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Carbon nanotube-Cu hybrids enhanced catalytic activity in aqueous media

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A B S T R A C T

In this work, we report the synthesis of a hybrid material, consisting of Cu nanoparticles (Cu-NPs) anchored on the surface of carbon nanotubes (CNTs), which is able to increase the catalytic behavior when compared to bare CuNPs. This enhanced activity was evaluated by the electrophoretic separation of three carbohydrates: sucrose, glucose and fructose. CNTs were first synthesized in the presence of minute amounts of oxygen, oxidized using H₂O₂-UV radiation and then decorated with Cu-NPs. The resulting hybrid structure was confirmed and characterized by X-ray photoelectron spectroscopy, transmission electron microscopy, high resolution transmission electron energy-dispersive X-ray spectroscopy, titration, thermogravimetric analysis, elemental analysis and Raman spectroscopy.

1. Introduction

Multi-walled carbon nanotubes (MWCNTs) were first imaged and their structure subsequently identified by Endo and Iijima, respectively [1,2]. Soon after, single-walled carbon nanotubes (SWCNTs) were synthesized and characterized [3]. Since then, carbon nanotubes (CNTs) attracted the attention of numerous scientists due to their fascinating electronic, mechanical, thermal, and electrochemical properties [4-6]. In order to modify the electronic properties of CNTs and induce surface reactivity, doping with B, N, BN, Si, P could

be achieved [7]. Basically, doping results in an excess or deficiency of electrons which could be then used to fabricate electronic devices [7,8].

Defect free and undoped CNTs are chemically inert and due to their large size (micrometers in length), CNTs are not readily dispersible in solvents. This fact makes difficult some applications needing uniform CNT dispersions in aqueous media. However, CNTs can be dispersed in water by a single step synthesis-functionalization with oxygen-derivatives [9]. In that case, oxygen-derivatives concentrate on the CNT surface and create the electrostatic stability required for creating

a uniform colloidal dispersion [10]. Furthermore, the combination of two nanomaterials such as CNTs and Cu-NPs could result in a novel hybrid material useful in the fabrication of sensors or catalysts [11,12]. Examples of catalytic applications can be found with Pd- and Pt-NPs anchored to CNTs [13–17], and alloys of Pt-Sn [18], Pt-Co [19], and Fe_3O_4 -Pt [20]. More recently, using a polymer assisted route, a variety of metal NPs (e.g. Au, Ag, Pd and Pt) were attached to the surface of CNTs. Interestingly, these materials exhibited a significantly enhanced catalytic activity in the reduction of 4-nitrophenol to produce 4-aminophenol [21]. In this context, the modification of CNTs with Cu-NPs or its oxides [22–24] also becomes an attractive possibility to use these hybrid materials as nano-electronic devices [23] or as novel catalysts when used as electrodes for the electrochemical sensing of carbohydrates [22,25–27].

In a variety of methods based on capillary electrophoresis (CE), oxidized CNTs were added to the background electrolyte (BGE) in order to enhance the resolution of electrophoretic separation [28]. However, for the detection of carbohydrates, CNTs were preferably used as a matrix so that Cu-NPs could be deposited on the outer surface of CNTs [22,27] or graphene [25,29]. It is noteworthy that the literature is very scarce on topics related to applications of metal NPs-CNTs hybrid materials in aqueous media. One reason could be due to the fact that CNTs tend to aggregate and metals are also insoluble (dispersible) in water. Therefore, having uniform dispersions of CNTs is a real challenge which must be overcome when dealing with analytical applications in aqueous media. Overall, the high surface-to-volume ratio of NPs, along with the ability to control the particle size, provides a unique opportunity for developing further catalytic applications.

In order to anchor NPs on the surface of CNTs, different methods such as the reduction of metal salts [30–33], deposition of NPs on CNTs by thermal evaporation [23] or using hyperbranched polymers [21] can be used. Specifically, for the deposition of Cu-NPs on CNTs, numerous authors have reported different approaches including calcination treatments [24], chemical reduction [22], and microwave radiation [34]. In this paper, we first report on the Cu-NPs encapsulation over the CNTs surface using microwave radiation (MW), a method which appears to be a very efficient when compared to conventional methods [35]. It is known that CNT reach very high temperatures and weld or reconstruct under short MW pulses [36]. The presence of impurities such as Fe (catalyst residues) or even amorphous carbon may also contribute to an intense heating (Joule effect).

