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Synthesis cerium oxide particles via polyelectrolyte controlled nonclassical crystallization for catalytic application

Mei Li,*[a,b] Yanghong Hu,[a,b] Cuicui Liu,[b] Jinguo Huang,[b] Zhaogang Liu,[b] Mitang Wang,[b] and Zhihua An*[c]

[a] School of Material Science and Engineering, Beijing University of Chemical Engineering, Beijing, 100029, China.
[b] School of Material and Metallurgy, Inner Mongolia University of Science and Technology, Key Laboratory of New Technologies of Modern Metallurgy and Application of Rare Earth Materials, Inner Mongolia University of Science and Technology, Baotou, 014010, China. Fax: +86 472 595 1505; Tel: +86 472 595 4390; E-mail: limei@imust.cn
[c] Department of Chemistry, New York University, 100 Washington Square East, New York, NY 10003, United States. Tel: +10 212 998 8475; E-mail: za6@nyu.edu

Experimental Section

Materials. $Ce_2(CO_3)_3$ was provided by Inner Mongolia Baotou Steel Rare-Earth Hi-Tech Co., Ltd of Baotou Steel (CeO2/ΣREO≥99.9%, ΣREO≥45%). $Ce(NO_3)_3$ solution was prepared by dissolving $Ce_2(CO_3)_3$ in nitric acid. $(NH_4)_2CO_3$, ethanol and Poly(sodium 4-styrenesulfonate) (PSS, $M_w \approx$ 70,000 g/mol)) were purchased from Sigma. Deionized (DI) water with a resistivity greater than 18 MΩ was obtained from a Millipore system. All chemicals were used as obtained without further purification.

Preparation of CeO_2 particles. In a typical preparation, 500 mL 0.14 M $Ce(NO_3)_3$ solution was mixed with 500 mL 1 g/L PSS solution in a 1L beaker. The final pH value of the mixture is adjusted to 4 by adding nitric acid. The final mixture solution contain 0.5 g/L PSS and 0.07 M $Ce(NO_3)_3$. The beaker was then covered with parafilm, which was punched three holes with a needle and placed in a desiccator. One watch glass of crushed $(NH_4)_2CO_3$powder (20 g) was also covered with parafilm with three holes and placed at the bottom of the desiccators. After 14 days of reaction, the beaker is removed from the desiccators. The precipitate precursor was rinsed with deionized water and ethanol alternatively for three times and allowed to dry at 60 ^oC for 8 hrs in a vacuum oven. Cerium oxide particles are obtained by calcination of the precursors at 500 ^oC for 2 hrs, the temperature acceleration speed is 200 ^oC/h. For comparison, cerium oxide particles are prepared without PSS with the same procedure.

Characterization. The particle size distribution of the samples was measured with Beckman Coulter LS230 laser diffraction particle size analyzer. Samples (0.05 g particles) were dispersed in 20 mL water containing 0.5% sodium hexametaphosphate as a stabilizing agent and sonicated for 5 min at 100 Hz. The results are calculated by diffraction data from Mie theory which is presented as a distribution curve of the differential volume versus particle diameter. The mean size of the particles is derived via statistical analysis of the distribution curve. Scanning election microscope (SEM) was used to characterize the samples. A thin film of gold (~2 nm) was sputtered onto the surface of the samples. A voltage of 5 kV was used during sample examination on a Zeiss AURIGA 55 SEM (Carl Zeiss, Inc.) with X-ray energy dispersive spectroscopy (EDS). Crystal structure of the samples was investigated with X-ray powder diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer ($\lambda_{Cu\text{-}K\alpha}$ = 1.54178 Å). The texture properties of the samples were characterized with QUADRASORB SI automated surface area analyzer and pore size analyzer. The samples were vacuumed for 3 hrs at 300 ^oC before measurement. N_2 isotherms are collected at -196 ^oC and the specific surface area, pore volume and pore size was calculated. Oxygen storage capacity (OSC) were measured using oxygen pulse gas chromatographic technique on a setup build by our lab, briefly, 200 mg samples were reduced in H_2 at a flow rate of 40 mL/min at 550 ^oC for 60 min and then flowed pure N_2 at a flow rate of 20 mL/min until the temperature was cooled down to 200 ^oC. Then O_2 was pulse injected at an interval of 2 min via six channel valves. A thermal conductivity detector (TCD) detector was used to collect the signal of the non-absorbed $O_{2.}$ The typical raw chromatograph is shown in Fig. S7. Then the pulse injection will stop once the sample was saturated with oxygen. The amount of uptake oxygen is calculated by subtracting the release amount of oxygen from the injection amount. Each measurement was repeated five times to get the average value. OSC is calculated by dividing the molar amount of uptake oxygen by the mass of sample (200mg of CeO_2). Fourier Transform Infrared (IR) spectroscopy was used to characterize the precursor sample on a SpectrumRX/BX FT-IR spectrometer (PerkinElmer). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a computerized Netzsch STA449F3 simultaneous TGA-DSC instrument. Samples were initially dried at 60 °C. Thermal measurements were conducted with a flow of O_2/Ar (1:4) gas at 20 mL/min from 25°C to 900°C at a

