Journal of Physical Sciences, Vol. 17, 2013, 179-184
ISSN: 0972-8791, www.vidyasagar.ac.in/journal
Published on 26 December 2013

A Low-temperature Synthesis and Characterization of Tetragonal-ZrO_2 Nanoparticles via Simple Hydrothermal Process

K. Anandan and V. Rajendran

Department of Physics, Presidency College
Chennai – 600 005, Tamilnadu, India
E-mail: anand.nanoscience@yahoo.com; ab.nanoscience@gmail.com

ABSTRACT

Tetragonal structure of zirconium oxide (ZrO_2) nanoparticles has been successfully synthesized by a simple hydrothermal process. The structural, morphological and optical properties of ZrO_2 nanoparticles are investigated using by the X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and photoluminescence (PL) emission spectroscopy analysis.

Keywords: ZrO_2; Hydrothermal Synthesis; Morphological studies; Optical properties

1. Introduction

Nanocrystalline particles play an important role in optoelectronic applications and mesoscopic physics research. These nanocrystalline particles exhibit size-dependent properties, and novel optical, electronic, magnetic, mechanical properties that cannot be achieved using their bulk counterparts [1–4]. Zirconium oxide is one of the most intensively studied materials owing to its technologically important applications in oxygen sensors, fuel cell electrolytes, catalysts and catalytic supports, metal oxide-semiconductor devices, superior thermal and chemical stability etc [5]. Many different methods of producing nanosize zirconium oxide powder were described in the literature, such as sol-gel processing, hydrothermal processing, and precipitation method [6]. Among these methods listed above, hydrothermal synthesis meets the increasing demand for the direct preparation of crystalline ceramic powders and offers a low temperature alternative to conventional powder synthesis technique in the production of anhydrous oxide powders. This technique can produce fine, high purity and stoichiometric particles of single and multi-component metal oxides. Furthermore, if the process conditions such as solution pH, solute concentration, reaction temperature, reaction time, seed materials, and the type of solvent are carefully controlled, the zirconium oxide particles with desired shape and size can be produced [7].

In this paper, we present the synthesis of zirconium oxide nanoparticles by simple hydrothermal process, and to investigate the effects of two different temperature conditions on particles size, morphology and optical properties.

2. Experimental procedure

2.1. Synthesis of ZrO_2 nanoparticles

All the reagents were of analytical grade and were used without any further purification. In a typical synthesis, 0.1M of $ZrOCl_2 \cdot 8H_2O$ dissolved in 80 ml of distilled water under vigorous stirring, after few minutes, 0.2 M of KOH was added into the above solution. Subsequently, sol solution was formed and transferred into stainless steel Teflon lined autoclave capacity of 100 ml and maintained it an oven at 160ºC for 24 hrs. The resulting precipitates were washed with distilled water and absolute ethanol to remove the soluble impurities and depress agglomeration, respectively. The final product was dried in vacuum at 60ºC for 5hrs and named as 'Z1'. The same procedure was followed for the preparation of 'Z2' at 190ºC instead of 160ºC.

2.2. Characterization of synthesized ZrO_2 nanoparticles

The crystal structure and size of the resulting products was characterized by X-ray powder diffraction (XRD) on a JSO-DEBYEFLEX 2002 X-ray diffractometer with Cu-Kα radiation (λ=0.1540nm), employing a scanning rate of 0.02º/s in the 2θ ranging from 20 to 80º. The functional groups of the materials were carried out by Fourier transformed infrared (FTIR) spectra on the Nicolet 205 spectrometer. The morphology of the products was observed by scanning electron microscopy (SEM, Hitachi S-4500 scanning electron microscope) and size of the products was further confirmed by transmission electron microscopy (TEM, JEOL-3010 operating at 200KV). Before TEM imaging, the products were ultrasonically dispersed in methanol. Optical properties of the products were carried out by Photoluminescence (PL, Fluoromax-4 spectrofluorometer with a Xe lamp as the excitation light source).

