CLICK CHEMISTRY OF MULTI-WALLED CARBON NANOTUBES-G-1,3-DIAZIDO-2-ISOPROPANOL WITH ALKYNE GROUPS

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Abstract. The click chemistry was employed on oxidized multiwall carbon nanotubes for their functionalization with 1,3-diazido-2-isopropanol (2N3OH). Phenylacetylene and propargylamine are used as alkyne groups, catalyzed with copper iodide (I). The chemical and structural characterization are described starting from the Raman and infrared spectroscopy as well as the realization of an elemental combustion analysis, transmission electron microscopy and nuclear magnetic resonance (NMR).

1. INTRODUCTION

The various allotropic forms of nanostructured carbon (i.e. nanotubes, fullerenes, graphene, etc.) constitute nowadays one of the most attractive elements for producing novel materials for a wide range of applications [1-5] due not only to their very attractive intrinsic properties [6-8], but also that they can be employed as a building block to fabricate novel materials due to hexagonal structure of this element that suggest strongest chemical bond in the most widely known systems in nature, where the nanotubes have different graphene sheets that are concentrically rolled [8-12], that by different chemical interactions, they can be present as nanocomposites (i.e. organic/organic, organic/inorganic) [13-17]. Accordingly, different works have been reported about of their properties, for example, the functionalization of carbon nanotubes, that since its discovery by Iijima [18], it has been studied a lot about them [19-21], due to influence of the diameter and chirality of the nanotubes as single-walled (SWNTs), double-walled (DWNTs) or multi-walled (MWNTs) [2,9-11,14,22] in the different properties of carbon nanotubes, such as mechanical, thermal...
and especially its surface area so vast, in addition to its importance in the purification and functionalization [10,13,14,22,23].

On the other hand, the functionalization is so vast, that different molecules play an important role in the chemistry of carbon nanotubes [24], where the azide anions (N₃⁻) are widely used as bridging groups in the reported compounds because of their effective exchange interactions with versatile coordination modes, which enables the construction of compounds with great diversity depending on the reaction environment [25]. Like hydrogen azide most other azides are also explosive substances that decompose with the release of nitrogen through the slightest input of external energy, for example, pressure, impact, or heat [26]. The nitrogen-rich azide compounds have a high heat of formation because they can release enormous amounts of energy, which is due to the average bond energies: N–N (160 kJ mol⁻¹), N=N (418 kJ mol⁻¹) and N≡N (954 kJ mol⁻¹) [25]. Industrial interest in organic azide compounds began with the use of azides for the synthesis of heterocycles such as triazoles and tetrazoles as well as with their use as blowing agents and as functional groups in pharmaceuticals [26].

To address the gap between a sophisticated function that is required for future advances in bio- and nanotechnology and the limited chemical control offered by many of the currently available synthetic materials’ processes, novel synthetic tools are needed. Click chemistry was developed to provide a simple method to join together organic molecules in high yields under mild conditions and in the presence of a diverse range of functional groups [27]. As a specific example of a click reaction, it’s suggested the copper-catalyzed Huisgen’s 1,3-dipolar cycloaddition of azides and terminal alkynes, which has now been used for a wide range of different applications [27–29]. The features of the click ligation reaction that are potentially useful in such applications are [27]: azides and alkynes can be attached to nucleic acids without greatly disturbing their biophysical properties, azides and unactivated alkynes are almost entirely unreactive towards the functional groups normally encountered in nature; they react only with each other, the triazole unit is extremely stable and is not toxic. The area of click chemistry is a highly creative area of research.

