Optics and Spectroscopy, 2023, Vol. 131, No. 11

00

Mechanisms of quenching of photoluminescence of carbon dots by metal cations

© A.M. Vervald[1], G.N. Chugreeva[1], K.A. Laptinskiy[1], I.I. Vlasov[2], T.A. Dolenko[1]

[1] Moscow State University, Moscow, Russia
[2] Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russia
E-mail: alexey.vervald@physics.msu.ru

Received May 12, 2023
Revised July 21, 2023
Accepted October 30, 2023.

The sensitivity of photoluminescence of carbon dots (CDs) to the presence of ions in the environment opens up prospects for creating optical nanosensors for heavy metal cations based on CDs, which requires knowledge of the mechanisms of the influence of ions on the photoluminescence characteristics of these nanoparticles. In this paper, for the CDs of hydrothermal synthesis the mechanisms of the quenching of their photoluminescence by five metal cations: Fe^{3+}, Cr^{3+}, Co^{2+}, Pb^{2+}, Mg^{2+}, were determined. It was found that for all ions a dynamic mechanism of quenching of photoluminescence of CDs makes a great contribution.

Keywords: photoluminescence, carbon dots, metal ions, quenching mechanisms, nanosensor.

DOI: 10.61011/EOS.2023.11.58035.5122-23

Carbon dots (CD) represent a wide class of zero-dimensional carbon nanomaterials, combining nanoparticles of different structures, compositions, synthesis methods and, as a consequence, having different properties [1,2]. Thus, the photoluminescence spectrum (PL) of CD can occupy the range from UV to IR [2], and the PL quantum yield ranges from fractions of a percent to 90% [2] . Photoluminescence of CD can originate from the carbon core of nanoparticles or be caused by local surface states [3]. The surface PL of nanoparticles is significantly affected by the environment: pH value [4], temperature [5], interactions with ions and molecules in the medium [6]. Based on this influence, sensors of environmental parameters of the CD, including metal ions (Me), which quenchh the PL of the CD, are being developed [6,7]. It is obvious that for the effective development of such nanosensors it is required to know the mechanisms of the influence of the environment on the PL of CD.

The most accepted classification of PL quenching mechanisms consists in the division of molecular mechanisms: dynamic (including FRET, PET, DET) and static types of quenching [8]. The static quenching mechanism is due to the fact that some of the phosphors of nanoparticles form non-photoluminescent complexes with quenchers. As a result of dynamic quenching, for example, collisions of CD with solution particles, a new channel for the decay of the excited state of phosphors appears. In multicomponent solutions, the internal filter effect can play a significant role, i.e. (re)absorption of exciting light and PL nanoparticles by solution components [8]. The mechanisms of formation and quenching of PL of specific CD, even within the class of CD of hydrothermal synthesis, depend on many factors: quenching by the same ion Fe^{3+} can occur due to both dynamic [9] and static [10] mechanisms. Therefore, it is required to study the mechanisms of the influence of environmental parameters on the FL of CD for each specific task.

In this work, the mechanisms of photoluminescence of CD quenching of hydrothermal synthesis by metal cations Fe^{3+}, Cr^{3+}, Co^{2+}, Pb^{2+}, Mg^{2+} in water, some of the most common in process and waste waters, were studied [11]. CD were synthesized from citric acid and ethylenediamine (1:1) by hydrothermal synthesis (for a detailed description of the synthesis and characterization of CD, see [12]). The objects of the study were solutions of CD with the addition of nitrates of the above cations in redistilled deionized water. The concentration of CD in all the experiments was equal to 0.005 g/l, the concentration of Me cations varied from 0 to 1 mM with steps of 0.1 mM.

