Electronic structure of hollow graphitic nanoparticles

Ilkiv B.I. [(1) *], **Foya O.O.** [(1)], **Petrovska S.S.** [(1)], **Sergiienko R.A.**[(2)], **Vasylyna O.V.**[3], **Zaulychnyy Ya.V.**[(1, 3)]

[(1)] Frantsevich Institute for Problems of Materials Science of NASU,
3 Krzhyzhanivsky Str., 03680 Kyiv, Ukraine
[(2)] Physics-Technological Institute of Metals and Alloys of NASU,
34/1 Vernadsky Ave., 03680 Kyiv, Ukraine
[(3)] National Technical University of Ukraine "Kyiv Polytechnic Institute", Engineering-physical Faculty, 35 Politekhnichna Str., 03056 Kyiv, Ukraine
[*]*E-mail: b_ilkiv@ukr.net*

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 causes necessity of study of the 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 interatomic interaction [4]. Therefore for study of the energy distribution of valence C*p*-electrons in carbon nanomaterials it is necessary to investigate their CK_α-bands. Ultra-soft X-ray emission spectroscopy allows getting 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 hollow graphitic nanoparticles.

Hollow graphitic nanoparticles CK_α noticeably differ from graphite one by possessing lower intensity of the π-sub-band. Different degrees of π-overlapping of p_z-orbitals in hollow graphitic nanoparticles appear due to increasing curvature of the spherical atomic surfaces when deepening into hollow graphitic nanoparticle. As a result degree of π-overlapping of the p_z-orbitals decreases over the surface and increases inside hollow graphitic nanoparticles. It has been revealed that *sp*-hybrid bonds form between carbon and residual iron atoms when high-energy 3*d*+4*s*-states overlap with sp^n-hybrid orbitals ($2<n<3$). This indicates that part of iron atoms can locate in hollow graphitic nanoparticles walls. Iron atoms could remain after washing in acids.

However CK_α spectrum of hollow graphitic nanoparticles 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 hollow graphitic nanoparticles walls due to larger diameter of particles.

Surfaces of hollow graphitic nanoparticles are less corrugated than surfaces of graphene nanosheets 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 hollow graphitic nanoparticles.

1. Novoselov K., Geim A.et al. Two-dimensional gas of massless Dirac fermions in graphene. Nature 2005; 438: 197-200

2. Katsnelson M.I. Graphene: carbon in two dimensions. Materials Today 2007; 10: 20-27

3. Novoselov K.S., Geim A.K., Morozov S.V., Jiang D., Zhang Y., Dubonos S.V., Grigorieva I.V., and Firsov A.A. Electric field effect in atomically thin carbon films. Science 2004; 306: 666–669

4. Nemoshkalenko V.V., Aleshin V.G. Electron spectroscopy of crystals. Kiev: Naukova Dumka, 1976. 288 p.