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Carbon Onion Films-Molecular Interactions of Multi-Layer Fullerenes

Raed A. Alduhaileb,[1] Virginia M. Ayres,[1] Benjamin W. Jacobs,[1] Xudong Fan,[1] Kaylee McElroy,[1] Martin A. Crimp,[1] Atsushi Hirata[2] and Mutsumi Horikoshi[2]
[1]College of Engineering, Michigan State University, East Lansing, MI 48824, U.S.A.
[2]Graduate School of Mechanical Sciences, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan

ABSTRACT

The evolution of carbon onion structure from spherical to polyhedral is correlated with changes in the sp^3/sp^2 ratio as a function of increasing synthesis temperature using electron energy loss spectroscopy, high resolution electron microscopy and scanning electron microscopy. Results, which are obtained using asymmetric f-variance and symmetric Gaussian deconvolution of electron energy loss spectrum, are compared. The possibility of a separate peak at 287 eV is also discussed.

INTRODUCTION

Multi-shell fullerenes, or carbon onions, are under investigation as a nano-property enabled solid lubricant. The potential applications for a carbon onion-based lubricant range from an environmentally benign option for wind power to a vacuum lubricant [1] for solar panel deployment in space. These uses of carbon onions depend on both their individual properties such as mechanical strength, and their interaction properties. When carbon onions are applied as a thin lubricating film, their stiction, rolling, and sliding interactions, with each other and with the wear surfaces govern their ultimate usefulness, in addition to their individual mechanical load-bearing characteristics.

Carbon onion physical structures are known to vary with synthesis temperature. Several authors have reported the structural evolution from spherical to polyhedral multi-shells as a function of increasing synthesis temperature [2,3]. It has been generally assumed that the structural evolution is accompanied by a change in the sp^3/sp^2 ratio, since a reduction in potential sp^3 defect sites, which are visible as broken shells in high-resolution electron microscopy (HRTEM) images, is observed. However, broken shells may also terminate in amorphous carbon networks that are more sp^2 than sp^3, while individual sp^3 point defects could be very hard to detect based on HRTEM images alone. Accurate knowledge of a systematic evolution of the sp^3/sp^2 ratio is important for the synthesis of carbon onions for an optimum lubricating film, especially at the nano-scale, since sp^2 carbons interact principally through p-electron overlap, while sp^3 carbons exhibit local dangling bond sites.

In the present investigations, electron energy loss spectroscopy (EELS) is used as a sensitive measure to quantitatively determine the sp^3/sp^2 ratio of a series of carbon onion samples grown at increasing synthesis temperatures of 1700^{o}C, 2000^{o}C and 2300^{o}C. This temperature series exhibits the spherical to polyhedral structural transition, as determined using HRTEM. Additionally, scanning electron microscopy (SEM) was used to characterize synthesis uniformity of carbon onions at the micron level.

EXPERIMENTAL DETAILS

Preparation of samples

Carbon onions were prepared from crystalline diamond nanoparticles having an average diameter of 5 nm. The diamond nanoparticles were heated in inert ambience in infrared gold image furnace. A graphite holder filled with 10 mg of diamond nanoparticles was placed inside the furnace, which was evacuated to approximately 1.3 Pa with a rotary pump; and slowly heated in argon gas flow at 1.5×10^5 Pa to 1700°C, 2000°C and 2300°C, respectively. The furnace temperature was held for one minute and then gradually cooled to room temperature in argon flow.

Carbon onion samples were suspended in ethyl alcohol and dispersed onto carbon lacey film 200 mesh copper grids. Large holes in the lacey film were utilized to ensure that EELS spectra contained only carbon onions.

Analytical techniques

EELS experiments were performed using an integrated Omega filter in a JEOL 2200FS. The energy resolution was around 1.5 eV, evaluated using the full width half max (FWHM) of the zero loss peak. EELS spectra were first corrected for instrument background and plural scattering using Gatan analysis software. The corrected spectra were then investigated using de-convolution based on asymmetric f variance area and symmetric Gaussian area fits (Peak Fit™ by SigmaPlot, version 4.12).

