

A NOVEL METHOD FOR SYNTHESIS OF METASTABLE TETRAGONAL ZIRCONIA NANOPOWDERS AT LOW TEMPERATURES

F. KAZEMI, A. SABERI*, S. MALEK-AHMADI**, S. SOHRABI***, H.R. REZAIE***, M. TAHRIRI****

*Department of Research and Development,
Hoor-Mehr-Sepahan Co., Isfahan, 81736-43513, Iran*

**Department of Material Science and Engineering, Faculty of Mechanical Engineering,
University of Tabriz, Tabriz, 51666-16471, Iran*

***College of Chemistry, Isfahan University of Technology, Isfahan, 84156, Iran*

****Department of Material Engineering and Metallurgy,
Iran University of Science and Technology, Narmak, Tehran, 16844, Iran*

*****Biomaterials Group, Faculty of Biomedical Engineering,
Amirkabir University of Technology, Tehran, 15875-4413, Iran*

E-mail: m-tahriri@aut.ac.ir

Submitted June 18, 2010; accepted January 20, 2011

Keywords: ZrO₂, Nanopowders, Precursors-organic, XRD, Crystallite, Electron diffraction

Zirconia (ZrO₂) nanopowder was synthesized using sucrose and fructose as a chelating agent from zirconium hydroxide. The synthesized powders were characterized by X-ray diffraction (XRD), simultaneously thermal analysis (STA), BET surface area, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The above-experimental results showed that the synthesized powders had particle sizes in the range 40-60 nm and mean crystallite sizes of 7-8 nm. Finally, in this research, chelating agents of sucrose and fructose were compared and the obtained results demonstrated that using fructose, nanopowder of zirconia with tetragonal phase was obtained.

INTRODUCTION

Zirconium oxide (ZrO₂) is considered as an important ceramic material due to its superior chemical, thermal and mechanical properties in a wide range of applications such as catalysts, oxygen sensors, fuel cells, engine parts and thermal barrier coatings on metal surfaces [1]. Recently, nano-crystalline materials, in particular zirconia (ZrO₂) nano-particles, have generated a lot of interest their unique physical and chemical properties, which are significantly different from their microcrystalline counterparts [2,3].

Metastable tetragonal zirconia, t-ZrO₂, can be produced at RT and at atmospheric pressure by thermal decomposition of zirconium salts, alkoxides and hydroxide or by ball-milling of monoclinic zirconia, m-ZrO₂. There are some evidences that metastable t-ZrO₂ can be also produced by ball-milling of zirconium hydroxide. The formation of t-ZrO₂ at room temperature and the conditions of its stability are still a matter of controversy [4]. Recently, Stefanic *et al.* investigated thermal decomposition products of three different zirconium salts. It was concluded that the formation of t-ZrO₂ is dependent on the nature of the starting salt [4].

One of the effective methods that recently have been developed is the citric acid and sucrose process, which is established for the preparation of fine oxide ceramic powders. In this technique, a uniform particle size powder is produced due to a homogeneous metal ion distribution in the solution, while other elements such as C, H, and N are easily removed during calcination. Therefore, the purity of the final powder does not get affected when citrate acid and sucrose are used as chelating agents and template materials [5,6].

The object of the present research is the synthesis of nanocrystalline tetragonal zirconia via introducing fructose as a novel chelating agent. Also the effects of particle size on zirconia phases are investigated.

EXPERIMENTAL

The raw materials utilized in this study were zirconium hydroxide, sucrose (product number S9378 Sigma-Aldrich), fructose (product number 239704 Sigma-Aldrich) and polyvinyl alcohol (PVA; product number 363065 Sigma-Aldrich average $M_w = 146,000-186,000$). Zirconium hydroxide was extracted from zircon sand by a novel hydrometallurgical method [7]. STA analysis

illustrated that the hydrated gel contains 45.05 wt% of zirconia. Chemical analysis by XRF (X-ray fluorescence) and the XRD pattern of the calcinated zirconium hydroxide at 1100°C for 1 h are shown in Table 1 and Figure 1, respectively.

Sucrose/fructose and PVA were added to 0.1 M solution of zirconium hydroxide which is prepared by solving 0.1 mole dried zirconium hydroxide in 1 l nitric acid (64 wt.%) solution. The molar ratio of zirconium cations to chelating agents (sucrose/fructose) and PVA was 1:4:0.5 for sucrose and 1:8:0.5 for fructose [6]. Then the pH was adjusted to 1 by dropwise addition of diluted nitric acid for 4 h. The addition of nitric acid causes to break sucrose into glucose and fructose. Also, this phenomenon causes to prevent sucrose re-crystallization [8]. The -OH and -COOH groups of the decomposed products promote binding of zirconia ions in homogeneous solution.

