Layer-by-layer synthesis of hollow spherical CeO₂ templated by carbon spheres

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Abstract CeO₂ hollow spheres were successfully prepared via a layer-by-layer (LBL) method using carbon spheres as sacrificial template and hexamethylenetetramine as precipitating agent. Transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectrum (XPS) were used for their characterization. The obtained products exhibit hollow spherical structure with a diameter of ca. 250 nm as well as the thin shell about ca. 20 nm composed of various oriented polycrystals, and the Brunauer–Emmett–Teller (BET) surface area was measured to be 126 m² g⁻¹. Calcination temperature is found to be crucial to the integrity of the hollow spheres and has to be below 973 K to achieve well defined hollow spheres. CO conversion was used as a catalytic test reaction revealing that the activity of the hollow spherical products was substantially higher than that of the non-hollow counterpart.

Keywords CeO₂ · Hollow spheres · Layer-by-layer · Carbon spheres

1 Introduction

In recent years hollow spheres of metal oxide have attracted burgeoning interests because of their wide variety of potential applications, including photonic crystal, catalysis, drug delivery, chemical sensors, chromatography, and waste removal [1–4]. To date, there have been several efforts in the synthesis of hollow oxides utilizing Ostwald ripening [5–8] or Kirkendall effect [9–11]. However, both of the methods are time-consuming, and have repeatability as well as uniformity issues. Alternatively, template synthesis serves as a prevailing approach to prepare inorganic hollow spheres due to its advantages in controllable uniformity and easy accessibility. The templates can be of different types, including silica [12], emulsions [13], reverse micelles [14], biological gelatin [15], polystyrene [16], beeswax [17], and even gas bubbles [18]. Among them, an interesting sacrificial core is represented by monodisperse carbon spheres produced by a hydrothermal treatment of aqueous solution of glucose. As demonstrated in Li's group [19–21], those carbon spheres carried functionalized groups and micropores on the surface which facilitated the precipitation of metal precursors and thus resulted in the formation of hollow spheres after the removal of carbon. More simplified strategy has been proposed by Thomas and co-authors and the one-pot synthesis uses carbohydrate [22] instead of carbon spheres to in situ form template cooperating with metal salts. In parallel to the development of templating methods, layer-by-layer (LBL) technique originally used to produce coated particles or films has been extended to fabricate hollow materials on the basis of electrostatic attraction or hydro-bonding which was firstly reported by Caruso et al. [23]. A number of hollow-structure inorganic compounds have been successfully prepared by LBL [24, 25].

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CeO₂ has been widely used as an active component in three-way catalysts (TWC) and is a promising candidate for applications in solid oxide fuel cells (SOFC) due to the redox activity between Ce (III) and Ce(IV) [26]. To achieve better catalytic performances, considerable efforts have been made to prepare porous structures of CeO₂ [27–30]. However, reports about CeO₂ hollow spheres still remain scarce. Herein, we report for the first time the synthesis of hollow spherical CeO₂ templated by carbon spheres in combination with a LBL preparation strategy. Hexamethylenetetramine (HMT) was adopted to slowly yield OH[−] so as to obtain a homogenous CeO₂ coating surrounding the spherical carbon core subsequently removed by a calcinations process. CO oxidation test indicated an enhanced catalytic activity of the hollow structure compared to non-hollow counterpart.

2 Experimental

2.1 Synthesis of carbon spheres

In a typical procedure, 10 g glucose (AR grade, Sinopharm Chemical Reagent Co, Ltd) was dissolved in distilled water (30 mL). The solution was stirred by ultrasonic stirrer at room temperature until a clear solution formed, and then was sealed in a 50 mL Teflon-lined autoclave and maintained at 453 K for 4 h. The brown products were washed by an alcohol–water solution for five times, and then dried at 353 K for 5 h.

