Preparation of homogeneous CNT coatings in insulating capillary tubes by an innovative electrochemically-assisted method

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Abstract

Preparation of homogeneous CNT coatings in insulating silica capillary tubes is carried out by an innovative electrochemically-assisted method in which the driving force for the deposition is the change in pH inside the confined space between the inner electrode and the capillary walls. This method represents a great advancement in the development of CNT coatings following a simple, cost-effective methodology.

1 Introduction

In the last decade innovation in the design of microfluidic systems [1,2] combined with a deeper understanding of the singularities of chemistry in confined spaces [3,4] has boosted new breath into the development of microreactors, i.e., those with at least two of their dimensions in the range of tens to hundreds of microns. Microreactors are considered a tool with the potential to push forward many industrial and lab processes which cannot be efficiently handled in conventional reactors [5,6]. It is well established that in many cases synthetic chemistry [7,3], clinical analysis [8,9] and power supply devices [10,11] can benefit from miniaturization. The reason behind these claims is mainly the optimization of heat and mass transfer due to their large surface-to-volume ratios. In addition the smart design of the reactor as a microfluidic system allows an increased control on the selectivity [3] and duration of critical reaction steps such as mixing or the chemical reaction itself. However, the spread of microreactors as a truly versatile tool depends highly upon the ability to provide microfluidic conducts with functional stationary phases [12]. To achieve this particular target, new strategies must still be developed in order to enable the generation of homogeneous coatings with the desired thickness throughout the microfluidic pipes without clogging the system.

The present work addresses the particular problem of the preparation of Carbon Nanotube (CNT) coatings as stationary phases inside capillary tubes. The CNT and graphene incorporation in microfluidic systems has recently drawn attention due to their remarkable properties for solid phase separation. However, a recent review points out the urge for further developments in the preparation procedures as well as understanding of the fundamentals [13]. Nevertheless, when it comes to the preparation of CNT films/coatings in a controlled manner a vast experience is already available in macroscopic as well as in patterned substrates. Authors usually choose between Chemical Vapor Deposition (CVD) [14–16] and Electrophoretic Deposition (EPD) [17,18]. CVD generates dense, vertically aligned forests of CNTs using an organic carbon source, a metallic catalytic seed and high temperatures in an inert atmosphere. On the other hand EPD is a method which specifically targets electrically conducting substrates and where already formed CNTs are provided in a liquid dispersion. The application of an electric field ~~of~~in the order of several tens of $V\ cm^{-1}$ in an electrolyte-free CNT dispersion induces the migration of anionic nanotubes towards the positively charged anode, followed by CNT coagulation and finally the formation of a deposit on the electrode which can retain CNT alignment in some cases [19]. CVD presents the best conditions for its adaptation to miniaturized devices [20], provided that a good seeding of the metallic catalyst is achieved throughout the target surface. However, from a purely fundamental point of view there are other concerns to be considered such as: (i) the use of temperatures higher than 600 °C necessary for the CNT preparation may affect the integrity of the reactor material, making it unsuitable for materials such as poly(methyl methacrylate) (PMMA), poly(carbonate) (PC), poly(styrene) (PS) or poly(dimethyl siloxane) (PDMS) [21]; and (ii) the requirement in many cases for additional post-treatment to either remove the metals present in native CNTs (purification) and/or grafting a supported catalyst, which can be complicated due to low accessibility and the corrosive action of acidic solutions used in the purification step.

Concerning EPD, the intrinsic need for a conducting surface to act as the substrate meets the additional requirement for an “open structure” (i.e., appropriate channel design), since tubular conducts would require a non-conventional electrode configuration in order to obtain a homogeneous distribution of the electric field along the inner cavity. These two limitations make EPD suitable for few specialty microreactor designs.

In the present study commercial fused-silica capillary tubes are used as a model insulator-based microreactor. To the best of our knowledge all reports dealing with the attachment of CNTs inside capillary tubes rely on the chemical modification of the inner silica wall to induce specific interactions with the CNTs [22–24]. Different interactions from Van der Waals [22] to electrostatic [23], to covalent binding [24] have been claimed as responsible for the CNT retention inside the capillary. The fact that a direct interaction between the capillary tube inner wall and the CNTs is needed generally limits the coating to a monolayer. In contrast to these approaches, here we present a method to prepare homogeneous coatings of pre-synthesized CNTs especially suitable for tubular micro-conducts made up of an insulating material while avoiding chemical pre-treatments. This simple method uses cheap and readily available equipment, reduces the number of necessary steps and avoids the use of toxic solvents. As in the case of EPD, electrochemistry is used for the deposition of the CNTs, but with a striking difference: the driving force is mainly the local pH shift produced at the electrode environment caused by redox reactions. This versatile technique has been successfully applied in the preparation of controlled deposits of different inorganic materials (see for example Refs. [25,26]) and even composites containing CNTs such as chitosan-CNTs [27], silica-CNTs [28], metal complexes-CNTs [29], and ~~hydrohyapatite~~hydroxyapatite-CNTs [30]. Moreover, this strategy has already ~~been~~ proven its usefulness in the preparation of patterned coatings of CNTs on conductive substrates [31]. The protocol for the successful deposition of CNTs coatings needs the preparation of pH sensitive CNT dispersions. Oxidized CNTs are known to be dispersed in water ~~in~~ under neutral to alkaline pH due to the presence of acidic O-containing groups such as carboxylic acids. At sufficiently high pH values, these groups release protons to give negatively charged CNTs where water molecules easily disrupt the π–π stacking interactions. It is well established that acidifying the solution leads to CNT coagulation due to the neutralization of these charges, although some groups [32] have reported the possibility of dispersing functionalized CNTs under acidic pH after undergoing harsh oxidation treatments, which may be due to the presence of defects on the surface of the CNTs apart from the surface oxygen groups. In the present study, water oxidation on an inert metal electrode is used to decrease the local pH inside the insulating capillary tube.

