



Nanoscale surface designing of Cerium oxide nanoparticles for controlling growth, stability, optical and thermal properties

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Abstract

The current work emphasises on the nanoscale surface designing of Cerium oxide (CeO₂) nanoparticles in surfactant media. The structural properties of surfactant functionalized nanoparticles were characterized by using UV–vis, PL, FTIR, XRD, TEM, DLS and DSC. The comparative effect of surfactants in relation with head groups and counterions over the modification of CeO₂ nanoparticles were also been assessed via analysing their thermal degradation mechanism and activation energy by TGA analysis. The comprehensive FTIR and TGA analysis were further been examined to investigate the stabilization mechanism of surfactants over CeO₂ nanoparticles. The kinetics of thermal decomposition for every surfactant has also been analyzed by employing different models. The synthetic approach developed in this work will have the potential to modify the band gap of CeO₂ nanoparticles which allow one to design new material with enhanced absorption activity, better control over growth, stability of nanoparticles which find potential impact in the development of solar cells.

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1. Introduction

The designing and synthesis of optical nano-colloids have been intensively practised in the past decade [1,2]. As a unique kind of these materials, rare earth oxides, especially Cerium oxide (CeO₂ with band gap ~3.1 eV) nanoparticles have engrossed special consideration as catalytic antioxidants in genetic systems [3,4]. CeO₂ nanoparticles have potential ability to scavenge free radicals in cell culture media [5–7]. CeO₂ nanoparticles also represent significant therapeutic agents for curing oxidative stress related disorders [8,9]. Besides several promising remedial roles, CeO₂ nanoparticles have also been used as fuel additive to reduce the quantity of particulate materials from diesel engines in the atmosphere [10,11]. CeO₂ nanoparticles have also shown several other technologically important applications including fuel cells, oxygen sensor, polishing material and UV blockers [12–15]. It has also been

claimed that the dispersion of acrylic-polyurethane with CeO₂ nanoparticles has provided better surface coating of wood [16].

From the technical and commercial outlooks, it is essential to scrutinize the preparation conditions of CeO₂ nanoparticles. The earlier synthetic strategies involve the use of high temperature and pressure conditions for the preparation of CeO₂ nanoparticles. For instance, ultrafine CeO₂ nanopowder has been synthesized via thermal decomposition at high temperature of around 1500 °C [17]. Zhang et al. [18] used the mixing room temperature conditions for synthesizing CeO₂ nanoparticles via directly mixing of cerium salts with hexamethylenetetramine. Masui et al. [19] have employed the hydrothermal process to produce CeO₂ nanoparticles. Yin et al. [20] presented the sonochemical method for preparing CeO₂ nanoparticles by employing cerium nitrate and azodicarbonamide as reactant materials with ethylenediamine or tetraalkylammonium hydroxide as additives. Besides, the conventional synthetic methods, colloidal methods via using soft templates of surfactants have also been employed for the synthesis of CeO₂ nanoparticles. The controlled growth of

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nanoparticles via surfactant-assisted pathways has been developed as easy and valuable in the view of environmental issues. Furthermore, the surface passivation with surfactants can provide extra stability and functionality to the NPs [21,22]. Moreover, by providing appropriate protective coatings of surfactants during nanoparticle synthesis can present two fold motives i.e. modification of optoelectronic properties and providing better stabilization against particle agglomeration [23,24]. Till date, various types of surfactants with different hydrophobic and hydrophilic portions have been employed for preparing CeO₂ nanoparticles [25,26].

Though, the evaluation of structural role of surfactants as stabilizers towards optical and photoluminescence properties during growth and ripening of CeO₂ nanoparticles has not been reported.

In this present paper, we have shown the simple optical spectroscopic based methods to explore the CeO₂-surfactant interfaces by illustrating the adsorption and photoluminescence behaviour of a series of surfactants functionalized ceria nanoparticles. Amongst the ionic surfactants, we have evaluated the function of four cationic surfactants with same chain length but different head group and counterions. On the basis of these results we had also examined the effects of surface curvature and anchoring strength of the surfactant heads on the surface of nanoparticles via using various techniques such as XRD, FTIR, TGA and DSC analysis. More significantly, the synthetic approach developed in this work will have the potential to modify the band gap of CeO₂ nanoparticles which will further allow one to design new material with enhanced absorption activity and significant importance in solar cells.