HRTEM experiments were performed in the same JEOL 2200FS at 200 kV. The HRTEM was used to correlate the EELS bond hybridization results with the carbon onion spherical to polyhedral structural changes.

SEM experiments were performed using a Hitachi S-4700II Field Emission Scanning Electron Microscope operated at 15 kV. SEM was used to assess synthesis uniformity, and identify unstable growth parameter regimes within the temperature series.

Structural characterization by HRTEM

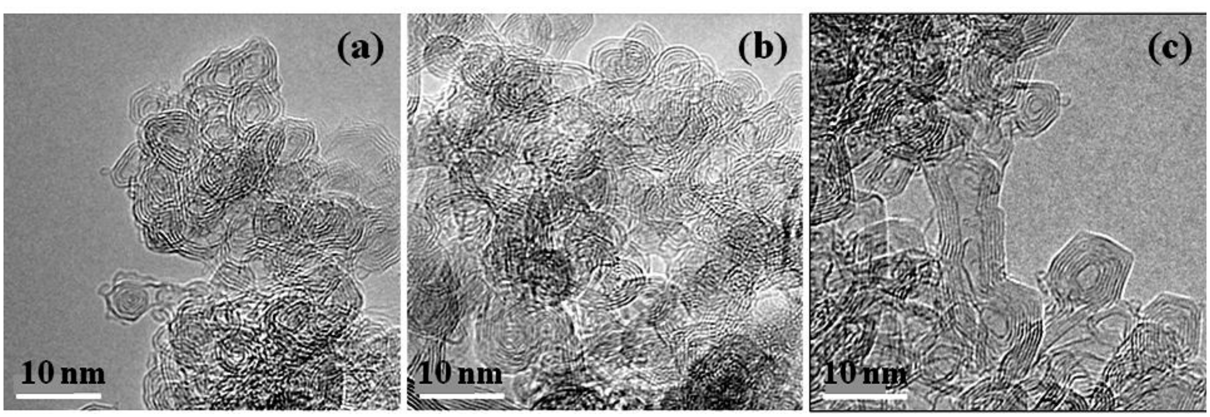

Figure 1. HRTEM of the structural transition from spherical to polygonal for carbon onions synthesized at temperatures (a) 1700^{o}C (b) 2000^{o}C and (c) 2300^{o}C.

HRTEM images confirmed that the previously reported spherical to polygonal structural transition is observed for our synthesis conditions over a temperature range of 1700°C to 2300°C. No evidence for a nanodiamond core was observed in any carbon onions; therefore HRTEM images also indicated that the nanodiamond starting material had been completely converted into the innermost carbon onion layers. The structural transition for these samples is shown in figure 1 (a-c).

sp^3/sp^2 characterization by EELS

EELS spectra were used to quantitatively measure the sp^3/sp^2 ratio in the carbon onion samples that were grown at increasing synthesis temperatures of 1700°C, 2000°C and 2300°C. Investigating the hybridized chemical bonding of all carbon onion samples revealed two major edges of sp^2 carbon in the EELS spectra. The first edge of the carbon K-edge spectra corresponds to the 1s to 2π* transition at 284.7 eV, and the second prominent edge corresponds to the 1s to 2σ* transition at 292.0 eV. Figure 2 (a) shows a typical EELS spectra for carbon onions prepared at 1700°C with the major edges identified. For a purely sp^2 material, the ratio of the integrated areas, which is given by equation (1), is close to 0.333 based on the energy density of states.

$$\frac{I^R_{\pi*}}{I^R_{\sigma*}} \tag{1}$$

This value is taken as the ratio reference (R) for the carbon onion (CO) sp^3/sp^2 ratio that is estimated as:

$$\frac{I^{CO}_{\pi*} \,/\, I^{CO}_{\sigma*}}{I^R_{\pi*} / \, I^R_{\sigma*}} \tag{2}$$

