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Sustained laser induced incandescence in carbon nanotubes for rapid localized heating

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Sustained laser-induced incandescence (LII) was observed when a continuous wave laser beam was focused on aligned multiwalled carbon nanotubes (CNTs) in vacuum. The sustained incandescence originated from radiative dissipation of heated CNTs due to laser-CNT interactions. Sustainability of the LII up to 2 h was achieved. Fittings of the LII intensity spectrum with Planck blackbody distribution indicate a rise of temperature from room temperature to ~2500 K in less than 0.1 s. This provides an effective way of achieving rapid high temperature heating at specific localized positions within CNT arrays. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3083554]

Carbon nanotubes (CNTs) have attracted widespread attention due to their remarkable thermal, mechanical, and electrical properties, which make them one of the most promising materials for future applications. The study of the rich laser-CNT interactions and their applications have been extensive.[1–3] We have previously developed a postgrowth processing technique which uses a focused laser beam to selectively destroy a localized region of CNTs, enabling one to create three-dimensional microstructures from aligned CNT arrays.[4] This technique is particularly effective for aligned CNT arrays due to its high absorption and low reflectance properties.[5] Amazingly when the CNTs were housed in a vacuum chamber, we observed a bright and sustained glow from the CNTs immediately upon focused laser irradiation. Furthermore the light emission from the laser-heated CNTs corresponds to a blackbody radiation at ~2500 K. Such strong incandescence behavior from a localized area within the CNT array can be maintained for more than 2 h. This phenomenon was denoted as sustained laser-induced incandescence (LII) of CNTs, borrowing the term from an established technique of heating carbon soot particles with laser to result in blackbody radiation emissions. While works on LII of carbon soot are abundant in the literature,[6–10] little has been explored for extended carbon structures such as CNTs. Notably, there has been isolated reports of optically induced ignition of CNTs.[11–16] Our studies on sustained LII of CNTs find several desirable features such as instantaneous localized heating, extremely high temperature, and long sustainability. Coupled with precise positional control of the focused laser beam on CNT array, this leads to an exciting way of heating and lighting CNTs.

Plasma-enhanced chemical vapor deposition was employed to grow arrays of aligned multiwalled CNTs on Si substrate using iron nanoparticles as catalysts. Details of the growth were reported elsewhere.[17] The sample used for the experiments presented here was a dense array of 10^7 CNTs/mm^2 with a relatively uniform height of ~50 μm. Figure 1 shows a schematic of the experimental setup of optical microscope-focused laser beam system. The laser beam was focused with a 50× objective lens (L) with a working distance of 8.3 mm. With the long working distance, the space between the lens and the sample can fit a transparent vacuum chamber for the sample to sit in. The power of the laser beam after passing through the system of lens and mirrors was reduced to ~30% of the original emitted power. The same objective lens was used to collect reflected and emitted light from the sample for viewing purposes. The laser used was usually a continuous wave diode laser with wavelength of 663 nm with a maximum output power of 80 mW. Other lasers of various wavelengths, namely, 532, 632, and 1064 nm were also able to produce sustained LII of CNTs. When the focused laser beam was incident upon the CNTs samples, it readily trimmed away the top portions of the CNTs.[4] In room ambient conditions, this was accompanied by flashes of LII at the instant when the laser beam hit the sample surface. A sustained glow was instead observed when the process was repeated with the sample in vacuum. The emissions were bright enough to be seen by the unaided eyes.[18] To study the optical characteristics of the LII, an optical fiber that is part of an optical spectrometer system was brought close to the sample. The spectrometer recorded the

