Surface Characterization of Carbon Materials by X-ray Photoelectron Spectroscopy

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Surface physicochemical properties are sensitive to preparation techniques, including physical and chemical treatments. Thus, surface treatments could induce significant changes in the surface modification of several materials. From its earliest days, X-ray photoelectron spectroscopy (XPS) was widely used as a powerful tool for understanding the nature of many different types of surfaces. Over the past 30 years many researchers have explored important aspects of the surfaces of treated materials. Also, XPS was an essential tool for understanding important aspects of natural and synthetic materials that cannot easily be investigated using other techniques. Today, carbon materials, such as carbon nanotubes, carbon nanofibers, graphene, activated carbons, and carbon blacks are being increasingly studied for many potential applications related to their superior chemical stability, mechanical strength, and thermal and electrical conductivity. In addition, the surface treatment of carbon materials could provide the various functionalities and affected their properties significantly through the functional groups induced onto the carbon materials. Therefore, the understanding of the surface features of carbon materials is very important. This chapter focuses on applications of XPS in several carbon material studies, surface treatment methods, and understanding and defining the surface characteristics of functionalized carbon materials using XPS.

Keywords: Surface properties, surface treatment, carbon materials

1. Introduction

Recently, the advent of green chemistry has significantly changed the science and technology of conventional materials. For example, silicon (Si) is known to be the key material of the 20th century and has been studied for uses in many electronic devices, such as semiconductors, mobile phones, and computers, tremendously enriching the quality of life. However, the scarcity and the high cost of Si limits its range of practical uses. Recently, carbon materials have been studied as possible replacements for conventional materials, such as silicon, metal, and ceramic. Carbon materials are an attractive alternative because of their abundance in the nature, large surface area, superior chemical stability, thermal and mechanical properties, and electric properties [1,2]. The word carbon was first proposed by Antoine L. De Lavoisier from the Latin carbo, charcoal in 1798 [3]. By the close of the 18th century, it was known that graphite and diamond occurs in different forms of the same element [4]. Elemental carbon in its chemical allotropes of graphite and diamond occurs in a great variety of species, such as carbon nanotubes, fullerene, whiskers, and carbon onions, and it has been developed as a structural and functional material for a large number of highly specialised applications, such as adsorbents, fillers, biomedical devices, and electronic devices, etc.. In addition, carbon plays a major role in the nano-sciences. For various applications and functionalizations of carbon materials, the surface characteristics of carbon materials are an important factor. The surface of carbon can be considered as a combination of basal planes of hydrophobic nature and polar sites at the edges of the carbon layers that form the graphite crystals. The edge-carbon atoms are frequently combined with different functional groups, such as oxygen, nitrogen, fluorine, carbonyl, and carboxyl groups, which act as primary sites for chemical reactions [5, 6]. For this reason, even the most hydrophobic or non-polar carbons can contain a certain amount of hydrophilic or polar sites, leading to the increase in the utilization of carbon materials.

Most surface properties, such as adsorption, wettability, hydrorepellence, and adhesion, of materials are strongly related to their microscopic properties, such as micro-porosity, roughness, and elemental and molecular composition. Knowledge of the surface dynamics of materials has recently allowed significant progress in many academic and scientific fields [7]. In recent years, many electron spectroscopy techniques have been developed as potential methods for surface analysis. Among these techniques, X-ray photoelectron spectroscopy (XPS), electron- and photon-induced vibrational spectroscopy, high-resolution electron-energy-loss spectroscopy (HREELS), and infrared spectroscopy have greatly improved our understanding of interfacial phenomena and surface characteristics of materials [8, 9]. Among these tools, XPS has rapidly developed in the last 10 years to become one of the most powerful techniques in obtaining accurate chemical information of both elemental and molecular composition of the surfaces. Also, this technique is sophisticated enough to distinguish different chemical states of the same element and to obtain their depth distribution at a range of thickness of about 5-10nm. In addition, an electron counter is capable of detecting emitted electrons allowing this technique to perform quantitative and qualitative analysis [10, 11]. Contrary to the Auger process, XPS is a one-electron process and the kinetic energy of the photoelectron depends on the energy of the excitation radiation. With the most commonly used excitation sources, the kinetic energy of
photoelectrons is approximately 0-1400 eV. XPS is less likely to produce surface damage and it can be preferable especially in non-conductive materials [12].

