Characterization of size and morphological composition of ablated nanoparticles of cerium dioxide after ultrasonic dispersion and centrifugation in aqueous solution

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Abstract. The paper investigates the size and morphological composition of ablated cerium dioxide nanoparticles after ultrasonic dispersion at centrifugation speeds from 800 to 13400 rpm. A nanodispersed solution of cerium dioxide was deposited onto silicon substrates by the drop method. To characterize the size and morphological composition of cerium dioxide nanoparticles, methods of scanning electron and atomic microscopy were used, and X-ray phase analysis was performed. It was found that ablated cerium dioxide particles in an aqueous solution agglomerated and without centrifugation their average size was 162 nm, after centrifugation their average size varied from 86 nm to 142.5 nm. X-ray phase analysis showed that with an increase in the centrifuge speed, the size of the coherent scattering region decreases, which affects the effectiveness of antioxidant properties, for example, in the Fenton reaction.

1. Introduction

Studies of the physicochemical properties of cerium dioxide are of interest from theoretical and practical points of view. Cerium dioxide has a wide range of applications in various fields, for example, as a catalyst in the afterburning of automobile engine exhaust, as an element of solid-state energy, in ceramics in the manufacture of photosensitive glasses for stabilizing color as the main component of polyrite, a powder for polishing optical parts, such as optical lenses [1]. But of particular relevance is the study of nanocrystalline cerium dioxide due to the change in its physicochemical properties during the transition to the nanoscale state.

One of the most important properties of cerium dioxide is its antioxidant activity, which determines the prospects for its use in biomedical direction. In works [2-4] it is indicated that nanocrystalline cerium dioxide exhibits antioxidant and antitumor properties; other studies [5, 6] note the ability of cerium dioxide nanoparticles to function as antioxidants, mimicking the behavior of a number of enzymes - catalase, superoxide dismutase, which indicates the possibility of its use in medicine. The photocatalytic properties of cerium dioxide nanoparticles, which are observed in various nanosized oxides, for example, in nanoparticles of copper (II) oxide are of great importance [7]. Photocatalytic properties can be used for various medical purposes [1].

The appearance of oxygen nonstoichiometry on the surface of cerium dioxide nanoparticles, where Ce$^{4+}$ ions are reduced to the Ce$^{3+}$ state upon the transition of cerium dioxide to the nanocrystalline
state is very interesting. It is assumed that oxygen nonstoichiometry determines the unique activity of cerium dioxide nanoparticles [8-10].

The method of obtaining nanoparticles of cerium dioxide is the method of laser ablation. The advantage of this method is the possibility of obtaining ablated nanoparticles with surface structural defects such as oxygen vacancies, which is the reason for an increase in the efficiency of their antioxidant properties [11-17].

The aim of this work is to obtain nanodispersed aqueous systems based on ablated cerium dioxide particles by ultrasonic dispersion and their subsequent centrifugation at different centrifuge speeds with an average particle size or agglomerates consisting of weakly bound cerium dioxide nanoparticles not exceeding 90 nm. The novelty in this work lies in the application of the centrifugation process to nanodispersed solutions of cerium dioxide and the study of the effect of this process on their antioxidant properties. In the solution the content of cerium dioxide particles decreases, but there is an increase in the proportion of nanosized particles, which are more active than particles with larger sizes due to an increase in the number of surface structural defects in nanoparticles.

2. Experimental materials and methods

In the experiments, we used reagent grade cerium dioxide in the form of a powder compressed into cylindrical tablets. Under the action of focused laser radiation, cerium dioxide was explosively sprayed, forming a flow of ablated particles. A coating of ablated nanoparticles was formed on a single-crystal silicon substrate located at a distance of 10–15 mm. A pulsed i terbium fiber laser was used as a source of laser radiation to obtain CeO\textsubscript{2} nanoparticles.

Figure 1 shows an experimental scheme for obtaining CeO\textsubscript{2} nanoparticles by laser ablation.

![Figure 1. Experimental scheme of the formation of layers of ablated CeO\textsubscript{2} particles on a silicon substrate.](image)

In this diagram, the curly arrow indicates pulsed laser radiation directed at the CeO\textsubscript{2} target, which is represented by a rectangle in the diagram. The symbol ↑ denotes the fluxes of ablated particles falling on a silicon substrate 1×0.5 cm in size (elongated rectangle), where a layer of CeO\textsubscript{2} nanoparticles is formed. The black rectangle marks the stand on which the target itself is located.

