Notes

Characterization of ZnO Nanoparticles Grown by Laser Ablation of a Zn Target in Neat Water

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The most frequently-employed technique to synthesize nanoparticles in liquid is the chemical reduction of metal ions. As an alternative, laser ablation of a metal target in liquid has proven to be a powerful tool to prepare nanoparticles in liquid.[1] In particular, it is an attractive technique for fabrication of various metal oxide nanoparticles emersed in liquid phase since it has overwhelming advantages, compared to the chemical reduction, such as technical simplicity, chemical pureness, and controlled synthesis. To be more concrete, nanoparticles can be formed in neat solvent like deionized water just by impinging on the target by a high-power pulsed laser beam without any supplementary chemicals.

The unique feature of laser ablation in liquid is the formation of dense plasma which brings about local and temporal non-equilibrium conditions. Accordingly, not only the chemical environment but also physical parameters including laser power and spot size, wavelength, and ablation time determine the characteristics of the resultant nanoparticles. In this respect, it will be certainly beneficial to verify the influence of such parameters not only for producing high-quality nanoparticles but also for deep understanding of the physical processes their-in.

Here, we present experimental results on the formation of ZnO nanoparticles *via* liquid laser ablation, which clearly demonstrate the effects of ablation time, aging, and laser power on the photoluminescence properties including the relative intensity of the UV and visible region.

Experimental

ZnO nanoparticles were produced by laser ablation of a Zn target (diameter = 25 mm, thickness = 4.0 mm, 99.99%) placed on the bottom of a glass vessel filled with 30 mL of deionized water. The Zn target was irradiated vertically by a Q-switched Nd- YAG laser (Quantel 980C, λ = 1064 nm) operating at 10 Hz. The laser beam was loosely focused using a lens with a focal length of 300 mm. The spot size of the focused laser beam was 2.0 mm in diameter. The vessel was continuously rotated to minimize the target aging effect and to give some stirring effect during the formation of nanoparticles.

The optical properties of the nascent nanoparticle solution was examined at room temperature by a UV-Vis absorption spectrophotometer (HP 8452A). The photoluminescence (PL) from the solution was measured using a He-Cd laser (λ = 325 nm) as an excitation light source. The irradiation time and laser power were varied to investigate the influence on the optical and PL properties. X-ray diffraction (XRD, Rigaku DMAX-IIIA) data for the dried film of nanoparticles were obtained using Cu Kα line. A transmission electron microscope (TEM, JEM-2000EX II) was employed to observe nanoparticles directly. The specimen for TEM was prepared by dropping the nanoparticle solution onto a Cu mesh coated with an evaporated carbon film. With a goal to elucidate the effect of UV illumination, the ZnO nanoparticle solution was irradiated using 266 nm laser beam (Spectra-Physics GCR 150, 10 Hz).

Results and Discussion

The XRD pattern of the ZnO nanoparticles formed by laser ablation of a Zn plate in deionized water at room temperature displayed in Fig. 1 reveals that they are crystalline and possess the hexagonal wurtzite structure. However, two wide peaks at

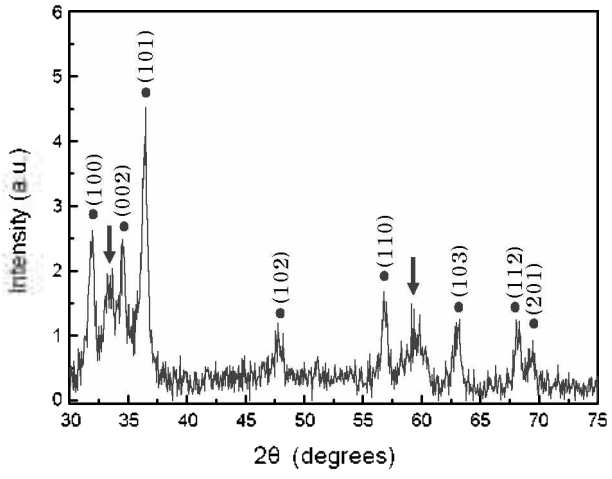

Figure 1. X-ray diffraction spectrum of ZnO nanoparticles formed *via* laser ablation of a Zn target in deionized water.

