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Mesoporous CeO\(_2\) nanoparticles assembled by hollow nanostructures: formation mechanism and enhanced catalytic property

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In this paper, a novel hierarchically mesoporous CeO\(_2\) nanoparticles assembled by hollow nanocores have been prepared through a facile solvothermal strategy using Ce(HCOO)\(_2\) as the precursor. X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), field-emission scanning electron microscopy (FE-SEM) and thermal gravimetric analysis (TGA) were utilized to characterize the products and research the formation mechanism. The whole synthesis process involves two steps: the formation of Ce(HCOO)\(_2\) nanoparticles constructed with nanocones at room temperature in an alkaline environment and oxidation induced phase transformation from Ce(HCOO)\(_2\) to CeO\(_2\) with the formation of hollow nanocores assembled by nanocrystals in the solvothermal process at 150 °C. The as-prepared mesoporous CeO\(_2\) nanoparticles with the average diameter of 500 nm displayed a high surface area of 147.6 m\(^2\) g\(^{-1}\) by N\(_2\) adsorption and desorption measurement. The H\(_2\)-TPR test showed its great reduction behavior in low temperature zone. By comparing the T\(_{100}\) temperature of CO conversion with commercial sample (above 350 °C) and other reported samples (above 300 °C) in the literatures, the mesoporous CeO\(_2\) nanoparticles (270 °C) presented an excellent catalytic activity for CO oxidation.

Introduction

Hierarchically nanostructured materials have attracted considerable interest due to their enhanced properties and potential applications.\(^{[1-8]}\) Up to now, a wealth of methods has been used for controlled synthesis of hierarchically nanostructured materials\(^{[9]}\), such as precursor template synthesis,\(^{[10]}\) liquid-liquid assisted route,\(^{[11]}\) hydrothermal/solvothermal synthesis.\(^{[12,13]}\) For example, 3D-hierarchical Cu\(_3\)Sn\(_4\) flowerlike microspheres have been successfully synthesized through a solvothermal process and the obtained Cu\(_3\)Sn\(_4\) photocatalysts without any loadings exhibit good photocatalytic activity.\(^{[14]}\) Novel hierarchical flower-like Bi\(_2\)MoO\(_6\) hollow spheres constructed with nanoflakes have been fabricated via a facile template-free solvothermal process in the presence of ethylene glycol.\(^{[15]}\)

As an important functional inorganic material, ceria has been under extensive investigation for its various applications in catalysts,\(^{[16]}\) chemical mechanical polishing materials,\(^{[17]}\) fuel cells,\(^{[18]}\) oxygen sensors,\(^{[19]}\) and UV blockers.\(^{[20]}\) Especially, many endeavors have been devoted to investigate the catalytic performances of the ceria-based nanomaterials. For example, Tang’s group studied the remarkably enhanced catalytic activity of core-shell Au@CeO\(_2\) nanocomposites for CO oxidation and the superior photocatalysts of multi-shelled CeO\(_2\) hollow microspheres for water oxidation in details.\(^{[21, 22]}\) The large contact areas and the mesopores promoted the catalytic oxidation of CO, while the triple-shelled hollow structure, the larger surface area and the more curved surfaces of the TScHSSs enhanced the photocatalytic oxidation of water. To date, considerable efforts have been focused on the fabrication of CeO\(_2\) 3D hierarchical structures constructed with nanoparticles, nanorods, nanoflakes, due to their enhanced properties.\(^{[23-26]}\) For example, Jeong’s group synthesized CeO\(_2\) with flowerlike microstructure through a cerium-based coordination polymers with a calcination process, later La\(_2\)O\(_3\) and Gd\(_2\)O\(_3\) were fabricated by the same method.\(^{[27]}\) Sun et al. fabricated nearly monodisperse flowerlike CeO\(_2\) microspheres via the calcination of a Ce(OH)\(_2\)CO\(_3\) precursor and the as-prepared CeO\(_2\) decorated with Cu showed excellent catalytic properties and marked hydrothermal stability for ethanol steam reforming.\(^{[28]}\) Without calcinations process, Sato’s group prepared 3D flowerlike CeO\(_2\) under subcritical and supercritical temperature of 350-380 °C via a solvothermal process and the as-formed flowerlike CeO\(_2\) decorated with 5% Gd displays higher catalytic activity than pure CeO\(_2\) for CO oxidation.\(^{[29]}\) However, these methods conventionally require either rigorous conditions or high temperature.

