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Optical Properties of Laser-Irradiated ZnO Nanoparticles in 2-Propanol

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Abstract

We investigate the effects of laser irradiation on the optical properties of ZnO nanoparticles in an organic solvent. ZnO nanoparticles are synthesized using normal precipitation methods in 2-propanol. Irradiating the nanoparticles in the solvent with unreacted reactants, which is colloidal solution without purification after the preparation, results in a reduction in the green luminescence, which is related to the number of surface oxygen defects, and an increase in the ultraviolet luminescence, which is related to the crystallinity of ZnO. Irradiation does not, however, significantly alter the nanoparticle diameter. Conversely, irradiation of purified (reactant-free) ZnO nanoparticles in the solvent does not change the ZnO photoluminescence intensity. We conclude that laser irradiation of the ZnO nanoparticles dispensed with reactants reduces the number of surface defects on the ZnO nanoparticles. Without the reactants, laser

irradiation of the ZnO nanoparticles in the solvent does not modify the surface defects concentration, nor does it increase the crystallinity.

1. Introduction

Nanoparticles have recently attracted significant research interest due to their vastly different properties as compared with the bulk material.¹⁻⁴⁾ These properties typically find their origin in the increase in surface-to-volume ratio characteristic of nanoparticles. Reducing the particles to nanoscale sizes leads to various phenomena such as an increase in the bandgap due to the quantum confinement effect.^{5,6)} Semiconductor nanoparticles are highly promising materials for lighting, display, bioimaging, etc. because it is possible to tune the fluorescence wavelength by exploiting the quantum confinement effect, and because nanoparticles offer high quantum yields owing to their core/shell structure.^{7,8)} However, to generate visible fluorescence, most of the widespread semiconductor nanoparticles include cadmium, which is cytotoxic.^{9,10)}

Zinc oxide (ZnO) is a wide-bandgap semiconductor material. With a bulk bandgap of approximately 3.37 eV, ZnO absorbs ultraviolet (UV) light. It is used for white pigments, cosmetics, medicine, and additive agents in rubber. For ZnO nanoparticles, various applications such as gas sensors,^{11,12)} varistors,¹³⁾ surface acoustic wave (SAW) filters,¹⁴⁾ UV laser diodes,^{15,16)} and solar cells are being studied.¹⁷⁻²¹⁾ ZnO nanoparticles may be synthesized using several methods²²⁾ such as spray pyrolysis,²³⁾ hydrothermal,^{24,25)} solvothermal,²⁶⁾ hot soap,^{27,28)} precipitation,²⁹⁻³³⁾ and solid-phase.³⁴⁾

ZnO emits UV light when electrons transit from the conduction band to the valence band, and green light when they transit from surface defect levels to the valence band after excitation into the surface defect level by UV light. The surface defect level related to the green luminescence is still controversial. Various models such as oxygen vacancies, interstitial oxygen, zinc vacancies, and interstitial zinc have been proposed for the surface defect.^{18,19,35)} One widely accepted theory points to oxygen defects. Some reports suggested a correlation between oxygen defects and the electron paramagnetic resonance (EPR) intensity at $g \sim 1.96$,³⁶⁾ while the others deny this relation.³⁷⁾

Laser irradiation (hereafter called irradiation) of a material is one of the prospective techniques to crystallize the material and to increase the material luminescence, and it has been applied to several types of thin films. Excimer laser annealing is an example of an industrial usage of this technique to crystallize amorphous silicon by exploiting the thermal energy of a UV laser beam.³⁸⁾ Various phosphor films on substrates have also been irradiated to increase crystallinity and luminescence.³⁹⁻⁴²⁾

