

X-ray Spectral Investigation of Carbon Nanoshells

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Carbon nanocapsules synthesized by plasma method in hexane were investigated using the ultra-soft X-ray emission spectroscopy method. It has been revealed that additional mixed $\pi+\sigma$ -overlapping form in nanocapsules in a result of folding of graphene sheets. It has been found that in nanocapsules sp -hybrid bonds between carbon and residual iron atoms form when overlapping high-energy $3d+4s$ -states with sp^n -hybrid orbitals ($2 < n < 3$).

Keywords: Carbon nanoshells, Graphene nanosheets, Emission spectra, Electronic structure.

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1. INTRODUCTION

Monoatomic layer of graphite possesses such unique properties like nontoxicity, high conductivity and significant mechanical strength [1-3]. These properties make graphene promising unit for formation of 3D structures. Such structures are desirable for use in energy technologies such as hydrogen storage, fuel cells, solar cells, lithium batteries, and capacitors, which have a strong requirement for superior storage devices. This cause necessity of study electronic structure of these materials that determine their properties. It is well-known that p -type electronic states in a variety of carbon modifications contribute mainly in its interatomic interaction [4]. Therefore for study of energy distribution of valence Cp -electrons in carbon nanomaterials it is necessary to investigate their CK_α -bands. Ultra-soft X-ray emission spectroscopy (USXES) allows to get full information about the energy distribution of occupied valence states lower Fermi level in carbon materials, for this reason the USXES method is useful instrument for investigation of the electronic structure of carbon nanoshells.

We report here ultra-soft X-ray emission spectroscopy investigations of carbon nanoshells synthesized by plasma method in hexane.

2. METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

A low current plasma discharge was generated between the pure wire Fe (99.7 % purity) anode and the bottom of the Fe tip (99.9 % purity) fixed on the top of a titanium ultrasonic horn, which served as cathode. Generation of plasma discharge begins with the ultrasonic cavitation and the end of the consumed anode assist the emission of electrons from the cathode. The voltage between the anode and cathode was held at

55 V and the upper limit of the current of the electrodes was set at 3.0 A throughout the experiment.

The carbon powder sample was separated from hexane by centrifugation, and the resulting dried powder was then etched in a 5M HCl solution for more than 10 h at 40 °C to remove exposed and insufficiently encapsulated iron carbide and iron oxide particles. After subsequent washing by water and drying in a vacuum at 40 °C, the powder samples were put in alumina pan and annealed in a pure argon gas flow at 1070 °C for 2 h. Then the powder was heat treated in argon with 1 % O₂ gas flow at 550 °C for 30 min and boiled in concentrated hydrochloric acid for 5-6 h at 105-110 °C. Obtained hollow graphitic nanoparticles were washed by water, ethanol and then dried.

A transmission electron microscope (JEM-3010, JEOL, Tokyo, Japan) operating at an acceleration voltage of 300 kV was used to obtain TEM images.

X-ray CK_α -emission bands representing the energy distributions of the occupied valence p -states in the samples were obtained using USXES. An X-ray spectrometer-monochromator RSM-500 (SCBXA, Burevestnik, St. Petersburg, Russia) was used. Measurements were carried out under a pressure in the spectrometer working volume of 5×10^{-6} Pa, obtained using oil-free pumping and additional freezing-out of hydrocarbons vapors by a nitrogen trap near the anode. The resolution of RSM-500 was $\Delta E \approx 0.2$ eV. The X-ray spectra were investigated at an accelerating voltage in the X-ray tube of $U_a = 5$ kV and an anode current of $I_a = 2.5$ mA. X-ray quanta were registered using a channel electron multiplier KBL1505 (Dr. Sjuts Optotechnik GmbH, Germany). The energy positions of the CK_α -bands in the samples were determined relative to that of CrL_i -line of the pure metal in the second order [5].

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3. RESULTS AND DISCUSSION

Since interlayer distances in nanocapsules are similar to those in graphite it is necessary to compare spectra of nanocapsules obtained in hexane with the graphite band (Fig. 1).

