

Supplementary Information

Crystallization Kinetics of Cerium Oxide Nanoparticles formed by Spontaneous, Room-temperature Hydrolysis of Cerium(IV) Ammonium Nitrate in Light and Heavy Water

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1. Apparent molar absorption coefficients

Apparent molar absorption coefficients for CAN in H₂O after 24 h of aging were estimated from the final absorption spectrum and the mass of added solute. In detail, 90 mg of CAN were dissolved in 50 mL of H₂O to obtain a final solution concentration of 3.3 mM. Absorption spectra were recorded in a 1 mm cuvette after 2, 6, and 24 h. The absorption spectrum changed minimally between 6 and 24 h, and a value of $3800 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$ was estimated at 289 nm (blue curve in Fig. 2). Following a similar procedure, the apparent molar absorption coefficient of CAN in 1 M HClO₄ solution was estimated to be $1,930 \pm 60 \text{ M}^{-1} \text{ cm}^{-1}$ at 291 nm (gold curve in Fig. 2). Note that uncertainties reported here and in the main text are twice the standard uncertainty (2σ). In Fig. 2, the absorption spectra of CAN in D₂O at 1 min and 24 hrs were scaled to have the same absorbance at the isosbestic wavelength of 368 nm.

2. XRD sample preparation and analysis

The nanoparticles were isolated for power XRD characterization by adding 20 mL of 1 M NaOH to 1 L of 4.1 mM CAN in H₂O solution that had been aged for five days. The solution pH before adding base was 1.8. A cloudy white precipitate formed immediately and the pH increased to 9.2. The cloudy white precipitate was filtered, rinsed, and dried in the air for three days to yield pale yellow crystals. A UV-Vis absorption spectrum of the filtrate matched that of nitrate ion and there was no evidence of absorption due to cerium. The pale yellow CeO₂ crystals were ground to a powder using a mortar and pestle and then mixed with ethanol to make a slurry. This was pipetted onto a glass microscope slide and then allowed to dry before the XRD patterns were measured (Fig. S1).

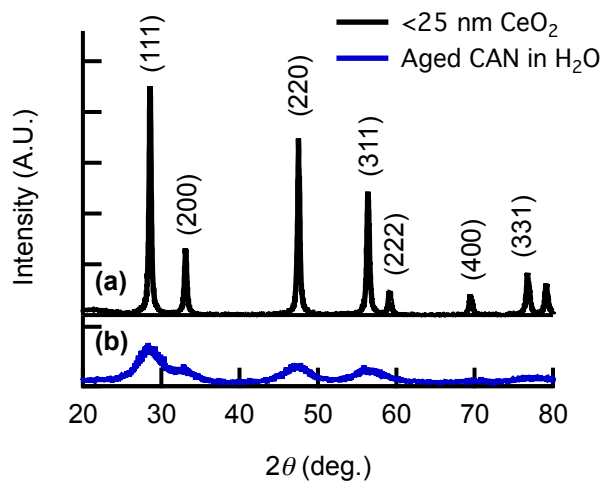


Fig. S1 XRD patterns of (a) commercial <25 nm nanoparticles and (b) ceria prepared by aging CAN in water. Peaks are labeled in panel (a) by the various CeO₂ crystal planes.

The 111, 200, 220, and 311 XRD peaks were analyzed using the Scherrer equation, $D = \frac{\kappa\lambda}{\beta_i \cos \theta}$ ^{1,2} to estimate the crystal grain size, where D is the diameter of the crystal grain, κ is a dimensionless shape factor ($\kappa = 1.07$ for sphere; $\kappa_{111} = 1.1547$, $\kappa_{200} = 1.0000$, $\kappa_{220} = 1.0607$, $\kappa_{311} = 1.1359$ for cube),² λ is the x-ray wavelength (0.154 nm for Cu K α), β_i is the integral width of the peaks, and θ is the Bragg angle. A diameter of 3.8 ± 0.3 nm was calculated assuming cubic nanocrystals, and a diameter of 3.7 ± 0.4 nm was calculated assuming spherical nanocrystals. Due to the large peak widths we assume that instrumental broadening is negligible. The integral peak widths were calculated by fitting to Gaussian functions using the Igor Pro program.

3. UV-Vis spectrum of the resuspended XRD sample

The precipitate obtained for XRD measurements was sonicated and resuspended in 1.0 M HClO₄. The resulting UV-Vis spectrum measured in a 1.0 mm path length cuvette (Fig. S2) closely matches the spectrum of an aged CAN in H₂O solution except at wavelengths shorter than 275 nm where the differences are attributed to absorption by nitrate ions present in the aged CAN in water solution, but absent in the washed precipitate. The agreement at longer wavelengths shows that the re-suspended particles have the same spectrum as the particles originally present in the aged CAN in water solution prior to precipitation with base. This demonstrates that even if precipitation causes particles to form by a different mechanism, the particles are nonetheless highly similar on the basis of their absorption characteristics.