2.2 Synthesis of CeO₂ hollow spheres

0.1 g as-prepared carbon spheres were dispersed in alcohol, and sonicated for 30 min. The resulting suspension was mixed with 0.01 g/mL Ce(NO₃)₃ solution. After thorough stirring, 0.5 g HMT was added to the solution and then transferred to a water bath keeping at 348 K. After reaction for 2 h, a resulting black precipitate was filtered, and then washed with distilled water and alcohol respectively for twice in each. The composite was dried at 333 K for 8 h. Afterwards, the carbon template was removed in a furnace by slowly increasing temperature from room temperature to 723 K (2 K min^{−1} ramping rate) and then keeping at 723 K for 30 min.

2.3 Characterization

TEM characterization was performed using a JEM-2010F transmission electron microscope operating at an accelerating voltage of 200 kV. The powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/MAX-2500PC diffractometer with Cu target (40 kV, 40 mA) at

scanning rate 8 K min^{−1}. Thermogravimetry and differential thermal analysis (TG-DTA) of the samples was carried out on an SDT Q600 instrument at a heating rate of 10 K/min from room temperature to 1073 K. Surface composition was determined by X-ray photoelectron spectroscopy (XPS) in an ion-pumped chamber (evacuated to 1.3×10^{-8} Torr) of an Axis Ultra (UK) spectrometer equipped with a focused monochromatised X-ray source at 225 W. FTIR spectra were obtained on a Nicolet Protege 460 spectrometer at 0.4 cm^{−1} resolution with a Nic-plan IR microscope. The N₂ sorption measurement was performed using Micromeritics ASAP 2010 at 77 K, the specific surface area was calculated using Brunauer–Emmett–Teller (BET) method.

2.4 Catalytic test

The catalytic reactions were conducted in a temperature-programmed reaction system using a thermal conductivity detector (TCD) in gas chromatograph (GC 950 system). In a typical reaction, 150 mg powder was loaded in a stainless tube reactor, and the reactor was heated from room temperature to 800 K at a rate of 2 K min^{−1}. The total gas flow amounted to 40 mL min^{−1} and the inlet gas composition was 1% CO and 5% O₂ with N₂ as balance.

2.5 Results and discussion

A simplified reaction mechanism of the formation of carbon spheres involves dehydration of the carbohydrate in the first step and subsequent carbonization of the so-formed organic compounds in the second step leading to a hydrophilic surface grafted with functional groups [22]. Elemental analysis indicates that the sphere has a carbon content of around 90% and the remaining mass can be attributed to oxygen and hydrogen atoms in the hydrophilic shell. A typical SEM image of carbon spheres is shown in Fig. 1 and the diameter is measured to be around 300 nm. Zeta potential analysis indicates that the surface of carbon spheres is negatively charged in water (pH 7, $\zeta = -38$ eV). However, the value changes to -20 eV when the spheres are suspended in Ce(NO₃)₃ solution and aged for 2 h before analysis. This suggests that the negatively charged surface facilitates the adsorption of the Ce³⁺ ions into the layer of the carbon spheres.

We propose that a strategy to obtain hollow CeO₂ using carbon sphere template can be as illustrated in Fig. 2 and the scheme includes (1) partial adsorption of cerium ions onto the surface layer facilitated by the functional groups; (2) LBL alternating deposition of Ce³⁺ combined with OH[−] slowly hydrolyzed from HMT driven by electrostatic attraction [31]; and (3) calcination of the composite spheres in air to remove the carbon core.

Fig. 1 SEM image of carbon spheres template

Functional groups on the carbon spheres are identified with FT-IR (curve “a” in Fig. 3). The bands at 1740 and 1650 cm^{-1} are attributed to C=O and C=C vibrations, respectively. The bands in the range 1000–1500 cm^{-1} , which include the C–OH stretching and OH bending vibrations, are indicative of the existence of large amounts of residual hydroxyl groups as well as trace carboxyl groups. The surface coating reactions decreased the number of organic functional groups, as revealed by curve “b” in Fig. 3. The O–H stretching band centered at 3500 cm^{-1} was weakened as well, which was consistent with the schematic illustration in Fig. 2. Further calcination leads to the formation of pure hollow CeO_2 spheres with few organic groups as seen in Fig. 3 (curve “c”).