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10°C/min heating rate. The thermal data were analyzed using Netzsch software programs supplied with the instrument.

EDS results.

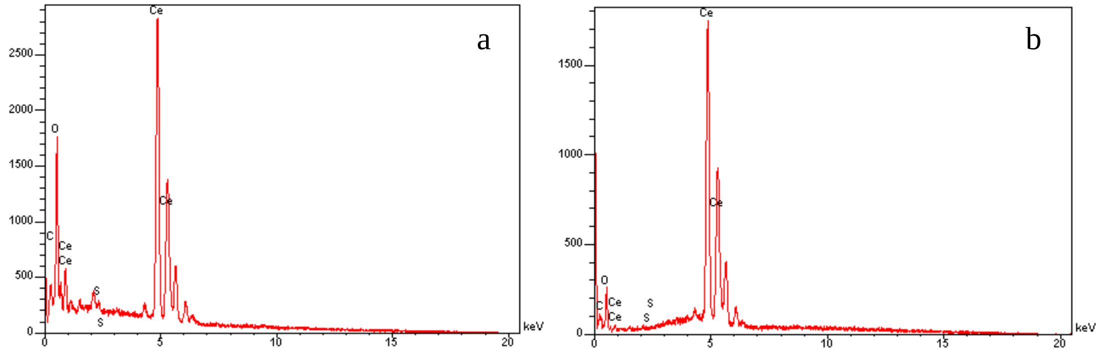

Fig. S1. EDS patterns of (a) as synthesized precursors and (b) CeO_2 obtained after calcinations of precursors. The disappeared sulfur peak in (b) indicates that PSS decomposed after calcinations.

Particle size distribution results.

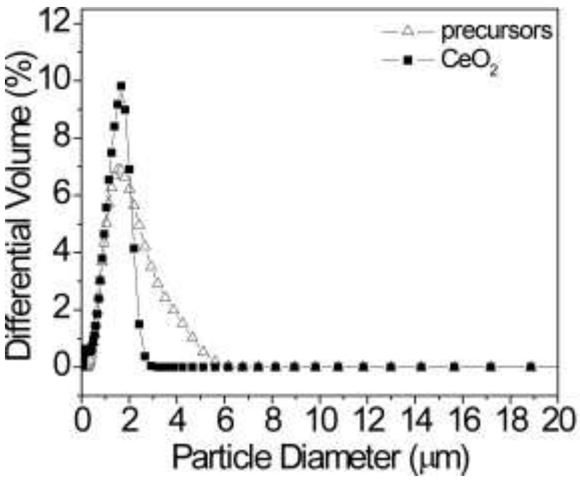

Fig. S2. The particle size distribution of as-synthesized precursor particles and CeO_2 particles synthesized with PSS. The mean particle size of precursors is 1.86 μm. The mean particle size of the obtained CeO_2 particles decreases to 1.33 μm.

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XRD Characterizaions of precursors.

