Control of the chemical composition and thickness of deposited coatings over carbon nanotubes using acrylic acid plasma

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Control de la composición química y espesor de los recubrimientos depositados sobre nanotubos de carbono empleando plasma de ácido acrílico.

Control de la composició química i del gruix dels recobriments dipositats sobre nanotubs de carboni emprant plasma d'àcid acrílic

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RESUMEN

En este estudio se demuestra que la superficie de los nanotubos de carbono pueden ser recubiertas con una película de tamaño nanometrico (nanorecubrimiento) con carácter químico controlado, mediante el tratamiento con plasma de ácido acrílico. El carácter químico del nanorecubrimiento polimérico puede ser hidrófilo o hidrófobo dependiendo del tipo de proceso que predomine durante el tratamiento de plasma: erosión o deposición, los cuales son producidos por las especies ionizadas presentes en el plasma. Así mismo, el proceso de deposición y erosión pueden ser controlados con la potencia a la cual se produce el tratamiento. Por ejemplo, el proceso de deposición es el predominante a 20 W de potencia, en donde se produce una cantidad significativa del nanorecubrimiento polimérico compuesto de grupos funcionales ácido carboxílico, los cuales aportan el comportamiento hidrófilo del nanorecubrimiento. Mientras que a 40 W predomina el proceso de erosión, en donde se deposita una menor cantidad del nanorecubrimiento polimérico con carácter hidrófobo, ya que no presenta los grupos funcionales ácido carboxílico en su estructura química. Sin embargo, se observó una competencia entre ambos procesos (deposición y erosión) produciendo nanorecubrimientos con diferentes caracteres químicos y espesores, que dependen principalmente del tiempo de tratamiento

Palabras clave: Nanotubos de carbono, funcionalización, hidrófilo, hidrófobo, nanorecubrimiento y plasma

SUMMARY

In this study, it is demonstrated that the surface of carbon nanotubes can be coated with a polymer nanometer size film (nanocoating) with tailored surface polar behavior when treated with acrylic acid plasma. The polar behavior of the polymer nanocoating can be hydrophilic or hydrophobic depending deposition and erosion processes caused by ionized species in the plasma. In turn, deposition and erosion can be controlled by plasma power. Deposition dominates at 20 W power, where a significant amount of polymer nanocoating is produced with carboxylic acid functional groups in the surface thus having an hydrophilic behavior. On the contrary, a smaller amount of polymer nanocoating with hydrophobic behavior (i.e. without any functional groups on its surface) suggests that erosion is the dominant process when 40 W power is used. Finally, a competition between deposition and erosion processes results in different polar behavior and amount of polymer nanocoating depending of the treatment time.

Keywords: Carbon nanotubes, functionalization, hydrophilic, hydrophobic, nanocoating and plasma.

RESUM

En aquest estudi es demostra que les superfícies dels nanotubs de carboni poden ser recobertes amb una pel·lícula de mida nanomètrica (nanorecobriment) amb caràcter químic controlat, mitjançant el tractament amb plasma d'àcid acrílic. El caràcter químic del nanorecobriment polimèric pot ser hidròfil o hidròfob depenent del tipus de procés que predomini durant el tractament de plasma: erosió o deposició, les quals son causades per les espècies ionitzades presents en el plasma. Tanmateix, el procés de deposició i erosió poden ser controlats amb la potència a la que es produeix el tractament. Per exemple, el procés de deposició és el predominant a 20 W de potència, on es produeix una quantitat significativa del nanorecobriment polimèric format per grups funcionals àcid carboxílic, els quals aporten el comportament hidròfil del nanorecobriment, mentre que a 40 W predomina el procés d'erosió, on es diposita una menor quantitat del nanorecobriment polimèric amb caràcter hidròfob, ja que no presenta els grups funcionals àcid carboxílic en la seva estructura química. No obstant això, es va observar una competència entre

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ambdós processos (deposició i erosió) produint nanorecobriments amb diferents caràcters químics i gruixos, que depenen principalment del temps de tractament.

Paraules clau: Nanotubs de carboni, funcionalització, hidròfil, hidròfob, nanorecobriment, plasma.

