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Electronic Structure Peculiarities of Graphite Nanosheets

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Electronic structure of graphite nanosheets and (CNCs)@(FePt) carbon nanocapsules was investigated using the ultra-soft X-ray emission spectroscopy method. It was revealed that magnetic separation of metal cores of (CNCs)@(FePt) carbon nanocapsules causes increasing overlapping of $p\pi$-orbitals over the surface of graphite nanosheets. It was found that mixing of $\sigma + \pi$ states in graphite nanosheets is smaller than that in (CNCs)@(FePt) nanocapsules and graphite nanosheets mixture since $p\pi$-orbitals overlap less with sp^2-orbitals of σ-type.

Keywords: Graphite nanosheets, Carbon nanocapsules, Emission spectra, Electronic structure.

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1. INTROSUCTION

Due to graphite nanosheets uniform thickness, as well as their high chemical, mechanical, and thermal stability, such materials are of high interest for a wide variety of applications. Whereas the as-synthesized Fe-Pt alloy included carbon nanocapsules can be considered for potential applications in biomedicine, e.g., in the transport of anticancer drugs. This causes necessity of study of the electronic structure of these materials that determine their properties. Ultra-soft X-ray emission spectroscopy allows to get full information about the energy distribution of occupied valence states lower Fermi level in carbon materials, for this reason this method is useful instrument for investigation of the electronic structure of graphite nanosheets and (CNCs)@(FePt) carbon nanocapsules.

2. METHODS OF SAMPLES MANUFACTURING AND ANALYSIS

2.1 Samples Manufacturing

The modified experimental apparatus for the synthesis of Fe-Pt alloy included carbon nanocapsules and graphite nanosheets has previously been presented [1]. For the synthesis of graphite nanosheets after the plasma discharge experiment, coarse metal particles settled to the bottom of the experimental glass vessel, while lighter carbon powder containing graphite nanosheets, amorphous carbon particles and the Fe-Pt alloy filled carbon nanocapsules remained in the liquid ethanol dispersion. As much as 60-100 mg of carbon powder was separated from the liquid ethanol by centrifugation. Oxidation with 15-20 % hydrogen peroxide solution at 90 °C for 12 h was used to remove the amorphous carbon. The carbon powder sample was then etched in aqua regia at 40 °C for 24 h to remove exposed Fe-Pt alloy nanoparticles. Finally, the Fe-Pt alloy filled carbon nanocapsules were removed by a magnetic separator.

2.2 Methods of Samples Analysis

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

The ultrasoft x-ray emission C$K\alpha$ ($K \rightarrow L_{II,III}$ transition) bands reflecting the energy distribution of the C2p-like states in the studied materials were obtained using RSM-500 spectrometer (SCBXA, Burevestnik, St. Petersburg, Russia) which allows analysis of spectra in the wavelength region 1-55 nm, where the CK_α-emission bands are located.

3. RESULTS AND DISCUSSION

Since carbon layer with thickness of 10 nm around the FePt core in (CNCs)@(FePt) carbon nanocapsules is similar to carbon onions with diameter of 5 nm [2] (Fig. 1) it is necessary to compare x-ray emission bands of (CNCs)@(FePt) carbon nanocapsules and graphite nanosheets mixture with spectrum of carbon onions (Fig. 2).

From this comparison it is clear that fine structure of the CK_α-bands is almost similar. However smaller surface curvature of carbon layers in (CNCs)@(FePt) nanocapsules causes lower intensity of the d and c' features that represent overlapping of p_z- and sp^n ($2 < n < 3$) orbitals (Fig. 2). Moreover a and b features of the CK_α of (CNCs)@(FePt) nanocapsules and graphite nanosheets mixture are shifted by 2 eV towards the low-energy side in comparison to those of carbon onions. It indicates the greater binding energy of electrons that provide the sp^n σ-bonds in carbon layers of nanocapsules, which curvature is lower than in carbon onions.