Subsequent heating at 80°C for 2 h on a hot-plate stirrer causes complex formation of the zirconia ions with sucrose or fructose [9]. The solution was heated in an electrical oven at 200°C for 4 h. During the heating process, the obtained gel converted to the black foam mass. Finally, the obtained mass was ground into powders and then calcined in an electrical furnace at 500, 600 and 700°C for 1 h. During the calcination process, the polymeric matrix is decomposed to gases such as CO₂ and H₂O which this phenomenon causes to release a large amount of heat. These produced gases prevent the agglomeration of calcined powders.

Further, a field emission scanning electron microscope (FE-SEM, LEO1-1530) and a transmission electron microscope (TEM, LIBRA1-200) were used for microstructural observation. The specific surface area

of the synthesized powders was measured by ASAP-2010, Gemini according to BET technique. The resulting samples were analyzed by XRD with Bruker AXS 2002 for evaluation of phase composition. Eventually, the mean crystallite size (D) of the zirconia powder was determined according to the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where k is a constant (shape factor, about 0.9), λ is the X-ray wavelength (1.5405 Å), β is the full width at half maximum (FWHM) of the diffraction line, and θ was the diffraction angle.

RESULTS AND DISCUSSION

The STA curve of the fructose precursor is shown in Figure 2. The small endothermic peak at about 270°C in DTA is assigned to the release of nitrate radicals. It is evident that, the second weight loss occurred between 200 and 550°C (about 70 %), corresponding to an exothermic curve in the DTA at 480°C. This is associated with the decomposition of precursor and burning of polymeric matrix.

Figures 3 and 4 illustrate XRD patterns of zirconia nanopowders produced with the sucrose and fructose precursors, respectively. The formation of tetragonal phase in the zirconia powders that synthesized with fructose precursor is also confirmed by the electron diffraction (ED) pattern which will be discussed later (see Figure 7).

Table 2. The approximate crystallite size of monoclinic and tetragonal phase and specific surface area of the zirconia powder calcined at different temperatures.

Calcination temperature (°C)	Crystallite size (nm)		
	Sucrose		Fructose
	Tetragonal phase (101)	Monoclinic phase (111)	Tetragonal phase (101)
500	9.2	20.8	7.2
600	15.8	22.9	12.6
700	15.9	30.6	22.9

Table 1. Chemical composition of calcined gel at 1100 °C.

Oxide	ZrO ₂ + HfO ₂	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
Percent (%)	99.88	0.06	0.03	0.03

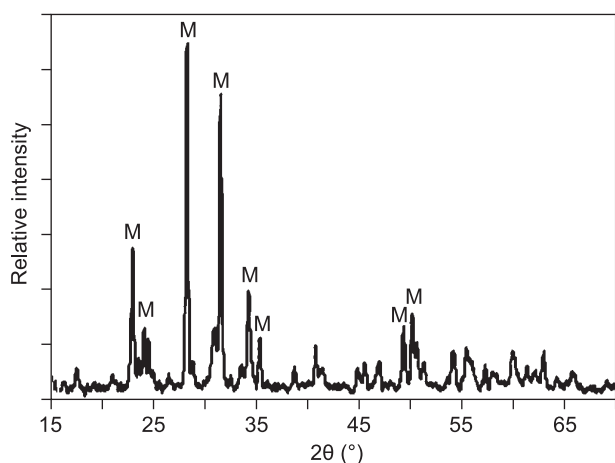


Figure 1. X-ray diffraction pattern of calcined zirconium hydroxide at 1100°C (M: monoclinic zirconia).

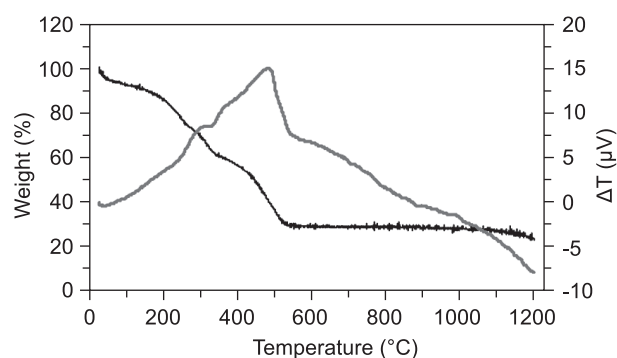


Figure 2. STA curves of the sucrose precursor.

