Pulse Laser Ablation System for Carbon Nano-Onions Fabrication

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A new laser ablation chamber design for KrF excimer laser synthesis of carbon nanomaterials, including nano-onions, is reported. The conditions for carbon nano-onions deposition, using excimer laser to ablate a commercial pure graphite target, were investigated. The transmission electron microscopy analysis of the collected deposits indicates that mainly nano-onions are obtained when pure graphite targets are ablated. Raman spectroscopy identified without doubt production of carbon nano-onions.

Keywords: laser ablation, carbon nano-onions, carbon nanotubes, carbon based nano-particles.

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INTRODUCTION

Carbon based nano-particles have been intensively studied in the last decade due to their remarkable electronic and structural properties, which makes them valuable for nanotechnology, magnetic storage materials, single electron devices, point source field emitters and electrochemical capacitors, as well as for their potential applications in advanced concepts for lubrication products [1–6]. Nowadays, carbon has been mimicked in the laboratory with the development of discrete chemical systems, such as the fullerenes, carbon nanotubes (CNT), and carbon nano-onions (CNO).

Carbon nano-onions, also called onion-like carbon (OLC), onion-like fullerenes (OLF), are a unique class of nanomaterial, often referred to as the zero-dimensional pendant to multi-wall carbon nanotubes.

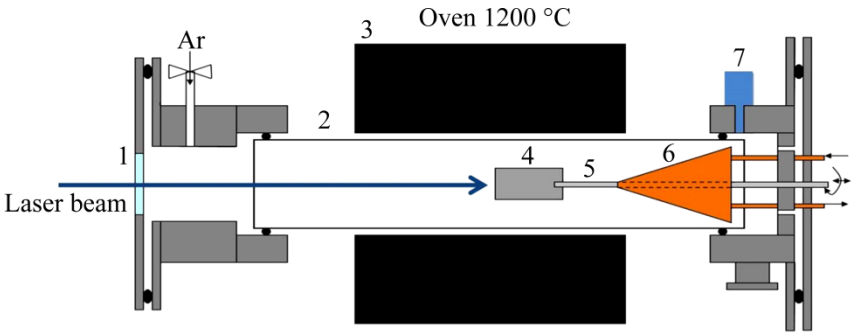
A critical element for CNOs synthesis is to master the fabrication of high quality, reliable CNOs. Various physical and chemical methods are reported for the synthesis of CNOs, such as arc discharge [7], laser ablation [8], plasma method [9], chemical vapor deposition (CVD) and high temperature annealing [10]. Two techniques were mainly reported in literature for fabrication of CNOs. The first of them, used in [11], reported the production of extremely pure CNOs in high yields by annealing carbon nano-diamond particles at temperatures above 1200°C. The second one, used in [12], reported the production of CNOs by arcing between two graphite electrodes under water. There are some drawbacks to both of these 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), obtained by the method in [11], as compared with large CNOs of 20–30 shells and about 15–25 nm, obtained by the method in [12]. Another drawback of these methods is related to the apparatus involved in the CNOs fabrication, which is very complex and highly specialized.

The recent developments of laser technologies offer unique opportunities for carbon nanostructures fabrication [13]. However, not many results have been reported so far on the use of laser emission in the UV domain for the growth of CNOs. Here we present a laser-assisted technique for fabricating high-quality CNOs by using an innovative design for the laser ablation chamber developed for the production of carbon nano-structures. This innovative chamber design is currently the subject of a patent application. The progress beyond state-of-the-art of the innovative chamber design related to the synthesis of high-quality single walled carbon nanotubes has been already presented elsewhere [14].

