

Supplemental Information

Solution Synthesis of Homogeneous Plate-like Multifunctional CeO₂ Particles

Shu YIN*, Yoshihiro MINAMIDATE, Shunsuke TONOUCHI, Takehiro GOTO, Qiang DONG,
Hisanori YAMANE and Tsugio SATO

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan

*E-mail: shuyin@tagen.tohoku.ac.jp

Table SI-1 Structure refinement and crystallographic data for Ce₂(CO₃)₃ · 8H₂O.

Empirical formula	Ce ₂ (CO ₃) ₃ · 8H ₂ O
Formula weight	604.40
Temperature	293(2) K
Diffractometer type	Rigaku RAXIS-RAPID
Scan mode	Ω
Crystal system	Orthorhombic
Space group	<i>Pmn</i> 2 ₁ (No. 31)
Unitcell dimensions	
<i>a</i> (Å)	9.5324(7)
<i>b</i> (Å)	8.4915(7)
<i>c</i> (Å)	8.9523(8)
Volume (Å ³)	724.64(10)
Calculated density (g cm ⁻³)	2.770
<i>Z</i>	2
Wavelength	0.71075 Å (Mo K α)
Absorption coefficient	6.292 mm ⁻¹
Crystal shape, color	platelet, transparent
Crystal size	0.100 x 0.007 x 0.112 mm
Absorption correction	numerical (NUMABS; Higashi, 1999)
Max. and min. transmission	0.962 and 0.599
Reflection collected	3321
Independent reflections	811 (<i>R</i> _{int} =0.079), (684 <i>I</i> > 2 σ (<i>I</i>))
θ range for data collection	3.12 to 20.82°
Limiting indices	<i>h</i> = -9 -> 9, <i>k</i> = -8 -> 8, <i>l</i> = -8 -> 8
Refinement method	Full-matrix least squares on <i>F</i> ²
Final <i>R</i> indices	<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] = 0.0410, <i>wR</i> (<i>F</i> ²) = 0.0973
Goodness-of-fit on <i>F</i> ²	1.088
Data/restraints/parameters	811/1/67
Weight	<i>w</i> = 1/[$\sigma^2(F_o^2) + (0.0222P)^2 + 4.8138P$], where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
Largest diff. peak and hole	2.23 and -1.03 eÅ ⁻³

Table SI-2 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce1	0.0181(7)	0.0333(9)	0.0121(7)	-0.003(3)	0.000	0.000
Ce2	0.0172(7)	0.0317(9)	0.0139(7)	0.002(3)	0.000	0.000

Table SI-3 Selected interatomic distances ($\text{\AA}$) of $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$.

Ce1 O4	2.494(12) x 2
Ce1 O3	2.511(12) x 2
Ce1 O3	2.511(12)
Ce1 O2(H ₂ O)	2.57(3) x 2
Ce1 O1(H ₂ O)	2.636(13) x 2
Ce1 O3(H ₂ O)	2.73(4) x 2
Ce1 O5	2.746(12) x 2
Ce2 O2	2.496(12) x 2
Ce2 O5	2.521(13) x 2
Ce2 O3	2.535(12) x 2
Ce2 O5(H ₂ O)	2.55(3) x 2
Ce2 O4(H ₂ O)	2.64(3) x 2
Ce2 O4	2.794(12) x 2
C1 O1	1.24(2)
C1 O2	1.34(4) x 2
C2 O5	1.275(19)
C2 O4	1.277(19)
C2 O3	1.28(2)

Table SI-4 The atomic coordinates, occupancies and isotropic atomic displacement parameters of $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$.