In this chapter, we will focus on the changes that various surface treatments create on the surface chemical structures of carbon materials. The surface treatments that will be discussed include wet and dry chemical treatments and the role of surface functional groups on carbon materials with regards to the wettability and electrical properties in the composite system. And, the XPS will be applied in order to determine the surface functional groups and surface dynamics of carbon materials.

2. Surface treatment of carbon materials

In recent years, carbon materials have become widely used as reinforcing materials in high-performance composite materials, adsorbents, biomedicine, electrochemistry, and energy storage materials. However, carbon surfaces are often difficult to adapt for various applications due to their low surface energy and chemical inertness. This statement is particularly applicable to low-surface-energy carbon materials which generally contain a very large proportion of C–C bonds, the strongest bonds found in organic compounds. Therefore, in order to improve the utilization of carbon materials, surface treatments are needed to promote the formation of functional groups, which increases surface energetics. The most widely used surface modification techniques involve wet treatments (such as chemical or electrochemical treatments and metallic coating) and dry treatments (such as photoirradiation, microwave, radiofrequency, and plasmas or fluorination using ionized gas). The ultimate goal of these treatments is to change the surface chemistry and the microstructure of the material and thus control a number of properties: biocompatibility, roughness, reactivity, conductivity, etc [13, 14].

2.1. Wet chemical treatment

2.1.1. Oxidation of carbon materials

Generally, the oxidation of carbon materials by wet chemical treatment is one of the basic methods that have been studied to obtain functionality of carbon materials by surface modification. The oxidative methods for the surface modification of non-polar carbon materials includes wet chemical methods (such as immersing in phosphoric acid or boiling in nitric acid) and oxidation on electrochemical oxidation using carbons as an anode in various electrolytes, and intercalation [15, 16].

![Figure 1. Schematic representation of the continuous electrochemical oxidation process for carbon fibers [17].](image)

The main aim of oxidation of a carbon surface is to obtain a more hydrophilic surface structure with a relatively large number of oxygen-containing surface groups. In general, the oxygen-containing groups behave as acids or bases, which possess ion-exchange properties. Various reagents have been used as oxidizers: concentrated nitric or sulfuric acid, sodium hypochlorite, permanganate, bichromate, and hydrogen peroxide. Among oxidation treatments, nitric acid oxidation is the most widely used method to increase the total acidity in a wet oxidation treatment. There are reports that the oxidation treatment of carbon materials in boiling nitric acid results in a significant increase in the acidic surface groups such as carbonyl and carboxyl groups.

2.1.2. Metal coating of carbon materials

In carbon-reinforced composite systems, the improvement in physical properties, the improvement of interfacial adhesion between carbon materials and matrix, is attributed to the presence of polar groups on the carbon surface,
which are able to interact with the active groups present in the matrix. Electroplating has been used to produce metal matrix composites reinforced with carbon materials. Carbon surfaces are metalized by electrolysis in molten salt solutions in the presence of a reductant. [18]. For example, the nickel process is based on a redox reaction in which the reducing agent is oxidized and Ni$^{2+}$ ions are reduced on the substrate surface. Once the first layer of nickel is deposited it acts as a catalyst for the process. As a result, a linear relationship between coating thickness and time usually occurs. The adhesion of electroplated metal/carbon composites has been shown to be excellent where the metal coating is grown from the carbon surface. In addition, the interaction between metal-plated carbon and the matrix is strong, mainly due to the higher metal surface energy that allows extensive wetting by the polymer. It indicates that the metal plating onto a carbon surface is a useful method for the increase of the utilization of carbon materials through introducing functionality.

