Synthesis of ZnO Nanoparticles by Spray Pyrolysis Method

Ghaffarian, Hamid Reza; Saiedi, Mahboobeh; Sayyadnejad, Mohammad Ali*[+]

Chemistry & Petrochemical Division, Research Institute of Petroleum Industry (RIPI),
P.O. Box 14665-137 Tehran, I.R. IRAN

Rashidi, Ali Morad

Gas Division, Research Institute of Petroleum Industry (RIPI), I.R. IRAN

ABSTRACT: *Zinc oxide (ZnO) nanoparticles were synthesized by spray pyrolysis method using an aqueous solution of zinc acetate at various concentrations from 5 to 25 wt%. The decomposition of precursor solutions was carried out at 800, 1000 and 1200ºC under different atomizing pressures. The crystal structure and morphology of synthesized nanoparticles were characterized by X-Ray Diffraction (XRD) spectrometry and Transmission Electron Microscopy (TEM), which indicated that ZnO nanoparticles were of hexagonal wurtzite structure. The XRD, TEM and BET analyses of prepared ZnO powders with concentrations of 5-20 wt% showed that the crystallite size diameter and specific surface area of particles were in the range of 10-25 nm and 44-56 m^2/g, respectively. It was found that impurity and unreacted zinc acetate appeared in the product with increase of precursor solution concentration beyond 20wt%.*

KEY WORDS: *ZnO, Spray pyrolysis, Nanoparticles, Specific surface area.*

INTRODUCTION

In recent years, nano zinc oxide has found wide ranging applications in various areas due to its unique and superior physical and chemical properties compared with bulk ZnO. The large specific surface area, high pore volume, nanostructured properties, low cost and low toxicity of nano ZnO [1] make it a promising candidate particularly in catalysts [2], chemical absorbents [3], polymer filler and additives [4], antiwear additives in oil lubricants [5] and advanced ceramics [6]. Zinc oxide nanoparticles have optical, electrical and photochemical activity [7], which can be used in photocatalysts [8], solar energy conversion cells [9,10], Ultra Violet (UV) detectors and UV emitting devices [11], chemical sensors sensitive to chemicals such as alcohol and benzene [12], and gas sensing materials for many sorts of gases such as ammonia, hydrogen and ozone [13-15]. Some researches have shown the performance of ZnO nanoparticles in degradation of some organic compounds [16], antibacterial effect [17] and killing human cancer cells [18].

Various chemical synthesis methods such as sol-gel [19], solvothermal [20], and microemulsion [21], and physical methods including chemical vapor deposition [22], thermal decomposition of organometallic precursors [23], arc plasma [24], laser ablation [25], and levitation gas condensation [26], have been used in preparation of ZnO nanoparticles. Physical methods are often advantageous compared to chemical ones, since such methods do not require some steps of wet chemistry such

* *To whom correspondence should be addressed.*
+ *E-mail: sayyadnejadma@ripi.ir*
1021-9986/11/1/ 6/$/2.60

as washing, drying and calcination and they can produce higher purity particles [27].

Spray pyrolysis is a physical method, which is relatively simple, reproducible, size controllable, low cost and continuous for synthesis of some nano metal oxides, mixed metal oxides and metals on metal oxides [28]. Powders prepared by this method, compared with those from wet chemical ones, are more crystalline, less agglomerated with higher purity and also have large specific surface areas [29]. Metal acetate, chloride and nitrate precursor solutions are used to synthesize metal oxides nanoparticles by spray pyrolysis methods [28]. Since the latter two compounds produce acid gases, which are environmental pollutants and corrosive, metal acetate is preferred. Furthermore, metal acetate precursors produce fine-grained, high specific surface area and aggregate-free powders due to their exothermic decomposition in the reaction whereas nitrate precursors produce strongly aggregated powders [30]. Many workers have applied zinc acetate for synthesis of ZnO nanoparticles [8,12,19,31,32]. In this research, spray pyrolysis method using zinc acetate and a tubular reactor were applied to synthesize ZnO nanoparticles and the effects of different parameters, concentration of starting material, temperature and atomizing pressure on the particle size diameter were investigated.

