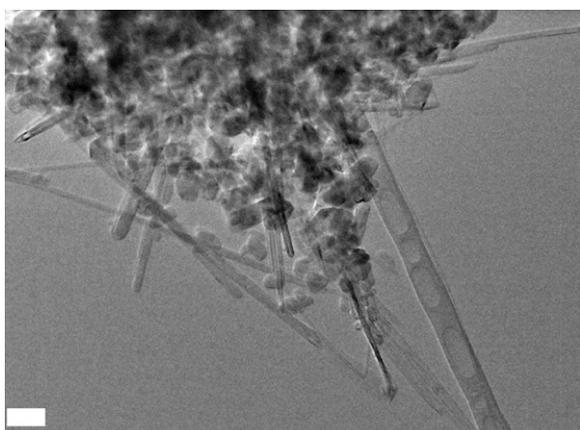
Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apsusc.2012.06.103>.

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**Fig. 4.** TEM image of as-received, non-purified multiwalled carbon nanotubes (scale bar is 100 nm).



**Fig. 5.** TEM image of  $\text{HNO}_3/\text{H}_2\text{SO}_4$  purified multiwalled carbon nanotubes (scale bar is 100 nm).

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