Template-free and non-hydrothermal synthesis of CeO_2 nanosheets via a facile aqueous-phase precipitation route and catalytic oxidation properties

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ABSTRACT

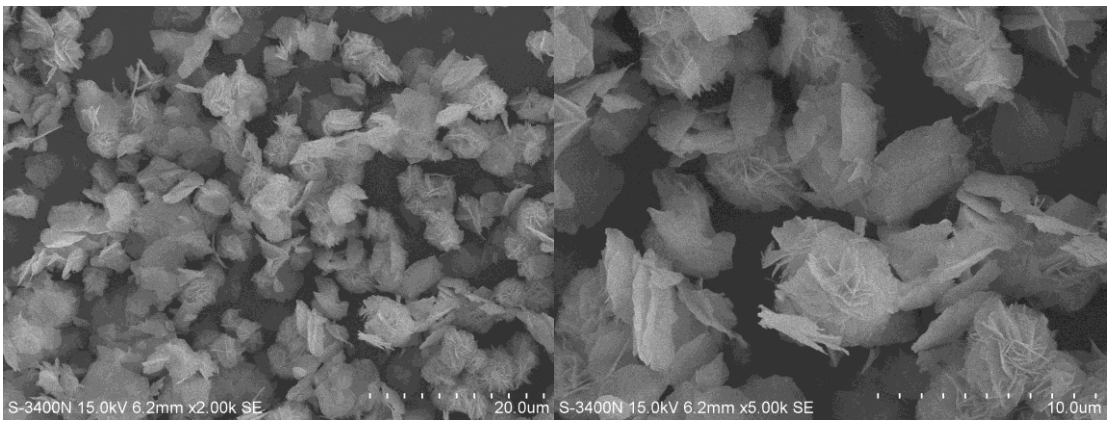
Two types of CeO_2 nanosheets, petal-like and belt-like, were synthesized via a facile aqueous phase precipitation method and NH_4HCO_3 as precipitant at 0 °C and 25 °C, without hydrothermal or solvothermal treatment, without template or surfactant and without organic solvent. The reaction temperature and supersaturation played key roles in the formation of ceria nanosheets, namely, lower temperature and higher supersaturation were favorable to the synthesis of sheet-like CeO_2 by oriented aggregation of CeO_2 nanocrystallines, while the elevated temperature could cause the dissolution-recrystallization of precursors and then formed polyhedral CeO_2 by Ostwald ripening process. Besides, the doping of heteroatoms was easy due to only adopting co-precipitation reaction, which could further extend the scope of application of CeO_2 nanosheets. Catalytic oxidation properties were investigated via catalytic oxidation of CO over CeO_2 and catalytic combustion of 1,2-dichloroethane over VOx/CeO_2. Compared with traditional CeO_2 nanoparticles, the ceria nanosheets showed more excellent catalytic oxidation activities.

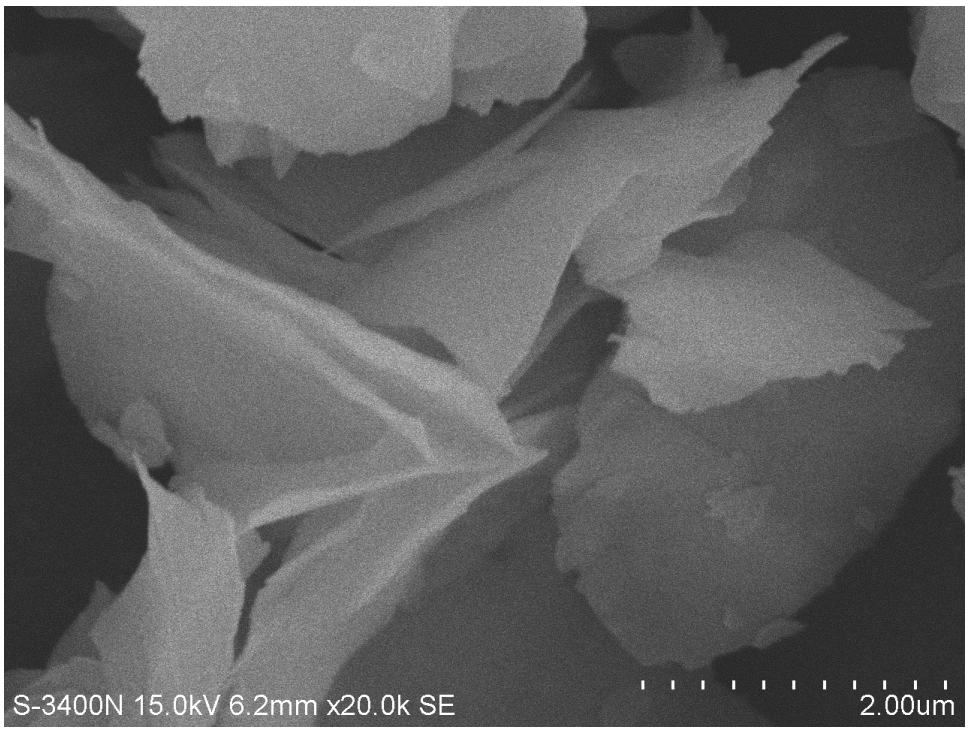
KEYWORDS: CeO_2, nanosheets, catalytic oxidation, carbon monoxide, 1,2-dichloroethane, vanadia

Effect of aging temperature

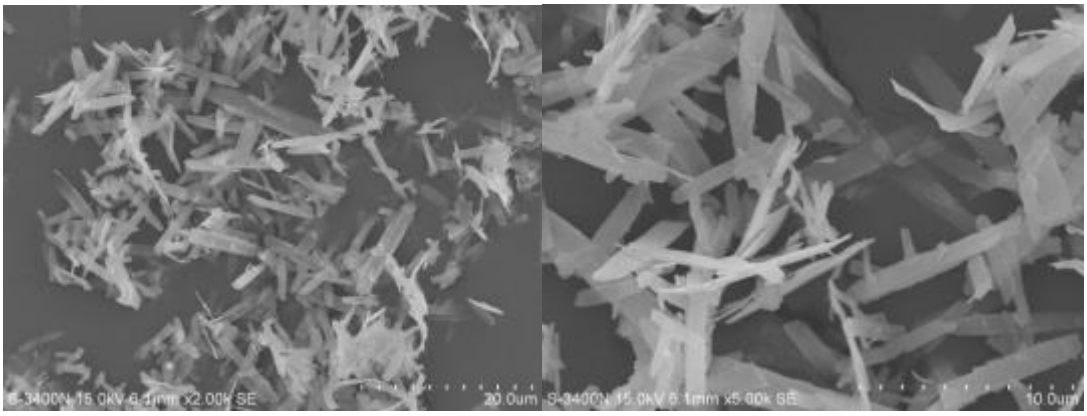
Fig.S1 Detail SEM of synthesized CeO_2 at different temperature

