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Mathematical modeling of interactions of the surface of carbon dots with metal ions using the method of molecular dynamics

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The interactions of a number of metal cations Co^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+} with the carboxylated surface of a carbon dot in water have been studied by the method of molecular dynamics. The analysis of the obtained time dependencies of the distances between cations and the carboxyl group showed the absence of ion adsorption on the surface of the carbon dot and their predominant interaction through a layer of water molecules. The results indicate that the quenching of photoluminescence of carbon dots by cations of the studied metals is dynamic.

Keywords: carbon dots, photoluminescence, molecular dynamics, photoluminescence quenching, adsorption.

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Introduction

Science and industry have been actively using the results of research into the microcosm, including nanoparticles in recent years [1]. Carbon nanoparticles, including carbon dots are among the most promising materials in various applications [2–4]. Carbon dots (CD) form a large class of carbon nanoparticles up to 10 nm in size, containing carbon in sp^3- and sp^2-hybridizations, as well as various impurity atoms and functional groups. The main characteristic of the majority of CDs, which makes them attractive for study and application, is their intense photoluminescence, which depends on many factors: the synthesis method and precursors, the structure and composition of particles, properties and environmental parameters [3–6]. This dependence opens up the prospects of using CDs as theranostic agents [7], photoluminescent markers [8], in the role of optical nanosensors for the determination of various substances and environmental parameters [9–11].

Currently, nanosensors based on carbon dots obtained by a simple and cheap hydrothermal synthesis method, are particularly actively developing [12]. There are numerous studies of the impact of environmental parameters on the photoluminescence intensity of CDs [5,6,12], as well as the studies of the dependence of the photoluminescence (PL) of nanoparticles on the salts and molecules in solutions [9–15]. Many groups have found a significant effect on the spectral characteristics of CD PL of dissolved ions, primarily metal ions [9–15]. It was found in the vast majority of experiments that the CD PL quenching takes place as a result of the interactions of CD with metal ions in the medium. Moreover, different ions change the intensity of CD PL to varying degrees [14]. These results provide broad prospects for the use of CDs as photoluminescent nanosensors of metal ions (including heavy metals) in technological and natural waters, as well as in biological tissues [9–13].

However, it is impossible to develop effective carbon nanosensors without studying the interactions between the surface groups of CD and surrounding ions and the mechanisms of the effect of these interactions on the nanoparticle PL. Despite numerous publications on the dependence of CD PL on the type and concentration of metal ions, these mechanisms have not yet been fully studied, although there are articles in which the authors explain the results obtained from the point of view of electronic processes. According to the research of the authors of Ref. [16,17], in the presence of ions in solution, the intensity of CD PL can decrease due to nonradiative transitions between singlet and triplet states of photoluminophores, as a result of transitions of photoluminophore electrons to unfilled quencher shells and the formation of complexes in the ground state, due to changes in the structure and number of surface states and traps.

An equally important issue for the use of CD as optical nanosensors is to determine the type of quenching of their PL by the studied ions. As is known, the main molecular mechanisms of phosphor fluorescence quenching are dynamic and static [14,17,18]. The dynamic extinguishing mechanism consists in the fact that when an excited photoluminophore collides with a quencher, nonradiative excitation is removed. The static mechanism, like the dynamic one, is also characterized by nonradiative removal of excitation from the phosphor, however, in this case a relatively stable non-photoluminescent complex is formed between it and the quencher. The results of experimental studies by the authors of Ref. [14] of the type of quenching of CD PL synthesized from citric acid and ethylenediamine with metal ions of Co^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+},

Zn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+} in water showed the possibility of both types of quenching — both static and dynamic. It is important to know the type of quenching to create a nanosensor for certain ions, since dynamic quenching ensures the reusability of the nanosensor due to repeated collisions of CD with ions. The nanosensor can only be single-use in case of static quenching, when complexes are formed (i.e., the ion is „adsorbed“ onto the CD), but it can remove metal ions as an adsorbent.