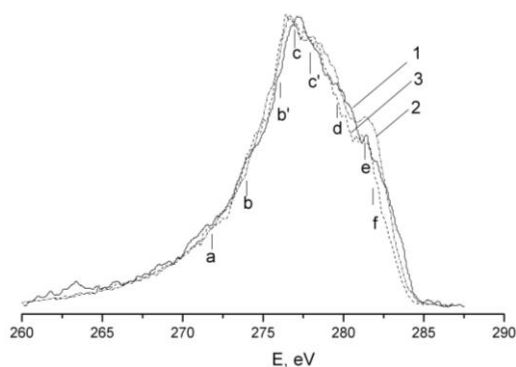


Fig. 1 – CK_{α} -bands of nanocapsules (1), graphite (2) and carbon onions (3)

From this comparison it is clear that spectra significantly differ. Long-wave contour of the CK_{α} -band of nanocapsules shifts towards the low-energy side relative to graphite spectrum by 0,2-0,5 eV due to increasing intensity of *a* and *b* features corresponding to sp^n -hybridized σ -bonds ($2 < n < 3$).

In near-peak region of nanocapsules spectrum additional feature *b'* appears probably due to formation of sp -hybrid bonds between carbon and residual iron atoms when high-energy $3d+4s$ -states overlap with sp^n -hybrid orbitals. This indicates that part of iron atoms can be in nanocapsules walls. Iron atoms can remain after washing in acids.

Nanocapsules CK_{α} noticeably differ from graphite possessing lower intensity of the π -subband *e* and *f* feature in a short-wave region as in carbon onions spectra (Fig. 1). Presence of *f* feature in nanocapsules spectra and absence of this peculiarity in graphite spectra indicates differences in π -interaction of p_z -orbitals. Obviously *e* and *f* features reflect different degree of π -overlapping of p_z -orbitals over spherical surface of nanocapsules. Different degrees of overlapping appear due to increasing curvature of the spherical atomic surfaces when deepening into nanocapsule. In a result degree of π -overlapping of the p_z -orbitals decreases over the surface and increases inside nanocapsules. Due to such non-stop change of π -overlapping degree *f* feature of the CK_{α} -band of nanocapsules is not sharp like in carbon onions spectrum.

However CK_{α} spectrum of nanocapsules is by 0,2-0,8 eV wider than that of carbon onions band due to larger contribution of the $pp\pi+pp\sigma$ -states overlapping in greater amount of nanocapsules walls due to larger diameter of particles.

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Since nanocapsules consist of folded graphene sheets it is necessary to compare emission bands of nanocapsules obtained in hexane and graphene nanosheets (Fig. 2). Shape of the CK_{α} -band of nanocapsules is similar to spectrum of graphene nanosheets with the exception of some narrowing of the band's top due to appearance of the *b'* feature and decrease of the intensity of *c'* feature.

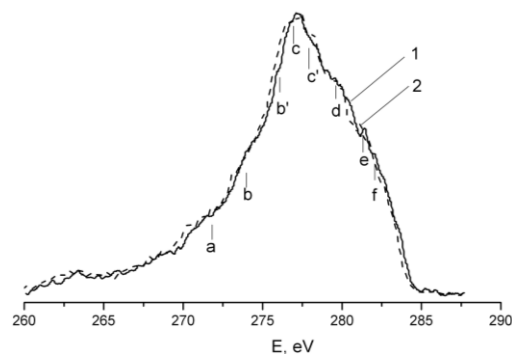


Fig. 2 – CK_{α} -bands of nanocapsules (1), graphene nanosheets (2)

Surfaces of nanocapsules are less corrugated (Fig. 3) therefore difference in degrees of overlapping of πp_z -states and sp^n -hybrid orbitals due to corrugation decreases whereas overlapping of these orbitals increases in a result of increasing curvature of layers when deepening into nanocapsules.

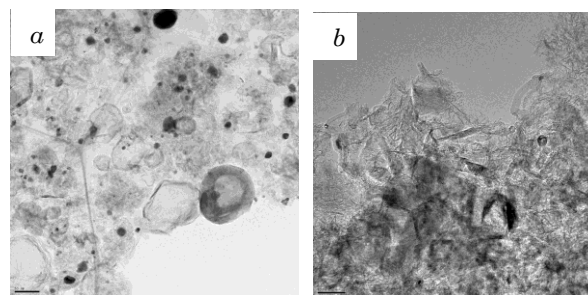


Fig. 3 – TEM images of nanocapsules synthesized in hexane (1), graphene nanosheets (2)

4. CONCLUSIONS

It was revealed that part of iron atoms can be in nanocapsules walls due to formation of sp -hybrid bonds between carbon and residual iron atoms when high-energy $3d+4s$ -states overlap with sp^n -hybrid orbitals.

Different degree of π -overlapping of p_z -orbitals over spherical surface of nanocapsules appears due to increasing curvature of the spherical atomic surfaces when deepening into nanocapsule.