3. Results and discussion

The purity and crystallinity of the obtained ZrO_2 nanoparticles were examined by using powder XRD analysis. Figure 1 show the XRD pattern of ZrO_2 nanoparticles prepared at 160 and 190°C, respectively. It can be seen from the Fig.1; both of them indexed tetragonal phase of zirconium oxide (JCPDS Card no. 79-1771) and sample 'Z1' exhibits broad diffraction peaks comparing than that of 'Z2', indicating the extremely small dimension of the ZrO_2 nanoparticles [8].

The average crystallite sizes of the ZrO_2 nanocrystallites have been estimated by Scherer's formula:

$$D = K\lambda/\beta\cos\theta$$

where K =0.9 is the shape factor, λ is the X-ray wavelength of Cu_Kα radiation (0.1542 nm), θ is the Bragg angle, and β is the experimental full-width at half-maximum (FWHM) of the respective diffraction peak (in units of radians). The average particles diameters of the ZrO_2 nanoparticles were calculated to be 5.12 and 7.09 nm for samples 'Z1' and 'Z2', respectively.

FTIR spectroscopy is a useful tool to understand the functional group of as-synthesized materials. Figure 2 show the FTIR spectra of the as-synthesized ZrO_2 nanoparticles Z1 and Z2, respectively. The broad and sharp peaks located at 3414 and 1620 cm^{-1} are associated with the –OH stretching and bending vibration of adsorbed water and the peak at 1426 cm^{-1} implied that the hydrated molecules could be in hydroxyl group [9]. The observation of a strong band observed different energetically bonding states. The band located at ~683cm^{-1} corresponds to Zr–O vibration of tetragonal

structure and the broadness of the band indicates that the ZrO_2 powders are nanocrystals [10].