It is possible to see that both static and dynamic types of PL quenching are determined by the relative position of the photoluminophore and the quencher. Thus, by conducting mathematical modeling of the interactions of certain functional surface groups of CD and the corresponding ions in solution, it is possible to draw theoretical conclusions about the mechanisms of these interactions and about the applicability of certain CD as reusable or disposable nanosensors of the studied metal ions. It is advisable to conduct such modeling using the molecular dynamics (MD) method for taking into account the impact of internal electron density distribution of CD surface groups, interactions with the local environment, solvent molecules, ions, other surface groups, and other factors on the properties of CD surface groups. The MD method allows obtaining information about changes of the length of hydrogen bonds between functional groups of nanoparticles and environmental molecules over time, about the dynamics of the interaction of diamond-like structures with the environment and the adsorption of ions into oxygen-containing groups [19], reproducing CD structures and tracking the dynamics of their changes over time [20,21]. All these factors also have a significant impact on the photoluminescent properties of the sample under consideration.

Molecular dynamic calculations are used to solve many problems related to the behavior of CD in various environments, usually using the interaction potential OPLS-AA (Optimized Potential for Liquid Simulations, All-Atom) [22]. For instance, the authors of Ref. [23] theoretically explained the decrease of viscosity of hydrolyzed polyacrylamide in case of the addition of CT. A generator of structurally diverse CD was developed in Ref. [24] and their structural dynamics were obtained in water and N,N-dimethylformamide. The authors of Ref. [25] used the potential of OPLS-AA to model the effect of the surface structure of detonation nanodiamonds and their environment on the dynamics of water molecules and changes of their hydrogen bonds near the surface of nanodiamonds. The structural changes of CD and other nanoparticles can be traced using the MD method, which, in turn, already makes it possible to correctly set the system parameters for calculations using quantum chemical mathematical modeling methods, which result in theoretical absorption and PL spectra that are in good agreement with experiment [26].

The interactions of the carboxylated surface of a carbon dot with metal nitrate ions $Al(NO_3)_3$, $Co(NO_3)_2$, $Cr(NO_3)_3$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, $Mg(NO_3)_2$, $Ni(NO_3)_2$, $Pb(NO_3)_2$ and $Zn(NO_3)_2$ in water was modelled in this paper using molecular dynamics for determining the type of CD PL extinguishing with the studied metal ions.

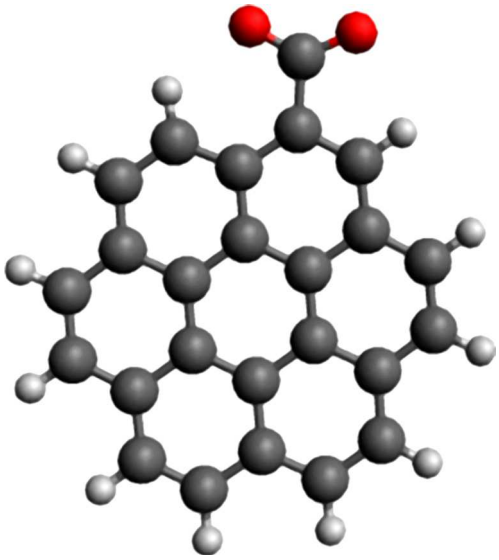

Figure 1. The chemical structure of the model of CD-COO-, excess charges in the group -COO− are distributed evenly over oxygen atoms. Carbon is shown by grey, hydrogen is shown by white coilor, and oxygen is indicated by red color.

Materials and methods

Objects under study

Each studied system consisted of one „carbon dot“, one dissociated metal nitrate molecule (Me^{n+} and $n^*(NO_3^-)$) and 500 water molecules. As a model of a carbon dot with sp^2-hybridization, we considered a 1 nm diameter graphene fragment composed of 7 aromatic carbon rings arranged in a circular pattern, featuring peripheral hydrogen atoms and one deprotonated carboxylic functional group $-COO^-$ (Fig. 1). The choice of the carboxylic group is attributable to the fact that it is the most chemically active, and also has a charge opposite to the cations, since it is usually deprotonated in an aqueous solution.

Calculations were performed for aqueous solutions of nitrates and metal ions Co^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+} and CD-COOH.

Theoretical calculations

The dynamics of the interactions of the CD-COOH surface with metal ions was studied using the molecular dynamics method.