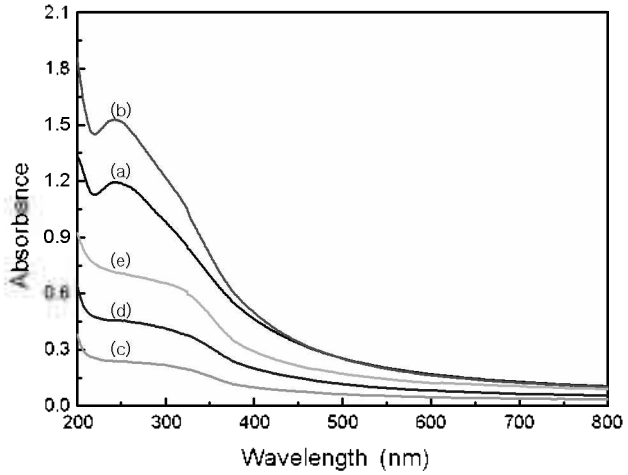

Figure 2. UV-Visible absorption spectra of ZnO nanoparticle solutions prepared at different ablation times. (a) 10 min, (b) 15 min, (c) 20 min, (d) 30 min, and (e) 50 min. The laser power was 100 mJ/pulse.

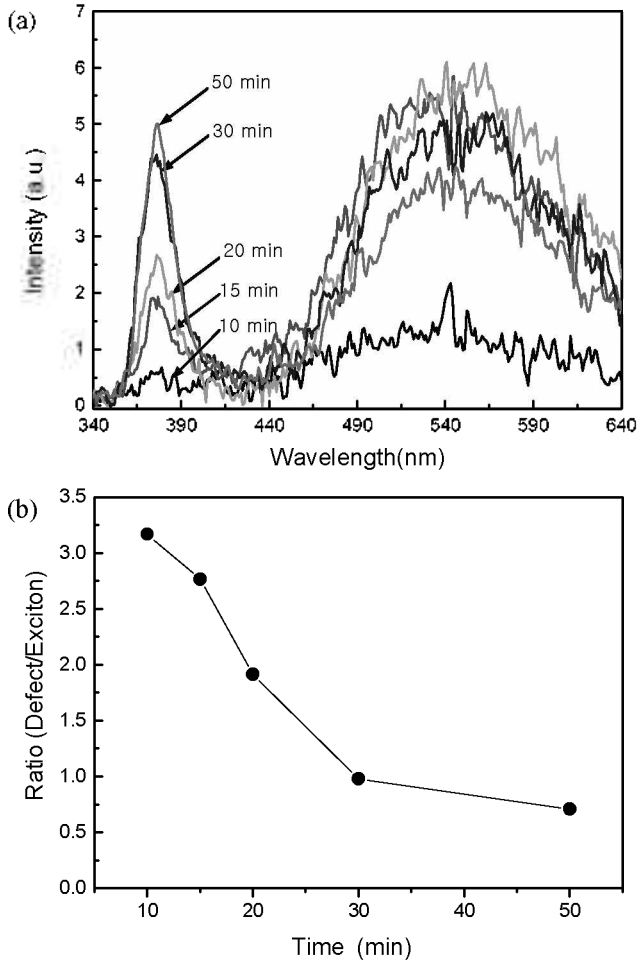

Figure 3. (a) PL spectra of ZnO nanoparticle solutions prepared at different ablation times. The laser power was 100 mJ/pulse. (b) The ratio of PL intensities at UV and visible region for ZnO nanoparticle solutions prepared at different ablation times.

2θ = 33.4° and 59.5° are not indexed for the ZnO wurtzite structure and they are considered to stem from the ZnOOH nanoparticles as pointed out by Singh *et al.*[2] They claimed that