Table 2 shows the crystallite size of the synthesized zirconia that is calculated by the Scherrer equation. According to the results, it is clear that the crystallite size of the monoclinic phase, presence in the sample that is synthesized with sucrose precursor, is significantly larger than the tetragonal phase synthesized with the fructose precursor.

It is important to point out the nanopowders are thermodynamically highly unstable [10] and therefore, the extra energy of a surface (surface energy anisotropy) with a radius of curvature, R , may be calculated as a stress (σ) in a Laplace equation:

$$\sigma = \frac{\gamma}{R} \quad (2)$$

where γ is the surface energy. In nanopowders, this sintering stress may reach very high values. For example, the sintering stress may be as large as 300 MPa in 10 nm particles compared to only 3 MPa for 1 μm particles, if γ has a typical value of 1.5 J/m² [11]. It is mentionable that for traditional sintering evaluations, the surface energy is assumed to be isotropic. The implications and difficulties brought about by this simplifying assumption in conventional powders, particularly for ceramics which are more anisotropic than metals, have been addressed [12]. For nano-sized particle with significant surface area, the anisotropy problem becomes even more critical. In fact, if the sintering process starts at a lower temperature, so the effects of surface energy anisotropy are more pronounced. Usually, if the temperature is sufficiently high, the surface energy anisotropy may be reduced.

The TEM evaluation of zirconia indeed showed that nanoparticles have a faceted appearance with anisotropic surface energies [13, 14]. Even for metals, a departure from the ideal spherical particle concept and, thus, isotropy is accentuated in the nanoscale range. Therefore, the highly anisotropic behavior of nanoparticle surfaces may be responsible for the crystallographic alignment, which has been often observed.

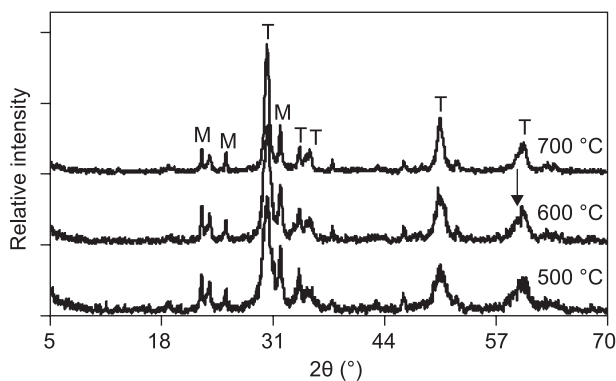


Figure 3. XRD patterns of the samples that synthesized with sucrose precursor calcined at different temperatures (M: m-ZrO₂, T: t-ZrO₂).

It is worth mentioning that if the particle size of zirconia became between 8-29 nm then, the tetragonal phase can be stabilized at room temperature [15].

Also, Dosev *et al.* [16] calculated the particle surface pressure dependence on particle size according to the hydrostatic balance of forces:

$$P = \frac{4\gamma}{D} \quad (3)$$

where D is the particle size. The estimated pressure for a particle with a diameter of 50 nm is 1.2×10^8 Pa (1.2 kbar). For small particles, the values of the surface pressures could be sufficiently large enough to permit the monoclinic structure to form and tetragonal phase might be stabilized. As the particle size increased, there is a corresponding decrease in surface pressure, resulting in a high proportion of the tetragonal phase.

Another possible reason for the existence of the metastable tetragonal phase of zirconia is due to the synthesized small particle size. Generally, in a single crystal, the monoclinic phase has significantly less bulk energy than the tetragonal phase. Thus, the thermodynamically stable phase at equilibrium conditions is the monoclinic phase. On the other hand, the specific surface energy of the tetragonal phase is considerably lower than that of the monoclinic phase. If the particle size decreases, the contribution of the surface energy to the total energy increases. Therefore, below a characteristic critical crystallite size, the tetragonal phase is more stable than the monoclinic phase that this critical particle size depends on the temperature [17,18].

As Table 2 shows, the monoclinic phases has a larger crystallite size than the tetragonal phase, but with increasing the calcination temperature the crystallite size of both monoclinic and tetragonal phase increases because of the dependence of critical particle size with temperature.

