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Effect of graphene oxide on spectral-luminescent properties of xanthene dye

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The effect of graphene oxide on the spectral and luminescent properties of xanthene dyes was studied. During the interaction of graphene oxide (GO) with a cationic dye, aggregation of Rhodamine 6G occurs, which is expressed as an increase in the optical density of the short-wavelength shoulder in the absorption spectrum of the dye. GO sheets can act as adsorption centers for dye molecules due to the influence of the Coulomb and intermolecular forces between GO and Rhodamine 6G. This effect is practically not pronounced for anionic dyes. The quenching of the dye fluorescence intensity in the presence of GO was observed. Fluorescence quenching was equal to 2.4 times for Eosin, 5.8 times for Bengal rose, and 22.1 times for Rhodamine 6G. As shown by spectral-kinetic measurements, the fluorescence lifetime was also decreased in this case. Dye fluorescence quenching occurs through the process of electron transfer from the dye to GO. The results obtained can be used for the photodegradation of organic dyes by using of composite materials with graphene oxide.

Keywords: graphene oxide; xanthene dyes; iconicity; absorption; fluorescence; spectral-luminescent properties, quenching

Introduction

Due to the unique properties of graphene and graphene oxide (GO), these materials have become widely studied [1–2]. Graphene has high charge-transport and mechanical strength characteristics, high transparency in the visible and IR ranges, good adsorption capacity and biocompatibility. These properties make it a very promising material for a wide variety of applications, including field-effect

transistors (FETs), gas and biomolecule sensors, transparent conductive films (TCFs) and graphene batteries [3–7].

Graphene oxide (GO) is a layered carbon structure with oxygen-containing functional groups (=O, -OH, -O-, -COOH) attached to both sides of the layer, as well as the edges of the plane [8–10]. GO can be synthesized by oxidizing of graphite to graphite oxide with following exfoliation into GO. The properties of GO are highly dependent on the synthesis method, which affects the final amount and type of oxygen-containing groups in the resulting GO. Unlike graphene, GO is hydrophilic, so its use in technological problems is more extensive. Highly oxidized forms of GO can be used as an electrical insulators with a band gap of approximately 2.2 eV. Due to the presence of various oxygen functional groups on the surface of GO, it can be used as a starting material for the synthesis of graphene derivatives, such as fluorographene, bromographene, graphane, and many others.

Due to its extended π -conjugated system and the presence of oxygen-containing groups, GO is an excellent medium for the incorporation of both organic and inorganic molecules. It was shown in Refs. [11–13] that GO can interact with various organic dyes and quantum dots. Based on these unique properties, various graphene-based sensors have been developed using photoinduced electron transfer or FRET [14–15]. In addition, studies of the interaction of graphene or GO with organic dyes are actively carried out in order to study and accelerate the processes of photocatalysis and adsorption of organic contaminants that is important problem for the environment [16–17].

Xanthene dyes such as Rhodamine 6G, Bengal rose and Eosin are well known and widely used compounds. Due to their high photostability, high quantum yield, and low cost, they are widely used as fluorescent probes in numerous studies [18, 19]. Similar to graphene, these dyes have a π -conjugated structure and therefore can effectively interact with graphene through π - π interactions. As a rule, such an interaction leads to fluorescence quenching, which is the result of photoinduced electron transfer from the dye to graphene.

The study of such processes has been intensively carried out [20, 21]. For example, fluorescence quenching of polymers by reduced graphene oxide [22], resonant energy transfer from a dye molecule to graphene [23], and interaction of graphene sheets with a dye using fluorescence quenching microscopy [24] have been reported. In addition, due to the growing attention to energy and environmental issues, many studies are focused on photocatalytic systems using graphene oxide and solar cells based on organic compounds, where dyes act as sensitizers. Therefore, the studies of the interaction and the process of electron injection from dye molecules to GO are very important. In this work the interaction between graphene oxide and xanthene dyes of different ionicity: cationic Rhodamine 6G (R6G) and anionic Eosin (E) and Bengal rose (BR) was studied.

Research methods

Structure of the studied dyes are shown in the Figure 1.

