Preparation of High Surface Area ZrO_2 Nanoparticles

Alaei, Mahshad*+; Rashidi, Ali Morad; Bakhtiari, Iida

Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI), P.O. Box 14665-137 Tehran, I.R. IRAN

ABSTRACT: *In comparison to the previous researches, ZrO_2 nanoparticles with higher surface area (85 m^2/g) have been synthesized in this research. The as-prepared ZrO_2 nanoparticles by co-precipitation method were characterized with X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The surface area of the sample was characterized by BET method. The effect of the growth parameters such as temperature, pH, Zr^{4+}/template ratio and kind of template on the growth and morphology of ZrO_2 nanoparticles have been investigated in detail. The results revealed that pH, temperature, Zr^{4+}/template and kind of template have an important effect on the morphology and size of the ZrO_2 nanoparticles. X Ray Diffraction (XRD) analysis of the superior nanoparticles that was prepared at pH=4, Temperature=70 ^oC, Zr^{4+}/template ratio=2 and by sorbitol as template indicates the formation of nanocrystalline ZrO_2 tetragonal phase structure. The average particle size of the product is about 4.45 nm that was calculated from XRD pattern by the Debye-Scherrer formula.*

KEY WORDS: *Zirconium Oxide, Nanoparticles, Co-precipitation method.*

INTRODUCTION

Specific properties of ZrO_2 nanoparticles such as low thermal conductivity, high coefficient of thermal expansion, high thermal stability, high oxygen ion conductivity, high strength, high fracture toughness and high thermal shock resistance, enables it to be used as thermal barrier coating, cutting tools, refractory material, and catalyst support (stable under a reducing atmosphere and photo irradiation) [1-3]. ZrO_2 nanoparticles can be used in fuel cells, sensors, advanced ceramics, transparent and optical devices [4-7].

Increasing the specific surface area and enhancement of the crystallinity increases its specific properties [8]. We are successfully prepared ZrO_2 nanoparticles with higher surface area (85 m^2/g) in comparison to the previous researches. Different methods have been proposed by researchers for the synthesis of ZrO_2 nanostructures such as sol–gel [9], hydrothermal [10], sputtering [11], Chemical Vapor Deposition (CVD) [12] and electrical arc discharge [13]. Many of these methods results in amorphous structures but co-precipitation method that was used in this research, produces crystallized ZrO_2 nanoparticles. Besides, compared with other techniques, from point of economical view and simple procedure, co precipitation is an attractive method with high yield of nanoparticles and capability of scaling up for mass production.

In the present study, we report a simple and inexpensive synthesis route of ZrO_2 nanoparticles with higher surface area (85 m^2/g) in comparison to the previous researches by co-precipitation method. We have

* *To whom correspondence should be addressed.*
+ *E-mail: alaiem@ripi.ir*
1021-9986/14/2/47 7/$/2.70

Table 1: Experimental conditions for the synthesis of the ZrO_2 nanoparticles by co precipitation method.

Sample	Zr^{4+}/template molar ratio	Kind of template	pH	Temperature (°C)	Average particle size (nm)
NO. 1	0.9	Sorbitol	10	70	4.10
NO. 2	2	Sorbitol	10	70	6.59
NO. 3	2	Poly Ethylene Glycol (PEG 4000)	10	70	4.15
NO. 4	2	Sorbitol	10	80	7.16
NO. 5	2	Sorbitol	10	60	3.58
NO. 6	2	Sorbitol	7	70	5.15
NO. 7	2	Sorbitol	4	70	4.45
NO. 8	2	Urea	10	70	amorphous

studied the effect of different reaction parameters such as temperature, pH, kind of template and molar ratio of precursor and template on the product average particle size and morphology.

EXPERIMENTAL SECTION

Materials and Characterization

All chemicals such as $ZrCl_4$, polyethylene glycol 4000, Urea, sorbitol and ammonia were of analytical grade and used without further purification.

The sample was characterized by Scanning Electron Microscopy (SEM) using a Holland Phillips XL30 microscope. XRD patterns of the samples were recorded in ambient air using a Holland Philips X-ray powder diffraction (Cu Kα, λ=1.5406 Å), at scanning speed of 2°/min from 20° to 80°. TEM images of the samples are prepared by Philips Analytical equipment (200 kV). Surface area of the desired sample was determined by Belsorp adsorption–desorption (BEL Japan Inc.).

