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Structural, Electronic, and Antioxidant Properties of Ablated Ceo2 Nanoparticles with Controlled Limiting Size

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Abstract

Ceria particles of nanodispersed composition have been obtained by laser ablation and subsequent treatment in an aqueous solution. Using techniques (TEM, XRD, Raman, EELS) of the nanostructural and electronic analysis, it is shown that the produced particles have structural defects that stabilize their internal structure. It is established that when the particle size decreases from 100 to 10 nm, the crystal lattice parameter lowers from 5.41 to 5.39 , and the elemental O/Ce composition changes from 1:1.83 to 1:1.76. The ablated CeO2 particles of nanodispersed composition exhibit high antioxidant activity due to the high concentration of functional defects on the surface of nanoparticles.

Keywords: Laser ablation • Cerium oxide • Nanoparticles • Structural defects • Electronic structure • Antioxidant activity

Introduction

Cerium dioxide is one of the most promising rare earth oxides, which, due to its unique physicochemical properties, such as UV absorption , high permeability and exchange capacity for oxygen ions , high-temperature stability, finds its application in many fields: biomedicine , solid-oxide fuel cells, solar screens , catalysis , etc. The functioning of CeO2 nanoparticles is due to the presence in their surface atomic layers of a large number of structural defects, in particular, oxygen vacancies . Oxygen vacancies (VO) on the surface of cerium can accumulate and release oxygen, and they also act as active centers for binding and neutralizing active oxygen radicals. So with a growth of the number of structural defects, its physicochemical activity increases [1].

Due to highly non-equilibrium conditions, the laser ablation makes it possible to obtain particles of transition metal oxides enriched with surface structural defects. However, its application is limited by the wide dimensional dispersion of ablated nanoparticles from nanometer to micrometer scales. We have developed a technique for separating the nanodispersed phase of ablated nanoparticles that have the highest concentration of surface structural defects. These defects should significantly improve their physicochemical properties . Thus, nanoparticles of transition metal oxides enriched with surface structural defects can have efficient antioxidant properties. This paper presents the characterization by transmission microscopy, optical spectroscopy, Raman, and EELS of the structural, electronic, and antioxidant properties of ablated CeO2 nanoparticles of the nanodispersed phase [2].

Materials and methods

Laser ablation of cerium dioxide nanoparticles was performed using an IPG Photonics diode-pumped fiber laser with wavelength of 1.06 μm. The intensity of the laser radiation was 109 W/m2. Ablated cerium dioxide nanoparticles were deposited on glass slides and then ultrasonic dispersed in an aqueous solution. Such colloidal systems were centrifuged in a Microspin Eppendorf high-speed microcentrifuge at rotor speeds of 500, 2000, 5000, and 13 400 rpm for 10 min. According to SAXS data, after centrifugation at 13 400 rpm, the limiting particle size in the colloidal system is reduced up to 30 nm [3].

Transmission electron microscopy (TEM) studies were performed using a Zeiss Libra-120 (Germany) microscope equipped with a HAADF detector and filter for electron energy loss spectroscopy (EELS). X-ray diffraction analysis was carried out on an X-ray diffractometer EMMA (Australia) equipped with a heat chamber up to 1600 °C. Size and morphological features of the ablated nanoparticles were studied using Small-angle X-ray scattering (SAXS) on an X-ray diffractometer SAXSess mc2 (Austria) equipped with a temperature chamber (-30 - 120 C). Raman studies were carried out on a Confocal Raman Spectroscopy system Nanofinder 30 (Japan) [4].

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The antioxidant activity of ablated nanoparticles was studied in the Fenton reaction by the oxidative degradation of the organic Methylene Blue (MB) dye. In this reaction, when iron sulfate FeSO4·7H2O interacts with hydrogen peroxide H2O2, reactive oxygen species are formed that can discolor organic dyes. In the presence of cerium dioxide nanoparticles, a controlled antioxidant Ce3+ ↔ Ce4+ cycle is realized on their surface, which neutralizes active radicals in an aqueous solution . Thus, the antioxidant activity of the nanoparticles can be determined from the kinetic curves of the residual concentration of methylene blue [5].

Results and Discussion

According to transmission electron microscopy (TEM) results, the size of ablated CeO2 nanoparticles varied in the range from 10 nm to several hundred nanometers. The nanoparticles had a predominantly faceted shape, which acquired a rounded shape with an increase in their size . After dispersion in aqueous solution and subsequent centrifugation, the limiting particle size in the colloidal system is reduced (Fig. 1.a,b,c). The pair-distance distribution function calculated by SAXS data for the CeO2 particles centrifuged at 13400 rpm. According to the results, the limiting particle size does not exceed 30 nm.