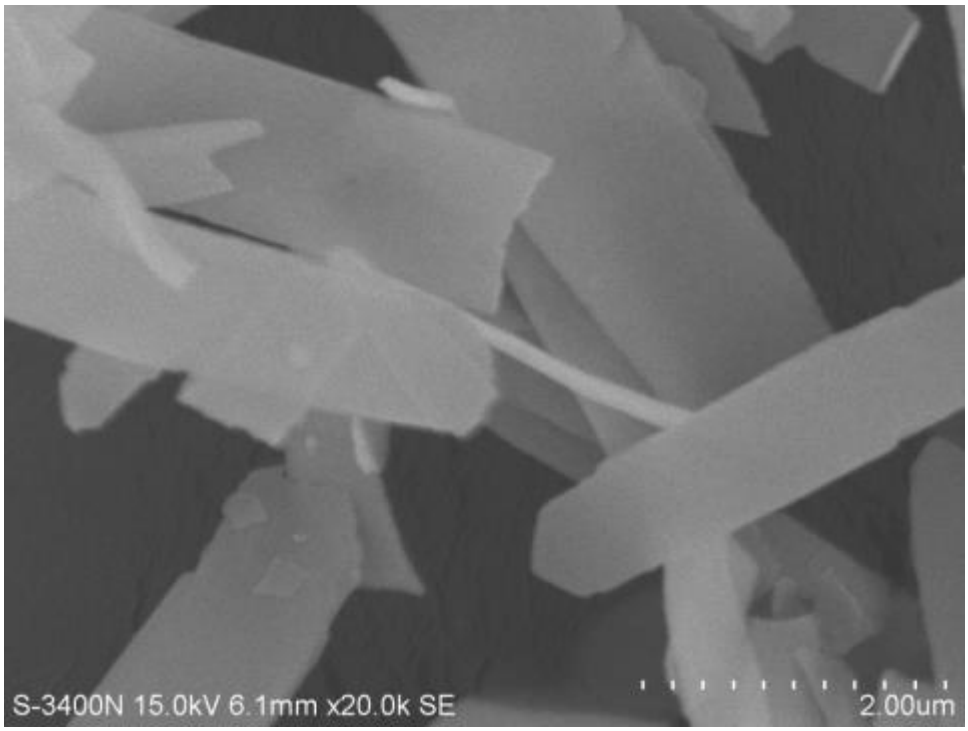
0°C,15h



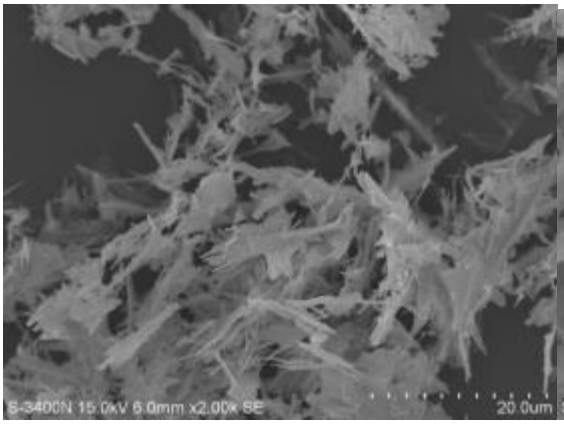


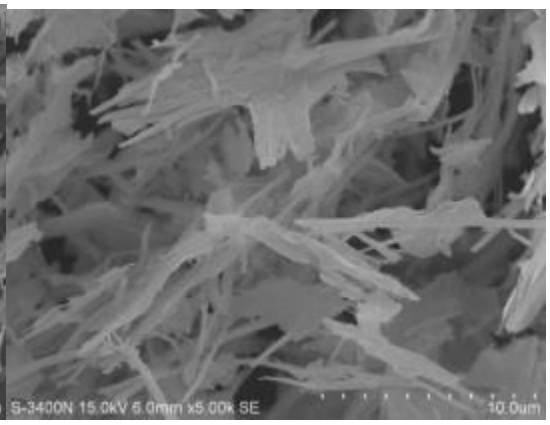
25°C,15h





50°C,15h


S-3400N 15.0kV 6.0mm x2.00k SE
20.0um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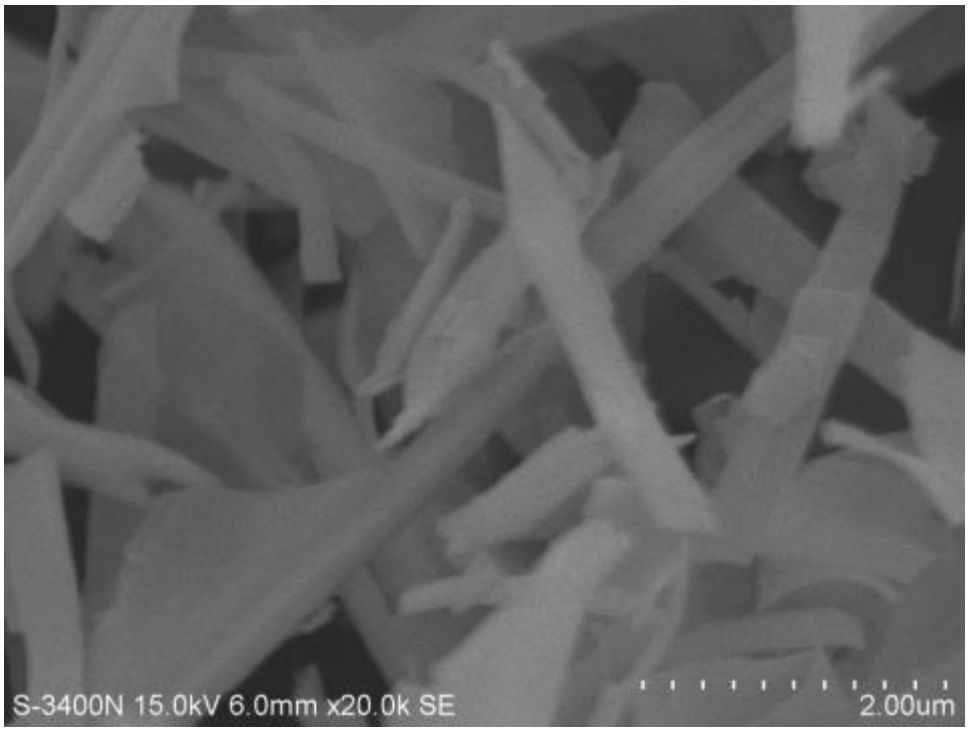
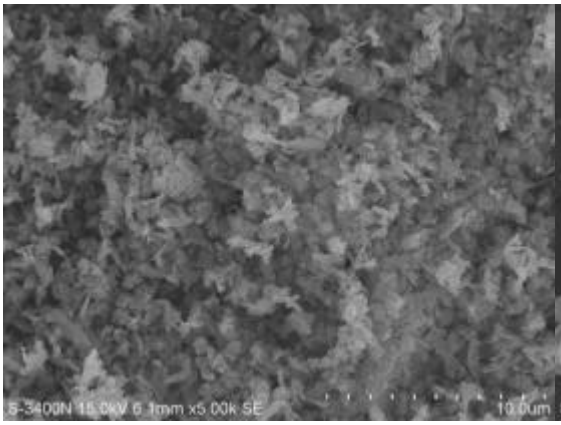
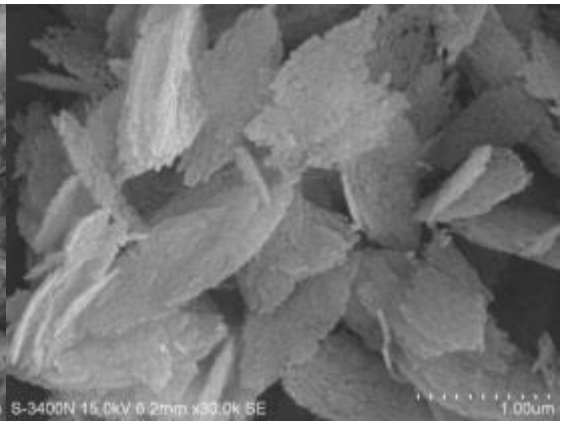
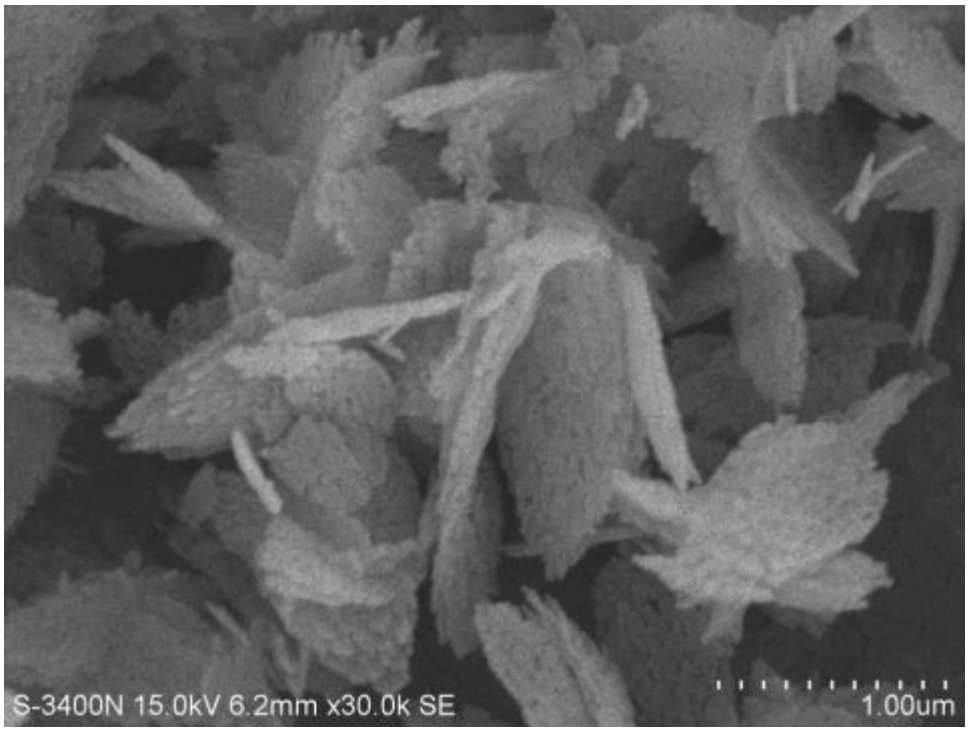
10.0um


S-3400N 15.0kV 6.0mm x20.0k SE
2.00um

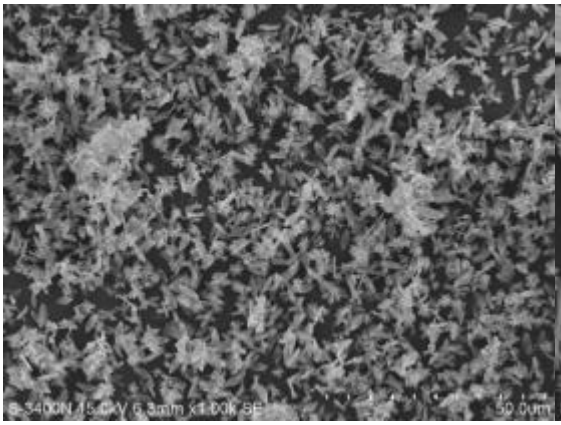
75°C,15h, under reflux condition

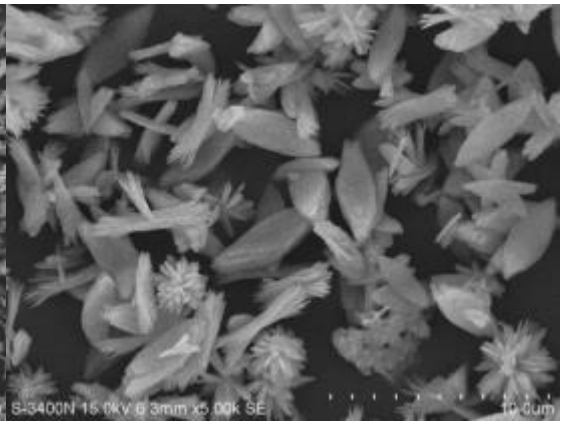


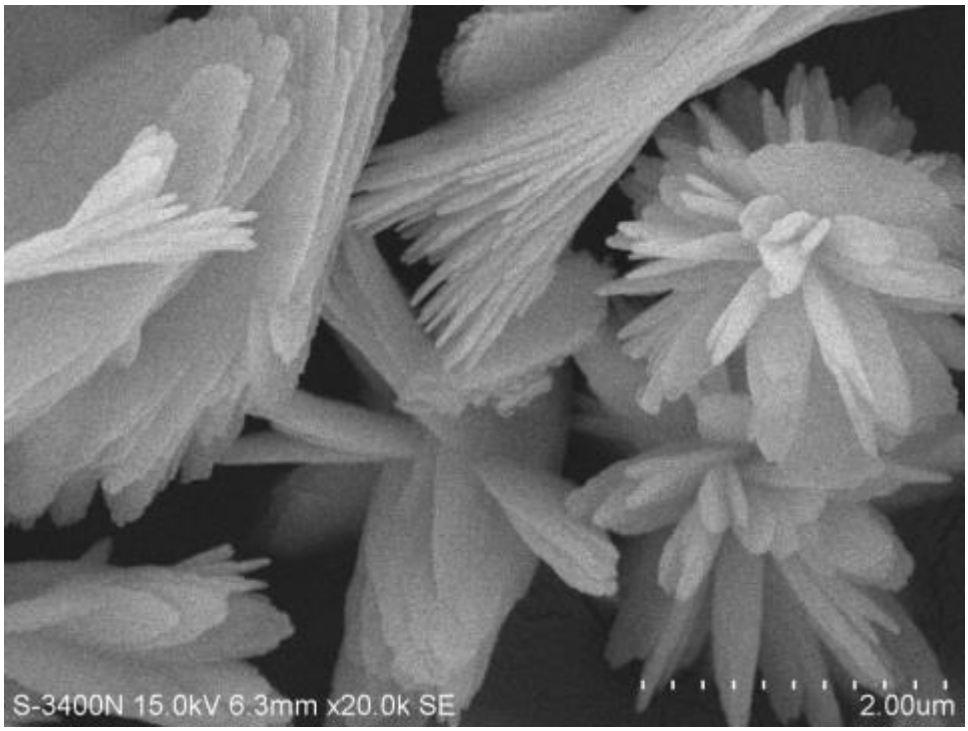




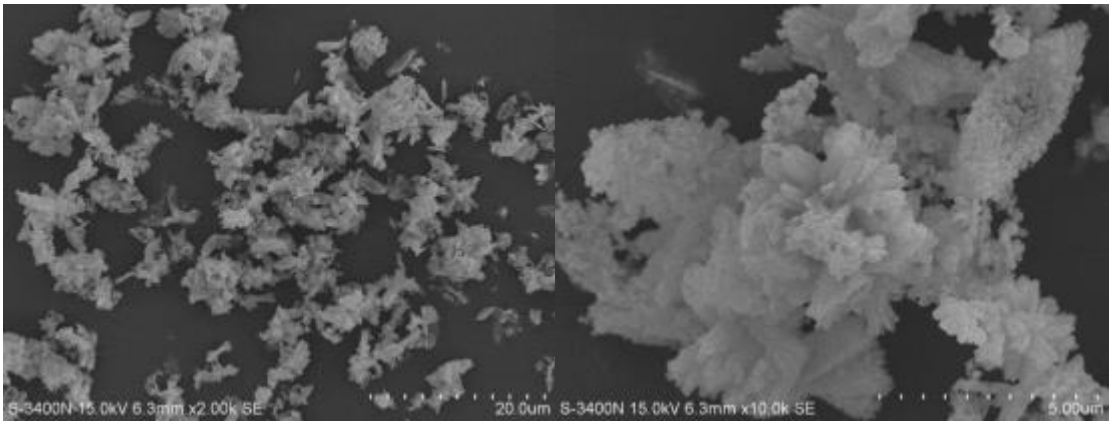
100°C,15h,under reflux condition







150°C,15h，under hydrothermal conditions



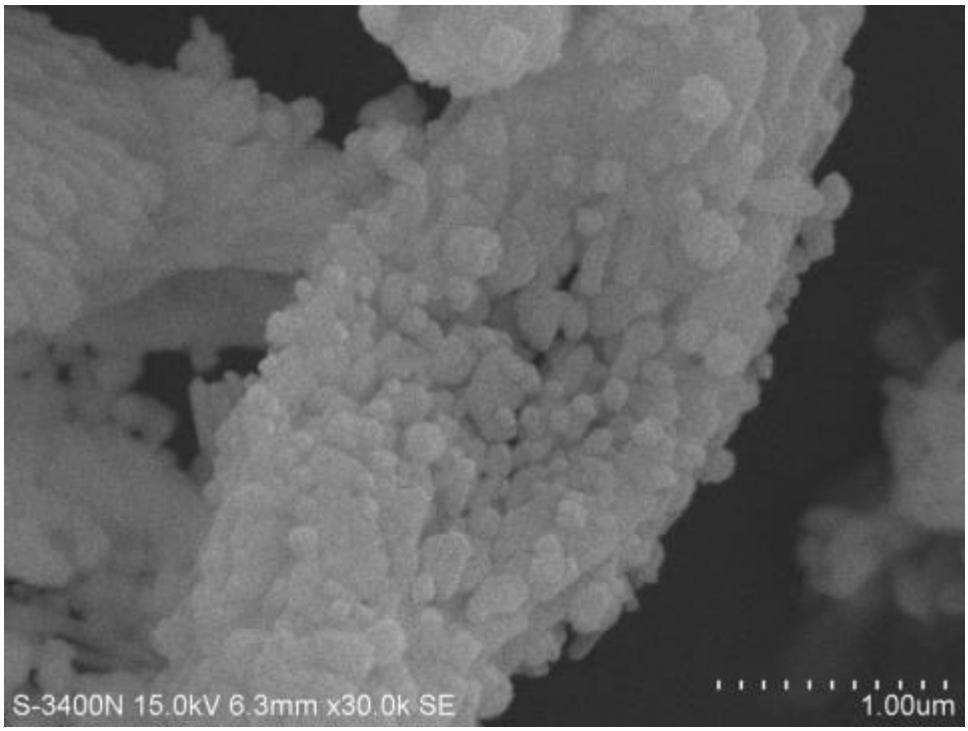
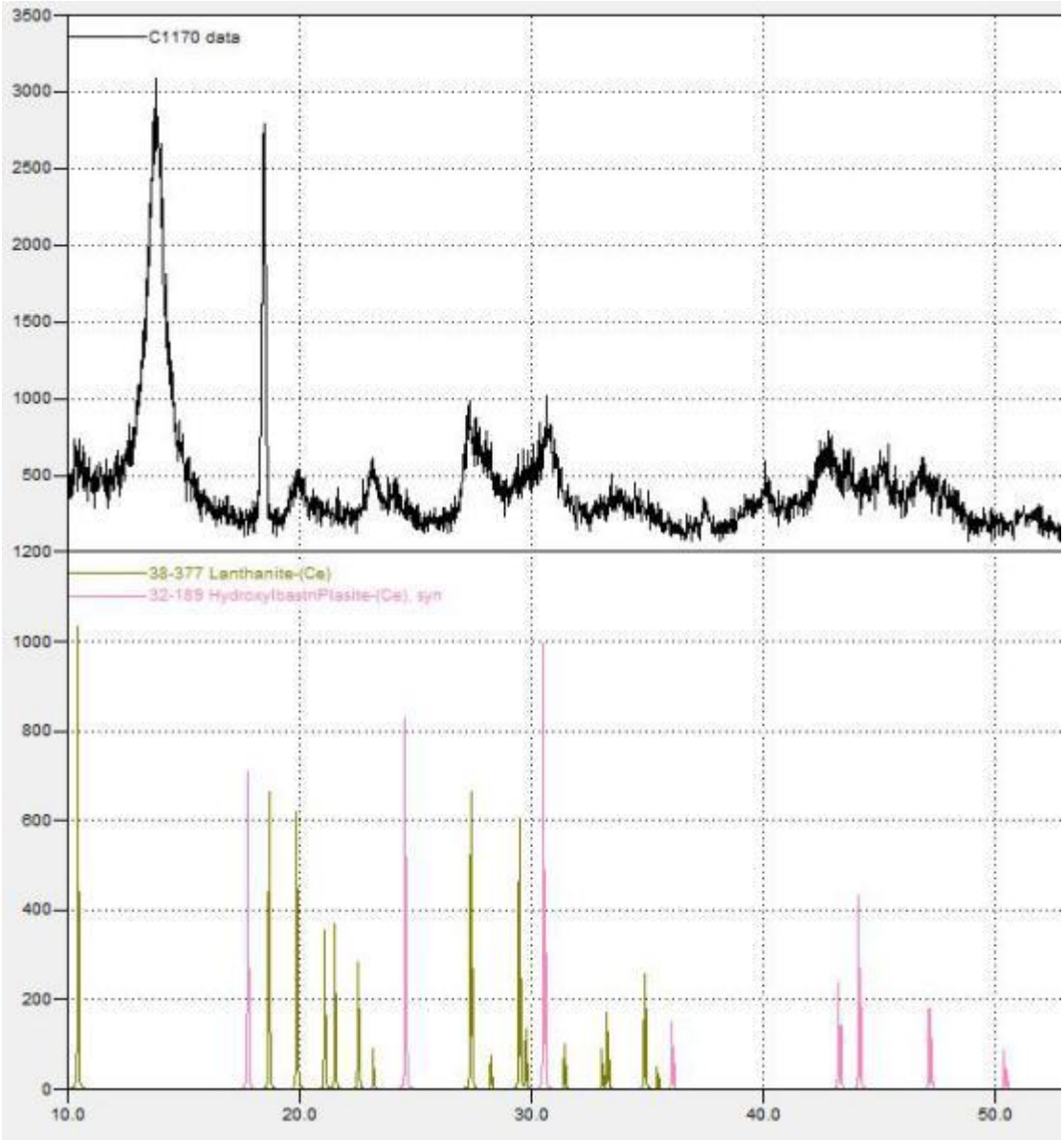


