Hydrogen Peroxide Detection Using Reversible Luminescent CeO_{2-x} and CeO_{2-x}:Eu^{3+} Nanocrystals

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Hydrogen peroxide (HP) is a prevalent industrial chemical used extensively for bleaching, cleaning, and disinfection. In biological systems, HP acts as a crucial signaling molecule and is involved in various enzymatic processes as a substrate or byproduct, such as those involving catalase, superoxide dismutase, and numerous oxidases and peroxidases. Thus, precise HP sensing is vital for monitoring its concentration in both industrial and biological contexts.

Traditional HP sensors based on dyes and enzymes often suffer from instability and irreversibility. In contrast, luminescent inorganic nanocrystals offer a promising alternative. Specifically, undoped (CeO_{2-x}) and Eu^{3+}-doped (CeO_{2-x}:Eu^{3+}) colloidal ceria nanocrystals facilitate HP detection through the reversible quenching of their luminescence bands at 590 nm (Eu^{3+}) and 430 nm (Ce^{3+}). Studying the quenching and recovery behavior of these luminescence bands during interactions with HP sheds light on the underlying mechanisms of HP detection by these nanoparticles.

CeO_{2-x} and CeO_{2-x}:Eu^{3+} luminescent sensors demonstrate reversible detection capabilities, with their recovery rates significantly accelerated by increased temperature and continuous UV irradiation. However, the introduction of Eu^{3+} ions, while beneficial for luminescence properties, negatively impacts the catalase-like activity of CeO_{2-x} nanoparticles and diminishes their antioxidant efficacy. This trade-off must be considered when deploying these sensors in biological environments.