2.2. Dry chemical treatment

The dry chemical treatments, such as a plasma treatment, an ozone treatment, oxidation in air, or fluorination, can remove impurities and introduce various functional groups, such as COOH, OH, and C=O, -F, on the surface of a carbon material. These techniques are simple and it is possible to control the quantity of new functional groups on carbon surfaces by the treatment conditions. Also, the dry chemical treatment does not cause the environment problems associated with wet chemical treatments. Therefore, many evaluations have been performed with carbon materials [19].

2.2.1. Plasma treatment

Plasma treatment is one of the most popular treatments for a variety of materials, including carbon materials. The interaction of a plasma treatment with carbon surfaces produces a highly active species. Depending on the nature of the gases used in the plasma zone, it may produce free radicals, ions, and meta stable species, which cause ablation, crosslinking, or oxidation reactions [20]. There are two principal advantages to using a mild plasma treatment method for materials: (1) the reaction takes place only on the material surface without significantly changing bulk properties, and (2) it is possible to utilize any atmosphere, such as oxidative, reductive, or inactive. This technique has become increasingly important owing to its high efficiency and operational simplicity. Surface energetics is also of importance because of the ability to exert careful control on the layer affected by the treatment, usually 0.02–50 µm in depth [21].

Figure 2. Schematic diagram of atmospheric-pressure plasma treatment apparatus [22].

2.2.2. Fluorination

Recently, several studies concerning the fluorination of carbon materials have been published. The outstanding reactivity of fluorine and fluorinating atmospheres has been demonstrated these last few decades by the synthesis of a wide variety of inorganic fluorine-based compounds and also by the drastic modification of their surface properties. One of the techniques to increase the surface polarity and functional groups of carbon materials is direct fluorination with oxygen in the presence of moderate temperature, which introduces hydrophilicity to surface carbon. For carbon materials, the oxygen-containing fluorination treatment offers several advantages over other treatments. One primary advantage is that the mechanical properties of carbon materials are not significantly degraded under optimum conditions. Other important advantages are related to the desire to development more environmental-friendly processes. The physical properties and chemical reactivity of organic molecules and carbon materials can be affected dramatically by fluorination. Today’s diverse commercial applications of organofluorine materials are clear evidence of the potential
beneficial effects of oxyfluorination as well as oxyfluorinated carbon materials. Actually, many of the characteristic effects of oxyfluorination could have been anticipated simply by comparing some of the fundamental atomic properties of fluorine with those of other elements. The modification of carbon materials is important for a variety of application fields, such as composite system or electronic devices. High reactive fluorination on the surface of carbon could provide carbon materials with advanced functionality, i.e. wettability or electrical properties.

Figure 3. Schematic diagram of fluorination reactor; (1) F$_2$ gas cylinder, (2) N$_2$ gas cylinder, (3) O$_2$ gas cylinder, (4) Buffer tank, (5) HF absorber (NaF pellet), (6) reactor, (7) pressure gauge, (8) F$_2$ absorber (Al$_2$O$_3$), (9) glass cock, (10) liquid nitrogen, (11) rotary vacuum pump [23].

3. X-ray photospectroscopy analyses of carbon materials

3.1 Oxidation of carbon fibers

Due to the improvement of their electrical conductivity and mechanical stiffness, the application of carbon fiber/polymer composites has greatly increased during the past decade, especially in the automobile and aerospace industries. To a large extent, the performance of such composites is dependent on the properties of the fibers developed during the manufacturing process and the surrounding matrix, but the interface between the two also plays a role. It is well known that the surface or interface properties of carbon fibers play an important part in real composite materials involving an organic matrix, since load stress transfers from one matrix to the other via the fiber [24]. For example, the interlaminar shear strength (ILSS) of composites is improved when the fibers are given treatments that increase surface functional group and roughness. There are numerous published surface modification methods in the literature that have been shown to change this interaction.

Among the various surface treatment methods, electrochemical oxidation treatments in basic electrolytes such as amines, diammonium hydrogen phosphate, and sodium hydroxide have been studied for their potential to increase oxidized functional groups on carbon fibers without the change of the surface area. In this study, the electrolyte used was 10 wt% phosphoric acid at a constant rate with different current densities (0 to 300 $\mu$A.m$^{-2}$).

