Pulsed Laser Annealing: Application to Nanoscale Carbon Materials

R. Vander Wal* and C. Gaddam

The Pennsylvania State University
John and Willie Leone Family Dept. of Energy and Mineral Engineering, & The EMS Energy Institute
* University Park, PA, USA, RandyVW@psu.edu

ABSTRACT

The terminology of laser derivitization refers to material transformation under the action of pulsed laser light. We have begun to use this technique as a processing tool to accentuate nanostructural differences in soot followed by HRTEM and image analysis.

Keywords: Carbon, laser, anneal, graphitize, HRTEM

1 INTRODUCTION

In prior work the author developed a laser based diagnostic, laser-induced incandescence (LII) to measure soot aerosol concentrations [1, 2]. In LII the final elevated temperature depends upon the laser intensity and fluence. Temperatures up and exceeding the vaporization temperature of carbon (~ 4000 K) are readily achievable with standard pulsed lasers. A consequence of the extreme condition, albeit unexpected given the short timescales involved were the structural transformation of the carbon particles. Because of the small particle size, radiative cooling occurs quickly, within 10's of nanoseconds. By 100 nsec the material temperature is lower than 2000 °C, a temperature at which mobility of carbon lamella becomes thermodynamically limited. The intriguing feature is the fast rate of cooling which effectively quenches the carbon transformation. In essence the nanostructure becomes frozen. Such short timescales do not allow for relaxation to thermodynamically stable graphite. The degree of growth and extent of realignment are dependent upon the initial nanostructure within the constraints of particle and aggregate morphology; each of which in turn depends upon the combustion conditions and fuel type.

2 RESULTS & DISCUSSION

Figures 1 and 2 are high-resolution transmission electron micrographs illustrating the comparative changes in nanostructure for spherical carbon particles along with their evolved nanostructure upon pulsed laser heating.

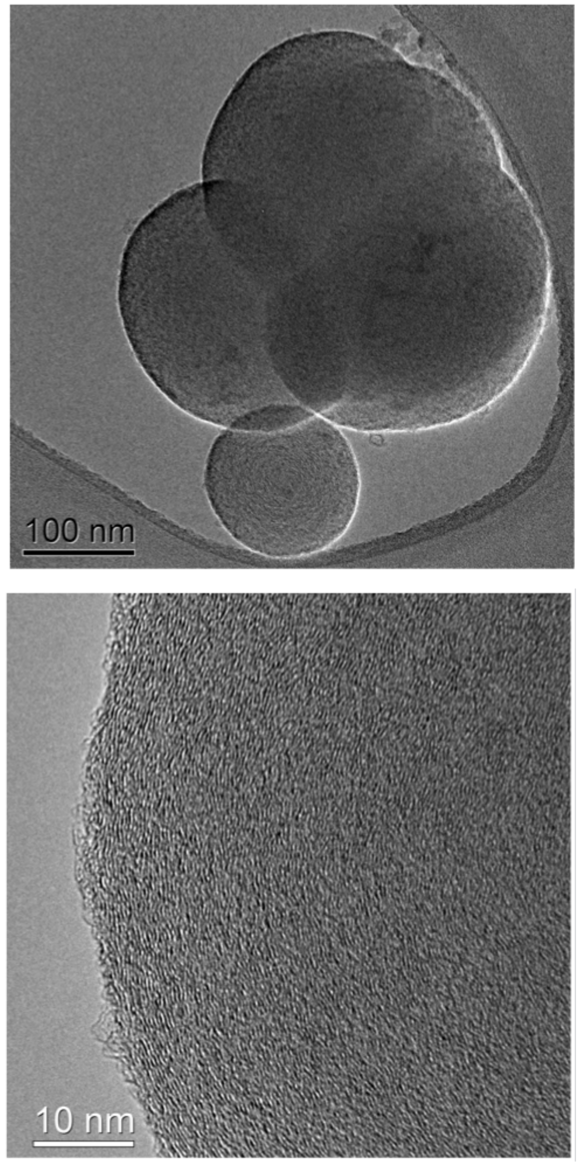

Figure 1. HRTEM images showing the original carbon at two different magnifications.