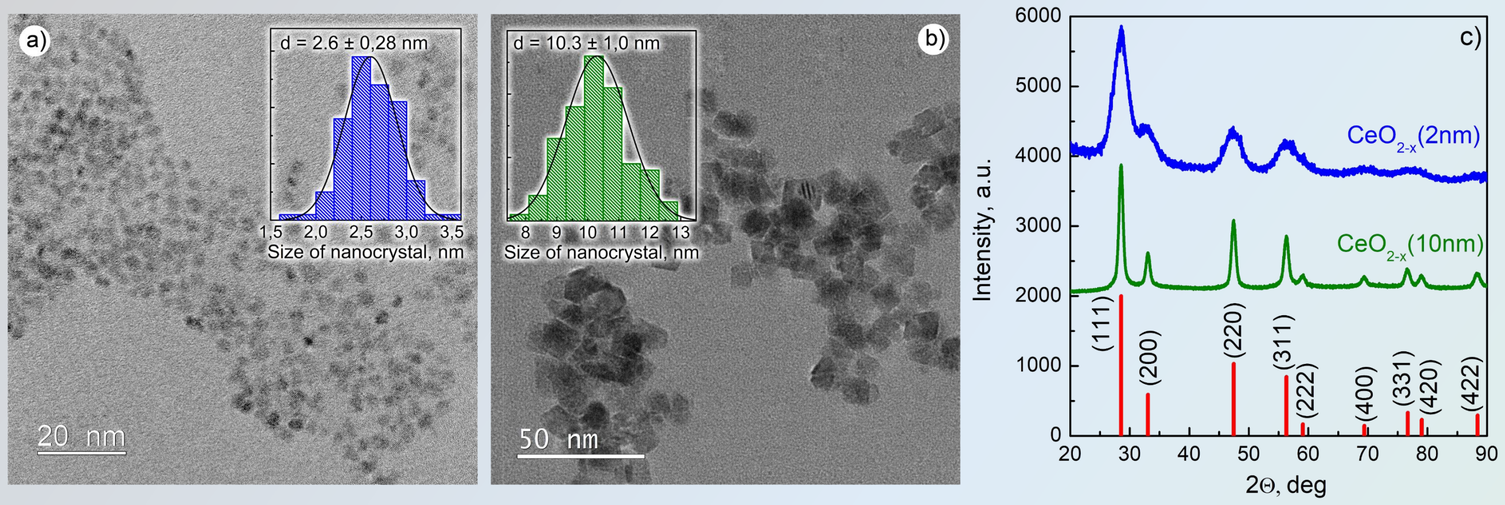

Fig1. TEM images (a-b) and XRD patterns (e) of CeO_2 NPs

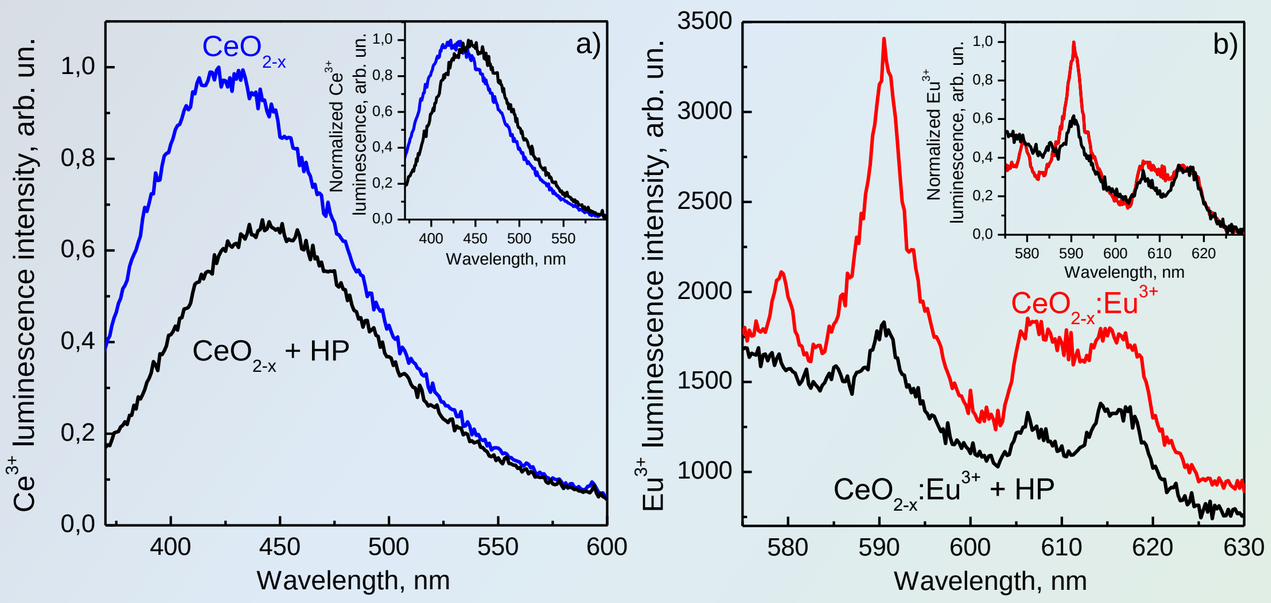

Fig2. Hydrogen peroxide sensing using HP-induced quenching of Ce^{3+} (a) and Eu^{3+} (b) luminescence of CeO_{2-x} (a) and CeO_{2-x}:Eu^{3+} (b) NPs.

