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X-ray Photoelectron Spectroscopy Study of Electronic Structure of Graphene Nanosheets

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Investigations of graphene nanosheets and oxidized graphene nanosheets were carried out using X-ray photoelectron spectroscopy. Scanning and transmission electron microscopy investigations were used in addition to X-ray photoelectron spectroscopy. It was found that functional carboxyl and epoxide groups were removed from samples due to argon bombardment in studies of oxidized graphene nanosheets with X-ray photoelectron spectroscopy. Thus the O*K*α-band was not revealed in oxidized graphene nanosheets owing to oxygen removal due to electron bombardment with the use of. ultra-soft X-ray emission spectroscopy.

Keywords*:* X-ray photoelectron spectroscopy, electronic structure, graphene nanosheets, oxidized graphene nanosheets

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Introduction

Discovery by Novoselov and Geim in 2004 [1] of graphene nanosheets (GNSs) opened a new field in science that still attracts tremendous interest from the scientific community. GNSs shows remarkable electric, optical, magnetic and mechanical properties, that provides the potential for the development of graphene-based transistors, highly selective gas sensors, electrodes in supercapacitors, light-emitting diodes, new materials etc. [2-5].

New methods of GNS synthesis were developed taking into account tremendous potential of GNSs application in different fields. Among the variety of the synthesis methods of GNSs it is worth to mention method of reduction of oxidized graphene nanosheets (OGNSs) [6].

The growing interest in graphene-based nanomaterials in the past few years, because of their interesting properties, has made it necessary to study these properties, which are determined mainly by the electronic structure, in detail.

It is well known that properties of materials are determined mainly by their electronic structure therefore it necessary to investigate GNS and OGNS electronic structure in order to improve methods of GNS synthesis and development of new materials on the GNS base.

Comprehensive reviews of the electronic structure of graphene-based materials are available [7-13], among which it is necessary to mark out results of investigations of GNSs [9-11] and OGNSs [12] using X-ray photoelectron spectroscopy. There is systematic report of electronic structure of GNSs in comparison to OGNSs [6]. Significant amount of oxygen atoms in OGNSs and some oxygen atoms in GNSs can interact with carbon forming chemical bonds and can lead to changes of shape of X-ray emission bands. Besides the low energy slope of the C*K*α band of the material should be superimposed with the O*K*α band recorded in the second order of reflection. However, any increase of the background of the C*K*α band near the end of its low-energy tail was not observed [6]. Therefore it is necessary to investigate the X-ray photoelectron spectra of OGNSs and GNSs to found out the reason of absence of the O*K*α-bands in the X-Ray emission bands of OGNSs and GNSs and to ascertain a fact of formation of chemical bonds between carbon and oxygen atoms.

We report here the results of XPS investigations of OGNSs and GNSs. In this work scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements were used in addition to XPS.

I. Materials and methods

2.1. Investigative techniques.

Investigations of XPS spectra of samples were carried out using XPS, PHI 5600. The spectra were excited by an Al$K\alpha$-source of X-ray radiation ($E = 1486.6$ eV) and were recorded at a constant pass energy of 25 eV. The energy scale of the spectrometer was calibrated by setting the measured Au 4f7/2 and Cu 2p3/2 binding energies to 84,00 ± 0,05 eB та 932,66 ± 0,05 eB, respectively, with respect to the Fermi energy, E_{F}. The charging effects were taken into account in reference to the 1s line (284.6 eV) of an adventitious carbon. Samples were mounted on the silicon substrates.

Droplets of the OGNSs, and GNSs dispersed in ethanol were deposited on a 150-mesh copper grid coated with a carbon-support film grid for TEM and SEM observations. A transmission electron microscope (JEM-3010, JEOL, Tokyo, Japan) equipped with a multi-scan charge-coupled device camera (Orius SC200D, Gatan Inc., Pleasanton, CA, USA) and Gatan digital micrograph software, operating at an acceleration voltage of 300 kV, was used to obtain TEM images. SEM images were obtained using a field-emission scanning electron microscope (FE-SEM; SU8000, Hitachi, Tokyo, Japan).

2.2. Materials.

OGNSs and GNSs were prepared using carbon nanofibres (CNFs) as the starting material. CNFs with fiber diameters ranging from ~ 30 nm to ~ 200 nm, and up to a few micrometers in length were purchased from Mitsubishi Materials Electronic Chemicals Co. Ltd (Tokyo, Japan). The CNF powder used in this investigation had the chemical composition shown in Table 1. Iron and cobalt served as catalysts in the CNF synthesis and remained after washing with acid.

The CNF oxidation was performed using $KMnO_4$ in concentrated H_2SO_4, using a modified Hummers method. [13]. This process affords OGNSs with the chemical composition presented in Table 1. Cl, K, Mn, Fe elements remained after oxidation and acid treatment with H_2SO_4, $KMnO_4$, and HCl. The Ti came from the Ti ultrasonic horn which was used for exfoliation of the graphite oxide in water.

