Surface Treatment of Zinc Oxide Nanoparticles by Silica Coating and Evaluation of Their Dispersibility and Photoluminescent Properties*

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We prepared silica-coated ZnO nanoparticles and evaluated the dispersibility and photoluminescent properties by comparing the properties of ZnO nanoparticle dispersion. It was confirmed that the Zeta-potential of the nanoparticles in saline was changed from 1.52 mV to −43.06 mV and the intensity of the exciton emission of ZnO was enhanced around 20 times by silica coating. These results indicated that the silica coating technique was effective for enhancing the dispersibility and controlling the fluorescence quenching of the emission of ZnO. [DOI: 10.1380/ejsnt.2015.451]

Keywords: Zinc oxide; Silica; Dispersibility; Photoluminescence; Exciton emission

I. INTRODUCTION

Zinc Oxide (ZnO) is a direct wide band gap (3.37 eV) compound semiconductor and regarded as a promising ultraviolet optoelectronic material [1–3]. To achieve efficient excitonic laser action at room temperature, the binding energy of the exciton must be much higher than the thermal energy (26 meV) [1]. In this regard, ZnO is a good candidate because its exciton binding energy is ~60 meV [1]. Besides, ZnO is a safe and a low price material used as a raw material of baby powders or cosmetics [4, 5]. Thus ZnO seems to be suitable for bioimaging applications. Organic dyes or Quantum dots are studied as fluorescent labeling reagents for bioimaging [6–13], but they have photobleaching behavior or toxicity for human body, hence ZnO is considered to be a candidate as the fluorescent labeling reagent which does not have these demerits. ZnO have been used as a fluorescent material using its broad (around 400 nm–600 nm wavelength) emissions, which are generated from oxygen vacancies (V_O), vacant zinc (V_{Zn}), zinc interstitials (Zn_i), anti-site defects (Zn_O), their ionized counterparts and complexes, and other defects in the crystalline lattices of ZnO, which is collectively called defect emission. Although the characterization of native point defects in ZnO is still a question of debate [14], the band energy of the typical defect emissions were reported as follows; for example, that of V_O , V_{Zn} , and Zn_i , were around 2.5 eV [15, 16], 2.35 eV [17, 18],

and 2.9 eV [19], respectively. Generally the exciton emission of ZnO nanoparticles is decreased in solvents [3]. There are many advantages to utilize the exciton emission of ZnO; first, the sharp emission is similar to the emission from quantum dots because the exciton emission has the atom-like energy level, second, to make relatively low price fluorescent reagents compared to quantum dots because we do not need controlling the size of ZnO nanoparticle with submicron order like quantum dots. Also we can use the emission wavelength around 380 nm which cannot be used by conventional fluorescent reagents to achieve strong fluorescence without the excitation saturation by using a fluorescent microscope with high excitation density. Therefore we are trying to apply the material as a fluorescence labeling reagent using the emission of ZnO exciton origin. However, ZnO nanoparticles are not dispersed in saline well, and the fluorescence quenching caused by energy/carrier transfer tend to be decreased the exciton emission of ZnO nanoparticles [20, 21]. Moreover, the toxicity of ZnO *in vivo* have been reported recently [22–25]. On the other hand, silica is known as a good insulator with large band gap energy [26], and silica-coating technique is investigated for capping toxic materials or modifying particle surface by functional group [27]. Thus we selected silica as a coating material for ZnO nanoparticles. There are many studies about silica-coated ZnO nanoparticles for bioimaging [28–32], their purpose are mainly reducing toxicity of ZnO or utilizing defect emissions of ZnO quantum dots which have more surface defects. In this study, we focused on controlling the fluorescence quenching of the exciton emission of ZnO, prepared silica-coated ZnO nanoparticle dispersions and evaluated the photoluminescent properties. Meanwhile, we also evaluated the dispersibility of the prepared nanoparticles.

