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In situ study of d-spacing variation under light irradiation in graphene oxide membranes modified with azobenzene

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Abstract

The article reports on the study of the effect of radiation and humidity on the interplanar distance of graphene oxide modified with azobenzene. It is shown that an increase in humidity contributes to an increase in the interplane distance of the studied sample.

Contents

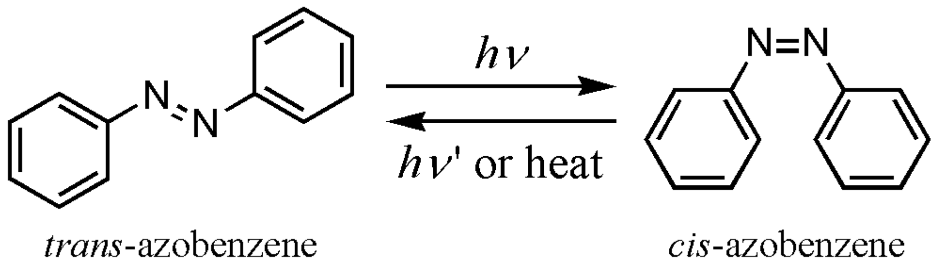
Introduction

Currently, there is a huge interest in the use of 2D materials in membrane technology. They are characterized by strong chemical bonds in the plane and weak bonds between the planes. Today, membranes based on graphene oxide nanosheets and transition metal dichalcogenides have already been used in gas separation processes. Some membrane materials can change the transport properties under the influence of external influences, for example, when exposed to an electric or magnetic field, which allows you to change the transport properties of the membrane without stopping the gas separation process. The issue of switchable membranes based on two-dimensional materials is poorly studied in the literature.

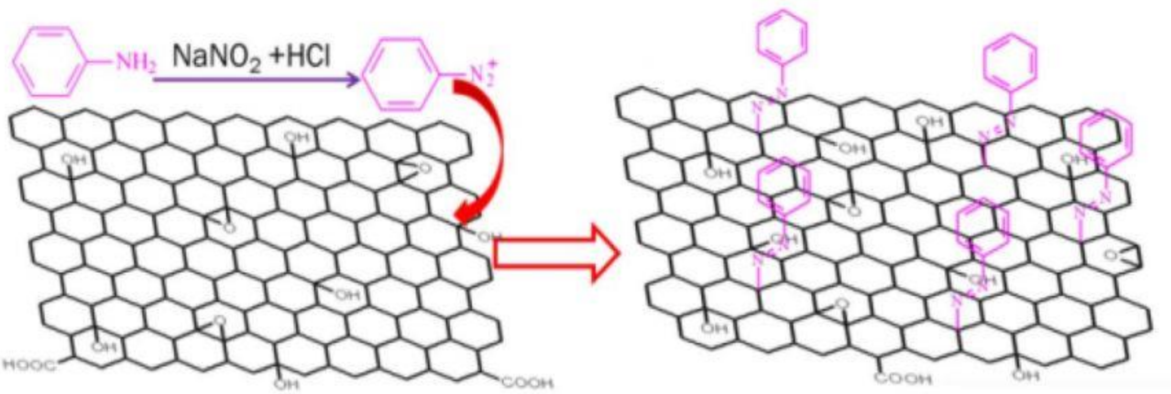
Theoretical part

Graphene oxide (GO) is a two-dimensional compound that is a sheet of graphene with carbonyl, hydroxyl, and carboxyl groups. It is worth noting that it has a two-dimensional sp^2-hybridized network with π-electrons delocalized along the rings [1]. Graphene oxide can be modified in various ways, which allows you to change its properties. Thus, for the manufacture of switchable membranes, graphene oxide modified with azobenzene can be used.

Azobenzene has two forms: *cis*-azobenzene and *trans*-azobenzene, which are mutually converted into each other under the influence of radiation. Reverse cis-trans isomerization occurs under the action of light or thermally in the dark.



Azobenzene can be formed as a result of the reaction of a compound between a diazonium salt and a binding agent. In the reaction of the compound, the benzene diazonium salt behaves as a weak electrophile and attacks the carbon atom with a high density of the electron cloud in the phenolic ring, such as hydroxyl (-OH) para - or ortho-carbon sites. Due to the fact that the edges and surfaces of graphene oxide are covered with-OH groups, it is possible to use it as a binding agent to obtain a hybrid containing a nitrogen atom in a diazo salt covalently bound to a carbon atom in the aromatic ring of graphene oxide [2].



