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Resonant excitation of precursor molecules in improving the particle crystallinity, growth rate and optical limiting performance of carbon nano-onions

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Abstract

A catalyst-free and highly efficient synthetic method for growing carbon nano-onions (CNOs) in open air has been developed through the laser resonant excitation of a precursor molecule, ethylene, in a combustion process. Highly concentric CNO particles with improved crystallinity were obtained at a laser wavelength of 10.532 μm through the resonant excitation of the CH_2 wagging mode of the ethylene molecules. A higher growth rate up to 2.1 g h^{-1} was obtained, compared with that without a laser (1.3 g h^{-1}). Formation of the CNOs with ordered graphitic shells is ascribed to the decomposition of polycyclic aromatic hydrocarbons (PAHs) into C_2 species. The optical limiting performances of the CNOs grown by the combustion processes were investigated. CNOs grown at 10.532 μm laser excitation demonstrated improved optical limiting properties due to the improved crystallinity.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon nano-onions (CNOs) are concentric multilayer giant fullerenes, which consist of multiple concentric graphitic shells to form encapsulated structures [1]. As an important member in the fullerene family, CNOs have been investigated extensively to replace fullerenes due to their extreme similarities shared with fullerenes but at a much lower cost [2–8]. A wide spectrum of applications have been envisioned for CNOs, including gas storage [9], supercapacitors [10], broad-band electromagnetic shielding [11], catalyst support structures [12], nano-lubricating additives [13] and water purification [2]. Due to their nonlinear optical properties, CNOs could also be used in optical limiters to protect delicate optical devices and human eyes from laser threats [14].

Due to their potential applications, scalable production of high quality CNOs is desired. Since the first report on obtaining CNOs from carbon soot by electron beam irradiation [1], a variety of synthetic strategies have been developed for growing CNOs, including chemical vapor deposition (CVD) [15] and nanodiamond phase transition [16]. However, metallic catalysts are required in conventional CVD methods [2, 15] and have to be removed before use. Thermal annealing of diamond nanoparticles requires high temperature processes and relatively expensive raw materials [16]. In 2004, Chio *et al* [17] reported a laser-assisted combustion process for growing CNOs in open air by using an infrared laser.

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However, the laser energy could not be efficiently coupled into the reaction regions for the growth of CNOs.

In this study, a highly efficient and scalable combustion process for CNO growth in open air was developed by using laser irradiation to achieve resonant excitation of precursor molecules. The laser energy was much more effectively coupled into the flame through the resonant excitation of ethylene molecules at 10.532 μm than at other non-resonant wavelengths. It was found that both growth rate and crystalline quality of the CNOs can be significantly improved by matching the irradiation wavelengths with the vibrational states of the ethylene molecules. Highly concentric CNO particles were obtained at a laser wavelength of 10.532 μm, which resonantly excites the CH_2 wagging mode (ν_7, 949.3 cm^{-1}) of the ethylene molecules. A growth rate up to 2.1 $g\,h^{-1}$ was recorded, which is higher than that without a laser (1.3 $g\,h^{-1}$). Optical limiting is an important material property which can be used for protecting delicate sensors and human eyes from optical damage. As a promising candidate of optical limiting among carbon-based materials [14, 18–20], carbon nanotubes (CNTs) [18] were reported to demonstrate a broad-band optical limiting ability because of the nonlinear scattering effect [14, 19]. However, the high cost and difficulties in the scalable production of CNTs prevent the extensive applications of CNTs. Herein, the optical limiting performance of the CNOs grown by the combustion process with resonant laser excitation was investigated. It is discovered that CNOs containing improved concentric structures have improved optical limiting performance.

