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Liquid Phase – Pulsed Laser Ablation: A route to fabricate different carbon nanostructures

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ABSTRACT

Carbon nanostructures in various forms and sizes, and with different speciation properties have been prepared from graphite by Liquid Phase – Pulsed Laser Ablation (LP-PLA) using a high frequency Nd:YAG laser. High energy densities and pulse repetition frequencies of up to 10 kHz were used in this ablation process to produce carbon nanomaterials with unique chemical structures. Dynamic Light Scattering (DLS), micro-Raman and High-Resolution Transmission Electron Microscopy (HRTEM) were used to confirm the size distribution, morphology, chemical bonding, and crystallinity of these nanostructures. This article demonstrates how the fabrication process affects measured characteristics of the produced carbon nanomaterials. The obtained particle properties have potential use for various applications including biochemical speciation applications.

1. Introduction

Over the last two decades, there has been a growing interest in developing efficient methods for production of carbon nanoparticles (CNPs) due to their vast array of applications including polymeric nanocomposites, functional fillers, super-capacitors, and water purification [1]. Pulsed laser ablation (PLA) is one of the well-known methods used to produce CNP [2]. This method has been widely studied within vacuum and controlled atmosphere. In the late nineties, the laser ablation of samples submerged within liquid media was utilised for colloidal nanoparticle suspension preparation. This process became known as the Liquid Phase – Pulsed Laser Ablation (LP-PLA). LP-PLA provides control over particle size and morphology, material allotropes, and functionalisation where organic solvents are used as liquid media. This approach does not produce any byproducts, is of low cost and is considered easier to implement compared to the more conventional use of controlled vacuum or gaseous media environments [3]. During the LP-PLA process, ablation plumes are produced at the laser–target interaction site, where the target surface and the surrounding liquid are vaporised forming micro-bubbles. The bubbles expand to reach a certain critical combination of pressure and temperature and then collapse [4,5]. Within the bubbles, the temperature reaches thousands of Kelvin and pressures in the range of kPa to several GPa are achieved, producing novel materials [3]. In previous works, LP-PLA was undertaken using a low pulse repetition frequency (PRF), typically in the range from 10 Hz to 30 Hz. In this study, the effect of using a Nd:YAG laser with a higher PRF in the range from 10 kHz to 14 kHz, and correspondingly an increased accumulated laser fluence (F) range, was investigated.

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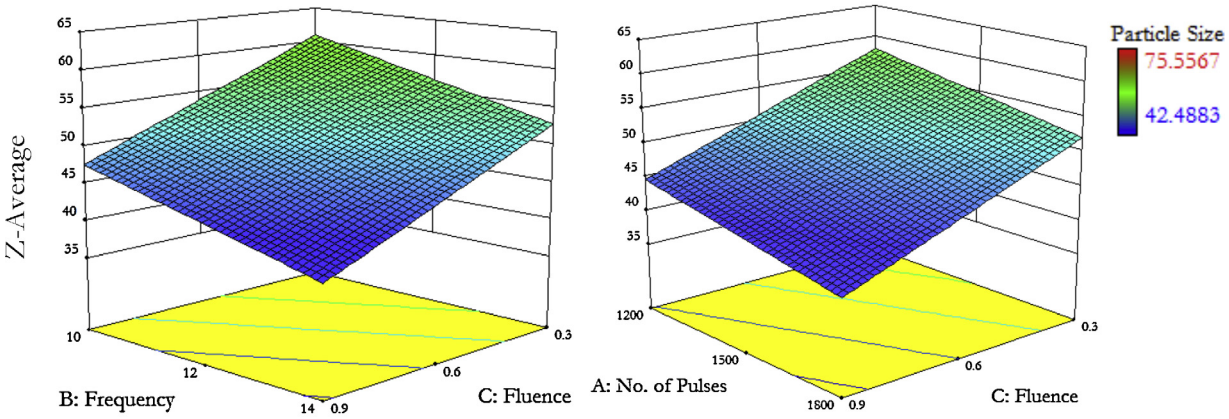

Fig. 1. Effects of number of pulses (N), PRF, and fluence (F) on fabricated particle sizes.