Thus, due to the modification of graphene oxide with azobenzene, the conformation of which has the ability to change reversibly under the influence of radiation, it is possible to change the interlayer distance in the structure of graphene oxide, which will lead to a change in transport properties.

The experiments were carried out on the P03 beam line (research station) of the PETRA III synchrotron source at DESY. P03 is the microfocus small - and wide-angle x-ray scattering beamline (MiNaXS) at PETRA III. This beamline exploits the excellent photon beam properties of the low emittance source PETRA III to provide micro- and nanofocused beams with ultra-high intensity and resolution in real and reciprocal space. The MiNaXS beamline exploits one of a high-β canted 2 m undulator pairs. The energy range of the beamline is 9 – 23 keV. In combination with Si(111) crystals, this demands a very high stability and precise positioning. To suppress higher harmonics, a planar double-mirror with low incidence angle compatible with the large energy range of the beamline is used.

Experimental part

In this work, a solution of graphene oxide modified with azobenzene applied to a silicon substrate by spin-coating was used as a sample.

A colloidal solution of graphene oxide was synthesized by a modified Hummers' method [3]. After synthesis, the graphene oxide suspension was subjected to repeated centrifugation and washing cycles with distilled water to pH = 4 and purified by dialysis. This procedure is described in more detail in [4].

The modification of graphene oxide with azobenzene was carried out according to the method described in [2], i.e. by diazotization. First, 10 mg of graphene oxide, exfoliated by ultrasound in 10 ml of deionized water to obtain an aqueous dispersion, was slowly added to a buffer solution of ammonia and ammonium chloride (90 ml, pH=9) and kept in an ice bath at 0-5 °C. Then 6 ml of sodium nitrite solution (0.69 g, 10 mmol) was slowly added to the aniline solution (0.93 g, 10 mmol) in hydrochloric acid (6 M, 10 ml) through a drip funnel for 10 minutes, after which the solution was strongly mixed for 20 minutes. The resulting solution of diazonium salt was slowly added to the buffer solution at 0-5 °C with stirring for 0.5 h, then kept at room temperature for 3 h. The resulting suspension was filtered and washed with DI-water until the pH of the filtrate reached 6-7, followed by drying under vacuum at 40 °C overnight.

The sample under study was analyzed by grazing incident X-ray diffraction, which is used to study surfaces and layers with a distance of about nanometers. The interplane distance of graphene oxide modified with azobenzene was estimated on the P03 beam line of the PETRA III synchrotron source in DESY. During the experiment, a photon beam with an energy of 15.01 keV (λ=0.827Å, $\Delta\lambda / \lambda < 3\cdot 10^{-4}$) was used. The beam was focused in the position of the sample using composite lenses Be with a size of (31×24) μm^2. To maximize the scattering intensity from the samples, an angle of incidence equal to 0.4° was chosen. Scattered X-rays were obtained using a 9 M Nexus Lambda detector (the pixel size is 55×55 mm^2). The distance from the detector to the sample was set to SDD1 = 610 mm. Before the GIWAXS experiment, we performed a standard calibration of the distance from the detector to the sample using silver begenate, which provides an uncertainty in the absolute distance d of less than 0.01 nm^{-1} for a distance d of 10 nm^{-1}. During the experiment, a camera with kapton windows was used to control the humidity level [5]. The humidity level was monitored using temperature and humidity sensors KIP-20 («Teplopribor», Russia) based on HIH-4000 sensors (Honeywell, accuracy is ±3.5% relative humidity) before and next to the experimental cell. The GIWAXS data were analyzed using the DPDAK software package [6]. High-quality UV LEDs (wavelength 365 nm) and IR LEDs (wavelength 850 nm) with a power of 15 W were used as radiation sources. At the initial stages of the experiment, an external standard light source in the experimental hatch was used for comparison, then it was turned off. The measurements are presented in Table 1.

