Photoemission spectroscopy of clean and potassium-intercalated carbon onions

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Hollow onionlike carbon (OLC), generated by annealing nanodiamond at 2140 K, has been studied by core-level and valence-band photoemission spectroscopy. Upon intercalation with potassium, core and valence states of the OLC show an almost rigid shift to higher binding energies, and the density of states at the Fermi level (E_F) is observed to increase. An asymmetric broadening of the C1s line from the OLC as intercalation proceeds indicates an increase in electron-hole pair excitations. Both core and valence-band spectra are consistent with charge transfer from the intercalated potassium to the OLC, and support the conclusion that the electronic structure of the carbon onions bears strong similarity to that of graphite, although differences do exist. In consequence the conclusion can be drawn that these species behave as graphite "nanocrystals" rather than as large fullerene molecules.

Although carbon onions were discovered in 1992 by Ugarte,[1] difficulties in preparation of large quantities have meant there have been few studies of this species, despite their interest as an intermediate form of matter bridging the fullerenes and graphite. Carbon onions are concentric spherical layers of graphite sheets with an interlayer distance of ~0.34 nm.[2] However, they can also be viewed as concentric fullerene shells or as another form of the fullerene family. The carbon onion structures may have a wide diameter range, from 1.4 nm for a two shell configuration such as C_{60}/C_{240} to tenths of a micron for carbon onions with hundreds of shells.[3] It has been suggested that carbon onions could be used as solid insulating lubricants,[4,5] as nanoscopic pressure cells, or more generally, as nanolaboratories for experiments on encapsulated small particles to gain direct insight into their structural behavior under high pressure.[6]

There are several methods to produce carbon onions: electron-beam irradiation of carbon soot in TEM,[1] annealing carbon soot,[7] annealing diamond nanoparticles,[8] high dose carbon ion implantation into silver substrates held at high temperature,[9,10] and most recently the synthesis of carbon "onions" in water.[11] Only a few methods produce large quantities of onions (milligrams) with a well controlled size distribution.[8,11]

Transmission electron energy-loss spectroscopy (TEELS) on carbon onions produced by the implantation of carbon ions in silver substrates at elevated temperature[10,12] has suggested that onions with a mean diameter as small as 4 nm have strongly graphitic character, and the optical properties derived for films of carbon onions are similar to polycrystalline disordered graphite.[13] Recent x-ray C K_α fluorescence measurements and calculations have also indicated similarities with polycrystalline graphite.[14] However, a scanning tunnelling spectroscopy (STS) study on arc-discharge produced carbon onions with a mean diameter of about 13 nm has suggested a more molecular character.[15]

In order to further investigate if the carbon onions behave as molecules or small graphitic nanoparticles we have undertaken synchrotron radiation excited photoemission measurements of potassium intercalated carbon onions produced by high-temperature vacuum annealing of ultradispersed diamond (UDD), or nanodiamond.[16,17] The hollow onionlike carbon (OLC) was produced by annealing the nanodiamonds at 2140 K in vacuum and were subsequently characterized by high-resolution transmission electron microscopy.[16,17] The OLC particles are 4–10 nm in diameter, are polyhedral, have a hollow inner space, and are strongly linked together by common extended curved graphitic layers. Photoemission spectroscopy provides a direct measure of the occupied electronic structure of the onions and their behavior under potassium intercalation which can provide insight into the degree to which this material may be regarded as "molecular" or "nanocrystalline."