The stock template solutions contained strong acids, which resulted in the hydrolysis of the sucrose molecules to form glucose and fructose which both molecules

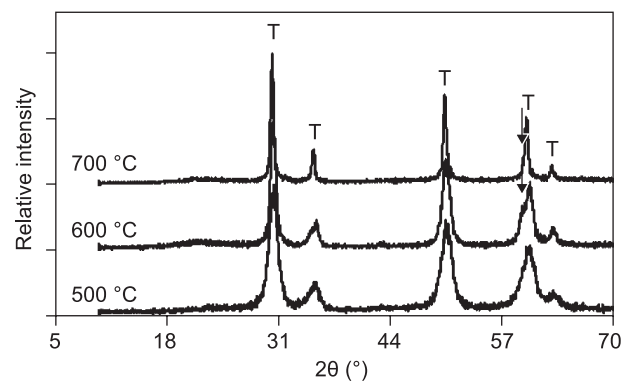
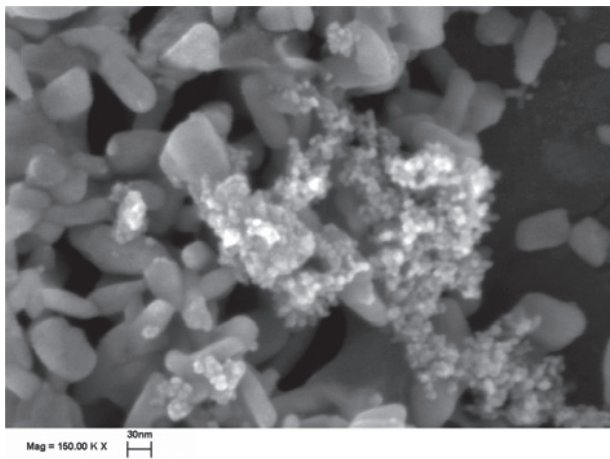


Figure 4. XRD patterns of the samples that synthesized with fructose precursor calcined at different temperatures (T: t-ZrO₂).

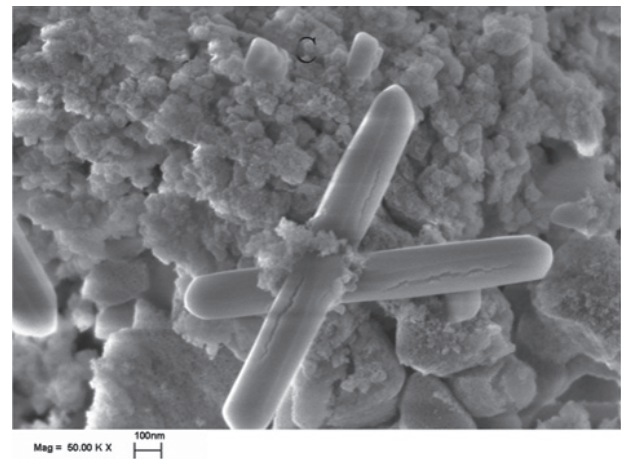
have the same molecular weight and chemical formula ($C_6H_{12}O_6$). However, glucose forms a 6-membered ring with one primary alcohol functional group while fructose forms 5-membered ring with two primary alcohols [19]. Diniz da Costa *et al.* [20] have investigated the effect of sucrose and its components (fructose and glucose) as a template material in the pore size tailoring of an acid catalysed sol-gel process. They have stated that with increasing the sucrose template concentration, structural parameters such as surface area, pore volume and mean pore size also increase. Therefore, this phenomenon leads to changing the gel matrix from microporous to mesoporous nanostructures. Also, fructose influenced the formation of large pore volumes and mean pore diameter while glucose was responsible for forming higher surface areas.

Figure 5 illustrates orientational growth of tetragonal zirconia particles. It seems that the size of particles that calcined at 500 °C is less than 50 nm.