In this study, we investigate the annealing effects of irradiation on ZnO nanoparticles dispersed in an organic solvent. Few reports exist on this topic, although

nanoparticles dispersed in solvent are useful in various fields. We selected ZnO in this study because of its technological potential, stability, and noncytotoxicity. We synthesized the ZnO nanoparticles using the normal precipitation method because of prevention of aggregation due to dispersion in solvent, and the controllability of particle size. Furthermore, the method is quite simple at room temperature. Irradiation of the ZnO nanoparticles in solvent with unreacted reactants, which is colloidal solution without purification after the preparation, decreases the green luminescence, giving a measure of the number of surface defects. It also slightly increases the UV luminescence of the nanoparticles. However, irradiation of purified (reactant-free) ZnO nanoparticles in solvent does not significantly modify the luminescence intensity (both visible and UV). In addition, the ZnO nanoparticle size does not significantly increase due to irradiation. With reactants, irradiation accelerates the synthetic reaction of highly crystallized ZnO on the nanoparticle surface, thereby decreasing the number of surface defects and leading to an increase in the UV luminescence.

2. Experiments

Zinc acetate dihydrate, sodium hydroxide, absolute 2-propanol, and hexane were procured from Kanto Chemical Corporation, and used without further purification.

Following the lead of many groups, we prepared the ZnO nanoparticles according to the procedure given in ref. 32. Zinc acetate dihydrate (0.5 mmol) was ultrasonically dissolved in 50 ml of absolute 2-propanol. Sodium hydroxide (0.5 mmol) was ultrasonically dissolved in 50 ml of absolute 2-propanol, and dropped into the zinc acetate solution vigorously stirred in an Erlenmeyer flask at room temperature, resulting in the immediate synthesis of the ZnO nanoparticles.

We divided the solution of the prepared ZnO nanoparticles into two portions, one being subjected to laser irradiation, and the other preserved without it. The twin solutions were characterized at the same time. As shown in Figure 1, the ZnO nanoparticle solution, contained in a quartz cell and stirred by a magnetic stirrer, was directly irradiated with a laser power of 50 mW at 325 nm wavelength, with a continuous wave He-Cd laser (Kimmon IK3552R-G).

We used a Rigaku RINT-2000 X-ray diffract meter to identify and characterize the synthesized nanoparticles. Due to their hydrophilic surface, the nanoparticles do not aggregate in polar solvents such as 2-propanol. To precipitate the nanoparticles, we added the nonpolar solvent hexane to the nanoparticle solution, leading to ZnO nanoparticle aggregates. The ratio of 2-propanol to hexane was 1:2. Three hours after adding hexane, a series of three centrifugation sequences separated the nanoparticle

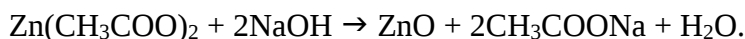
aggregates from the solvent. We observed the nanoparticle morphology using a field emission transmission electron microscope (FE-TEM; JEOL JEM-2010F) with an accelerating voltage of 200 kV.

The ZnO nanoparticles were dispersed in carbon tetrachloride and dropped on a carbon membrane on a copper grid. The solvent was removed by drying in a vacuum oven. We acquired room temperature photoluminescence (PL) spectra of as-synthesized and purified (reactant-free) nanoparticles in the solution using a Hitachi High-Technologies F-7000 fluorescence spectrophotometer. Purification of the nanoparticles involved removing the unreacted reactants such as zinc acetate and sodium hydroxide, using the procedure given above to remove the aggregates from the solution. The nanoparticle solution absorption spectra were acquired at room temperature using a Shimadzu MultiSpec1500 spectrometer (the nanoparticle solutions were contained in quartz cells for the measurements).

3. Results and Discussion

We identified the nanoparticles in 2-propanol via the X-ray diffraction pattern (XRD) of the precipitated nanoparticles (Fig. 2). The broad peaks are due to the small size of the particles. The peak height and angle of the XRD pattern correspond to the

PDF data of ZnO (PDF 36-1451). We therefore conclude that ZnO is successfully synthesized in 2-propanol. The synthetic reaction of ZnO is⁴³⁾



We also investigated the morphology of the ZnO nanoparticles in 2-propanol. Figure 3 shows an FE-TEM image of the nanoparticles. The particle size on the copper grid is approximately 5 nm, and the shape is nearly spherical. Lattice fringes indicating crystal structure are also observed on the nanoparticles.