In particular, potassium is strongly electropositive, and one would expect an ionic bond to form between the onionlike carbon and the intercalated potassium, with charge donated from potassium to the OLC. Graphite is a semimetal with a low density of states near the Fermi level (E_F) and one would expect, from a simple model of the band structure of graphite near E_F,[18] that charge transfer to nanocrystalline graphite particles would to lead to a continuous shift of the occupied density of states (DOS), with an increase in DOS at E_F as intercalation continues. On the other hand, if the OLC is molecular in character, one would expect to observe pinning of E_F within the lowest unoccupied molecular orbital (LUMO) upon initial doping,[19] then as intercalation continues occupation and finally complete filling of the LUMO with a sudden shift in binding energy when the LUMO is fully filled.[19] Saturation may occur at this point, or occupation of higher molecular orbitals may occur, as observed in C_{60} and the higher fullerenes at large akali to fullerene ratios.[20,21]
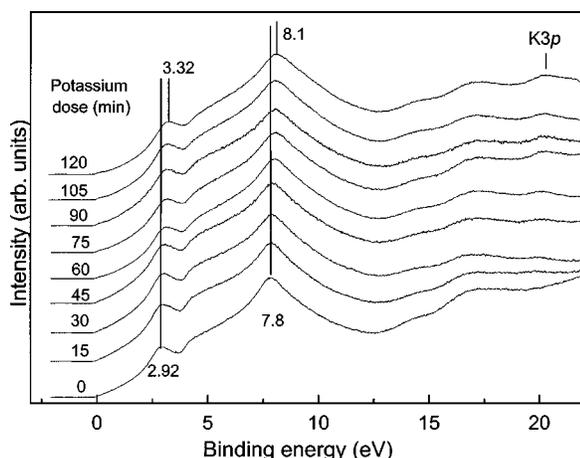
FIG. 1. Valence-band spectra of a thick onionlike carbon film as a function of potassium intercalation. Spectra were obtained in normal emission geometry at a photon energy of 40 eV.
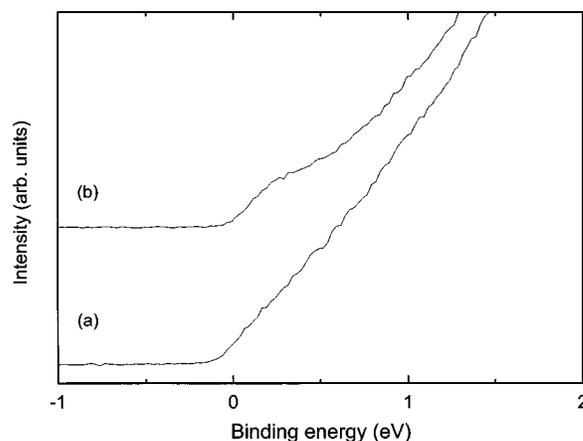

FIG. 2. Near Fermi edge region of valence-band spectra obtained at 40 eV from (a) clean carbon onions and (b) fully intercalated carbon onions. The spectra demonstrate the increased photoemission intensity at the Fermi level after potassium intercalation.

Several studies have been performed on onionlike carbon (OLC): high-resolution transmission electron microscopy (HRTEM),[16,17,22] Raman spectroscopy,[23] x-ray photoelectron spectroscopy (XPS),[24] electron energy-loss spectroscopy (EELS),[25] and electron-spin resonance (ESR).[2,25] Prior to this work the onionlike carbon valence band has been studied by x-ray emission spectroscopy but no intercalation of these particles has been performed.[14] In this paper, XPS and valence-band spectra are measured to investigate the electronic structure of the carbon onions under the intercalation of potassium.

