Size controlled ZnO nanoparticles synthesized by liquid phase deposition and polymer hybridization

*Yuri Tabata*, Tomohiro Sakai*, Nobuya Hiroshiba, Yo Ichikawa

1Graduate School of Engineering, Nagoya Institute of Technology
2Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

* Corresponding author: Fax: 81-52-735-7314, e-mail: (Y.T.) cju16556@stn.nitech.ac.jp (N.H) n.hiroshiba.648@nitech.jp

We demonstrated a simple solution synthesis method of ZnO nanoparticles to explore the probability of controlling diameter and shape by the synthesis conditions. The optimized synthesis condition of ZnO nanoparticles was found for application of NIR scatterer. The ZnO nanoparticles with an average diameter of 370 nm, which is suitable diameter for NIR scatterer, were observed. The diameter of observed 76% nanoparticles was under 500 nm. The synthesized ZnO nanoparticles were hybridized with transparent amorphous polymers (PMMA) for the purpose of film applications as NIR scatterer. The optical properties of ZnO-polymer materials were examined in the UV-VIS and FT-IR. We confirmed that the transmittance of ZnO-polymer (containing 10 wt% of ZnO nanoparticles) in NIR region is clearly reduced. To achieve effective NIR scattering film, ZnO-polymer ratio should be optimized.

Key words: ZnO, micro crystal, nanoparticle, hybrid materials, polymer

1. INTRODUCTION

Our final goal of this study is to fabricate near infrared (NIR) scattering film which consist of transparent polymer and size-controlled nanoparticles for future applications as smart intelligent windows[1]. In recent years, the development of UV absorber and NIR scatterer using hybrid nano-materials is crucial for resolving urban life problems such as heat island effect and UV damages[2-3]. Zinc oxide (ZnO) nanoparticles are one of candidate materials, since oxide semiconductors absorb UV light owing to its wide band gap. In addition, NIR light can be scattered by ZnO nanoparticles with diameter under 500 nm[2]. To effective UV absorber and NIR scattering films, controlling method of a shape and size for ZnO nanoparticles synthesis is needed. However, size and shape controlling method of ZnO nanoparticles synthesis is not fully investigated for the purpose of NIR scattering films. In this study, we examined the shapes and size dependence of ZnO nanoparticles using simple solution process by changing of solution conditions. The synthesized ZnO nanoparticles were hybridized with transparent polymers; Poly-methyl methacrylate (PMMA) to investigate the probability of NIR scattering film.

2. EXPERIMENTAL

2.1 Shape dependence of ZnO crystals

The pH dependence of morphological change in shapes of ZnO nano-crystals was investigated. All regents used in this experiment were obtained from Wako Pure Chemical Industries Ltd. (each purity is 99% for NaOH and Zn(NO$_3$)$_2$・6H$_2$O). The ZnO nano-crystals samples were prepared as the following procedure: An aqueous solution of NaOH (45ml 0.2M) added to an aqueous solution of Zn(NO$_3$)$_2$・6H$_2$O (50 ml 0.1 M) 4-7. An aqueous solution of NaOH (1.5 M) added to the mixture of above solutions for adjusting to pH10, 11, and 12. This pH controlled solutions were kept at 25 degrees for 3 days. The settled out ZnO nanoparticle samples were dried in ambient atmosphere.

2.2 Size dependence of ZnO nanoparticle

To decrease average diameter, hydrothermal synthesis is improved8-12. An aqueous solution of NaOH (10 ml, 0.1 M) added to the Zn(NO$_3$)$_2$・6H$_2$O solution (10 ml 0.1 M) 8*. The obtained Zn(OH)$_2$ sol was separated by centrifugation at 3000 rpm for 5min. It was repeated three times. A stable Zn(OH)$_2$ sol was dispersed in ethylene glycol kept at 35 degrees for 24 hours. After 24 hours, an aqueous solution of NaOH (15 ml, 0.1M) was added to the Zn (OH)$_2$ sol dispersed ethylene glycol solution. The obtained precipitate was separated by centrifugation at 3000rpm for 5min. Finally, condensed ZnO nanoparticles gel was obtained from the precipitate.

2.3 ZnO-polymer hybridization

After synthesis, ZnO nanoparticles gel was hybridized with transparent amorphous polymers (PMMA). The ZnO nanoparticle gel (0.3 ml) was added to two types of density of PMMA (5 wt% and 10 wt%) acetone solution. The mixture solution of dispersed ZnO was span-coat on glass substrate at 500 rpm 10 second then at 2000 rpm for 5 second. Before spin-coating, glass substrates were cleaned by ultra-sonication in acetone for 30 min, and followed by surface treatment with UV-Ozone cleaner for 15 min to remove organic pollutions and to get hydrophilic surface. After spin-coating, the substrates were dried under ambient atmosphere. Typical film thickness of these samples is approximately 0.3 µm.
3. RESULTS AND DISCUSSION

