Single-Walled Carbon Nanotubes, Carbon Nanofibers and Laser-Induced Incandescence

Randy L. Vander Wal
National Center for Microgravity Research, Cleveland, Ohio

Thomas M. Ticich
Centenary College, Shreveport, Louisiana

Gordon M. Berger and Premal D. Patel
National Center for Microgravity Research, Cleveland, Ohio

April 2004
Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.

- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- E-mail your question via the Internet to help@sti.nasa.gov
- Fax your question to the NASA Access Help Desk at 301–621–0134
- Telephone the NASA Access Help Desk at 301–621–0390
- Write to:
  NASA Access Help Desk
  NASA Center for AeroSpace Information
  7121 Standard Drive
  Hanover, MD 21076
Single-Walled Carbon Nanotubes, Carbon Nanofibers and Laser-Induced Incandescence

Randy L. Vander Wal
National Center for Microgravity Research, Cleveland, Ohio

Thomas M. Ticich
Centenary College, Shreveport, Louisiana

Gordon M. Berger and Premal D. Patel
National Center for Microgravity Research, Cleveland, Ohio

Prepared for the
Carbon 2004
sponsored by the American Carbon Society
Providence, Rhode Island, July 11–16, 2004

Prepared under Cooperative Agreement NCC3–975

National Aeronautics and Space Administration

Glenn Research Center

April 2004
Acknowledgments

This work was supported by a NASA NRA 97–HEDs–01 combustion award (RVW), and a Director’s Strategic Research Fund, administered through NASA cooperative agreement NCC3–975 with the National Center for Microgravity Research on Fluids and Combustion (NCMR) at NASA Glenn Research Center. The authors thank David R. Hull for the HRTEM imaging.

This report contains preliminary findings, subject to revision as analysis proceeds.

This report is a preprint of a paper intended for presentation at a conference. Because of changes that may be made before formal publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at http://gltrs.grc.nasa.gov
Single-Walled Carbon Nanotubes, Carbon Nanofibers and Laser-Induced Incandescence

Randy L. Vander Wal  
National Center for Microgravity Research  
Glenn Research Center  
Cleveland, Ohio 44135

Thomas M. Ticich  
Centenary College  
Shreveport, Louisiana 77134

Gordon M. Berger and Premal D. Patel  
National Center for Microgravity Research  
Glenn Research Center  
Cleveland, Ohio 44135

Introduction

Many reacting flows are aerosols composed of multiple elements. Such is the case for catalyzed aerosols whose products will be chemically and physically different than the catalyst particle. One of the most sought aerosols is carbon nanotubes (CNTs). Aerosol synthesis of CNTs is currently the method of choice for both purity and yield of CNTs and offers the opportunity for both continuous processing and scalability. Catalyzed by metal nanoparticles in hydrocarbon or CO gas mixtures at elevated temperatures, these nanostructures are comprised mainly of elemental carbon. Depending upon the structural details of the catalyst particle, the nanotube morphology will vary between single-walled nanotubes (SWNTs), multi-walled nanotubes (MWNTs) and nanofibers. Currently, yield measurements and synthesis conditions are characterized by collecting samples for subsequent processing and electron microscope analysis, steps which do not provide real-time feedback. Clearly, process control and optimization of nanotube/nanofiber production could benefit from a real time, in situ diagnostic. One such potential diagnostic is laser-induced incandescence (LII).

LII has been widely tested and used for measurement of carbonaceous aerosols in reacting flows [2]. LII has been applied to soot measurements within a wide variety of combustion systems including simple laboratory scale diffusion and premixed flames [3-8], in situ engine measurements [9], and aircraft engine exhaust [10]. The foundational principle of LII is the use of pulsed laser heating to elevate the temperature of the irradiated soot to temperatures near the vaporization temperature of carbon, far above that of the ambient flame gases and the surrounding particulate matter. Consequently, the spectral emission is both dramatically increased and blue-shifted relative to the non-laser heated soot and flame gases. Through selective spectral and temporal detection, this incandescence emission may be detected apart from the non-laser heated soot and flame gases and quantified for absolute soot volume fraction determination [2,11].