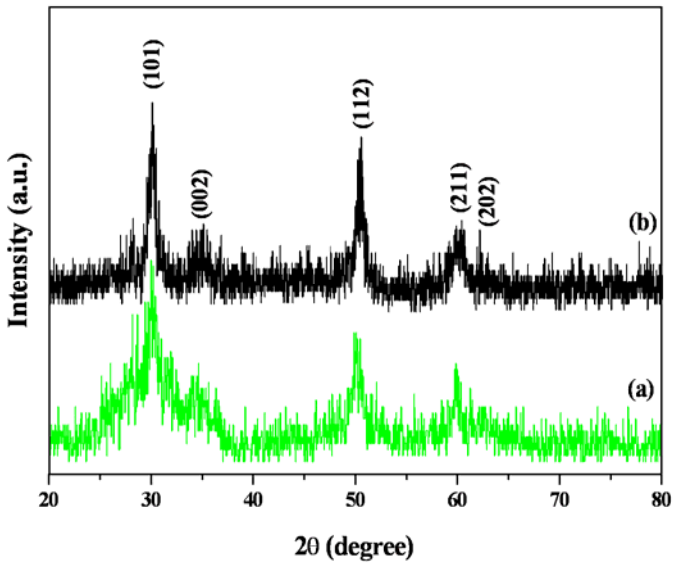

Figure 1: XRD patterns of prepared ZrO_2 nanoparticles: (a) Z1 and (b) Z2

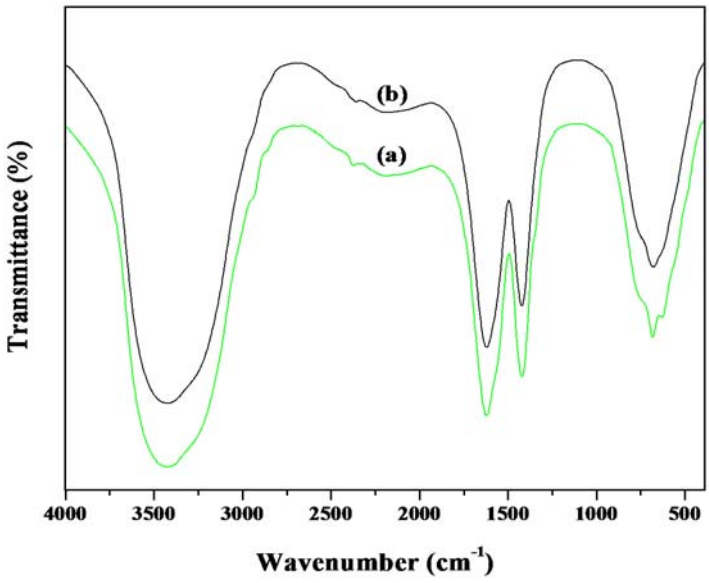

Figure 2: FTIR spectra of as-synthesized ZrO_2 nanoparticles: (a) Z1 and (b) Z2

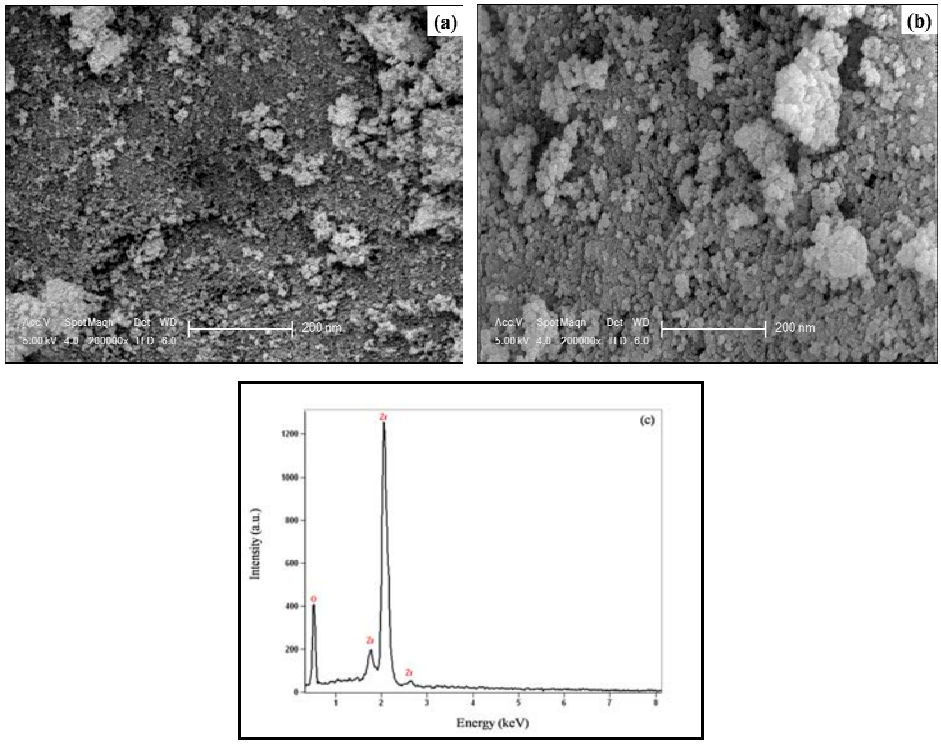

Figure 3: SEM images of ZrO_2 nanoparticles: (a) Z1, (b) Z2 and (c) EDX spectrum of Z1

Figure 3 (a-b) shows the surface morphological study of the zirconium oxide nanoparticles. The samples exhibited spherical-like morphologies; however, there is variation in size of particles diameter between the samples prepared at 160 and 190°C temperatures. Figure 3(c) shows an elemental analysis of the ZrO_2 nanoparticles, in which the peaks of Zr and O are pronounced. The formation and composition of crystalline ZrO_2 nanoparticles are justified from quantitative analysis, which reveals that the Zr and O as the only elementary species in the sample indicate that, high purity and no any other impurity in the sample.

