Supplementary Information

Globular pattern formation of hierarchical ceria nanoarchitecture

Noboru Aoyagi[1]*, Ryuhei Motokawa[1,2], Masahiko Okumura[3], Takumi Saito[1,4],

Shotaro Nishitsuji[5], Tomitsugu Taguchi[6], Takumi Yomogida[7] and Atsushi Ikeda-Ohno[1]

[1]Advanced Science Research Centre (ASRC), Japan Atomic Energy Agency (JAEA), Tokai-mura, Ibaraki 319-1195 Japan

[2]Materials Sciences Research Centre (MSRC), Japan Atomic Energy Agency (JAEA), Tokai-mura, Ibaraki 319-1195 Japan

[3]Centre for Computational Science and e-Systems, JAEA, Kashiwa, Chiba 277-0871, Japan

[4]Nuclear Professional School, School of Engineering, The University of Tokyo, Ibaraki 319-1188 Japan

[5]Graduate School of Science and Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan

[6]National Institutes for Quantum and Radiological Science and Technology, Tokai-mura, Ibaraki 319-1106, Japan

[7]Nuclear Science and Engineering Centre (NSEC), Japan Atomic Energy Agency (JAEA), Tokai-mura, Ibaraki 319-1195 Japan

Author Note

*E-mail: aoyagi.noboru@jaea.go.jp

TABLE OF CONTENTS

1. A set of Ce^{IV} concentration parameters for nanoclusters and ions obtained from SAXS analysis

The SAXS intensity $I(q)$ obeys the following relationship:

$$I(q=0)=\phi_s \cdot V_s \cdot (\rho_s - \rho_m)^2, \quad \text{(S1)}$$

where ϕ_s [N.D.] is the volume fraction of the secondary clusters of our concern, V_s [cm^3] is the volume of a single secondary particle, ρ_s and ρ_m are the scattering length density [cm^{-2}], respectively. Here, the summation of the volume fraction is

$$\phi_w + \phi_s + \phi_m = 1 \quad \text{(S2)}$$

with the volume fraction of water, ϕ_w, and of matrix, ϕ_m, respectively. The matrix includes all of the ionic species in the system: $Ce_m(OH)_n^{(4m-n)+}$. In the present study, we assume m=1 and n=4 as the representative parameters with the one having close formula to the density available for relevant species ρ_s given in Table S1. Remember that this leads to a discrimination to obtain a proper solution of the polynomial in the present case.

Table S1. Chemical formula, the density of the compounds, and scattering line density in the literature. 1-6

Chemical formula	density, D_x [Mg/m^3]	S.L.D. [$Å^{-2}$]		S.L.D. [cm^{-2}]		Ref.No.
		Re	Im	Re	Im	
H_2O	0.998 (25℃)	9.52E-06	-3.17E-06	9.52E+10	-3.17E+10	
Ce (Metal)	6.77	4.61E-05	-8.23E-06	4.61E+11	-8.23E+10	
CeO_2	7.20	5.13E-05	7.21E-06	5.13E+11	7.21E+10	1
$Ce^{III}(OH)_3$	4.57	3.40E-05	4.15E-06	3.40E+11	4.15E+10	2
$Ce^{III}(NO_3)_3(H_2O)_6$	2.40	1.97E-05	9.99E-07	1.97E+11	9.99E+09	3
$[NH_4]_2[Ce^{IV}(NO_3)_6]$	2.49	2.05E-05	1.08E-06	2.05E+11	1.08E+10	4
$[Ce^{IV}{}_2(\mu_2\text{-}OH)_2(NO_3)_6(H_2O)_8]$	2.48	2.02E-05	1.08E-06	2.02E+11	1.08E+10	5
$[Ce_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(NO_3)_8]$	3.85	2.93E-05	2.71E-06	2.93E+11	2.71E+10	6

The volume fraction of the second clusters, ϕ_s [cm^3], is

$$\phi_s := \frac{C_s M_s}{d_s} \frac{[\mathrm{mol}][\frac{\mathrm{g}}{\mathrm{mol}}]}{[\frac{\mathrm{g}}{\mathrm{cm}^3}]}, \qquad \text{(S3)}$$

Where C_s [mol] is the number of the secondary clusters, M_s [g/mol] is the formula weight of the primary particle, d_s [g/cm^3] is the density of the particle. In the similar manner, we have the following fractions with C_m [mol] is the number of Ce ions in the matrix medium M_m [g/mol] is the formula weight of the ionic species, d_m [g/cm^3] is the density of the ionic species. Each fraction defines

$$\frac{\phi_w := \left(10^3 - \frac{C_s M_s}{d_s} - \frac{C_m M_m}{d_m}\right)}{10^3}, \qquad \text{(S4)}$$

and

$$\phi_m := \frac{C_m M_m}{10^3 d_m}, \qquad \text{(S5)}$$

where, the eq. S3 with concentration [mol/L] description provides dimensionless fraction for $k = w, s, \text{or } m$:

$$\phi_i = \frac{C_k M_k}{10^3 d_k}. \qquad \text{(S6)}$$

In the meantime, the scattering length density ρ_m in the eq(S1) is the summation of that of water and the matrix by a factor of their volume fraction χ_w and χ_I, respectively. The actual matrix contains a variety of the ionic species; however, we select $Ce(OH)_4$ as a presumable species in a succinct model case with a density of D_x = 2.49 [g/cm^3] (Table S1). As long as we investigated, no data is available for the density of $Ce(OH)_4$. This might be due to an extensive hygroscopic nature or the reason the determination of the hydration number

and the subsequent structures is very difficult. Therefore, we used $D_x = 2.49$ [g/cm^3] that is the value for CAN, instead. Some possible density candidates are listed in Table S1, ranging from 7.20 for CeO_2 to 2.40 for $Ce^{III}(NO_3)_3(H_2O)_6$. In reality, the system of our interest has a complicated mixture of the multiple components—the optimal value for the present second cluster might exist in between.

Note that ρ_I represents a scattering length density for the corresponding ion: $Ce(OH)_4$.

$$\rho_m = \chi_w \rho_w + \chi_i \rho_i \qquad \text{(S6)}$$

with

$$\chi_w = \frac{10^3 - \frac{C_s M_s}{d_s} - \frac{C_i M_i}{d_i}}{10^3 - \frac{C_s M_s}{d_s}} \qquad \text{(S7)}$$

and

$$\chi_i = \frac{\frac{C_i M_i}{d_i}}{10^3 - \frac{C_s M_s}{d_s}} \qquad \text{(S8)}$$

Total concentration of Ce^{4+} [mol/L] ions preserves;

$$\frac{C_t}{10^3} = \frac{C_s}{10^3} + \frac{C_i}{10^3} \qquad \text{(S9)}$$

In the case of $C_{Ce^{IV}} = 0.05$ [M], which is the second series in the Procedure and Apparatus section, we substitute $\frac{C_t}{10^3} = 0.05$ [M] for the total concentration. With the eq (S7) and the eq (S8), the eq (S6) turns into

$$C_i = -\frac{d_i}{d_s}\frac{M_s}{M_i}\frac{\rho_w - \rho_m}{\rho_w - \rho_i} C_s + 10^3 \frac{d_i}{M_i}\frac{\rho_w - \rho_m}{\rho_w - \rho_i} . \qquad \text{(S10)}$$

And thus, one obtains the following simple solvable problem with a third order polynomial of ρ_m by using parameters in Table S2 and erasing C_i and C_s from the eq (S10) in combination with the eq (S9):

$$\rho_m^3+b_2\rho_m^2+b_1\rho_m+b_0=0 \qquad \text{(S11)}$$

Table S2. Parameters used for the calculation.

Given variables	value	unit	remark
$I(q=0)$	231.77	cm^{-1}	Exp.
V_s	8.01E-11	cm^{-2}	Exp.
ρ_w	9.44E+10	cm^{-2}	Exp.
ρ_s	5.20E+11	cm^{-2}	Exp.
ρ_i	1.88E+11	cm^{-2}	Exp.
b_2	−1.135E+12		numerical
b_1	3.67E+23		numerical
b_0	−2.564E+34		numerical

The numerical solutions of the eq (S11) are complex numbers with the negligible imaginary parts. Two of the solutions give the negative numbers for C_i. Therefore, an effective solution is:

$$\rho_m = 9.58E+10 \ cm^{-2} \qquad \text{(S12)}$$

Finally, the corresponding concentrations are

$$C_i = 6.97E{-}03 \text{ M}, \quad \text{(S13)}$$

and

$$C_s = 4.30E{-}02 \text{ M}. \quad \text{(S14)}$$

2. The determination of the aggregation number (n_A) in a single secondary cluster

The volume of the secondary cluster satisfies the following relation with that of the primary cluster (V_p), the association number (n), and a filling factor (ζ)

$$V_s = V_p \cdot n \cdot \zeta \ , \qquad \text{(S15)}$$

Where the maximum number allowed is $\zeta_{max} \sim 0.64$ for a hexagonal closest packing. In the present spherical approximation, $V_s = (\frac{3}{4})\pi R_s^3$ and $V_p = (\frac{3}{4})\pi R_p^3$ provide the mean aggregation number of the secondary clusters: $\overline{n}$=27.0. The following scheme is an updated scheme described in the Introduction section via the present discussion.