Successful implementation of LII relies upon judicious choice of excitation and detection conditions [11-13]. Excitation conditions encompass choice of excitation wavelength and laser fluence. Detection conditions include choice of detection wavelength, spectral bandpass about the central wavelength and detection delay and duration relative to the excitation laser pulse usually corresponding to the peak of the signal intensity. Though many of these issues have been addressed for LII applied to soot, a homogeneous aerosol consisting mainly of carbon, metal catalyzed carbon nanotubes and nanofibers are physically and chemically heterogeneous.
Specific Objectives

Application of LII to a chemically and physically heterogeneous aerosol, such as carbon nanotubes or nanofibers brings forth several questions. Questions include:

1. Does the metal nanoparticle catalyzing the carbon nanotube or nanofiber also simultaneously incandesce? Can this even be determined?
2. If the particle does incandesce, can this emission be detected separately from that arising from the laser-heated carbon nanostructure as a measure of the metal particle concentration?
3. Will vaporization wipe out incandescence from SWNTs, because there is no solid material left to incandesce?
4. Can the laser initiate reactions between the catalyst metal particles and the carbon?
5. Does the incandescence scale with the mass fraction of aerosol? Can this be validated against an independent technique?

Despite this range of possibilities, it is expected that some questions could be answered by impact on the spectral and/or temporal evolution of the LII signal. For example, incandescence from metal nanoparticles ought to be readily recognizable by the appearance of structured emission and the different decay rate of such emission relative to that from the near blackbody emission of the carbon nanotube or nanofiber [14]. Emission from electronically excited vaporized material ought to be identifiable by its distinctly different spectral and temporal evolution compared to incandescence. The onset of vaporization ought to be identifiable from fluence dependence measurements. The vaporization effect(s) upon the emission signal ought to be identifiable by the variation of the signal temporal evolution with laser fluence. Emission arising from condensed phase reaction products (whose synthesis was initiated by the pulsed laser heating) ought to again produce distinctly different spectral and temporal emission relative to that from unreacted material [15], namely the portion of the carbon nanotube that would be uninfluenced by the catalyst particle.

Thus to examine the viability of LII for measuring these aerosols, we investigated the capability of LII applied to CNTs within a reacting flow. The work presented here characterizes LII applied to CNTs within a flame environment.

Experimental

Light at 1064 nm, generated by a Nd:YAG laser, was directed to pass through the flame between two steel chimneys, 1 inch O.D. and 3 inches long. A 1/4 inch diameter aperture through a 1/16 inch thick steel disk trimmed the beam spatial intensity profile to approximate a top-hat profile within the near field. LII was collected by a quartz optical fiber bundle. A commercial quartz lens assembly was placed on the fiber to accommodate the fiber’s numerical aperture. A second telescope served to relay the laser beam image onto the commercial lens. The relay telescope was formed by two quartz lenses, each 50.5 mm diameter, with 100 and 250 mm focal lengths. The other end of the fiber bundle terminated in a rectangular geometry matching the entrance slit for the spectrograph or spectrometer. An intensified cooled CCD, under computer control, captured spectra at selected times relative to the excitation laser pulse. The pulser for the camera intensifier was synchronized to the laser by a digital delay generator. Spectral resolution was determined by the entrance slit and was found to be 5 nm by comparison to Hg lamp spectral emission lines. Spectral wavelength calibration was achieved by comparison to tabulated Hg emission lines.

A PMT attached to a spectrometer detected the temporal emission of the LII at selected wavelengths. Operated at 900 V, the PMT temporal resolution was judged to be approximately 2 ns. The temporal evolution data was captured by a digitizing oscilloscope with GHz bandwidth. Spectral and temporal data was processed using commercial software.
Single-walled nanotubes and nanofibers were synthesized within a pyrolysis flame configuration. Nebulization of an ethanol solution of iron nitrate or nickel nitrate at a concentration of 6mg/ml produced an aerosol of metal nitrate particles. This mist was entrained using a mixture of CO, H2 and He, (0.25 SLPM for each gas) for the iron solution or C2H2, H2 and CO (0.1, 0.5, 0.5 SLPM) for the Ni solution. These gas mixtures yielded nearly exclusively SWNTs with Fe nanoparticles and nanofibers with Ni particles. Further details of the tested gas mixtures, solution concentrations and solvent effects are reported elsewhere [16,17]. The aerosol and reactive gas mixture formed the fuel for the pyrolysis flame.

**Background**

Metal catalyzed SWNTs and nanofibers represent a unique measurement challenge to optical diagnostics. First, the aerosol to be measured is composed of two elements in intimate association. Additionally, each of these may exist in a variety of forms. In the case of SWNTs, as Fig. 1 shows, numerous Fe nanoparticles are distributed along the nanotube walls. Though difficult to observe, many are likely at the tips of the nanotubes as suggested by the yarmulke formation mechanism [18]. In contrast, for the Ni catalyzed nanofibers, Ni nanoparticles are clearly observed at the ends of the nanofibers. Isolated Ni nanoparticles are generally not observed. As shown in Fig. 1, these catalyst nanoparticles are partially covered by or contained within the nanofiber. Finally, the Ni particles are much larger than the Fe nanoparticles.

