THE NON-CLASSICAL CRYSTALLIZATION OF CeO$_2$ NANOPARTICLES

by

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To mom, dad, Lincoln, and Ben
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LIST OF ABBREVIATIONS

CAN: Cerium(IV) ammonium nitrate, $(\text{NH}_4)_2\text{Ce(NO}_3)_6$
HR-TEM: High-resolution transmission electron microscopy
EELS: Electron energy loss spectrum
STEM: Scanning transmission electron microscopy
HAADF-STEM: High angle annular dark field scanning transmission electron microscopy
FFT: Fast Fourier transform
XRD: X-ray diffraction
ABSTRACT

Over the past couple of decades, new in situ characterization techniques such as liquid-cell TEM have revitalized efforts to understand the mechanisms of crystal formation. The spontaneous, room-temperature crystallization of CeO$_2$ from mM concentrations of cerium(IV) ammonium nitrate (CAN) in water was studied using UV-Vis absorption spectroscopy, transient absorption spectroscopy, x-ray diffraction, and high-resolution transmission electron microscopy. Characterization of the final nanoparticles revealed polycrystalline CeO$_2$ nanoparticles that are stable from aggregation over a period of months. Most of the nanoparticles are between 3 and 9 nm, although a small proportion of larger particles between 10 and 150 nm were also detected. Crystallization is accompanied by a large change in absorption which can be modeled by the presence of just two species. These species are argued to be an amorphous, hydrated intermediate that is converted to nanocrystalline CeO$_2$ over a period of minutes to hours. The rate-limiting step of the amorphous to crystalline transition involves a proton transfer reaction, as evidenced by a solvent kinetic isotope effect of $\sim$10. Ultrafast transient absorption measurements show a drastic difference between the optical properties of the crystalline nanoparticles and the amorphous precursors. This system is an excellent model system for studying non-classical crystallization because the minutes-to-hours time scale and the small sizes of the nanoparticles and precursors allow for in situ observation of crystallization using steady-state absorption spectroscopy. This system would also lend itself well to characterization by other techniques such as liquid-cell TEM or x-ray absorption spectroscopy.
CHAPTER ONE

INTRODUCTION

The research presented in this dissertation began as an effort to clarify the mechanism of the oxidation of water by Ce$^{4+}$. Baur observed in 1908 that oxygen evolution accompanies the photoreduction of Ce$^{4+}$ to Ce$^{3+}$ in aqueous Ce$^{4+}$ solutions.\(^1\) This result was confirmed in 1937 by Weiss and Porret, who reported the following overall reaction upon photolysis with 254 nm light.\(^2\)

\[
4 \text{Ce}^{4+} + 2 \text{H}_2\text{O} + h\nu \rightarrow 4 \text{Ce}^{3+} + 4 \text{H}^+ + \text{O}_2 \quad (1.1)
\]

Further research over the decades measured Ce$^{4+}$ reduction as opposed to O$_2$ evolution, and resulted in a myriad of proposed mechanisms. Some attributed the photoreduction quantum yield dependence on Ce concentration to the photolysis of a Ce$^{4+}$ dimer.\(^3\)-\(^4\) The reaction mechanism for producing molecular oxygen was not described, but the authors did suggest specific dimer species (coordinated waters are omitted), including [Ce$^{IV}$–O–Ce$^{IV}$]$^{6+}$, [Ce$^{IV}$–O–Ce$^{IV}$–OH]$^{5+}$, [HO–Ce$^{IV}$–O–Ce$^{IV}$–OH]$^{4+}$, and [Ce$^{IV}_2$(µ–OH)$_2$]$^{6+}$. Other researchers concluded that O$_2$ is evolved via an ^OH intermediate produced from direct oxidation of H$_2$O (eq 1.2a),\(^5\) and suggested that H$_2$O$_2$ could also be involved (eq 1.2b and 1.2c).\(^2\)-\(^6\)

\[
\text{Ce}^{4+} \cdot \text{H}_2\text{O} + h\nu \rightarrow \text{Ce}^{3+} + \text{H}^+ + ^\text{OH} \quad (1.2a)
\]

\[
2 ^\text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (1.2b)
\]

\[
2 \text{Ce}^{4+} + \text{H}_2\text{O}_2 \rightarrow 2 \text{Ce}^{3+} + 2 \text{H}^+ + \text{O}_2 \quad (1.2c)
\]
Evans and Uri argued that 'OH is instead produced via the photooxidation of a complexed hydroxide ligand,

\[
[\text{CeOH}]^{3+} + h\nu \rightarrow \text{Ce}^{3+} + \text{H}^+ + '\text{OH}
\]

before reacting in a manner consistent with eq 1.2b and 1.2c. Ce\(^{4+}\) was proposed to be regenerated in small amounts through backreactions between 'OH or H\(_2\)O\(_2\) and Ce\(^{3+}\),\(^{2,6-7}\) and photooxidation of Ce\(^{3+}\) was shown to occur inefficiently for excitation wavelengths of 254 nm.\(^{4,8}\)

Interest in the water oxidation mechanism by Ce\(^{4+}\) has waxed and waned with the decades. However, with increased interest in photocatalytic water splitting, whereby a catalytic chemical system uses sunlight to convert water into molecular hydrogen and oxygen, understanding how simple systems oxidize water has taken on a new importance.\(^9\) Better understanding of the properties that make water oxidation possible is applicable to the rational development of an efficient water splitting system. Therefore, we originally set out to define the mechanism by which this “simple” metal center produces molecular oxygen from water.

While attempting to determine whether there is a solvent kinetic isotope effect (KIE) for the photolysis of Ce\(^{4+}\), the perplexing observation was made that the UV-visible absorption spectrum of cerium(IV) ammonium nitrate (CAN) was seemingly irreproducible, and that the differences were especially apparent when H\(_2\)O was replaced with D\(_2\)O. Upon further investigation, significant spectral changes following dissolution of CAN in water emerged as the reason for these differences in absorption, with a ten-times slower spectral evolution when CAN is dissolved in D\(_2\)O instead of H\(_2\)O. If the
solutions age for long enough (~1 hr in H₂O and ~10 hrs in D₂O), the absorption spectrum of a solution stops changing, and is furthermore identical to the absorption spectrum of any other aged CAN in water solution, regardless of isotopic substitution. In addition to the odd steady-state observations, ultrafast transient absorption measurements on cerium(IV) ammonium nitrate (CAN) in 1 M HClO₄ show a strong ground state bleach signal that decays rapidly (τ = 1.3 ps) to a constant offset. These transient absorption signals differ drastically from the longer-lived, power-law like decays of aged CAN in water.

The lack of scattering initially led us to hypothesize that the formation of a small hydrolysis product was the cause of the absorption change, but a publication by Ikeda-Ohno et al.¹⁰ showing formation of CeO₂ nanoparticles when the pH is raised above 0.5 prompted the investigation into whether the observed spectral changes were a result of the crystallization of CeO₂ nanoparticles. Following the confirmation that CeO₂ nanoparticles result from the aging of CAN in water, this research transitioned into a study focused on determining the crystallization mechanism of CeO₂ nanoparticles formed by hydrolysis of CAN.

