Reversible luminescent hydrogen peroxide sensors based on CeO_{2-x} and CeO_{2-x}:Eu^{3+} nanocrystals

Pavel Maksimchuk, Yevhen Neuhodov, Kateryna Hubenko, Andrey Onishchenko, Svetlana Yefimova, Vladyslav Seminko

Yu.V.Malyukin Department of Nanostructured Materials, Institute for Scintillation Materials, NAS of Ukraine

pavel.maksimchuk@gmail.com

Yu.V.Malyukin department of nano structured materials

Hydrogen peroxide (HP) is a widespread industrial chemical widely used for bleaching, cleaning, and disinfection. HP also plays an indispensable role in living organisms being a ubiquitous cell signaling molecule and a substrate or byproduct of a number of enzymes (including catalase, superoxide dismutase, and a number of oxidases and peroxidases). So, HP sensing is required for reliable quantification of HP content in these systems.

HP sensors based on luminescent inorganic nanoparticles can be considered as a perspective alternative to traditional dye- and enzyme-based sensors which usually are unstable and non-reversible. Undoped (CeO_{2-x}) and Eu^{3+}-doped (CeO_{2-x}:Eu^{3+}) colloidal ceria nanoparticles provide HP detection by reversible quenching of Eu^{3+} (590 nm) and Ce^{3+} (430 nm) luminescence bands. The dynamics of Eu^{3+} and Ce^{3+} luminescence quenching and recovery during HP-nanoceria interaction provides an insight into the microscopic mechanisms of HP sensing by CeO_{2-x} and CeO_{2-x}:Eu^{3+} nanoparticles.

Both CeO_{2-x} and CeO_{2-x}:Eu^{3+} luminescent sensors are reversible and their recovery rates can be sufficiently increased by temperature and continuous UV irradiation. At the same time, Eu^{3+} ions deteriorate the catalase-mimetic activity of CeO_{2-x} NPs and worsen their antioxidant properties that should be keep in mind while using these sensors in biological media.