![Fe Catalyzed SWNTs and Ni Catalyzed Nanofibers](image)

Figure 1.—HRTEM images of Fe catalyzed SWNTs and Ni catalyzed nanofibers collected from the pyrolysis flame. The images show the material as sampled directly from the flame, without purification or processing.
The carbon nanostructures are also different sizes, as seen by comparison of the SWNTs in Fig. 1 and the nanofibers in Fig. 1. As illustrated by the HRTEM images in Fig. 1, the structure of the SWNTs is that of a single atomic layer of carbon, forming a hollow cylinder. SWNTs are, however, frequently found as bundles or ropes consisting of a few to several nanotubes that are physically not chemically bound together [18]. Hence, these nanostructures possess widely varying aspect ratios. In contrast to the SWNT, nanofibers are comprised of stacked graphene segments. As seen in Fig. 1, the nanofibers may possess a variety of morphologies depending upon the length and orientation of the graphene segments with respect to the filament axis.

These structures are formed via a different growth process involving carbon solvation into, diffusion through and precipitation from the catalyst particle [19]. As a dual element system with each element in different forms and exhibiting varying “phases” or levels of organization, such as graphitic quality; widely different signals could be expected. Moreover, the intimate “attachment” of the catalyst particles to the catalyzed carbon nanostructures introduces further possible complications related to reactions between the metal nanoparticle and carbon upon pulsed laser heating, as discussed previously.

**Results and Discussion**

**Spectrally Resolved Emission**

As a starting point for identifying suitable spectral regions for detection of incandescence and spectral interferences, temporally resolved emission spectra were obtained. These were collected at the highest available laser fluence, 0.8 J/cm² to best detect possible spectral interferences from vaporized species.

In comparison to LII spectra obtained on metal aerosols [14], there is absence of structured emission in the spectra shown in Fig. 2. This suggests an absence of electronically excited atoms or molecules produced by the pulsed laser heating. Similar results have been attained with LII applied to soot, when using 1064 nm excitation [3,12]. This apparent absence of Fe or Ni and atomic, molecular or small cluster emission potentially offers straightforward interpretation of the emission as arising from SWNTs and nanofibers.

![Figure 2.—Spectrally resolved emission signals collected at the indicated times after the excitation laser pulse. The blackbody curve fits are the solid lines.](image-url)
Yet these spectra differ substantially from blackbody emission characteristic of a carbonaceous aerosol. As shown for both the Fe and Ni pyrolysis flames, the fitted temperatures of the initial spectra are substantially higher than those associated with the vaporization temperature of carbon, roughly 4000 K. It should be noted that carbon has the highest vaporization temperature of the materials within the flame environment used here. Only ionic, atomic and molecular emission can create such apparent elevated temperatures, not a superheated, solid nanostructure. These species likely exist within a laser vaporized plasma. With increasing time after the excitation laser pulse, the spectra become consistent with blackbody emission commensurate with “solid” carbon material (i.e. < 4000 K). Collisional quenching and radiative cooling of electronically excited species will occur at a far faster rate than conductive cooling of a solid nanostructure [20]. Essentially, spectra collected at times delayed after the excitation laser pulse allow for plasma dissipation processes after which only incandescence becomes detectable.

**Temporally Resolved Emission**

In order to clarify/identify the origins of the wavelength resolved emission spectra, temporally resolved signals were collected at fixed detection wavelengths of 300, 450 and 600 nm. The same value of laser fluence, 0.8 J/cm² as used for the temporally resolved emission spectra generated these signals. These data are plotted in Fig. 3 for both the Fe and Ni pyrolysis flames. The signal intensities have been scaled to a common peak intensity in order to examine differences in the temporal decays. As shown, for both the Fe and Ni based systems, there is little variation in the temporal decay with increasing detection wavelength. Moreover, for any given detection wavelength, there is little difference in the decay rate between the Fe and Ni systems, despite the quite different sizes for the catalyst particles and carbon nanostructures between these two systems, as shown in Fig. 1.

![Figure 3](image)

**Figure 3.**—Temporally resolved emission signals collected at the nominal indicated wavelengths for the Fe and Ni based pyrolysis flame systems.