The optical absorption spectra of all CD solutions with Me salts were obtained on a Shimadzu UV-1800 spectrophotometer, and PL spectra on a Shimadzu RF-6000 spectrofluorimeter. The optimal excitation for the PL of the studied CD is radiation at a wavelength of 345 nm (Fig. 1, *a*). As a result of analysis of the PL spectra, it was found that the interaction of CD with all studied Me cations leads to a decrease in the PL intensity with increasing Me concentration (Fig. 1, *b*). It should be noted the peculiarity of the ions Fe^{3+}, which have significant absorption in the PL CD 400-550 nm region (Fig. 1, *a*). This absorption means that the main mechanism for quenching PL CD by iron ions is the effect of the internal filter — (re)absorption of incident light and PL by solutions of metal salts [8].

Other mechanisms of PL CD quenching by Me ions was analyzed on the basis of PL spectra corrected for absorption using the following formula [13]:

$$I_{corr} = I_0 10^{\left[\frac{\mathrm{Ab}(\lambda_{exc})+\mathrm{Ab}(\lambda_{em})}{2}\right]}, \qquad (1)$$

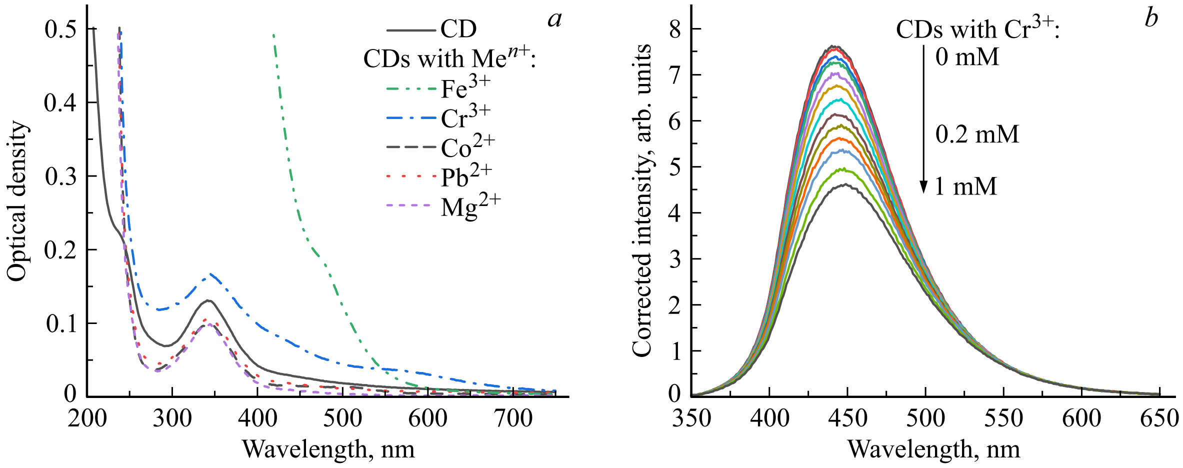

Figure 1. (*a*) Optical absorption spectra of solutions of CD with salts of various Me (Me concentration 1 mM) and (*b*) photoluminescence spectra of solutions of CD with Cr^{3+}salts with concentration in the range 0–1 mM, adjusted for absorption.

where I_0 and I_{corr} — PL signal intensity observed before and after correction for absorbance; Ab — absorbance of the solution; λ_{exc} and λ_{em} —excitation and emission wavelengths. See Fig. 1 for the examples of the obtained spectra, *b*.

To study the mechanisms of quenching of PL CD by Me ions, the Stern-Volmer theory (SV) was used: the dependences of the change in the integral intensity of PL CD F_0/F on the concentration of quenchers [Q] were plotted, where F_0 and F — intensity PL in the absence and presence of a quencher with concentration [Q], respectively (Fig. 2). It turned out that the obtained dependences are either well approximated by a straight line, or are nonlinear and deviate towards the abscissa axis. Linear dependence in coordinates SV