Table 1. Conditions for measuring the interplanar distance

№	Ongoing experiment
1	Measurement of the interplane distance without a source at zero humidity.
2	Measurement of the interplane distance at a humidity of 49% with a light source.
3	Measurement of the interplane distance at a humidity of 49% without a light source.
4	Measurement of the interplane distance at a humidity of 49% under the influence of UV radiation (365 nm), as well as the study of the relaxation of the sample structure after exposure to UV radiation (365nm).
5	Measurement of the interplane distance at a humidity of 49% under the influence of IR radiation (850 nm), as well as the study of the relaxation of the sample structure after exposure to IR radiation (850nm).
6	Measurement of the interplane distance at a humidity of 100%
7	Measurement of the interplane distance at 100% humidity under the influence of IR radiation (850 nm), as well as the study of the relaxation of the sample structure after exposure to IR radiation (850nm).
8	We put a drop of water next to the sample (100% humidity), turned on UV radiation (365 nm), then turned on IR radiation (850 nm). In all cases, the interplane distance was measured.

Results and discussions

The measurement of the interplane distance between the nanolayers of graphene oxide modified with azobenzene showed that this indicator in the absence of light and zero humidity is on average 0.8696 nm.

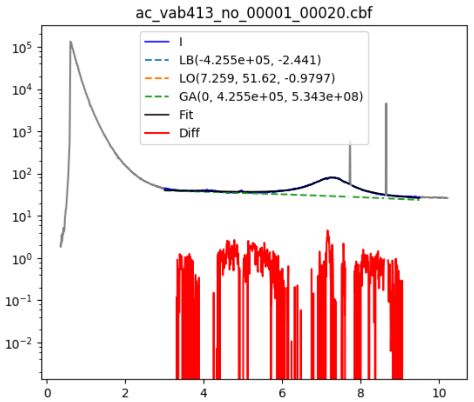


Fig. 1. Processing of the results obtained without a source at zero humidity in the DPDAK program.

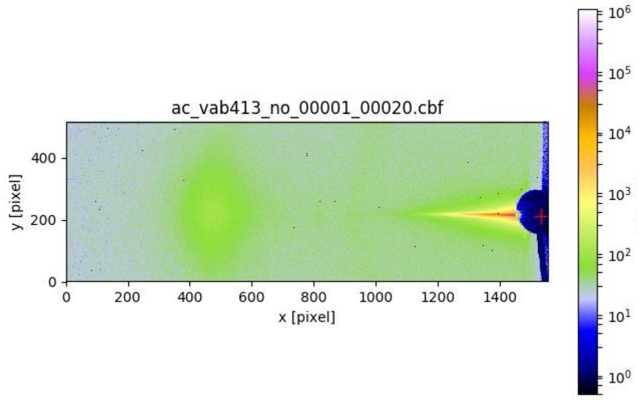


Fig. 2. Two-dimensional scattering pattern characteristic of a sample taken in the absence of a source and zero humidity.

When the humidity increases to 49%, the interplane distance is 0.9873 nm and 1.0172 nm in the presence and absence of light, respectively.

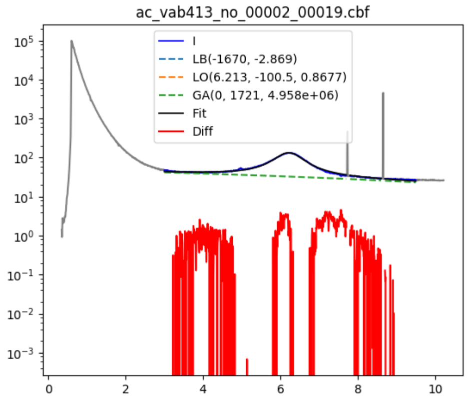


Fig. 3. Processing of the results obtained in the presence of light and humidity of 49% in the DPDAK program.

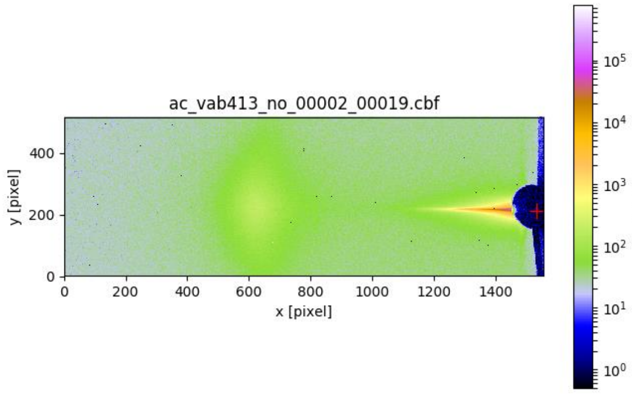


Fig. 4. Two-dimensional scattering pattern characteristic of a sample taken in the presence of light and humidity of 49%.