Among the more interesting examples is the application of the Cu-catalyzed azide–alkyne cycloaddition (CuAAC) for the click reaction [28,29], towards chemical functionalization of nanomaterials, such as the carbon nanotubes [30–34]. In this case, alkyn groups introduced onto the surface of the nanotubes offered a route towards highly specific post-modification [28]. On the other hand, in this investigation, the synthesis of 1,2,3-Triazoles are generally prepared by the cycloaddition of an alkyne with an azide, which can be promoted thermally or by metal catalysis. This cycloaddition reaction of an azide and an alkyne is a typical ‘Click’ reaction, that is, a highly efficient and reliable general reaction that can be used for linking moieties for various purposes, such as in combinatorial chemistry [35]. For this paper, the azide group is grafted to multi-walled oxidized carbon nanotubes (MWOHs), where the click is promoted in the functionalization of 1,3-diazido-2-isopropanol (2N3OH) with two different alkynes; phenylacetylene (CMWN3) and propargylamine (CMWN3H3), see Fig. 1.

2. EXPERIMENTAL

As-received multi-walled carbon nanotubes (MWNTs) were obtained from Sun Nanotech Co., which produced them by chemical vapor deposition, with a diameter from 10 to 30 nm and 1 to 10 µm long, with a purity >90% and of 90 to 350 m²/g [36]. The other reactive were purchased from Sigma-Aldrich Co. LLC., and used without further purification. Based on previous reports [37–42], the purification/oxidation of the MWNTs was achieved in liquid phase with a 3:1 mix of NH₄OH (95%) and H₂SO₄ (98%) at 85 °C for 3 h in a reflux process. The resulting material was vacuum-washed to a neutral pH with deionized water. On other hand, for the graft of the azide in the carbon nanotubes, different experiments based by other reports [43,44] were used, however, with the synthesis of 1,3-diazido-2-isopropanol (2N3OH) [45–47], the graft was accomplished.

2N3OH was obtained in 76% yield by 25.6 mmol of epichlorohydrin in 45 ml of 2:1 v/v of CH₂CN:H₂O were dissolved. Later 61.5 mmol of NaN₃ were added to a flask equipped with a reflux condenser and a magnetic stir bar to 65 °C by 24 h, subsequently, the solvent evaporated under vacuum. The mixture was extracted with dichloromethane, the organic phase dried over Na₂SO₄ and filtered, and the solvent evaporated under vacuum to give the crude product with 1.23 g cm⁻³ of density.

MOND. 2N3OH was reacted with MWOHs (3:1 w/w), where the esterification is carried out by the reaction mechanism that promotes the N-diciclohexilcarbodiimide (DCC) in 20 ml of tetrahydrofuran (THF). The mixed was added to a flask equipped with a reflux condenser and a magnetic stir bar under nitrogen to 65 °C for 18 h. Fi-

Fig. 1. A graphic description of the purification and oxidation of MWNTs and the synthesis of 1,3-Diazido-2-isopropanol (2N3OH), where the reaction sequence is the esterification between MWOHs and 2N3OH, where the N-diciclohexilcarbodiimide (DCC) as catalyst, the carboxyl (-COOH) of the MWOHs and hydroxyl of the 1,3-Diazido-2-isopropanol, form the ester. The consequent reaction is the azide of the carbon nanotubes (MOND) with the alkynes; phenylacetylene (CMWN3) and propargyl-amine (CMWN3H3).

Finally, the sample was washed with deionized water and dried under vacuum.

Click Chemistry CMWN3 and CMWN3H3. The reaction conditions for both samples are the same, only change the alkyne groups, phenylacetylene and propargylamine respectively. 2 ml of ethanol and 5 mg of CuI and 0.9 mmol of the alkyne group were mixed in a flask to homogenize, subsequently, the MOND sample and other 2 ml of ethanol were added, with stirring and without exposure to light for twenty four hours. The mixture was washed with deionized water for 24 hours and dried under vacuum for three hours. Finally it was stored in an amber bottle and refrigerated.

