

Ultrasonic-induced synthesis of high surface area colloids $\text{CeO}_2\text{--ZrO}_2$

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Abstract The nanostructures of high surface area ceria–zirconia colloids have been successfully synthesized via a sonochemical method in the presence of polyethylene glycol 600. Their structural characteristics have been investigated using powder XRD, FESEM, BET surface area, TG, and other techniques. The average size of $\text{CeO}_2\text{--ZrO}_2$ nanoparticles is estimated to be 3.7 nm using Debye–Scherrer’s equation. The BET analysis indicates that colloids $\text{CeO}_2\text{--ZrO}_2$ have a remarkably high surface area of $226 \text{ m}^2 \text{ g}^{-1}$.

Keywords Ceria–zirconia colloids · Ultrasonic synthesis · High surface area · Oxygen storage capacity · Nanoparticles

Introduction

Cerium–zirconium colloids have more advantages over simple cerium oxide, which lies in the presence of defects due to the insertion of the

smaller Zr^{4+} ion into the CeO_2 lattice (Mamontov et al. 2000; Sugiura 2003). Recently, $\text{CeO}_2\text{--ZrO}_2$ colloids are under focus because of their applications in the field of catalysis, particularly in the technology of the three-way catalysts (TWCs) used for eliminating toxic gases in automobile exhaust (Ozawa et al. 1993; Ranga Rao et al. 1994; Kaspar et al. 1999). These materials have also been used as solid-state conductors for their good ionic mobility (Kawamura et al. 2001; Izu et al. 2000). The remarkable properties of $\text{CeO}_2\text{--ZrO}_2$, such as catalysis, oxygen storage capacity (OSC), are directly related with its surface area. Higher surface area would offer more active sites for carrying out catalytic reactions. Various methods, such as hydrothermal synthesis (Cabanas et al. 2001), coprecipitation (Reddy et al. 2005), sol–gel (Rossignol et al. 1999), and gel-combustion (Lamas et al. 2003), have been employed to synthesize $\text{CeO}_2\text{--ZrO}_2$ with high surface area. In recent years, ultrasound irradiation has been extensively used for the preparation of novel materials with unusual properties. Ultrasound irradiation can induce the formation of particles with much smaller size and higher surface area than those produced with other methods. However, only a few studies on sonochemical synthesis of colloids $\text{CeO}_2\text{--ZrO}_2$ have been reported (Yu et al. 2003). In the present work, colloids $\text{CeO}_2\text{--ZrO}_2$ with ultrahigh surface area were prepared via ultrasound irradiation without thermal post-treatment.

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Experimental

All chemicals were of analytical grade and were used as purchased without further purification. $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (purity > 99.0%), $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (purity > 99.0%), $\text{NH}_3 \cdot \text{H}_2\text{O}$, and NaOH were all obtained from Shanghai Chemical Reagent Company. Deionized water was used throughout.

Soft chemical routes with ultrasound were employed to generate colloids $\text{CeO}_2\text{--ZrO}_2$. In a typical procedure, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ were dissolved separately in excess deionized water and mixed together in a molar ratio of 1:1. Then, polyethylene glycol (PEG) 600 was added to the solution until its content (w/w) was up to 2%. Dilute aqueous ammonia (2.6 mol/l) was added gradually dropwise to the aforementioned mixture solutions with vigorous stirring until precipitation was complete (pH = 9). After 5 ml NaOH solution (0.3 mol/l) was added as mineralization, the colloidal precipitates, which still exist in the solution, were exposed to high-intensity ultrasound irradiation under ambient air for 2 h with a pulse of 5 s on and 5 s off. Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (Xinzhi Co., China, JY92-2D, 0.6 cm diameter; Ti-horn, 20 kHz, 60 W cm^{-2}) immersed directly in the reaction solution. The temperature was kept under 323 K throughout the reaction by a cooling system. After cooling to room temperature, the precipitates were centrifuged and washed several times with deionized water and absolute ethanol in sequence to remove the surfactant. Then, after being dried in vacuum at room temperature, pale yellow powders were obtained. The obtained samples were characterized by X-ray Diffraction (XRD), Field Emission Scanning Electronic Microscope (FESEM), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS), BET surface area, and other techniques. A portion of the colloids $\text{CeO}_2\text{--ZrO}_2$ was calcined at 773 K for 2 h and was also characterized. The direct sonochemical method without surfactants and the hydrothermal method were employed to prepare nanoparticles for comparison (Cabanac et al. 2001).