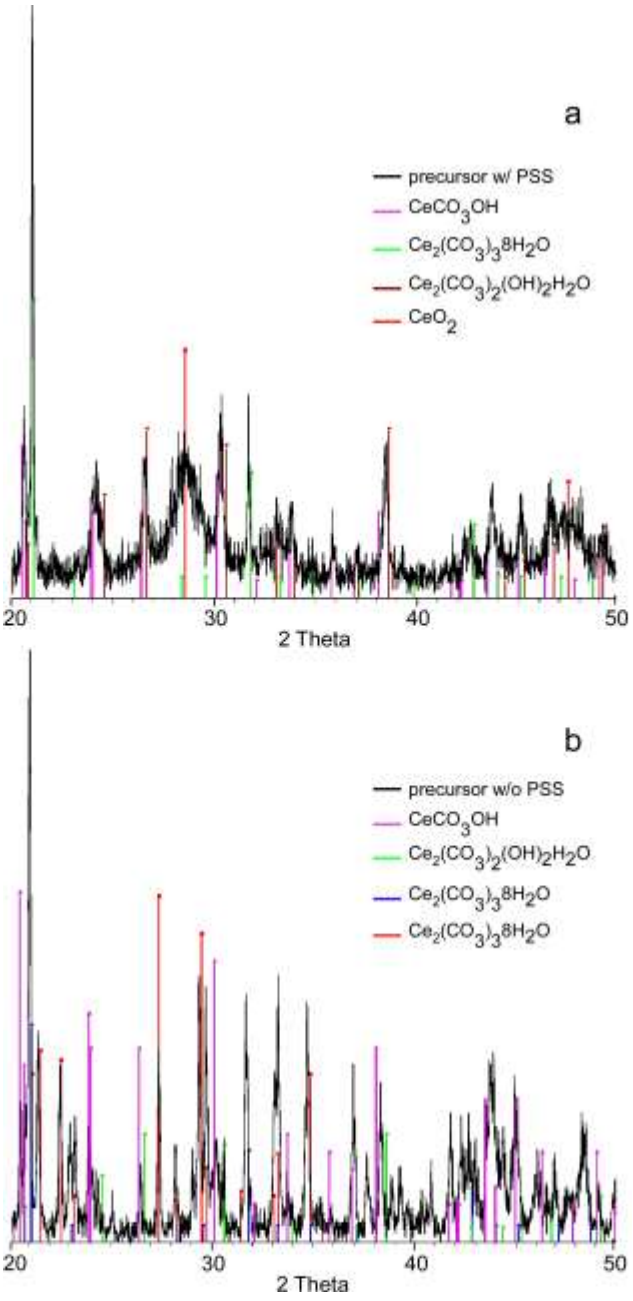

Fig. S3. XRD patterns of precursor particles prepared (a) in the presence of PSS and (b) in the absence of PSS. All samples are dried at 60°C. The XRD data analysis indicate that the precursors prepared with and without PSS additives are both mixtures of cerium (III) carbonate hydrates ($Ce_2(CO_3)_38H_2O$) and cerium (III) basic carbonates hydrates ($CeCO_3OH$ and $Ce_2(CO_3)_2(OH)_2H_2O$). The precursors obtained with PSS also contain very fine CeO_2 particles. This might due to the oxidation and decomposition of cerium (III) hydroxide produced at the earlier stage of the gas diffusion process. There are two different lattice parameter for the orthorhombic cerium carbonate hydrates ($Ce_2(CO_3)_38H_2O$) in the precursors obtained without PSS, however, it is not show up in the precursors obtained with PSS addition.

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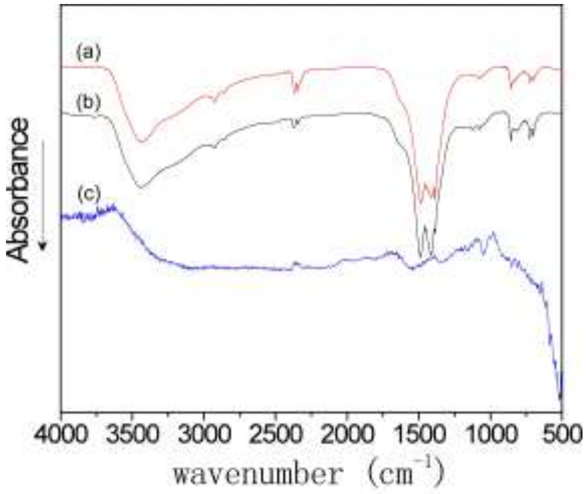

Fig. S4. IR spectra of precursor particles prepared (a) in the absence of PSS and (b) in the presence of PSS. All samples are dried at 60°C. (c) IR spectrum of CeO_2 obtained after calcination of precursors at 900 °C.

Table S1. Position of IR absorptions and functional groups in precursors.

