Research Paper Nanotechnology

Synthesis and Characterization of Cerium Oxide Nanoparticles by Using Rapid Precipitation Method

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ABSTRACT

In the present study, nano-sized ceria (CeO2) powders were prepared using rapid precipitation method, without any stabilizers, using cerium chloride as a starting material and sodium hydroxide as a precipitating agent. The synthesized ceria powders were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) to determine crystallite size, crystallinity and shape respectively. It was found that the crystallite size obtained in the synthesis methods were below 30 nm. The particle size, morphology, shape and crystalline structure of resulting particles were also discussed.

KEYWORDS Cerium Oxide nanoparticles (CeO2), Precipitation method, XRD, FTIR, SEM

INTRODUCTION

Nanotechnology is one of the fastest-growing fields today, and it represents a projected 20–30 billion dollar market value by 2015 (McWilliams 2010). Nanotechnology is the study of manipulating material at molecular scale to develop novel engineering products with enhanced physical and chemical properties. Nanoparticles can be defined as ultrafine particles ranging in between 1 - 100 nm in size with varying physical and chemical properties (Moore, 2006 and Nel *et al.,* 2006).

Most recently, cerium oxide (CeO_2) nanoparticles have been tested for their ability to serve as free radical scavengers to provide protection against chemical, biological, and radiological insults that promote the production of free radicals. Cerium oxide nanoparticles (CeO_2 NPs), also known as nanoceria, are one of the most economically valuable manufactured nanoparticles currently in production (Wang et al. 2008). They are used in catalysts (Zheng et al. 2005), solar panels, fuel cells (Murray et al. 1999; Corma et al. 2004), as diesel fuel additive (Park et al. 2008a,b), and for glass and ceramic applications (Eom and Choi 2009). Cerium is a lanthanide series rare earth element that can either exist as a free metal or cycle between the cerium (III) and cerium (IV) oxidation states (Heckert et al. 2008). Nanoceria also cycle between the Ce (III) and Ce (IV) valence states, and they contain oxygen vacancies that allow the nanoparticles to act as an regenerative catalyst (Heckert et al. 2008).

Numerous Methods have been proposed to synthesize nano-sized CeO_2 particles with promising control of properties, such as hydrothermal, reverse micelles, sonochemical, pyrolysis and rapid precipitation. Among them, owing to the advantages of simple process, easy scale-up, low cost, cheap salt precursors and low-temperature operation, the rapid precipitation method has attracted the most extensive attentions. An attempt has been made to synthesize cerium oxide nanoparticles via rapid precipitation method. Therefore, the present work, was attempted to study the yielding of hydroxide precipitates on the formation of CeO_2 particles. The synthesized cerium oxide nanoparticles was characterized using various techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM).

MATERIALS AND METHODS

Cerium chloride ($CeCl_3$), Sodium hydroxide (NaOH), Ethanol (100%) and Double distilled water were used for the synthesis of iron oxide nanoparticles. All chemicals were of reagent grade and used without further purification. Precipitation method was used to synthesis CeO_2 nanoparicles. The synthesized nanoparticles were characterized by various physical techniques such as X-ray diffraction (Seifert), Fourier transform infrared spectroscopy (Bruker, Vortex-70) and morphology by scanning electron microscope (SEM, FEI Quanta 200). XRD patterns were obtained using Cu-Kα radiation (λ = 1.54056 Å) between 20◦ and 80◦. FT-IR spectrum was recorded at 400–1400 cm–1 wavelengths using KBr pellets. The morphology of the synthesized nanoparticles were obtained by scanning electron microscope.

Synthesis of CeO_2 by rapid precipitation method

Cerium chloride, (0.1M) solutions was prepared and (0.3M) sodium hydroxide was dissolved in distilled water separately and was kept ready. The sodium hydroxide solution was then added drop wise to the cerium chloride solution under constant stirring using a magnetic stirrer (Remi Model).The aqueous clear solutions turned yellowish white initially but as the reaction proceeds, it converts into light yellow colloidal suspension. The reaction was allowed to proceed for 4 h after the complete addition of sodium hydroxide solution under stirring at room temperature (35 ± 2°C).After the reaction, the precipitate was washed three times with distilled water and ethanol. After complete washing, the product was dried at 100 °C for 3 h to complete the conversion of Ce(OH)3 to CeO_2. After complete conversion, to obtain CeO_2 powder. This powder is then heated in the muffle furnace at 500 °C for 3 h, yellowish white powder is obtained (light yellowish in na-

ture) cooled, ground by mortar, and checked for yield.

