Supporting Information for

(Hydro)peroxide Ligands on Colloidal Cerium Oxide Nanoparticles

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Materials and Instrumentation.

All chemicals and solvents were purchased commercially and used without further purification. Anhydrous H₂O₂ was prepared from 50% aqueous H₂O₂ by published procedure¹ and stored as DCM-d₂ solution over MgClO₄. The concentration was measured by ¹H NMR using hexamethyl benzene as internal standard. ¹H and ³¹P NMR spectra were collected on A500a Agilent DD2 500 MHz spectrometer using TMS and 85% H₃PO₄ respectively as external standards. UV-vis spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer using 1 cm quartz cuvettes. FT–IR spectra were measured as solid samples on Bruker Alpha IR spectrometer with ATR attachment. Powder X-ray diffraction (PXRD) patterns were obtained on Bruker D8 Focus Powder X-Ray Diffractometer with sealed Cu-anode tube ($\lambda = 0.154$ nm) as X-ray source. TEM images were obtained on FEI Tecnai Osiris 200kV transmission electron microscope operating at 200kV. 5 µL of 1mM nanoceria solution in cyclohexane were deposited on a lacey carbon 400 mesh Cu grid (Ted Pella, Inc.). The size and the distribution of NPs were obtained by counting >1000 nanocrystalline particles using ImageJ software. Inductively-coupled plasma mass spectroscopy (ICP-MS) was carried out using a Perkin Elmer ICP-MS Elan DRC-e instrument.

Nanoparticle Preparation.

Ceria NPs were synthesyzed following a published procedure with minor modifications.² Sodium oleate ($C_{17}H_{33}COONa$, STREM, 99%, 1.06 g, 3.5 mmol) was dissolved in 15 mL of warm double distilled water (DDW), then cooled to room temperature and added dropwise to a stirring solution of 1.92 g (3.5 mmol) ammonium cerium nitrate ((NH₄)₂Ce(NO₃)₆, Sigma Aldrich, 99.9%) in 15 mL DDW. Subsequently, 4.5 mL of aqueous ammonia solution (28 wt%, Sigma Aldrich) was added dropwise under vigorous stirring to the reaction mixture. After 30 minutes of stirring, the crystalline products were collected by centrifugation (6500 rpm for 15 min), followed by decantation, and washed twice with distilled water to remove excess starting materials. After the last centrifugation and decantation, pale-brown solid materials were placed in a glass vial and dried at 90 °C for 24 h in tube furnace under air. The resulting brown solid was brought into an N₂ glovebox, and dissolved in DCM, although some small amount of precipitate remained. These precipitates were removed by centrifugation at 6500 rpm for 10 min. Then, clear brown solution was stored under N₂ in the freezer (-35 °C).

Calculation of Cerium Concentration.

Cerium concentration was determined using ICP-MS analysis. An aliquot (0.1 mL) of room temperature CeO_{2-x} NPs in DCM was dried under vacuum, and the sample was calcined at 400 °C for 4 hours to remove residual organic matter. After calcination, samples were digested in a 1 mL mixture of 1:1 concentrated H₂SO₄ and 50% aqueous H₂O₂, and diluted to a volume of 10 mL with DDW in a volumetric flask. Five samples were then prepared for ICP analysis and the concentration determined by the method of standard additions.

Calculation of Nanoparticle Concentration.

The average volume of each CeO_{2-x} NP was calculated assuming a spherical NP with V = $4/_3\pi r^3$, where r is the radius determined from the TEM analysis (see above). Then the average mass of the NP is given by m=d*V, where d – density (d = 7.13 g/cm³ for cerium oxide nanopowder).³ Then, from the measured concentration of Ce atoms in solution (ICP-MS, above), the concentration of cerium oxide in mass per volume is known (g/L, using formula weight of 172.1 g/mol), and by dividing this to a mass of a single NP and Avogadro's number we can calculate the concentration of ceria NPs in that solution. At last, the ratio between the concentration of cerium atoms and the ceria NPs in solution will give us the number of Ce atoms per NP.

Characterization of Cerium Oxide Nanoparticles.



Figure S1. Powder X-Ray diffraction pattern of oleate-capped CeO_{2-x} NCs, evaporated from DCM solution. Scan rate 0.3 deg/min. The standard data for CeO_2 (JCPDS card 34-0394) presented in red.



Figure S2. TEM image (left) and size distribution histogram (right) of oleate-capped CeO_{2-x} NCs.

UV-Visible Studies of Addition of H₂O₂ to Nanoceria.

All UV-Visible studies were performed at room temperature on 0.25 mM stirred cerium oxide NP solutions in DCM upon in situ additions of different amounts of H_2O_2 , as stated in the text. The reactions were followed during first 1000 sec, with spectra taken every 10 sec (to obtain kinetic profiles). Each time different amount of H_2O_2 was added to a new solution of nanoceria.



Figure S3. Correlation between delta OD at λ_1 (285nm) vs. λ_2 (380 nm) at different amounts of H₂O₂ added (from the Fig. 1B). As can be seen from the figure, there is no linear correlation between the two wavelengths.



Figure S4. Kinetic profiles for the changes in optical density for 285 nm and 380 nm, in 0.25 mM nanoceria upon addition of 0.25 mM H_2O_2 (The process shown in Fig. 1A).



Figure S5. The optical spectra of CeO_{2-x} NPs in 2 mL cyclohexane (CHX) (0.25 mM) upon addition of ^tBuOOH (2.5 mM). The initial spectrum (sky blue, lowest) is immediately prior to the addition of ^tBuOOH.

¹H NMR Studies of Addition of H₂O₂ to Nanoceria.

