

Cryochemical Synthesis of Zinc-salt Nanoparticles

Andrei Baranov, Young-Jei Oh[†], and Masahiro Yoshimura^{*}

Korea Institute of Science and Technology, Seoul, Korea,

Fax: 82-2-958-6720, e-mail: [†]youngjei@kist.re.kr

^{*} Tokyo Institute of Technology, Yokohama, Japan

Fax: 81-45-924-5360, e-mail: yoshimura@mssl.titech.ac.jp

To avoid agglomeration of zinc-salt nanoparticles we used freeze-drying of zinc nitrate/sodium chloride aqueous solutions with molar ratio 0.06 (or 0.006) M $Zn(NO_3)_2$ / 4 M NaCl. Zinc nitrate/sodium chloride solution was precipitated by ammonia or butylamine before spraying into liquid nitrogen. Some samples were sprayed into liquid nitrogen without preliminary precipitation. Final product was a micron-sized sodium chloride crystals with non-agglomerated nanosized (10~30 nm) zinc-salt particles placed on the surface of NaCl crystals (pristine nitrate and precipitated by butylamine solutions). For the solution precipitated by ammonia formation of nanosized zinc-salt particles on the surface of NaCl crystals was not observed. Subsequent heat treatment of all the samples for the decomposition of zinc-salt to zinc oxide even at 400°C leads to agglomeration and photoluminescence spectra show similar to bulk zinc oxide behavior.

Key words: cryochemical synthesis, nanoparticles, NaCl substrate, Zn-salt

1. INTRODUCTION

Novel optical, electrical and other unique properties of semiconductor oxide nanomaterials based on ZnO arose enormous interest to the synthetic methods for ZnO nanoparticles [1,2]. The most reliable and rather simple synthesis can be realized in solutions where nanosized particles form stable colloid solution. Many of the well known techniques for the water elimination from aqueous solution such as freeze-drying, spray-drying, or hydrothermal decomposition result in the strongly aggregated powders [3,4]. In this report we suggest a new way for the cryochemical synthesis of non-aggregated and nanosized Zn-salt particles.

2. EXPERIMENTAL

Starting aqueous solutions listed in Table 1 were precipitated by equimolar amount of butylamine (samples #1) or ammonia (samples #2) and after that were sprayed into liquid nitrogen.

Table 1. Composition of starting solution and Zn-salt nanoparticles

N	Composition of starting solution	Precipitation before spraying by	Presumable composition of Zn-salt nanoparticles
1	0.06 M $Zn(NO_3)_2$ 4 M NaCl	Butylamine	$Zn(OH)_2$ • nH_2O
2	0.06 M $Zn(NO_3)_2$ 4 M NaCl	Ammonia	$Zn(OH)_2$ • nH_2O
3	0.06 M $Zn(NO_3)_2$ 4 M NaCl	None	$Zn(NO_3)_2$ • nH_2O
4	0.006 M $Zn(NO_3)_2$ 4 M NaCl	None	$Zn(NO_3)_2$ • nH_2O

Samples #3 and #4 were sprayed into liquid nitrogen without preliminary precipitation. After evaporation of liquid nitrogen frozen micro droplets in metal trays were subjected to freeze-drying at $P = 5$ Pa using Alpha 2-4

(Christ, Germany) laboratory freeze drier. As-obtained fine powders were studied by HRSEM (Fig 1-6) and TEM. Before TEM measurements samples were thinned by water (Fig.7). Selected area of electron diffraction was taken after electron beam treatment for the crystallization of amorphous zinc-salt particles (Fig.7 inset). Finally all the samples were calcined for 1 hour at 400°C for the decomposition of Zn-salt into ZnO. Photoluminescence (PL) spectra were measured at fixed 320 nm excitation wavelength in the range of 360~700 nm.

3. RESULTS AND DISCUSSION

Scanning and transmission electron microscopy studies of freeze-dried zinc nitrate/sodium chloride aqueous solutions revealed the formation of rather large (size ranges 0.5~4 μm for the samples #1,3,4 and up to 10 μm for the sample #2) and well crystallized grains of sodium chloride (Fig. 1-3). Sodium chloride prevents aggregation of a Zn-salt nanoparticles (presumable composition of Zn-salt nanoparticles see in the Table 1) and plays role as a substrate after elimination of water from the aqueous solution during freeze-drying.

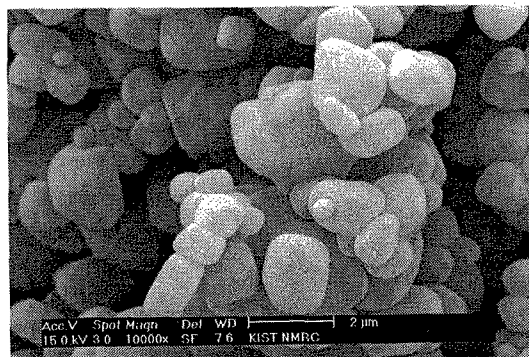


Fig.1. SEM photo of sample #1.