The morphology and size information of the sample was further investigated by TEM analysis. Figure 4 shows the TEM image of the ZrO_2 nanoparticles obtained at 160°C along with corresponding particles size distribution. The well dispersed spherical-like morphology of nanoparticles was obtained; its size was about 5 nm on average. The particle size histogram of zirconium oxide nanoparticles (Figure 4(b)) shows that the particles range in size from 3 to 7 nm. The size of the particles observed from the TEM studies are in good agreement with average size obtained from the XRD results.

The room temperature photoluminescence emission spectra of ZrO_2 nanoparticles are as shown in Figure 5. The spectra show the broad emission bands at ~510 nm for both samples. The PL emission bands in the present ZrO_2 might be due to the transitions from the surface trap states in the conduction band to lower energy levels close to the valance band. This is in agreement with the results reported in the literature [11, 12]. Due to a very narrow particle size distribution, it can be mentioned that the small particle size was

the main reason for the broad fluorescence band [13, 14]. The bands observed at ~482 and 492 nm might be due to the presence of oxygen vacancies [12]. The prepared ZrO_2 nanoparticles provide a great potential in future optoelectronic nanodevice applications.

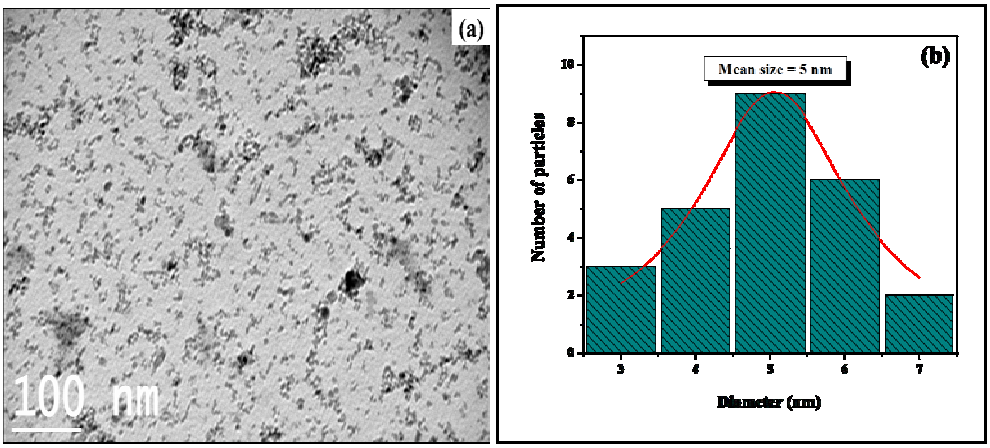

Figure 4: TEM image of Z1 and corresponding particles size histogram

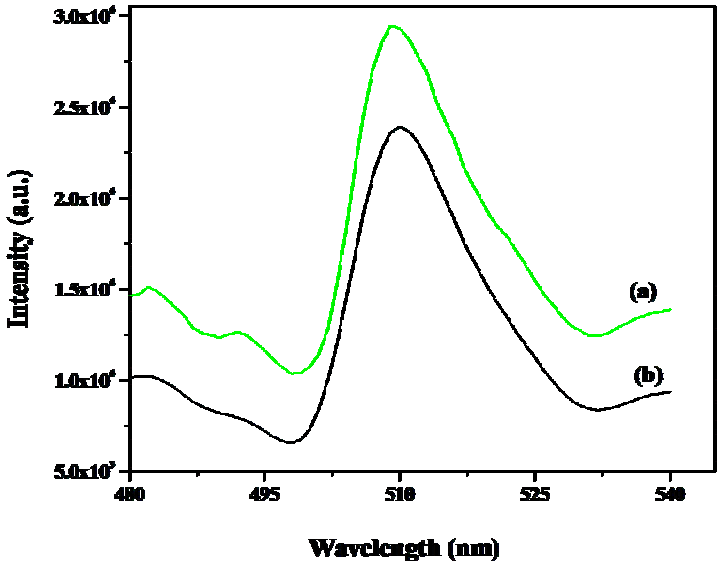

Figure 5: PL emission spectra of ZrO_2 nanoparticles: (a) Z1 and (b) Z2

4. Conclusion

A simple low-temperature hydrothermal process using to prepare small sized tetragonal-ZrO_2 nanocrystallites. The spherical shaped particles with average sizes of 5 and 7 nm were obtained, which was confirmed by SEM, XRD and TEM studies. The room temperature PL emission spectra revealed that the obtained emissions bands were