2. Experimental

2.1. Material and methods

Cerium (III) chloride anhydrous beads, Hexadecyl trimethyl ammonium bromide (CTAB), Hexadecyl trimethyl ammonium chloride (CTAC), cetyl pyridinium bromide hydrate (CPB > 98%) and cetyl pyridinium chloride (CPC) were purchased from Sigma-Aldrich. Ammonia solution (NH₄OH, about 25%) was purchased from Merck. Absolute ethanol was provided by Changshu Yangyuan chemical China. All the chemicals were used as purchased without any further purification.

2.2. Synthesis of Cerium oxide nanoparticles

CeO₂ nanoparticles were prepared by an aqueous precipitation method in surfactant media. Briefly describing, 0.05 mol of cerium (III) chloride were taken into an aqueous solution of respective surfactant (10 M), ethanol (1.3 mol), deionized water (50 ml), and ammonium aqueous solution (0.25 mol). The mixture of the reactants was then consequently stirred at 40 °C for 24 h to obtain yellow colour particles. The characteristic UV–vis absorption bands observed between 300–400 nm (Fig. S1 Supplementary data). The bands are assignable to bandgap absorption in CeO₂ nanoparticles caused by the charge-transfer shifts among the O 2p

and Ce 4f states in O²⁻ and Ce⁴⁺. The obtained particles were then extracted from the reaction mixture by centrifugation and subsequently washed with water and ethanol to remove the impurities.

2.3. Characterization

The crystalline phase of surfactant functionalized CeO₂ nanoparticles were determined by using Cu-K α radiation ($\lambda=1.5418$ Å) on Panalytical, D/Max-2500 x-ray Diffractometer over the range 10–90°, with a count time of 0.5 s. Crystallite size of as functionalized CeO₂ nanoparticles were further evaluated by applying Scherer's formula [27].

Fourier transformed infrared (FTIR) spectra of powders were obtained using a Perkin-Elmer (RX1) FTIR spectrometer in the frequency range 4400–350 cm⁻¹ with a resolution of 1 cm⁻¹. The optical absorption spectra were evaluated in the range of 200–800 nm using a UV–vis Jasco V550 spectrometer. Photoluminescence measurements were recorded with a Hitachi F-7000 Photo-luminescence spectrophotometer. The samples were excited at 340 nm at 500 V and 10 mm slit width. The size and shape of particles were examined by a Hitachi H 7500 electron microscope operating at 80 kV. Particle size estimations (90° optics) were carried out with a Nano S 90 (Red badge) Malvern Instruments Corporation model no. ZEN 1690. The synchronized TG–DTG (Thermo gravimetric analysis) plots were attained through a thermal analysis method; model SDT Q-600, from TA Instruments. DSC measurements were performed with a DSC TA Q20 instrument equipped with a refrigerated cooling system (TA Instruments, New Castle, DE). Nitrogen with a flow rate of 50 ml min⁻¹ was used as purge gas.

3. Results and discussion

The availability of various hydroxyl groups over the surface of bare CeO₂ nanoparticles makes it more hydrophilic in nature and enhances their agglomeration tendency via strong particle–particle interactions. Therefore, to overcome the generation of such aggregations, further stabilization process was carried out in the presence of cationic surfactants of same chain length and varied head group and counter-ions. The comparative role of different surfactants over the agglomeration was clearly visualized from the TEM images of the as formed particles. In the absence of surfactant, the agglomeration tendency was more (Fig. 1a), whereas in the presence of surfactant the particles were well separated with spherical morphology. It was further observed that the concentration of surfactant have the significant effect on the final structure of the formed CeO₂ nanoparticles. Fig. 1 shows the TEM images of CeO₂ nanoparticles prepared under different concentrations of surfactants. At low concentration of surfactants ([surfactant] < cmc), the agglomerated patterns with closely joined particles are often generated as compared to the [surfactant] > cmc. The behavioural variation was explained on the basis of improper surface coverage of CeO₂ nanoparticles by surfactants at lower

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