Fig.S2 Detail XRD of as-synthesized CeO_2 (Precursor)

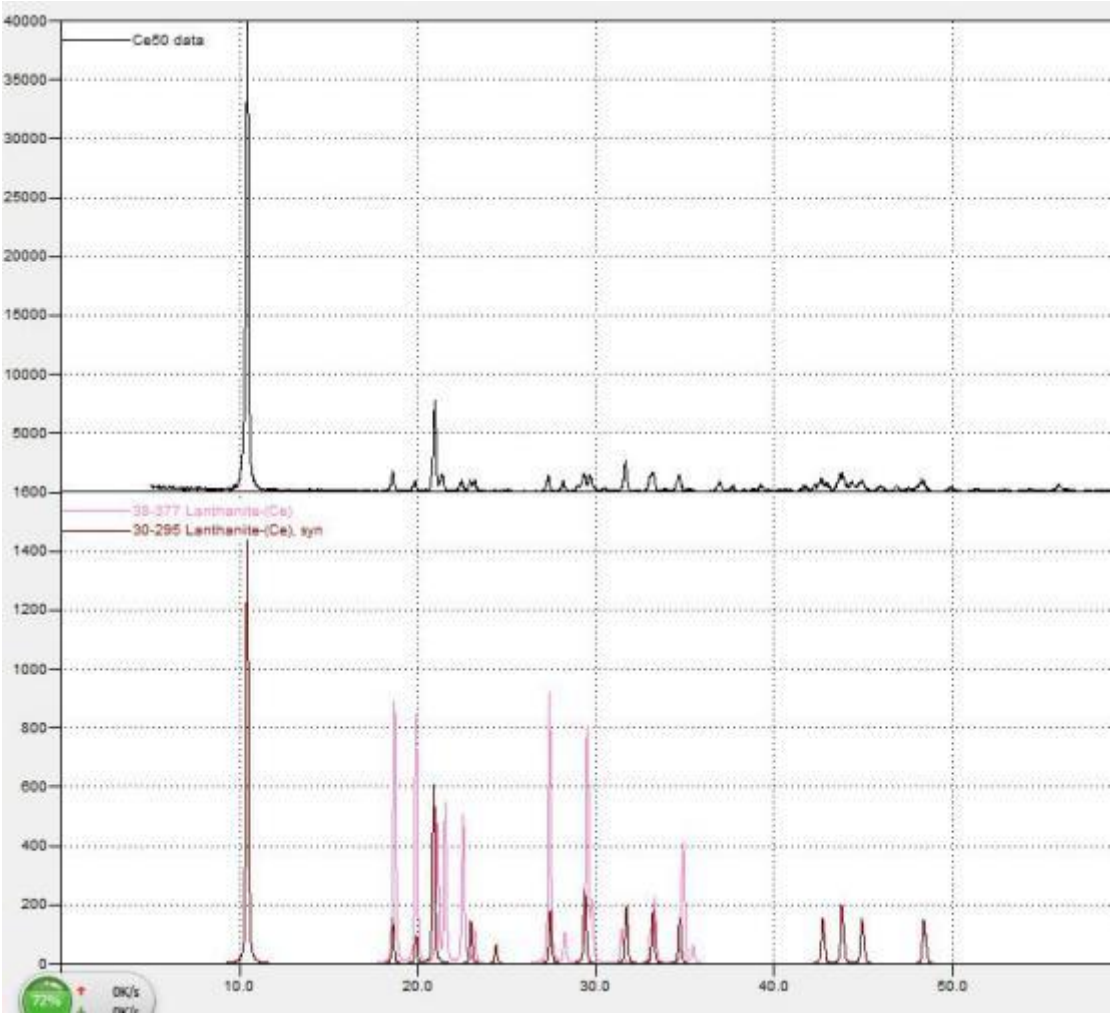
XRD pattern of as-synthesized precursor at 25℃

Cerium Carbonate Hydrate ($Ce_2(CO_3)_3$•8 H_2O, JCPDS 38-377)



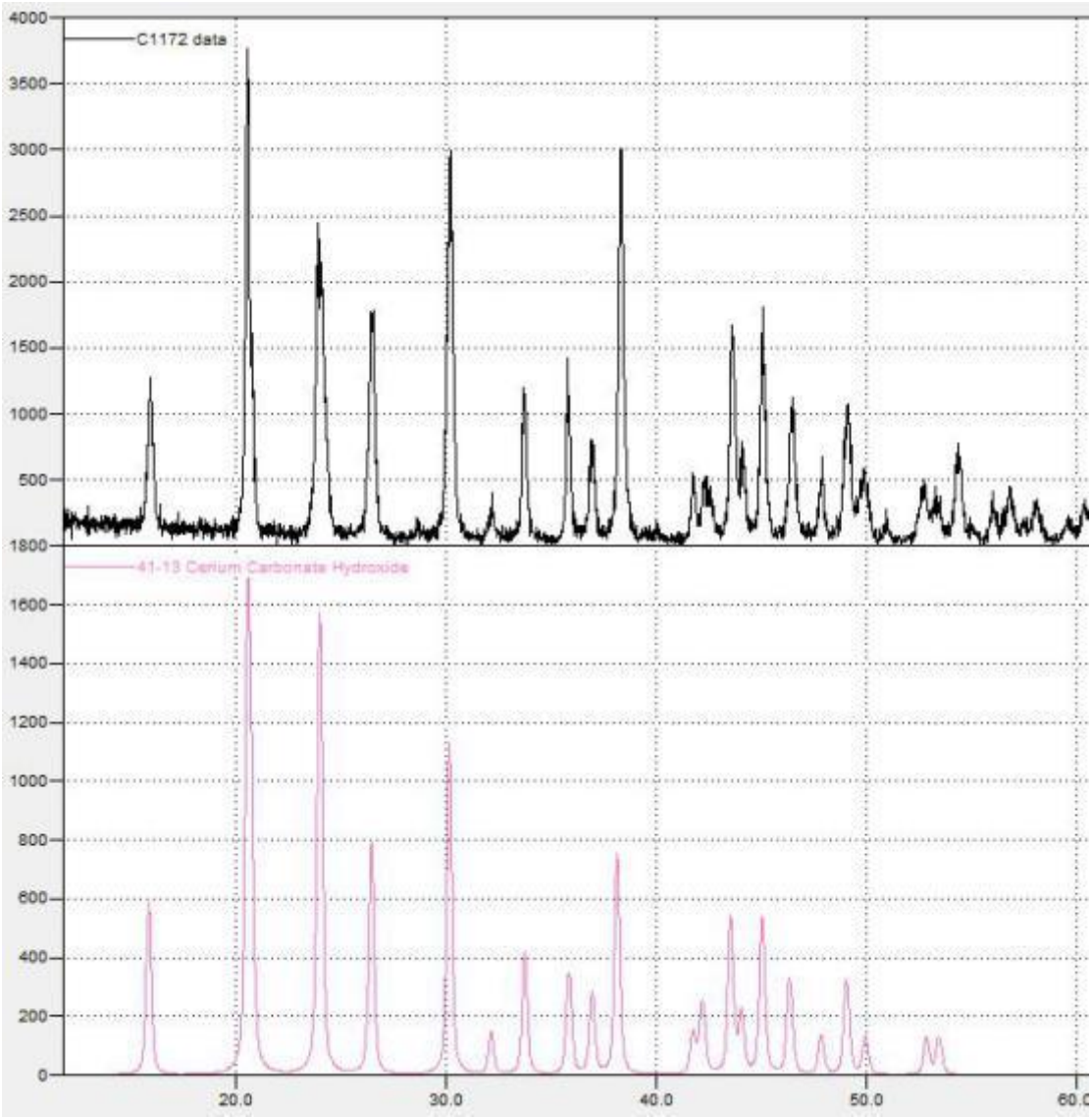
XRD pattern of as-synthesized precursor at 50℃

Orthorhombic Cerium Carbonate Hydrate ($Ce_2(CO_3)_3$•6 H_2O, JCPDS 30-295)



XRD pattern of as-synthesized precursor at 100℃

orthorhombic $CeOHCO_3$ (JCPDS 41-13)



Card Information

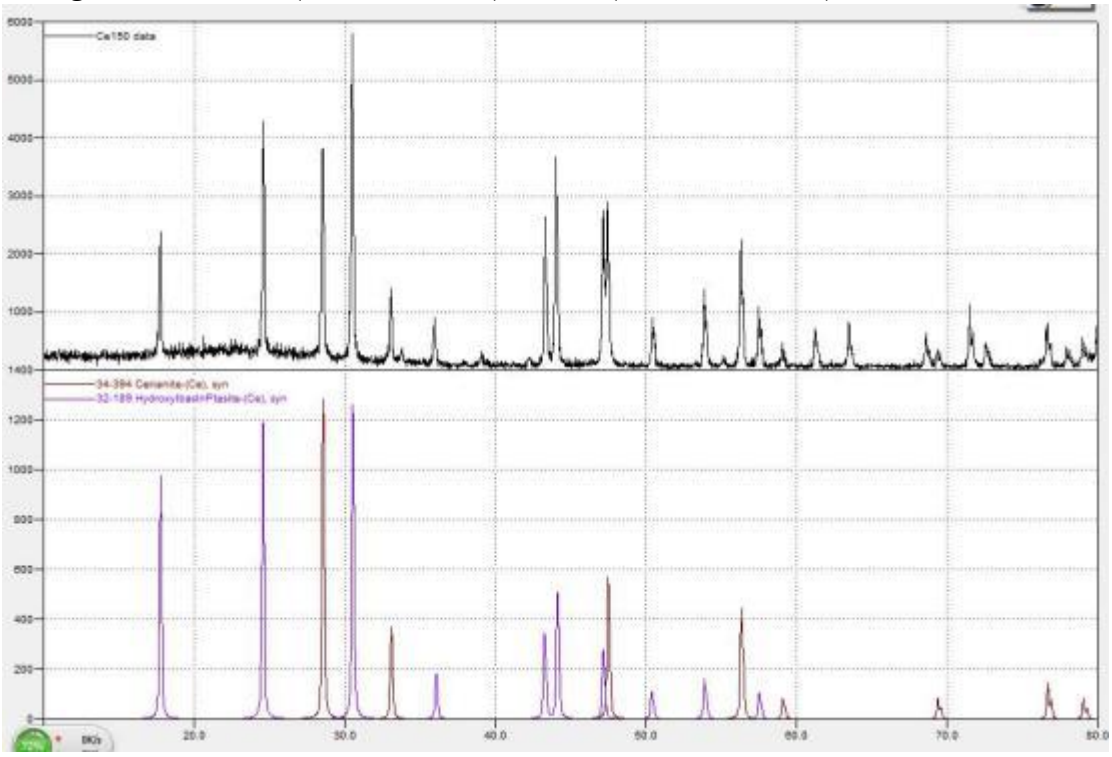
Names:	Cerium Carbonate Hydroxide
Formula:	Ce C O_3 O H
PDF Number:	41-13
Quality:	indexed
Subfiles:	inorganic

