O U R N A L O F

Ceramic Processing Research

One-step synthesis of ceria (CeO₂) nano-spheres by a simple wet chemical method

Mahsa. Zarinkamar, Majid. Farahmandjou and Tahereh. Pormirjafari. Firoozabadi

Department of Physics, Varamin Pishva Branch, Islamis Azad University, Varamin, Iran

In this research a new synthesis of CeO_2 nanoparticles using cerium chloride as precursor have been investigated. Samples were obtained by wet chemical method and characterized by the Powder X-ray Diffraction (PXRD), Scanning Electron Microscopy (SEM), high resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectrophotometer. Particle size has been obtained as 50 nm for annealed nanoparticles increasing with the increase of the annealing temperature and they changed from sphere-like shaped to cubic-like shaped with increasing annealing temperature. Detailed measurements of XRD spectra exhibited cubic structure of nanocrystals. The surface morphological studies from SEM depicted a change in shape and crystality of particles with formation of clusters for calcined particles. The particle size of CeO₂ was around 50 nm as estimated by XRD technique and direct HRTEM observation. The sharp peaks in FTIR spectrum determined the purity of CeO₂ nanoparticles and absorbance peak of UV-Vis spectrum showed the small bandgap energy of 3.26 ev.

Key words: CeO₂ nanoparticles, Wet chemical, Synthesis, Crystalline particle.

Introduction

Cerium oxide (CeO₂) has been widely investigated because of its multiple applications such as in catalysis, as an electrolyte material for solid oxide fuel cells, as a material with high refractive index, and as an insulating layer on silicon substrates [1, 2]. Rare earth oxide nanoparticles have exceptional luminescence, magnetic and electronic properties due to their unfilled 4f electronic structure. As such, rare earth-based phosphors, magnetic materials, hydrogen storage material and high surface area support catalyst are being widely developed. Most of the applications require the use of nonagglomerated nanoparticles, as aggregated nano-particles lead to inhomogeneous mixing, poor sinter-ability and compromised quantum properties [3]. However, nanocrystallites with a primary particle size < 5 nm have a stronger tendency to agglomerate, making processing very difficult. As such, the benefits expected from highly crystalline nano-particles are easily lost during the manufacture of components unless weakly agglomerated nano-particles can be produced [4]. Ceria (CeO₂) is widely used as an oxygen ion conductor in solid oxide fuel cells, oxygen pumps and ampere-metric oxygen monitors because of its high oxygen ion conductivity [5-10]. Ceria has also received much success in redox and combustion catalysts due to its ability to shift between reduced and oxidized state as a result of change in gas phase oxygen concentration [11]. As an oxygen storage

Fax: +982122482091

component, ceria act as an oxygen buffer providing oxygen under lean conditions and removing it under rich conditions for optimal conversion in three-way catalyst system [6, 7]. Under working conditions, the catalysts are exposed to alternating O2 deficient to excess O₂ environment. Ceria, in this situation, has the ability to donate its oxygen for the removal of CO and hydrocarbons during the O₂ deficient part of the cycle while absorbing and storing oxygen from O2, NO and water during the excess O₂ environment [8]. This unique feature of ceria is thus termed as oxygen storage capacity (OSC). Crystalline ceria nanoparticles have previously been synthesized using a variety of methods including room temperature solution precipitation, sonochemical synthesis, hydrothermal crystallization, microemulsion, mechanochemical processing, thermal decomposition, spray pyrolysis, sol-gel method, thermal hydrolysis, and solvothermal synthesis [12, 13]. These techniques mainly require high pressure, salt-solvent mediated high temperature conditions or surface capping agents and the ceria particles generated are relatively large. Therefore, a simple approach for a low-cost, lower-temperature, large-scale, and controlled growth process to produce ceria nanostructures at atmospheric pressure is essential [14, 15]. CeO₂ was chosen because it has interesting economic and physicochemical properties compared to other metal oxides. Cerium dioxide is abundant, nontoxic, and inexpensive. Furthermore, CeO₂ is a semiconducting material that absorbs light in the near UV and also slightly in the visible region. Cerium dioxide is, therefore, a promising material that can be used in heterogeneous photocatalytic reactions [16-21]. The aim of this work is to prepare CeO₂ nanoparticles by

^{*}Corresponding author:

Tel:+989122976922

E-mail: farahmandjou@iauvaramin.ac.ir

new wet chemical synthesis in the absence of a capping agent. The prepared nanoparticles were characterized and their crystal structure and surface morphology was studied by XRD, HRTEM, SEM, FTIR and UV-vis spectroscopy analyses.

Experimental Detail

Wet chemical synthesis was employed to synthesize cerium oxide nanoparticles from of precursors (cerium choloride). Materials used were cerium coloride (CeCl₂ \cdot 5H₂O), hydrocholeric acid (95% HCl) and ethanol (100% C₂H₅OH) all of which were from Merck.