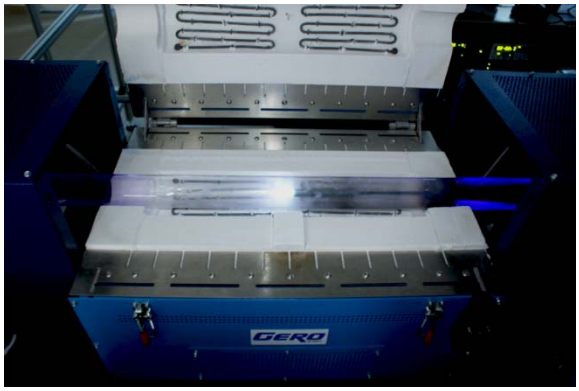
EXPERIMENTAL

Laser-assisted CNOs formation has been performed in a novel custom designed laser ablation chamber for carbon nano-structures synthesis by the UV laser vaporization. A scheme and photographs of the experimental set-up are presented in Fig. 1. Complete technical details about the novelty of the used ablation chamber are reported elsewhere, together with obtained progress beyond state-of-the-art [14]. Figure 1a present a cut-away side view of the novel, experimental set-up used in our research for the laser ablation of the 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 flow-meter (*7*). The flow can be varied from 0 to 300 L/h.



(a)



(b)

(c)

Fig. 1. Schematics and photograph of the novel laser ablation chamber design for KrF excimer laser: (a) Design of PLV system; (b) top view and (c) front view. Chamber schematics: 1 – Quartz laser window; 2 – Quartz tube; 3 – Electrical Oven; 4 – Target; 5 – Graphite transfer rod; 6 – Cold Finger; 7 – Vacuum gauge.

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. Figures 1b and c are photographs of the novel chamber after installation.

Pulsed laser vaporization experiments were carried out using a Compex Pro 205 excimer laser, operating with a wavelength of 248 nm, 25 ns pulse length and 10 Hz repetition rate. The laser beam was focused on a 20 mm^2 spot perpendicularly directed on a pure graphite commercial target surface. The pressure inside the reactor was fixed at 7 Torr, while the 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*). The temperature of the oven was kept constant at 900^{o}C during the entire experiment.

The samples for transmission electron microscopy (TEM) observations were prepared by sonicating the powdery products in distilled water for 15 min. Using a thin glass dropper, a droplet was collected from the solution and then the suspension was dropped onto a holey-carbon TEM grid. JEOL-ARM200F TEM equipment was used for the morphological and microstructural characterization of the ablation products.

Raman spectroscopy of unpurified ablation products was performed at room temperature using a Horiba LabRam 800 with an excitation wavelength of 532 nm, in the spectral range 100–2500 cm^{-1}.

RESULTS AND DISCUSSIONS

Characterization by Transmission electron microscopy

The morphologies and microstructure of unpurified CNOs as collected after ablation were observed by high-resolution transmission electron microscopy (HRTEM). As depicted in Fig. 2, the products obtained by ablating the pure graphite target look like well-defined nano-onions, both individual and clustered through an amorphous carbon matrix. Figure 3 is showing a cluster of CNOs, while Fig. 4 is showing just one CNO. It has to be understood that the CNOs are not bounded in the cluster and they can be easily dispersed under treatment in ultrasounds baths with 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.

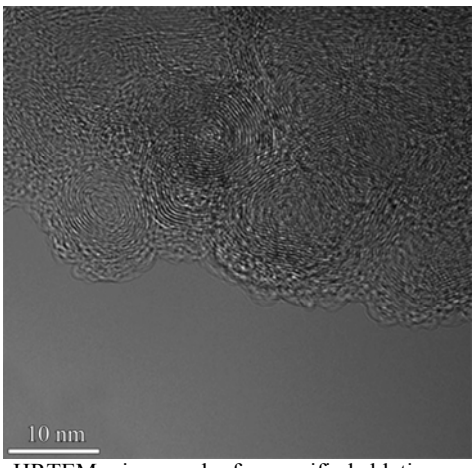


Fig. 2. HRTEM micrograph of un-purified ablation products.

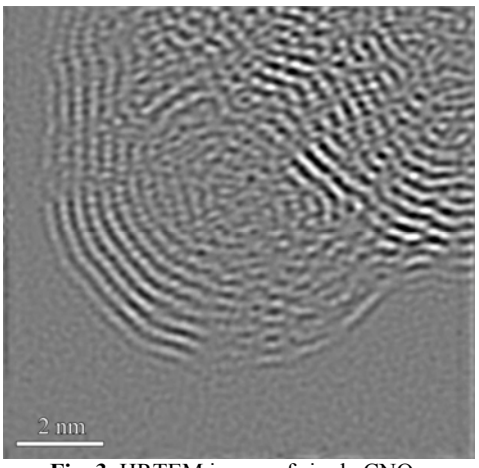


Fig. 3. HRTEM image of single CNOs.

