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Rapid purification/oxidation of multi-walled carbon nanotubes under 300 kHz-ultrasound and microwave irradiation†

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The use of ultrasound (US) and microwaves (MW) in the oxidation and purification of multi-walled carbon nanotubes (MWCNTs) was investigated. These techniques, in particular US at a frequency of 300 kHz, strongly accelerate the process and avoid the heavy structural damage, observed at the 20–35 kHz classic range, even at low power. Due to the residual metal catalyst on the head of MWCNTs, MW heating is strongly absorbed, causing the rupture of the tip and the loss of the metal. All our chemico-physical treatment types were performed by suspending the CNTs in a 3:1 H_2SO_4/HNO_3 mixture. The resulting samples were investigated by TEM microscopy, TGA analyses and Raman spectroscopy, while the degree of oxidation was estimated by colourimetric analyses.

Introduction

The exceptional interest in single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs respectively) resides in their possible technological applications in many fields like as gas adsorbents, templates, actuators, composite reinforcement, catalyst support, probes, chemical sensors, nanopipes and nano-reactors.[1,2,3] In particular, the potential applications of CNTs in medicinal chemistry are of great interest given their capacity to interact with macromolecules such as proteins and oligosaccharides.[4,5] The main difficulty with regards to the integration of such materials into biological systems is derived from their lack of solubility in physiological solutions. Different methods have been proposed to address the problem of their solubility in water.[6,7]

It is known that diluted acid solutions (e.g. HCl) remove the metal catalyst, but preserve the structure of the CNTs,[8] while strong oxidizing agents (e.g. HNO_3) cause the formation of defects, leading to the formation of oxygen-containing groups, such as hydroxyl, ether, quinone and carboxylate groups on the tube walls via covalent functionalization.[9,10] Oxidized CNTs can be functionalized at their carboxylic groups, through elaborate methods, which allow to attach organic moieties directly onto the nanotube sidewalls through

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cycloaddition, electrophilic, nucleophilic or radical addition, attaching of dichlorocarbene and polymerization techniques.[11]

The research on non-conventional techniques such as ultrasounds (US) and microwaves (MW) in the synthesis and modification of CNTs has been thorough. Recent literature reports on the advantages and drawbacks of sonication[12] and dielectric heating[13,14] on carbon materials. Although the mechanism of CNTs/MW interaction has not yet been completely understood, MW have been widely used for the purification of raw CNTs, for their oxidation or to provide a reactive environment to promote further functionalization.[13,15]

As far as the oxidation of CNTs surfaces is concerned, high-energy US may cause serious damages and produce bundles of carbon ribbons together with amorphous carbon nanoparticles. As a matter of fact, US frequency was found to be a critical parameter in sonochemical action. It can affect cavitation in several ways: by modifying bubbles size and number, cavitation threshold, and the temperatures reached during collapse.[16] Most CNT oxidations under US have been carried out at 20-35 kHz, a condition that maximizes the mechanical effect causing many ruptures in carbon structures. However, irradiation around 300 kHz reduces the dimension of cavitation bubbles and consequent mechanical CNT structure damages. Its higher oxidative capacity can be attributed to a greater generation of free radicals.[17,18,19]

In this work the effectiveness of the Mitsui MWCNTs oxidation under 300 kHz irradiation will be highlighted.

Experimental

For US treatment we employed two specific pieces of equipment: namely a US-probe with a Pyrex® horn (20 kHz) inserted inside a MW cavity (MicroSYNTH Milestone - Bergamo). This is a hybrid tool which has already been exploited for improved extractions[20] and fast digestion[21]. The high power cavitating tube for irradiation at 300 kHz showed in Figure 1, was successfully applied for advanced oxidation processes[19]. Both have been realized by Danacamerini (Torino) in collaboration with the corresponding author's group and are commercially available.

Figure 1. A high-power 300 kHz US-reactor with cooling system.