Part of the disagreement in the water oxidation mechanism by Ce⁴⁺ (eq 1.1) is a result of difficulties in determining hydrolysis equilibria. Metal ions can act as Lewis acids and ionize water into a proton and a hydroxide ligand.

\[ \text{M}^{n+} + \text{H}_2\text{O} \rightarrow [\text{M}^{n+} - \text{OH}]^{+n-1} + \text{H}^+ \quad (1.4) \]

The [Mⁿ⁺–OH]ⁿ⁻¹ complexes can complex additional OH⁻, or go on to form poly-nuclear complexes. For those interested, Baes and Mesmer offer a thorough discussion of metal
hydrolysis in ref. 15. During the first half of the 20th century, researchers did not address the possibility of poly-nuclear complexes of Ce$^{4+}$ existing in acidic conditions.$^{2, 11-12}$ While several potentiometric and photometric studies published around 1950 did point to the existence of polynuclear hydrolysis products in acidic solutions,$^{3-4, 11, 13-15}$ problems existed in predicting the extent of polymerization and the species involved. As King and Pandow noted, the methods used to demonstrate the existence of polymeric hydrolysis products were unable to determine the identity of the polymeric species or the equilibria between them.$^3$ In addition, undetected crystallization above pH ~0.5 may have influenced predictions of hydrolysis species at lower pH values, while assumptions of the identity of the “least hydrolyzed species” may have been faulty. For example, Danesi$^{11}$ argued in 1967 that Ce$^{4+}$ is unhydrolyzed in 3 M nitrate when the pH is less than 0.7, but also noted that his data did not disprove that the least hydrolyzed species is a different Ce$^{4+}$ species such as [Ce$^{IV}$OH]$^{3+}$. His reasoning was that the Ce$^{4+}$/Ce$^{3+}$ reduction potential is independent of pH for nitric acid concentrations ranging between 0.5 and 1.0 M and Ce$^{4+}$ concentrations ranging between 10 and 100 mM. However, a recent study showed that Ce$^{4+}$ speciation favors formation of a µ$_2$-oxo-bridged dimer, [(H$_2$O)$_{6-7}$Ce$^{IV}$–O–Ce$^{IV}$](H$_2$O)$_{6-7}$]$^{6+}$, when CAN is dissolved into 3 M nitric acid for Ce$^{4+}$ concentrations between 0.04 and 0.4 M.$^{16}$ Another recent EXAFS study shows that the dominant Ce$^{4+}$ species in 2 M perchloric acid containing 0.05 M Ce$^{4+}$ is the same µ$_2$-oxo-bridged dimer, although a Ce$^{4+}$ trimer, a single hydroxo-bridged dimer, and a double hydroxo-bridged dimer were also detected.$^{17}$
Spectral and potentiometric changes that occur between pH 0.5 and 3.5, the pH above which Ce$^{4+}$ visibly precipitates, were repeatedly attributed to the formation of polynuclear complexes rather than CeO$_2$. For example, Danesi observed slow equilibration over hours to days for Ce$^{4+}$ solutions when the nitric acid concentration was less than 0.5 M,$^{11}$ and attributed it to the formation of trimers, tetramers, and dodecamers. Meanwhile, Ardon and Stein observed the formation of a “colloidal polymer” above pH 0.7, but were hesitant to make an assignment.$^{18}$ Instead, they noted that the observed colloid is likely related to dimers$^{3,13}$ and trimers$^{3}$ reported by other authors. Even as late as 2002, researchers were reporting the existence of [Ce(OH)$_x$]$^{4-x}$ in the pH range from 1 to 3.$^{19}$ Rather than monomers,$^{19}$ dimers, trimers, or polymers, Hayes et al., Ardon and Stein, and Danesi were likely synthesizing CeO$_2$ nanoparticles in a method similar to Ikeda-Ohno et al.$^{17}$

The recent EXAFS work that points to the prevalence of a μ$_2$-oxo bridged Ce$^{4+}$ dimer in acidic solutions over a 10-fold change in Ce$^{4+}$ concentration, from 0.04 to 0.4 M,$^{10,16-17}$ should not be extended without question to other concentration and pH regimes. Decades-old spectrophotometric studies show that absorbance by Ce$^{4+}$ does not follow Beer’s law when the Ce$^{4+}$ concentration is varied at constant ionic strength and proton concentration,$^{3,13}$ while photoreduction quantum yield measurements show a strong dependence on Ce$^{4+}$ concentration.$^{4}$ When coupled to the observation that CeO$_2$ is formed at a pH as low as 0.5, it becomes obvious that even after a century of research, the speciation of CeO$_2$ is still not well understood.
We faced similar barriers to understanding the process by which solvated and/or hydrolyzed Ce\(^{4+}\) ions self-organize into crystals as those faced by researchers trying to understand the photoreduction of Ce\(^{4+}\)—how can a mechanism be assigned when the initial speciation is unknown? Further difficulty is added when the initial state is unstable and unable to be isolated. However, while most systems undergo processes such as Ostwald ripening, oriented attachment, and recrystallization that obscure any hints of intermediate phases,\(^{20}\) HR-TEM images of our CeO\(_2\) samples showed that crystal grains are preserved within the nanoparticles in this system long after crystallization is complete. We argue that rather than a mixture of small hydrolytic dimers and oligomers, large amorphous polymers give way to nanocrystalline CeO\(_2\).

A major product of this work is the discovery of a facile, room temperature hydrolysis route to polycrystalline CeO\(_2\) nanoparticles at mM concentrations of Ce(IV). Recent research concerning crystallization of inorganic solids has made it clear that multiple pathways to a final crystalline product exist, even within the same system.\(^{21}\) This is in contrast to classical nucleation theory, which states that crystals are assembled “ion by ion” through the addition of monomers to growing nuclei.\(^{22}\) The mechanism detailed in the following chapter presents itself as an excellent model system for non-classical nucleation. It does not undergo Ostwald-ripening, or recrystallization following non-oriented attachment, and instead retains multiple crystal grains within a single nanoparticle. Additionally, the nanoparticles do not undergo oriented attachment or aggregate, which allows for observation of crystallization by optical methods without having to account for scattering. These results are presented in the manuscript in Chapter
2, while the supplementary information and additional experiments are included in the appendices.
CHAPTER TWO

CRYSTALLIZATION KINETICS OF CERIUM OXIDE NANOPARTICLES FORMED
BY SPONTANEOUS, ROOM-TEMPERATURE HYDROLYSIS OF CERIUM(IV)
AMMONIUM NITRATE IN LIGHT AND HEAVY WATER

Contribution of Authors and Co-Authors

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Contributions: Synthesized nanoparticles. Performed steady-state and transient absorption studies. Prepared samples for all microscopy and XRD experiments. Generated figures and wrote manuscript.

Co-Author: Robert E. A. Williams

Contributions: Acquired HR-TEM and HAADF STEM images and EELS spectra.

