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Laser assisted synthesis of carbon nanoparticles with controlled viscosities for printing applications

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ABSTRACT

High-quality carbon nanoparticles with controlled viscosity and high aqueous stability were prepared by liquid-phase laser ablation of a graphite target in deionized water. The size distribution was found to vary from 5 nm to 50 nm with mean size of 18 nm, in the absence of any reducing chemical reagents. Efficient generation of short chain polyynes was recorded for high laser repetition rates. Homogeneous and stable nanoparticle suspensions with viscosities ranging from 0.89 to 12 mPa.s were obtained by suspending the nanoparticles in different solvent mixtures such as glycerol–water and isopropanol–water. Optical properties were investigated by absorption and photoluminescence spectroscopy. Raman spectroscopy confirmed graphitic-like structure of nanoparticles and the surface chemistry was revealed by Fourier-transform infrared spectroscopy demonstrating sufficient electrostatic stabilization to avoid particle coagulation or flocculation. This paper present an exciting alternative method to engineer carbon nanoparticles and their potential use as a ligand-free nano-ink for ink jet printing (jetting) applications.

1. Introduction

In the last decade, rapid progress has been made in the synthesis of a variety of carbon-based nanomaterials for novel applications in diverse areas such as electronics, sensors, and energy. Specifically, carbon nanoparticles (CNPs) have emerged as a new class of carbon-based nanomaterial with several desirable photophysical properties, chemical inertness, stability, high (aqueous) dispersity [1]. The superior biological properties of CNPs, such as low toxicity and biocompatibility, has significantly contributed in replacing traditional semiconductor quantum dots by CNPs in bioimaging, biosensor and biomolecule/drug delivery applications [2,3]. Exceptional optical and electronic properties of CNPs, include their ability for photoinduced electron transfer, photoluminescence and exceptional conductivity due to their dual role as electron donors and acceptors. CNPs can therefore be integrated within existing technologies for creating nanoscale optoelectronic devices [4] and nanosensors [5]. To date, a variety of techniques have been developed to prepare CNPs. In general, these techniques can be classified into top-down and bottom-up approaches. Top-down strategies include electrochemical synthesis [6], laser ablation [7], and arc discharge [8]. Bottom-up strategies include ultrasonic methods [9], microwave assisted synthesis [10], and hydrothermal treatment [11].

Specific technological applications require particular surface activity of the nanomaterials, as for instance in the ink-jet printing of nanomaterials for surface coating of electronic/photonic devices [12]. In this case, it is highly desirable to obtain nanoparticles without any precursor residues and stabilizing ligands. The molecules (ligands) on the surface of a nanoparticle decrease its activity which in turn decreases its electrical conductivity. Hence this requirement has led to expensive follow-up treatments and cleaning steps after nanoparticle synthesis, such as the calcination of catalyst supports or the filtration of nanomaterials [13].

Alternatively, Pulsed Laser Ablation in Liquids (PLAL) has emerged as a versatile technique to fabricate a variety of nanomaterials [14]. As a general strategy, an intense laser beam is irradiated on the surface of a solid target resulting in the generation of a plasma plume at the liquid–solid interface. This results in the simultaneous formation and ejection of nanoclusters of the target material into the confining medium, thus leading to the formation of ultrapure colloidal nanoparticles in solution [15]. By changing

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the laser parameters, target material and liquid media, the size, morphology and surface chemistry of the nanoparticles can be precisely controlled [16,17]. Several studies have been published reporting PLAL as an effective method for the generation of interesting carbon-based nanomaterials including nanoparticles [18] and polyynes [19]. Polyynes are of significance in materials science due to their one-dimensional electronic structures, size-dependent band gaps [20] and nonlinear optical properties [21].

In this work, we exploit this unique technique (i.e. PLAL) to generate nanoparticles with novel functionalities to be used as nano-inks in ink-jet printing (jetting) technology. Over the years, ink-jet printing techniques have become attractive alternatives to conventional photolithography or screen-printing for patterning various functional materials such as organic light emitting diodes (OLED), printed scaffolds for growth of living tissues, and building 3D objects [22]. An important advantage of nanoparticle based inks is the large surface/volume ratio that these particles offer. This can allow low annealing temperature, short process time, high conductivity [23] and high density functionalisation to obtain a wide variety of surface chemistries for different ink-jet printing applications [24].

The present work focuses on the use of laser assisted method, PLAL, for preparation of high-quality carbon nanoparticles based colloids with controlled viscosity. To the best of our knowledge, this is the first time demonstration of laser generated carbon nanoparticles, towards their application as nano-inks in jetting technology. Optical properties were investigated by absorption and photoluminescence spectroscopy. Raman and Fourier-transform infrared (FTIR) spectroscopy were performed to reveal the chemical structure of the nanoparticles. Viscosity measurements in different solvent mixtures were performed in order to optimize the viscosity of the CNP based colloids.

