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Formation of carbon nanospheres via ultrashort pulse laser irradiation of methane

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HIGHLIGHTS

- Carbon nanospheres can be synthesized via irradiation of gaseous methane.
- Sphere size varies with pressure of methane.
- Spheres are composed of amorphous carbon.

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ABSTRACT

Irradiation of methane with intense, spatially- and temporally-shaped femtosecond laser pulses forms a spatially confined microplasma that produces carbon nanospheres. The morphology and composition of the nanospheres are characterized by transmission electron microscopy (TEM), ultraviolet (UV) Raman spectroscopy, and infrared spectroscopy (IR). Increasing the pressure of methane from 6.7 to 133.3 kPa results in a decrease of the median diameter of the spheres from ~500 nm to 85 nm. At pressures of 101.3 kPa and higher, particles with non-spherical morphologies are observed in TEM analysis. The morphology of the nanospheres is determined to be amorphous, containing both sp^2 and sp^3 hybridized carbon atoms, based on the presence of the carbon D and T peaks in the UV Raman spectrum. The red shift of the G peak and a high fluorescence background in the Raman spectrum indicates that the hydrogen content of the spheres is at least 30%. The presence of hydrogen is supported by the IR spectrum, which shows the presence of C—H bonds in the nanosphere product.

1. Introduction

Carbon nanomaterials such as fullerenes [1], nanotubes [2] and graphene [3] have been widely researched in the last few decades due to their high mechanical strength, thermal conductivity, electrical conductivity, and ability to undergo organic functionalization reactions [4–6]. Carbon nanospheres constitute another class of carbon nanomaterials that have applications in the biomedical, electronic, and environmental fields [7–9]. The surface chemistry of carbon nanospheres can be tuned through organic functionalization and doping, making them useful in a range of applications that include bulk electrode synthesis [10,11], molecular transport across biological membranes [12], and for use as tailored catalysts [13–15].

A variety of methods including hydrothermal synthesis [9,16] and pyrolysis [17–20] have been used to synthesize carbon nanospheres. These methods typically require high substrate temperatures, catalyst supports, and post-processing of the sample. Plasma-enhanced chemical vapor deposition (CVD) is also commonly used to produce carbon nanospheres. CVD experiments are typically conducted at pressures <1.33 kPa using a flow of either single or mixed gases [21,22], with the substrates heated to 50 °C or higher [22,23].

Carbon nanosphere formation has been proposed to originate

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from pentagonal rings formed in nascent graphitic flakes, which continue to grow into a spiral shell. Growth of large spheres in the gas phase results from pentagonal-heptagonal carbon rings organized in hexagonal networks that allow single-atom-thick graphite layers to deposit with the proper curvature onto the surface of an already growing sphere [24]. Prior studies in which carbon spheres were generated by relatively high temperature methods (e.g. pyrolysis of organic precursor) have shown that the material can be deposited on substrates for analysis or further processing [17]. An application such as carbon coating of electrodes, which requires the delicate deposition of carbon at a low substrate temperature, could benefit from the development of new low-temperature, spatially-controlled synthetic methods [25].

This work investigates a novel synthetic route to carbon nanospheres via the irradiation of gaseous methane with intense, spatially- and temporally-shaped femtosecond (fs) laser pulses that create a microplasma reaction zone. The resulting carbon nanospheres deposited on a room temperature substrate are characterized with UV Raman spectroscopy, IR spectroscopy, and TEM. In particular, the bonding structure of the carbon atoms in the nanospheres and the size distribution and morphology of the product as a function of methane pressure are determined. Both neutral and ionized fragments produced during fs laser irradiation of methane were observed in previous studies using fluorescence spectroscopy [26] and mass spectrometry [27–29]. This contribution demonstrates that the spatially confined microplasma formed by focusing an intense fs laser pulse produces solid photoproducts from methane, in this case, carbon nanospheres.

