





Ultrasound-assisted modification of MWCNTs with citric acid

Modificación asistida por ultrasonido de MWCNT con ácido cítrico

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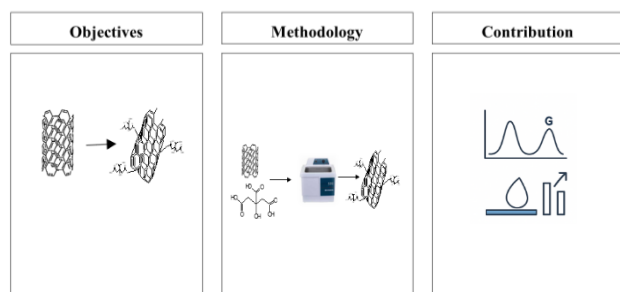


Abstract

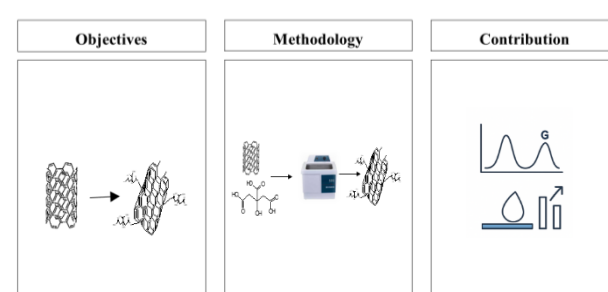
Multi-walls carbon nanotubes (MWCNTs) were modified by ultrasound-assisted with citric acid (MWCNTs-citric acid). This modification was assisted by ultrasonic irradiation by 4 hours and 60°C. MWCNTs-citric acid were characterization by spectroscopy FT-IR (ATR) show the characteristics bands of carboxylic acids, and RAMAN spectroscopy shows the D and G bands to relation to sp^2 bonds, showing order and disorder structural. MWCNTs-citric acid contact angle value indicates the hydrophilic nature of nanostructure. MWCNTs-citric acid turbidity assay using different solvents is increase to MWCNTs. The measure of percentage of acid groups is 16.5%. The different characterizations are a probe of excellent superficial modification of MWCNT using ultrasonic energy.

Resumen

Los nanotubos de carbon de pared multiple (NTCPM) fueron modificados empleando energía ultrasonica y ácido cítrico (NTCPM-ácido cítrico). Estas modificaciones se llevaron acabo por 4 horas a 60°C. Los NTCPM-ácido cítrico fueron caracterizados por FT-IR(ATR) mostrando bandas características del ácido carboxílico, espectroscopia RAMAN mostrando las bandas D y G relacionadas con los enlaces sp^2 , mostrando el orden y el desorden estructural. El valor de ángulo de contacto indicó la naturaleza hidrofóbica de las nanoestructuras. Los ensayos de turbidez indicaron que esta propiedad incrementa en los NTCPM-ácido cítrico. Las mediciones del % de grupos ácido fue del 16.5%. Las diferentes caracterizaciones son una prueba de la excelente modificación superficial de los NTCPM usando energía de ultrasonido.



NTCPM, Ultrasound, Acid citric



NTCPM, Ultrasonido, Ácido Cítrico

Area: Promotion of frontier research and basic science in all fields of knowledge

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Introduction

Carbon nanotubes (CNTs) are allotropes of carbon such as diamond, graphite and fullerenes; which are presents in 1991 by Sumio Iijima, when he was worked in electronic microscopic showed tubular molecules (Iijima, 1991). CNTs have a structure with carbon atoms in hexagons and pentagons and sp^2 hybridization. Nanotubes are classified as simple-walls (SWCNTs) or multi-walls carbon nanotubes (MWCNTs), formed by single or multiple layers of graphene rolled up into a seamless tube. Since discovery of these nanostructures, multiple researches are focused in different research areas because exceptionally high material properties such as electrical and thermal conductivity, strength, stiffness, and toughness (Maubert *et al.*, 2009).

MWCNTs showed several applications and technological solutions in different areas like automotive industry, optoelectronic, medicine, and water treatment. However, the major problem in several applications is the poor dispersion and solubility of nanomaterials of carbon. MWCNTs superficial modification might to help and change the poor dispersion. Several ways to performed superficial modification by covalent and not covalent bond of functional groups and molecules are reported (Sujata *et al.*, 2013)

These modifications are accompanied by “green” modification methods. In the global effort to reduce hazardous waste generated by industry, the green chemistry philosophy is integrating and re-designed processes. Green chemistry bases in 12 fundamental principles. These principles are a guide in minimizing the use of unsafe reagents and maximizing the efficiency of chemical processes. One of the most important principles is the sixth, Design for Energy Efficiency, which states that the energy requirements of chemical processes should be acknowledged for their environmental and economic impacts and should be minimized. The ultrasound is an alternative energy source that reduces reaction time, decrease reagents and solvents, and contributes to an efficient process (Li *et al.*, 2009).

