Manipulation of ZnO/Polymer Nanocomposites Generated by Nanosecond Laser Ablation in Organic Liquid

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We present experimental results on the production of ZnO nanoparticles with second harmonic of pulsed nanosecond Nd:YAG laser ($\lambda = 532$ nm, pulse duration = 5 ns) in tetrahydrofuran with 0.0 wt% and 0.8 wt% concentrations of polystyrene by high (200 mJ pulse energy) and moderate (80 mJ pulse energy) pulse energies. The produced colloids were characterized by ultraviolet-visible absorption, transmission electron microscopy, room temperature photoluminescence emission and dynamic light scattering. The mean size of nanoparticles decreased from 40 nm to 22 nm by adding polymer (0.8 wt%) and increasing the pulse energy. The colloidal nanocomposites showed a shoulder at 360 nm in ultraviolet-visible absorption spectra and were found very stable for one month. We observed two photoluminescence emission peaks in UV region at 380 nm and 400 nm attributed to exciton transition. Dynamic light scattering indicated that the size and aggregation of nanocomposites were controlled by polymer concentration and pulse energy.

1. Introduction

Recently, many researchers have prepared a series of novel nanostructures by using pulsed-laser ablation (PLA) of target in liquid media [1–7]. Compared with other chemical or physical methods, PLA is much more simple and controllable procedure. On the other hand, the products obtained by PLA have high chemical pureness. 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 good candidates in a broad range of applications. Particularly, metal and metal oxide nanoparticles have increasing applications in nonlinear optics [8], optoelectronics [9], biomedical engineering [10, 11], electro-optical devices [12], chemical catalysts [13] and lasing materials [14].

The synthesis of ZnO nanoparticles using laser ablation in an aqueous solution was intensively studied during the last years [15–23]. 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. In the photoluminescence spectra of ZnO, there are different emission bands in the UV [24], visible (violet [25], blue [26], green [27], yellow and orange-red [28]) 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 [29]. The UV peak is usually considered as the characteristic emission of ZnO and attributes to exciton transition. Wang et al. [26] 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 [29]. In this paper we report generation of ZnO nanocomposites by nanosecond laser ablation of zinc (Zn) target in tetrahydrofuran (THF) and in THF with 0.8 wt% concentration of polystyrene (PS). We try to exhibit the roles of pulse energy and polymer concentration in controlling of size, shape, composite and agglomeration of ZnO nanocomposites.

2. Experimental

ZnO nanocomposites were produced using laser ablation of a Zn (99.95%) target in THF (> 99.9%) with different concentrations of PS as liquid media. A Zn target was fixed on a vertical flat bracket in front of a laser beam in a teflon chamber filled with a 45 mL solution of THF with specific concentration of PS (Sigma-Aldrich), which was continuously stirred. Laser ablation was performed by Nd:YAG laser (Quantel, Briliant b class4, 5 ns pulse duration, 10 Hz repetition rate, 4.5 W maximum average power and 450 mJ maximum pulse energy, 7 mm diameter) operating at second harmonic with the wavelength of 532 nm. The laser beam was focused by a lens with the focal length of 100 mm on the surface of the target. Different pulse energies 80 mJ/pulse and 200 mJ/pulse and different concentrations of PS 0.0 wt% and 0.8 wt% were selected. The nanocomposites were characterized by transmission electron microscopy (TEM, Zeiss, Em900), ultraviolet-visible spectroscopy (UV-VIS spectrometer, V-530, JASCO), dynamic light scattering (ZS-Malvern zeta sizer) and room temperature photoluminescence emission spectroscopy (fluores-

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cence spectrophotometer, Varian Cary Eclipse, excitation wavelength was 350 nm).

3. Results and discussion

Figure 1a and b shows TEM pictures and size distributions of nanocomposites fabricated in THF by 80 mJ pulse energy and in THF with 0.8 wt% of PS by 200 mJ pulse energy, respectively. The nanoparticles had spherical shapes and their average size decreased obviously from 40 nm to 22 nm by increasing polymer concentration and laser pulse energy.
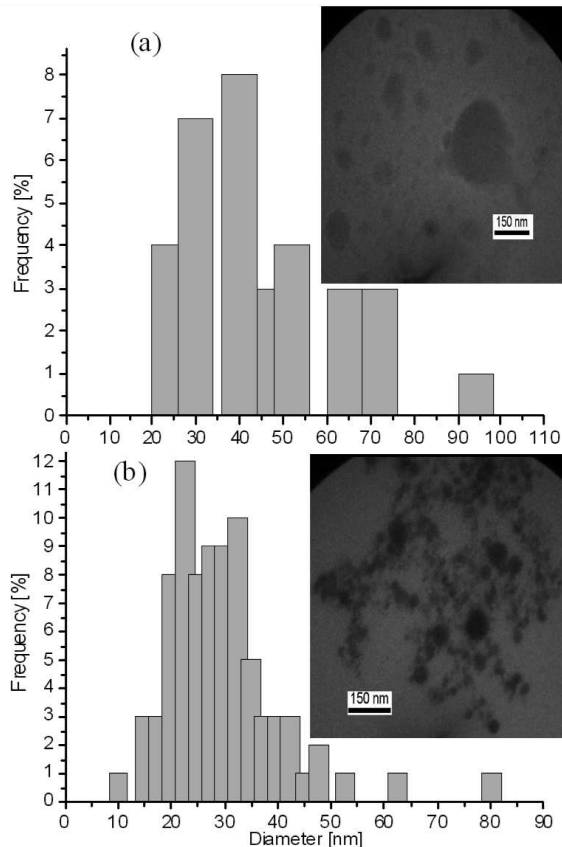

