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Increase in the fluorescence intensity of ZnO nanoparticle by laser irradiation

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Abstract

We increased fluorescence intensity of ZnO nanoparticles by irradiation of laser to nanoparticles in solvent. The intensity of laser-irradiated nanoparticles became 1.4 times larger than that of non-irradiated one. The ZnO nanoparticles were synthesized by precipitation method. The laser for irradiation to ZnO nanoparticles was He-Cd cw laser. It was found that the average particle size was slightly increased during laser irradiation by red-shifted absorbance onset. These highly-fluorescent nanoparticles in solvent are useful for biomedical field such as biological imaging.

Key words

ZnO, nanoparticle, fluorescence, laser

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1. Introduction

Extensive studies have recently been carried out on fluorescence of nanoparticles, because of unique optical properties [1]-[4]. ZnO is one of most promising materials in many fields [5]-[8]. ZnO nanoparticles were easily obtained by precipitation method [9]-[14]. ZnO is known as green phosphor. Increase in fluorescence intensity of nanoparticle is important in many applications of nanoparticle. To increase fluorescence intensity of phosphor, they were usually sintered in electric furnace. In this way, nanoparticles adhered to a wall of a container because the solvent was evaporated in the furnace when it was sintered. However, nanoparticles are usually used in solvent in the case of biomedical use because nanoparticles for markers of biological imaging are conjugated with DNA, cell and tissue in solvent. Therefore, it is important to increase fluorescence intensity of nanoparticles in solvent without adhesion to a wall of a container by evaporation of solvent.

In this study, we found that fluorescence intensity of ZnO nanoparticles in ethanol was increased by irradiation of UV laser. It is known that laser annealing increases fluorescence intensity of films, which consists of ZnS:Mn,Pr nanoparticles [15]. To our knowledge, few experiments to measure the optical properties after laser-irradiation to inorganic nanoparticle in solvent have been performed. Fluorescent nanoparticles in

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solvent are important in many fields, especially in biomedical use for biological imaging and so on.

2. Experiments

Synthesis of ZnO nanoparticle was based on reference [14], which had been referred by many groups. In this study, ethanol was used for solvent instead of 2-propanol. Zinc acetate dihydrate (0.5mmol) was dissolved in 50ml of ethanol ultrasonically. This Zn^{2+}-containing solution was stirred in Erlenmeyer flask vigorously. Sodium hydroxide (0.5mmol) was also dissolved in 50ml of ethanol ultrasonically. This OH^--containing solution was dropped to above Zn^{2+}-containing solution at room temperature. By this procedure, ZnO nanoparticles were synthesized. Laser beam was directly irradiated to ZnO nanoparticles in ethanol for 1 hour. He-Cd cw laser (Kimmon, IK3552R-G), whose wavelength was 325nm, was used. The solution was in quartz cell during the irradiation. To investigate ZnO nanoparticles, following apparatuses were used. The synthesized nanoparticle was identified with ZnO by X-ray diffractometer (RIGAKU, RINT-RAPID). ZnO nanoparticles were synthesized several times to obtain adequate amounts of ZnO nanoparticles for XRD measurement. Powder of ZnO nanoparticles were obtained by centrifugation after addition of hexane as poor solvent.

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Absorbance spectra were measured at room temperature by spectrometer (SHIMADZU, MultiSpec1500). Photoluminescence excitation spectra and photoluminescence spectra of ZnO nanoparticles in ethanol were measured at room temperature by fluorescence spectrophotometer (SHIMADZU, RF-5300PC).

3. Results and discussion

Figure 1 shows X-Ray diffraction pattern of ZnO nanoparticle as synthesized. All the patterns exhibited the hexagonal wurtzite structure of ZnO (PDF 36-1451). Lower bar graph indicated PDF data of ZnO. Peak height and angle of this XRD pattern corresponded to the PDF data of ZnO. Miller indexes were indicated in figure 1. Therefore, ZnO was successfully synthesized. However, these peaks were broad because of the size of ZnO nanoparticle. The average crystallite size of the ZnO nanoparticles was estimated 4.5nm by Scherrer equation [16].

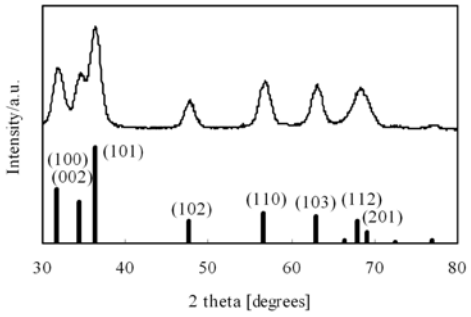

Figure 1

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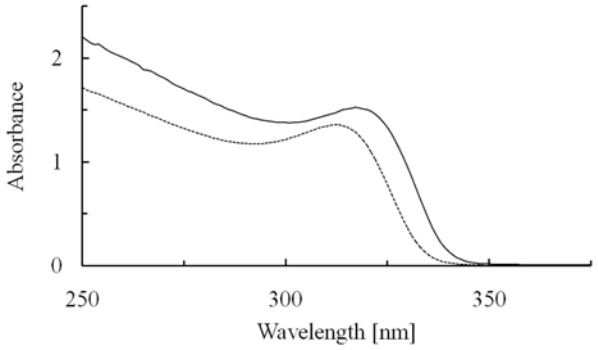

Figure 2

Figure 2 shows absorbance spectra of laser-irradiated ZnO nanoparticles and non-laser-irradiated ones in solvent. As particle size decreased, the band gap increases and absorption edge is blue-shifted comparing to that of bulk [1]-[4]. Particle size was estimated from absorption onset in figure 2 by using the effective mass model [17]-[19]. Average diameter of non-laser-irradiated ZnO nanoparticles was about 3.3nm because absorption onset was 326nm, while the average diameter of non-laser-irradiated ones was about 3.4nm because of 332nm. Absorbance onset was slightly red-shifted. Particle size was slightly increased, although these estimated values were slightly different from crystallite size of Scherrer equation in figure 1. The irradiation of laser to nanoparticles might coarsen them by thermal effect.

