

Vacuum Ultraviolet Assisted Photoreduction of Graphene Oxide Nanosheets

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Films of graphene oxide nanosheets have been prepared by deposition from an aqueous alcohol emulsion onto a Teflon FEP substrate. The behavior of the films exposed to monochromatic vacuum UV radiation at a wavelength of 123.6 nm has been studied. The decrease of water content and the amount of hydroxyl (OH) groups as well as the increases of the concentration of double bonds in the film has been found after irradiation. At the same time the amount of C=O remains constant in the carboxyl and ketone groups.

Keywords: Graphene oxide nanosheets, Vacuum ultraviolet irradiation, XPS, FTIR spectroscopy.

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1. INTRODUCTION

The reduction of graphene oxide (GO) nanosheets by the action of UV radiation is quite attractive from the standpoint of manufacturing polymer compositions of graphene when a suspension of GO nanosheets is introduced into a solution of a transparent polymer and the reduction is carried out after the formation of a final sample. In [1] we have found that CO₂, CO, H₂O, and O₂ released to the gas phase during UV induced photoreduction of graphene oxide nanosheets with 253.7 nm light from Hg lamp. According to the results obtained in [2], the photoreduction does not occur unless the excitation quantum energy exceeds 3.2 eV.

In this paper we present the results concerning the reduction of the graphene oxide nanosheets films with the aid of vacuum UV irradiation (wavelength 123.6 nm, quantum energy 10.0 eV). The films were prepared by deposition from aqueous alcohol suspensions on to Teflon FEP. The techniques of FTIR and X-ray photoelectron spectroscopy were used in the study.

2. EXPERIMENTAL

2.1 Materials

Thin GO films were prepared by deposition from an aqueous alcohol suspension on transparent samples of 25 mm in diameter and 120 μm in thickness made from Teflon FEP (85% : 15% copolymer of tetrafluoroethylene with hexafluoropropylene) manufactured by DuPont Films, USA. Before deposition, the substrate was treated for 30 min at air pressure of 333 Pa by KrR-2A krypton resonance lamp with vacuum UV radiation at a wavelength of 123.6 nm and intensity of 8×10^{14} photon/(cm²s) to generate the oxygen containing polar groups CF₂C(O)F and CF₂COOH on the hydrophobic polymer surface and, as a consequence, to enhance the adhesion of GO nanosheets to the polymer substrate. In the process of photoreduction the films of GO nanosheets on the Teflon FEP substrate were irradiated in a vacuum (10⁻⁵ Pa) with 123.6 nm light from a KrR-2A krypton lamp at a distance of 3 cm from the

lamp window. The light intensity of the lamp monitored with an FD-34 solar-blind photodiode (GOI, St. Petersburg) was 8×10^{14} photon/(cm² s).

2.2 Instruments

IR spectra were recorded over the range of 4000–675 cm⁻¹ with Perkin-Elmer Spectrum 100 Fourier transform spectrometer equipped with ATR attachment.

X ray photoelectron spectra were measured on a PHI-550 spectrometer. Photoelectron emission was excited with Mg Kα radiation at 300 W power. The analyzed area was 1.2 mm². The base pressure in the XPS analysis chamber did not exceed 1×10^{-9} torr. The intensities of photoelectron peaks were converted into concentrations of the corresponding elements with the use of the appropriate ionization cross sections.

3. RESULTS AND DISCUSSION

3.1 IR spectra

Figure 1 presents the ATR FTIR spectra of the untreated graphene oxide film on a Teflon FEP substrate (curve 1) and irradiated in a vacuum (~10⁻⁵ Pa) with light from the KrR-2A krypton lamp for 215 (curve 2) and 500 min (curve 3). Exposition of the film to monochromatic VUV radiation leads to substantial changes in its chemical composition, primarily due to photoreduction and a decrease in concentration of oxygen-containing groups. Thus, the total concentration of OH groups, which exhibit the absorption band at 3000–3700 cm⁻¹, considerably decreases already after 215 min of irradiation. At the same time, the shoulder at 1620 cm⁻¹ attributed to bending vibrations of water molecules almost completely disappears and the intensities of the absorption bands at 1360–1380 and 1060–1080 cm⁻¹ due to vibrations of the C–OH bond and phenylhydroxyl groups, respectively, significantly decrease. The further VUV irradiation leads to the complete disappearance of the bands corresponding to the presence of the hydroxyl in the C–OH groups (1220–

1230 cm^{-1}) or attached to the phenyl group (1060–1080 cm^{-1}). However, the intensity of the absorption band due to C = O stretching (1730 cm^{-1}) remains practically unchanged after both 215 and 500 min of irradiation with 123.6 nm light. Note that the intensity of the absorption line at 1590 cm^{-1} attributed to allowed double bond vibrations of the conjugated carbon rings in the basic plane significantly increases in this case. Therefore the abstraction of hydroxyl groups seems to initiate the recovery of double bonds.