XPS is a useful tool in determining the chemical compositions of carbon fiber surfaces. As shown in Table 1, the amount of surface oxygen groups increases as the current densities of the treatments increases up to 70$\mu$Am$^{-2}$, whereas nitrogen groups are not influenced by variations in current density. This results in increasing the surface acidity or hydroxyl and carboxyl groups on the fibers that have been anodized in phosphoric acid solution.
Therefore, it is expected that the increasing of oxygen functional groups on the fibers plays an important role in improving the degree of adhesion at interfaces between fibers and polymer matrix.

<table>
<thead>
<tr>
<th>Current density (µA·m⁻²)</th>
<th>C₁S Eb (eV) AT (%)</th>
<th>N₁S Eb (eV) AT (%)</th>
<th>O₁S Eb (eV) AT (%)</th>
<th>O₁S/C₁S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>284.7  74.3</td>
<td>400.7  1.4</td>
<td>532.5  24.3</td>
<td>0.327</td>
</tr>
<tr>
<td>30</td>
<td>284.7  73.5</td>
<td>400.9  1.4</td>
<td>533.9  25.1</td>
<td>0.342</td>
</tr>
<tr>
<td>70</td>
<td>284.6  68.8</td>
<td>400.3  0.7</td>
<td>532.3  30.6</td>
<td>0.445</td>
</tr>
<tr>
<td>130</td>
<td>284.6  72.1</td>
<td>400.8  1.4</td>
<td>532.6  26.5</td>
<td>0.368</td>
</tr>
<tr>
<td>300</td>
<td>284.7  69.7</td>
<td>401.0  1.5</td>
<td>532.8  28.9</td>
<td>0.414</td>
</tr>
</tbody>
</table>

It is generally accepted that moderate surface treatments do not lead to essential morphological surface changes. Figure 4 shows the SEM photographs of carbon fibers with and without anodic surface treatments. The axial striations from the extrusion process can again be seen in the untreated fiber image. As one compares the untreated and the treated fibers, it can be seen that acidic anodic oxidation does lead to a change in surface morphology at the microscopic scale. It was observed that there is a tendency for “surface smoothing” or “crystallite stacking diminishing” on fibers to be largely dominant as the current density is increased. This seems to be a consequence of the surface destruction of the fibers, preferentially prismatic planes. This is suggestive of the strong decomposing interaction between basic carbon and acidic electrolyte, even if the treatments are carried out at low current densities. At the higher densities, there exists a severe structural heterogeneity, such as “micro-etching spots”, aligned along the fiber axis. This may lead to enhancing the lack of overall distance for physical interaction between fibers and matrix, resulting in lowering the composite mechanical properties [17].

Figure 4. SEM photographs of the carbon fibers studied: (a) untreated; (b) 30 (µA·m⁻²); (c) 70 (µA·m⁻²); (d) 300 (µA·m⁻²).

3.2. Metal coating of carbon fibers

The physical and chemical properties of carbon fibers are usually modified to achieve adequate adhesion between the reinforcement and the matrix materials. To enlarge the surface polarity of non-polar carbon fibers, electroplating is a useful method because of the high surface energy of metal. In this study, the electrolytic plating of metallic nickel on a
The carbon fiber surface has been carried out in order to improve the interfacial adhesion and the mechanical properties in carbon fiber/phenolic matrix composite systems. Figure 5 shows the SEM photographs of non-treated (A) and nickel-plated (B–E) carbon fibers as a function of current density for the surfaces. As the electrodeposition current density was increased, the nickel coating thickness increased significantly. The metal coating appeared to cover the entire surface of the fiber (at >10~<30 Am⁻²). Also, above 30 Am⁻² current density, the nickel coating formed rod-like microstructures. The amounts of nickel on the fibers were determined by AAS, which showed the range of 0 ~ 12.3 mg/g with increasing current density. These SEM micrographs of the coated carbon fibers, as shown in Figure 5, suggest that nickel first deposits on the fiber surface at energetically favored sites, such as kinks, edges, corners, and other structural irregularities, and then cover the entire surface of the fiber.