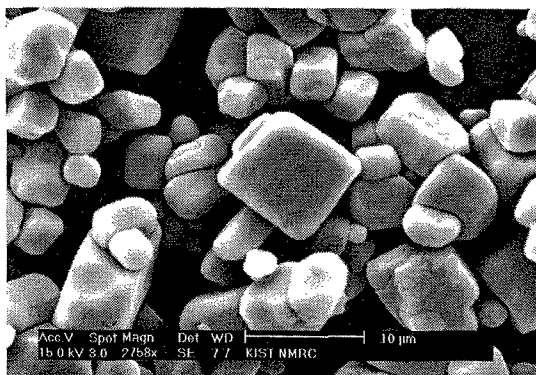


Fig.2. SEM micrograph of sample #2.

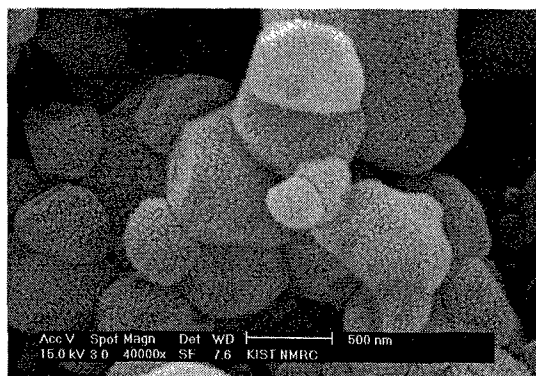


Fig.3. SEM micrograph of sample #3.

At higher (from x40,000 up to x200,000) magnification the formation of nanosized (average size of 10~30 nm) particles is clearly seen on the surface of sodium chloride crystals (Fig.4,5).

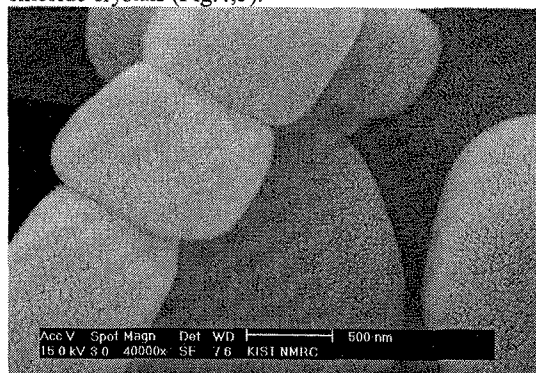


Fig.4. SEM micrograph of sample #1 with x40,000.

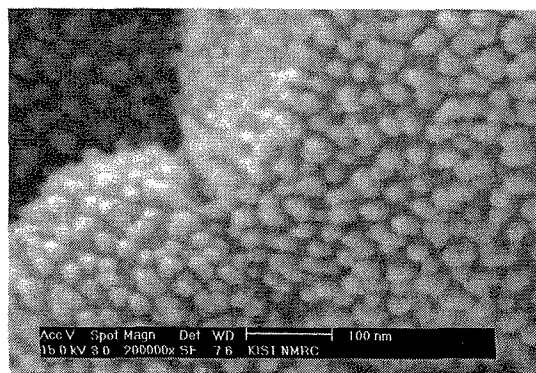


Fig.5. SEM micrograph of sample #3 with x200,000.

Preliminary precipitation of zinc nitrate by butylamine from zinc nitrate/sodium chloride solution before freeze-drying leads to the similar particle size distribution in contrary with precipitation by ammonia where formation of ultra fine zinc-salt particles has no longer been observed (Fig. 2). In the case of zinc nitrate/sodium chloride solution with the mole ratio 1:650 (sample #4) characteristic size of zinc-salt particles is the same but its density on the surface of sodium chloride crystals is obviously less than previous one (Fig.6).

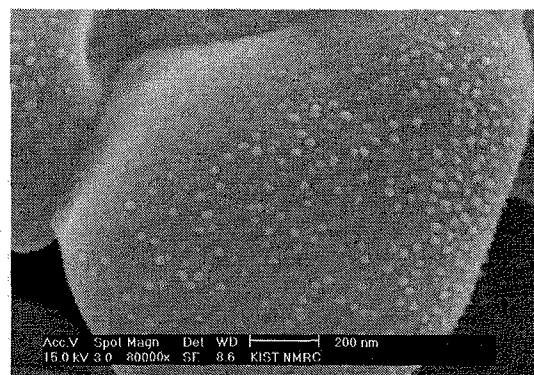


Fig.6. SEM micrograph of sample #4.

There are two possible compositions - $Zn(OH)_2 \cdot nH_2O$ and $Zn(NO_3)_2 \cdot nH_2O$ for the final state of Zn-salt nanoparticles in accordance with the prehistory. As was shown by TEM measurements the reflections on the selected area of electron diffraction photos after electron beam treatment correspond to the zinc oxide hexagonal structure. Beam treatment of Zn-salt nanoparticles leads to the decomposition and crystallization of ZnO.

