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Spontaneous formation of carbon nanotubes and polyhedra from cesium and amorphous carbon

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Carbon nanotubes, nested onions and polyhedra are a subset of the carbon polymorphs called fullerenes [1-12]. In each case, the formation of these materials involves high-temperature processes. Herein, we describe new results showing carbon nanotubes and polyhedra can be formed spontaneously — under mild conditions — at temperatures as low as 50°C. This transition from structural disorder to order is brought about by the interaction of elemental cesium with non-crystalline, nanoporous carbon.

The nanoporous carbon (NPC) was prepared by pyrolysis of a mixture of poly-(furfuryl alcohol) and poly-(ethylene glycol) [13-16].¹ NPC prepared in this way does not display an X-ray diffraction pattern but simply weak and diffuse lines in the vicinity of those observed for well-ordered graphite. Skeletal densities of the materials range between 60 and 70% that of graphite [14] and hydrogen content is less than 0.01 wt% [14,16]. The free volume in the structure is bimodally distributed between nanopores with a mean dimension of 0.5 nm and mesopores with a mean dimension of 7.0 nm [16].

The transition to ordered structure was achieved by following the methods we developed for the preparation of strong base catalysts [13]. One gram of NPC was pretreated by heating under vacuum for 18 h at 450°C and placed in a stainless-steal tube. Two grams of metallic cesium were warmed to liquefaction and added to the carbon. Upon mixing, there was a mild, but detectable, exotherm. The tube containing the mixture was sealed, placed in a close-fitting furnace, heated at 50°C for 16 h and then cooled to room temperature. The resultant Cs/NPC solid was free flowing and showed no signs of gross Cs inclusions. Due to the pyrophoric nature of the metallic cesium, all the steps described were conducted within the confines of an argon atmosphere glovebox. Two additional samples were prepared in an identical manner with the exception that the Cs treatments were conducted at 350 and 500°C.

The Cs/NPC samples were prepared for transmission electron microscopy (TEM) on a dry basis. The materials were removed from the glovebox in closed containers which were opened to air slowly. The samples were ground into fine powders using an agate mortar and pestle, and deposited directly onto holey-carbon-coated Cu TEM grids. Excess and loose powders were removed from the grids by gentle shaking.

The HREM images of the Cs-treated materials and that of the starting amorphous NPC displayed

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¹ A 75:25 (wt/wt) mixture of poly-(furfuryl alcohol) and 8000 avg. MW poly-(ethylene glycol) was pyrolized at 850°C for 8 h under flowing helium.



Fig. 1. HREM images of (a) NPC prior to Cs^o treatment, but after heating in vacuum for 18 h at $T = 450^{\circ}$ C (________, 10 nm). (b) NPC after treatment with Cs^o and post-treatment at $T = 50^{\circ}$ C for 3 h (_______, 10 nm). (c) Post-treatment at $T = 350^{\circ}$ C. (d) Post-treatment at $T = 500^{\circ}$ C.

notable differences. The NPC that had not been treated with cesium, displayed the typical amorphous nanopore structure [14,15]. On a length scale of 1.5-3.0 nm there is no reproducible ordering (Fig. 1a). Low-magnification TEM examination of the Cs/NPC materials indicated each contained regions that were Cs-rich and regions that contained essentially no cesium as confirmed by energy-dispersive spectroscopic elemental (EDS) analysis.

Ordered arrays of carbon nanoparticles, such as short nanotubes (typical aspect ratios in the 5-10 nm range), nanopolyhedra, and onion-like structures were observed in the TEM image of the carbon-rich regions of the sample prepared at 50°C (Fig. 1b). Similar structures, as well as sub-graphitic and

graphitic sheets, were present in each of the samples treated at 350 and 500°C (Fig. 1c,d). None of these features were present in the amorphous NPC starting material (Fig. 1a). The surfaces of all of these ordered carbon nanoparticles were coated with thin layers of disordered carbon. From an analysis of the various micrographs taken of the samples, it is evident that the carbon nanoparticles were more ordered, as well as being present in larger numbers, in the materials heated to 350 and 500°C following addition of cesium. Nonetheless, it is quite significant that carbon nanopolyhedra, tubes and onions were observed even in the sample heated to only 50°C.