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Contributions: Wrote and aided in the preparation of the manuscript and figures.
CHAPTER TWO

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BY SPONTANEOUS, ROOM-TEMPERATURE HYDROLYSIS OF CERIUM(IV)
AMMONIUM NITRATE IN LIGHT AND HEAVY WATER

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The electronic supplementary information (ESI) is presented in Appendix A.

Abstract

A stable sol of cerium oxide nanoparticles forms spontaneously when cerium(IV) ammonium nitrate (CAN) is dissolved in room-temperature water at mM concentrations. Electron microscopy experiments reveal the formation of highly crystalline cerium oxide particles several nm in diameter and suggest that they are formed from amorphous particles that are similar in size. Under the low pH conditions of the experiments, the nanoparticles form a stable dispersion and show no evidence of aggregation, even many months after synthesis. The absence of particles large enough to scatter light significantly makes it possible to observe the crystallization kinetics through dramatic changes in the
UV-visible absorption spectra that occur during solution aging. Measurements show that the cerium oxide nanocrystals are formed roughly an order of magnitude more slowly in D$_2$O than in H$_2$O solution. This large solvent kinetic isotope effect ($k_{H}/k_{D} \sim 10$), which is reported here for the first time for the crystallization of a solid metal oxide phase, indicates a rate-determining proton transfer reaction, which is assigned to the conversion of hydroxy to oxo bridges. In D$_2$O solution, the absorption per mole of cerium ions increases by over 400% at 290 nm as the weakly absorbing precursor phase is transformed into nanocrystalline cerium oxide. An isosbestic point is detected at 368 nm, and the absorption spectra can be modeled throughout aging by the sum of spectra of just two interconverting species. Preliminary ultrafast transient absorption experiments confirm that the optical properties of the amorphous precursors differ greatly from those of the final, nanocrystalline phase. Crystallization of CeO$_2$ from CAN in water has much in common with the crystallization of iron oxides from iron(III) salts, including the importance of non-classical nucleation and growth pathways. It is an outstanding system for studying the poorly understood events that cause molecularly solvated ions to self-assemble into nanocrystals, following hydrolysis. At the same time, the strong susceptibility of CAN to spontaneously form CeO$_2$ nanocrystals under the mildest of reaction conditions indicates that caution is needed when working with this common sacrificial oxidant.
Despite much investigation, the molecular events behind the homogeneous nucleation and growth of inorganic crystals and nanocrystals from solution-phase precursors are still unclear. There is growing recognition\textsuperscript{20,23} that crystallization pathways for many systems are at odds with the tenets of classical nucleation theory, which predict that crystals are assembled by the addition of small monomeric units (e.g., single ions) to growing crystals.\textsuperscript{24} Instead, clusters or disordered polymers containing up to hundreds of metal ions may be important intermediates along the crystallization pathway.\textsuperscript{25} Diverse non-classical mechanisms exist and may even operate concurrently in some systems.\textsuperscript{26}

The crystallization of iron(III) oxides has received especially close scrutiny due to the importance of terrestrial iron minerals. The concept of non-classical nucleation pathways mediated by amorphous polymer intermediates in iron(III) oxides was first discussed many years ago,\textsuperscript{27-29} but has received increased attention recently.\textsuperscript{30-32} Uncertainty over the pathways leading to crystal formation persists as illustrated by two recent studies of the events leading to solid iron(III) oxide phases, following the hydrolysis of simple iron(III) salts in acidic aqueous solutions.\textsuperscript{32-33} Zhu et al.\textsuperscript{33} report that the iron(III) hexaaqua ion, \([\text{Fe(H}_2\text{O)}_6]^{3+}\), and the singly-bridged \(\mu\)-oxo dimer, \([\text{(H}_2\text{O)}_5\text{Fe-O-F(H}_2\text{O)}_2]^{4+}\), are the only detectable intermediates when iron(III) nitrate is transformed by hydrolysis into ferrihydrite nanoparticles at room-temperature. They propose that the conversion of a \(\mu\)-oxo dimer to a dihydroxy-bridged dimer is the rate-determining step, and the high reactivity of the latter species is suggested to maintain its concentration below detectable levels.\textsuperscript{33}
On the other hand, Scheck et al.\textsuperscript{32} conclude from their study of the hydrolysis of dilute solutions of FeCl\textsubscript{3} that rapidly formed olation (= hydroxy-bridged) polymers, which are 1 – 2 nm in diameter, are present initially in dynamic equilibrium with free ions. These heavily hydrated polymers, which are only about one quarter as dense as ferrihydrite, are suggested to be prenucleation clusters of the kind discussed in ref. \textsuperscript{30}. They are proposed to form the final solid phase through aggregation initiated by the conversion of large numbers of hydroxy bridges into oxo bridges (oxolation).

In essence, the two studies propose starkly contrasting rate-determining steps: oxo to hydroxy bridge conversion in small units (dimers)\textsuperscript{33} vs. hydroxy to oxo bridge transformation in much larger building blocks (polymers).\textsuperscript{32} It is important to note that differences in counterions and concentrations could result in different crystallization mechanisms, but the contrasting proposals illustrate the challenges in elucidating the underlying reaction steps. Here, we present a kinetic study of the formation of cerium oxide (CeO\textsubscript{2} or ceria) nanocrystals, which form spontaneously when the common chemical oxidant cerium(IV) ammonium nitrate (CAN) is dissolved in water in mM concentrations. The evidence strongly suggests that ceria crystallization occurs via non-classical pathways, and similarities and differences with the better-studied iron(III) systems are noted.

Ceria is a technologically important and earth-abundant material that is valued for catalysis\textsuperscript{34} and for its role as a scavenger and source of reactive oxygen species in biological systems.\textsuperscript{35-37} Although the precipitation of various iron(III) oxides from aqueous solution has been investigated for many years, the mechanism behind ceria
crystallization has been the subject of only a few studies.\textsuperscript{10, 38} Our results show that hydrolysis of CAN in heavy water (D\textsubscript{2}O) slows the formation of nanocrystalline ceria by an order of magnitude. This large kinetic isotope effect, which has not been reported previously, provides new insights into the mechanisms behind crystal nucleation and growth, and could lead to new avenues for controlling nanocrystal composition and morphology.

The synthesis of ceria by CAN hydrolysis has distinctive characteristics that recommend it as a model system for investigating crystallization kinetics, including non-classical aspects. Although iron(III) oxides crystallize in at least four distinct structures,\textsuperscript{39} ceria only crystallizes in the fluorite lattice, eliminating competitive and possibly complex pathways to multiple solid phases. The crystallization of ceria may also be relevant to the formation of actinide oxides like PuO\textsubscript{2} that also crystallize in the fluorite structure. Colloidal PuO\textsubscript{2} and other “eigencolloids” play a role in the environmental transport of radioactive contaminants in groundwater.\textsuperscript{40}

2.2 Results and Discussion

Our observation of spontaneous ceria nanoparticle formation in aqueous CAN solutions was fortuitous. In the course of preparing aqueous CAN solutions for femtosecond transient absorption experiments, we discovered that the UV-vis absorption spectrum of a freshly prepared mM CAN solution undergoes large changes on the minutes time scale (Figure 1). These concentrations were originally chosen to yield appropriate absorbance values at 265 nm for transient absorption measurements in a 1.0
mm path length based on molar absorption coefficients reported for hydrated Ce\(^{4+}\) ions at UV wavelengths. CAN is highly soluble in water, and the crystals dissolve completely in a few seconds. The pH of the solution immediately drops to a value near 2 due to the strong Lewis acidity of the salt. During aging, the pH decreases in a slower process by an additional 0.1 to 0.2 pH units. A similar, slow drop in pH is observed during the aging of Fe\(^{3+}\) solutions.