In this paper, we report the CNT functionalization with carboxylic oxygen-derivatives, and the simultaneous anchorage with Cu-NPs using H_2O_2 in conjunction with UV radiation. Furthermore, this hybrid material is easily dispersible in water. The anchorage of Cu-NPs to the CNT surface was studied as a function of the exposure time to microwave radiation. The produced materials were characterized by a combination of different spectroscopic and microscopy techniques. In order to assess their analytical and catalytic characteristics, the synthesized hybrid material was used for the carbohydrates reduction in aqueous media, in order to improve the detection of different carbohydrates including glucose, fructose and sucrose via CE.

2. Experimental

2.1. Chemical methods

Hydrogen peroxide 30% was supplied by Panreac; ethanol, ferrocene (FeCp_2), toluene and aqueous solutions of 0.01 N sodium hydroxide volumetric standards were supplied by Sigma Aldrich; sodium hydroxide and Cu standard solutions of 1000 mg/L were purchased by Scharlau Chemie. Nitric acid (65%) was supplied by Suprapur. Sucrose, D-glucose, and D-fructose standards, from Supelco Analytical, were prepared in aqueous solution at 500 ppm.

CNTs synthesized in the presence of minute amounts of oxygen (COx) were synthesized by chemical vapor deposition (CVD) as described by Botello-Méndez et al. [9]. Concentrations of 1% ethanol, 5% ferrocene and 94% toluene were selected because they provided highly crystalline CNT materials. For comparison purposes CNTs were also prepared under the same conditions but in the absence of alcohol; they are labelled as MWCNT in the text. As produced CNTs (COx) were then mixed with ethanol before the microwave treatment because it has been observed that the liquid reduces overheating (Joule effect). Subsequently, oxidized CNTs (oxdCOx) were prepared by a method reported in our previous publication by Martin et al. [10]. In particular, UV radiation (at 254 nm) was applied to CNTs suspensions in water peroxide during 30 min. The suspensions were then filtered, washed and dried several times. This treatment permits the carboxylation of CNTs increasing their dispersion ability when compared to pristine CNTs.

Fig. 1 shows the schematics depicting the experimental approach used in this work for anchoring Cu-NPs to CNTs, employing $\text{Cu}(\text{NO}_3)_2$ as a precursor and microwave radiation as the driver for promoting Cu-NPs encapsulation.

In a typical experiment, 100 mg of oxdCOx were dispersed in a 0.1 N ethanol solution of $\text{Cu}(\text{NO}_3)_2$ which was dispersed ultrasonically during 5 min. This dispersion was then introduced in a microwave oven for domestic use and then heated for different times. This resulted in the encapsulation of Cu-NPs by graphene-like layers (see below). The dispersions were

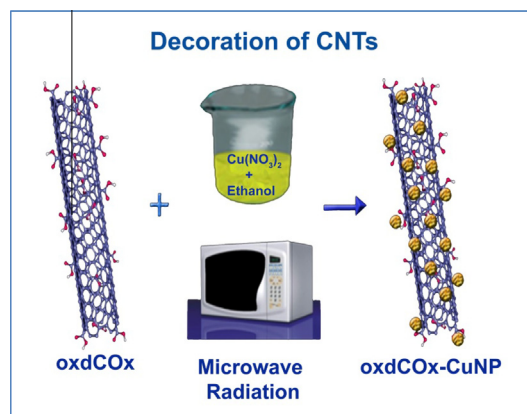


Fig. 1 – Schematic representation of the experimental approach used to anchor Cu-NP on the CNTs surface. (A colour version of this figure can be viewed online.)

then cleaned and filtered several times. Two treatment times were used: 1 and 2 min. Sample Cu2min presented the best dispersibility so this study was concentrated on this sample.

2.2. Instrumentation

X-ray photoelectron spectroscopy (XPS). Two XPS instruments were used: an Axis-Ultra (Kratos) and an Omicron. Surface chemical analysis was performed by N₂ adsorption measurements at 77 K with a BELSORP-max (Bel Japan Inc). Samples were pressed into small pellets of 15 mm diameter, mounted on the sample holder and introduced into the chamber where they were degassed and vacuumed.

Titration. Carboxylic group concentration present within the CNT surface was measured using a Methrom 916 Ti-Touch Potentiometric compact titrator equipped with a Methrom 800 Dosino and a Unitrode pH-meter. In a typical experiment, 10 mg of CO_x or oxdCO_x were added to 40 mL of Milli-Q water and then ultrasonicated for 1 min (VCX 500-750 of Sonics&Materials, 750 W and 20 kHz). Subsequently, a 0.01 N NaOH solution was added at a rate of 1 mL/min by 0.01 mL increments during mechanical stirring and the carboxylic acid concentration was determined from the equivalence point.