attributed to the surface defects and oxygen vacancies in the material. This work would be meaningful to provide a methodology to synthesize ultrafine nanomaterials. This method can be applied to a wide range of materials for various branched nanostructures, which may serve as potential building blocks in different advanced nanodevices.

REFERENCES

1. A.P. Alivisatos, Semiconductor Clusters, Nanocrystals, and Quantum Dots, Science 271 (1996) 933–937.
2. S.A. Majetich and Y. Jin, Magnetization Directions of Individual Nanoparticles, Science 284 (1999) 470–473.
3. K.Gupta, P.C. Jana and A.K.Meikap, Synthesis and properties of polyaniline samarium nanocomposite, J. Phys. Sci., 16 (2012) 209–216.
4. K. Anandan and V. Rajendran, Rose-like SnO2 nanostructures synthesized via facile solvothermal technique and their optical properties, J. Phys. Sci., 14 (2010) 227–234.
5. R.J. Liu, Y. Li, H. Zhao, F.Y. Zhao and Y.Q. Hu, Synthesis and characterization of Al_2O_3 hollow spheres, Mater. Lett., 62 (2008) 2593–2595.
6. D.S. Bae, E.J. Kim, S.W. Park and K.S. Han, Synthesis and characterization of nanosized $Zn_xMn_{1-x}Fe_2O_4$ powders by glycothermal process, Mater Sci Foru, 486 (2005) 436−439.
7. D.S. Bae, K.S. Han, S.B. Cho and S.H. Choi, Synthesis and characterization of the ultrafine $ZnFe_2O_4$ powder by glycothermal, Kor Assoi Crys Grow, 1 (1997) 167−173.
8. H. Zhu, D. Yang, Z. Xi and L. Zhu, Hydrothermal Synthesis and Characterization of Zirconia Nanocrystallites, J. Am. Ceram. Soc., 90 (2007) 1334–1338.
9. Y.F. Gao, Y. Masuda, H. Ohta and K. Koumoto, Room-Temperature Preparation of ZrO_2 Precursor Thin Film in an Aqueous Peroxozirconium-Complex Solution, Chemist. Mater., 16 (2004) 2615–2622.
10. C. Pecharroman, M. Ocana and C.J. Serna, Optical constants of tetragonal and cubic zirconias in the infrared, J. Applied Phys., 80 (1996) 3479–3483.
11. B. Neppolian, Q. Wang, H. Yamashita and H Choi, Synthesis and characterization of ZrO_2–TiO_2 binary oxide semiconductor nanoparticles: Application and interparticle electron transfer process, Appl. Catal. A, 333 (2007) 264–271.
12. L.J. Lai and C.S. Su, Luminescence excitation and near edge X-ray absorption spectra of Er_2O_3 dopant on zirconia ceramics, Mater. Chem. Phys., 62 (2000) 148–152.
13. M.N. Tahir, L. Gorgishvili, J. Li, T. Gorelik, U. Kolb, L. Nasdala and W. Tremel, Facile synthesis and characterization of monocrystalline cubic ZrO_2 nanoparticles, Solid State Sci., 9 (2007) 1105–1109.
14. J. Joo, T. Yu, Y.W. Kim, H.M. Park, F. Wu, J.Z. Zhang and T. Hyeon, Multigram scale synthesis and characterization of monodisperse tetragonal zirconia nanocrystal, J. Am. Chem. Soc., 125 (2003) 6553–6557.