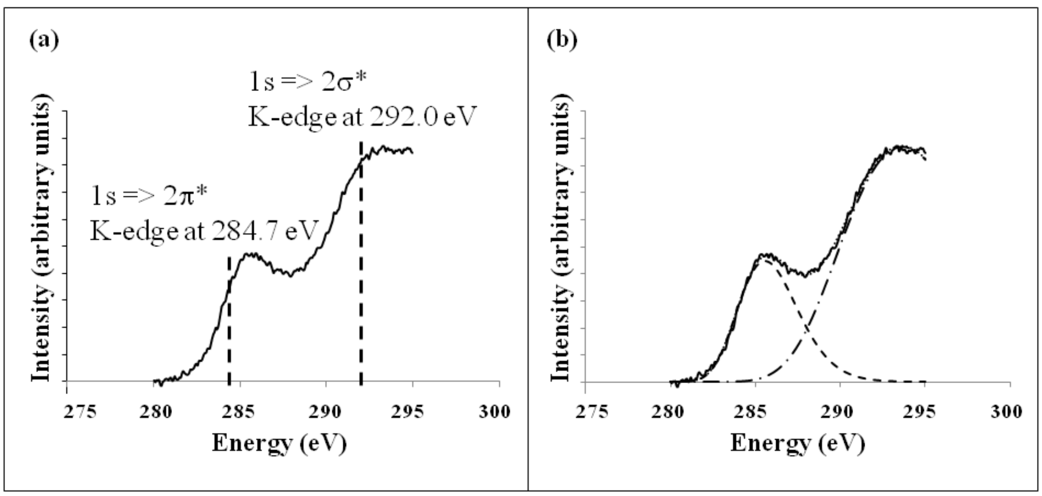

Figure 2. EELS spectrum from carbon onions prepared at 1700°C showing (a) the main transition K-edges and (b) 2-peak fit by f-variance deconvolution.

Deconvolution must be used to identify and evaluate the integrated areas that correspond to the carbon onion 1s to 2π* and 1s to 2σ* transitions. In the present work, we experiment with using an asymmetric f-variance fit, to reproduce the characteristics of the leading edge, which is a delta function symmetrically broadened by the energy resolution of the instrument, and the higher energy states, which are the asymmetric contributions from all available energy levels in the energy density of states [4]. The results of 2-peak fitting by asymmetric f-variance deconvolution are shown in Table I. A typical deconvolution for carbon onions prepared at 1700^{o}C is shown in figure 2 (b). All samples had a coefficient of determination (CoD) of 0.97 or above using the 2-peak asymmetric fit.

Table I. EELS results obtained using f-variance area deconvolution and 2-peak fit.

Temperature	CoD	$I_{\pi*}$	$I_{\sigma*}$	$I_{\pi*}/I_{\sigma*}$	sp^3/sp^2
1700^{o}C	0.999	39547.39	95377.24	0.41	1.2452
1700^{o}C	0.993	65823.27	156490.00	0.42	1.2631
2000^{o}C	0.978	117590.00	295790.00	0.40	1.1938
2000^{o}C	0.998	125260.00	437990.00	0.29	0.8588
2000^{o}C	0.997	369690.00	728380.00	0.51	1.5242
2300^{o}C	0.999	166230.00	358740.00	0.46	1.3915
2300^{o}C	0.996	225710.00	479510.00	0.47	1.4135

Analysis of sp^3/sp^2 ratio in the literature is typically based on symmetric Gaussian deconvolution of the EELS spectra. A question has arisen over the need for a separate feature at about 287 eV in addition to the known 1s to 2π*and 1s to 2σ* transitions at 284.7 eV and 292.0 eV. The interpretation of such a 287 eV feature, as due to a C-H contribution [5] or to several possible molecular sp^2 contributions [6], is also under discussion. Therefore, in this work, we have investigated (a) whether inclusion of a 287 eV feature is required in a 2-peak fit by Gaussian deconvolution and (b) whether inclusion of a 287 eV feature in a 3-peak fit by Gaussian deconvolution produces a good fit, identified as a high CoD.