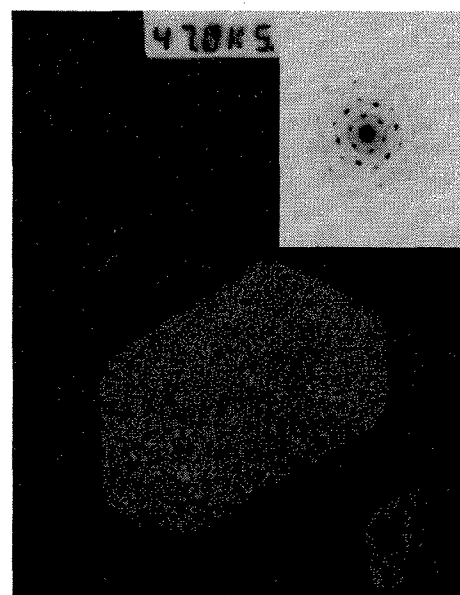


Fig. 7. TEM photo of thinned by water NaCl crystal with Zn-salt nanoparticles (sample #1).

Inset - Selected area of electron diffraction was taken after electron beam treatment from decomposed and crystallized Zn-salt nanoparticles.

From the results obtained by SEM it is possible to propose the following model for the formation of zinc-salt nanoparticles on the surface of sodium chloride crystals (Fig. 8).

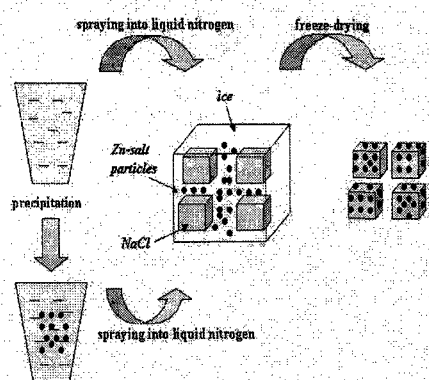


Fig. 8. Model of zinc-salt nanoparticles formation on the surface of NaCl crystals in the cryochemical process.

For the samples #1, #3, and #4 it is reasonable to assume the formation of Zn-salt nanoparticles (black droplets on the scheme). Frozen in a liquid nitrogen aqueous solution (transparent cube on the scheme) is constituted from the crystals of NaCl (gray cubes on the scheme) and mixture of Zn-salt particles and ice. At the next stage all the water molecules (except hydrated ones) are eliminated by vacuum and non-aggregated Zn-salt particles coat the surface of NaCl crystals.

Heat treatment at 400°C leads to the decomposition of Zn-salt to the ZnO phase and to the aggregation of nanosized Zn-salt particles to the bulk ZnO forms. It may be explained by not enough thermal stability of NaCl crystals at the 400°C temperature. Another possible explanation deals with melting of Zn-salt hydrates in a crystallization water.

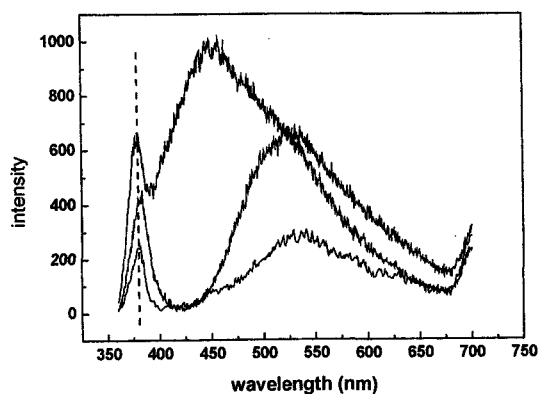


Fig. 9. PL spectra of samples #1~#3 calcined at 400°C. Dashed line corresponds to the position of luminescent maximum for the bulk ZnO – 380 nm.

The PL spectra are shown on the Fig. 9. Upper curve (at 380 nm) corresponds to the ammonia precipitated sample #2, in the middle – curve for the nitrate sample #3 and lower line is for the sample #1. It is clear from these spectra that the final state of all the samples after calcination is the same. There is no any shift of PL maximum of spectra to the ultraviolet zone as was expected from the (10~30 nm) size of the Zn-salt nanoparticles before heat treatment and obviously that luminescent properties of calcined samples are similar to the bulk ZnO.

4. CONCLUSIONS

1. The cryochemical method for preparation of nanosized and non-aggregated zinc-salt particles was developed.

2. Formation of zinc-salt nanoparticles strongly depends on precipitation conditions and was not observed for ammonia.

3. Formation of zinc-salt nanoparticles is possible without precipitation from 4M NaCl+0.06M $Zn(NO_3)_2$ and 4M NaCl+0.006M $Zn(NO_3)_2$ aqueous solutions with the same 10~30 nm size. 4. Luminescent properties of samples annealed at 400°C are similar to the bulk ZnO that means aggregation of nanoparticles during heat treatment.

5. ACKNOWLEDGMENTS

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6. REFERENCES

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