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$_4$HCO$_3$ 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
75°C, 15h, under reflux condition
$100^\circ C, 15\text{h, under reflux condition}$
150°C, 15h, under hydrothermal conditions
Fig. S2 Detail XRD of as-synthesized CeO$_2$ (Precursor)

XRD pattern of as-synthesized precursor at 25°C
Cerium Carbonate Hydrate (Ce$_2$(CO$_3$)$_3$$\cdot$8 H$_2$O, JCPDS 38-377)
XRD pattern of as-synthesized precursor at 50°C
Orthorhombic Cerium Carbonate Hydrate (Ce₂(CO₃)₃•6 H₂O, JCPDS 30-295)
XRD pattern of as-synthesized precursor at 100°C
orthorhombic CeOHCO$_3$ (JCPDS 41-13)
XRD pattern of as-synthesized precursor at 150°C
Hexagonal CeOHCO$_3$ (JCPDS 32-189) +CeO$_2$ (JCPDS 34-0394)
XRD pattern of as-synthesized precursors hydrothermally treated at 150°C and 170°C

Hydrothermal treatment of as-synthesized precursors(0°C) at 150°C

Hydrothermal treatment of as-synthesized precursors(0°C) at 170°C
XRD pattern of as-synthesized precursor (CeO$_2$-SC)
Orthorhombic Cerium Carbonate Hydrate (Ce$_2$(CO$_3$)$_3$$\cdot$6 H$_2$O, JCPDS 30-295)
Effect of precipitant (at 0°C)

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°C)

Fig.S4 Detail SEM of synthesized CeO₂ 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°C)

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$_3$)$_3$•6H$_2$O) and 0.75 g ammonium bicarbonate (NH$_4$HCO$_3$) 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$6H$_2$O) and 0.75 g ammonium bicarbonate (NH$_4$HCO$_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$_3$)$_3$•6H$_2$O) and 0.75 g ammonium bicarbonate (NH$_4$HCO$_3$) 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$_3$)$_3$•6H$_2$O) and 0.75 g ammonium bicarbonate (NH$_4$HCO$_3$) 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$_2$O) and 0.75 g ammonium bicarbonate (NH$_4$HCO$_3$) were dissolved in 200 ml deionized water at 0 °C under magnetic stirring, respectively. The NH$_4$HCO$_3$ solution was slowly dropped into the Ce(NO$_3$)$_3$ solution at ratio of 2.5 ml/min.
Fig. S7 XRD and IR of as-synthesized precursors by dropping way

Orthorhombic Cerium Carbonate Hydrate (Ce$_2$(CO$_3$)$_3$•8 H$_2$O, JCPDS 38-377)
Card Information

Names:  Cerium Carbonate Hydrate  Lanthanite-(Ce)
Formula:  Ce₂(C₂O₄)₃·₉H₂O
PDF Number:  38-377
Quality:  indexed
Subfiles:  inorganic mineral

Cell and Symmetry Information
System:  orthorhombic  Space Group:  Pbnm  (no. 56)
a:  9.482  b:  16.938  c:  8.965
Density (Dm):  2.760  Density (Dx):  2.790  Z:

Instrument Information
Radiation:  CuKα  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)