Table 1

Chemical composition of CNF, OGNSs, GNSs

Element concentration, mass % / Sample	carbon	oxygen	iron	cobalt	S, Cl, K, Mn, Si, Ti
CNFs	91.7	3.4	4.4	0.5	
OGNs	68	25.5			6.5
GNSs	87	8.7			4.3

The OGNSs were reduced with hydrazine hydrate at room temperature for 24 h and were mainly of thickness less than 1 nm and chemical composition of GNSs is shown in Table 1.

II. Results and discussion

3.1. Characterization of OGNS, and GNS morphological features.

Results of X-ray diffraction investigation of OGNSs and GNSs were presented in [6]. The SEM observations did not allow observation of individual OGNSs, but white edges of OGNSs, with thicknesses less than 5 nm, were clearly defined [6]. After chemical reduction with hydrazine hydrate, the OGNSs were reduced to GNSs and restored to an ordered crystal structure. Fig. 1, a shows the agglomerated GNSs, with a curled morphology with average thickness of the graphene nanosheet at a curled edge less than 2 nm (Fig. 1, a).

The XRD patterns of the GNSs do not exhibit a diffraction peak at 11.8°, instead, a broad diffraction peak for carbon (002) centered at $2\theta = 24.4^{\circ}$ appeared [6]. This indicates that during the reduction process, the OGNSs were re-assembled and oxygenated functional groups were removed. The broad carbon diffraction peak at (002) can be interpreted in terms of a decrease in the size of the coherent-scattering region along the *c*-axis in

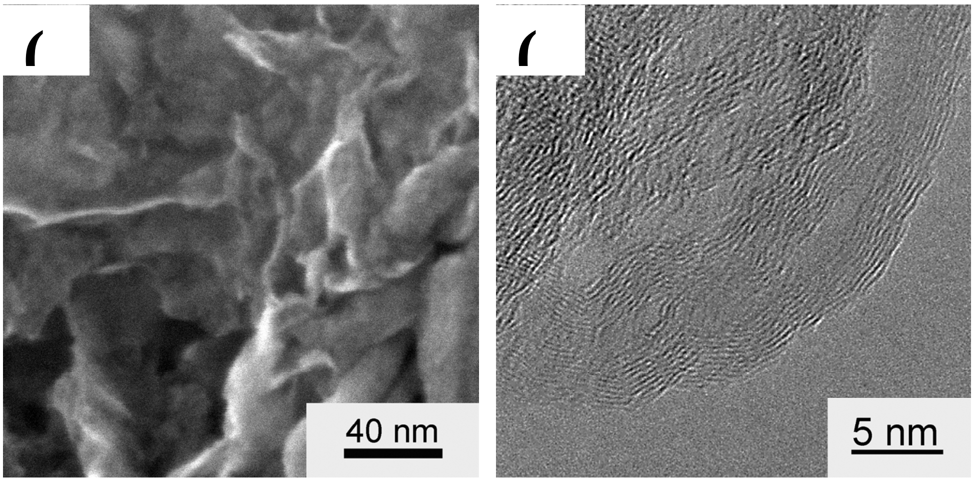

Fig. 1. (a) SEM image of GNSs (б) HRTEM image of randomly selected area of GNSs.

the stacked graphene layers.

TEM investigations showed that after reduction of the OGNSs, the GNS structures were formed. Fig 1b demonstrates many GNSs with turbostratic stacking, in which there are random relative orientations of successive graphene layers. It is possible because of intact defects and vacant sites in the base planes of the GNSs after elimination of oxygenated functional groups and chaotic re-assembling of the reduced OGNSs to form GNS structures.

3.2. XPS investigation.

The O*K*α-emission bands were not revealed in OGNSs and GNSs in [6] in the energy region corresponding to oxygen *K*α-band in the first and second order of the X-ray emission spectra. Therefore we studied the X-ray photoelectron spectra before and after argon bombardment of these materials (Fig. 2 and Fig. 3).

From Fig. 2 it is clear that before argon bombardment C1*s*-line of OGNSs splits into three peaks corresponding to the binding energies of the C1*s*-electrons. Peak separation of the C1*s*-spectrum resulted in a main first peak located at 284.60 eV, corresponding to the binding energy of the C1*s*-electrons involved in C–C, and C=C bonds; the second and third peaks (286.7, 288.7 eV) appeared as a result of C1*s*-electrons of carbon atoms involved in bonds with oxygen (namely epoxide C-O-C and carboxyl C=O functional groups [14, 15]). As a result of treatment of OGNSs and GNSs samples using an argon ion beam the additional second and third peaks disappeared because of the removal of carbon atoms in oxygen containing groups C-O-C, C=O (Fig. 2, 3). Similarly electron bombardment removes oxygen during investigations of the emission C*K*α-bands of OGNSs and GNSs using ultra-soft X-ray emission spectroscopy [6]. Most probably, the oxygen was removed as gas molecules (CO_2, H_2O) [15]. Therefore the OKα-emission band in second order of X-ray emission spectra was not revealed [6].