Fig. 1. TEM pictures and size distributions of produced nanocomposites in (a) THF by 80 mJ/pulse; (b) THF with 0.8 wt% of PS by 200 mJ/pulse.

Figure 2a–e depicts typically the UV-VIS absorption spectra of generated nanocomposites in THF with 0.8 wt% concentration of PS by 80 mJ pulse energy and 200 mJ pulse energy at two different times within a month and Fig. 2e shows the UV-VIS absorption spectra of the nanocomposites produced in pure THF by 200 mJ/pulse, respectively. We observe obviously a shoulder at 360 nm (3.37 eV) for all of the colloids correspond to ZnO exciton absorption. Comparing parts (a)–(d) confirmed that the stability of nanocomposites produced in THF with 0.8 wt% of PS is high and the characteristic absorption peak of ZnO nanocomposites

(360 nm) was observed after one month. This shoulder was not clear for the nanocomposites in pure THF after one month because of high aggregation of nanocomposites.
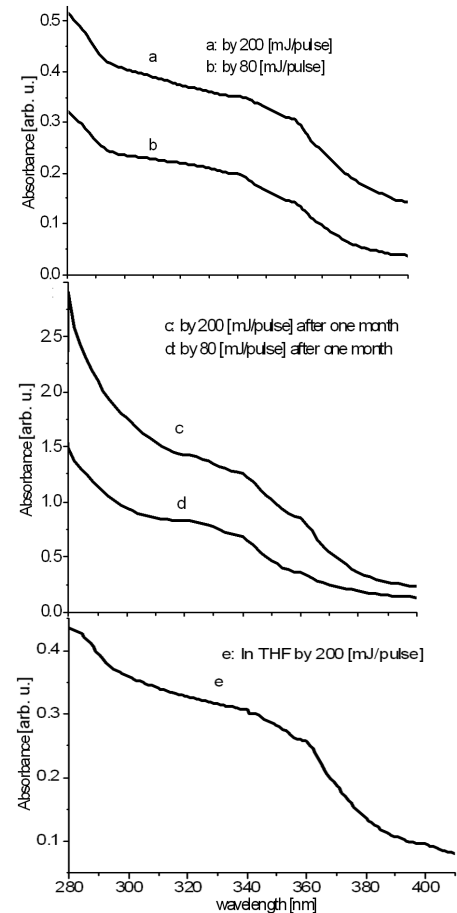

Fig. 2. UV-VIS absorption spectra of produced nanocomposites in THF with 0.8 wt% concentration of PS by 80 mJ/pulse and 200 mJ/pulse (*a*) and (*b*) at first day, (*c*) and (*d*) after one month, (*e*) in THF by 200 mJ/pulse at first day.

Figure 3a–c depicts photoluminescence emission spectra (excitation wavelength was 350 nm) of ZnO nanocomposites produced in THF with 0.8 wt% concentration of PS by 80 mJ pulse energy and by 200 mJ pulse energy and in pure THF by 80 mJ pulse energy, respectively. We observed two characteristic emissions of ZnO nanocomposites, UV emission at 380 nm and violet emission at 400 nm. The photoluminescence of ZnO may be associated with different origins. Except for UV photoluminescence emission of ZnO, which is usually attributed to exciton transition, the origins of the visible photoluminescence emissions of ZnO are still being discussed. Wang et al. [25] attributed violet emission to the electronic transition from conduction band states to valence band states.