Recently, our research group has been focused on fabrication of CeO\(_2\) with satisfactory structure in a mild solution route.\(^{[30-33]}\) We have reported a simple solvothermal method to obtain Ce(HCOO)\(_2\), followed by annealing the Ce(HCOO)\(_2\) at high temperature to obtain CeO\(_2\) three dimensional micro/nanostructures.\(^{[30]}\) Based on this work, we had designed a one-step and facile strategy to synthesize mesoporous CeO\(_2\) nanoflowers derived from Ce(HCOO)\(_2\) and Ce\(_2\)(C\(_2\)O\(_4\))\(_3\)·10H\(_2\)O through a solvothermal or hydrothermal route.\(^{[31, 32]}\) Even though we have reported self-assembly of ceria nanocrystals starting from Ce(HCOO)\(_2\) in the neutral condition.\(^{[33]}\) In our current work, we synthesized a novel hierarchically mesoporous CeO\(_2\) nanoparticles assembled by hollow nanocores derived from Ce(HCOO)\(_2\) under the changed experiment condition and studied...
the formation mechanism in detail. It is worth mentioning that there were few reports about the mesoporous hollow cone-like structure according to our knowledge. The whole process involved two steps: 1. the preparation of the Ce(HCOO)$_3$ nanoparticles constructed with nanocones in a short time in an alkaline environment at room temperature; 2. the transformation from Ce(HCOO)$_3$ to CeO$_2$ with the formation of hollow nanocones by the oxidation of H$_2$O$_2$ in the solvothermal process. The final product displayed a high surface area of 147.6 m$^2$ g$^{-1}$ and excellent catalytic activity for CO oxidation.

**Experimental Section**

**Materials**

All the reactants were analytical grade and used without further purification. Cerium(III) nitrate hexa-hydrate [Ce(NO$_3$)$_3$·6H$_2$O, >99.0%] and cerium(IV) oxide powders (CeO$_2$, >99.0%) were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. Formic acid (HCOOH, >99.0%), Polyoxyethylene(10) octylphenyl ether (OP:10, 99.0%), hydrogen peroxide (H$_2$O$_2$, 30 %) were obtained from Sinopharm Chemical Reagent Co. Ltd. NH$_3$·H$_2$O solution with a concentration of 10 M was obtained by diluting commercial ammonia solution (NH$_3$·H$_2$O, >99.0%), Cerium(IV) oxide powders from Tianjin Kemiou Chemical Co. Ltd. NH$_3$·H$_2$O solution with a concentration of 10 M was obtained by diluting commercial ammonia solution (NH$_3$·H$_2$O, >99.0%), Hydrogen peroxide (H$_2$O$_2$, 30 %) was obtained from Sinopharm Chemical Reagent Co. Ltd. Formic acid (HCOOH, >99.0%), Polyoxyethylene(10) octylphenyl ether (OP:10, 99.0%), hydrogen peroxide (H$_2$O$_2$, 30 %), and the ammonia solution (NH$_3$·H$_2$O, 25 %) were obtained from Sinopharm Chemical Reagent Co. Ltd. NH$_3$·H$_2$O solution with a concentration of 10 M was obtained by diluting commercial ammonia solution (NH$_3$·H$_2$O, 25%). Deionized water and absolute alcohol were used throughout.

**Synthesis of CeO$_2$ nanoparticles**

In a typical procedure, 0.117 g (0.27 mmol) Ce(NO$_3$)$_3$·6H$_2$O was dissolved in 15 mL of absolute alcohol under vigorous stirring, then 130 µL OP-10 and 100 µL HCOOH was added. Subsequently, a white colloidal solution was obtained immediately after the rapid addition of 500 µL 10 M NH$_3$·H$_2$O. After continuous stirring for 20 min, the color of the colloidal solution turned to brown with the addition of 100 µL H$_2$O$_2$ (30%). Finally, the as-formed brown solution was transferred into a Teflon-lined autoclave with a capacity of 20 mL and heated for 6 h at 150 °C. After the autoclave was cooled to room temperature naturally, light brown products were collected and washed with deionized water 3 times. Then the products were washed with absolute alcohol, and dried at 60 °C for 8h.