2. Experimental section

CNO growth was performed through a laser-assisted combustion process in the open air using C_2H_4 and O_2 as precursors. Figure 1 shows the schematic diagram of the experimental set-up. A welding torch with a 1.5 mm orifice tip was used to generate the flames. The fuel was a mixture of ethylene (C_2H_4) and oxygen (O_2) with a gas flow ratio of 5:3. A wavelength-tunable CO_2 laser (PRC, spectral range from 9.2 to 10.9 μm) was used. The laser beam at a wavelength of 10.532 μm was used to resonantly excite the CH_2 wagging mode (ν_7, 949.3 cm^{-1}) of the ethylene molecules to achieve effective energy coupling. The laser beam was directed right above the top of the nozzle and perpendicularly to the flame axis. The laser beam was focused using a ZnSe convex lens (focal length = 254 mm) to 2 mm in diameter. Silicon wafers with dimensions of $5 \times 5 \times 0.6$ mm^3 were placed on top of the flames to collect the CNOs.

The as-grown CNOs were characterized by a field-emission transmission electron microscope (FEI Tecnai G2 F30, 300 kV) and a Renishaw inVia dispersive micro-Raman spectrometer with a 514 nm excitation source. The experiments on optical limiting were conducted using a Q-switched Nd:YAG laser (Powerlit Precision II 8010, 532 nm, τ = 6 ns, 10 Hz) laser. The CNO suspension (0.025 $g\,l^{-1}$) was loaded into a PMMA cuvette. A magnetic stirrer was used to keep the CNO particles from agglomeration and precipitation.

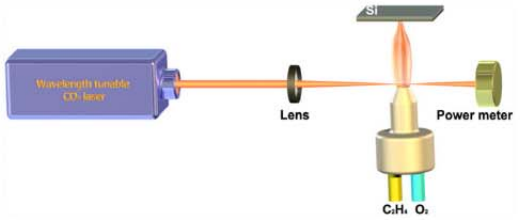

Figure 1. Illustration of the experimental set-up for CNO growth with resonant excitation by a wavelength-tunable CO_2 laser.

3. Results and discussions

Figure 2(a) shows a photograph of the ethylene–oxygen flame without laser excitation. When a laser beam of an arbitrary non-resonant wavelength, such as 10.333 μm, was used to irradiate the flame, no obvious change was observed in both shape and luminosity of the flame, as shown in figure 2(b). The flame shape and luminosity changed drastically when a laser beam of the resonant wavelength, 10.532 μm, was used, as shown in figure 2(c). The flame became much brighter and shorter than the flames shown in figures 2(a) and (b).

To study the influence of laser wavelength and laser power on the CNO growth, CNOs grown under different conditions, including without laser excitation and with laser excitation at 10.333 and 10.532 μm, were investigated. The transmission electron microscopy (TEM) micrographs of the CNOs grown under different conditions are shown in figures 2(d)–(f). Figure 2(d) shows the TEM image of the CNOs grown without laser irradiation. Typical amorphous carbon structures [21], containing random graphitic striations, are observed. The CNO particles contain entangled and rippled graphitic striations in the inner cores and on the outer layers, separately. Similar amorphous structures are found in CNOs grown with laser excitation at 10.333 μm, as shown in figure 2(e). However, distinctively different concentric structures containing long-range ordered graphitic striations are observed in the CNOs grown with laser excitation at 10.532 μm, as shown in figure 2(f). The inner cores of the CNOs grown at 10.532 μm appear to be transparent, indicating the hollow cores of the CNOs.

Figure 2(g) shows typical Raman spectra of CNOs grown under different conditions without laser excitation and with laser excitation at 10.333 and 10.532 μm, respectively. The inset shows a zoomed view of the second-order Raman peaks. In the Raman spectra, two dominant Raman shifts at 1350 and 1590 cm^{-1} are observed and ascribed to the D and G bands, respectively [22]. The D and G bands were fitted into five different bands (G, D1, D2, D3 and D4) [23], as shown in figure 2(h). Among them, the D3 band is ascribed to the amorphous carbon [23] and its relative intensity ($R3 = I_{D3}/(I_{D3} + I_{D2} + I_G)$) is proved to be a reliable parameter for evaluating the crystallinity of graphite-like and amorphous carbon [24]. Therefore, $R3$ and the full width at half-maximum (FWHM) of the G band were analyzed to study the crystallinity of CNOs grown in this study. Mean values of the spectral

