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UNDERSTANDING THE LACK OF FULLERENES IN FULLERENE-LIKE CARBONS

Jacob W. Martin,[1,2] * Leonard Nyadong,[3] Caterina Ducati,[4] Merilyn Manley-Harris,[5] Alan G. Marshall,[6] and Markus Kraft[1,2,7]

[1]Department of Chemical Engineering and Biotechnology, University of Cambridge, West Site, Philippa Fawcett Drive, Cambridge, CB3 0AS, United Kingdom. [2]Cambridge Centre for Advanced Research and Education in Singapore (CARES), Singapore, 138602. [3]Phillips 66 Research Center, OK 74003-6607, United States. [4]Department of Materials Science and Metallurgy, University of Cambridge, United Kingdom. [5]School of Science, University of Waikato, New Zealand. [6]National High Magnetic Field Laboratory, Florida State University, FL 32310-4005, United States. [7]School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459

*Presenting author's e-mail: jwm50@cam.ac.uk

Introduction

Significant evidence has been demonstrated for fullerene-like curved carbon networks in non-graphitising carbons such as polygonalised structures [1] and non-hexagonal rings [2]. However, many mass spectrometry studies of charcoals have found a lack of fullerenes, such as C_{60} and C_{70} [3]. One of the ions of interest is the mass-to-charge (m/z) 701 ion, near the m/z of C_{60}, which has been found in glassy carbon and in many charcoal samples [3]. We have previously interpreted this ion as belonging to a planar graphitic fragment and developed a microcrystalline model of charcoal [3]. Recently, we explored the thermal annealing of fullerenes in arc carbon into a polymerised structure with evidence for giant fullerenes and found the magic number fullerenes were consumed and oxygen integrated into the nanostructure of fullerene arc-carbon [4].

In this work, making use of a range of highly sensitive and accurate mass spectrometers we have explored the nanostructure of gasification charcoal. We compare the results with heat treated fullerene arc-carbon finding a similar nanostructure supported by Raman spectroscopy and electron microscopy.

Methods

We made use of a laser desorption ionisation time-of-flight, Fourier transform ion cyclotron resonance and electrospray ionisation time-of-flight-mass spectrometers. An FEI Tecnai F20 electron microscope was used at an accelerating voltage of 200 kV. Raman spectra were collected on a Horiba LabRAM HR spectrometer. Reactive molecular dynamics making use of the REBO-II reactive forcefield were used to explore the surface reconstruction and topology of this network.

Results and Discussion

We were unable to detect any magic number fullerenes C_{60} or C_{70} in the gasification charcoal samples using LDI-TOF MS or the highly sensitive FT-ICR MS method. The m/z 701 ion, near the m/z of C_{60}, was found to be a breakdown product of pyrolysis and not a persistent part of the nanostructure. When ablating the charcoal using a high laser power (12.8 mJ/cm^2) oxygenated ions were generated, separated by m/z 24, suggesting cage-like oxygenated carbon fragments. Similar

distributions of oxygenated ions were found for the thermally annealed arc-carbon suggesting a shared nanostructure **(Figure 1).** This indicates that small magic number fullerenes are not stable in solid state thermal annealing and polymerise along with intercalating oxygen. This suggests that an annealed fullerene-like nanostructure would not be expected to contain small unstable magic number fullerenes.

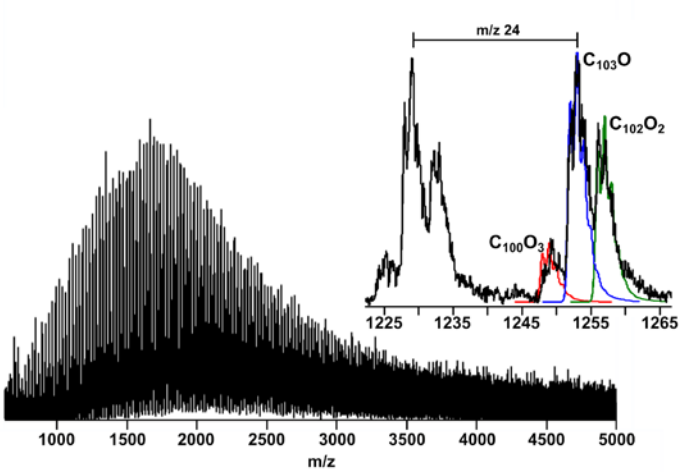

Figure 1. LDI-TOF mass spectrum of charcoal with inset showing the peak structure.

High resolution transmission electron microscopy (HRTEM) showed highly curved nanostructures. *Onion-like* structures were also observed. Layered regions were also observed alongside the curved features. Raman spectroscopy showed significant intensity between the D and G bands which has recently been computationally found to arise from the pentagonal ring breathing mode which is upshifted from the hexagonal breathing mode D band. A carbon surface was reconstructed using reactive molecular dynamics. The curvature is found to be integrated from non-hexagonal rings as well as non-sp^2 defects which close the surface of the solid providing a surface of low reactivity. Simulated HRTEM images reveal curved and layered fringes, leading us to suggest (along with the experimental results) a *stacked, fulleroid-like nanostructure* for this material.

Conclusions

No magic number fullerenes were found in a gasification charcoal but larger oxygenated fragments were found and were also found in thermally annealed arc-carbon. These results, along with HRTEM and Raman spectroscopy, support a *stacked, fulleroid-like nanostructure*.

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