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SPECTROSCOPIC MANIFESTATIONS OF RNA PHOTOSTABILIZATION BY CERIUM DIOXIDE NANOPARTICLES

A spectroscopic study of the influence of cerium dioxide (CeO_2) nanoparticles on the photostability of ribonucleic acid (RNA) in aqueous solution is presented. Optical absorption, fluorescence, and phosphorescence spectroscopy were employed to analyze the interaction of RNA with CeO_2 nanoparticles approximately 6 nm in size. It has been shown that the presence of CeO_2 nanoparticles does not significantly alter the electronic structure of RNA, while it markedly affects the relaxation pathways of excited electronic states. A decrease in the fluorescence intensity accompanied by an increase in the phosphorescence intensity was observed for RNA in the presence of CeO_2 nanoparticles, indicating a redistribution of radiative relaxation channels involving triplet states. Photodegradation studies revealed a reduced degradation rate of RNA upon the addition of CeO_2 nanoparticles, without changes in the shape of the absorption spectra. The obtained results demonstrate a photostabilizing effect of cerium dioxide nanoparticles, which can be attributed to the suppression of radical photochemical processes and a reduction in the efficiency of radical degradation pathways.

Keywords: CeO_2 nanoparticles, RNA, optical spectroscopy, fluorescence, phosphorescence, photostability, excited states.

1. Introduction

Cerium dioxide (CeO_2) nanoparticles have attracted considerable attention in modern condensed matter physics and materials science due to their combination of size-dependent optical properties, the presence of mixed valence states Ce^{3+}/Ce^{4+}, and a high concentration of structural defects, in particular, oxygen vacancies. It is these features that determine the ability of CeO_2 nanoparticles to participate in electron-exchange processes and substantially influence the course of photochemical reactions in complex molecular systems [1–3].

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In the last decade and a half, a significant number of works have been devoted to the study of antioxidant and photoprotective properties of CeO_2 nanoparticles, mainly in the context of biomedical and biophysical applications [4–6]. It has been shown that nanosized CeO_2 can reduce the rate of photodegradation processes in biological environments, which is usually associated with the inhibition of radical photochemical reactions and the deactivation of photochemically active forms. At the same time, most of these studies are focused on the final biological effects, while the physical mechanisms of the interaction of CeO_2 nanoparticles with biomacromolecules remain poorly understood.

Nucleic acids are among the biopolymers most sensitive to ultraviolet and visible radiation, since photoexcitation of their chromophore fragments can lead to the initiation of radical degradation channels. In this context, studies aimed at elucidating how external nanostructured components affect the relaxation processes of excited electronic states of nucleic acids

and the efficiency of photochemical degradation channels are of particular interest [7].

Optical spectroscopy of absorption, fluorescence, and phosphorescence is a powerful tool for studying such processes because it makes it possible to directly analyze changes of the electronic structure and the redistribution among radiative and non-radiative relaxation channels. In particular, an analysis of the ratio between the fluorescence and phosphorescence components of the emission enables conclusions to be drawn about the participation of triplet states and the efficiency of radical photochemical processes [8–14].

Despite the intensive development of research on CeO_2 nanoparticles, spectroscopic works aimed at studying their influence on the photostability of nucleic acids at the molecular level remain isolated. In particular, the issues of the redistribution among the relaxation channels of excited states and the reduction in the efficiency of radical photochemical processes in the presence of CeO_2 nanoparticles are insufficiently studied.

In this regard, the aim of this work is to establish the effect of CeO_2 nanoparticles on the photostability of ribonucleic acid in aqueous solution using the methods of optical spectroscopy of absorption, fluorescence, and phosphorescence.