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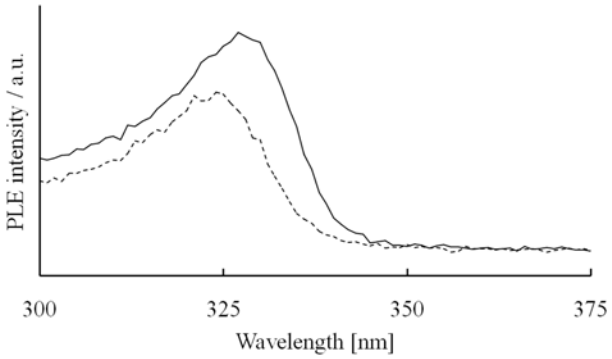

Figure 3

Figure 3 shows photoluminescence excitation spectrum of laser-irradiated ZnO nanoparticles and non-irradiated ones. Emission wavelength of PLE spectra was 500nm. The peak intensity of irradiated one was more than 1.4 times larger than that of non-irradiated one, although peak wavelength was shifted.

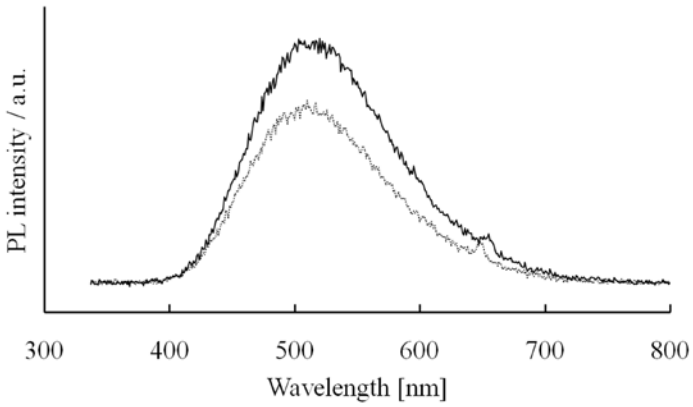

Figure 4

Figure 4 shows photoluminescence spectrum of laser-irradiated ZnO nanoparticles and non-irradiated ones. Diameter of ZnO nanoparticles were slightly increased by laser-irradiation. To eliminate the effect of red-shift in absorbance spectra, excitation wavelength of PL spectra was set at wavelength of maximum intensity of excitation spectra,

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whose emission wavelength was 500nm. Excitation wavelengths of laser-radiated nanoparticles and non-laser-irradiated ones were 327nm and 324nm, respectively. Peaks around 650nm were secondary scattering of excitation wavelength. The intensity of irradiated one was more than 1.4 times larger than that of non-laser-irradiated one. In this study, UV emission was not observed. It was considered that so many defects related to nonradiative relaxation existed in our ZnO nanoparticles because ZnO was synthesized at room temperature. This optical property might be related to experimental conditions. ZnO nanoparticles radiating no UV light are suitable for biological imaging, because UV light damages living creatures. It was considered that luminescence of green was increased by the increase of colors center related to green luminescence and/or the decrease of defects related to nonradiative relaxation. Local maximum peak height of absorbance spectra and photoluminescence excitation spectra increased by irradiation of laser to ZnO nanoparticles. These increases in absorbance might be related to increase in the number of color centers. In the case of ZnO, various models, which are O vacancies, interstitial O, Zn vacancies, interstitial Zn and so on, have been proposed to explain color center of green luminescence [6], [7], [20]. O vacancies is one of widely-accepted models. Irradiation of laser to ZnO nanoparticles might increase O vacancies in nanoparticles by desorption of oxygen. At the same time, laser annealing effect might decrease the defects related to nonradiative relaxation. It has been investigated

that irradiation of laser to metal nanoparticles increase temperature of them, which is several hundred degrees [21], [22]. This experiment was performed by pulse laser. It was considered that temperature was more increased in the case of cw laser because heat by pulse laser was likely to be removed than that by cw laser.

4. Conclusion

In conclusion, we found that fluorescence intensity of ZnO nanoparticles was increased by laser irradiation. The intensity of laser-irradiated ZnO nanoparticles was more than 1.4 times larger than that of non-laser-irradiated one. The irradiation of laser might increase O vacancies related to color center of green luminescence of ZnO nanoparticles.

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Figure captions

FIG. 1. XRD pattern of ZnO nanoparticle as synthesized. Lower bar graph indicates PDF data (PDF No. 36-1451, ZnO, the hexagonal wurtzite structure).

FIG. 2. Absorbance spectra of laser-irradiated ZnO nanoparticles and non-irradiated ones in ethanol at room temperature. Non-laser-irradiated nanoparticles: dashed line, laser-irradiated nanoparticles: solid line.

FIG. 3. Photoluminescence excitation spectra of laser-irradiated ZnO nanoparticles and non-laser-irradiated ones in ethanol at room temperature. Non-laser-irradiated

nanoparticles: dashed line, laser-irradiated nanoparticles: solid line.

FIG. 4. Photoluminescence spectra of laser-irradiated ZnO nanoparticles and non-laser-irradiated ones in ethanol at room temperature. Non-laser-irradiated nanoparticles: dashed line, laser-irradiated nanoparticles: solid line.