INTRODUCTION

Characteristics of carbon nanotubes (CNTs) such as high aspect ratio and surface area, as well as unique electrical, thermal, and mechanical properties, turn them into excellent candidates for applications in different fields of science and technology, including medicine, energy, environment, among others.[1-5]However, the application of CNTs is restricted by the presence of highly toxic impurities and also by their non-polar or hydrophobic character, particularly when added to polar systems.[6, 7] These negative aspects of the CNTs may be solved by coating or encapsulating them with a thin film, avoiding in this way the exposure of their impurities and changing their hydrophobic nature to a hydrophilic one allowing them to interact with polar molecules. Hydrophilic CNTs could be applied in electronic components, biomedical materials, water purification processes, among others.[8, 9] Different processes have been developed to functionalize the CNTs, being the coating deposition of polar polymers the preferred one. This type of functionalization can be either non-covalent or covalent, depending on the required surface characteristics. In the former, the coating may get detached easily, while in the latter the reaction forming covalent bonds may also damage the nanotubes; thus, in both cases the functionalization may be deficient. Conversely, the plasma functionalization using polar monomers (plasma polymerization) does not produce a significant damage to the CNTs and is of covalent type. Thus, this type of coating deposition may reduce the toxicity problems and also change the nature of the nanotubes from hydrophobic to hydrophilic. For these two reasons this process has been used in the modification of the surface of nanostructures, although few works on the control of the chemical composition of the surface of nanoparticles by plasma polymerization have been reported.[10-13] In this case, the plasma treatment conditions determine the ionization of the monomer as well as the rate of deposition of the generated ionic species over the substrate. In the present work, it is shown that depending on the treatment conditions of acrylic acid plasma it is possible to control the chemical composition of deposited thin films over CNTs, as well as the thickness (amount) of the deposited coating; thus, tuning the chemical nature (polar and non-polar) and the coating thickness of CNTs can be tailor made for specific needs.

MATERIAL AND METHODS

Materials

Pristine MWCNTs (purity >95%) from Nano-lab with an external diameter of 30 ± 15nm, a length from 1 to 5 mm and a surface area of 400 m^2g^{-1}. Reactive grade acrylic acid was obtained from Sigma Aldrich (purity >95%).

Methods

Plasma Process: Treatment of MWCNTs with plasma of acrylic acid: 0.05 g of MWCNTs were introduced in a Plasma glass reactor and put under vacuum.[14] Then, the acrylic acid flow was fixed at 0.15 cm^3min^{-1} while the pressure was maintained at 8 x 10^{-2} mbar. The plasma treatment conditions were: treatment time of 30, 60, and 90 minutes and plasma powers of 20, 40, and 100 W.

Characterization

Infrared spectra of treated MWCNTs were obtained in an infrared spectrophotometer from Thermo Nicolet® (model MAGNA 550). Measurements were performed at 100 scans with a 4 cm^{-1} resolution, using the KBr pills technique. The high-resolution micrographs were taken in a transmission electron microscopy (TEM) from Philips TITAN® (model JSM-74101F) at a voltage of 30.0 kV. Contact angle measurements were performed with a Ramé-Hart goniometer (model 100-00). The dispersion in water tests were carried out as follows: The MWCNTs were dispersed in water (10 mL) under vigorous magnetic stirring (30 rpm) during 15 minutes; next, the stirring was stopped allowing the solution to settle up for 3 hours; finally, a photograph of each solution was captured. The TGA analysis were performed with TA-Q500 equipment in temperature range 25 to 600 °C, nitrogen atmosphere with continuous flow of 50 mL min^{-1} and heating rate of 10 °C min^{-1}. Once 600 °C is reached, an oxygen flow was used.

RESULTS AND DISCUSSION

The acrylic acid plasma treated nanotubes were characterized by dispersion in water tests; contact angle measurements and Fourier transform infrared spectroscopy (Figure 1, 2 and 3). The dispersion in water tests demonstrated that the as received nanotubes behave differently compared to those nanotubes treated with acrylic acid plasma (Figure 1).

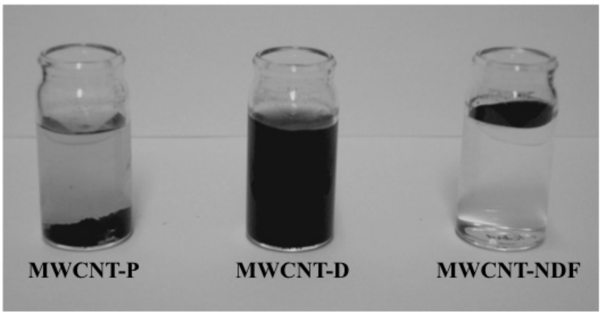


Figure 1. *Dispersion in water tests of pristine nanotubes (MWCNT-P) and plasma treated nanotubes: MWCNT-D and MWCNT-NDF.*

