Phase tuning of zirconia nanocrystals by varying the surfactant and alkaline mineralizer

A. Uma Maheswari[a,*], Sreedevi R. Mohan[a], S. Saravana Kumar[b], M. Sivakumar[a]

[a]Department of Sciences, Amrita School of Engineering, Amrita Vishwa Vidyapeetham, Amritanagar, Coimbatore 641 112, India
[b]Department of Physics, NSS College, Pandalam, Pathanamthitta District 689 501, India

Abstract

The influence of cationic (CTAB)/neutral polymeric (PVP) surfactants and strong (NaOH)/weak (NH$_4$OH) alkaline mineralizers on phase stabilization of zirconia nanocrystals synthesized by chemical precipitation is investigated. X-ray diffraction and micro-Raman analysis of the as-prepared samples show that tetragonal zirconia is predominant as compared to monoclinic using PVP with NH$_4$OH. The phases are also evident from lattice fringes of TEM images and the corresponding SAED pattern. Photoluminescence spectra of samples reveal oxygen vacancies present in the zirconia nanocrystals. The group H Raman vibration modes identified are attributed to surface defects and quantum size effects of nanocrystals. The phase stabilization of zirconia nanocrystals is explained using the polymerization rate of tetramers during synthesis. The rate can be varied by proper selection of the surfactant and the mineralizer. A slow polymerization rate with PVP and NH$_4$OH favors the formation of tetragonal zirconia. Thus, a simple method for phase stabilization of zirconia nanocrystals at room temperature using chemical precipitation by varying the surfactant and the mineralizer is demonstrated.

1. Introduction

Recently there has been a renewed interest in exploring phase dependent properties of zirconia nanocrystals due to their technological importance. Generally zirconia exists in three temperature dependent polymorphs namely thermodynamically stable monoclinic (below 1170 °C), metastable tetragonal (between 1170 and 2370 °C) and cubic (above 2370 °C) [1]. Among these, tetragonal zirconia has high strength and fracture toughness which makes it suitable for the fabrication of structural ceramics [2] and functional materials [3]. Its excellent mechanical properties are due to stress induced martensitic tetragonal-to-monoclinic transformation which results in toughening [4]. In addition, tetragonal zirconia has high chemical and dimensional stability and hence used as a ceramic biomaterial for dental restorations [5]. Tetragonal zirconia coatings enhance stainless steel's resistance to corrosion and wear [6]. It is also used in thermal barrier coatings of gas turbine parts owing to its low thermal conductivity/high thermal expansion coefficient when compared to monoclinic zirconia [1]. Thin films of tetragonal zirconia are used as gate for microelectronic devices due to their high dielectric constant [7]. The ionic conductivity of tetragonal/cubic zirconia is high due to the presence of oxygen vacancies at grain boundaries and hence they are used as solid electrolytes for oxygen sensors [8] and oxide fuel cells [9]. Zirconia modified with sulphate anions is well suited for catalytic reactions like hydrogenation and isomerisation [10]. The presence of acidic, basic hydroxyl groups and coordinatively unsaturated Lewis acidic-base Zr^{4+}O^{2-} pairs can enhance its phase dependent catalytic reactions. For instance, sulfated tetragonal zirconia can act as an active catalyst for *n*-butane isomerization [11] whereas monoclinic zirconia is used for selective hydrogenation of CO$_2$ to produce methanol [12]. Zirconia nanocrystals exhibit phase dependent luminescence and used for the fabrication of eco-friendly photonic systems [13].

*Corresponding author. Tel.: +91 422 2685000×5617;
fax: +91 422 2656274.
E-mail address: a_umamaheswari@cb.amrita.edu (A. Uma Maheswari).

Since the applications of zirconia are structurally dependent, it is essential to investigate the factors influencing phase stabilization during synthesis. Bulk zirconia at room temperature is monoclinic because of its low equilibrium lattice energy. Tetragonal and cubic phases of zirconia can be stabilized at room temperature by reducing the grain size to few nanometers or by doping which introduces defects (oxygen vacancies) in the lattice [14]. There are several chemical methods to synthesize zirconia nanocrystals. The solution based synthesis methods are chemical precipitation [15], hydrothermal [16], sol–gel [17], microemulsion [18], and microwave [19]. Among these, chemical precipitation is a low cost method for controlled synthesis of zirconia nanocrystals. Investigations revealed that structure of nanocrystals is influenced by various factors such as precursor [20], pH of solution during hydrolysis [21], surfactants [22], mineralizers [15], processing conditions [23] and calcination temperature [24] during synthesis. The phase stabilization of nanocrystals is significantly influenced by the type of surfactant and alkaline mineralizer. In CTAB assisted hydrothermal synthesis, tetragonal zirconia is obtained at relatively lower temperature (523 K) [25]. The interaction of dissolved surfactant and Zr^{4+} ions with water molecules also influences the morphology of nanocrystals. Eltejaei et al. [22] reported that increased Zr^{4+} ions concentration in aqueous solution reduces surface area of nanocrystals by lowering the probability of surfactant hydrophobic head adsorption on the particle surface. This in turn reduces repulsive force between nanoparticles and enhances their aggregation. However, increasing the concentration of surfactant reduces size of nanocrystals. Hence, a suitable ratio of Zr^{4+} ions and surfactant can increase the surface area of nanocrystals.

