Pulsed Laser Ablation Synthesis of Carbon Nano-Structures: Effect of Target Composition and Laser Ablation Condition on Their Yield and Morphology

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Abstract. This work is organized to provide a snapshot of our approach, achievements and understanding on the topic of carbon nano-particles, specifically carbon nano-onions and carbon nanotubes. The experiments have been performed employing a new and innovative laser ablation chamber design. The conditions for carbon nano-onions deposition, using excimer laser to ablate a commercial pure graphite target, are reviewed and confirmed by transmission electron microscopy analyses. We also reviewed results about UV laser ablation on metal doped carbon-based targets under different temperatures and laser pulse repetition rates to reveal the influence of the temperature and pulse frequency on the single wall carbon nanotubes synthesis and its yield.

1. Introduction

Carbon nano-particles have been intensively studied in the last decade due to their remarkable electronic and structural properties, which make them valuable for nanotechnology, magnetic storage materials, single electron devices, point source field emitters and electrochemical capacitors, and for their potential applications in advanced concepts for lubrication products [1]. Nowadays, carbon has been mimicked in the laboratory with the development of discrete chemical systems, such as fullerenes, *Carbon Nano-Onions* (CNOs) and *Carbon NanoTubes* (CNTs).

Carbon nano-onions, also *called Onions-Like Carbon* (OLCs), *Onion-Like Fullerenes* (OLFs), are a unique class of nanomaterials, often referred to as the zero-dimensional pendant to multi-wall carbon nanotubes.

A critical element for CNOs synthesis is to master the fabrication of high quality, reliable CNOs. Two techniques were mainly reported in literature for

fabrication of CNOs. The first of them, also called Kuznetsov method [2], reported the production of extremely pure CNOs in high yields by annealing carbon nanodiamond particles at temperatures above 1200°C. The second one, called Sano method [3], is reporting production of CNOs by arcing between two graphite electrodes under water. There are some drawbacks to these two methods. The main drawback is related to the fact that the CNOs obtained by these methods are quite different: small CNOs with 6–8 shells (5 nm) are obtained by Kuznetsov's method as compared with large CNOs of 20–30 shells and about 15–25 nm in the case of Sano's technique. Another drawback of these two methods is related to the apparatus involved in CNOs fabrication, which is very complex and highly specialized.

The recorded reports of carbon nanotubes (CNTs) belong from early '50 when the Russian researchers Radushkevich and Lukyanovich [4] reported first their observation. Later on 1976 the single (or double) walled carbon nanotubes were reported by Oberlin *et al.* [5].

The recent history of the CNTs start by 1991 when Sumio Ijima, from Nippon Electric Corporation (NEC) Research Laboratory in Japan, has been the first scientist who described the multiwalled carbon nanotubes (MWCNTs) preparation process after a random event during the test of a new arc evaporation method for C_{60} carbon molecule fabrication [6]. Two years later, in 1993, the first reports about the growth process of single walled carbon nanotubes (SWCNTs) are published almost simultaneously in two separate works from Iijima *et al.* and Bethune *et al.* [7, 8]. Since this time, the SWCNTs have been one of the hottest topics in both physics and material science.

The rolling of a single graphene layer, which is a hexagonal network of carbon atoms, led to form a single tube, *i.e.*, a SWCNT (Fig. 1). When two or more concentric tubes are placed one into another, MWCNTs are formed.



Fig. 1. Wrapping of graphene sheet to form SWCNT [7].

Due to remarkable electronic and structural properties, SWCNTs have started to revolutionize various applications areas, from electronics, electromagnetic devices, to composite materials and optics, to biomaterials and biomedical devices. Studies in biological and pharmaceutical fields were extensively reported by literature, proving that CNTs can act as a part of biosensors, drug and vaccine delivery vehicles [9, 10, 11, 12, 13, 14, 15, 16].

During the challenge of the wonderful world of CNTs several techniques were examined with the aim to produce high quality CNTs. Nowadays, three main synthesis methods are mastered on the CNTs production field: arc discharge, laser ablation and chemical vapor deposition (CVD).

In between them, the arc discharge and chemical vapor deposition methods are widely applied for the formation of MWCNTs. Many studies were made to improve either the quality or the quantity of the produced material by optimizing the synthesis process. As a result some types of CVD methods were discovered such as plasma-enhanced, microwave-enhanced, radiofrequency-enhanced CVD. Nowadays, the laser vaporization is the best reported method to grow high-quality, high-purity SWCNTs. The laser ablation technique favors the growth of higher purity SWCNTs (about 90% pure) with a better graphitized structure than those produced in the arc process. By this synthesis technique, the MWCNTs are generated only employing special reaction conditions.

