



Synthesis and characterization of stable and crystalline Ce_{0.6}Y_{0.4}O_{1.8} nanoparticle sol

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ABSTRACT

Ce_{0.6}Y_{0.4}O_{1.8} (40YCO) nanoparticle sol was synthesized via the hydrolysis of a Ce–Y–triethanolamine (TEA) complex derived from the reaction of hydrate cerium (III) nitrate (Ce(NO₃)₃·6H₂O), yttrium nitrate (Y(NO₃)₃·6H₂O) and TEA in alcohol solution at room temperature. The resultant sol possessed excellent UV shielding ability and high transparency in visible light region, and can be stable for one month. Transmission electron microscopy (TEM) showed a particle size distribution of 4.1 ± 0.7 nm for 40YCO. X-ray diffraction (XRD) as well as selected area electron diffraction (SAED) gave evidence that the as-synthesized nanoparticles were well crystalline. The formation of a solid solution was monitored by XRD and ICP-MS. Moreover, zeta potential measurement and infrared spectra were employed to study the YCO particles.

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1. Introduction

CeO₂-based material is of potential interest as an ultraviolet (UV) radiation blocking material and gain much attention because of their relatively lower catalytic activity for the oxidation of organic materials compared to pure CeO₂ [1–4]. It offers an attractive way for conventional applications such as coating, personal-care products, wood varnishes and finishing. In general, all of these applications demand nanoparticle certain features such as monodispersity, nonagglomeration and be as sol in a suitable solvent.

As yttrium oxide absorbs widely in the UV part of the spectrum, the Y/Ce substitution is expected to shift efficiently the absorption edge of CeO₂ towards shorter wavelengths, the latter usually being slightly located in the visible. Tessier et al. [5] investigated the UV absorption properties of a Ce_{0.7}Y_{0.3}O_{1.85} nanometric aqueous suspension which exhibits good stability and excellent UV absorption ability. They find doping the yttrium into CeO₂ does not cause a modification in the position of the absorption edge located around 390 nm, but leads to a steeper edge.

Various methods have reported the synthesis of Ce_{1-x}Y_xO_{2-x/2} (YCO) nanoparticles, including citrate and glycine methods [5], carbonate coprecipitation [6], thermal decomposition of trichloroacetates [7] and urea-based homogeneous precipitation [8]. Most of these methods involve extensive heat treatment. The

yttrium doped CeO₂ solid-solutions can also be synthesized by several other approaches such as hydrothermal method [9,10], microwave-induced combustion [11], coprecipitation technique [12] and azeotropic distillation process [13]. Among them, most focus on yielding powders rather than stable suspension or sol. For these methods, it is difficult to allow an efficient control of the granulometry and achieve monodispersed and stable sol in aqueous media. In the case of Tessier et al. [5], colloidal route is followed to prepare YCO nanometric suspension, nitric acid is used as peptizing agent, and the resultant suspension is at low pH value. However, in the extreme of pH value, other undesirable effects such as dissolution may occur, since partial dissolution of the yttria occurs mainly in the acid region, whereas no dissolution occurs under basic or neutral condition [14].

Triethanolamine (TEA) is a versatile polyfunctional ligand that may bond to many metal ions to form complex. It has been applied in the synthesis of nano-CeO₂ and binary or ternary systems such as ZrO₂–Y₂O₃, MgO–Al₂O₃, PbO–ZrO₂–TiO₂, Y₂O₃–Al₂O₃ and La₂O₃–CuO₂ [15–20]. Generally, TEA is used as a complexing agent, to keep the metal ions in homogeneous solution, which leaves sufficient flexibility for the system to exist homogeneously throughout the reaction without undergoing precipitation. Nevertheless, to our knowledge, the preparation of CeO₂–Y₂O₃ binary through using TEA as complexing agent is not reported.

We report here the synthesis and characterization of Ce_{0.6}Y_{0.4}O_{1.8} nanoparticle sol, we aim to prepare neutral YCO nanoparticle sol with excellent UV-shielding capacity and high dispersion stability. A homogeneous precipitation method by hydrolysis of a Ce–Y–TEA complex at low temperature was applied. This method does not involve extensive heat treatment

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and relatively high synthesis temperature. TEA was not only used as a complex agent, but also used as a precipitating agent, no peptizing agent and other surfactant were added. Furthermore, the present study is the first investigation for using a Ce–Y–TEA complex as precursor to synthesize YCO sol.

2. Experimental

2.1. Preparation procedures

$Ce_{1-x}Y_xO_{2-x/2}$ ($x=0.1, 0.2, 0.3, 0.4$) nanoparticles were all produced by the same method. They will later be referred to as 10–40YCO for convenience. All chemicals $Ce(NO_3)_3 \cdot 6H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, TEA and ethyl alcohol were reagent grade and used without further purification. Stoichiometric amounts of $Ce(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were firstly dissolved into ethyl alcohol to form a solution, where the total concentrations for metal ions were 1.0 mol L^{-1} . Then the requisite amount of TEA was added into the solution, where the TEA to metal ions mole ratio was maintained at 7:1. Under constant stirring at room temperature for some time, the solution turned muddy with a brown precipitate being yielded, and a slurry was formed when the reaction lasted for 1.0 h. Subsequently, given amounts of distilled water was added into the slurry under continuous stirring at 15°C and a feed aqueous solution for hydrolysis was achieved. Finally, the as-prepared feed aqueous solution was put into water bath at 30°C . After some time, a khaki yellow precipitate was generated. When the hydrolysis lasted 1.0 h, the obtained precipitate was separated by centrifugation and washed repeatedly with distilled water until the supernatant solution was tested neutral by litmus paper. The washed sample was then redispersed in distilled water to be aged at room temperature until it turned whitish yellow.

