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Abstract. The evolution of energy spectra of X-ray photoelectron spectroscopy observed with increasing annealing temperature of graphene oxide (GO) samples is being investigated. The main attention in the work is focused on the region investigation determined by multiple electron energy losses due to \(\pi\) and \(\pi + \sigma\) plasmon excitations. Such a study allows one to understand an entire structural evolution of GO during thermal reduction process. \(\pi\) plasmon peak becomes prominent only for the samples annealed at the temperatures above 200 \(\degree\)C. Comparison of acquired graphene oxide spectrum (annealed at 1000 \(\degree\)C) with spectrum of highly oriented pyrolytic graphite (HOPG) has been carried out.

1. Introduction

Graphene has unique chemical and physical properties that opens great opportunities for its utilization in electronics, electrochemistry, solar energetics and other fields of science and engineering. Graphene oxide (GO) is known as a precursor for the cost-effective and mass production of graphene-based materials [1]. Thermal annealing reduction of GO is one of the most perspective method of graphene production [2–6]. Investigation of physical and chemical changes occurring in GO samples during annealing process at different temperatures is high of interest. This problem was studied by different authors using different measurement techniques. In [7], Hall measurements were used to define conductivity of graphene-like samples obtained from GO at different heating temperatures. Authors of [4] used the X-ray diffraction analysis to study thermal recovery dynamics. Combination of diffractional scanning calorimetry, thermogravimetric analysis, mass-spectroscopy and X-ray photoelectron spectroscopy (XPS) allowed authors of [3] to determine thermodynamic properties of thermal recovery of GO and define the evaporating gas compounds. The authors of [8] have studied the evolution of the chemical composition of GO samples experienced by the thermal treatment using the XPS method and determined the structural changes in multi-layered GO utilizing X-ray diffraction analysis. The dynamics of changes of XPS spectra and other physical and chemical characteristics of thermally reduced GO has been studied in [9].

Common methods of XPS investigate only no-loss peaks of emitted electrons from certain shells. In the present work multiple elastic and inelastic electron scattering processes are taken into account.
This permitted us to determine the contribution of plasmon oscillations into the electron energy loss spectrum and connect it with the electron conduction of the partially reduced GO samples.

2. Experimental

2.1. GO sample preparation

The Hummers method [10] was used to produce all GO samples. The standard synthesis procedure has resulted in production of a paper-like multi-layer GO film of 40–60 μm in thick. The film was cut onto samples of about 30×15 mm in size that were subjected to the thermal treatment at different temperatures and studied in detail. Heat treatment of the samples was performed in high temperature oven setup Planar GROW-2S, designed for carbon nanotube growth by chemical vapour deposition (CVD). The samples placed into quartz container with the length of 20 cm, width of 3 cm and height 2.5 cm which was brought into the oven. Slow argon flow (50 cm³/min) and up to 10 torr pressure was performed during oven heating and samples heat treatment where performed. Only the slow heating process leads to the stable reproducible results as it was shown by the experiments. For example, if the heating temperature is about 1 °C/s uncontrolled “explosion” like damage occurs to the sample.

2.2. XPS measurements

Photoelectron spectra of the samples were measured on Kratos Axis Ultra DLD experimental setup. Energy pass for wide energy loss spectra was set on 160 eV, for small energy range near C 1s peak – 60 eV. Four samples were places in the measurement plate simultaneously. Al Kα anode monochromatic X-Ray source was used for the measurements. Measurements of samples which suffered heat treatment at 100 °C were performed with neutralizer because of charging. Samples annealed at higher temperature had enough conductivity not to cause charging effect thus no neutralizer was used. The experimental data are shown in figure 1.

![Figure 1](image_url)

**Figure 1.** Experimental XPS spectra of GO for different annealing temperature groups: (a) – 200–400 °C; (b) – 600–1000 °C. Δ = BE_C1s − E.

3. Spectra analysis technique

We consider a single layer illuminated by the X-ray irradiation. Let \( Q(\tau, \Delta, \mu_0, \mu, \phi) \) be the photoelectron flux density function, \( \tau = z/\ell_{tot} \) is the dimensionless layer thickness, \( z \) is the geometrical thickness of the layer, \( \ell_{tot} = [n (\sigma_{el} + \sigma_{in})]^{-1} \) is the total mean free path, \( n \) is the concentration of scatters, \( \sigma_{el} \) and \( \sigma_{in} \) are integral elastic and inelastic scattering cross sections, respectively, \( \Delta \) is the energy loss, \( \mu_0 \) is the cosine of the incident polar angle \( \theta_0 \), \( \mu \) is the cosine of the photo-electron emission polar angle \( \theta \), \( \phi \) is the azimuthal angle between incident and emission directions. The function \( Q \) is considered as the XPS spectrum. Within the partial intensity approach [11, 12] \( Q(\tau, \Delta, \mu_0, \mu, \phi) \) can be expanded into a series of \( k \)-fold inelastic electron scatterings:

\[
Q(\Delta, \tau, \mu_0, \mu, \phi) = Q_0(\tau, \mu_0, \mu, \phi) \delta(\Delta) + \sum_{k=1}^{\infty} Q_k(\tau, \mu_0, \mu, \phi) \chi^k_{in}(\Delta)
\]  

(1)
where \( x_{in}(\Delta) \) is probability distribution of the energy loss in a single inelastic event (also referred to as normalized differential inverse inelastic mean free path DIIMFP or NDIIMFP), and \( x_{in}^k(\Delta) \) is the spectrum of energy losses after \( k \) successive inelastic scattering events. The method of determining the functions \( Q(\tau, \Delta, \mu_0, \mu, \phi) \) and \( x_{in}(\Delta) \) is presented in detail in [13].

