Electron-beam analysis of polymerized KC_{60}

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We have conducted high-resolution transmission electron microscopy (HRTEM) and electron-energy-loss spectroscopy (EELS) studies on polymerized KC_{60}. The chainlike structure proposed for the polymerized material is confirmed. Lattice constants extracted from the HRTEM images are consistent with those determined earlier by x-ray diffraction. The fine structure in the EELS spectrum of KC_{60} shows the sp^2 nature of the carbon bonds along with features which distinguish the bonding in this alkali fulleride from that of other fullerenes. Both the HRTEM and EELS studies show that polymerized KC_{60} is exceedingly resilient against damage induced by a 200-keV electron beam, in sharp contrast to the behavior of pristine C_{60}.

Since the discovery of a method to produce macroscopic quantities of C_{60} and its related structures,[1] much interest has been generated for the study of fullerene materials. The unusually large size (7 Å diameter) (Ref. 2) of this molecule places it within the resolution of imaging using high-resolution transmission electron microscopy (HRTEM). Iijima has imaged nested fullerenes where the innermost ball was the size of a C_{60} molecule.[3] Yet because at room temperature the C_{60} molecules in pristine crystals are rotating,[4,5] imaging a single C_{60} molecule in C_{60} compounds is problematic. Recently an alkali-fulleride compound, AC_{60} (A=K, Rb, Cs), has been synthesized which forms an air stable, conducting polymer.[6] X-ray studies suggest bulk KC_{60} is composed of polymeric fullerene chains.[7] We have used HRTEM and electron-energy-loss spectroscopy (EELS) analyses to image and study the bonding nature of this material. We confirm its chainlike structure and find KC_{60} to be remarkably immune to 200 keV electron-beam-induced structural damage.

Crystals of KC_{60} were produced by a slow-cooled technique[6] described in detail elsewhere.[8] In order to avoid any effects of solvents on the material, samples were prepared for HRTEM analysis simply by grinding the crystals between two glass slides and mounting powdered specimens onto holey carbon grids. HRTEM images were produced using a JEOL JEM 200CX microscopy using a 200-keV accelerating voltage.

Figure 1 is a high-resolution electron micrograph of KC_{60} taken under phase contrast imaging conditions. From the lattice fringes, we observe the sample to be crystalline over fairly large domains. The variation in lattice spacing arises from the different orientations of the individual crystalline domains. The edges appear amorphous in some regions but this is due most likely to the possible curling effects of the thin crystals at the unsupported edges. The lattice spacings extracted from HRTEM images are $a=9.0$ Å, $b=10.1$ Å, $c=14.3$ Å. The values are consistent with those determined from previous x-ray-diffraction studies, which find $a=9.138$, $b=10.107$, $c=14.233$.[7]

Figure 2 is a high magnification micrograph of crystalline KC_{60} imaged with the electron beam perpendicular to the polymerized direction (a axis). The lower region of the image distinctly reveals the chainlike structure of this material; the inset (not to scale) is a schematic showing the spacing seen in the micrograph. From the clarity with which the dominant units (C_{60}) can be imaged, we deduce that the C_{60} balls are not rotating in KC_{60}, in contrast to their behavior in pristine, van der Waals bonded C_{60}. The strong on-chain covalent bonding in the polymerized fullerene seems to hinder the rotation of the balls.

In order to further study the bonding in polymerized alkali fulleride, we conducted an electron-energy-loss spectroscopy study. Figure 3 shows the EELS spectrum taken from a KC_{60} crystal. We note the characteristic 284-eV K edge onset for the carbon in the material; the potassium L edge lies at 294 eV and therefore rides on the carbon edge and cannot be distinctly observed in the spectrum. The fine structure of the carbon peak in this spectrum is different than the standard sp^2 bonding seen in graphite. Thus, while the carbon atoms
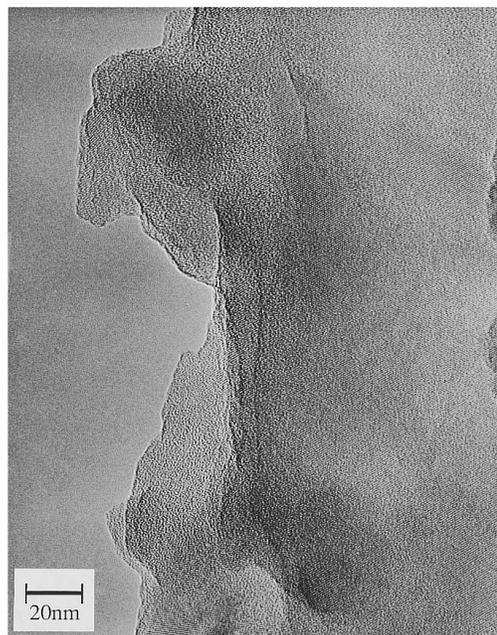
FIG. 1. High-resolution transmission electron micrograph of KC_{60} showing large crystalline domains.
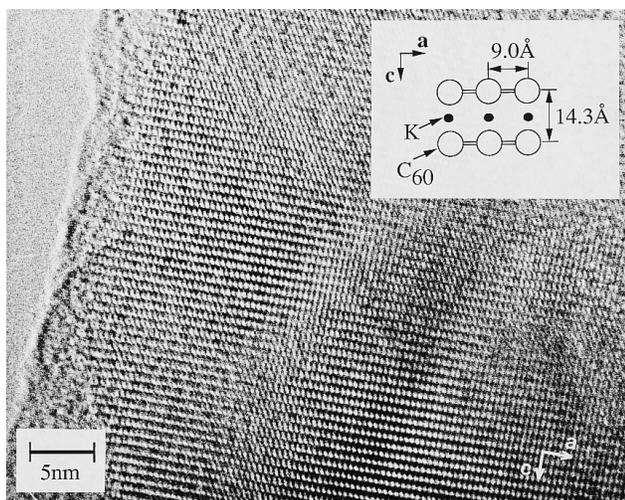
FIG. 2. Higher magnification image of KC_{60} showing the chain-like structure of the polymerized material.