3. Results and discussion

A JEOL 6610LV scanning electron microscope was used to study the size and morphology of centrifuged ablated cerium dioxide particles. Sample preparation was carried out in the following way: after obtaining particles by laser ablation they were dispersed in an aqueous solution for at least 40 minutes and then they were centrifuged in a microcentrifuge, the speed range of which was from 5000 to 13400 rpm with a fixed time of 5 minutes. After centrifugation, 80% solutions of their total volume were taken from 2 ml microtubes with a syringe. The obtained samples of a dispersed solution of cerium dioxide were applied dropwise onto silicon substrates in the amount of one drop per each substrate. After preparation of the samples, studies were carried out using a scanning electron microscope. In the images of scanning electron microscopy, objects that are limited, probably, by a water film, inside which there are particles of cerium dioxide are observed (figure 2). The reason for the appearance of such structures is the agglomeration of cerium dioxide particles in an aqueous solution.
Figure 2. SEM images of agglomerates of ablated CeO$_2$ particles a - 0 rpm; b - 800 rpm; c - 2000 rpm; d - 5000 rpm; e - 10000 rpm; f - 13400 rpm.

The obtained SEM images were used to construct histograms of agglomerate size distributions for each centrifuge speed (figure 3).

The presented histograms show a decrease in the size of agglomerates in the volume of a microtube equal to 1.6 ml with an increase in the centrifuge speed, which shows the efficiency of the centrifugation process in obtaining agglomerates or particles with sizes of the order of 20-180 nm.
Figure 3. Granulometry of agglomerates of ablated CeO$_2$ particles according to SEM images a - 0 rpm; b - 800 rpm; c - 2000 rpm; d - 5000 rpm; e - 10000 rpm; f - 13400 rpm.

Analysis of the size and morphology of cerium dioxide nanoparticles using SEM and AFM microscopy found that ablated cerium dioxide particles in an aqueous solution agglomerated and without centrifugation their average size was 162 nm, after centrifugation at a speed of 13400 rpm their average size was 86 nm; 10000 rpm – 107 nm; 5000 rpm – 134 nm, 2000 rpm – 141.6 nm, 800 rpm – 142.5 nm.

An atomic force microscope was used to study the size and morphology of centrifuged ablated cerium dioxide particles. Sample preparation was carried out in the following way: after obtaining particles by laser ablation they were dispersed in an aqueous solution for at least 40 minutes and then they were centrifuged in a microcentrifuge, the speed range of which was from 5000 to 13400 rpm with a fixed time of 5 minutes. After centrifugation, 80% solutions of their total volume were taken from 2 ml microtubes with a syringe. The obtained samples of a dispersed solution of cerium dioxide were applied dropwise onto silicon substrates in the amount of one drop per each substrate. On an
electric furnace at a temperature of 120°C, these droplets evaporated. After preparation of the samples, studies were carried out using an atomic force microscope (figure 4).

![AFM images and profilograms of dispersed ablated agglomerates of cerium dioxide particles at centrifugation speeds a - 0 rpm; b - 5000 rpm; c - 10000 rpm; d - 13400 rpm.](image)

**Figure 4.** AFM images and profilograms of dispersed ablated agglomerates of cerium dioxide particles at centrifugation speeds a - 0 rpm; b - 5000 rpm; c - 10000 rpm; d - 13400 rpm.

On the profilograms, it is observed that the limiting values of particles decrease in the volume of a microtube equal to 1.6 ml with an increase in the centrifugation speed. During the analysis, it was found that the ablated particles of cerium dioxide in an aqueous solution agglomerated.
The sizes and morphology of ablated cerium dioxide nanoparticles were studied on an EMMA X-ray powder diffractometer with a thermal chamber up to 1600°C. Sample preparation was carried out in the following way: cerium dioxide sprayed onto silicon wafers was subjected to dispersion in an ultrasonic bath for at least 40 minutes. Subsequently, dispersed CeO₂ solutions were centrifuged in a microcentrifuge with a constant time of 5 minutes at various speeds ranging from 800 to 13400 rpm with a volume of at least 50 ml. After centrifugation, 80% solutions of their total volume were taken from 2 ml microtubes with a syringe. Then, the resulting solutions were applied dropwise onto silicon wafers, which were installed on a furnace with a heating temperature of 120°C for accelerated evaporation of sample droplets. The drip process lasted an average of 12 hours for samples that were centrifuged from 800 to 5000 rpm and 26 hours for samples centrifuged at 10000 and 13400 rpm. After preparing the samples together with a non-centrifuged sample of a dispersed solution of cerium dioxide, their X-ray phase analysis was carried out (figure 5).

