

XPS of carbon nanostructures obtained by underwater arc discharge of graphite electrodes

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Abstract

Carbon nanostructures, obtained by underwater arc discharge of graphite electrodes, were studied by X-Ray Photoelectron Spectroscopy (XPS). It was observed that the spectra of the samples taken from the floating part of the synthesis products, composed basically by Carbon nano-onions (CNO), present differences with those obtained from the precipitate, which contains a mixture of CNOs and multi-walled Carbon Nanotubes (MWCNT). These differences are related with the presence of atoms of carbon located in orbitals with different degree of hybridization (sp^2 - sp^3), which in turn is related to the diverse grade of curvature of the planes of carbon in the nanostructures present in the samples. The obtained results indicate that XPS can be an important element in the characterization of the products obtained by the above-mentioned method of synthesis.

Key words: X-ray photoelectron spectroscopy; carbon nanotubes; graphite; raman spectroscopy; synthesis; transmission electron microscopy.

XPS de nanoestructuras de carbono obtenidas por descarga de arco de electrodos de grafito sumergidos en agua

Resumen

Se utilizó la Espectroscopia Fotoelectrónica de Rayos X (XPS) para estudiar nanoestructuras de carbono obtenidas por descarga de arco de electrodos de grafito sumergidos en agua. Se observó que los espectros de las muestras tomadas de la fracción flotante de los productos de la síntesis, compuestas básicamente por nano-cebollas de carbono (CNO), presentan diferencias con los de las muestras obtenidas del precipitado, que contiene una mezcla de CNOs y nano-tubos de carbono de capas múltiples (MWCNT). Estas diferencias están asociadas con la presencia de átomos de carbono localizados en orbitales con diferente grado de hibridación (sp^2 - sp^3), lo que a su vez se relaciona con las diferentes curvaturas de los planos de carbono en las nanoestructuras presentes en la muestras. Los resultados obtenidos indican que XPS puede ser un elemento importante en la caracterización de los productos obtenidos por el citado método de síntesis.

Palabras clave: espectroscopia fotoelectrónica de rayos X; nanotubos de carbono; grafito; espectroscopia raman; síntesis; microscopía electrónica por transmisión.

Introduction

Carbon nanostructures, such as graphene, nano-tubes, nano-onions, nano-diamonds, and other, are being studied intensely by the scientific community, due to their current and potential applications in Electronics, Healthcare, Environmental Protection, Industry and many other fields. Their peculiar physical properties are also of special interest [1,2].

One of the most popular and simple method for obtaining carbon nanostructures, especially nano-onions and nano-tubes, is the synthesis by underwater arc discharge of graphite electrodes, described by Sano in

2002 [3]. Since then, several authors have been using this technique to synthesize carbon nano-onions [4].

Due to the fact that the morphology and some physical properties of the nanostructures depend of the synthesis method used, it is very important to study in detail the characteristics of the nanomaterials obtained by underwater arc discharge. For example, recent studies by Transmission Electron Microscopy (TEM) and Raman Spectroscopy shown that an important fraction of the nano-onions obtained by this technique has polyhedral structure [5,6], instead of the common spherical one obtained by other methods of synthesis [7, 8].

In order to obtain further information about the nanostructures obtained by the synthesis of arc discharge in water, in the present work several samples resulting of the synthesis have been studied using X-Ray Photoelectron Spectroscopy (XPS). This powerful technique has resulted very useful for the study of carbon nanostructures produced by other methods [9,10], but so far with a very little application to those obtained with this particular synthesis procedure.

This research emphasize on the difference in the spectra obtained from the floating part of the synthesis products, very rich in nano-onions, with respect to those from the precipitated, which contains an important fraction of MWCNT. The presence of oxygen in the products and its chemical form is also investigated.

Materials and methods

The nanostructures were obtained in a home-made workstation consisting of two graphite electrodes submerged in distilled water with resistivity of 1.2 MΩ. The arc discharge starts by contacting the 99.9% pure graphite anode (6 mm diameter) with a graphite cathode (10 mm tip diameter) of similar purity submerged to a depth of 5 cm. The discharge voltage and current were 16–17 V and 30 A, respectively. This set up is described in more detail in reference [6].