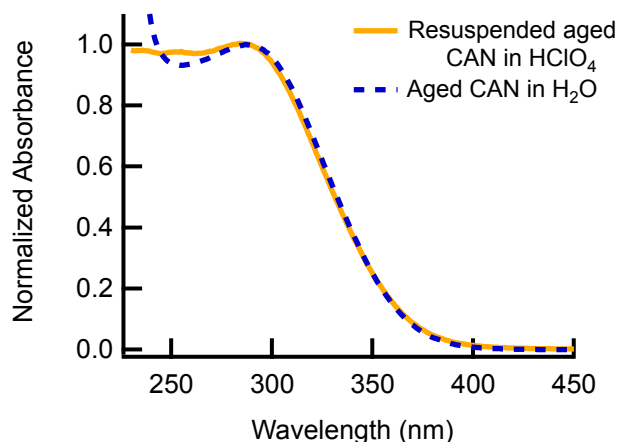


Fig. S2 UV-vis spectra of aged CAN in H₂O (dashed blue curve) and of the precipitate obtained by adding NaOH to aged CAN in H₂O, followed by washing, drying, and resuspension in 1.0 M HClO₄ (gold curve). The weak bump at 255 nm in the latter spectrum is assigned to a small amount of Ce³⁺(aq) produced by photoreduction of the nanoparticles by laboratory lights. Absorption at wavelengths shorter than 250 nm by aged CAN in H₂O (dashed blue curve) is due to NO₃⁻ counterions, which are not present in the resuspended sample (gold curve).

4. One-day-old CAN in H₂O TEM

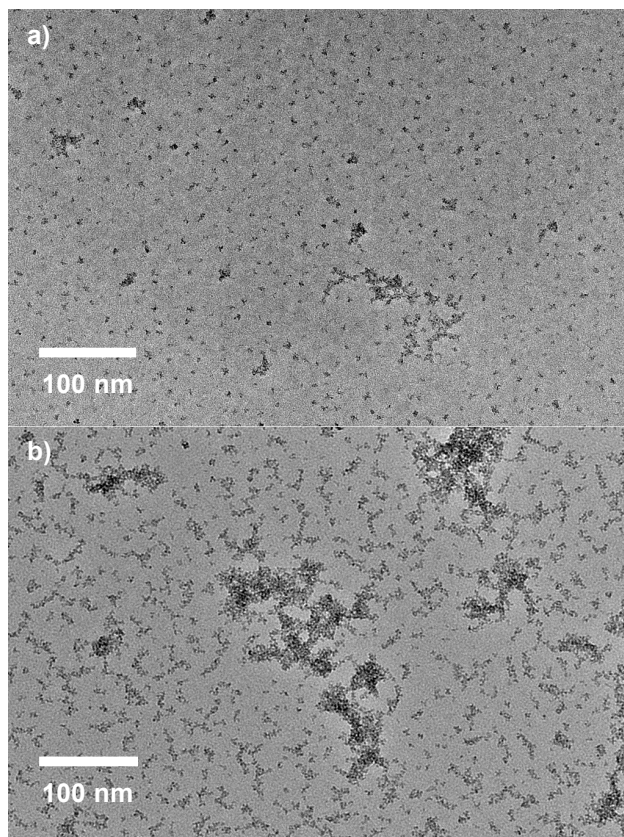


Fig. S3 TEM images of aged CAN in H₂O. The images were taken of different areas of the same TEM grid. While b) shows an area with higher nanoparticle coverage and extensive clustering, a) shows an area with well-dispersed particles. Fig. 3 in the main text shows HR-TEM images of nanoparticles in area a).

5. Transient absorption calculations

The initial precursor absorbance, $A_{P, 266 \text{ nm}}(t = 0)$, and final nanocrystal absorbance, $A_{\text{CeO}_2, 266 \text{ nm}}(t = \infty)$, were estimated from the measured absorbance of 0.75 at 266 nm after 4 minutes of aging using the second-order kinetic model in the following form,

$$A_{266 \text{ nm}}(t) = \frac{A_{P, 266 \text{ nm}}(t = 0) \left[t_{1/2} + t \cdot \frac{A_{\text{CeO}_2, 266 \text{ nm}}(t = \infty)}{A_{P, 266 \text{ nm}}(t = 0)} \right]}{t_{1/2} + t} \quad (\text{S1})$$