**Characterization**

The phase purity of the sample was examined by using a D8 Advance X-ray diffractometer with a graphite monochromator and Cu-K radiation (λ=0.15418nm). The nanostructure and morphology of the products were characterized using an Advance X-ray diffractometer with a graphite monochromater for Cu:K radiation (λ=0.15418nm). The nanostructure and morphology of the products were characterized using a field-emission scanning electron microscope (FE-SEM, Hitachi, S4800). Thermogravimetric analysis (TGA) was carried out to monitor the mass loss of products at a heating rate of 10 °C min$^{-1}$ from 25 to 800 °C under an air atmosphere (Mettler Toledo, TGA/SDTA851°). Temperature-programmed reduction under a H$_2$ environment (H$_2$-TPR) was carried out on a PCA-1200 instrument. Typically, 50 mg CeO$_2$ catalyst was pretreated under O$_2$ stream at 500 °C for 0.5 h. After cooling down to room temperature, the sample was purged with 30 mL min$^{-1}$ of N$_2$ for 30 min to remove the excess O$_2$. Then a flow of 5% H$_2$-N$_2$ was introduced into the CeO$_2$ sample with a flow rate of 30 mL min$^{-1}$ and the temperature was raised to 1000 °C at a rate of 10 °C min$^{-1}$. N$_2$ adsorption-desorption isotherms were measured on a QuadraSorb SI at 77.3K. Before the measurement, the samples were outgassed at 200 °C under vacuum for 6 h. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution was calculated from the desorption branch using the Barrett-Joyner-Halenda (BJH) theory.

**Measurement of catalytic activity**

The catalytic activity of the as-obtained samples was evaluated by a continuous flow fixed-bed microreactor operating under atmospheric pressure. In a typical experiment, catalyst particles (50 mg) were placed in the reactor. Then, the samples were treated in O$_2$ gas with a flow rate of 30 ml/min and heated at 300 °C for 2 h. After cooling down to room temperature, the gas stream was switched to the reaction atmosphere, i.e., CO oxidation in excess O$_2$: 1% CO and 10% O$_2$ balanced with N$_2$, with a flow rate of 60 ml/min. The composition of the gas exiting the reactor was analyzed with an online infrared gas analyzer (Gasboard-3121, China Wuhan Cubic Co.) which simultaneously detects CO and CO$_2$ with a resolution of 10 ppm.

**Results and discussion**

**Physical characterization of Ce(HCOO)$_3$ precursor**

![Fig. 1](image-url) (a) XRD pattern, (b1) TG, and (b2) DSC curves of the Ce(HCOO)$_3$ precursor obtained before adding H$_2$O$_2$

At the early stages of our synthesis process, a white colloidal solution was obtained immediately with the addition of the ammonia solution (10 M). The white colloids were centrifuged, dried and characterized by XRD, TGA and TEM. Fig. 1a shows the XRD pattern of the precursor, and all the diffraction peaks could be easily indexed to the rhombohedral pure phase [space group: R3 (146)] of Ce(HCOO)$_3$ (JCPDS card No. 49-1245). To investigate the thermal behavior of the Ce(HCOO)$_3$, thermogravimetry analysis was carried out under air from 30 to 800 °C with a temperature ramp of 10 °C min$^{-1}$. The TG curve (Fig 1b1) indicates that the weight loss (36.81%) is approximately in agreement with the theoretical value of the conversion from Ce(HCOO)$_3$ to CeO$_2$. Only one peak is found in the DSC curve (Fig 1b2) during 30 to 800 °C, which is 347.2 °C. All the decomposition behaviors demonstrate that the chemical formula of the as-formed precursor is Ce(HCOO)$_3$ without crystal water.
The size and morphology of the Ce(HCOO)₃ precursor were examined by transmission electron microscope (TEM) and scanning electron microscope (SEM). Fig. 2a shows a panoramic TEM image of the as-formed precursor, which indicates the nanoparticles are relatively uniform and monodisperse. It can be clearly seen from Fig. 2 that these nanoparticles are composed of many nanocones and the average diameter of these nanoparticles is about 500 nm. It is necessary to separate the nucleation from the growth for the final product with uniform size. However it is hard to obtain completely uniform particles with a rapid process of nucleation and growth in an alkaline environment at room temperature, especially for 3D-hierarchical nanostructure.