After the discharge, part of the products of the synthesis are floating at surface of water and the rest of the products precipitate. Samples were obtained from both fractions and studied separately.

The XPS spectra were obtained in a spectrometer Alpha 110 from Thermo Fisher Scientific. The equipment has a hemispherical electron analyzer with seven channels. The X-rays were obtained from a monochromatic source of Aluminum (Al Kα). A survey spectrum was taken from each sample, and, subsequently, high resolution spectra at the neighborhood of the bands of special interest (C 1s and O 1s) were obtained.

The high resolution spectra were deconvoluted with combinations of Gaussian and Lorentzian curve profiles, using the fitting tool kit of MATLAB. Different combinations were tested and those with better determination coefficient¹ (R^2) were chosen for the analysis.

Results and discussion

The XPS survey spectrum taken from one of the samples of the floating part is displayed in figure 1. The most prominent features of this spectrum are the very sharp peaks located at binding energies near 284 and 531 eV. According to the literature [11], these peaks correspond

to the levels 1s of carbon (C1s) and oxygen (O1s), respectively. The last one is an evidence of the presence of oxygen in the products of the synthesis, which is a consequence of the synthesis in water. The other important feature is the band present around 1000 eV, which corresponds to KLL Auger electrons from oxygen, and corroborates the presence of this element in the samples. This survey spectrum is very similar to those taken from the rest of the samples of the floating fraction as well as those taken from the precipitate. Then, in order to detect differences between the samples from the floating part and the precipitate it was necessary to analyze the high resolution spectra. One of such spectra for the line C1s of the samples obtained from the floating part is presented in figure 2. There is also displayed the result of the deconvolution of the spectrum.

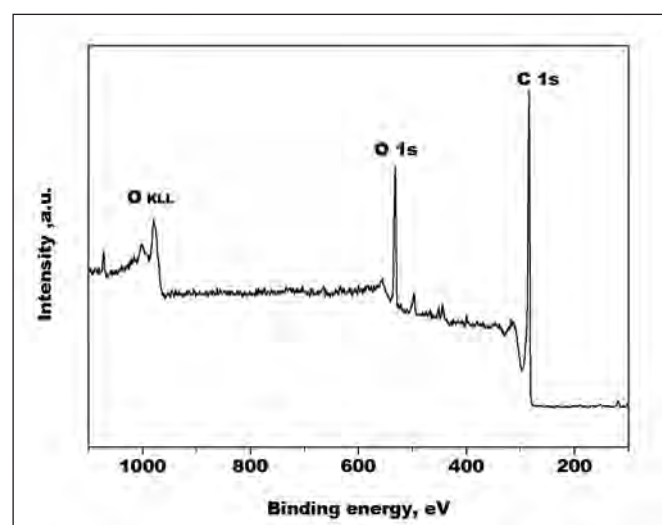


Figure 1. XPS survey spectrum of one of the samples taken from the floating part of the synthesis products.

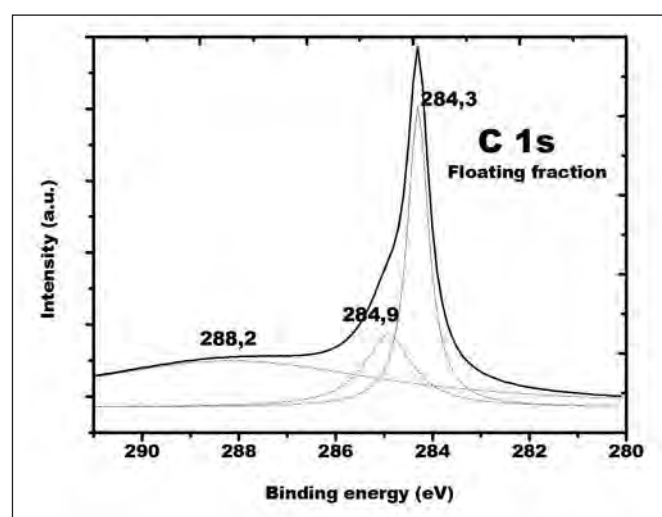


Figure 2. High resolution XPS spectrum of the C1s zone from the samples of the floating fraction.

