

CATALYTIC ACTIVITY OF CERIUM OXIDE NANOPARTICLES

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Abstract

Cerium oxide (CeO₂) nanoparticles present an interesting material for various applications in biotechnology and medicine. The mechanism of CeO₂ nanoparticles biological activity is supposed to be related to the presence both Ce³⁺ and Ce⁴⁺ ions on the surface of the nanocrystal. We studied and compared the catalytic activity of CeO₂ nanoparticles synthesized by chemical and physical methods. The cerium oxide was found to demonstrate catalase-like and peroxidase activity. CeO₂ nanoparticles obtained by a chemical method showed more pronounced catalytic properties. In addition, this material catalyzed the decomposition of hydrogen peroxide by the enzyme horseradish peroxidase.

Keywords: Nanoparticles, luminescence, defects, cerium dioxide, catalytic activity, enzymes, catalase

1. INTRODUCTION

Cerium oxide (CeO₂) nanoparticles present a promising object for various applications, including biomedical research [1-3]. The CeO₂ nanoparticles are characterized by a high oxygen non-stoichiometry. The formation of oxygen vacancies leads to the reduction of cerium ions to the Ce³⁺ state on the particle surface. Such property correlates with the catalytic activity of cerium oxide nanoparticles and is probably responsible for their biological activity.

Many studies have reported on the multienzyme activity of cerium oxide nanoparticles, acting like superoxide oxidase [4] catalase [5] and oxidase [6] enzymes. CeO₂ nanoparticles catalyze the reactive oxygen species decomposition such as superoxide radical and hydrogen peroxide. Compared with natural analogues of enzymes, enzyme-like substances based on nanomaterials provide lower cost, the ability to change their catalytic activity and improved stability under harsh conditions. As shown in [7], CeO₂ nanoparticles possess enzyme-like catalytic activity and are stable over a wide range of pH values and temperatures, in contrast the natural enzyme horseradish peroxidase. Moreover, on the surface of nanomaterials there can be a larger number of catalytic centers as compared to natural enzymes, which have only one active center in the molecule [8]. The catalytic activity based on the cerium oxide nanoparticles ability to participate in the cycles of reduction and oxidation.

The majority of researches are devoted to the study of cerium oxide nanoparticles obtained by various chemical methods (co-precipitation method, hydrothermal synthesis, sol-gel technique, etc.). During chemical synthesis, the nanoparticles surface may be coated with an organic shell [9-10]. This shell helps to improve the aqueous sols stability and allows subsequent conjugation with biological molecules. In addition, the organic coating can protect the CeO₂ nanoparticles from oxidation, i.e., keep mixed valence states of cerium on the surface.

At the same time, the features of physical methods for producing this material are less considered. As we showed earlier, CeO₂ nanoparticles, obtained as a result of strongly nonequilibrium gas-phase synthesis

method conditions exhibit pronounced luminescent properties [11]. This fact allows us to assume the cerium ions of different valences presence on the nanoparticles surface.

The purpose of the present work is to study and compare the catalytic properties of CeO₂ nanoparticles produced by a gas-phase method and chemical technique.

2. EXPERIMENTAL

We studied two group of nanoparticles produced by different methods. The first group of CeO₂ nanoparticles was obtained by a pulsed electron beam evaporation in a low-pressure gas on a NANOBIM-2 installation. The details of nanomaterial synthesis correspond to paper [12]. The second group of CeO₂ nanoparticles was produced by chemical method according to paper [13] and coated with maltodextrin. We denote the first group as CeO₂ (P), the second group - CeO₂ (C).

We used the suspensions of nanoparticles for catalytic activity research. The nanoparticles were dispersed in distilled water in concentrations of 5 mg/ml. The sodium citrate was used as a suspension stabilizer for the first group of nanoparticles. The dispersion was thoroughly mixed and treated with ultrasound for 40 min.

The catalase-like activity of CeO₂ nanoparticles was studied by measuring the optical absorption of the suspensions before and after the addition of hydrogen peroxide (3%). The optical absorption spectra were recorded with a Helios Alpha spectrophotometer ($\lambda=190-1000$ nm) equipped with the Vision 32 software. The peroxidase activity of CeO₂ was determined using the TMB reagent (tetramethylbenzidine) by ELISA method.

