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Size and Shape Tailoring of ZnO Nanoparticles

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Abstract. ZnO nanoparticles were successfully synthesized via the co-precipitation method using zinc nitrate and sodium hydroxide as raw materials. Size and shape of ZnO nanoparticles were well controlled by varying the ratio of sodium hydroxide solutions (0.5-0.9 mole) and the synthesized temperatures (65, 75 and 85 °C). ZnO nanoparticles exhibited a high degree crystallinity with wurtzite hexagonal structure for all conditions carried out using SEM, XRD, EDS and Raman. It was clearly observed that both sodium hydroxide solution and synthesized temperatures strongly affected on the size and shape of ZnO nanoparticles. The smallest ZnO nanoparticle was observed to be 47 nm with 0.7 mole of sodium hydroxide solution at 75 °C. Uniformed ZnO nanoparticles were obtained at synthesized temperatures above 65 °C. Optical properties of ZnO nanoparticles were also studied and carried out as absorbance spectra. In addition, optical energy band gap of ZnO nanoparticles was in the range of 3.24-3.35 eV.

Introduction

Due to their significant electrical and optical properties, a requirement for the development of nanocrystals semiconducting materials is rising. These noteworthy properties are greatly useful for invention the electronic devices. Owing to their unique and advantage properties of ZnO n-type oxide semiconductor nanocrystals; a very small in size, high surface-to-volume ratio, non-toxic and environmental friendly, it has been used in widely applications such as a gas sensor device [1], dye-sensitized solar cell [2], UV detector [3] and optoelectronic devices [4]. These potentially devices were currently found in commercial market. Many synthesized techniques have been developed for achieved the ZnO nanocrystals. Consequently, variety shapes of ZnO nanocrystals so-called nanowires, nanorings, nanobelts, nanorods, nanotetrapods, nanosheets and nanoparticles were obtained. These unique nanocrystals showed promising properties as report earlier [5-7]. However, ZnO nanoparticles (*ZNPs*) have some advantage over other nanocrystals shape. N. Yamazoe and K. Shimanoe reported that a sphere-like nanocrystals (nanoparticles) exhibited higher gas sensing response over plate-like (nanorods) and also column-like (nanosheets) [6]. This useful evident could be applied for the development of UV detector and dye-sensitized solar cell applications.

In this work, *ZNPs* were synthesized via co-precipitation technique since it is a low-cost, no advance apparatus needed and simply technique [8, 9]. The effect of synthesized temperatures and ratio of starting materials on growth of *ZNPs* were carried out.

Experimental

ZNPs were successfully synthesized via the co-precipitation method using zinc nitrate ($Zn(NO_3)_2$, 99.9% Sigma-Aldrich) and sodium hydroxide (NaOH, 97% Sigma-Aldrich) as raw

materials. Using distilled water (DI) as the solvent, 0.1 M $Zn(NO_3)_2$ solution (500 ml, 15 sets) and 2 M NaOH solution (500 ml) were separately prepared. $Zn(NO_3)_2$ solution was stirred at desired temperatures (65, 75 and 85 °C) for 20 min in glass container. Then, amount of NaOH solution was slowly added drop-wise into a mixed container and successively stirred for 20 min. The mole ratio between $Zn(NO_3)_2$ and NaOH solutions was set to be 1:0.5, 1:0.6, 1:0.7, 1:0.8 and 1:0.9. After that, the mixed solution was allowed to cool down naturally in air and precipitated for 24 h. The white product on the bottom of the container was collected, washed by DI water for 4 times, dried in the air for 24 h and following by annealed at 600 °C for 6 h under air atmosphere to receive *ZNPs*.

ZNPs were characterized using scanning electron microscope (SEM), energy dispersive X-ray spectrometer (EDS), X-ray diffractometer (XRD), Raman spectrometer (Raman) and UV-Vis spectrophotometer (UV-Vis).