$$F_0/F = 1 + K_{SV}[\mathrm{Q}] \tag{2}$$

corresponds to the presence of one of two possible mechanisms: static or dynamic; K_{SV} — SV constant of the corresponding process. The static quenching mechanism implies the formation of non-luminous complexes with quenchers by some of the phosphors, while dynamic quenching implies the emergence of a new collision channel for the disintegration of the excited state of the phosphors. The resulting nonlinearity of the dependence in the SV coordinates and its deviation towards the abscissa is explained by the inaccessibility of a fraction of phosphors for quenching. In the case where only the fraction f_1 of phosphors is subject to quenching, dependence (2) is converted to the form

$$F_0/F = (1 + K_{SV}[\mathrm{Q}])/(1 + (1 - f_1)K_{SV}[\mathrm{Q}]). \tag{3}$$

Figure 2 and the table show the results of approximation of the $F_0/F([\mathrm{Q}])$ dependences for all salts by function (3).

The analysis of the obtained dependences SV and their approximations shows that the degree of quenching by different ions PL CD can differ by three orders of magnitude (Table). The accuracy of the approximation depends directly on the degree of PL quenching: against the background of weak quenching by the, Co^{2+}, Pb^{2+}, and especially Mg^{2+} ions, the experimental measurement error is large, which prevents the unambiguous determination of the approximation parameters. For the Fe^{3+} and Cr^{3+} ions, which significantly quench the photoluminescence, there is a high quality of approximation of the SV dependences by equation (3).

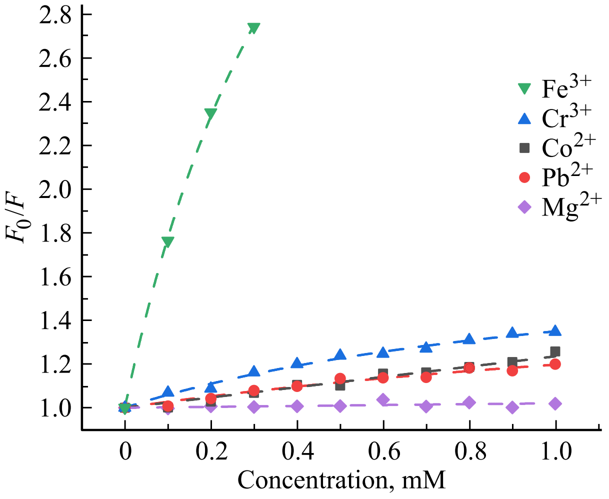

Figure 2. $F_0/F([\mathrm{Q}])$ SV dependences for all the cations under study. The dashed line shows the results of approximation of the dependences by equation (3).

The quality of the obtained approximations suggests that the quenching of CD by Me cations occurs mainly due to one of two mechanisms — dynamic or static. To understand which of these two mechanisms is responsible for the observed PL quenching, the FL CD lifetimes were measured. In the absence and presence of Me cations with a concentration of 1 mM in solutions, the lifetime of the main

Results of approximation of the dependences $F_0/F([\mathrm{Q}])$ of quenching PL CD by salts of different cations by the function (3)

Ion Me^{n+}	K_{SV}, M^{-1}	Quenching fraction of phosphors f_1, %	Coefficient determinationR^2
Fe^{3+}	11300 ± 500	82 ± 1	0.99967
Cr^{3+}	1500 ± 200	43 ± 3	0.99113
Co^{2+}	230 ± 200	100 ± 70	0.97273
Pb^{2+}	730 ± 30	39 ± 9	0.97084
Mg^{2+}	21 ± 14	95 ± 61	0.23144

component of the PL intensity varies from 3.6 ns to 3.3, 2.9, 3.0, 3.0 and 3.5 ns for Fe^{3+}, Cr^{3+}, Co^{2+}, Pb^{2+}, Mg^{2+} respectively. The change in lifetimes means a dynamic mechanism of FL CD quenching.