The XPS and valence-band spectra were acquired at Beamline 4.1 of the Synchrotron Radiation Source in Daresbury (UK). OLC in powder form was placed in isopropanol and sonicated in a normal ultrasonic bath to obtain a uniform suspension. The suspension was dropped on a germanium substrate, so as to obtain a thick film and was then immediately loaded into an ultrahigh vacuum chamber (UHV) (pressure less than 10^{-10} Torr). The sample was then annealed at 300 °C to remove adsorbates such as condensed water and traces of isopropanol. Films of hollow onionlike carbon (OLC) samples were also prepared on different substrates, such as Si, Ag, and Pt and showed the same results. Photoemission spectra were acquired with a SCIENTA SES-200 analyzer using Mg K_α x rays (1253.6 eV) from a conventional x-ray gun for core-level [x-ray photoelectron spectroscopy (XPS)] spectra and 40 eV photons for the valence band. Binding energies were calibrated for the XPS spectra by measuring the position of the Pt $4f_{7/2}$ (~71.2 eV) peak from a platinum foil in good electrical contact with the sample, while for valence-band spectra the Fermi edge from the same foil was used as a reference. The overall energy resolution was 0.8 eV for the XPS and 0.3 eV for the valence band estimated from the Pt $4f_{7/2}$ linewidth and Fermi cutoff, respectively. Potassium was deposited onto the carbon onion films at room temperature by evaporation from a well outgassed commercial (SAES) getter source. Typically pressures were 2×10^{-9} Torr during potassium intercalation. For each film the evolution of photoemission spectra was studied for

several potassium doses until saturation, meaning that no substantial further change in the peak positions of the valence band and in the C1s core level could be observed. In this work we call the result of this saturation dose a "fully intercalated film." During the experiment frequent checks were made for contamination, and no oxygen could be observed.

Figure 1 shows valence-band spectra of a clean and potassium intercalated thick film of carbon onions on germanium, obtained with a photon energy, $h\nu=40$ eV. We observe two prominent peaks at 2.92 and 7.84 eV and one shoulder at ~4.24 eV for the clean carbon onion film. The first peak arises from states associated with π bonding, while the second peak is associated with σ bonding, in accordance with graphite.[14,26] The shoulder at ~4.24 eV is related to a mixed σ-π state according to recent x-ray C K_α fluorescence measurements and calculations.[14] Upon potassium intercalation a new, rather broad peak at ~19.8 eV is observed which increases with potassium dose and is assigned to the K3p shallow core level. For adsorption of potassium on graphite at low coverage the K3p peak has been observed at ~19.3 eV,[18] which is reasonably close to the observed value in this work, particularly given the difficulty of accurately obtaining the position of this broad and weak feature. Significant changes occur in the valence-band photoemission spectra of the carbon onions as a function of the potassium intercalation. An increase in density of states (DOS) at the Fermi level is observed (shown in detail in Fig. 2) coupled with a continuous shift of valence-band features to higher binding energy. For example, from the shoulder at 2.92 eV shifts to 3.32 eV at saturation, a shift of ~0.4 eV, while the peak at 7.8 eV, which is harder to locate, shifts upwards in energy by about 0.3 eV to 8.1 eV.

The observed increase in DOS at E_F and the measured shift of valence-band features to higher binding energy can be explained within a simple model applicable to graphite,[18] in which E_F is located at a region where the DOS is small. If the carbon onions behave as graphite nanocrystals a small but continuous density of states should exist on either side of
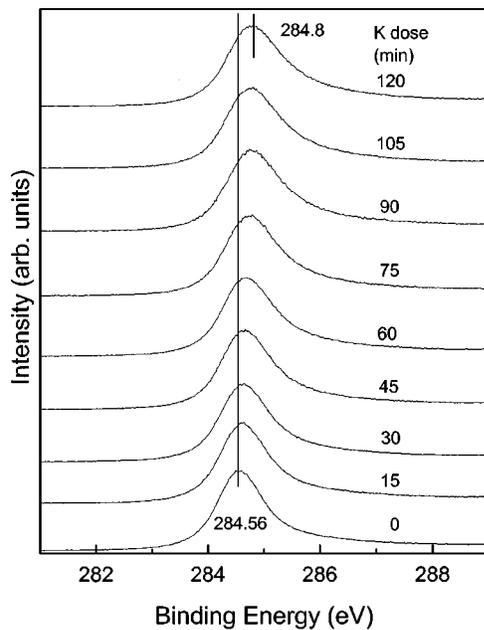
FIG. 3. C1s core-level spectra as a function of potassium intercalation showing the continuous shift in C1s binding energy as intercalation increases.

the Fermi level of the pristine material, increasing as one moves further away from E_F. As potassium is intercalated within the film, charge is transferred from the potassium to the carbon onions. The low DOS around E_F means that transfer of charge into unoccupied states leads to a measurable, yet continuous, motion of the Fermi level ''up'' the DOS. Since spectra or plotted referenced to the Fermi level this leads to a shift of the DOS spectrum to higher binding energy. If the carbon onions were behaving as a molecular system discrete states would be visible in the valence band and changes in binding energy would be discontinuous as molecular states became filled.