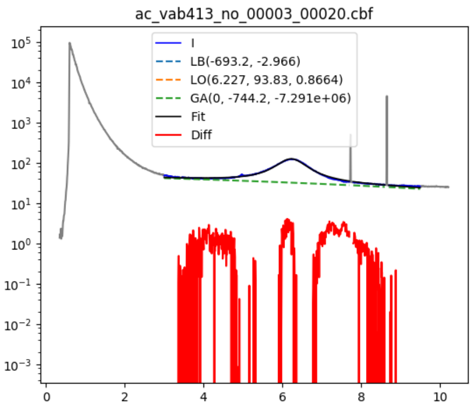


Fig. 5. Processing of the results obtained in the absence of light and humidity of 49% in the DPDAK program.

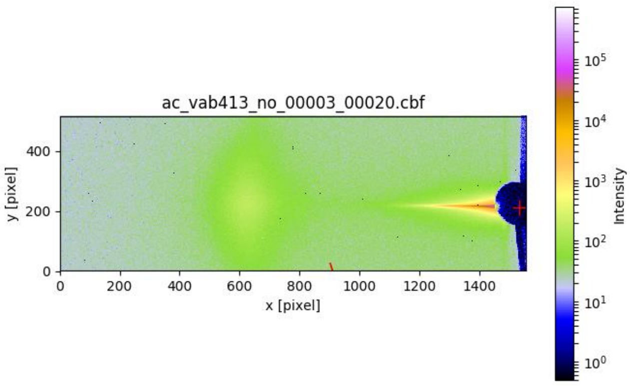


Fig. 6. Two-dimensional scattering pattern characteristic of a sample taken in the absence of light and humidity of 49%.

Subsequent measurements were carried out under the action of UV and IR radiation.

At a humidity of 49% and exposure to UV radiation on the sample, the interplane distance between the nanolists of modified graphene oxide is 0.9314 nm, i.e. the interplane distance decreases relative to this indicator at 49% humidity and the absence of light. When the UV radiation is turned off, relaxation occurs, as a result of which we can observe an increase in the interplanar distance to almost the original value.

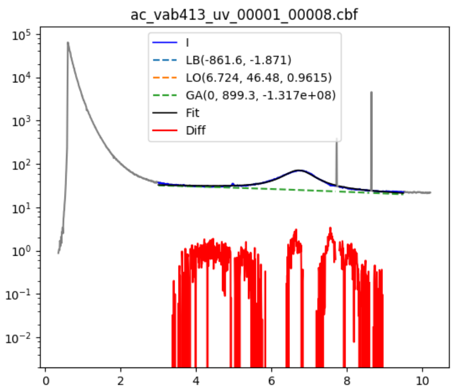


Fig. 7. Processing of the results obtained under the influence of UV radiation and humidity of 49% in the DPDAK program.

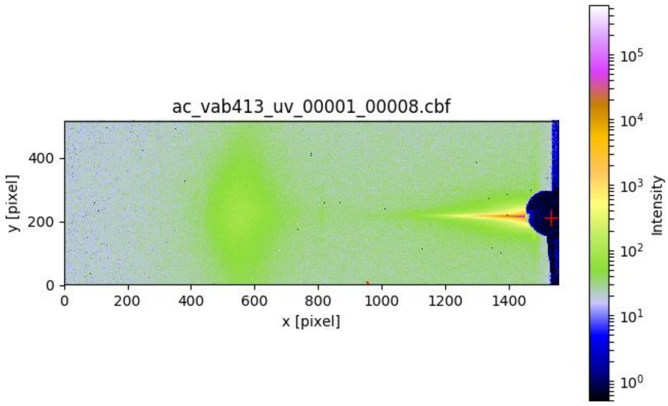


Fig. 8. Two-dimensional scattering pattern characteristic of a sample taken under the influence of UV radiation and humidity of 49%.

