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Topology and Electronic Structure of Onion-Like Carbon and Graphite/Diamond Nanocomposites.

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ABSTRACT

Annealing of nanodiamond at moderate temperature makes it possible to produce structures being intermediate in the carbon transformation from sp^3 - to sp^2 -state (graphite/diamond nanocomposites) and onion-like carbon (OLC). Electron microscopy shows such structures involve cage shells with spacing close to graphite. X-ray emission spectroscopy has been applied to examine the electronic structure of OLC and graphite/diamond nanocomposites. The $CK\alpha$ -spectra of OLC produced in the temperature range of 1600-1900 K were found to be markedly different from the spectrum of particles formed at 2140 K and characterized by better ordering of graphitic shells. The latter spectrum was shown to be very similar to the $CK\alpha$ -spectrum of polycrystalline graphite, while the former ones exhibited a significant increase of high-energy maximum that might be caused by the holed defect structure of graphitic networks forming at the intermediate annealing temperatures. To interpret experimental spectra, the quantum-chemical semiempirical AM1 calculation of icosahedral C_{540} cage and that with holed defects was carried out. The lack of at least 22% atoms in an internal carbon cage was found to be essential to provide an increase of density of high-energy electronic states similar to that observed in the spectrum of OLC produced at 1900 K.

INTRODUCTION

Onion like carbon (OLC) is one of the nanostructured forms of carbon consisting of fullerene like shells enclosed each into another. It can be formed via two principally different approaches. First approach uses a condensation of carbon atoms or small clusters in gas phase during an electric arc discharge [1] or in metal matrix [2]. Another approach is based on the transformation of condensed carbon under high-energy treatment. So Ugarte has found the curling and closure of graphitic networks of carbon soot into OLC particles under electron beam irradiation [3]. Later we developed technique, which allows producing hundreds of grams OLC by heat treatment of nanodiamond (ND) [4]. Two different types of OLC carbon can be produced by these mentioned methods, one contains spherical shells another one consists of polygonized shells. The latter contains fullerene like spheres with twelve pentagons, which preferentially responsible for the formation of polygonized structure. It should be mentioned that

polygonized OLC is usually formed after heat treatment of carbon soot [5] or spherical OLC [4] at the temperature higher than 2000 K.

To explain the sphericity of onions formed under electron beam irradiation of carbon [6] the structural models including combinations of pentagons and octagons have been proposed by Terrones [7]. Recently, we proposed that the sphericity of onions produced by ND annealing at the intermediate temperature (1400–1900 K) can be explained by the formation of holed structure of onion shells [8]. Here we used a combination of X-ray fluorescence spectroscopy and quantum-chemical simulation for the characterization of the electronic structure of OLC and graphite/diamond nanocomposites produced via the controlled annealing of ND.

EXPERIMENTAL AND CALCULATION DETAILS

In this work we used ND powders with average particle sizes of 4.7 nm, obtained by explosion of TNT/RDX mixture [9]. Non-diamond forms of carbon were removed by boiling the sample in a 1:1 mixture of concentrated H_2SO_4 and HClO_4 at 130–200°C [10]. The annealing of ND samples was performed in a high vacuum chamber at temperatures 1170, 1600, 1900, and 2140 K (samples I, II, III, and IV respectively). The micrographs of the products were obtained with a JEM-2010 transmission electron microscope.

X-ray fluorescence spectra of ND and ND annealing products and non-textured polycrystalline graphite ($\text{CK}\alpha$ spectra) were recorded with X-ray spectrometer “Stearat” using a crystal-analyzer from ammonium biphthalate [11]. The samples were deposited on copper supports and cooled down to liquid nitrogen temperature in the vacuum chamber of the X-ray tube operating with copper anode ($U=6$ kV, $I=0.5$ A). Determination of X-ray band energy was accurate to ± 0.15 eV with spectral resolution of ~ 0.5 eV.

The quantum-chemical calculations of carbon cages were carried out using semiempirical AM1 method [12]. The fullerene molecule C_{540} being a third inner shell of ideal spherical onion [13] was chosen as a model of a closed graphitic cage. The cages C_{456} and C_{420} were obtained by removing all pentagonal rings and respectively two or five neighboring atoms from the I_h C_{540} . Theoretical $\text{CK}\alpha$ spectra were built in the framework of the frozen orbital approximation (Koopman’s theorem) on the basis of calculation of the ground state of compound. X-ray transition intensity was calculated by summing the squared coefficients for carbon 2p atomic orbitals (AOs) in the real occupied molecular orbital (MO). The energy location of intensity corresponded to the MO eigenvalue. Intensities so obtained were normalized by maximal value and broadened by convolution with Lorentzian functions of 0.6 eV half width at half maximum (HWHM).