**Figure. 5.** SEM micrographs of the nontreated and nickel-plated carbon fibers (×5000, original magnification). (A) 0, (B) 5, (C) 10, (D) 30, and (E) 60 A m⁻².

XPS spectra of non-treated and nickel-coated carbon fibers are shown in Figure 6. As expected, the non-treated carbon fibers (Figure 6a) show a C₁s peak and a substantial O₁s peak at 284.6 and 532.8 eV, respectively. The O₁s peak is probably due to intrinsic surface carbonyl or carboxyl groups. Otherwise, for the nickel-plated carbon fibers (Figures 6b–e), carbon, oxygen, and nickel (BE=857.6 eV) peaks are observable in XPS. The O₁s peak of nickel-plated carbon fibers (Figures 6b–e) is probably due to NiO, C=O, –OH, and O–C–O groups.

**Figure 7A** shows expanded scale O₁s XPS spectra for carbon fibers coated with nickel at 10 Am² current density. The O₁s spectra reveals the presence of three peaks corresponding to NiO groups (peak 1, BE=529.6 eV), C=O, or –OH groups (peak 2, BE=531.6 eV), and O–C–O groups (peak 3, BE=532.6 eV) groups. The Ni₂p peak is shown on an expanded scale in Figure 7B for nickel-coated carbon fibers. In the case of the nickel-coated carbon fibers in Figure 7B, several subpeaks are seen in addition to the main peak (BE=858.5 eV). These subpeaks which are separated computationally in Figure 7B indicate that Ni metal (Peak 1, BE=852.7 eV, and Peak 4, BE=858.5 eV), NiO (Peak 2, BE=854.6 eV), and Ni(OH)₂ (Peak 3, BE=856.4 eV) are present as a result of electrolytic nickel plating. However, these peaks are never seen for the non-treated carbon fibers. For the non-treated and nickel-plated carbon fibers, the O₁s/C₁s composition ratios of nickel-coated carbon fibers are increased compared to non-treated due to the deposition of more active forms, such as, NiO, Ni(OH)₂, and Ni metal on the inactive carbon. However, nitrogen of carbon fiber surfaces has no significant changes when the concentration and distribution are varied.
From the XPS experimental results, it was found that the surface composition of carbon fibers changed substantially as a result of nickel plating. The carbon content of nickel-plated fibers decreased when the fibers are plated with metallic nickel, whereas the oxygen and nickel contents of coated fibers are higher than for non-treated fibers. The active groups on the carbon fiber surfaces after nickel plating may help to change the polarity and the functionality of fiber surfaces.

3.3. Fluorination of carbon blacks

As mentioned above, surface modification techniques are widely used because they have many advantages, such as they are inexpensive, they require only simple equipment, and they can be completed quickly. Among the many surface modification techniques, the physical properties and chemical reactivities of organic molecules or carbon materials are two that can be dramatically affected by fluorination. The high ionization potential of fluorine and its relatively low polarizability result in weak intermolecular interactions, low surface energies, and low refractive indexes for perfluorocarbon.