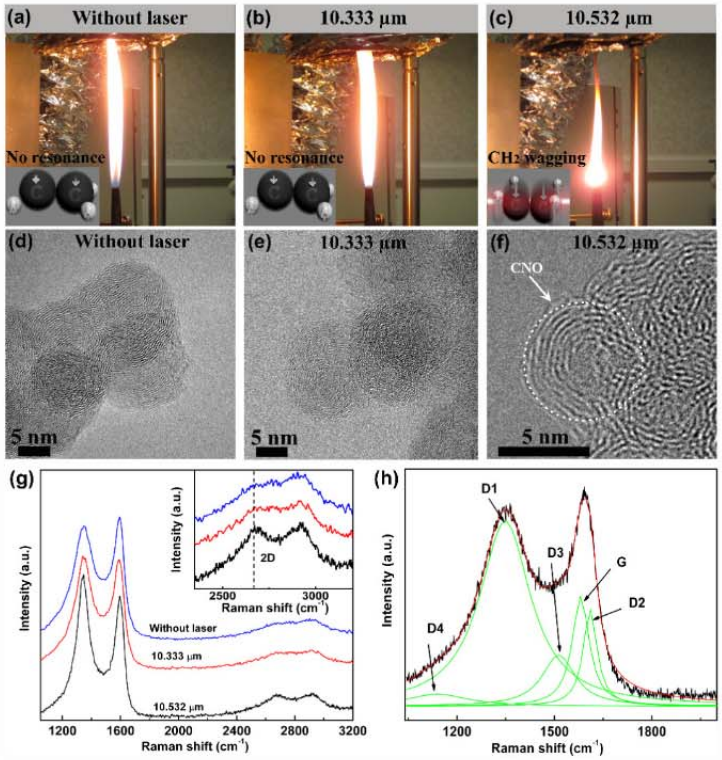

Figure 2. Photographs of ethylene–oxygen flames: (a) without laser excitation, (b) excited at 10.333 μm and (c) excited at 10.532 μm. (The insets show molecular vibration under the excitation conditions.) TEM images of CNOs grown (d) without laser excitation and with laser excitation at (e) 10.333 and (f) 10.532 μm. (g) Raman spectra of CNOs grown without laser excitation and with laser excitation at 10.333 and 10.532 μm (The inset shows the magnified view of the second-order Raman spectra.) (h) Typical curve fitting of a first-order Raman spectrum.

parameters discussed below were obtained from four spectra recorded from different regions of each sample collected on Si substrates. Table 1 summarizes the FWHM of the G bands and the relative intensities of the D3 bands of CNOs grown under the conditions without laser excitation and with laser excitation at 10.333 and 10.532 μm, respectively. By comparing the CNOs grown under different circumstances, the reduced G-band FWHM and $R3$ ratio indicate the improvement in the crystallinity of the CNOs grown with resonant excitation at 10.532 μm. For the CNOs grown at 10.333 μm, however, the Raman analysis does not show an obvious crystallinity improvement even using a high laser power up to 1000 W. Additionally, an obvious intensity increase in the 2D band ($\sim$2690 cm^{-1}), which is closely related to the crystallite size, was observed in the CNOs prepared at 10.532 μm, indicating a crystallinity improvement [23]. The CNO growth rate at 10.532 μm was measured to be around 2.1 g h^{-1}, which was higher than those at 10.333 μm (0.3 g h^{-1}) and without a laser (1.3 g h^{-1}). Therefore, the resonant excitation of the C_2H_4 molecules at 10.532 μm not only improves the crystallinity of CNOs but also increases the growth rate.

Table 1. Summary of G-band FWHM and $R3$ for CNOs grown without laser excitation and with excitation at wavelengths of 10.333 and 10.532 μm at 1000 W.