Pristine nanotubes (MWCNT-P) do not disperse in water (precipitate just after the stirring is stopped). In contrast, nanotubes treated at powers of 20 and 100 W disperse quite well in water (MWCNT-D). Unexpectedly, nanotubes treated at 40 W (MWCNT-NDF) do not disperse but float and concentrate in the upper side of the liquid. Both MWCNT-P and MWCNT-NDF showed high contact angles when a drop of water was deposited on them indicating a high surface tension typical of hydrophobic materials; the measured contact angle for these two nanotubes was 141 and 130°, respectively (Figure 2). On the contrary, MWCNT-D showed a hydrophilic behavior since they got wet with no water drop formation. The hydrophobic/hydrophi-

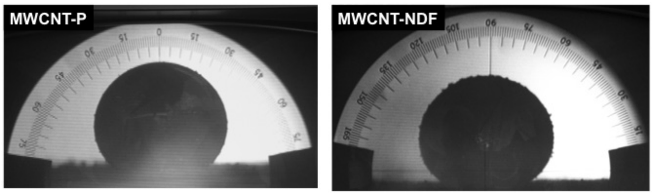


Figure 2. *Pictures showing the contact angle of water on MWCNT-P and MWCNT-NDF.*

lic behavior of CNTs was related to the absence/presence of polar groups as observed by fourier transform infrared spectroscopy (FTIR) (Figure 3).

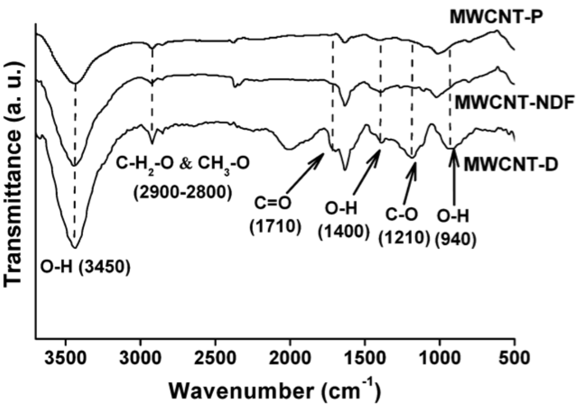


Figure 3. *FTIR spectra of MWCNT-P, MWCNT-NDF, and MWCNT-D.*

The lack of FTIR signals associated with polar groups (OH-, C=O- and CO-) suggests a hydrophobic nature for both MWCNT-P and MWCNT-NDF, while signals of functional groups of carboxylic acid indicate a hydrophilic nature for MWCNT-D. These signals are a carbonyl stretch (C=O) at 1710 cm^{-1}; a hydroxyl stretch (OH) at 3450, 1400 and 940 cm^{-1}, and a carbon-oxygen stretch (C-O) at 1210 cm^{-1}. Furthermore, an increase in the intensity of the symmetric and asymmetric stretches of the carbon-hydrogen group that belongs to the CH$_2$-O (2920 cm^{-1}) and CH$_3$-O (2834 cm^{-1}) groups was observed. These results indicate that the acrylic acid plasma treatment had a significant effect on the chemical composition of CNTs and depending on the plasma power the resulting nanotubes are hydrophobic or hydrophilic in nature.

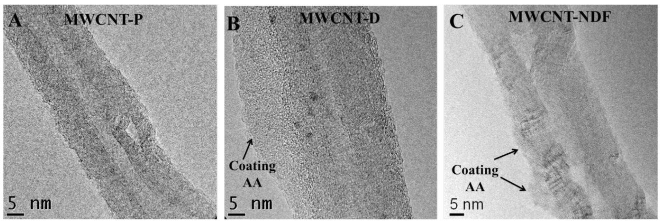


Figure 4. *A) Micrograph of uncoated MWCNT-P; B) Micrograph of MWCNT-D treated with plasma at 20 W for 30 min; C) Micrograph of MWCNT-NDF treated with plasma at 40 W for 30 min*

High-resolution transmission electron microscopy (HR-TEM) was used to determine the features of the coating (Figure 4). MWCNT-P showed a typical morphology of uncoated nanotubes (Figure 4 A). On the other hand, a coating was observed for both hydrophilic and hydrophobic nanotubes, with thicknesses ranging from 1.5 to 13.7 nm (Figures 4 B and 4 C). No differences in texture were observed by HR-TEM between hydrophilic and hydrophobic coatings.

