# КОНДЕНСАЦИЯЛАНҒАН КҮЙДІҢ ФИЗИКАСЫ
# ФИЗИКА КОНДЕНСИРОВАННОГО СОСТОЯНИЯ
# PHYSICS OF THE CONDENSED MATTER

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## Optical properties of ablated graphene oxide in aqueous dispersions

The effect of laser radiation on the structural and optical properties of graphene oxide dispersed in water was studied. It was shown that under laser ablation a significant reduction in the size of graphene oxide sheets can be achieved. In this case, the resulting main parts of particles have a size of about 110–120 nm, and are similar to graphene quantum dots. The Raman spectra indicate the reduction of graphene oxide during laser radiation. The thickness of the formed particles practically was not changed, since the $I_D/I_G$ ratio has close values. The prepared dispersions of graphene oxide exhibit wide luminescence bands in the region of 400–600 nm with a maximum of about 450 nm and a lifetime of 1.6 ns. It was shown that by laser ablation it is possible to achieve a significant increasing in the luminescent ability of graphene oxide in an aqueous solution. In this case, the luminescence intensity increased by almost 2 times, while the optical density of the solution was increased by only 5 % relative to the initial dispersion. The results can be used to create organic luminescent materials, in optical nanotechnology, as well as in photovoltaics, biophysics and bioimaging.

*Keywords*: graphene oxide, laser ablation, dispersion, size distribution, structure, absorbance, luminescence, lifetime kinetics.

### *Introduction*

Carbon is one of the most common chemical elements. Carbon materials that include graphite, diamonds, fullerenes, carbon nanotubes and graphene have been well known for a long time.

Graphene is widely used in energy and environmental materials [1], such as energy storage [2], photovoltaics [3], photoelectrochemical [4] and photocatalytic [5–8] generation of hydrogen/hydrocarbon fuels and photocatalysis of organic pollutants.

It is known that graphene is a superconducting material with zero band gap. In this case, graphene oxides are semiconductors with a controlled band gap width by resizing sheets and the degree of its oxidation. Graphene oxide and its modifications, unlike graphene, is a more convenient material for researchers, since it is easy to obtain and also used for practical purposes.

The quantum confinement effect is applicable not only to graphene, but also to graphene oxide. This led to the emergence of a new type of carbon nanostructures — graphene quantum dots. Such quantum dots have a discrete band gap and exhibit photoluminescent properties. Graphene quantum dots of various shapes and sizes exhibit unusual photoluminescence, which is associated with a circular polygonal shape and the corresponding edge effects of graphene quantum dots [8].

Compared to traditional semiconductor quantum dots and organic dyes, photoluminescent carbon-based quantum dots have high solubility in aqueous solutions, chemical inertness, and resistance to photobleaching. For example, electron generation and transport at graphene dots were used for solar cells [9–11], organic light emitting diodes (OLED) [12], photodetectors, photocatalysts [13] and supercapacitors [14]. Extinction-

controlled fluorescence was developed for sensors of biomolecules, metal ions, and toxic/hazardous substances [15, 16].

Also, an its advantage is low toxicity and high biocompatibility compared to semiconductor quantum dots, which makes them very promising for biophysical and medical applications, for example, for bioimages, biosensors, drug delivery, and medical diagnostics [17, 18]. In addition, graphene dots can be easily modified both by the addition of functional groups and by doping with heteroatoms. It may be useful for fluorescent nanocomposites, functional hybrids, and materials with a high refractive index [18].

Over the past few years, significant progress has been made in the synthesis, study of the properties and practical applications of carbon-based and graphene quantum dots. There is two approaches are distinguished among the methods for the obtaining of graphene dots: «bottom-up» and «top-down». However, the synthesis used in these approaches often require the usage of aggressive reagents, critical reaction conditions, are time-consuming and, often, expensive procedures, since they involve several stages.

Pulse laser ablation in a liquid can be used as a one-step, low-cost and fast method for preparing graphene dots with controlled parameters. Currently, very few papers have been published on the preparation of graphene quantum dots by laser ablation [19, 20].

