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### Hydrolysis of Tetravalent Cerium for a Simple Route to Nanocrystalline Cerium Dioxide: An In Situ Spectroscopic Study of Nanocrystal Evolution

Atsushi Ikeda-Ohno,<sup>\*[a, b, c]</sup> Christoph Hennig,<sup>[a]</sup> Stephan Weiss,<sup>[a]</sup> Tsuyoshi Yaita,<sup>[d]</sup> and Gert Bernhard<sup>[a]</sup>



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**Abstract:** Despite the rapid developments in recent nanocrystal research and their expanding applications, the evolution mechanism of nanocrystals remains veiled for the most part due to the lack of appropriate analytical techniques. Here we demonstrate one promising multi-spectroscopic approach for the in situ investigation of nanocrystal evolution. That is, the for-

mation of nanocrystalline cerium dioxide (NC-CeO<sub>2</sub>) has been probed by dynamic light scattering (DLS), X-ray absorption spectroscopy (XAS) and highenergy X-ray scattering (HEXS). The

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obtained results indicate that the fine colloidal particles of NC-CeO<sub>2</sub> are formed in an acidic aqueous solution simply through the hydrolysis of the initial precursor of small oligomer Ce<sup>IV</sup> species. This information on how NC-CeO<sub>2</sub> evolves is fundamental to simplifying and alleviating the synthetic strategy for NC-CeO<sub>2</sub> production.

#### Introduction

The hydrolysis of metal cations is a fundamental reaction not only for the aqueous solution chemistry of metal cations, but also for wet chemical processes of metals. For instance, the sol–gel process, which is often employed to produce metal oxide compounds, is based on the polymerization and aggregation initiated by hydrolysis.<sup>[1]</sup> More recently, sol–gel processes are further being developed for the fabrication of metal nanocrystals (NCs).<sup>[2]</sup> Metal NCs, whose size is generally less than 100 nm at least in one dimension,<sup>[3]</sup> exhibit a unique "intermediate" character between bulk crystals and atoms.<sup>[4]</sup> This often enhances their chemical activities, such as catalytic or redox activity, as compared with those of the chemically identical bulk materials.<sup>[5]</sup> Owing to these remarkable properties, metal NCs are steadily drawing consid-

- [a] Dr. A. Ikeda-Ohno, Dr. C. Hennig, S. Weiss, Prof. Dr. G. Bernhard Institute of Resource Ecology Helmholtz-Zentrum Dresden-Rossendorf P.O.Box 510119, 01314 Dresden (Germany) Fax: (+49)351-260-3553
  [b] Dr. A. Ikeda-Ohno
- School of Civil and Environmental Engineering The University of New South Wales UNSW, Sydney, NSW 2052 (Australia) Fax: (+61)2-9385-5033 E-mail: a.ikeda@unsw.edu.au aikeda@lax.kuramae.ne.jp
- [c] Dr. A. Ikeda-Ohno
  Institute for Environmental Research
  Australian Nuclear Science and
  Technology Organisation
  Locked Bag 2001, Kirrawee DC
  NSW 2232 (Australia)
  Fax: (+61)2-9717-3111
  E-mail: atsushi@ansto.gov.au

[d] Dr. T. Yaita
 Quantum Beam Science Directorate
 Japan Atomic Energy Agency
 Kouto 1-1-1, Sayo-cho, Sayo-gun
 Hyogo-ken 679-5148 (Japan)
 Fax: (+81)791-58-0311

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erable attention across a range of technological and medical applications.<sup>[6,7]</sup>

One significant on-going challenge in metal NCs research is to control their shape and size, because the physical/chemical properties of metal NCs largely depend on these factors.<sup>[7]</sup> The establishment of synthetic strategy to tailor metal NCs with desirable shape and size requires the elucidation of their fundamental formation mechanism, that is, the evolution from initial metal precursors into NCs, as the morphology and size distribution of the resultant NCs are determined predominantly by their evolution route.<sup>[7,8]</sup> The formation mechanism of metal NCs, however, remains undiscovered for the most part due to the lack of appropriate experimental techniques. That is, the most frequently used tools to characterize NCs thus far are electron microscopy (e.g., SEM and TEM) and X-ray diffraction. These methods are powerful enough to visualize the shape, size, and lattice images of NCs, as well as to acquire their lattice parameters. The intrinsic limitation of these methods is, however, that they are applicable exclusively to solid state samples, but neither to solution samples nor to wet ones. Given the fact that major syntheses to fabricate metal NCs, including the sol-gel process, are performed in solution, a new analytical approach to observe in situ the evolution of metal NCs in solution is imperative for further expanding the research of metal NCs as well as their applications.

Based on these backgrounds, the aim of this paper is to demonstrate one promising analytical strategy for probing the evolution of metal NCs in solution. That is, we herein combine dynamic light scattering (DLS), X-ray absorption spectroscopy (XAS), and high energy X-ray scattering (HEXS) based on pair-distribution function (PDF) analysis,<sup>[9]</sup> for in situ monitoring of the formation of nanocrystalline cerium dioxide (referred to as "NC-CeO<sub>2</sub>", hereafter) triggered by the hydrolysis of tetravalent cerium ( $Ce^{IV}$ ). The initial purpose of this study was to systematically investigate the hydrolysis behavior of Ce<sup>IV</sup>. The hydrolysis of Ce<sup>IV</sup> is a very primary step of many wet syntheses for fabricating NC-CeO<sub>2</sub>,<sup>[10]</sup> although all the reported synthetic methods require additional processes (e.g., heating, adding organic solvents, or calcination) subsequent to the initial hydrolysis step to finally yield NC-CeO<sub>2</sub>. However, the present study reveals, unexpectedly, that NC-CeO<sub>2</sub> is already produced at the

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early stage of the hydrolysis of Ce<sup>IV</sup>. As a consequence, we have succeeded in observing the whole evolution process from the precursor species into NC-CeO<sub>2</sub>.

Because of the flexibility between the tri- and tetravalent oxidation states, cerium is known to be the only rare earth element (REE) forming a stable pure stoichiometric dioxide compound  $(M^{IV}O_2)$  with a fluorite-type structure, whereas most others (except Pr and Tb) form a sesquioxide compound (M<sup>III</sup><sub>2</sub>O<sub>3</sub>).<sup>[11]</sup> Owing to this chemical specificity along with the highest natural abundance of Ce among all REEs,<sup>[12]</sup> the application of NC-CeO<sub>2</sub> has spread out over a variety of fields, including the catalysts for harmful gas treatment<sup>[13]</sup> and the water-gas shift reaction,<sup>[14]</sup> electrodes for solid oxide fuel cells (SOFC),<sup>[15]</sup> polishing materials for advanced integrated circuits,<sup>[16]</sup> sunscreen cosmetics,<sup>[17]</sup> and a medical use as an artificial superoxide dismutase.<sup>[6]</sup> These versatile applications of NC-CeO<sub>2</sub> still require a simpler and more efficient synthetic strategy. This study provides a primary concept to potentially simplify the NC-CeO<sub>2</sub> synthesis merely based on hydrolysis. This is also a representative example which demonstrates the importance of fundamental understanding of the formation mechanism of metal NCs for further development of NCs research.

#### Results

Visual observation of hydrolysis behavior of Ce<sup>IV</sup>: Figure 1 shows the color change of a 0.1 M Ce<sup>IV</sup> solution in 1.0 M HNO3 titrated with NaOH. The initial color of the solution ("pH 0.0" in Figure 1) had a strong and clear yellow color.



Figure 1. Color change of 0.1 M Ce<sup>IV</sup> in 1.0 M HNO<sub>3</sub> as it is being titrated with NaOH. The photo was taken immediately after sample preparation.