Variation in the time evolution at these different wavelengths can reveal contributions to the observed laser induced emission in addition to incandescence from the laser heated nanostructures. If only blackbody radiation were contributing to the signal, a more significant decrease in the temporal decay rate would be expected with increasing detection wavelength. That such behavior is not observed indicates a different origin of the emission. The close similarity in the emission decay rates between the Fe and Ni systems indicates vaporization producing a super-heated plasma, producing a “blackbody” continuum emission. Under severe vaporization, if any solid material remains to incandesce at longer times, [13,15], its contribution to the detected radiation will be small. The solid material may arise either from condensation of plasma species or material heated by the wings of the near top-hat beam profile.
Fluence Dependencies

Having determined that vaporization occurs at these fluences, leaving little or no material from either SWNT or nanofibers, we collected fluence dependence data. Fluence dependencies serve as a starting point for determining the onset of vaporization and its contribution to the observed signal. The data shown in Fig. 4 were generated using a “prompt” signal collection gate, beginning with the peak LII intensity, for the indicated signal integration times following the laser pulse as indicated in the Figure. As seen in Fig. 4, for both the Fe and Ni systems, the signal increases, reaches a near maximum and then decreases. Traditionally, the decrease has been attributed to laser induced vaporization resulting in mass loss leaving less material to incandesce subsequent to the laser pulse [5,13,15]. The point of decreasing signal has been referred to as the vaporization threshold.

Two Laser Pulse Measurements

Two-laser pulse measurements are used to further probe the effects of laser induced changes upon the optical signal. Two-laser pulse experiments reveal that other material changes are produced at fluence below the apparent vaporization threshold, leading to nanostructures with different optical and thermal properties. Results from these measurements will be conveyed during the presentation.

Conclusions

In conclusion, it is likely, based on previous studies of LII applied to metal aerosols, that the catalyst particles contribute to the incandescence and/or plasma emission, the particular process depending upon the laser fluence. The super-elevated temperatures, derived from blackbody fits to spectrally resolved emission, observed using laser fluences of 0.8 J/cm², suggest continuum emission from a laser generated plasma. The absence of atomic, molecular and cluster electronic emission upon the “blackbody” (plasma) radiation is surprising, but highlights the utility of 1064 nm excitation in order to avoid electronic excitation of plasma species.
Unlike previous observations, LII from the metal nanoparticles does not produce distinct spectral signatures. Thus, their relative contribution to the emission signal is not readily extracted from that arising from the carbon nanotubes or nanofibers. Additionally, it is not readily rejected, spectrally nor temporally. The short temporal existence of the emission signal from Fe-SWNT system and Ni-nanofiber system confirms that vaporization occurs at high laser fluences, e.g. 0.8 J/cm². In this case there is no remaining solid incandescence. Fluence dependencies reveal the onset of laser induced vaporization as commensurate with that of pure carbonaceous material, approximately 0.6 J/cm².

References

**REPORT DOCUMENTATION PAGE**

<table>
<thead>
<tr>
<th>1. AGENCY USE ONLY (Leave blank)</th>
<th>2. REPORT DATE</th>
<th>3. REPORT TYPE AND DATES COVERED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>April 2004</td>
<td>Final Contractor Report</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4. TITLE AND SUBTITLE</th>
<th>5. FUNDING NUMBERS</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>6. AUTHOR(S)</th>
<th>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Randy L. Vander Wal, Thomas M. Ticich, Gordon M. Berger, and Premal D. Patel</td>
<td>National Center for Microgravity Research 21000 Brookpark Road Cleveland, Ohio 44135</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>8. PERFORMING ORGANIZATION REPORT NUMBER</th>
<th>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E–14453</td>
<td>National Aeronautics and Space Administration Washington, DC 20546–0001</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>10. SPONSORING/MONITORING AGENCY REPORT NUMBER</th>
</tr>
</thead>
<tbody>
<tr>
<td>NASA CR—2004-212977</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>11. SUPPLEMENTARY NOTES</th>
</tr>
</thead>
</table>

12a. DISTRIBUTION/AVAILABILITY STATEMENT

<table>
<thead>
<tr>
<th>Unclassified</th>
<th>Distribution: Nonstandard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subject Categories: 23 and 31</td>
<td></td>
</tr>
</tbody>
</table>

Available electronically at [http://gltrs.grc.nasa.gov](http://gltrs.grc.nasa.gov)

This publication is available from the NASA Center for AeroSpace Information, 301–621–0390.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Laser induced incandescence applied to a heterogeneous, multi-element reacting flows is characterized by a) temporally resolved emission spectra, time-resolved emission at selected detection wavelengths and fluence dependence. Laser fluences above 0.6 J/cm² at 1064 nm initiate laser-induced vaporization, yielding a lower incandescence intensity, as found through fluence dependence measurements. Spectrally derived temperatures show that values of excitation laser fluence beyond this value lead to a super-heated plasma, well above the vaporization of temperature of carbon. The temporal evolution of the emission signal at these fluences is consistent with plasma dissipation processes, not incandescence from solid-like structures.

14. SUBJECT TERMS

Laser induced incandescence; Carbon; Carbon aerosol detection; Nanotubes

15. NUMBER OF PAGES

13

16. PRICE CODE

Standard Form 298 (Rev. 2-89) Prescribed by ANSI Std. Z39-18 298-102

NSN 7540-01-280-5500