

Fluorescence Labeling and Quantification of Oxygen-Containing Functionalities on the Surface of Single-Walled Carbon Nanotubes

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Fluorescence labeling of surface species (FLOSS) was applied to identify and determine the concentration of oxygen-containing functionalities on single-walled carbon nanotubes (SWCNTs), subjected to two different purification processes (air/HCl and nitric acid treatments) and compared to as-received (nonpurified) SWCNTs. The fluorophores were selected for their ability to covalently bind, with high specificity, to specific types of functionalities (OH, COOH, and CHO). FLOSS revealed that even as-received SWCNTs are not pristine and contain ~0.6 atomic % oxygen functionalities. FLOSS showed that, after nitric acid treatment, SWCNTs are ~5 times more functionalized than SWCNTs after air/HCl purification (5 versus 1 atomic % oxygen functionalities), supporting the idea that the former purification process is more aggressive than the latter. FLOSS demonstrated that carbonyls are the major functionalities on nitric-acid-purified SWCNTs, suggesting that chemical derivatization strategies might consider exploiting aldehyde or ketone chemistry.

1. Introduction

1.1. Importance of Functional Groups on Carbon Nanotubes (CNTs). The unique geometry of the CNTs provides them with outstanding mechanical and electronic properties.^{1,2} For this reason, CNTs and, especially, single-walled carbon nanotubes (SWCNTs) have potential applications in different areas from producing the smallest nanotransistors^{1,2} to drug delivery.³ One of the obstacles that hinders industrial-scale applications of CNTs is the presence of impurities that compromise the desirable properties of as-produced CNTs and make their characteristics irreproducible. In general, there are two types of impurities: (i) particles of the metallic catalyst (which are inevitably used in the production of SWCNTs), encapsulated by CNT or covered with amorphous carbon, and (ii) carbon impurities, comprised of different forms of carbon other than CNTs.¹ Among the numerous purification strategies,^{4–7} two methods are frequently used: air/HCl treatment⁸ and nitric acid treatment.⁹ Because both methods use oxidizing agents, the CNTs become oxidized after purification. The oxygen-containing groups on the surface of

purified CNTs affect their properties.^{10–14} In some cases, chemical modification of CNTs can improve their properties, e.g., solubility,¹⁰ adsorption behaviors,¹³ and catalytic activity.¹¹ Functionalized CNTs find uses in a number of applications, e.g., as capacitors,¹² sensors,¹⁴ and probes for atomic force microscopy.¹⁵ Thus, it is important to identify and ultimately control the type and concentration of oxygen-containing functional groups on CNTs.

1.2. Methods To Identify and Quantify Functional Groups on CNTs. X-ray photoelectron spectroscopy (XPS),^{16,17} infrared spectroscopy (IR),^{18–20} and Raman spectroscopy^{20,21} are the most widely used techniques to investigate functional groups on CNTs. Nevertheless, each method has its limitations.²²

Using XPS, it is hard to distinguish between signals from different oxygen-containing functionalities because of the close proximity of the peaks in the C(1s) region.^{17,23} To overcome this difficulty, XPS was combined with derivatization reactions to identify and quantify separately different oxygen-containing functional groups on polymers,^{24,25} carbon fibers,²⁶ and black

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carbons.¹⁷ The detection limit of this XPS labeling technique was estimated as $\sim 10^{14}$ groups/cm² (10^{-10} mol/cm²).²⁷

IR spectroscopy is not able to determine species that have no IR-active vibrational modes. IR detects vibrational resonances associated with particular chromophores but does not necessarily identify the functional groups. For example, while an IR peak might be interpreted as arising from a C–O bond, condensed-phase IR data alone cannot unambiguously distinguish whether this C–O is associated with an ether or alcohol group. In addition, IR spectroscopy provides little absolute quantitative information.^{18–20} In the best cases, the detection limit of IR spectroscopy is estimated as $\sim 10^{14}$ groups/cm² (~ 2 – 3 atomic %).²⁸

Not all vibrational modes are IR-active. For this reason, Raman spectroscopy is commonly used in combination with IR measurements to obtain the most complete vibrational information. Raman spectroscopy is sensitive to the diameters of the nanotubes,²⁹ their chirality,²⁹ and purity.⁷ On the other hand, Raman spectroscopy is not sensitive to many functional groups, e.g., alcohols, carboxyls, and carbonyls, that might be present on CNTs.^{20,21}