2 Experimental

2.1 Carbon nanotube functionalization

Commercial Multiwalled CNTs (MWCNT, NanoBlack, Columbian Chemicals Co.) with a typical diameter of 14 nm and lengths ranging from few hundred nanometers to several microns, and a measured BET area of 253 $m^2\,g^{-1}$ [33], were used without further purification. Considering the MWCNT coatings, the geometric coverage on a flat surface was estimated as $S_{covered} = S_{BET}/\pi = 80\ m^2\,g^{-1}$, by assuming an ideal rod-shaped form for the CNTs. Functionalization of the MWCNT surface (*f*MWCNT) with O-containing groups was achieved by reaction with ammonium persulfate (APS, Merck) in aqueous solution (0.5 g of MWCNT in 100 mL, 20% w/v APS), for 24 h at 25.0 ± 0.1 °C. The ~~partially~~ *f*MWCNT were recovered by centrifugation, and purified by re-dispersion in ultra-pure water aliquots ~~a number of~~several times followed by subsequent centrifugation steps. TG-MS analysis was performed on the sample in order to analyze the amount of surface oxygen groups on the MWCNT.

2.2 Preparation and characterization of the Pd catalyst

Pd-decorated partially oxidized Multi-Walled Carbon Nanotubes, *f*MWCNT-Pd, were prepared by direct impregnation of the *f*MWCNT, where previously formed Pd nanoparticles were spontaneously attached to the carbon support after spending several days in suspension. Pd nanoparticles were provided in the form of a stable colloidal suspension in methanol, prepared using a method from the literature [34]. After 72 h stirring at room temperature, the already formed catalyst was recovered by filtering. Non-specifically attached Pd and capping agent excess were removed by subsequent washing with refrigerated water–ethanol mixture prepared with equivalent volumes.

2.3 Preparation of stable *f*MWCNT dispersions in water and estimation of their concentration

To obtain highly concentrated solutions, 100 mg of the solid sample were dispersed in 10 mL ultra-pure water using sonication. The mixture was centrifuged in order to separate the stable dispersion from the non-soluble fraction. This fraction can be used to prepare new CNT dispersions by repeating the whole process over again. The first or the second aliquot is usually the highest concentrated for the *f*MWCNT-Pd, while for *f*MWCNT the highest value is obtained after 6–7 water extractions. For the estimation of the concentration as well as for the studies on CNT leaching the π-plasmon band in UV analysis (245 nm) was used. The MWCNT dispersions were diluted 1:35 v/v in ultra-pure water and the UV–Vis–NIR spectrum was obtained in a JASCO (V-670) spectrophotometer. The difference between the absorbance at 1300 nm (baseline) and 350 nm was used as the indicative parameter. This value multiplied by a factor 1.085 – the slope of the calibration curve – gives a good estimate of the real concentration in mg mL^{-1}.

2.4 Electrochemically-assisted *f*MWCNT deposition

An electrochemical column-shaped glass cell (10 cm long; 1.5 cm inner diameter) sealed by rubber septa at both ends was employed. Commercial fused silica capillary tubes for chromatography (Agilent, 0.250 mm inner diameter) were used as received. Capillary tube segments employed were typically 18–23 cm long. One end of the capillary tube was fixed to a syringe by means of epoxy adhesive, to allow its filling and emptying, and then was inserted in the electrochemical cell through the upper septum. A Pd wire (Goodfellow, 0.050 mm diameter) was passed all the way through the capillary segment, exiting the cell through the lower septum. Copper self-adhesive tape was used to immobilize the tip of the Pd inner electrode, providing a stiff point for the electric contact. A coiled Pt wire (Goodfellow, 1.0 mm diameter) acted as the auxiliary-outer-electrode. The lower end of the capillary tube almost reaches the bottom of the glass cell, lying only a few millimeters away from both the septum and the outer electrode. In the present configuration a very small volume (1–2 mL) of the fMWCNT~~-~~/~~-~~fMWCNT-Pd aqueous dispersion was required. Once the components were placed as indicated in Fig. 1, a DC power source (Phywe) was connected to the electrodes, always setting the Pd -inner~~-~~electrode as the anode (+). After a 1 h treatment at a voltage of 30 V, the capillary tube and the Pd wire were removed from the cell jointly. The inner solution was drawn out with the syringe and the tube was dried at 80 °C under dynamic vacuum before carefully removing the wire to avoid scratching of the CNT coating.