2. Materials and methods

Five millimetre diameter graphite rods of 300 mm length, MCCA medium grade, were obtained from Olmec Advanced Materials Ltd. The rods were cut to provide 6 mm lengths. A procedure for sample set-up before processing was composed of controlled steps to avoid possible contamination of the graphite rods. These steps were sample cleaning with deionised water, placement of the sample within the well plate reservoir which was 11 mm in height, filling of the well with deionised water, placement of a cleaned 200 μm thick slide of soda lime glass on top of the well plate, and then positioning of the sample onto the laser ablation stage mount. This left a 5 mm gap between the graphite rod surface and the glass surface. Then, an area of 3 mm × 3 mm was ablated from the graphite target using a WEDGE HF 1064 nm wavelength and 700 ps pulse width Nd:YAG laser.

Typically, breakdown of the carbon material with pulses of 700 ps will occur via avalanche ionisation. For pulse durations longer than a few tens of picoseconds, energy is transferred from the laser-excited electrons to the lattice on the time scale of the pulse duration. Avalanche ionisation is therefore very efficient for pulses longer than a few picoseconds because the long pulse duration allows more time for exponential growth of the electron density. This energy is carried out of the focal volume by thermal diffusion. Damage then occurs when the temperature of the material in the irradiated region becomes high enough for the material to melt or fracture. The electron temperature increases within a few tens of femtoseconds and the laser energy is transferred from electron-to-lattice typically on the order of 10 ps. After this and within the laser-supported combustion range of laser intensities, a plasma is formed above the workpiece which starts to shield the incident power from the material surface [6]. As this plasma expands radially, energy within the plasma is coupled to the surface. The calculation of exact energy quality transfer to the surface is therefore convoluted by these effects. Higher fluences however still be expected to lead to increased initial electron temperatures, higher energy diffusion through the workpiece, better coupling from plasma to the workpiece surface, and ultimately to higher energy transmission to the target.

The number of pulses (N), PRF, and F were varied to investigate their effects on the carbon nanostructures produced. These parameters were adjusted according to a Box-Behnken experimental design (with 15 points in the experimental design space including three repetitions of the central point). The number of pulses was set to 1200, 1500 and 1800; frequency was set to 10, 12, and 14 kHz; and laser fluence was set to 0.3, 0.6, and 0.9 J/cm^2. The laser fluence was kept below 1 J/cm^2 as this was the maximum energy density available from the laser system at 14 kHz. Fluences below 0.3 J/cm^2 produced some ablation but did not produce any detectable levels of carbon nanoparticles. Laser ablation of the graphite rod surface produced a fine colloidal suspension within the deionised water consisting of carbon nanostructures. From each experiment, this colloid was pipetted into 1.5 mL Eppendorf centrifuge tubes using a glass pipette for subsequent characterisation. The colloids were sonicated for 10 min, and then filtered using 200 nm syringe filters. The carbon nanoparticles were characterised for size distribution and appearance with a ZS90 Zetasizer (Malvern Instruments) and an FEI Tecnai F20, high resolution transmission electron microscope (HR-TEM). Chemical composition was analysed using a Jobin-Yvon Horiba LabRam® HR800 micro-Raman system at 20 mW and 1 μm^2 spot size (with Ar^+ 488 nm air cooled laser). Ten separate samples were prepared and average results calculated for the presented Zetasizer results.

3. Results and discussion

3.1. Particle size analysis

The average size and associated distribution differed depending on the laser processing parameters. Two distributions of nanostructure sizes were detected from all of the produced samples. Thus, all samples were separated into two different fractions by filtration, one fraction containing particles with sizes below 200 nm and the other with sizes above 200 nm. The *z*-average hydrodynamic size (intensity average by cumulants analysis), of sample fractions with particle sizes below 200 nm, is presented in Fig. 1. The figure shows the effects of N, PRF, and F on the size of the particles obtained. These 3D graphs were generated, in Design Expert®, using

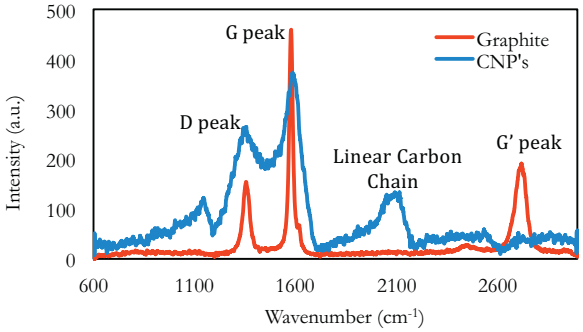

Fig. 2. Micro-Raman spectra for sample CNPs produced with 1500 pulses, 10 kHz, 0.9 J/cm^2, and pure graphite.