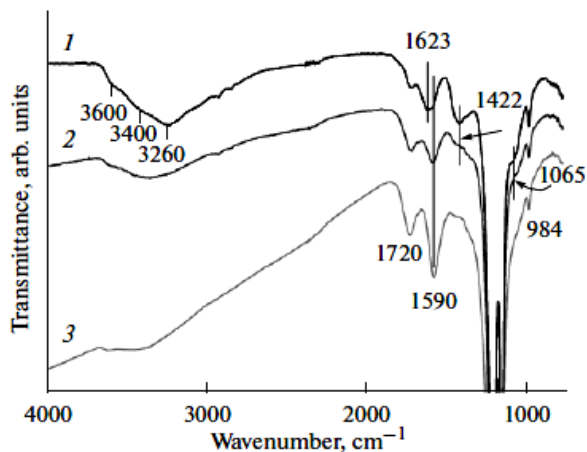


Fig. 1 – FTIR spectra of graphene oxide film on the FEP substrate before (1) and after irradiation (2, 3) for 215 and 500 min, respectively

3.2 XPS

The concentrations of carbon, oxygen and traces of fluorine and nitrogen calculated from the survey X-ray photoelectron spectra are presented in Table 1

Table 1 – Surface layer composition (in at. %) of the graphene oxide films before and after VUV photoreduction (500 min)

:	C	O	N	F
Virgin	70,0	20,0	2,5	7,5
After reduction	76,0	15,0	2,0	7,0

The C1s line of the virgin sample is composed of two distinct peaks with maximums at 285.0 and 287.0 eV and an extended shoulder on the high binding energy side of these peaks (Fig. 2). According to literature, the peak at $E_b = 285.0$ eV is due to carbon atoms surrounded in their close environment by other carbon atoms only. The second peak (287.0 eV, Table 1) is attributed by most investigators to carbon atoms linked by one

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bond with oxygen, i.e., epoxy (>C–O–C<) or hydroxy (>C–OH) groups. Finally, the appearance of peak 3 is supposed to be due to carboxyl (–COOH) groups. Low intensity peaks 4 and 3 can be attributed to carbon atoms of the fluorinated substrate. In addition, the intensity of the π -plasmon line separated from the base peak by 5–7 eV increased after irradiation with the increase of the concentration of double bonds.

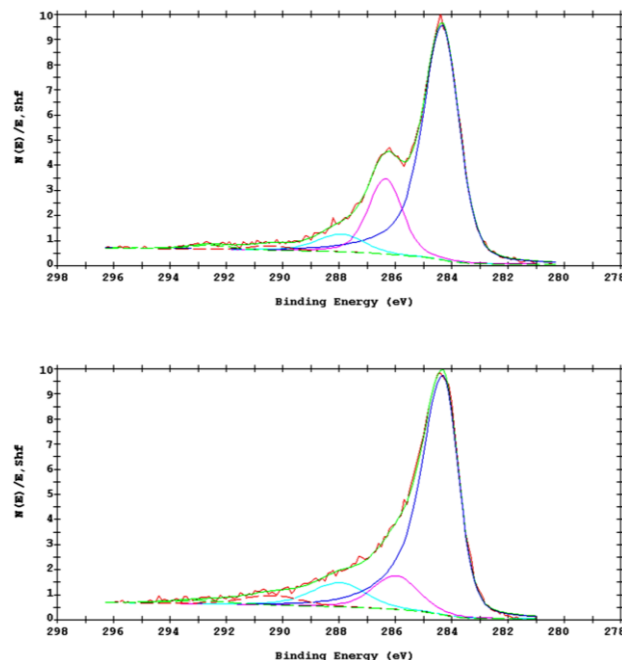


Fig. 2. – The C1s XPS spectrum graphene oxide film on the FEP substrate before (top) and after irradiation (bottom)

In summary, the vacuum ultraviolet assisted reduction of GO nanosheets leads to a decrease in concentration of carbon atoms linked with oxygen by one bond. It has been also found that VUV irradiation decreases the water content and increases the concentration of double bonds in the film. At the same time, the irradiation does not change the amount of C = O groups in carboxyl (COOH) groups or ketones.

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