2. Experimental Technique

We used the solutions of yeast ribonucleic acid (RNA), CeO_2 nanoparticles, and RNA systems with CeO_2 nanoparticles in the citrate buffer (the concentration $C = 3 \times 10^{-6}$ M, pH = 6.4). The sol of citrate-stabilized CeO_2 nanoparticles was synthesized by Ph.D., senior research fellow O.B. Shcherbakov as described in Ref. [15] and was kindly provided for this study. Yeast RNA was preliminarily purified by triple phenol deproteinization, precipitated, and repeatedly washed with ethanol [16]. RNA systems with CeO_2 nanoparticles were prepared by directly mixing the RNA solution and the nanoparticle sol in a ratio of 1:10.

Optical absorption spectra were registered on a Cary 60 UV-Vis spectrophotometer (Agilent, USA) at room temperature. The absorption spectra of the solutions were registered in standard quartz cuvettes 1 cm in thickness and width (a transmission interval of 170÷1000 nm). Luminescence spectra (fluorescence and phosphorescence) were recorded on a Cary Eclipse fluorescence spectrophotometer (Varian, Australia) at the temperature $T = 77$ K within a wide range of excitation wavelengths ($\lambda_{\text{sb}} = 250$–320 nm). A cuvette with a sample was shock-frozen in liquid nitrogen and placed into an Optistat DN cryostat (Oxford Instruments, United Kingdom), which was already filled with liquid nitrogen. The temperature $T = 77$ K was controlled by means of an Intelligent Temperature Controller ITC503S (Oxford Instruments). The determination errors for the wavelengths and the optical density were standard for the Cary 60 UV-Vis spectrophotometer: the spectral width of the slit was 1.5 nm, the determination accuracy of the wavelength was 0.5 nm, and the repeatability of the optical density measurements was 3%. Similar errors were obtained for the Cary Eclipse spectrophotometer: the spectral width of the slit was 5 nm (for fluorescence) and 10 nm (for phosphorescence), and the determination accuracy of the wavelength was 1.5 nm.

To study the photostability, the samples of examined substances were irradiated with a DRT-1000 mercury lamp. Then, the corresponding absorption spectra were registered from time to time. The obtained numerical data were processed using the application software package Microcal Origin.

3. Results and Their Discussion

3.1. Absorption spectra

The ultraviolet absorption spectra of CeO_2 nanoparticles are characterized by a broad band in an interval of 200–400 nm (Fig. 1, curve *1*). Within this band, two overlapping peaks are observed. The short-wave component (≈220–260 nm) corresponds to transitions associated with Ce^{3+} states, whereas the long-wave part of the spectrum (≈290–400 nm) is associated with the presence of Ce^{4+} ions. A relatively large value of the optical density of the short-wave band testifies to a substantial fraction of Ce^{3+} surface states, which is typical for CeO_2 nanoparticles with sizes of the order of several nanometers [17].

The absorption spectrum of RNA (Fig. 1, curve *2*) demonstrates a characteristic maximum (at $\lambda = 260$ nm) related to $\pi \rightarrow \pi^*$ ($S_0 \rightarrow S_1$) transitions of nucleotide bases [8, 9]. A small peak at $\lambda = 320$ nm may be associated with the presence of a certain number of complexes located directly between the nucleotides (for example, in a single-stranded frag-

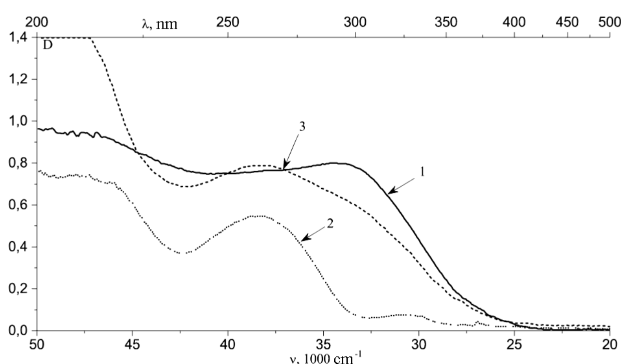

Fig. 1. Optical absorption spectra of the solutions of CeO_2 nanoparticles (*1*), RNA (*2*), and RNA + CeO_2 system (*3*) in the citrate buffer (concentration $C = 3 \times 10^{-6}$ M). $T = 293$ K