Atom	site	occ.	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{\AA}^2)^{\text{a}}$
Ce1	2 <i>a</i>	1.0	0	0.50146(13)	0.5135(4)	0.0211(4)
Ce2	2 <i>a</i>	1.0	0	0.56276(14)	0.0135(4)	0.0209(4)
C1	2 <i>a</i>	1.0	0	0.212(3)	0.011(8)	0.039(6)
C2	4 <i>b</i>	1.0	0.2471(18)	0.437(2)	0.308(2)	0.017(5)
O1	2 <i>a</i>	1.0	0	0.067(2)	-0.006(4)	0.058(7)
O2	4 <i>b</i>	1.0	0.0929(12)	0.2991(14)	0.0869(13)	0.028(3)
O3	4 <i>b</i>	1.0	0.2425(12)	0.4087(16)	0.4482(13)	0.033(4)
O4	4 <i>b</i>	1.0	0.3630(12)	0.4184(15)	0.2383(13)	0.025(4)
O5	4 <i>b</i>	1.0	0.1341(13)	0.4789(16)	0.2428(14)	0.025(3)
O6(H ₂ O)	4 <i>b</i>	1.0	0.3657(12)	0.2360(16)	0.0787(13)	0.040(4)
O7(H ₂ O)	4 <i>b</i>	0.5	0.076(3)	0.245(4)	0.643(3)	0.005(8)
O8(H ₂ O)	4 <i>b</i>	0.5	0.071(4)	0.233(5)	0.364(4)	0.051(14)
O9(H ₂ O)	4 <i>b</i>	0.5	0.409(3)	0.187(3)	0.369(4)	0.024(9)
O10(H ₂ O)	4 <i>b</i>	0.5	0.389(3)	0.189(4)	0.622(4)	0.039(11)
O11(H ₂ O)	4 <i>b</i>	0.5	0.128(4)	-0.003(4)	0.357(4)	0.045(12)
O12(H ₂ O)	4 <i>b</i>	0.5	0.159(4)	0.023(5)	0.640(5)	0.059(13)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

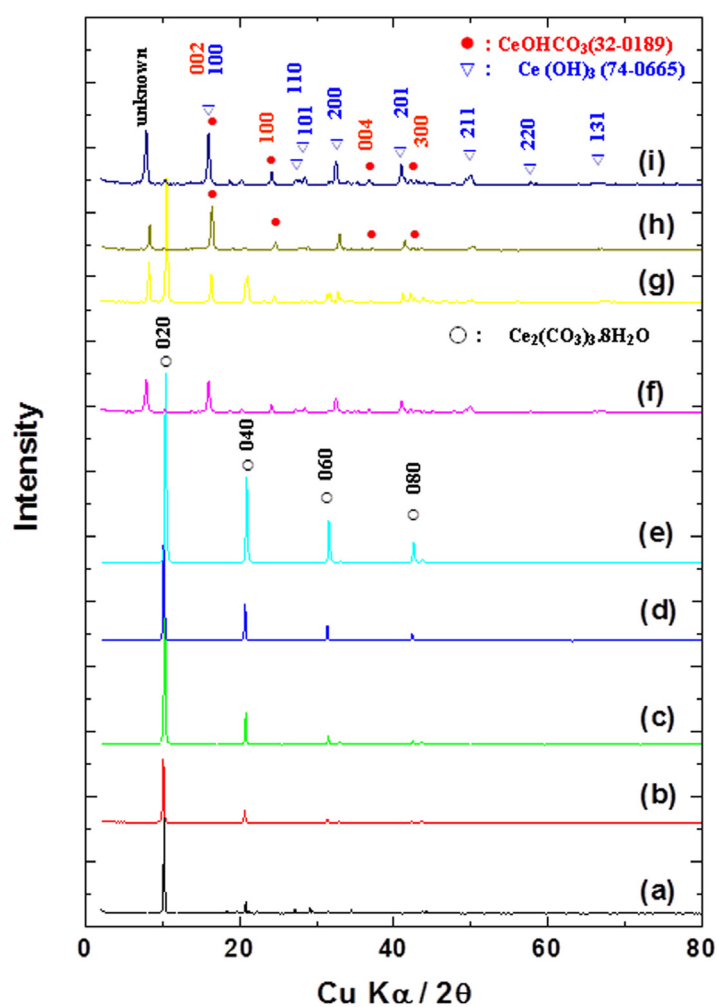


Fig.SI-1 XRD patterns of the cerium precursors prepared at (a)pH 4.81, (b)pH5.66, (c)pH5.74, (d)pH5.99, (e)pH6.04, (f)pH6.74, (g)pH6.87, (h)pH8.69, and (i) pH9.83