With increasing pH, the yellow color began to fade at around pH 0.5 and became almost colorless above pH 0.7. The solution remained transparent until the production of hydrolytic precipitate above pH 3.0. The precipitate initially had a pale-yellow color (e.g., "pH 3.0" in Figure 1). It then turned into purple (e.g., "pH 8.0" in Figure 1) when the solution became basic (pH > 7.0). It should be noted that, as far as pH 0.5 (i.e., from pH 0.0 (initial) up to 0.5), the pH value of the sample solution increased in proportion to the amount of NaOH added. However, at around pH 0.5, at which the solution color began to fade, the pH value became transiently unchanged regardless of the addition of NaOH. Continuous addition of NaOH resulted in the re-increase of pH in due course. After that, the pH value rose proportionally again. We refer this pH value of 0.5 as "the critical pH" hereafter. The same behavior was observed when either the Ce concentration was increased up to 1.0 M, or an NH<sub>3</sub> solution was used for titrant.

Dynamic light scattering: DLS is a powerful technique to determine the size distribution of particles dispersed in solution.<sup>[18]</sup> The Ce<sup>IV</sup> solutions shown in Figure 1 have been studied first by DLS to investigate the presence of colloidal species in the solutions. No DLS signals were detected for the solutions below the critical pH (i.e., pH < 0.4), meaning that the scattered light intensities were equal to those of a pure solvent (i.e., aqueous HNO<sub>3</sub>). On the other hand, the solutions at the critical pH or higher (i.e.,  $pH \ge 0.5$ ) showed detectable DLS signals, suggesting a significant increase of scattered light intensities as compared with that of the pure solvent and, hence, the formation of colloidal species in the solutions exceeding the critical pH. The tetravalent cations of Th<sup>IV[19]</sup> and U<sup>IV,[20]</sup> ionic radii of which are similar to that of Ce<sup>IV[21]</sup> are known to produce colloidal solution being composed of their oxyhydroxide compounds. Considering the chemical similarity among these tetravalent cations, the Ce<sup>IV</sup> particles formed above the critical pH are likely to be the hydrolytic colloid of Ce<sup>IV</sup> or possibly the mixture of Ce<sup>IV</sup> and reduced Ce<sup>III</sup>. Figure 2(a) shows the particle size distributions of the colloidal species formed at different pH values. There is a broadening trend in the particle size distribution with increasing pH. The local pH excursion caused by the base titration process possibly produces aggregated species with larger particle sizes. This is possibly the cause of the observed broadening trend in particle size distribution as the pH increases. The morphology of colloidal particles is also influenced by metal concentration and the type of basic reagents employed for pH adjustment. That is, the lower concentration of Ce in the initial solution results in the narrower particle size distribution of the resultant colloids, and the pH adjustment with NH<sub>3</sub> provides finer and more homogeneous colloid than that with NaOH (Sections 1 and 2 in the Supporting Information). The particle size and homogeneity of the Ce colloid also vary with aging. As shown in Figure 2(b), the freshly formed colloid exhibits a wide particle size distribution and, thus, is very heterogeneous (the top-most histogram in Figure 2(b): "1 hour"). With aging, the particle size distribution gradually narrows and the mean hydrodynamic diameter of the particles becomes smaller. After approximately one month of aging, the particle size of the Ce colloid becomes significantly homogeneous (the bottom-most histogram in Figure 2(b): "672 h") with a finer particle size (mean values of the dominant hydrodynamic diameter =  $(3.0 \pm 0.7)$  nm when the pH is adjusted with NH<sub>3</sub>, and  $(4.2\pm0.8)$  nm with NaOH (Sections 1 and 2 and Figure S5 in the Supporting Information). The DLS instrument employed in this study has a minimum detection limit of <1 nm for particle size estimation, according to the specification document. Therefore, the particle size of 3-4 nm diameter is closed to the minimum detection limit, but it is still detectable. In general, DLS intensity is proportional to the sixth power of a particle diameter.<sup>[18]</sup> This means that





Figure 2. (a) Particle size distribution of Ce colloid formed in 1.0 M HNO<sub>3</sub> at different pH values adjusted with NaOH; [Ce]=0.1 M. DLS data were collected 48 h after sample preparation. (b) Time variation of particle size distribution of Ce colloid formed in 1.0 M HNO<sub>3</sub> at pH 0.5; [Ce]=0.1 M. NH<sub>3</sub> was employed for pH adjustment.

the presence of a small amount of larger particles may lower the sensitivity for smaller particles. However, the error of DLS signals becomes significantly smaller with time (Figure S5 in the Supporting Information), suggesting that there is little contribution of larger particles to the detection of 3–4 nm particles. Hence, we conclude that the obtained hydrodynamic diameter of 3–4 nm is above the limit of minimum detection. To summarize the DLS results, the apparently transparent Ce<sup>IV</sup> solutions with pH 0.5–2.0 in Figure 1 are, in fact, a colloidal solution of fine particles. The hydrodynamic diameter and size distribution of these fine particles are influenced by the Ce concentration, pH, the type of basic reagent, and aging.

**X-ray absorption spectroscopy**: To acquire the information on Ce oxidation states and local structural arrangement of Ce species, the Ce<sup>IV</sup> samples in Figure 1 were further investigated by XAS including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses. The analysis of Ce K-edge XANES spectra in conjunction with spectrofluorometry suggests that the oxidation state of Ce remains mostly tetravalent at any pH value (Section 1–1 in the Supporting Information). This means that the change of solution color observed in Figure 1 is likely to be attributed not to the reduction from Ce<sup>IV</sup> to colorless Ce<sup>III</sup>, but to the change in Ce<sup>IV</sup> speciation.

Figure 3 shows the  $k^3$ -weighted Ce K-edge EXAFS spectra (left, labeled (a)) for 0.1 M Ce<sup>IV</sup> solutions at different pH values along with reference data of a 0.05 M Ce<sup>IV</sup> solution in 2.0 M HClO<sub>4</sub> and CeO<sub>2</sub> powder, and their corresponding Fourier transforms (FTs) (right, labeled (b)). Our recent study combining EXAFS with DFT calculations has revealed that the primary aqua species of Ce<sup>IV</sup> in an aqueous perchloric acid (grey colored spectra at the top most in Figure 3) is not a simple mononuclear hydrate complex, but an oxo- or/and hydroxo-bridging dinuclear complex(es).<sup>[22]</sup> Such smaller oligomer complexes can be readily identified on EXAFS-FT data by the presence of a distinguishable peak at around  $R + \Delta = 3.5 - 3.7$  Å, which is derived from the Ce-O<sub>bridging</sub>-Ce arrangement.<sup>[22]</sup> This characteristic peak at around  $R + \Delta = 3.5 - 3.7$  Å appeared also in the spectrum for 1.0 M HNO<sub>3</sub> without an addition of basic reagent ("0.0" with a deep blue color in Figure 3). Coordination of nitrate ions  $(NO_3^{-})$  may also give an EXAFS-FT peak at around R+ $\Delta = 3.6 - 3.7 \text{ Å},^{[23]}$ potentially overlapping with the Ce-O<sub>bridging</sub>-Ce peak. However, tetravalent actinides (An<sup>IV</sup>), which are often referred to as analogues of Ce<sup>IV</sup>, are coordinated by two NO<sub>3</sub><sup>-</sup> at best in lower nitrate concentrations like 1.0 M,<sup>[23c,24]</sup> exhibiting small and indistinctive EXAFS-FT peaks related with NO<sub>3</sub><sup>-</sup> coordination.<sup>[23c]</sup> Taking into account this fact along with the observed spectral identity between the grey and deep-blue colored spectra in Figure 3 (see Section 1-3 in the Supporting Information), we conclude that the oxo/hydroxo-bridging dinuclear complexes are the dominant form of Ce<sup>IV</sup> in 1.0 M HNO<sub>3</sub> at pH 0.0, albeit the present EXAFS results do not completely exclude the co-existence of higher oligomer complexes at this stage. These results indicate that these small oligomer complexes, not a mononuclear hydrate complex, are the precursors that finally evolve into NC-CeO<sub>2</sub> through hydrolysis, as will be discussed in the following sections. When the pH is increased from "0.0" to "0.3" (deep- and normal-blue-colored data in Figure 3), Peak 3 in Figure 3(b) is split into two with an additional peak at a shorter R range of  $R + \Delta = 3.0$  Å.