Cell and Symmetry Information

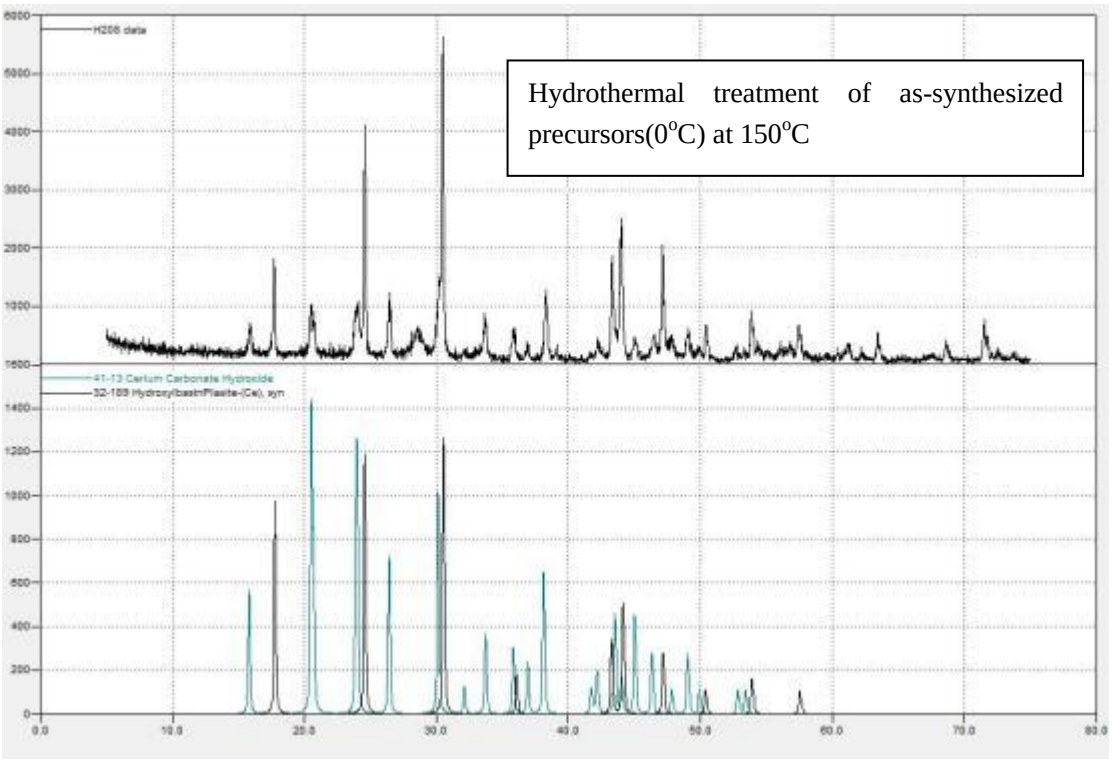
System:	orthorhombic		**Space Group:**	(no.	0)
a:	5.015	**b:**	8.565	**c:**	7.337
Density (Dx):	4.545	**Z:**	4		

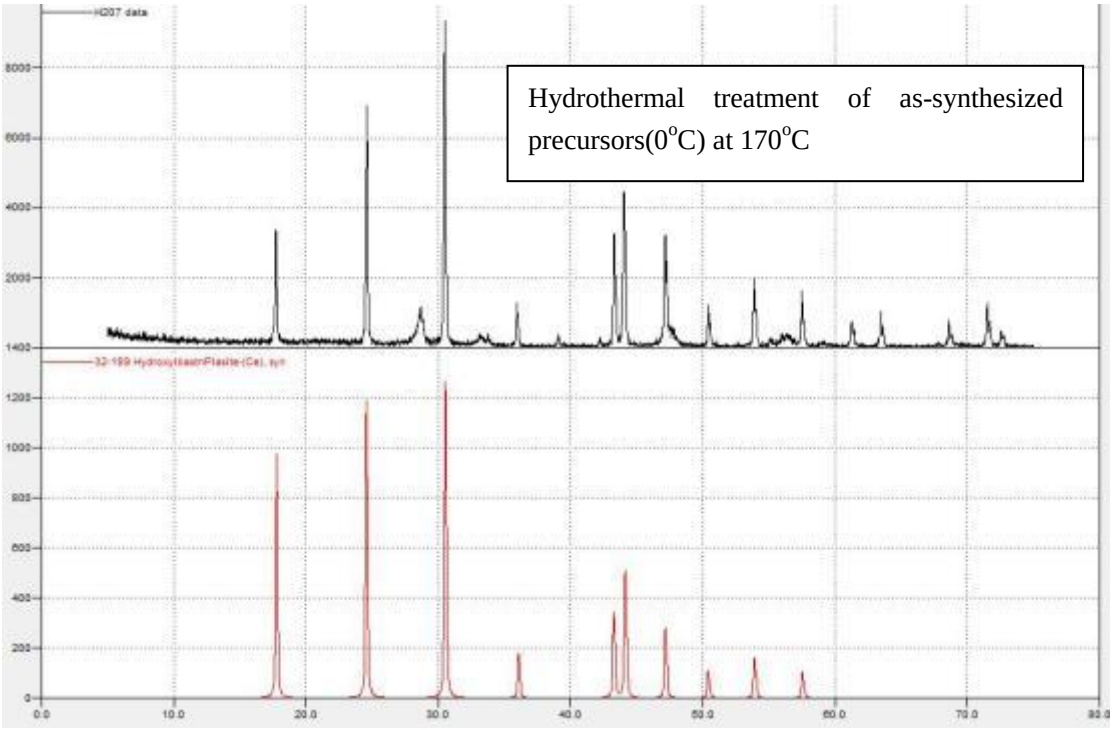
XRD pattern of as-synthesized precursor at 150℃

Hexagonal $CeOHCO_3$ (JCPDS 32-189) +CeO_2 (JCPDS 34-0394)



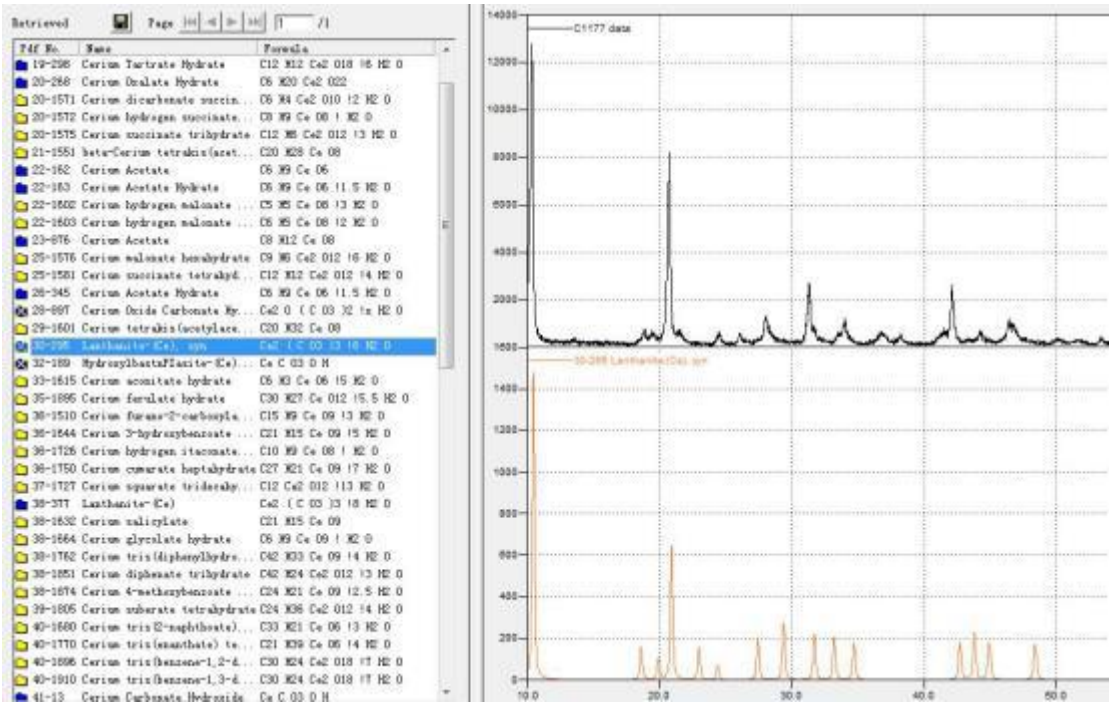
XRD pattern of as-synthesized precursors hydrothermally treated at 150℃ and 170℃





XRD pattern of as-synthesized precursor (CeO_2-SC)

Orthorhombic Cerium Carbonate Hydrate ($Ce_2(CO_3)_3$•6 H_2O, JCPDS 30-295)



Card Information

Names:	Cerium Carbonate Hydrate
	Lanthanite-(Ce), syn
Formula:	Ce_2 (C O_3)$_3$!$_6$ H_2 O
PDF Number:	30-295
Quality:	questionable
Subfiles:	inorganic mineral

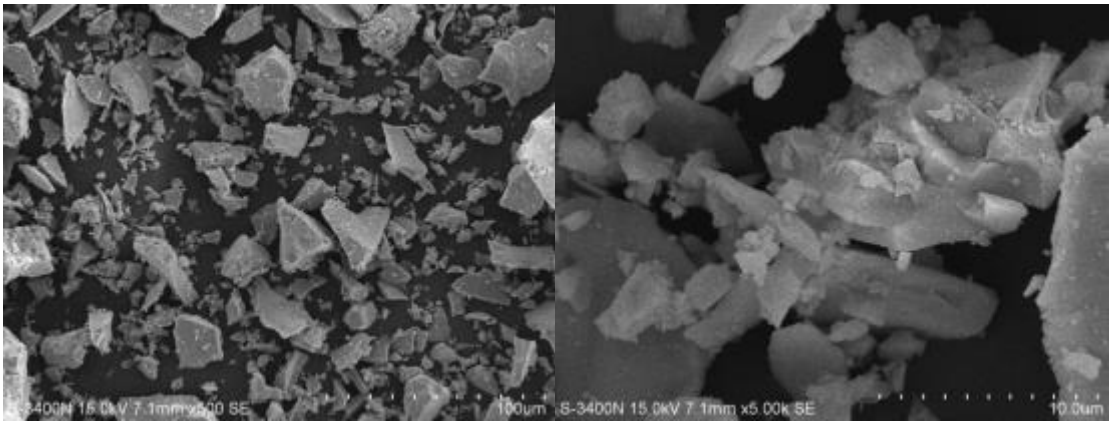
Cell and Symmetry Information

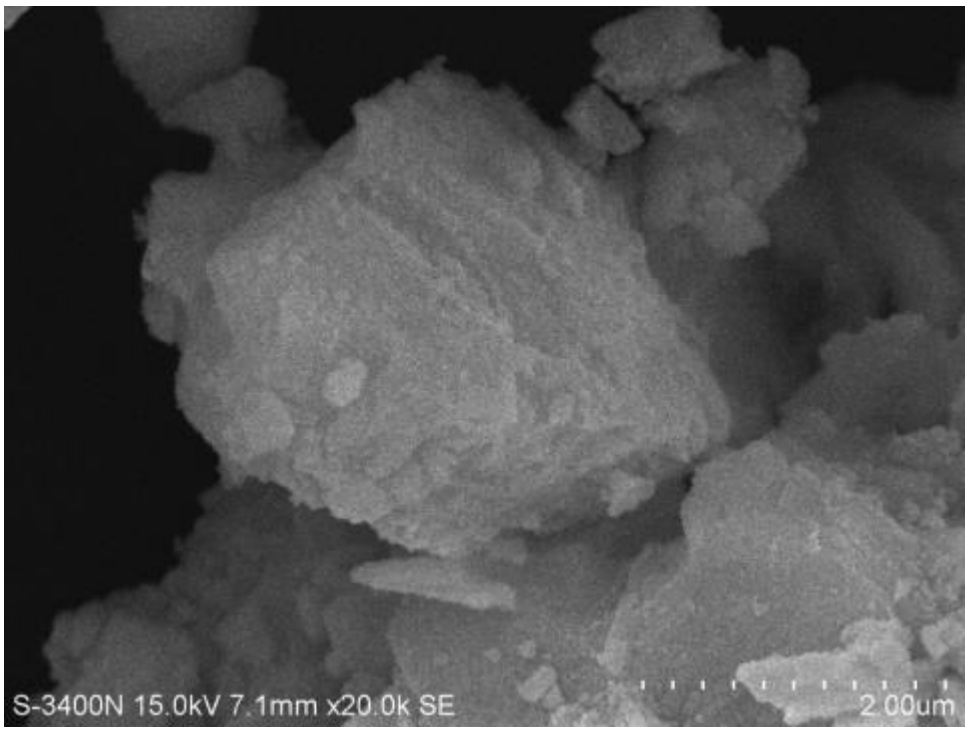
System:	orthorhombic		**Space Group:**	Pbnb	(no. 56)
a:	9.470	**b:**	16.902	**c:**	8.929
Z:	4				