All the ¹H NMR spectra were measured as DCM-d₂ solutions at room temperature. The amounts of nanoceria used in each experiment refer to the amount of Ce atoms, measured by ICP.



Figure S6. ¹H NMR spectrum of free oleic acid, 50 mM solution in DCM- d_2 , along with the integration and the assignment of the peaks.

Calculation of the Amount of Capping Ligand.

The amount of the oleate capping ligand was calculated from the total integrated area under the broad visible peaks of the aliphatic region, Fig. S7. The integration of the separated peaks is less effective in this case, since they are very broad and mostly overlap with the big peak at δ = 1.27 that corresponds to 20 aliphatic H atoms. The resulting amount of the capping ligand was 8.2 µmol of oleate in solution of 8 µmol of nanoceria, Fig. S7, which is, within an error, equivalent to the amount of Ce atoms. Therefore, roughly 180 oleate ligands are associated with every NC in solution (see the calculation of NP concentration, above).



Figure S7. ¹H NMR spectrum of ceria NPs with internal standard. 0.5 μ mol hexamethyl benzene (HMB), 8 μ mol ceria, DCM-d₂.





Figure S8. ¹H NMR spectra of ceria NPs upon addition of various amounts of H_2O_2 . (A) 0 µmol; (B) 2 µmol; (C) 4 µmol; (D) 8 µmol; (E) 16 µmol; (F) 32 µmol. 8 µmol nanoceria, 0.5 µmol hexamethyl benzene (HMB), DCM-d₂.

Discussion of the amount of capping ligand being released.

The estimation of the amount of released ligand was done by calculating the difference in integrated intensity of selected H atoms during the course of addition of H_2O_2 . Since the total amount of ligands shouldn't change upon their displacement, the increase in the integrated intensity is proportional to the increase in amount of free ligand and can be calculated as percent of total ligand present at the end. The most outstanding peak belongs to the $C_{\alpha}H_2$ at δ =2.3, however it can be detectable only after addition of 0.5 equivalents H_2O_2 . Hence, two additional resonances were examined, of allylic CH₂ groups (δ =2.02) and of primary CH₃ group (δ =0.88). Both were compared with the $C_{\alpha}H_2$ over the course of partial change, and no significant difference was observed.

Notably, the calculated amount of the total ligand in solution after the last addition (based on either $C_{\alpha}H_2$ or CH_3 groups) is equal, within an error, to the amount of ligand calculated from the total integrated intensity before the addition of H_2O_2 (above).

H ₂ O ₂ eq	H-α	H-allyl	H-Met	HMB
0	ND	2.18	1.72	1.00
0.25	ND	2.32	1.84	1.00
0.5	1.24	2.42	1.93	1.00
1	1.41	2.69	2.18	1.00
2	1.66	3.12	2.53	1.00
4	2.01	3.90	3.02	1.00
Partial increase, % $0.5 \rightarrow 4 \text{ eq}$	100%*(2.01-1.24)/2.01 = 38.3%	100%*(3.9-2.42)/3.9 = 37.9%	100%*(3.02-1.93)/3.02 = 36.1%	-
Total increase, % 0 → 4 eq	-	100%*(3.9-2.18)/3.9 = 44.1%	100%*(3.02-1.72)/3.02 = 43.0%	-



Figure S9. ¹H NMR spectrum of oleate-capped ceria NPs with free oleic acid added. 10 μ mol ceria, 10 μ mol free oleic acid, DCM- d_2 .

FTIR spectra of nanoceria before and after the addition of water.



Figure S10. FTIR spectra of oleate-capped ceria NPs before (black) and after (green) the addition of H_2O . Both samples were precipitated from solution, washed and dried *in vacuo* before solid-state IR spectra were taken.

Stability of ceria NPs and reactions with PPh₃

The peroxo/hydroperoxo groups are quite stable. They degrade spontaneously only after several days at room temperature or only after several weeks at 4°C (as indicated by increased optical density around 400 nm). All the reactions were followed under ambient conditions in air and no change in stability was observed under dry atmosphere in N₂ box.

No products of ligand oxidation were observed by ¹H NMR.

 PPh_3 was prepared as DCM solution and stored under N_2 . Nanoceria itself does not react with PPh_3 . All reactions were run at room temperature.



Figure S11. ³¹P NMR spectra after addition of PPh₃ to H_2O_2 -treated nanoceria powder. 5 µmol PPh₃, 1:1 THF/DCM-d₂, solids obtained from reaction of 8 µmol ceria with 24 µmol H_2O_2 , followed by precipitation and several washing steps. According to integration, 2 µmol of Ph₃P=O was formed.



Figure S12. UV-Visible spectra for the reaction of PPh₃ with H_2O_2 -treated nanoceria solution. Starting ceria spectrum shown in green. Ceria after reaction with H_2O_2 is red, 1 hour and 24 hours after addition of PPh₃ are shown in blue and purple, respectively. 0.5 µmol ceria, 0.5 µmol H_2O_2 , 2 µmol PPh₃, 2 mL DCM.

References

- 1 A. G. DiPasquale and J. M. Mayer, J. Am. Chem. Soc., 2008, **130**, 1812.
- 2 T. Taniguchi, T. Watanabe, N. Sakamoto, N. Matsushita and M. Yoshimura, *Cryst. Growth Des.*, 2008, **8**, 3725.
- 3 (a) Nanoceria density d_{nano} = 7.13 g/cm³, http://www.us-nano.com; Sigma-Aldrich catalog, CAS Number 1306-38-3; (b) Cerium dioxide bulk density, d_{bulk} = 7.65 g/cm³, https://www.webelements.com/compounds/cerium/cerium dioxide.html