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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.

Keywords: ZnSe nanocrystals; *Z*-scan technique; Optical nonlinearity; Absorption

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 Bi_2O_3 [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, $ZnNO_3 \cdot 6H_2O$ was dissolved in deionized water. The Se powder was added into KBH_4 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 mm^3). 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 Kα 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 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.

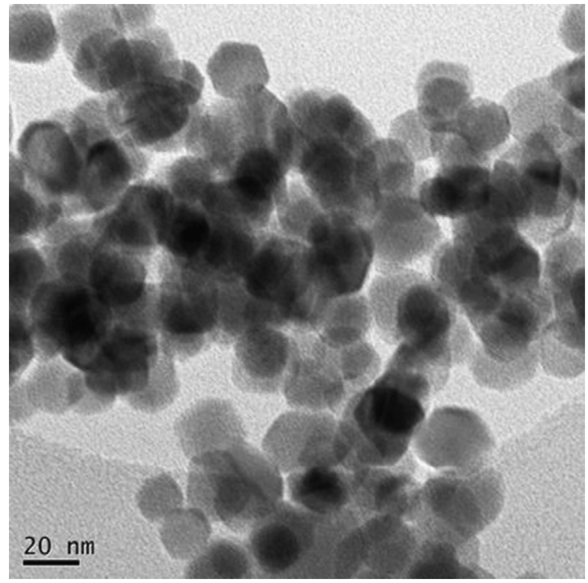

Fig. 2. The TEM image of ZnSe nanocrystals dispersed in acetone.

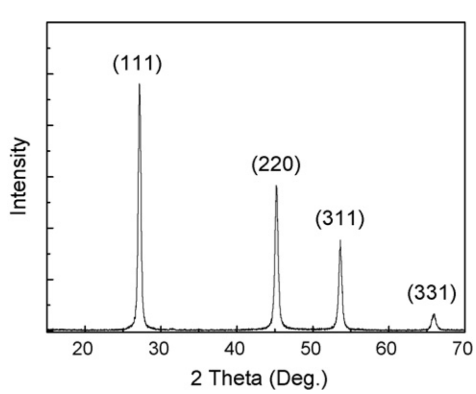

Fig. 1. XRD pattern of ZnSe nanocrystals synthesized by hydrothermal method.

3.2. Absorption spectra

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

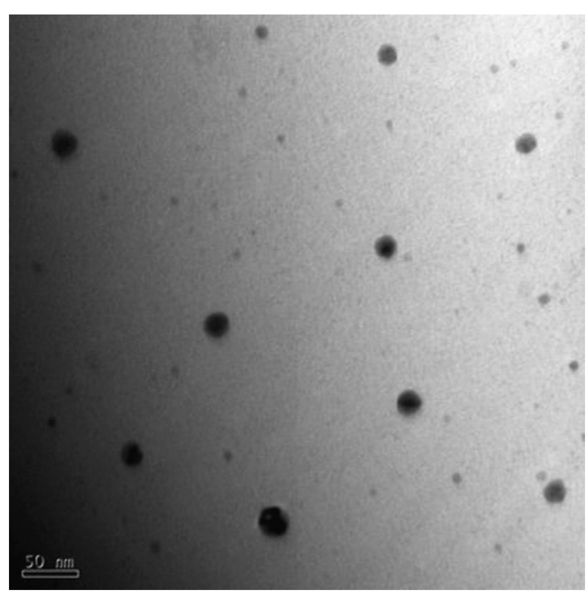

Fig. 3. The TEM image of ZnSe nanocrystals embedded in epoxy resin matrix.

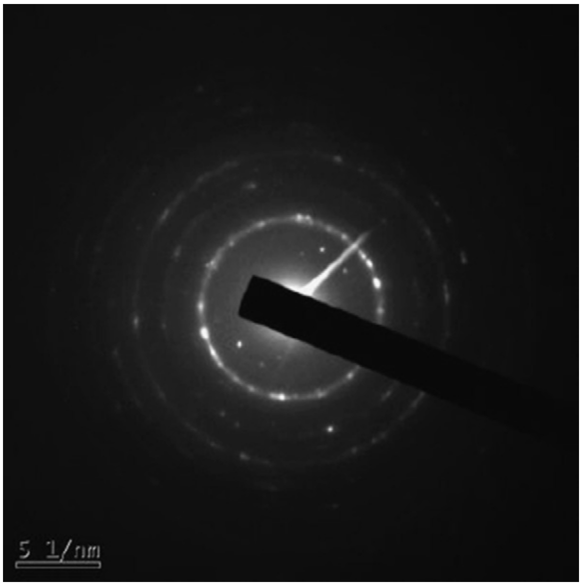

Fig. 4. The electron diffraction pattern of the ZnSe nanocrystals embedded in epoxy resin matrix.

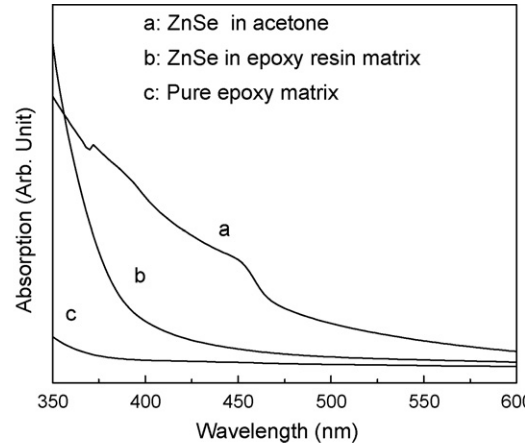

Fig. 5. The spectra of ZnSe nanocrystals dispersed in acetone solution (a), ZnSe nanocrystals embedded in epoxy resin matrix (b) and pure epoxy resin (c), respectively.