Unfortunately, the growth of SWCNTs by laser vaporization is not yet fully controlled or fully understood. Thus, their potential technological applications, which depend on the growth rates and the possibility of large-scale production are affected by this lack of fundamental understanding.

This work is organized to provide a snapshot of our approach, achievements and our understanding on the topic of CNTs. Our approach consists in proposing a new design of the laser vaporization apparatus. The new design aim to eliminate the major drawbacks of the prior-art designs such as complexity and costs. The important role of the synthesis parameters is outlined. The results summarized in this work are essentially the studies from the last few years. While the level of our understanding accumulated during this period is vast, here is presented what are certainly the strongest achievements.

2. Synthesis Apparatus

The pulsed laser-ablation process for the production of single-wall carbon nanotubes was developed by Guo *et al.* [17].

Figure 2 depict a schematic of the oven laser-vaporization apparatus proposed by Guo's group.

Typically, a laser shot is directed to a carbon target (1) and vaporizes a small amount of material inside of an oven heated up to1200°C [17, 18, 19, 20]. During ablation, an uniform and smooth face for ablation is ensured by laser beam scanning across the target surface under computer control system. The soot produced by the laser vaporization is usually swept by the flowing working gas (Ar, N₂, etc.) from the high-temperature zone, and deposited onto a water-cooled copper collector (2) positioned outside the furnace.



Fig. 2. Schematic of the Guo synthesis apparatus for CNTs by laser ablation technique [17]. The key elements of apparatus are the ablation target (1), the water-cooled copper collector (2) and the quartz tube (3).

On a single laser shot, the vaporized material self-assembles to form a high volume fraction of SWCNTs.

One disadvantage of using this design of laser ablation apparatus is the small carbon deposit. The cause is a complex design of the reaction apparatus that also led to both difficult manipulation and expensive apparatus.

Noticeable improvements of the design for the laser ablation apparatus was recently reported by Enachescu's group [21, 22]. Figure 3 present a cut-away side view of the novel, experimental set-up by Enachescu's group for the laser ablation of the carbon targets. The laser ablation chamber consists of a quartz tube (2), 60 mm in diameter, mounted inside a hinged tube furnace (3). The temperature of the furnace can be varied from 30° C up to 1200° C and the quartz tube is O-ring sealed to ensure pressure control from 10^{-3} Torr up to atmospheric pressure.

The ablation gas is entering the chamber just after the quartz window (1), controlled by a flowmeter. The gas flow can be varied from 0 to 300 L/h. As novelty, the length of the oven has been increased to 675 mm compared to prior art reactor designs, of only 305 mm, which would ensure a quite constant temperature zone or a smaller temperature gradient inside the chamber.



Fig. 3. Chamber schematics: 1) Quartz laser window; 2) Quartz tube; 3) Electrical Oven;4) Target; 5) Graphite transfer rod; 6) Cold Finger; 7) Vacuum gauge.

Pulsed laser vaporization experiments were carried out using a Compex Pro 205 excimer laser from Coherent, operating with a wavelength of 248 nm, 25 ns pulse length and 10 Hz repetition rate. The laser beam was focused on a 20 mm² spot perpendicularly directed on a pure graphite commercial target surface. The pressure inside the reactor was fixed at 7 Torr while an Argon flow was kept at about 300L/h. The observed plume resulting from the laser interaction with the graphite target (4) was 20-30 mm long and the ablation products condensed on the water-cooled cold finger (6).

3. Target Composition

Already the first Guo's laser ablation experiments has pointed out that the composition of the target material is a crucial factor in the CNTs synthesis. The first used target was made of pure graphite, which was machined to be a cylinder. Previous reported results, including here our reported achievements, has demonstrated that laser ablation on a pure graphite targets yield fullerenes and nano-onions by laser ablation [23, 24, 25].

SWCNTs are obtained when simultaneously with carbon, a small percentage of catalyst transition metal are mixed. There are studies which has evaluated a series of mono- and bi-metal catalysts pointing-out that binary metal mixtures can significantly enhance SWCNTs yields [23, 24, 25].

Isolated SWCNTs were formed when monometallic Co or Ni/graphite target has been used. It was demonstrated that a high amounts of SWCNTs bundles are obtained applying bimetallic graphite catalyst Ni/Y (Yttrium) with the concentration of Ni always higher than that of Y, or Ni/Co in equal concentration [26, 27].