Figure 3. (a)  $k^3$ -weighted Ce K-edge EXAFS spectra for  $0.1 \text{ M Ce}^{IV}$  in  $1.0 \text{ M HNO}_3$  with different pH values and reference spectra for  $0.05 \text{ M Ce}^{IV}$  in 2.0 M HClO<sub>4</sub> (grey) and CeO<sub>2</sub> (red): solid lines, experimental data; dotted lines, theoretical curve fits. NaOH was used for pH adjustment. (b) Fourier transforms of EXAFS spectra in (a): the experimental data is given as solid lines; theoretical curve fits are given as dotted lines; *k* range for Fourier transformation,  $k = 2.0-15.0 \text{ Å}^{-1}$ ; phase shifts ( $\Delta$ ) are not corrected. Peak  $1 = \text{Ce}-\text{O}_{\text{oxo}}/\text{O}_{\text{hyd}}$ , Peak  $2 = \text{Ce}-\text{O}(\text{H}_2\text{O})$ , Peak 3 = Ce-Ce, Peak  $4 = \text{Ce}-\text{O}_{\text{oxo}}(\text{CeO}_2)$  (see the main text for more details). The magnitude of the data for CeO<sub>2</sub> powder (red) is reduced by one third relative to the *y* axes for facilitating comparisons of the spectra.

The Ce–Ce distance in Ce<sup>IV</sup> oligomers is expected to shorten as they grow from dimers into larger oligomers.<sup>[22,25]</sup> The thermodynamic data suggests the presence of only di-, tri-, and hexanuclear complexes for soluble Ce<sup>IV</sup> oligomer species in an aqueous solution.<sup>[26]</sup> This has been further supported by DFT calculations.<sup>[25]</sup> Given these facts, the EXAFS-FT peak at  $R+\Delta=3.0$  Å for the blue-colored spectra "0.3" in Figure 3 (b) possibly implies the partial evolution of Ce<sup>IV</sup> species from smaller to larger oligomer complexes. As a matter of fact, the EXAFS curve fitting for the data "0.3" calculates a shorter Ce–Ce distance of 3.28 Å (Table 1), which may be comparable with 3.35 Å found in the trinuclear Ce<sup>IV</sup> complex optimized by a DFT calculation.<sup>[22]</sup> A further increase in pH leads to a drastic change in EXAFS spectra. That is, at pH 0.4 and over, EXAFS oscillation in a higher *k* range (k > 8 Å<sup>-1</sup> in Figure 3(a)) becomes more emphatic, producing an intense peak at  $R + \Delta = 3.5$  Å (Peak 3 in Figure 3(b)) on EXAFS-FT spectra. The position of this intense peak is consistent with that for the nearest Ce–Ce arrangement in CeO<sub>2</sub> (red-colored data in Figure 3(b)). Besides, the EXAFS oscillation cycle for the samples exceeding the critical pH (pH 0.5–12.0) coincides with that of CeO<sub>2</sub> especially in the higher *k* range (Figure 3(a)). Therefore, the EXAFS-FT peak at around  $R + \Delta = 3.5$  Å for the samples "pH 0.4–12.0" can be reasonably assigned to the Ce–Ce arrangement of CeO<sub>2</sub> or similar structure. The calculated Ce–

Table 1. Summary of EXAFS structural parameters obtained from theoretical curve fitting. A complete list of the obtained parameters is provided in the Supporting Information (Table S1).

Sample	Form	Peak 1 or 4 in Figure 3 (b)		Peak 2 in Figure 3 (b) $Ce=O(H_{2}O)$		Peak <b>3</b> in Figure 3 (b)		Peak <b>3</b> in Figure 3 (b)	
bumpie		$CN^{[a]}$	<i>R</i> [Å] <sup>[b]</sup>	CN <sup>[a]</sup>	$R [Å]^{[b]}$	CN <sup>[a]</sup>	R [Å] <sup>[b]</sup>	CN <sup>[a]</sup>	$R [Å]^{[b]}$
2.0 м HClO <sub>4</sub> <sup>[c]</sup>	liquid	1.0	2.03	7.1	2.46	0.8	4.05		
1.0 м HNO <sub>3</sub> (pH 0.0)	liquid	0.7	2.02	7.4	2.43	1.1	4.05		
1.0 м HNO <sub>3</sub> (pH 0.3)	liquid	1.8	2.08	6.9	2.44	1.1	4.05	0.5	3.28
1.0 м HNO <sub>3</sub> (pH 0.4)	liquid	4.0	2.35	3.5	2.47	5.3	3.83		
1.0 м HNO <sub>3</sub> (pH 0.5)	liquid	5.5	2.29	3.4	2.46	5.8	3.81		
1.0 м HNO <sub>3</sub> (pH 0.8)	liquid	8.2	2.28			7.9	3.82		
1.0 м HNO <sub>3</sub> (pH 1.0)	liquid	8.3	2.28			8.8	3.81		
1.0 м HNO <sub>3</sub> (pH 2.0)	liquid	8.2	2.28			11.6	3.81		
1.0 м HNO <sub>3</sub> (pH 5.0)	precipitate	8.0	2.30			11.7	3.82		
1.0 м HNO <sub>3</sub> (pH 12.0)	precipitate	7.7	2.31			11.7	3.82		
CeO <sub>2</sub>	powder	8 <sup>[d]</sup>	2.35			12 <sup>[d]</sup>	3.83		

[a] CN: coordination number; error  $\leq \pm 15$  %. [b] R: interatomic distance; error  $\leq \pm 0.01$  Å. [c] Values taken from Ref. [22]. [d] Fixed values.