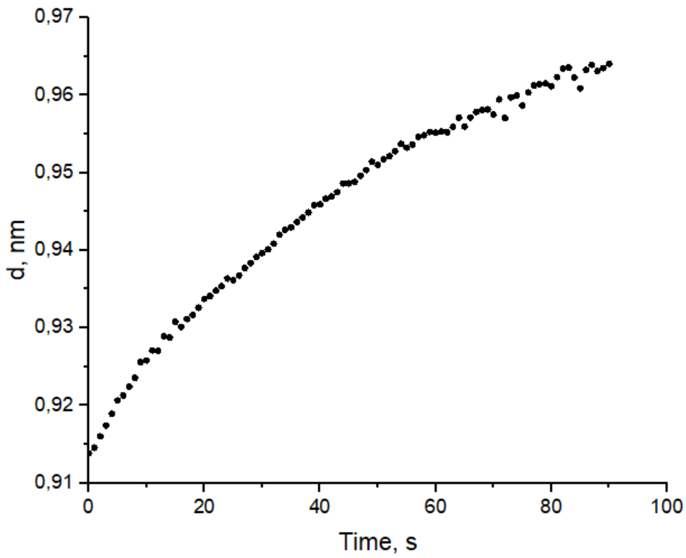


Fig. 9. Change in the interplane distance during relaxation after exposure to UV radiation on the sample.

At a humidity of 49% and exposure to IR radiation, the interplane distance is 0.9262 nm, i.e. it also decreases relative to this indicator at 49% humidity and the absence of light. In the absence of exposure to IR radiation, relaxation occurs, as a result of which we observe a slight increase in the interplane distance of the interplane distance (we observe a sharp jump in the interplane distance, after which this parameter also sharply decreases to approximately the initial state and practically does not change over time).

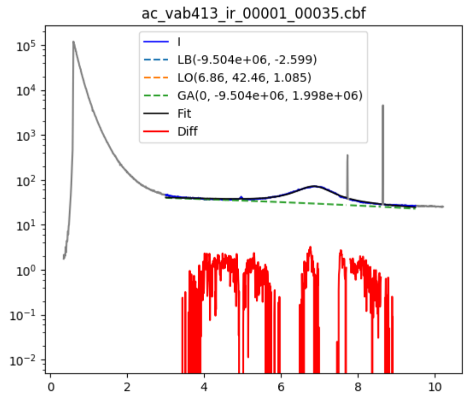


Fig. 10. Processing of the results obtained under the influence of IR radiation and humidity of 49% in the DPDAK program.

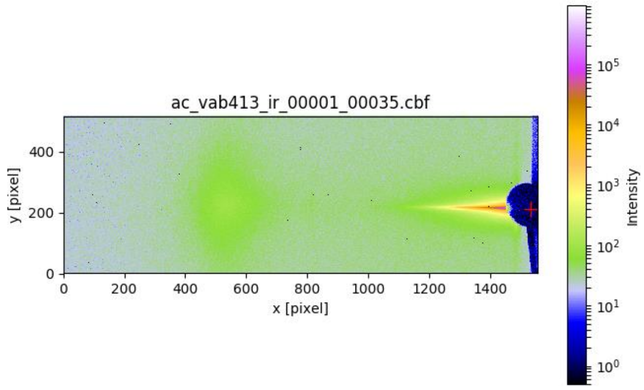


Fig. 11. Two-dimensional scattering pattern characteristic of the sample taken under the influence of IR radiation and humidity of 49%.

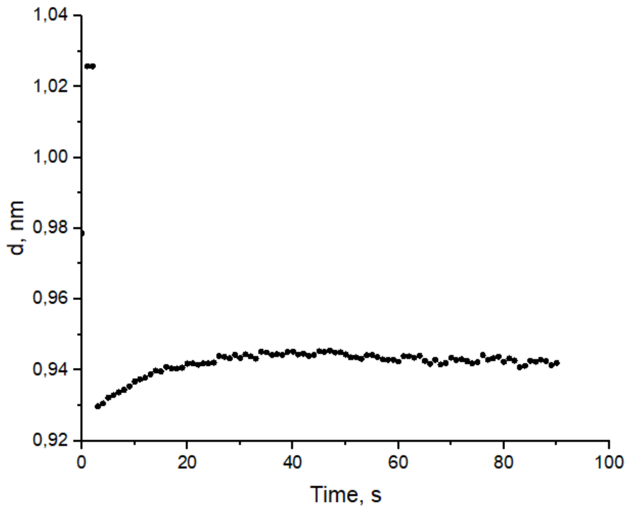


Fig. 12. Change in the interplane distance during relaxation after exposure to IR radiation on the sample.

