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TRAJECTORIES OF GRAPHITIZABLE ANTHRACENE COKE AND NON-GRAPHITIZABLE SUCROSE CHAR DURING THE EARLIEST STAGES OF ANNEALING VIA CO_2 LASER HEATING

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Introduction

The structural transformation of carbons with dependence upon Heat-Treatment-Temperature (HTT) has received extensive study.[1,2] A vast accumulation of knowledge has been gained regarding HTT studies. However, HTT studies are purely based on thermodynamics (i.e. temperature) and little attention has been directed towards annealing kinetics. Measuring kinetics of solid-state reactions at temperatures above 2,000 °C are challenging experimentally. The experimental challenge is in the control of achieving short time durations at precise elevated temperatures. Lasers can heat carbon materials to graphitization temperature within nanoseconds to milliseconds, depending on laser light source.[3,4] On these extremely short time scales, the extent of material transformation is kinetically limited by time above temperature. Laser heating can be used to study the rates and trajectories of carbon annealing.[5] Short heating durations enable the annealing pathway of graphitizable and non-graphitizable carbons to be followed and contrasted. Franklin's original non-graphitizable model is broadly correct, but the key to the model lies in the cross-links and the structure of these cross-links is unknown, thus the key to non-graphitizing behavior is not adequately explained.[6,7] The discovery of the C60 fullerene stimulated much research. The key defining feature of fullerenes is the 5-membered pentagonal ring. The idea that odd membered rings are the defects in chars that lead to cross-linking and non-graphitizability has been proposed.[8–10] However, direct visualization of odd-membered ring structures with transmission electron microscopy (TEM) in chars prior to heat treatment is difficult as the material is amorphous. Monitoring the materials trajectory with respect to time at temperature can provide insight into the nature and formation mechanism of cross-links found in heat-treated non-graphitizable carbons.

Materials and Methods

Anthracene and sucrose were selected as model graphitizing and non-graphitizing compounds based on historical precedence.[6,11,12] Samples were prepared by carbonization in a tube bomb reactor. Ten grams of precursor was loaded into a 25 mL reactor body. The reactor was purged of oxygen with nitrogen. A sand bath was used to bring the reactor to temperature. Heating duration and temperature were 5 h and 500 °C. Carbonization occurred under autogenous pressure (no pressure control), pressures reached ~ 6.9 MPa. A Centorr Vacuum Industries series 45 graphitization furnace was used to provide reference materials. Heat treatment temperature of 2600 °C was used to anneal samples for a duration of 1 hour. Anthracene coke and sucrose char were

laser heated with a 250 W CO_2 laser to 2600 °C for 0.25–300 s.[5] The laser was operated at full power. The laser spot size was 4 mm in diameter. Time-Temperature-Histories (TTHs) were determined by spectrally resolving the laser-induced incandescent signal and applying multi-wavelength pyrometry. Samples were ground to a fine powder and pressed into a thin disc (~ 100 µm) for heating. Thin samples were used to promote uniform heating. This approach was determined appropriate based on TTHs collected from underneath a thin layer. Samples were heated under an argon atmosphere. TEM was used for direct visualization of nanostructure before and after annealing. Oxygen content was assessed with Energy Dispersive X-ray Spectroscopy (EDS) in the TEM. X-Ray Diffraction (XRD) was utilized for crystal structure determination. The experimentally observed unraveling of sucrose char was simulated using ReaxFF based reactive molecular dynamics.

Results and Discussion

Sucrose and anthracene derived carbons displayed overlapping TTHs.[5] Samples reached 2,600 °C in 1.4 ms. The traditional furnace annealing pathway is followed for CO_2 laser heating as based upon equivalent end structures.[3,5]

Anthracene Coke. Graphitizable anthracene coke followed the well-known thermodynamically based HTT steps as first described by Oberlin.[1] The as-prepared materials represent stage 1, basic structural units (BSUs) formed via mesophase. The 4 stages are separated by increasing temperature. A time series of short duration isothermal laser heating at 2,600 °C showed stage 2 to occur after 0.25 s. After 1 s the distorted columns of BSUs from stage 2 were converted to wrinkled layers representing stage 3, that typically occurs around 1,000 °C. The distorted layers stiffened and become relatively flat after 5 s at 2,600 °C.[5] Following the 4 HTT stages, the layer plane spacing decreases (i.e. graphitization) as layers assume graphitic lattice spacing at temperatures above 2,200 °C. As prepared anthracene coke has a turbostratic structure with a layer plane spacing of 3.44 Å as measured with XRD. The spacing does not decrease until the 2-dimensional annealing is completed (after 5 s at 2,600 °C). The spacing reduction initially occurs at a faster rate and progressively slows.[5]

