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Fabrication of ZnO nanocomposites by picosecond laser ablation of zinc in tetrahydrofuran solution of thermoplastic polyurethane

S. Faramarzi[1,*], M. R. Jalilian-Nosrati[1], S. Barcikowski[2]

[1]*Department of Physics, Faculty of Science, Islamic Azad University, Central Tehran Branch, Tehran, Iran*
[2]*Laser Zentrum Hannover, Hollerithallee 8, 30419 Hannover, Germany*

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Abstract

Laser ablation of a Zn target in tetrahydrofuran with different concentrations of thermoplastic polyurethane was performed with picosecond pulses. The results of ultraviolet-visible absorption, photoluminescence emission and X-ray diffraction pattern indicated that ZnO nanocomposites were produced. The influence of pulse energy, polymer concentration and argon degassing on production rate, size distribution and composite structure of nanocomposites were investigated. We tried to improve the control of size, agglomeration and composite structure of nanoparticles by polymer concentration and degassing with argon. The average particle diameters of nanocomposites which produced by 75μJ pulse energy in the liquid with 0.4 Wt% polymer concentration were in the range of 0.5 nm to 16 nm. The typical size of nanocomposites was decreased from 8 nm to 6 nm by 0.1 Wt% increasing in polymer concentration. In addition we could control agglomeration of nanocomposites by degassing with argon and increasing of polymer concentration up to 0.5 Wt%. We obtained maximum production rate by maximum laser pulse energy, 125 μJ. Polymer concentration and argon degassing were not effective in production rate.

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Keywords: *Production rate; Laser fluence; Photoluminscence emission; Polymer solution*

1. Introduction

Fabrication of nanoparticles has attracted great attention due to their unusual properties that differ from bulk materials. The size dependent properties of nanoparticles allow them to be candidates in a broad range of applications. Particularly, metal and metal oxide nanoparticles have increasing applications in nonlinear optics [1], optoelectronics [2], biomedical engineering [3-4], electro-optical devices [5], chemical catalysts [6] and lasing materials [7]. Among different preparation methods for producing nanoparticles [8], laser ablation technique has been successfully developed and laser ablation in liquid has been recognized as an important technique for the fabrication of nanoparticles [9-10]. In this method by adding surfactants to liquids, size and aggregation state of nanoparticles can be controlled and material with much higher purity can be produced [11]. The development of new pulsed laser sources (e.g. nano-, pico- and femtosecond pulses) has attracted much attention to ablation of solid target in various liquids [12-15]. Zinc oxide (ZnO), with a wide band-gap energy of 3.37 eV at room temperature and exciton binding energy of 60 MeV, is a semiconductor with a large number of applications. Because of particular optical properties of ZnO nanoparticles, it is a promising material for optoelectronic and electro-optical devices [5,16]. In the photoluminescence spectra of ZnO, there are different emission bands in the UV [17], visible (violet [18], blue [19], green [20], yellow and orange-red [21]) regions. The origins of different defect emissions are not understood completely but some hypotheses have been suggested to explain the mechanism of different defect emissions [22]. The UV peak is usually considered as the characteristic emission of ZnO and attributes to exciton transition. Wang et al.[18] observed a violet photoluminescence at 402 nm from ZnO films and attributed it to the electronic transition from conduction band states to valence band states. For understanding the defect emission mechanism of the violet photoluminescence in ZnO, more investigations are needed [22]. To explain the green emission, various mechanisms have been proposed, such as oxygen vacancies, interstitial oxygen, Zn vacancies, and Zn interstitials [20]. The orange-red emission is also commonly attributed to the presence of excess oxygen in the samples. Surface dislocations and zinc interstitials [22] are other proposes for orange-red emission. In addition to different preparation methods for fabrication of ZnO nanoparticles [23], ablation of Zn metal target in aqueous solution [24-26] has attracted more attention recently. Generation of metal and metal oxide nanocomposites by different preparation methods [27] and by laser ablation [28] in different solutions of polymers have been reported before. ZnO nanocomposites have been produced by some different methods [29], but there is no report on fabri-

*Corresponding author:S. Faramarzi;
E-mail: sh_faramarzi@iauctb.ac.ir
Tel: (+98) 21 88385787
Fax: (+98) 21 88385777

cation of ZnO nanocomposites by laser ablation in solution of polymer in organic liquid. In this paper we report generation of ZnO nanocomposites by picosecond laser ablation of zinc target in tetrahydrofuran (THF) with different concentrations of thermoplastic polyurethane (TPU). The generated nanocomposites by this method and in these liquids have smaller size and narrower size distribution compared to the nanoparticles which have been reported by other workers on this area recently [24-26].