Powder XRD measurements were performed on an X'Pert Pro Diffractometer (Cu $K\alpha$ radiation, $\lambda = 0.15418$ nm, from Philips company). The morphology of the $\text{CeO}_2\text{--ZrO}_2$ powders calcined was studied by FESEM (JEOL, JSM-6700F), with an EDS

probe for the analysis of the element. The TEM measurements were obtained with JEM-2010. The specific surface area of the powders was determined from N_2 adsorption isotherms in a Micromeritics 2100 automatic apparatus.

Results

The powder XRD patterns of colloids $\text{CeO}_2\text{--ZrO}_2$ generated via three methods are shown in Fig. 1. It is seen that all the three patterns are similar to each other. This indicates that the structures of the nanoparticles prepared by the three different methods are isomorphous. The diffraction peaks of (111) (200) (220) and (311) corresponding to the *Fm-3m* fluorite structure of $\text{CeO}_2\text{--ZrO}_2$ are identified in all the three patterns.

N_2 BET surface areas and particle size of different kinds of colloids $\text{CeO}_2\text{--ZrO}_2$ are presented in Table 1. The average size of the nanoparticles is estimated from the X-ray line widths of well-resolved and most intense (111) and (220) peaks using Debye–Scherrer's equation. The sizes of colloids $\text{CeO}_2\text{--ZrO}_2$ are 3.7, 4.2, and 13.5 nm via the different methods of PEG-assisted sonochemical, direct sonochemical, and hydrothermal, respectively. Colloids $\text{CeO}_2\text{--ZrO}_2$ prepared by the two kinds of sonochemical methods have smaller size than the hydrothermal samples. The

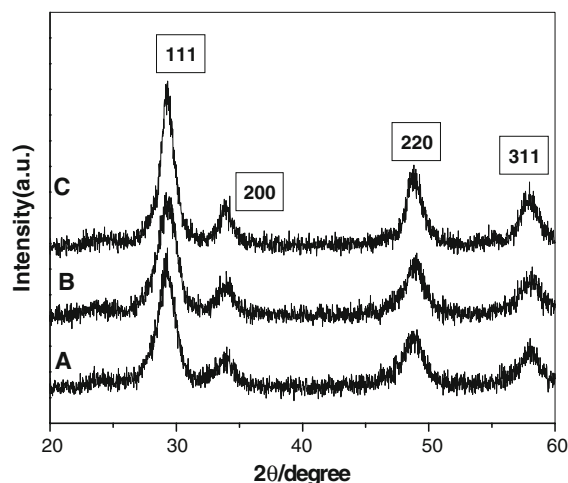


Fig. 1 Powder XRD patterns of colloids $\text{CeO}_2\text{--ZrO}_2$ generated via different methods. (A) PEG-assisted sonochemical method, (B) direct sonochemical method, and (C) hydrothermal method

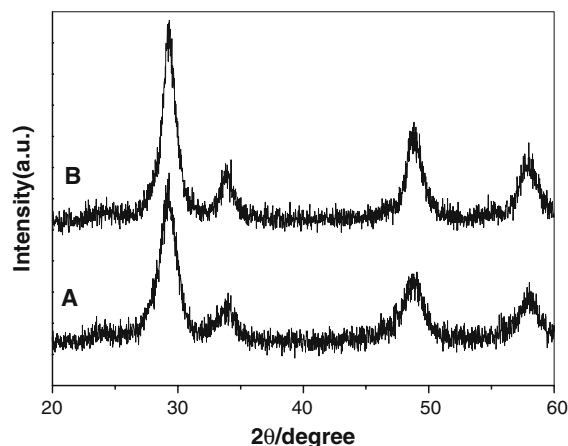
Table 1 BET surface area (S_{BET}), nanoparticles size (d), and OSC of different colloids $\text{CeO}_2\text{-ZrO}_2$

