Electronic Supplementary Information

Photoreductive Dissolution of Cerium Oxide Nanoparticles and Their Size-Dependent Absorption Properties

Natasha W. Pettinger, Jennifer M. Empey, Sascha Froebel, and Bern Kohler*

Department of Chemistry and Biochemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, United States

[†] Permanent address: Covestro Deutschland AG, Kaiser-Wilhelm-Allee 60, 51373 Leverkusen, Germany

*Corresponding Author: Bern Kohler, kohler.40@osu.edu, Tel: +1 614-688-2635

1. Quantum Yield Measurements: Additional Details

The quantum yield, Φ , for the photoreductive dissolution of CeO₂ is defined as follows,

$$\Phi = \frac{\# \text{ of } Ce^{3+} \text{ ions released}}{\# \text{ of photons absorbed by } CeO_2} = \frac{\# \text{ of } CeO_2 \text{ formula units reduced}}{\# \text{ of photons absorbed by } CeO_2}.$$
 (eq. SI-1)

The number of Ce^{3+} ions released to the solvent is assumed to equal the number of CeO_2 units that are lost from the particle. The latter quantity is determined after each irradiation interval from the change in absorbance at 290 nm and the absorption coefficient per mole of CeO_2 formula units of 4100 ± 200 M⁻¹ cm⁻¹ for ceria-AA or 3800 ± 1300 M⁻¹ cm⁻¹ for ceria-CAN, determined as discussed below. Because a hydrated Ce^{3+} ion absorbs very weakly at 290 nm compared to the absorption of CeO_2 per formula unit, the decrease in absorbance was assumed to arise solely from a decrease in the number of CeO_2 formula units in the nanoparticle. As shown in Figure 3, the normalized difference spectra recorded during irradiation agree at all times for the ceria-AA sample and they agree up until approximately 50% of the cerium ions in the ceria-CAN sample have been ejected to the solvent (Figure 3 in the main text). Radicals formed when glycerol is oxidized by holes in the nanoparticle are unlikely to absorb strongly at 290 nm, the wavelength used to determine the quantum yields, but if they did the quantum yield would be underestimated.

The number of incident photons was estimated from the power measured at the sample position with a power meter. Due to the high absorbance (~3 in a 1 cm path length) of the suspensions virtually all photons passing through the front face of the cuvette were absorbed by the nanoceria, and it was not necessary to correct for the transmission of the incident beam. Furthermore, the very small size (< 10 nm) of the vast majority of nanoparticles means that scattering can be neglected and the solutions were non-turbid and optically clear. To estimate the actual power incident on the solution, the measured power was corrected for Fresnel (reflection)

losses from the front window in the fused silica cuvette. Using a fused silica window with the same thickness as the front window of the cuvette, the transmission was measured to be 90.3% and 90.6% at 265 nm and 300 nm, respectively.

The absorbance measured as a function of irradiation time was used to graph the number of Ce⁺⁻ ions ejected to the solvent vs. the number of absorbed photons. The initial slope of the line, corresponding to an absorbance decrease of never more than 5%, was used to calculate the quantum yield using eq. SI-1. Identical quantum yields within experimental uncertainty were measured when the aging time of the ceria-CAN suspension was varied between 1 day and 4 months. Quantum yields were calculated from a minimum of three trials.

Determination of the molar absorption coefficient of fully oxidized nanoceria. Ceria nanoparticles were completely dissolved to Ce^{3+} (aq) by UV irradiation and then the literature absorption coefficient of the latter species (750 ± 70 M⁺cm⁺ at 254 nm)⁺ was used to estimate the original quantity of Ce present. For ceria-AA, a value of 4100 ± 200 M⁻¹ cm⁻¹ was determined at 290 nm (λ_{max}), and this value was used to scale the measured UV-vis absorption spectrum to yield the red curve in Figure 1 in the main text. The absorption coefficient of the ceria-CAN nanoparticles was determined using the same method to be 3800 ± 1300 M⁻¹ cm⁻¹ (blue curve, Figure 1). In ref.², the absorption coefficient of a sample of ceria-CAN nanoparticles was estimated from the mass of the cerium(IV) salt used to synthesize ceria-CAN nanoparticles to be 3800 ± 200 M⁻¹ cm⁻¹ in good agreement with the molar absorption coefficient determined here by complete photochemical dissolution.

2. Scherrer Analysis of XRD Peak Broadening

The XRD characterization methods for the ceria-CAN particles is described in detail in ref.². To characterize the ceria-AA particles, ceria-AA powder was isolated via rotary evaporation at 35 °C for XRD analysis (D8 Advance X-Ray Powder Diffractometer, Bruker).