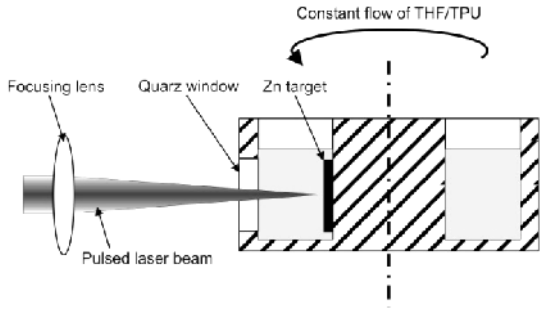

Fig. 1. Set up used for laser ablation of Zn in stirred TPU solution of THF

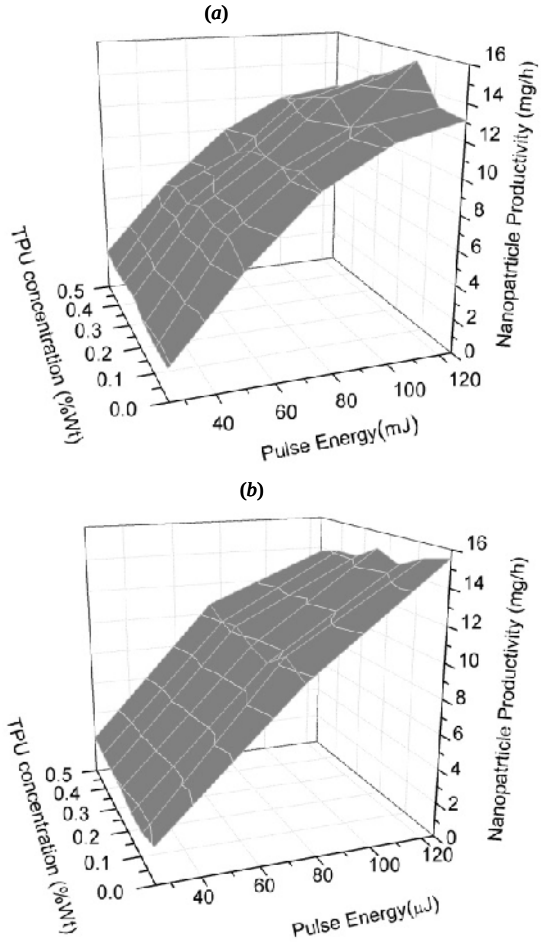

Fig. 2. (a) Production rate for one hour without argon, (b) Production rate for one hour with argon

2. Experimental details

ZnO nanocomposites were produced by laser ablation of a Zn target in THF with different concentrations of TPU as a liquid media. Zinc plate (purity 99.58 Wt%) was fixed on a vertical flat bracket in front of laser beam in a Teflon chamber filled with 30 mL solution of THF with specific concentration of TPU, which was continuously stirred. Ablation performed for 10 min by a picosecond pulsed laser (Trumpf, TruMicro 5250, 25 W power, 515 nm wavelength, pulse duration about 7 Ps, 125 µJ max pulse energy and 200 kHz max repetition rate). The laser beam was focused on the metal plate using a telecentric F-Theta lens with a focal length of 56 mm and a scanner (Harryscan II-14/ Scanlab). The setup applied to produce nanocomposites in liquid media is shown in Fig. 1. Different pulse energies from 25 µJ to 125 µJ and different concentrations of TPU up to 0.5 Wt% were selected. Repetition rate during the experiments was 33.3 kHz and scan speed was fixed to 3300 mm/s. The colloids were characterized by transmission electronic microscopy