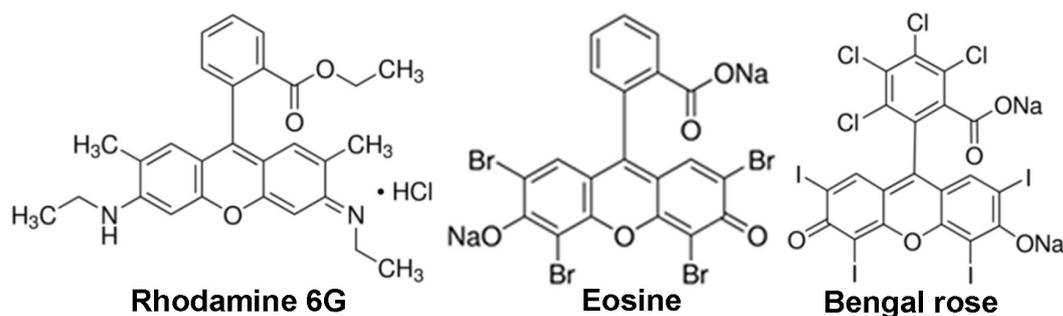


Figure 1. Structural formulae of xanthene dyes.

To prepare a dispersion of GO, single-layer graphene oxide (SLGO, Sigma Alsdric) was used, which was sonicated in an aqueous solution for a long time (30 minutes). The resulting dark brown solution was centrifuged at 3000 rpm to remove large particles. Subsequently, a transparent dispersion was used to prepare mixed dye-GO solutions. The dye content in all samples was constant and equal to 8.5×10^{-6} mg/mL ($C = 3.6 \times 10^{-5}$ mol/L). The concentration of GO was varied and was equal to 0.008, 0.016, 0.033 and 0.066 mg/mL.

The absorption spectra of the studied solutions were measured on a Cary-300 spectrophotometer, and the fluorescence spectra, on an Eclipse spectrofluorimeter (Agilent). The lifetimes of the excited state of the dyes were estimated from the fluorescence decay kinetics measured with a picosecond-resolution pulsed spectrofluorimeter with registration in the time-correlated photon counting mode (Becker&Hickl, Germany) upon excitation with a 488 nm laser.

Results and discussion

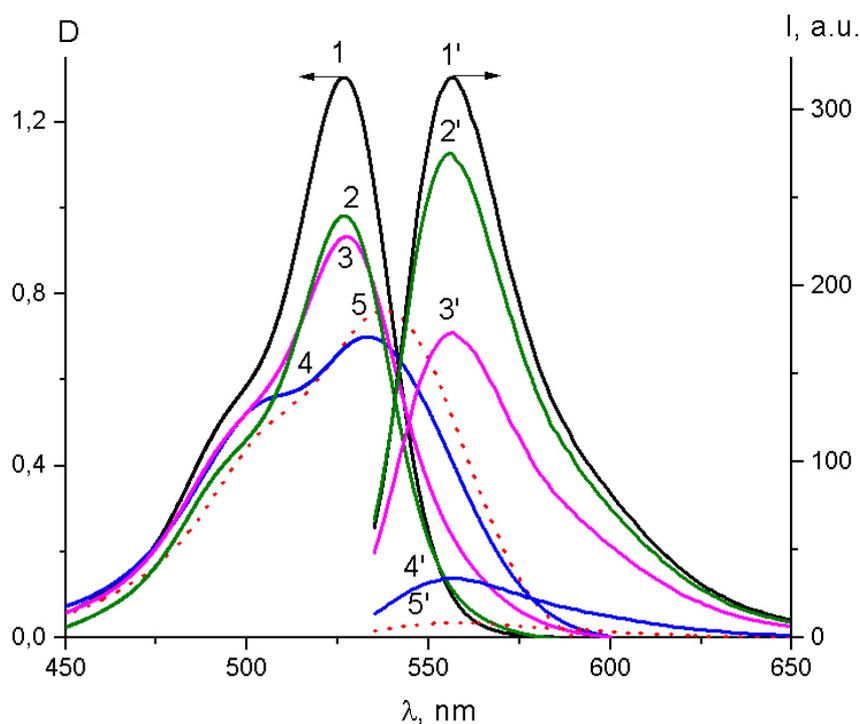
In the absorption spectra of the dye solutions, an increase in the concentration of GO lead to the decrease in the optical density of the solutions, and a noticeable broadening of the spectrum (almost 2 times) with a shift of the maximum to the long wavelength region are observed (Table 1). At the same time, in the short-wavelength part of the spectrum, a shoulder with a maximum at about 495–505 nm is observed, the intensity of which practically was not changed. However, the ratio of the optical density recorded at the maximum of the absorption spectrum and in the short-wavelength shoulder (D_{shw}) increases.

The fluorescence spectra, as can be seen from the Figure 2, do not shift in this case. When the solutions were illuminated with light with a shorter wavelength, no noticeable shift or change in the shape of the absorption bands was recorded. As can be seen from the Figure 2, even a slight impurity of GO in the dye solution leads to a noticeable quenching of the fluorescence intensity (by 15 percents). Further increases in the GO concentration almost completely quench the luminescence of the dye. At the same time, as can be seen from Figure 2, a noticeable broadening of the fluorescence spectrum is observed.