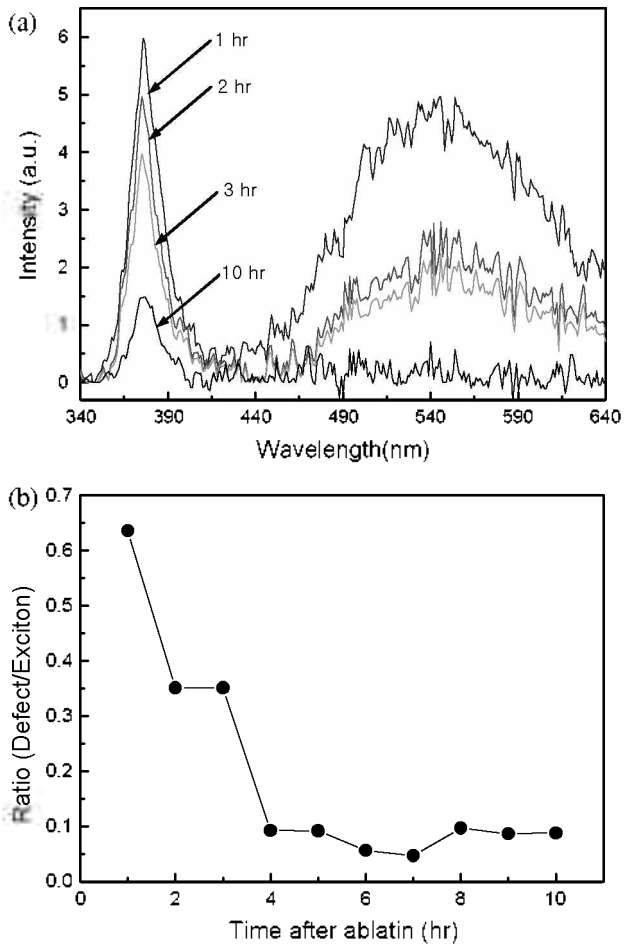

Figure 4. (a) PL spectra of ZnO nanoparticle solutions obtained with the increase of the aging time. The ablation time was 40 min with the laser energy of 100 mJ/pulse. (b) The ratio of PL intensities at UV and visible region for ZnO nanoparticle solutions prepared at different aging times.

unstable ZnO_2 formed via reaction of Zn nanoparticles with O_2 may react further with hydroxide ion to produce ZnOOH. Formation of such oxyhydroxides has been previously reported for Al[3] and Ga[4] target.

Figure 2 presents optical absorption spectra of ZnO nanoparticle solutions, each prepared by varying the ablation time which ranges from 10 to 50 min. A shoulder at ~ 350 nm indicates the excitonic peak of ZnO. For ablation times of 10 and 15 min, a clear absorption peak appears at 242 nm, which comes from the surface plasmon resonance (SRS) of Zn nanoparticles.[5] However, the Zn SRS peak disappears at longer ablation times, suggesting that Zn clusters turn into ZnO nanoparticles with the increase of ablation time. In particular, the abrupt decrease in the optical absorption in the UV region after 20 min is highly striking. This indicates that there is a certain critical density of Zn clusters to initiate the formation of ZnO. It is expected that the highly active Zn clusters formed in the Zn plasma react with H_2O to produce $Zn(OH)_2$ and H_2. Subsequently, $Zn(OH)_2$ decomposes to ZnO and H_2O.

Photoluminescence properties of the solution are also dependent on the ablation time as illustrated in Fig. 3(a). The PL intensity of the near band edge emission at 376 nm increases

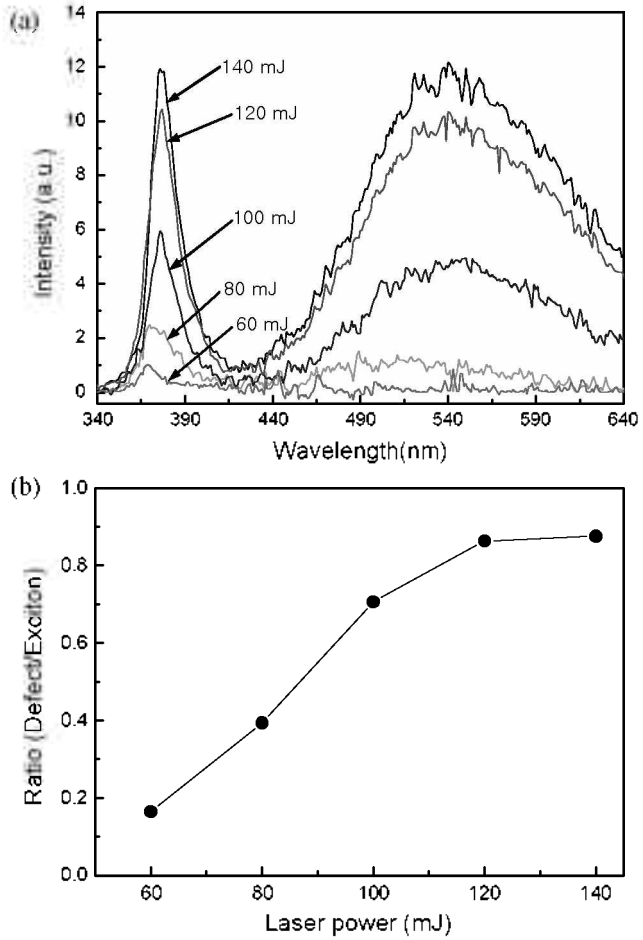

Figure 5. (a) PL spectra of ZnO nanoparticle solutions prepared with various ablation laser energies. The ablation time was 40 min. (b) The ratio of PL intensities at UV and visible region for ZnO nanoparticle solutions prepared at different laser energies.