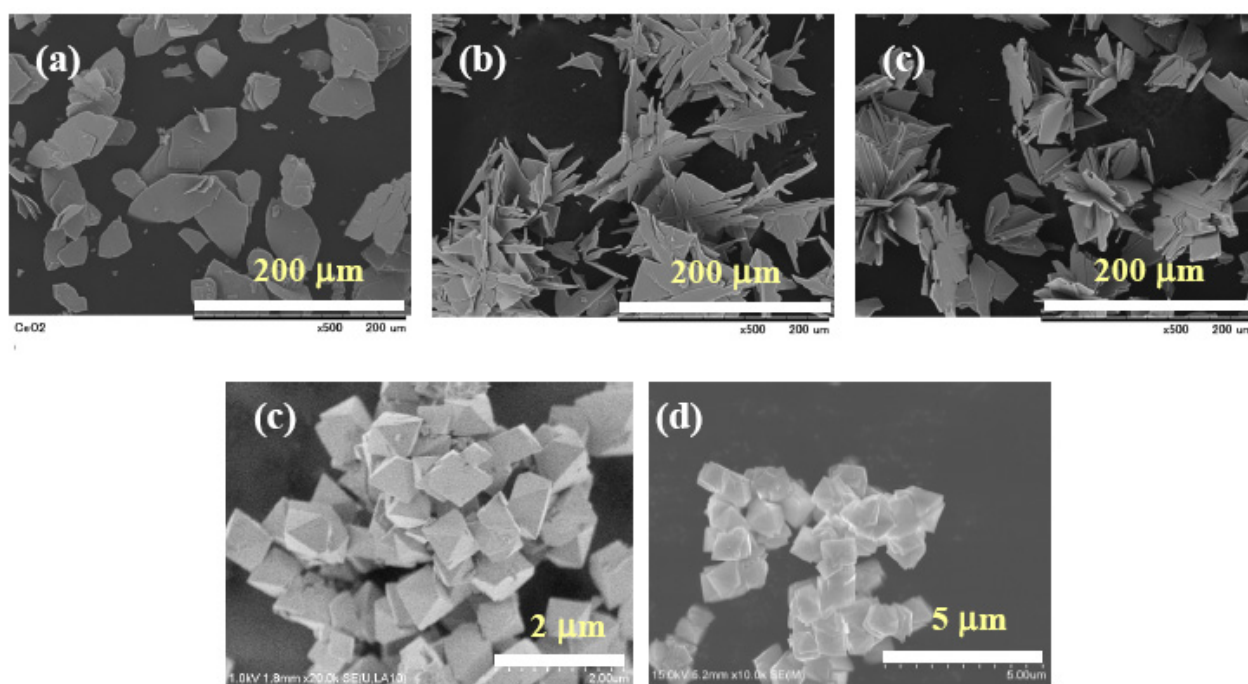


Fig.SI-2 SEM images of the particles synthesized in 0.1M $\text{Ce}(\text{NO}_3)_3$ solution (a) 25°C, (b) 50°C, (c) 75°C, (d) 100°C and (e) 200°C, using 0.3M NaHCO_3 solution as precipitator.