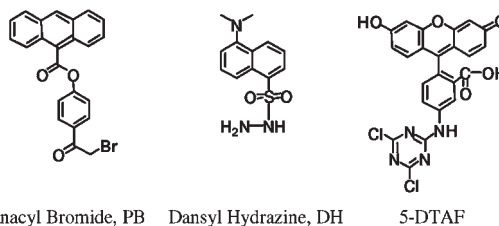
Fluorescence spectroscopy is an extremely sensitive technique, with the ability to detect single molecules.³⁰ Fluorescence has been used to characterize CNTs.³¹ Several groups studied the covalent attachment of fluorescent molecules to functional groups on carbon nanotubes.^{32,33} Fluorescence microscopy was used to visualize CNTs.³⁴ Georgakilas et al. reported an approach to the organic functionalization of nanotubes with a fluorescent moiety (pyrene), which has led to a high level of solubility of the resulting products.³⁵ Zhu et al. incorporated a naphthalimide fluorescent molecule onto SWNT via amidation.³⁶ Such modifications can change the electronic structure of nanotubes.^{35,36} In addition, chromophore emission can be significantly quenched by the process of attachment to nanotubes.^{34,36} This makes the quantification of chromophores on the nanotube surface complicated.

Our previous study on the use of fluorescence labeling of surface species (FLOSS) to detect functional groups on self-assembled monolayers (SAMs)³⁷ and activated carbon fiber (ACF)³⁸ showed that FLOSS has the advantage of a lower minimum detection limit compared to other techniques, such as XPS and IR. Recently, it has been demonstrated that the detection limit of FLOSS can be as low as $\sim 10^9$ groups/cm².³⁹

Table 1. Properties of SWCNTs

	as received	air/HCl treated	nitric acid treated
SSA (m ² /g)	307 ± 21	737 ± 31	21 ± 4
catalyst (Ni) content (wt %)	30	9	3.5

Scheme 1. Structures of the Dyes Used as Labels



Panacyl Bromide, PB Dansyl Hydrazine, DH 5-DTAF

2. Experimental Section

2.1. Arc-Produced SWNTs and Their Properties. The solid as-received and nitric-acid-treated arc-produced SWNTs were purchased from Carbon Solutions, Inc. The specific surface area (SSA) of each of the samples was determined by adsorption of nitrogen at -196 °C using an ASAP 2020 instrument (Micromeritics Instrument Corporation) and employing the Brunauer–Emmett–Teller (BET) method for the calculations⁴⁰ (Table 1). Thermogravimetric analysis (TGA) (Perkin Elmer, Pyris 6 TGA) was run for the samples to determine the catalyst content (i.e., to compare efficiency of the purification techniques) (Table 1 and Figures S17–S19 in the Supporting Information).

2.2. Fluorescence Labeling Pathways and Detection. To exclude issues related to the specificity/nonspecificity of any given dye to label selectively (i.e., exclusively) only the functional groups of the interest, dye labels successfully used in the selective labeling functional groups on polymers and biomaterials were selected.^{27,41,42} Panacyl bromide (4-(9-anthroyloxy)phenacyl bromide, Molecular Probes) (PB),⁴¹ dansyl hydrazine (5-dimethylaminonaphthalene-1-sulfonyl hydrazine, Molecular Probes) (DH),^{27,42} and 5-(4,6-dichlorotriazinyl)aminofluorescein (Molecular Probes) (5-DTAF) (Scheme 1) were used to label carboxylic, carbonyl, and alcohol groups on SWCNTs, respectively (Figure 1). The concentration of functional groups was determined by measuring the intensity of the fluorescence of the dye in solution before contact with SWCNTs and after the labeling reaction, with the labeled SWCNTs removed from the solution. This “depletion” approach is feasible because of the large SSA of the materials. The depletion of the fluorescence signal was then related to the concentration of functional groups on SWCNTs using a fluorescence calibration curve, the mass (and SSA) of the sample, and the stoichiometry of the given labeling reaction. All fluorescence measurements were performed in 10 mm rectangular quartz cuvettes in a Fluoromax-2 instrument (Jobin Yvon) using a right-angle geometry. All manipulations with dyes were performed in the room lighted only by a red bulb.