3. RESULTS AND DISCUSSION

The catalase-like activity of CeO₂ nanoparticles was evaluated by the suspensions change in the optical absorption in the region of about 400-450 nm after the H₂O₂ addition (**Figure 1**). There is an expressed change in optical density for the CeO₂ nanoparticles produced by chemical method. At the same time, a similar effect is not observed for CeO₂ nanoparticles synthesized by a pulsed electron beam evaporation. A small decrease in the optical density of a CeO₂ (P) sample may be associated with effects of agglomeration and sedimentation.

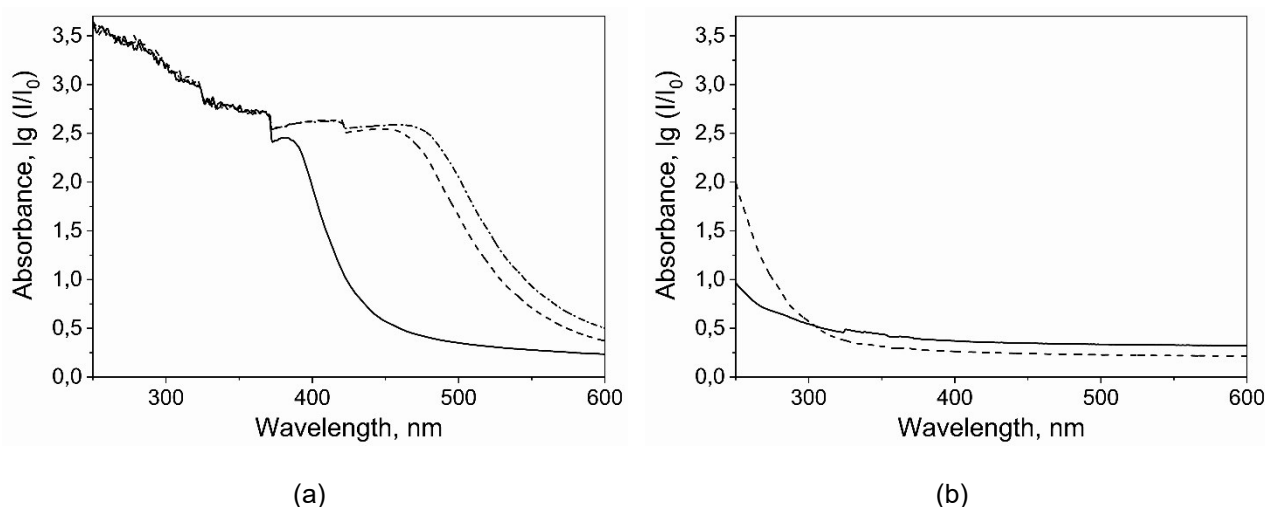


Figure 1 Change on optical absorption of CeO₂ nanoparticles during interaction with H₂O₂: the solid line - before H₂O₂ adding (pure), the dashed line - after H₂O₂ adding (in 1 min); the dash-dotted line - after H₂O₂ adding (in 5 min). a) CeO₂ (C), b) CeO₂ (P)

Figure 2a shows the CeO₂ (C) nanoparticles differential optical absorption spectra before and after adding H₂O₂ in 1 min and 5 min. Relative changes in the optical density of H₂O₂-containing samples were used for evaluation the catalase-like activity. The study results of the catalase-like activity dependence on concentration are presented in **Figure 2b**.