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Ce distances for the spectra "pH 0.4-12.0" range from 3.81 to 3.83 Å (Table 1), being in agreement with that found in the crystal structure of CeO<sub>2</sub> (3.83 Å).<sup>[27]</sup> The EXAFS-FT peaks observed at  $R + \Delta = 1.5 - 2.0$  Å (Peaks 1 and 2 in Figure 3(b)) reflect the primary coordination sphere of Ce<sup>IV</sup>. The present Ce<sup>IV</sup> samples are composed of H<sub>2</sub>O, HNO<sub>3</sub>, and NaOH. Taking into account the fact that NO<sub>3</sub><sup>-</sup> are unlikely to interact directly with Ce<sup>IV</sup>, the coordinative ligands potentially found in the primary coordination sphere are water molecules, hydroxide ions (OH<sup>-</sup>) and oxo-oxygens (-O-), all of which are O-coordinating ligands. The peaks 1 and 2 for "HClO<sub>4</sub>" in Figure 3(b), grey-colored data) correspond to the bridging oxo/hydroxo oxygen  $(O_{oxo}/O_{hvd})$  and water molecules, respectively.<sup>[22]</sup> Peak 2 is observable from pH 0.0 to the critical pH of 0.5, indicating the presence of hydrate species. Peak 4 in Figure 3(b) corresponds to the nearest Ce-O<sub>oxo</sub> arrangement in CeO<sub>2</sub> (red-colored spectra). Peak 4 is dominant also for the precipitate samples (pH "5.0" and "12.0" in Figure 3(b)). This suggests that the local coordination arrangement of Ce<sup>IV</sup> in the precipitate formed above pH 2.0 is similar to that in CeO<sub>2</sub>. The structural parameters obtained for these precipitate samples are also well consistent with those for the reference CeO<sub>2</sub> sample (Table 1 and Table S1 in the Supporting Information). For the solution samples (pH "0.0"-"2.0"), Peak 1 becomes distinguishable with a slight fluctuation of peak position as an increase in pH, being dominant in the primary coordination sphere above the critical pH. Since Peak 1 appears in a shorter distance than Peak 2 relating to water molecules, Peak 1 can be attributed to stronger O ligands than water molecules, such as O<sub>oxo</sub>/O<sub>hvd</sub> or OH<sup>-</sup>. This suggests that, with increasing pH, hydrated water molecules are transformed into oxo/hydroxo ligands, which potentially bridge Ce4+ cations through oxolation and olation reactions<sup>[28]</sup> finally to form colloidal species. The solution samples above the critical pH display Peaks 1, 3, and 4 (pH "0.8"-"2.0" in Figure 3(b)), indicating that the colloidal species in these samples are a mixture of CeO<sub>2</sub>-like species and other Ce<sup>IV</sup> oligomers.

The present EXAFS results clearly demonstrate the structural transition of Ce<sup>IV</sup> species from the initial oligomer complexes to CeO<sub>2</sub>-like precipitate through the potential formation of small oligomers. However, it is difficult to fully identify the Ce<sup>IV</sup> colloid forming above the critical pH only by EXAFS, as presumable species (oligomers like hexamer,<sup>[29]</sup> hydroxide species,<sup>[30]</sup> and CeO<sub>2</sub><sup>[27]</sup>) are expected to have similar Ce–Ce distances and, hence, they all would exhibit Peak 3 at similar position in Figure 3 (b). Therefore, additional information is required to further characterize the Ce<sup>IV</sup> colloid.

**High energy X-ray scattering**: HEXS combined with PDF analysis has been recently demonstrated to be a powerful tool for the structural analysis of chemical species in solution and colloidal systems,<sup>[31]</sup> being complementary to EXAFS.<sup>[31c,32]</sup> To acquire additional structural information particularly on the Ce<sup>IV</sup> colloid, HEXS data were collected for selected transparent solutions, colloidal and precipitate

samples. For making the discussion in the following sections clearer, the term "colloid/colloidal" hereafter refers to any particulate forming a colloidal suspension, regardless of the chemical structure of the particulate. The term "crystalline" refers to a compound having a long-range structural order (<1 nm), whereas the term "amorphous" is used for a compound without the long-range structural order.

Figure 4 shows the two-dimensional images of X-ray scattering patterns from the Ce<sup>IV</sup> solution without pH adjustment (pH 0.0, (a) on the left) and the solution at pH 1.0 ((b) on the right). The colloid-free solution at pH 0.0 exhibits a featureless scattering image, whose scattering intensity is de-



Figure 4. Two-dimensional X-ray scattering images (colored circular image), integrated scattering curves (inset graph with a white line) and sample appearance (inset photo) of  $0.5 \text{ M Ce}^{IV}$  in  $1.0 \text{ M HNO}_3$  at pH 0.0 (a) and at pH 1.0 (b). NaOH was employed for pH adjustment. Data were collected 14 days after the sample preparation.

creased monotonously from the scattering center outward (i.e., toward higher scattering angles, inset graph of Figure 4 (a)). This is a typical scattering pattern often called "diffuse scattering",<sup>[9]</sup> representing the absence of long-range order in the sample (e.g., liquid or glass). On the other hand, the solution at pH 1.0, which contains the Ce<sup>IV</sup> colloid, shows clear ring patterns producing Bragg peaks on its integrated scattering curve (inset graph of Figure 4 (b)). This is a clear indication that the particles of the Ce<sup>IV</sup> colloid have a crystalline structure, not an amorphous one. Since (oxy)hydroxide compounds are generally amorphous<sup>[19]</sup> and do not exhibit Bragg peaks, the Ce<sup>IV</sup> colloid formed is most likely a crystalline oxide compound of Ce<sup>IV</sup>.

The collected HEXS data were further treated to extract the total scattering structure function  $(S^{\text{total}}(Q))^{[9]}$  derived only from the Ce<sup>IV</sup> colloid, and finally to produce its pairdistribution functions (PDF; g(R)),<sup>[9]</sup> which represent the radial distribution of the interatomic distances of atomic pairs present in the colloid. Figure 5(a) shows the  $S^{\text{total}}(Q)$ of the Ce<sup>IV</sup> colloid formed at different pH values, along with a reference data of CeO<sub>2</sub> powder. Although the colloid formed at a lower pH of 0.5 displays weaker peak intensity, the position of each peak is almost identical for all the colloid samples, regardless of pH. Besides, the peak positions observed for the Ce<sup>IV</sup> colloid are in good agreement with those for CeO<sub>2</sub> (red-colored data in Figure 5(a)). The PDFs shown in Figure 5(b) further indicate the structural similari-





Figure 5. (a) Total scattering structure functions ( $S^{\text{total}}(Q)$ ) of Ce<sup>IV</sup> colloid ([Ce]=0.1 M) formed at different pH values and a reference compound of CeO<sub>2</sub> powder. (b) Pair-distribution functions (PDFs, g(R)) derived from  $S^{\text{total}}(Q)$  in (a): dotted lines; the positions corresponding to the Ce–Ce pairs found in the CeO<sub>2</sub> structure.<sup>[27]</sup> NaOH was employed for pH adjustment. Data were collected 14 days after the sample preparation.

ty between the Ce<sup>IV</sup> colloid particles and crystalline CeO<sub>2</sub>. That is, all the colloid samples display clear peaks at the positions corresponding to the Ce–Ce distances of the CeO<sub>2</sub> structure (dotted lines in Figure 5 (b)). These results reveal that the colloidal Ce<sup>IV</sup> species formed above the critical pH is actually the nano-sized particles of crystalline CeO<sub>2</sub> (i.e., NC-CeO<sub>2</sub>). The Ce<sup>IV</sup> colloid once formed is no longer soluble even if the solution is re-acidified to pH 0.0 (Section 1–5

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and Figure S12 in the Supporting Information). This also supports the identification of  $CeO_2$  in the colloid particles, as  $CeO_2$  is known to be hardly soluble even in a strong acid, whereas other hydroxide or hydrous oxide compounds are readily soluble in an acidic solution.

The Ce-Ce distances in the colloid structure can be estimated directly from the obtained PDFs. Table 2 summarizes the Ce-Ce distances in the colloid samples prepared in different conditions, along with those for reference CeO<sub>2</sub> powder. The Ce-Ce distances for CeO<sub>2</sub> powder listed in Table 2 agree well with those of the reported crystal structure.<sup>[27]</sup> The Ce<sup>IV</sup> colloid samples exhibit similar Ce-Ce distances as those found for the CeO<sub>2</sub> powder within the average distance error of  $\approx 0.02$  Å, regardless of the type of basic reagent used for pH adjustment, the pH, or the concentration of Ce. This indicates that, unless precipitated, the hydrolysis of Ce<sup>IV</sup> results in the formation of NC-CeO<sub>2</sub> at any condition above the critical pH (Section 1-5 in the Supporting Information). The PDF of the Ce<sup>IV</sup> colloid exhibits an obvious cut-off in correlation peaks at around 2.5-2.6 nm (Figure S15 in the Supporting Information), suggesting that the colloid particles keep their structural order up to 2.5-2.6 nm.