2.2.1. Fluorescence Labeling of Carbonyl Groups. An aliquot of solution of DH (with HCl, used as a catalyst) of known concentration (~ 0.1 mM, see the Supporting Information for details) in methanol (JT Baker) was allowed to react with a known mass of sample in a glass beaker while stirring. After the reaction, the solution supernatant was transferred into an empty flask. The remaining sample was washed in the beaker with neat solvent (methanol), and the supernatant was transferred into the same flask. The washing of the sample (and transferring of the

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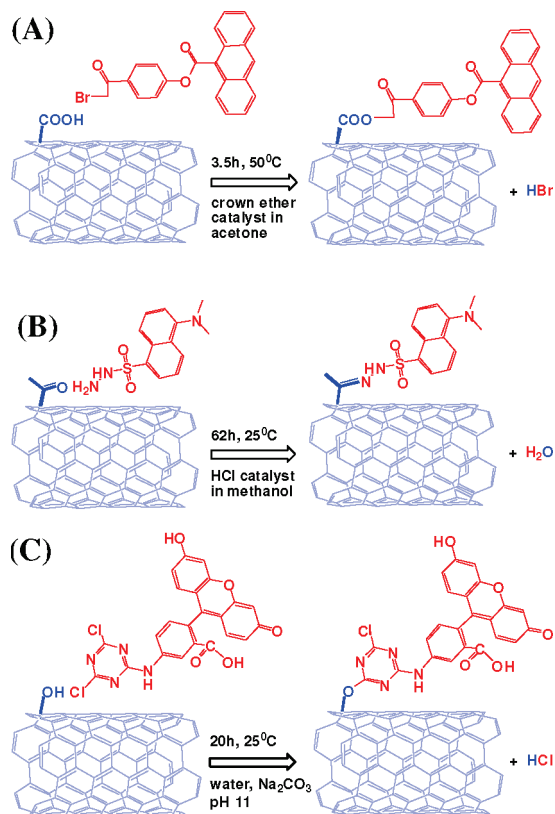


Figure 1. Labeling reaction schemes: (A) carboxylic groups with panacyl bromide, (B) aldehyde groups with dansyl hydrazine, and (C) alcohol groups with 5-DTAF.

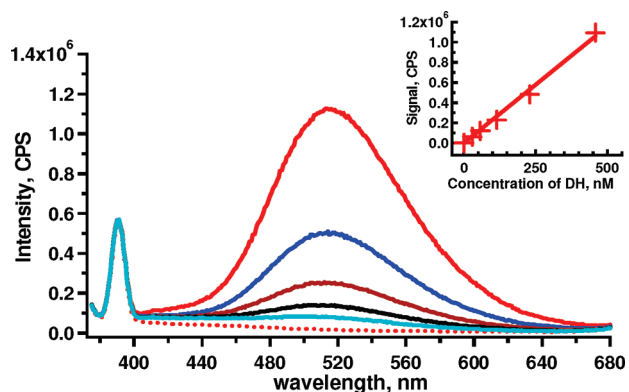


Figure 2. Emission spectra of dansyl hydrazine of different concentrations: 458 nM (red solid line), 229 nM (blue solid line), 115 nM (brown solid line), 57 nM (black solid line), and 29 nM (cyan solid line); neat acetone + HCl (red dotted line) excited at 350 nm. Inset: calibration plot of fluorescence intensity at 510 nm versus the DH concentration.

supernatant) was repeated several times (4–5 times). The collected supernatant was diluted with acetone (~100 nM range), and the fluorescence spectrum of the solution was recorded (excitation at 350 nm). This procedure was implemented twice for as-received, air/HCl-treated, and nitric-acid-treated SWCNTs. The depletion of the fluorescence signal was measured and compared to the fluorescence intensity of the dye after the control experiment (labeling reaction with no sample in the beaker) (Figures 2–5).

2.2.2. Fluorescence Labeling of Carboxylic Groups. Carboxylic groups were labeled with PB following a scheme similar to the one described above (Figures S1–S4 in the Supporting Information).