Results and Discussion

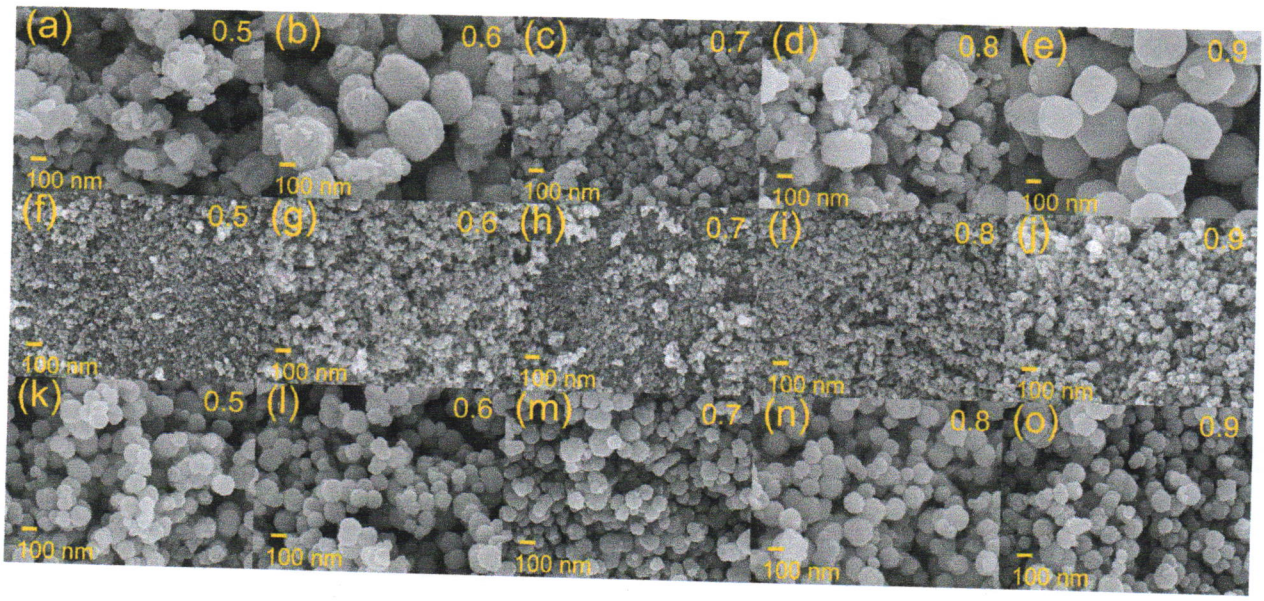

Fig. 1 SEM images of *ZNPs* synthesized at 65 °C (a-e), 75 °C (f-j) and 85 °C (k-o).

Fig. 1 showed SEM images of *ZNPs* synthesized from different NaOH contents; (a-e) for 65 °C, (f-j) for 75 °C and (k-o) for 85 °C. It was observed that the *ZNPs* greatly affected by both temperatures and NaOH contents, and the best condition was observed at 75 °C. Smallest *ZNPs* was obtained with 0.7 mole of NaOH solution for all synthesized temperatures; 115.2, 47.0 and 172 nm for 65, 75 and 85 °C, respectively. At 65 °C, it was clearly seen that synthesized *ZNPs* were not uniformed. Particle size increased from 158.2 nm (Fig. 1(a)) to 202.1 nm (Fig. 1(b)) and, then, dereased to 115.2 nm (Fig. 1(c)) with the increasing of NaOH contents. After that, particle size increased. It should be noted that macaron-like *ZNPs* were clearly observed in Fig. 1(b) and Fig. 1(e). The similar tendency was also observed at 85°C; 159.9, 186.3, 172.1, 210.1 and 235.1 nm for 0.5-0.9 mole NaOH solutions as displayed in Fig. 1(k-o). The average *ZNPs* size was shown in Fig. 2(a), 65 > 85 > 75 °C. Chemical composition of *ZNPs* was investigated, and Zn and O atom were detected in EDS data confirmed that synthesized products were *ZNPs* with the mole ratio about 1.

XRD spectra of *ZNPs* synthesized at 75 °C was demonstrated in Fig. 2(b). Those peaks in the spectra were corresponding to (100), (002), (101), (102), (110), (103), (200), (112) and (201) diffraction planes in accodance with International Centre for Diffraction Data (79-0206). No impurities peaks were detected in the XRD spectra. All samples exhibited similar peaks patterns and showed a high degree crystallinity with a pure hexagonal wurtzite structure. Average crystallite size was in the same trendency with average size that shown Fig. 2(a). In addition, a lattice parameter c of *ZNPs* was presented in Fig. 3(a), decresing with the rise of NaOH contents; however, it increased

at the highest NaOH contents for 65 and 85 °C. This result was in contrast with at 75 °C. The change of the lattice parameter c corresponded to a shift of (002) peak as presented in Fig. 3(b) and Fig. 3(c). The higher the shift degree the more contract the lattice parameter c.