3. RESULTS AND DISCUSSION

The as-received multi-walled carbon nanotubes (MWNTs), oxidized (MWOHs), with 1,3-diazido-2-isopropanol (2N3OH) and just as the nanotubes clicked with the phenylacetylene (CMWN3) and propargyl-amine (CMWN3H3) alkynes, were characterized by FTIR and Raman spectroscopy and elemental combustion analysis (ECA); furthermore, MWNTs and MWOHs samples were evaluated by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). On the other hand, the 1,3-diazido-2-isopropanol (MOND) was evaluated by FTIR spectroscopy and nuclear magnetic resonance (NMR) or confirming its chemical structure with the literature.

3.1. 1,3-diazido-2-isopropanol (2N3OH)

The use of nuclear magnetic resonance (NMR) in carbon nanotubes was impossible, due to different nanoparticles used in the synthesis that are still presented in them, however, the characterization of (2N3OH) by $^{13}$C and $^1$H were possible. To confirm the functional groups of that chemistry structure, the characterization for FTIR spectroscopy was used.

For FTIR (Fig. 2), according to different sources that have studied this molecule [45-47] and literature specialized on this spectroscopy [48-51], the chemistry structure of the diazide this at 2090 cm$^{-1} \nu_1$(N$_3$), 645 cm$^{-1} \nu_2$(N$_3$) and 1270 cm$^{-1} \nu_3$(N$_3$). On the other hand, the vibrations that characterize the carbons that make up the structure is at 2867 cm$^{-1} \nu$(CH$_2$), 2930 $\nu$(CH$_3$) cm$^{-1}$ y 1444 $\nu$(CH) cm$^{-1}$. Finally, the OH groups of the isopropanol, is between 3700-3100 cm$^{-1} \nu$(R-OH).
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By NMR spectroscopy (See Fig. 3), coinciding with the cited literature [46], the 1,3-diazido-2-propanol is similar to synthesized by other publications, where 1H NMR (CDCl3) δ 2.64 (br s, 1H), 3.36–3.46 (m, 4H), 3.90–3.97 (m, 1H), and by 13C NMR (CDCl3) δ 54.1, 69.7, are present. Thus, forming the structure C₃H₆N₆O with a 142.12 g mol⁻¹ of molecular weight, verifying the structure of 1,3-diazido-2-isopropanol (2N3OH).

3.2. Multi-walled carbon nanotubes, from as-received to its modifications

With 1,3-diazido-2-isopropanol (2N3OH) characterized, the functionalization of this structure on the multi-walled oxidized carbon nanotubes (MOND) and subsequent clicked with alkynes (CMWN3 and CMWN3H3) was evaluated, however, is very important evidence the difference between as-received and oxidized carbon nanotubes (MWNTs and MWOHs respectively).

**FTIR:** Regardless of the characteristic peaks of the carbon nanotubes (see Fig. 4), that describe at normal modes of vibration at ~1580 cm⁻¹ for E₁u and ~800 cm⁻¹ for A₂u in multi-walled carbon nanotubes (MWNTs), confirmed by different authors [3,52-55] and increases in other bands that identify in the oxidation of multi-walled oxidized carbon nanotubes (MWOHs) as between 1750–1550 cm⁻¹ for ν(C=O), 1466 cm⁻¹ for δ(O-H) and between 1300–950 cm⁻¹ for ν(C-O) due to vibrations of the carboxyl groups, 3443 cm⁻¹ for isolated surfaces of νₛ(OH) [13,55-57]. However, the most important in that characterization is the presence of the azide on MWNTs (see
where this signal is commonly reported to be a very strong band representing antisymmetric stretching $\nu_1(N_3)$ between 2000-2100 cm$^{-1}$ frequency [58-64], however, reported that the internal modes of the azide ion occurs in two other frequencies, such as flexural mode $\nu_2(N_3)$ between 660-600 cm$^{-1}$ and symmetric stretching $\nu_3(N_3)$ between 1360-1300 cm$^{-1}$ frequency [61], furthermore, there vibrations may suggest the presence of nitrogen in the absence of azide, as $\nu(NH_2)$ between 3415-3375 cm$^{-1}$ frequency [58-63], at 3162-3134 cm$^{-1}$ the $\nu(NH)$ [58,63], at 1625-1602 cm$^{-1}$ the $\nu(C=N)$ [58-60,63], at 1555-1541 cm$^{-1}$ the $\nu(N=C)$ [58,63], at 1165-1132 cm$^{-1}$ the $\nu(N-N)$ [58,63] and stretching vibrations of $\nu(C-H)$ between 3000-2900 cm$^{-1}$ frequency[60]. Triazols are obtained by forming the click with the carbon nanotubes (See Fig. 4). With the propargylamine (CMWN3H3) the primary amine N-H is manifested at 3300 cm$^{-1}$ where is affiliated with two bands, the first by scissor vibration of NH$_2$ at 1630 cm$^{-1}$ and the second at 720 cm$^{-1}$ by twisting vibration [51,65-67]. For the other alkyn, the group phenyl of the phenylacetylene (CMWN3) presents different peaks characterizing the ring at 1628, 1430, 750, and 685 cm$^{-1}$, this according to some authors [51,68-70].