Effect of precipitant (at 0℃)

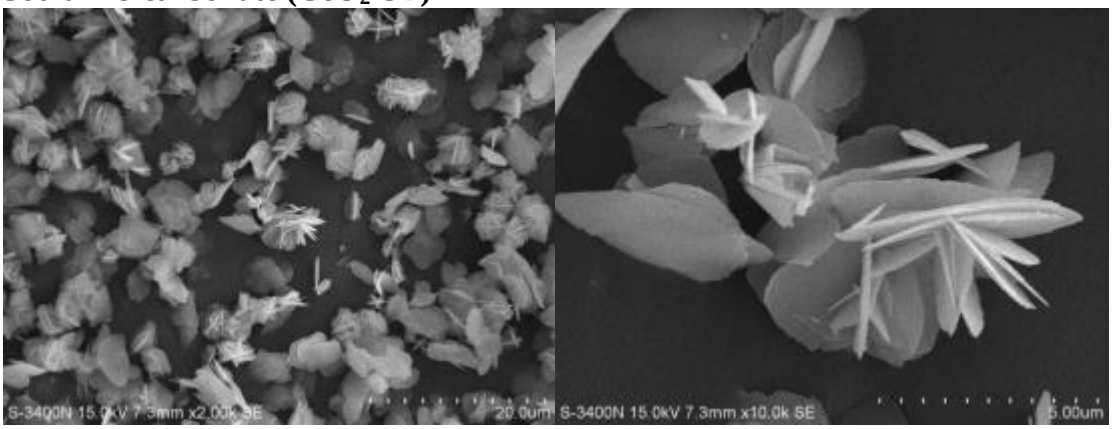
Fig.S3 Detail SEM of synthesized CeO_2 using different precipitants

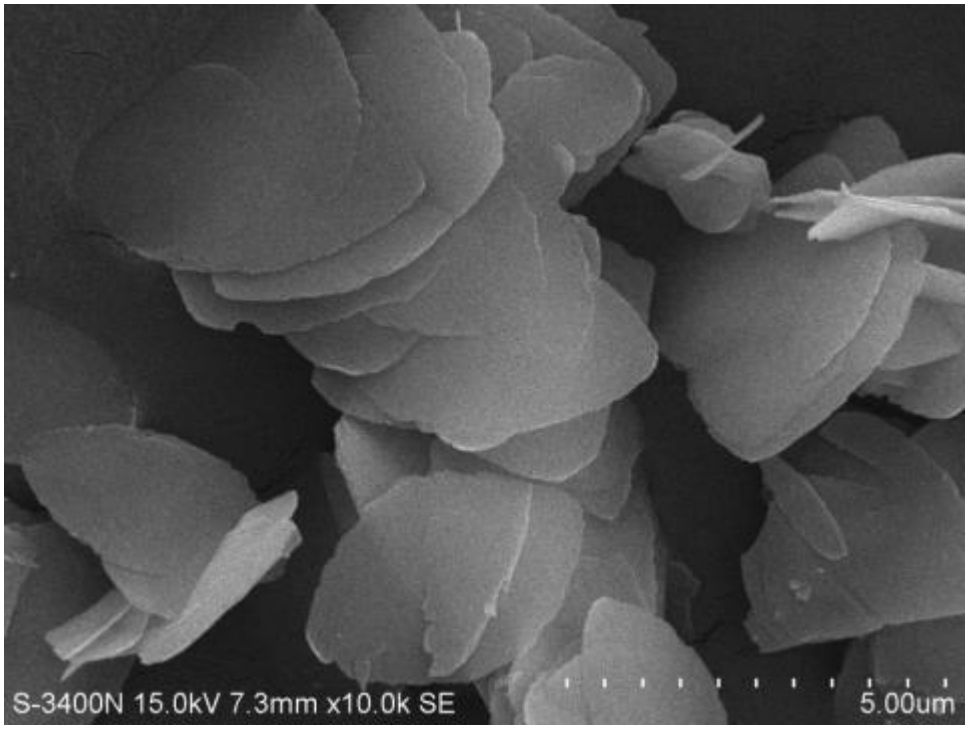
Aqueous ammonia (CeO_2-AA)



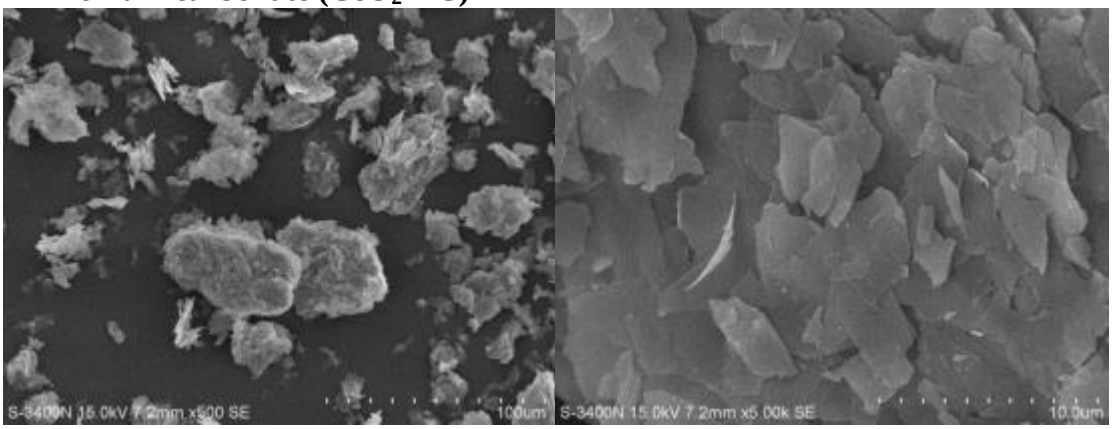


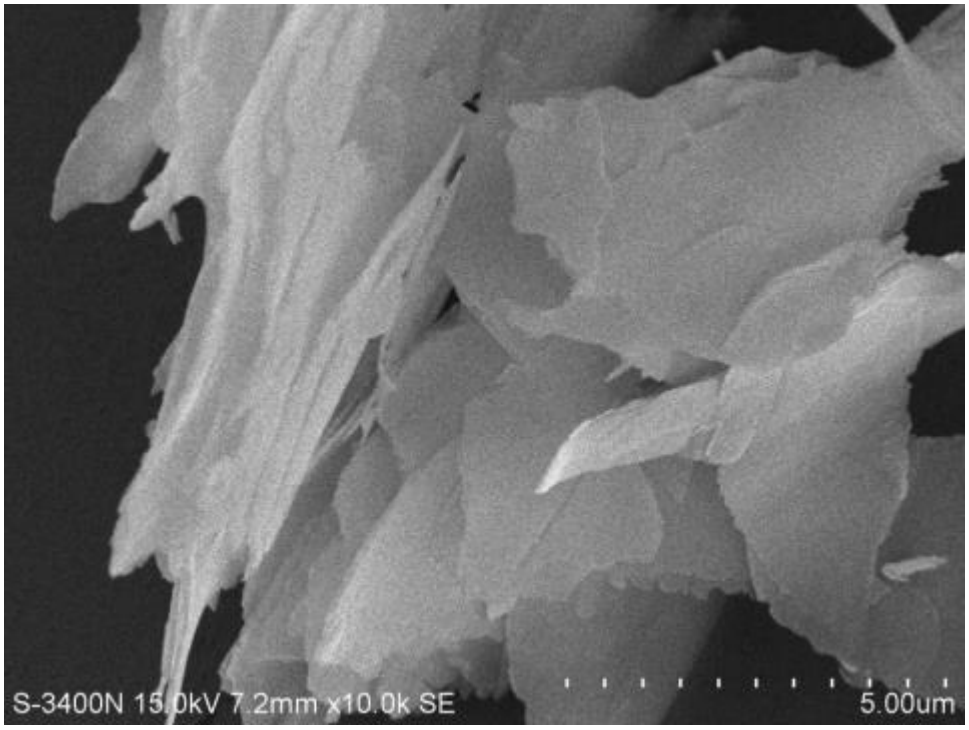
Sodium bicarbonate (CeO_2-SB)



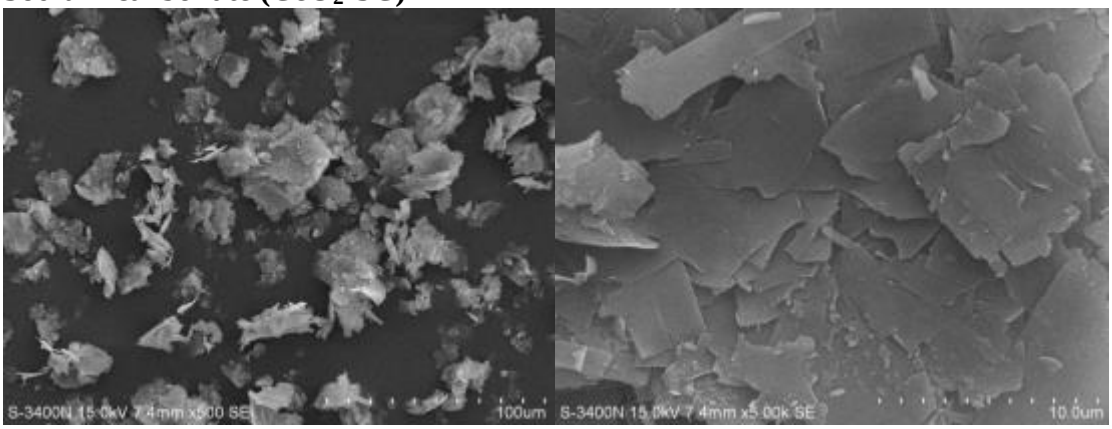


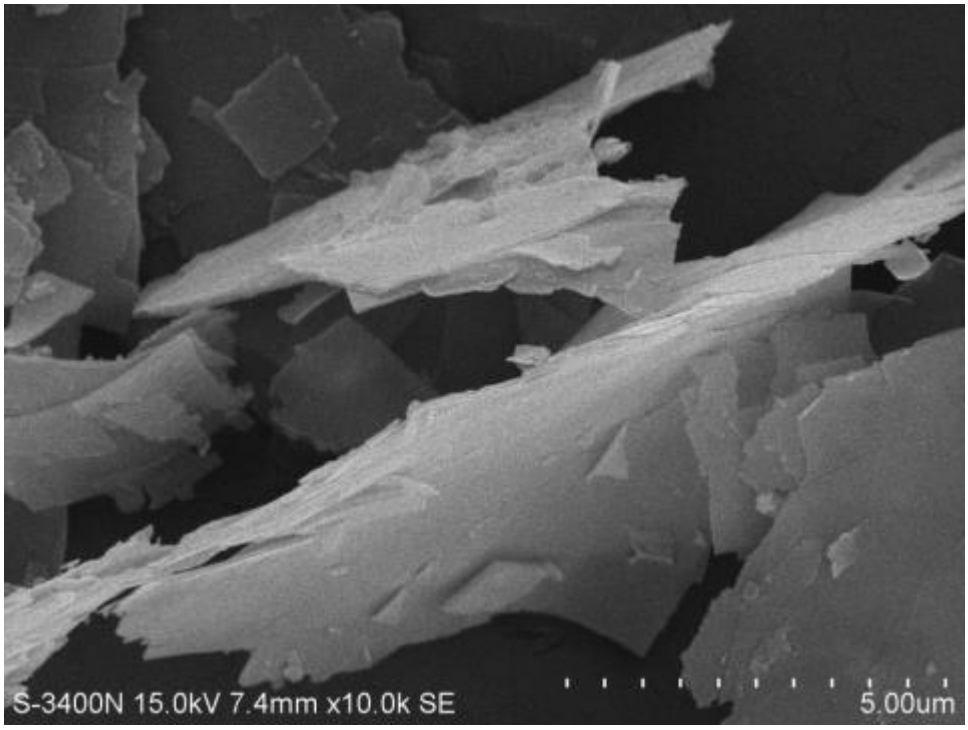
Ammonium carbonate (CeO_2-AC)





Sodium carbonate (CeO_2-SC)

