Influence of pH on the redox properties of nanoparticles based on rare-earth elements in the lipid peroxidation system

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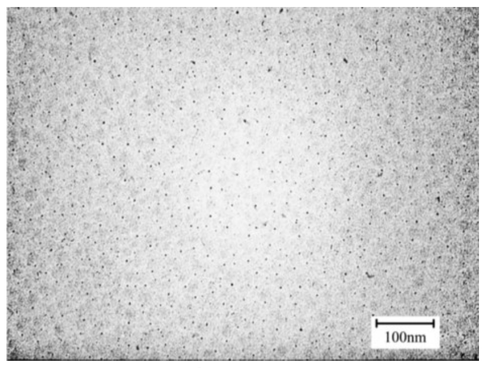
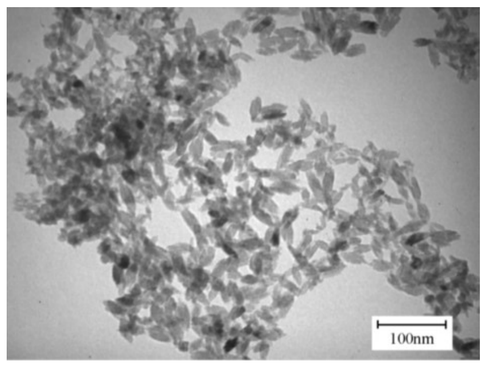
Nanoparticles (NPs) with reversible redox properties presents a new wave in the antioxidant therapy for prevention and treatment of diseases associated with oxidative stress

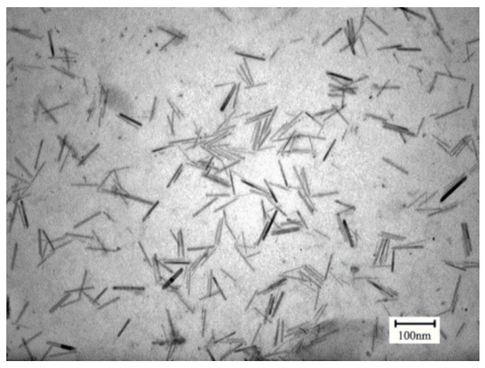
Five types of the unmodified particles were used