with the increase of ablation time, while that of the green emission, presumably associated with the oxygen vacancies on the surface of nanoparticles, reaches its maximum intensity at 20 min and decreases with ablation time. The ratio of the defect and exciton emission progressively decreased with increase in the ablation time as shown in Fig. 3(b). This indicates that the average size of the nanoparticles becomes larger to reduce the concentration of defects on the surface as the number density of nanoparticles grows with prolonged irradiation. Figure 4 demonstrates the aging effect of the ZnO nanoparticle solution. Both exciton and defect emission intensity decreased with aging time. The defect emission, however, was suppressed more during the aging process as clearly shown in Fig. 4(b), which implies that the surface defects such as oxygen vacancies decreased owing to either the growth of nanoparticles *via* aggregation process or the occupancy of the oxygen vacancy by dissolved oxygen with aging.

Figure 5 shows the effects of the ablation laser power on the PL spectra. The near band edge emission peak shifts to blue as the laser fluence decreases, which suggests that the size of ZnO nanoparticles becomes smaller at lower laser powers.[6] The green emission intensity grows more rapidly than the UV emission as the laser power increases. This leads us to conclude

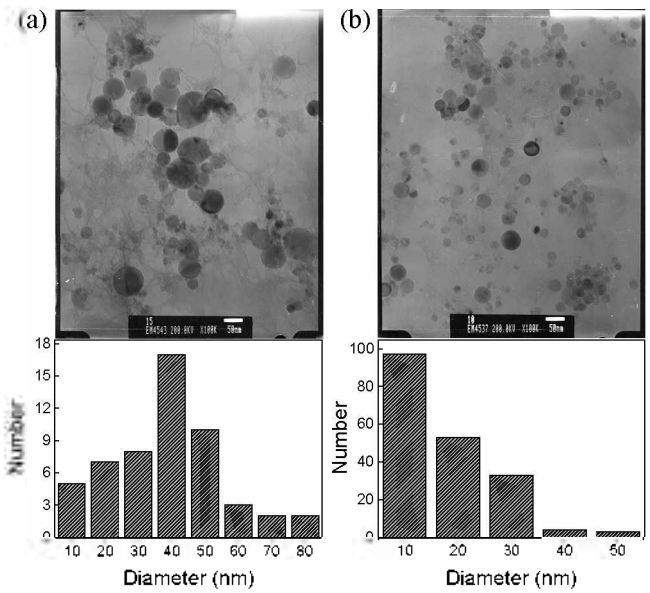

Figure 6. TEM images and size distribution of ZnO nanoparticles (a) before laser irradiation, (b) after laser irradiation. The nanoparticle solution was originally prepared *via* irradiating the Zn target with the laser energy of 100 mJ for 40 min. The photodissociation laser wavelength was 266 nm (30 mJ, collimated).

that, at high laser power, the size of nanoparticles is relatively large but their densities of surface defects remain still high.

The effects of UV irradiation on the ZnO nanoparticle solution were examined as shown in Fig. 6. Before irradiation, the average size of nanoparticles obtained from TEM images was 38.7 nm in diameter. The size was drastically reduced by irradiation and the average diameter became as small as 17.5 nm. The coagulation of nanoparticles has been reported to be accelerated by irradiation of light at the plasmon frequency as the van der Waals force is enhanced.[7] In case of ZnO nanoparticles, fragmentation induced by 266 nm irradiation is dominant, which causes substantial reduction of particle sizes.

In conclusion, the size and surface properties of ZnO nanoparticles produced by liquid laser ablation in deionized water, as deduced by their PL spectra, are strongly dependent on the experimental parameters such as laser power, ablation time, and aging. Therefore, care has to be taken in the control of ablation parameters to optimize and reproduce the characteristics of the nanoparticles fabricated by laser ablation of a solid target in liquid phase.

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