The crystallite (domain) size of the Ce<sup>IV</sup> colloid can be estimated from the peak width of their extracted scattering curves (in  $2\theta$ ) based on the Scherrer equation.<sup>[33]</sup> As shown in Figure 6, the intensity of each scattering peak grows larger as an increase in Ce concentration, although their scattering patterns are identical. The domain size was esti-



Figure 6. X-ray scattering curves (in  $2\theta$ ) of Ce<sup>IV</sup> colloid formed at pH 2.0 with different Ce concentrations: Energy of incident X-ray; 87.1 keV ( $\lambda$ =0.142 Å), pink colored data; NH<sub>3</sub> was employed for pH adjustment, orange colored data; NaOH was employed for pH adjustment. Black lines with numbers at the bottom denote the *hkl* indices of CeO<sub>2</sub>.<sup>[27a]</sup> Data were collected 14 days after the sample preparation.

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Table 2. Summary of Ce–Ce distances for Ce<sup>IV</sup> colloid and CeO<sub>2</sub> powder. The values are obtained by direct reading of x coordinates of the corresponding peak tops on PDFs. The error in Ce–Ce distances is estimated to be  $\pm 0.001$  nm based on 95% height of peak maximum.

[Ce]	pН	Basic	Form $R_{Ce-Ce}$ [nm] $ R_i(CeO_2) $									$ R_i(\text{CeO}_2) - R_i _{\text{average}}$ <sup>[b]</sup>	
[M]	-	reagent <sup>[a]</sup>		1	2	3	4	5	6	7	8	9	[nm]
	0.5			0.383	0.537	0.664	0.767	0.854	1.016	1.153	1.211	1.386	0.0024
0.1	1.0	$NH_3$	colloid	0.383	0.537	0.662	0.767	0.855	1.014	1.151	1.212	1.384	0.0017
	2.0			0.383	0.539	0.664	0.763	0.857	1.014	1.154	1.212	1.384	0.0023
	0.5		colloid	0.384	0.557	0.656	0.770	0.857	1.012	1.162	1.246	1.376	0.0078
	1.0		colloid	0.384	0.544	0.661	0.769	0.856	1.016	1.155	1.214	1.382	0.0014
0.1	2.0	NaOH	colloid	0.383	0.549	0.662	0.767	0.854	1.015	1.149	1.213	1.381	0.0019
	5.0		precipitate	0.381	0.540	0.663	0.767	0.856	1.015	1.151	1.209	1.383	0.0021
	$0.0^{[c]}$		colloid	0.383	0.546	0.661	0.767	0.854	1.015	1.149	1.212	1.381	0.0017
0.5	2.0	NaOH	colloid	0.383	0.545	0.660	0.770	0.856	1.017	1.154	1.215	1.382	0.0022
1.0	2.0	NaOH	colloid	0.383	0.549	0.662	0.767	0.854	1.015	1.149	1.212	1.381	0.0019
CeO <sub>2</sub>			powder	0.384	0.543	0.663	0.768	0.855	1.013	1.152	1.213	1.380	
CeO <sub>2</sub>			crystal structure <sup>[d]</sup>	0.3826	0.5411	0.6627	0.7652	0.8556	1.0123	1.1478	1.2099	1.3795	

[a] Type of basic reagent used for pH adjustment. [b]  $R_i = R_{Ce-Ce}$  for each peak (*i*=1–9),  $R_i(CeO_2) = R_{Ce-Ce}$  for reference CeO<sub>2</sub> powder (listed on the second bottom line on the table). Therefore, the value " $|R_i(CeO_2) - R_i|_{average}$ " is a measure indicating the conformity of each sample with CeO<sub>2</sub>. Sample "[Ce]=0.1 M, pH 0.5 with NaOH" (the 4th line from the top) indicates a large " $|R_i(CeO_2) - R_i|_{average}$ " value of 0.078 Å, mainly due to a large noise level on its spectrum (light-green-colored data in Figure 5 (b)). [c] The sample was first adjusted at pH 2.0 to produce Ce<sup>IV</sup> colloid, and re-acidified to pH 0.0 by using HNO<sub>3</sub>. [d] Values taken from Ref. [27b].

mated from the full widths of half maximum for three distinguishable scattering peaks attributed to (220), (311) and (331) reflections. Table 3 summarizes the domain sizes estimated from their scattering peaks. Interestingly, the domain size in the Ce<sup>IV</sup> colloid particles is little influenced by the formation conditions (i.e., type of basic reagents for pH adjustment, pH value, or Ce concentration), and is calculated to be almost constant (2.6 nm assuming a cubic shape, or 2.9 nm assuming a spherical shape). This domain size is well consistent with the cut-off distance of correlation peaks in PDF (2.5–2.6 nm) and also in line with those of the reported

Table 3. Domain size of Ce<sup>IV</sup> colloid formed in different conditions. The listed values are the average of those derived from the full widths of half maximum (FWHM) or integral widths of (220), (311), and (331) reflection peaks in Figure 6. A detailed description of the domain size estimation based on the Scherrer equation<sup>[33]</sup> is given in Section 1–7 of the Supporting Information.

			Cubic	shape <sup>[a]</sup>	Spherical shape <sup>[b]</sup>			
[Се] [м]	pН	Basic reagent <sup>[c]</sup>	Domain size [nm]	St. dev. (±) [nm]	Domain size [nm]	St. dev. (±) [nm]		
0.1	0.5 1.0 2.0	NH <sub>3</sub>	2.63 2.70 2.43	0.21 0.10 0.08	2.91 3.01 2.72	0.08 0.19 0.17		
0.1	1.0 2.0	NaOH	2.59 2.61	0.21 0.24	2.87 2.84	0.13 0.14		
0.5	2.0	NaOH	2.66	0.26	2.92	0.21		
1.0	2.0	NaOH	2.61	0.15	2.82	0.04		

[a] Domain size  $(D_{hkl}(\text{cubic}) \text{ Å}^{-1}) = 0.94\lambda/\beta_{1/2}\cos\theta$ , in which  $\lambda = 0.142 \text{ Å}$ and  $\beta_{1/2} = \text{FWHM}$  of (hkl) peak. [b] Domain size  $(D_{hkl}(\text{spherical}) \text{ Å}^{-1}) = 1.07\lambda/\beta_i\cos\theta$ , in which  $\lambda = 0.142 \text{ Å}$  and  $\beta_i = \text{integral}$  width of (hkl) peak. [c] Basic reagent employed for pH adjustment. NC-CeO2 synthesized by hydrolysis-related methods (2-3 nm).<sup>[34]</sup> The derived domain size of 2–3 nm is smaller than those estimated by DLS (approximately 4-8 nm, Figure S5 in the Supporting Information). The particle size derived from DLS corresponds to the hydrodynamic diameter, which includes the interfacial double layer surrounding the particle, and also reflects agglomerated particles. Hence, it is theoretically larger than the physical diameter of an individual particle (i.e., domain size). Besides, the domain particles would agglomerate to each other to form larger particles. The particle size estimation by DLS involves these factors, calculating a larger particle size than a single domain size. Another possible scenario could be that DLS is sensitive to a different part of the size distribution, whereas the domain size determination by HEXS is sensitive to only small particle sizes. This is also a possible reason why the domain size derived from HEXS is different from the particle size estimated by DLS. The type of countercations (i.e., Na<sup>+</sup> or  $NH_4^+$  in the present case) also affects the thickness of the interfacial double layer and agglomeration properties. In fact, the NC-CeO<sub>2</sub> prepared by adding NaOH exhibits a wider particle size distribution than that prepared by adding NH<sub>3</sub> (Figure S4 in the Supporting Information). Given the fact that the domain size of the resultant NC-CeO<sub>2</sub> is unchanged regardless of their formation conditions (Table 3), the type of basic reagent for pH adjustment (i.e., countercations) has an influence mainly on the thickness of the interfacial double layer and/or the agglomeration properties of the domain particles, but not on the domain size itself. The NC-CeO<sub>2</sub> with several-nanometer size is composed of just hundreds of atoms, bearing internal structural strain more easily than the rigid and orderly crystal structure in CeO<sub>2</sub> powder. This is probably the cause of the 0.02 Å difference

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in Ce–Ce distances between NC-CeO<sub>2</sub> and a reference CeO<sub>2</sub> powder ( $|R_i(CeO_2)-R_i|_{average}$  in Table 2). The scattering curve of NC-CeO<sub>2</sub> precisely reproduces the *hkl* families of CeO<sub>2</sub> without anomalous reflections (Figure S13 in the Supporting Information), suggesting that the NC-CeO<sub>2</sub> has a high crystallinity and is characterized as a fluorite-type CeO<sub>2</sub> structure.

