

Optical linearity and nonlinearity of ZnSe nanocrystals embedded in epoxy resin matrix investigated by Z-scan technique

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Abstract

The ZnSe nanocrystals were synthesized by hydrothermal method. Through mixed with epoxy resin in vacuum at high temperature environment, the nanocrystals embedded in an epoxy resin matrix structure were obtained. This nanocomposite sample was characterized by transmission electron microscope (TEM) and electron beam diffraction, showing the nanocrystals were dispersed homogeneously and their structures were zinc blende structure. The nanocomposite structure was also confirmed by the blue-shift of the absorption edge. The nonlinear refraction index and two-photon absorption (TPA) coefficient were measured by the Z-scan technique, using a single Gaussian beam of Nd:YAG laser (532 nm). The result shows that ZnSe nanocrystals embedded in epoxy resin matrix have higher nonlinear refraction index and lower TPA coefficient than that of bulk ZnSe.

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1. Introduction

In recent years, semiconductor nanocrystals have been investigated extensively due to their promising applications for various optoelectronic devices. The nanometer size structure makes the electronic energy states discrete. When the diameter of nanocrystals is decreased, the energy separation and quantum effect will be enhanced. Size dependent shifts of the absorption and emission spectra in semiconductor nanocrystals have been widely reported [1–4]. In addition, at the effect of pump laser, the enhancement of electron cloud deformation and optical Kerr effect makes the nanometer materials have large third-order optical nonlinearities than that of the bulk ones [5,6]. This change in refractive index leads to self-focusing or defocusing of light beam within materials with appreciable n_2 values. The typical transmission with peak-valley shape dependent on the change in refractive index acts like an ON–OFF switch. Some large third-order optical nonlinearities materials, such as CdTe [7], and Bi₂O₃ [8],

had been reported, which indicates that these quantum structures can be used for optoelectronic devices.

Currently, nanocrystals can be synthesized by a variety of methods, such as sol–gel methods [9,10], hydrothermal method [11], chemical vapor deposition (CVD) [12,13], and molecular beam epitaxy (MBE) [14,15], etc. For all of these methods, hydrothermal method, which has advantages of low reaction temperature, simple equipment and less consumption of energy, has been used widely. In addition, the hydrothermal method is also an effective method to form well-crystallization structure with fewer defects.

In this paper, the ZnSe nanocrystals were synthesized by hydrothermal method, and then the ZnSe nanocrystals were dispersed into the epoxy resin matrix to form a composite structure. At last, the Z-scan technique was employed to measure the sign and the magnitude of the nonlinear refraction index and two-photon absorption coefficient of the sample.

2. Experimental procedure

Firstly, ZnNO₃·6H₂O was dissolved in deionized water. The Se powder was added into KBH₄ aqueous solution to mix together at 60 °C water bath under an atmosphere of argon. Secondly, these

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two kinds of solution were mixed and became milk-yellow immediately. NaOH aqueous solution was added after reacting for a while. Thirdly, the solution was put into the autoclave (teflon inside, 70 mm³). Finally, the autoclave was heated to a certain temperature and kept for a certain time. The ZnSe nanocrystals were collected by centrifugation after purification with deionized water and ethanol, respectively, under ultrasonic condition, and then dried in vacuum condition at 60 °C.

The dried ZnSe nanocrystals were dispersed in acetone solutions and confect to a saturated and stable solution, and then 10 mL saturated solutions were extracted to 50 g liquid state epoxy resin and stirred for 2 h under an atmosphere of argon. The curing agent was added to the mixture solution as follow. When the solution became sticky, the mixture solution was transferred to vacuum case. For prevent occurring drastic reaction, we increased the temperature and decreased the pressure in vacuum case step by step. After keeping 12 h at 80 °C, the ZnSe nanocrystals embedded in epoxy resin matrix were synthesized. By the following polishing and cutting, the transparent and yellow nanocomposite sample with 1 mm thickness was achieved.

3. Results and discussion

3.1. Structural characterization

The X-ray diffraction (XRD; Model D\max-2400, Rigaku) patterns were obtained using Cu K α radiation (1.54065 Å). X-ray diffraction patterns of nanocrystals synthesized by hydrothermal method are shown in Fig. 1. The diffraction peaks of (1 1 1), (2 2 0) and (3 1 1) associated to zinc blende structure can be clearly observed. On the other hand, a broadening of the diffraction peaks is detected due to the nanoscale grain size. The Debye–Scherrer formula was utilized to calculate the average grain size of the sample. The average grain size of the ZnSe nanocrystals is 20 nm.