We now discuss the photoluminescence of the ZnO nanoparticles in 2-propanol. Figure 4 shows the photoluminescence spectra of the irradiated and nonirradiated ZnO nanoparticles with reactants in 2-propanol, with an excitation wavelength of 300 nm. Note that for these measurements, unreacted reactants such as zinc acetate and sodium hydroxide are present in the 2-propanol solution. Figure 4(a) shows the entire photoluminescence spectrum spanning from 300 to 700 nm. The green luminescence of the irradiated nanoparticles is approximately 13% lower than that of the nonirradiated ones, and the peak wavelength is slightly red shifted. Figure 4(b) shows the photoluminescence spectrum in the UV region, spanning from 320 to 380 nm. The UV luminescence of the irradiated nanoparticles is slightly more intense than that of the nonirradiated ones, and the peak wavelength is also slightly red shifted. Figure 5 shows

photoluminescence spectra of the irradiated and nonirradiated nanoparticles in reactant-free 2-propanol. As mentioned in the experimental section, we added the nonpolar solvent hexane to the nanoparticle solution to precipitate the nanoparticles by aggregation, then separated them by centrifugation, before redispersing them ultrasonically into 2-propanol. The unreacted reactants such as zinc acetate and sodium hydroxide were thus removed from the ZnO nanoparticle solution. Figure 5(a) shows the entire photoluminescence spectrum of this solution, spanning from 300 to 700 nm and Figure 5(b) shows the photoluminescence spectrum in the UV region, spanning from 320 to 380 nm. We observe no significant change in the intensity compared with Figure 4, although the green luminescence of the irradiated nanoparticles is slightly weaker than that of the nonirradiated ones, and the peak wavelength is slightly red shifted.

Figure 6 shows the luminescence intensity difference between the irradiated and nonirradiated ZnO nanoparticles as a function of the irradiation time. The UV luminescence intensity increases linearly with time, indicating that irradiation strongly influences the UV luminescence of the ZnO nanoparticles.

To investigate the nanoparticle size, we measured the absorbance spectra of the irradiated and nonirradiated nanoparticles in 2-propanol with reactants, which are

shown in Fig. 7. Due to quantum confinement, a decrease in particle size will cause an increase in the band gap, leading to a blue shift in the absorbance edge¹⁻⁴. We estimate the particle size from the absorbance onset shown in Fig. 7, using the effective mass model⁴⁴⁻⁴⁶) and find that the nonirradiated and irradiated ZnO nanoparticles are 3.6 and 3.8 nm, respectively. These data indicate that the ZnO nanoparticle size is not significantly influenced by laser irradiation. Thus, the observed change in the green and UV luminescence is not related to the size of the ZnO nanoparticles.

Figures 4 and 5 indicate that irradiation of the ZnO nanoparticles with reactants decreases the green luminescence intensity, and that irradiation of the reactant-free nanoparticles does not significantly change the green luminescence. In general, luminescence intensity is related to nanoparticle size. However, as discussed above, the change in the green luminescence intensity because of irradiation is not attributable to a change in nanoparticle size because, as shown in Fig. 7, the irradiated nanoparticles are almost the same size as the nonirradiated ones. Each effect of zinc acetate and sodium hydroxide were investigated to understand the mechanism of the intensity change. Figure 8 indicates photoluminescence spectra of the purified nanoparticles in 2-propanol with zinc acetate. The unreacted reactants such as zinc acetate and sodium hydroxide were removed from the nanoparticle and then only zinc acetate was added. The

nanoparticles were irradiated by laser for 30 min in 2-propanol with zinc acetate. We observe a reduction in green luminescence and no significant change in UV luminescence. Peak at 600 nm is the second order scattering of grating. Figure 9 indicates photoluminescence spectra of the purified nanoparticles in 2-propanol with sodium hydroxide. A drastic reduction in green luminescence and no significant change in UV luminescence were observed. The drastic reduction in green luminescence should relate to the dissolution of ZnO in sodium hydroxide. Therefore, both reactants are required to decrease the green luminescence and to increase UV luminescence.