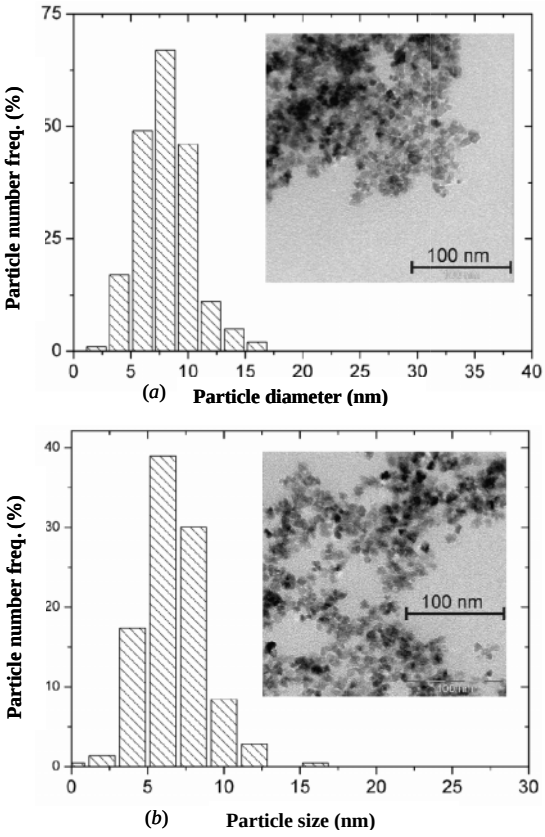

Fig. 3. (a) TEM image and primary particle size distribution of nanocomposites produced in THF with 0.4 wt% TPU concentration by 75 µJ pulse energy, (b) TEM image and primary particle size distribution of nanocomposites produced in THF with 0.5 wt% TPU concentration by 75 µJ pulse energy.

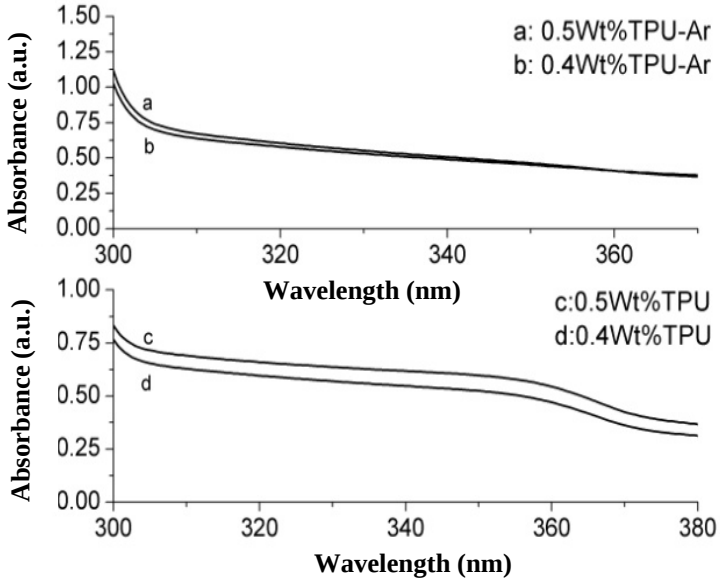

Fig. 4. Ultraviolet-visible absorption of nanocomposites produced by 75 µJ pulse energy in THF (curve-a) with 0.5Wt% of TPU and argon degassing (curve-b) with 0.4Wt% of TPU and argon degassing (curve-c) with 0.5Wt% of TPU without argon degassing (curve-d) with 0.4Wt% of TPU without argon degassing.

(TEM, Zeiss LIBRA®120 PLUS) to measure real size, optical absorption spectra (1650 Pc, Shimadzu ultraviolet–visible spectrometer), room temperature photoluminescence (Fluorescence Spectrophotometer F-4500 with Xe lamp, Excitation wavelength was 350 nm (3.65 eV)) and X-ray diffraction (Stadi P Stoe diffractometer using CuK_α radiation ($\lambda = 1.54$ Å)) for characterizing structure of nanocomposites. For controlling oxidation reaction of nanocomposites during ablation, we degassed the liquids before ablation with argon for 40 min and performed the same experiments in three different pulse energies, 25 µJ, 75 µJ and 125 µJ. Ablation rate determination was carried out by weighting the material before and after the ablation process (Sartorius M3P) with an accuracy of 0.001 mg. For observing photoluminescence emission of productions, two samples were prepared by ablation in the liquid with 0.4 Wt% TPU concentration. Ablation time increased to one hour at two different pulse energies of 75 µJ and 125 µJ.