In particular, this method was used in Ref. [19] to obtain graphene oxide nanostructures. It was shown that in the process of ablation, occurs the formation of graphene oxide nanostructures with various shapes: ribbons, flakes and quantum dots with simultaneous photoreduction of graphene oxide. The quantum dots of graphene oxide have blue photoluminescence, which is the result of recombination of charge carriers localized on zigzag edges. The luminescence intensity varies for dots obtained at different irradiation times.

Also, this method was used for the synthesis of graphene oxide dots in Ref. [20]. The diameter of the resulting structures varies from 5 to 30 nm, and they have good stability and crystallinity. The luminescence spectrum of the resulting nanostructures is located in the yellow-green region, which is atypical for graphene quantum dots. The authors showed that these dots have high optoelectronic properties and were used as markers for displaying cancer cells.

In this work, we studied the effect of laser radiation on the structural and optical properties of graphene oxide dispersed in water.

## *Experimental*

For the preparation of dispersions, a single-layer graphene oxide (GO, Cheaptubes) was used. Since it was shown earlier in our work [21], GO dispersed into particles of various sizes and stability in various organic solvents. Here we selected water. Deionized water was purified using the AquaMax system. The specific resistance of water was equal to 18.2 MΩ/cm. The surface tension of water was equal to 72.8 mN/m at pH=5.6 and a temperature of 22 ºC.

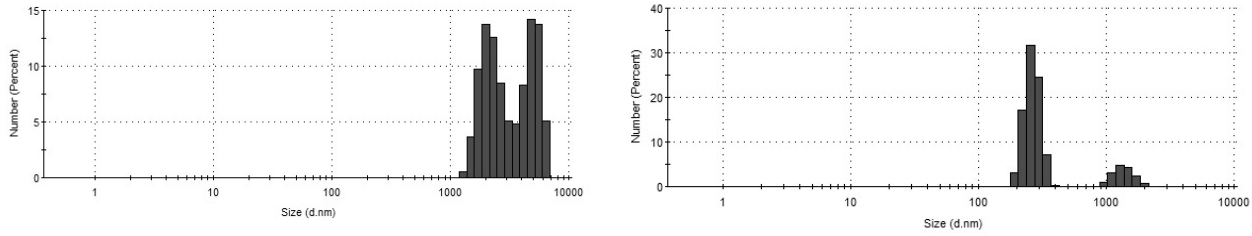
The GO concentration in the solution was equal to 0.25 mg/ml. To obtain dispersion, it was treated with ultrasound for 30 minutes. The GO dispersion was undergo to laser ablation with the second harmonic of a solid-state Nd:YAG laser with a generation wavelength at 532.0 nm, a pulse duration of 10 ns, and an pulse energy of ~16 J/cm$^2$. The height of the ablated liquid was 0.8 cm. The particle size of graphene oxide in the solutions was determined by dynamic light scattering method using a Zetasizer nano analyzer (Malvern).

The absorption and fluorescence spectra of the samples were measured on Cary and Eclipse (Agilent) spectrometers, respectively. Raman spectra of the prepared samples were recorded using Confotec MR520 (3D Scanning Raman Confocal Microscope, Sol Instruments) with laser excitation at a wavelength of 532 nm.

The fluorescence lifetimes of dispersions were determined using the TCSPC system (Becker&Hickl) at an excitation wavelength of $\lambda_{ex}$ = 488 nm. The fluorescence lifetimes were determined from decay kinetics processing with SPCImage software (Becker&Hickl). All measurements were performed in 1 cm quartz cuvettes at room temperature.

## *Results and discussion*

Measurements showed that after dispersing of GO in water and before laser irradiation, about half of the particles have an average size of 4900 nm, and the second half of sizes are in the order of 2300 nm (Fig. 1*a*).