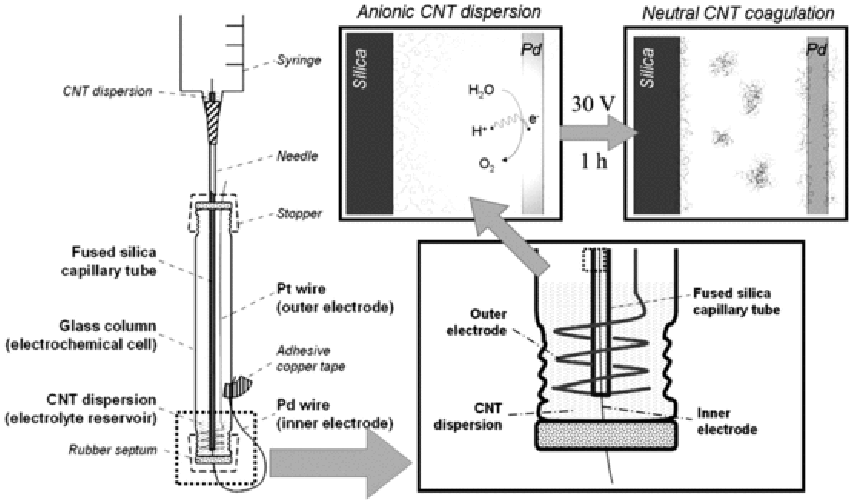

Fig. 1 Illustration (Please substitute Figure 1 with the image attached in this galley proof document. Thank you very much) of the experimental setup for the electrochemically-assisted deposition of MWCNT inside capillary tubes. Insets corresponding to a close-up view (lower right) of the bottom of the cell and the suggested deposition process (top right).

2.5 Sample characterization

The obtained samples were characterized by Scanning Electron Microscopy (SEM, JEOL JSM-840), with an acceleration voltage of 15 kV. The capillary segments were beveled with a scalpel blade in order to uncover the inner face of the tube. Samples were coated with a thin gold layer prior to analysis. ~~The~~CNTs samples were also characterized by Transmission Electron Microscopy (TEM, JEOL JEM-2010) with an accelerating voltage of 200 kV.

Quantification of the Pd loading in the catalysts was performed by the analysis of the solutions obtained through the acidic digestion of an fMWCNT-Pd sample with the Inductively Coupled Plasma-Optical Electron Spectroscopy technique (ICP-OES, Perkin Elmer, Optima 4300 DV).

Thermal analyses of the samples were ~~performed~~carried out in a Differential Scanning Calorimetry-Thermogravimetric Analysis (DSC-TGA) equipment (TA Instruments, SDT 2960 Simultaneous) coupled to a mass spectrometer (Thermostar, Balzers, GSD 300 T3). About 10 mg of the sample were heated up to 940 °C (heating rate of 10 °C/min) under a helium flow rate of 100 mL/min.

Electrochemical studies of the fMWCNT-Pd coated capillary tubes were performed in a standard 3 electrode electrochemical cell, using a reversible hydrogen electrode (RHE) as the reference electrode and a platinum wire as the counter-electrode. Cyclic voltammetry was ~~performed~~measured in a 0.5 M H_2SO_4 electrolyte, thoroughly purged with N_2 (g) prior to each experiment, at a scan rate of 10 mV s^{-1}. The fMWCNT-Pd coated capillary tube used as the working electrode was prepared in such a way that electric contact with the inner CNT layer could be easily made. For such a purpose the capillary was beveled at the upper end and then covered with a thin layer of sputtered gold, covering the tip inside and outside. Then a conducting silver-epoxy adhesive was used to bind the metalized end of the capillary tube to the needle of a syringe. Electrical contact to the CNT coating was made directly through the needle. Fine control of the electrolyte level in the capillary was achieved by means of a pro-pipette adapted to the syringe through a flexible rubber conduct. An eDAQ potentiostat and recorder were used to ~~perform~~ record the cyclic voltamm~~etry~~ogram.

3 Results and discussion

The functionalization treatment significantly increased the amount of surface oxygen groups present in the MWCNT ~~used in this study~~ without altering their morphology. For the fMWCNT sample the combined presence of CO_2 and H_2O evolution in the region below 300 °C is highly characteristic of the presence of carboxylic acid groups, Fig. 2. The CO desorption at higher temperatures is due to decomposition of other O-containing surface groups such as anhydrides,

~~lactones,~~ phenols, ethers, quinones and carbonyl groups. Quantification of CO_2 and CO signals at the mass spectrometer revealed that the oxygen content after functionalization rose to 5.4 wt%, from the 1.5 wt% typical of as received MWCNT.