2.2. Characterization

A Tecnai G2 F30 S-Twin (Philips) microscope operated at 300 kV was used for TEM and SAED studies of the final product. The crystalline phase was determined by X-ray diffraction analysis (Bruker D8 FOCUS, 40 kV/40 mA). The UV-shielding properties of the particles were evaluated by measuring the suspensions with UV-vis spectrophotometer (Shimadzu UV-2500PC), where the oxide concentration was 1.0 g L^{-1} . Dispersion stability of the samples was investigated by the method of UV absorbance. Dynamic light scattering (DLS) was used to analyze the change in light intensity with time to study the stability of the samples in solution at shorter times. Scattering experiments were performed using a BI-200SM and BI-9000AT digital correlator (Brookhaven Instruments, USA). The light source was a 532 nm, 15 mW, semiconductor laser, The scattering angle was 90° and the temperature was $25 \pm 1^\circ\text{C}$. The FT-IR spectra were recorded with a FTIR Nicolet 5700 instrument. Zeta Potentiometric analyzer (PSA NANO2590) was applied to analyze the zeta potential of the particles on dilute suspensions containing 0.1 wt.% solid oxide, and the pH value was adjusted with a given concentration HCl and NaOH solution and measured by a fine pH measuring instrument (PHS-32, China). The inductively coupled plasma mass spectrometry (ICP-MS) was employed to determine the contents of Y and Ce elements in the samples.

3. Results and discussion

3.1. Preparation of the YCO sol

TEA is a weak base and would dissociate and release hydroxide ion in aqueous solution. When mixing Ce^{3+} and TEA aqueous solution, white $Ce(OH)_3$ precipitate was prone to be generated and

oxidised spontaneously to khaki yellow $Ce(OH)_4$ precipitate by oxygen. Besides, Ce^{4+} possesses high hydratability which is resulted from its high positive charge and strong Lewis acidity. Therefore, it is difficult to produce Ce–Y–TEA complex in aqueous solution. For this reason, we modified the preparation process of Ce–Y–TEA complex. This process was performed in alcohol solution.

The Ce–Y–TEA complex precursors were solid. They are insoluble in alcohol, but can be dissolved in given amount of water. Hydrolysis of the Ce–Y–TEA complex took place during isothermal holding of the complex aqueous solution and the rate was influenced by temperature. The hydrolysis was extremely slow and the solution had no obvious changes for over 48 h at a temperature lower than 15°C , and yet, when raising the temperature, the hydrolysis accelerated. The color of the fresh precipitate led to our suggestion that Ce^{3+} was oxidized to Ce^{4+} in the preparation process of the complex, because $Ce(OH)_4$ is khaki yellow, whereas $Ce(OH)_3$ is white. In our synthesis experiment, although gaseous Ce^{4+} existed in the hydrolysis solution, their existence form was water-soluble complex. The chelated complex has reduced the electrophilic character of Ce^{4+} , and the reduction lowered the hydrolysis and condensation rates, leaving sufficient flexibility for achieving CeO_2 – Y_2O_3 homogeneous coprecipitate. Furthermore, when the yttrium content increased, the hydrolysis and condensation rates slowed down, and when the yttrium content rose up to 30–40 mol%, loose gel rather than powder sediment was formed. In addition, raising the volume of water would also promote the hydrolysis. Therefore, to ensure appropriate hydrolysis rate and achieve desirable yttrium doped CeO_2 gel, the total concentrations for metal ions in aqueous solution for hydrolysis were maintained at 0.1 – 0.08 mol L^{-1} .

Since the hydrolysis of the Ce–TEA complex produced a hydrated CeO_2 , a deprotonation was necessary for the formation of CeO_2 crystallites, and generally, the deprotonation reaction was performed at high temperature. In the present study, in order to alleviate the agglomeration, the deprotonation was completed in aqueous media at room temperature although it would take about one and half a month for the 40YCO. More importantly, the dispersion stability of all samples was improved gradually in the deprotonation process, and for the 40YCO gel, the gel–sol transition took place simultaneously, namely the khaki yellow gel changed gradually to a whitish yellow sol.

The obtained sol was very stable, and only significantly little sedimentation occurred at the bottom of the container after holding the sol for one month. Its stability was confirmed by the UV absorbance (Fig. 1) and DLS measurement (Fig. 2) of the sol. It was also found that the yttrium content was relevant to the dispersion stability, i.e., decreasing the yttrium content would reduce the dispersion stability.

3.2. IR and zeta potential analysis

In order to ascertain the reason for the high dispersion stability of the 40YCO sol, we performed a FT-IR spectra and zeta potential analysis. The FT-IR spectra are shown in Fig. 3. Characteristic absorption bands at 1051, 1606, 2346, 3131, and 3441 cm^{-1} can be observed, respectively. A strong peak at 1400 cm^{-1} is attributed to stretching vibrations of Ce–O [21]. The strong and broad bands at 3130, 3446 and 1600 cm^{-1} are assigned to stretching vibrations of O–H and bending vibration of H–O–H (ν_{O-H} and δ_{H-O-H}). Moreover, the intensity of these absorption bands for YCO was stronger than that of undoped CeO_2 and increased with an increase in yttrium content. This result demonstrated a higher degree of surface hydration of YCO compared to undoped CeO_2 , and the higher dopant concentration, the higher degree of surface hydration.

As shown in Fig. 3, there is also an absorption band around 2346 cm^{-1} caused by CO_2 absorbed on CeO_2 . For higher yttrium

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