However, previous publications have focused on using targets that have been obtained by hot pressing, using Graphite Cement GC-8010B supplied by Metal Forming Lubricants, Inc. or pressing followed by temperature curing [23, 24, 25]. These methods are time consuming and usually more expensive. We have proposed a novel target preparation method that eliminates the need for pressing or hotpressing and the associated difficulties related to it. The novel preparation procedure involves mixing mono- and bi-metal catalysts powders (particle size $0.10-0.45 \mu m$) with the graphite cement. To our knowledge, carbon cement supplied by Dylon has been used with the addition of graphite powder [24]. Our preparation method did not include any additional graphite. The mixture was placed in a PTFE mold in which the 2 cm in diameter target is formed. The mixture was cured at 130°C for 4 hours. This ensures the reaction of the resin from the graphite cement. Finally, the target was removed from the mold and heated to 800°C for one hour in an inert atmosphere in order to remove the unreacted resin. The mass loss during the temperature treatments was 39%. This new method is very easy and straight forward to implement, with great results for SWCNTs synthesis.

The performance of the novel design for the laser ablation apparatus proposed by Enachescu's group have been highlighted by several experiments in details reported in scientific papers. As comparison, experiments in the same conditions as the ones reported in the literature by using a prior-art apparatus have been performed [28]. As in the Braidy experiments, the ablation setup was including an KrF excimer laser, producing 25 ns pulses at 248 nm with 100 to 700 mJ energy. The laser was focuses the laser beam on a 20 mm² rectangle spot on the target.

Two types of targets have been ablated in our new design of ablation reactor without the use of an inner tube: a pure graphite target and a Co/Pt doped cement target prepared by the new procedure proposed by Enachescu's group. It must be emphasized that except the preparation procedure, the Co/Pt doped cement targets used in both experiments have been of the same chemical composition. The ablation parameters for these targets are mentioned in Table 1.

Parameter	Pure graphite Target	Co/Pt doped cement target
Laser Energy	700 mJ	700 mJ
Pulse frequency	10 Hz	30 Hz
Temperature	900 °C	1100°C
Argon flow	300 L/h	250L/h
Pressure	10 Torr	500 Torr

Table 1. Ablation parameters

The collected products were studied using *Transmission Electron Microscope* (TEM) and *High Resolution Transmission Electron Microscopy* (HRTEM).

As depicted in Fig. 4, the products obtained by ablating the pure graphite, target look like very well-defined nano-particles, both individual and clustered. Isolated CNOs on the TEM experimental grid is a probabilistic difficult to catch due to the fact that many times the individual CNOs are dragged to form a cluster even in the solution deposited on the TEM grids. Statistic measurements show that they have diameters between 6–25 nm. The individual nano-particles are usually spherical and have a concentric shell structure.

On the other hand, as depicted by Fig. 5, the TEM and HRTEM images performed on the ablation products of the target with Co/Pt as catalysts make evidence of the presence of SWCNTs surrounded by amorphous carbon. Moreover, the presence of the catalyst can also be seen as nanoparticles a few nanometer in diameter. The nanotubes are isolated or bundled up. This is in accordance to the findings of Braidy's reported results on SWCNTs obtaining in similar ablation conditions but using a prior-art apparatus.



a)



Fig. 4. TEM and HRTEM images of the nano-onions obtained by ablating a pure graphite target at 700 mJ and 300 L/h.





Fig. 5. HRTEM image on SWCNTs obtained by the ablation of the Pt/Co doped target.

Further structural analysis has been performed by means of micro-Raman spectroscopy. In Fig. 6, a typical Raman spectrum of the products obtained by laser ablation of the pure graphite target is presented.



Fig. 6. Micro-Raman spectra of nano-onions obtained by laser ablation of graphite target.

The spectrum shows the presence of the D band centered at 1349 cm^{-1} and the G band with a maximum peak at 1592 cm^{-1} . The presence of the G band in the Raman spectra indicates sp² carbon hybridization while the D band is usually attributed to defect-induced Raman features [29].

The micro-Raman spectrum of the products obtained by laser ablation of the Co/Pt doped target is presented in Fig. 7 alongside the Raman spectrum of commercial SWCNTs from Sigma Aldrich, used as reference sample.



Fig. 7. Micro-Raman spectra of SWCNTs obtained by laser ablation of Co/Pt doped target.