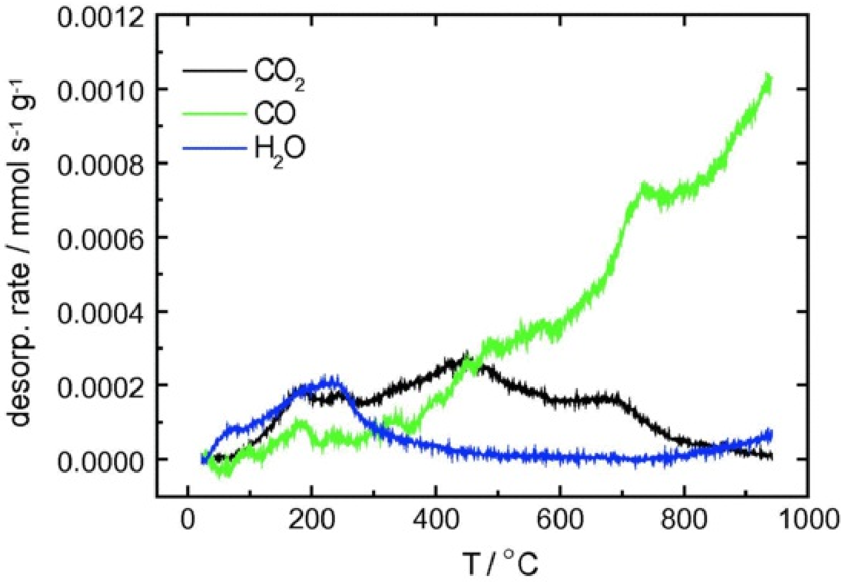

Fig. 2 CO_2, CO and H_2O desorption rate profiles as a function of the temperature for the fMWCNT sample. (A color version of this figure can be viewed online.)

TEM analysis of the sample *f*MWCNT-Pd revealed that the Pd nanoparticles were very well distributed on the surface of the carbon support (Fig. 3), without any visible agglomeration. The Pd loading in the catalyst was 1.33 ± 0.02 wt% according to the ICP-OES analysis.

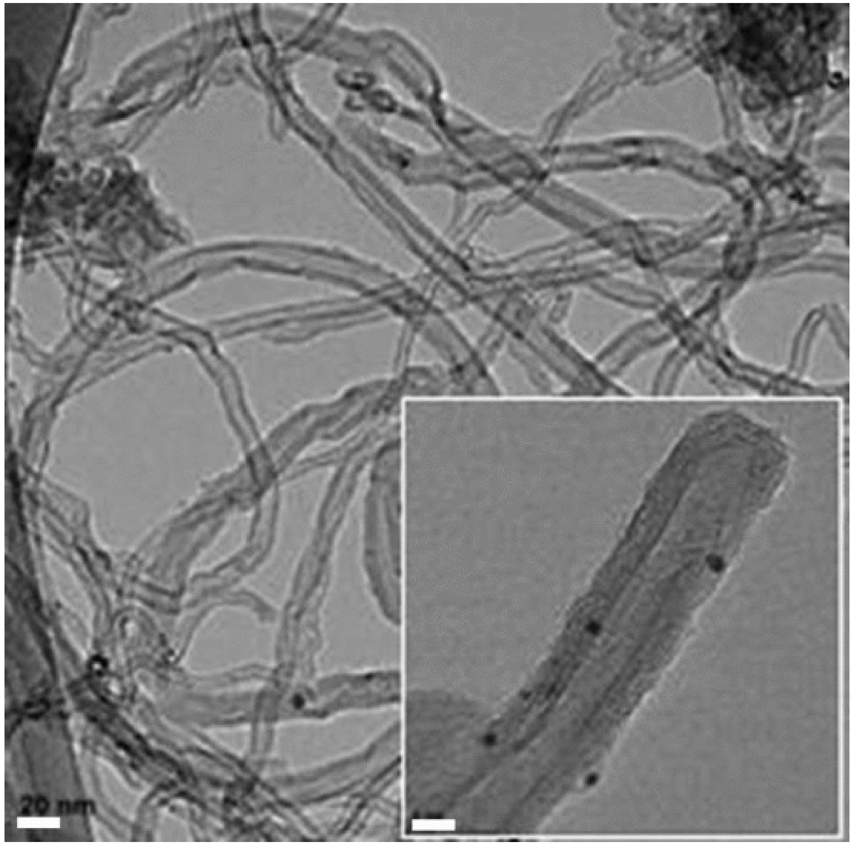

Fig. 3 TEM images of *f*MWCNT-Pd deposited from a stable water dispersion. Scale bar: 20 nm; inset scale bar: 5 nm.