spectrometer in the range of 350–600 nm at room temperature. These absorption spectra exhibit the blue-shift arose by ZnSe nanocrystals both in acetone solution and epoxy resin matrix. There is distinct salience at 450 nm in curve (a); this is due to the aggregation of ZnSe nanocrystals in acetone solution. In curve (b), there is an abrupt absorption edge. The optical bandgap was estimated to be 3.10 eV (400 nm) from the linear extrapolation of the absorption edge, which is 0.42 eV blue-shift compared with bulk ZnSe (2.58 eV). According to Brus's formula [16]:

$$E(R) = E_g + \frac{\hbar^2\pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon_2 R} + \frac{e^2}{R}\overline{\sum_{n=1}^{\infty}\alpha_n\left(\frac{S}{R}\right)^{2n}} \tag{1}$$

where E_g is the band gap energy of bulk ZnSe material, ε_2 is the dielectric constant of ZnSe. m_e and m_h are effective masses of electron and hole. The second term is regards as quantum energy of localization, increasing as R^{-2} for both electron and hole. The third term is the Coulomb attraction; and the last term is considered as the polarization energy of the charge carriers. The calculated result shows that the grain sizes in epoxy resin matrix are 2.0 nm, which is corresponding to the smallest isolated particles in the sample. For the larger particles about 20 nm in Fig. 3, they belong to weak confinement region, where the Brus's formula cannot be used [2].

3.3. Nonlinear optical properties

The nonlinear refraction index and two-photon absorption coefficient of the sample were determined by the well-known Z-scan method in a single-beam single-wavelength geometry given by Sheik-Bahae et al. [17]. A Nd:YAG Q-switched laser (GCR170, Spectra-Physics, Inc.), with the pulse width of 7 ns, full width at half-maximum, was used as the light source. A lens of 160 mm focal length was used to focus the laser beam onto the tested sample, which was moved along the optical axis (Z direction) through the focus by a step motor driver. The laser beam waist (ω_0) was 25 μm. Both of the transmitted beam energy and the reference beam energy were recorded by energy radiometers (Rjp-637, Laser Probe, Inc.). The sample used for nonlinear measurement has the thickness of 1 mm, which is much smaller than the diffraction length of the beam z_0. The transmittance after passing through the sample was measured simultaneously as a function of position z by using closed-aperture in the far field of the lens (Fig. 5).

Fig. 6 shows the normalized transmittance versus the sample position (z) measured with closed-aperture Z-scan technique using the pump laser intensity of $I = 6.5$ GW/cm^2. Some information can be acquired directly. First, the curve exhibits a typical peak-valley characterization, which indicates the sign of nonlinear refractive index of the ZnSe embedded in epoxy resin is negative. Second, the part of valley occupies larger depth and area, which is due to the nonlinear absorption. As mentioned above, the bandgap of ZnSe nanocrystals embedded in epoxy resin matrix is 3.10 eV, and the energy of our pump laser is

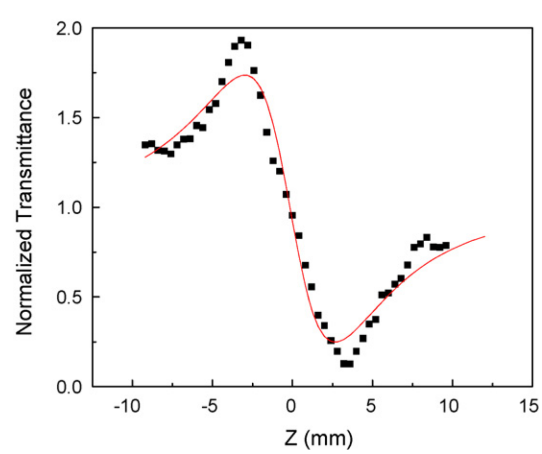

Fig. 6. Normalized Z-scan curves of ZnSe nanocrystals embedded in epoxy resin matrix.

$h\nu = 2.33$ eV (532 nm), so $E_g/2 < h\nu < E_g$ is tenable and the two-photo absorption is permitted [18].

Considering the nonlinear refraction and the two-photo absorption (TPA) always present together for closed-aperture measurement, Yin et al. [19] and Liu et al. [20] proposed the following modificatory fitting formula:

$$T(x) = 1 - \frac{2(\rho x^2 - 2x + 3\rho)}{(x^2+9)(x^2+1)}\Delta\Phi \quad (2)$$

where $x = z/z_0$, $z_0 = k\omega_0^2/2$ is the diffraction length of the beam, and ρ is the parameter, which is direct proportion with ratio of TPA coefficient and nonlinear refraction index.

According to Eq. (2), both of the nonlinear refractive index and TPA coefficient can be extracted from the fitting closed Z-scan measurement. The calculated results show that the nonlinear refraction coefficient $n_2 = -1.31 \times 10^{-9}$ esu, which is about 40 times greater than that of bulk ZnSe [21], and the TPA coefficient $\beta = 3.96$ m/GW, which is about two order magnitude lower than that of bulk ZnSe [21].

4. Conclusions

ZnSe nanocrystals were synthesized by hydrothermal method. Through mixing with epoxy resin in vacuum at high temperature environment, the nanocrystals embedded in an epoxy resin matrix structure were obtained. The transmission electron microscopy confirmed that the ZnSe nanocrystals were dispersed homogeneously in the matrix. The absorption spectra exhibit the blue-shift both in acetone solution and epoxy resin matrix. The nonlinear refraction index and TPA coefficient of the ZnSe nanocrystals embedded in epoxy resin matrix were measured by the Z-scan technique. The result shows that the nanocomposite sample has the larger refraction index and lower TPA coefficient than that of bulk ZnSe. These properties make offer promising applications in future optical devices.

Acknowledgments

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