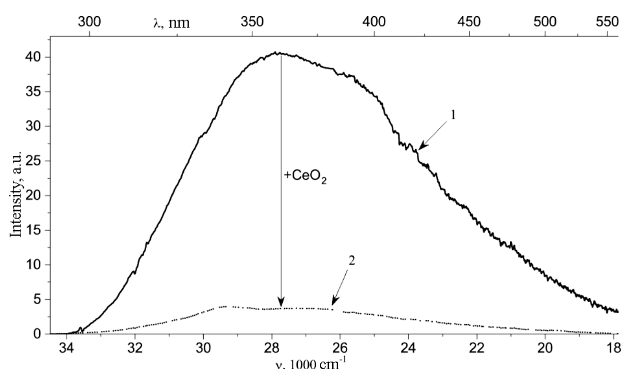

Fig. 2. Fluorescence spectra of the solutions of RNA (*1*) and RNA + CeO_2 system (*2*) in the citrate buffer (concentration $C = 3 \times 10^{-6}$ M). $T = 77$ K, $\lambda_{exc} = 300$ nm

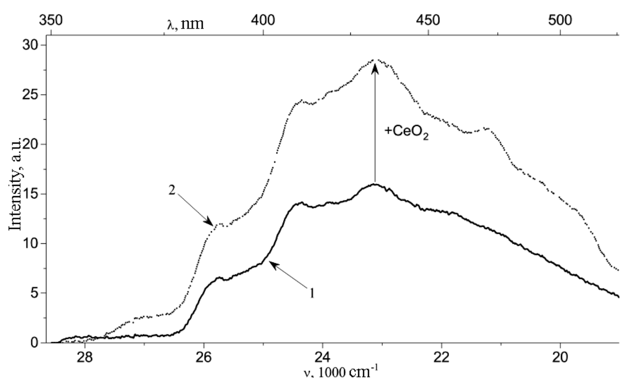

Fig. 3. Phosphorescence spectra of the solutions of RNA (*1*) and RNA + CeO_2 system (*2*) in the citrate buffer. $T = 77$ K, $\lambda_{exc} = 300$ nm

ment of telomeric DNA [10]). When CeO_2 nanoparticles are added, the longest-wavelength band in the absorption spectrum of the RNA + CeO_2 system (Fig. 1, curve *3*) practically coincides with the sum of the bands in the absorption spectra of RNA and CeO_2. Such a behavior testifies to a weak but reproducible interaction of RNA with the surface of CeO_2 nanoparticles, without a considerable rearrangement of the electronic structure of the macromolecule. A slight redistribution of the electron density (optical electrons) from Ce atoms to atoms constituting the π-electron systems of nucleotides is possible. As a result, the optical properties of the RNA + CeO_2 complex depend mainly on the π-electron systems of nucleotides.

3.2. Luminescence properties

Luminescence studies (fluorescence and phosphorescence) were carried out in a wide interval of excitation wavelengths (λ_{exc} = 250–320 nm). In this spectral interval, the positions of the main fluorescence and phosphorescence bands of the RNA and RNA + CeO_2 systems were practically independent of the excitation wavelength. These studies have shown that the addition of CeO_2 nanoparticles substantially affects the radiative characteristics of RNA. In the presence of CeO_2, a decrease in the fluorescence intensity (Fig. 2) and a simultaneous increase in the phosphorescence intensity (Fig. 3) are observed, but the shapes of the corresponding spectra practically do not change.

The preservation of the spectral shape means that the local electronic structure in the chromophore fragments of the RNA macromolecule remains unchanged so that the observed effects are mainly associated with the redistribution among the relaxation channels of excited states. As in the case of pure RNA, the fluorescence emission of the RNA + CeO_2 system is close to a linear combination of guanine and cytidine chromophores (which have the lowest energy values of their singlet states), and the phosphorescence emission is determined by the contribution of adenine fragments [8, 9]. This conclusion is consistent with the "classical" ideas about the dominant role of adenine in triplet processes in nucleic acids [11, 12] (the adenine link in RNA is the most stable to photodegradation in comparison with other nucleotides [9]).

