Preparation and Characterization of zirconia-core ceria -shell composites and its formation mechanism

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Abstract. In this work, a strategy was developed for the synthesis of nano-sized, zirconia-core ceria -shell composites directly via chemical precipitation method in mixed solvents. The as-synthesized ZrO₂@CeO₂ composites were characterized by X-ray diffraction (XRD), zeta potential analysis, field emission scanning electron microscope (FESEM), energy dispersive spectrum (EDS) and transmission electron microscopy (TEM). The results indicated that the fabricated ZrO₂@CeO₂ composites were irregular spheroids and were uniformly coated by cubic fluorite CeO₂ nanoparticles. Based on the effects of pH value on coating performances, a possible formation mechanism of zirconia-ceria composite was deduced and summarized.

1. Introduction

Over last few years, the study on fabricating nanocoating or core-shell structure particles had been promoted rapidly, principally due to such composite particles possessed special structure and morphology, which would exhibit novel performances that were substantially different from those of the cores, thus making them attractive from both scientific and technological viewpoints.[1-3] With the fabrication, the applications of nanocoating or core-shell structure materials therewith fill our daily life nearly in every aspect, ranging from LCD materials,[4] fuel cells[5] and other civilian areas to stealth materials[6] in military.

As a vital sort of rare earth resources, nanocrystalline ceria is a multifunctional material with a wide range of applications in exhaust treatment,[7] UV absorber[8] and surface lapping and polishing materials.[9] However, with the exploitation and export of rare earth being limited, the international price shows a drastic rising trend. So, on the premise of the properties of product being guaranteed, the interest is spurred to reduce the mixed rare earth cerium as much as possible in above-mentioned fields. In this context, as a practical approach for minimizing Ce loading on nanomaterials, manufacturing core-shell composites have prompted an unprecedented interest in related fields.

Currently, the preparation of core-shell materials are mainly based on two feasible means. One is to make the cores treated with coupling agents (e.g., silane-coupling agents) so as to form chemical bonds between core and shell particles. Another way is making an appropriate treatment to cores with either using surfactants or adjusting pH value to enhance or reverse surface charge to form strong electrostatic attractions between the cores and the shells. Armini et al.[10] prepared PMMA-core ceria-shell composites by adjusting pH value and investigated their CMP behavior for SiO₂ dielectric layers. Zheng et al.[11] fabricated Ag/C core-shell composite materials by chemical deposition, and the results indicated that the pH value and surfactants imposed significant influences on silver coating. In addition. All these experimental results indicated that core-shell composites resulted in reducing the coating-materials loading, but improving the functional performance in evidence.

In view of ceria and zirconia have a certain similarity in terms of physical, chemical and thermal stability[12], ZrO₂-CeO₂ nanocomposites can be used as a substitute in many ceria application fields. To the best of our knowledge, no report has been devoted to the preparation of zirconia-core ceria -shell composites by chemical precipitation method in situ. Hence, we attempt to produce inorganic CeO₂-coated ZrO₂ composites. In this work, our studies are aimed at preparing zirconia-core ceria...
-shell composite by chemical precipitation method in situ and summarizing its formation mechanism via turning the pH condition.

2. Experimental

2.1 Materials.

Zirconium dioxide was purchased from Aladdin Industrial Corporation (Shanghai, China). Hexamethylene tetramine (HMT) were obtained from Kelong Chemical Reagent Co. Ltd (Chengdu, China). Remaining chemical reagents, including cerium nitrate hexahydrate (Ce(NO$_3$)$_3$$\cdot$6H$_2$O), sodium hydroxide (NaOH) and absolute ethanol were of analytical grade and were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All reagents were used without any further purification. Deionized water was used throughout the experiment.

2.2 Synthesis of ZrO$_2$@CeO$_2$ composite particles.

Preparation of ZrO$_2$ suspensions—ZrO$_2$ powder was dispersed in absolute ethanol under magnetic stirring, and then added 2M NaOH aqueous solutions. To get homogeneous suspension, the resulting mixture was treated by ultrasonic for 1 h under room temperature, and then preserved for further use in experiments.