In the search of novel strategies of reaction process, the ultrasound is an excellent method to MWCNTs dispersion and energy activation in the superficial modifications of MWCNTs.

The literature reports several approaches to MWCNTs modification using H_2SO_4/HNO_3 and ultrasound and high temperature. Additionally, other oxidizing agents, such as stearic acid, H_2SO_4 , and $KMnO_4$, have also been employed in ultrasound-assisted modifications of CNTs (Chen *et al.*, 2005).

Actually, it's proposed the use of novel methods less aggressive to add functional groups on MWCNTs. For example, the Sonochemistry in MWCNTs modifications with citric acid; an organic acid of natural source, which found it in several fruits such as lemon, orange, plum, etc. Citric acid is a carboxylic acid used in pharmaceutical, food and cosmetics products (Wang *et al.*, 2006).

Sonochemistry is used to development chemistry bonds in nanometric particles. Literature reports showed the use of ultrasound to MWCNT dispersion and activation of chemistry bonds to promote the superficial modification (Xu *et al.*, 2012). In this article, present the results about the superficial modification of MWCNT's with citric acid using ultrasound like alternative activation.

Methodology

Develop give the meaning of the variables in linear writing and important is the comparison of the used criteria.

Materials

MWCNTs industrial grade with 90% of purity, 20-50 nm of diameter, 5-15 μm of length and superficial area of 200 m^2/g were used. Citric acid of analytical grade (Faga Lab) is used.

Superficial modification of MWCNT's

A saturate solution of citric acid (20 g in 25 mL of distillate water) was prepared. Then adding MWCNTs (0.04 mg). Placed this mixture into an ultrasonic bath (Branson 5510, 20-50 kHz and 10-60 Kw/ m^2 of intensity) at 60 °C by 4 hours. Finish time of sonication, the mixture was filtered and washed with distilled water several times. Finally, dried the MWCNTs were dried into a stove at 40 °C for 24 hours.

Spectroscopic characterization

Infrared using a spectrophotometer Perkin-Elmer GX00 with ATR (Attenuated Total Reflectance) dispersive and diamond tip performed spectroscopic characterization. The samples were analyzed in powder form without prior treatment, using 32 scans at room temperature within the 4000–600 cm^{-1} range (Skoog, 2008).

Raman studies were development in a spectrophotometer Micro Raman (RENISHAW), Neon laser of 633 nm of length with 40 seconds of integrations and 6% of potency. Deposited the Samples on holder and stick with double-face tape and not previous preparation (Ferrari & Robertson, 2000).

Contact angle determination

Samples were compacted to form tablets. Then added a drop of 100 to surface of sample and the angle contact between the sample tablets and measured the water drop. For these experiments, a Rame-Hart contact angle goniometer (model 100-00) was used.

Turbidity determination

The turbidity was determined in the solvents water, ethyl acetate, methanol, and ethanol (polar) and hexane and petroleum ether (nonpolar). For this determination, 0.02 mg of the sample in 8 mL of solvent was used as well as a Hach model 2100P turbidimeter for determinations.

Determination of percentage of acid groups by titration

Acid groups determination was carried out to weight 0.00125 mg of sample and then was put into a Schlenk flask, added a mixture of 0.01 N of NaOH (5 mL) and NaCl (0.01 N). The flask was hermetic closed and stirred by 4 hours in nitrogen atmosphere. Then the sample is filtered and added 2 drops of phenolphthalein like indicator and titillated with solution of NaOH (0.01 N). Executed the experiments by triplicate (Boehm, 1994).

Results

FTIR (ATR)

The performed MWCNTs modification in mild conditions using citric acid under ultrasonic irradiation. First, to demonstrate the modification, FTIR (ATR) of sample of MWCNTs performed the characterization and MWCNTs modified with citric acid (MWCNTs-citric acid). Fig.1 shows FTIR (ATR) spectrum of MWCNTs unmodified. The expected spectrum of the nanostructure not exhibits important bands, which is due to only C-H bond present in the structure. In contrast, Fig. 2 shows the FTIR (ATR) of MWCNT-citric acid.

The spectrum of the MWCNTs-citric acid exhibits important IR bands. For example, the O-H stretching (2900 cm^{-1}), the C=O stretching (1700 cm^{-1}) and the O-C-H bending (1390 cm^{-1}). These IR bands are an important suggestion of the superficial modification of MWCNTs and the presence of carboxylic acid group of the citric acid. In conforming to literature reports, (Chen *et al.*, 2005) reported a study about MWCNTs modification with citric acid promoted by ultrasound.