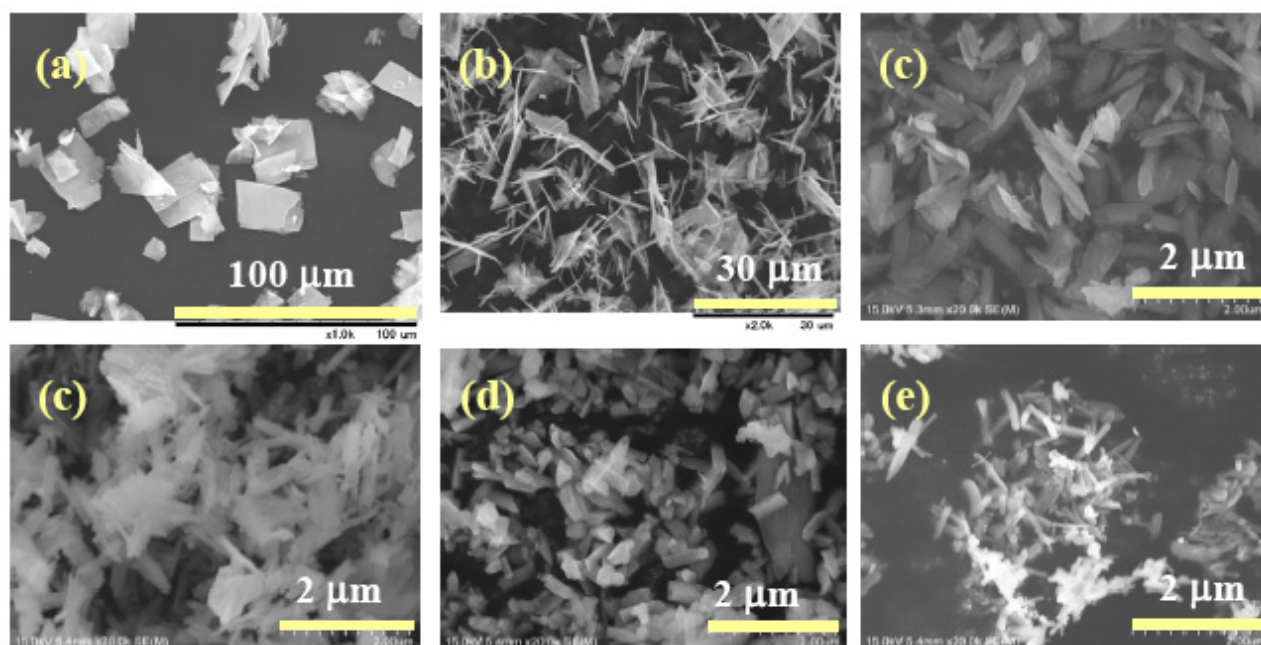


Fig.SI-3 SEM images of the particles synthesized in 0.1M $\text{Ce}(\text{NO}_3)_3$ solution (a) 25°C, (b) 50°C, (c) 75°C, (d) 100°C, (e) 150°C and (e) 200°C, using 0.27M NaHCO_3 / 0.03M Na_2CO_3 mixed solution as precipitator.