The XRD peak broadening of the ceria-AA particles was analyzed using the Scherrer equation,³

$$D = \frac{\kappa\lambda}{\beta_i \cos\theta}$$

Where *D* is the diameter of the crystal grain, κ is a dimensionless shape factor,⁴ λ is the x-ray wavelength (0.154 nm), β_i is the integral width of the peaks, and θ is the Bragg angle in radians. The XRD pattern was fit to 8 Gaussian functions using the Multipeak Fitting 2 package in Igor Pro to obtain the integral peak widths of each peak (Figure S1). The calculated particle sizes are reported in Table S1.



Figure S1. XRD pattern for ceria-AA (a) and ceria-CAN (b) particles (grey lines) and Gaussian fits to the peaks (red lines).

Table S1. Fit parameters and calculated crystallite sizes for the ceria-AA (a) and ceria-CAN particles (b).

hkl	ĸ ^a	eta_i	heta	$D_{\text{cube}} (\text{nm})$	D_{sphere} (nm)
111	1.1547	0.02840	0.4936	6.4561	5.9825
200	1.0000	0.02338	0.5715	6.8647	7.3453
220	1.0607	0.03097	0.8216	5.7523	5.8028
311	1.1359	0.02988	0.9761	6.6287	6.2441
222	1.1547	0.03204	1.0169	6.3546	5.8885
400	1.0000	0.02579	1.2038	7.2434	7.7505
331	1.1262	0.03221	1.3303	6.8444	6.5028
420	1.0733	0.02463	1.3678	8.6567	8.6301
			Average:	6.9 ± 0.7	6.8 ± 0.8
(b)	Ceria-CAN				
hkl	ĸ ^a	eta_i	heta	$D_{\text{cube}} (\text{nm})$	$D_{\text{sphere}} (\text{nm})$
111	1.1547	0.06858	0.4969	2.9497	2.5545
200	1.0000	0.05602	0.5739	3.2733	3.2733
220	1.0607	0.07261	0.8255	3.3173	3.1275
311	1.1359	0.08602	0.9848	3.6771	3.2371
			Average:	3.3 ± 0.3	3.1 ± 0.3

(a) Ceria-AA

 ${}^{a}\kappa$ values are for cubic particles from ref. ⁴. κ values for all lattice planes for spherical particles are equal to 1. Uncertainties are 95% confidence intervals estimated using the Student's *t*-distribution.

3. TEM Images of Ceria-AA and Ceria-CAN Particles.

TEM grid preparation and imaging methods for the ceria-CAN particles are described in ref. ², while a \sim 30 µM sample of ceria-AA in 6.7 mM HClO₄ was dropped onto a thin carbon film grid for TEM imaging (Tecnai G² F30 TWIN TEM microscope, FEI).



Figure S2. TEM images of ceria-AA (a) and ceria-CAN (b) nanoparticles.



Figure S3. HR-TEM images of ceria-CAN showing polycrystalline nanoparticles with irregular shapes.



Figure S4. HR-TEM images of ceria-AA showing the particle crystallinity and irregular crystallite shapes.

4. Absorption Spectra of Ceria-CAN after UV Irradiation



Figure S5. Absorption spectra recorded after UV irradiation of ceria-CAN nanoparticles in pH 2 aqueous suspension for the times indicated (open circles) and linear combinations of the initial ceria-CAN spectrum (0 min) and Ce(ClO₄)₃ in water (solid curves).

5. TEM Images of irradiated and nonirradiated nanoparticles: Ceria-AA

Ceria-AA in pH 2 HClO₄ was irradiated in a carousel photoreactor equipped with mercury arc lamps in a 1 cm cuvette while stirring until 90% of the ceria absorbance at 290 nm disappeared. A \sim 30 μ M sample was then dropped onto a thin carbon film grid and imaged using a Tecnai G² F30 TWIN TEM microscope (FEI).



Figure S6. Representative TEM images of unirradiated ceria-AA (a) and ceria-AA after 90% of the Ce ions have been released as aqueous Ce^{3+} (b) used to determine particle sizes.



Figure S7. Particle diameters of the ceria-AA particles before irradiation (a) and after the absorbance of the solution at 289 nm decreased by 90% due to dissolution of Ce^{3+} (b). Particles were sized manually using the Image-J software. The mean particle diameter decreased from 5.7 nm to 3.6 nm.