Fluorinated carbon blacks (CBs) have recently been fabricated as a new class of reinforcing or conducting fillers. The reaction of CB with elemental fluorine via proprietary processes can adjust both surface energy and electrical conductivity of CB due to the creation of a layer of strong carbon-fluorine (C-F) bonds at the surfaces. The main objectives of this work are to investigate the positive temperature coefficient (PTC) and negative temperature coefficient (NTC) phenomena of fluorinated CB-filled high-density polyethylene (HDPE) composites at a fluorination pressure of 0.1-0.4 MPa. The changes in surface properties of fluorinated CB are investigated using X-ray photoelectron spectroscopy (XPS) and contact angle measurements.
It is well known that XPS has been used as a powerful analytical technique to evaluate compositions of the CB. XPS analysis was, therefore, performed in order to obtain information about the surface composites (up to a sample depth of about 10 nm). Figure 8 shows the broad scan XPS spectra of fluorinated CB (which is C\textsubscript{19}S and F\textsubscript{19}S) and XPS analysis curves of fluorinated CB measured at different fluorination pressures. Noticeable changes were observed in the materials between before fluorination and after fluorination. Binding energy (E\textsubscript{b}) of the band assigned to graphitic carbon (C-C), undergoes a slight shift (0.01 – 0.1 eV) towards lower E\textsubscript{b} because of a lowering of the Fermi level (E\textsubscript{F}) and a subsequent decrease of the energy gap between the C\textsubscript{1s} core level and E\textsubscript{F}. In the C\textsubscript{19}S spectra, the peak intensity decreases with increasing fluorination pressure. Also, the component (C=O) (with E\textsubscript{b} = 286.83 ± 0.06 eV) is connected with non-fluorinated C in the position of C-F bonds. The slight shift from (C-C) arises from the weak excess of positive charge, which is located on these atoms because of the presence of neighboring F. Since the work of Mallouk and Bartlett, it has been known that the graphene layers are associated with a physical type E\textsubscript{b} (1 ≤ x ≤ 2) groups that present on the surface of the CB or at structural defects. Consequently, by increasing the amount of fluorination on the surface, the content of carbon decreases, whereas the relative amount of C-F increases with increasing fluorination pressure.

The wetting of a solid surface by a liquid and the concept of contact angle (θ) was first formalized by Young [25],

\[
y_S = y_{SL} = y_L \cos \theta
\]  \[1\]

where γ\textsubscript{L} is the surface energy of the liquid, γ\textsubscript{SL} is the interfacial energy of solid/liquid interface, and γ\textsubscript{S} is the surface energy of solid.

Fowkes has suggested that the surface free energy of substances consists of two parts, the London dispersive and specific (or polar) components,

\[
y = y^L + y^{SP}
\]  \[2\]

where the superscript L refers to the contribution due to London dispersive forces which are common to all substances, and superscript SP relates to the specific polar contribution.

In the context of surface energetic studies, Owens and Wendt [26] derived the following equation for the interfacial energy between liquid and solid assuming a geometric mean combination of the London dispersive and specific components:

\[
y_{SL} = y_S + y_L - 2(\gamma^L \cdot \gamma_S^{1/2}) - 2(\gamma^L \cdot y_S^{SP})^{1/2}
\]  \[3\]

Combining Eqs. [1] and [3] yields a linear equation,

\[
y_L (1 + \cos \theta) = 2(\gamma^L \cdot \gamma_S^{1/2}) + 2(\gamma^L \cdot y_S^{SP})^{1/2}
\]  \[4\]

where γ\textsubscript{L}, γ\textsubscript{S}, γ\textsubscript{SP}, and γ\textsubscript{L} are known for the testing liquids [27] and γ\textsubscript{S}, γ\textsubscript{L}, and γ\textsubscript{SP} can be calculated by the contact angle measurements.

Based on “harmonic” mean and force addition, Wu [28, 29] proposed the following equations:

\[
y_{SL} = y_S + y_L - \{4 y_L (\gamma^L - y_S^{1/2}) - 4 y_S (y_L^{SP} + \gamma_L^{SP})\}
\]  \[5\]

The equation can be written as follows with the aid of Eq.:

\[
y_L (1 + \cos \theta) = \{4 y_L (\gamma^L - y_S^{1/2}) - 4 y_S (y_L^{SP} + \gamma_L^{SP})\}
\]  \[6\]

Wu claimed that this method applied accurately between polymers and between a polymer and an ordinary liquid.
Figure 9 shows surface free energy of fluorinated CB as a function of fluorination pressure. The surface free energy of fluorinated CB decreases with increasing fluorination pressure. The resulting higher fluorine content on the CB surfaces appears in relation to decreasing of the surface free energy. In other words, it seems that the polar part of the surface free energy increases at higher degrees of fluorination with increasing fluorination pressure. The nature of the C-F bonding is affected mainly by the fluorine content and the fluorination temperature. The decrease in the dispersive component (γSL) of the surface free energy may be caused by the destruction of the graphitic character of the CB surface due to fluorination. The γSL values are usually assumed to be fairly independent of the method of surface modification of carbon materials. It is assumed that the specific component (γSSP) reflects the essential surface characteristics of carbon or the partial graphitized carbon framework of the particles. In contrast, we observe a distinct dependence of the values of the fluorine content on the CB surfaces. When a certain amount of fluorine is present on the CB surfaces, the amorphous part of the surface is eliminated; therefore, the amount of graphite must decrease, in accordance with the results of surface analysis.