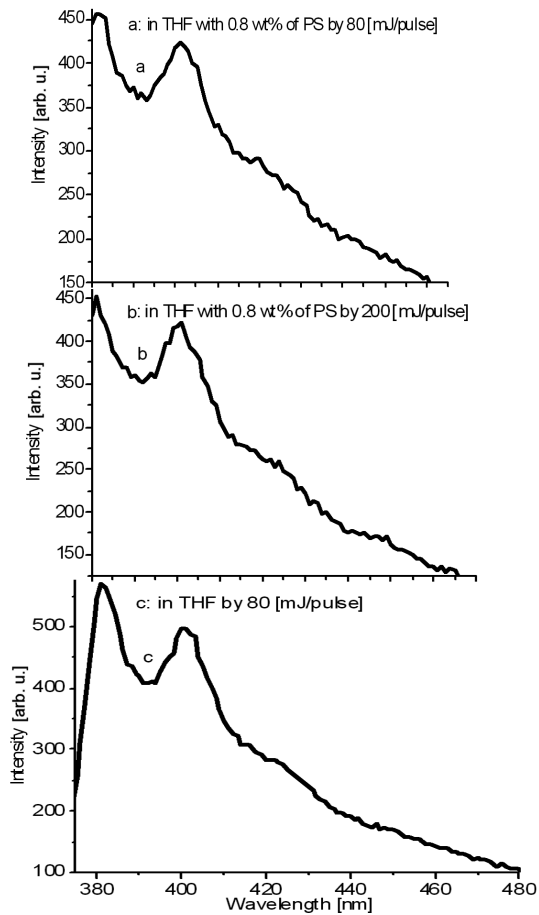Figure 4a and b shows the dynamic size distribution of ZnO nanocomposites produced by 80 mJ pulse energy in

Fig. 3. Photoluminescence emission spectra of produced nanocomposites (excited by 350 nm) in THF with 0.8 wt% concentration of PS (a) by 80 mJ/pulse, (b) by 200 mJ/pulse, (c) in THF by 80 mJ/pulse.
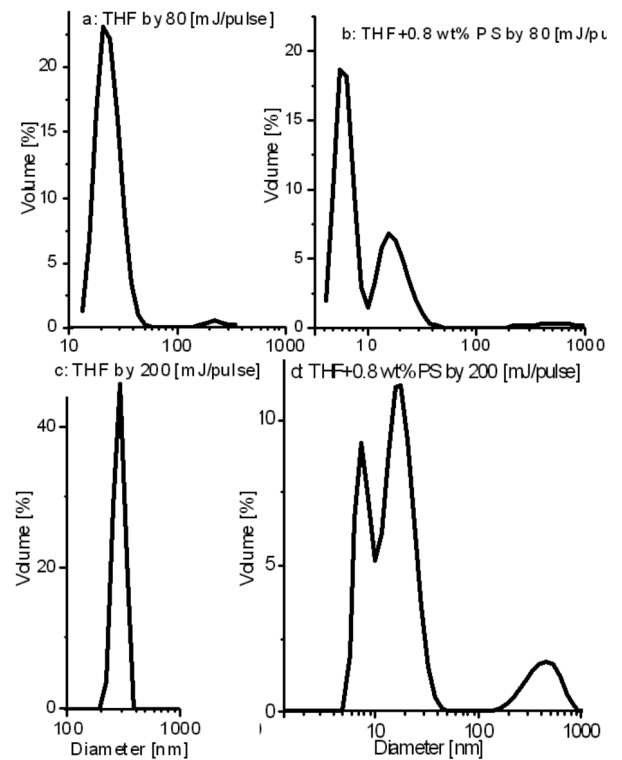

Fig. 4. Dynamic size distribution of produced nanocomposites in (a) THF by 80 mJ/pulse, (b) THF with 0.8 wt% of PS by 80 mJ/pulse, (c) THF by 200 mJ/pulse, (d) THF with 0.8 wt% of PS by 200 mJ/pulse.

THF and in THF with 0.8 wt% of PS. Figure 4c and d indicates the dynamic size distribution of the nanocomposites fabricated by 200 mJ pulse energy in THF and in THF with 0.8 wt% of PS, respectively. Comparing parts (a) and (b) as well as (c) and (d), left to right, indicates by adding polymer the agglomeration and dynamic size of nanoparticles reduced which is attributed to the capping of polymer (PS) on the ZnO nanoparticle surfaces. On the other hand, comparing parts (a) and (c) as well as (b) and (d), up to down, indicates although by increasing pulse energy smaller nanoparticles were produced but more aggregate was observed for nanoparticles and larger dynamic size was found for ZnO nanocomposites fabricated by high pulse energy.

4. Conclusion

Pulsed nanosecond laser ablation was performed for fabrication of ZnO nanocomposites in polymer solution. We tried to improve the control of size, shape, composition and agglomeration of nanoparticles by polymer concentration and pulse energy. In consequence for produc-

tion of smaller nanoparticles with less agglomeration, we have to use moderate pulse energy and more polymer concentration in the solutions during the ablation.

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