Physical Characterization of CeO₂ nanoparticles

Fig. 3 XRD pattern of the CeO₂ products after solvothermal treatment at 150 °C for 6h

Fig. 3 shows the typical diffraction pattern of the CeO₂ products. All diffraction peaks are in good agreement with a pure phase face-centered cubic [space group: Fm3m (225)], which is consistent with the JCPDS file of ceria (JCPDS No. 34-0394). It can be seen that there are no signals corresponding to Ce(HCOO)₃ in Fig. 3, indicating the high purity of the sample. Furthermore, the broadening of the peaks manifested that the sample is made up of primary small crystal particles. In addition, the product obtained by annealing Ce(HCOO)₃ precursor is also detected by XRD (ESI, Fig. S1†) and the diffraction peaks are consistent with a pure face-centered cubic phase of ceria (JCPDS No. 34-0394).

To identify the internal structures of nanoparticle thoroughly, more details of the nanoparticles have been investigated by the HRTEM (Fig. 5). As shown in Fig 5a, the full view of a single nanoparticle indicates that the structures are made of several hollow nanocones which is in line with the high-magnification SEM image (ESI, Fig. S2†). The magnified part of a hollow nanocone (Fig 5c) confirms the nanocones are made of numerous nanocrystal particles with a crystallite size about 3-5nm. As shown in Fig. 5d, the visible lattice fringes with a spacing of about 0.27 nm clearly corresponded to the spacing of the (200) planes of ceria. Furthermore, the color contrast of the image (Fig. 5d) indicates the mesoporous structure of CeO₂ nanoparticles which is consistent with the BJH analysis. The mesoporous structure favoured for molecule accessibility to the active surface of the nanocrystals and mass transport. As shown in Fig. 5b, the selected area electron diffraction (SAED) pattern of a single CeO₂ nanoparticle (Fig. 5b) indicates the typical polycrystalline nature. Therefore we could come to a conclusion that the
nanoparticles were composed of many tiny crystal particles.

The textural porosities of the CeO\textsubscript{2} products were furthermore characterized by N\textsubscript{2} adsorption–desorption measurement. The N\textsubscript{2} adsorption–desorption isotherms are displayed in Fig. 6 and the inset part is the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution plots. The obvious hysteresis loop ranging from 0.4 to 1.0 in the relative pressure suggests the existence of mesostructure in the CeO\textsubscript{2} nanoparticles. The calculated surface area of the CeO\textsubscript{2} nanoparticles is 147.6 m\textsuperscript{2} g\textsuperscript{-1}, which is much higher than that of the commercial CeO\textsubscript{2} (8.5 m\textsuperscript{2} g\textsuperscript{-1}).\textsuperscript{[38]} Because the high surface area exhibits numerous crystal facets which are considered as the active sites for the adsorption of CO, the CeO\textsubscript{2} nanoparticles could be an ideal catalytic support for CO conversion.\textsuperscript{[31, 39]} From the BJH pore size distribution plots of the CeO\textsubscript{2} nanoparticles, the mesopores (5-60nm) can serve as tunnel structure for the contact between the catalytic surfaces and CO molecules.\textsuperscript{[37, 40, 41]} The N\textsubscript{2} adsorption-desorption isotherms measurement was also used to test the calcined CeO\textsubscript{2} powders via cerium formate precursor (ESI, Fig. S4†) and the BET surface area of the calcined product is 114.9 m\textsuperscript{2} g\textsuperscript{-1}.