![X-ray diffraction patterns from ablated cerium dioxide particles centrifuged at various speeds from 800 to 13400 rpm.](image)

Figure 5. X-ray diffraction patterns from ablated cerium dioxide particles centrifuged at various speeds from 800 to 13400 rpm.

The measurements were carried out in the 2θ range of angles from 25° to 65°. The characteristic peaks of cerium dioxide are at 2θ = 28.55, 33.08, 47.49, 56.35, 59.09. The data on characteristic peaks were taken from the database of the "Match" program, which is used for processing X-ray diffractograms. On the diffraction patterns, most of the peaks of cerium dioxide can be clearly traced, for example, samples of 800 and 1000 rpm in almost the entire measurement range. However, in the samples of 10000 and 13400 rpm, some of the characteristic peaks are poorly visible in comparison with other samples, for example, the peaks at 2θ = 47.49, 56.35. This is due to the fact that with an increase in the speed of centrifugation, the number of particles with small sizes in the solution increases and the characteristic peaks are "blurred", that is, the width of the reflection at half-height δ increases. At a value of 2θ = 59.09, the peaks for all samples are not visible at all, which indicates an insufficient thickness of the formed film to obtain this characteristic peak.

In addition to the characteristic peaks of cerium dioxide, we can observe characteristic peaks from silicon oxide in the diffractogram. The appearance of characteristic peaks of silicon oxide is associated with the oxidation of the silicon wafer during the drop deposition of samples at a temperature of 120°C.

After analyzing the X-ray diffractogram (figure 5), additional measurements were performed in the 2θ ranges, which contained only peaks from ablated cerium dioxide particles. Figure 6 shows a
piecewise X-ray diffraction pattern that has been measured with increased 2θ steps and exposure to obtain accurate results.

![X-ray diffraction patterns from ablated particles of cerium dioxide, centrifuged at various modes from 800 to 13400 rpm, with peaks of cerium dioxide at 2θ ≈ 28.55; 33.08; 47.49; 56.35.](image)

Subsequently, the diffraction patterns were approximated in the "Origin" software environment by a Gaussian curve according to the formula:

\[ y = y_0 + A \exp \left[ -\frac{(x - x_c)^2}{2w^2} \right]. \] (1)

The diffraction peaks were used to estimate the sizes of the coherent scattering regions using the Scherer equation:

\[ D = \frac{k\lambda}{\delta \cos \theta}, \] (2)

where \( k \) is a constant; \( \delta \) is the width of the diffraction maxima at the half-amplitude level; \( \theta \) is the Bragg scattering angle; \( \lambda \) is the radiation constant = 0.154 nm for Cu on the Kα line.

The values of the center of the peaks \( x_c \) and the variance \( w \), which are necessary for calculating the sizes of the coherent scattering regions, were taken from the approximated diffraction patterns. Using the obtained values according to formula (3), we calculated the width of the diffraction maxima at the half-amplitude level.

\[ \delta = 2w \cdot (\ln 4)^{1/2}, \] (3)

From the values of 2θ diffraction peaks from ablated cerium dioxide particles, their crystallographic planes that cause these peaks are determined. Table 1 shows the results of evaluating the sizes of the coherent scattering regions of cerium dioxide particles for four crystallographic planes.