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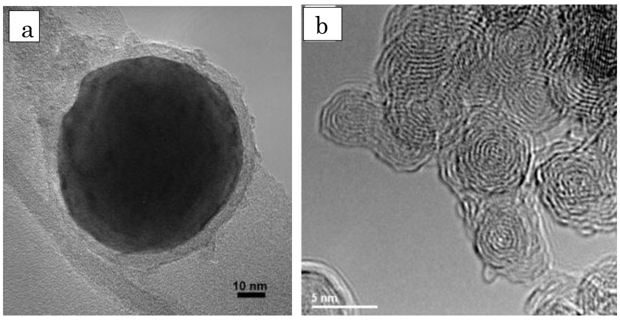

Fig. 1 – HRTEM images of (CNCs)@(FePt) carbon nanocapsules (a) and carbon onions (b)

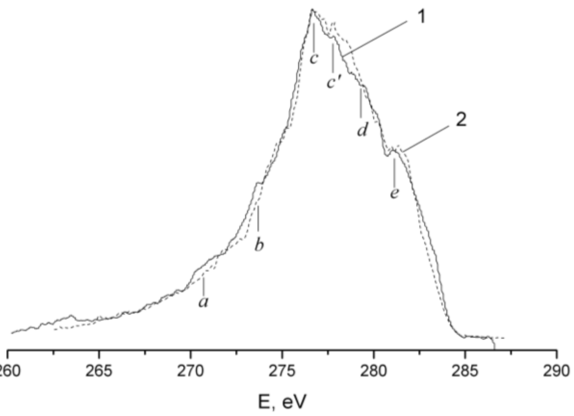

Fig. 2 – CK_α-emission bands of (CNCs)@(FePt) nanocapsules and graphite nanosheets mixture (1) and carbon onions (2)

After magnetic separation of metal cores in (CNCs)@(FePt) nanocapsules carbon layers brake and their curvature decreases. Overlapping of $p\pi$-orbitals over the surface of graphite nanosheets increases approaching to that in graphite. However intensity of π-subband is much lower than that in graphite probably due to orientational dependence of π-sub-band intensity on angle of X-ray quanta yield when electron move from p_π to 1s state [3].

Comparison of the CK_α-bands obtained from carbon layers in (CNCs)@(FePt) nanocapsules and graphite nanosheets mixture with spectrum of graphite nanosheets showed that spectra are almost similar (Fig. 3).

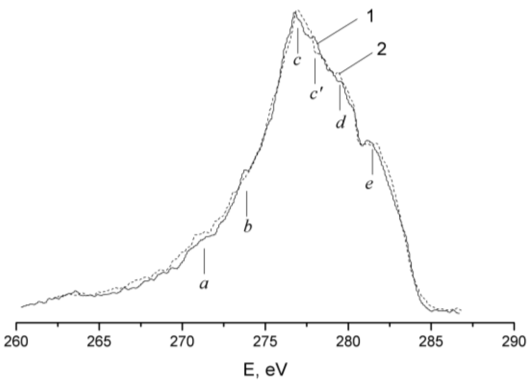

Fig. 3 – CK_α-emission bands of (CNCs)@(FePt) nanocapsules and graphite nanosheets mixture (1), graphite nanosheets (2)

Almost similar intensity of π-sub-band of (CNCs)@(FePt) nanocapsules and graphite nanosheets mixture and graphite nanosheets obtained after magnetic separation indicates randomness of nanosheets location relative to direction of x-ray quanta emission. Width of c peak in the graphite nanosheets CK_α decreases that indicate lower mixing of $\sigma + \pi$ states since graphite nanosheets become flat and $p\pi$-orbitals overlap less with sp^2-orbitals of σ-type.

4. CONCLUSIONS

Investigations of the electronic structure of (CNCs)@(FePt) nanocapsules and graphite nanosheets mixture and graphite nanosheets obtained after magnetic separation of the mixture allowed to reveal the followings:

1. Binding energy of electrons providing sp^n $(2 < n < 3)$ σ-bonds in carbon layers of (CNCs)@(FePt) nanocapsules is greater than that in carbon onions;
2. After magnetic separation of metal cores of (CNCs)@(FePt) nanocapsules overlapping of the $p\pi$-orbitals over the surface of graphite nanosheets increases approaching to that in graphite;
3. In graphite nanosheets smaller mixing of $\sigma + \pi$ states occurs in comparison to (CNCs)@(FePt) nanocapsules and graphite nanosheets mixture since nanosheets after magnetic separation became flat and $p\pi$-orbitals overlap less with sp^2-orbitals of σ-type.

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