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	d (nm)	OSC (%)
PEG-assisted sonochemical	226	3.7	0.46
PEG-assisted sonochemical (calcined at 773 K)	190		
Sonochemical	161	4.5	0.45
Sonochemical (calcined at 773 K)	60		
Hydrothermal	63	13.5	0.37

surface area of hydrothermal samples is $63 \text{ m}^2 \text{g}^{-1}$. In contrast to this, the colloids $\text{CeO}_2\text{-ZrO}_2$ synthesized by the two kinds of sonochemical methods have higher surface area: Colloids $\text{CeO}_2\text{-ZrO}_2$ synthesized by direct sonochemical method show the surface area of $161 \text{ m}^2 \text{g}^{-1}$, which is very close to $168 \text{ m}^2 \text{g}^{-1}$ reported by Yu et al. (2003), and colloids $\text{CeO}_2\text{-ZrO}_2$ freshly prepared by PEG-assisted sonochemical method exhibit remarkably high surface area of $226 \text{ m}^2 \text{g}^{-1}$, which is higher than those ever reported for colloids $\text{CeO}_2\text{-ZrO}_2$. These results approve the advantage of ultrasound irradiation in the synthesis of nanoparticles. It can induce the formation of particles with much smaller size and higher surface area.

To evaluate the potential applications of $\text{CeO}_2\text{-ZrO}_2$ in TWCs, the thermal behavior of $\text{CeO}_2\text{-ZrO}_2$ freshly prepared by sonochemical method was investigated. The surface area of $\text{CeO}_2\text{-ZrO}_2$ calcined at 773 K was measured. As is shown in Table 1, the surface area of $\text{CeO}_2\text{-ZrO}_2$ prepared by PEG-assisted sonochemical method could be kept as high as $190 \text{ m}^2 \text{g}^{-1}$ even after being calcined at 773 K. But for the samples made by direct sonochemical method, the surface area is only $60 \text{ m}^2 \text{g}^{-1}$ after being calcined at 773 K. The decrease of its surface area is much higher than that of the samples generated via PEG-assisted sonochemical method. It is suggested that $\text{CeO}_2\text{-ZrO}_2$ prepared by PEG-assisted sonochemical method possesses better thermal stability than the direct sonochemical samples.

To investigate the lower surface area decrease of PEG-assisted sonochemical samples, the XRD pattern of PEG-assisted sonochemical $\text{CeO}_2\text{-ZrO}_2$ was measured after it was calcined at 773 K. As is shown in Fig. 2, the XRD patterns showed that the microstructures of colloids $\text{CeO}_2\text{-ZrO}_2$ generated by

**Fig. 2** Powder XRD patterns of colloids $\text{CeO}_2\text{-ZrO}_2$. (A) PEG-assisted sonochemical samples. (B) PEG-assisted sonochemical samples calcined at 773 K for 2 h

PEG-assisted sonochemical method do not undergo remarkable change after being calcined at significantly elevated temperatures of 773 K. This indicates that the primary colloids $\text{CeO}_2\text{-ZrO}_2$ keep their size and do not easily recrystalline. The colloids $\text{CeO}_2\text{-ZrO}_2$ could keep their surface area calcined even at high temperature due to their stable structures. Moreover, the significant difference between the surface area decrease of PEG-assisted sonochemical samples and direct sonochemical samples calcined at high temperature depicts that PEG-600 is the key factor in the crystallization period of $\text{CeO}_2\text{-ZrO}_2$. Also, the addition of PEG-600 in the sonochemical process can enhance the thermal resistance of colloids $\text{CeO}_2\text{-ZrO}_2$.