RESULTS AND DISCUSSION

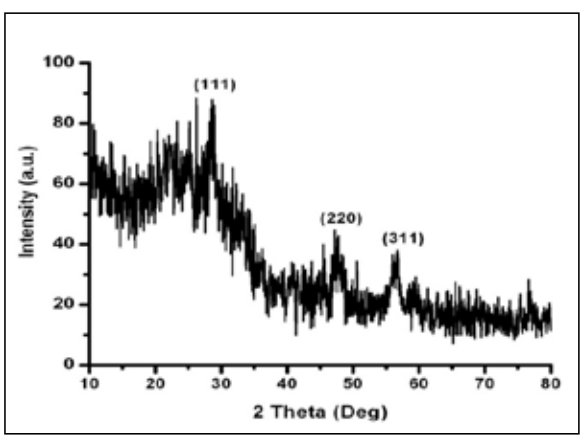
X-Ray Diffraction (XRD)

The X-ray diffraction pattern of developed differently shaped cerium oxide (CeO_2) nanoparticle prepared at calcinations 500°C temperature using Cerium chloride and water as a solvent. The 2θ values observed and correspond to diffraction planes of cerium form of CeO_2. The Sharp and intense diffraction peaks in the pattern match well with cerium oxide nanoparticles having lattice constants of c = 3.92717 Å. The data was well agreed with the standard data of Joint Committee on Powder Diffraction Standards.

For the synthesized CeO_2 samples, the XRD pattern (Fig.1) shows four main reflections (111), (220), and (311) characteristic of CeO_2 cubic phase structure (Ref.JCPDS card 34-394). The intense peaks suggested the good crystallinity of cerium oxide. The crystallite particle sizes were determined using debye- scherrer formula. The Debye–Scherrer equation is used frequently in X-ray analysis of materials, particularly powder diffraction of metal oxides. It relates the peak breadth of a specific phase of a material to the mean crystallite size of that material. It is quantitative equivalent of saying that the larger the material's crystallites are, sharper are the XRD peaks. According to the full width at half-maximum (FWHM) of the diffraction peaks, the average size of the particles (crystallite) are estimated from the Scherrer equation.

The element particle and its size can be calculated from the XRD spectrum employing the above equation and affirms it is cerium oxide and its particle size ranges from 18-27 nm.

Fig.1. XRD pattern of synthesized CeO_2nanoparticles



Fourier transform infrared spectroscopy Study

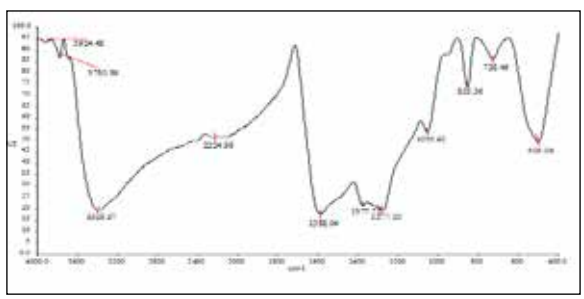
Fourier transform infrared spectroscopy measurements were performed to identify any functional groups adsorbing species onto the surface of the as-prepared cerium oxide nanoparticles and to detect molecular structure. Fourier transform infrared (FTIR) absorption spectra were measured at room temperature using a Perkin–Elmer FTIR spectrometer (GX model), in the wave number range of 4000–400 cm–1) using potassium bromide (KBr) pellet technique.

The formation of cerium oxide (CeO_2) nanoparticles and the presence of different chemical functional groups were evaluated by the Fourier Transform Infra Red Spectroscopy (FT-IR) spectra (Fig.2) respectively. The diagrammatic representation has revealed that the peak values for the different functional group (Table 1). FT-IR spectra of cerium oxide (CeO_2) synthesised nanoparticles depict in (Fig.2). The relative intensities and tentative assignments of fundamental Infrared absorption frequencies are shown in table (1).