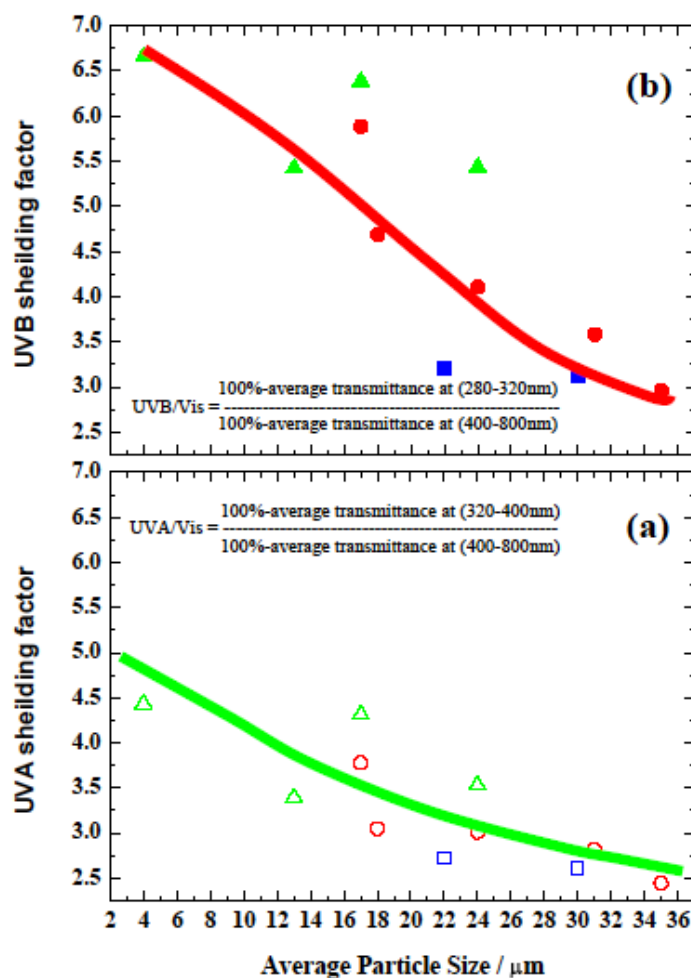


Fig.SI-4 The relationship between average particle size and (a) UVA/Vis shielding factor; (b) UVB/Vis shielding factor. Different marks indicated the samples synthesized in different solvents. ●, ○: aqueous solution; ▲, △: ethylene glycol solution; ■, □: ethanol solution.

$$\text{UVA/Vis} = \frac{100\% - \text{average transmittance at (320-400nm)}}{100\% - \text{average transmittance at (400-800nm)}}$$

$$\text{UVB/Vis} = \frac{100\% - \text{average transmittance at (280-320nm)}}{100\% - \text{average transmittance at (400-800nm)}}$$

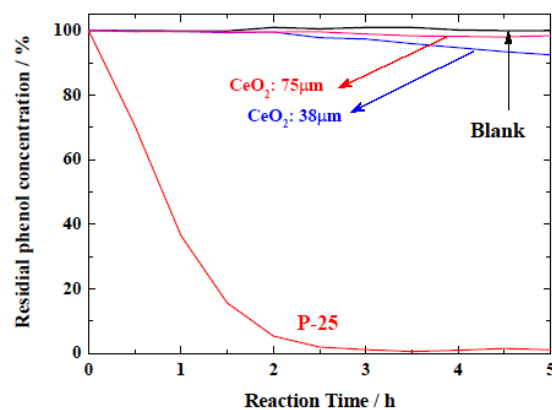


Fig.SI-5 Photocatalytic catalytic activity of plate-like cerium oxides, together with those of blank test and commercial titania particles P-25.