Preparation of ZrO_2 nanoparticles

An appropriate amount of $ZrCl_4$ was dissolved in 300 mL distilled water in order to form 0.06 M solution (Solution **A**). Different quantities of template (poly ethylene glycol 4000, urea and sorbitol) was added separately to the desired amount of ammonia solution and well mixed by stirring for 5 min. The as-prepared solution was added drop wise to the Solution **A** at room temperature under stirring. The mixture was heated to reaction temperature of 60, 70 or 80°C and kept for few minutes. Experiments were carried out in two molar ratios of Zr^{4+} source/template including 0.9, and 2 while the pH value was adjusted in 10 during the reaction time. As the reaction completed, the as-prepared white solid products were washed with distilled water and ethanol to remove the ions possibly remaining in the final products, and finally dried at 60°C. The product was calcined at 550 °C for 2h. To study the effect of other growth parameters on morphology and size of the ZrO_2 nanoparticles, reaction parameters such as kind of template, pH and temperature were tuned during the synthesis to obtain the desired size of nanoparticles that can be used for different applications.

RESULTS AND DISCUSSIONS

Effect of template and Zr^{4+}/template molar ratio

Table 1 depicts the experimental conditions studied to achieve a controllable growth of ZrO_2 nanoparticles by finding the most effective parameters. Different sizes of ZrO_2 nanoparticles were obtained through the influence of template. The average particle size of the products was calculated from XRD pattern by the Debye-Scherrer formula.

$$D = \frac{0.89\lambda}{(\beta \cos\theta)}$$

Where the λ is X-ray wavelength (0.1540 nm for Cu-K_α), β is the width at half maximum of the diffraction peak and θ is Bragg diffraction angle.

Poly ethylene glycol 4000 (PEG 4000), sorbitol and Urea were examined as template in the similar experimental conditions. It is also worth nothing that applying the sorbitol, decreases the cost of product. The surface morphology of ZrO_2 nanoparticles was evaluated

by SEM and TEM. Figs. 1 & 2 show X-ray diffraction patterns of all samples that were prepared in this research. Most of the diffraction peaks in the XRD patterns could be indexed to the tetragonal structure of ZrO_2 nanoparticles (79-1769 JPDS card).

The results indicate that the variation of template can alter the morphology and average particle size of ZrO_2 nanoparticles. The formation of ZrO_2 nanoparticles may be due to the creation of nuclei by the addition of template firstly [14]. Figs. 3 & 4 show Scanning Electron Microscopy (SEM) images of all samples that were prepared in this research. From the images, it can be seen that by using PEG 4000 and sorbitol as template, crystalline tetragonal ZrO_2 nanoparticles and by using urea amorphous ZrO_2 were obtained. We suppose that urea acted by different mechanism in this reaction. In aqueous solution, the following reaction will be happen.

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$$

Sorbitol and PEG 4000 have hydroxyl group and can form suitable complexes with Zr^{4+}(aq). On the other hand, SEM images indicate that agglomeration of the product nanoparticles will be observed by using PEG 4000 as template. It may be due the polymeric structure and high molecular weight of PEG 4000 that causes stereo stric problems. As a result, sorbitol was selected as the superior template in this reaction.

In order to investigate controllable growth of ZrO_2 nanoparticles, different Zr^{4+} source/template ratios were used, employing sorbitol as template. The ratios were 0.9 and 2. The SEM results showed that the growth of ZrO_2 nanoparticles will be more uniform and individual through tuning the ratio from 0.9 to 2 (Samples 1,2).

The effect of different ratios on the synthesis of nano products has been discussed in the other research. *Zhang et al.* [15] obtained a change in morphology of products as a result of different ratios.

Effect of reaction temperature

It is expected that by increasing the temperature reaction, the average particle size of the products will be increased [16]. SEM images that was presented in Figs. 3 & 4 emphasis this truth.