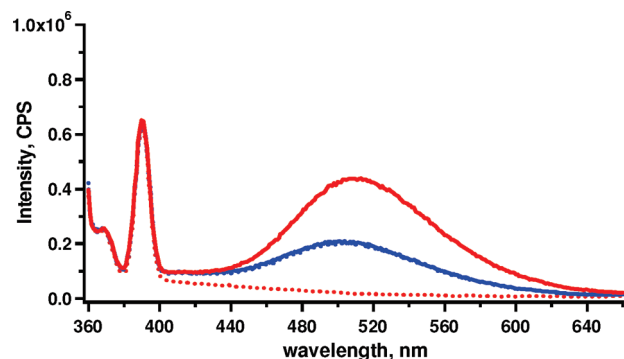


Figure 3. Emission spectra of dansyl hydrazine reacted with carbonyls of as-received SWCNTs: control experiment without SWCNTs (red solid line), after reaction with 26.4 mg of SWCNTs (blue solid line), and after reaction with 23.9 mg of SWCNTs (blue dotted line); neat acetone (red dotted line). Excitation at 350 nm.

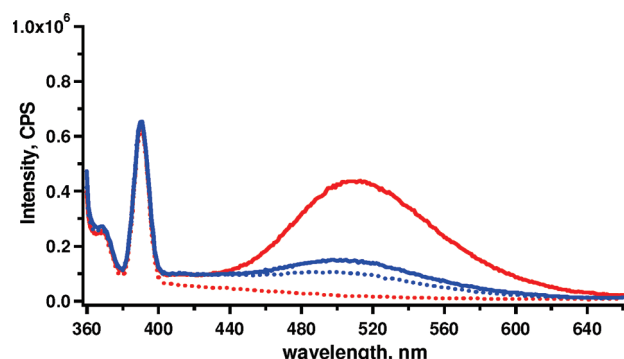


Figure 4. Emission spectra of dansyl hydrazine reacted with carbonyls of air/HCl-treated SWCNTs: control experiment without SWCNTs (red solid line), after reaction with 15.0 mg of SWCNTs (blue solid line), and after reaction with 19.4 mg of SWCNTs (blue dotted line); neat acetone (red dotted line). Excitation at 350 nm.

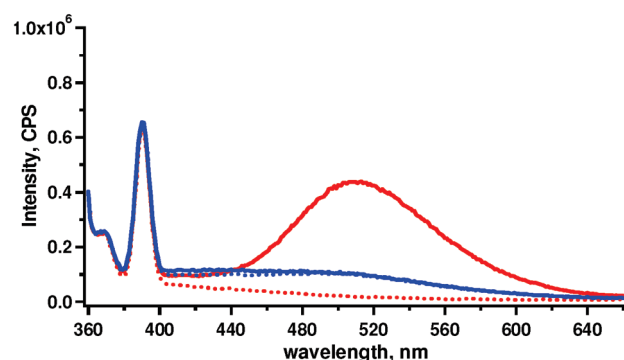


Figure 5. Emission spectra of dansyl hydrazine reacted with carbonyls of air/HCl-treated SWCNTs: control experiment without SWCNTs (red solid line), after reaction with 56.3 mg of SWCNTs (blue solid line), and after reaction with 48.2 mg of SWCNTs (blue dotted line); neat acetone (red dotted line). Excitation at 350 nm.

2.2.3. Fluorescence Labeling of Alcohol Groups. Alcohol groups were labeled with 5-DTAF following a procedure similar to the one described above (Figures S5–S8 in the Supporting Information).

3. Control Experiments

3.1. Physi/Chemisorption. To determine the contribution of physisorption of the dyes on samples to the observed depletion,

Table 2. FLOSS Results (Atomic Percent and Surface Coverage) of Various Oxygen-Containing Functional Groups on SWCNTs

SWCNT samples	functional groups					
	–COOH (carboxylic)		–COH (aldehyde, ketone)		–OH (alcohol)	
as received	< 10 ¹² groups/cm ²	< 0.03 atomic %	1.0 × 10 ¹³ groups/cm ²	0.3 atomic %	–5.8 × 10 ¹² groups/cm ²	< 0.6 atomic %
air/HCl treated	< 10 ¹² groups/cm ²		1.1 × 10 ¹³ groups/cm ²		2.1 × 10 ¹³ groups/cm ²	
	1.3 × 10 ¹³ groups/cm ²	0.4 atomic %	2.0 × 10 ¹³ groups/cm ²	0.5 atomic %	3.8 × 10 ¹³ groups/cm ²	< 1.1 atomic %
HNO ₃ treated	1.6 × 10 ¹³ groups/cm ²		1.8 × 10 ¹³ groups/cm ²		4.6 × 10 ¹³ groups/cm ²	
	7.3 × 10 ¹³ groups/cm ²	1.9 atomic %	1.2 × 10 ¹⁴ groups/cm ²	2.9 atomic %	–1.3 × 10 ¹⁴ groups/cm ²	< 3.5 atomic %
dye	7.2 × 10 ¹³ groups/cm ²	PB	1.0 × 10 ¹⁴ groups/cm ²	DH	1.3 × 10 ¹⁴ groups/cm ²	5-DTAF