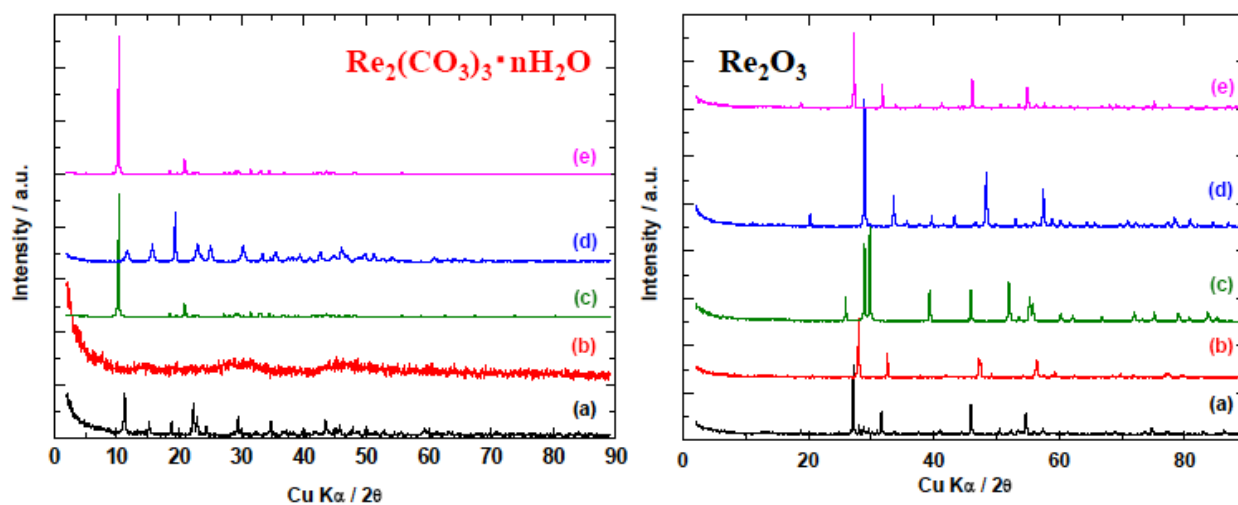


Fig. SI-6 XRD patterns of plate-like rare earth carbonates $\text{Re}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$ (left) and rare earth oxides Re_2O_3 (Re = Sm (a), Tb (b), La (c), Y (d), and Eu (e)) particles synthesized by the similar manner in 0.3M NaHCO_3 solution at 25°C, followed by calcination in air.

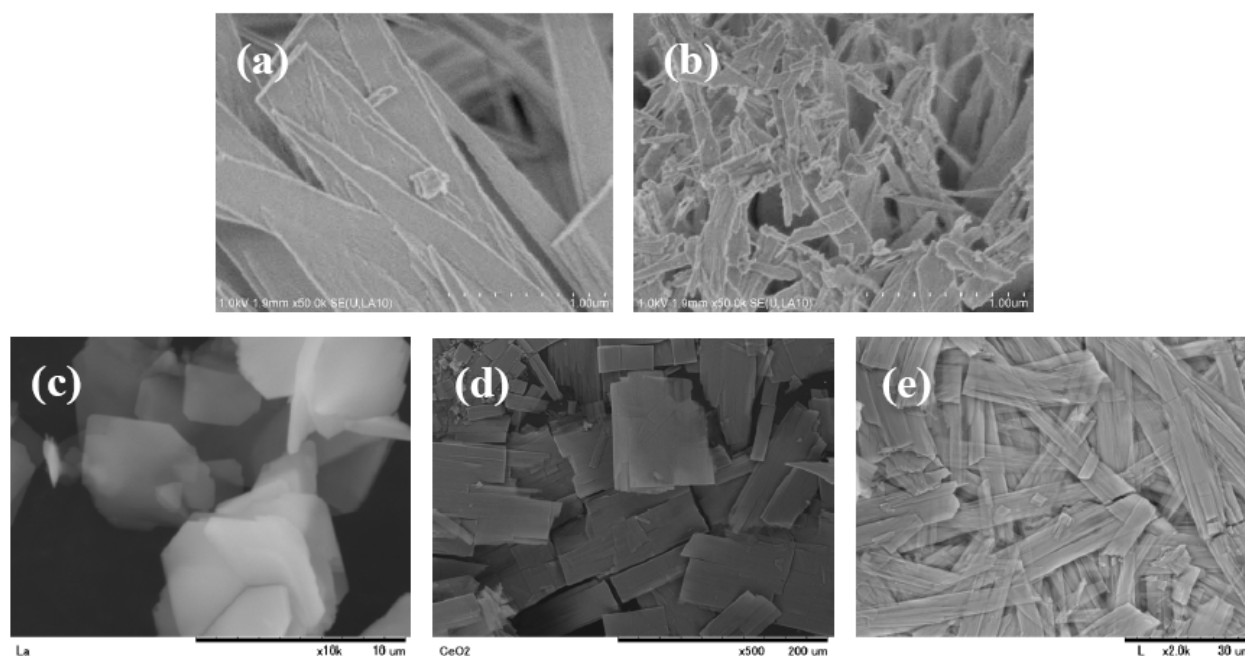


Fig.SI-7 SEM images of (a) Sm_2O_3 , (b) Tb_2O_3 , (c) La_2O_3 , (d) Y_2O_3 , and (e) Eu_2O_3 plate-like particles synthesized by the similar manner in 0.3M NaHCO_3 solution at 25°C, followed by calcination in air.