The experimental setup employed for the electrochemically-assisted coating process consisted basically on a DC power source and an electrochemical cell, provided with two inert electrodes (metal wires), where the capillary tube is held vertically. The configuration of the different elements is illustrated in Fig. 1. A Pd wire (Ø = 50 µm, inner electrode) in passed through the capillary tube, exiting the cell through a rubber septum at the bottom of the cell. An auxiliary electrode is provided in the form of a Pt coil (counter electrode) with one end exiting the upper rubber septum. The solution used as electrolyte was a concentrated dispersion of *f*MWCNT or a dispersion of fMWCNT-Pd in ultra-pure water (see Section 2.3).

The electrochemical treatment consisted in the application of a high voltage (30 V) between the inner (anode, +) and outer (cathode, ~~)~~−) electrodes. The applied voltage must be high enough to produce the oxidation of water molecules at the Pd wire, but not too high in order to prevent gas evolution as a result of the massive formation of dioxygen. As water electrolysis proceeds protons are released over the inner electrode, acidifying the solution confined within the capillary tube, Fig. 1.

Confinement is expected to enhance the local pH shift by limiting proton diffusion to the electrolyte reservoir at the bottom of the cell. This change in the local pH inside the capillary causes the CNTs to coagulate, favouring the massive deposition of the newly formed aggregates on the capillary surface and the Pd wire used as anode. After 1 h of electrochemical treatment the capillary tube inner wall was nearly covered with a homogeneous CNT coating along the length of the fused silica capillary, as revealed by SEM images in Fig. 4~~-~~A~~-~~–D, at the magnification scale used. As evidenced from these images, dense layers of *f*MWCNT may be deposited on an insulating substrate with a complex geometry by a simple methodology in which no pre-treatment of the substrate is necessary and which, moreover, does not require the use of high temperatures, aggressive chemicals, or noxious solvents. A control experiment was performed in which no current was passed through the circuit in order to verify that the CNTs were indeed deposited by an electrochemically-assisted process. The control experiment did not yield any appreciable CNT deposits.

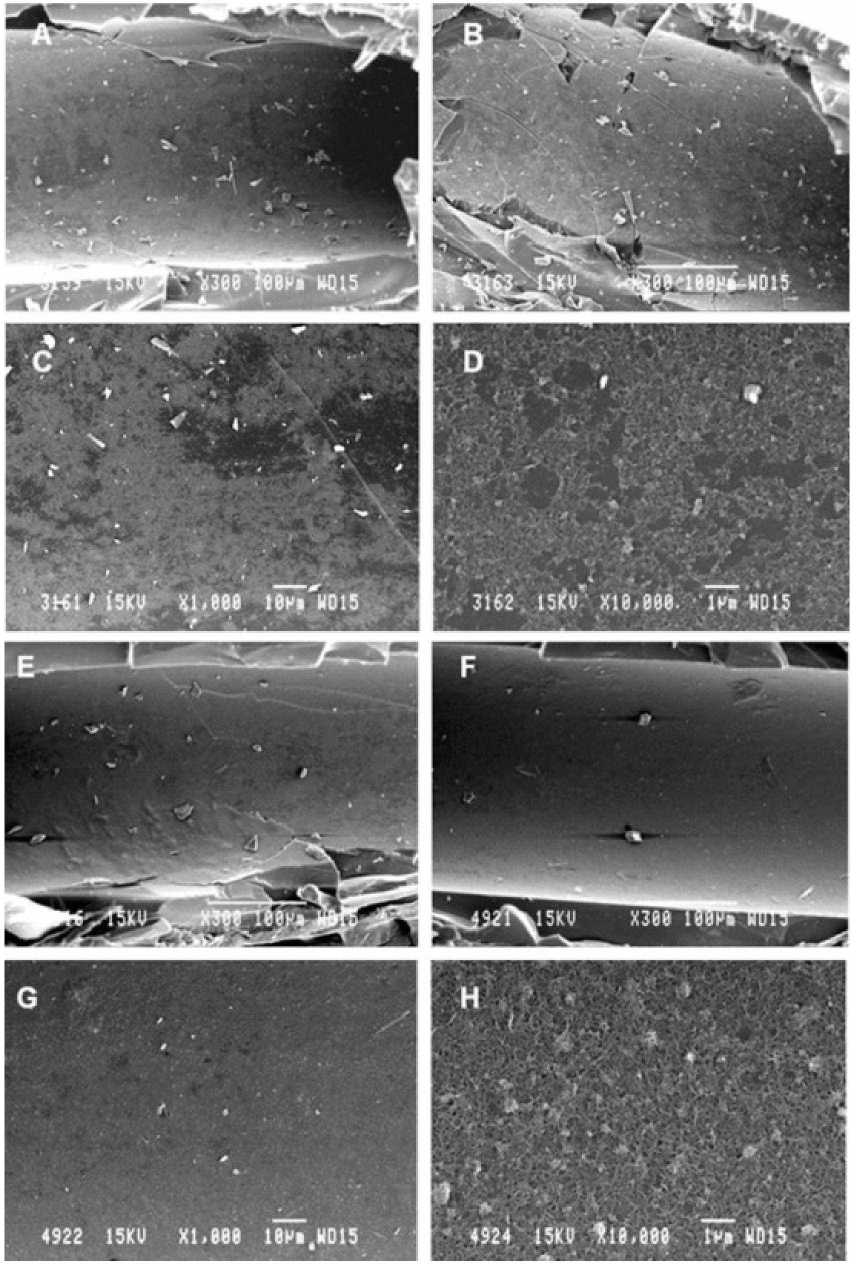

Fig. 4 SEM images of the inner wall of *f*MWCNT (A–D) and *f*MWCNT-Pd (E–H) coated capillary tubes. Silica splinters (sharp-edged fragments) and fractures are artifacts produced as a result of the incision with the scalpel blade.