EXPERIMENTAL SECTION

Starting materials

Zinc acetate dehydrate (Zn $(CH_3COO)_2 2H_2O$) with purity of 99.5% was purchased from Aldrich Chemical Company. The precursor solutions were prepared from above zinc acetate and distilled water. A few drops of glacial acetic acid were then added to stabilize the solution. To obtain the optimal concentration of starting material, the concentration of zinc acetate in precursor solution was chosen to be 5, 15, 20 and 25 wt%. Dry air was used as the carrier gas for carrying precursor solutions into the nebulizer and also supplying the required pressure for atomizing the solutions. Bulk zinc oxide with a purity of 99.5% was purchased from Pars Company (Iran).

Apparatus

Fig.1 shows a convenient system, which was assembled in our investigation for preparation of size controlled ZnO nanoparticles by spray pyrolysis method.

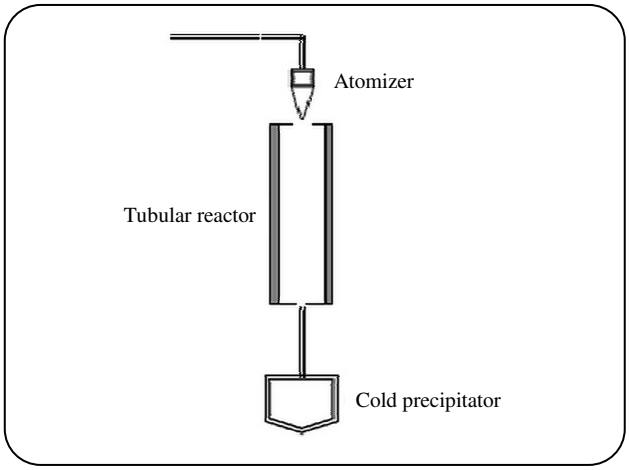

Fig. 1: Schematic illustration of spray pyrolysis apparatus used for synthesis of zinc oxide nanoparticles.

This system consists of three main parts: (1) a twin fluid nebulizer, which atomizes the precursor solutions and converts them to droplets, (2) a vertical tubular reactor (length: 130 cm, diameter: 5 cm) with controllable temperature zones from 200ºC to 1200ºC, and (3) a precipitator to collect prepared nanoparticles.

A Phillips PW 1840 x-ray diffractometer with Cu-Kα radiation source in the range of 20º to 80º was used to determine the crystal phase and crystallite size analysis of prepared particles. A Bruker AT-210 transmission electron microscope was applied to investigate morphology of synthesized nano size samples. A Bruker IFS 88 Fourier Transform Infrared spectrophotometer (FT-IR) was employed for identification of unreacted compounds in the ZnO nanoparticles. The Specific Surface Area (SSA) of nano samples were measured by N_2 adsorption method using Brunauer-Emmet-Teller (BET) technique.

Synthesis

To synthesize ZnO nanoparticles, at first the precursor solution was atomized by nebulizer under the pressure of air (7 bar). The droplets decomposed inside the reactor, where the temperature was 1200ºC. The obtained nanoparticle product was collected into the cold precipitator and dried in an oven at 100ºC. Unreacted zinc acetate present in the product can be removed by washing the nanoparticles with water.

Four samples with concentrations of 5,15,20 and 25 wt% zinc acetate were synthesized at 1200ºC and designated ZnO-5, ZnO-15, ZnO-20 and ZnO-25, respectively.