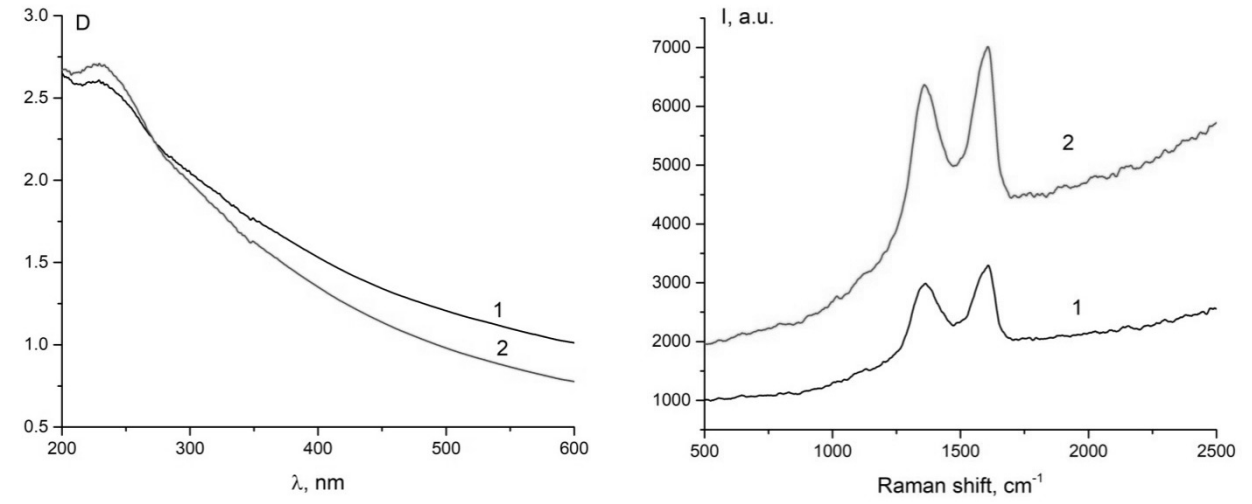

*a* *b*

Figure 1. Size distribution of GO particles in water before (*a*) and after (*b*) laser irradiation

After ablation (Fig. 1*b*), a darkening of the GO solution was registered and a decrease in the average particle size to 200–250 nm were observed. And about 13 % of the particles have a diameter of about 1400 nm.

Measurements of the optical characteristics showed (Fig. 2) a wide absorption band with a maximum of about 230 nm of the prepared dispersion, which is formed by transitions between orbitals of ππ*-nature in C–C aromatic bonds [22, 23]. A shoulder of about 300 nm is associated with n→π* transitions in C=O bonds, and it is almost indistinguishable in the absorption spectra.

It can be seen from the spectrum that the optical density of the dispersion of graphene oxide in water after ablation is higher than before irradiation. It is a result of uniform distribution and increase in the concentration of GO particles after laser treatment. As well as the fact that prior to ablation, graphene oxide flakes were clearly distinguishable in solution. After laser treatment, the solution became more transparent and intensely colored due to the uniform distribution of graphene oxide particles.




*a* *b*

Figure 2. Absorption (*a*) and Raman (*b*) spectra of GO dispersion before (1) and after (2) ablation

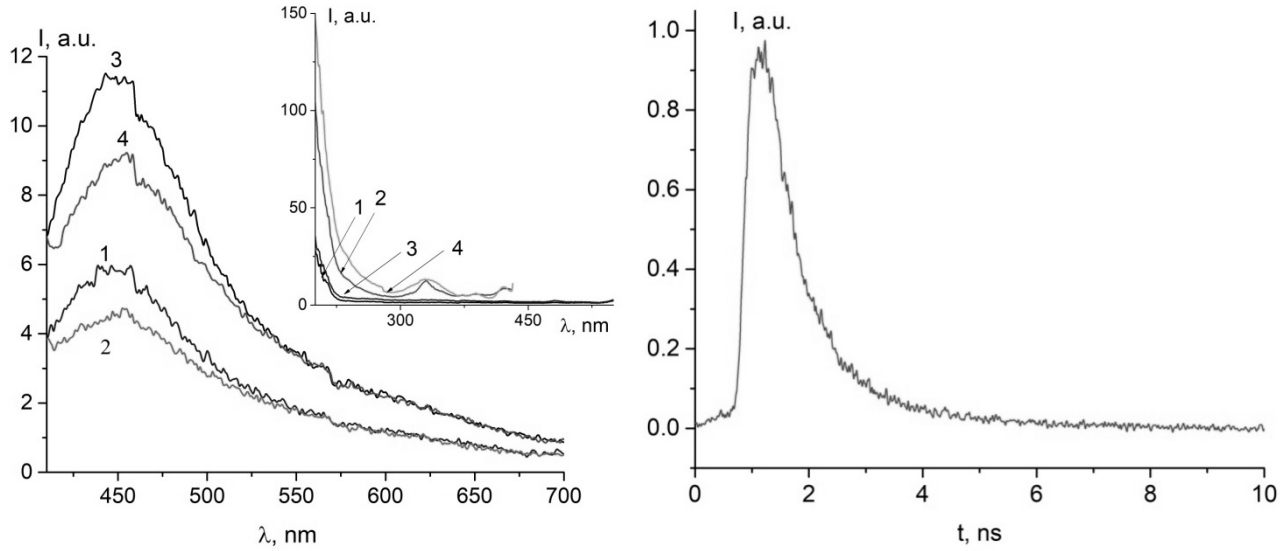
The effect of laser ablation on the structural properties of graphene oxide is shown in Figure 2*b*. Two intense bands in the region of 1300 and 1600 $cm^{-1}$ were registered in the Raman spectrum of GO. The G-band of GO is located at 1605 $cm^{-1}$ and is shifted to higher frequencies compared to the position of this band in graphite (1581 $cm^{-1}$) due to the presence of separate double bonds that resonate at higher frequencies [24, 25]. After complete reduction of graphene oxide to graphene, a bathohromic shift usually occurs. As can be seen from the figure, it was not occurred after laser ablation.