6. TEM Images of irradiated and nonirradiated nanoparticles: Ceria-CAN

HR-TEM images of irradiated ceria-CAN particles were recorded using an image-corrected TitanTM 60-300 (S)TEM operated at 300 kV. Ceria-CAN samples were prepared by dissolving cerium(IV) ammonium nitrate into water to make a solution that was 0.3 mM in Ce(IV). This solution was allowed to age for one day and the nanoparticle suspension was then exposed to UV irradiation in the mercury lamp photoreactor until the initial absorbance had decreased by two thirds. Acid was not added to buffer the pH during UV-induced dissolution.

The irradiated suspension was then diluted 100-fold and pipetted onto ultrathin carbon TEM grids (Cu 400 mesh, UL). The excess liquid was wicked away with a laboratory tissue and the grid was allowed to dry in a desiccator under light vacuum for 15 minutes. Images of the nonirradiated ceria-CAN particles were recorded as described in ref.².



Figure S8. Representative HR-TEM images of unirradiated ceria-CAN (a, b) and ceria-CAN after 67% of Ce ions have been released as aqueous Ce^{3+} (c, d) used to determine crystallite sizes. The sample pH was not held fixed during irradiation, which may have led to the agglomeration observed in the images above. For better comparison, agglomerated nonirradiated ceria-CAN particles are shown to match the agglomeration state of the irradiated particles.



Figure S9. Crystallite diameters of the ceria-CAN particles before irradiation (a) and after 67% of the nanoparticle absorbance was converted to the absorbance of aqueous Ce^{3+} (b) measured from HR-TEM images using Image-J software. The mean crystallite diameter decreased from 3.1 nm to 2.0 nm.

7. Red-shifting of the CeO₂ absorption onset upon adsorption of glycerol



Figure S10. (a) Suspending CeO₂-CAN in water containing 1 M glycerol (yellow curve) leads to a slight red shift in the absorption onset compared to a suspension of CeO₂-CAN in water (blue curve). On the other hand, there is barely any change in absorbance by CeO₂-AA upon addition of 1 M glycerol (b).

8. Number of Ce atoms per nanoparticle

The number of Ce atoms in the two nanoparticles studied were calculated from the average crystallite diameters (from Scherrer analysis) and the CeO₂ lattice parameter of a = 0.5412 nm reported in ref. ⁵. Because CeO₂ crystallizes in the fluorite crystal structure, there are 8 oxygen atoms and 4 cerium atoms per cubic unit cell, which has a volume of 0.1585 nm³. All calculations were performed assuming spherical particles. The results of these calculations are in Table S2 below.

Table S2. Estimates of total Ce ions and Ce ions on the surface of the two nanoceria samples.

	$CeO_2\text{-}CAN (3.0 \text{ nm } \emptyset)$	$CeO_2\text{-}AA \ (6.8 \text{ nm } \emptyset)$
Ce ions per crystallite	360	4,200
Ce ions on crystallite surface	190 ^{<i>a</i>} , 140 ^b	990 ^{<i>a</i>} , 700 ^b
% of Ce ions on crystallite surface	53% ^{<i>a</i>} , 39% ^{<i>b</i>}	24% ^{<i>a</i>} , 17% ^{<i>b</i>}

^{*a*} Assuming only 100 facets.

^bAssuming only 110 facets.

9. References

- (1) Heidt, L. J.; Smith, M. E. Quantum Yields of the Photochemical Reduction of Ceric Ions by Water and Evidence for the Dimerization of Ceric Ions. *J. Am. Chem. Soc.* **1948**, *70*, 2476-2481.
- (2) Pettinger, N. W.; Williams, R. E. A.; Chen, J.; Kohler, B. Crystallization Kinetics of Cerium Oxide Nanoparticles Formed by Spontaneous, Room-Temperature Hydrolysis of Cerium(IV) Ammonium Nitrate in Light and Heavy Water. *Phys. Chem. Chem. Phys.* 2017, 19, 3523-3531.
- (3) Patterson, A. L. The Scherrer Formula for X-Ray Particle Size Determination. *Phys. Rev.* **1939**, *56*, 978-982.
- (4) Langford, J. I.; Wilson, A. J. C. Scherrer after 60 Years Survey and Some New Results in Determination of Crystallite Size. *J. Appl. Crystallography* **1978**, *11*, 102-113.
- Paun, C.; Safonova, O. V.; Szlachetko, J.; Abdala, P. M.; Nachtegaal, M.; Sa, J.; Kleymenov, E.; Cervellino, A.; Krumeich, F.; van Bokhoven, J. A. Polyhedral CeO₂ Nanoparticles: Size-Dependent Geometrical and Electronic Structure. *J. Phys. Chem. C* 2012, *116*, 7312-7317.