CNOs	FWHM of G band (cm^{-1})	$R3 = I_{D3}/(I_{D3} + I_{D2} + I_G)$
Without laser	71.4	0.24
10.333 μm	64.6	0.23
10.532 μm	59.5	0.19

Figure 3 shows the TEM micrographs of the CNOs prepared using different laser powers at 10.532 μm. Above a threshold laser power of 400 W, CNOs containing concentric graphitic shells were fabricated, as shown in figures 3(b)–(d). As observed in Raman spectra, figure 3(e), the FWHM of the G band and the intensity of $R3$ decrease with the increasing laser power. However, the 2D-band intensity increases with the increasing laser power. Both changes indicate the improved crystallinity of the CNOs.

To study the influence of laser-induced resonant excitation of ethylene molecules on the CNO growth, laser absorption

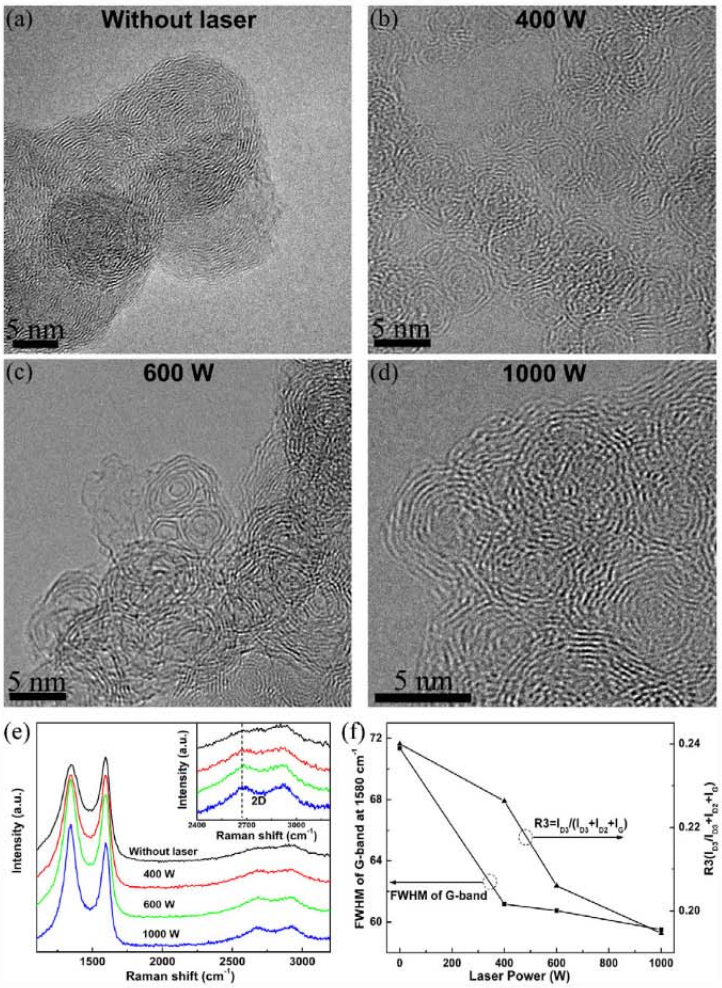

Figure 3. TEM images of CNOs grown (a) without laser excitation and with different laser powers of (b) 400, (c) 600 and (d) 1000 W at 10.532 μm. (e) Raman spectra of CNOs grown with different laser powers. (The inset shows the magnified view of the second order Raman spectra.) (f) G-band FWHM and *R*3 of CNOs as functions of the laser power.