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II. EXPERIMENTAL

ZnO nanoparticles were prepared by using a gas evaporation method. A Zn metal (99.99%; The NILACO, Tokyo, Japan) was melted and evaporated by the arc discharge between a carbon cathode and a Zn metal anode, and the ZnO nanoparticles were formed by the reaction of evaporated zinc and oxygen in the air [3]. The conditions of the arc discharge were the pressure of 20 kPa, the current of 50 A, and the air flow rate of 5 L/min. To prepare ZnO particle dispersions, 0.1 g ZnO nanoparticles were dispersed in 20 mL solvent (ethanol or water) by using an ultrasonic homogenizer VCX-500 (SONICS & MATERIALS, Newtown, CT, USA). The dispersions were centrifuged at 3000 g for 1 min at room temperature to remove large/aggregated particles. To prepare silica-coated ZnO particles, the ZnO-ethanol dispersions were prepared by same way as described previously. Silica-coated ZnO particles were prepared by the hydrolysis and polycondensation of tetraethoxysilane (TEOS) in the ZnO-ethanol dispersions. ZnO dispersion of 12.5 mL was put into 30 mL vial container with magnet stirrer, and 28% ammonia water of 0.1 mL, ultrapure water of 0.9 mL, and TEOS (> 95%; KANTO CHEMICAL, Tokyo, Japan) of 1 mL were added into the ZnO dispersion, and then stirred for 24 hours at room temperature. The prepared particles were washed with ethanol and ultrapure water by centrifugation and were dispersed in ultrapure water by using an ultrasonic homogenizer. To confirm the dispersibility of the particles, the prepared particles were also dispersed in saline (0.9% sodium chloride water; OTSUKA PHARMACEUTICAL, Tokyo, Japan) by using an ultrasonic homogenizer. In the case of observing the morphology of silica-coated ZnO particles, the particles-water dispersion was dried, and the dried particles were fixed on the holder for a scanning electron microscope (SEM). The morphology of prepared particles was observed by a field emission scanning electron microscope JSM-7001FA (JEOL, Tokyo, Japan). The particle size distribution of prepared particles was analyzed by using a dynamic light scattering particle size analyzer LB-550 (HORIBA, Kyoto, Japan). The Zeta-potential of prepared particles was measured by using a Zeta-potential analyzer ELSZ-1 (OTSUKA ELECTRONICS, Hirakata, Osaka, Japan). The photoluminescent properties of prepared particles were measured by using a spectrofluorometer Fluoromax 4 (HORIBA, Kyoto, Japan) with irradiating 325 nm light from a xenon lamp.

III. RESULTS AND DISCUSSION

Figure 1 is a SEM image of silica-coated ZnO nanoparticles. It was observed that the shape of the particles was rod-like. In the image, the blighter parts (the core part of particles) showed ZnO and darker parts (the shell part of particles) showed silica because Zn tends to emit more secondary electrons than Si by irradiating electrons. It was confirmed that the surface of ZnO particles was coated with silica with thickness around several tens nm. Figure 2 shows the particle size distributions for both ZnO particles and silica-coated ZnO particles in water and in

FIG. 1. SEM image of prepared silica-coated ZnO nanoparticles.

TABLE I. Zeta-potentials for both ZnO particles and silica-coated ZnO particles in water and in saline.

solvent	Zeta-potential [mV]	
	ZnO	Silica-coated ZnO
water	41.30	-46.14
saline	1.52	-43.06

saline.

ZnO particles were dispersed better in water than in saline. On the other hand, silica-coated ZnO nanoparticles were dispersed well in both water and saline. Table I shows the Zeta-potential values for both ZnO particles and silica-coated ZnO particles in water and in saline. It was confirmed that ZnO and silica-coated ZnO particles showed positive and negative potentials respectively and the absolute values of Zeta-potential corresponded to the dispersibility. In water dispersion, both ZnO and silica-coated ZnO particles showed high absolute values of Zeta-potential. However, in saline dispersion, the absolute value of silica-coated ZnO particles was high but that of ZnO particles was very low. These results indicated that the dispersibility of ZnO in saline was highly enhanced by silica coating. According to Derjaguin-Landau-Verwey-Overbeck (DLVO) theory, the agglomeration and stability of particle dispersions are determined by the sum of the attractive (van der Waals) and electrostatic repulsive forces between individual particles [33, 34]. In the case of ZnO-dispersed saline, the van der Waals force between ZnO particles become dominant and the agglomeration of the particles was occurred. On the other hand, in the case of silica-coated ZnO-dispersed saline, the electrostatic repulsive force was dominant; as a result, silica-coated ZnO-saline dispersion was stable. Figure 3 shows the photoluminescent spectra of ZnO dispersion and silica-coated ZnO dispersion. The exciton emission of ZnO and the defect emission were observed at around 380 nm and the

FIG. 2. Particle size distributions for both ZnO particles and silica-coated ZnO particles in water and in saline. (a) ZnO particles in water. (b) ZnO particles in saline. (c) Silica-coated ZnO particles in water. (d) Silica-coated ZnO particles in saline.

FIG. 3. Photoluminescent spectra of ZnO dispersion and silica-coated ZnO dispersion. (The wavelength of excitation light was 325 nm.)

broad range over 400 nm in these spectra, respectively. It was confirmed that the intensity of the exciton emission of ZnO was enhanced around 20 times by silica coating. As for the exciton emission of ZnO, it was considered that the

silica layer contributed blocking the transition of the carrier energy because the band gap of silica was larger than that of ZnO, which leading to the fluorescence quenching reduction and emission intensity enhancement. As for the defect emission of ZnO, we also observed the enhancement of the defect emission which is not as strong as the exciton emission. Therefore the emission was mainly arisen from the donor-acceptor pair emission or the internal defects, not the surface defects. These results indicated that the carrier confinement and the surface passivation due to the core-shell structures were carried out successfully by coating ZnO nanoparticles with silica.

IV. CONCLUSIONS

We had successfully prepared silica-coated ZnO nanoparticles. We confirmed that the dispersibility of ZnO in saline was enhanced by silica coating. Also we confirmed that the intensity of the exciton emission of ZnO was enhanced around 20 times because of the carrier confinement of ZnO by silica. These results suggested that the surface passivation of ZnO nanoparticles by silica coating is effective for enhancing the emission of ZnO and controlling the surface defect of ZnO.

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