The CNTs were treated by acrylic acid plasma at different times (30, 60 and 90 min) and resulting treated CNTs were studied by TGA. In Figure 5 A it is demonstrated that all nanotubes treated with acrylic acid plasma lose weight at percentages ranging from 8.5 to 59.3 wt%, in the range of temperatures between 150 to 550 °C, whereas for the MWCNT-P no weight loss was observed. In Figure 5 B a weight loss versus plasma treatment time plot is shown, those percentages were obtained at a temperature of 550 °C from TGA. This figure shows that the amount of the deposited coating for hydrophobic nanotubes (MWCNT-NDF, 40 W) increases only 1.4 wt% each 30 minutes while that for the hydrophilic nanotubes MWCNT-D, 20 W increases 19.5 wt% each 30 minutes. For the MWCNT-D (100 W) the weight loss behavior is quite irregular and it will be discussed later. The derivative of the weight loss (Figure 6) shows the decomposition process between 200 and 500°C is typical for the pyrolisis of the chain groups of poly (acrylic acid) (PAA). Chen et al. reported two main weight-loss regions for MWCNT grafted with PAA.[15] The carboxyl groups of PAA are likely to decompose in the first region (~150-270 °C), whereas the polymer backbone and hydroxyethyl groups decompose in the second region (~270-500 °C). According to the TGA themograms, the nanocoating observed by HR-TEM is plasma-polymerized

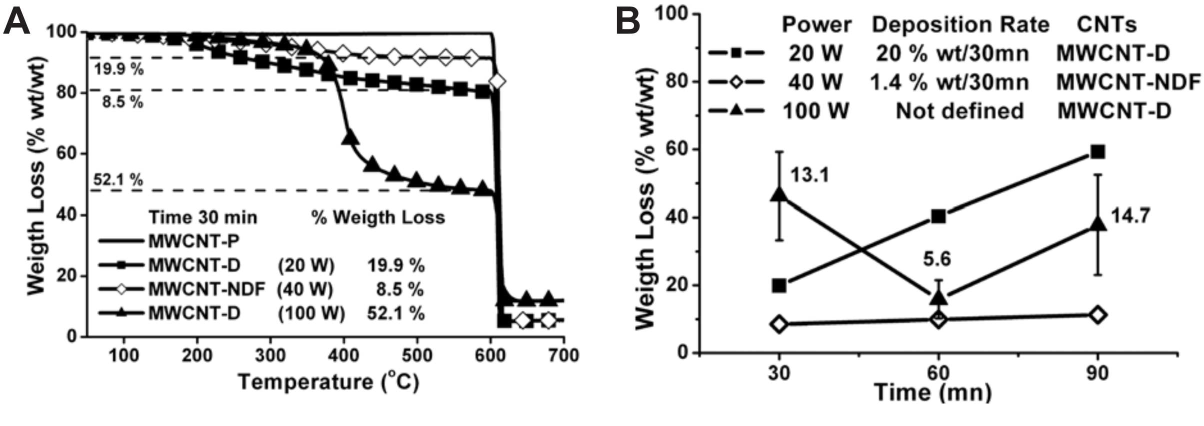


Figure 5. *A) TGA of MWCNTs treated with plasma; B), TGA data for MWCNTs treated with plasma.*

poly (acrylic acid) (PP-PAA) of either hydrophobic or hydrophilic character.

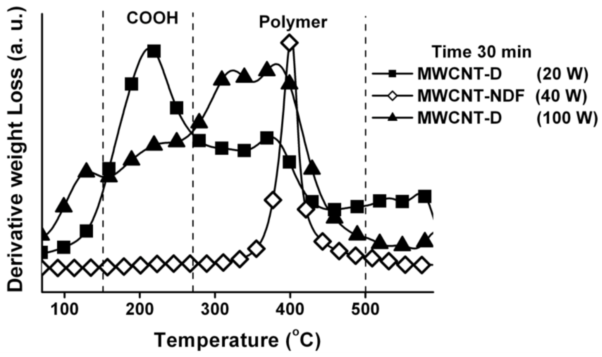
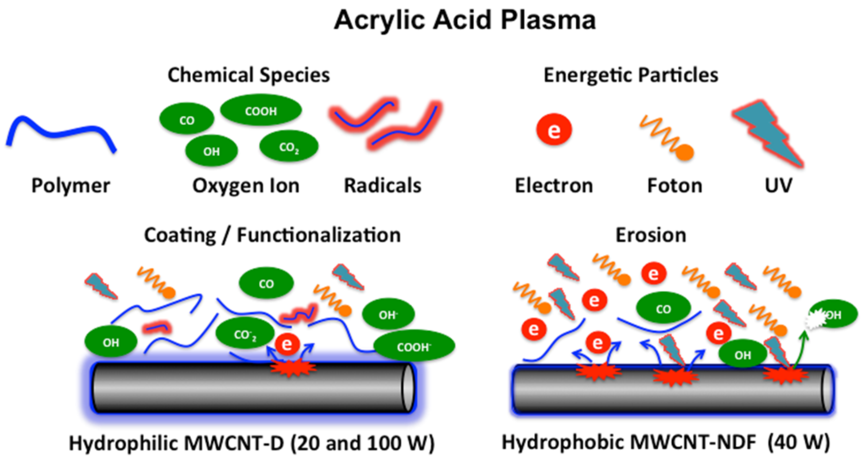