Thus, the presence of CeO_2 nanoparticles favors a reduction in the fluorescence channel efficiency and a growth in the phosphorescence quantum yield, which can be interpreted as an enhancement of the role of triplet states in the relaxation of excited electronic states of RNA.

3.3. Photostability of RNA

The photostability of RNA solutions, CeO_2 nanoparticles, and RNA + CeO_2 systems was studied by irradiating these samples with high-intensity ultraviolet and visible radiation from a DRT-1000 mercury lamp and registering the absorption spectra on the Cary 60 UV-Vis spectrophotometer. For pure RNA, a monotonic decrease in the optical density at the maximum of the longest-wavelength band in the absorption spectrum (associated with the $S_0 \rightarrow S_1$ transition) as the irradiation time increased was observed, which corresponds to the macromolecular photodegradation. The optical density of the RNA absorption spectrum decreases by about 60% after 100 min of irradiation. Similar data were previously obtained by us for DNA and RNA samples of various origins, as well as for synthetic polynucleotides [9, 13, 14].

In the presence of CeO_2 nanoparticles, the rate of the optical density decrease is substantially lower (by about 19%), which testifies to a higher RNA photostability. At the same time, the shapes of the absorption spectra of both pure RNA and RNA + CeO_2 systems remain unchanged during photodegradation, which points to the absence of selective photochemical damage to separate nucleotide fragments and is consistent with the assumption of the suppression of radical photochemical processes, whereas degradation occurs relatively uniformly over the macromolecule.

Separate experiments showed that CeO_2 nanoparticles themselves undergo photodegradation faster than the RNA and RNA + CeO_2 systems: after about 20 min of irradiation, the absorption spectrum of CeO_2 changed considerably. Such a behavior may evidence the "sacrificial" role of the nanoparticles in photochemical processes and reducing the efficiency of RNA degradation through radical channels.

Having plotted the relative dependences of the optical density at the absorption maximum (normalized to the corresponding optical density values for the initial/undamaged samples) on the irradiation time for the samples of pure RNA, RNA + CeO_2 complex, and CeO_2 nanoparticles (Fig. 4), one can clearly see that the addition of CeO_2 nanoparticles reduces the rate of RNA degradation by about 19%.

Thus, the interaction of CeO_2 nanoparticles with the RNA macromolecule reduces the rate of RNA photodegradation. This is in contrast to, for example, platinum-containing drugs, which, when incorporated into the biomacromolecule chain, increase the photodegradation rate of these biomacromolecules and are used for anticancer chemotherapy and photodynamic therapy [13]. The reduction of the photodegradation rate provides a basis for the application of CeO_2 nanoparticles as a photostabilizer in biological systems and for the creation of appropriate drugs.

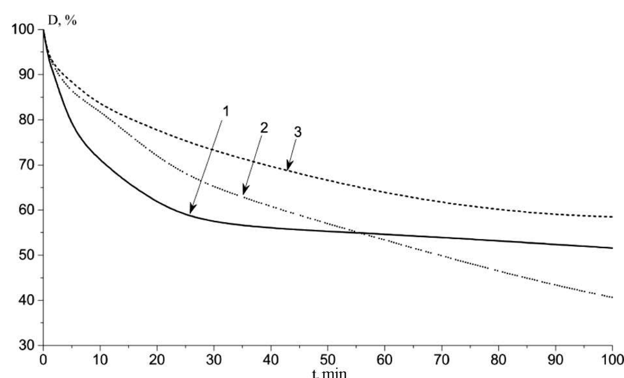

Fig. 4. Time dependences of the ratio (in %) between the optical density of CeO_2 nanoparticles (*1*), RNA (*2*), and RNA + CeO_2 system (*3*) at the maximum of the absorption spectrum and the corresponding value for the initial/intact sample

3.4. Discussion of mechanisms

The obtained spectroscopic data testify that the photostabilizing effect of CeO_2 nanoparticles on RNA is not associated with a change in the electronic structure of the macromolecule. Instead, the main role is played by a redistribution among the relaxation channels of excited states and the suppression of radical photochemical processes.

