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Microwave assisted sol-gel synthesis of tetragonal zirconia nanoparticles

to be the reason for smaller particle sizes.

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ABSTRACT

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1. Introduction

The development of zirconia (ZrO₂) nanoparticles has attracted much attention due to their multifunctional characteristics. Nanoparticles have been recognized to have potential in the area of photonic applications. It is known that the main crystal phases of ZrO₂ are cubic (c), tetragonal (t) and monoclinic (m) and their main IR frequencies are 480, 435 and 270 cm⁻¹ for cubic, tetragonal and monoclinic phases, respectively. This indicates that phonon energy of the ZrO₂ host varies on the crystal phases. The monoclinic phase is thermodynamically stable up to 1100°C, the tetragonal phase exists in the temperature range 1100-2370 °C and the cubic phase is found above 2370°C. It has several applications such as solid oxide fuel cell, bio-sensors, H₂ gas storage material, oxygen sensor, catalyst and catalyst support [1–5]. In addition, zirconia is used as piezoelectric material, electro-optic material and dielectric material [6–8]. It is also used as support to disperse various noble and transition metals for distinct catalytic applications. Zirconia is a well-known solid acid catalyst and an n-type semiconductor material [9]. ZrO₂ is used as toughening ceramics in thighbone and oral planting [10]. Recently it has been reported that the oxide nanoparticles are promising for photonics, however principal role from technological point of view play their mono-dispersion and appropriate contact with the surrounding medium [11].

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A simple and fast synthesis of zirconia nanoparticles by microware assisted citrate sol-gel method is

reported. The formation of nanoparticles was characterized by performing powder X-ray diffraction

(XRD) of the samples calcined at higher temperatures. The physico-chemical characterizations were

done employing techniques of Raman spectroscopy and BET surface area measurements. Fourier trans-

form infrared spectroscopy (FTIR) was performed to analyze the band structure and functional groups. High-resolution transmission electron microscopy (HRTEM) was done for analyzing the morphology of

nanoparticles and estimating the crystallite sizes. The prepared material was found to have tetragonal

symmetry. The average particle sizes were found ranging \sim 5–10 nm. Gelation and fast combustion seems

The existence of metastable tetragonal (t-ZrO₂) at low temperature has been reported and synthesized by several methods. Some of the methodologies such as oxidation of ZrCl₂ by molecular oxygen [12], molten hydroxides method [13] non-hydrolytic sol-gel reaction between isopropoxide and ZrCl₄ [14], sol-gel template technique [15,16] are developed to prepare nanocrystalline ZrO₂. Microwave assisted synthesis of nanocrystalline materials has attracted much attention in recent years because of its several advantages such as unique synthetic pathways, rapid heating rates, short processing durations, uniformity and low power requirements [16–24]. Microwave assisted citrate gel combustion method is similar to solution combustion process (SCP) reported earlier [25].

In the present work combustion synthesis has been performed under microwave using citric acid as fuel and zirconium oxychloride as oxidizer. To the best of our knowledge, there is no report on the synthesis of tetragonal zirconium oxide (ZrO₂) employing microwave assisted technique. The present problem was therefore undertaken with a view to develop a cheap and fast microwave assisted synthesis of t-ZrO₂ and to characterize the samples for

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Fig. 1. Representative powder XRD pattern for ZrO₂ nanoparticles calcined at 450 °C.

their structural and optical properties employing various physicochemical methods.

2. Experimental details

High purity chemicals, zironium oxychloride (S.D. Fine Chemicals) and anhydrous citric acid (LOBA Chemie Pvt. Ltd.) were used for the preparation of the zirconia (ZrO_2) nanoparticles. In the present set of experiment, 9.78 g of zirconium oxychloride ($ZrOC_1 \cdot 8H_2O$) was mixed with 7.68 g of citric acid ($C_2O_4H_2$) in a 250 ml corning glass beaker. De-mineralized water was added to have homogenous slurry of pH 2. The solution was evaporated to dryness by exposing it to microwave for 2 min. The material swells into a white colored gel. The product obtained was grinded and kept for calcination in a tubular furnace at a temperature of 450 °C for 4 h. On calcination a black colored residue was obtained which was grinded in a motor-pastel to make a fine powder.