![Absorption spectra](image)

Figure 1. Absorption spectra of 3.3 mM CAN in D\(_2\)O solution at 2, 5, 8, 13, 24, 34, 53, and 161 min (orange curves). The isosbestic wavelength (368 nm) is shown by an asterisk. The dashed curves are fits to a second-order kinetic model (eq 1) with the initial and fully-aged spectra colored green and red, respectively. Spectra at intermediate times are shown in blue. The region near the isosbestic point is magnified in the inset.

The spectral changes occur much more slowly in D\(_2\)O than in H\(_2\)O, making it easier to observe the kinetics of aging in heavy water. Results in D\(_2\)O solution are shown in Figure 1 for a CAN concentration of 3.3 mM (1.8 mg mL\(^{-1}\)). Similar results were obtained for CAN concentrations of between 0.2 and 4.6 mM.

In D\(_2\)O, the absorption spectrum recorded one minute after mixing decreases nearly monotonically with increasing wavelength above 250 nm (Figure 1). The strong
absorption below 250 nm is due to the nitrate counter ions. Two very weak shoulders are seen at 260 and 315 nm in the initial spectrum. Several minutes later, a broad peak grows in near 290 nm, while the weak tail seen at wavelengths greater than 380 nm decreases. The latter change causes the pale yellow color of a freshly prepared solution to fade to colorless. An isosbestic point is seen at 368 nm (asterisk in Figure 1) in both H₂O and D₂O solution. The same spectral changes are observed regardless of whether solutions are maintained in the dark or exposed to fluorescent laboratory lights, indicating that they are not due to photochemical reactions.

Several hours after CAN is added to the water, the absorption spectrum ceases to change and identical spectra are observed in D₂O and H₂O within experimental uncertainty (solid blue and dashed red curves in Figure 2). In contrast to the strong growth in absorption when CAN is dissolved in neat water, the spectrum of CAN in 1.0 M HClO₄ (yellow curve in Figure 2) does not change with time, even several months after preparation as long as the solution is maintained in the dark to prevent photoreduction of Ce⁴⁺ to Ce³⁺.
Figure 2. Absorption spectra of freshly prepared CAN in D₂O (solid red curve), CAN in H₂O aged for 23 h (blue curve), CAN in D₂O aged for 24 h (dashed red curve; scaled to match the blue curve), and CAN in 1.0 M HClO₄ in H₂O (gold curve). The procedure used to measure apparent molar absorption coefficients (ε) is described in the ESI.
The clear and colorless solutions are sols of suspended ceria nanocrystals. High-resolution transmission electron microscopy (HR-TEM) images recorded from a 1.3 mM solution of CAN in H$_2$O after aging for one day reveal highly crystalline domains a few nm in diameter (Figure 3). FFTs of the nanocrystals shown in Figure 3 show reflections corresponding to CeO$_2$ ($d_{111} = 3.12$ Å, $d_{200} = 2.71$ Å, and $d_{400} = 1.35$ Å). The independent reflections reveal that multiple crystalline orientations are present within each nanoparticle. The particles are similar in appearance to small nanocrystalline ceria particles imaged previously.$^{10, 41}$ Analysis of an XRD spectrum of precipitated nanocrystals (Figure A1) yields an average crystalline domain size of $3.7 \pm 0.4$ nm in good agreement with sizes observed in HR-TEM images.
Figure 3. Image-corrected HR-TEM images of several nm nanoparticles a) and c) present in a day-old 1.3 mM solution of CAN in water and their respective FFT images b) and d) showing the lattice spacings characteristic of CeO$_2$. The well-dispersed nature of the nanoparticles is shown in e).

HR-TEM images reveal both well-dispersed single nanoparticles and aggregates (Figure A3). However, because the solutions remain clear and non-turbid even after many months of aging, aggregates are most likely artifacts of sample drying.$^{42}$ Covered solutions show no change in absorption after one year of storage on a laboratory shelf at room temperature. In contrast, sols formed from Fe(III) salts eventually become turbid.
and precipitate,\textsuperscript{28, 43-44} although particle settling can be avoided for up to several weeks.\textsuperscript{33} If the particles were to grow large enough to scatter light, then the absorbance should increase at all wavelengths, but the absorbance at wavelengths longer than 368 nm actually decreases with time. The fact that the nanocrystals do not grow beyond a few nm in size also suggests that growth does not occur by aggregation (see below).

The pronounced changes seen in the absorption spectra and the absence of light scattering make UV-vis spectroscopy an excellent in situ technique for observing the kinetics of ceria crystallization. Kinetic traces monitored near the maximum of the long-time spectrum at 289 nm are strongly biphasic (Figure 4). After 2.5 h of aging in D\textsubscript{2}O (red circles), the solution absorbance is 4.1 times larger than the value measured 45 s after mixing. A smaller increase of 2.9 is observed in H\textsubscript{2}O (blue circles) during the same time period, but the data in Figure 4 likely fail to capture the faster kinetics. In contrast, more modest absorbance increases are seen in time-dependent UV-vis spectra measured during iron(III) oxide crystallization.\textsuperscript{33}

![Figure 4. Absorbance growth at 289 nm by CAN in H\textsubscript{2}O, [Ce\textsuperscript{IV}] = 1.1 mM (blue circles scaled by 2.1) and CAN in D\textsubscript{2}O, [Ce\textsuperscript{IV}] = 2.5 mM (red circles). The red and blue curves are fits to eq 1.](image-url)
The time-dependent UV-vis spectra in Figure 1 are internally linear, meaning that each can be reproduced by a linear combination of just two basis spectra. More than two chemical species could be present in significant concentrations and still yield internally linear spectra when their interconversion is governed by a single chemical reaction. However, it is highly unlikely that the crystallization of ceria can be described by a single reaction among three or more cerium species. Instead, internal linearity and the isosbestic point seen during aging are best explained by a two-state model in which a precursor is steadily converted into nanocrystalline ceria.

Identification of the final product as ceria is confirmed by XRD (Figure A1) and XEDS coupled with lattice spacing measurements from image-corrected HR-TEM. As will be discussed below in more detail, the precursor is proposed to be an amorphous hydrolytic polymer and not a mononuclear Ce(IV) ion. Additional species could be present, but only in concentrations that are too low to influence the UV-vis spectra.