**Formation Mechanism**

Based on our previous work, we used H\textsubscript{2}O\textsubscript{2} as an oxidant to control the transformation from Ce(HCOO)\textsubscript{3} to CeO\textsubscript{2} under the protection of ammonia solution. At an early stage, a white colloidal solution was formed immediately after the addition of ammonia solution (10M) to the solution containing Ce\textsuperscript{3+}, H\textsuperscript{+} and HCOO\textsuperscript{-} ions. In the past research, the injection method of base is often overlooked. Herein, we find that the rapid injection method of strong ammonia (10M) is the key to obtain nano-cone constructed Ce(HCOO)\textsubscript{3} precursor. However, the mechanism and influencing factors for the formation of the Ce(HCOO)\textsubscript{3} precursor need to be further discussed. Even though the morphology of Ce(HCOO)\textsubscript{3} was influenced by the dosage of ammonium hydroxide, we can see from Fig. 7c-d that the final products all inherited the shape and dimensions of the Ce(HCOO)\textsubscript{3} template after solvothermal reaction. Furthermore, the textural porosities of the corresponding products were tested by N\textsubscript{2} adsorption–desorption measurement and the BET surface area of the solid nanospheres and dispersive cone-like nanostructure are 105.7 m\textsuperscript{2} g\textsuperscript{-1} and 142.6 m\textsuperscript{2} g\textsuperscript{-1} respectively.

In a solution route, because the molecular interactions including Van der Waals forces and hydrogen bonds between capping agents benefit the interaction potentials between the particles, these nanocones organized into ordered nanoparticles spontaneously via an oriented attachment (OA) mechanism.\textsuperscript{[44, 45]} In addition, the nonionic surfactant OP-10 we used here instead of PVP we frequently used before may also play a crucial role on the formation of final products due to its stabilizing behavior.\textsuperscript{[46]} In the presence of PVP, CeO\textsubscript{2} nanoparticles assembled by solid nanocones were obtained (ESI, Fig. S5b†). The products without adding of OP-10 were also tested by TEM (ESI, Fig. S5c†).

**Fig. 6** N\textsubscript{2} adsorption-desorption isotherms of the CeO\textsubscript{2} nanoparticles; inset is corresponding BJH pore size distribution curve.

**Fig. 7** The TEM images of the obtained Ce(HCOO)\textsubscript{3} precursors (a, b) and corresponding final products (c, d) when the dosage of the NH\textsubscript{3}H\textsubscript{2}O (10M) were 400 µL and 600 µL, respectively.
Fig. 8 XRD pattern of the products obtained after the addition ((a) ammonium solution, (b) H$_2$O$_2$) at room temperature and different solvothermal times illustrated as ((c) 20 min, (d) 40 min, (e) 1 h, (f) 2 h (g) 3 h).

Fig. 9 The TEM images of the products obtained at different solvothermal times illustrated as ((a) 20 min, (b) 40 min, (c) 60 min, (d) 120 min)

To get a better understanding of the phase transformation from Ce(HCOO)$_3$ to CeO$_2$ and the formation of the cone-like hollow structure, a series of time-dependent experiments were made. As shown in Fig. 8, the evolution process was examined by XRD. We obtained the TEM images of the products at different solvothermal times as shown in Fig. 9. At first, the XRD pattern (Fig. 8a) of white precipitation is well indexed to the characteristic peaks of Ce(HCOO)$_3$. The XRD pattern (Fig. 8b) of the brown precipitation after the addition of 100 µL H$_2$O$_2$ (30%) reveals that the samples were also pure phase Ce(HCOO)$_3$. After the following solvothermal treatment in the autoclave at 150 ºC for 20 min, the Ce(HCOO)$_3$ at the surface of these nanocones had been oxidized by H$_2$O$_2$ and dissolved, but CeO$_2$ nuclei can not be seen from Fig. 9a. So the peaks indexed to ceria can not be seen clearly from Fig. 8c due to the absence of CeO$_2$ precipitation. As shown in Fig. 9b, the formed CeO$_2$ nuclei aggregated randomly at the surface of these noncones, and the peaks indexed to the face-centered cubic phase of ceria, such as (111) and (220), appeared as shown in Fig. 8d. Fig. 9c indicates that after 60 min solvothermal treatment, the core-shell structure formed with the dissolution of the inner Ce(HCOO)$_3$. The XRD analyses (Fig. 8e) identified the typical mixed peaks of Ce(HCOO)$_3$ (marked with *) and CeO$_2$ due to the remained inner Ce(HCOO)$_3$ cores and the CeO$_2$ shell wall. When the reaction time was prolonged to 2 h, the peaks assigned to Ce(HCOO)$_3$ almost completely disappeared, which together with Fig. 8d indicates that the transformation of Ce(HCOO)$_3$ to CeO$_2$ took place at this time. At the same time, the ceria nanocones with extended cavities were obtained and the inner Ce(HCOO)$_3$ cores disappeared as shown in Fig. 9d. After 3 h, the sample with a better crystallization can be observed from the XRD pattern (Fig. 8g), but no peaks of Ce(HCOO)$_3$ can be seen any more, which suggest that the phase transformation have completed.
Based on the above XRD, TEM results and our previous work on the synthesis of flowerlike CeO$_2$ through an oxidation-coordination-assisted dissolution process, the phase transformation can be deduced as the following equations:

$$\text{Ce}^{3+} + 3\text{HCOOH} + 3\text{NH}_3\cdot\text{H}_2\text{O} \rightarrow \text{Ce(HCOO)}_3 + 3\text{NH}_4^+ + 3\text{H}_2\text{O} \quad (1)$$

$$\text{Ce}^{3+} + 3\text{HCOOH} \rightleftharpoons \text{Ce}^{4+} + 3\text{HCOO}^− \quad (2)$$

$$\text{NH}_3\cdot\text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^− \quad (3)$$

$$2\text{Ce}^{3+} + \text{H}_2\text{O} + 2\text{OH}^− \rightarrow 2\text{Ce(OH)}_2^{2+} \quad (4)$$

$$\text{Ce(OH)}_2^{2+} (aq) + 2\text{OH}^− \rightarrow \text{CeO}_2 (s) + 2\text{H}_2\text{O} \quad (5)$$

The formation mechanism could be illustrated in Fig. 10. At the early stage, Ce(HCOO)$_3$ crystal seeds were generated immediately when NH$_3$·H$_2$O was added to the solution following eqn (1). In a short time, nano-cone constructed Ce(HCOO)$_3$ nanoparticles were obtained due to the anisotropic crystal growth and oriented attachment of Ce(HCOO)$_3$ crystal seeds. Then a small amount of H$_2$O$_2$ was used as oxidant which broke the dissolution-recrystallization equilibrium of Ce(HCOO)$_3$ and promoted the conversion from Ce$^{3+}$ to Ce$^{4+}$ complex (Ce(OH)$_2^{2+}$)\textsuperscript{31, 39}. Due to an appropriate dielectric constant of ethanol, the reaction rate of eqn (4) could be slowed down.\textsuperscript{47} Under the alkaline environment CeO$_2$ was formed due to supersaturation of Ce(OH)$_2^{2+}$, thus Ce(HCOO)$_3$ was dissolved gradually with the continuous conversion of Ce(HCOO)$_3$(s) to Ce(OH)$_2^{2+}$(aq). Therefore, an oxidation-coordination-assisted dissolution was involved during the whole process. The formed CeO$_2$ nuclei would aggregate randomly at the surface of these nanocones to decrease the surface energy of the system. Meanwhile, the porous structure was formed at the outer layer of these nanocones. The porous structure at the outer layer would further provide the channels for the diffusion of the inner Ce$^{3+}$ cation and outer H$_2$O$_2$, which ensures the complete transformation of Ce(HCOO)$_3$ to CeO$_2$. In the case of the partially oxidized Ce(HCOO)$_3$, since most of the outer wall had been oxidized to CeO$_2$ nuclei, the oxidation-coordination-assisted dissolution process continued inside the nanocones; thus, the ceria nanocones with extended cavities formed finally.\textsuperscript{48} During this process, the amount of H$_2$O$_2$ should be controlled to avoid acceleration of the reaction (4), thus the dissolution-recrystallization process could occur slowly.