The Raman spectrum shows 3 main bands. The first, centered at 164 cm⁻¹, is attributed to the *Radial Breathing Mode* (RBM) of the SWCNTs. The RBM corresponds to the vibration of the C atoms from the nanotube in the radial direction [28]. Another strong feature in the Raman spectrum is the G band with a maximum at 1589 cm⁻¹. The G band is characteristic for sp² carbon hybridization. The G band corresponds to the vibration of C atoms in the transversal and longitudinal direction [29]. A broad band centered at 1340 cm⁻¹ and usually named the D band is also present in the SWCNTs spectrum. This is characteristic for scattering from defect sites, *i.e.*, sp³ carbon hybridization. Previous studies show that the RBM peak for MWCNTs is too weak to be observable in the Raman spectra [29]. Thus, the RBM band centered at 164cm⁻¹ confirms that the nanotubes are single walled.

According to these results, the performances of the new laser ablation apparatus design for KrF excimer laser synthesis of carbon nanomaterials, including here nano-onions and carbon nano-tubes, has been well evidencieted *versus* prior-art apparatus [28].

4. Results and Discussions

In our studies, results about the morphologies and microstructure of un-purified ablation products, as collected after ablation of a pure graphite target were obtained by Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HRTEM) analysis.

As depicted in Fig. 8, the products look like well-defined carbon nano-onions (CNOs), both individual and clustered through an amorphous carbon matrix.



Fig. 8. Characteristic HRTEM micrograph of un-purified ablation products showing nano-onions like structures surrounded by an amorphous matrix.

Figure 9a) is showing a cluster of CNOs while the Fig. 9b) is showing just one CNO. It has to be understood that the CNOs are not bounded in the cluster and they are easy to be dispersed in an ultrasounds baths treatment done in distilled water. However, to catch just isolated CNOs on the TEM experimental grid is a probabilistic difficult process while many times the individual CNOs are dragged to form a cluster even in the solution deposited on the TEM grids. Usually, individual CNOs are obtained after functionalization treatments specially performed to avoid the electrostatically agglomeration of fabricated CNOs.





Fig. 9. HRTEM image of a) clustered CNOs and b) single CNOs.

Statistic measurements of the diameter of the observed CNOs were found in the range of 10 to 25 nm. The individual nano-onions are spherical and formed by 10-20 concentric shells. The graphitic interlayer distance of the CNOs was estimated in 10 different samples and the mean value was found to be 0.35 nm, as evidenced by the inset in Fig. 10, which is close to the ideal graphitic interlayer spacing [30].



Fig. 10. HRTEM micrograph showing the graphitic interlayer of the CNOs. The measurement of the interlayer distance is coming from the insert.

However, the structures that are observed in the HRTEM look like carbon onions with hollow core. As observed, no amorphous carbon can be found inside of the shell; thus pure carbon nano-onions have been obtained. As seen, the hollow core of the onion is regular and very small (less than 5 nm). The inter-atomic distance in between the carbon atoms was also measured in 10 different samples and the mean value was found to be 0.24 nm as evidenced by the inset in Fig. 11.



Fig. 11. HRTEM micrograph of a CNO used for calculation of the interatomic distance. The result of the measurement for the interatomic distance is presented in the insert.

TEM and HRTEM analysis have been performed on the ablation products obtained from graphite target doped with bi-component catalysts by Enachescu's group [31] (see Fig. 12). The SWCNTs are embedded within the amorphous carbon. The presence of the catalyst can also be seen as nanoparticles a few nanometer in diameter. The nanotubes are isolated or bundled up. This is in accordance to the findings of other groups on SWCNTs obtained by laser ablation [32, 33, 34].



a)

b)



Fig. 12. TEM a), b) and c) HRTEM image on SWCNTs obtained by the ablation of the bi-component doped target.

Thermo-Gravimetric Analysis (TGA) was used to measure the purity of the SWCNTs obtained. The weight loss of the collected products has been measured. The temperature was gradually increased by 5°C/min under furnace 21% Oxygen atmosphere at normal pressure. The mass loss versus temperature curve is presented in Fig. 13.



Fig. 13. Thermo-gravimetric analysis used to estimate the purity of synthesized SWCNTs.

The mass loss between 300°C and 450°C can be attributed to the oxidation of SWCNTs. The purity of the ablation can be estimated to be about 70%. The ablation byproducts are amorphous carbon that oxidizes at lower temperatures and catalyst nanoparticles covered in graphitic layers of carbon.

4. The Effect of the Laser Parameters

Generally, the effect of laser intensity and furnace temperature on diameter distribution, yield and physical characteristics of SWCNTs was extensively studied and documented in the literature [35, 36, 37].