Preparation of ZrO$_2$@CeO$_2$ composites—in a typical process, a certain concentration of Ce(NO$_3$)$_3$$\cdot$6H$_2$O solutions were added slowly into well dispersive ZrO$_2$ suspension. By the mixture slowly heated to 75 ℃, excessive amounts of hexamethylenetetramine (HMT) as precipitant were added in drops into the mixture under continuously stirring. After the titration of HMT solutions, the mixture was deposited for 2 h under room temperature. Then the resulting precipitates were centrifuged and washed with deionized water and ethanol to remove any possible remnants. Final products were collected by drying overnight at 60 ℃ in air and calcination at 600 ℃ for 2 h.

2.3 Characterization.

The XRD measurements of synthesized products were attained by a DX-2700 X-ray diffractometer (Fangyuan Ltd, China) using Cu Kα radiation (λ= 0.154056 nm). Zeta potential versus pH curves of samples was determined by using a ZetaPALS instrument (BIC, USA). Scanning electron microscope (SEM) micrographs were attained by Ultra 55 (carl zeiss SMT Pte Ltd, Germany). The morphology of the products was examined by using a Transmitting Electron Microscope (Libra 200FE, carl zeiss SMT Pte Ltd, Germany) with an acceleration of 10 kV.

3. Results and discussion

3.1 The effect of pH value on coating performance.

Electrostatic attractive interaction was acknowledged as a prime mechanism for the formation of core-shell structure materials. The surface charge characteristic of cores would reflect the electrosorption rate or whether the electrostatic attractions will happen between cores and shell particles. Surface charge against ZrO$_2$ cores is shown in Fig. 1. The electrophoretic mobility measurements gave a zeta potential of 10mV at neutral pH. With pH value increasing, the potential of ZrO$_2$ shown a decreasing trend and reached isoelectric point (IEP) at the pH value of 7.9.

![Zeta potential of ZrO$_2$ as a function of the pH values.](image)
The pH value of the ZrO₂ suspensions was measured 6.5 and in this condition the ZrO₂ particle carried positive charge, as shown in Fig. 1, which conflicted with electrostatic attractions of ZrO₂(core) and Ce³⁺ cations(shell). To exert strong electrostatic attractive behavior between ZrO₂ cores and Ce³⁺ cations, it is feasible to change the surface charge of zirconia particles by adjusting pH value. The hydroxyl concentration of Ce(OH)₃ precipitation generating was calculated using Eq.(1). The conversion of hydroxyl concentration and pH value was measured using Eq.(2) and Eq.(3).

Ksp (Ce(OH)₃) = [Ce³⁺][OH⁻]³.                                                                                     (a)
POH = -log c(OH⁻).                                                                                                        (b)
POH + PH = 14.                                                                                                             (c)

Here, Ksp is a constant of 1.5×10⁻²⁰ at 25 °C.[13]

Therefore, we turned the pH value of ZrO₂ suspensions to 8.1 using 2M sodium hydroxide aqueous solution before the addition of HMT solution.

Fig. 2 shows the XRD patterns of ZrO₂@CeO₂ composites. Compared with original zirconia particles (Fig. 2a), the spectrum of Fig. 2b-c revealed well-developed reflection of cubic fluorite-type structure ceria (JCPDS 34-0394). Furthermore, the diffraction peak at around 28.2 had broaden distinctly and the main diffraction peaks of zirconia remained but obviously weakened, which might attribute to the coating of the CeO₂ particles around ZrO₂ cores partly.[14]

Fig. 3 displays the zeta potential of ZrO₂@CeO₂-NaOH composites. The IEP value of CeO₂ and ZrO₂ was around 6.8 and 7.9 respectively, while the IEP of ZrO₂@CeO₂-NaOH composites was 7.1, which shown a significant shift toward pure CeO₂. Herein, it suggested that the ceria-coated zirconia composite particles had been synthesized in some degree. As for the IEP of composites did not coincide with ceria absolutely, it might owe to the ceria shell was incomplete or the ZrO₂ core still exerted effects on the zeta potential of the CeO₂ particle comprising the shell.[15]
Fig. 4 shows the SEM and EDS results of ZrO$_2$@CeO$_2$-NaOH and ZrO$_2$@CeO$_2$ composites. Compared with ZrO$_2$ particles (Fig. 4a), the significant change was the composite particles presented rough surfaces and on closer examination the size of composites was really increased. Besides, the EDS results both confirmed that there was a significant amount of Ce and O on the surface of zirconia, which was in accordance with XRD and Zeta analysis results. The data in Table 1 revealed that the amount of Ce element on the surface of ZrO$_2$@CeO$_2$ composites was lower than that of ZrO$_2$@CeO$_2$-NaOH composites.