The calculated spectrum is sought with taking into account the instrumental function of the energy analyzer and the Doppler broadening which depends on experimental parameters and can be described with the Gaussian function. To calculate XPS spectra it is necessary to consider effects that lead to the asymmetric form of the photoelectron line [14]. Different chemical shifts due to different chemical bonds are taken into account.

4. Results and discussion

In this study we analyse a set of experimental XPS spectra of GO (figure 1) treated at different temperatures on the base of PES approach. The spectra where measured with high resolution what allows us to study not only the no-loss peaks but analyse the electrons energy losses in detail which provide us with a significant additional information of the samples. The first part of this study and detailed description of chemical shifts of oxygen-containing groups can be found in [9]. The deoxidization process with annealing can be clearly recognized from the compound intensities changes. The most significant changes appear at the temperature of about 200 °C and no oxide is observed at 1000 °C. The proposed framework allows obtaining qualitative characteristics of the studied process. Nevertheless, here we focus on electronic structure evolution analysis. The \( x_{in}(\Delta) \) values were retrieved from each of XPS spectra using method similarly to present in the work [15].

Extracted from PES spectra DIIMFP are presented on figure 2.

![Figure 2. Retrieval \( x_{in}(\Delta) \).](image)

![Figure 3. Dependency of \( \pi \) plasmon excitation probability and conductivity of partially reduced GO samples on the annealing temperature.](image)

For the samples annealed at the temperature of 200 °C and higher the appearance of \( \pi \) plasmon mode and its further intensity increasing with temperature is observing. This phenomenon is caused by the conductivity appearance which is the reason of structure evolution. As it was said before the most significant changes in inelastic cross sections and, consequently, in the electronic structure of the annealed GO samples occur at the heating temperatures of 200–400 °C (figure 2). The conductivity of the samples rapidly increases by several orders of magnitude due to the percolation transition. Whereas the intensity of \( \pi \) plasmon also increases at these temperatures and then remains almost constant (figure 2). This behaviour is due to the properties of the percolation chain formed by the conductive fragments of the reduced GO. According to this, the resistance of the material is determined mainly by the resistance of the contacts between the fragments. The reduction of GO is also accompanied by a decrease in the density of the material. The removal of oxygen makes the sample more brittle. The measurements indicate that the thermal treatment does not change the thickness of the samples, so that the observed changes in the density of the material due to annealing...
are caused by the removal of oxygen and other elements engaged into the structure of graphene oxide. The results of density measurements showed [9], heating the samples up to 800 °C results in a decrease of their density by about 2.4 times, from 1.2 to 0.5 g/cm³. The density of graphite is about 2.2 g/cm³, which exceeds that of our 800 °C sample about 4.5 times. Therefore the average distance between the graphene fragments in the 800 °C sample is 4–5 times larger than that in graphite so one can expect that the inter-layer interaction in our reduced graphene layers is negligible.

Figure 4. EELS spectra of one, two, five and several layers of graphene (taken out of [17]).

Figure 5. XPS spectra of the GO sample annealed at 1000 °C and HOPG from XPS Handbook [18].

Electron spectroscopy allows determining DIIMFP values which provide us with the full information concerning electron properties and structural features of studied samples. For example, electron energy losses are clearly dependent on the considered allotrope, so different allotropic forms of carbon have different energy loss functions [16]. In figure 3 electron energy loss (EELS) spectra evolution with different number of graphene layers is illustrated [17]. The energy shift towards greater energy losses of both π and π+σ plasmon peaks is clearly seen with the increasing of the number of layers. The shape and intensity of these peaks also strongly depend on the number of graphene layers that allows us to determine whether it is graphene, multi-layered graphene or graphite. It is also possible to distinguish between different allotropic forms of carbon based on XPS spectra analysis. The comparison of XPS spectra of GO and HOPG is performed in figure 4, the spectra have a similar shape that demonstrates the similar electronic properties. This also shows that reduced graphene oxide is far from graphene structure but closer to graphite’s one in spite of that there is a big difference between these materials in Raman spectra (figure 6).

Figure 6. Raman spectra of graphene oxide samples annealed at different temperatures. The lower black curve is the Raman spectrum of defect-free graphite.
This difference is associated with different scales of plasmon and Raman excitations determined by the corresponding wavelengths. The wavelength of plasmon excitations has the order of one angstrom and for Raman scattering, this value is more than thousands of angstroms.

5. Conclusions

The differential inelastic cross section reconstruction method proposed in the work based on the partial intensity method [11, 12] leads to good correspondence between calculated and measured spectra of emitted photo-electrons for energy losses up to 60 eV from C1s peak. The proposed framework allows us to retrieve not only no-loss peaks but also complete XPS spectra including energy losses and a background formed by photoionisation from the lower binding energy shells. Using the calculation routine of the framework the reconstructed DIIMFP can be used to describe EELS and XPS spectra of the samples [9].

It is shown that photo-electron spectra can provide a great amount of information about processes that take place during GO samples annealing. Heat treatment of the GO samples at the temperature from the range of 150–170 °C causes the percolation transition, at which the conductivity of the material increases by 5 orders of magnitude. The correlation between the conductivity and π plasmon intensity was demonstrated. Widely used peak shape analysis allows to determine components contributions but doesn't provide enough information about ongoing the allotropic state changes of the GO samples. The correspondence of allotropic state of carbon with its differential inelastic cross sections was also shown previously [16].

The analysis shows that a material has been obtained has electronic properties of graphite but its density is much lower. This very interesting fact makes reduced graphene oxide a unique material.

Acknowledgments

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