A $t_{1/2}$ of 18 min was used for CAN in D₂O and a value of 2.79 was used for the ratio of $A_{\text{CeO}_2, 266 \text{ nm}}(t = \infty)$ to $A_{P, 266 \text{ nm}}(t = 0)$ at 266 nm. The calculated absorbances were $A_{P, 266 \text{ nm}}(t = 0) = 0.57$ and $A_{\text{CeO}_2, 266 \text{ nm}}(t = \infty) = 1.58$. These values were used in eq. 1 from the main text to generate $A_{266 \text{ nm}}(t)$ in column 2 of Table S1. The calculated absorbance matched well with the measured absorbance after 8 minutes ($A_{266 \text{ nm}, \text{ calc.}} = 0.88$ vs. $A_{266 \text{ nm}, \text{ meas.}} = 0.85$).

The first transient absorption scan was started approximately one minute after mixing. Each TA trace corresponds to one scan of the optical delay line from negative to positive delay times. It took 9 minutes to acquire each scan. The absorbance values were estimated 2 minutes into each 9-minute scan (1st column of Table S1), corresponding to when the TA signal near time zero was measured. In calculating the absorbances at 266 nm (second and third columns of Table S1), we neglected any reduction of Ce^{IV} resulting from pump laser excitation. These absorbance values were used to calculate a relative ΔA in the fourth column of Table S1. The final column reports the experimental transient absorption amplitude values at 500 fs of the 266 nm pump, 350 nm probe experiments shown in Fig. 5 of the main text.

Table S1. Transient Absorption Amplitudes

Aging time / min	A^a	$A_{\text{CeO}_2}^b$	$\Delta A \propto (1 - 10^{-A}) \frac{A_{\text{CeO}_2}}{A}$	ΔA_{exp}^c
3	0.71	0.23	0.26	0.77
12	0.97	0.63	0.58	1.50
21	1.11	0.85	0.71	2.09
30	1.20	0.99	0.77	2.58

^a Absorbance values in this column and in columns 3 and 4 are measured at the pump wavelength of 266 nm.

^b $A_{\text{CeO}_2}(t) = \frac{A_{\text{CeO}_2}(\infty) \cdot t}{t_{1/2} + t}$ with $A_{\text{CeO}_2}(\infty) = 1.58$, $t_{1/2} = 18$ min, and the aging time t given in column 1.

^c Experimental TA signal amplitudes ($\times 10^3$) at 500 fs for the 266 nm pump, 350 nm probe data (Fig. 7, main text).

6. pH changes

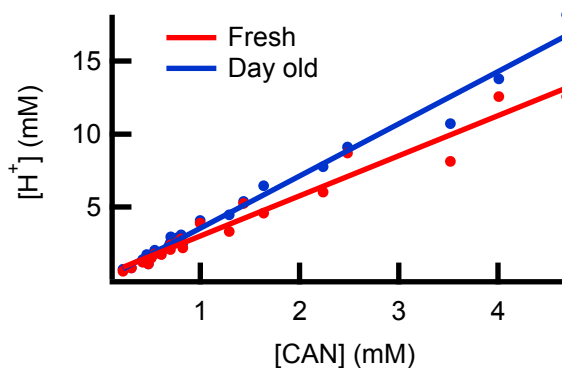


Fig. S4 The H^+ vs. CAN concentration of fresh (red) and day-old (blue) CAN solutions. The initial pH was measured within the first 30 s after dissolution. The CAN concentration, $[\text{CAN}]$, was calculated from the absorbance of the aged solution using our measured absorption coefficients. The pH was fit to $[\text{H}^+] = m[\text{CAN}] + b$ in order to calculate m , the number of protons released per Ce(IV) ion. Initially, 2.8 ± 0.3 (2σ) protons were released per Ce(IV). After one day, this increased to 3.6 ± 0.2 (2σ).

7. Spectrophotometer corrections

Because approximately 1 minute is needed to record a single absorption spectrum with our spectrophotometer and because aging occurs on a similar timescale, the spectra shown in Fig. 1 were corrected for the scan speed of the spectrophotometer. Using the actual time of each absorbance measurement, kinetic traces were generated at wavelengths 5 nm apart. The spectra at the times shown in the fig. captions were then obtained from these traces by interpolation.

8. References

1. Patterson, A. L. The Scherrer formula for x-ray particle size determination. *Phys. Rev.* **1939**, *56*, 978-982.
2. Langford, J. I. & Wilson, A. J. C. Scherrer After 60 Years - Survey And Some New Results In Determination Of Crystallite Size. *J. Appl. Cryst.* **1978**, *11*, 102-113.