Catalyst-Free Synthesis of Carbon Nanotubes with Low-Intensity Lasers

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ABSTRACT

We have discovered a novel method of synthesizing carbon nanostructures such as single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs) and carbon onions without catalyst. The method uses low-intensity continuous-wave laser irradiation of functionalized fullerenes at ambient temperature and pressure. Formation of SWNTs vs. MWNTs can be controlled by varying the wavelength and dose of laser irradiation. Complete graphitization of MWNTs can be achieved. Potential applications include *in situ* synthesis of CNTs, doped CNTs for bioimaging or hydrogen storage and electrical connects.

Keywords: Fullerenes, Carbon nanotubes, Catalyst, Laser, Onions

1 INTRODUCTION

Carbon nanotubes have unique optical, electrical and mechanical properties. Since Ijima's report in 1991, carbon nanotubes have been synthesized by various techniques such as arc-discharge, laser ablation, chemical vapor deposition and templated synthesis [1, 2]. The arc-discharge and laser ablation methods usually use graphite as the source of carbon, whereas in chemical vapor deposition and templated synthesis the source of carbon is carbon monoxide or other hydrocarbons [1]. Carbon nanotubes have also been synthesized by thermal treatment of carbon nanostructures. Thermal treatment and annealing at 800–1200°C result in single-walled carbon nanotubes (SWNTs). Annealing at a temperature of 1600–2000°C results in coalescence of SWNTs [3]. Above 2200°C, multi-walled carbon nanotubes (MWNTs) begin to form, while SWNTs dissappear. Only MWNTs are present at temperatures higher than 2400°C [4].

SWNTs and double-walled carbon nanotubes (DWNTs) have been synthesized by coalescence of pristine fullerenes with thermal or laser treatments. In the case of thermal treatment, the temperature is around 1200°C [5]. Guan et al., have achieved coalescence of fullerenes at 550°C by doping the SWNTs with iodine to lower the energy barrier for coalescence of fullerenes present inside SWNTs [6]. To our knowledge, MWNTs have not previously been synthesized by coalescence of either pristine or functionalized fullerenes.

Coalescence of pristine fullerenes by laser treatment to form SWNTs or DWNTs requires intensities in the range of 1–3 MW/cm^2 [7, 8]. Although oxygen-free conditions are generally employed for coalescence of pristine fullerenes by laser, Manfredini et al. have reported that oxidative conditions are required for coalescence of fullerenes by laser irradiation [9]. Formation of carbon schwarzites by laser irradiation of pristine fullerenes has also been reported [10]. Formation of carbon nantoubes by laser irradiation of either pristine or functionalized fullerenes at room temperature and in absence of catalyst has not been reported.

Recently, we reported our discovery on optical heating, ignition and transformation of functionalized fullerenes. [11]. Functionalized fullerenes glow under laser irradiation in an oxygen-free environment (e.g., vacuum or nitrogen atmosphere). The white-light emission is blackbody radiation and the emission spectrum corresponds to a 4500 K emission temperature. We have also discovered that in an oxygen-free environment, laser irradiation of functionalized fullerenes results in extensive molecular reconstruction of functionalized fullerenes, leading to formation of carbon nanotubes, carbon onions and carbon schwarzites. We are the first group to synthesize carbon nanotubes, onions and schwarzites by laser irradiation of fullerenes in absence of catalyst and at room temperature and pressure [11].

2 MATERIALS & METHODS

Optical transformation experiments were carried out with polyhydroxy fullerenes (PHF) and carboxy fullerenes (CF) [11]. PHF or CF was coated on a silica wafer (1x1 cm^2). The sample was equilibrated with argon in a glove-box. After 24 hours of equilibration, the PHF film was exposed to a 785 nm laser with an optical fiber (400µm diameter). The output power of the laser was varied from 0.5–1.5 W. The irradiated area was approximately 1 mm in

diameter. The functionalized fullerene samples glowed under laser irradiation with emission intensity increasing with higher incident laser intensity. The sample was irradiated at different locations for up to 30 seconds at any single spot. After completion of the experiment, the sample was placed in a Petri dish and the dish was sealed with Parafilm while still within the argon atmosphere of the glove-box. The black spots were scraped from the film and collected for imaging by high resolution transmission electron microscopy (HR-TEM).

3 RESULTS & DISCUSSION

Laser irradiation of functionalized fullerene coated silica substrate was marked with white and black spots. The white spots are believed to be due to melting and recrystallization of silica. HR-TEM (up to 500,000x magnification) revealed that the black spots contained numerous single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs), carbon onions, carbon schwarzites and other carbon nanostructures (Figures 1 & 2). The MWNTs ranged from 2 nm to greater than 1000 nm in length. Higher resolution images revealed that the walls of the MWNTs are graphitized. Complete graphitization of MWNTs occurs above 2400°C [1]. Some of the MWNTs were welded together. Tour et al. have patented the use of electromagnetic irradiation for welding of carbon nanotubes [12]. Our observations indicate that the size, shape, number of walls, graphitization and alignment of nanotubes varies. Control of these properties should be possible through manipulation of synthesis parameters such as nature of functionalized fullerenes, sample preparation (e.g., matrix, film thickness), and intensity and duration of irradiation.

Laser irradiation induced conversion of functionalized fullerenes to carbon nanostructures has many potential applications, some of which are listed below.