A thorough microscopic analysis along the main axis did not display significant changes in the CNT deposit as a function of the distance to the bottom of the cell. Fig. 4A and ~~4~~B feature two spots from the capillary separated by 10 cm with almost identical coverage.

The same procedure was repeated with a dispersion of *f*MWCNT-Pd. The coverage featured by the SEM images (Fig. 4, ~~-~~E~~-~~–H) is slightly higher than that of the bare *f*MWCNT, rendering an almost homogeneous coating of at least one monolayer thick. This improvement may be related to the 4-fold increase (0.9~~to~~–3.9 mg · mL^{-1}) in the concentration of the *f*MWCNT in water when loaded with palladium nanoparticles, as evidenced from the UV–Vis analysis of the samples (Fig. 5). This increase in maximum dispersion of the MWCNT was probably due to the presence of the capping agent poly(*n*-vynilpyrrolidone) (PVP) that protects the nanoparticles from aggregation. It should be highlighted that for a good coverage of the capillary tube, working electrolyte solutions should be as concentrated as possible, thus the necessity of increasing the amount of surface oxygen-containing groups of the starting material.

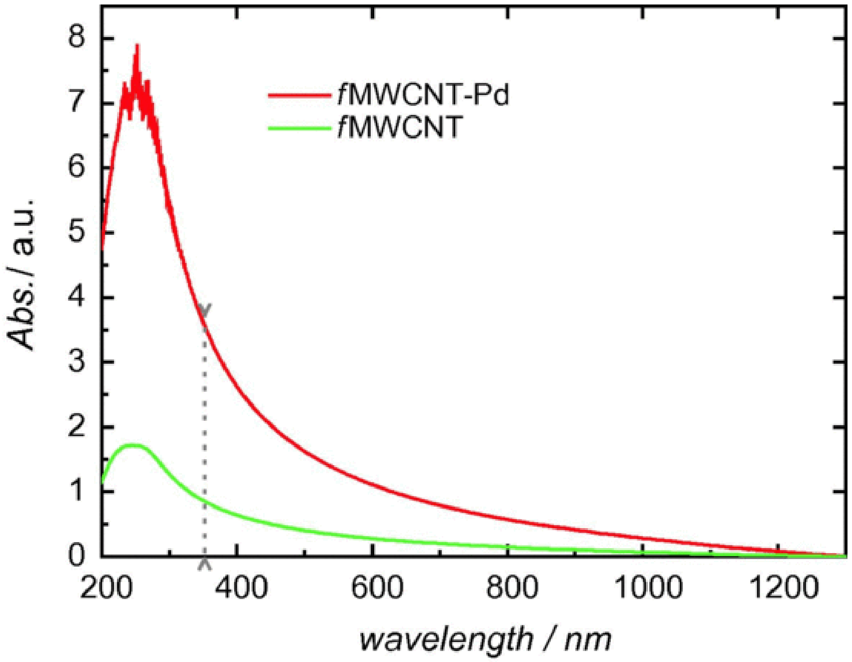

Fig. 5 UV–Vis–NIR spectra of the different stable CNT dispersions employed in the present study, after 1:35 dilution in water. The difference between the absorbance at 1300 nm (baseline) and 350 nm was used as the indicative parameter. (A color version of this figure can be viewed online.)

It must be noted that for comparison purposes, the same electroassisted deposition process was applied to a conventional conductive support (flat ITO glass). After undergoing deposition under the same conditions as those described in this study, a continuous deposit of CNTs was observed on the surface of the glass slide (results not shown). Moreover, using this configuration the CNT assisted-electrodeposi~~o~~tion could be obtained at voltages as low as 2 V, as reported by Aziz and Yang [31]. In this respect, the use of comparatively high voltages is necessary when using the fused silica capillaries due to their being insulating materials.

SEM offers valuable qualitative information about the degree of immobilization and distribution of CNTs on the silica walls. Nevertheless, a quantification of the amount of CNTs inside the capillary using Air-TG was also attempted. As the flexible polyimide coating found over the silica capillary could also be oxidized at the same temperature range of the CNTs, its removal is critical to avoid misassignments. In order to do this, the electrochemically-assisted deposition was performed as described previously, but using a silica capillary tube where the polymer coating had been carefully burned off with a conventional flame burner. After deposition, a 10 mg sample of the capillary tube was cut into small segments of few mm. The conditions and the equipment for TG-MS were the same as for the TPD except for the injected gas, replaced now by synthetic air (H_2O and $CO_2 < 5$ ppm). A clear increase for the CO_2 MS-signal was observed in the region between 500 and 700 °C, Fig. 6. A control experiment performed with a polyimide-free capillary tube in the absence of the CNT deposit clearly shows that the previously found CO_2 desorption must be due to the combustion of the CNT coating. The area under the peak was quantified giving a 0.023~~-~~ wt% for the CNT deposit related to the total mass of the coated capillary tube.