Box 1

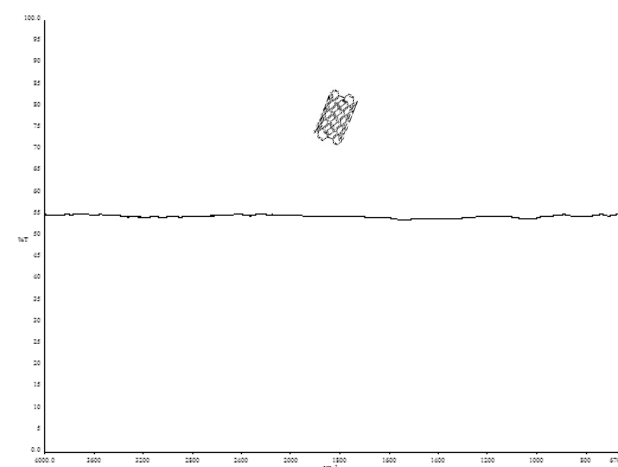
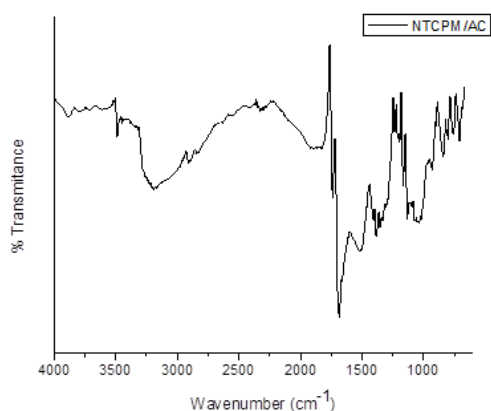


Figure 1

FT-IR (ATR) spectrum of MWCNTs

Source [in italic]

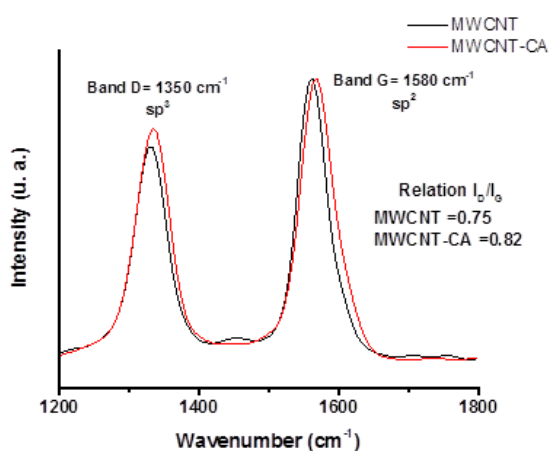
Box 2**Figure 2**

FT-IR (ATR) spectrum of MWCNTs-citric acid.

Source [in italic]

Raman characterization

In the Fig. 3 is present the Raman spectrum in which are observed the characteristic peaks in 1350 cm^{-1} (D band) and 1580 cm^{-1} (G band), to assigned to ordered and disordered structured of C-C layers respectively. Maiti and col. (2013) reported a study in which MWCNTs showed in 1331 cm^{-1} and 1604 cm^{-1} the D and G bands and assignation to C-C sp^2 hybridization (Maiti *et al.*, 2013).

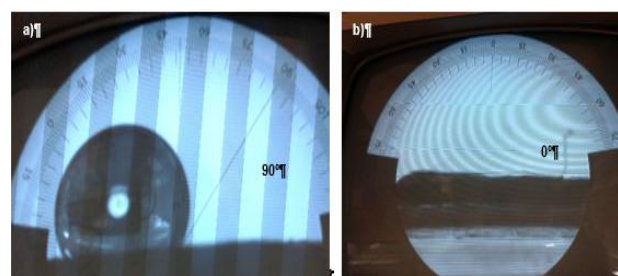
Box 3**Figure 3**

RAMAN spectra of MWCNTs and MWCNTs-citric acid

Source [in italic]

MWCNTs and MWCNTs-citric acid contact angle determination

Contact angle characterization determine the hydrophilic or hydrophobic nature sample. In this case, the contact angle of MWCNTs and MWCNTs-citric acid determination was performed using a tablet of MWCNTs and MWCNTs-citric acid. The results show that MWCNTs formed a 90°C contact angle between the sample table and the drop of water. This is indicative that not exist interaction between MWCNTs and the water because the character hydrophobic of the nanostructure. In the other hand, the contact angle of MWCNTs-citric acid was 0°C , because the sample tablet and the drop of water have an excellent interaction, Fig. 4. This behavior indicates that the modification of MWCNTs with citric acid was performed because the character on superficial nanostructure changes of hydrophobic to hydrophilic. The hydrophilic MWCNTs-citric acid is due to different interactions such as hydrogen bonds, Van der Waals and others.