Therefore our conclusions, drawn on the basis of photoemission measurements, differ from those of previous scanning tunneling microscopy and spectroscopy (STM/STS) measurements of carbon onions[15] in which it was concluded that the onionlike carbon measured is more likely to be of molecular character, on basis of similarities of with (STS) of C_{36}.[27] In the measurements of Hou *et al.*[15] the carbon onions were reported as having an ellipsoidal shape, with typical dimensions 11×14 nm. The onions investigated in the experiments reported here are of similar size (4–10 nm diameter), and would also show ''moleculelike'' behavior, if this were the correct model for the physical properties of OLC. Hence it is probable that the STS data[15] reflect aspects of that measurement (perhaps the DOS of the STM tip or tip instabilities) additional to the electronic structure of the carbon onions.

The behavior of the OLC valence band under intercalation differs significantly from that observed for potassium adsorption onto the graphite surface, in which a constant 0.4-eV shift in valence band and C1s core level was observed at all except for the lowest alkali coverage.[18] We attribute these differences to the small potassium to carbon ratio in our ex-
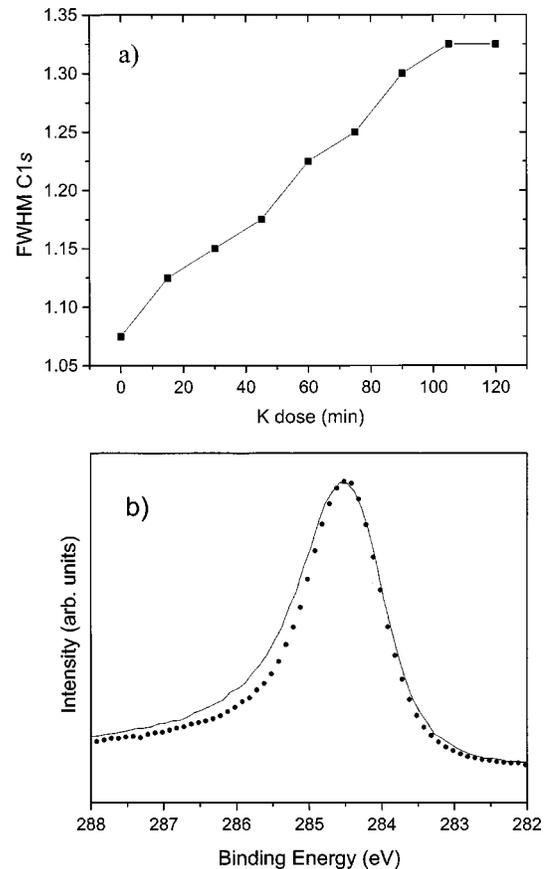
FIG. 4. (a) Variation of the FWHM of the C1s line of onionlike carbon as a function of potassium dose. FWHM were found by fitting the C1s line with an asymmetric Gaussian-Lorentzian line shape. (b) Comparison between the line shapes of C1s peaks from pristine and fully intercalated onionlike carbon (dots and continuous line, respectively). The C1s line from the fully intercalated material has been shifted 0.24 eV to lower binding energy to facilitate comparison.

periment, even at saturation, demonstrated by the low intensity of the K3p peak with respect to carbon derived features in Fig. 1, and the fact that our experiment was carried out at room temperature, allowing the potassium to intercalate into the onion film rather than simply residing at the surface which increases the degree of charge transfer possible.