![Graph showing surface free energy of fluorinated CB as a function of fluorination pressure.](image)

**Figure 9.** Surface free energy of fluorinated CB as a function of fluorination pressure.

3.4. Air oxidation of carbon nanotubes

Carbon nanotubes (CNTs) have attracted increasing interest since Iijima first discovered them in 1991 [30]. Studies on the application of CNTs as electrode materials for electric double layer capacitors (EDLCs) have been performed, and the results show that CNTs are a promising candidate for the electrode materials of EDLCs. CNTs have potential advantages over activated carbons due to having a hollow structure, nanometer diameters, narrow size distribution, highly accessible surface area, low resistivity, and high stability. These properties make them potentially quite suitable for application in the fabrication of EDLCs. However, the specific capacitance of EDLCs based on CNTs is not very high at present, and the specific capacitance of CNT EDLCs using organic electrolyte is only about 20–30 F/g. It has been found that CNTs oxidized with CO$_2$ have about two times the capacitance of CNTs without oxidization. Therefore, in this study, we are to evaluate the specific capacitance of CNT-based polarizable electrodes in EDLCs after air-oxidation at various temperatures.

![Graph showing XPS wide scan spectra of the pristine and MWCNTs air-oxidized at various temperatures.](image)

**Figure 10.** XPS wide scan spectra of the pristine and MWCNTs air-oxidized at various temperatures.
XPS analysis was also applied to determine the chemical species introduced by air-oxidation. Figure 10 shows XPS spectra of the pristine and the air-oxidized MWCNTs. The peaks at 283.7 and 531.9 eV are attributed to C$_{1s}$ and O$_{1s}$, respectively. As expected, the oxygen peak intensity of the air-oxidized MWCNTs was increased according to the oxidation temperature. The content of elements on the surfaces of the MWCNTs was calculated by the area of each element.

The atomic ratio of oxygen and carbon in pristine MWCNTs is 0.033, while that of the MWCNTs air-oxidized at 600 °C is 0.157. In addition, it can be seen that the C–C peak both before and after the air-oxidation is the major surface carbon functional component. Due to the surface oxidation process in the MWCNTs, the percentage of C–C is lower and the percentage of C=O or C–O is higher than that of the pristine MWCNT sample, as shown in Figure 10. These functional groups could affect the electrochemical properties of the pristine MWNTs. Indeed, the MWNT electrodes air-oxidized at 600°C show the highest specific capacitance, 50 F/g, more than twice as high as that of the electrodes made of pristine MWCNTs (25 F/g), owing to the different structures and the changes of surface characteristics (increment of oxygen functional groups) of the MWCNTs [31].

3.5. Plasma treatment of graphite nanofibers

The surface modification of carbon materials is of great importance in a wide variety of fields. As mentioned previously, untreated carbon fiber surfaces are, as a result of their manufacture under high temperatures, non-polar in nature and have a low surface energy. Therefore, carbon fibers are unable to form strong adhesive bonds between their surfaces and the matrix. One promising procedure to enhance the surface energy and wettability is to generate polar groups on the fiber surfaces and modify the surface morphology by applying a plasma treatment. Thereby, oxygen functional groups (hydroxyl, carbonyl, carboxyl groups, etc.) can be formed on the surface, which simultaneously reacts with the polymer matrix and improves adhesion and wettability [32].

The aim of the present investigation is to enhance the overall adherence of vapor-grown graphite nanofibers to a surrounding polymer matrix by forming polar groups at their surfaces and by modifying the surface morphologies. The surface characteristics of graphite nanofibers (GNFs) that have been modified by an atmospheric plasma treatment are investigated using XPS.