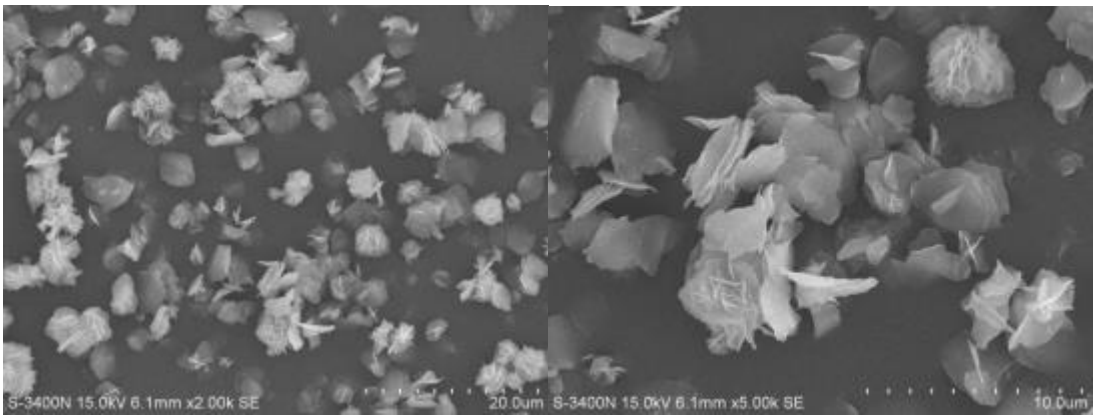


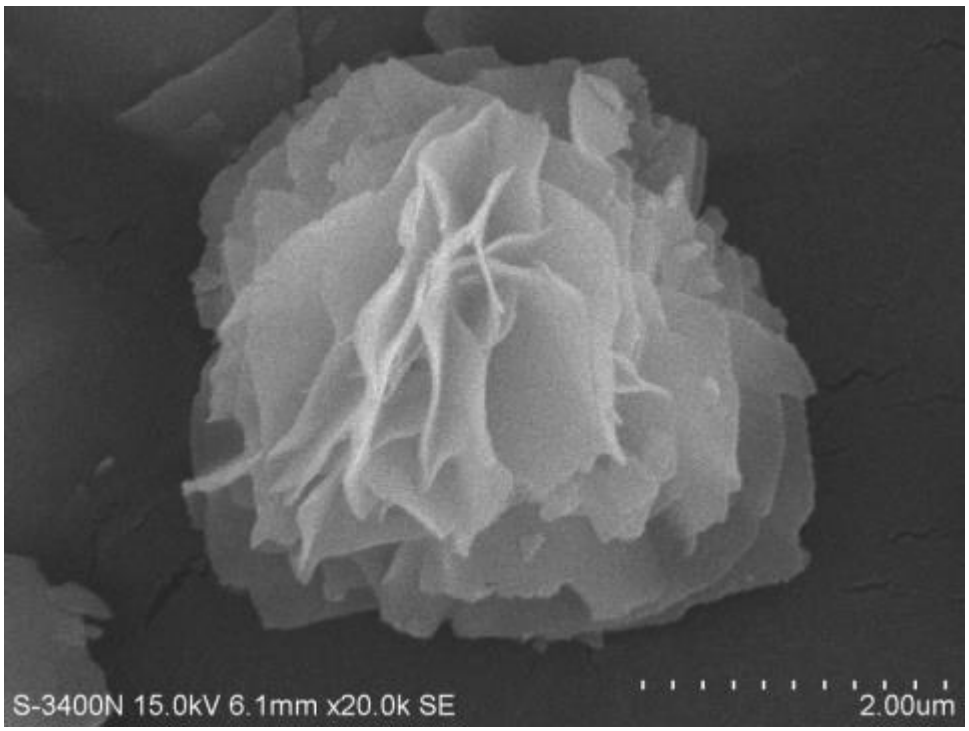


Effect of aging time (at 0℃)