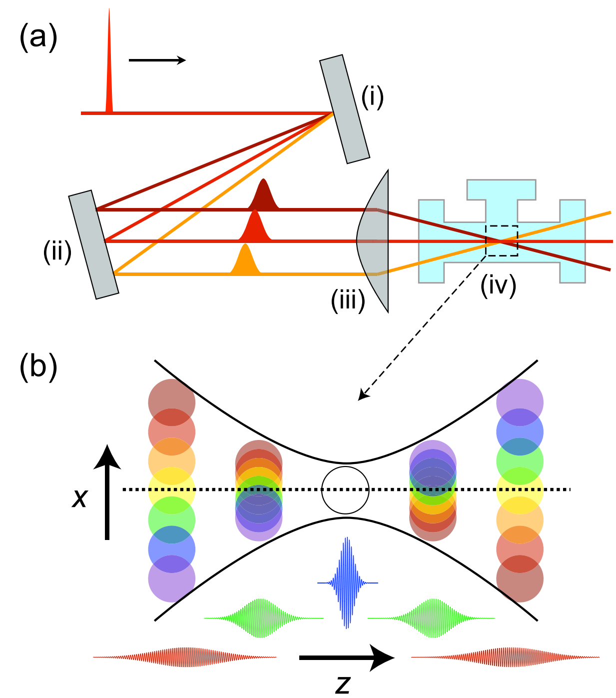

Fig. 1. A schematic of the experimental ultrashort laser pulse irradiation apparatus. (a) The laser pulse is spatially dispersed by a pair of gratings (elements (i) and (ii)) and subsequently focused by an aspheric $f = 10$-cm lens (iii) into the reaction chamber (iv). (b) A schematic representation of simultaneous spatial and temporal focusing. The spatially separated spectral components recombine at the geometric focus (white circle) leading to the formation of the shortest, and thus the highest intensity, pulse. Before and after the focus the intensity is much lower because the pulse is delocalized in space and time.

2. Experimental

2.1. Materials

Gaseous methane (99.0% purity) was obtained from Airgas. The gas was used without any further purification.

2.2. Instrumentation

A titanium-sapphire-based chirped-pulse amplifier with bandwidth centered at 790 nm provided 35 fs, 5 mJ pulses at a 1 kHz repetition rate. In order to avoid self-phase modulation of the laser pulse in the reaction chamber and to ensure homogeneous energy deposition at all gas pressures, we employed simultaneous spatial and temporal focusing (SSTF) [30–32]. The SSTF apparatus was comprised of a grating pair (1200 l/mm) that spectrally and temporally dispersed the pulse. An aspheric $f = 10$-cm lens focused the pulse into the center of the reaction chamber (shown in Fig. 1a) while concurrently compressing the pulse in time, as illustrated in Fig. 1b. The grating pair left an uncompensated negative frequency chirp on the pulse at the focus, resulting in pulse duration of ~36 ps at the focus.

Fig. 2 shows a more detailed schematic of the reaction chamber and a photograph of the laser plasma in the chamber without the top flange. The microplasma in the center of the chamber appears white in Fig. 2 due to fluorescence and Bremsstrahlung emission from ions and excited neutral species in the laser focus (the photograph was taken in air) [33]. The use of SSTF suppresses filamentation (which elongates the focal volume and limits the attainable laser intensity) [34], leading to a well-defined focal spot size for input energies of up to several mJ [35]. All experiments were conducted with a pulse energy of 4 mJ and an irradiation time of 2 h except for the experiment conducted at a methane pressure of 6.7 kPa, where an irradiation time of 3 h was used in order to deposit sufficient product for analysis. Based on the measured spot size of $w_0 = 20$ μm and the 36 ps pulse duration, the pulse peak intensity was calculated to be ~8.8×10^{12} Wcm^{-2} in the focus.

Samples were prepared by evacuating the reaction chamber to <0.02 kPa and then filling the chamber to the desired pressure of methane (between 6.7 kPa and 133.3 kPa). The chamber was then sealed and remained under static pressure during laser irradiation. After irradiation, any remaining gas was evacuated before opening the chamber to remove the sample. A carbon type-A 300 mesh copper TEM grid (Ted Pella Inc., Redding, CA) positioned on a stainless steel plate 5 mm below the laser focus was used to collect particles produced during laser irradiation (Fig. 2). The sizes and shapes of particles deposited on the TEM grid during laser irradiation were characterized without any post-reaction processing using a JEOL JEM-1400 TEM operating at 120 kV. One sample was additionally characterized using a JEOL JEM-2100 (operating at 200 kV) in order to obtain high-resolution images (<0.2 nm). Size information and statistical analysis were performed using ImageJ and MATLAB, respectively.

Samples for Raman analysis were collected on polished silicon wafers placed at the same location in the reaction chamber as the TEM grids. Carbon nanospheres deposited on the silicon wafer exhibited a density gradient (Supporting Information, Fig. S1). The particle density was lowest directly below the laser spot and increased as the laser defocused away from the center of the spot. These samples were analyzed without any further processing using a LabRAM HR Evolution Raman microscope (Horiba Scientific) with a 325 nm HeCd laser source. Raman spectra were measured using a 40× UV objective in the range of 400–4000 cm^{-1}. To avoid damage to the sample from UV radiation, the power of the laser on the sample was kept below 0.002 mW. At this power, no visible damage of the sample was observed during measurements. Spectra were