Thus, in this work it was found that all the metal ions studied, within the limits of their concentration 0–1 mM, quench photoluminescence of CD of hydrothermal synthesis. Meanwhile, the degree of this quenching is different and decreases in the series: $\mathrm{Fe}^{3+} \gg \mathrm{Cr}^{3+} > \mathrm{Co}^{2+} \sim \mathrm{Pb}^{2+} > \mathrm{Mg}^{2+}$ in 10^3 times. For all the ions, a dynamic PL quenching mechanism has been determined. For Fe^{3+}, a significant contribution to the quenching of nanoparticle PL is made by the internal filter effect. In this case, some of the phosphors turn out to be inaccessible for dynamic quenching.

Funding

The study was supported by a grant from the Russian Science Foundation No 22-12-00138, https://rscf.ru/project/22-12-00138/ (AMV, KAL, IIV, TAD). This work of CFG was supported by Theoretical Physics and Mathematics Advancement Foundation „BASIS“ (project № 22-2-1-75-1).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J. Liu, R. Li, B. Yang. ACS Cent. Sci., **6** (12), 2179 (2020). DOI: 10.1021/acscentsci.0c01306

[2] N.A.S. Omar, Y.W. Fen, R. Irmawati, H.S. Hashim, N.S.M. Ramdzan, N.I.M. Fauzi. Nanomaterials, **12** (14), 2365 (2022). DOI: 10.3390/nano12142365

[3] L. Ai, Y. Yang, B. Wang, J. Chang, Z. Tang, B. Yang, S. Lu. Sci. Bull., **66**, 839 (2021). DOI: 10.1016/j.scib.2020.12.015

[4] M.Yu. Khmeleva, K.A. Laptinsky, P.S. Kasyanova, A.E. Tomskaya, T.A. Dolenko. Opt. i spektr., **130** (6), 882 (2022) (in Russian). DOI: 10.21883/OS.2022.06.52630.36-22
[M.Yu. Khmeleva, K.A. Laptinskiy, P.S. Kasyanova, A.E. Tomskaya, T.A. Dolenko. Opt. Spectrosc., **130** (6), 697 (2022). DOI: 10.21883/EOS.2022.06.54706.36-22].

[5] Z. Mua, J. Huaa, Y. Yanga. Spectrochim. Acta A Mol. Biomol. Spectrosc., **224**, 117444 (2020). DOI: 10.1016/j.saa.2019.117444

[6] O.E. Sarmanova, K.A. Laptinskiy, S.A. Burikov, G.N. Chugreeva, T.A. Dolenko. Spectrochim. Acta A, **286**, 122003 (2023). DOI: 10.1016/j.saa.2022.122003

[7] M. Batool, H.M. Junaid, S. Tabassum, F. Kanwal, K. Abid, Z. Fatima, A.T. Shah. Crit. Rev. Anal. Chem., **52**, 756 (2020). DOI: 10.1080/10408347.2020.1824117

[8] F. Noun, E.A. Jury, R. Naccache. Sensors, **21** (4), 1391 (2021). DOI: 10.3390/s21041391

[9] W. Wang, J. Peng, F. Li, B. Su, X. Chen, X. Chen. Microchim. Acta, **186**, 32 (2019). DOI: 10.1007/s00604-018-3140-8

[10] N. Hashemi, M.H. Mousazadeh. Opt. Mater., **121**, 111515 (2021). DOI: 10.1016/j.optmat.2021.111515

[11] L.F. Dolina. *Sovremennaya tekhnika i tekhnologii dlya ochistki stochnykh vod ot soley tyazhelykh metallov* (Kontinent, Dnepropetrovsk, 2008), 227 s. (in Russian).

[12] K. Laptinskiy, M. Khmeleva, A. Vervald, S. Burikov, T. Dolenko. Appl. Sci., **12** (23), 12006 (2022). DOI: 10.3390/app122312006

[13] J.R. Lakowicz. *Principles of Fluorescence Spectroscopy*, 3rd ed. (Springer, NY., 2010), p. 56.

Translated by E.Potapova