The growth of the phosphorescence intensity together with a simultaneous reduction of the fluorescence intensity points to a more active participation of triplet states in the relaxation of excited electronic states of the RNA macromolecule (a similar situation was observed by us for molecular complexes with the fragments of the DNA macromolecule of various lengths [13,18]). As a result, the probability of triggering radical photochemical reactions may decrease, which leads to macromolecule degradation.

Thus, CeO_2 nanoparticles can be considered as an effective photostabilizing component, which reduces the efficiency of radical channels of RNA photodegra-

dation. This statement is confirmed by both luminescence and absorption spectroscopic data.

4. Conclusions

1. Using optical absorption, fluorescence, and phosphorescence spectroscopy methods, the influence of cerium dioxide (CeO_2) nanoparticles on the photostability of ribonucleic acid in an aqueous medium has been studied. It was shown that CeO_2 nanoparticles do not substantially change the electronic structure of RNA, which is confirmed by the preservation of the shape of absorption spectra.

2. It was found that the presence of CeO_2 nanoparticles significantly affects the radiative properties of RNA: it decreases the fluorescence intensity and simultaneously increases the phosphorescence intensity. This testifies to a redistribution among the relaxation channels of excited electronic states, with an increase of the role of triplet states.

3. Photodegradation studies showed that CeO_2 nanoparticles enhance the photostability of RNA by reducing the rate of degradation under the action of ultraviolet and visible radiation. At the same time, the absence of changes in the shape of the absorption spectra of RNA points to the suppression of radical photochemical processes, without selective damage to separate chromophore fragments.

4. It was found that CeO_2 nanoparticles undergo photochemical changes faster than RNA, which allows them to be considered as a photostabilizing component that reduces the efficiency of radical channels of macromolecule photodegradation.

5. The obtained results demonstrate the informative value of spectroscopic methods for studying the mechanisms of interaction of nanomaterials with biomacromolecules and confirm the promising use of CeO_2 nanoparticles as photostabilizing additives in systems sensitive to optical radiation.

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СПЕКТРОСКОПІЧНІ
ПРОЯВИ ФОТОСТАБІЛІЗАЦІЇ РНК
НАНОЧАСТИНКАМИ ДІОКСИДУ ЦЕРІЮ

У роботі представлено спектроскопічне дослідження впливу наночастинок діоксиду церію (CeO_2) на фотостабільність рибонуклеїнової кислоти (РНК) у водному розчині. Методами оптичної спектроскопії поглинання, флуоресценції й фосфоресценції досліджено особливості взаємодії РНК з наночастинками CeO_2 розміром близько 6 нм. Показано, що присутність наночастинок CeO_2 не призводить до суттєвих змін електронної структури РНК, проте істотно впливає на процеси релаксації збуджених електронних станів. Виявлено зменшення інтенсивності флуоресценції й одночасне зростання інтенсивності фосфоресценції РНК за наявності наночастинок CeO_2, що свідчить про перерозподіл випромінювальних каналів із залученням триплетних станів. Дослідження фотодеградації показали, що додавання наночастинок CeO_2 призводить до зменшення швидкості деградації РНК без зміни форми спектрів поглинання. Отримані результати вказують на фотостабілізуючу роль наночастинок CeO_2, пов'язану з пригніченням радикальних фотохімічних процесів і зменшенням ефективності радикальних каналів деградації.

Ключові слова: наночастинки CeO_2, РНК, оптична спектроскопія, флуоресценція, фосфоресценція, фотостабільність, збуджені стани.