Examination of the Cs-rich regions on the TEM



Fig. 2. Powder X-ray (Cu–K α) diffraction line patterns of (a) NPC prior to Cs^o treatment, but after heating in vacuum for 18 h at $T = 450^{\circ}$ C. (b) NPC after treatment with Cs^o and post-treatment at $T = 50^{\circ}$ C for 3 h. (c) Post-treatment at $T = 350^{\circ}$ C. (d) Post-treatment at $T = 500^{\circ}$ C.

grids indicated that they were extremely electron beam sensitive and degraded very rapidly to highly disordered structures. Thus these regions were not amenable to any meaningful imaging.

Analyses of the materials by X-ray powder diffraction (Cu-K α), after air exposure, revealed that significant structural reorganization and ordering of these materials had taken place. In comparison to the amorphous starting material (Fig. 2a), each of the diffraction patterns of the Cs-treated samples showed a high degree of crystallinity. All the Cs-containing samples have sharp lines at 2θ values of 13, 26 and 39°. The reflection at $13^{\circ}-2\theta$ corresponds to an interlayer spacing of 0.67 nm. When these samples were washed with water and re-analyzed, the X-ray diffraction lines disappeared, but the HREM images after water treatment indicated that the nanostructures remained intact. Thus, the line patterns arise as a direct consequence of cesium residing between the layers of the nanostructures that we see in the HREM images. Once the cesium was removed from these layers, they relaxed back to structures with too few carbon layers to provide the requisite X-ray coherence length (≈ 0.2 nm) necessary for diffraction. Therefore, the Cs-containing structures that gave rise to the notable crystallinity were likely to have been those regions of the sample that were too electron beam sensitive to image.

Consistent with these arguments, based upon the X-ray diffraction results and the TEM images, we note that each of the Cs-treated carbons showed strong electron-diffraction patterns indicative of significant levels of ordering. A representative electron diffraction pattern is shown for the 350°C material (Fig. 3).

That the cesium is able to promote nanostructuring of NPC spontaneously near room temperature is quite remarkable. This ordering process is very different than those high-energy processes that have been reported to lead to these forms of carbon. The NPC prepared at 850°C is rich in sp² carbon, and is laden with defects. The high energy of this material is evident in its heat of formation which is at least 20 kJ/mol carbon above that of graphite, its low density and high magnetic susceptibility. It is this free energy that must be released upon combination with elemental cesium. The nanostructures represent local free energy minima that lie at levels above graphite

Fig. 3. Electron diffraction pattern from NPC treated with cesium and post-treated at $T = 350^{\circ}$ C.

but below NPC. It may be the extraordinary reducing power of cesium, the most electropositive element (electron affinity = 0.4715 eV), that provides the chemically mediated pathway to these nanostructures under very mild conditions. It is likely that the donation of the Cs electrons to aromatic nanodomains forms carbanions by completion of bonds left dangling in the NPC. These structures may, in turn, set off a catalytic polymerization process that leads to concatenation and ordering of the carbon. The spontaneity of the reaction, is evidenced in the exotherm of mixing of the starting materials. Alternatively, the cesium may act as a solvating medium for the carbon. The cesium may migrate through the nanoporous structure, aggregate, then dissolve the carbon and precipitate it in ordered form. Thus, the carbon-saturated elemental cesium would leave in its wake the ordered structures that we observe.

We note that the process of structural ordering continues at room temperature over the course of time. HREM examination of samples that have been analyzed and then stored for 6 weeks in the inert atmosphere box, indicates that the degree of ordering



figure 3

continues to rise at room temperature with time. Most notably, the level of graphitic-like material increases in each sample. We have attempted to use thermal siphoning to remove the cesium after posttreatment; preliminary experiments indicate that more than 66% of the original mass of cesium can be recovered in this manner. These results lend further credence to the notion that the cesium may be acting catalytically in transforming carbon from disordered to ordered nanodomains.

In contrast to this result with cesium, the arc-discharge process for nanotube formation begins with well-ordered graphite that is heated to high temperature (2000°C) causing vaporization and, hence, defect formation. Under such conditions the nanotubes form on the face of the cathode, the electrode that is bombarded with electrons. Logically, given its electropositive character, the role of cesium is to supply electrons to the carbon, a step necessary to set off the process of ordering. The required temperature is low because the NPC begins in a highly strained form that is rich in defects. The addition of electrons provides the pathway for release of this free energy. Therefore Cs-promoted ordering may be thought of as approaching nanostructures from a higher-free-energy starting material (NPC) rather than from one of lower-free-energy (graphite). This line of reasoning may serve to explain both the spontaneous nature of the reaction and the unprecedented formation of nanostructures under such mild conditions. Additional work is underway to uncover the mechanism of this new nanostructure-forming process.

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