**Transmission electron microscopy**: The  $Ce^{IV}$  colloid (i.e., NC-CeO<sub>2</sub>) formed above the critical pH was further investigated by TEM to characterize its dried state. Figure 7 shows



Figure 7. A high-resolution transmission electron micrograph of the dried  $Ce^{IV}$  colloid (left) and fast Fourier transformations of Areas (i) and (ii) (right). The sample was prepared by drying a  $Ce^{IV}$  colloid solution (1.0 M  $Ce^{IV}$  in 1.0 M HNO<sub>3</sub>, pH 2.0 adjusted with NH<sub>3</sub>) in the air.

a high-resolution TEM image of the dried Ce<sup>IV</sup> colloid particles formed at pH 2.0 (left) and its Fourier transformation (FT) images (right). The FT image of Area (i) is well consistent with two independent CeO<sub>2</sub>(111) reflections ( $d_{111}$  = 3.12 Å, dihedral angle =  $70.5^{\circ}$ ), whereas the FT image of Area (ii) is in good agreement with  $CeO_2(200)$  and  $CeO_2$ -(022) reflections  $(d_{200}=2.71 \text{ Å}, d_{022}=1.91 \text{ Å}, \text{ dihedral})$ angle = 90°). These results demonstrate that the NC-CeO<sub>2</sub> formed in the solution phase retains its crystalline structure even when it is dried up. The individual domains seem to be agglomerated during the dving process. The size of individual particles of the dried NC-CeO<sub>2</sub> is estimated to be 2-3 nm, being in line with the HEXS and DLS results, as well as the size of the reported NC-CeO<sub>2</sub> particles.<sup>[34]</sup> To generate a lattice image on TEM, several atoms are needed to be lying in the direction of electron beam. Therefore, the clear lattice image shown in Figure 7 suggests that the NC-CeO<sub>2</sub> prepared in this study is highly crystalline.

#### Discussion

Evolution mechanism of nanocrystalline cerium dioxide: The EXAFS results have demonstrated that the initial precursor species, which finally evolve into NC-CeO<sub>2</sub>, is a smaller oligomer species of Ce<sup>IV</sup>, such as a dinuclear complex. An increase in pH will transform such a smaller oligomer species into larger ones before the formation of NC-CeO<sub>2</sub>. The thermodynamical data on the hydrolysis of

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Ce<sup>IV</sup> suggests the formation of hydrolytic Ce<sup>IV</sup> species of up to hexamer.<sup>[26]</sup> A recent DFT study by Aubriet et al.<sup>[25]</sup> has further suggested that, among the possible hydrolytic CeIV oligomers, trimer and hexamer tend to be stabilized during the hydrolysis in particular. It should be noted that tetravalent actinides (An<sup>IV</sup>), the chemical analogues of Ce<sup>IV</sup>, can form stable hexanuclear complexes in aqueous solution only in the presence of strongly coordinating functionalized ligands, such as carboxylic ligands, which can bridge and link adjacent M<sup>IV</sup> centers to reinforce and stabilize the hexanuclear core framework.<sup>[35]</sup> The present system contains NO<sub>3</sub>as a potentially coordinating ligand. However, the coordination of NO<sub>3</sub><sup>-</sup> towards Ce<sup>IV</sup> is expected to be much weaker than that of carboxylic ligands and, hence,  $NO_3^-$  is probably unable to serve as a bridging ligand to stabilize the hexanuclear core structure. Taking into account these facts, the dominant precursor species to finally evolve into NC-CeO<sub>2</sub> are considered to be dimer and trimer species. Of course, the potential presence of other oligomer species cannot be completely excluded, particularly as transition species from dimer/trimer to NC-CeO<sub>2</sub>. However, their lifetime must be very short and, therefore, it is difficult to prove their existence by the present experimental capability. Recently developed time-resolved spectroscopic techniques<sup>[36]</sup> may be able to gain more insight into the dynamics of the formation of these minor oligomer species.

When a basic reagent is added into the system, the following three fundamental reactions will occur with respect to the hydrolysis of  $Ce^{IV}$ :

 $Ce(aq.) + OH^{-} \rightarrow Ce - OH$  (1)

$$Ce(aq.)-OH_2+Ce-OH \rightarrow Ce-OH-Ce+H_2O \tag{2}$$

$$Ce-OH + Ce-OH \rightarrow Ce-O-Ce + H_2O$$
 (3)

Both olation and oxolation reactions (Equations 2 and 3, respectively) can promote the transformation of the initial dimer species into trimer and other oligomer species, as these polynuclear complexes are bridged by oxo- and hydroxo ligands.<sup>[22,25,29]</sup> Here we note that the oxolation reaction (Equation 3) consumes OH<sup>-</sup> to form an oxo-bridge, whereas the stoichiometric amount of OH<sup>-</sup> is unchanged in the olation reaction (Equation 2). It has been mentioned in the section "Results: Visual observation of hydrolysis behavior of Ce<sup>IV</sup>" that the pH value of the Ce<sup>IV</sup> solution increases proportionally to the volume of the basic reagent added from the initial pH (pH 0.0) until the critical pH of 0.5. This increase in pH is stopped at the critical pH, at which the formation of NC-CeO<sub>2</sub> begins, and the pH value becomes constant transiently regardless of the addition of basic reagent. These facts clearly indicate that the olation reaction is dominant in the region of pH 0.0-0.5 to increase hydroxo-bridging species, whereas the oxolation reaction is accelerated suddenly at the critical pH of 0.5 to convert the hydroxo-bridging species to the oxo-bridging ones, which further evolve into CeO<sub>2</sub>.