One of the ablation parameters that has not been thoroughly documented is the laser pulse frequency, or repetition rate. Few attempts are reporting about the influence of the laser repetition rate and concluding that an increase from 1 to 30 Hz of a Nd:YAG laser pulse leads to a small decrease in the mean SWCNTs diameter: from 1.25 nm to 1.21 nm [38]. Similar results are reported when a laser ablation was performed using a KrF excimer laser (248 nm wavelength) and the repetition rate was increased from 30 Hz to 150 Hz [39]. According to these reported studies, the increase in repetition rate has led to an increase in the ratio of nanotubes with diameter 1.49nm compared to SWCNTs with a diameter of 1.22nm.

We compared TEM images of recorded ablation products obtained at 1100° C using a 248 nm wavelength KrF excimer laser operating at and 10, 30 and 50 Hz. The ablated target used for this studies was a Co/Ni doped target. The ablation environment inside the ablation reactor was consisting in an Argon flux of 250 L/h at a pressure of 500 Torr.

Characteristic TEM and HRTEM micrographs of our ablation products obtained

at 50 Hz show similar morphology with those for the ablation products at 10 Hz and 30 Hz respectively (see Fig. 14).



Fig. 14. TEM micrographs of the ablation products at 1100°C and a) 10Hz, c) 30 Hz and e) 50 Hz. The b), d) and f) images shows corresponding HRTEM micrograph on an individual SWCNT growth at 10Hz, 30 Hz and 50 Hz respectively.

f)

e)

The ablation products consist of SWCNTs bundles, amorphous carbon and catalyst nanoparticles. The obvious difference observable when comparing the three characteristic morphologies is the bundle size of the SWCNTs. At 50 Hz, the measured diameters of the bundles of SWCNTs are generally higher, ranging from a few nanometers up to 55 nm, triple in size as compared to the bundles found in the products obtained by laser ablation at 10 Hz and doubled compared to the bundles obtained by laser ablation at 30 Hz. It is obvious that a higher repetition rate enhances further the formation of larger bundles of nanotubes having a narrower diameter distribution. Such an enhancement is thought to be a consequence of the extra local heating of the target surface under high repetition rate conditions.

The micro-Raman spectroscopy analysis performed on ablations products from 10, 30 and 50 Hz repetition rate have shown that a higher repetition rate enhances further the formation of larger bundles of nanotubes having a narrower diameter distribution.

All the recorded spectra of the SWCNTs present in the ablation products presents two regions of interest. Fig. 15 shows the Raman spectra of the products obtained by the ablation at 10, 30 and 50 Hz.



Fig. 15. Low frequency Raman spectra on ablation products at 10, 30 and 50Hz using 532 nm excitation wavelength.

At low wavenumbers, 100 to 300 cm⁻¹ a band entitled the Radial Breathing Mode (RBM) is characteristic for SWCNTs. The Raman frequency in this region is inversely proportional to the SWCNTs diameter by the following equation:

$$\omega_{RBM} = \frac{c_1}{d} + c_2 \tag{1}$$

where ω_{RBM} is the radial breathing mode frequency (in cm⁻¹), d is the SWNT

diameter (in nm), c_1 and c_2 are constants with values of $c_1 = 215 \text{ cm}^{-1}$ and $c_2 = 18 \text{ cm}^{-1}$ respectively[40].

According to quotation (1) there are small variations between the products obtained at these three repetition rates pointing-out that the nanotube diameters are not influenced by the repetition rate used. The diameters calculated with the above equations are in the 1.3 to 1.5 nm range.

Figure 16 shows the high frequency region of the Raman spectra, 1200 to 1700 cm⁻¹, of the products obtained by ablation at 10, 30 and 50 Hz, and the D band centered at 1340 cm⁻¹ is observed. The second characteristic band present in the Raman spectra is centered on around 1600 cm⁻¹. This is the G band and its split can be observed. The lower frequency component of the G band is ascribed to vibrations along the circumferential direction of the nanotubes (G⁻) and it is attributed to resonance effect in metallic nanotubes. The other one, at higher frequency, is associated to vibrations along the direction of the nanotube axis (G⁺) and is associated with semiconducting nanotubes[41]. The high similarity of the G bands from the Raman spectra indicates that the electronic character of the SWCNTs in the sample was not influence by the laser repetition rate.



Fig. 16. High frequency Raman spectra on ablation products at 10, 30 and 50Hz using 532nm excitation wavelength.