**H$_2$-TPR Reduction Behaviors**

![H$_2$-TPR profiles](image)

Fig. 11 H$_2$-TPR profiles of the as-obtained solvothermal CeO$_2$ nanoparticles (a), calcined spherical CeO$_2$ (b) and the commercial CeO$_2$ sample (c). H$_2$-TPR tests can reveal the property of oxygen vacancies for the CeO$_2$ which is an important factor to affect the catalytic activity.\textsuperscript{49} H$_2$-TPR measurements were performed on the as-formed hollow nano-cone constructed CeO$_2$ nanoparticles, the calcined CeO$_2$ and commercial CeO$_2$ samples to reveal their redox properties (Fig. 11). All samples show two major reduction peaks below 1000 °C, which are consistent with the TPR spectra...
of the pure CeO₂ samples. The first peak at the lower temperature (300-600 °C) is due to the reduction of the surface oxygen species or reduction of the ceria surface, while the reduction of bulk oxygen and the formation of Ce₂O₃ lead to the second peak at the higher temperature region (above 700 °C). Furthermore, there is a direct proportion relationship between the peak areas of the curves and the amount of H₂ consumption. The above three samples (a ~ c) based on the peak areas in TPR profiles are shown with a sequence a > b > c, which indicates the solvothermal CeO₂ sample has the best reduction behavior, followed by the calcined CeO₂ and the commercial CeO₂ sample. The more surface oxygen species due to the high surface area of the mesoporous CeO₂ nanoparticles led to the high peak area in low temperature zone which indicates the excellent catalytic property.

Catalytic properties

![Graph showing CO conversion vs. temperature for different methods: CeO₂ after solvothermal method, CeO₂ after calcination method, and commercial CeO₂.]

Fig. 12 Conversion of CO over (a) CeO₂ nanoparticles after solvothermal method, (b) ceria after calcination method and (c) commercial ceria

To evaluate the catalytic activity of our CeO₂ samples, the CO conversion reaction was selected as a model reaction. Fig. 12 shows the catalytic profiles of the as-obtained solvothermal CeO₂ sample along with that of the calcined CeO₂ sample and commercial CeO₂ powders for comparison. It can be seen clearly that the hollow nano-cone constructed CeO₂ sample displayed much higher catalytic activity followed by the calcined CeO₂ and then the commercial CeO₂ sample. The CO conversion of the CeO₂ nanoparticles increase rapidly with raised reaction temperature from 100 °C to 300 °C, but that of the calcined CeO₂ and commercial CeO₂ ascends slowly. For example, at 250 °C, the CO conversion is 95% for the CeO₂ sample after solvothermal method, and 71% for the calcined CeO₂ sample, while only 13% for commercial CeO₂ powders. When the CO conversion is 50%, the temperatures are about 200 °C and 245 °C for the CeO₂ sample after solvothermal and calcination method respectively.

Based on our speculation, the better catalytic activity of the CeO₂ nanoparticles is attributed to the small size of the nanocrystals and high specific surface area which give many catalytically active sites, as well as the porous structures favoured for molecule accessibility to the active surface of the nanocrystals and mass transport. Because the recycling performance of the catalyst is crucial to the practical applications, the catalytic tests are performed six cycles. The recycling catalytic profiles were represented and compared in Fig. S6. Obviously, the catalytic performance remains well and all the CO conversion temperature almost keep the same. The CeO₂ nanoparticles after the catalysis were collected and tested by TEM (ESI, Fig. S7†). The well retained original morphology also indicated its excellent recycling performance.

Conclusion

A one-step facile and mild solvothermal strategy was developed to synthesize hollow nano-cone constructed CeO₂ nanoparticles via a formate precursor. H₂O₂ was used as an oxidant to achieve the phase transformation from Ce(HCOO)₂ to CeO₂ in the solvothermal process instead of the calcination of cerium formate precursor. Oxidation-coordination-assisted dissolution-recrystallization process contributed to the formation of the hollow structure. The excellent catalytic property is attributed to the small size of the nanocrystals, high surface area and mesoporous structure of the CeO₂ nanoparticles. Because the high surface area and the porous structures, the CeO₂ nanoparticles sample can be used as not only an effective catalyst towards the conversion of CO₂ but also an ideal support material for noble metals load and the detailed studies are still under investigated. Besides, our strategy may be further extended to synthesize other metal oxides 3D hierarchical structures.

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Notes and references