At 100% humidity in the dark, an increase in the interplane distance to 1.3341 nm is observed compared to zero humidity, which may be due to the sorption of water vapor in graphene oxide at high humidity [5]. With subsequent exposure to IR radiation, the value of the interplane distance increases, and when the exposure is stopped, it decreases almost to the initial value at 100% humidity.

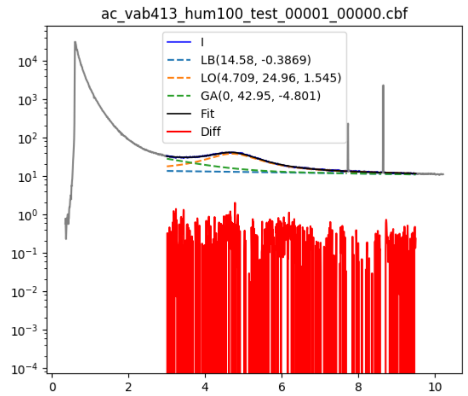


Fig. 13. Processing of the results obtained under the influence of IR radiation and 100% humidity in the DPDAK program.

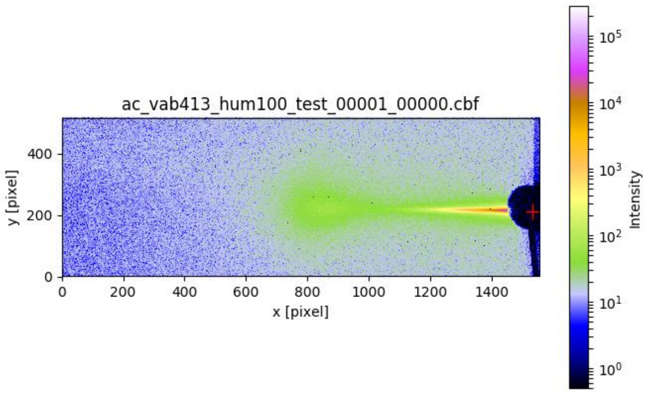


Fig. 14. Two-dimensional scattering pattern characteristic of a sample taken under the influence of IR radiation and humidity of 100%.

If you place a drop of water next to the sample, which is equivalent to creating almost 100% humidity, and measure the interplane distance in the dark, then when exposed to UV radiation, and then exposed to IR radiation, this indicator will be 1.3150 nm, 1.2502 nm and 2.3248 nm, respectively.

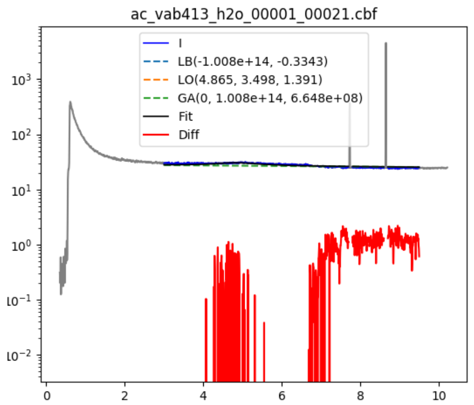


Fig. 15. Processing of the results obtained in the dark when placing a drop of water next to the sample in the DPDAK program.

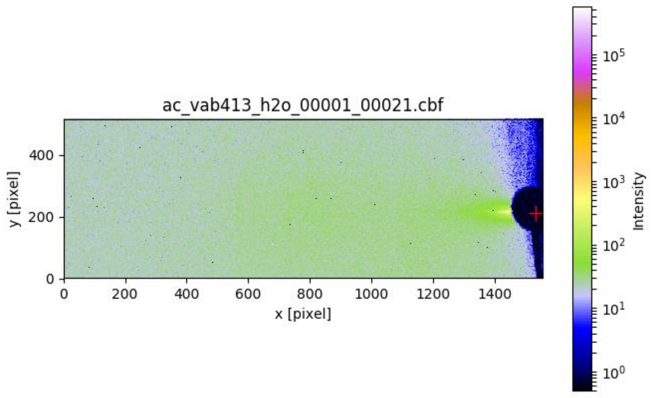


Fig. 16. Two-dimensional scattering pattern characteristic of a sample taken in the dark when a drop of water is placed next to the sample.