The calculations were performed in the LAMMPS software package [27] using OPLS-AA potential [22]. This potential is usually used to model the behavior of organic molecules in liquid solutions. The OPLS-AA potential, originally developed for describing liquids, has also shown

Table 1. Parameters of the OPLS/AA potential for the studied ions: ε is the depth of the quantum well, σ is its position for the Lennard-Jones potential [29,30]

Ion	ε, kcal/mol	σ, Å
Co^{2+}	0.0164	1.40
Cu^{2+}	0.0427	2.07
Mg^{2+}	0.6200	2.40
Ni^{2+}	0.0366	2.19
Pb^{2+}	0.8000	3.00
Zn^{2+}	0.0150	1.90
Al^{3+}	0.2166	1.45
Cr^{3+}	0.0264	2.67
Fe^{3+}	0.1910	2.17
N in (NO_3)-	0.1700	3.25
O in (NO_3)-	0.2100	2.96

itself well in calculations of the behavior of molecules of solids in liquid media.

The values of the OPLS-AA potential parameters for the CD-COOH model used were obtained using the LigParGen package [28]. The three-point model SPC-E was used as a water model [29]. The interaction coefficients for the studied salt ions in the OPLS-AA potential were borrowed from publications [29,30] and presented in Table 1. The cross-interactions in this potential are calculated according to a geometric rule.

To set the initial state of the system, all its components — CD-COO-, metal salt ions, water molecules — were placed in the nodes of a programmatically defined lattice, after which the system was brought to thermodynamic equilibrium in an isothermal isobaric ensemble (NPT) at a temperature of 300 K and a pressure of 1 bar. The resulting volume of the equilibrium system turned out to be 27 nm^3, which corresponds to the concentration of CD with carboxylic surface groups of the order of 25 g/L, and the salt concentration of 0.29 M. After that, the volume of the system was fixed, and further calculations were performed in the canonical ensemble obtained using the Nose–Hoover thermostat (NVT). One calculation step was 1 fs, the total calculation time of each system was 1000 ns (1 μs, 10^9 steps). The equations of motion were integrated according to the Störmer–Verlet method. The thermal regulation was performed every 100 steps. The boundary conditions of the system were periodic.

As an example of the dynamics of the interaction of CD with cations calculated by the MD method, Fig. 2 shows the positions of the carbon dot, iron ions Fe^{3+} and three nitrate anions NO_3 relative to each other at different time points.

Results and discussion

The time dependences of the distances between cations Me^{n+} and C atoms in the -COO^--group were studied during the entire calculation time of 1 μs as a characteristic of the dynamics of the interaction of ions of salts Me^{n+} with the surface groups of the carbon dot. The dependence of the distance from the ion Cr^{3+} to the deprotonated carboxylic group on the CD surface on the time for the first 100 ns of the calculation is shown in Fig. 3 as an example. The obtained time dependences of the distance from all the studied metal cations to the atom from the deprotonated group -COO^- behave in a similar way: the distance from the cations to the group -COO^- varies from 4.5 Å to about 25 Åduring 1000 ns.

The modeling results showed that cation adsorption does not occur on the surface of the nanoparticle even in the case of significant Coulomb attraction between metal ions and surface carboxylic groups, i.e. no complexes are formed. Moreover, the ion never comes close to the group; in the best case, it stays for some time at a distance of about 4.5 Å from it, which corresponds to the size of one water molecule (Fig. 4). Thus, calculations have shown that the quenching of photoluminescence of CD with a carboxylated surface by the studied metal cations is attributable only to a dynamic mechanism.

As a measure of interaction, it was decided to use the fraction of time from the total calculation time (this time was the same for all cations and was 1000 ns), during which the cation remains in the position closest to the group -COO^-. The range of 4.3–4.7,Åwas used to estimate this position. Table 2 shows the results of calculation of this fraction of time for all the studied cations.