The prepared zirconia nanoparticles were examined by powder X-ray diffraction using Cu K α radiation (λ = 1.5406 Å, Rigaku Geiger Flex X-ray diffractometer) to confirm the phase and structure. The diffuse reflectance Fourier transform infrared spectroscopy, FTIR (Jasco-660 plus Fourier transform spectrophotometer) was used to determine the functional groups present in the material. The morphology and sizes of the zirconia nanoparticles were analyzed by transmission electron microscopy in high-resolution mode. The sample for TEM observation was prepared by suspending the particles in ethanol by ultrasonification and drying a drop of the suspension on a carbon coated copper grid. Philips Technai G²-20 (FEI) electron microscope operating at 200 kV was used for TEM experiments. BET surface area was measured using ASAP 2020 V3.04 H, BET analyzer in a N₂ absorption apparatus, using the single point BET method. Raman records were taken on a Labram HR800 micro Raman spectrometer using Labspec software. Raman spectrum in the range 50–4000 cm⁻¹ were recorded using 488 nm wavelength Ar⁺ laser source at the energy of 2.53 eV with recording time of 10 s.

3. Results and discussion

Tetragonal zirconium oxide (t-ZrO₂) nanoparticles were prepared by microwave assisted citrate sol-gel technique using zirconium oxychloride as oxidizer. Powder XRD patterns of the prepared nanoparticles calcined at different temperatures were recorded. The representative powder XRD for the sample calcined at 450 °C is shown in Fig. 1. The XRD pattern reveals the fact that the single tetragonal phase of ZrO₂ is crystallized. The calcination temperature has important role to play in formation of crystalline phase and the particle size. The calcination temperature was optimized, and 450 °C was found effective to crystallize the desired tetragonal phase. It was observed that the full width at half maximum of the reflection peaks decreases and also becomes sharp as the calcining temperature increases. This suggests that the crystallinity of prepared zirconia nanoparticles is increasing at higher temperatures. The representative XRD pattern obtained for the samples calcined at 450°C was taken into consideration and all



Fig. 2. (a) Representative TEM micrograph for ZrO₂ sample annealed at 450 °C. (b) High-resolution TEM micrograph for samples annealed at 450 °C. The corresponding SAD patterns are inserted into micrographs.

peaks have been indexed and match with the t-ZrO₂ (JCPDF card file, no. 79-1771). The lattice parameters were calculated for t-ZrO₂ from the XRD data. The parameters were; a = 5.083 Å, c = 5.185 Å and the tetragonality, c/a = 1.0201. The diffraction characteristic peaks were obtained with the (h k l) values of (1 0 1), (1 1 0), (1 1 2), (2 1 1), and (2 2 0). The particle sizes were calculated from FWHM (Full Width Half Maximum) of reflections of t-ZrO₂ structured zirconia nanoparticles using Debye–Scherer formula [26]. The particle sizes were found varying \sim 5–10 nm range.

Transmission electronic microscopy (TEM) in high-resolution mode is best tool to analyze the morphology and the sizes of the prepared nanoparticles [27-29]. Fig. 2(a and b) shows the TEM micrographs taken for the samples calcined at 450 °C. The corresponding selected area diffraction patterns are inserted into the micrographs. Fig. 2(a) shows a typical TEM image for the dried powders. The powders are very fine and agglomerated. Electron diffraction analysis reveals that they have amorphous characteristics due to small particle sizes. The micrograph shown in Fig. 2(a)indicates the formation of nanoparticles with sizes ranging from few nanometers to few tens of nanometers. The corresponding diffraction pattern shows the presence of few clear spots along with connecting diffraction rings. The presence of spots along with the streaks shows the presence of crystallite of reasonably sufficient sizes to diffract. The connecting streaks indicating the short-range order due to presence of some smaller size particles as well. The high-resolution electron micrograph for the samples annealed at 450 °C is shown in Fig. 2(b). The clarity in the fringe patterns inside the crystallite indicates the formation of single phase ZrO₂ with the long-range order in the structure. The distance between two adjacent lattice planes is about 0.28 nm (see Fig. 2(b)), which is close to



Fig. 3. FTIR spectrum of ZrO_2 in the range of 3500-500 cm⁻¹.

the spacing of (101) planes of the t-ZrO₂. The corresponding SAD pattern is inserted into the micrograph. The clear spots in SAD pattern suggest that the crystallites are of sufficiently large size. The absence of rings in the SAD pattern is indicative of the crystalline order, larger particle size and long-range order in the crystallites. The TEM results also suggest the successful preparation of tetragonal phase of ZrO₂ nanocrystals with the crystallite sizes ranging \sim 5–10 nm.