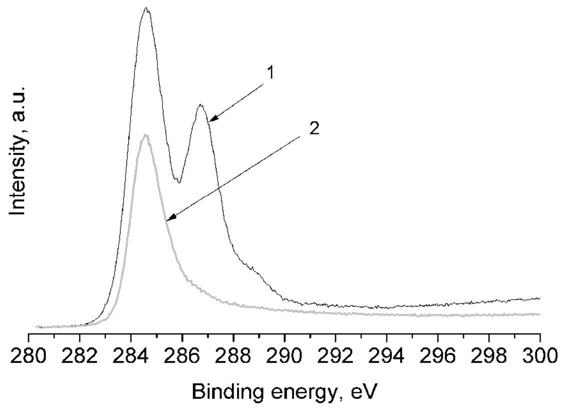

Fig. 2. XPS C1*s*-lines of OGNSs before (1) and after argon ion beam bombardment (2).

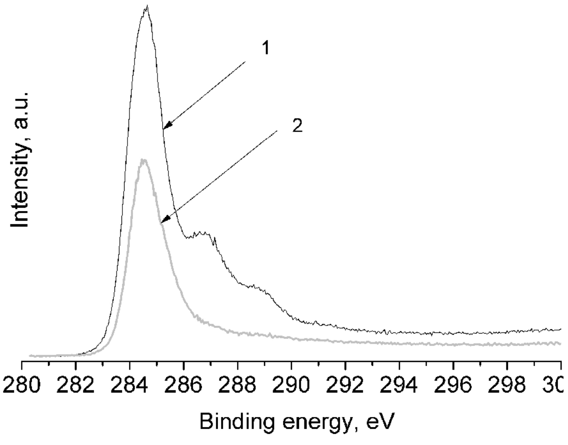

Fig. 3. XPS C1*s*-lines of GNSs before (1) and after argon ion beam bombardment (2).

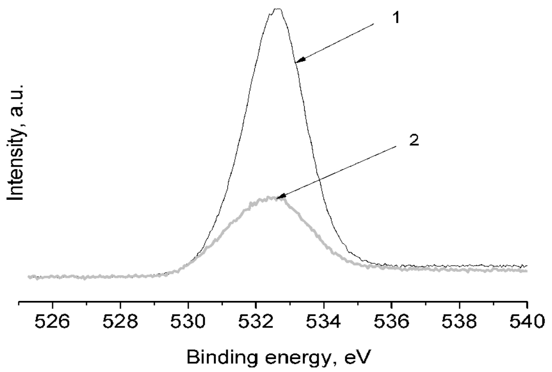

Fig. 4. XPS O1*s*-lines of OGNSs before (1) and after argon ion beam bombardment (2).

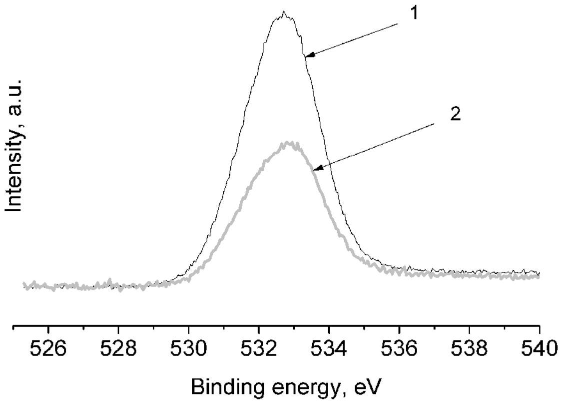

Fig. 5. XPS O1*s*-lines of GNSs before (1) and after argon ion beam bombardment (2).

Removal of oxygen-containing epoxide and carboxyl groups is confirmed by the significant decrease in the intensity of the O1*s*-lines in the OGNSs and GNSs spectra after treatment with the argon ion beam (Fig. 4 and Fig. 5).

Conclusions

The argon ion beam bombardment that removes oxygen-containing epoxide and carboxyl groups C-O-C, C=O. Thus absence of the O*K*α-emission bands in the OGNSs and GNSs in the energy region corresponding to oxygen O*K*α-band in the first and second order of X-ray emission spectra is connected with removal of oxygen from samples as a result of electron bombardment during ultra-soft X-ray emission spectroscopy investigations.

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Дослідження електронної структури графенових нанолистів методом рентгенівської фотоелектронної спектроскопії

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Дослідження графенових нанолистів та окислених графенових нанолистів, було проведене методом рентгенівської фотоелектронної спектроскопії (РФС). На додаток до рентгенівської фотоелектронної спектроскопії зразки досліджували методами скануючої та просвічуючоючщі мікроскопії. Встановлено, що аргонне бомбардування усуває функціональні карбоксильні та епоксидні групи зі зразків. Відсутність емісійних О*K*α-смуг в ОГНЛ та ГНЛ пов'язана з видаленням зі зразка кисню в результаті електронного бомбардування при дослідженні зразка методом ультрам'якої рентгенівської емісійної спектроскопії.

Ключові слова*:* рентгенівська фотоелектронна спектроскопія, електронна структура, графенові нанолисти, окислені графенові нанолисти/