In order to understand these spectra it is important to bear in mind that the floating fraction is composed mainly from nano-onions, mostly with polyhedral morphology [6]. These polyhedral nano-onions have plane regions very similar to graphite and regions where the carbon lattice is curved, in order to close the polyhedron.

¹ This coefficient is defined by:

$$R^2 = \frac{\sum_{i=1}^n (y^{fit} - \bar{y})^2}{\sum_{i=1}^n (y^{exp} - \bar{y})^2}$$

where y^{fit} and y^{exp} are the values of the independent variable (Binding energy in this work) obtained from the fitting and from the experimental data, respectively; and \bar{y} is the mean value of the experimental values

The main component of the spectrum is the peak located at 284,3 eV, which corresponds to the position of the core level 1s of the carbon with hybridization sp^2 . Consequently, this peak can be associated with the plane faces of carbon in the polyhedral nano-onions.

Although the core levels do not participate directly in the bonds of the atoms, it is well known that the kind of hybridization of the external orbital has influence in the position of the core levels, and then in the XPS spectra. Consequently, the other peak, shifted to the right in the binding energy axis, at 285 eV, can be identified with the curved zones of the nano-onions, where the orbitals are a mixture of sp^2 and sp^3 hybridizations [5]. Finally, there is a broad band with a center in 287,9 eV. Some compounds of carbon with oxygen can give peaks in this zone. The specific compound will be analyzed later on, using the high resolution spectra from O 1s.

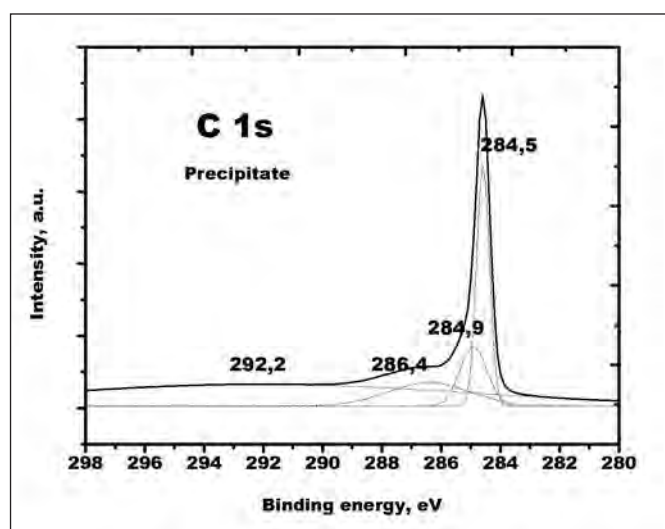


Figure 3. High resolution XPS spectrum of the C1s zone from the samples of the precipitate.

Figure 3 corresponds to the high resolution XPS spectra of the band C 1s of the samples taken from the precipitate. These samples contain an important quantity of MWCNT besides nano-onions. In this spectrum there are also two peaks similar to those found in the spectrum of the floating part, but in this case located at 284,4 and 284,6 eV respectively. These peaks can be assigned to the plane and curved parts of the nano-onions, respectively. Nevertheless there are differences between the two spectra. In the spectrum of the precipitate, the peak at 287,9 eV is missing and there are two new bands, one at 285,9 and other very broad at 291,3 eV. Due to the fact that these samples contain nanotubes, the first of these peak can be associated to the curved planes of the MWCNT, which present orbitals with mixed hybridization sp^2 - sp^3 . The position of the peak is different to that of the curved part of the nano-onions because, in general, the ratio sp^2/sp^3 is different in the nano-tubes and in the nano-onions. Different ratios sp^2/sp^3 can also be related with the presence of nano-onions of different diameters.