Transmission electron microscopy (TEM) analyses were carried out using a Zeiss EM-10C with a field emission gun operating at 60-100 kV. A suspension of CNTs in isopropanol was prepared ultrasonically and a drop was deposited onto lacey carbon grids.

High resolution transmission electron microscopy (HRTEM) and energy-dispersive (EDX) analyses were performed in a JEOL-200 FX II microscope operated at 200 keV. TEM grids were prepared as described above taking the precaution of using Ni grids instead of Cu grids and identify the presence of Cu-NPs.

Thermogravimetric analysis (TGA) was performed in a Perkin Elmer 6000STA system heating from 50 °C to 900 °C. Approximately 5 mg of sample were heated in an open Pt crucible at a rate of 10 °C/min under an air flow (20 mL/min).

Elemental analysis (EA) were carried out with a Perkin Elmer 1100B atomic absorption spectrophotometer, and by dispersive energy fluorescence X-ray (ED-XRF) in a SPECTRO XEPOS spectrometer in a He atmosphere with a Pd window, 50 W X-ray excitation source and SDD detector. Determination of Cu was done digesting 4 mg of samples in HNO₃ during 15 min in a 600 W microwave chamber (Milestone Ethos D), and dissolved in 50 mL of Milli-Q water prior to measurements. Analysis of the as-synthesized CNTs had 3.3 wt% Fe; once oxidized, iron content was reduced to 1.8 wt%. Cu-NPs concentration in the hybrid CNTs materials yielded 0.27 ± 0.01 mg Cu/g and 0.41 ± 0.03 mg Cu/g for Cu1min and Cu2min, respectively.

Raman spectroscopy measurements were carried out in via Renishaw confocal microscope based Raman spectrometer using the 514.5 nm laser excitation. For each sample, various spectra were recorded in different places in order to verify the homogeneity of the sample.

Capillary electrophoresis (CE) experiments were carried out using a PA-800plus system from Beckman Coulter equipped with a DAD detector, set at 265 nm. Silica capillaries of 75 µm (inner diameter) were purchased from Polymicro Tech-

nologies. They were cut in pieces with a total length of 58 cm (48 cm effective length). New capillaries were conditioned with 1 M sodium hydroxide (10 min, 20 psi) and Milli-Q water (5 min, 20 psi). Fused silica capillaries were flushed with 0.1 M NaOH during 10 min, then, Milli-Q water was flowing during 3 min, and finally 75 mM NaOH BGE during 7 min, at 20 psi. Carbohydrate samples consisting of fructose, glucose and sucrose were diluted in Milli-Q water at 500 ppm, and they were then injected at 0.5 psi within 10 s period. Separations were performed at a constant voltage of 12 kV and cassette temperature of 20 °C. CO_x, oxdCO_x and Cu2min (from 0.003 to 0.008 mg/mL concentrations) were dispersed in 75 mM NaOH using a 6 mm probe sonicator (model VCX-130-130 W from Biotech) during 10 min at 60 Hz.

3. Results and discussion

3.1. As produced and oxidized CNTs

The functionalized surface of CNTs is crucial for achieving uniform dispersions in aqueous media. In this context, XPS analyses were used to characterize as produced and oxidized CO_x CNTs. XPS provides insightful information regarding the binding energies of carbon compounds. Fig. 2 plots deconvoluted XPS C1s and O1s spectra indicating the percentages of carboxylic (by O—C=O peak), alcoholic (by C—O peak) and lactones (by C=O peak) groups identified on the CNTs surface.

Deconvolution of the C1s peak for CO_x CNTs(left) shows a main peak centered at 284.5 eV, which is attributed to the graphitic structure (sp² hybridized carbon bonding) [24]. Peaks centered at 285.9, 287.3.0 and 289 eV correspond to functional groups consisting of carbon atoms attached to different oxygen-containing moieties such as alcohol, lactones and carboxylic groups, respectively [37]. XPS analysis of the O1s peak (Fig. 2, CO_x) also confirms the presence of carboxylic groups on the CNTs surface (binding energy of 534.0 eV). Another peak was also identified at 530.7 eV, which corresponds to CO_x CNTs containing a large number of alcoholic groups (36.7%), probably due to the presence of ethanol during synthesis. It is noteworthy that after the oxidation treatment there is a significant increase in the number of defects within the CNTs samples such as the increase of aliphatic groups, from 15.87% (CO_x) to 23.90% (oxdCO_x). In addition, the concentration of carboxylic groups (see C1s plots) increased from 6.49% (CO_x) to 8.54% (oxdCO_x) after oxidation; the nanotube dispersibility in aqueous media enhances significantly after oxidation (see below).