All chemicals were purchased from Sigma-Aldrich (solvents from Carlo Erba SpA) and were used without further purification. MWCNT were provided by Mitsui (Japan). Samples of Mitsui MWCNT were oxidized with a mixture of 3:1 concentrated H_2SO_4/HNO_3 under different techniques and conditions, namely MW, US and combined MW/US irradiation. After the oxidation treatment, the CNTs were washed several times with distilled water (at least 5 times) to achieve neutrality and then freeze dried. Such oxidized CNTs, placed in aqueous solution form stable suspensions for several days (5-7 days). The morphology of the samples was investigated by means of TEM (JEOL 3010-UHR instrument operating at 300 kV, equipped with a 2k x 2k pixels Gatan US1000 CCD camera) and AFM (Park Scientific Instrument Auto Probe LS) microscopies (see TOC). The surface properties were investigated by Raman spectroscopy. Raman spectra were acquired using an integrated confocal Raman system, which included a Horiba Jobin-Yvon HR800 microspectrometer, an Olympus BX41 microscope, and a CCD air-cooled detector operating at -70 °C. A polarized solid state Nd 80 mW laser operating at 532.11 nm was used as the excitation source. The software LabSpec 5 (Horiba Jobin-Yvon) was used to analyze the spectra.

The stability of the oxidized materials was investigated by thermogravimetric analyses under N2 flow (ramp, 10 °C/min) by TA instrument Q600 SDT Simultaneous DSC-TGA heat flow analyzer.

Result and discussion

According to HRTEM images, pristine MWCNTs, 10-15 μm in length and with external diameters of 20-100 nm, have a pronounced aspect ratio and are very straight and defect-free with a narrow, centered cavity of 2-10 nm, surrounded by regularly spaced walls with closed endings (Fig. 2a). It is worth noting that, due to the very high temperature of the annealing treatment (2000-2500 °C), catalyst nanoparticles vaporize and disappear from the inner cavity of the nanotubes to form metal aggregates, hundreds of nanometers in size, which are rarely dispersed in CNT bundles (data not shown for the sake of brevity). The external motif shows a peculiar amorphous layer which is a few nm thick (Inset of Fig. 2a). A Raman spectrum of the pristine sample confirms the high-crystallinity, the high-quality together with the defect-free properties (Fig. 2a'). In this figure, the well spaced characteristic first order D and G bands with maxima at 1351 cm^{-1} and 1577 cm^{-1}, are shown. Furthermore, the small shoulder at 1620 cm^{-1}, is ascribed to a disorder due to the finite particle size or lattice distorsion (D'-band).[22] Therefore, the high crystalline MWCNTs were treated by wet chemistry under MW and/or US irradiation at specifically selected power and for a suitable treatment time and compared with pristine untreated MWCNTs. The aim of this treatment was to induce local defectivity, but to preserve the CNT structure integrity. As it is widely recognized, the formation of defects gives rise to covalent functionalization.[23]

The sonication and/or microwave treatments in 3:1 H_2SO_4/HNO_3 solutions may selectively affect the crystalline order of samples, by removing the external (amorphous), by making in general the surface structures more reactive and finally by altering the internal carbon structure integrity (more crystalline phase). It is interesting to note that the MW irradiation treatment gives rise to selective ruptures of CNT endings, which act as antennas that can cause local superheating (Fig. 2b).

The characteristic crystallinity is almost preserved and the removal of the amorphous external layer is quite complete (inset of HRTEM image in Fig. 2b). The Raman spectrum of the samples (Fig. 2b') shows an increased ID/IG band ratio (see Fig. 2b'), which confirms the partial formation of defects.