The photoemission data presented here cannot provide information regarding the topographical structure of the films, only the electronic and chemical structure. However, the diffusion of potassium into the carbon onion film should be very similar to that for graphite[18] or for C_{60} thin films,[19] and hence it is almost certain that at room temperature potassium atoms are highly mobile within the carbon onion film. This leads to two possibilities for the location of the potassium atoms, first that the potassium atoms are between carbon onions, in interstitial sites, or second that they are located within the carbon onions. Although the first possibility is more likely, the second cannot be ruled out because recent theoretical and x-ray C K_α fluorescence studies have shown that OLC cages are probably defective,[14] giving rise to a finite probability for penetration of potassium atoms into the body of the OLC particles.

Figure 3 shows C1s core-level spectra as a function of potassium intercalation. The C1s line is observed to shift to higher binding energy as a function of potassium dose, in a similar manner to that observed for the valence band. The C1s spectra were fitted with an asymmetric Gaussian-Lorentzian line shape, the results of fitting indicating that the C1s line moves from its initial binding energy of 284.56 eV saturating at approximately 284.81 eV, a shift of $\sim$0.24 eV. The shift in the C1s line is smaller than that of the leading-edge valence-band feature. This slightly smaller shift of C1s core level compared with the valence-band shift can be ascribed to more efficient screening of the core hole with increasing potassium intercalation, associated with the increase in DOS at E_F. This effect of additional screening compensates some of the "rigid shift" induced purely by the filling of the unoccupied states near the Fermi level by the charge donated from the potassium. The valence-band spectra are less affected by such increased screening because of the considerably shorter photohole lifetime at low binding energies. This behavior is in contrast to the rigid shift in C1s line and valence band associated with potassium adsorption on graphite[18] where charge transfer from the potassium made little difference to core hole screening. Instead the behavior is similar to that observed in a recent photoemission study of potassium multiwall carbon nanotubes.[28]

Inspection of Fig. 3 shows that a considerable broadening of the C1s line is observed as the intercalation proceeds. The full width at half maximum (FWHM) of C1s peaks are plotted in Fig. 4(a). The increase in FWHM upon doping is primarily due to a broadening to the high binding-energy (BE) side of the line, while the low BE half width at half maximum (HWHM) stays approximately constant. Figure 4(b) shows a comparison of C1s lines obtained from pristine and fully intercalated samples and highlights the nature of this broadening, which is consistent with the presence of additional low-energy electronic excitations associated with the charge transferred from the potassium to the onionlike carbon. It is known that the asymmetry of C1s peak towards higher binding energy may be explained as due to electron-hole pair excitations. The degree of asymmetry depends on the magnitude of the DOS near E_F which we observe to increase upon potassium intercalation. Thus the C1s line shape can also be used as an independent confirmation that the charge is donated from the intercalated potassium to the carbon onions.

We must also discuss the possibility of the presence of graphite particulates with the OLC film, which could influence the photoemission measurements. To test the quality of the OLC material we performed atomic force microscopy (AFM) measurements of low-density carbon onions deposited on graphite and oxidized silicon surfaces. In these measurements (not shown) we did not observe any obvious graphite particulates and found features 2–9 nm in diameter with an average size of $\sim$4.5 nm which we associate with the OLC.[28]

In conclusion, photoemission measurements of the intercalation of onionlike carbon with potassium reveal a nonrigid shift of valence-band states and the C1s core level. The absence of clearly defined molecular states and the continuous increase in binding energy of spectral features upon intercalation indicate that the carbon onions behave as small graphite crystals—nanocrystals—and hence display bulklike rather than moleculelike behavior even at such small diameters. However, the small size of the carbon onions does appear to influence the screening of the core-ionized states, which is observed to change with potassium intercalation, in contrast to potassium adsorption at the surface of a macroscopic graphite sample.

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