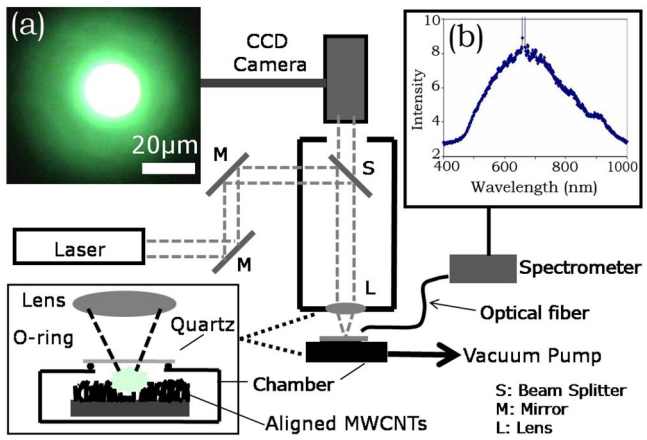

FIG. 1. (Color online) Schematic of the experiment setup to achieve sustained LII of CNTs. Inset (a) shows a snapshot of the LII as seen through the optical microscope. Inset (b) shows the raw intensity profile of the LII captured by the optical spectrometer.

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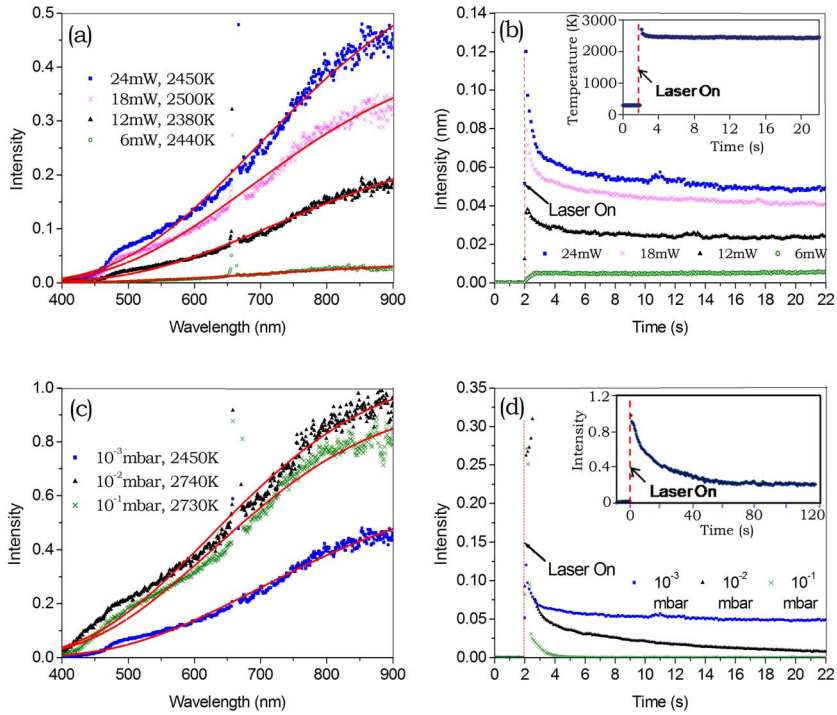

FIG. 2. (Color online) (a) Intensity vs wavelength profile of the LII taken at an instant after laser irradiation for various laser powers. Solid lines are the corresponding fittings of the data with the Planck blackbody radiation equation. (b) Intensity vs time evolution of LII at various laser powers. Laser was irradiated on the sample at $t=2$ s. Inset in (b) shows the temperature-time evolution of the CNTs undergoing LII with the laser power of 24 mW. Air pressure is kept at 2.0×10^{-3} mbar. [(c) and (d)] Intensity profiles at various vacuum levels. Inset in (d) shows a long duration spectrum of a sustained LII that was allowed to last for more than 2 h. A laser power of 24 mW was used.