The combined MW/US 20 kHz irradiations entirely remove the amorphous layer on the surface, as well as cause a considerable destruction of the multiwalled structures favoring longitudinal ruptures among internal walls, with formation of new channels along the carbon nanotubes axis (see arrows in Fig. 2c). The more drastic effects on the structure integrity are confirmed by the increased band ratio ID/IG (Fig. 2c')

US irradiation at 20 kHz produces strong mechanical action (Fig. 2d). Even if the CNT endings are preserved, the amorphous layer is rather removed (inset in top right part of Fig. 2d) and graphene sheet fragments are formed by the external local exfoliation of the carbon nanotubes (see arrows in the bottom part of Fig. 2d). In addition, longitudinal breaks in the internal structure give rise to new internal cavities generated along the nanotube axis between neighbouring walls (inset in top right part of Fig. 2d). The defect formation under more severe conditions are confirmed by the Raman spectrum shown in Fig. 2d', where the highest ID/IG band ratio was observed. The shoulder at 1615 cm^{-1} (D' band) is much more defined. Finally HRTEM images of the sample sonicated at 300 kHz are reported in Fig. 2e. In this figure, the end of a CNT is shown. The overall structure of the nanotube was preserved and the amorphous external layer was almost completely removed (inset of Fig. 2e). The Raman spectrum shown in Fig. 2e' confirms the high integrity of CNTs from the reduced ID/IG band ratio and the low intensity of the shoulder at 1617 cm^{-1}. On the basis of the effects produced by the different treatments shown in Fig. 2, we can state that sonication performed at 300 kHz preserves the integrity of the

CNT structure, while the 20 kHz sonication causes the most disastrous effects, namely damage to the resulting wall stacking and formation of some graphene sheet portions.
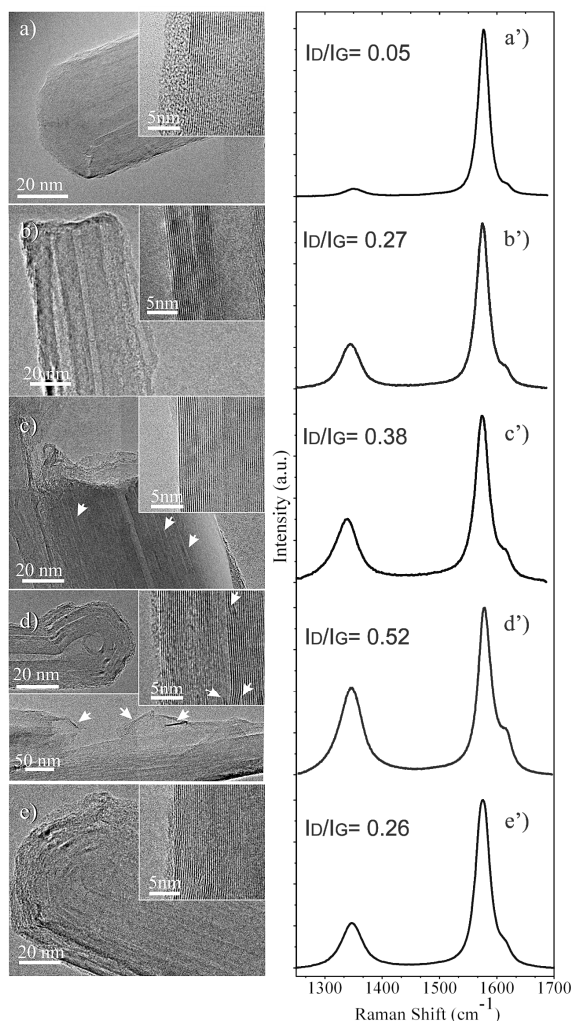

Figure 2. TEM images (left part) and Raman spectra (right part) of MWCNTs treated under different techniques (Tab. 1): a/a' pristine MWCNTs; b/b' MW; c/c' sequential MW/US 20 kHz; d/d' US 20 kHz; e/e' US 300 kHz, respectively. The arrows shown in the insets of figure 3d show the resulting stacking faults (inset top part) and graphene sheet fragments.