The possible reactions in an aqueous solution can be expressed as follows:

$$NH_3 + H_2O \rightleftarrows NH_3.H_2O \rightleftarrows NH_4^+ + HO^-$$

$$Zr^{4+} + 6\,NH_3 \rightleftarrows Zr(NH_3)_6^{4+}$$

$$Zr(NH_3)_6^{4+} + 4HO^- \rightleftarrows ZrO_2 + 6NH_3 + 2H_2O$$

$$Zr^{4+} + 6HO^- \rightleftarrows Zr(OH)_6^{2-}$$

$$Zr(OH)_6^{2-} \rightleftarrows ZrO_2 + 2H_2O + 2\,HO^-$$

$$ZrCl_4+C_6H_{14}O_6+15/2\,O_2 \rightarrow ZrO_2+2Cl_2+6CO_2+7H_2O$$

It can be seen that ZrO_2 nuclei are obtained by the dehydration of $Zr(OH)_6^{2-}$ or $Zr(NH_3)_6^{4+}$. It is expected that adsorption of ions on the substrate will play an important role in determining the particle size. For lower density of nuclei (higher temperature) the crystal grows larger in size before being blocked (the possibility of getting blocked is low), in comparison to the situation where a high density of nuclei (lower temperature) results in small crystals before being blocked. The higher density of nuclei enhances the possibility of a crystal to get blocked [18]. By increasing the temperature, bigger particles can be formed. In comparison to sample No. 2, sample No.4 reaction at higher and sample No.5 reaction at lower temperature were performed. As can be seen, by increasing the reaction temprature, the product particle size will be incresed and by decreasing the reaction temprature, the product particle size will be decreased.

Effect of pH

pH was found to be an important parameter affecting ZrO_2 nanoparticle synthesis.

Figs. 3 & 4 shows that the particles formed at pH=4 were predominantly spherical in shape, relatively uniform in size, with average particle size about 4.46 nm (sample No. 7). Nanoparticles synthesised at pH 7 (sample No. 6) and pH=10 (sample No. 2) have average particle size about 5.15 nm and 6.59 nm respectively. As a result by increasing the pH, the average particle size of products will be increased [17]. Addition of pH causes the formation of bigger aggregates because of the stable nuclei that was formed on the substrate during the reaction lead to the formation of a contacting crystal to which two or more crystals are associated at the higher pH value of the solution [18,19].

The further characterization of the samples is performed by TEM. Fig. 5 and Fig. 6 depict Transition Electron Microscopy (TEM) images of samples 2 and 7 with average particle size about 6.59 nm and 4.45 nm respectively in comparison to the previous researches with reported average particle sizes such as 20, 16.5, 26.5 nm [10,13,20].