RESULTS AND DISCUSSION

$\text{CK}\alpha$ -spectra of the ND and its annealing products are presented in figure 1 together with high-resolution transmission electron microscopy (HRTEM) images of the samples. The $\text{CK}\alpha$ -spectrum of sample I exhibits one broad maximum around 279 eV and is almost coincident with

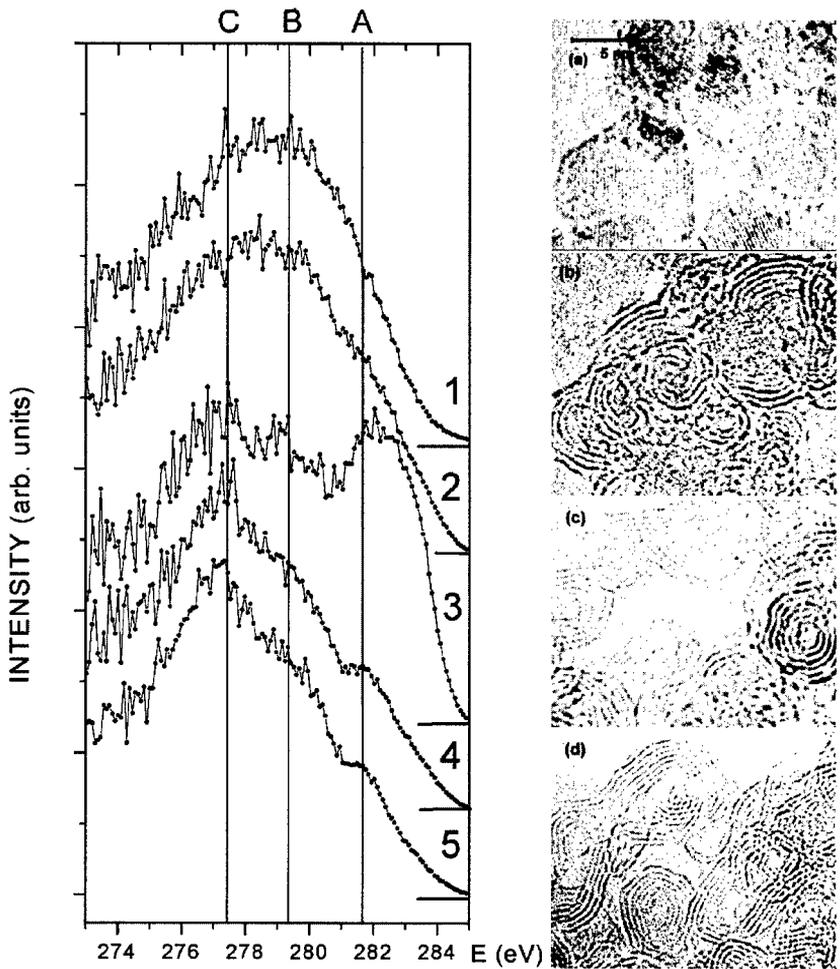


Figure 1. CK α -spectra of the samples produced at 1170 K (1), 1600 K (2), 1900 K (3), and 2140 K (4), and of non-textured polycrystalline graphite (5). HRTEM images of measured samples: (a) – sample I, the dark contrast lines in micrographs indicate the (111) crystallographic diamond layers, which are separated by 0.206 nm; (b) – sample II, (c) – sample III, and (d) – sample IV. The dark contrast closed circles lines in micrographs (b), (c) and (d) correspond to graphite-like sheets. The distance between these sheets (~ 0.35 nm) is closed to that of graphite (0.34 nm).

the spectrum of diamond single crystal [14]. A presence of interference fringes spaced by 2.06 Å (figure 1(a)) is evidence for the diamond particles in this sample. The CK α -spectrum of sample II is slightly different from the former spectrum by somewhat more pronounced high-energy shoulder A. The image of the sample II demonstrates the rearrangement of ND surface into graphite layers with the retention of a portion of diamond particles (figure 1(b)). As CK α -spectrum measures the density of 2p-occupied states for all carbon atoms in a sample, the enhanced intensity of the shoulder A in the spectrum of sample II is caused by the atoms forming graphitic layers. The CK α -spectrum of sample III consisted of OLC (figure 1(c)) exhibits three maxima at 277.5, 279 and 282 eV. The further heating of ND above 2140 K led to the polyhedral hollow OLC particles (sample IV depicted in figure 1(d)). The CK α -spectrum of this sample has the main maximum C around 277.5 eV, the high-energy shoulder B around 279.2 eV, and the short-wave maximum A at 281.6 eV and it is in good agreement with the spectrum of polycrystalline graphite (figure 1). Some variation in the location of the main maximum and in the relative intensities for the former spectrum may be attributed to the contribution of the edge states of polyhedral particles.

Inspection of the spectra indicated the electronic state of carbon particles produced at the initial and final stage of ND annealing mainly corresponds to that characteristic of diamond and graphite respectively. Although the sample of OLC (sample III) is intermediate product in the transformation from ND particles to polyhedral graphitic particles, its spectrum is considerably different from another measured spectra. Maximum A in the CK α -spectrum of sample III is comparable with main maximum C by intensity. Furthermore, this maximum is shifted by 0.4 eV toward the high-energy spectral region relative to the position of maximum A in the graphite spectrum. These two effects indicate the enhanced localization of weakly bonding electrons in OLC. The localization might result from defects in the curved graphitic networks, namely, the dangling bonds. The origin of such defects accompanying of the OLC formation can be explained in terms of deficit of diamond carbon atoms in the graphite/diamond interface to form perfect fullerene-like shells [8]. When the temperature of ND treatment reaches about 2100 K and mobility of carbon atoms increases the defects in OLC anneal out.