SEM images of the pH dependence of ZnO crystals were shown in Figure 1. The protuberance shapes on ZnO microcrystals decrease with the increase of pH value. The crystals prepared only from pH10 (Fig. 1(a)) have a variety of shapes of surface morphology. We suggest that the balance of hydroxide ion (OH⁻) and Zn(OH)₄²⁻ ions density at pH12, respectively. In these cases, almost crystals shape is having regular polyhedron at pH11 and spherical shapes at pH12, respectively. We suggest that the balance of hydroxide ion (OH⁻) and Zn(OH)₄²⁻ ions is important parameter for forming ZnO particle by hydrothermal synthesis. From Mie scattering theory, spherical shaped object scatter irradiated light along this relationship as follows;

\[ K(\rho) = \frac{4}{\rho} \sin \rho + \frac{4}{\rho^2} (1 - \cos \rho) \]

Here, \( \rho = 2(n - 1) \), and \( n \) is refractive index. From this equation, the ideal diameter region of spherical shaped object for scattering NIR wavelength sunlight (900-1800 nm) is 100-300 nm. If ZnO nanoparticles hybridize to PMMA, we needed to 500 nm or below diameter of ZnO nanoparticles.

The crystallinity of ZnO samples were examined using XRD measurement. The results were shown in Fig. 2. All specific peaks of XRD patterns were identified as zinc oxide crystal structure(10). The relative peak intensities of ZnO 100, 002 and 101 are changed by the pH conditions. The 002 peak intensity increases with the increasing of pH value comparing to 100. The intensity ratio of 002 per 100 are 0.77, 0.54, and 0.23, respectively. From this tendency, we conclude that the crystal growth along c-axis of ZnO becomes dominant with increase of pH of the aqueous solution.

![Fig. 2 XRD patterns of the ZnO micro crystals. The nanoparticles synthesized at r.t. for 3days under (a) pH10, (b) pH11, and (c) pH12 solutions. After synthesis, they dried at 80 degree for 20 hours.](image)

To decrease the average diameter of ZnO, ethylene glycol dispersion solution method(9) was used. Figure 3 shows the SEM image of the synthesized ZnO nanoparticles using ethylene glycol dispersion solution.

![Fig. 3 SEM image of the ZnO nanoparticles. This nanoparticles synthesized by ethylene glycol dispersion solution(NaOH (aq, 10 ml, 0.1 M) and Zn(NO₃)₂·6H₂O (aq, 10 ml 0.1 M) dispersed in ethylene glycol (50 ml)) under pH12 for 24hours.](image)

The ZnO nanoparticles with a diameter of 100-300 nm were observed in SEM image. The dispersion in diameters of synthesized ZnO nanoparticles was statistically counted as shown in Fig. 4. The average particle size of the ZnO nanoparticles is approximately 370 nm. The number of 76% of ZnO nanoparticles has below 500 nm in diameter. The ZnO-sol controlled crystal growth by dispersing in ethylene glycol.

![Fig. 4 Distribution of ZnO nanoparticles.](image)
Fig. 4 Particle size distribution of ZnO nanoparticles synthesized by ethylene glycol dispersion solution (NaOH (aq, 10 ml, 0.1 M) and Zn(NO$_3$)$_2$·6H$_2$O (aq, 10 ml, 0.1 M) dispersed in ethylene glycol (50 ml)) under pH12 for 24 hours.

The optical properties of hybridized ZnO-polymer materials using UV-VIS and FT-IR transmittance measurement were carried out. The result was shown as Fig. 5. Transmittance falls in a visible and NIR range. The NIR transmittance of PMMA density 10 wt% is lower than that of 5 wt% hybridized with ZnO nanoparticle gel. This result indicates that higher PMMA density is effective for NIR scattering. However, the optimization of ZnO-PMMA ratio of this hybridization film should be carried out as a continuation of this study.

Fig. 5 The optical transmittance spectra measured by UV-VIS and FT-IR measurement system. The measured ZnO-polymer hybrid films were: (a) PMMA only (5 wt% and 10 wt%) (b) ZnO-gel and PMMA 5 wt% (c) ZnO-gel and PMMA 10 wt%.

4. CONCLUSION
In this study, we demonstrated a simple solution synthesis method of ZnO nanoparticles to control diameter and shape by the synthesis conditions. The ZnO nanoparticles with an average diameter of 370 nm were observed by optimal synthesis condition using ethylene glycol dispersion solution. The synthesized ZnO nanoparticles were hybridized with transparent amorphous polymers (PMMA) for the purpose of application as NIR scatterer. The optical properties of ZnO-polymer materials were examined in the UV-VIS and FT-IR. We confirmed that the transmittance of ZnO-polymer in NIR region is clearly reduced comparing to neat-PMMA film. To achieve effective NIR scattering film, ZnO-polymer ratio should be optimized as a continuation of this study.

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6. REFERENCES

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