Table 1; FTIR functional groups representation of CeO_2 nanoparticles

Sl. No.	CeO_2 Nps (Transmittance cm-1)	Definition of the spectral assignment
1	3393.97	Hydroxy group. H-bonded OH stretch
2	2224.99	Thiocyanate (-SCN)
3	1588.04	Open – chain imino (-C=N-)
4	1377.71	Organic sulfates
5	1277.10	Dialkyl group
6	1055.92	PO_2 – symmetric stretching: nucleic acids and phospholipids C-O stretch: glycogen
7	728.46	Aliphatic bromo compounds, C-Br stretch
8	855.36	C N+ C stretch: nucleic acids
9	503.08	Aliphatic iodo compounds, C-I stretch

Fig.2. FTIR Spectrum of CeO_2 nanoparticles

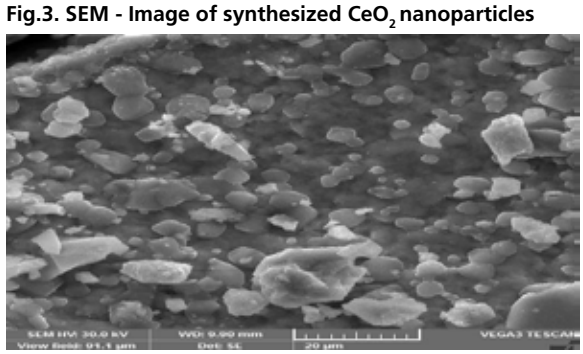


Scanning Electron Microscopy (SEM)

SEM images show agglomeration of primary nanoparticles into the secondary microparticles, a general phenomenon observed in CeO_2 nanoparticles synthesis. The morphology of the resulting cerium oxide nanopowder was examined using scanning electron microscopy.

The SEM micrographs of the CeO_2 calcined at different calcination temperature in (Fig. 3) show that the material is formed in single phase and spherical in nature. Depending on precursor concentration, temperature and many other factors the morphology of the nanoparticles were reported to vary. It is also clear from the SEM image of synthesized CeO_2 sample was porous in nature.

Fig.3. SEM - Image of synthesized CeO_2 nanoparticles



To understand the crystalline nature and purity of the Cerium oxide nanoparticles XRD was performed. Rapid Precipitation method CeO_2 nanoparticles XRD patterns were compared with reference JCPDS file 01-075-0390 according to that cubic CeO_2 showed the similar peaks and planes matching with the reference file (Fig.1).

Figure 2 shows the FTIR spectra of CeO_2 nanoparticles. The Rapid precipitation method CeO_2 nanoparticles showed strong peak at 3393 cm^{-1} corresponds to the (O–H) mode of (H-bonded) water molecules (Zhang et al., 2001). The peaks in the regions of 2900–2800 cm^{-1} and 1562–1543 cm^{-1} correspond to the stretching and bending modes of the hydrocarbon chain. The peak observed at 503,728 and 855 cm^{-1} corresponds to the (Ce–O–O) stretching mode of vibration (Finocchio et al., 1999). The sizes of the individual particles are marked in the SEM images (Figure 3). Depending on precursor concentration, temperature and many other factors the morphology of the nanoparticles were reported to vary (Palard et al., 2010).

Cerium oxide nanoparticles produced by precipitation method showed a flaky morphology and by optimization the individual particles were obtained. The choice of precursors for Cerium oxide nanoparticles yielded relatively different results in terms of crystalline nature, crystallite size and specific surface area. Cerium oxide nanoparticles can be used in various applications.

ACKNOWLEDGMENT

The authors are thankful to the UGC-Dr. D.S. Kothari Post Doctoral Fellowship, New Delhi for providing financial support (Ref No: F.4-2/2006(BSR)/13-911/2013). They are also grateful to the authorities of Alagappa university for the Instrumentation facilities in the Department of Oceanography & CAS, Alagappa University, Thondi campus.

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