Figure 6. *DTGA of MWCNTs treated with plasma.*

All plasma treated CNTs showed a PP-PAA nanocoating, however, their chemical composition and thickness were different from one experiment to the other. The acrylic acid plasma coats the nanotubes with oxygen-containing radical ions or polymer chains. The control over the deposition of each one of these chemical species depends on two processes occurring during the plasma treatment: erosion arising from the collision of plasma species and coating with chemical species. The colliding species are electrons, which damage (atoms and/or chemical group abstraction) the surface of CNTs. On the contrary, the coating consists in the plasma deposition of chemical species (covalently linked) over the surface of the CNTs; by controlling this process, functionalized or coated nanotubes may be produced. Then, these two processes (erosion and deposition) can be controlled with plasma power as shown below.

Effect of plasma power

At a plasma power of 40 W, the erosion process prevails and the resulting coating lacks of polar oxygen groups (coating of hydrophobic nature). In contrast, at a power of 20W the deposition process is dominant producing a coating composed of a polymer layer with carboxylic acid polar groups (coating of hydrophilic nature). In addition, the highest deposition of material was observed at this power, increasing as the plasma treatment time was increased. The functionalization of the nanotubes is produced at a power of 20 W because in the plasma gas the number of chemical species (polymers and oxygen ions) may be larger than the number of generated electrons. Results of the treatment at a plasma power of 100 W suggest a lack of control because at a treatment time of 30 minutes the deposition process prevails, generating hydrophilic nanotubes, however, at 60 minutes erosion was the dominant process resulting in hydrophobic nanotubes, although showing a low degree of modification. At a treatment time of 90 minutes, the deposition process is once again dominant because the nanotubes are hydrophilic, but the coating is thinner than the one obtained in the first 30 minutes of treatment at this power. The competition between erosion and deposition at a power of 100 W may arise from the ionization of a larger number of monomer molecules, which produces a larger number of colliding chemical species (electrons) but at the same time accelerates the deposition of the chemical species (radicals). The variation in both the chemical composition and the thickness (amount) of the deposited coating seems to be contradictory in comparison to previous works on the treatment of MWCNTs with acrylic acid plasma.[11, 12]. It is worth mentioning that experiments were repeated three times and the error is significant (Figure 5B). Nevertheless, it should be considered that reactive species of acrylic acid plasma might have an important role on the erosion process. The erosion is probably related to the presence of oxygen in the acrylic acid plasma, since this gas may cause degradation, purification, and functionalization of the MWCNTs.[16-18] The presence of oxygen in the plasma treatment is originated from the carboxylic acid dissociation (ionization), which depends on the plasma power. Thus, plasma power induces either, the formation of new chemical groups or the removal of chemical groups formed and deposited during plasma treatment. Normally, the deposition of acrylic acid plasma species may result in hydrophilic nanotubes, however for high plasma powers the deposited coating was hydrophobic, indicating a simultaneous coating/erosion process where the erosion seems to eliminate most polar groups. In the scheme 1 a diagram of the coating, functionalization, and erosion processes of the acrylic acid plasma treatment of MWCNTs is presented. This behavior may also occur with other polar monomer plasma, although it would depend on the number of functional groups in the monomer, the plasma treatment conditions and the plasma reactor design. The control of the processing parameters (power and



Scheme 1. Scheme of the functionalization and erosion processes during plasma treatment of MWCNTs with acrylic acid.

treatment time) allows fine tuning of the chemical composition and thickness of plasma monomer coatings over MWCNTs, thus power and treatment time are critical in many technological applications of CNTs.

CONCLUSION

Surface of carbon nanotubes was successfully coated with a polymer nanocoating with either hydrophilic or hydrophobic character through plasma of acrylic acid. The polar character and thickness of the nanocoating were controlled with power of plasma treatment. Deposition of chemical species predominated at 20 W, yielding hydrophilic nanocoatings with thickness ranging from 5 to 40 nm. At 40 W erosion seems to dominate since hydrophobic nanocoatings with a low amount of organic material were obtained. A lack of control predominates at 100 W, thus it is not possible to predict the chemical composition and the amount of coating on the nanotubes surface.

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