Figure 6 shows the TEM micrographs of the zirconia nanoparticles. As can be seen, there is still some agglomeration present and the mean crystallite size is about 8 nm. Roy *et al.* [21] reported the same XRD pattern as shown in Figure 4 for cubic phase zirconia, but this interpretation is highly disputable. A. Ghosh *et al.* [22] investigated tetragonal and cubic yttria stabilized zirconia (YSZ). They showed that the XRD pattern of nanocrystalline zirconia for tetragonal and cubic stabilized phases are the same but as the particles are calcined at higher temperatures there will be peak of the $2\theta\sim 35^\circ$ and $2\theta\sim 59^\circ$ peaks (identification mark for the presence of tetragonal phase). Lamas *et al.* [23]

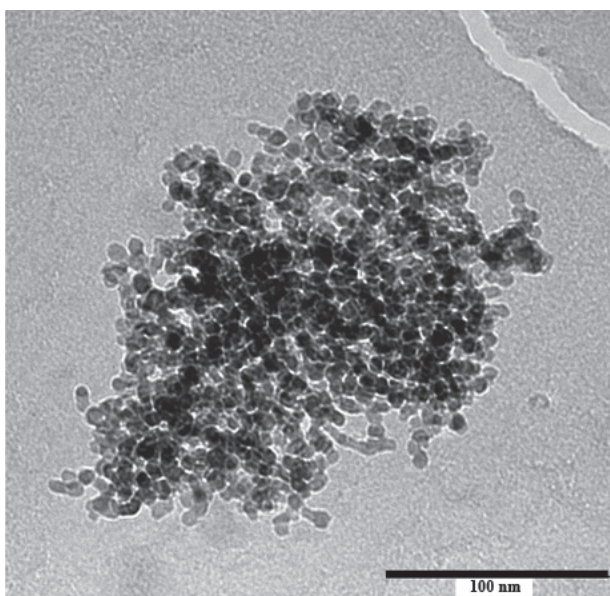


a) calcined at 500°C for 1 h

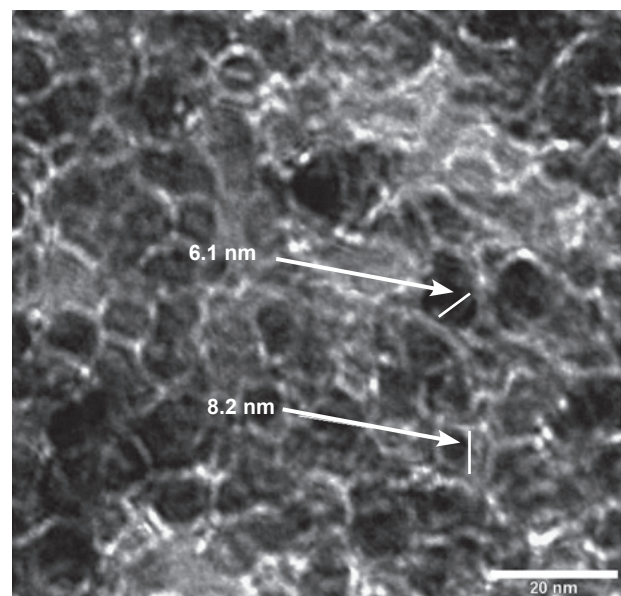


b) calcined at 600°C for 1 h

Figure 5. SEM micrograph of the zirconia nanopowders prepared with fructose precursor.



a) calcined at 500°C for 1 h



b) calcined at 600°C for 1 h

Figure 6. TEM micrographs of the zirconia nanopowders prepared with fructose precursor calcined at 500°C for 1 h.

proposed (112) plane as a characteristic for the presence of tetragonal phase.

Figure 7 shows an electron diffraction pattern of the sample that synthesized with fructose that calcined at 500°C for 1 h. It is noticeable that the (112) plane is distinguished in this figure but is not shown in the XRD pattern (that shown in Figure 4) clearly because of the peak intensity that related to the (112) plane is weak. Also, it is worth mentioning that the XRD pattern could not always give sufficient data to determine the phase of the zirconia nanopowders while electron diffraction could do this job.

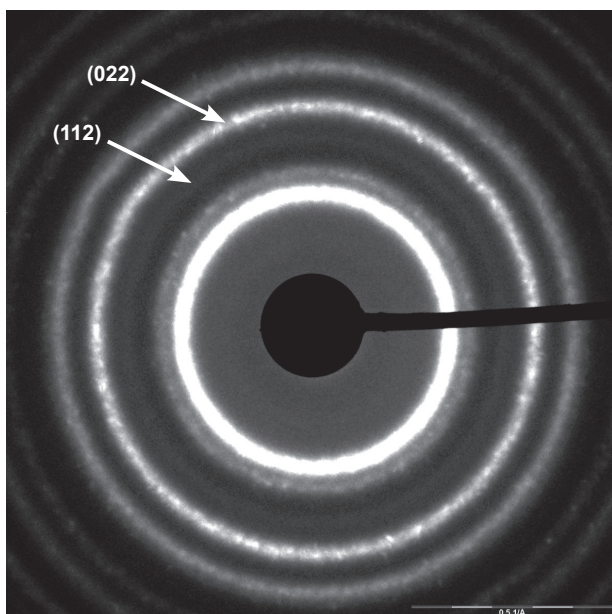


Figure 7. Electron diffraction pattern of the zirconia nanopowders prepared with fructose precursor calcined at 500°C for 1 h.