Consistent with previous report by some of us[24] (Turci et al, 2010), ultrasound in heterogeneous systems may act on suspended particles through two different cavitation mechanisms, depending on US resonance frequency and particle size.[25] When operated at 20 kHz, the impact of US on CNTs is firstly mechanical in nature. On the other hand, higher frequency reduces the mechanical stress, favouring the formation of highly reactive species, usually radicals.
Conversely, the effects of MW treatments are localized on the nanotube endings, where, apart from the removal of the caps, the structure maintains a high degree of integrity.
Thermogravimetric analyses (TGA/DTGA) of samples made under N_2 flow are shown in Figure 3. In the top part of this figure, the weight loss of the treated samples are compared with those of the pristine MWCNTs. DTGA plots are illustrated in the bottom part of the plot. From these, several decomposition rate signals can be seen, in the 100-340°C, 350-550 °C ranges for all the samples.

According to some authors,[26] beside a weight loss centered around 100 °C associated with a release of physically desorbed water, two broad bands in the 200-550 °C interval are assigned to single and/or adjacent carboxylic and phenolic groups.
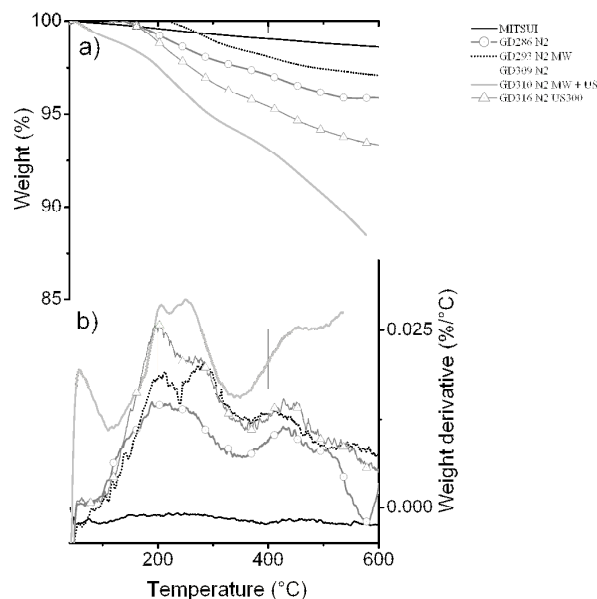

Figure 3. a) TGA and b) DTGA analysis of: pristine MWCNTs (black curves), samples treated under MW (black dotted curves), sequential MW/US 20 kHz treatments (gray curves), US 20 kHz (gray curves, circles) and 300 kHz sonication (gray curves, triangles).

When thionin acetate (THA) ethanolic solution (4.3 x 10^{-6} M) is added to a weighed sample of MWCNTs (ca. 2 mg), the purple color fades to colorlessness in function of the presence of carboxylic groups.[27] This cationic dye interacts with the negative charged surface of CNTs giving rise to either electrostatic bonds with carboxylic groups or unspecific hydrophobic interactions with the graphitic surface. A small decrease in color intensity was also observed, when the THA solution was mixed with pristine CNTs, used as a reference, showing that pristine CNTs have a tendency to adsorb thionin molecules unspecifically. The amount of fluorophore taken in by CNT was evaluated by comparing the difference after adsorption with the initial content of THA. The carboxylic group content was calculated by subtracting the amount due to unspecific interaction of equal weight of the corresponding non oxidized CNT sample, and considering 1:1 stoichiometry between THA cation and oxidized CNT carboxylated groups. It was expressed as mmol of -COOH/mg of oxidized CNTs. Time, power and temperature are showed in Table 1. The

amount of -COOH groups normalized per mg of oxidized CNT is reported in Figure 4. The thermal treatment within an oil bath induce the formation of ca. 4×10^{-5} mmol of -COOH groups per mg of CNTs.

