

# PRODUCTION AND CHARACTERIZATION OF CARBON NANO-ONIONS BY LASER ABLATION

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**Abstract.** We report about the synthesis of carbon nano-onions (CNOs) by means of KrF excimer laser ablation. A pure graphite target has been ablated under a 300L/h flux of Argon. The products have been investigated by high resolution transmission electron microscopy (HRTEM) and Raman-confocal micro-spectroscopy. The laser synthesized CNOs, at a furnace temperature of 900°C, have a diameter distribution between 13nm and 25nm.

## 1. Introduction

The discovery of fullerenes [1] and carbon nanotubes [2] has sparked intensive efforts to produce and characterize different nano-structured carbon materials with unique properties.

Carbon nano-onions (CNOs) have been first discovered in 1992 [3] by intense electron beam irradiation of graphitic structures. The two main synthesis methods for CNOs have been the annealing of carbon nanodiamond particles at temperatures above 1200°C [4] and the arc-discharge between graphite electrodes under water [5].

Possible applications for CNOs include their use as lubricants or in the fabrication of supercapacitors. This has intensified the research for obtaining and characterizing CNOs.

Pulsed Laser Vaporization has been shown to produce CNOs using an excimer laser [6]. The ablation has been carried out at room temperature using a mixture of O<sub>2</sub> and Ar. The targets used were Co/Ni doped graphite and yielded CNOs and multi-wall carbon nanotubes (MWCNTs)

In the present work we report a successful synthesis of CNOs in a novel design ablation chamber. The laser employed in our experiments was a KrF excimer laser with 25ns pulses at 248nm. One of the main differences from previous studies consists in the target used as well as novel ablation chamber. Pure graphite and a target obtained from graphite cement have been shown to produce CNOs under ablation. The ablation gas used in our setup has been Argon as opposed to experiments performed with Oxygen.

## 2. Experimental

The custom designed laser ablation chamber, presented in figures 1 and 2, consists of a 1260mm long quartz tube, 60mm in diameter, placed inside an electrical oven. The 675mm long oven can control the temperature in the reactor from room temperature, up to 1200°C. The laser used was a Compex Pro 205 excimer laser from Coherent.

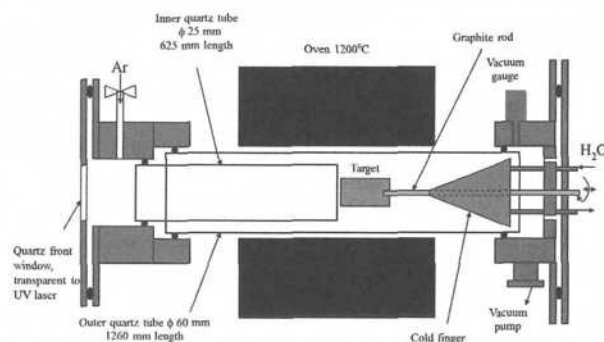


Figure 1. Side view of the experimental ablation reactor

The ablation reactor has several modifications in comparison to previous reactors used for laser ablation of carbonaceous targets. The quartz tube and oven have been designed longer so that a more uniform temperature is achieved in the reactor. The cold finger has also been elongated to 260mm in order to provide a big surface for the ablation products to condense onto, while having a temperature gradient of the cold finger.



Fig. 2. Photographs of the chamber: a) front view; b) top view; c) back view

The first target used was a graphite rod 120mm long and 20mm in diameter. The target is mounted on a graphite rod that keeps the target centred in the ablation chamber and transfers a rotational motion from an electric motor. The rotational motion ensures that the ablation takes place uniform on the entire surface of the target.

The second target has been prepared from Graphite Cement GC-8010B supplied by Metal Forming Lubricants, Inc. The graphite cement forms 100% carbonaceous bonds after temperature treatment. The mixture was placed in a PTFE mould in which the 20mm 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%. Both targets yielded similar results in the ablation conditions presented below.

The ablation was carried out for 1 hour at 900°C under a 300L/h flux of Argon. The pressure inside the ablation reactor was maintained at 500Torr with a rotary vane pump mounted at the back of the reactor. The laser was operated at 30Hz with a pulse energy of 600mJ.

The products collected from the cold finger were investigated by transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and Raman-confocal micro-spectroscopy. The TEM microscope was an EM-410 Philips microscope working with a 80kV acceleration voltage. The HRTEM micrographs were performed with a JEOL-ARM200F TEM equipment.

The TEM and HRTEM micrographs were performed on un-purified ablation products. These were collected from the cold finger and dispersed in ethanol after 30 minutes in an ultrasound bath.

The products have been investigated without any purification or processing by Raman micro-spectroscopy. The spectra were recorded with a Horiba LabRam800 Raman-confocal micro-spectrometer

### 3. Results

The micrographs presented in figure 3 show the presence of nanoparticles with diameters between 13nm and 25nm.