In order to confirm the presence of functional groups, acid-base titration experiments were also carried out to determine the concentrations of carboxylic groups on the CNTs surface (see Table S1 in Supplementary data). For example, the carboxylic acid deposited on the CNT surface increased up to 21% after the H₂O₂/UV oxidation treatment. The dispersion stability also significantly increased in time as illustrated in Fig. 3. Clearly, oxdCO_x possess a better liquid stability and the suspension remained homogeneously dispersed after 10 days. CO_x CNTs are only stable for few days after the dispersion preparation, whereas the pristine CNTs (pure carbon) settle down immediately after sonication.

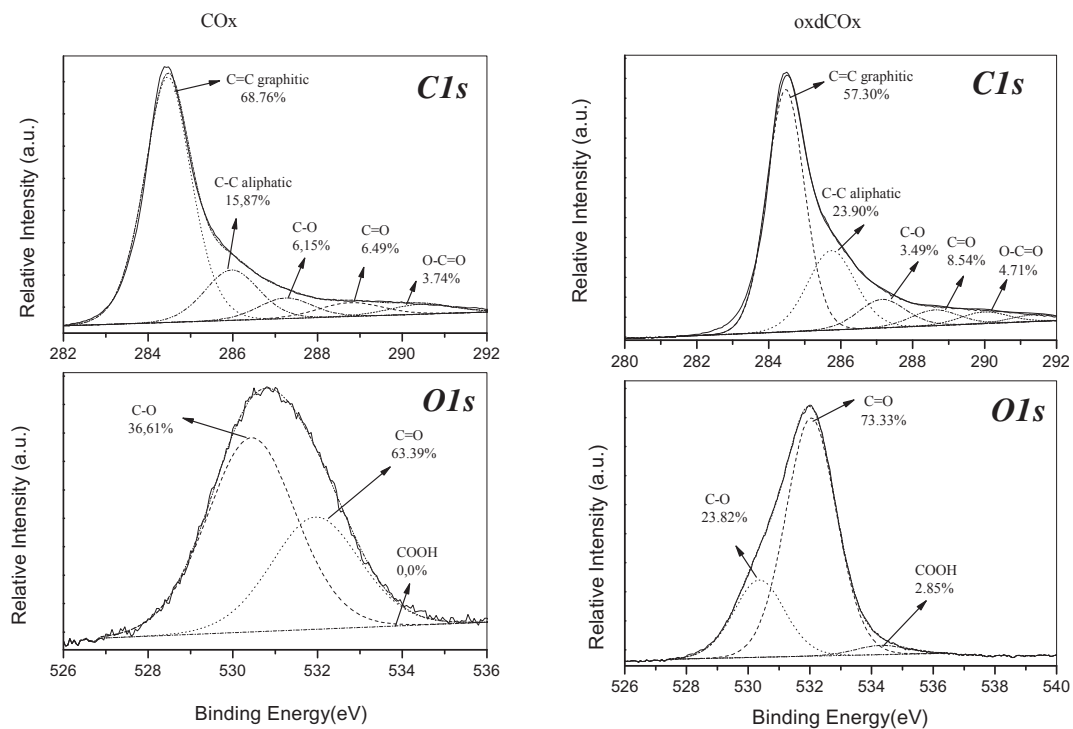


Fig. 2 – XPS spectra corresponding to the carbon (C1s) and oxygen (O1s) binding energy of COx (left) and oxdCOx (right). The spectra were deconvoluted and the percentage (m/m) of the differential functional groups of alcohols (C–O), lactones (C=O) or carboxylic (COOH) are indicated.