Fig.S4 Detail SEM of synthesized CeO_2 at different aging time

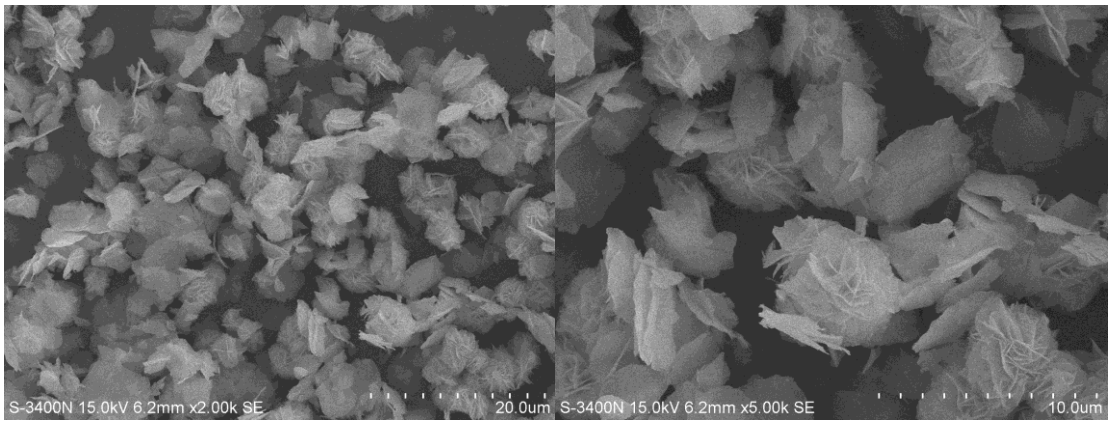
no aging

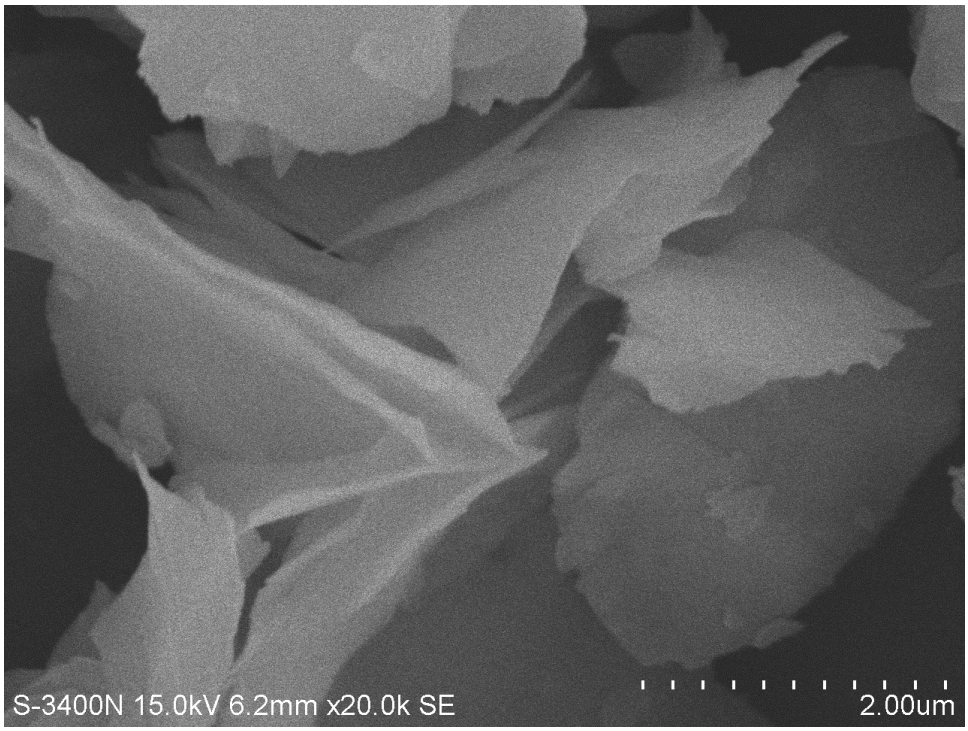




Thickness: 30-40nm

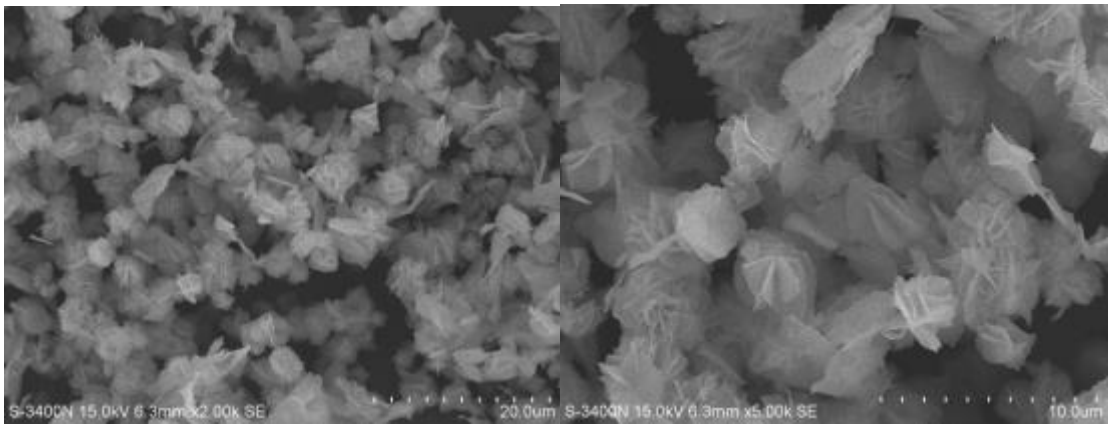
aging for 15h

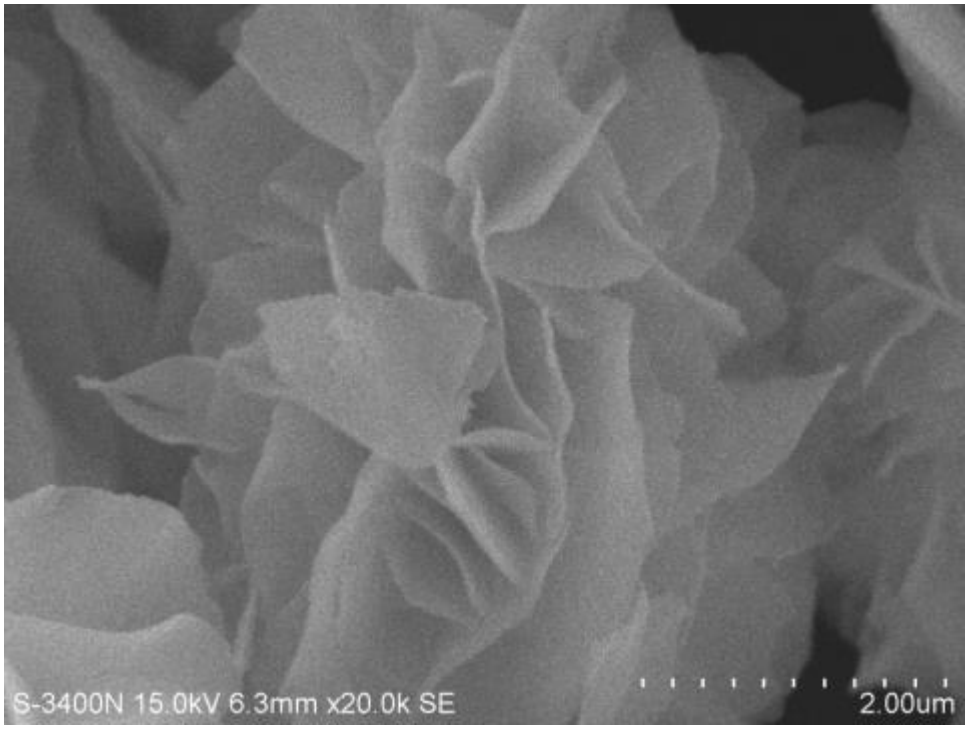




Thickness: 40-70nm

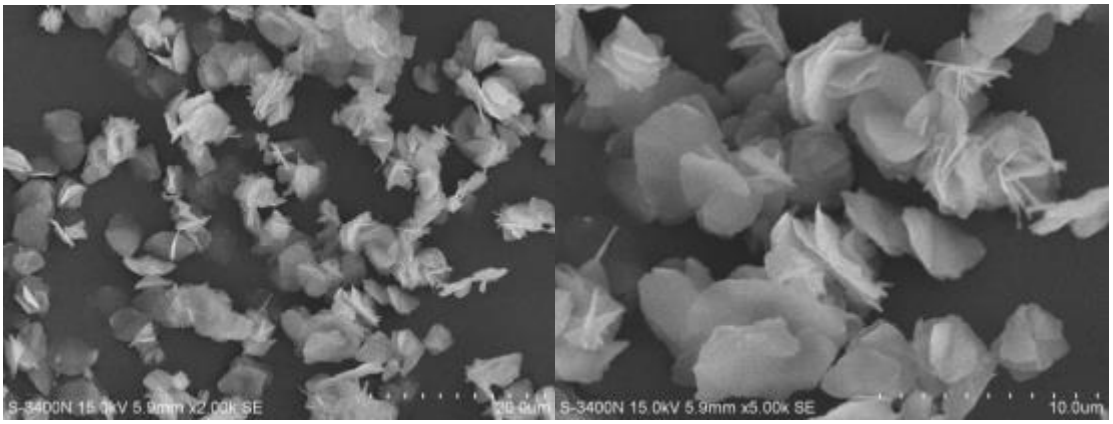
aging for 24h

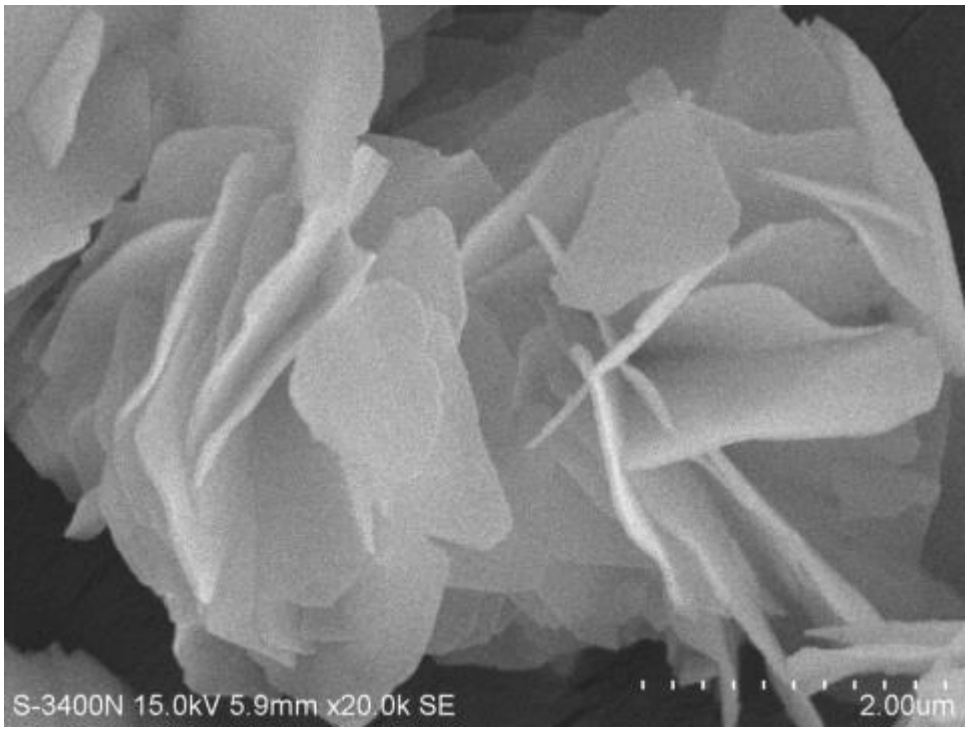




Thickness: 30-50nm

aging for 48h





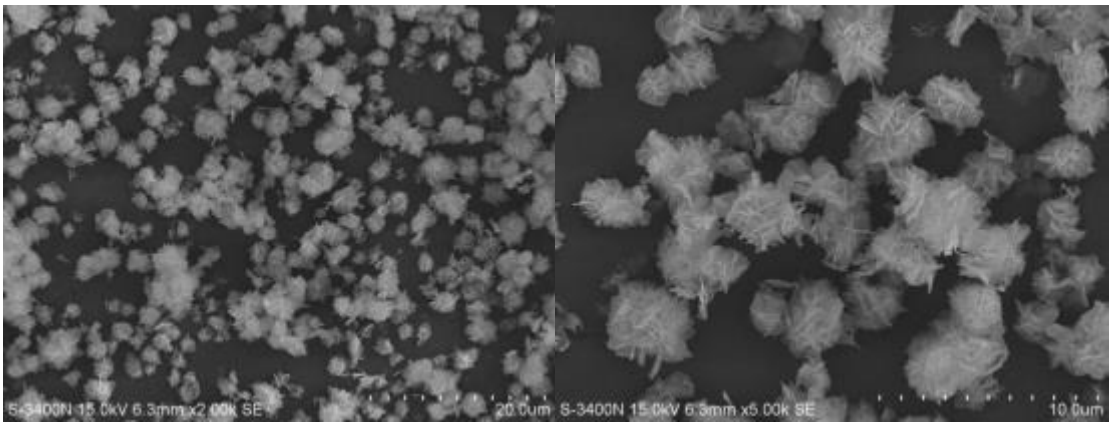
Thickness: 70-100nm

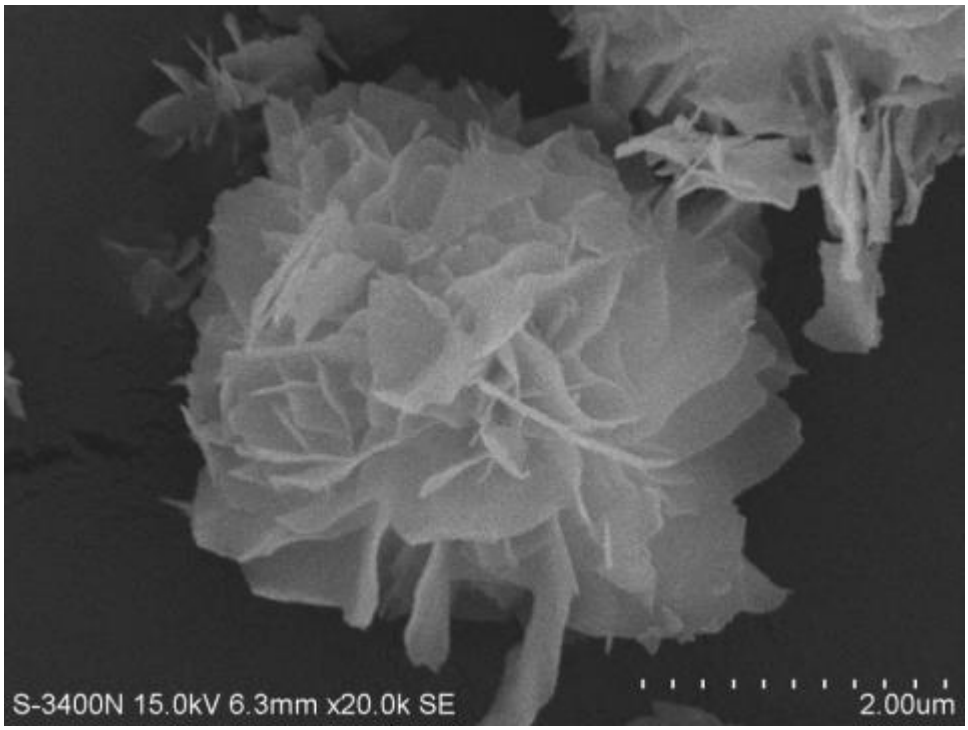
Effect of water content (aging for 24 h at 0℃)

Fig.S5 Detail SEM of synthesized CeO_2 at different water content

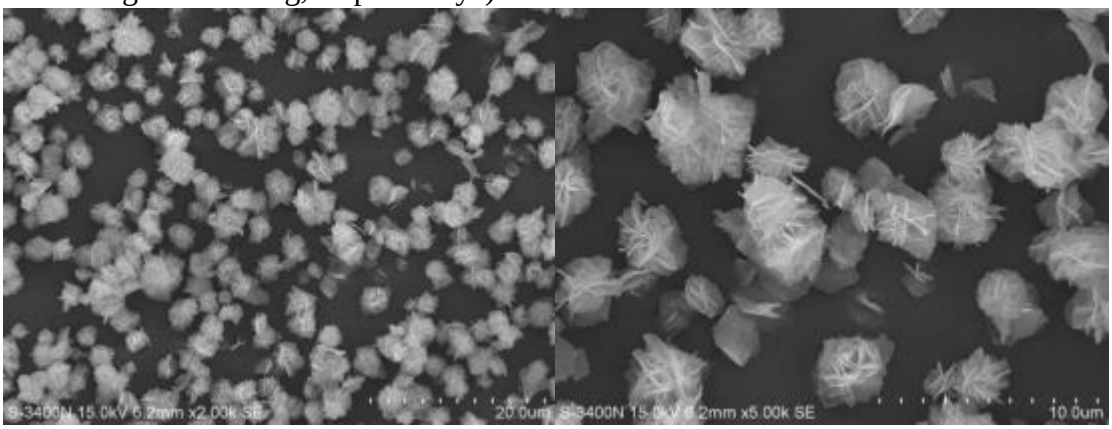
petal-like CeO_2 nanosheets

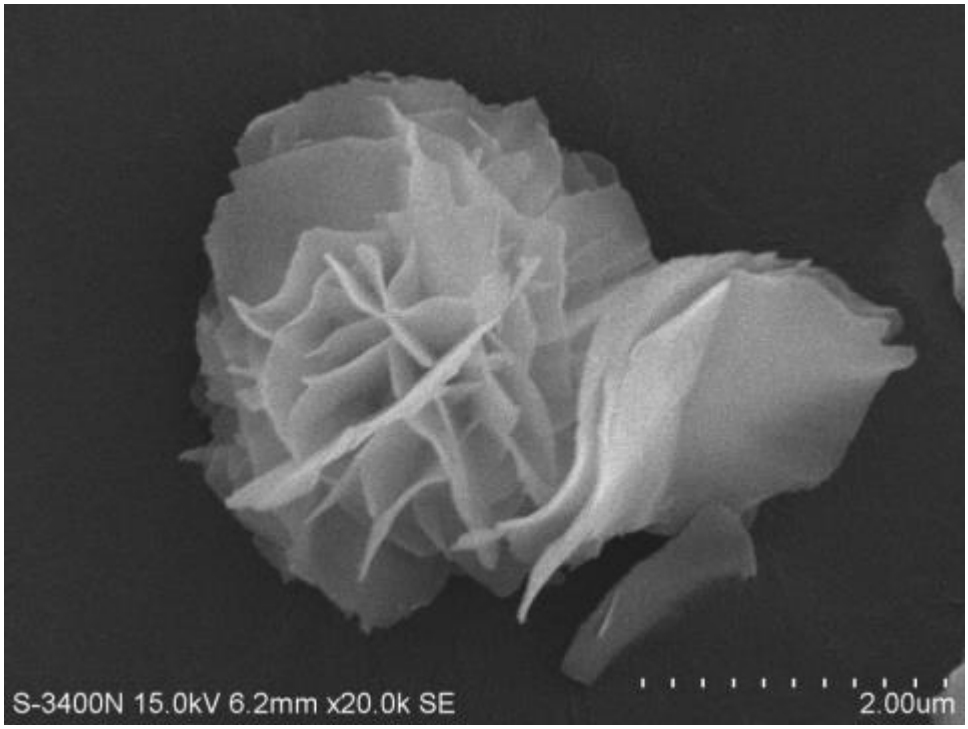
50ml water (1.39 g cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and 0.75 g ammonium bicarbonate (NH_4HCO_3) were dissolved in 25 ml deionized water at 0 °C under magnetic stirring, respectively.)





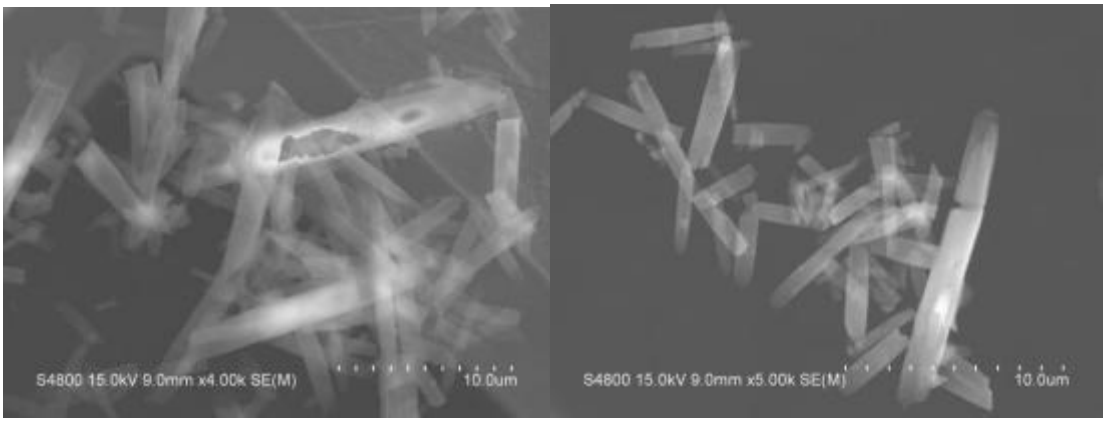
100ml water (1.39 g cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and 0.75 g ammonium bicarbonate (NH_4HCO_3) were dissolved in 50 ml deionized water at 0 °C under magnetic stirring, respectively.)



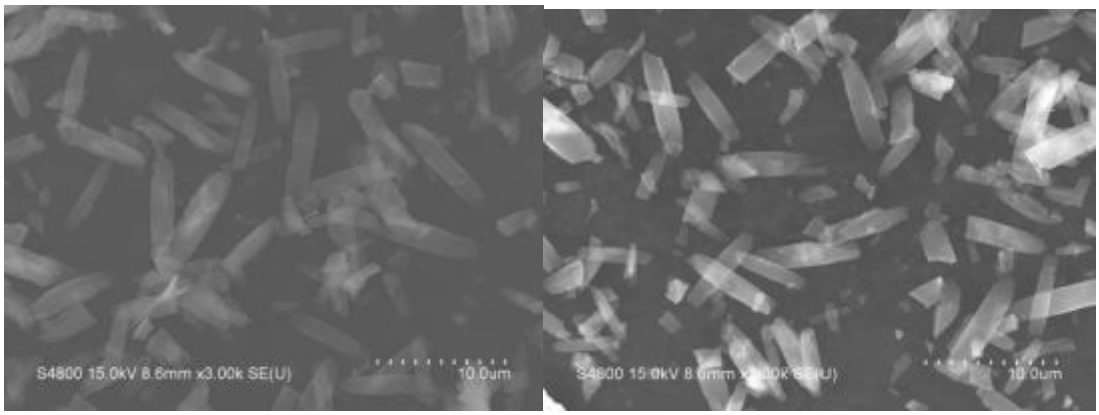


belt-like CeO_2 nanosheets

100ml water (1.39 g cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and 0.75 g ammonium bicarbonate (NH_4HCO_3) were dissolved in 50 ml deionized water at 25 °C under magnetic stirring, respectively.)