5. The Effect of Temperature

It is a fact that all the work reported to date on the laser vaporization based synthesis of SWCNTs was carried out using lasers emitting either in the visible or in the infrared domains. There are not so many studies reported on the use of lasers emitting in the UV domain for the growth of SWCNTs. Braidy *et al.* have reported that for UV laser synthesis of SWCNTs the growth temperature is a key parameter that strongly favors the formation of the SWCNTs. According to their results, increasing the growth temperature from 550 to 1150°C is leading to higher yield of SWCNTs and an increase of the diameter distribution [32].

Our results, already published elsewhere [24], are confirming the Braidy findings: the increase in ablation temperature has led to an increase in SWCNTs productivity. This was visible from both the TEM and HRTEM micrographs and from Raman micro-spectroscopy.

Morphological characterizations of the products obtained consisting of TEM and HRTEM micrographs were obtained with a Phillips EM410 operating at 80 kV and a Jeol-ARM200F with a resolution of 0.2 nm and 0.11nm respectively. In Fig. 17 characteristic TEM micrographs of the ablation products at 700, 900 and 1100°C are presented.



Fig. 17. TEM micrographs of the ablation products obtained at a) 700°C; b) 900°C; c) 1100°C.

In Fig. 17 a) can be seen that the products resulted from the ablation carried out at 700°C consists mainly of amorphous carbon and catalyst particles. At 900°C (Fig. 17b), the TEM micrographs reveals the presence of small amounts of SWCNTs together to amorphous carbon and catalyst particles. At the highest used growing temperature, *e.g.*, 1100°C, the ablation yielded the highest purity of SWCNTs as visible from the TEM micrographs (see Fig. 17c). Micro-Raman spectra of the ablation products have been performed and characteristic spectra are presented in Fig. 18.



Fig. 18. Raman spectra of the ablation products obtained at 700, 900 and 1100°C with 532 nm excitation wavelength.

All the acquired spectra depict a maximum in the RBM band at around 188 cm⁻¹. A low intensity peak at 279 cm⁻¹ peak can also be seen in the spectrum from 700°C. Using equation (1), the SWCNTs diameters are calculated and the obtained values are ranging from 1.26 nm to 0.82 nm respectively. The spectrum of the products of the 900°C ablation presents three maximums in the RBM region, at 176, 183 and 190 cm⁻¹. The estimated diameter range for this interval would be between 1.25 and 1.36 nm. The RBM region from the Raman spectrum of the 1100°C ablation products presents two maximums at 164 cm⁻¹ and 183 cm⁻¹ which represents a diameter distribution from 1.3 nm to 1.5 nm.

As depicted by Fig. 18, to bands are visible at high frequency. The first one is the D band centered at around 1340 cm⁻¹. This band is usually attributed to the scattering on sp³ hybridized carbon atoms from defect sites and amorphous carbon. The second one, centered at around 1587cm⁻¹ is named G band and is characteristic for scattering on sp² hybridized carbon atoms. The ratio of the normalized intensity of these two bands is a good indication of the quality of the sample, *i.e.*, the higher D band intensity indicating more amorphous carbon or defects in the sample [41]. The I_G/I_D ratios for the 700, 900 and 1100°C samples are 1.5, 2.0 and 7.7, indicating a decrease in the amorphous carbon and/or defects in the ablation products obtained at higher temperatures. This is in good accordance with the TEM and HRTEM micrographs that show an increase in SWCNTs production with increasing the growing temperature.

6. Conclusions

Some of the most critical topics about the synthesis of carbon nano-structures by UV laser ablation process have been discussed. It was described in details how the target composition is influencing the type of nano-structures growth.

Synthesis of carbon nano-onions by UV laser vaporization technique on a pure graphite target, in a new laser ablation chamber design, using a KrF excimer laser have been discussed. HRTEM analysis shows that the synthesized CNOs were typically 25–30 nm in diameter. The observed individual nano-onions were spherically shaped and have a concentric shell structure, formed by 10-20 shells with a hollow core. The HRTEM images recorded on obtained ablation products look like well-defined nano-onions, both individual and clustered through an amorphous carbon matrix. Isolated CNOs on the TEM experimental grid is probabilistic difficult to catch due to the fact that many times the individual CNOs are dragged to form a cluster even in the solution deposited on the TEM grids.

The ablation of metal doped target has yielded SWCNTs, documented via TEM, micro-Raman spectroscopy, as well as TGA measurements. The new chamber demonstrated production up to 70% purity of the SWCNTs, showing that the new design of the ablation apparatus is suitable for SWCNTs production. The ablation of catalyst doped carbonaceous targets has been carried out at various

temperatures: 700, 900 and 1100°C, and repetition rates: 10, 30 and 50Hz. The influence of the temperature and repetition rate on the ablation products has been investigated with TEM and Raman-confocal micro-spectroscopy.