Also, in the Raman spectrum of GO, there is exhibits a D band of about 1360 $cm^{-1}$, which characterizes the defectness of graphene and is active only if defects participate in double resonance scattering near the Brillouin zone [24]. Therefore, the $I_D/I_G$ intensities ratio is often used to determine the size of domains with $sp^2$ hybridization in carbon materials. The data obtained showed that the ratio of the intensities of the G and D bands was changed from 1.10 to 1.05, which indicates a partial reduction of graphene oxide during laser ablation.

Under the studying the luminescent properties of the prepared dispersions, the spectra shown in Figure 3 were obtained.

A wide band with a maximum of about 450 nm was registered in the GO luminescence spectrum. When the luminescence excitation wavelength was changed from 320 nm to 350 nm, the position and shape of the fluorescence band was not changed. The fluorescence intensity in this case was increased by ~20 %.

After ablation, the luminescence spectrum also practically was not changed in its shape, however, the luminescence intensity was increased almost in 2 times for both excitation wavelengths. This fact could be explained by growth in the optical density *D* of the solution after ablation. However, the *D* value was increased by only 5 %. Therefore, growth in the luminescence intensity is associated with other processes. As shown by the measured fluorescence excitation spectra (on the inset in Fig. 3*a*), the main contribution to the GO fluorescence is made by the centers actively absorbing light in the region of 320–340 nm. After laser ablation, their changes practically do not occur. When the excitation spectrum was recorded at the long-wavelength edge of the luminescence (at ~580 nm), a spectrum that was similar in shape to the absorption spectrum of GO was obtained. At present, the mechanism of the occurrence of fluorescence in graphene nanostructures remains incompletely studied, but most authors [24, 25] believe that it can be assigned to different emitting groups or localized electron–hole pairs due to the isolation of $sp^2$ clusters inside the $sp^3$ matrix. In any case, this will be the basis for our further studies.




*a*— Fluorescence spectra of the GO dispersion before (1, 2) and after (3, 4) ablation: 1, 3 — $\lambda_{ex}$=320 nm; 2, 4 — $\lambda_{ex}$=350 nm. In the inset — the fluorescence excitation spectra at registration of spectrum at: 1,3 — 450 nm, 2,4 — 580 nm

*b* — the fluorescence decay kinetics of GO, $\lambda_{reg}$ = 450 nm

Figure 3

When measuring the lifetime of GO luminescence in solutions, the excitation was carried out at a wavelength of 375 nm (Figure 3b). The decay kinetics of GO is described by a bi-exponential equation. The average fluorescence lifetime of GO at λ = 455 nm is equal to $\tau_{fl}$ = 1.6 ns for the initial dispersion. After ablation, $\tau_{fl}$ has changed little and it was equal to 1.57 ns. This indicates a similar nature of luminescence before and after laser ablation of a graphene oxide dispersion.