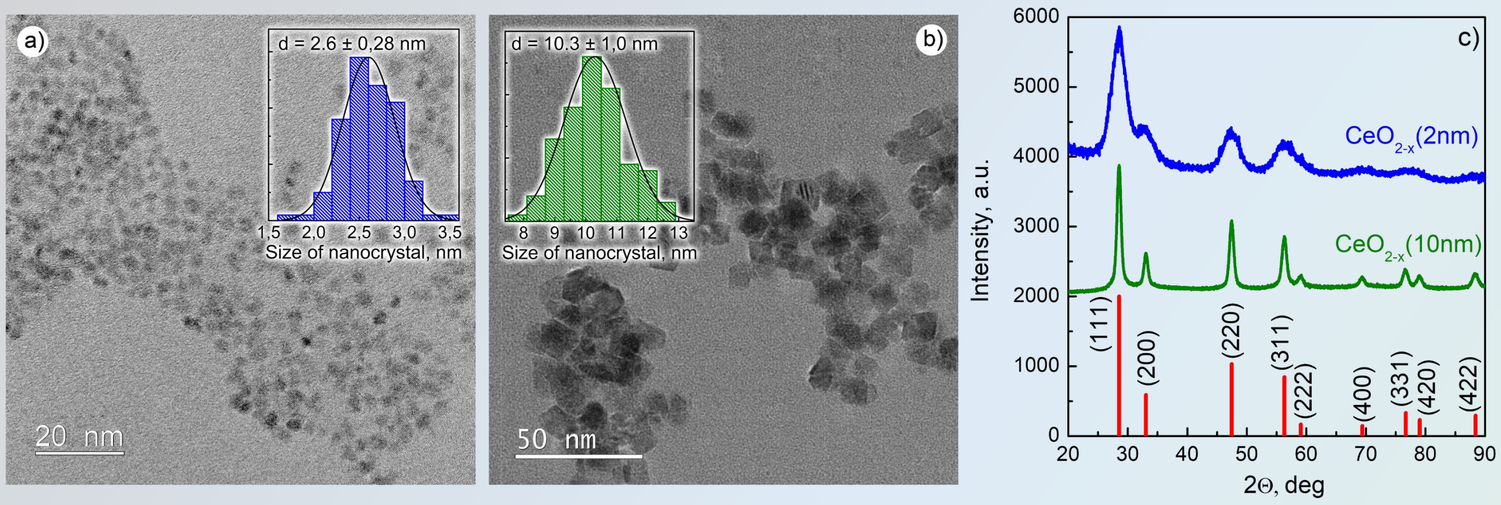

Fig1. TEM images (a-b) and XRD patterns (e) of CeO_2 NPs

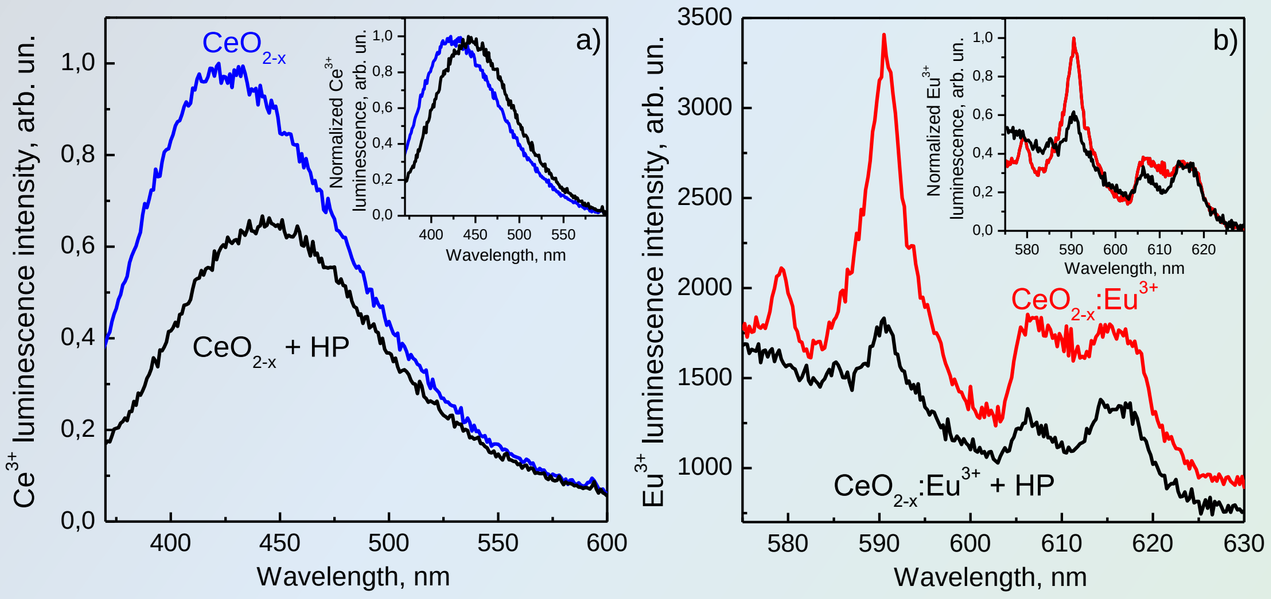

Fig2. Hydrogen peroxide sensing using HP-induced quenching of Ce^{3+} (a) and Eu^{3+} (b) luminescence of CeO_{2-x} (a) and CeO_{2-x}:Eu^{3+} (b) NPs.