Box 4**Figure 4**

Contact angle of a) MWCNTs and b) MWCNTs-citric acid. The photographs show an angle of 90°C and 0°C respectively.

Source [in italic]

(Ellis & Ingham, 2012) reported that MWCNTs are hydrophobic nature, but with the superficial modification with acetic acid is changed to hydrophilic. This previous report shows that the modification of MWCNTs is possible using a green organic acid. For instance, the results in the contact angle determination are according with the literature.

Turbidity determination

Several technological applications of carbon nanostructures have not been developed due to their poor dispersion in various solvents and matrices.

The surface modification of CNTs improved their dispersion, potentially addressing the issue of poor solubility. Turbidity determination is a physical analysis that shows if a nanomaterial is modified or unmodified to change this property. In the Fig. 5 are show the results in the turbidity assay, performed in different solvents; the MWCNTs-citric acid sample has a good dispersion because the light in the determination was not cross the MWCNTs-citric acid dispersion. The measure of turbidity in the solvents ethanol, pentanol and petroleum ether was not determinate because an excellent dispersion of the nanoparticles. In addition, MWCNTs-citric acid in ethyl acetate is different with the MWCNTs.

Box 5

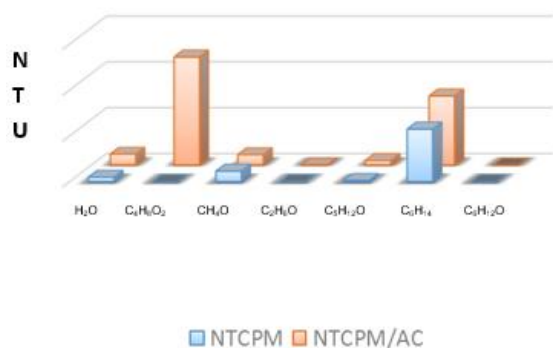


Figure 5

Turbidity determination in different solvents.

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Acid groups quantification by titration

The determination of acid groups in MWCNTs-citric acid treated by titration in an assay by triplicate. The amount of acid groups in percentage of MWCNTs-citric acid was 16.5%. In according to literature, Cabello and col. reported a percentage of acid groups to MWCNTs-citric acid of 18.57%, using a treatment of 8 hours in the ultrasound irradiation (Cabello *et al.*, 2014). In contrast, in the present work, MWCNT–citric acid composites were obtained through ultrasound-assisted treatment, requiring only 4 hours of irradiation.

MWCNTs covalent modification is possible due to the superficial defects in the nanostructure. It is important to mention that the percentage of acid groups should not be to high value because a total modification of the nanostructure may be to affect the MWCNTs properties.

Conclusions

In conclusion, citric acid superficial modification of MWCNTs performed by ultrasound assisted. FT-IR (ATR), Raman, contact angle determination, turbidity and measure of percentage of acid groups, characterized this modification. FT-IR (ATR) results show characteristic bands in MWCNTs-citric acid. Raman spectroscopy results show order and disorder in nanostructures. Turbidity results show that the dispersion of MWCNTs is poor in contrast with MWCNTs modified in different solvents such as ethanol, methanol, and petroleum ether. For polar solvents the electronegative atoms may be interact with the polar groups in MWCNTs-citric acid by hydrogen bond principally and the increase the dispersion. In the case of nonpolar solvents interacts with MWCNTs-citric acid by Van der Waals interactions. Contac angle in MWCNTs-citric acid is decrease in comparison with the MWCNTs. Finally, the percentage of acid groups is a measure of superficial modification of MWCNTs by covalent bond.

Declarations

Conflict of interest

The authors declare no interest conflict. They have no known competing financial interests or personal relationships that could have appeared to influence the article reported in this article.

Author contribution

Díaz-Silvestre, Sergio E: Contributed to investigation, writing –original draft and editing.

Ramírez-Mendoza, Leticia: Contributed to the project idea, research method and technique.

Vazquez-Aguilar Mario: Contributed to review amp; amp; editing.

Availability of data and materials

Further information regarding the data is available upon request. Please contact the corresponding author for inquiries.

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Article

Abbreviations

CNTs	Carbon nanotubes		
FT-IR	Fourier-transform	infrared	
MWCNTs	spectroscopy	Multi-walls	carbon nanotubes

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