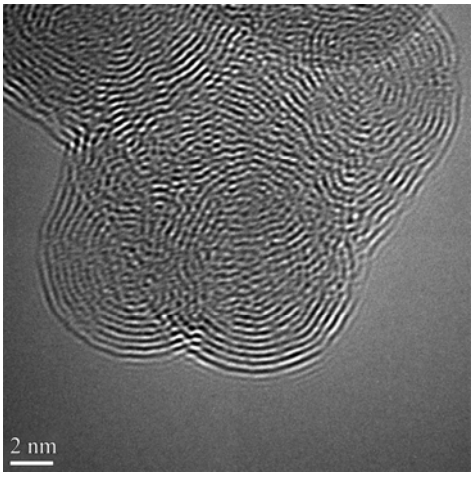


Fig. 4. HRTEM image of clustered CNOs.

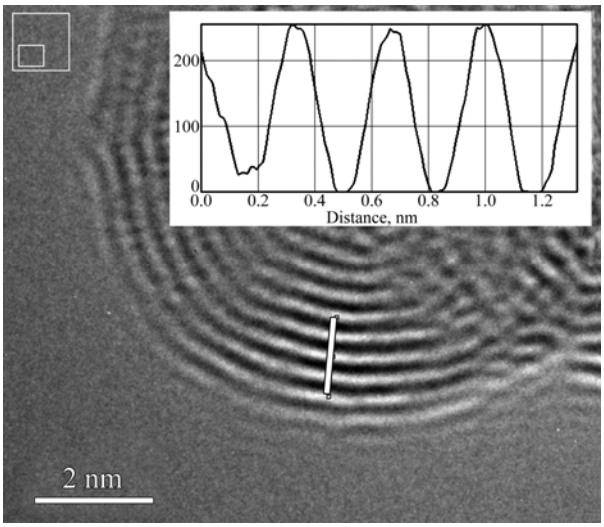


Fig. 5. HRTEM micrograph of the graphitic interlayer of the CNOs. The calculation of the interlayer distance is shown in the insert.

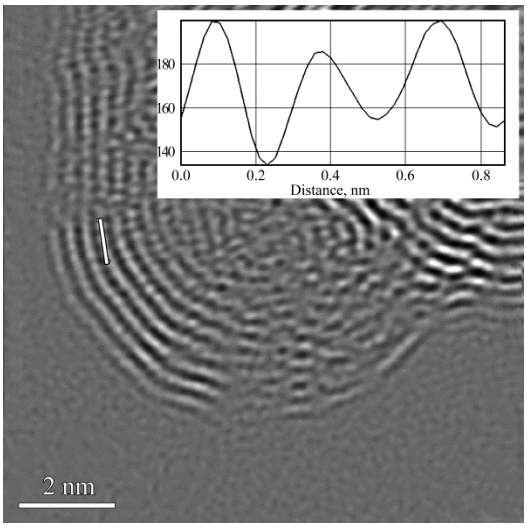


Fig. 6. HRTEM micrograph of the CNOs used for calculation of the interatomic distance. The result of the measurement for the interatomic distance is presented in the insert.

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 shell layers. 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. 5, which is close to the ideal graphitic interlayer spacing [15]. These structures are larger than the nano-onions synthesized by the technique as in [11] and similar to those reported by using the technique from [12]. However, the structures that are observed in the HRTEM look like carbon onions with a hollow core. As observed, no amorphous carbon can be found inside the shell; thus pure carbon nano-onions have been obtained. Hence, the

hollow core of the onion is regular and very small (less than 5 nm). The obtained CNOs are comparable with those obtained by the technique as in [12]. The interatomic 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. 6.