Table 1.

Spectral parameters of Rhodamine 6G at different concentrations of GO in solutions.

C_{GO} , mg/mL	λ_{absmax} , nm	$\Delta\lambda_{1/2}$, nm	D_{max}	λ_{shw} , nm	λ_{flmax} , nm	$\Delta\lambda_{1/2}$, nm	I, a.u.
0	526	37	1.3	495	557	37	319
0.008	529	39	0.98	495	557	39	277
0.016	528	50	0.93	495	557	43	173
0.033	534	70	0.70	505	557	50	34
0.066	538	70	0.76	505	557	56	9

Figure 2. Absorption (1 – 5) and fluorescence (1' – 5', $\lambda_{exc} = 530$ nm) spectra of Rhodamine 6G at various concentrations of GO, mg/mL: 1, 1' – 0; 2, 2' – 0.008; 3, 3' – 0.016; 4, 4' – 0.032; 5, 5' – 0.066.

The measurements of fluorescence excitation spectra of the studied solutions have shown that the spectra recorded coincide in shape with the absorption spectra of pure Rhodamine 6G. When GO was added to the solution, the dye excitation intensity decreases.

Thus, as can be seen from the presented data, GO have influence on the spectral and luminescent properties of Rhodamine 6G in solution. When they interact, a bathochromic shift and deformation of the absorption bands occur with the observed pronounced quenching of the dye luminescence intensity associated with dye aggregation.

We also measured the decay kinetics of Rhodamine 6G fluorescence in solutions at various GO concentrations (Figure 3). As can be seen from the presented data, with an increase in the GO concentration, not only the luminescence inten-

sity of the dye decreases, but also the lifetime of fluorescence (Table 2), which indicates the dynamic nature of the observed quenching.

Table 2.

Spectral-kinetic data of dye solutions at various GO concentrations.

C_{GO} , mg/mL	I , a.u.	τ , ns	I/I_0	τ_0/τ
Rhodamine 6G				
0	25876	4.91	1	1
0.008	17649	4.62	1.47	1.06
0.016	11474	4.21	2.26	1.17
0.033	2548	3.85	10.16	1.27
0.066	1169	3.79	22.14	1.30
Eosine				
0	18800	1.50	1	1
0.008	16343	1.48	1.15	1.02
0.016	15939	1.45	1.18	1.04
0.033	12395	1.38	1.52	1.09
0.066	7756	1.31	2.42	1.15
Bengal rose				
0	25600	0.29	1	1
0.008	24567	0.35	1.04	0.82
0.016	16260	0.31	1.57	0.93
0.033	7421	0.16	3.45	1.81
0.066	4385	0.21	5.84	1.38

The result of the study of spectral and luminescent characteristics of Eosine and Bengal rose in the presence of GO are shown in Table 3. It can be seen that in the presence of GO, the absorption spectra of both Eosine and Bengal rose do not exhibit any significant shifts or shape changes. However, in the absorption spectrum of Eosine, as well as for Rhodamine 6G, a decrease in the absorption density of the dye was observed with an increase in the GO concentration.

For Bengal rose, a similar result was obtained only at $C_{GO}=0.066$ mg/mL. In this case, the fluorescence spectra of dyes are slightly red-shifted and broadened by 1–2 nm relative to the emission spectra of pure Eosine and Bengal rose.

As in the case of Rhodamine 6G the addition of GO leads to a decrease in the fluorescence intensity of the dyes. Thus, a decrease in fluorescence intensity by 2.4 times for Eosine and 5.8 times for Bengal rose was registered. As the spectral-kinetic measurements showed (Table 2), the fluorescence lifetime also decreases.

