SUPPORTING INFORMATION

Cell Uptake, Intracellular Distribution, Fate and Reactive Oxygen Species Generation of Polymer Brush Engineered CeO_{2-x} NPs

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Fig. S1: TEM images of CeO_{2-x} NPs with different polymer brush coatings:a) bare NPs; b) coated with PMETAC; c) coated with PSPM CeO_{2-x} NPs were all pretreated with uranyl acetate to visualise the polymer coating._The arrows in images b) and c) indicate the polymer brush.

Table S1: Size and ζ -potential of CeO_{2-x} NPs measured by DLS at 25° C in10 mM NaCl and cell culture medium.

	10 mM NaCl		Cell culture medium	
	Size (nm)	Zeta (mV)	Size (nm)	Zeta (mV)
CeO ₂ NPs	894.2±47.6	8.2±0.4	161.2±7.2	-10.3±1.2
CeO ₂ @PSPM NPs	159.3±5.1	-31.9±3.9	163.4±8.5	-11.3 ± 0.3
CeO ₂ @PMETAC NPs	247.7±9.0	25.7±0.3	208.4±6.0	-10.6±0.7

XPS

CeO_{2-x} NPs with different polymer coatings were also characterised by X-ray photoelectron spectroscopy (XPS). All samples were measured at 12.5 kV and 300 W in a SPECS SAGE HR 100 XPS system using a non-monochromatic Al K α X-ray source at 12.5 kV and 300 W. The pass energy was 30 eV for survey scan and 10 eV for narrow scans.. The analysis consisted of satellite removal, Shirley background subtraction, calibration of the binding energies to the C 1s C-C peak at 285 eV, and peak fitting with Gaussian-Lorentizan line shapes.



Fig. S2: XPS spectra of (a) Ce 3d 5/2; (b) O1s for CeO₂ NPs.



Fig. S3: XPS spectra of (a) Ce 3d 5/2;(b)O1s; (c) N 1s; (D)S 2p for CeO₂@PSPM NPs.



Fig. S4: XPS spectra of (a) Ce 3d 5/2;(b)O1s; (c) N 1s; for CeO₂@PMETAC NPs.



Fig. S5: Fluorescence emission spectra of Alexa FluorTM 488 free probe and of Alexa FluorTM 488 labelled CeO_{2-x} NPs in distilled water. 488 nm excitation.



Fig. S6: Raman spectra of CeO_{2-x} NPs with different coatings.



Fig. S7: ICP-MS measurements of cellular uptake of label free CeO2-x after incubation with HEK293 cells of 1h and 48h.

Calculation of amine group on the surface of CeO_{2-x} NPs

The calculation of amine group on the surface of CeO_{2-x} NPs is presented as follows:

Volume of single NP = $4/3 \times 3.14 \times (15/2 \times 10^{-9} \text{ m})^3 = 1.77 \times 10^{-24} \text{m}^3 = 1.77 \times 10^{-18} \text{ cm}^3$ (we consider the shape of a single NP as a sphere). Since there is a layer of atoms in the outer surface of NPs. Thickness of the layer is assumed to be a half of the lattice constant (The lattice constant of a cerium oxide crystal is 5.39 Å).

Volume of single unit cell (a^3) = (5.39×10⁻¹⁰ m)³= 1.57×10⁻²⁸m³ (volume of a cube)

Thickness of outer layer = $1/2 \times 5.39 \times 10^{-10}$ m = 2.69×10^{-10} m

Radius of the inner part = $15/2 \times 10^{-9}$ m- 2.69×10⁻¹⁰m=7.23×10⁻⁹ m

Volume of the inner part = $4/3 \times 3.14 \times (7.23 \times 10^{-9} \text{ m})^3 = 1.58 \times 10^{-24} \text{ m}^3$

Volume of the outer layer = $1.77 \times 10^{-24} \text{ m}^3 - 1.58 \times 10^{-24} \text{ m}^3 = 1.9 \times 10^{-25} \text{ m}^3$ (Volume of one NP subtracts volume of the inner part)

The number of unit cell on the outer layer $=1.9 \times 10^{-25}/1.57 \times 10^{-28}=1200$ (Volume of outer layer / Volume of single unit cell)

Since each unit has 8 oxygen ions,

the number of oxygen ions on the outer layer $=8 \times 1200 = 9600$

Weight of single NPs = 1.77×10^{-18} cm³×7.44g/ cm³ = 1.32×10^{-17} g (The density of CNPs is 7.44g/ cm³ and the volume of single NP 1.77×10^{-18} cm³)

So in 100mg NPs,

the number of single NPs = $0.1 \text{ g} / 1.32 \times 10^{-17} \text{ g} = 7.6 \times 10^{15}$

And in 100mg NPs,

the amount of oxygen ion in the outer layer = $9600 \times 7.6 \times 10^{15} \times N_A$ (Avogadro constant) = 121 μ mol

Let us consider the silane covered the surface of all the NPs completely, then in 100mg NPs the amount of amines on the surface of NPs =121 μ mol /3=40 μ mol (one sliane molecule has 1 amine and consumes 3 oxygen ion in the outer layer)

For the fluorescence labelling, the molar ratio between the fluorophore Alexa 488 and the silane is 1 to 100.

This means for 100 mg silanised CeO_{2-x} NPs,

the required weight of Alexa 488 = 643.41 g/mol×($40 \times 10^{-6}/100$) mol =257 µg



Fig. S8: Size distribution of the CeO₂ NPS as measured by Dynamic Light Scattering