

FLUORESCENCE LABELING OF SURFACE FUNCTIONALITIES ON CARBON MATERIALS: ACTIVATED CARBON FIBER AND SINGLE WALLED CARBON NANOTUBES (SWNTs)

Xue Feng^{1,2}, Wenguo Feng², Radisav Vidic², Eric Borguet¹

1 Chemistry Department and Surface Science Center, University of Pittsburgh

2 Department of Civil and Environmental Engineering, University of Pittsburgh

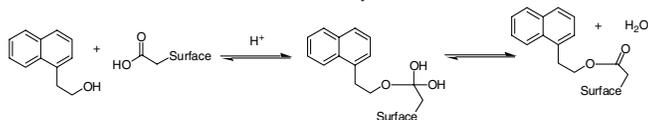
Introduction

Many uses of carbon materials, including activated carbon, activated carbon fibers and carbon nanotubes are influenced by the oxygen containing surface functional groups of these materials [1, 2]. Several methods have been applied to detect and quantify oxygen functional groups on carbon material surfaces. Infrared (IR) spectroscopy [3], X-ray photoelectron spectroscopy (XPS) [4], temperature programmed desorption (TPD) [5], elemental analysis [6] and Boehm titration [6] are the most frequently used methods. Although the Boehm titration is a valuable technique, it is limited to a few special functional groups, i.e. phenolic, lactonic and carboxylic [7]. TPD only provides the total number of groups without detailed information about their types. Quantitative analysis of XPS and IR data is not straightforward [7]. Fluorescence detection is a technique that has been broadly used in biological science. We have previously used fluorescence labeling to detect low concentrations of surface functionalities on a self assembled monolayer (SAM) [8]. The present experiments showed that covalent fluorescent labeling of surface species (FLOSS) can effectively detect and quantify oxygen containing surface functional groups located on the carbon material surface.

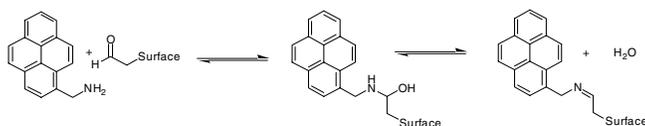
Experimental

The commercially available activated carbon fibers, ACF-25, used in this study were supplied by Kynol Inc. The solid as-received HiPco SWNTs were purchased from Carbon Nanotechnologies Incorporated. HiPco SWNTs were purified by flowing moist air (0.2L/min) through as-received nanotubes for four hours at 498K. The nanotubes were then soaked in 3N HCl solution for another 4 hours [9]. Three chromophores with appropriate functionalities were selected to covalently label CHO, COOH and OH groups, respectively, as shown in schemes 1 to 3, as described previously[8]. After the FLOSS reactions the samples were rinsed copiously in neat solvent. Detailed descriptions of IR, XPS and Boehm titration experiments are described elsewhere[10].

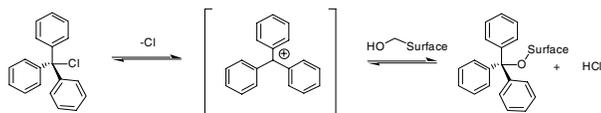
Scheme 1 Attachment of 1-naphthaleneethanol to COOH



Scheme 2 Attachment of 1-pyrenemethylamine to CHO



Scheme 3 Attachment of triphenylmethylchloride to OH



Results and Discussion

a) FLOSS of ACF

The presence of COOH and CHO groups on the fiber surface is indicated, in the data shown in Figures 1a and 1b, by the dominant monomer emission peak near 340nm and 398nm respectively. [8] One open question was whether these peaks came from chemisorption or from non-specific physisorption of chromophores on the fiber surface. An estimation of the amount and effect of residual, non-specific adsorption was made by running the FLOSS reaction with unsubstituted chromophores that could not covalently bind to the fiber surface. The spectra from these controls are also shown in Figure 1. The significantly lower fluorescence suggests that physisorption provides only a small contribution and that the FLOSS spectrum really corresponds to chemisorbed chromophores. The absence of a significant dimer emission peak at 410-420 nm on Figure 1a suggests little chromophore aggregation occurs on the surface. This is consistent with the FLOSS result that the concentration of COOH groups on ACF is very low.