Positions (cm^{-1})	**(a) precursors w/o PSS**	**(b) precursors w/ PSS**	**(c) CeO_2**
3349	-OH (stretch) and water of hydration (stretch)	-OH (stretch) and water of hydration (stretch)	-
2926, 2923	overtones of CO_3^{2-} asymmetric stretch	overtones of CO_3^{2-} aymmetric stretch and $–CH_2$ asymmetric stretch	-
1480, 1491	CO_3^{2-} asymmetric stretch	CO_3^{2-} asymmetric stretch	-
1203, 1126	-	SO_3^{2-} asymmetric stretch	-
1075	CO_3^{2-} symmetric stretch	CO_3^{2-} symmetric stretch	-
857, 858	CO_3^{2-} out-of-plane bend	CO_3^{2-} out-of-plane bend	-
697-725	CO_3^{2-} bend	CO_3^{2-} bend	-
557	C-O-Ce stretch	C-O-Ce stretch	
518, 586	-	-	O-Ce-O stretch

The IR results revealed that the precursors are carbonate hydrates and possibly contain –OH groups. The bands in the 1075 cm^{-1} and 1480-1500 cm^{-1} regions are attributable to carbonate stretch vibration mode and are virtually identical to the ones previously reported for cerium carbonate hydrates.[1,2] Other bands corresponding to the bend vibration modes of carbonate are also seen in the 697-725cm^{-1} and 850 cm^{-1} regions, which is consistent with the reported results.[3] It also clearly indicated that the precursors obtained in the presence of PSS contain SO_3^{2-} groups, while the precursors obtained in the absence of PSS does not contain this band. The obtained CeO_2 after calcinations exhibits only Ce-O stretch bands in the 518 cm^{-1} and 580 cm^{-1} regions, which is consistent with the previously reported results. [4] This indicates that the obtained product after calcination is pure CeO_2.

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TGA and DSC analysis of precursors.

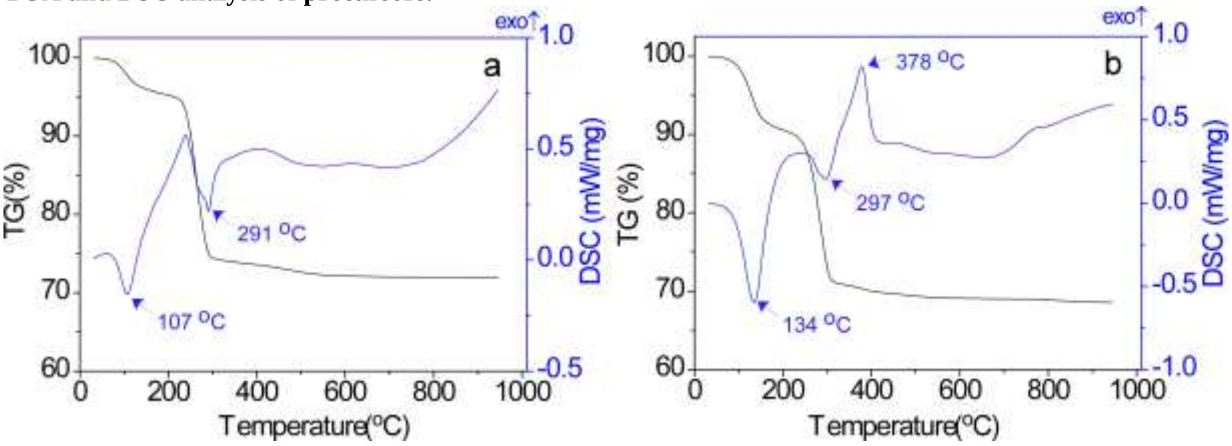

Fig. S5. TG and DSC curves of precursor particles prepared (a) in the absence of PSS and (b) in the presence of PSS. All samples are dried at 60°C and measured in a O_2/Ar (1:4) gas flux.

The thermogravimetric analysis was carried at an oxidizing atmosphere by using O_2/Ar (1:4) gas flux. The results revealed that the endotherms around 100°C -200°C are due to the loss of bulk water and hydrate water in both of the precursors (Fig. S5 a&b). The precursors obtained in the absence of PSS contain less hydrate water (4.51%) than the precursors obtained in the presence of PSS (9.38%). The endotherms (a&b) around 240-330°C were assigned to the decomposition of cerium carbonate and basic cerium carbonate, which is consistent with reported results.[5] The only slightly endothermic character of the decomposition of cerium carbonate and basic cerium carbonate can be explained in terms of the exothermic oxidation of Ce (III) by O_2 to Ce (IV), which takes place simultaneously in the absence of PSS. However, the exothermic peak in the precursors obtained in the presence of PSS (b) indicates that the decomposition of cerium carbonate and the exothermic oxidation of Ce (III) by O_2 to Ce (IV) occurred nonsimutaneously.[5]