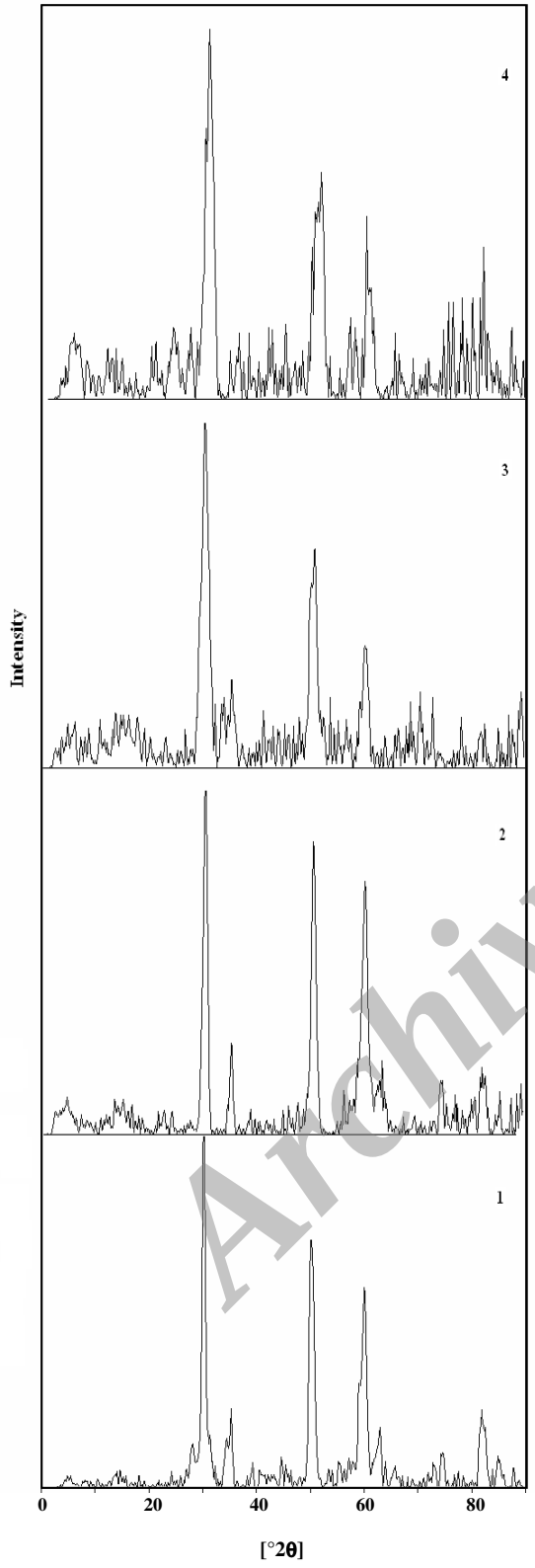

Fig. 1: XRD patterns of the as-prepared ZrO_2 nanoparticles (Samples 1,2,3,4).

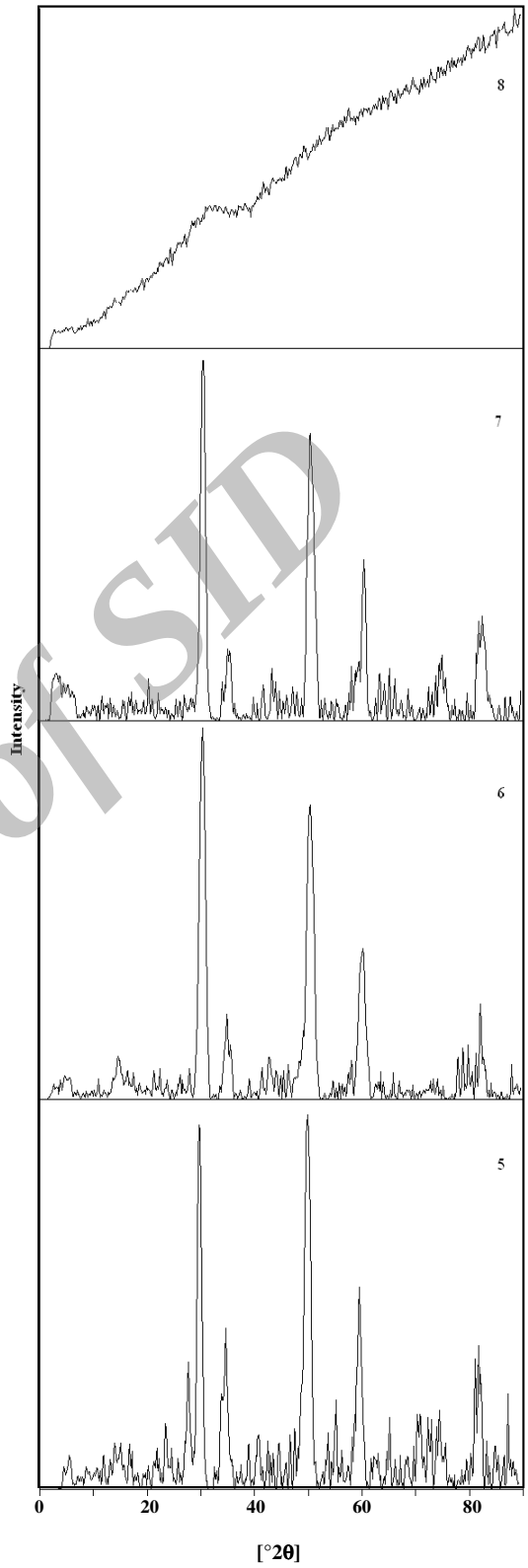

Fig. 2: XRD patterns of the as-prepared ZrO_2 nanoparticles (Samples 5,6,7,8).