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The HEXS results indicate that the NC-CeO<sub>2</sub> particles formed above the critical pH have a constant domain size of 2-3 nm. This size is consistent with the smallest size of 2-3 nm for the reported NC-CeO<sub>2</sub> prepared by different methods.<sup>[10b, 37]</sup> The domain particles do not seem to grow larger, even if solution conditions are modified (i.e., Ce concentration, pH, or type of basic reagent). Assuming that the domain particle of NC-CeO<sub>2</sub> has a polyhedral shape with an average diagonal length of 2.6 nm based on the HEXS results, the number of the Ce-Ooxo-Ce unit on one diagonal line of the polyhedron is calculated to be 6-7 (Section 1-6 in the Supporting Information). Tetravalent plutonium (Pu<sup>IV</sup>), whose ionic radius is very close to that of Ce<sup>IV</sup> (hexagonal:  $Pu^{IV} = 0.86 \text{ Å}; Ce^{IV} = 0.87 \text{ Å}, \text{ octahedral: } Pu^{IV} = 0.96 \text{ Å},$ Ce<sup>IV</sup>=0.97 Å),<sup>[21]</sup> is known to form a stable nano-sized oxide cluster of  $[Pu_{38}O_{56}]^{40+}$  in an aqueous solution.<sup>[31d]</sup> The structure of this Pu<sup>IV</sup> cluster is based on the fluorite-type PuO<sub>2</sub> arrangement, in which three Pu-Ooxo-Pu units are lying on a diagonal line. Given the fact that CeO<sub>2</sub> is also based on the fluorite structure, the present NC-CeO<sub>2</sub> is highly likely to form a similar but slightly larger oxide cluster. Assuming that the domain particle of the Ce<sup>IV</sup> colloid is forming a cubic polyhedral cluster (Figure S13 in the Supporting Information), the cluster possesses a huge specific surface. That is, of the 146 Ce atoms, 102 are the end member atoms constituting the cluster surface. This suggests that 69% of Ce atoms in the Ce<sup>IV</sup> cluster are still surrounded by OH<sup>-</sup> and/ or water molecules in solution. Hence, the EXAFS-FT Peak 1 observed for the Ce<sup>IV</sup> colloid samples in Figure 3(b) (pH "0.5"-"2.0") is probably attributed to the Ce-O(OH<sup>-</sup>) bonding of the end-member Ce atoms on the cluster surface, as the Ce-O(OH<sup>-</sup>) distance can be shorter than that of Ce-O<sub>oxo</sub> in the rigid crystal structure of CeO<sub>2</sub>.<sup>[22]</sup>

DLS results suggest that the hydrodynamic diameter of the Ce<sup>IV</sup> colloid and its size distribution are controlled by several factors. As discussed in the "Results: High energy X-ray scattering" section, the difference in hydrodynamic diameter could be attributed to the different thickness of the interfacial double layer around the domain NC-CeO<sub>2</sub> particles, as well as the agglomeration property of the particles. The observed particle size distribution can be interpreted by the agglomeration of domain particles. That is, the domain NC-CeO<sub>2</sub> particles agglomerate to form larger clusters.<sup>[31d, 34a]</sup> The surface of the domain particles is more hydroxidized as an increase in pH, prompting the condensation of the domain particles through the olation reaction. This reasonably explains the observed broadening trend in particle size distribution with increasing pH (Figure 2(a)). A higher metal concentration increases the number of domain particles in the system, augmenting the opportunity for the domain particles to be agglomerated. This is also in line with the broadening trend of particle size distribution with increasing Ce concentration (Figure S3 in the Supporting Information). However, these agglomerated clusters are not stable thermodynamically for a long period of time, as they are disassembled gradually with time and the particle size distribution finally becomes homogeneous with the domain

size of 2-3 nm (Figure 2(b)). The aggregation of the domain particles can be also minimized by adjusting pH at around the critical pH (pH 0.5 in the present condition), which can be readily identified by the observation of pH variation during the titration process.

Simple preparation of nanocrystalline cerium dioxide: Thus far, the synthesis of NC-CeO<sub>2</sub> has required involving "not gentle" chemical processes, such as calcination or use of organic solvents/emulsion, to produce homogeneous and fine particles. Based on the results obtained in this study, the synthetic process for NC-CeO2 can be simplified and alleviated. Firstly, the formation of CeO<sub>2</sub> does not necessarily require a highly basic condition or calcination. The strong olation/oxolation tendency of Ce<sup>IV</sup> is sufficient to produce CeO<sub>2</sub> even in an acidic condition without heating. Besides, NC-CeO<sub>2</sub> powder is obtained simply by evaporating the solution of the Ce<sup>IV</sup> colloid formed above the critical pH. Secondly, NC-CeO<sub>2</sub> seems to possess an intrinsic nature to be stabilized with a specific domain size (2–3 nm in the present conditions). Therefore, the effort for adding organic solvent/ emulsion or physical/chemical processes (e.g., pyrolysis, mechanochemical- or sonochemical process) to homogenize the particle size distribution can be saved. Thirdly, the homogeneousness of NC-CeO2 particles can be controlled by optimizing pH values, Ce concentration, and the type of basic reagents for pH adjustment. The particle size distribution of NC-CeO<sub>2</sub> colloid also tends to become homogeneous with aging. This aging effect may be accelerated by gentle heating. The size of NC-CeO<sub>2</sub> particles can be possibly controlled simply by selecting the type of basic reagents (i.e., countercations), which play an important role in stabilizing nanocrystals with a specific size in solution.<sup>[38]</sup>

#### Conclusion

The present study has demonstrated that a combination of DLS, XAS, and HEXS is a very powerful and comprehensive approach to study in situ the evolution of nanocrystalline materials in solution. This multiple spectroscopic approach has been applied to the formation of NC-CeO<sub>2</sub> induced by the hydrolysis of Ce<sup>IV</sup>. The obtained results have proven that, with increasing pH, the initial precursor Ce<sup>IV</sup> species of small oligomer complexes, such as a dinuclear complex, grow into larger ones through olation/oxolation reactions, finally producing a colloid being composed of CeO<sub>2</sub> with a uniform domain size of 2-3 nm. In the solution conditions studied, the NC-CeO<sub>2</sub> colloid is already formed at a critical pH of 0.5, which is very acidic. The formation of NC-CeO<sub>2</sub> in an acidic condition, as well as the presence of the initial hydroxo/oxo-bridging dinuclear complexes, stems mainly from the strong olation/oxolation tendency of Ce<sup>IV</sup>. Based on these findings, the synthetic route to NC-CeO<sub>2</sub> can be simplified and alleviated. That is, a simple evaporation of the Ce<sup>IV</sup> colloidal solution, which is prepared by a careful pH adjustment with a selected basic reagent, will result in the production of fine NC-CeO<sub>2</sub> powder. Besides, this simple synthetic method can be potentially applied to the production of other nanocrystalline metal oxides, such as TiO<sub>2</sub> from Ti<sup>IV,[39]</sup> or ZrO<sub>2</sub> from Zr<sup>IV,[40]</sup> as these oxides can be prepared through the hydrolysis of the corresponding tetravalent cations. The key to establishing the hydrolysisbased simple route to nanocrystalline metal oxides is to identify the critical pH condition at which the nanocrystals begin to form. To this end, the present multi-spectroscopic analytical approach serves as a promising tool for optimizing the synthesis conditions to obtain nanocrystalline metal oxides, as it is a versatile approach applicable to any other solution or colloidal system.

#### **Experimental Section**

Sample preparation: A weighted amount of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Rare Metallic Co. Ltd., or Sigma-Aldrich Co., 99.99%) was dissolved into 1.0 M HNO<sub>3</sub> (100 mL) to give a Ce concentration of 0.1, 0.5, or 1 M. The solution was then electrolyzed at 1.9  $V^{\rm [22]}$  to oxidize  $Ce^{\rm III}$  to  $Ce^{\rm IV}$  by using a potentiostat (ALS Electrochemical Analyzer Model 600C or Metrohm Autolab PGSTAT12/30/302) with a three electrode system (Pt-plate working and counter electrodes, and a Ag/AgCl reference electrode). After the electrolysis, the Ce oxidation state in the solution was confirmed to be tetravalent by fluorescence spectroscopy (Figure S1 in the Supporting Information) and Ce K-edge XANES spectroscopy (Figure S2 in the Supporting Information). The resultant solution was employed as a stock solution for subsequent pH titration experiments. That is, the stock solution was sequentially titrated by a NaOH or NH<sub>3</sub> solution to prepare a series of Ce<sup>IV</sup> solution samples with different pH values. To minimize the local pH excursion effects, which potentially produce larger aggregate species, the titrand solution was stirred vigorously and the basic concentration and titrant volume added were minimized in the course of pH adjustment. At each pH, a small portion of the titrated solution was collected for spectroscopic measurements. The whole titration process involved less than 5% decrease in solution volume. Therefore, we consider that a suite of the collected solution samples has a constant Ce concentration. The pH measurement was performed by using a pH meter (HORIBA F-52 or inoLab WTW-pH720) calibrated with four different pH buffer solutions (pH 1.68, 4.01, 6.86, and 9.18 at 298 K). All sample preparation and sealing were performed in an inert glove box filled with N2 to avoid the penetration of atmospheric oxygen or carbon dioxide into the sample solutions. Additionally, deionized water used for sample preparation was degassed and deoxygenated by purging N2 prior to its use.