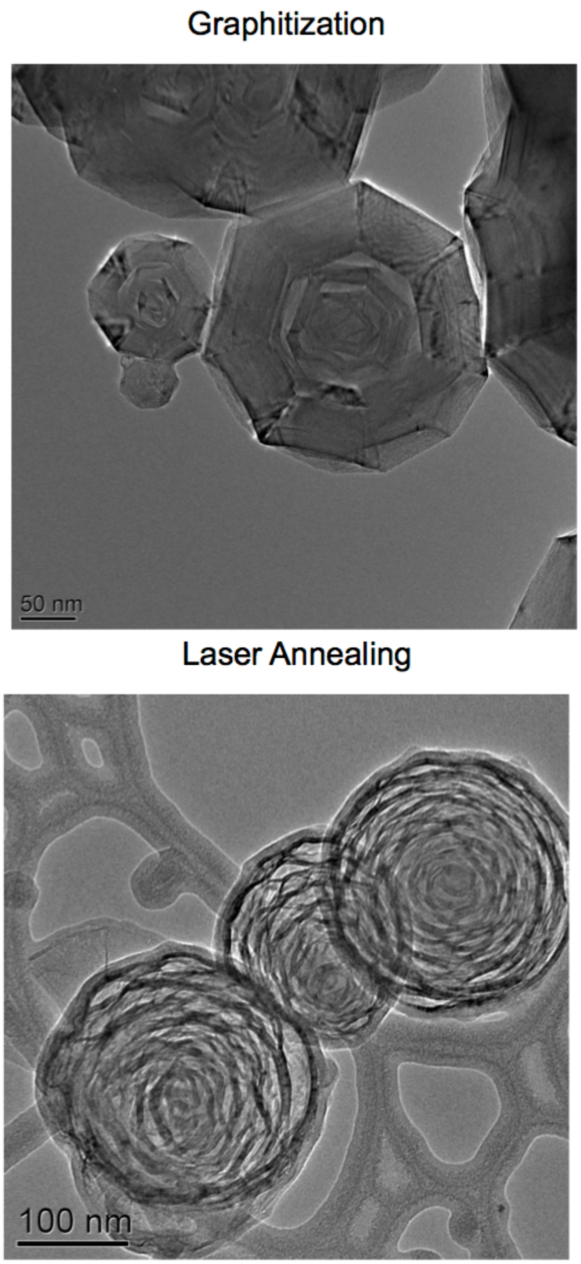

Figure 2. HRTEM images showing the carbon subjected to high temperature (3000 C) thermal graphitization (left) and laser annealed carbon (right) at the same magnification.

Figures 3 and 4 show lower magnification HRTEM images of two different laser annealed carbons. Figure 3 is the same material as shown in Figs. 1 & 2. The internal voids are not easily resolved but the uniformity of the process is readily seen. As represented by the image, the interconnected nature of the carbon particles is shown, this being inherent to the starting material. Figure 4 shows the internal microporosity created by laser annealing but starting with a different carbon source material. Both surface area and micropore volume increased. Relative to the former carbon, these values were different suggesting that source selection can be used as a variable by which to further tailor final carbon structure.

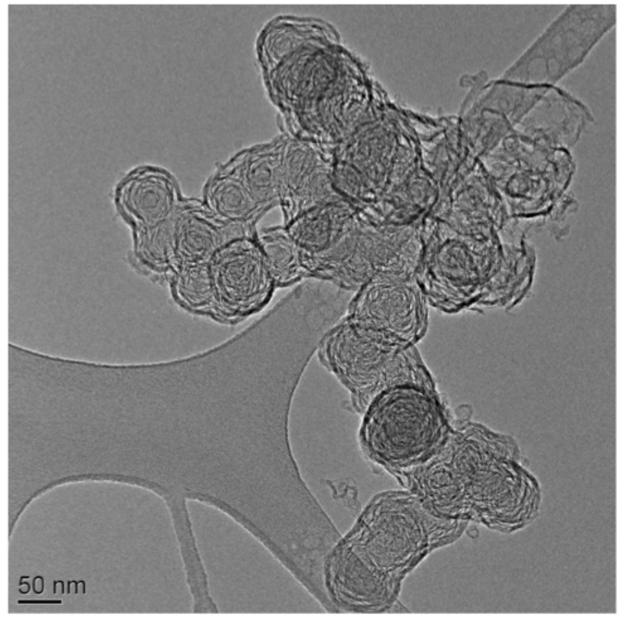

Figure 3. HRTEM image of the laser annealed carbon showing macrostructure of connected particles and the uniformity of the processed carbon.

