Luminescence properties and ROS scavenging activity of ceria nanoparticles

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The unique redox properties of cerium oxide (CeO_{2-x}) nanoparticles, which are determined by two stable oxidation states of cerium ions (Ce^{3+} and Ce^{4+}) and relatively low reduction potential for Ce^{3+}/Ce^{4+} switching, have led to extensive biomedical applications of nanoceria for the treatment of various deceases. Currently, besides antioxidant activity, a pronounced antibacterial anticancer, anti-diabetic, and tissue regeneration activity of nanoceria was described. In contrast to most inorganic materials, nanoceria is able to decompose hydrogen peroxide (HP) without formation of hydroxyl radicals, so its activity can be considered as enzyme-like. At the same time, as the mechanisms of redox activity of nanoceria, so the optimal conditions for effective ROS scavenging are still discussed.

The role of the surface defect structure in formation of antioxidant activity of ceria-based nanoparticles was revealed using the methods of optical spectroscopy. The variation of the type of doped ions allowed to show that while $^{\bullet}OH$ scavenging ability of nanoceria depends simply on the content of Ce^{3+} ions on the surface of nanoparticle, the mechanism of HP decomposition depends on the type and the content of Ce^{3+}-V_o-Ce^{3+} (or Re^{3+}-V_o-Ce^{3+}) complexes. The interaction of HP molecule with Re^{3+}-V_o-Ce^{3+} surface complexes can be accompanied by oxidation of one or both ions in the complex, and, accordingly, the decomposition of HP molecules can occur both with (CeO_2:Eu^{3+} and CeO_2:Y^{3+} nanocrystals) and without (CeO_{2-x} and CeO_2:Tb^{3+} nanocrystals) generation of hydroxyl radicals [1]. The different mechanisms of HP decomposition by nanoparticles lead to variation of HP decomposition rate as well. The dynamics of HP decomposition by CeO_{2-x} and CeO_2:Tb^{3+} nanocrystals can be described using the mathematical model usually used for description of enzyme kinetics (Michaelis-Menten equation). The maximum rate of HP decomposition shows clear dependence on the size of nanoparticles i.e. on the number of available surface sites for binding of HP molecules. At HP concentrations, for which almost all Ce^{3+}-V_o-Ce^{3+} sites are involved into HP decomposition, the process of slow $Ce^{3+}\rightarrow Ce^{4+}$ oxidation turns into fast redox cycling and Ce^{3+}/Ce^{4+} oscillations are observed [2].

5d→4f luminescence of Ce^{3+} ions in CeO_{2-x} nanocrystals opens the possibility of controlling the interaction of reactive oxygen species with ceria nanocrystals [3]. Intensity of 5d→4f luminescence of Ce^{3+} ions in nanoceria can be used for study of the dynamics of nanoceria-ROS interaction, and as a measure of its antioxidant activity. Presence of 5d→4f luminescence makes these NPs a new type of antioxidants with ability both to scavenge reactive oxygen species and to visualize the change in ROS concentration during this process.

[1] V. Seminko, P. Maksimchuk, G. Grygorova, E. Okrushko, O. Avrunin, V. Semenets, Yu.V. Malyukin, Switching the type of redox activity of colloidal nanoceria by Re^{3+} (Re = Y, Eu, Tb) doping, Chemical Physics Letters, V. 767, 138363 (2021).
[2] V. Seminko, P. Maksimchuk, G. Grygorova, E. Okrushko, O. Avrunin, V. Semenets, Yu.V. Malyukin, Mechanism and Dynamics of Fast Redox Cycling in Cerium Oxide Nanoparticles at High Oxidant Concentration The Journal of Physical Chemistry C, V. 125, P. 4743–4749 (2021).
[3] V. Seminko, P. Maksimchuk, G. Grygorova, O. Avrunin, V. Semenets, V. K. Klochkov, Yu.V. Malyukin, Catalytic Decomposition of Hypochlorite Anions by Ceria Nanoparticles Visualized by Spectroscopic Techniques, J. Phys. Chem. C, V. 123, № 33, p. 20675–20681 (2019).