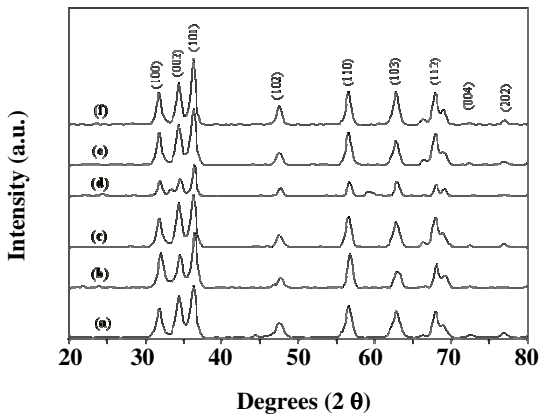

Fig. 2: XRD patterns of synthesized samples: (a) ZnO-5, (b) ZnO-15, (c) ZnO-20, (d) ZnO-25, (e) ZnO-20a, (f) ZnO-20b.

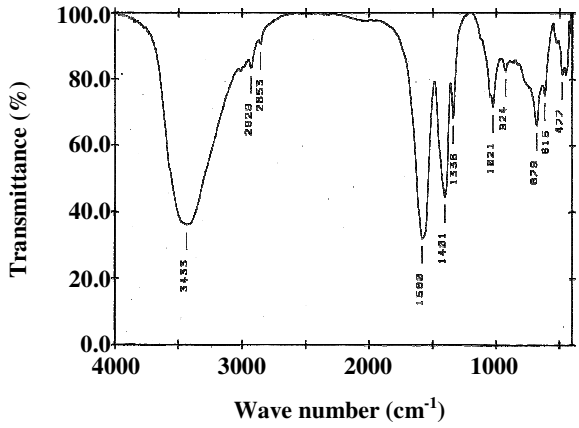

Fig. 3: FT-IR spectrum of extracted zinc acetate from ZnO-25.

Two samples were also synthesized with 20 wt% concentration of zinc acetate at 1000ºC under atomizing pressure of 7 and 4 bar and designated ZnO-20a and ZnO-20b, respectively.

RESULTS AND DISCUSSION

Figs. 2(a)-(d) show the XRD patterns of ZnO nanoparticles, synthesized using different concentrations of starting materials at 1200ºC. Figure 2(e) and 2(f) represent the XRD patterns for samples ZnO-20a and ZnO-20b prepared using 20wt% zinc acetate as a precursor solution at 1000ºC under the atomizing pressure of 7 and 4 bar, respectively.

Diffraction peaks of all samples except ZnO-25 can be well indexed to the hexagonal wurtzite structure of ZnO reported in international center diffraction data (JCPDS 36-1451) and no peaks from other phase of zinc oxide and impurities were detected, which indicated that pure products were formed. Peaks at 2θ: 33.2 and 59.6 in XRD patterns of sample ZnO-25 in Figure 2(d) correspond to impurity. In addition, FT-IR analysis of ZnO-25 indicated the presence of unreacted zinc acetate in the sample. Therefore, extraction of zinc acetate was carried out with distilled water. The solvent was evaporated and the sample was then dried in an oven at 100ºC. Fig.3 shows the FT-IR spectrum of obtained sample from ZnO-25. The absorption broad bands at 1580 and 1401 cm^{-1} in the spectrum are due to asymmetric and symmetric stretching vibrations of carbonyl group (COO-Zn) in the zinc acetate, respectively. In spray pyrolysis method, the reaction temperature, concentration and residence time of precursor solutions inside the reactor are the most important parameters, which can affect size and morphology of nanoparticles as well as the purity of product. It seems that the atomized droplets of sample ZnO-25 do not decompose in the core of reactor because of their high concentrations, which do not allow heat from hot walls of the reactor to reach the droplets. Therefore, the zinc acetate of these droplets remains in the product as the impurity.

The ZnO crystallite diameter size D was calculated using the Debye-Sherrer formula $D=K\lambda/\beta\cos\theta$, where K is Sherrer constant, λ is the x-ray wavelength (1.54 Å), ß is full width at half-maximum of the peak, and θ is the Bragg diffraction angle. The particles size and Specific Surface Area (SSA) of nano ZnO samples and bulk ZnO are shown in Table 1.