Crystal defect was investigated using Raman technique. Vibration modes observing in the spectra were corresponded to $E_2(H)$-$E_2(L)$ ~332 cm^{-1}, $A_1(TO)$ ~388 cm^{-1}, $E_1(TO)$ ~412 cm^{-1}, $E_2(H)$ ~438 cm^{-1}, $A_1(LO)$ ~533 cm^{-1} and $E_1(LO)$ ~585 cm^{-1}, respectively (not shown). No defect or other impurities peaks were detected in the spectra. This result confirmed that *ZNPs* were a high degree crystallinity

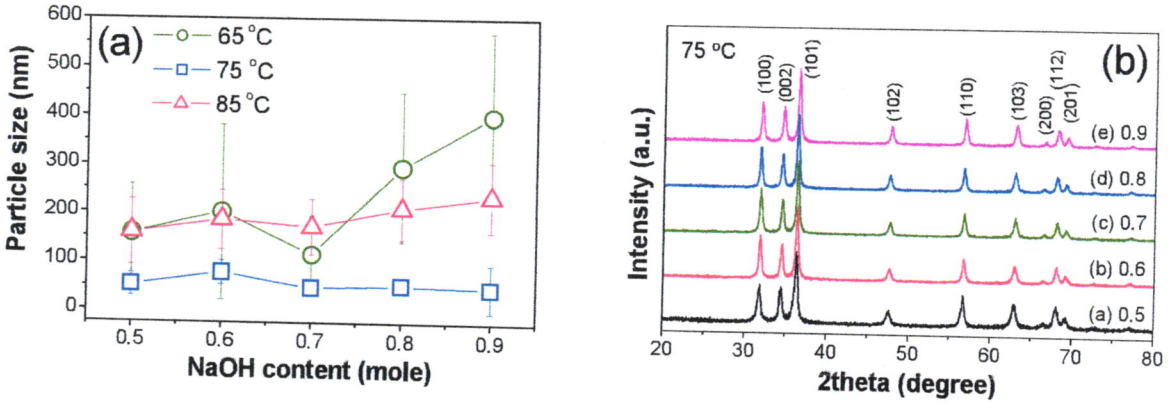

Fig. 2 (a) average *ZNPs* size and (b) XRD pattern of *ZNPs* synthesized at 75 °C.

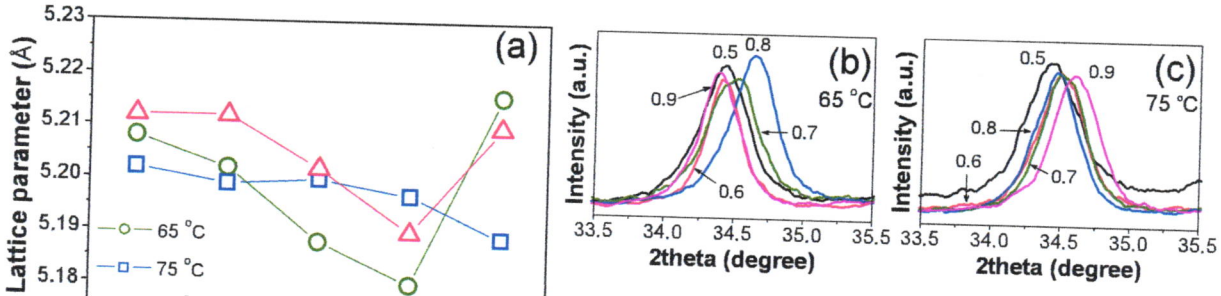

Fig. 3 (a) lattice parameter c of all samples, and the shift of (002) peak in XRD spectra for *ZNPs* synthesized at (b) 65 °C and (c) 75 °C.