Figure 4 shows typical TEM images of CeO_2 -coated carbon micro-spheres. The Ce^{3+} ions appear to be adsorbed to precipitate in a surface layer of about 15 nm rather than grafted on the surface. Corresponding FFT of the HRTEM exhibits diffused rings, implying that the wall is composed of poly-crystalline grains with some amorphous components. It should be noted that during the assembly of nanoparticles onto the template surface, the amorphous components could serve as “glue” so as to interconnect the

grains densely [32]. Carbon spheres own polysaccharide-like surface that can chelate Ce^{3+} ions and at the same time effectively prevent them from heterogeneous coagulation [19, 20] during the adsorption of Ce^{3+} . Under slow hydrolyzing of HMT, the oppositely-charged OH^- is released in the solution which can be represented by the following equation:

Consequently, $\text{Ce}^{3+}/\text{OH}^-/\text{Ce}^{3+}/\text{OH}^- \dots$ deposit onto the carbon sphere following a LBL assembly, which is consistent with the illustration in Fig. 2. In the mean time, a spontaneous CeO_2 precipitation is believed to occur due to its intrinsic crystallization tendency. The resulting shell thus formed is a compact composite largely composed of uniform grains of CeO_2 , the Eq. 3 given below is believed to be responsible for this phenomenon.

Figure 5 shows a TG-DTA curve of the CeO_2 coated carbon spheres. Initially, a slow weight loss occurs below 523 K and it can be attributed to a process of further dehydration and densification of the composite spheres. Fast weight loss happens between 533 K and 693 K corresponding to a gradual decomposition of carbon sphere template. DTA peaks at 575 K indicating this removal process is endothermic. It is noticed that the endothermic peak for the CeO_2 coated carbon composite spheres is lower than the DTA peak 698 K for Ga_2O_3 coated carbon spheres in a previous report [19]. It is plausible that the intrinsic redox transition between Ce^{3+} and Ce^{4+} may accelerate the inner oxidation.

Figure 6a shows some typical CeO_2 hollow spheres after the removal of carbon templates by a calcination process. The hollow spheres have an average diameter of about 250 nm, roughly 50 nm smaller than the starting sphere. The amount of shrinkage is considerably larger in this method than in the cases when traditional sacrificial-core templates, such as silica, biological gelatin and beeswax,

Fig. 2 Schematic for the formation of CeO_2 hollow spheres using carbon spheres as template and LBL precipitation

Fig. 3 FTIR spectra of the samples: (a) carbon spheres, (b) CeO₂-coated carbon spheres and (c) CeO₂ hollow spheres

are used [12–17]. Nonetheless, the easy removability of carbon was beneficial for the formation of hollow spheres as compared to those templates. It is believed that the additional shrinkage is caused by a process of the dehydration of the more loosely cross-linked shell structure surrounding the carbon spheres. The thickness of the shell after carbon removal is about 20 nm, a little higher than the previous coating thickness corresponding to Fig. 4b, confirming the shrinkage phenomenon. BET measurement demonstrates that the hollow spheres possess specific surface area of 126 m² g⁻¹, which is much higher than that of the ordinary CeO₂ nanoparticles. HRTEM reveals that the wall of the hollow sphere consists of small nanocrystals of an average size of 5 nm, as shown in Fig. 6b with a nanocrystal highlighted and the {111} and {200} interplanar spacing indicated. A typical SAED pattern from the hollow sphere is shown in Fig. 6c and is indexable as from the face-centered fluorite CeO₂.

Further characterization by XPS is shown in Fig. 7 and it reveals that the hollow spheres contain mostly cerium and oxygen with some residual carbon probably from contamination. The fact that no other elements such as nitrogen are

Fig. 5 TG-DTA curves of the CeO₂-coated carbon sphere composite

detected suggests that the reactions involving the precursors are complete. The Ce 3d spectrum (Fig. 7, inset) confirms that the cerium mainly exists as the Ce(IV) oxidation state (881.85 eV) [33]. In addition, the O 1s peak centered at 529.1 eV corresponds to the lattice O²⁻ contribution associated with cerium rather than oxygen absorbent. The binding energies of Ce 3d and O 1s are in good agreement with those of the standard CeO₂.