Femtosecond transient absorption (TA) signals measured during aging of CAN in D$_2$O reinforce the conclusion that two species are responsible for the spectral changes seen in Figure 1. The signals measured just after dissolving CAN in water are very weak and close to zero at a probe wavelength of 300 nm (Figure 5). The initial signal at 350 nm (Figure 5a) is a little stronger and appears as a weaker version of the fully aged signal. After nine minutes of aging, the signal amplitude increases substantially at both probe wavelengths. When normalized to the peak signal amplitude, the traces overlap with the exception of the 1-10 min trace at 300 nm. The transient signals fit well to a second-order kinetic model, but the underlying dynamics are not the subject of this study.
Figure 5. Femtosecond transient absorption signals of CAN in D$_2$O recorded as a function of aging time (colored curves with time after mixing shown in the legend). The pump wavelength was 266 nm and the probe wavelength was a) 350 nm and b) 300 nm (b). The solid black curves are fits of a second-order kinetic model to the blue traces.

TA signal amplitudes depend on the number density of excited states created by the pump pulse and scale as $1 - 10^{-A}$, where $A$ is the total absorbance of the sample at the pump wavelength.\textsuperscript{46} If only a single absorbing species were present, then the absorbance increase from 0.71 to 1.20 measured during the 36 minutes needed to record the TA traces shown in Figure 5 would cause the signal to increase by 16%, but the actual percentage increase is an order of magnitude larger. Two species—a precursor and the final nanocrystalline ceria—are needed to explain the large increase in the TA signal strength. The very weak TA signals measured during the first 9 minutes of aging indicate that the precursors contribute only weakly to the TA signals at both probe wavelengths. The subsequent strong signal growth (Figure 5) indicates that nanocrystalline ceria yields much larger TA signals than the precursors.
The traces in Figure 4 were fit using a second-order kinetic model in which a precursor is progressively converted irreversibly to nanocrystalline ceria. Reasonable fits could also be obtained using a biexponential model, and we hesitate to attach significance to a particular kinetic model. Regardless of what model is used, however, the data clearly indicate that rapid initial changes in absorbance are followed by slower changes.

According to the second-order model, the absorbance at time \( t \), \( A(t) \), is given by,

\[
A(t) = A_p(t) + A_{ceO_2}(t) = \frac{A_p(t=0) t_{1/2} + A_{ceO_2}(t=\infty) t}{t_{1/2} + t}
\]  

(2.1)

where \( A_p \) and \( A_{ceO_2} \) are the absorbances as a function of time of the precursor and nanocrystalline ceria, respectively, and \( t_{1/2} \) is the half-life for the disappearance of the precursor. Note that eq 1 provides excellent fits at times \( t > 0.5 \) min, but points at \( t < 7.5 \) min in \( D_2O \) solution do not fit well due to an initial induction period, and were excluded from the fit. The half-life in \( D_2O \) (17.6 ± 0.5 min) is over ten times longer than in \( H_2O \) (1.50 ± 0.04 min) solution.

Eq 1 was also used to fit the time-dependent spectra in Figure 1 at each wavelength simultaneously. The good agreement between the data and fits (orange and blue dashed curves in Figure 1) shows that only two states are needed to describe the spectral evolution during aging. The time-zero spectrum (precursor) and the \( t = \infty \) spectrum (ceria) determined from the fit are shown by the green and red curves in Figure 1, respectively.

Returning to the transient absorption signals in Figure 5, the presence of two species with unequal TA signal strengths explains the dramatic growth in the TA signal
amplitudes. In a multicomponent solution, the signal contribution from each ground-state species is weighted by the ratio of its absorbance to the total solution absorbance.\textsuperscript{46} If the TA signal from the precursor can be neglected compared to that from ceria, then the signal at each delay time between pump and probe pulses depends on the absorbances measured after a fixed period of aging according to,

\[ \Delta A \propto \left(1 - 10^{-4}\right) \frac{A_{\text{CeO}_2}}{A} \]  

(2.2)

where \( A_{\text{CeO}_2} \) is the absorbance due only to nanocrystalline ceria. The right-hand side of eq 2 was evaluated using \( A \) and \( A_{\text{CeO}_2} \) values obtained from fits using eq 1 (with \( t_{1/2} = 18 \text{ min} \) for CAN in D\textsubscript{2}O) to initial and final spectra of the sample used in the TA measurements (Table A1). The results predict that the TA signal obtained 30 minutes after the dissolution of CAN in D\textsubscript{2}O should be 300\% stronger than the signal recorded after 3 minutes of aging in good agreement with the 340\% increase actually observed in the 350 nm signal at 500 fs (Figure 5).

To investigate the nature of the precursor, STEM images were recorded as close as possible to the start of aging by adding CAN crystals to D\textsubscript{2}O, shaking for several seconds, and immediately preparing a TEM grid as described in the methods section. Images obtained in this manner (a typical image is shown in Figure 6a) reveal bright regions that are commensurate in size with the final nanoparticles. EELS measurements (Figure 6a inset) confirm that these particles are made of Ce\textsuperscript{4+} ions, but HR-TEM images obtained on the same region lack the lattice features that are prominent in the aged samples.
Figure 6. a) STEM image of fresh CAN in D$_2$O with the corresponding EELS spectrum shown in the inset. The Ce M4 and M5 peaks at 883.75 and 901.25 eV are labeled. Nanodiffraction of the same area showed no evidence of crystallinity. b) A probe corrected STEM image of CAN in D$_2$O aged 30 min with crystalline lattice (blue area) and less ordered regions (red area).

Importantly, probe-corrected HAADF-STEM images, recorded from a 1 mM CAN in D$_2$O sample that was aged for 30 min (Figure 6b), show evidence of small crystalline particles (an example is shown inside the blue dashed circle), which are connected to disordered, non-crystalline regions (red dashed circle). The crystalline domains in the 30 min old D$_2$O sample are of similar size (2 – 6 nm) as ones detected in the fully aged CAN in H$_2$O sample. We assign the amorphous precursors seen in the
STEM images (Figure 6a) to polymers formed when heavily hydroxylated monomers rapidly condense by olation (i.e., hydroxy bridge formation). We argue below that these amorphous particles can form on the seconds time scale from the initial hydrolysis species.

The rapid pH drop due to hydrolysis of CAN provides the driving force for ceria nanocrystal formation. Earlier, Ikeda-Ohno et al.\textsuperscript{10} showed that sols of nanocrystalline ceria form once the pH of a 0.1 M Ce(IV) solution initially at pH 0.0 is raised above 0.5 by titration with NaOH or NH\textsubscript{3}. Raising the pH to 3.0 or higher triggered precipitation.\textsuperscript{10} Our results show that it is not necessary to add base because aqueous mM CAN solutions spontaneously attain a pH value within the range (0.5 – 2.0) identified by Ikeda-Ohno as producing sols of ceria nanocrystals.

Water molecules coordinated to a Ce\textsuperscript{4+} ion are rendered sufficiently acidic by the metal that they deprotonate to the solvent, leaving ligated hydroxide ions behind. In our experiments, higher CAN concentrations produce lower initial pH values. A graph of the initial hydronium ion concentration ([H\textsuperscript{+}]) vs. the initial CAN concentration can be fit to a straight line over the range of concentrations investigated. The slope of the best-fit line for freshly prepared solutions corresponds to the release of 2.8 ± 0.3 (2\textsigma) moles of protons per mole of Ce\textsuperscript{4+} ions (Figure A4). After 24 hours of aging this quantity increases slightly to 3.6 ± 0.2 (2\textsigma) moles of protons.