The potential oxygen storage capacity (OSC) was tested by oxygen release characteristics of the powders in the temperature range 293–773 K. The weight change of $\text{CeO}_2\text{-ZrO}_2$ was measured by thermogravimetry (TG) under cyclic heat treatments in flowing nitrogen or dry air. The heat cycle consisted of heating the samples to 773 K, cooling to 293 K, and again heating to 773 K. All heating and cooling rates were 10 K min^{-1} . The OSC was the weight loss of samples during the second heating cycle. As is shown in Table 1, the OSCs of colloids $\text{CeO}_2\text{-ZrO}_2$ are 0.46, 0.45, and 0.37% via the different methods of PEG-assisted sonochemical, direct sonochemical, and hydrothermal, respectively. It is depicted that $\text{CeO}_2\text{-ZrO}_2$ prepared by ultrasound has better OSC properties than hydrothermal samples.

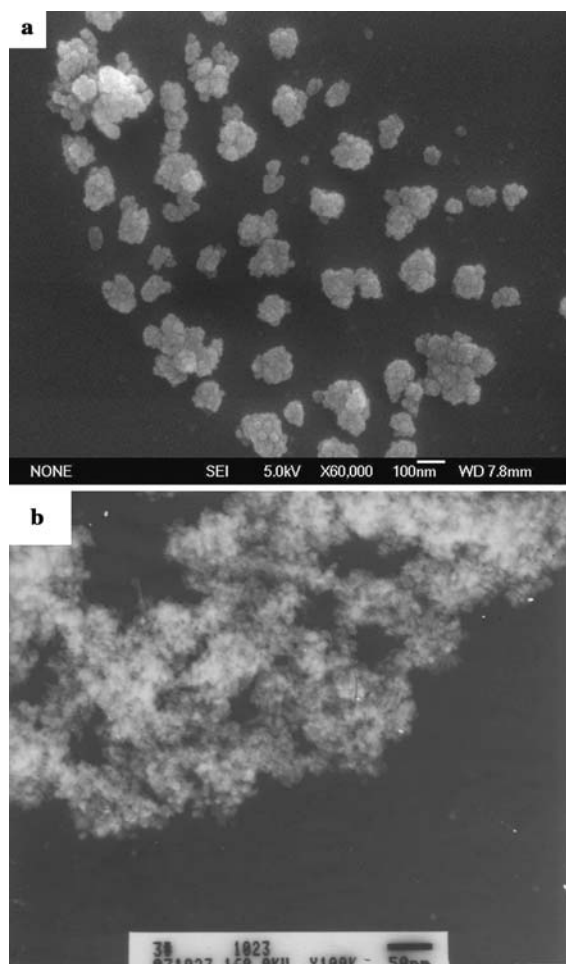


Fig. 3 SEM (a) and TEM (b) images of colloids $\text{CeO}_2\text{-ZrO}_2$. The magnification is 60 K (a) and 100 K (b), respectively

The microstructures of PEG-assisted sonochemical colloids $\text{CeO}_2\text{-ZrO}_2$ are studied by SEM (Fig. 3a, $\times 60$ K) and TEM (Fig. 3b, $\times 100$ K). The particle sizes estimated from TEM images are consistent with those calculated from the XRD patterns. It is shown in Fig. 1 that monodispersed colloids $\text{CeO}_2\text{-ZrO}_2$ are clustered in agglomerates with a narrow distribution of particle sizes, and the pore sizes of colloids $\text{CeO}_2\text{-ZrO}_2$ are in the microporous range. The EDS analysis of selective area confirms the 1:1 molar ratio of Ce/Zr.

In conclusion, a novel PEG-assisted sonochemical strategy for the fabrication of nanoporous colloids $\text{CeO}_2\text{-ZrO}_2$ has been established. It is a convenient, mild, efficient, and environmentally friendly method. With this method, homogeneous fluorite structure of crystalline $\text{CeO}_2\text{-ZrO}_2$ has been obtained. The

surface areas of fresh samples are significantly as high as $226 \text{ m}^2 \text{ g}^{-1}$, and the decrease of surface area is very small even after being calcined at 773 K. It is indicated that the microstructure of $\text{CeO}_2\text{-ZrO}_2$ nanoparticles generated by this method is stable, and they can keep their size and do not recrystalline after calcination. This character could make colloids $\text{CeO}_2\text{-ZrO}_2$ find their way in their practical applications, especially for use as catalysts in TWCs.

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