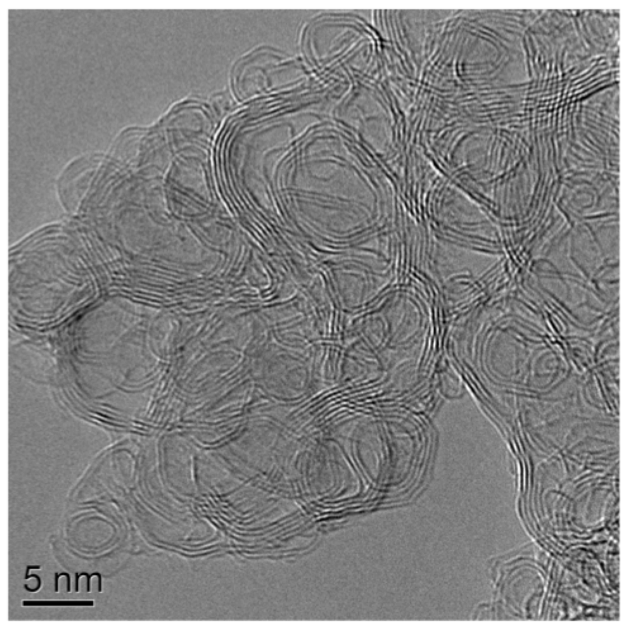

Figure 4. HRTEM image of the laser annealed carbon showing macrostructure of connected particles and the uniformity of the processed carbon.

The significance of pulsed laser heating is that the transformed material has extensive internal voids, i.e. microporosity. Volatiles have escaped or decomposed at the elevated temperatures. Lamellae have grown, aligned and reoriented, aided by removal of cross-links and bonding enabled by radical sites created under thermal action. In general the lamellae are now distinct and highly recognizable. Unlike graphitization, transport across the lamellae is yet possible, as evident by the measured increase surface area and micropore volume.

That such amorphous carbons change, morphologically, structurally and chemically in response to heat treatment is well known [3]. Generally the process is termed "graphitization". Appropriate given that under thermal equilibrium conditions the carbon transforms towards graphite. The degree depends upon temperature, time of heating and most importantly, the initial carbon material. Though extremes of temperature can induce large changes, carbons exhibit high initial variability and broadly two classes of carbons are so-called graphitizing and non-graphitizing, with meanings as the names imply [4]. Of course there is a virtual continuum in between these two limits with the degree of graphitization defined by the extent of long-range order resembling that of graphite. That such bulk materials can manifest such divergence based upon initial composition and structure even more applies to nanocarbons where size and morphological effects could also contribute to promotion or inhibition of structural changes towards or perhaps away from the lattice structure of graphite.

3 CONCLUSIONS

Our preliminary evidence suggests that the initial carbon nanostructure in conjunction with the chemistry of construction governs the material transformation under pulsed laser annealing. As the figures suggest, nanostructural differences are visually recognizable as dependent upon the starting material. Upon action of pulsed laser light, these differences become magnified. Therein the action of the laser light is to differentiate the nanostructure to accentuate the differences in the process termed laser derivitization.

4 ACKNOWLEDGEMENTS

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REFERENCES

1. Vander Wal, R. L., Using Laser-induced Incandescence to Measure Soot/Smoke Concentrations, (Invited Feature Article) Laser Focus World (1998).
2. Vander Wal, R. L., Laser-Induced Incandescence: Excitation and detection conditions, material transformations and calibration. Appl. Phys. B 96:601-611 (2009).
3. Gadiou, R., Didion, A., Saadallah, S.-E., Couzi, M., Rouzaud, J.-N., Delhaes, P., and Vix-Guterl, C., Graphitization of carbons synthesized in a confined geometry. Carbon 44:3348-3378 (2006).
4. Oberlin, A., Carbonization and graphitization. Carbon 22:521 (1984).