Table 3. FLOSS Results Compared to Results of Other Techniques^a

samples (SWCNTs)	functional groups							
	–COOH (carboxylic)		–COH (aldehyde, ketone)		–OH (alcohol)		total O content ^b	
	FLOSS (%)	other techniques (%)	FLOSS (%)	other techniques (%)	FLOSS (%)	other techniques (%)	FLOSS (%)	other techniques (%)
as received	< 0.03	0 ⁴⁴ (XPS)	0.3	not found	0.3	not found	~0.5	0 ⁴⁷ (TGA, RS)
air/HCl treated	0.4	not found	0.5	not found	0.7	not found	~1	1 ⁴⁷ (TGA, RS)
HNO ₃ treated	1.9	2.2 ⁴⁶ (BT), 2.7 ⁴⁴ (XPS)	2.9	not found	1.4	not found	~5	~4 ⁴⁸ (VIS–NIR, RS, AFM), ~5 ⁴⁹ (COGE)

^a XPS, X-ray photoelectron spectroscopy; BT, Boehm titration; TGA, thermogravimetric analysis; RS, Raman spectroscopy; VIS–NIR, visible and NIR spectroscopy; AFM, atomic force microscopy; COGE, carbon oxides gas evolution measurements. ^b Total O content = content (–COOH) + content (–COH) + content (–OH).

a series of control experiments was run. Fresh (nonlabeled) SWCNT samples were mixed in solution under reaction conditions with deactivated (pre-reacted) dyes for the period of the FLOSS reaction time (or longer). Pre-reacted dyes have their reactive functional group protected, e.g. DH would be reacted with acetone so that it could not covalently bind to aldehyde/ketone groups on the sample. Control experiments did not show any significant depletion for DH and PB dyes, suggesting that the depletion after the FLOSS reactions was due to the covalent attachment only and the extensive washing procedure was sufficient to remove most physisorbed dyes (Figures S2 and S9–S11 in the Supporting Information). On the other hand, control experiments with 5-DTAF (Figures S12–S14 in the Supporting Information) did show depletion (~50% of the intensity of the peak from 5-DTAF in the solution before the contact with SWCNTs) after the contact of deactivated dye with the samples, suggesting that the concentration of alcohol groups determined by 5-DTAF is overestimated and thus should be considered as the upper limit of the actual surface concentration.

Control experiments (see the Supporting Information) indicate that the FLOSS measurements involving panacyl bromide and dansyl hydrazine apparently are not significantly affected by the presence of small quantities of SWCNTs in the supernatant. The measurements with 5-DTAF, however, are more significantly affected, i.e. there is an apparent depletion that could result in overestimates of the surface hydroxyl groups by a factor of 2 in some cases. This compounds the problems associated with 5-DTAF physisorption.

3.2. Time Control Experiments. To investigate if the duration of the reaction was sufficient for all accessible groups to be functionalized by the dyes, labeled samples were subjected to contact with fresh portions of the solution of each of the dyes. This second run did not show additional depletion for any of the dyes, suggesting that the reaction time was long enough for the functional groups to be labeled (Figures S15 and S16 in the Supporting Information).

4. Results and Discussion

4.1. Fluorescence Detection of Functional Groups. The FLOSS results are summarized in Table 2. One can see that the

data are reproducible to within 10% (data on labeling –OH groups were not taken into account). Several general tendencies are apparent: (i) As-received SWCNTs are the least functionalized of the samples. Nevertheless, they contain more than 0.5 atomic % (fraction of SWCNT carbon atoms that have oxygen-containing functionality⁴³) of oxygen functionality. Therefore, even as-produced tubes may not be considered pristine. The concentration of the carboxylic groups was below the FLOSS detection limit (0.03 atomic %). (ii) Air/HCl-treated samples contain 2 times more –COH and –OH groups and, at least, 10 times more –COOH groups compared to nonpurified, as-received SWCNTs. (iii) In comparison to as-received SWCNTs, nitric acid treatment increases –COOH, –COH, and –OH groups by a factor of 100, 10, and 5, correspondingly.