The prompt release of ~3 protons per Ce\textsuperscript{4+} ion is consistent with the formation of a highly hydroxylated monomer such as [Ce(OH)\textsubscript{3}]\textsuperscript{+} (ligated water molecules have been omitted). The elementary proton transfer reactions that produce hydrolyzed monomeric
ions of high valent metal ions are thought to attain equilibrium in a fraction of a second. We propose that these initial mononuclear Ce(IV) species then undergo rapid polymerization (olation) to form amorphous structures in which many Ce ions are extensively connected by OH bridges.

The lability of bound water molecules is thought to be the most important factor determining olation rates. Exchange rates for water molecules have not been measured for very many tetravalent ions, but values of $5.4 \times 10^6$ s$^{-1}$ and $> 5 \times 10^7$ s$^{-1}$ have been reported for U$^{4+}$ and Th$^{4+}$, respectively. These values and the high rate constants of $10^7$ M$^{-1}$ s$^{-1}$ pertinent to iron(III) oxide formation suggest that small and extensively hydroxylated oligomers are fully formed before our earliest UV-vis spectra or TEM images have been recorded.

Several factors likely contribute to the rapid formation (< 10 s) of olation polymers. The reduced charge of the monomers attenuates Coulombic repulsion and facilitates their rapid condensation. A recent molecular dynamics simulation suggests that iron(III) dimers and trimers joined by hydroxy bridges can form in just tens of ps. In addition, the rates of water loss that control the kinetics of olation are highest for the most heavily hydroxylated (and lowest charged) monomers.

Both oxo bridges and bound water molecules may be present in the amorphous Ce(IV) olation polymers, but the high degree of hydroxylation is confirmed by experiments showing that the polymer reacts with strong acid. In particular, adding 1.0 M HClO$_4$ before aging is complete instantly alters the absorption spectrum and halts the spectral evolution. At the moment acid is added, the component of the absorption
spectrum arising from the long-time product (CeO$_2$) is unchanged, but the precursor contribution is replaced by the spectrum of CAN in 1.0 M HClO$_4$ (Figure 7).

Figure 7. The absorption spectrum taken 5 minutes after preparing a pH 1.81 CAN in H$_2$O solution is shown by the solid blue curve. 1.0 mL of the solution was then acidified to pH 0.37 by adding 0.75 mL of 1.0 M HClO$_4$ and a new spectrum was recorded (gold curve). The dashed blue curve is a linear combination of the aged CAN in water spectrum (1.3 mM) and the CAN in 1.0 M HClO$_4$ spectrum (2.5 mM).

These changes arise because the ceria nanoparticles are unreactive toward acid, but the OH bridges in the hydrolytic polymers are cleaved by acid to yield smaller species as seen also with iron(III) hydrolytic polymers. The vulnerability of OH bridges to attack by acid suggests that the olation polymers are constantly being remodeled through competition between acid-catalyzed cleavage and the addition of monomers or small oligomers. This competition is proposed to favor the formation of polymer masses having compact shapes.

The much slower crystallization rate of ceria nanoparticles in D$_2$O vs. H$_2$O and the presence of amorphous cerium(IV) polymers support a mechanism in which an initial period of rapid olation gives way to rate-determining oxolation. Livage and
coworkers described oxolation in metal oxide systems as proceeding via nucleophilic attack by OH on a second metal center followed by 1,3-proton transfer. However, reactions in which oxygen acts as a nucleophile generally display only modest kinetic isotope effects (KIEs) as seen, for example, in the case of the hydroxide ion. On the other hand, proton transfer can show much larger KIEs. The substantial deuterium kinetic isotope effect observed here is consistent with a rate-determining proton transfer reaction during the rearrangement of amorphous polynuclear Ce(IV) species to crystalline CeO$_2$.

Instead of joining Ce(IV) monomers by oxo bridges, we propose that oxolation describes the process by which hydroxy bridges in a highly dynamic olation polymer are converted to oxo bridges. This intramolecular (or intracluster) process can occur by the transfer of a proton on a hydroxo bridge to a more distant OH ligand connected to the first via one or more water molecules. It could also occur by slow loss of the proton of the OH bridge to the solvent, consistent with the slow pH decrease observed during aging. By transferring protons from OH ("ol") bridges to complexed hydroxides, amorphous polynuclear Ce(IV) domains are converted to nanocrystalline CeO$_2$.

Surprisingly, deuterium KIEs, which might be anticipated in metal oxide crystallization due to the putative role of proton transfer in oxo bridge formation, have rarely been mentioned in the literature. Knight and Sylva noted that the precipitation of solid iron oxide particles is roughly a factor of two slower in D$_2$O than in H$_2$O, but the underlying reasons were not discussed.
The observation of co-existing amorphous and nanocrystalline regions in probe-corrected STEM measurements (Figure 6b) provides strong evidence in favor of a non-classical nucleation and growth mechanism. Nevertheless, there are a diversity of such mechanisms, and it is difficult to tell the precise pathway from present results. One possible model is that the amorphous olation polymers play a role similar to the magic sized cluster intermediates observed by Cossairt and co-workers during the nucleation and growth of InP quantum dots. In this case, the polymers would act as reservoirs for monomers that later add ion-by-ion to nuclei that form separately from, and more slowly than the polymers.

On the other hand, instead of being off-pathway intermediates, polymers could play a more direct role in the nucleation and growth of the nanocrystals. De Yoreo and coworkers recently observed a non-classical pathway in which a crystal is formed from an amorphous particle, while both remain in contact. A recent cryo-TEM study of CaCO₃ nucleation also suggests that crystalline domains can nucleate within amorphous structures.

Our HR-TEM images showing that many of the particles consist of just a few nanocrystalline domains or grains within each nanoparticle (Figs. 3a and 3c) support this picture. These structures cannot arise from aggregation or by sweeping single crystals together during drying as both effects would be expected to produce a number of larger particles containing more than just the two or three domains actually observed. Furthermore, the lack of precipitation even after a year of aging indicates that aggregation
does not occur, likely due to coulombic repulsion between the nanoparticles and adsorbed nitrate ions in the low pH conditions.\textsuperscript{57}

The details of how crystalline domains nucleate within the amorphous particles—and the relation of nucleation to oxolation—require further study. Nevertheless, our findings are consistent with a picture in which two or more nucleation events occur within an amorphous particle, causing individual nanocrystalline CeO\textsubscript{2} domains to grow together, forming distinct grain boundaries until the amorphous precursor is fully consumed.

The preliminary picture obtained in this study for ceria crystallization from mM aqueous CAN has much in common with the non-classical mechanism for iron(III) oxide crystallization proposed by Scheck et al. for mM concentrations of FeCl\textsubscript{3}. In both systems, the rate determining step is oxolation within large olation polymers.\textsuperscript{32} On the other hand, Zhu et al.\textsuperscript{33} observed no intermediate species larger than dimers in their study of more concentrated (0.2 M) iron(III) nitrate solutions and proposed that the conversion of $\mu_2$-oxo bridged dimers to the more reactive bis(hydroxy) dimer is the rate-determining step.