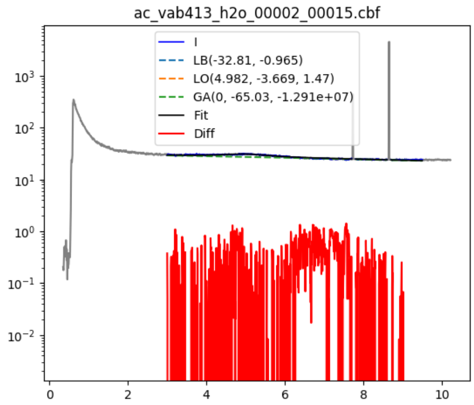


Fig. 17. Processing of the results obtained when exposed to UV radiation and placing a drop of water next to the sample in the DPDAK program.

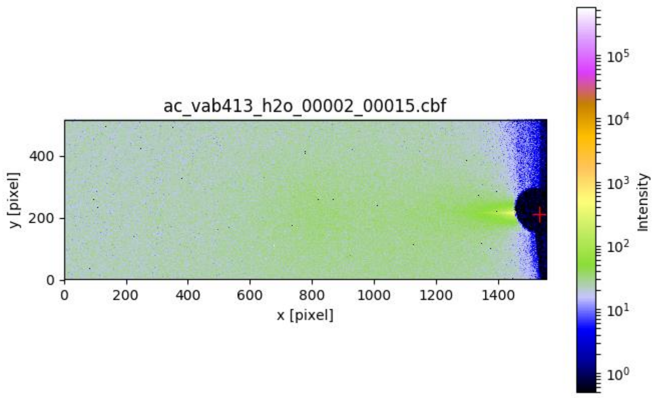


Fig. 18. Two-dimensional scattering pattern characteristic of a sample taken when exposed to UV radiation and a drop of water is placed next to the sample.

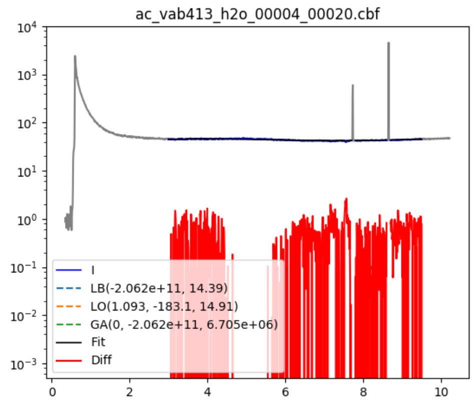


Fig. 19. Processing of the results obtained when exposed to IR radiation and placing a drop of water next to the sample in the DPDAK program.

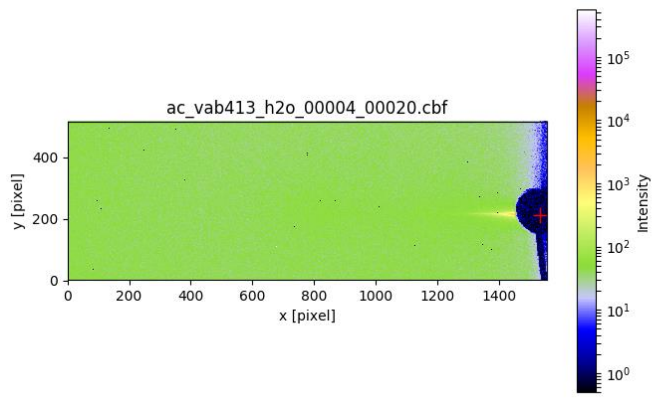


Fig. 20. A two-dimensional scattering pattern characteristic of a sample taken when exposed to IR radiation and a water drop is placed next to the sample.

The change in the interplane distance between the nanolayer of graphene oxide modified with azobenzene under the action of radiation may be due to the mutual conversion of cis - and trans - forms of azobenzene. Since two hydrogen atoms from different phenyl rings end up in the same place in the cis isomer, their repulsion leads to the twisting of the molecule and the destruction of a single system of generalized π-orbitals. In the trans-isomer, such a conflict does not occur, and a single system of seven conjugated π-bonds is formed, which makes it more stable.

Conclusions

1.In the course of the work, changes in the interplane distance of graphene oxide modified with azobenzene were studied under various conditions.

2. It has been experimentally shown that an increase in humidity leads to an increase in the interplanar distance.

3. It is noted that the interplane distance in the case of close to 100% humidity decreases when exposed to UV radiation, and increases when exposed to IR radiation, which may be due to the mutual conversion of cis - and trace forms of azobenzene.

4. It was found that a greater interplane distance of graphene oxide modified with azobenzene is observed when exposed to IR radiation, which is in good agreement with the trans-form of azobenzene.

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