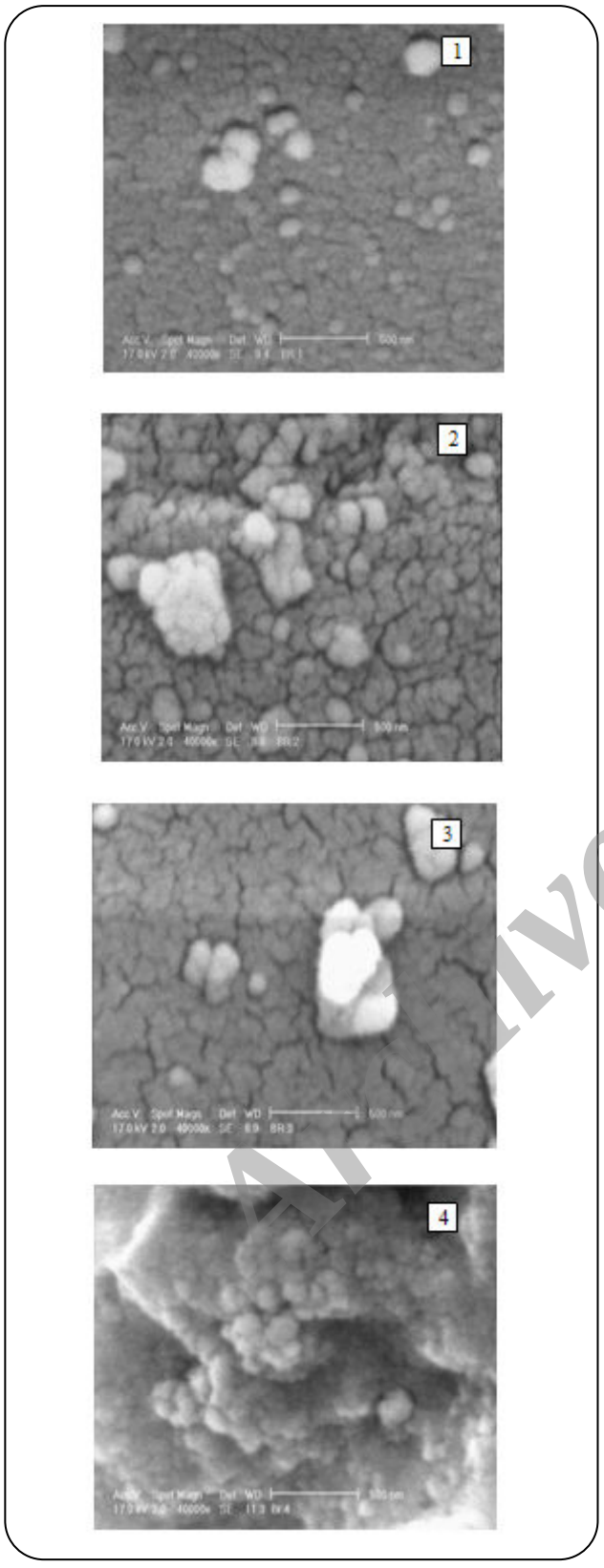

Fig. 3: SEM images of the as- prepared ZrO_2 nanoparticles (Samples 1,2,3,4).