To reveal the effect of a portion of dangling bonds on the density of occupied 2p-electronic states the quantum-chemical calculations of carbon cages (figure 2) were performed using AMI method. The theoretical spectrum of icosahedral C₅₄₀ has three features A, B, and C, which intensity and energetic separation are in good agreement with corresponding values in the CK α -spectrum of sample IV. The maxima C and A correspond to σ - and π -like MOs, while the shoulder B is formed by both types of orbitals. The spectra of cages C₄₅₆ and C₄₂₀ show a sequential increasing of the maximum A relative to that in the C₅₄₀ spectrum.

Formation of the holes causes a disruption of joint π -system in C₅₄₀ and, hence, π -electron localization. This localization however cannot provide the increase of density of weakly bonding states observed in the experiment. It is evident that the electrons of dangling bonds contribute to the maximum A of spectra of the holed cages. The localization of electron density on the zigzag sites of graphitic edges was found in [15,16]. The edges of holes in the C₄₅₆ cage are actually zigzag-like, while those in the C₄₂₀ cage are armchair-like. Considerable increasing of the maximum A in the C₄₂₀ spectrum compared to that in the C₄₅₆ one indicates that the shape of boundary of a hole is not important. The governing factor is a portion of the dangling bonds, that is about 15% and 22% in the cages C₄₅₆ and C₄₂₀ relative to the perfect C₅₄₀ shell.

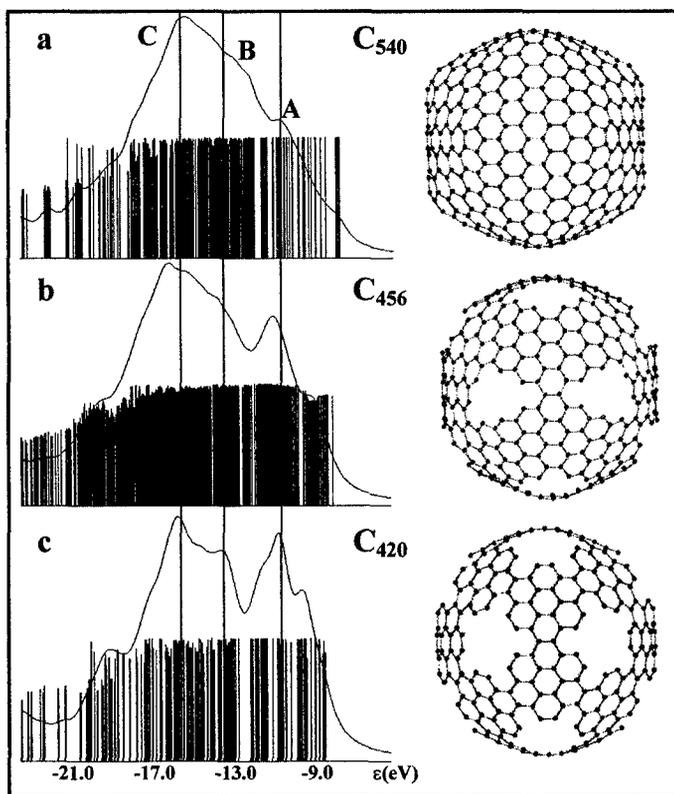


Figure 2. Theoretical $CK\alpha$ -spectra plotted by the result of AM1 calculation on the carbon cages C_{540} (a), C_{456} (b), and C_{420} (c).

Accidental near degeneracy in energy of the localized π -states and electron states of the dangling bonds provides the high total density observed in the high-energy region of the holed carbon cages (figure 2). At the same time one can observe increasing of the density of states around -9.0 eV that is in the correspondence with the detected shifting of the maximum A in the $CK\alpha$ -spectrum of sample III. The changes found from the comparison between the spectra of C_{540} and C_{420} cage are similar to those observed in the $CK\alpha$ -spectra of polyhedral particles (sample IV) and OLC (sample III). We suggest the network of OLC prepared by ND annealing incorporates the handling bonds in an internal carbon cage, which portion is about 22% or some more.

CONCLUSION

X-ray fluorescence spectroscopy investigation of OLC and graphite/diamond nanocomposites produced at various temperatures of ND annealing detected the enhanced density of weekly bonding states in the former material. Quantum-chemical calculations on the carbon cages showed such enhancement is more likely explained by the occurrence of dangling bonds in an internal carbon cage, which may significantly modify the chemical and physical properties of OLC compared to the polyhedral graphitic particles prepared on the final stage of ND annealing. The holes in OLC may cause unusual effects in its transport, magnetic and optic properties [17].

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