Supplementary Materials

New facets of nanozyme activity of ceria: lipo- and phospholipoperoxidaselike behaviour of CeO₂ nanoparticles

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An analysis of the prooxidant activity of CeO₂ nanoparticles with respect to hydrogen peroxide was carried out according to a previously published protocol.¹



Figure S1. Chemiluminograms of citrate-stabilised CeO₂ sol and a colloidal solution of carboxymaltose Fe(III) (Ferinject[®]) in a phosphate buffer solution (100 MM, pH 7.4) + luminol $(50 \mu mol/L) + H_2O_2$ (250 $\mu mol/L$).



Figure S2. Chemiluminograms of (a) citrate-stabilised CeO₂ sol in a phosphate buffer solution (100 mM, pH 7.4) + luminol (50 μ mol/L) + H₂O₂ (250 μ mol/L); (b) light sum dependence (S_{CL} , × 10³ imp) on the concentration of CeO₂ sol. The dependence of the analytical signal on the concentration of CeO₂ nanoparticles was described by the equation: $S_{CL} = (0.36 \pm 0.04) \times c$ (CeO₂, μ mol/L) + (25 ± 2), r = 0.992 (P = 0.95, n = 4).



Figure S3. Chemiluminogram of ammonium citrate in a phosphate buffer solution (100 MM, pH 7.4) + coumarin 334 (50 μ mol/L) + PCOOH (the concentration of hydroperoxide groups was $98 \pm 10 \mu$ mol/L).



Figure S4. Chemiluminograms of (a), (b) citrate-stabilised CeO₂ sol (7.0, 3.5 mM) and (c), (d) deoxyhemoglobin (Hb) solution (5.0, 2.5 nM) in a phosphate buffer solution (100 mM, pH 7.4) + coumarin 334 (50 μ mol/L) + LOOH (concentration of hydroperoxide groups was 100 ± 12 μ mol/L) at various temperatures.



Figure S5. Chemiluminograms of (a), (b) citrate-stabilised CeO₂ sol (1.0, 0.5 μM) and (c), (d) deoxyhemoglobin (Hb) solution (5.0, 2,5 nM) in a phosphate buffer solution (100 mM, pH 7.4) + coumarin 334 (50 μmol/L) + PCOOH (concentration of hydroperoxide groups was 98 ± 10 μmol/L) at various temperatures.

Quantification of lipo- and phospholipoperoxidase-like activity of CeO₂ nanoparticles

To quantitatively compare lipo- and phospholipoperoxidase-like activities of citratestabilised CeO₂ sol the following algorithm was used. For three different concentrations of CeO₂ sol, the values of prooxidant capacity (light sum of chemiluminescence which is proportional to the number of free radicals) were calculated using the equation: $S = A \times c + B$, where A and B coefficients were calculated from the experimental dependencies of the light sum on the concentration of the CeO₂ sol. Thus, prooxidant capacity of CeO₂ sol for linoleic acid hydroperoxide substrate was calculated as

 S_{CL} (L-OOH) = (1.50 ± 0.29) × c (CeO₂, mmol/L) + (16 ± 2),

for phosphatidylcholine hydroperoxide substrate -

$$S_{CL}$$
 (PC-OOH) = (22 ± 3) × c (CeO₂, μ M) + (35 ± 5).

The ratio S_{CL} (PC-OOH)/ S_{CL} (L-OOH) demonstrates the difference between the phospholipo- and lipoperoxidase-like activities of CeO₂ NPs.