**Table 1.** Dimensions of coherent scattering regions of cerium dioxide particles centrifuged at speeds from 800 to 13400 rpm for four crystallographic planes.

| {hkl} | 0 (rpm) | 800 (rpm) | 1000 (rpm) | 2000 (rpm) | 5000 (rpm) | 10000 (rpm) | 13400 (rpm) |
|-------|---------|-----------|------------|------------|------------|-------------|-------------|
| 111   | 18.6    | 23.3      | 28.7       | 22.6       | 19.5       | 16.5        | 19.2        |
| 200   | 20.2    | 37.6      | 26.8       | 20.6       |            | 15.8        |             |
| 220   | 11.3    | 16.3      | 25.4       | 19.9       | 19.4       | 16.4        | 18.5        |
| 113   | 23.6    | 17.4      | 24.6       | 23.9       | 27.9       | 16.5        | 12.8        |
A reduced $D$ value in comparison with the granulometric data can be characterized by a violation of the crystallinity of objects. Namely in the particles of cerium dioxide there are structural defects, such as an oxygen vacancy, and as a result of the partial absence of oxygen atoms in the crystal lattice, the values obtained by X-ray diffractometric analysis differ from the values of the particle sizes obtained by other research methods. The study of the phase composition of the ablated particles showed that with an increase in the centrifuge rotation frequency, the dimensions of the coherent scattering region decrease.

4. Conclusions
As a result of the work, it was found that the centrifugation process for nanodispersed solutions of cerium dioxide affects the particle size, namely, with an increase in the centrifugation speed, the dispersion of particles in size is carried out in a smaller range than without centrifugation in a microtube volume equal to 1.6 ml, which in turn increases the effectiveness of various properties of cerium dioxide nanoparticles, including antioxidant ones, as shown by the authors in an earlier work [18].

Acknowledgments
The work was carried out with the financial support of the Russian Foundation for Basic Research within the framework of scientific project № 20-02-00599. This work was also supported by the Ministry of Education and Science of The Russian Federation (g/z 2020 № 0851-2020-0035).

References
[1] Aneggi E, de Leitenburg C, Boaro M, Fornasiero P and Trovarell A 2020 Cerium Oxide (CeO$_2$): Synthesis, Properties and Applications ed S Scirè and L Palmisano (Amsterdam: Elsevier) pp 45–108
[2] Vazirov R A, Sokovnin S Y and Ulitko M 2017 Radiation and Applications 2 139–41
[3] Filippi A et al 2019 RSC Advances 9 11077–81
[4] Eriksson P et al 2018 Scientific Reports 8 6999
[5] Vazirov R A, Sokovnin S Y, Ilves V G, Bazhukova I N, Pizurova N and Kuznetsov M V 2018 J. Phys. Conf. Ser. 1115 032094
[6] Heckert E G, Karakoti A S, Seal S and Self W T 2008 Biomaterials 29 2705–9
[7] Pugachevskii M A, Hein K A, Mamontov V A, Tan M M and Kuzmenko A P 2020 Proceedings of the Southwest State University Series: Engineering and Technologies 10 72–85 [in Russia]
[8] Alexander E B, Olga S P, Vladimir K I and Yuri D T 2010 RSC Advances 12 3531–3
[9] Gunawan C, Lord M S, Lovell E, Wong R J, Jung M S, Oscar D, Mann R and Amal R 2019 ACS Omega 4 9473–9
[10] Singh K RB, Nayak V, Sarkar T and Singh R P 2020 RSC Advances10 27194–214
[11] Abid S A, Taha A A, Ismail R A and Mohsin M H 2020 Environ. Sci. Pollut. R. 27 30479–89
[12] Lapin I N, Shabalina A N and Svetlichnyi V A 2016 Key Eng. Mat. 683 281–7
[13] Yoshihiro T and Fumitaka M 2014 Chem. Phys. Lett. 599 110–5
[14] Trenque I et al 2020 CrystEngComm 22 1725–37
[15] Aung N V, Mamontov V A and Pugachevskii M A 2019 Collection of articles of the X All Russian Scientific and Practical Conference "Nanotechnologies: education, science, innovation" (Kursk: Kursk State University) pp 132–4
[16] Pugachevskii M A 2017 Tech. Phys. Lett. 43 698–700
[17] Pugachevskii M A, Mamontov V A, Aung N V, Chekadanov A S and Kuzmenko A P 2020 Tech. Phys. Lett. 46 1032–5
[18] Pugachevskii M A, Mamontov V A, Kuzmenko A P and Neruchev Yu A 2021 Proceedings of the Southwest State University. Series: Engineering and Technologies 11 61–74 [in Russia]