![Figure 11. XPS wide-scan spectra of the oxygen-plasma-treated graphite nanofibers: (a) GNFs-0, (b) GNFs-1, (c) GNFs-2, (d) GNFs-3, and (e) GNFs-4.](image)

XPS analysis of surface-treated graphite nanofibers (GNFs) under different plasma conditions was performed to investigate the influence of gas pressure. The power was kept constant and the pressure was varied by 30 mbar by changing the flow rate. Figure 11 shows the typical wide-scan photoelectron spectra of oxygen-plasma-treated GNFs, where, for example, the spectrum of the fibers after 10 min of O$_2$-plasma treatment shows additional strong oxygen lines and a weak nitrogen line, resulting from the formation of oxygen functional groups such as hydroxyl, carbonyl, and carboxyl groups. Generally, it is known that the C$_{1s}$ lines are fitted by five or six component lines with different binding energies, corresponding to different functional groups. The atomic concentrations of these groups are given in Table 2 for the samples before and after plasma treatment.
Table 2. Atomic concentrations of plasma-treated graphite nanofibers (GNFs) obtained by XPS measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic concentration (%)</th>
<th>Binding energy (eV)</th>
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<tbody>
<tr>
<td></td>
<td>Grap. (284.5)</td>
<td>CHx (285.0)</td>
</tr>
<tr>
<td>GNFs-0</td>
<td>96</td>
<td>1.6</td>
</tr>
<tr>
<td>GNFs-1</td>
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<td>GNFs-3</td>
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<tr>
<td>GNFs-4</td>
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</tbody>
</table>

Regarding fibers that have undergone plasma-treatment for 10 min, the sample generates functional groups such as hydroxyl or ether groups (C–OR), carbonyl groups (C=O), and carboxyl groups (COOR). The total oxygen concentration amounts to 7.5 wt%. Further plasma treatment does not enlarge this amount significantly and the concentration of superficial hydrocarbon (CH\textsubscript{x}) is nearly fixed. Consequently, a plasma treatment time of 10 min is sufficient and longer times do not significantly change the total oxygen concentration. And the composition of the gases used does not seem to play a decisive role in the formation of functional groups on the GNFs and their proportions to each other. However, the power (W) seems to be one of the key factors that affect the surface composition of the GNFs, as shown in the oxygen content of GNFs-4. Depth profiling using an ion beam for sputter erosion of the surface is normally an appropriate method of determining the thickness and the composition of a layer. In the present case, however, this kind of depth profiling is mainly hampered by two facts: (1) A loss of chemical information: the ion beam, having energy level of 3 keV, changes or decomposes the functional groups, and this can be accompanied by a loss of oxygen, (2) Differentially strong sputter erosion: the ion beam hits the fibers under different angles due to the curvature of the fibers. Therefore, the estimate of the thickness determined from the decay of the measured depth profile only gives an idea of the true thickness and represents an upper limit for the thickness of the layer. Furthermore, the takeoff angle for the photoelectrons is 0° with respect to the surface normal of the pressed pellets, while the incident ion beam strikes this surface under an angle of 55°; i.e., some photoelectrons will always come from the unsputterable parts of the fibers.

Summary

The discussion in this chapter included the application of a variety of surface treatments (such as electrochemical oxidation treatment, metal plating, fluorination, and plasma treatment) on carbon surfaces and the XPS analysis of the surface characteristics of surface treated carbon materials. It was found that the surface polarity of non-polar carbon materials was significantly increased by different surface treatment methods and conditions, and these surface treatment methods led to an enhanced surface energy of carbon materials, indicating that surface treatment of the materials could provide an increase of the utilization, such as wettability and electrical properties of the carbon materials when compared to conventional carbon materials. In addition, XPS data showed excellent qualitative results on the surface characteristics and the chemical composition of the surface treated carbon materials. Consequently, the XPS method is a powerful tool capable of determining the surface features of carbon materials as well as other materials.

References