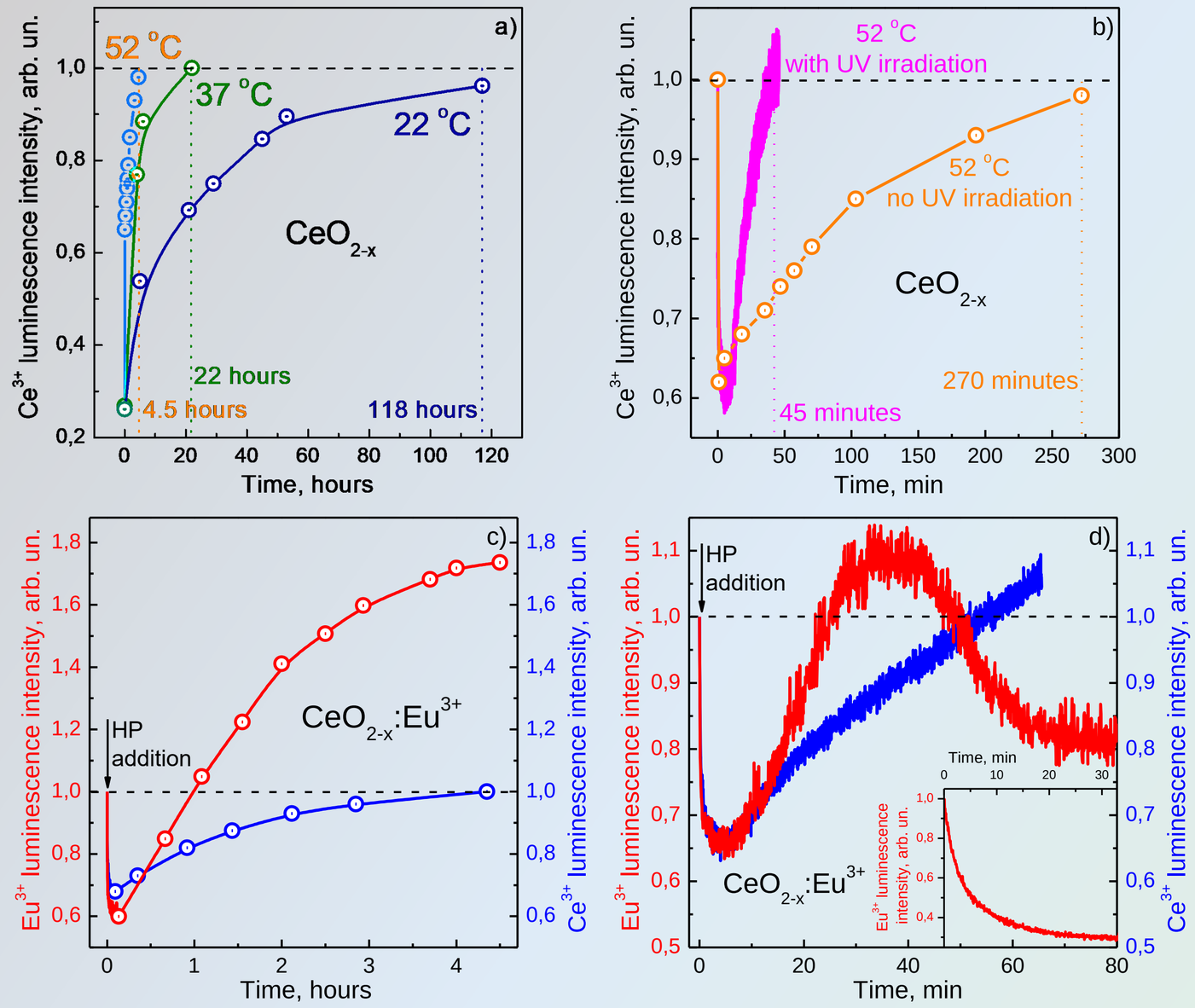

Fig3. Recovery of luminescence intensity of CeO_{2-x} (a, b) and CeO_{2-x}:Eu^{3+} (c, d) NPs after HP addition without irradiation (a, c) and with UV irradiation (b, d).