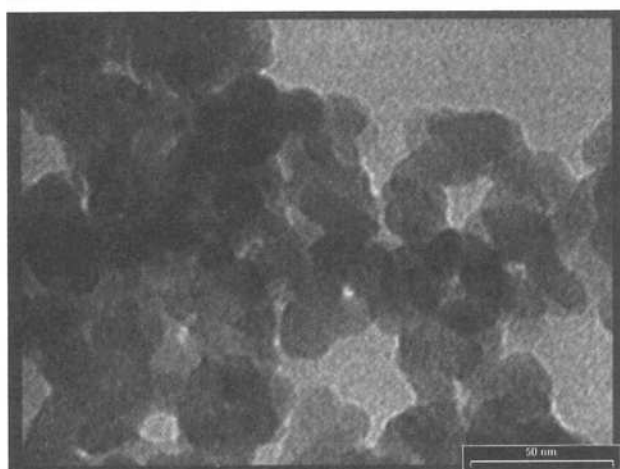


Figure 3. TEM micrograph of the ablation products.

In figure 4 a HRTEM micrograph confirms the concentric structure of the nano-onions. The interplanar distance was estimated about 0.34nm, as shown in figure 5.

The nanoparticles are not perfectly spherical and tend to agglomerate. Similar structures, named nano-onions, have been first reported by Ijima [7] as concentric shell structures with 3-5 nm in diameter.

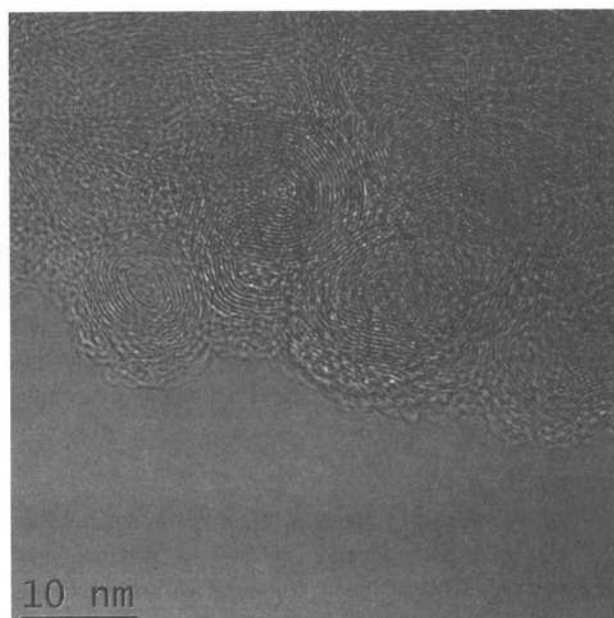


Figure 4. HRTEM micrograph on CNOs showing the concentric structure.

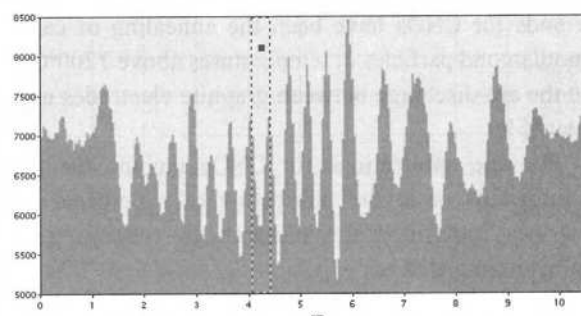


Figure 5. HRTEM measurements of the distance between the concentric graphitic planes.

The production of nano-onions and SWCNTs has also been confirmed by micro-Raman spectroscopy. Figure 6 presents the Raman spectrum, of the obtained products, in the 100cm<sup>-1</sup> to 2800cm<sup>-1</sup> region. The excitation wavelength has been 532nm.

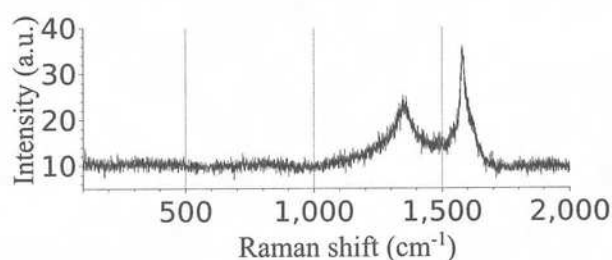


Figure 6. Raman spectrum of CNOs obtained by laser ablation.

The spectrum shows the presence of a broad band centred at 1349 cm<sup>-1</sup>. This band is called the D band and is characteristic for scattering on carbon atoms with sp<sup>3</sup> hybridization. Another prominent feature in the Raman spectrum is the G band with a maximum peak at 1592cm<sup>-1</sup>. The G band is attributed to scattering on sp<sup>2</sup> hybridized carbon atoms.

#### 4. Conclusions.

The chamber design used has been shown to be suitable for production of CNOs by laser ablation of graphite targets.

The CNOs obtained have been characterized by TEM, HRTEM and Raman-confocal micro-spectroscopy. The size of the obtained CNOs has been estimated by TEM and HRTEM to be between 13 and 25nm.

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