The results of 2-peak fitting by symmetric Gaussian deconvolution are shown in Table II. In at least one instance (row identified with bold border), a 3-peak fit that included a peak at about 287 eV was required to obtain a 0.989 CoD

Table II. EELS results obtained using Gaussian deconvolution and 2-peak fit.

Temperature	CoD	$I_{\pi*}$	$I_{\sigma*}$	$I_{\pi*}/I_{\sigma*}$	sp^3/sp^2
1700^{o}C	0.998	28384.32	106570.00	0.27	0.7998
1700^{o}C	0.989	38044.33	160220.00	0.24	0.7131
2000^{o}C	0.992	64570.15	359260.00	0.18	0.5397
2000^{o}C	0.997	81883.80	484740.00	0.17	0.5073
2000^{o}C	0.998	288310.00	813370.00	0.35	1.0645
2300^{o}C	0.998	114530.00	419090.00	0.27	0.8207
2300^{o}C	0.993	142900.00	565360.00	0.25	0.7590

The results of 3-peak fitting by symmetric Gaussian deconvolution with inclusion of a third feature at 287 eV are shown in Table III. All samples had CoD of 0.97 or above using the 3-peak asymmetric fit. A typical deconvolution for carbon onions prepared at 1700^{o}C is shown in figure 3.

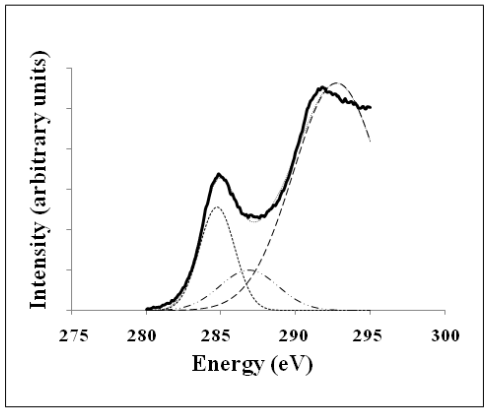

Figure 3. EELS spectra from carbon onions prepared at 1700°C showing 3-peak fit by Gaussian deconvolution.

Table III. EELS results obtained using Gaussian deconvolution and 3-peak fit.

Temperature	CoD	$I_{\pi*}$	$I_{\sigma*}$	$I_{\pi*}/I_{\sigma*}$	sp^3/sp^2
1700°C	0.990	23974.79	32161.78	77124.92	0.9335
1700°C	0.981	45052.71	22508.18	155460.00	0.8703
2000°C	0.974	67397.28	81505.44	273040.00	0.7413
2000°C	0.995	109060.00	36756.27	419600.00	0.7805
2000°C	0.999	256560.00	58267.76	783520.00	0.9833
2300°C	1.000	92994.61	27554.33	409640.00	0.6817
2300°C	0.993	133940.00	38433.95	534010.00	0.7532