FIG. 3. Electron-energy-loss spectrum of the KC_{60} material. Carbon K edge at 284 eV is clearly visible while the potassium L edge at 294 eV rides on the carbon peak and cannot be separately distinguished.

in a pristine C_{60} molecule are believed to have mostly sp^2 bonding with some sp^3 character due to the slight curvature on the ball, KC_{60} clearly shows some sp^2 character but has a distinctly different bonding overall as compared to other fullerenes. Due to the closeness in energy of the carbon K edge and potassium L edge, extraction of further information of the carbon bonding in the KC_{60} spectrum is not meaningful.

We comment on the remarkable stability of KC_{60} when subjected to a 200-keV electron beam, during both the HRTEM and EELS studies. The crystallinity of KC_{60} in the HRTEM studies was observed to be unaffected by irradiation from the 200-keV electron beam for the duration of the imaging experiment, about 1 h. This structural stability is in sharp contrast to the behavior of pristine, unpolymerized fullerene material. Previous HRTEM studies[9] on pristine C_{60} and C_{70} have demonstrated that pristine, unpolymerized fullerene materials turn amorphous within a matter of minutes under 200-keV electron-beam irradiation. Our own studies on pristine C_{60} confirm these findings. Consistent with what was seen while imaging, the KC_{60} EELS spectrum (obtained using 200-keV electrons) did not change over time. In contrast, our EELS spectra of pristine C_{60} reflect the decrystallization of the material over time where the C_{60} balls break apart and turn into amorphous carbon.[9] Under EELS examination, the carbon signature in pristine unpolymerized C_{60} was found to transform to an amorphous carbon signature within 5 min. Both the HRTEM and EELS results show directly that KC_{60} is exceedingly robust against electron-beam structural damage, which lends support to the idea of strong covalently bonded chains of C_{60} in the polymerized KC_{60}
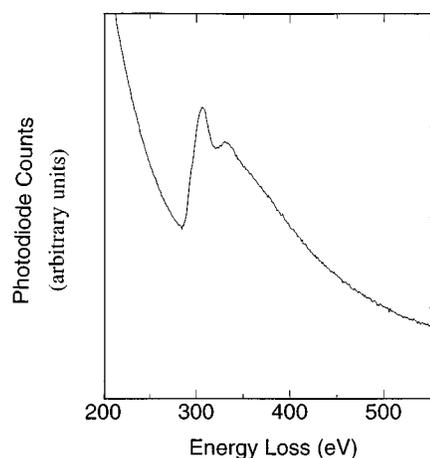
material. The breakup of the C_{60} balls in pristine C_{60} but not in polymerized KC_{60} also implies that the changes made to the carbon bonding when the material is polymerized using potassium strengthens the C_{60} molecule and prevents it from damage under the electron beam. It is possible that the metallization plays an important role in the carbon-bond energy absorption of polymerized KC_{60}.

In summary, our HRTEM images clearly resolve in real space the chainlike structure of KC_{60} confirming the polymerization of this alkali-fulleride material. We find, through both HRTEM and EELS studies that the KC_{60} material, unlike pure C_{60} crystals, remains crystalline and is unaffected by a 200-keV electron beam. Because this alkali-fulleride compound shows extensive resilience under the electron beam and has properties such as air stability and metallic conductivity, KC_{60} stands out as among the most inert of conducting fullerene materials.

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