The detection and quantification of OH was performed using triphenylmethyl chloride, which is known to react with hydroxyl groups [8]. The fluorescence spectra for fibers exposed to triphenylmethylchloride are shown in Figure 1c. The fibers exposed to non-functionalized chromophore (triphenylmethane) showed almost the same signal level indicating non-specific attachment (partially contributed by emission from activated carbon fiber itself) on the surface.

b) XPS of ACF

The curve fitting and deconvolution of C1s region XPS spectra of ACF25 are shown in Figure 2a and 2b. The dominant peak at 284.8 eV in Figure 2a was assigned to graphitic carbon in the fiber [11]. The 286.2 eV peak is assigned to the carbon in -C-O-C- and/or C-OH [11]. The binding energy of carbon in carbonyl groups is reported to be 287.5~288.1eV [11]. No evidence of carbonyl groups was detected in the C1s XPS. The O1s feature shown in Figure 2b is composed of only one peak at 533.4eV, which corresponds to oxygen in C-O groups (alcohol or ether groups) [12]. The oxygen double bond carbonyl peak was expected to be at 530.4-530.8 eV [11]. Existence of carbonyl groups, that could either be characteristic of aldehyde or carboxylic acid functionality, could not be detected by XPS in this case.

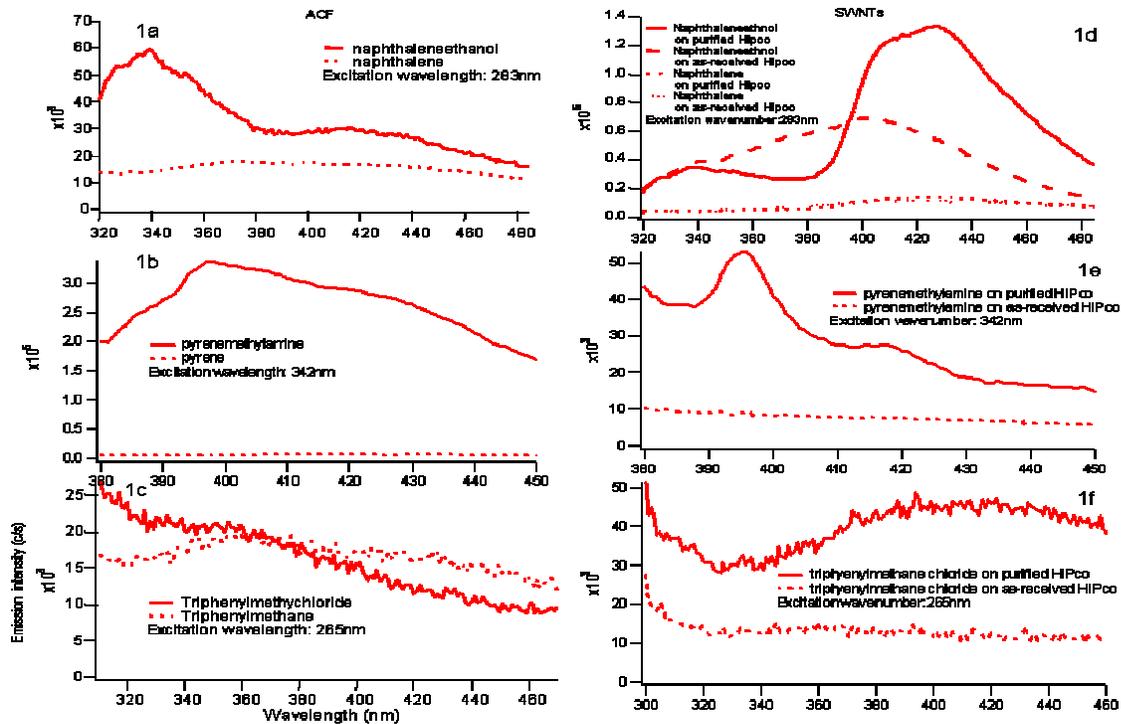


Figure1: Emission spectra of 1a: naphthaleneethanol (solid) and naphthalene (dashed), 1b: pyrenemethylamine (solid) and pyrene (dashed), 1c: triphenylmethylchloride (solid) and triphenylmethane (dashed) reacted activated carbon fiber and 1d: naphthaleneethanol and naphthalene 1e: pyrenemethylamine, 1f: triphenylmethylchloride reacted with both as-received HIPco and purified HIPco nanotubes.