In the previous work, it was demonstrated that nature of alkaline mineralizer can affect the polymerization rate of tetramers which in turn influences structure of zirconia nanocrystals [15]. For a given mineralizer, the type of surfactant can also influence the polymerization rate and structure of zirconia. Studies pertaining to the combined influence of mineralizer and surfactants on phase stabilization of zirconia nanocrystals have not been reported. In this context, the present work is aimed to investigate the effect of cationic (CTAB)/polymeric (PVP) surfactants and strong (NaOH)/weak (NH$_4$OH) alkaline mineralizers on the structure of zirconia nanocrystals. The as-prepared samples are analyzed using X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), photoluminescence (PL) and micro-Raman spectroscopy techniques. The phase stabilization mechanisms are also discussed.

2. Experimental methods

2.1. Synthesis of zirconia nanoparticles

The reagents used for synthesis are $ZrOCl_2 \cdot 8H_2O$ (precursor), cetyl trimethylammonium bromide (CTAB)/polyvinyl-pyrrolidone (PVP) (surfactants), xylene and NaOH/NH$_4$OH (mineralizers). Initially 3.66 g of CTAB is added to 100 ml of distilled water and stirred for 10 min. Then 0.63 ml of xylene is added and stirred for 10 min. In this solution, 1.8 g of $ZrOCl_2 \cdot 8H_2O$ is added and the mixture is stirred for 2 h. Finally the metal hydroxide precipitate is obtained by adding 5 M alkaline mineralizer NaOH/NH$_4$OH till pH of the solution becomes 9. The precipitate is then reflexed at 85 °C for 3 h in an oil bath and is cooled down to room temperature followed by 24 h stirring. The precipitate is washed using distilled water to remove impurities, and finally with ethanol for three times and filtered. The wet zirconium hydroxide is dried at 100 °C for 18 h and calcined at 500 °C for 4 h for getting zirconium oxide nanocrystals. The above said procedure is repeated using PVP as a surfactant. The as-prepared samples synthesized using surfactants CTAB and PVP with the alkaline mineralizer NH$_4$OH are labelled as A and B, and samples prepared using NaOH as the mineralizer with same surfactants as C and D respectively.

2.2. Characterization

The as-prepared samples are analyzed using XRD, TEM, photoluminescence and micro-Raman spectroscopy techniques. The X-ray diffractogram of samples was recorded using a "Bruker AXS D8 Advance model" X-ray powder diffractometer with vertical (2θ) geometry. CuKα (1.5405 Å) is used as a radiation source and Si (Li) PSD as the detector. The spectra were recorded for diffraction angles (2θ) ranging from 20° to 90° in the continuous scan mode at 0.02°/step. The TEM images of samples were obtained using a JEOL-JEM2100 microscope by employing an accelerating voltage of 200 kV. For recording TEM images first sample is ultrasonically dispersed in ethanol. A drop of this solution is placed on carbon-coated copper grid and dried at 50 °C. The fluorescence spectra of samples dispersed in ethanol were recorded using a Horiba-Jobin Yvon FluoroMax-4P spectrofluorimeter using quartz cell polished on four sides with 10 mm path length. Raman active modes of samples were identified from the spectra obtained by a laser Raman microspectrometer (HORIBA Jobin Yvon, model Lab-RAM HR, France) with an operating wavelength of 514.5 nm.

3. Results and discussions

3.1. XRD and TEM analysis

The X-ray diffractograms of samples A, B, C and D are shown in Fig. 1. The structural details are analyzed by comparing the spectra with JCPDS cards 37-1484, 65-2357 (monoclinic), 14-0534, 17-0923, 42-1164 (tetragonal) and 27-0997 (cubic). The spectra of samples A and B showed intense peaks at 2θ values 29.9°, 34.8°, 50.1° and 59.9° due to diffraction from lattice planes (101), (110), (200) and (311) respectively which corresponds to tetragonal zirconia. The peaks at 81.02° and 81.8° of samples A and B are attributed to monoclinic and tetragonal zirconia respectively. Further, the shoulder observed at 29.9° peak of sample A that corresponds to the monoclinic phase is absent in sample B. On the other hand, X-ray diffractograms of samples C and D showed both monoclinic and tetragonal phases. The prominent monoclinic peaks of sample C are at 27.8°, 31°, 49.89° and 81° due to