BET surface area was measured for the prepared zirconia samples calcined at 450 °C for 4 h. The average values calculated for surface area was $38.7767 \text{ m}^2/\text{g}$ and pore size was 3.85247 nm. FTIR spectra of the samples in the range $400-4000 \text{ cm}^{-1}$ were recorded. Fig. 3 shows the FTIR spectrum for the zirconia nanoparticles in absorbance mode. The prominent band at 2355 cm^{-1} and 2323 cm^{-1} corresponds the structural O–H stretching of the nanomaterials. In the bending mode region two bands are observed at 1554 cm^{-1} and 1523 cm^{-1} , which are due to the O–H bending. In addition the broad band at $900-1000 \text{ cm}^{-1}$ can be assigned to the Zr–O bond for t-ZrO₂.

Raman spectroscopy is sensitive to the polarizability of the oxygen ions and therefore it can be used to determine the symmetry of a crystal system. In fact Raman spectroscopy is a technique more sensitive to short-range order than X-ray diffraction, and it can show the peaks for anatase or rutile as well as monoclinic zirconia along with that of tetragonal zirconia. The Raman spectra of ZrO₂ calcined at the temperatures of 600 °C and 800 °C are plotted in Fig. 4. The assignment of the observed bands was made on the basis of the comparison of the observed spectra with that of reported in the literature [24,25,30]. The vibrational Raman active modes are classified as:

$$\Gamma = A_{1g} + 2B_{1g} + 3E_g$$

In A_{1g} mode oxygen atoms move in the *z*-direction only. The B_{1g} modes also involve motion in the *z*-direction, however now Zr and O both the atoms participate. In E_g modes, Zr as well as O atoms move in the *x*-*y* plane. Pictorial description of the modes can be found elsewhere [31]. Fig. 4 shows the Raman spectra of ZrO₂ nanoparticles precipitated at pH 2 and calcined at different temperatures. Fig. 4(A) represents the Raman spectra for the sample calcined at 400 °C. The band appeared at 643 cm⁻¹ can be assigned to A_{1g} mode since it involves movement of two oxygen atoms only and is expected to appear at higher wave number. The next two bands appeared at 470 and 382 cm⁻¹ are assigned to doubly degenerate E_g



Fig. 4. Raman spectra of ZrO_2 precipitated at pH 2 and calcined at different temperatures.

modes on the simple reasoning that these two modes also does not involve movement of Zr atoms. The remaining three modes namely two B_{1g} modes and one E_g mode are assigned to the remaining three band appearing at 259, 146 and 123 cm⁻¹, respectively. The spectrum of sample calcined at 600 °C is shown as curve (B) in Fig. 4. The above bands appeared in the Raman spectra for both the samples are assigned to t-ZrO₂. In addition, few faint bands at 563, 536, 381, 293, 176 cm⁻¹ have appeared which are due to the co-existence of small amount of monoclinic phase.

4. Conclusions

Zirconia nanoparticles were synthesized by the simple and most convenient microware assisted citrate sol-gel method. The formation of tetragonal crystalline phase t-ZrO₂ was confirmed by powder XRD analysis on calcined samples. The morphology, particle size and microstructure were analyzed using high-resolution transmission electron microscopy. The HRTEM data also confirms the formation of single phase t-ZrO₂. The high-resolution TEM micrograph and SAD pattern show the crystalline perfection and long-range order in the prepared zirconia nanoparticles. The crystallite sizes were found in the range of \sim 5–10 nm. Raman spectra further supports and confirms the crystalline phase as well as the specific bands to show the modes of vibration in Zr–O system.