CONCLUSION

In conclusion, the single-phase tetragonal zirconia nanopowders have been synthesized by a polymer matrix method with fructose/sucrose and PVA as a chelating agent at low temperatures. The crystallite size is in the range of 7-10 nm, and its particle size is smaller than 50 nm in the sample that calcined at 500°C. This chemical synthesis through the polymer matrix technique comprising fructose is applicable and cost effective compared to other processes for the preparation of nano-sized zirconia particles. Eventually, the electron diffraction pattern of zirconia nanoparticles can distinguish cubic and tetragonal phase while XRD patterns can not make a difference between these of two phases.

References

- Mueller R., Jossen R., Pratsinis S.E., Watson M., Akhtar M.K.: *J. Am. Ceram. Soc.* 87, 197 (2004).
- Limaye A.U., Helble J.J.: *J. Aerosol Sci.* 35, 599 (2004).
- Cao G.: *Nanostructures and Nanomaterials: Synthesis, Properties and Applications*; p. 47-75, Imperial College Press, London 2004.
- Štefanić G., Music S., Popović S., Sekulić A.: *J. Mol. Struct.* 408/409, 391 (1997).
- Pati R.K., Ray J.C., Pramanik P.: *Mater. Lett.* 44, 299 (2000).
- Saberi A., Alinejad B., Negahdari Z., Kazemi F., Almasi A.: *Mater. Res. Bull.* 42, 666 (2006).
- Kazemi F., Sohrabi S., Malek-Ahmadi S., Rezaie H.R., Allah-Karam S.R.: *Proc. International Conference on Ultrafine Grained and Nanostructured Materials*, Center of Excellence for High Performance Materials School of Metallurgy and Materials Engineering University College of Engineering, University of Tehran, Nov. 17th-18th 2007.
- Lessing P.A.: *Am. Ceram. Soc. Bull.* 68, 1002 (1989).
- Wu Y., Bandyopadhyay A., Bose S.: *Mater. Sci. Tech.* A 380, 349 (2004).
- Koch C.C.: *Nanostructured materials, Processing, Properties and Potential Applications*, p. 45-64, William Andrew, New York 2002.
- Porter D.A., Easterling K.E.: *Phase Transformations in Metals and Alloys*, 2nd ed., p. 134-156, Chapman and Hall, London 1992.
- Johnson D.L.: *Solid State Sintering Models*, in: *Sintering Processes*, p. 97-106, MRS, Plenum Press, New York 1980.
- Rankin J., Sheldon B.W.: *Mater. Sci. Eng. A* 204, 48 (1995).
- Carim A.H.: *Microstructure in Nanocrystalline Zirconia Powders and Sintered Compacts*, in: *Nanophase Materials, Synthesis-Properties- Applications*, p. 283-286, Kluwer Academic Publication, Amsterdam 1994.
- Garvie R.C.: *J. Phys. Chem.* 82, 218 (1978).
- Dosev D., Guo B., Kennedy I.M.: *J. Aerosol Sci.* 37, 402 (2006).
- Benfer S., Knozinger E.: *J. Mater. Chem.* 9, 1203 (1999).
- Tok A.I.Y., Boey F.Y.C., Du S.W., Wong B.K.: *Mater. Sci. Eng. B* 130, 114 (2006).
- Baum S.J.: *Introduction to Organic and Biological Chemistry*, Macmillan Publishing Co., p. 280-284, New York 1978.
- Diniz da Costa J.C., Coombs S., *J. Sol-Gel Sci. Tech.* 31, 215 (2004).
- Roy S., Ghose J.: *Mater. Res. Bull.* 35, 1195 (2000).
- Ghosh A., Suri A.K., Pandey M., Thomas S., Rama Mohan T.R., Rao B.T.: *Mater. Lett.* 60, 1170 (2006).
- Lamas D.G., Rosso A.M., Suarez Anzorena M., Fernandez A., Bellino M.G., Cabezas M.D., Walsøe de Reça N.E., Craievich A.F.: *Scripta Mater.* 55, 553 (2006).