As shown in Table 1, the prepared ZnO nanoparticles with concentrations in the range of 5-20 wt% at 1200ºC have 14.3-17.1 nm diameter size and 50-56 m^2/g specific surface area range. Comparing the obtained results for samples ZnO-5, ZnO-15 and ZnO-20 in Table 1 exhibited that the 20wt% is the optimal zinc acetate concentration for synthesis of nano ZnO at 1200ºC in spray pyrolysis method. To lower energy consumption, the experiment with this concentration was also carried out at 800 and 1000ºC under the atomizing pressure of 7 and 4 bar. It was observed that when the reaction temperature decreased from 1200ºC to 1000ºC at atomizing pressure of 7 bar, the diameters of obtained nanoparticles decreased from 17.1 to 10.0 nm and when the atomizing pressure of solution decreased from 7 to 4 bar,

Table 1: Diameter size and BET specific surface area of different ZnO nano particles.

Sample	Zinc acetate concentration wt%	Reactor T(°C)	Atomizing pressure (bar)	Crystal size (nm)	BET-SSA(m^2/g)
ZnO-5	5	1200	7	14.3	56
ZnO-15	15	1200	7	15.3	51
ZnO-20	20	1200	7	17.1	50
ZnO-20a	20	1000	7	10.0	54
ZnO-20b	20	1000	4	25.1	44
Bulk ZnO	-	-	-	243.0	5