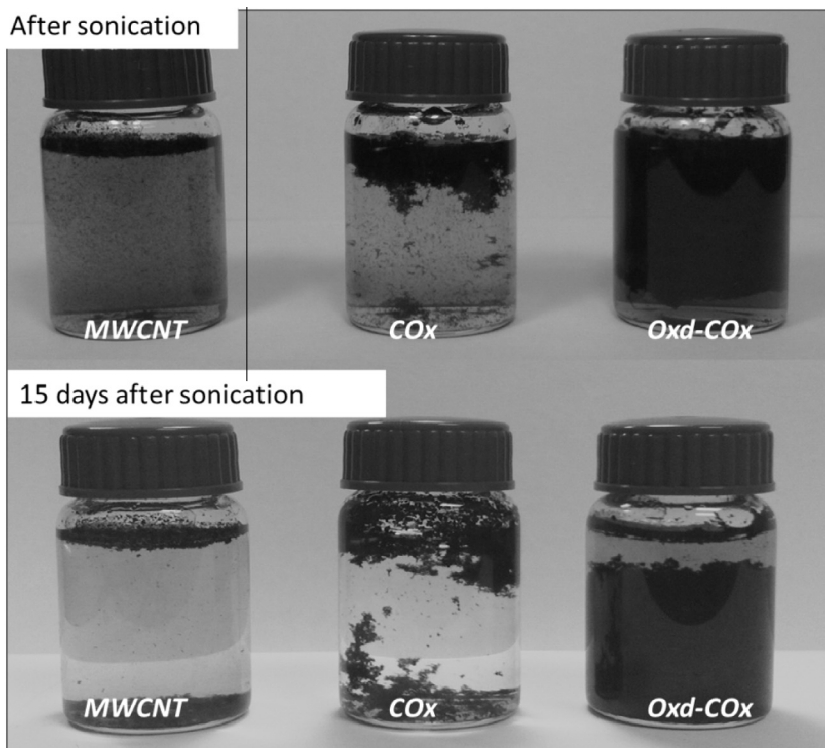


Fig. 3 – Photographs of aqueous CNT suspensions showing MWCNT, COx, and oxdCOx immediately after sonication and 15 days after sonication.

3.2. Encapsulation of Cu-NPs on carbon nanotubes

Since oxdCOx displays a more stable dispersion when compared to COx CNTs, this sample was selected as support for depositing Cu-NP following the procedure described in the Section 2. TEM studies were used to confirm the anchorage of Cu-NP on the surface of oxdCOx.

Fig. 4 shows TEM images of as synthesized CNT samples (COx), oxidized (oxdCOx) and the hybrid material after a 2 min microwave treatment. These images reveal a high amount of Fe-containing particles inside CNTs and also points that Cu-NPs were deposited in a very low proportion on the surface of CNTs. No visible changes in the morphology of CNTs were observed after the Cu-NPs were anchored. This result is noteworthy since strong chemical oxidation of multi-walled CNTs usually damages the tubes surface [37]. According to our measurements, the Cu-NPs size distribution is centered at 10 ± 2 nm.

In order to confirm that the anchored particles on the surface of the tubes consisted of Cu, EDX analyses were carried out using nickel TEM grids. In Fig. 5 the EDX spectrum of a spot (upper) is presented. The presence of Cu was clearly observed by observing the Cu-K (8.6 keV) and Cu-L (1.0 keV) transitions. In addition, Fe and Ni signals can be observed also; the signal from Fe could arise from the catalyst residues observed within the nanotubes (see Fig. 4) and the Ni signal must come from the grid background. Elemental analyses show that the Fe:Cu atom ratio is 50:1, a very high ratio that makes difficult the determination of Cu by dispersive techniques. To prove that Fe particles are not at the surface of the CNTs a surface technique must be used.

The morphology of hybrid Cu2min and the way Cu-NPs anchored on CNTs were also studied by HRTEM. Fig. 6 shows

an image of the Cu2min sample showing a Cu-NP with lattice fringes of ca. 0.208 nm. This interlayer spacing is consistent with the (111) planes of Cu [29]. The (111) Fe plane also has a similar spacing but the fact that the examined particle is at the surface of a tube makes us to attribute this particle to Cu.

To ascertain if Fe particles could be located not only within the tubes but also at their surface, XPS analysis was performed. Fig. 7 shows the results for the energy region corresponding to Cu for two samples, the oxidized COx and Cu2min. It can be clearly observed the signal from Cu (933 keV) although its intensity is very low. No signal could be detected for Fe (see complete XPS spectrum in Supplementary data Fig. S3). Since XPS signals can only come from a very few atom layers from the surface, the absence of Fe signal is a clear indication that Fe particles are located within the tubes and that Cu particles are at the surface.

We also noted that Cu-NPs deposited on CNTs appear encapsulated by a few graphitic layers. This observation is noteworthy since it is not common to find Cu-NPs surrounded by graphitic layers after carrying out a chemical NP anchorage [24]. Similar results have been reported when depositing NPs under abrupt conditions [38]. Therefore, Cu-NPs appear to be firmly anchored to the surface of CNTs, thus making Cu-NPs highly stable in alkaline aqueous solutions used for the analytical studies described below (see Section 3.3).