The results of calculations using the MD method listed in Table 2 allow constructing the following series for reducing the degree of interaction of the metal cation with the carboxylic group of CD-COO^-:

$$Fe^{3+} > Pb^{2+} > Cr^{3+} > Mg^{2+} > Cu^{2+}$$

$$\sim Ni^{2+} > Zn^{2+} \sim Co^{2+} > Al^{3+}.$$

If we divide it by the valence of the ion, we obtain

$$Fe^{3+} > Cr^{3+} > Al^{3+}$$

for trivalent cations of Me and

$$Pb^{2+} > Mg^{2+} > Cu^{2+} \sim Ni^{2+} > Zn^{2+} \sim Co^{2+}$$

for divalent cations Me.

The authors of Ref. [14] experimentally obtained the following series according to the degree of photoluminescence quenching for the same set of metal cations:

$$Fe^{3+} > Cr^{3+} > Cu^{2+} > Co^{2+} > Pb^{2+} > Ni^{2+}$$

$$\sim Al^{3+} > Mg^{2+} \sim Zn^{2+},$$

from which it is possible to make separate corresponding series for trivalent and divalent ions:

$$Fe^{3+} > Cr^{3+} > Al^{3+},$$

$$Cu^{2+} > Co^{2+} > Pb^{2+} > Ni^{2+} > Mg^{2+} \sim Zn^{2+}.$$

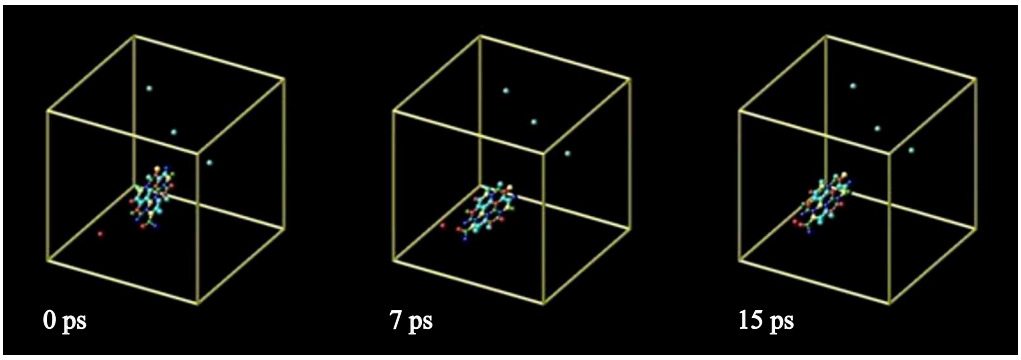

Figure 2. The position of CD-COO (size 1 nm) with a deprotonated carboxylic group relative to iron ions Fe^{3+} and three nitrate anions NO_3 at different time points (water and oxygen molecules in the nitrate ion are not shown). The edge size of the cube is 3 nm.

Table 2. Fractions of the time during which the cations remained at a distance of 4.3–4.7 Å from the CD-COO^- group for a time of 1000 ns

Cation	Co^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}	Mg^{2+}	Pb^{2+}	Al^{3+}	Cr^{3+}	Fe^{3+}
Fraction of timethe cation remained in the position of maximum proximity to group -COO^- ,%	6.9	7	8.7	8.8	12.9	14.2	4.9	13.2	19.7

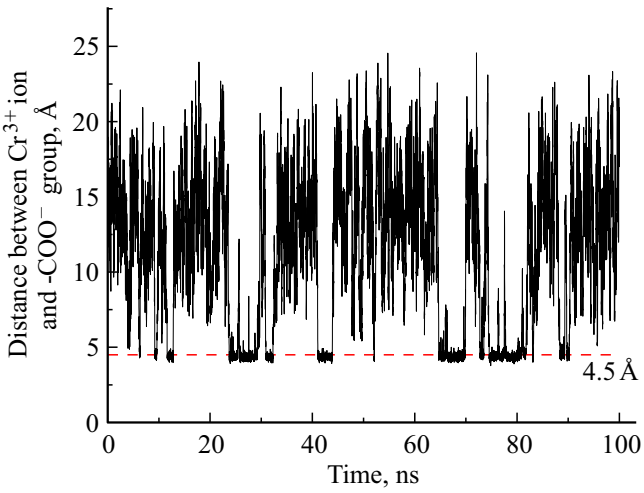

Figure 3. The time dependence of the distance from the ion Cr^{3+} to the carbon of the carboxylic group CD-COO.