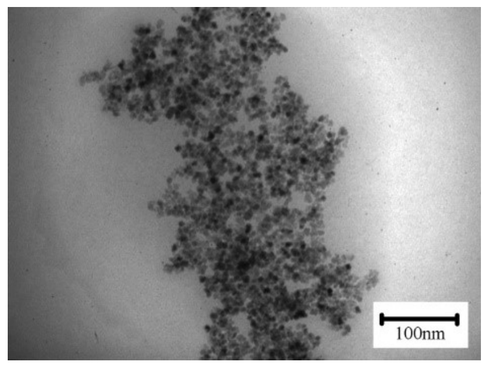
$GdYVO_4:Eu^{3+}$ (2nm) - spherical



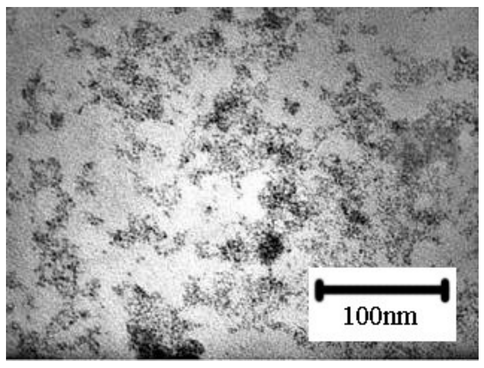
$GdVO_4:Eu^{3+}$ (8×25nm) - spindle



$LaVO_4:Eu^{3+}$ (8×80nm) - rod-like



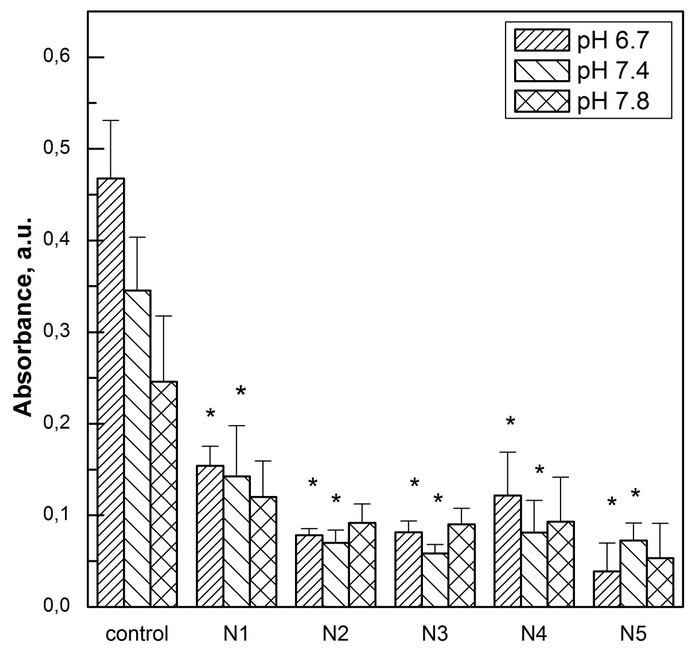
CeO_2 (2нм) - spherical



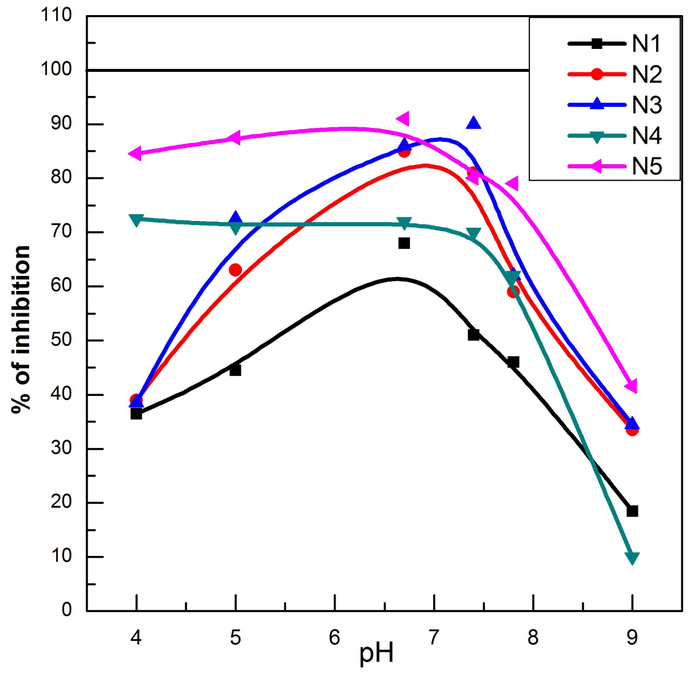
CeO_2 (9нм) - spherical

In a number of works the transition from antioxidant effects of NPs to prooxidant ones under an pH influence were reported. The dependence of the redox properties of NPs of the pH of the medium is considered as one of the promising approaches in overcoming the resistance of tumor cells to the action of antitumor drugs.

Antioxidant properties of NPs were evaluated by their ability to inhibit the formation of diene conjugates.
Two different methods of activation of lipid peroxidation were used: auto-oxidation and oxidation induced by tert-butylhydroperoxide (t-BHP).
The formation of conjugates was studied at different pH values: 4, 6.7, 7.4, 7.8, and 9.0.



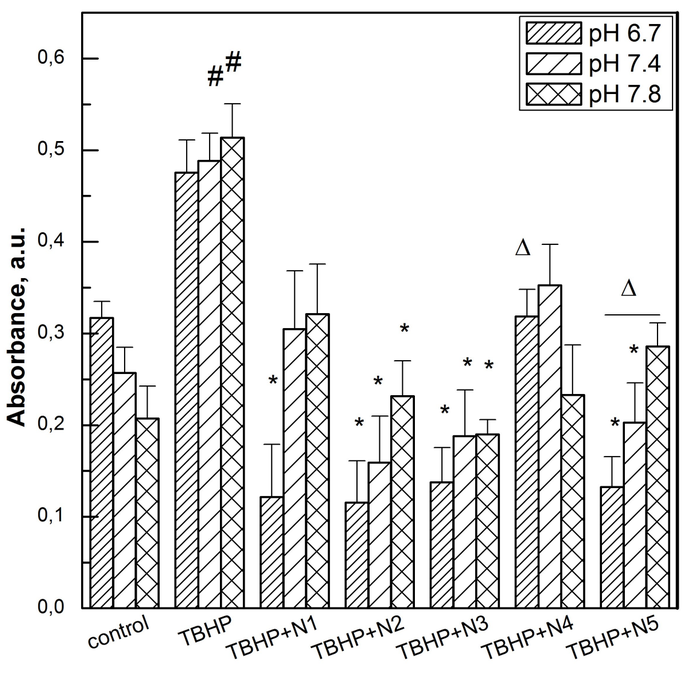
The level of diene conjugates during autooxidation of phosphatidylcholine in the presence of NPs at different pH