Therefore at triazole formation, the azide band disappears from the spectrum (≈2100 cm$^{-1}$) [29-32].

**Raman:** For many authors, Raman spectroscopy is considered as the fingerprint of carbon nanotubes [71-76], that’s why is very important make a deep analysis on the oxidation, purification and modification in the structure of the outer walls of carbon nanotubes. In Raman spectroscopy (see Fig. 5), the peaks to $\approx$1570 cm$^{-1}$ (G band), $\approx$1340 cm$^{-1}$ (D band), and $\approx$2684 cm$^{-1}$ (G’ band) were studied and have been analyzed by different authors [13,75,77-86]. To verify the oxidation/purification of the multi-walled carbon nanotubes (from MWNTs to MWOHs), some publications [87,88] consider the G band (≈1590 cm$^{-1}$) as an indicator of purity due to the excellent graphitic orientation that this represents in the carbonaceous materials by its sp$^2$ hybridization, free of broken links or other hybridizations present including sp$^3$, however, other papers [89,90], they evaluate the purity of carbon nanotubes with the D band (≈1350 cm$^{-1}$), because it is sensitive to the carbonaceous impurities and structural defects.
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Table 1. Relationship of the characteristics bands of nanotubes oxidized with the MOND, CMWN3, and CMWN3H3 samples in Raman spectroscopy.

<table>
<thead>
<tr>
<th>Samples</th>
<th>D</th>
<th>G</th>
<th>G'</th>
<th>G'/G</th>
<th>G'/D</th>
<th>D/G</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNTs</td>
<td>72,068</td>
<td>79,955</td>
<td>81,314</td>
<td>1.02</td>
<td>1.13</td>
<td>0.90</td>
</tr>
<tr>
<td>MWOHs</td>
<td>40,546</td>
<td>52,738</td>
<td>51,791</td>
<td>0.98</td>
<td>1.28</td>
<td>0.77</td>
</tr>
<tr>
<td>MOND</td>
<td>91,522</td>
<td>150,383</td>
<td>87,009</td>
<td>0.58</td>
<td>0.95</td>
<td>0.61</td>
</tr>
<tr>
<td>CMWN3</td>
<td>57,373</td>
<td>83,518</td>
<td>46,338</td>
<td>0.55</td>
<td>0.81</td>
<td>0.69</td>
</tr>
<tr>
<td>CMWN3H3</td>
<td>144,659</td>
<td>195,188</td>
<td>123,017</td>
<td>0.63</td>
<td>0.85</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Table 1. Relationship of the characteristics bands of nanotubes oxidized with the MOND, CMWN3, and CMWN3H3 samples in Raman spectroscopy.