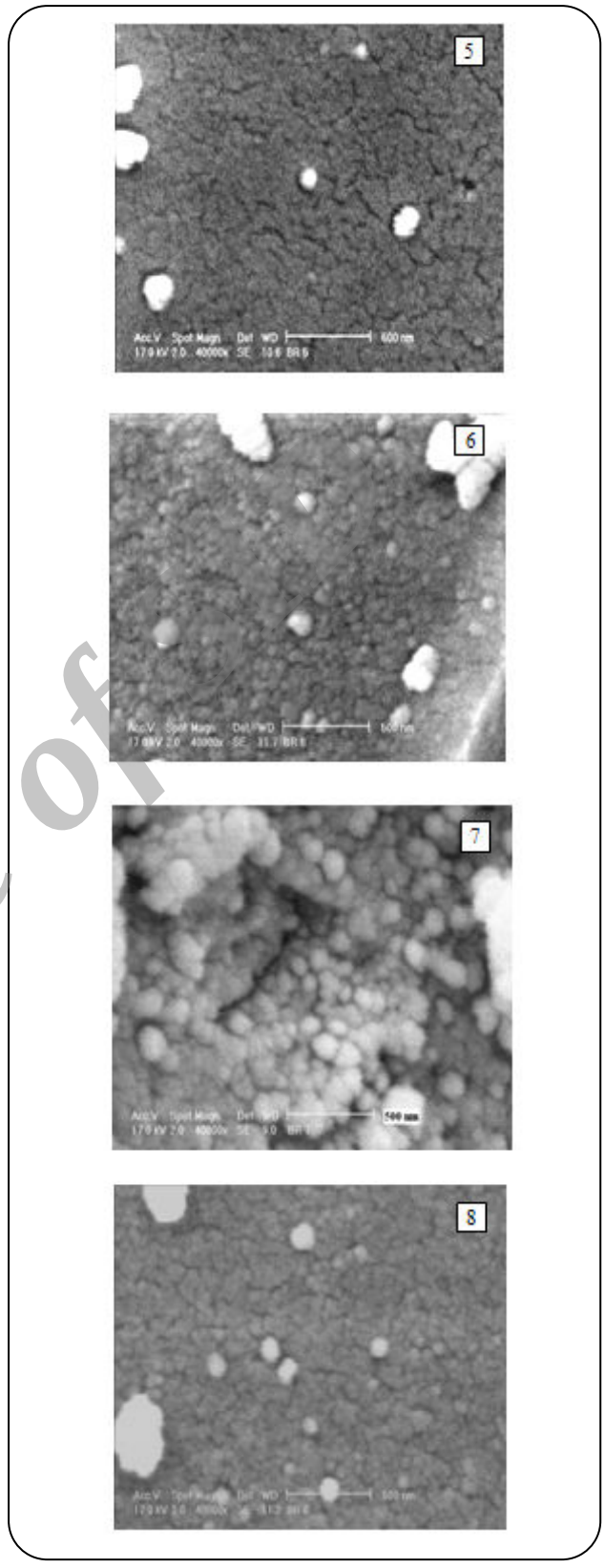

Fig. 4: SEM images of the as- prepared ZrO_2 nanoparticles (Samples 5,6,7,8).

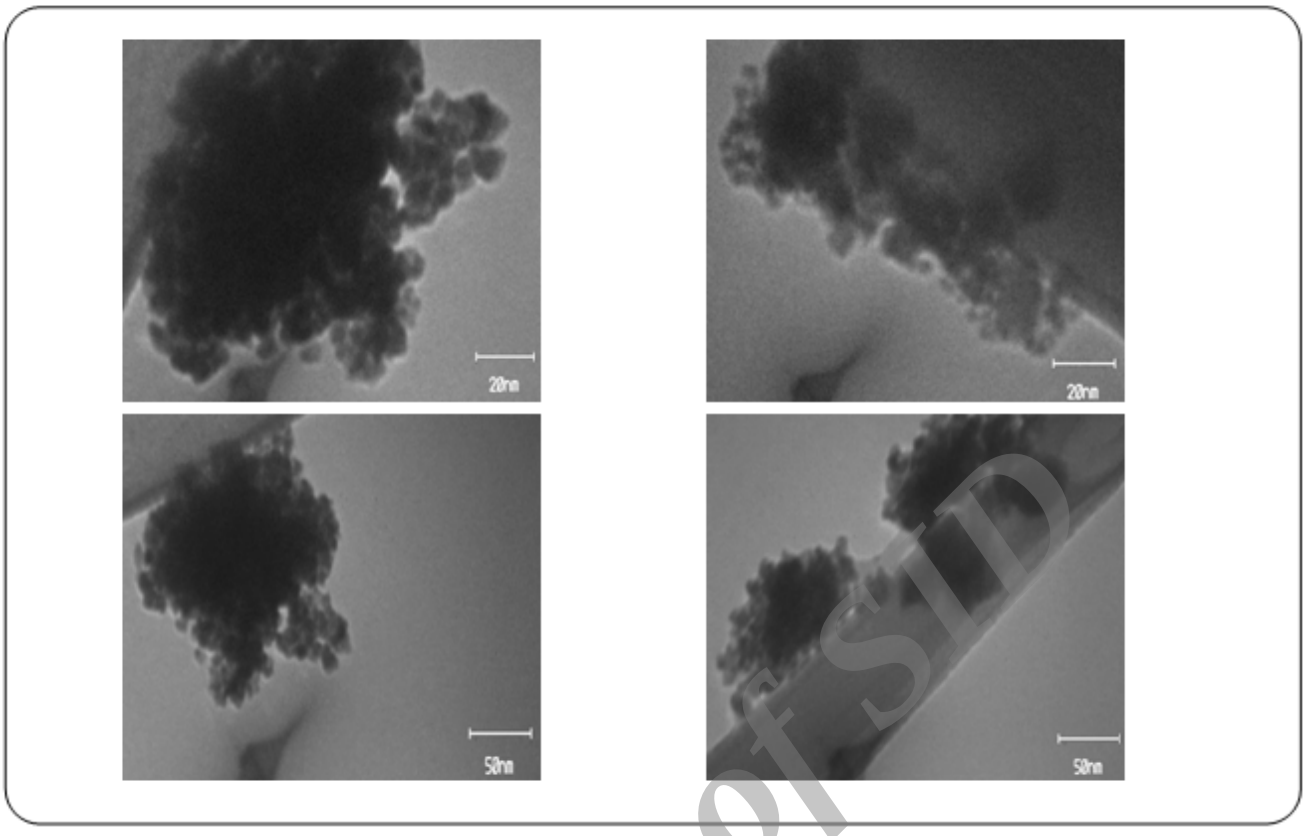

Fig. 5: TEM image of the as- prepared ZrO_2 nanoparticles (Sample 2).