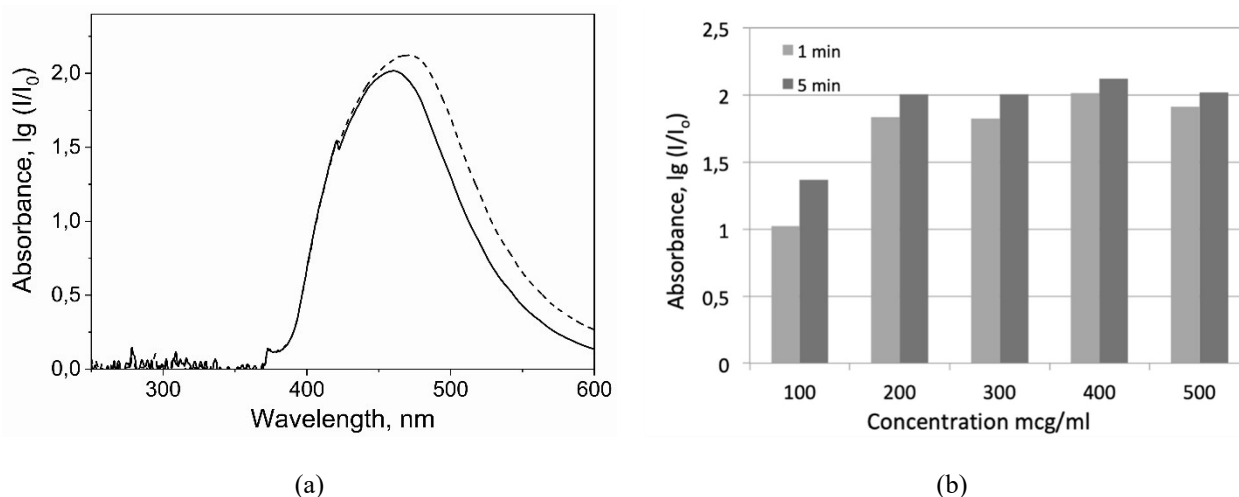


Figure 2 a) Difference between optical absorption spectra of CeO₂ (C) nanoparticles before and after adding H₂O₂ in 1 min (the solid line) and 5 min (the dashed line); b) The relative change dependence in the optical density of CeO₂ (C) samples in the 450-500 nm region after the H₂O₂ addition to concentration

The results of study on the peroxidase activity are presented in **Figures 3-4**. **Figure 3** presents the study results of the CeO₂ effect on the tetramethylbenzidine (TMB) oxidation. The synergistic effect of CeO₂ nanoparticles and the enzyme horseradish peroxidase when interacting with TMB are shown in **Figure 4**.

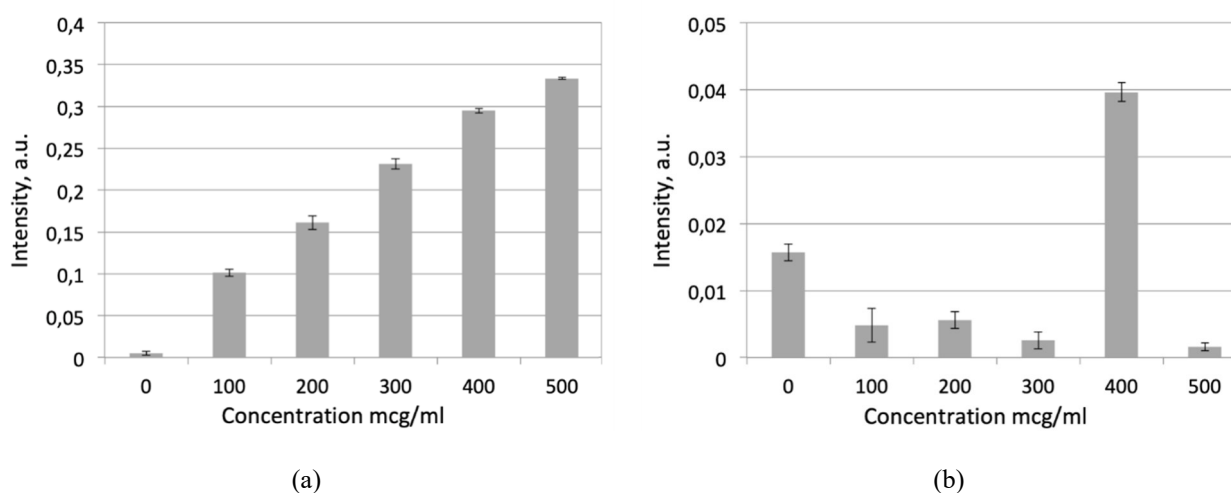


Figure 3 Concentration dependence of the CeO₂ nanoparticles effect on the TMB oxidation: a) CeO₂ (C), b) CeO₂ (P)

The study's results of the CeO₂ nanoparticles catalytic activity show their catalase-like and peroxidase-like activity. The CeO₂ nanoparticles action mechanism as a catalase enzyme involves a two-step process: Ce⁴⁺ ion is first reduced by H₂O₂ to Ce³⁺ state, and a hydroperoxyl radical (HO•) is formed, then this radical is involved in the Ce⁴⁺ state in Ce³⁺ reduction. Common reaction products are Ce³⁺ ions, protons, water, and molecular oxygen [14]. Recent studies have shown the oxidation of Ce³⁺ into Ce⁴⁺, induced by H₂O₂, leads to

the stable intermediate particles, such as peroxy- or hydroperoxyforms, associated with the nanoparticle surface [15]. The peroxidase-like activity mechanism also consists in the transformation of the hydrogen peroxide to water and molecular oxygen reduction [16].