3. Results and discussion

Fig. 2a and Fig. 2b show particle production rate per one hour by different laser pulse energies in THF with different concentrations of polymer without and with argon degassing, respectively. The ablation rates increased continuously with laser pulse energy. Ablation rate is approximately constant at constant pulse energy for different liquids with different concentrations of TPU.

TEM pictures and analyzed particle size distributions of nanocomposites prepared in THF with different concentrations of TPU ,0.4 Wt% and 0.5 Wt%, at 75 µJ energy are shown in Figs. 3a and 3b, respectively.

Fig. 4 shows typically the ultraviolet-visible optical absorption spectra of generated nanocomposites at 75 µJ pulse energy in the liquids with 0.4 wt% and 0.5 wt% TPU concentration without and with argon degassing. Obviously in ultraviolet-visible absorption spectra (Fig. 4, curves c and d) there is one shoulder at 360 nm (3.37 eV) which correspondes to ZnO nanocomposites. The shoulder is shown by nanocomposites which generated in the liquids without argon degassing and disappears in ultraviolet-visible spectra of nanocomposites which produced in the liquids with argon degassing. Since ZnO exciton absorption peak is located at about 360 nm, this shoulder should correspond to ZnO nanocomposites.

Fig. 5 depicts photoluminescence emission spectra of ZnO nanocomposites which produced by 125 µJ pulse energy during one hour. There is a green emission at about 538 nm. Except for exciton-related UV photo-

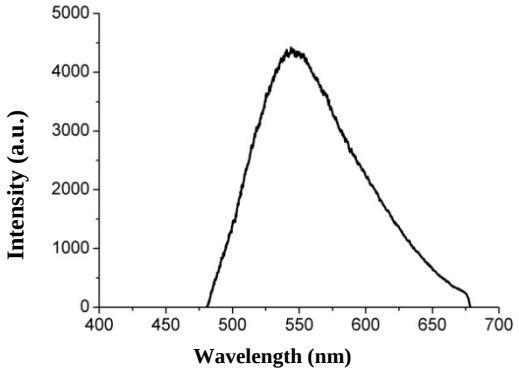

Fig. 5. Photoluminescence of nanocomposites produced in THF with 0.4Wt% of TPU by 125 µJ pulse energy.

luminescence emission of ZnO, the origins of the visible photoluminescence emissions of ZnO are still open up to now. To explain the origin of green photoluminescence emission for generated ZnO nanocomposites, we propose either oxygen vacancies or Zn interstitials [69-70].

Fig. 6 shows the typical XRD pattern for the sample obtained by laser ablation in the liquid with 0.4Wt% of TPU concentration which was produced by 75 µJ pulse energy. Three peaks in XRD pattern were characterized as belonging to hexagonal structure of bulk ZnO with lattice constants of a = 3.249 Å and c = 5.206 Å.

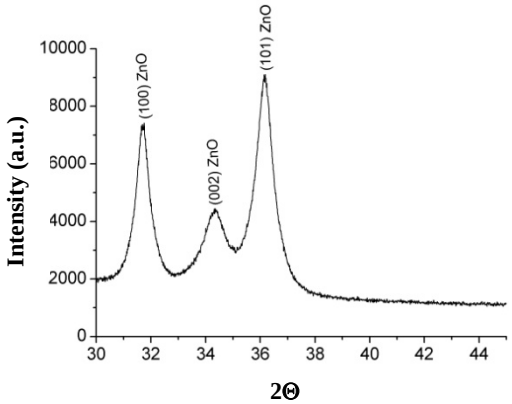

Fig. 6. XRD pattern recorded from the ZnO nanocomposites produced in THF with 0.4 wt% of TPU by 75 µJ pulse energy.

4. Conclusion

For the first time we have used picosecond laser ablation for fabrication of ZnO nanocomposites in polymer solution. We tried to improve the control of size, agglomeration and composite structure of nanoparticles by polymer concentration and degassing with argon. Moreover, we studied the influence of laser pulse energy on the production rate in the liquids with different concentrations of TPU. In this work fabrication of ZnO nanocomposites were aimed because of biomedical applications.

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