by the flames at the non-resonant wavelength of 10.333 μm and the resonant wavelength of 10.532 μm was investigated, as shown in figure 4. In the measurements, a laser power meter was used to monitor the absorption of the laser power by the flames by comparing the measured powers before and after going through the flames. By irradiating the laser beam through the C_2H_4/O_2 flames used for laser-assisted growth of CNOs, as shown in figure 4, a much stronger absorption was observed at the wavelength of 10.532 μm, as compared with that at the wavelength of 10.333 μm. The obvious absorption at 10.532 μm by the C_2H_4/O_2 flames is ascribed to the resonant excitation of the CH_2 wagging mode (ν_7, 949.3 cm^{-1}) of the C_2H_4 molecules. A C_2H_4 molecule in the CH_2 wagging mode vibrates like a butterfly. By absorbing laser energy at 10.532 μm, the CH_2 wagging vibrational mode is resonantly excited. The strong absorption of the laser energy through resonant excitation at 10.532 μm indicates the proposed method to synthesize CNOs is highly efficient.

In this study, optical emission spectroscopy was used to study the effects of the resonant laser energy coupling on the formation of CNOs. Figure 5 shows the optical emission spectra of the flame without laser excitation, and with laser excitation at 10.333 μm and 10.532 μm, respectively. For the flame without laser excitation, C_2 and polycyclic aromatic hydrocarbon (PAH) species which contribute to the formation of CNOs [25] were observed in the spectra. For the flame with laser excitation at 10.333 μm, an obvious black body radiation background was observed besides the C_2 and PAH species,

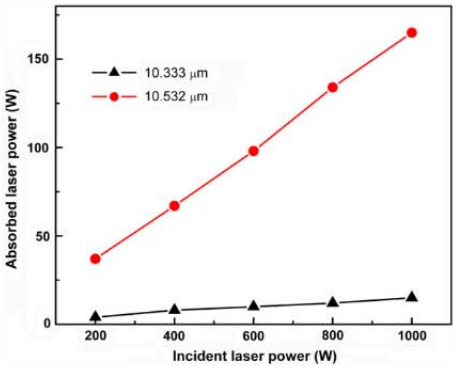

Figure 4. The laser powers absorbed by the combustion flame at the wavelengths of 10.333 and 10.532 μm as functions of the incident laser power.

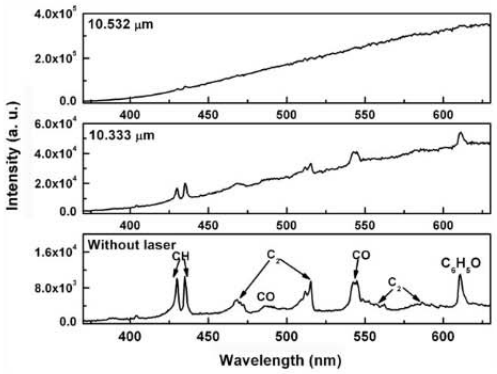

Figure 5. Optical emission spectra of the flame without laser excitation, and with laser excitation at 10.333 μm and 10.532 μm, respectively.

which indicates that a certain amount of CNO particles are formed. When the laser energy was resonantly coupled into the flame at 10.532 μm, the black body radiation band intensity was stronger than that at 10.333 μm, which indicates that many more CNO particles are formed. These results suggest that laser resonant excitation of ethylene molecules at 10.532 μm promotes CNO formation.

Chio *et al* [17] reported that high quality shell-shaped carbon particles can be obtained by coupling sufficient laser energy into an acetylene flame. In this study, laser energy was coupled into the flame more efficiently through resonant excitation of the ethylene precursor molecules. The total absorbed laser power is much higher at an excitation laser wavelength of 10.532 μm, which can resonantly excite the CH_2 wagging mode (ν_7, 949.3 cm^{-1}) of the ethylene molecules, than a non-resonant one, such as 10.333 μm, as shown in figure 4. At the laser wavelength of 10.532 μm, starting from the threshold laser power of 400 W, a sufficiently high temperature in the flame is reached by the efficient coupling of the laser energy through resonant excitation to decompose PAHs into C_2 species, which favor the formation of more ordered graphitic layers [25]. Hence, CNOs with long-range ordered concentric graphitic shells are formed. At 10.333 μm, however, the laser energy absorbed by the flame is low. The growth of PAHs in the flame is more favored than decomposition. Hence, the main mechanism to form the CNOs is through PAH addition [25]. Since various PAHs with different sizes and shapes exist in the ethylene flame, continuous addition of PAHs onto the surface of carbon particles will introduce disconnected graphitic segments. As a result, highly ordered CNOs with long-range ordered concentric graphitic shells cannot form, even though the laser power was increased up to 1000 W, as shown in figure 2(e).