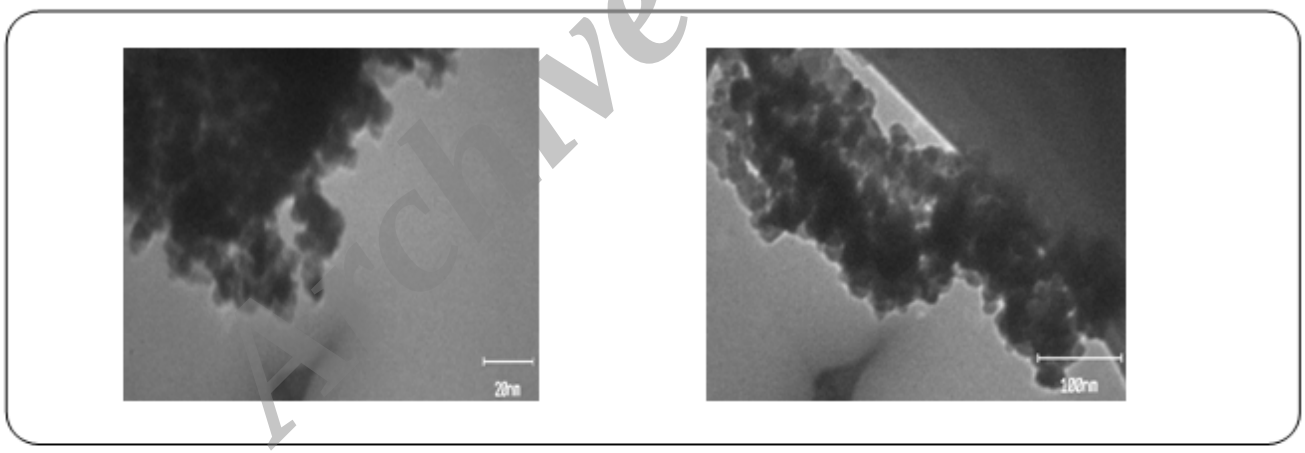

Fig. 6: TEM image of the as- prepared ZrO_2 nanoparticles (Sample 7).

These samples indicated better properties such as crystalline nanostructure with individual and distinct nanoparticles in comparison to the other samples. From the TEM images, it can be seen that the morphology of the sample 7 is better than the sample 2. This is logical result because the sample 7 was formed in lower pH.

CONCLUSIONS

In conclusion, a simple and economical method was successfully utilized for the synthesis of ZrO_2 nanoparticles, in which average particle size is 4.46 nm with higher surface area ($85 m^2/g$) in comparison to the previous similar researches. Effective reaction parameters were investigated in detail. Average particle size

of the product will increase at higher temperatures and pH. Among the three kind of selected templates, sorbitol is the best because of the formation of suitable complex structure with Zr^{4+}(aq.). By tuning of Zr^{4+}/template from 0.9 to 2, the morphology of the product will be better and more distinct and individual nanoparticles will be obtained.

Acknowledgement

This work was supported by Research Institute of Petroleum Industry (RIPI). The authors would like to express their thanks to the RIPI, Tehran, Iran for their financial support of this project.

Received : Oct. 3, 2011 ; Accepted : Mar. 9, 2014

REFERENCES

[1] Shukla S., Seal S., Int., Mechanisms of Room Temperature Tetragonal Phase Stabilization in Zirconia, *Mater. Rev.,* **50**(1): 45-64 (2005).

[2] Liang J., Jiang X., Liu G., Deng Z., Zhuang J., Li F., Li Y., Characterization and Synthesis of Pure ZrO_2 Nanopowders via Sonchemical Method, *Mater. Res. Bull.*, **38**: 161-168 (2003).