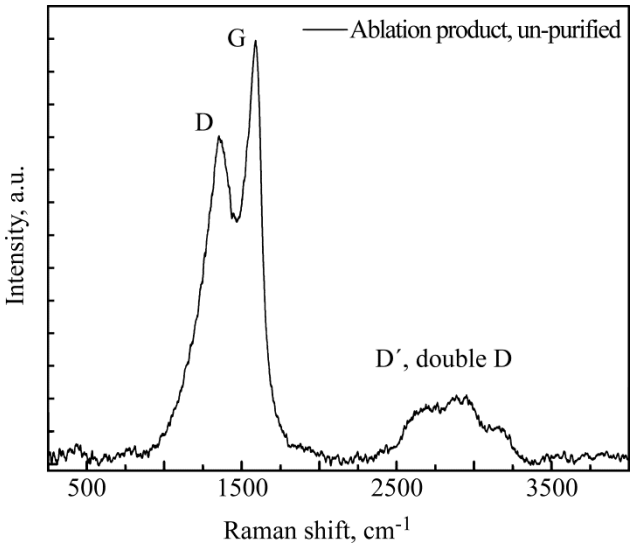


Fig. 7. Raman spectra of CNOs, with a 532 nm excitation wavelength.

Characterization by micro-Raman Spectroscopy

The quality of the synthesized carbon nano-onions was investigated by micro-Raman spectroscopy. A representative Raman spectrum of the un-purified carbon onions is shown in Fig. 7. Two broad peaks centered at about 1351 and 1589 cm^{-1} can be seen on the recorded Raman spectrum. The first Raman features, centered at 1351 cm^{-1}, are attributed to the *D* band, which indicates the vibration of carbon atoms with dangling bonds for atoms in a two dimensional hexagonal lattice [16]. The second observed Raman features from 1589 cm^{-1} are associated with the *G* band, which is attributed to sp^2 carbon networks formed by the bonded carbon atoms in a two-dimensional hexagonal lattice [16]. The observed Raman features in the range of 2500–3200 cm^{-1} (linear carbon chains) are attributed to sp^3 and *sp* carbon networks [17, 18]. The intensity ratio of *D* to *G* band (I_D/I_G), which implies the degree of the crystalline perfection, is calculated to be 0.63, which is in good agreement with the HRTEM observations. These values reveal that the CNOs synthesized by laser vaporization have a high crystallinity. The ratio of *D* and *G* band (I_D/I_G) is used in the empirical formula proposed by Pimenta to determine the in-plan crystallite size L_a [19]:

$$L_a = \frac{560}{E_{laser}^4}\left(\frac{I_D}{I_G}\right)^{-1}$$

$$L_a = \left(2.4\cdot 10^{-10}\right)\lambda_{laser}^4 \cdot \left(\frac{I_D}{I_G}\right)^{-1} \quad (1)$$

where E_{laser} is the excitation energy in eV (2.33).

Thus obtained L_a value is about 30 nm, which is in good agreement with those obtained by the TEM analysis (about 25 nm).

CONCLUSIONS

Carbon nano-onions have been successfully produced by the laser vaporization technique in a laser ablation chamber of the novel design using a KrF excimer laser. The HRTEM analysis shows that the collected CNOs are typically 10–25 nm in diameter. The observed individual nano-onions are spherically shaped and have a concentric shell structure, formed by 10–20 shells with a hollow core.

The HRTEM images recorded on the 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 a probabilistic difficult object to catch because many times individual CNOs are dragged to form a cluster even in the solution deposited on the TEM grids.

Micro-Raman analysis has been performed to evaluate the crystallite size of produced CNOs. Using Pimenta's formula, the obtained value for crystallite size has been found to be 30 nm, which is in good agreement with the values estimated by the HRTEM.

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Реферат

Представлена разработка новой камеры лазерной абляции для KrF-эксимерного лазера, используемого для синтеза наноматериалов, включая нанолуковицы (наночастицы, напоминающие луковицу). Изучены условия осаждения углеродных нанолуковиц при использовании эксимерного лазера для абляции стандартного чистого графита. Анализ материала с помощью трансмиссионной лазерной микроскопии показал, что нанолуковицы, главным образом, получают при лазерной абляции чистого графита. Рамановская спектроскопия, несомненно, подтвердила образование углеродных нанолуковиц.

Ключевые слова: лазерная абляция, углеродные нанолуковицы, углеродные нанотрубки, углеродные наночастицы.