Electronic Supplementary Information

Controlling the Surface Chemistry of Cerium Oxide Nanoparticles for Biological Application

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Figure 1S Schematic of synthesis of dextran coated doped cerium oxide nanoparticles (CNPs)



 Rare earth doping elements (La, Sm or La)

Figure 2S

X-ray diffraction pattern of doped CNPs with dextran CNP exhibit the fluorite structure represent a fluorite structure correspond to commercially available CNP. Presence of dextran of CNPs surface and reduction in particle size are attributed to peak broadening. Absence of additional peaks suggests the formation of doped CNPs and dopants do not form additional oxide because of phase separation.



Figure 3S

(a) HRTEM micrographs of 20 mole% Sm doped CNPs showing uniform distribution of nanoparticles of 2-7 nm size. Indexed selected area diffraction pattern belong to FCC fluorite crystal structure.

(b) Energy dispersive X-ray analysis spectrum of 20 mole% Er doped CNPs shows the elemental composition corroborating the presence of Yb, Er, in cerium oxide. Presence of Cu is from copper TEM grid.







Figure 4S

Particle size distribution of 10 mole% Sm doped CNP after one year of synthesis showing the colloidal stability and higher shelf life of nanoparticles.



Figure 5S

Superoxide dismutase activity (SOD) of doped CNPs. (a)-(c) at basic pH 8 and (d)-(e) at acidic pH 4.5. SOD activity represents the scavenging of super oxide radicals and measured at 565nm.



Where Blank 1: Water (20μL) + WST working solution (200μL) + Enzyme working solution (20μL)
Blank 2: Sample solution (20μL) + WST working solution (200μL) + Dilution buffer (20μL)
Blank 3: Water (20μL) + WST working solution (200μL) + Dilution buffer (20μL)
Sample (SS): Sample solution (20μL) + WST working solution (200μL) + Enzyme working solution (20μL)

Figure 6S

% SOD Improvement =
$$\left[\frac{\% SOD \ activity_{sample}}{\% SOD \ activity_{Dex \ CNPs}}\right] * 100$$

Percentage improvement in SOD activity with doping element and concentration with reference to dextran CNPs.



Figure 7S

Catalase mimetic activity of doped CNPs. (a)-(c) at basic pH 8 and (d)-(e) at acidic pH 4.5. Catalase activity represents the conversion of hydrogen peroxide into oxygen with time and remaining hydrogen peroxide levels measured at 240nm.



HEPES Buffer pH 8.0

Acetic Acid Buffer pH 4.5

Figure 8S

Intracellular ROS scavenging properties of CNPs using confocal microscopy. Pretreatment with CNPs with or without doping (1 μ M final concentration) able to decrease intracellular ROS induced by H₂O₂ (10 μ M final concentration) for six hours. Scale bar 100 μ m.



Table 1S

Summary of surface oxidation state of Ce from XPS and zeta potential

Material	Ce ³⁺ (%)	Ce ⁴⁺ (%)	Zeta Potential (mV)
Dextran CNP	48.75	51.25	-15.33±0.98
5mole% La-CNP	67.95	32.05	-11.20±2.77
5mole% Sm-CNP	63.80	36.20	-3.89±0.65
5mole% Er-CNP	57.32	42.68	-22.73±0.31
10mole% La-CNP	55.12	44.88	-20.93±1.68
10mole% Sm-CNP	54.83	45.17	-10.9±0.46
10mole% Er-CNP	59.69	40.31	-21.33±0.95
20mole% La-CNP	63.81	36.19	-7.73±1.68
20mole% Sm-CNP	51.68	48.32	-7.90±0.46
20mole% Er-CNP	62.46	37.54	-18.23±0.23