LII intensities with a broadband of wavelengths. Figure 1 also shows a snapshot of the LII captured by the charge-coupled device camera through the optical microscope [inset in Fig. 1(a)] as well as a typical intensity profile as collected by the spectrometer [inset in Fig. 1(b)]. Calibration of the absolute spectral response of the spectrometer used was performed with a standard calibrated tungsten halogen light source (Ocean Optics LS-1-CAL). Optical spectrum of the light source was measured and compared against the calibrated values to obtain the wavelength dependent detection efficiency of the spectrometer. This detection efficiency factor is then multiplied to the raw data to obtain the corrected spectrum. The data was fitted with the Planck blackbody distribution

$$I(\lambda,T) = A\frac{2\pi hc^2}{\lambda^5(e^{hc/\lambda k_B T}-1)}, \tag{1}$$

where A is the scaling factor to account for the geometrical factor for the measuring setup and the detection efficiency of the spectrometer. The temperature T of the incandescence may be obtained conveniently by taking the ratio of intensities at two wavelengths (λ_1,λ_2), yielding the expression

$$T = \frac{hc}{k_B}\frac{1/\lambda_1 - 1/\lambda_2}{\ln(\lambda_2^5 I_2) - \ln(\lambda_1^5 I_1)}. \tag{2}$$

In this work, the LII intensity profile, the dependence of LII intensity, temperature and lifetime on laser power, and air pressure were studied in detail. Figure 2(a) shows corrected intensity versus wavelength profiles and their corresponding Planck blackbody distribution fittings at various laser powers, taken at the onset of focused laser irradiation on aligned multiwalled CNTs at 10^{-3} mbar vacuum. We see that despite a clear correlation between laser power and LII intensity, the temperature of LII remained at ~2500 K. This implies that while the number of incandescent CNTs increases with laser power, the temperature of the incandescent CNTs is ~2500 K regardless of the laser power. Figure 2(b) complements Fig. 2(a) to show the intensity time evolution of the LII. The sharp peak of LII intensity immediately after laser irradiation followed by a decline toward a constant intensity is typical for higher laser powers. This is explained by the initial destruction of the top portions of the CNTs that are directly under the focused laser beam, producing an avalanche of hot graphitic fragments which contributes to LII intensity. When these graphitic fragments are scattered away or coated back onto the remaining CNTs and no further destruction of CNTs occur, the LII intensity drops to give a sustained glow. The inset in Fig. 2(b) shows the evolution of temperature for LII at 24 mW laser power and at 10^{-3} mbar vacuum. Extremely rapid heating from room temperature to >2500 K within a time step of 0.1 s and a stable temperature of ~2500 K was subsequently maintained. Figures 2(c) and 2(d) and real time videos of LII (Ref. 18) at various pressures show strong dependence of LII characteristics on the vacuum condition. We find that a vacuum level of 10^{-3} mbar is essential for the sustainability of LII, which at this pressure may last more than 2 h,[18] as shown in the inset in Fig. 2(d). At lower vacuum levels of 10^{-1} and 10^{-2} mbar, the intensity peaks were higher than that at 10^{-3} mbar but the lifetimes were much shorter. The same laser power of 24 mW was used for the pressure-dependence studies. We suggest that in lower vacuum conditions, interactions between laser-heated CNTs and the surrounding gas molecules may result in exothermic reactions to further increase the temperature. This also results in the massive destruction of CNTs that we have observed at lower vacuum levels, leading to the diminished LII intensities at later times. Preliminary data from experiments of LII in various controlled gaseous environments shows that oxygen gas plays a vital role in the air pressure-dependence of the LII. Detailed studies of LII in controlled environment will be presented elsewhere.

The morphologies of CNTs before and after laser treatment in vacuum (10^{-3} mbar) were studied using scanning electron microscopy (SEM) as shown in Figs. 3(a)–3(c). Figures 3(a) and 3(b) show the top view of as-grown CNTs and