In-situ synthesis of CNTs in polymer matrix

Carbon nanotubes (CNTs) have been incorporated in polymer matrices to improve the mechanical, electrical and optical properties of the polymer. A major limitation associated with current techniques is low solubility of CNTs and therefore low dispersability. Functionalized fullerenes are soluble in polar as well as non-polar solvents, thereby overcoming the dispersion issue. *In-situ* synthesis of CNTs, presently unique to our discovery, can be controlled for size, type, graphitization, dispersion, alignment and precise positioning of nanotubes. CNT-polymer composites have a wide range of applications, including bullet-proof materials, conducting polymers, high-mechanical strength materials and transparent display panels. Additionally, irradiation of functionalized fullerenes in a polymer matrix can lead to formation of welded CNTs, which can further improve properties of polymer composites.

Hydrogen storage

Carbon nanotubes are being widely researched as potential candidates for hydrogen storage because of their ability to adsorb hydrogen as well as their high surface area. According to our discovery, MWNTs synthesized in a hydrogen atmosphere can provide a route for trapping hydrogen inside MWNTs.

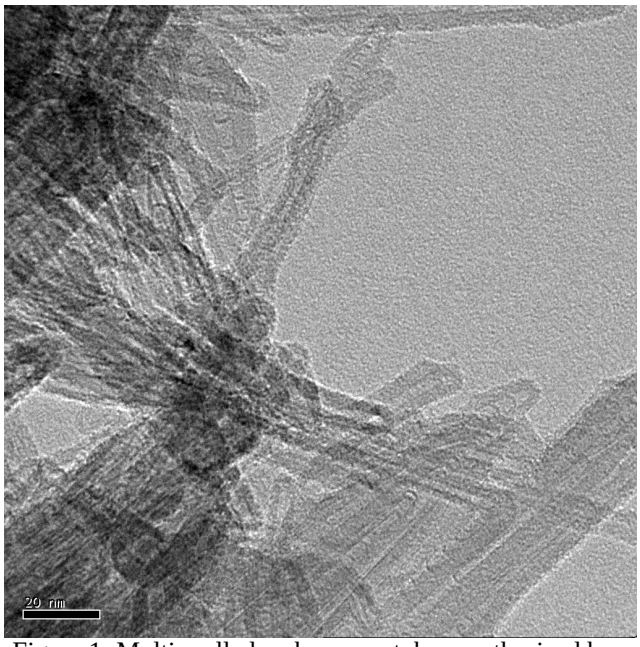

Figure 1: Multi-walled carbon nanotubes synthesized by laser irradiation of functionalized fullerenes at room temperature and pressure and in absence of catalyst.

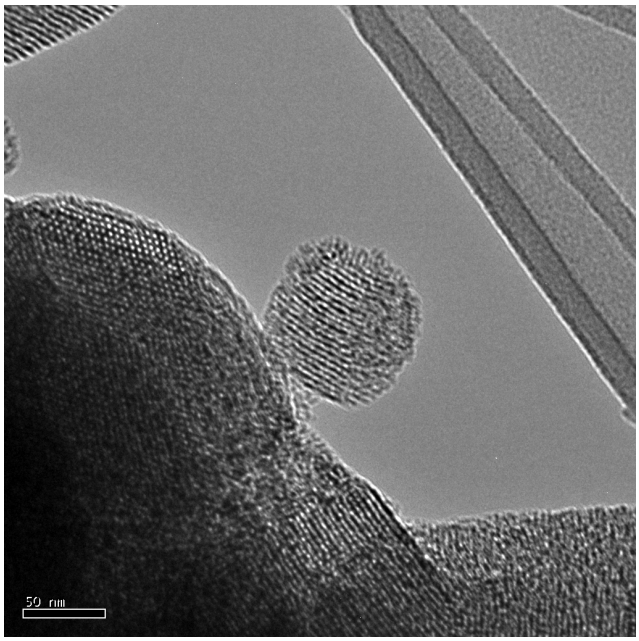

Figure 2: Carbon nanostructures synthesized by laser irradiation of functionalized fullerenes at room temperature and pressure and in absence of catalyst.

Electronics

Carbon nanotubes are being extensively researched for various electronic applications, including electrical connects, field emission devices and displays. One of the major hurdles for successful application of CNTs in these areas is the low dispersability of CNTs and the presence of impurities, such as metal catalysts. *In-situ* synthesis of CNTs with functionalized fullerenes can overcome these barriers. For example, CNTs can be synthesized in place to act as connects between electrical components. This can be accomplished by first coating the connect area with functionalized fullerenes dissolved in an appropriate solvent and then scanning the connect area with a narrow-beam-width laser in an oxygen-free environment. Functionalized fullerenes that remain after CNT synthesis can be removed by laser irradiation in the presence of oxygen. The solvent compatibility of functionalized fullerenes is a major advantage for coating them on or incorporating them within various substrates. A transparent substrate (e.g., glass, polymer) coated on one side with functionalized fullerenes can be irradiated to form an aligned and uniform matrix of CNTs, which can be used as a panel for displays or for other transparent electronic devices. Fabrication of other features (e.g., electrodes) in micro/nano electromechanical systems can also be easily achieved through *in-situ* synthesis of CNTs using the disclosed technology.

Doped CNTs

Elements or isotopes that impart novel capabilities (e.g., detection, therapeutics) can be incorporated within the core or walls of CNTs using suitable functionalized fullerenes. These modified CNTs can be used as sensors for detection of biological or chemical agents. For example, irradiation of $Gd@C_{60}(OH)_x$ in oxygen-free environment can produce Gd doped CNTs, which can be used as contrast agents for magnetic resonance imaging (MRI). The modified CNTs can also be applied for therapeutic properties such as drug delivery.

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