The increase in ablation temperature has led to an increase in SWCNTs productivity of about 70%.

This was visible from both the TEM and HRTEM micrographs and micro-Raman spectroscopy has been used to depict the way in which the target composition and the ablation conditions affects the carbon nanotubes formation and yield. TEM micrographs have made evidence of the fact that the amount of amorphous carbon decreases with increasing ablation temperature. Raman spectra of the ablation products have also shown that the average diameter of the obtained SWCNTs increases with increasing ablation temperature.

The SWCNTs bundle diameter has been shown to increase with the increase in laser repetition rate. The laser pulse frequency did not have an observable impact on the nanotube diameter under the ablation conditions used. The I_G/I_D ratios for the 700, 900 and 1100°C samples are 1.5, 2.0 and 7.7, indicating a decrease in the amorphous carbon and/or defects in the ablation products obtained at higher temperatures.

The purity of the SWCNTs in the ablation products has been shown to increase with increasing the laser pulse repetition rate.

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References

- K.W. STREET, M. MARCHETTI, R.L. VANDER WAL, A.J. TOMASEK, Tribol Lett, 16, pp. 143, 2004.
- [2] V.L. KUZNETSOV, A.L. CHUVILIN, Y.V. BUTENKO, I.Y. V.M. MALKOV, Titov, Chem. Phys. Lett., 222, pp. 343, 1994.
- [3] N. SANO, H. WANG, M. CHLOWALLA, I. ALEXANDROU, G.A.J. AMARATUNGA, Nature, 414, pp. 506, 2001.
- [4] L.V. RADUSHKEVICH and V.M. LUKYANOVICH, Zh. Fiz. Khim., 26, pp. 88, 1952.
- [5] A. OBERLIN, M. ENDO and T. KOYAMA, J. Cryst. Growth, **32**, pp. 335, 1976.
- [6] S. IIJIMA, Nature, **354**, pp. 56, 1991.
- [7] S. IIJIMA and T. ICHIHASHI, Nature, **363**, pp. 603, 1993.
- [8] D.S. BETHUNE, C.H. KIANG, M.S. DEVRIES, G. GORMAN, R. SAVOY, J. VAZQUEZ and R. BEYERS, Nature, 363, pp. 605, 1993.
- [9] B.T. YAKOBSON, R.E. SMALLEY, Am. Sci., 85, pp. 324, 1997.
- [10] V.N. POPOV, Mat. Sci. Eng. R: Reports, 43, pp. 61, 2004.