The tension between these pictures is likely due to the very different total metal ion concentrations in the two studies. It seems quite reasonable that the two mechanisms correctly describe crystallization pathways that vary strongly with concentration of the salt that undergoes hydrolysis. Earlier Trysted et al.\textsuperscript{38} investigated ceria nanoparticles prepared in a hydrothermal synthesis by in situ X-ray scattering. They found no evidence of Ce(IV) intermediates larger than dimers and suggested that the assembly of dimers is
rate determining. This result, which was obtained on a concentrated (1 M) Ce(IV) solution parallels the finding of Zhu et al.\textsuperscript{33} on concentrated Fe(III) solutions, and does not contradict the importance of amorphous olation polymers at lower concentrations. Ceria crystallization from amorphous polymers may occur significantly more rapidly than the crystallization of iron oxide phases from iron(III) olation polymers, and this could inhibit the aggregation of partially oxolated precursors that eventually lead to precipitation in the iron system.\textsuperscript{32}

2.3 Conclusions

In summary, we have shown that nanocrystalline ceria forms spontaneously at room temperature by simply dissolving mM concentrations of CAN in water without the addition of a strong base or heating. It is difficult to imagine a simpler synthetic procedure for preparing nanocrystals that are just several nm in diameter from a common laboratory salt. Nanocrystal nucleation and growth by aqueous CAN solutions can easily go unnoticed because the resulting solutions do not scatter light or undergo precipitation. CAN is a popular sacrificial oxidant used in studies of water oxidation catalysts,\textsuperscript{58-59} and researchers who work with aqueous CAN solutions should be aware of its very strong tendency to form nanocrystalline CeO\textsubscript{2}.

UV-vis spectroscopy is a useful in situ probe of the kinetics of nanocrystal formation in this system. The results also establish that hydrolysis of CAN in heavy water slows the formation of nanocrystalline CeO\textsubscript{2} by an order of magnitude. The isotope effect is consistent with rate-determining oxolation reactions. The results further suggest that
ceria crystallization does not proceed via ion-by-ion assembly as suggested by classical nucleation theory, but instead occurs by oxolation and dehydration reactions that take place within an amorphous polymer precursor.

This study provides the first evidence that a proton transfer reaction is the rate-limiting step in metal oxide nanocrystal formation. In view of the considerable body of knowledge surrounding proton transfer reactions, this observation should lead to more refined mechanistic understanding. The slower growth in heavy water could potentially be used to control metal oxide nanocrystal characteristics such as morphology and size as has been done previously for noble metal nanoparticles.60-61

Finally, our results reveal that there is a clear separation in time scales between the formation of amorphous precursors and the appearance of crystalline domains. The mild conditions required for this transformation, the convenient reaction times in heavy water (minutes), and the formation of small crystals that do not aggregate or precipitate make this an outstanding system for study by real-time, in situ electron microscopy and other techniques that can paint a more complete picture of the nanoscale events that occur during metal oxide crystallization.

2.4 Materials and Methods

2.4.1 Sample Preparation

Ammonium cerium(IV) nitrate ((NH₄)₂[Ce(NO₃)₆], (CAN) was purchased in 98% purity grade from Sigma-Aldrich (St. Louis, MO) and used as received. The CAN in H₂O and CAN in D₂O samples were made by dissolving CAN in purified water from a
Millipore Synergy water purifier (Billerica, MA) and D$_2$O (D, 99.9%, Cambridge Isotope Laboratories, Inc., Andover, MA). All pH measurements were performed using an Orion Star A 121 pH meter (Thermo Scientific) with an Orion 9110DJWP electrode (Thermo Scientific). The pD value in D$_2$O solutions was estimated by adding 0.41 to the reading from a pH meter. pH corrections in the acidification experiments (Figure 7) were made with 1.0 M HClO$_4$ (Sigma Aldrich, 34288 FLUKA).

2.4.2 Steady-State and Transient Absorption Spectroscopy

UV-Vis absorption spectra were recorded using a Lambda 25 spectrophotometer (Perkin-Elmer, Wellesley, MA). Unless specified, a 1.0 mm path length cell was used. For femtosecond transient absorption measurements and UV-Vis aging experiments, CAN in D$_2$O solutions were prepared to have an initial absorbance of ~0.3 at 289 nm because the absorbance increased over the course of measurements. Solutions were shaken for thirty seconds prior to measurement. During aging, absorption spectra of CAN solutions were measured in 1 to 10 minute intervals over the course of a few hours. The spectrophotometer scan speed was 240 nm/min, leading to some distortion of the initial spectra. The method of correcting this skew is described in the ESI. Single-wavelength TA signals were also recorded during solution aging.

Femtosecond TA measurements were performed with UV pump pulses at 266 nm generated via third harmonic generation of the fundamental pulses from a commercial Ti:sapphire femtosecond laser system (Libra, Coherent Inc., Santa Clara, CA). Tunable probe pulses were generated from an OPA (OperA solo, Coherent Inc., Santa Clara, CA) pumped by the 800 nm fundamental pulses. The pump pulses were chopped at 333 Hz by
a mechanical chopper (New Focus, Santa Clara, CA) and then passed through a half waveplate and a polarizer. The angle between the linear polarizations of pump and probe pulses was set to the magic angle (54.7º). The pump pulse energy was controlled via a half wave plate and polarizer. The pump pulse energy was 0.75 μJ with a spot size of ~0.48 mm (FWHM) at the sample.

A motorized optical delay stage was used to delay the probe pulses. The probe beam was focused at the sample to a ~0.15 mm (FWHM) spot size. After the sample, the probe beam was directed to a monochromator and then detected by a photomultiplier tube (Hamamatsu 1P28) connected to a lock-in amplifier (Stanford Research System Inc., Sunnyvale, CA).

2.4.3 Electron Microscopy

TEM images were recorded at The Ohio State University’s Center for Electron Microscopy and Analysis (CEMAS) using an image-corrected Titan™ 60-300 (S)TEM and a probe-corrected Titan™ 80-300 (S)TEM operated at 300 kV. EELS measurements were collected as spectrum images using a Gatan Enfina spectrometer. XRD experiments were performed using a Scintag X1 Diffraction System with an accelerating voltage of 45 kV, a current of 40 mA, and a Copper K-alpha x-ray source (λ = 0.154 nm).

Grids for electron microscopy were prepared as follows. After the desired amount of aging, the CAN solution of interest was diluted with water (1:4 for aged CAN in H₂O, 1:50 for CAN in D₂O) to reduce the final concentration of particles, and a single drop was transferred by pipette onto ultrathin carbon on 400 square Cu mesh TEM grids. (Cu 400 mesh, UL) The liquid was immediately wicked away with a tissue and the grid was
placed in a desiccator and dried under vacuum for 15 minutes before introduction into the electron microscope. Just under a minute elapsed between diluting the solution and placing the grid in the desiccator.