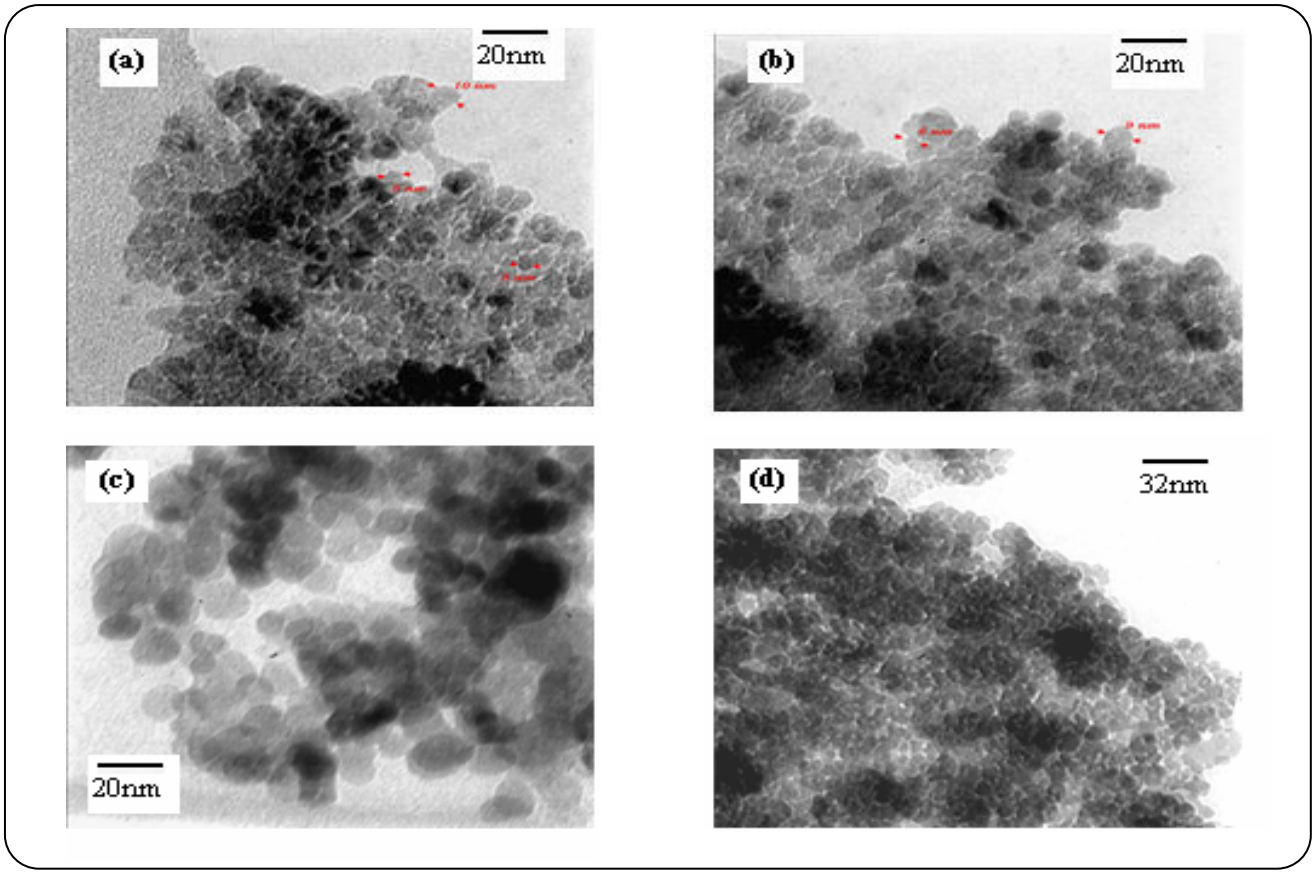

Fig. 4: TEM images of synthesized samples: (a) ZnO-5, (b) ZnO-15, (c) ZnO-20, (d) ZnO-20a.

the diameters of particles increased from 10.0 to 25.1 nm (Table 1). Increasing the heating temperature increases the diameters of particles because of the higher growth of ZnO crystals at higher temperature. Decreasing the atomizing pressure increases the droplet diameter, which results in increasing particles diameter. FT-IR analysis of powder synthesized at 800°C showed the presence of too much unreacted zinc acetate in the sample, which indicated that the heat from hot walls of reactor is not sufficient to decompose zinc acetate inside the droplets.

Figs. 4(a)-(d) show typical TEM images of samples ZnO-5, ZnO-15, ZnO-20 and ZnO-20a, respectively. As shown in Fig. 4, the ZnO nanoparticles size of all samples is less than 20nm, which is in agreement with those of ZnO diameter size calculated from the XRD diffraction peaks (Table 1).

To investigate the performance of prepared nanoparticles, they were used for removal of hydrogen sulfide (H_2S) in water based drilling mud and their performances were compared with those of bulk ZnO.

Zinc oxide nanoparticles were completely capable of removing H_2S from mud in just 15 minutes, whereas bulk zinc oxide could remove 2.5% of H_2S in as long as 90 minutes under the same conditions. Details have been fully described elsewhere [3].

CONCLUSIONS

Spray pyrolysis, which is a simple, size controllable and continuous method, was used to synthesize ZnO nanoparticles. Obtained results from XRD data show that all nano powders prepared with concentrations of 5-20 wt% zinc acetate at 1000 and 1200ºC have wurtzite hexagonal phase without any impurity. FT-IR analysis of obtained powder from precursor solution containing 25wt% zinc acetate reveals that increasing precursor solution concentration beyond 20wt%, results in an impurity and unreacted zinc acetate in the products. It was observed that the decrease in reaction temperature from 1200 to 1000ºC decreased the crystallite diameter size from 17.1 to 10.0 nm and with decreasing the atomizing pressure of precursor solution, increased crystallite size. The higher particle size at lower atomizing pressure can be explained by increasing the droplet size produced in atomizer, which results in increasing particles diameter.

Received : Jan. 13, 2009 ; Accepted : Jun. 29, 2010

REFERENCES

[1] Franklin N.M., Rogers N.J., Apte S.C., Batley G.E., Gadd G.E., Casey P.S., Comparative Toxicity of Nanoparticulate ZnO, Bulk ZnO, and $ZnCl_2$ to a Fresh Water Microalgae; *Pseudokirchneriella Subcapitata*: The Importance of Particle Solubility, *Environ .Sci. Tech.*, **41,** p. 8487 (2007).