The band at 291,3 eV have been found in several carbonaceous materials [9] and it is identified as a plas-

monic band. This kind of band is the result of the interaction of the photoelectrons emitted from the core levels with the near-free electrons in the valance band. The lack of this band in the spectra of the samples from the floating part is not clear and will be the object of further researches.

In order to obtain more information about the presence of oxygen in the products of the synthesis, high resolution spectra were measured in the neighborhood of the O 1s peak. The spectrum corresponding to one sample taken from the floating part is shown in figure 4. After the deconvolution, two peaks can be clearly identified: one at 532,2 eV and other at 534,4 eV. The comparison of these values with those reported in the literature [11] allows to associate the first peak with the carbonyl group, $C=O$, and the second with the group $C-OH$. These two groups are the main components of the graphene oxide [12]. In the spectra of C 1s, the peak of the carbonyl group is located at 288 eV, then the third peak in the spectrum of the figure 2 can be associated to this group.

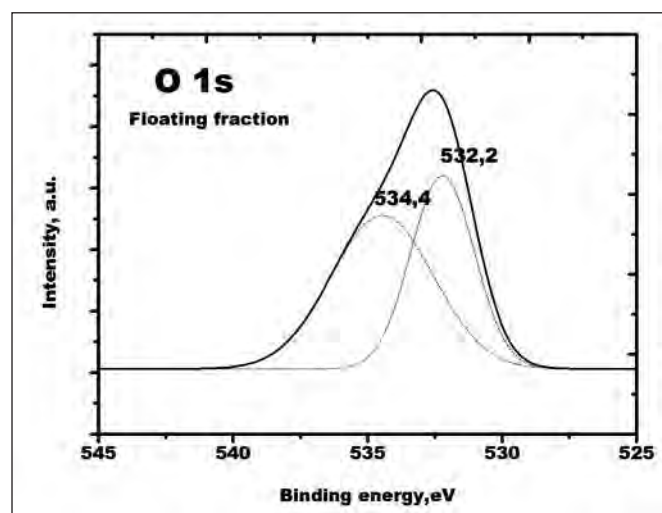


Figure 4. High resolution XPS spectrum of the O1s zone from one sample of the floating fraction.

The corresponding peak of $C-OH$ can be found near 286,5 eV, then we can suppose that it overlaps with the broad peak of carbonyl group in the high resolution spectra of C1s in these samples. The spectra of O1s from the rest of the samples are similar to the one shown in figure 4, but the relation of intensities of the two peaks can be different. In most samples, the prevailing peak is the corresponding to carbonyl group. In some of them the peak from group is absent.

The formation of oxygen-containing groups indicates the presence of edges in graphitic layers of these samples. These edges can be found in carbon nanotubes with open ends, which could exist in the samples of the precipitate, but in low quantities. The most feasible explanation for the existence of these groups is the presence of incomplete graphitic layers in the nano-onions. The formation of defective nano-onions have been reported by other authors [3].

Conclusions

Carbon nanostructures synthesized by the method of underwater arc discharge of graphite electrodes are studied using X-Ray photoelectron spectroscopy (XPS). The high resolution spectra of C1s taken from the floating part are different from those of the precipitate. The main difference is related with the presence of peaks that correspond to C atoms in orbitals with mixed hybridization sp^2 and sp^3 , but with different ratio sp^2/sp^3 , due to the presence of nanotubes in the precipitate whose C planes have different curvature relative to the nano-onions. Different ratios sp^2/sp^3 can also be related with the presence of nano-onions of different diameters. On the other hand, the high resolution spectra of O1s show the presence of oxygen-containing groups in the samples that can be formed mainly in defective zones of the graphitic planes of the nano-onions.

The results of this work demonstrate that XPS can be a useful tool for the characterization of the products synthesized by arc discharge in water, in conjunction with the traditional methods like Transmission Electron Microscopy and Raman spectroscopy.

Acknowledgments

Authors are grateful to Dr. Celia Lizeth Gómez Muñoz for her valuable technical support in XPS measurements.

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Recibido: 13 de febrero de 2018

Aceptado: 29 de mayo de 2018