**Dynamic light scattering:** Sample solutions enclosed in a Pyrex glass cuvette were irradiated by an argon ion laser LEXEL 95 (LEXEL Laser, 400 mW, 514.5 nm wavelength) at a constant temperature of 298 K. The intensity of scattered light from the samples was detected at a right angle to the incident light by using a BI-90 Particle Size Analyzer (Brookhaven Instruments Co.) with a 120 second duration. The measurement was repeated ten times for each sample and the collected data were averaged. The autocorrelation functions, C(r), were calculated from the fluctuations of the scattered light intensity to estimate the hydrodynamic radii (i.e., Stokes radii) of the particles in the samples.<sup>[18]</sup> The Cumulant expansion and the CONTIN analysis were employed to derive the particle size information based on the obtained C(r).<sup>[41]</sup> For the measurements of aging effect, the samples were triply sealed in a glass cuvette and stored in a N<sub>2</sub>-filled inert glove box between the measurements, to avoid possible penetration of air into the samples.

X-ray absorption spectroscopy: X-ray absorption spectra, including both XANES and EXAFS regions, were collected at Ce K-edge (40.447 keV) in quick-scanning mode at the JAEA Quantum Dynamics Beamline BL11XU,<sup>[42]</sup> SPring-8, under the ring operating conditions of 8 GeV and

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99 mA with top-up mode. A liquid N2-cooled Si(311) double crystal was employed to monochromatize white X-rays from the synchrotron ring. All spectra were collected in transmission mode by using ionization chambers filled with an Ar/N<sub>2</sub> mixture (Ar/N<sub>2</sub>=5:5) at ambient temperature and pressure. Prior to the measurement of each sample, the energy of incident X-rays was corrected by measuring the first inflection point of the Ce K-edge spectrum (defined as 40.447 keV) for reference CeO<sub>2</sub> powder. For each sample, a single scan from 40.07 to 41.92 keV was completed in 60 seconds, and the scan was repeated 20 times. The obtained 20 spectra were then averaged for data analysis. The pH adjustment of sample solutions was carried out in a N2-filled glove box immediately before the measurement. The sample solutions were enclosed in a doubly sealed plastic cuvette with an optical path length of 10 mm in the same N2-filled glove box, and transferred to the beamline directly. The whole measurement process, including pH adjustment, sample sealing, sample transport, and collecting XAS spectra was completed within 30 min. Precipitate samples were measured as a "wet" form, in which the precipitate was gathered at the bottom of the sample cuvette by spontaneous sedimentation, without removing solution phase or evaporation. EXAFS data analysis was performed according to the standard procedure<sup>[43]</sup> by using a dedicated program WinXAS (version 3.2).<sup>[44]</sup> EXAFS structural parameters were obtained by theoretical curve fitting both in k space (i.e., EXAFS oscillation spectra) and in R space (i.e., Fourier-transformed spectra). The threshold energy,  $E_{k=0}$ , was defined as the first inflection point of each spectrum. Theoretical phase and amplitude required for the curve fitting were calculated by a program code FEFF 8.20<sup>[45]</sup> based on the reported crystal structures of CeO<sub>2</sub>,<sup>[27b]</sup> Ce<sup>IV</sup> dinuclear complexes<sup>[46]</sup> and DFT-optimized Ce<sup>IV</sup> oligomer complexes.<sup>[22]</sup> All significant single-scattering- (SS) and multiple-scattering (MS) paths, whose relative amplitude was calculated to be more than 15%, were taken into account on the curve fitting. The amplitude reduction factor,  $S_0^2$ , was fixed at 0.9, and the shifts in the threshold energy,  $\Delta E_{k=0}$ , were constrained to be the same value for all shells, to reduce the free parameters on the curve fit procedure as much as possible.

High energy X-ray scattering: HEXS measurements were performed on beamline ID15B at the ESRF by using a 87 keV ( $\lambda = 0.142$  Å) monochromatic X-ray beam selected by a single Si(511) bent Laue crystal. The cross section of the beam was adjusted to 0.1×0.1 mm<sup>2</sup> by tungsten slits in front of the sample. Two-dimensional scattering images were recorded at room temperature on a mar345 image plate detector (Marresearch GmbH) in transmission geometry. The distance between the sample and the detector was 300 mm. Samples were sealed in a polycarbonate capillary (2.0 mm in diameter) with epoxy and packaged in a  $N_2$ -filled sample container having a Kapton window. The scattering data of an empty capillary and Ce-free blank solutions (i.e., aqueous HNO<sub>3</sub> with NaOH or NH<sub>3</sub>) were also collected for background subtraction. Data reduction and PDF analysis were carried out on a software package IGOR Pro (version 6.0) with the dedicated macro commands developed by S. Skanthakumar and co-workers at Argonne National Laboratory, according to the same procedure described previously by the same group.[31,47] Fourier transformation from Q space  $(Å^{-1})$  into R-space (Å) was performed in the range of  $Q = 1.0 - 21.0 \text{ Å}^{-1}$ .

**Transmission electron microscopy**: A Titan 80-300 electron microscope (FEI) operating at 300 kV was employed for acquiring TEM images in bright field. The instrument is equipped with a field emission gun, a SuperTWIN- $\alpha$  lens, and an image corrector providing a point resolution of 0.10 nm. Samples for TEM measurement were prepared by dropping a 5 or 10  $\mu$ L of a sample solution on a 400-mesh copper grid coated with carbon film (10 to 15  $\mu$ m in thickness, Plano GmbH), wicking away the solution with a filter paper, and drying in a desiccator for one day.

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#### Nanomaterials -

A. Ikeda-Ohno,\* C. Hennig, S. Weiss, T. Yaita, G. Bernhard ......

Hydrolysis of Tetravalent Cerium for a Simple Route to Nanocrystalline Cerium Dioxide: An In Situ Spectroscopic Study of Nanocrystal Evolution



**Nanocrystal evolution**: A multi-spectroscopic approach has revealed that the hydrolysis of tetravalent cerium  $(Ce^{IV})$  produces a colloidal solution of fine cerium dioxide  $(CeO_2)$  nanocrystals (see figure). A simple synthetic concept of nanocrystalline metal oxides is proposed based on the obtained results.



#### CeO<sub>2</sub> nanocrystals

Simple hydrolysis of aqueous tetravalent cerium (Ce<sup>IV</sup>), that is, without additional physical or chemical processes, gives nanosized crystalline cerium dioxide (CeO<sub>2</sub>) particles. Multispectroscopic analysis shows that the transformation of small oligomeric Ce<sup>IV</sup> complexes into nanosized cerium dioxide proceeds through olation/oxolation reactions. The study outlines a simple and conceptually new way of preparing metal oxide nanocrystals and a strategy for analyzing nanocrystal evolution in situ. For more details, see the Full Paper by A. Ikeda-Ohno et al. on page **I**ff.