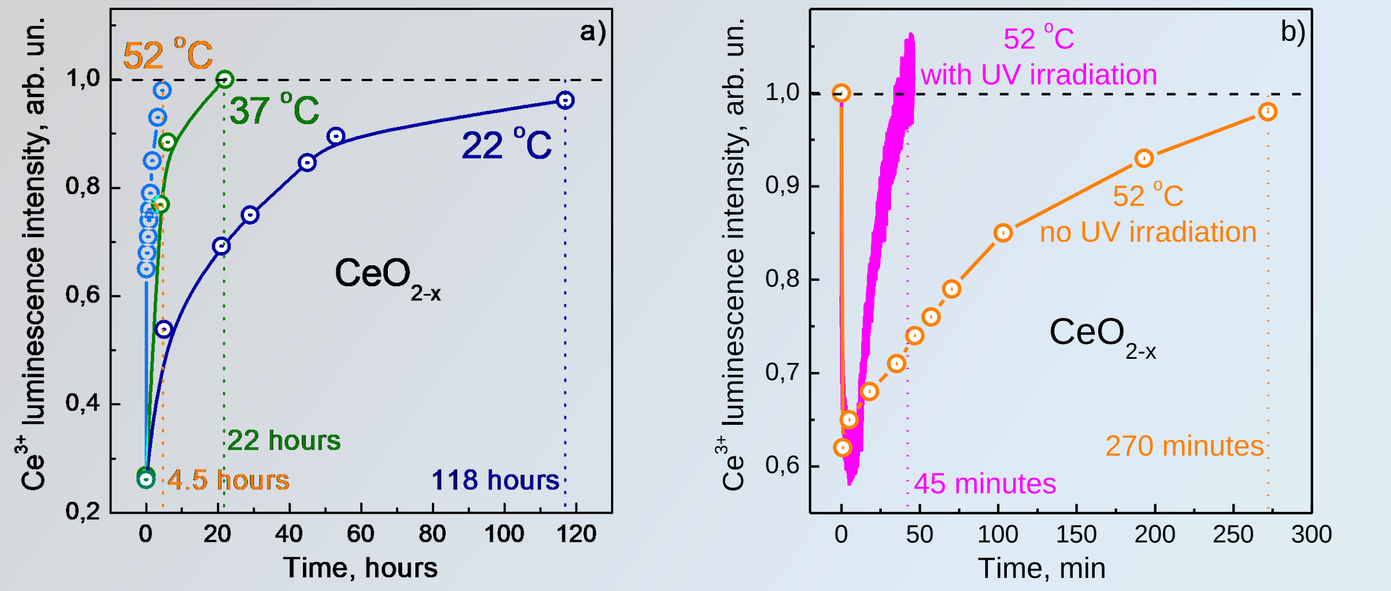

Fig3. Recovery of luminescence intensity of CeO_{2-x} (a, b) and CeO_{2-x}:Eu^{3+} (c, d) NPs after HP addition without irradiation (a, c) and with UV irradiation (b, d).

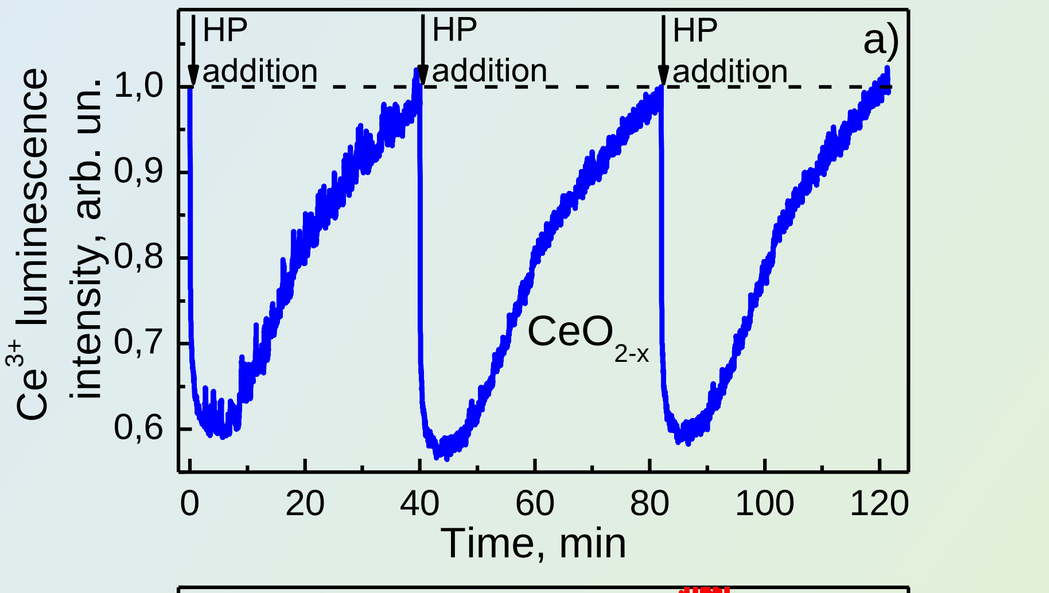

Fig4. Dynamics of Ce^{3+} luminescence intensity of CeO_{2-x} NPs (a) and Eu^{3+} luminescence intensity of CeO_{2-x}:Eu^{3+} NPs (b) at multiple HP addition and continuous UV irradiation (t = 52 °C).

Conclusions

Undoped and Eu^{3+}-doped colloidal ceria nanoparticles provide effective HP detection by quenching of Ce^{3+} (as a result of Ce^{3+}→Ce^{4+} oxidation) and Eu^{3+} (as a result of energy transfer from Eu^{3+} ions to hydroxyl groups) luminescence bands. CeO_{2-x} and CeO_{2-x}:Eu^{3+} luminescent sensors are reversible and the recovery rates can be sufficiently increased by temperature and/or continuous UV irradiation. As a result, the times of full recovery of luminescence signal for both sensors can be decreased from few days to less than 1 hour.

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