The nanocrystals dispersed in acetone solutions were measured by transmission electron microscopy (TEM; Model JEM-3010, Tokyo, Japan) at room temperature. The image of TEM (Fig. 2) shows that the most probable value of the grain size is 20 nm, which is in agreement with the XRD results. Though the nanocrystals often aggregate, it is easy to distinguish every particle. Fig. 3 provides the evidence that the ZnSe nanocrystals

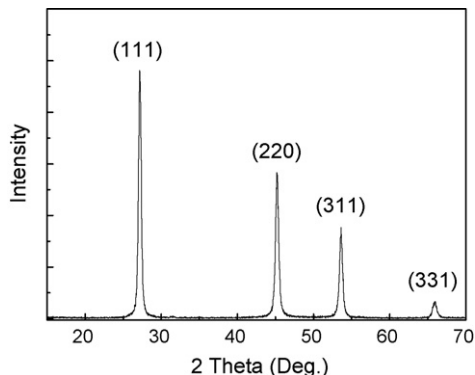


Fig. 1. XRD pattern of ZnSe nanocrystals synthesized by hydrothermal method.

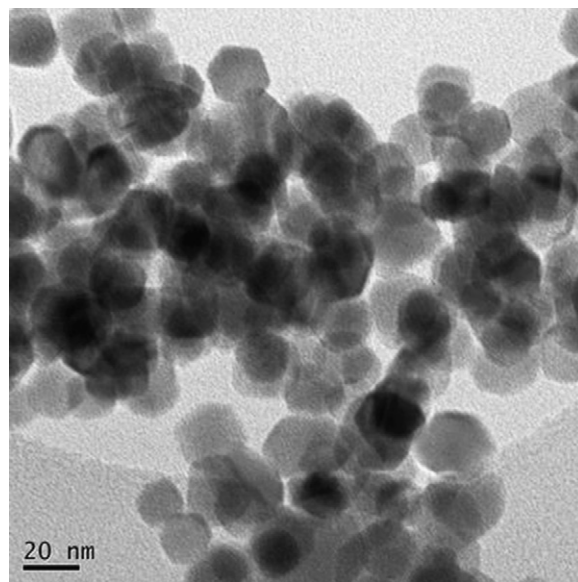


Fig. 2. The TEM image of ZnSe nanocrystals dispersed in acetone.

synthesized by hydrothermal method have been embedded homogeneously in epoxy resin matrix. Compared with Fig. 2, the nanocrystals in Fig. 3 are mainly about 20 nm and the particles are isolated, which reveals that the composite process is capable of separating the aggregate nanocrystals effectively. The electron diffraction pattern (Fig. 4) also confirms ZnSe nanocrystals embedded in epoxy resin are zinc blende structure, which is also consistent with the conclusion drawn from XRD.

3.2. Absorption spectra

Fig. 4 shows the linear absorption spectra of ZnSe nanoparticles dispersed in acetone solution (a), ZnSe nanoparticles embedded in epoxy resin (b) and pure epoxy resin (c), respectively. The spectra were recorded by a JASCO V-570

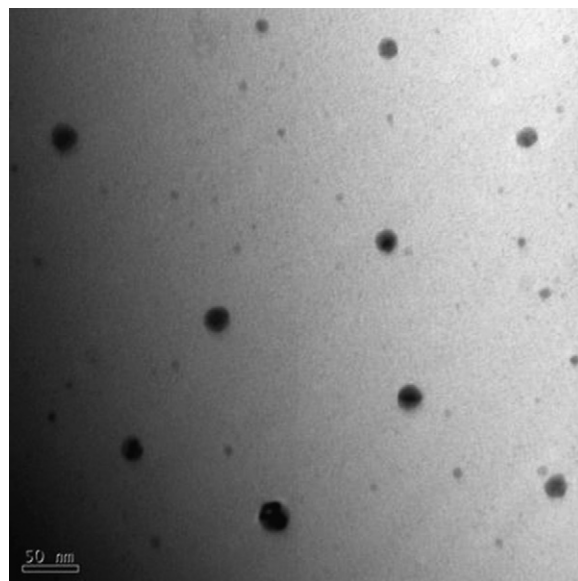


Fig. 3. The TEM image of ZnSe nanocrystals embedded in epoxy resin matrix.

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