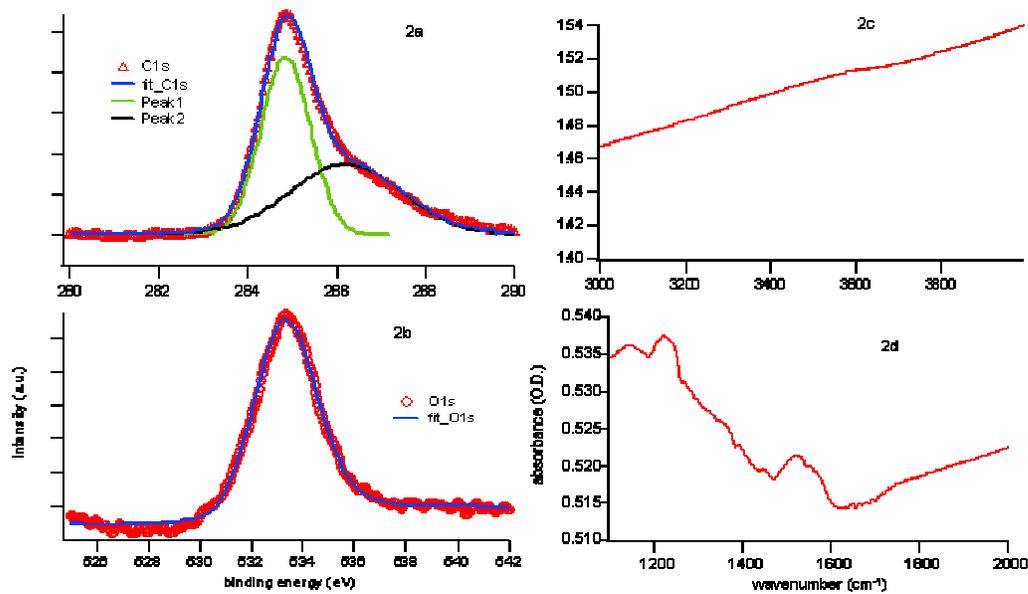


Figure2, a: XPS C1s, b: XPS O1s spectra of activated carbon fiber and IR spectra of activated carbon fiber at c: 3000-4000 cm^{-1} region and d: 1100-2000 cm^{-1} region.

c) IR of ACF

The infrared spectrum from 1100 to 1800 cm^{-1} shown in Figure 2d did not reveal any evidence of carbonyl groups (usually around 1700 cm^{-1}) on the fiber surface. The peak in the 1200-1250 cm^{-1} region is associated with alcohol (-OH) on phenol group or ether type structures (C-O-C). The peak in the 1500-1600 cm^{-1} region is assigned to aromatic C=C band and various substitution modes of the aromatic ring [13]. The -OH region spectrum in Figure 2c showed no evidence of OH groups.

d) FLOSS of SWNTs

The existence of COOH groups on both as-received and purified HiPco SWNTs is clearly shown in Figure 1d. For both nanotube samples, two peaks are visible at 340 and 420 nm, representing monomer and dimer, in the spectra. The dimer peak suggests high local concentrations of fluorescent molecules. It is well known that most of the functional groups on nanotubes surface exist on defects sites, which are unlikely to be homogeneously distributed on the surface. Furthermore, a defect site may actually be a cluster of sites, e.g. an opening in the SWNT side wall, which can be decorated with a number of functional groups. After the purification process, the monomer peak didn't change significantly. However, an enhancement of the dimer peak was observed, indicating an increase in local concentration of COOH groups. That means that new COOH groups are likely to form near the existing COOH groups, where the defects sites are located. It is commonly accepted that the defects are easier to attack than the perfect structure.

The detection of CHO groups by the fluorescence signal of pyrene is illustrated in Figure 1e. The concentration of CHO groups on as-received nanotubes is too small to be detected by fluorescence labeling. Also OH groups were barely observed on as-received nanotubes, as shown in Figure 1f. The inability to completely remove the non-specifically adsorbed chromophores prohibited the detection of the apparently low concentrations of CHO and OH groups on the surfaces evaluated in this study. It is clear from the increase in fluorescence observed for purified as compared to as received SWNT, Fig 1e and 1f, that CHO and OH groups are introduced during the purification.

These results provide insight into the purification process. HiPco nanotubes were made by the catalytic decomposition of CO at high pressure and temperature with iron as a catalyst. As-received HiPco SWNTs contains some COOH groups and negligible amounts of CHO and OH groups. After purification, 90% of iron was removed due to the acid extraction and more oxygen containing functional groups (e.g. COOH, CHO and OH) appear, presumably on the defects sites oxidized by the reaction with the moist air.

Conclusions

FLOSS is an effective method to detect and quantify low concentrations of functional groups on the outer surfaces of carbon materials, e.g., activated carbon fiber and nanotubes, especially when IR and XPS data are not conclusive for the existence of COOH and CHO groups. The presence of COOH and CHO groups was indicated by the fluorescence signal from covalently bonded chromophores. FLOSS showed the existence of COOH groups on as-received nanotube sample, while concentrations of

CHO and OH groups were below the detection limit. The purification process introduced more oxygen containing groups to the purified nanotubes. Moreover, FLOSS suggested that the functional groups are distributed heterogeneously on the nanotube surface. New functional groups grew on the defect sites as a result of the purification process.

FLOSS is a useful surface sensitive technique for determining a specific type of functional groups and useful for detailed analysis of the surface chemistry of carbon materials. FLOSS is not limited to COOH, CHO and OH groups studied here because other groups can be detected by selection of suitable chromophores and functional groups.

Acknowledgement

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