[2] Jung H., Choi H., Catalytic Decomposition of Ozone and Para-Chlorobenzoic Acid (p CBA) in the Presence of Nanosized ZnO, *Appl. Catal. B*, **66,** p. 288 (2006).

[3] Sayyadnejad M.A., Ghaffarian H.R., Saeidi M., Removal of Hydrogen Sulfide by Zinc Oxide Nanoparticles in Drilling Fluid, *Int. J. Environ. Sci.Tech.*, **5**, p. 565 (2008).

[4] Carrion F.G., Sanes J., Bermudez M.D., Influence of ZnO Nanoparticle Filler on the Properties and Wear Resistance of Polycarbonate, *Wear,* **262,** p. 1504 (2007).

[5] Hernandez Battez H, Gonzalez R., Viesca J.L., Fernandez J.E., Dlaz Fernandez J.M., Machado A., Chou R., Riba J., CuO, ZrO_2 and ZnO Nanoparticle as Antiwear Additive in Oil Lubricants, *Wear,* **265,** p. 422 (2008).

[6] Rao K.J., Mahesh K., Kumar S., A Strategic Approach for Preparation of Oxide Namomaterials, *Bull. Mater. Sci.,* **28,** p. 19 (2005).

[7] Kumpika T., Thongsuwan W., Singjai P., Optical and Electrical Properties of ZnO Nanoparticle Thin Films Deposited on Quartz by Sparking Process, *Thin solid Films*, **516,** p. 5640 (2008).

[8] Park S.B., Kang Y.C., Photocatalytic Activity of Nanometer Size ZnO Particles Prepared by Spray Pyrolysis, *J. Aerosol Sci.,* **28,** p. S473 (1997).

[9] Rao A.R., Dutta V., Achivement of 4.7% Conversion Efficiency in ZnO Dye Sensitized Solar Cells Fabricated by Spray Deposition Using Hydrothermally Synthesized Nanoparticles, *Nanotechnology*, **19**, p. 445712 (2008).

[10] Wei D., Unalan H.E., Han D., Zhang Q., Niu L., Amaratunga G., Ryhanen T., A Solid-State Dye-Sensitized Solar Cell Based on a Novel Ionic Liquid Gel and ZnO Nanoparticles on a Flexible Polymer Substrate, *Nanotechnology*, **19,** p. 424006 (2008).

[11] Carrey J., Carrere H., Khan M.L., Chaudret B., Marie X., Respaud M., Photoconductivity of Self-Assembled ZnO Nanoparticles Synthesized by Organometallic Chemistry, *Semicond. Sci. Technol.*, **23,** p. 025003 (2008).

[12] Ge C., Xie C., Hu M., Gui Y., Bai Z., Zeng D., Structural Characteristics and UV-Light Enhanced Gas Sensitivity of La-Doped ZnO Nanoparticles, *Mater. Sci. Eng. B*, **141**, p. 43 (2007).

[13] Rout C.S., Hegde M., Govindaraj A., Rao C.N.R., Ammonia Sensors Based on Metal Oxide Nanostructures, *Nanotechnology*, **18,** p. 205504 (2007).

[14] Rout C.S., Raju A.R., Govindaraj A., Rao C.N.R., Hydrogen Sensors Based on ZnO Nanoparticles, *Solid State Commun,* **138**, p. 136 (2006).

[15] Kenanakis G., Vernardou D., Koudoumas E., Kiriakidis G., Katsarakis N., Ozone Sensing Properties of ZnO Nanostructure Grown by the Aqueous Chemical Growth Technique, *Sens. Actuators B*, **124**, p. 187 (2007).

[16] Wang H., Xie C., Zhang W., Cai S., Yang Z., Gui Y., Comparison of Dye Degradation Efficiency Using ZnO Powders with Various Size Scales, *J. Hazard. Mater.*, **141**, p. 645 (2007).

