

XAFS study of fluorides and aminofluorides graphite and few layered graphene

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The important problem for graphene-based materials is control of electronic properties. One of the important approach is its chemical functionalization. The chemical functionalization of few-layered graphene (FLG) such as introduction of heteroatoms and chemical groups, creation of defects in a graphene layer, electron doping can significantly enhance the properties of materials based on few-layered graphene. Layered low-dimensional fluorinated graphene nanostructures are considered as very promising candidates. Experimental studies showed that the number of fluorinated graphene layers influences on the composition and chemical properties of these materials. Introduction of different functional groups also affects the properties of fluorinated graphene layers. Particularly, introduction of nitrogen atoms can considerably enhance various properties of graphene-based materials.

The mechanism of influence of composition, structure and size effects on the electronic structure and its interrelation with the properties of graphene-based materials are very important problems. XAS and XPS methods are most effective methods for the study of electronic structure. In this work we presented the results of study of composition, local atomic and electronic structure fluorides and aminofluorides of graphite and few-layered graphene layers based on analysis of XPS and XAS of C K, N K, F K-absorption edge spectra. Samples of fluorides of C_2F composition with different thicknesses were obtained by fluorination of initial graphite (thickness of 300 μm), expanded graphites with different thicknesses (10-90 nm), few-layered graphenes (3-4 nm) and graphene papers (0.335-1.34 nm). Aminofluorides are obtained by interaction of graphene fluorides with ammonia/

At the interaction of NH_3 with C_2F reaction of substitution of fluorine by amine group as well as reduction reaction removing the fluorine atoms from fluorinated graphene layers proceed. The characteristic influence of the size effects appears at the average thickness of graphene layers of 3-4 nm changing the composition of aminofluorides. Along with amine groups, products of the reduction reaction is intercalated in graphite aminofluorides, for example, N_2 is observed in NK edge spectra for a long time. For fluorinated FLG intercalation capacity is lacking.

Ferrocene molecule was intercalated in C_2F and aminofluoride of graphite. In this case, the reduction reaction takes place (F concentration ~4%). According to XPS, in the products of reaction is observed ferrocene and Fe(III) species. Fe K XANES shifted to the higher energies. According to EXAFS data, the radius of the first coordination shell is decreased at interaction. From EXAFS fitting, we found that in the case of aminofluoride the local surrounding of Fe can be interpreted as formation of new species with both C and F atoms in the first coordination shell and the presence of ferrocene and FeF_3 . For C_2F case, we observed only superposition of ferrocene and FeF_3 . Chemical reactions proceeding inside fluorinated graphite matrix and formation of FeF_3 can be interesting for various applications.

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