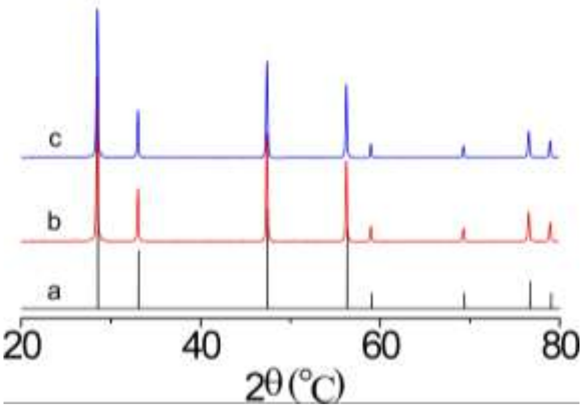

Fig. S6. XRD patterns of the products after thermal analysis measurement on the precursors obtained in the absence of PSS (b) and in the presence of PSS (c) comparison with the standard CeO_2 XRD data (a). The results reveal the final products after thermal analysis are cerium (IV) oxide.

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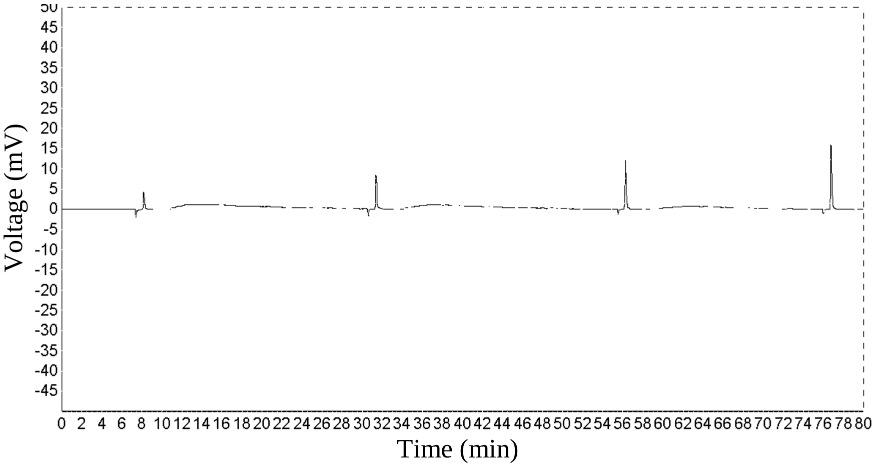

Fig. S7. A typical pulse gas chromatograph of OSC measurement. TCD signals (in mV) vs time (in min) indicated the quantity of the non-absorbed oxygen after each pulse injection.

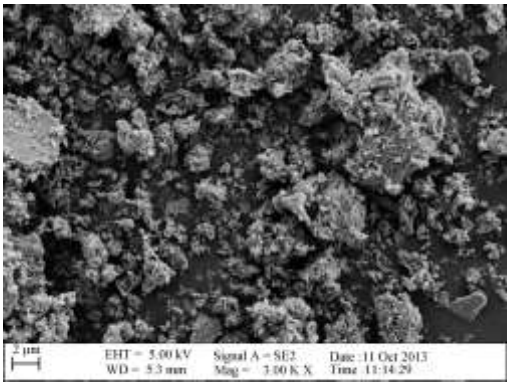

Fig. S8. A SEM image of CeO_2 powder prepared by evaporation and calcination of the mixture of cerium nitrate solution with PSS.

The following control experiment was carried out to confirm that the PSS controlled nonclassical crystallization methodology with gas diffusion technique is necessary for obtaining mesoporous CeO_2 particles with spherical morphology. The solution contain 0.5 g/L PSS and 0.07 M $Ce(NO_3)_3$ was evaporated and calcinated at 500^oC to get the solid CeO_2. The results reveal that this procedure yields CeO_2 powder without any regular morphology (Fig. S8). In other words, the morphology of obtained CeO_2 particles is not controllable via this method. Using PSS controlled nonclassical crystallization methodology with gas diffusion technique, the precursor nanocrystallines are self-assembled with the aid of PSS into spherical particles. The obtained CeO_2 particles inherit the spherical morphology from the precursors. Furthermore, the obtained CeO_2 particles are mesoporous with slit-like pores which provide high surface area and pore volume, both of which are favorable for catalysts.

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