Many researchers have proposed that the green luminescence of ZnO nanoparticles is related to the electron transition at the defect level.^{18,19,35)} It is conceivable that the reduction in the green luminescence from ZnO nanoparticles is due to a reduction in lattice defects (i.e., improved crystallinity). Because nanoparticles have large surface-to-volume ratio compared to the bulk materials, the nanoparticle surface has a greater influence on the material properties. We thus conclude that a reduction in the green luminescence indicates in particular an increase in the crystallinity at the ZnO nanoparticle surface. The claim that the UV irradiation increases the crystallinity is supported by the observation that the change in luminescence intensity is proportional to the irradiation time, as shown in Fig. 6. The excitation of an electron from the

valence band to the conduction band promotes the synthetic reaction on the surface of ZnO when nanostructured ZnO is irradiated with UV light.^{47,48)} When zinc acetate and sodium hydroxide exist, UV laser beam promote the synthesis of ZnO on the surface of nanoparticle. The laser irradiation may raises the surface temperature of the ZnO nanoparticles, which also promotes the synthesis of ZnO.

Therefore, we conclude that highly crystallized ZnO is synthesized on the nanoparticle surface and that the reduction in surface defect numbers leads to a reduction in the green luminescence. UV laser irradiation promotes the synthetic reaction at the ZnO nanoparticle surface, thus raising the nanoparticle temperature.

4. Conclusions

Laser irradiation of the ZnO nanoparticles in the solvent with reactants increases the UV luminescence and decreases the green luminescence, the latter of which is related to surface defects. Laser irradiation of purified (reactant-free) ZnO nanoparticles in the solvent does not significantly change the luminescence intensity (green or UV). Furthermore, the ZnO nanoparticle size does not significantly increase due to laser irradiation. Laser irradiation of nanoparticles with unreacted reactants accelerates the synthetic reaction of highly crystallized ZnO on the nanoparticle surface, leading to a

reduction in surface defects and an increase in the UV luminescence.

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Figure captions

Figure 1. Schematic and photograph of laser irradiation of a solution of the ZnO nanoparticles in a quartz cell.

Figure 2. XRD pattern of the precipitated nanoparticles.

Figure 3. FE-TEM image of the ZnO nanoparticles.

Figure 4. PL spectra of the ZnO nanoparticles with the reactants in 2-propanol excited at 300 nm. The solid (dashed) line corresponds to the (non) laser-irradiated ZnO nanoparticles. (a) Green luminescence (emission wavelength: 300–700 nm). (b) UV luminescence (emission wavelength: 320–380 nm).

Figure 5. PL spectra of the ZnO nanoparticles without the reactants in 2-propanol excited at 300 nm. The solid (dashed) line corresponds to the (non) laser-irradiated ZnO nanoparticles. (a) Green luminescence (emission wavelength: 300–700 nm). (b) UV luminescence (emission wavelength: 320–380 nm).

Figure 6. Difference in luminescence intensity between the laser-irradiated and (non) laser-irradiated ZnO nanoparticles as a function of laser-irradiation time.

Figure 7. Absorbance spectra of the laser-irradiated and (non) laser-irradiated ZnO nanoparticles in 2-propanol. The solid (dashed) line corresponds to the (non) laser-irradiated ZnO nanoparticles.

Figure 8. Photoluminescence spectra of the purified ZnO nanoparticles in 2-propanol with zinc acetate excited at 300 nm. The solid (dashed) line corresponds to the (non) laser-irradiated ZnO nanoparticles.

Figure 9. Photoluminescence spectra of the purified ZnO nanoparticles in 2-propanol with sodium hydroxide excited at 300 nm. The solid (dashed) line corresponds to the (non) laser-irradiated ZnO nanoparticles.

ZnO
nanoparticle
solution