*Conclusion*

Thus, it has been shown that by laser ablation of graphene oxide in water, a significant reduction in the size of GO sheets can be achieved. In this case, the resulting particles have a size mainly of about 110–120 nm, and are similar to graphene quantum dots. The measured Raman spectra indicate the reduction of graphene oxide during laser ablation. In this case, the thickness of the formed particles practically does not change, since the $I_D/I_G$ ratio has close values.

It was shown that by laser ablation it is possible to achieve a significant increase in the luminescent ability of GO in an aqueous solution. In this case, the luminescence intensity was increased by almost 2 times, while the optical density of the solution was increased by only 5 % relative to the initial solution. The recorded fluorescence excitation spectra indicate that the main contribution to the GO luminescence is made by the centers actively absorbing light in the region of 320–340 nm. After laser ablation, changes in the fluorescence excitation spectra practically do not occur.

The results can be used to create organic luminescent materials, in optical nanotechnologies, as well as in photovoltaics, biophysics and bioimaging.

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## Су дисперсиясындағы аблирленген графен оксидінің оптикалық қасиеттері

Суда дисперсияланған графен оксидінің құрылымдық және оптикалық қасиеттеріне лазерлік сәулеленудің әсері зерттелген. Графен оксидін суда лазерлік абляциялау арқылы графен оксиді парағының мөлшерін едәуір азайтуға болатындығы көрсетілді. Бұл жағдайда алынған бөлшектердің мөлшері шамамен 110–120 нм болады және ол графен кванттық нүктелеріне ұқсас. Раман спектрін өлшеу лазерлік сәулелендіру кезінде графен оксидінің қалпына келетіндігін көрсетті. Бұл жағдайда қалыптасқан бөлшектердің қалыңдығы іс жүзінде өзгермейді, өйткені $I_D/I_G$ қатынасы жақын мәндерге ие. Графен оксидінің дайындалған дисперсиялары 400–600 нм аймақта максимум 450 нм және өмір сүру ұзақтығы 1,6 нс болатын кең люминесценциялық жолақтарды көрсетті. Лазерлік абляция арқылы су ерітіндісінде графен оксидінің люминесценттік қабілетінің едәуір артуына қол жеткізуге болатындығы көрсетілген. Бұл жағдайда люминесценцияның қарқындылығы 2 есе өсті, ал ерітіндінің оптикалық тығыздығы бастапқы ерітіндімен салыстырғанда 5 %-ға өсті. Алынған нәтижелерді органикалық люминесцентті материалдарды, оптикалық нанотехнологияларды жасау үшін, сонымен қатар фотоэлектриктерде, биофизика мен биобейнелеуде қолдануға болады.

*Кілт сөздер:* графен оксиді, лазерлік абляция, дисперсия, өлшемдердің таралуы, құрылымы, жұтылу, люминесценция, өмір сүру кинетикасы.

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## Оптические свойства аблированного оксида графена в водных дисперсиях

Изучено влияние лазерного облучения на структурные и оптические свойства оксида графена, диспергированного в воде. Показано, что путем лазерной абляции оксида графена в воде можно добиться значительного уменьшения размеров листов оксида графена. При этом образующиеся частицы имеют размер преимущественно около 110–120 нм и схожи с графеновыми квантовыми точками. Измеренные раман-спектры указывают на восстановление оксида графена в процессе лазерного облучения. При этом толщина образуемых частиц практически не изменяется, так как отношение $I_D/I_G$ имеет близкие значения. Приготовленные дисперсии оксида графена проявляют широкие полосы свечения в области 400–600 нм с максимумом около 450 нм и временем жизни 1,6 нс. Показано, что путем лазерной абляции можно добиться значительного увеличения люминесцентной способности оксида графена в водном растворе. При этом интенсивность свечения возросла почти в 2 раза, тогда как оптическая плотность раствора увеличилась лишь на 5 % относительно исходного раствора. Полученные результаты могут быть использованы для создания органических люминесцентных материалов в оптических нанотехнологиях, а также в фотовольтаике, биофизике и для биоимиджинга.

*Ключевые слова:* оксид графена, лазерная абляция, дисперсия, распределение по размерам, структура, поглощение, люминесценция, кинетика времени жизни.

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