[17] Padmavathy N., Vijayaraghavan R., Enhanced Bioactivity of ZnO Nanoparticles-an Antimicrobial Study, *Sci. Technol. Adv. Mater.*, **9,** p. 035004 (2008).

[18] Hanley C., Layne J., Pannoose A., Reddy K.M., Coombs I., Feris K., Wingett D., Preferential Killing of Cancer Cells and Activated Human T Cells Using ZnO Nanoparticles, *Nanotechnology*, **19,** p. 295103 (2008).

[19] Kaur R., Singh A.V., Sehrawat K., Mehra N.C., Mehra R.M., Sol-Gel Derived Yttrium Doped ZnO Nanostructures, *J. Non-Crystalline Solids*, **352,** p. 2565 (2006).

[20] Tonto P., Mekasuwandumrong O., Phatanasri S., Pavarajarn V., Praserthdam P., Preparation of ZnO Nanorod by Solvothermal Reaction of Zinc Acetate in Various Alcohols و *Ceram. Int.,* **34**, p. 57 (2008).

[21] Singhal M., Chhabra V., Kang P., Shah D.O., Synthesis of ZnO Nanoparticles for Varistors Application Using Zn-Substituted Aerosol of Microemulsion, *Mater. Res. Bull.,* **32,** p. 239 (1997).

[22] Guan Y.F., Pedraza A.J., Synthesis and Alignment of Zn and ZnO Nanoparticles by Laser-Assisted Chemical Vapor Deposition, *Nanotechnology*, **19,** p. 045609 (2008).

[23] Rataboul F., Nayral C., Casanove M.J., Maisonnat A., Chaudret B., Synthesis and Characterization of Monodisperse Zinc and Zinc Oxide Nanoparticles From the Organometallic Precursor $[Zn(C_6H_{11})_2]$., *J. Organomet. Chem.*, **643,** p. 307 (2002).

[24] Shoushtari M.Z., Parhoodeh S., Farbod M., Fabrication and Characterization of Zinc Oxide Nanoparticles by DC Arc Plasma, *J. Phys.: Conf. Ser.*, **100,** p. 052017 (2008).

[25] Sakai K., Oyama S., Noguchi K., Fukuyama A., Ikari T., Okada T., Optical Properties of Nanostructured ZnO Crystal Synthesized by Pulsed-Laser Ablation, *Physica E,* **40,** p. 2489 (2008).

[26] Uhm Y.R., Han B.S., Lee M.K., Hong S.J., Rhee C.K., Synthesis and Characterization of Nanoparticles of ZnO by Levitational Gas Condensation, *Mater. Sci. Eng. A*, **49,** p. 813 (2007).

[27] Madler L., Liquid-Fed Aerosol Reactors for One-Step Synthesis of Nano-Structure Particles, *KONA*, **22,** p. 107 (2004).

[28] Okuyama K., Lenggoro I.W., Preparation of Nanoparticles via Spray Route, *Chem. Eng. Sci.*, **58,** p. 537 (2003).

[29] Kodas T.T., Hampden-Smith M.J., "Aerosol Processing of Materials", 1st ed., New York, Wiley-VCH (1999).

[30] Gardner T.T., Messing G.L., Preparation of MgO Powder by Evaporative Decomposition of Solution, *Am. Ceram. Soc. Bull.*, **63,** p. 1498 (1984).

[31] Shen L., Bao N., Yanagisawa K., Domen K., Gupta A., Grimes C.A., Direct Synthesis of ZnO Nanoparticles by a Solution-Free Mechanochemical Reaction, *Nanotechnology*, **17**, p. 5117 (2006).

[32] Hong R., Pan T., Qian J., Li H., Synthesis and Surface Modification of ZnO Nanoparticles, *Chem. Eng. J.*, **119,** p. 71 (2006).