- [11] M. PARADISE, T. GOSWAMI, Mat. Design, 28, pp. 1477, 2007.
- [12] J.C. GRUNLUM, A.R. MEHRABI, M.V. BANNON, J.L. BAHR, Adv. Mat., 16, pp. 150, 2004.
- [13] P.R. SUPRONOWICZ, P.M. AJAYAN, K.R. ULLMAN, B.P. ARULANANDAM, D.W. METZGER, R. BIZIOS, J. Biomed. Mat. Res. A59, pp. 499, 2002.
- [14] H. KOERNER, G. PRICE, N.A. PEARCE, M. ALEXANDER, R.A. VARIA, Nature Mater., 3, pp. 115, 2004.
- [15] R. SEN, B. ZHAO, D. PEREA, M.E. ITKIS, H. HU, J. LOVE, E. BEKYAROVA, NanoLett., 4, 459, 2004.
- [16] Y. LIN, S. TAYLOR, H. LI, S.K.A. FERNANDO, L. QU, W. WANG, L. GU, B. ZHOU, Y.P. SUN, J. Mater. Chem., 14, pp. 527, 2004.
- [17] T. GUO, P. NIKOLAEV, A. THESS, D.T. COLBERT and R.E. SMALLEY, Chem. Phys. Lett., 236, pp. 419, 1995.
- [18] A. THESS, R. LEE, P. NIKOLAEV, H. DAI, P. PETIT, J. ROBERT, C. XU, Y.H. LEE, S.G. KIM, A.G. RINZLER, D.T. COLBERT, G.E.SCUSERIA, D. TOMANEK, J.E. FISHER, R.E. SMALLEY, Science, 273, pp. 483, 1996.
- [19] M. YUDASAKA, T. ICHIHASHI, T. KOMATSU and S. IIJIMA, Chem. Phys. Lett., 299, pp. 91, 1999.
- [20] A.G. RINZLER, J. LIU, H. DAI, P. NIKOLAEV, C.B. HUFFMAN, F.J. RODRIGUEZ-MACIAS, P.J. BOUL, A.H. LU, D. HEYMANN, D.T.COLBERT, R.S. LEE, J.E. FISHER, A.M. RAO, P.C. EKLUND, R.E. SMALLEY, Appl. Phys. A: Mater. Sci. Process., 67, pp. 29, 1998.
- [21] P.M. BOTA, D. DOROBANTU, I. BOERASU, D. BOJIN, M. ENACHESCU, Surface Engineering and Applied Electrochemistry, 50(2), 2014, (in press).
- [22] P.M. BOTA, D. DOROBANTU, D. BOJIN, M. ENACHESCU, accepted for publication in Materials Research Innovations, 2014.
- [23] S. IIJIMA, J. Cryst. Growth, 50, pp. 675, 1980.
- [24] T.W. EBBESEN, P.M. AJAYAN, Nature, **358**, pp. 220, 1992.
- [25] D. DOROBANTU, P.M. BOTA, I. BOERASU, D. BOJIN, M. ENACHESCU, Surface Engineering and Applied Electrochemistry, 50(3), 2014 (in press).
- [26] W.K. MASER, E. MUNOZ, A.M. BENITO, M.T. MARTÍNEZ, G.F. de la FUENTE, Y. MANIETTE, E. ANGLARET, J.-L. SAUVAJOL, Chem. Phys. Lett., 292, pp. 587, 1998.
- [27] W.K. MASER, A.M. BENITO, E. MUOZ, G.M. de VAL, M.T. MARTINEZ, A. LARREA, G.F. de la FUENTE, Nanotechnology, 12, pp. 147, 2001.
- [28] N. BRAIDY, M.A. EL KHAKANI, G.A. BOTTON, Chemical Physics Letters, **354**, pp. 88. 2002.
- [29] D. ROY, M. CHHOWALLA, H. WANG, N. SANO, I. ALEXANDROU, T.W. CLYNE, G.A.J. AMARATUNGA, Chem. Phys. Lett., 373, pp. 52, 2003.
- [30] G. RADHAKRISHNAN, P.M. ADAMS, F.D. ROSS, Journal of Physics: Conference Series, 59, pp. 424, 2007.
- [31] P.M. BOTA, D. DOROBANTU, I. BOERASU, D. BOJIN, M. ENACHESCU, Journal of Experimental Nanoscience, accepted for publication 2014.
- [32] G. RADHAKRISHNAN, P.M. ADAMS, L.S. BERNSTEIN, Appl. Surf. Sci., 253, pp. 7651, 2007.
- [33] A.A. PURETZKY, D.B. GEOHEGAN, X. FAN, S.J. PENNYCOOK, Appl. Phys. A70, pp. 153, 2000.
- [34] S. AREPALLI, P. NIKOLAEV, W HOLMES, S. BRADLEY, Appl. Phys. Lett., 78, pp. 11, 2001.
- [35] V. LE BORGNE, B. AISSA, M. MOHAMEDI, Y.A. KIM, MORINOBU ENDO, M.A. El KHAKANI, J Nanopart Res, 13, pp. 5759, 2011.
- [36] S. BACHILO, S. STRANO, C. KITTREL, R.E. SMALLEY, R.B. WEISMAN, Carbon. Nanotub Sci., 298, pp. 2361, 2002.

- [37] S. BANDOW, S. ASAKA, Y. SAITO, A.M. RAO, L. GRIGORIAN, E. RICHTER, P.C. EKLUND, Phys Rev Lett., **80**, pp. 3779, 1998.
- [38] O. JOST, A. GORBUNOV, L.C. CIACCHI, W. POMPE, X. LIU, T. PICHLER, L. DUNSCH, M.S. GOLDEN, J. FINK, in H. Kuzmany *et al.* (Ed.) AIP Conference Proceedings, **591**, 341, 2001.
- [39] N. BRAIDY, M.A. El KHAKANI, G.A. BOTTON, Chemical Physics Letters, **354**, pp. 88, 2002.
- [40] S.S. HARILAL, C.V. BINDHU, R.C. ISSAC, V.P.N. NAMPOORI, C.P.G. VALLABHAN, J. App. Phys., 82, pp. 2140, 1997.
- [41] A. JORIO, M.A. PIMENTA, A.G. SOUZA FILHO, R. SAITO, G. DRESSELHAUS, M.S. DRESSELHAUS, New Journal of Physics, 5, pp. 1391, 2003.