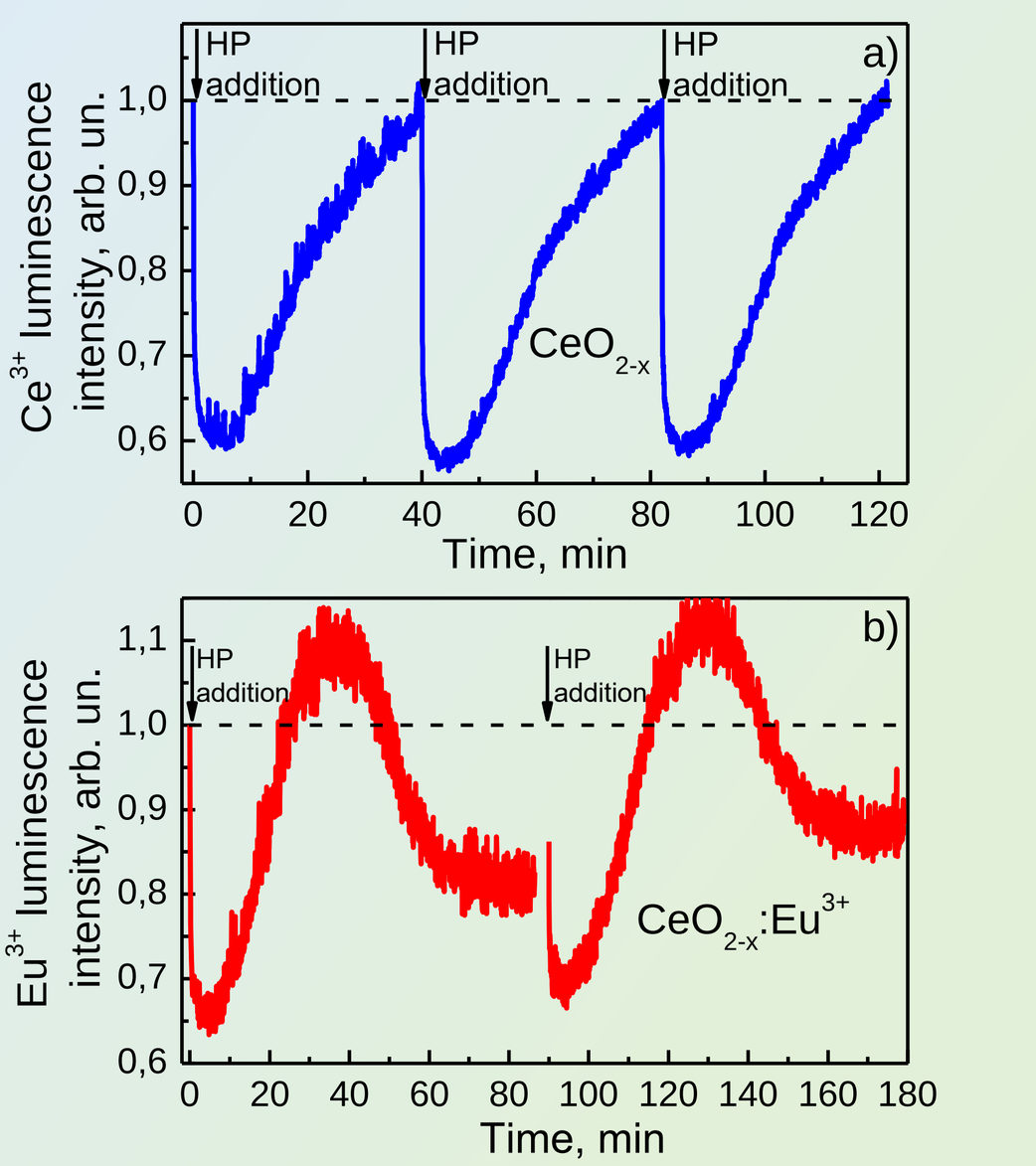

Fig4. Dynamics of Ce^{3+} luminescence intensity of CeO_{2-x} NPs (a) and Eu^{3+} luminescence intensity of CeO_{2-x}:Eu^{3+} NPs (b) at multiple HP addition and continuous UV irradiation (t = 52 °C).

Conclusions

Undoped and Eu^{3+}-doped colloidal ceria nanoparticles provide effective HP detection by quenching of Ce^{3+} (as a result of $Ce^{3+}\rightarrow Ce^{4+}$ 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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