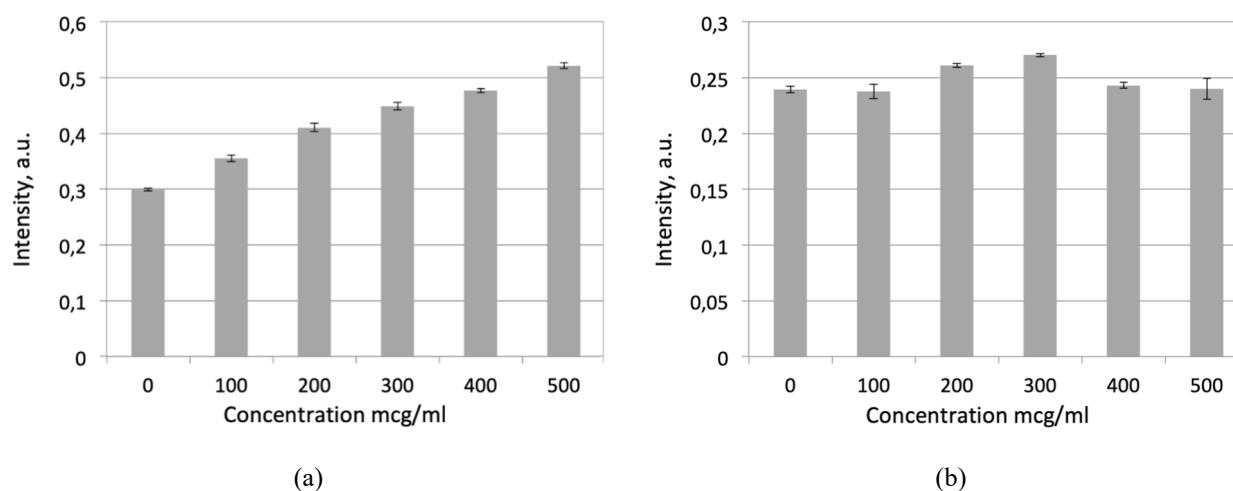


Figure 4 Concentration dependence of the CeO₂ nanoparticles and horseradish peroxidase synergistic effect on the TMB oxidation: a) CeO₂ (C), b) CeO₂ (P)

The observed enzyme-like activity is most appeared for the nanopowder obtained by the chemical method. This may be due to the fact the maltodextrin shell obstructs the natural CeO₂ oxidation processes and thus preserves the Ce³⁺ and Ce⁴⁺ ions presence on the particle surface. CeO₂ nanoparticles obtained by the gas-phase method have a rather high different valence cerium ions ratio [17]. However, strongly nonequilibrium evaporation conditions by an electron beam lead to a significant structural defects number, including on the nanoparticle surface [11]. The presence of structural defects leads to the formation of complex defects associated with Ce³⁺ ions and oxygen vacancies. This complicates the participation of Ce³⁺ ions in redox reactions and, probably, is a reason for the less expressed catalytic activity of these samples.

Note, the maltodextrin-coated CeO₂ nanoparticles exhibit catalytic activity that depends linearly on concentration. This is probably due to a sufficiently equable nanoparticles distribution in the sol. At the same time, the nanopowders obtained by the gas-phase method are characterized by the micrometer-sized elements presence as a synthesis result [12]. This can lead to a non-equitable nanoparticles' agglomeration distribution and a sol stability deterioration.

4. CONCLUSION

This paper presents a catalytic properties study of CeO₂ nanoparticles produced by a gas-phase method and chemical technique. Catalase-like and peroxidase-like activity of nanoparticles were detected. The most expressed catalytic activity is observed for nanoparticles obtained by a chemical method. Nanoparticles obtained by the gas-phase method are characterized by a non-equitable agglomerates distribution in size, and, accordingly, a lower sol stability. Probably, this may be the reason for the lower catalytic samples' activity obtained by this method. The CeO₂ nanoparticles and the horseradish peroxidase enzyme synergistic effect has been demonstrated. This allows to consider this object as a potential hydrogen peroxide biosensor in an enzyme-linked immunosorbent assay.

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