Higher calcination treatment leads to the formation of discrete CeO₂ nanoparticles from the collapse of hollow structure apparently due to the growth of the nanoparticles (Fig. 8a). The enhanced exposure of lattice fringe as well as the brighter rings in Fig. 8b and c respectively provide the evidence of higher crystallinity compared to that in Fig. 6b and c. Specific surface area from BET measurement drops remarkably to 45 m² g⁻¹ primarily as a result of the disappearance of interior pores. Calcination temperature is found to be one of the key factors for the formation of CeO₂ hollow spheres. A systematic screening experiment suggests that a calcination temperature lower than 973 K is necessary to maintain the integrity of the hollow structure.

Fig. 4 **a** Typical TEM images of CeO₂-coated carbon spheres. **b** HRTEM image of the interface. **c** Corresponding FFT image

Fig. 6 **a** TEM image of CeO₂ hollow spheres. **b** HRTEM image showing the structure of the shell wall. **c** Corresponding SAED pattern

Fig. 7 XPS wide spectrum and Ce 3d spectrum (*inset*) of CeO₂ hollow spheres

Figure 9 shows the XRD patterns of the samples calcined at various temperatures, no obvious peaks can be found corresponding to carbon in the uncalcined composite (Fig. 9a), which is attributed to the amorphous structure of carbon spheres, however it could be confirmed that the carbon template were coated by CeO₂ semi-crystals combined with the result from FFT pattern in Fig. 4c, since all

of the reflection peaks could be indexed to the face-centered cubic structure according to JCPDS 34-0394. The narrower peaks imply the increasing of the crystal size as well as crystallinity which is consistent with the result from the SAED patterns.

Catalytic activity of the hollow sphere CeO₂ was evaluated by CO oxidation. Figure 10 shows the temperature dependence of the total conversion for both hollow and non-hollow CeO₂ samples (specific BET surface area: 12 m² g⁻¹, obtained directly from Ce(NO₃)₃ thermal decomposition), the CO conversion increased with increasing reaction temperature for both samples. The *T*₅₀ (temperature for 50% conversion) of the hollow sample is 543 K while it is 752 K for the non-hollow sample, suggesting a considerable enhancement in catalytic property by the hollow CeO₂ spheres. In addition to the increased specific surface area as confirmed by the N₂ sorption measurement with BET method, the hollow structure is also believed to provide substantial space for the adsorption and desorption of gas molecules. As for CO oxidation, CO reacts with the catalyst surface meanwhile forming an oxygen vacancy, which is then replenished by gas-phase oxygen thereby completing the cycle by the formation and desorption of CO₂. The interconnected hollow structure in our sample enables better contact with the gas molecule due to the existence of interior spaces and penetrable shell. Therefore, they reasonably exhibit better performance compared with the non-hollow counterparts.

Fig. 8 **a** Typical TEM image of a collapsed CeO₂ hollow sphere. **b** HRTEM image of the shell wall. **c** Corresponding SAED pattern

Fig. 9 XRD patterns of as-prepared sample (a) and samples calcined at 723 K (b) and 973 K (c)

Fig. 10 Plots of CO conversion of hollow CeO_2 spheres and non-hollow analogues

3 Conclusions

In conclusion, hollow CeO_2 spheres are successfully fabricated by LBL bonding and reactions of the precursors surrounding functionalized carbon sphere template and a following calcinations procedure. The hollow spheres have a diameter of about 250 nm with uniform shell thickness of about 20 nm. Calcination temperature is found to be critical to the integrity of the hollow spheres and has to be below 973 K to achieve well defined hollow spheres. Catalytic test shows that the hollow spherical CeO_2 has significantly increased catalytic activity for CO oxidation in comparison to the non-hollow analogues.

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