The Raman spectra (see Fig. S1 in Supplementary data) were recorded for pristine COx, the oxidized CNTs (oxdCOx) and Cu2min samples. Each spectrum consists of three characteristic bands, namely the D-band located at ca. 1360 cm^{-1} (induced by the presence of amorphous carbon and defective sites embedded in sp^2 hybridized lattices), the G-band located at ca. 1588 cm^{-1} (related to the in-plane tangential stretching

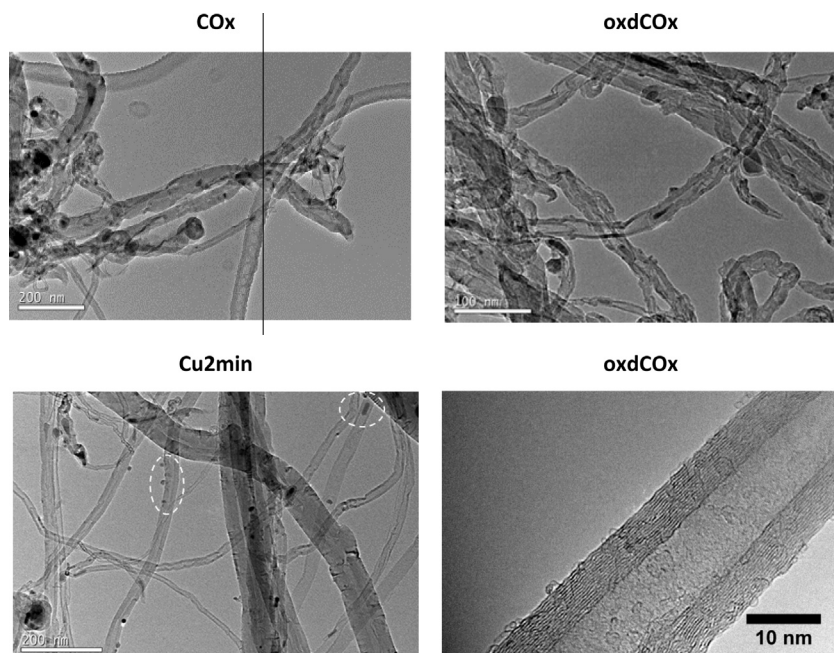


Fig. 4 – TEM images corresponding to COx and oxdCOx (upper) and Cu2min sample and oxdCOx magnification (bottom). For Cu2min some particles can be identified at the surface of a CNT; at the upper right, dotted line shows an iron particle inside a CNT and at the left, Cu particles in the surface of CNT.

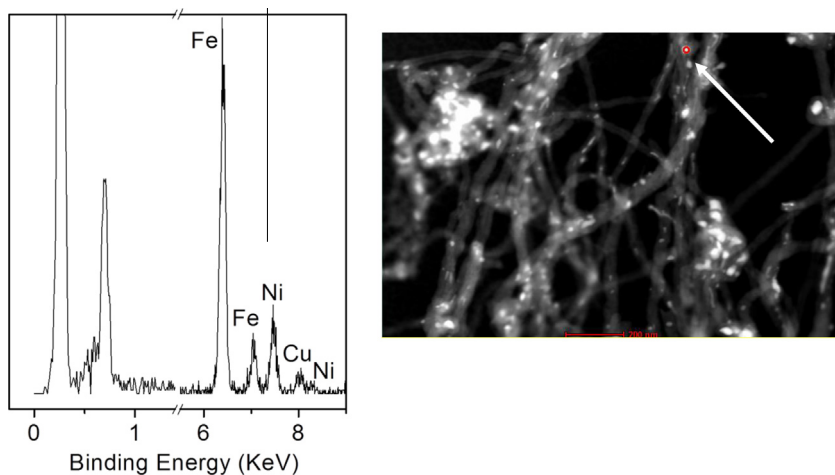


Fig. 5 – Spot beam EDX spectra (Ni grid) of Cu₂min hybrid sample. Arrow shows the spot location. (A colour version of this figure can be viewed online.)

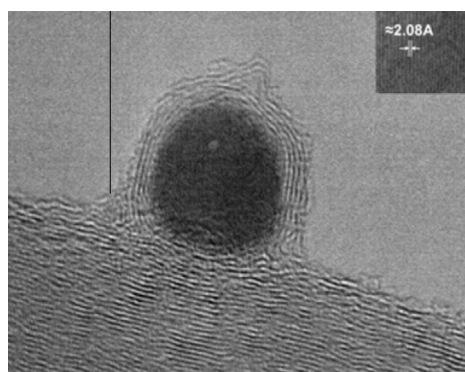


Fig. 6 – HRTEM images of a 10 nm Cu-NP showing an interlayer distance of ca. 2.08 Å that belong to the (111) plane of Cu.