[3] Chandra N., Singh D.K., Sharma M., Upadhyay R.K., Amritphale S.S., Sanghi S.K., Synthesis and Characterization of Nano-Sized Zirconia Powder Synthesized by Single Emulsion-Assisted Direct Precipitation, *J. Colloid Interface Sci*., **342**: 327-332 (2010).

[4] Zhu B., Xia C.R., Luo X.G., Transparent Two-Phase Composite Oxide Thin Films with High Conductivity, *Thin Solid Films*, **385**: 209-214 (2001).

[5] Petrik N.G., Taylor D.P., Orlando T.M., Laser-Stimulated Luminescence of Yttria-Stabilized Cubic Zirconia Crystals, *J. Appl. Phys.*, **85**: 6770-6776 (1999).

[6] Bastianini A., Battiston G.A., Gerbasi R., Porchia M., Daolio S., Chemical Vapor Deposition of ZrO_2 Thin Films Using $Zr(NEt_2)_4$ as Precursor, *J. Phys. IV France 05*, **4**(5): C5-525-C_5-531 (1995).

[7] Corma A., Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions, *Chem. Rev*., **95**: 559 (1995).

[8] Tian G., Pan K., Fu H., Jing L., Zhou W., Enhanced Photocatalytic Activity of S-Doped TiO_2–ZrO_2 Nanoparticles Under Visible-Light Irradiation, *J. Hazard. Mater*., **166**: 939-944 (2009).

[9] Ehrhart G., Capoen B., Robbe O., Boy P., Turrell S., Bouazaoui M., Structural and Optical Properties of n Propoxide Sol Gel Derived ZrO_2 Thin Films, *Thin Solid Films*, **496**: 6-12 (2006).

[10] Torres-Huerta A.M., Dominguez-Crespo M.A., Ramirez-Meneses E., Vargas-Garcia J.R., MOCVD of Zrconium Oxide Thin Films: Synthesis and Characterization, *Appl. Surf. Sci.*, **255**: 4792-4795 (2009).

[11] Tahir M.N., Gorgishvili L., Li J., Gorelik T., Kolb U., Nasdala L., Tremel W., Facile Synthesis and Characterization of Monocrystalline Cubic ZrO_2 Nanoparticles, *Solid State Sci.*, **9**: 1105-1109 (2007).

[12] Rozo C., Jaque D., Fonseca L.F., Sole J.G., Luminescence of Rare Earth-Doped Si–ZrO_2 Co-Sputtered Films, *J. Lumin.*, **128**: 1197-1204 (2008).

[13] Ashkarran A.A., Ahmadi Afshar S.A., Aghigh S.M., Kavianipour M., Photocatalytic Activity of ZrO_2 Nanoparticles Prepared by Electrical Arc Discharge Method in Water, *Polyhedron*, **29**: 1370-1374 (2010).

[14] Habibi R., Towfighi Daryan J., Rashidi A.M., Shape and Size-Controlled Fabrication of ZnO Nanostructures Using Novel Templates, *Journal of Experimental Nanoscience*, **4**: 35-45 (2009).

[15] Zhang H., Feng J., Wang J., Zhang M., Preparation of ZnO Nanorods Through Wet Chemical Method, *Mater. Lett*., **61**: 5202-5205 (2007).

[16] Anandan K., Rajendran V., Size Controlled Synthesis of SnO_2 Nanoparticles: Facile Solvothermal Process, *Journal of Non-Oxide Glasses*, **2**: 81-89 (2010).

[17] Gericke M., Pinches A., Biological Synthesis of Metal Nanoparticles *Hydrometallurgy*, **83**: 132-140 (2006).

[18] Joshi R.K., pH and Temperature Dependence of Particle size in Pb1-xFexS Nanoparticle Films, *Solid State Commun*., **139**: 201-204 (2006).

[19] Salehi S., Ryukhtin V., Lukas P., Biest O.V., Vleugels J., Two-D Analysis of the Thermo-Mechanical Properties of ZrO_2-Based Composites, *International Journal of Chemo Informatics and Chemical Engineering,* **2**(1): 25-39 (2012).

[20] Ashkarran A.A., Aghigh S.M., Ahmadi Afshar S.A., Kavianipour M., Ghoranneviss M., Synthesis and Characterization of ZrO_2 Nanoparticles by Arc Discharge Method in Water, *Metal-Organic, and Nano-Metal Chemistry*, **41**: 425-428 (2011).