in the graphitic sp$^2$ networks samples (this contrary to the G band), therefore, we can conclude that the relationship between the intensities of these two bands is related to the purity of carbon nanotubes, but with the disadvantage, according to Anne C. Dillon [90], that only not the intensity is important, the full-width-at-half-maximum (FWHM) of the D band is much broader than that of the nanotube D-band, from 86 cm$^{-1}$ to 57 cm$^{-1}$ of graphite to 42 cm$^{-1}$ to 17 cm$^{-1}$ of carbon nanotubes. The G' band, according to Roberta A. DiLeo [91], is characteristic to the purity of carbon nanotubes, because its intensity is proportional to the purity of the multi-walled carbon nanotubes due to the presence of nano-carbons (disordered phase) in the samples. For all the reasons described above, in this work, we related the areas of the G'/G, G'/D, and D/G bands to find a relationship purity to the averaging these values (see Table 1).

The samples on multi-walled carbon nanotubes supported were analyzed. To know the different structural characteristics modification in the outer walls of carbon nanotubes and oxidized carbon nanotubes (MWNTs and MWOHs) due to graft of the 1,3-diazido-2-isopropanol (MOND) on MWOHs and the subsequently click with the alkyynes (CMWN3 and CMWN3H3). The different studies about the G, D, G' bands in the spectrum, there are summarized in Table 1 and the graph of Fig. 5.

The dimensionless values of the areas of the G, D, and G' bands and the relationship of them, suggest the purification of the MWNTs in the oxidation with acids MWOHs due to the decrease in the ratio D/G and the increase in the ratio G'/G and G'/D by the removal of carbonaceous material, however, in the other samples, the values G'/G, G'/D show lower values like to D/G, because they increase the defects in the outer walls of carbon nanotubes by the presence of organic molecules and not by the presence of other carbon allotropes, thus proving by Raman the graft of 1,3-diazido-2-isopropanol (MOND) and the click chemistry with phenylacetylene and propargyl-amine alkyynes (CMWN3 and CMWN3H3).

EAC: To support the presence of nitrogen atomic in the grafted of the 1,3-diazido-2-isopropanol with the MWOHs (MOND) and the click chemistry with phenylacetylene and propargyl-amine alkyynes (CMWN3 and CMWN3H3) in the walls of carbon nanotubes, the studies of elemental analysis by combustion (EAC) and X-ray Photoelectron Spectrometer (XPS) are the key to that (See Figs. 6 and Fig. 7 respectively). For EAC, the results are summarized in Figure R7, where is clear the presence of nitrogen in the samples are presents the graft of the 2N3OH on MWOHs and the click chemistry with the alkyynes (CMWN3 and CMWN3H3). With a quality control, the sulfanilamide was used as a standard. The experimental results were N = 16.23%, C = 41.80%, H = 4.65%, and S = 18.61%, with the theoretical values of N = 16.25%,

Fig. 7. X-ray photoelectron spectroscopy (XPS) spectrum with the deconvolution of the bands and the analysis of the areas of MWNTs and MWOHs for every molecule.

C = 41.81%, H = 4.65%, and S = 18.62%, and the recovery percent is 99.94%, 99.95%, 99.78%, and 100.11% for N, C, H, and S, respectively. By X-ray photoelectron spectroscopy (XPS), was possible the characterization to identify the different elements of the graft of azide with multi-walled oxidized carbon nanotubes (MOND) and the “click” of them with alkynes, which correspond to carbon (C: 294-281 eV), oxygen (O: 537-528 eV) and nitrogen (N: 406-396 eV) mainly.

The presence of nitrogen in MOND is due at diazide in the structure of the outer walls of the carbon nanotubes, with a 8.09% (w/w), on the other hand, the atomic percentage of nitrogen in CMWN3 and CMWN3H3 (3.82 and 5.42%, respectively) due to the addition of these organic molecules, where reflected increased carbon and hydrogen with alkynes and therefore, proportional reduction of nitrogen in the samples, where the click chemistry with propargyl-amine, the atomic percentage of nitrogen is higher due to the amino group. The atomic nitrogen of the azide has been reported by this technique by different authors [25,92,93].