Investigation of structural evolution by SEM

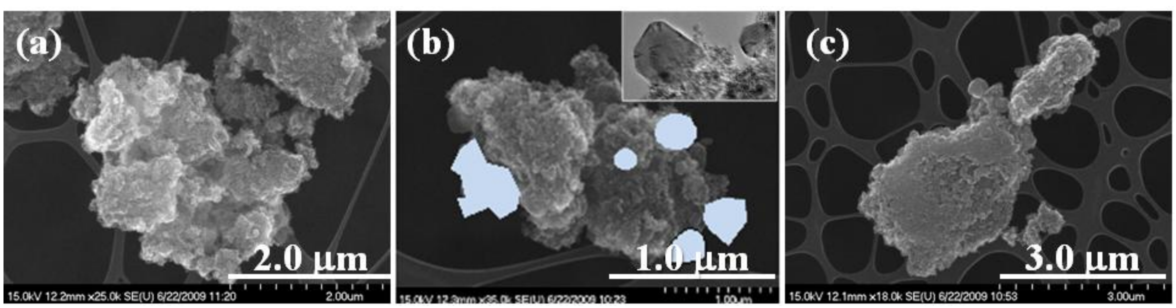

Figure 4. SEM surface images of carbon onions synthesized at temperatures (a) 1700°C (b) 2000°C and (c) 2300°C.

SEM images, which are shown in figure 4 (a-c), indicated that synthesis uniformity issues may be present. Synthesis was fairly uniform for carbon onions grown at 1700°C. However, carbon onions grown at 2000°C showed evidence of microcrystallite graphite formation in addition to carbon onion synthesis. Carbon onions grown at 2300°C showed better uniformity than those grown at 2000°C but less uniformity than samples grown 1700°C, with some microcrystallite graphite formation observed.

DISCUSSION

The EELS spectra of the carbon onion samples showed an increase in the sp^3/sp^2 ratio based on comparison of the results from the 1700°C synthesis and 2300°C synthesis. The results from the 2000°C were variable. SEM and TEM results indicated that synthesis uniformity issues were present for the 2000°C carbon onions. Therefore, synthesis uniformity should be considered in analysis of the sp^3/sp^2 ratio based on EELS.

In the present work, we use an asymmetric f-variance fit, to reproduce the characteristics of the leading edge, which is a delta function symmetrically broadened by the energy resolution of the instrument, and the higher energy states, which are the asymmetric contributions from all available energy levels in the energy density of states. The results of 2-peak fitting by asymmetric f-variance deconvolution produced fits with CoDs of 0.97 or above (typically above) for all samples. 2-peak fitting by symmetric Gaussian deconvolution required an additional feature at 287 eV for at least one sample, and 3-peak fitting by symmetric Gaussian deconvolution with inclusion of a 287 eV feature produced fits with CoDs of 0.97 or above for all samples.

CONCLUSIONS

The evolution of carbon onion structure from spherical to polyhedral is correlated with changes in the sp^3/sp^2 ratio as a function of increasing synthesis temperature using electron energy loss spectroscopy, high resolution electron microscopy and scanning electron microscopy. High CoD fits were obtained without inclusion of a separate peak at 287 eV using asymmetric f-variance deconvolution of electron energy loss spectra.

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REFERENCES

1. A. Hirata, M. Igarashi and T. Kaito, *Tribol. Int.* **37**, 899 (2004).
2. O. O. Mykhaylyka, Y. M. Solonin, D. N. Batchelder and R. Brydson, *J. Appl. Phys.* **97**, 074302 (2005).
3. S. Osswald, G. Yushin, V. Mochalin, S. O. Kucheyev and Y. Gogotsi, *J. Am. Chem. Soc.***128**, 11635 (2006).
4. R. Egerton, "Chapter 3: Electron Scattering Theory," *Electron Energy Loss Spectroscopy in the Electron Microscope* (Plenum Press, New York, NY, 1986) pp. 129-228.
5. R. Brydson, Z. Zhili and A. Brown, "Revisiting the Determination of Carbon sp^3/sp^2 Ratios via Analysis of the EELS Carbon K-edge," *EMC 2008: Vol 1: Instrumentation and Methods*, edited by M. Luysberg, K. Tillmann and T. Weirich (Springer-Verlag, Berlin, Germany, 2008) pp. 357-358.
6. A. J. Papworth, C. J. Kiely, A. P. Burden, S. R. Silva and G. A. Amaratunga, *Phys. Rev.* **B62**, 12628 (2000).