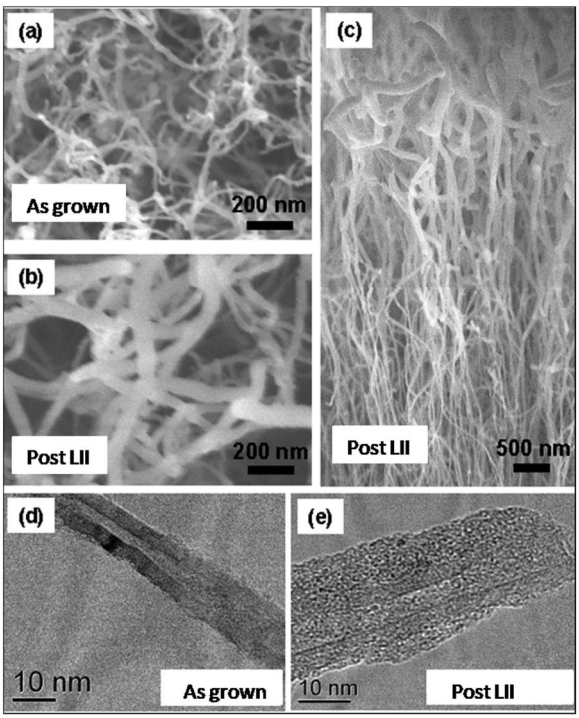

FIG. 3. [(a) and (b)] SEM images of CNTs before and after LII reveal thickened structure of post-LII CNTs. (c) Cross-sectional SEM shows that only the thickened structures are restricted to the top sections of the post-LII CNTs. [(d) and (e)] TEM images of CNTs before and after LII show coatings of possibly amorphous carbon on individual post-LII CNTs.

remaining CNTs after the LII process in vacuum, respectively. Figure 3(c) shows a cross-sectional view of the CNT sample after LII in vacuum. Evidently the top portions of the remaining CNTs became much thicker after laser treatment. Further observations with TEM shown in Figs. 3(d) and 3(e) indicate that the thickened structure consists of CNT coated with a thick layer of amorphous carbon. The amorphous carbon was produced when the focused laser destroyed the CNTs. The thickening of the CNTs suggests that the amorphous carbon produced during laser pruning were likely to have adhered onto the CNTs in vacuum. Such phenomenon was not observed when the CNTs were laser treated in an ambient setup.

We propose a mechanism for the sustained LII of aligned CNT array. The CNTs under focused laser beam efficiently absorbed light energy and were instantly heated up. The intense heat generated caused the CNTs to partially sublime into fragments of graphitic carbon aggregates or amorphous carbons. From the focused laser spot on the sample, heat spread radially out of the laser spot to surrounding CNTs by conduction in the entangled network of CNT forest. While the sample continually absorbs laser energy from the laser beam, heat was also lost to the environment through the conduction with molecules in the air. In the vacuum condition, the latter was greatly minimized, resulting in the build up of heat in the mesh of CNTs and amorphous carbons, which in turn raised the temperature to a point where incandescence took place. As suggested by Rinzler *et al.*,[19] heated C_n chains extending off the open tips of the CNTs are primary sources of incandescent glow. It is reasonable to expect that the defective CNTs rich with dangling bonds and amorphous carbons produced by laser pruning contain many of such C_n chains. Together with laser induced heating, an extended and bright incandescence emitter was thus obtained.

Our calculated temperature of ~2500 K is similar to the estimated sublimation temperature of the CNTs.[20] Our laser treatment however does not completely break the bonds to give gaseous carbon (small atom clusters of C, C_2, and C_3) as such process will require a temperature of ~4000 K.[21] Rather, we believe that the CNTs disintegrate into fragments of small graphite sheets or amorphous carbon aggregates. At high laser intensity an avalanche of amorphous carbons and open CNTs are produced. These hot amorphous carbons and open CNTs may dissipate heat via conduction, convection, and radiation, with radiation being the dominant mechanism in vacuum, resulting in the observed sustained LII.

The study of LII of these arrays allows one to better understand the focused laser-CNT interaction. LII of CNTs may pave the way for more future applications of CNTs. The incandescence with a stable temperature of ~2500 K induced by the focused laser can be used as a localized high temperature heat source. Such localized heating can be achieved with a low laser power of 6 mW and is sustainable for more than 2 h. The use of laser to generate an almost instantaneous heating enables remote ignition to trigger reactions in CNT arrays. The broadband light emissions may be useful for a wide range of optically induced endothermic reactions in "nanotesttubes." Finally LII can be used as a technique to coat CNTs with graphitic materials as sacrificial or protective coatings.

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