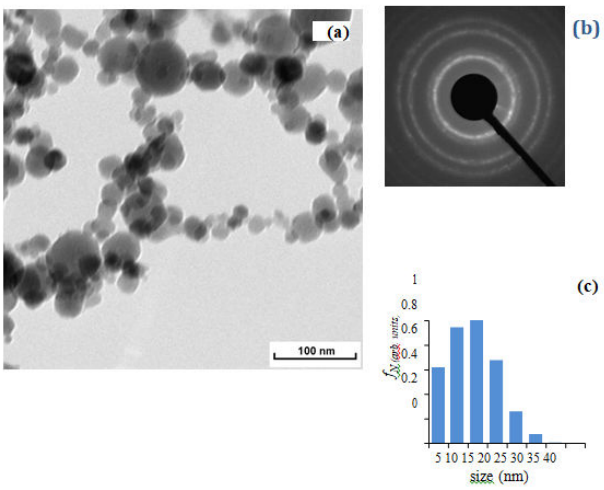

Figure 1: TEM images of ablated CeO2 nanoparticles produced by laser ablation (a); electron diffraction pattern (b) and granulometry data (c) of CeO2 nanoparticles centrifuged at 13400 rpm.

Phase studies carried out using both X-ray and electron diffractometry indicate a high nanocrystalline nature of the ablated CeO2 nanoparticles . Thus, electron diffraction patterns are coaxial superposition of diffraction rings. In addition X-ray diffraction patterns show a significant increase in FWHM (full width half maximum) of the diffraction peaks. The crystal lattice in terms of interplanar distances determined by both electron and X-ray diffraction corresponds to the cubic structure of CeO2. However, CeO2-x phases with diffraction peaks are also detected in ablated nanoparticles. These phases are derivatives of CeO2, strongly enriched in oxygen vacancies.

According to calculations based on TEM and X-ray data, the lattice parameter of the CeO2 nanoparticles is much smaller than the values characteristic of bulk material, and it tends to decrease with decreasing particle size. This result is not obtained for CeO2 nanoparticles by chemical synthesis, where the lattice parameter increases with decreasing particle size. In this case, the number of oxygen vacancies in synthesized nanoparticles increases; it leads to the appearance of Ce3+ and an increase in the lattice parameter due to a growth of the radius of Ce3 + and the Ce–O bond length . On the contrary, in our case, the lattice parameter shrinkage can be explained as follows: in ablated particles, due to the physical features of the laser ablation process, such as ultrafast cooling of molten matter under sharply nonequilibrium conditions, thermoelastic stresses develop in amorphized surface atomic layers. These stresses can compress the internal crystal structure of particles, thereby stabilizing their metastable state.

However, as the particle size decreases below 10 nm, the lattice parameter begins to increase due to a significant decrease in electrostatic forces. This behavior is consistent with the results of our first-principles calculations of the structures of cerium oxide particles with a size of 1.06–3.25 nm with the chemical composition Ce19O32, Ce44O80, Ce85O160, and Ce231O448.

Structural and electronic properties of ablated CeO2 nanoparticles were also studied by characteristic electron energy loss spectroscopy . Background subtraction is performed on all the raw data. These spectra were analyzed according to. The Ce4+ peak components at energies of 885.0 and 902.9 eV were distinguished in the figure. In addition, the curves show the Ce3+ peak components at 879.7 and 896.7 eV. It can be seen that the intensity of the Ce3+ peaks increases with the growth of the centrifugation rate. A change in the oxidation state from Ce4+ to Ce3+ indicates an increase in the VO concentration in the surface atomic layers of nanoparticles.

The modes in the Raman spectra correspond to the lattice of fluorite with structural defects. The F2g Mode (450 cm-1) exhibits a pronounced asymmetry and a shift towards lower energies relative to bulk cerium oxide. Modes in the range 640-720 cm-1 are second-order combination modes due to the presence of oxygen vacancies in cerium oxide. These modes are presented in all samples of ablated CeO2 nanoparticles. However, with decreasing particle size, the relative intensity of the VO peaks increases.

Conclusions

The ablated CeO2 nanoparticles of nanodispersed composition were successfully obtained by ultrasonic dispersion and subsequent centrifugation in an aqueous solution. The dependence of the lattice parameters on the particle size has been established. It is shown that with a decrease in the particle size from 100 to 10 nm,the crystal lattice parameter decreases from 5.41 to 5.39. It has been determined that the concentration of structural defects increases with decreasing particle size. The highest antioxidant activity is manifested in nanodispersed solutions of CeO2 particles with a limiting size of 30 nm. The high antioxidant activity of nanoparticles is determined by the high concentration of functional defects on the surface of nanoparticles obtained under acutely nonequilibrium conditions of laser ablation.

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