Sucrose Char. Material restructuring is observed in sucrose char after 0.25 s. Compared to the as-prepared char, the annealed sample lamellae are slightly longer with more pronounced curvature.[5] The oxygen content is below the EDS detection limit after 0.25 s. Oxygen departs early in the annealing process and impacts trajectory through the structure it imparts on the carbon skeleton and not by direct C-O-C cross-linking as is commonly suggested. After 1 s closed shell nanoparticles appear to be forming.[5] The material is comprised exclusively of closed shell nanoparticles after 5 s at 2,600 °C as displayed in Figure-1A. This structure suggests an abundance of odd-membered rings are present in the structure as it is unlikely such a structure could exist without the inclusion of odd-membered rings. The odd-membered rings likely originated in the as prepared material and/or formed upon early oxygen loss. The closed shells unravel with additional time at temperature and give rise to the irregular pore structure displayed in Figure-1B. The disorganized carbon structure from heat treated sucrose char has been described as ribbon-like. However, ribbon-like implies the fringes in Figure-1B are projections of curtain-like structures and not cages or pores as they are. Upon rotating the specimen it is observed that these materials are cage-like and can better be imaged as crumbled up paper.[13] The distorted structure is not due

to imping growth of BSUs as is commonly suggested[14] but is from the unravelling of closed shell particles. Thus, it is odd-membered rings that are responsible for the non-graphitizability of sucrose char.

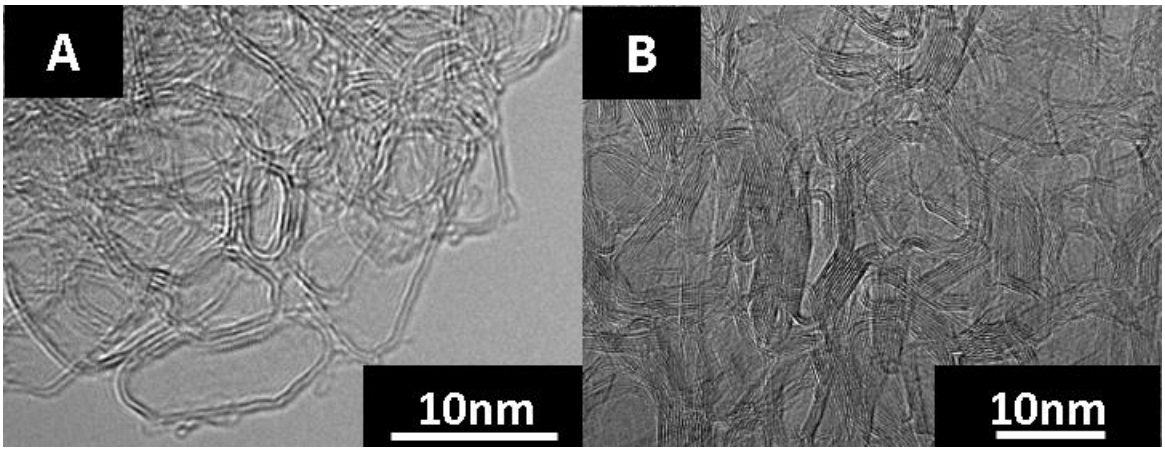

Figure 1. TEM micrograph of CO_2 laser annealed sucrose char. A) after 5 seconds, B) After 20 seconds.

ReaxFF was used to simulate the unravelling of the closed shell structure. Simulations resulted in the formation of a structure resembling a multiwall carbon nanotube MWCNT from two multiwall spherical nanoparticles.[5] The result is analogous to the annealing observed in peapod CNTs.[15]

Conclusions

The MWCNT endcap like structures found in furnace annealed sucrose char are really the remnants of once closed fullerenic-like nanoparticles. Odd-membered rings are required for the existence of such structures. Therefore, the odd-membered carbon ring induced curvature found in furnace annealed sucrose char is not manufactured during annealing via impinging growth, but rather the odd-membered rings are present in the virgin char.

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