XPS: To confirm the multi-walled oxidized carbon nanotubes, the X-ray photoelectron spectroscopy (XPS) was used. With Gaussian deconvolution components of carbon (C1s) and oxygen (O1s) bands, the MWNTs and MWOHs were characterized, where the dimensionless values of the area under the curve of every band are obtained.

With the aim of obtaining a standard value in the deconvoluted bands, according to what has been published by various research groups [3,94-101], the state of art suggest different functional groups for every component at deconvolution (see Table 2).

To the deconvolution of the C1s carbon peak, the percentage occupied in the band of sp² and sp³ hybridizations carbon and the carbon bonded to the hydroxyl, carbonyl, carboxyl, carbonate and electronic π-π* transition of the outer layers of the multi-wall carbon nanotubes are obtained. Furthermore, when analyzing the oxygen O1s band, the percentage occupied in the band, the molecules of carboxyl, carbonyl, hydroxyl, carbonate and water are

| Table 2. Binding energies for every deconvoluted band of the C1s and O1s peaks. |
|-----------------|-----------------|
| Carbon C1s      | Oxygen O1s      |
| sp²: 284.5      | -COOH: 531.2    |
| sp³: 285.6      | O=C: 532.1      |
| –OH: 286.6      | O–C: 533.4      |
| C=O of carbonyl: 287.6 | C–O*–C=O: 534.3 |
| –COOH: 288.6   | Carbonate: 290.0 |
| π-π* Transitions: 290.9 | Water: 535.5   |

The publication details are: 20% of the text is long sentences, 20% of the text is short sentences, 20% of the text is paragraphs, 20% of the text is tables, 20% of the text is figures.
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In Table 2, different binding energies corresponding to the bands for each molecule of carbon and oxygen are shown. In the Fig. 7, the row of the part a), is clear the deconvolution of the C1s peak for MWNTs and MWOHs, well as the proportional area under curve of the deconvoluted bands, furthermore, the row of the part b), the values and deconvolution of the O1s peak for every sample are present. In the bar graphs, so much for C1s peak as for the O1s peak, the carboxyl and hydroxyl bands of the MWOHs are higher than the MWNTs, thereby confirming the oxidation of the carbon nanotubes and the generation of hydroxyl groups for the subsequent esterification. A very important point is the complement with Raman, where the exfoliation of the outer walls is evident due to increasing of the sp^2 deconvoluted band and the decreasing sp^3 deconvoluted band of the MWOHs regarding to MWNTs.

TEM: The TEM micrographs of the oxidized nanotubes (MWOHs) in Fig. 8, similarly to the case of the as-received MWNTs, show heptagons (H) and pentagons (P) carbon rings, according to reported, but, interestingly, the outside diameters, decrease as compared to the as-received MWNTs, with values ranging from 19 to 41 nm. The micrograph of image MWOHs(b) shows nanotubes with open ends with 24 nm of outside diameter, probably due to the action of the acids employed for the oxidation. In that image also shows the possibility of found fullerene according to similar images to work about the sensitivity of single-walled carbon nanotubes. However, when the azide is grafted in the walls of carbon nanotubes, it is possible to see a lot of kind of noise in said walls (Fig. 8), due to a functionalization of the 1,3-diazido-2-isopropanol.

4. CONCLUSIONS

The modification on multiwall carbon nanotubes with azide was successful due to oxidation-purification of them, that subsequently, the “Click Chemistry” with alkyne groups was possible. The characterization of the azide (2N3OH) and all carbon nanotubes modified, describe in detail the implementation of this synthesis. The use of these materials can be in different fields of organic chemistry, as well as new technology generation, due to the different functional groups present.

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