References

- [1] G.K. Chuach, Catal. Today 49 (1999) 131–139.
- [2] G.K. Chuach, S. Jaenicke, Appl. Catal. A 145 (1996) 267-284.
- [3] N.Q. Minh, J. Am. Ceram. Soc. 76 (3) (1993) 563–588.
- [4] A.B.F. Martinson, J.W. Elam, J.T. Hupp, M.J. Pellin, Nano Lett. 7 (2007) 2183–2187.
- [5] E.C. Subbarao, H.S. Maiti, Adv. Ceram. 24 (1988) 731-748.
- [6] J.D. Kim, S. Hana, S. Kawagoe, K. Sasaki, T. Hata, Thin Solid Films 385 (2001) 293-297.
- [7] M. Laurent, U. Schreiner, P.A. Langjahr, J. Eur. Ceram. Soc. 21 (2001) 1495-1498.
- [8] H.L. Lee, J.T. Kim, G.G. Hong, J. Korean Ceram. Soc. 25 (2) (1988) 117-122.
- [9] B.M. Reddy, A. Khan, Catal. Rev. 47 (2005) 257–296.
- [10] K. Prabakaran, S. Kannan, S. Rajeswari, Trends Biomater. Artif. Organs 18 (2005) 114–116.
- [11] A. Majchrowski, J. Ebothe, E. Gondek, K. Ozga, I.V. Kityk, A.H. Reshak, T. Łukasiewicz, J. Alloys Compd. 485 (2009) 29–32.
- [12] J.L. Gole, S.M. Prokes, J.D. Stout, O.J. Glembocki, R.S. Yang, Adv. Mater. 18 (2006) 664–667.
- [13] L. Wang, K.F. Cai, Y.Y. Wang, J.L. Yin, H. Li, C.W. Zhou, Ceram. Int. 35 (2009) 2499–2501.
- [14] J. Joo, T. Yu, Y.W. Kim, H.M. Park, F.X. Wu, J.Z. Zhang, T. Hyeon, J. Am. Chem. Soc. 125 (2003) 6553–6557.

- [15] H.Q. Cao, X.Q. Qiu, B. Luo, Y. Liang, Y.H. Zhang, R.Q. Tan, M.J. Zhao, Q.M. Zhu, Adv. Funct. Mater. 14 (2004) 243–246.
- [16] S. Shukla, S. Seal, Rev. Adv. Mater. Sci. 5 (2003) 117-120.
- [17] D.R. Baghurst, D.M.P. Mingos, J. Chem. Soc. Chem. Commun. 12 (1988) 829-830.
- [18] D.R. Baghurst, A.M. Chippindale, D.M.P. Mingos, Nature 332 (1988) 311-312.
- [19] N.H. Sutton, Am. Ceram. Soc. Bull. 68 (1989) 376-386.
- [20] C.C. Landry, A.R. Barron, Science 260 (1993) 1653-1655.
- [21] S. Komarneni, E. Breval, R. Roy, in: W.H. Sutton, M.H. Brooks, I.J. Chabinsky (Eds.), Microwave Processing of Materials, 124, Materials Research Society, Pittsburgh, PA, 1988, pp. 235–238.
- [22] E.J.A. Pope, Am. Ceram. Soc. Bull. 70 (1991) 1777–1778.
- [23] T.T. Meek, C.E. Holcom, N. Dykes, J. Mater. Sci. Lett. 6 (1987) 1060-1062.

- [24] P.D. Ramesh, K.J. Rao, Bull. Mater. Sci. 18 (1995) 447-465.
- [25] S. Park, D.W. Lee, J.C. Lee, J. Am. Ceram. Soc. 86 (2003) 1508-1512.
- [26] B.D. Cullity, Elements of X-ray Diffraction, second ed., Addison-Wesley, MA, 1978.
- [27] K.S. Bartwal, S. Kar, N. Kaithwas, M. Deshmukh, M. Dave, N.P. Lalla, H. Ryu, Adv. Mater. Res. 26–28 (2007) 667–670.
- [28] N. Kaithwas, M. Dave, S. Kar, S. Verma, K.S. Bartwal, Cryst. Res. Technol. 45 (2010) 1179–1182.
- [29] S. Kar, S. Verma, K.S. Bartwal, J. Alloys Compd. 495 (2010) 288-291.
- [30] B.K. Kim, J.W. Hahn, K.R. Han, J. Mater. Sci. Lett. 16 (1997) 669-671.
- [31] A.P. Naumenko, N.I. Berezovska, M.M. Biliyand, O.V. Shevchenko, J. Mater. Sci. Lett. 9 (2008) 121–125.