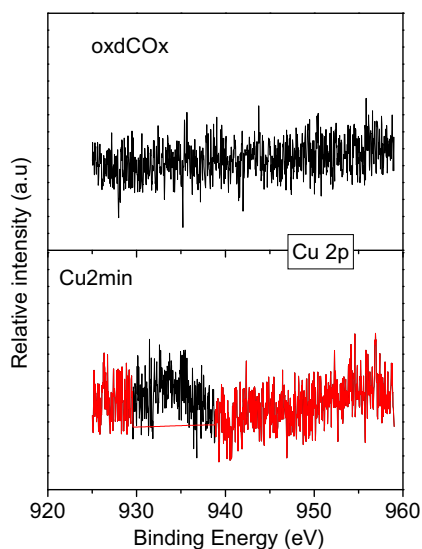


Fig. 7 – XPS spectra corresponding to the copper (Cu₂p_{3/2}) binding energy of oxdCO_x (left) and oxdCO_x-CuNP (right). (A colour version of this figure can be viewed online.)

Table 1 – Raman shifts for the D- (ω_D) and G- (ω_G) bands and the intensity ratio of the D- and G-bands (I_D/I_G). HT refers to heat treatment (see text for details).

Sample	ω_D	ω_G	I_D/I_G
CO _x	1360.6	1588.2	0.51
oxdCO _x	1358.9	1588.2	0.47
Cu ₂ min	1360.8	1589.4	0.48
oxdCO _x HT	1358.9	1589.5	0.53

carbon-carbon bonds in graphene sheets), and the 2D band centered at ca. 2707 cm^{-1} . Raman shifts of the D- and G-bands and the intensity ratio of both bands (I_D/I_G) are shown in Table 1.

The intensity ratio I_D/I_G could be used to indicate the degree of crystallinity within sp^2 -hybridized carbon samples, that is, the smaller the number the more crystalline with fewer defects the sample becomes [39]. No significant variations in the spectral shape or Raman shifts were detected, in accordance with previous results [10], although a slight decrease in the I_D/I_G ratio was observed as CNTs get oxidized and Cu-NPs get anchored on the tube surfaces. These differences are within variations between different batches produced identically. Sample oxdCO_x was treated at 500 °C for 1 h under N₂ to create a slightly more defective surface, as the slight increase in I_D/I_G ratio reflects. This sample was used to confirm that catalytic activity was due to Cu-NPs and not to surface interactions with the tubes (see Section 3.3).

Different structural forms of carbon can exhibit different oxidation behavior depending of the functionalities anchored to their surface [37]. For example, defects embedded in sp^2 hybridized carbons tend to oxidize at around 500 °C [40] due to their low activation energies, whereas nanocarbons exhibiting a high degree of crystallinity start to oxidize at a higher temperature, between 600 and 700 °C [41].

In our studies, TGA analysis (Fig. 8) revealed a decrease of the thermal stability of the oxidized sample (oxdCO_x) when compared to the pristine nanotube sample [10]. In particular,

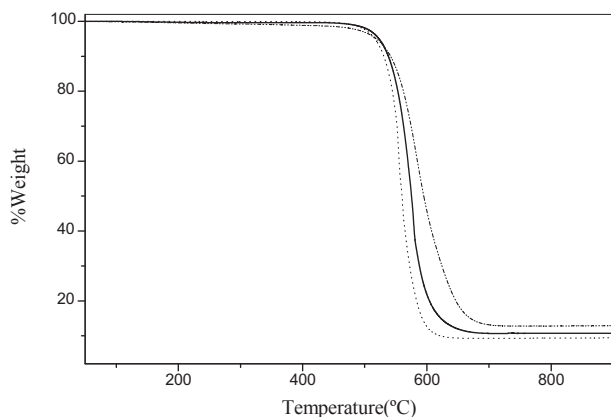


Fig. 8 – Thermogravimetric analysis (TGA) of different samples: COx (solid line); oxdCOx (dashed line); Cu2min (dashed dotted line).

the maximum oxidation rate for the COx sample appeared at 578 °C whereas for the oxdCOx appeared at 550 °C. However, the Cu2min sample presented the best thermal stability since a maximum weight loss rate appeared at 587 °C. This stabilization effect created by Cu-NPs could be due to the fact that Cu-NPs are first deposited on defective sites, thus inhibiting oxidation sites within tubes. In addition, the microwave treatment which induced graphitization of carbon layers around the Cu-NPs, was also responsible for creating more crystalline graphitic surfaces; in agreement with the Raman observations described above.