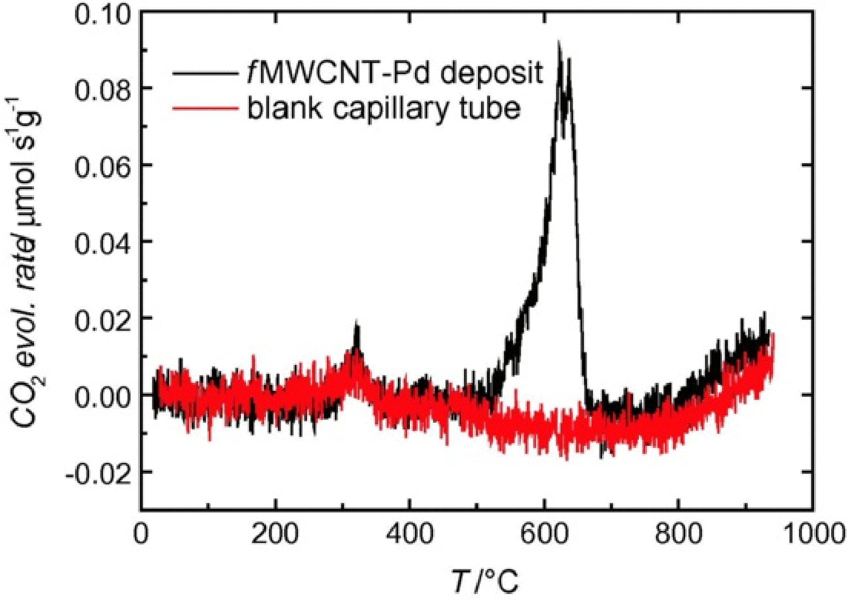

Fig. 6 CO_2 desorption rate profile as a function of the temperature, during the combustion of silica capillary tubes in synthetic air. (A color version of this figure can be viewed online.)

The pristine MWCNT used in the present study are known to cover a geometric area of about 80~~-~~ m^2 g^{-1}, leading to an estimated coverage value of 0.250~~-~~ cm^2 per 1 cm length (pcl). To put these figures into context it must be emphasized that the specific surface of the inner wall of the capillary tube is just 0.078~~-~~ cm^2 pcl, which would mean that the method reported in this study can deliver a coating of MWCNT with an estimated thickness of three monolayers.

In order to properly test the homogeneity and coherence of the CNT deposit, cyclic voltammetry was performed inside the capillary tube using the CNT layer as the working electrode (WE) in a 3 electrode-electrochemical cell. By filling the capillary with growing amounts of electrolyte solution a broadening in the double layer of the cyclic voltammogram was observed, Fig. 7. This is due to an increase in the WE surface area immersed in the electrolyte. In addition, quantification of the broadening registered at 1.05 V, rendered average current values of 13.3, 23.5 and 35.6 nA for electrolyte filling levels of 2, 4 and 6 cm, respectively. The increase in the area immersed follows a 1:~~-~~1.8:~~-~~2.7 ratio as the electrolyte level is increased inside the capillary, confirming that the distribution of the CNTs along the tube surface is homogeneous, with a slight enrichment at the lower section of the capillary. ~~The elongationshifting of the voltammograms towards lower intensities below 0.5 V as the capillary length is increased may be related to CNT agglomeration (this may arise from diffusional limitations), which would be a direct result of the deposition method reported in this study (vide supra).~~