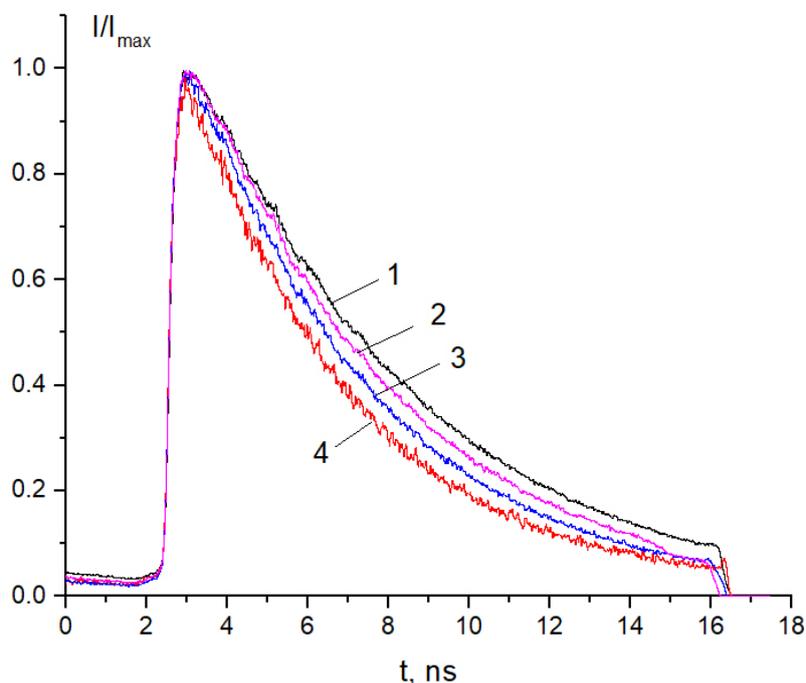


Figure 3. Fluorescence decay kinetics of Rhodamine 6G at various concentrations of GO, mg/mL: 1 – 0; 2 – 0.008; 3 – 0.016; 4 – 0.033.

Table 3.

Spectral parameters of Eosin and Bengal rose at different concentrations of GO in solutions.

C_{GO} , mg/mL	λ_{absmax} , nm	$\Delta\lambda_{1/2}$, nm	D_{max}	λ_{shw} , nm	λ_{flmax} , nm	$\Delta\lambda_{1/2}$, nm	I , a.u.
Eosine							
0	516	34	1.39	482	540	34	93
0.008	516	34	1.34	482	540	35	82
0.016	516	34	1.29	482	541	35	75
0.033	516	34	1.13	482	541	35	52
0.066	518	35	0.85	482	542	36	41
Bengal rose							
0	526	33	1.54	490	553	36	185
0.008	526	33	1.58	490	553	36	170
0.016	526	34	1.51	490	553	36	162
0.033	526	34	1.67	490	554	37	134
0.066	526	35	1.39	490	554	37	105

In this case, the ratio of τ/τ_0 for Eosine and Bengal rose is also smaller than for Rhodamine 6G. It can be said that, in the presence of GO, the quenching of the luminescent properties of xanthene dyes corresponds to the Rhodamine 6G>Bengal rose>Eosine dependence.

As can be seen from the data, the absorption spectra of the rhodamine dye are bathochromically shifted upon the addition of GO. In this case, the broadening

and deformation of the spectra was registered, as evidenced by the increase in the optical density of the short-wavelength shoulder in the absorption spectrum of the dye. Meanwhile, under the photoexcitation of Rhodamine 6G solutions with a wavelength of $\lambda = 530$ nm, only a decrease in the fluorescence intensity and broadening of the spectra was observed without changes in their shape. This indicates that only monomeric molecules give fluorescence. Thus, it can be concluded that in the presence of graphene oxide particles, molecular aggregation of positively charged rhodamine molecules is observed. In this case, GO sheets can act as adsorption centers [25] for dye molecules due to the influence of Coulomb and intermolecular forces between the oxygen-containing groups of GO (-OH, -COOH, =O) and the positively charged xanthen fragment of Rhodamine 6G. For Eosin and Bengal rose, these changes are not so pronounced due to the predominance of the negative charge on the molecules, which is expressed in the predominance of repulsive forces during interaction with GO.

Quenching of fluorescence in an electronically excited state can occur through a nonradiative transition to the ground state, either as a result of energy or electron transfer, depending on the properties of the chromophore, bonds, and local environment. Obviously, there is no overlap between GO and the fluorescence spectrum of the dyes, so dye fluorescence quenching occurs through an electron transfer process. In this case, the interaction between the excited dye and GO leads to a decrease in the fluorescence yield of the dye, and such quenching is the process of charge transfer from the excited dye to the graphene surface.

Conclusion

The effect of GO on the spectral and luminescent properties of xanthen dyes was studied. It was shown that during the interaction of GO with a cationic dye, aggregation of Rhodamine 6G occurs, which is expressed as an increase in the optical density of the short-wavelength shoulder in the absorption spectrum of the dye. GO sheets can act as adsorption centers for dye molecules due to the influence of the Coulomb and intermolecular forces between GO and Rhodamine 6G. This effect is practically not pronounced for anionic dyes.

The quenching of the dye fluorescence intensity in the presence of GO was observed. Fluorescence quenching was equal to 2.4 times for Eosin, 5.8 times for Bengal rose, and 22.1 times for Rhodamine 6G. As shown by spectral-kinetic measurements, the fluorescence lifetime was also decreased in this case. Dye fluorescence quenching occurs through the process of electron transfer from the dye to GO. The results obtained can be used for the photodegradation of organic dyes by using of composite materials with graphene oxide.

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