It is interesting to note, that carboxylic groups are not the most abundant functional groups on nitric-acid-treated or Air/HCl-treated samples. The concentration of aldehyde and ketone groups is at least 50% higher than that for carboxylic groups. This result explicitly supports previous tentative suggestions about the predominant presence of aldehyde and ketone groups on nitric-acid-treated SWCNTs.⁴⁴ From this perspective, it might be recommended to use the chemistry of carbonyls, in addition to that of carboxyls, for the subsequent derivatization of SWCNTs.

The extremely small SSA of the nitric-acid-treated SWCNTs (see Table 1) is consistent with the FLOSS results, indicating the presence of high concentrations of functionalities in the sample. Functional groups can increase bundling of the SWCNTs, reducing the accessible nitrogen adsorption as nonpurified SWCNTs.⁴⁵

FLOSS results were compared to previously reported concentrations of functional groups on SWCNTs, determined

(43) Atomic fractions (i.e., “atomic %”) were calculated by dividing concentrations of functional groups (for each functional group), expressed as the number of functional groups/cm² by 3.85 × 10¹⁵ C atoms/cm², the surface density of carbon atoms in SWCNTs. This can be derived from honeycomb with a side of 0.1415 nm (the smallest distance between closest carbon atoms in SWCNTs).

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by titration,⁴⁶ XPS,^{44,47} X-ray spectroscopy,⁴⁸ and evolution of CO₂ and CO gases⁴⁹ (Table 3).

As seen from Table 3, the FLOSS results are generally consistent with the preceding reports whenever data are available. The scarcity of quantitative literature information about different functionalities on SWCNTs can be related to the difficulty in identifying functional groups present in low concentrations using conventional techniques and the difficulty in determining absolute concentrations.

The fact that FLOSS gave similar results, within experimental error, as titration (1.9 and 2.2% of carboxylic groups on HNO₃-treated SWCNTs, according to FLOSS and titration, respectively⁴⁶) (Table 3) means that the size of the label molecules (e.g., DH, PB, and 5-DTAF used in FLOSS compared to NaHCO₃ and NaOH used in titration⁴⁶) does not limit the number of functional groups accessible for the labeling (unlike the results of labeling of functional groups on activated carbon fibers, reported elsewhere.³⁸ The better accessibility of the functional groups on SWCNTs compared to the activated fibers is most likely related to the bigger size of the micropores of SWCNTs.³⁸

It should be mentioned here that the concentrations of the functional groups, determined in this work, represent concentrations of the functional groups that are *accessible* to the fluorophores, i.e., mostly the functional groups on the exterior surfaces

of the bundles of SWCNTs. Despite the limitations that bundling may have on the results of any of the conventionally used techniques (XPS, Raman, and UV-vis-NIR)^{50–52} to characterize CNTs, information about functional groups that are *accessible* to the probe is important for a number of applications, e.g., the further modifications of SWCNTs and applications where SWCNT functional group chemistry is used.

5. Conclusions

FLOSS was used to identify and quantify functional groups on as-received, air/HCl-treated, and HNO₃-treated SWCNTs. The densities of carboxylic, carbonyl, and hydroxyl groups were determined by FLOSS. The concentration of hydroxyl groups, although, was overestimated because of the strong nonspecific adsorption of the corresponding dye to SWCNTs. The combination of high sensitivity of the fluorescence technique together with the selectivity of covalent chemistry allowed for the unambiguous detection of the presence of carboxylic, aldehyde/ketone, and hydroxyl groups on as-received, air/HCl-treated, and nitric-acid-treated SWCNTs. It was revealed that carbonyl groups are the most abundant groups on any type of SWCNTs, making chemistry of carbonyls another plausible route of further derivatization of SWCNTs in the material chemistry.

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Supporting Information Available: Fluorescence labeling of carboxylic, carbonyl, and alcohol groups, control experiments, and thermogravimetric analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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