![Fig. 4 FESEM images (left) and EDS spectra (right) of composites. (a) ZrO$_2$, (b) ZrO$_2$@CeO$_2$-NaOH and (c) ZrO$_2$@CeO$_2$.](image)

| Elements | ZrO$_2$@CeO$_2$-NaOH composites (wt%) | ZrO$_2$@CeO$_2$ composites (wt%) |
|----------|--------------------------------------|----------------------------------|
| O        | 30.41                                | 35.06                            |
| Cu       | 2.01                                 | 1.69                             |
| Ce       | 23.71                                | 15.08                            |
| Zr       | 43.87                                | 48.17                            |

TEM provides an intuitively effective tool to observe the morphologies of products. Fig. 5 shows the TEM images of ZrO$_2$ and ZrO$_2$@CeO$_2$ composites. It was observed that the obtained composites were irregular spheroids. Compared with the original ZrO$_2$, the loaded ZrO$_2$ particles exhibited a rough appearance and the size of composite particles increased by about 5 nm, which finally confirmed that the CeO$_2$ shells were formed on the ZrO$_2$ surface. Based on the results of XRD, zeta potential, SEM and TEM analyses, the structure of the prepared composites could be deduced: the cubic fluorite CeO$_2$ shells with good crystal structure were formed on the surfaces of the ZrO$_2$ cores. Fig. 5c shows the TEM image of ZrO$_2$@CeO$_2$ composites. Compared with Fig. 5b, the results shown that CeO$_2$ particles did not coat ZrO$_2$ cores compactly after calcinations.
3.2 Formation mechanism.

Based on the typical theory of electrostatic attraction, we might describe the formation mechanism of zirconia-core ceria-shell composites as follows: the first step involved the preparation of negative-charged ZrO$_2$ particles. Secondly, with the addition of Ce(NO$_3$)$_3$ solution, Ce$^{3+}$ cations were absorbed on ZrO$_2$ particles driven by electrostatic attraction. With the OH$^-$ slowly released from the hydrolyzing of HMT, Ce$^{3+}$ cations combined with OH$^-$ into Ce(OH)$_3$ precipitate. Then, followed by dryness and calcination process, Ce$^{3+}$ was oxidized to Ce$^{4+}$ and the CeO$_2$ shell was formed. The synthesis procedure is illustrated in Scheme 1.

![Scheme 1 Electrostatic attraction for the synthesis of ZrO$_2$@CeO$_2$ composite particles.](image)

However, in the coating process, heterogeneous nucleation was inevitable in the presence of ZrO$_2$ particles. The heterogeneous nucleation surface coating process is a method based on the theory of LaMer crystallization, which takes advantage of the heterogeneous nucleation and growth of shell particles on substrate to form coating layer. As shown in Fig. 9, once the generated Ce(OH)$_3$ precipitate exceeded its rate of dissolution (i.e., $C > C1$), the existence of dispersed ZrO$_2$ particles would result in the heterogeneous nucleation of Ce(OH)$_3$. When the concentration of Ce(OH)$_3$ in solution reached $C2$, not only would the heterogeneous nucleation and growth of Ce(OH)$_3$ occur around ZrO$_2$ particles, but also the homogeneous nucleation and growth of Ce(OH)$_3$ would generate as the reaction progress. The results obtained from Fig. 2c, Fig. 4c and Fig. 5c confirmed that, in the coating process, the heterogeneous nucleation of Ce(OH)$_3$ exerted a crucial influence on coating performance in the absent of electrostatic attraction between shell particles and cores. Therefore, we could suggest that in the preparation of zirconia-core ceria-shell composites by chemical precipitation method, but the electrostatic attraction, heterogeneous nucleation might also play a vital role in a certain extent.
Fig. 6 The LaMer diagram of nucleation area. where $C_1$ and $C_2$ are the equilibrium concentration of solute with the bulk solid and the critical concentration as the minimum for nucleation, respectively.

4. Conclusions

A chemical precipitation method was firstly developed to coat tetragonal phase zirconia particles with shells of cubic fluorite phase ceria. XRD, zeta potential, SEM and TEM results confirmed that zirconia-core ceria-shell composites were successfully synthesized. Based on the experimental results, we concluded that it was an effective means to improve the coating performance by adjusting pH value. Moreover, we confirmed that, in the coating process, heterogeneous nucleation of precipitates played a vital role as well as the electrostatic attraction. Applications of these new materials will be published elsewhere.

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