In separate burettes, Cerium choloride solution was prepared by dissolving 30 g, CeCl₂ · 5H₂O in 100 mL HCl solution. Similarly, 100 mL of ethanol and 100 mL disstiled water were mixed. The solution of cerium chloride was added drop by drop to the solution of ethanol and water with stirring. The constant Ph = 2was maintained during the synthesis. Resulting CeO₂ were dried at 70 °C for 4 hours, cooled to room temperature Then, the product was calcined at different temperatures 500 °C and 1000 °C for 4 hours without any washing and purification. The specification of the size, structure and morphological properties of assynthesis and annealed CeO2 nanoparticles were carried out. X-ray diffractometer (XRD) was used to identify the crystalline phase and to estimate the crystalline size. The XRD pattern were recorded with 2è in the range of 4-85° with type X-Pert Pro MPD, Cu-K_{α}: $\lambda = 1.54$ Å. The morphology was characterized by field emission scanning electron microscopy (SEM) with type KYKY-EM3200, 25 kV and high resolution transmission electron microscopy (HRTEM) with type Zeiss EM-900, 80 kV. All measurements were carried out at room temperature.

Result and Discussion

X-rar diffraction (XRD) at 40 Kv was used to identify crystalline phases and to estimate the crystalline sizes. Figure 1 shows the XRD morphology of CeO₂ nanoparticles annealed at 1000 $^{\circ}$ C for 4 hours.

The exhibited picks correspond to the (111), (200), (220), (311), (222), (400), (331) and (420) of a cubic fluorite structure of CeO_2 is identified using the standard data [22, 23]. The mean size of the ordered CeO_2 nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula according to equation the following:

$$D = \frac{0.89\lambda}{B\cos\theta} \tag{1}$$

where, 0.89 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The mean size of as- maximum intensity (FWHM) in radians, and θ is the Bragg angle. The mean size of as-prepared CeO₂ nanoparticles was 50 nm from this Debye-Sherrer equation.

Figure 2 show the SEM images of the as-prepared and annealed CeO₂ nanoparticles prepared by wet chemical method. Figure 2(a) shows the as-synthesis CeO₂ with particle size ranges from 30-80 nm in diameter. Figure 2(b) shows the particles annealed at 500 °C for 4 hours and figure 2(c) shows the particles annealed at 1000 °C for 4 hours. It can be seen that with increasing temperature the morphology of the particles changes from sphere-like shape to cube-like shape with less agglomerate.

The transmission electron microscopic (TEM) analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of the crystallites. Figure 3 shows the as-synthesized TEM image of spherical CeO_2 nanoparticles prepared wet chemical route with a diameter in the range of 20-100 nm.

According to figure 4, the infrared spectrum (FTIR) of the synthesized CeO_2 nanoparticles was in the range of 400-4000 cm⁻¹ wavenumber which identify the chemical bonds as well as functional groups in the compound. The large broad band at 3415 cm⁻¹ is ascribed to the O-H stretching vibration in OH groups. The absorption picks around 1464 cm⁻¹ is assigned to the bending vibration of C-H stretching. The strong band below 700 cm⁻¹ is assigned ti the Ce-O stretching mode [24]. The broad band, corresponding to Ce-O





Fig. 2. SEM images of the CeO₂ nanoparticles.



Fig. 3. TEM image of the CeO₂ nanoparticles.



Fig. 4. FTIR spectrum of CeO₂ sample.



Fig. 5. UV-Vis absorption spectra of CeO_2 nanoparticles.

stretching mode of CeO_2 is seen at 500 cm⁻¹.

UV-visible absorption spectral study may be assisted in understanding electronic structure of the optical band gap of the material. Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. UV-Vis absorption spectra of asprepared and annealed CeO₂ nanoparticles are shown in Figure. 5. For as-synthesized CeO₂ nanoparticles, the strong absorption band at low wavelength near 380 nm correspond to bandgap energy of 3.26 ev (figure 5a) and for annealed CeO₂ nanoparticles the strong absorption band at low wavelength near 385 nm correspond to 3.22 ev (figure 5b). In comparison with UV-visible absorption spectrum of CeO2 nanoparticles, band/peak in the spectrum located at around 400-700 nm are observed to be shifted towards lower wavelength side, which clearly shows the blue shift. It indicates the absorption positions depend on the morphologies and sizes of CeO₂. The UV absorption ability of CeO₂ is related with band gap energy. The UV-absorption edge provides a reliable estimate of the band gap of any system.

Conclusions

CeO₂ nanoparticles were obtained using CeCl₂.5H₂O and HCl solution in the absence of any capping agent by wet chemical synthesis. XRD spectra showed cubic fluorite structure of CeO₂ was identified using the standard data. SEM images showed that with increasing temperature the morphology of the particles changed from sphere-like shaped to cube-like shaped with less agglomeration. HRTEM image exhibited the spherical CeO₂ nanoparticles prepared with smallest particle about 20 nm in diameter. FTIR data confirmed the presence of Ce-O stretching mode of CeO₂. The Ceria nanoparticles revealed a strong UV-vis absorption below 400 nm with a well-defined absorption peak at 380 nm and the direct band gap was found to be 3.26 eV.

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