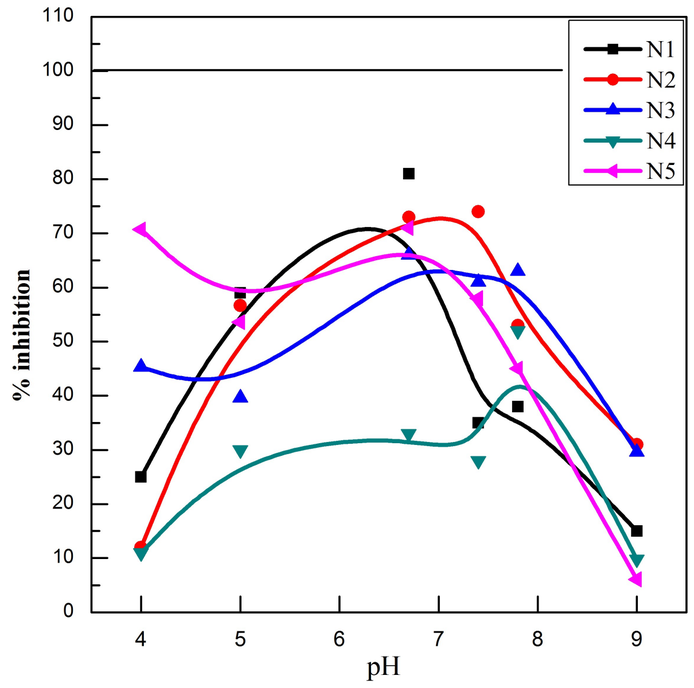
Inhibition of phosphatidylcholine autooxidation by NPs at different pH

During autooxidation of phosphatidylcholine, inhibition of lipid peroxidation is observed at physiological pH values for all types of studied NPs.
In the acidic pH range, both types of CeO_2 are stronger antioxidants than orthovanadate NPs.
Small spherical NPs – CeO_2 and $GdYVO_4:Eu^{3+}$ show the least pronounced antioxidant effect in the physiological range, and spherical $GdYVO_4: Eu^{3+}$ NPs are weaker antioxidants than CeO_2.

N1 – $GdYVO_4:Eu^{3+}$ (2нм) – spherical;
N2 – $GdVO_4:Eu^{3+}$ (8×25нм) – spindle;
$LaVO_4:Eu^{3+}$ (8×80нм) – rod-like;
N4 – CeO_2 (2нм) – spherical;
N5 – CeO_2 (9нм) – spherical;



The level of diene conjugates during t-BHP - induced oxidation of phosphatidylcholine in the presence of NPs at different pH



Inhibition of phosphatidylcholine t-BHP - induced oxidation by NPs at different pH

During t-BHP - induced lipid oxidation, small CeO_2 particles show the weaker antioxidant activity in whole pH range compared to the same orthovanadate NPs apparently due to low ability to bind/neutralize organic molecules, and the lack of stabilizing effect on the lipid layer in contrast to the anisometric orthovanadate NPs or larger NPs of CeO_2.

N1 – $GdYVO_4:Eu^{3+}$ (2нм) – spherical;
N2 – $GdVO_4:Eu^{3+}$ (8×25нм) – spindle;
$LaVO_4:Eu^{3+}$ (8×80нм) – rod-like;
N4 – CeO_2 (2нм) – spherical;
N5 – CeO_2 (9нм) – spherical;

For the studied NPs prooxidant properties have not been observed in the whole range of pH values.
Antioxidant action for different types of NPs is determined not only by their structure and shape, but also by the nature of the radicals formed in the system and depends on the pH of the medium.