A lower degree of oxidation was achieved using MW only and sequential MW and US power. A better result in terms of amount of –COOH (4.3×10^{-5} mmol/mg) was obtained with US only, operated at 20 kHz. Among the methods investigated, US operated at 300 kHz induced the highest formation of oxidized groups (5.3×10^{-5} mmol/mg), while the crystalline structure of CNTs was maintained quite unaltered (see TEM and Raman results).

Figure 4. Colorimetric assessment of -COOH groups on oxidized CNTs. The amount of oxidized functions is reported as mmol of -COOH per unit mass of nanotubes.
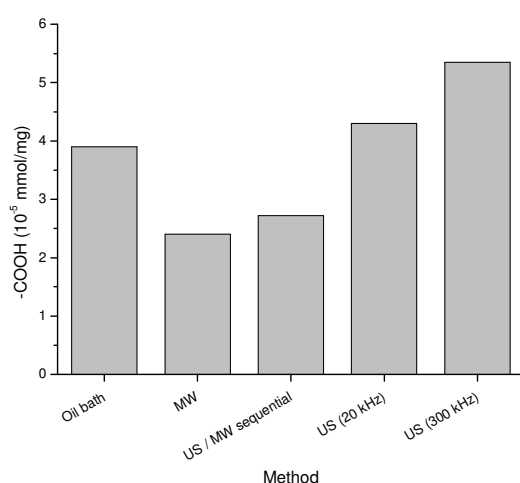

Table 1. General reaction conditions.

Entry	Method	Time (min)	Power (W)	T (°C)
1	Oil bath	40	-	60
2	MW	40	30	60
3	US/MW sequential[a]	10/40	30/40	60
4	US (20 kHz)[b]	45	50	45
5	US (300 kHz)	60	250	40

[a] Cooling system with circulating fluid. [b] Thermostatted bath.

Conclusions

In conclusion, we tested several non-conventional techniques (MW and/or US) for the fast oxidation and purification of MWCNTs in a H_2SO_4/HNO_3 mixture.

CNT oxidation occurs through surface modification, which depends on the degree of damage caused by the different types of irradiation. A thorough investigation by TEM showed the damage caused to the surface. After numerous tests, by varying methods, times and powers, we concluded that each selected procedure enabled CNT oxidation.

The Mitsui CNT structure is usually defects-free, with a characteristic amorphous layer, even if some activity towards water at room temperature has been also shown. It is interesting to note that MW irradiation caused the systematic rupture of the CNT tip, due to the higher metal concentration, the residual catalyst on which the CNT was grown, that caused superheating. On the other hand this procedure determined the efficient removal of metal catalysts. The resulting metal-free highly oxidized CNTs (-OH and -COOH on the surface) can be further functionalized for specific applications.

By comparing the colourimetric tests with the TEM/Raman and TGA analyses we can conclude that the effects of the US/MW treatments on MWCNTs can produce both surface and structure defectivity, constituted by carboxylic groups (topological defects) and line/planar defects (i.e. dislocations, stacking faults). Raman and TGA techniques give an indication of the average defectivity/functionalization, while TEM and colorimetric analyses are able to individuate more specific defectivities (structure and –COOH functional groups). From these results, we can state that upon oxidation conditions the formation of other surface functional groups, like phenolic and lactone groups (-OH, =O), is considerable.

Combined MW/US irradiation removed the amorphous layer, with the formation of defects favoring oxidation, but prolonged thermal treatment affected the surface until a point where the CNT was considerably damaged.

US irradiation at 20 kHz showed a marked mechanical effect, with the removal of the amorphous layer together with a partial breaking of the structure. The 300 kHz US allowed oxidation and maintained the structural integrity of oxidized CNTs. In other words it preserved the typical tubular shape with an excellent oxidation rate. In the light of recent sonochemical protocols for the fabrication and the modifications of graphene-like materials,[28] work is in progress to apply our findings in this emerging field.

Acknowledgment

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