In this study, optical limiting characteristics of the CNOs prepared under different conditions (without laser excitation and with laser excitation at 10.532 μm) were investigated. An Nd:YAG laser (532 nm) was used as a light source for the optical limiting measurements. CNO powders of 0.1 mg were dispersed in 4 ml deionized water. The optical limiting responses of the CNOs grown at the wavelength of 10.532 μm and without laser excitation are shown in figure 6(a). When the incident laser fluence is low, the transmittance of the CNO suspensions is constant, which agrees with Beer's law [18]. With the increase in the incident laser fluence, the transmittance decreases remarkably. Figure 6(b) shows the normalized transmittance as a function of the incident fluence. When the influence of the incident laser is increased

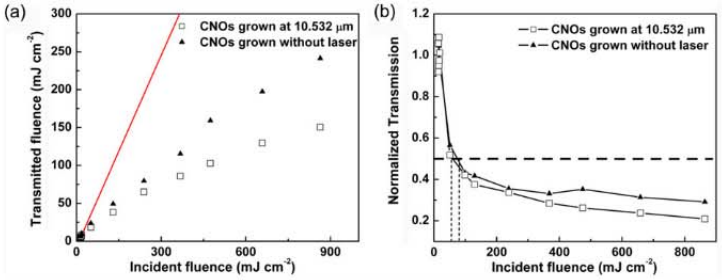

Figure 6. (a) Transmission of the CNO suspension as a function of the incident laser fluence. (The red guideline in the figure is the linear fitting of the transmitted laser fluence at the low laser fluence for CNOs grown at 10.532 μm. At low laser fluence, the transmittance is constant, which matches Beer's law.) (b) Normalized transmission for the CNO suspension.

to 870 mJ cm^{-2}, the normalized transmittance shows a decrease of 70%–80% compared with the linear Beer's law estimations for the CNO samples prepared without and with laser excitation, respectively. The optical limiting thresholds, defined as the incident influence at which the transmission reduces by 50%, are 52 and 80 mJ cm^{-2}, respectively, for the CNOs grown with and without 10.532 μm laser excitation. CNOs prepared using the 10.532 μm laser excitation show an obviously lower optical limiting threshold. The optical limiting effect is ascribed to the nonlinear scattering [19]. The thermal effect of the solvent surrounding the CNOs generates solvent bubbles which effectively attenuate the incident laser beam. This thermally induced mechanism strongly depends on the thermal conductivity of the optical limiters [20]. Increased thermal conductivity could improve the nonlinear scattering effect [20]. Because the long-range ordered concentric graphitic lattice can transfer crystal lattice vibrations more efficiently, CNOs with improved crystallinity grown at 10.532 μm exhibit an increased thermal conductivity. Thus CNOs grown at 10.532 μm demonstrated improved optical limiting performance as compared with those grown without laser excitation.

4. Conclusions

In conclusion, a highly efficient synthetic method has been developed for CNO growth in open air through the laser resonant excitation of precursor molecules. CNOs containing distinct concentric graphitic shells were obtained at the incident wavelength of 10.532 μm. A high growth rate up to 2.1 g h^{-1} was obtained. Formation of the CNOs with ordered graphitic shells is ascribed to the decomposition of PAHs into C_2 species. CNOs grown at 10.532 μm demonstrated improved optical limiting properties due to the improved crystallinity, which suggests potential applications as an optical limiter to protect delicate optical devices and human eyes.

Acknowledgments

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