2. Materials and methods

2.1. Synthesis

Laser ablation experiments were carried out using a Nd:YAG laser system (WEDGE HF 1064, Bright Solutions) providing pulses centred at 1064 nm and with a pulse width of 700 ps at the repetition rate set at 7 kHz for production of CNPs and 10 kHz for generation of polyynes. The graphite target (99.999% pure from Sigma Aldrich) in cylindrical form with a diameter of 6 mm and height of 8 mm was placed on the bottom of a glass cuvette (dimension $10 \times 10 \times 50$ mm). The cuvette was filled with 2 mL deionised water (DI water) which corresponded to 1 cm of liquid above the surface of the target. The target was mechanically polished, and then washed with deionised water several times to remove any impurities from the surface. The laser beam was focused onto the target material using a lens with a focal length of 30 cm. During all the experiments, the graphite target was placed in the focal plane of laser beam. A 2-dimensional scanning galvanometer (SS-12, Raylase) was used to scan the laser beam across the top of the graphite target in a circular pattern, at a scan rate of 1.2 mm/s. The laser fluence was measured experimentally using a 30A-P-17 OPHIR® power meter. The laser ablation parameters are defined as follows, unless indicated otherwise. For the production of CNPs, the ablation was carried out at an energy density ranging from 0.02 J.cm^{-2} to 0.71 J.cm^{-2} for a 30 min irradiation time, and for the generation of polyynes the laser fluence was fixed at 0.40 J.cm^{-2} for a 10 min irradiation time. Additionally, the effect of ablation time on production of nanoparticles was also investigated at a fixed laser fluence. The formation of carbon nanostructures could be estimated by the slight change of the colour (from transparent to varying tones of grey) of the liquid during ablation. However it should be noted that changes in the colour of the colloidal solution were only recorded for high levels of fluence. The sample preparation for each characterization measurement was performed one day after preparation of the colloids.

2.2. Characterization

Optical absorption spectra were recorded in a quartz cuvette (10 mm pathlength, Helma) with Varian Cary® 50 UV–Vis spectrophotometer. The scan range was 200–1200 nm with a 600 nm/min scan rate. Photoluminescence of the colloidal solution was measured using a Jasco FP-8500 fluorescence spectrometer. All the optical spectra were corrected for water absorption, by subtracting the contribution of water from the recorded spectrum.

Transmission Electron Microscopy (TEM) was performed with a FEI titan instrument, operating at 300 kV, equipped with a Field Emission Gun (FEG), spherical aberration corrector system (Cs-corrector) of the objective lens. The samples were prepared by drop casting the colloidal solution onto carbon coated 300 mesh copper grid and left to evaporate at room temperature.

The nanoparticles were sonicated in distilled water for 20 min and then their stability in water was studied in a dynamic light scattering (DLS) experiment using a Zetasizer Nano ZS (Malvern Instruments Ltd). Micro-probe Raman measurements were performed with Jobin-Yvon Horiba LabRam® HR800 system at 20 mW and 1 μm^2 spot size (with Ar+ 488 nm air cooled laser, accumulation time = 20 s) in a backscattering configuration with resolution of about 1.1 cm^{-1}. Sample preparation for Raman measurements was done by depositing colloidal CNP solution over the substrate by drop casting method. The excess of liquid was then left to evaporate at room temperature leading to the formation of a "coffee ring". This technique is commonly accepted as the property of the material in the coffee ring remains the same as in the original sample [25]. Various measurements were performed at different position on the coffee ring. Fourier Transform Infrared spectroscopy (FTIR) was performed on a Perkin–Elemer Spectrum 100 FTIR spectrometer. The data was acquired in transmission and ATR imaging modes over the spectral range the 600–4000 cm^{-1}. Viscosities of the CNP suspensions were measured with an Anton Paar MCR 301 Rheometer system with maximum torque capability of 200 mNm, resolution of 0.1 nNm, and a maximum angular velocity of 628 rad/s.

3. Results and discussion

3.1. TEM characterization

TEM characterization was carried out to obtain information about the morphology and size distributions in the colloidal solutions produced by laser ablation of the graphite target in deionized water. Fig. 1 shows TEM images of NPs obtained at 0.40 J.cm^{-2} laser irradiance for 5 min. Isolated and uniformly distributed CNPs could be observed at low (Fig 1a) and high magnification (Fig 1b).

3.2. Optical measurements

CNPs solutions were produced by laser ablation of a graphite target in deionized water, using picosecond laser pulses emitting at 1064 nm at 7 kHz, by varying the laser fluence 0.02, 0.40, 0.50, 0.60 and 0.70 J.cm^{-2} for a fixed irradiation time of 30 min. Fig. 2 shows the UV–visible absorption measurements of the obtained colloid solutions. The spectra of each colloidal solution consisted of a broad continuous band between 200 and 500 nm and a distinctive shoulder at around 260 nm, except for the solution obtained at lowest energy density. A strong increase in the UV absorption band