3.3. Analytical application: electrophoretic separation of carbohydrates

Three carbohydrates (sucrose, glucose and fructose) were selected as analytes of interest for this work. However, their analysis in aqueous media by CE with UV-detection has been a challenge due to the lack of sensitive detection methods, because of the absence of charge at neutral pH and the absence of chromophore groups when they are underivatized [42]. In this context, some strategies have been proposed in order to overcome these problems [43]. Among those methods reported in the literature to separate and detect those underivatized carbohydrates, an aqueous BGE based on NaOH has been selected as a reference. This BGE favors the ionization of sugars due to their catalyzed hydrolysis under alkaline conditions [44,45]. Hydroxide ions initiate proton removal from the anomeric hydroxyl, followed by ring opening that produces their enolization, thus gaining enediolate anions with negative charge. The absorbance of the conjugated carbonyl groups will be higher than the original sugar, allowing its detection by UV-VIS at 265–270 nm [46,47], and being easily separated by CE as shown in Fig. 9. Moreover, from enols it is also possible to produce a large variety of oxidized products in an alkaline medium [45].

In this work, the separation of the carbohydrates using the conventional NaOH BGE has been compared to that produced by dispersions of oxdCOx (without Cu-NPs) and of the synthesized hybrid material Cu2min in NaOH as BGEs. oxdCOx and Cu2min samples were dispersed in 75 mM NaOH BGE in a

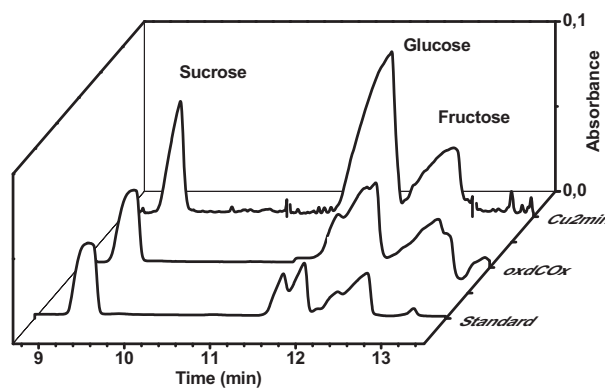


Fig. 9 – Sucrose, glucose, and fructose at 500 ppm were separated using as BGEs the standard 75 mM NaOH aqueous solution and the same aqueous solution containing 0.008 mg/mL of oxdCOx or Cu2min as indicated in the axis.

concentration range 0.003–0.008 mg/mL. This concentration range was selected according to previously published ranges [28,48,49], and Cu2min was chosen because it forms homogeneous dispersions, and because of the high amount of Cu efficiently anchored on the CNTs surface. The most relevant data, corresponding to the 0.008 mg/mL CNTs concentration are shown in Fig. 8.

The use of oxdCOx in the BGE leads to an improved sensitivity of glucose and fructose when compared to the BGE medium without CNTs. However, as observed in Fig. 8, the most impressive result appears with the Cu2min sample, which increases the sensitivity in the detection of these reducing carbohydrates by a factor of ca 5. The sensitivity enhancement can be attributed to a heterogeneous catalysis effect of Cu-NP on the glucose hydrolysis producing enolate anions in alkaline medium as fragmentation products [44]. Other synergistic effects on the oxidation of glucose in alkaline solution have been described in other combination of carbon nanostructures and CuNPs, including Cu-graphene [26,50,29]. The mechanism is not well understood although it has been proposed that the Cu(III)/Cu(II) pair may take part as an electron transfer mediator [50]. However, the presence of Cu ions is hard to accept in our system due to the encapsulation of Cu-NPs with graphitic layers. In order to verify that the sensitivity enhancement is only attributed to the presence of Cu-NPs and not to the surface defects created during the oxidation process, we induced more defects on oxdCOx by heating the sample to 500 °C for 1 h in a N₂ atmosphere. The high value of I_D/I_G for this sample (see Table 1) confirms a higher defective surface but no significant changes were detected in the electropherogram (see fig. s2 in Supplementary data).

4. Conclusions

An easy approach has been successfully developed for the preparation of a hybrid system consisting of Cu-NPs encapsulated on the surface of CNTs. The results indicate that, under our experimental conditions, the amount of Cu is relatively low (0.2–0.4 mg Cu/g, the size of Cu-NPs is about 10 nm and are strongly anchored to the surface of oxidized CNTs. The

dispersibility of the Cu-NPs hybrid material in aqueous solutions is high due to the presence of carboxylic groups formed on the surface of CNTs. We have used alkaline dispersions of these hybrid nanotubes as BGE for electrophoresis of a mixture of carbohydrates: sucrose, glucose and fructose. We have demonstrated that 0.008 mg/mL of Cu₂min (0.41 mg Cu/g sample) is enough to achieve a sensitivity enhancement of 5 times (S/N) in glucose when compared to media containing any nanostructure. The observed signal enhancement has been attributed to a heterogeneous catalysis of the carbohydrates fragmentation process due to the presence of Cu-NPs.

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