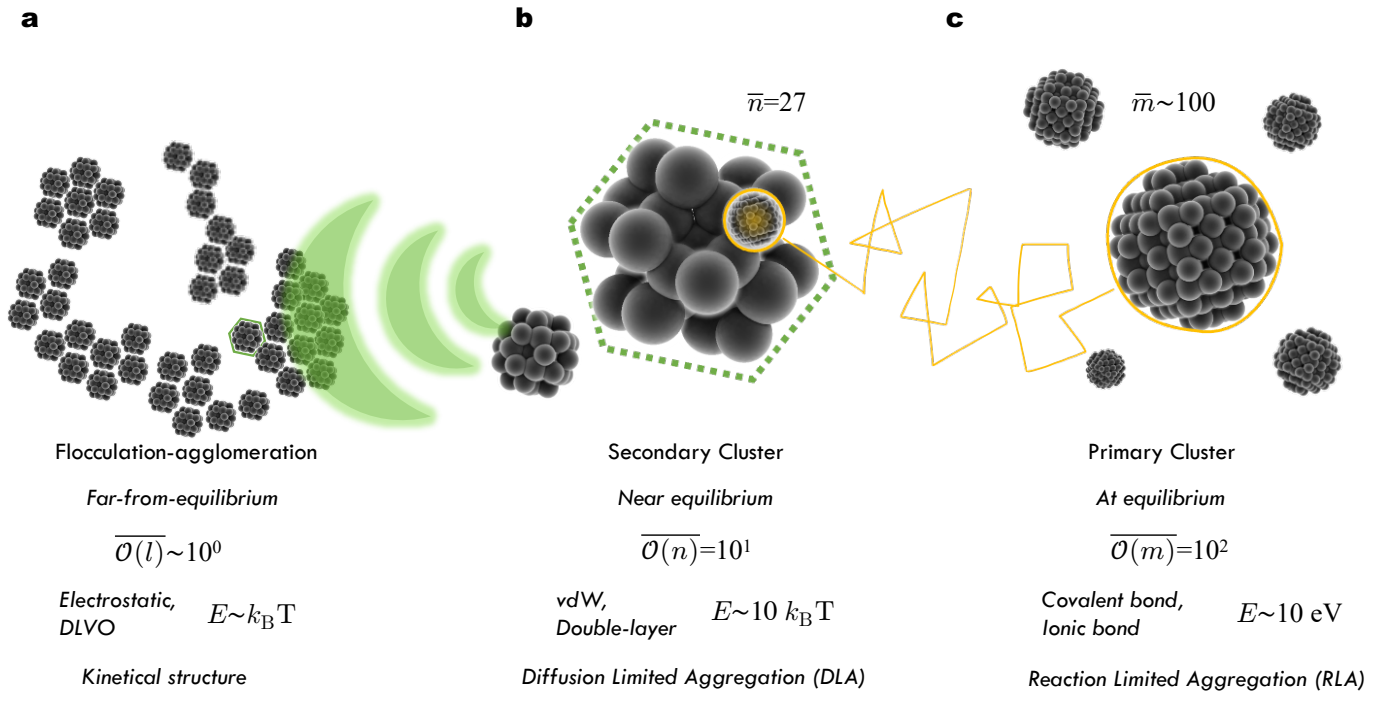

Fig. S1. A hierarchical nanoarchitecture concluded in the present study. **a** Flocculation–agglomeration model. Common in kinetical structure observed on a carbon-coated copper microgrid. **b** Secondary cluster with the mean value of aggregation number $\overline{n}$ = 27. Diffusion Limited Aggregation is in control; that is, the Brownian motion (orange solid line segments represent a zigzag trace) is a key path. **c** Primary cluster with the mean value of Ce^{IV} in a single particle $\overline{m}$ ~ 100.

References

(1) Itoh, T.; Mori, M.; Inukai, M.; Nitani, H.; Yamamoto, T.; Miyanaga, T.; Igawa, N.; Kitamura, N.; Ishida, N.; Idemoto, Y., Effect of Annealing on Crystal and Local Structures of Doped Zirconia Using Experimental and Computational Methods. *J. Phys. Chem. C* **2015,** *119*, 8447-8458.

(2) Mullica, D. F.; Oliver, J. D.; Milllgan, W. O., Cerium trihydroxide. *Acta Crystallographica Section B* **1979,** *35*, 2668-2670.

(3) Milinski, N.; Ribar, B.; Sataric, M., PENTAAQUATRINITRATOCERIUM(III) MONOHYDRATE, CE(H2O)5(NO3)3.H2O. *Crystal Structure Communications* **1980,** *9*, 473-477.

(4) Beineke, T. A.; Delgaudio, J., Crystal structure of ceric ammonium nitrate. *Inorg. Chem.* **1968,** *7*, 715-721.

(5) Guillou, N.; Auffrédic, J. P.; Louër, D., Synthesis, Crystal Structure, and Thermal Behavior of Cerium(IV) Oxide Nitrate Ce2O(NO3)6(H2O)6 · 2H2O. *Journal of Solid State Chemistry* **1994,** *112*, 45-52.

(6) Calvez, G.; Daiguebonne, C.; Guillou, O.; Le Dret, F., A New Series of Anhydrous Lanthanide-Based Octahedral Hexanuclear Complexes. *Eur. J. Inorg. Chem.* **2009,** *2009*, 3172-3178.