Formation of *ZNPs* could be explained as following. Firstly, zinc nitrate solution acted as the source of Zn^{2+}; while aqueous sodium hydroxide alkali salt was used to supply OH^- ions in the reaction. Secondly, the reaction of those two solutions resulted in a formation of $Zn(OH)_2$. By hydrolysis and condensation processes of zinc nitrate with the help of sodium hydroxide in DI medium at low temperatures, finally, *ZNPs* could be formed [10]. It was noticed that Zn^{2+} and OH^- concentrations played as key factors on growth of *ZNPs*, via pH value. At low OH^- ions, a high Zn^{2+} concentration presented which strongly influenced on the formation of *ZNPs*. In this state, more ZnO nuclei could be produced and ZnO nuclei might fused together forming large ZnO cores which could be resulted in large particles. As the raised of OH^- ions, Zn^{2+}concentration gradually decreased reached a lowest value at 0.7 mole NaOH, resulted in smallest nanoparticles [9] and pH of the mixture was also reduced from 5.8-5.5 at 65 °C. With highest NaOH contents, pH of the mixture increased up to 6.1. Therefore, particles size was enlarged.

In addition, effect of synthesized temperatures on aqueous pH was observed; 65 > 85 > 75 °C, closely related to *ZNPs* size. The influence of synthesized temperatures on *ZNPs* size was obviously observed in good agreement with previously work [11]. Besides, uniformed *ZNPs* were received at high temperature, and the effect of NaOH contents was diminished as shown in Fig. 1. Moreover, the optical property of *ZNPs* was investigated in term of absorbance spectra (not shown). All

samples showed the absorption band edge around 370-384 nm, and optical energy band gap was calculated to be 3.27-3.33 eV, 3.31-3.35 eV and 3.24-3.28 eV for 65, 75 and 85 °C, respectively.

Summary

ZNPs were synthesized via simple and low-cost co-precipitation method. The size and shape of *ZNPs* were successfully tuned by varying the synthesized temperatures and NaOH contents. *ZNPs* exhibited a pure hexagonal wurtzite crystal structure. It was evidenced that NaOH played a key role on *ZNPs* size through pH value by adjusting Zn^{2+}/OH^- ratio. The synthesized temperature, another key factor, also tuned solution pH in the reaction process impacted on *ZNPs* size and also prevented a change in *ZNPs* size at high temperature. The unique morphology so-called macaron-like shape *ZNPs* was found. These results are beneficial to achieve the nanoparticles.

Acknowledgment

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303	Palpu Chongi Gisul/Journal of Korea Technical Association of the Pulp and Paper Industry	j	Q3 0,214	7	48	180	692	68	180	0,41	14,42	
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307	Proceedings of the Institution of Mechanical Engineers, Part N: Journal of Nanoengineering and Nanosystems	j	Q3 0,212	6	18	73	331	40	72	0,40	18,39	
308	Journal of Nano- and Electronic Physics	j	Q3 0,212	6	180	479	2.371	159	479	0,37	13,17	
309	Mechanics and Industry	j	Q3 0,210	3	53	91	951	58	88	0,66	17,94	
310	International Heat Treatment and Surface Engineering	j	Q3 0,209	5	34	108	457	28	94	0,27	13,44	
311	Kung Cheng Je Wu Li Hsueh Pao/Journal of Engineering Thermophysics	j	Q3 0,207	15	458	1.716	4.605	434	1.716	0,25	10,05	
312	Key Engineering Materials	k	Q3 0,207	36	3.945	9.159	40.734	2.037	8.996	0,26	10,33	
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314	Journal of Failure Analysis and Prevention	j	Q3 0,205	13	118	267	1.619	77	242	0,30	13,72	
315	Journal of Natural Fibers	j	Q3 0,205	10	26	72	740	42	71	0,60	28,46	
316	Materiaux et Techniques	j	Q3 0,202	4	39	188	771	44	174	0,34	19,77	
317	International Journal of Nanoscience	j	Q3 0,201	14	21	348	567	147	341	0,33	27,00	
318	Problems of Atomic Science and Technology	j	Q3 0,201	6	223	838	2.377	179	836	0,24	10,66	
319	High Temperature Materials and Processes	j	Q3 0,200	20	61	311	1.359	114	306	0,45	22,28	
320	Pollack Periodica	j	Q4 0,197	6	42	156	489	22	153	0,16	11,64	
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