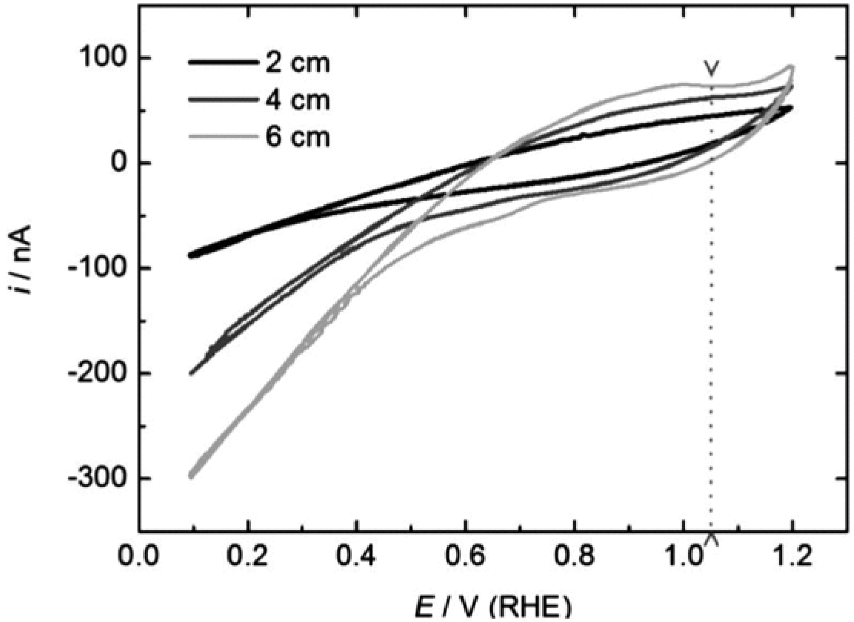

Fig. 7 Cyclic voltammograms obtained in 0.5 M H_2SO_4 for the capillary tube coated with *f*MWCNT-Pd, for increasing levels of the electrolyte inside the tube. Scan rate of 10 mV s^{-1}.

Finally the adherence of the *f*MWCNT coating to the silica wall in hydrodynamic conditions was studied. These preliminary tests consist in flowing water aliquots through the *f*MWCNT and *f*MWCNT-Pd modified capillary tubes at a controlled rate (10 mL s^{-1} ≡ 4 m s^{-1}). Each capillary segment was treated with nearly 10^4 times its inner volume. SEM images obtained after the treatment showed non-significant CNT loss in either *f*MWCNT or *f*MWCNT-Pd coated capillary tubes, Fig. 8. As no large parts of the deposit were missing, UV–Vis spectroscopic analysis of water aliquots was employed in order to trace the possible dispersion of individual nanotubes or small bundles. The π-plasmon MWCNT characteristic signal centered at 245 nm was absent in all cases, suggesting that CNT concentration in the aliquot must fall below the detection limit of the technique, experimentally determined to be 10 ng mL^{-1}. According to these results CNT leaching beyond 2 wt% under harsh hydrodynamic conditions can be ruled out. This method can be listed as environmental-friendly as organic solvents are not required and no significant MWCNT leaching from the coating takes place.

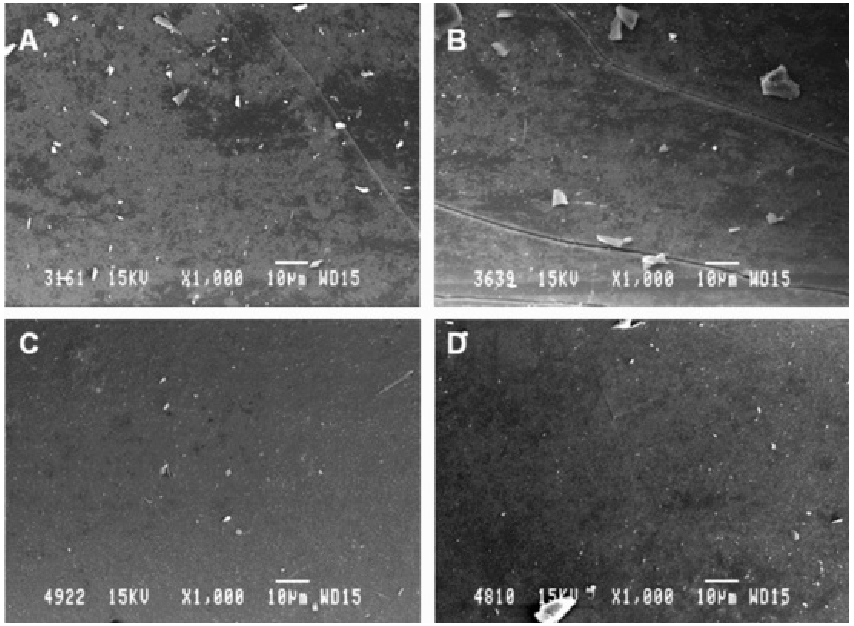

Fig. 8 SEM images corresponding to fused silica capillary tubes coated with *f*MWCNT before (A) and after (B) the hydrodynamic treatment, and with *f*MWCNT-Pd before (C) and after (D) the same treatment.

4 Conclusion

In summary, a simple, robust and innovative electrochemically-assisted method for the generation of homogeneous CNT coatings inside fused-silica capillary tubes has been demonstrated using a very simple principle (aggregation–deposition of CNTs when submitted to a pH change) and readily-available instrumentation. Due to the simplicity of the operational principles, CNT-supported-catalysts can be easily prepared as coatings too. While no pre-treatment of the target surface was required, this method may be applied to complex reactor architectures and avoids problems derived from the use of high temperatures required for CVD. Unlike for EPD, insulating materials and closed micro-conducts are perfectly suited substrates for CNT deposition. This method can be listed as environmental-friendly as organic solvents are not required and no significant MWCNT leaching from the coating takes place, even under harsh hydrodynamic conditions. The possible use of SWCNT, scalability and production of thicker coatings are the matter of ongoing research but the simplicity of the present strategy offers good prospects for all these purposes.

Acknowledgments

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