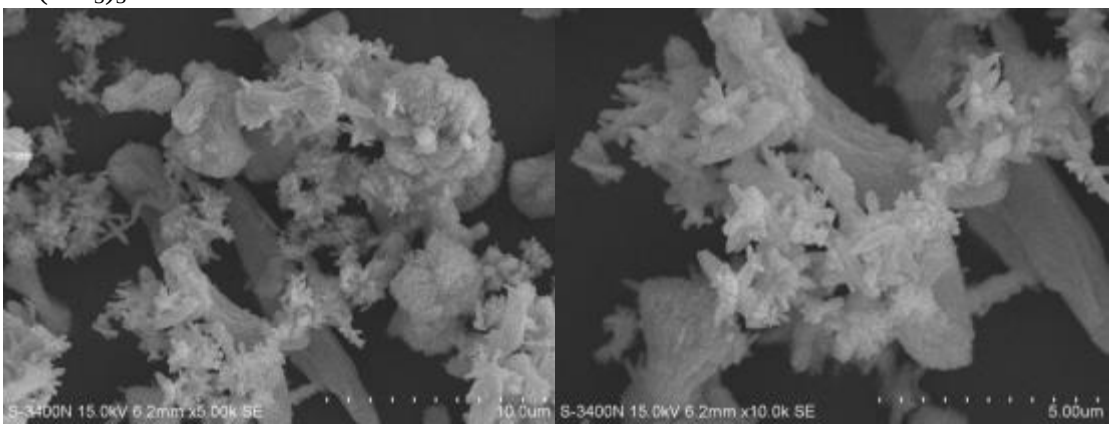
50ml water (1.39 g cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and 0.75 g ammonium bicarbonate (NH_4HCO_3) were dissolved in 50 ml deionized water at 25°C under magnetic stirring, respectively.)



Effect of adding way (aging for 24 h at 0°C)

Fig.S6 Detail SEM of synthesized CeO_2 at dropping way

1.39 g cerium (III) nitrate hexahydrate ($Ce(NO_3)_3•6H_2O$) and 0.75 g ammonium bicarbonate (NH_4HCO_3) were dissolved in 200 ml deionized water at 0 °C under magnetic stirring, respectively. The NH_4HCO_3 solution was slowly dropped into the $Ce(NO_3)_3$ solution at ratio of 2.5ml/min.



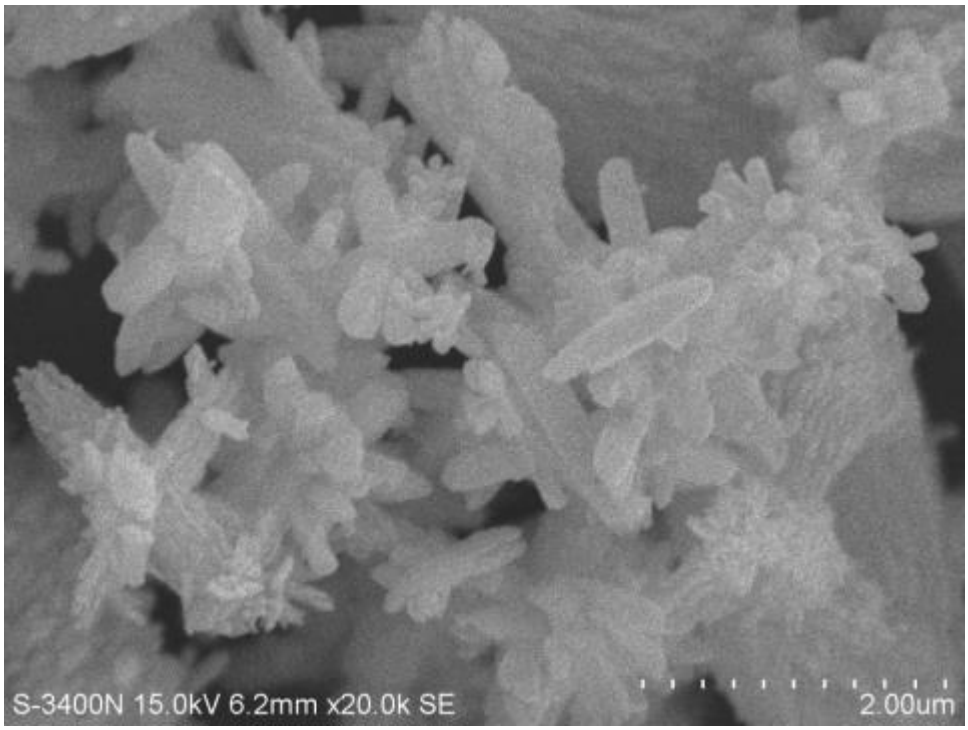
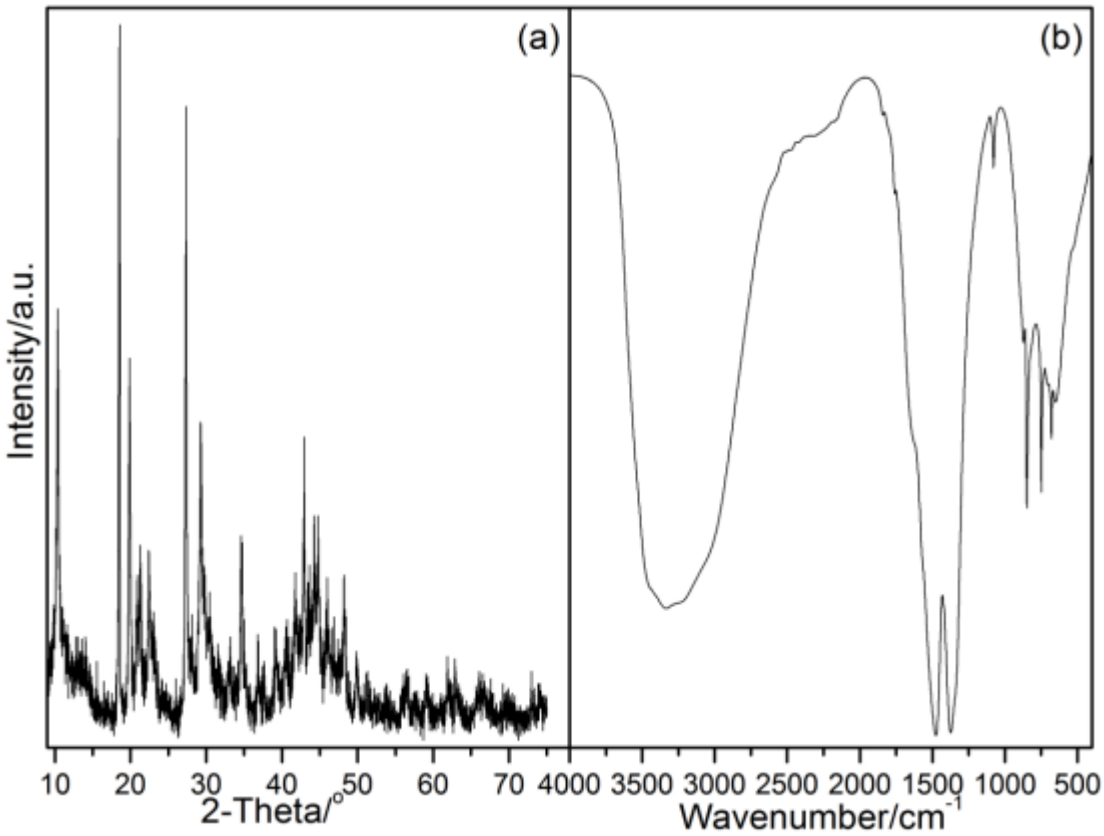
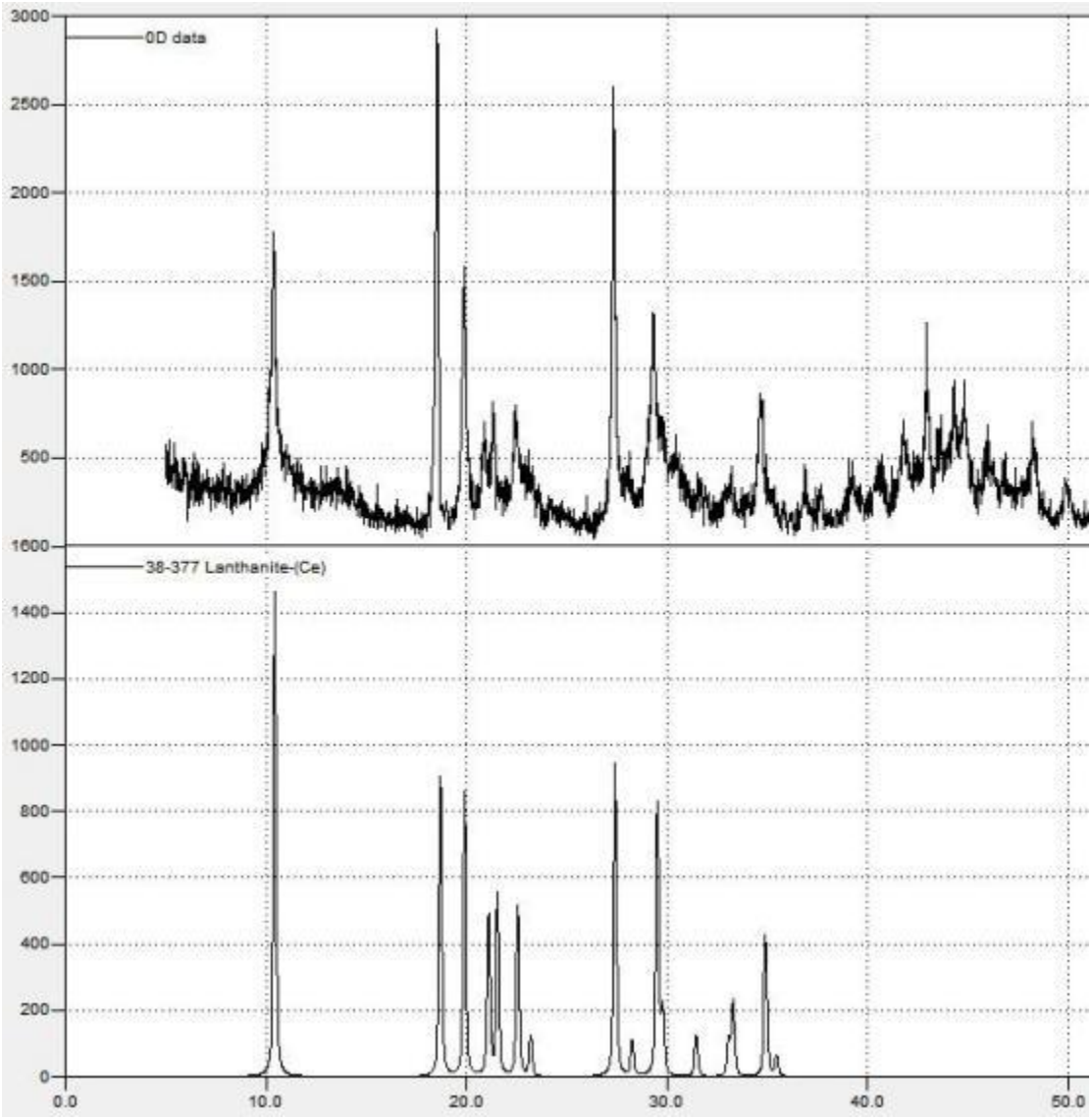


Fig.S7 XRD and IR of as-synthesized precursors by dropping way

Orthorhombic Cerium Carbonate Hydrate ($Ce_2(CO_3)_3$•8 H_2O, JCPDS 38-377)





Card Information

Names:	Cerium Carbonate Hydrate
	Lanthanite-(Ce)
Formula:	$Ce_2(CO_3)_3 \cdot 8H_2O$
PDF Number:	38-377
Quality:	indexed
Subfiles:	inorganic mineral

Cell and Symmetry Information

System:	orthorhombic		**Space Group:**	Pbnb	(no. 56)
a:	9.482	**b:**	16.938	**c:**	8.965
Density (Dm):	2.760	**Density (Dx):**		2.790	**Z:**

Instrument Information

Radiation:	CuKa	**Wavelength:**	1.5418	**Filter:**	Ni
Instrument(d):	Debye-Scherrer				
Instrument(I):	densitometer		**I type:**	unknown	

Fig. S8 SEM images of the CeO_2 particles prepared by thermal decomposition method (CeO_2-TD)