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Notes

The authors declare no competing financial interest.
APPENDICES
APPENDIX A

ELECTRONIC SUPPLEMENTARY INFORMATION FOR “CRYSTALLIZATION KINETICS OF CERIUM OXIDE NANOPARTICLES FORMED BY SPONTANEOUS, ROOM-TEMPERATURE HYDROLYSIS OF CERIUM(IV) AMMONIUM NITRATE IN LIGHT AND HEAVY WATER”
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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A1 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 ± 200 M⁻¹ 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 ± 60 M⁻¹ 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.

A2 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. A1).

Figure A1 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 CeO$_2$ crystal planes.

The 111, 200, 220, and 311 XRD peaks were analyzed using the Scherrer equation, $D = \frac{\kappa \lambda}{\beta_i \cos \theta}$, to estimate the crystal grain size, where $D$ is the diameter of the crystal grain, $\kappa$ 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), $\lambda$ is the x-ray wavelength (0.154 nm for Cu Kα), $\beta_i$ is the integral width of the peaks, and $\theta$ is the Bragg angle. A diameter of $3.8 \pm 0.3$ nm was calculated assuming cubic nanocrystals, and a diameter of $3.7 \pm 0.4$ 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.
The precipitate obtained for XRD measurements was sonicated and resuspended in 1.0 M HClO$_4$. The resulting UV-Vis spectrum measured in a 1.0 mm path length cuvette (Fig. A2) closely matches the spectrum of an aged CAN in H$_2$O 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.

![Figure A2](image)

**Figure A2.** UV-vis spectra of aged CAN in H$_2$O (dashed blue curve) and of the precipitate obtained by adding NaOH to aged CAN in H$_2$O, followed by washing, drying, and resuspension in 1.0 M HClO$_4$ (gold curve). The weak bump at 255 nm in the latter spectrum is assigned to a small amount of Ce$^{3+}$ (aq) produced by photoreduction of the nanoparticles by laboratory lights. Absorption at wavelengths shorter than 250 nm by aged CAN in H$_2$O (dashed blue curve) is due to NO$_3^-$ counterions, which are not present in the resuspended sample (gold curve).
A4 One-day-old CAN in H₂O TEM

Figure A3. 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).

A5 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,
\[ A_{266\text{ nm}}(t) = \frac{A_{\text{P,266 nm}}(t=0) t_{1/2} + t \cdot \frac{A_{\text{CeO}_2,266\text{ nm}}(t=\infty)}{A_{\text{P,266 nm}}(t=0)}}{t_{1/2} + t} \]  

A \( t_{1/2} \) of 18 min was used for CAN in D_2O and a value of 2.79 was used for the ratio of \( A_{\text{CeO}_2,266\text{ nm}}(t=\infty) \) to \( A_{\text{P,266 nm}}(t=0) \) at 266 nm. The calculated absorbances were \( A_{\text{P,266 nm}}(t=0) = 0.57 \) 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 A1. 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 A1), corresponding to when the TA signal near time zero was measured. In calculating the absorbances at 266 nm (second and third columns of Table A1), we neglected any reduction of Ce^{IV} resulting from pump laser excitation. These absorbance values were used to calculate a relative \( \Delta A \) in the fourth column of Table A1. 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 A1 Transient Absorption Amplitudes

<table>
<thead>
<tr>
<th>Aging time / min</th>
<th>$A^a$</th>
<th>$A_{\text{CeO}_2}^b$</th>
<th>$\Delta A \propto \left(1 - 10^{-t}\right) \frac{A_{\text{CeO}_2}}{A}$</th>
<th>$\Delta A_{\text{exp}}^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.71</td>
<td>0.23</td>
<td>0.26</td>
<td>0.77</td>
</tr>
<tr>
<td>12</td>
<td>0.97</td>
<td>0.63</td>
<td>0.58</td>
<td>1.50</td>
</tr>
<tr>
<td>21</td>
<td>1.11</td>
<td>0.85</td>
<td>0.71</td>
<td>2.09</td>
</tr>
<tr>
<td>30</td>
<td>1.20</td>
<td>0.99</td>
<td>0.77</td>
<td>2.58</td>
</tr>
</tbody>
</table>

$^a$ 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).

### A6 pH changes

Figure A4. 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, [CAN], was calculated from the absorbance of the aged solution using our measured absorption coefficients. The pH was fit to $[H^+] = m[\text{CAN}] + b$, in order to calculate $m$, the number of protons released per Ce(IV) ion. Initially, $2.8 \pm 0.3$ (2σ) protons were released per Ce(IV). After one day, this increased to $3.6 \pm 0.2$ (2σ).
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.
APPENDIX B

CRYSTALLIZATION BY DILUTION OF A STOCK SOLUTION
B1 Crystallization through dilution

Adding a stock solution of 1.0 M CAN in 1.0 M HClO₄ to enough water to yield a final CAN concentration of 1 to 6 mM causes similar spectral changes as when CAN is dissolved directly in neat water (Figure A3). The pH after dilution varies between 1.6 and 2.3, depending on the total CAN concentration, but does not vary significantly during aging. An isosbestic point is still seen at 368 nm, and each intermediate spectrum can still be modelled as a linear combination of the initial and final spectra. The kinetics of the increase in absorption that is indicative of crystallization happen half as slowly when CAN in H₂O is prepared by dilution as opposed to dissolution. Fits to equation 2.2 reveal a half-life of 3.47 ± 0.11 min for CAN in H₂O prepared by dilution, which is over twice as long as the 1.5 ± 0.04 min half-life for CAN in H₂O prepared by dissolution.

The spectra during aging of 1 M CAN in 1.0 M HClO₄ diluted in H₂O were analyzed using the same procedure as aging of CAN in D₂O (Figure 1). However, the calculated precursor spectrum likely undershoots the actual spectrum in this system because there are not enough data points to collect the initial kinetics. Sampling the initial behavior is much more important in this system than in the D₂O system given the almost 10-fold increase in rate. Even so, every spectrum can still be modeled as a linear combination of any two spectra in the dataset, consistent with two-state behavior.
Figure B1 Scan-speed corrected (described in Appendix 1.7) absorption spectra of 5 µL of 1 M CAN in 1 M HClO$_4$ diluted with 2 mL of H$_2$O recorded 2, 3, 5, 9, 20, 58, and 175 minutes after dilution. The absorbance increases or decreases as shown by the arrows. The isosbestic wavelength (368 nm) is marked by an asterisk.

**B2 Crystallization via hydrolysis of different Ce$^{IV}$ salts**

In an effort to determine the role of nitrate in the crystallization of CeO$_2$, Ce(SO$_4$)$_2$ was dissolved into water. However, the insolubility of this salt, even in 1 M acid, did not allow for the observation of the absorption spectrum. An alternative method to determining the role of nitrate is to use the salt (NH$_4$)$_2$Ce(SO$_4$)$_3$, which may have better solubility than Ce(SO$_4$)$_2$. A similar experiment to determine the role of ammonia in the crystallization of CeO$_2$ would be to use a K$_2$Ce(NO$_3$)$_6$ salt in place of CAN.
REFERENCES CITED