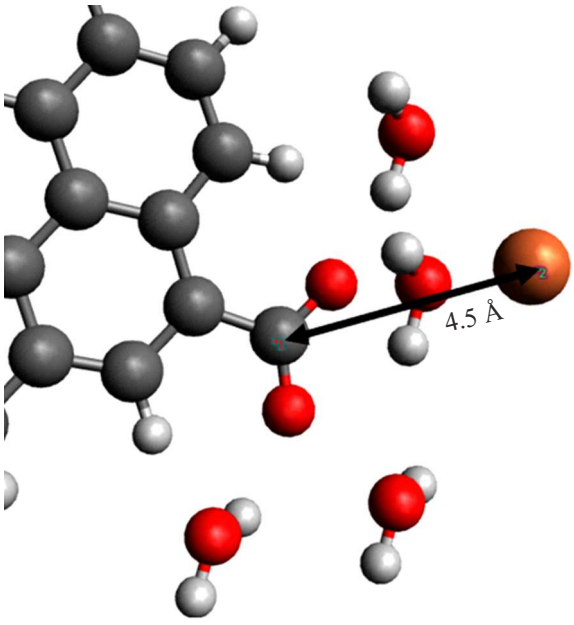

Figure 4. The relative position of the cation Fe^{3+} and the CD carboxylic group at the maximum approximation of the cation to the CD carboxylic group.

It should be noted that the calculations considered a carbon dot model with carboxylic surface groups, while the experimental studies of the authors of Ref. [14] used CDs synthesized from citric acid and ethylenediamine by the hydrothermal method, having simultaneously carboxylic, hydroxylic and amide groups (Fig. 1, *b*) of article [14]).

As follows from the comparison of theoretical and experimental results, the series for the quenching of CD PL by trivalent metal cations are completely consistent with each other, and the series for divalent ions differ significantly, although there is a partial correlation between them.

Obviously, the discrepancy is explained by the different composition of the surface functional groups of the „model" and „experimental" carbon dots. For this reason all metal cations in water can interact not only with the CD carboxylic groups, but also with hydroxylic groups in the experiment. Moreover, the interaction of nitrate anions with

amide groups is also added. Nevertheless, the complete agreement of the theoretical and experimental series on the degree of quenching of CD PL by trivalent metal cations once again shows that the carboxylic groups are the most chemically active on the surface of CD, and the interactions between the functional groups of nanoparticles and cations are mainly attributable to Coulomb forces.

Conclusion

The interactions of carboxylic surface groups of a carbon dot with ions of metal nitrates $Al(NO_3O_3$, $Co(NO_3)_2$, $Cr(NO_3O_3$, $Cu(NO_3)_2$, $Fe(NO_3O_3$, $Mg(NO_3)_2$, $Ni(NO_3)_2$, $Pb(NO_3)_2$ and $Zn(NO_3)_2$ in water was mathematically modelled using the method of molecular dynamics for determining the type of quenching of CD PL by the studied metal ions.

It was found that the studied cations Co^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+} are not adsorbed onto the carboxylated surface of CD. They approach the surface of the CD-COO^- as a result of the Coulomb interaction and remain near it for a certain time at a distance corresponding to the size of one water molecule. Thus, it has been established that the main contribution to the quenching of CD-COO^- PL by metal cations is made by a dynamic mechanism.

The calculated time fractions from the total calculation time (1000 ns) during which each metal cation resided in closest proximity to the -COO^- groups enabled ranking of the cations by their interaction strength with CD carboxylic groups:

$$Fe^{3+} > Pb^{2+} > Cr^{3+} > Mg^{2+} > Cu^{2+} \sim Ni^{2+} > Zn^{2+} \sim Co^{2+} > Al^{3+}.$$

The theoretical results obtained require further experimental confirmation.

The established dynamic type of quenching of PL of CD-COOH by metal cations Co^{2+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+} in water opens up wide opportunities for the development of reusable nanosensors based on CD-COOH for the diagnosis of metals in technological and natural waters, as well as in biological tissues.

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Conflict of interest

The authors declare that they have no conflict of interest.

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