

Study on nonlinear optical thin films of CdZnSe quantum dots

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Abstract: By one pot method prepared high quality $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ uniform quantum dots, and the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ quantum dot film with uniform thickness was prepared by rotating coating method on the surface of FTO glass. The thickness and surface morphology of the quantum dots were measured and characterized by using a bench and scanning electron microscope. Third order nonlinear optical properties of quantum dots film was investigated by Z-scan method. The results show that at a wavelength of 532 nm laser induced, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ quantum dots film perform out of the excellent reverse saturable absorption effect, the third order nonlinear refractive index n_2 is 8.2×10^{-12} esu, third-order nonlinear absorption beta coefficient of 2.3×10^{-5} m/W.

1. Introduction

Due to its special size, quantum dots have many unique and excellent properties such as quantum confinement effect, nonlinear optical property and surface effect, which have been the research frontier [1-3] in the field of materials in recent years. Its nonlinear optical effect is far higher than the corresponding body material, which has great potential applications in laser protection[4].

In the experiment, we found that $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dot in toluene solvent showed excellent nonlinear characteristic, and belongs to the anti-saturation absorption [5]. Therefore, by improving the experimental method, the size of the quantum dots is made more uniform, and a more pure $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dot is prepared, and then a high quality $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dot is prepared by a rotary coating method film.

2. Experimental Method

2.1 Preparation And Characterization of Quantum Dots

(1) Preparation of Quantum Dots

Through the improvement and adjustment of the one-pot method for preparation of CdSeS by Professor JiangYang's group, $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dot was synthesized from morphine oleate solvent by using zinc oxide and chromium oxide as the cation source and selenium powder as the anion source[6]. Weigh 0.5mmol (0.0407g) of ZnO and 0.5mmol (0.0642g) of CdO was added to oleic acid and octadecene ratio of 1: 1 10mL solvent, the mixed liquid was heated to pale yellow transparent and then cooled down to 120 °C under the protection of nitrogen. Weigh 1mmol selenium powder (0.0790g), the selenium powder was added to 10mL oleic acid morpholine solvent heated under magnetic stirring until completely dissolved and cooled to 120 °C, the solution was golden yellow transparent. The above selenium solution was added to a solution containing zinc oxide and chromium oxide, rapidly heated to 210 °C for 10 minutes after being uniformly stirred under the protection of



nitrogen. The reaction liquid was added to 15mL toluene solution to terminate the reaction, and then a proper amount of methanol solution was added to precipitate the quantum dots. Pure $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dot can be prepared by repeated high-speed centrifugal cleaning.

(2) Characterization of Quantum Dots

The structure of quantum dots was analyzed by X-ray diffraction (XRD). The instrument used was a SHIMADZU XRD-7000 X-ray diffractometer using a CuK α target with a wavelength of 0.154056nm.

The surface topography and particle size of quantum dots were observed and analyzed by using High-resolution transmission electron microscopy, the composition of quantum dots and the ratio between the components were analyzed and obtained by using X-ray photoelectron spectroscopy. The instrument used was a JEM-ARM200F atomic resolution electron microscope with an operating voltage of 200KV.

2.2 Preparation and Characterization of Thin Film

(1) Preparation of the thin film

The solution of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dot dissolved in toluene was applied to the FTO glass surface after a complicated process of cleaning and dedusting by spin-coating method. The 150 μL quantum dot toluene solution using a pipette drops to the surface of FTO glass, in the rotating speed of 2000r/min under the condition of continuous spin coating for 20ses, and then in a glove box at 150°C under nitrogen atmosphere quenching 10mins, making the quantum dot film can be more firmly coated on the FTO glass surface.

(2) Characterization of the Thin Film

The thickness of the sample film is measured using a Step Profiler and the surface flatness of the sample can be analyzed by the scanning curve of the stepper. The experimental equipment used was a Dektak XT Bruker stepper with a vertical resolution of 0.1nm and a vertical measurement range of up to 1 mm.

The absorption spectrum of the sample film was analyzed by ultraviolet-visible spectrophotometer, the experiment was performed at room temperature with a wavelength range of 300-800nm. The instrument used in the experiment was UV-2550 ultraviolet-visible spectrophotometer.

2.3 Nonlinear Experiment of Thin Film

Some interesting phenomena occur in nonlinear optical materials under strong laser light. The absorption coefficient and refractive index change regularly with the laser light intensity [7]. In order to explore the relationship of all parameters and the laser intensity of this type of material, Sheik.Bahae and others first proposed the concept of Z-scan method in 1997. After nearly 20 years of development, the Z-scan method has gradually become the preferred method for the measurement of nonlinear optical properties [8]. In this paper, the nonlinear optical properties of the sample are tested by Z- scan.

Experimental conditions: Nd: YAG laser, repetition rate of 10Hz, the center wavelength of 532nm, pulse width 6.5ns, focusing lens focal length f is 395mm focused beam radius of 40.4 microns.

Experimental method: The sample moves along the Z axis before and after the focus, and the Z-scan normalized experimental curve is obtained by data processing.

The following diagram shows the Z-scan experimental schematic:

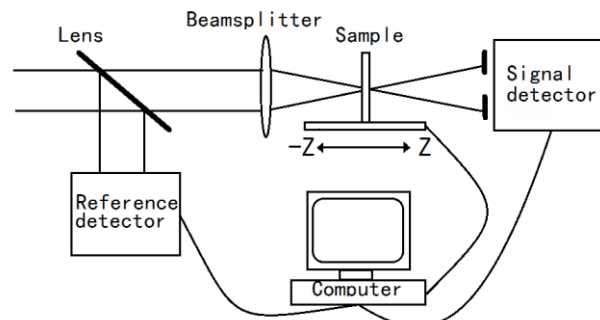


Fig.1 Schematic Diagram of Z-scanning Experiment

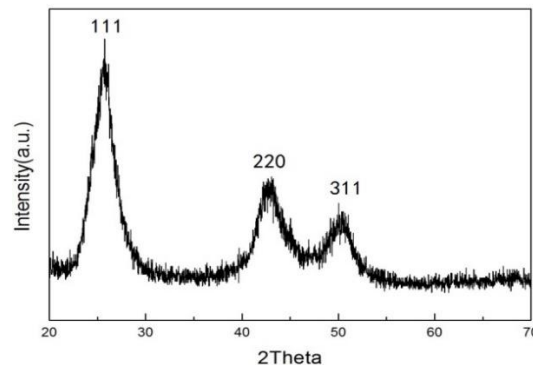
3. Results and Discussion

3.1 Quantum dot structure, appearance and composition

It can be seen from Figure 2 that the XRD pattern has three strong diffraction peaks corresponding to the (111), (220) and (311) planes of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dots respectively. There are no extra peaks in the spectrum, which indicates that the prepared quantum dots are more pure. The size of quantum dot particles can be calculated by Deby-Scherrer formula [9].

$$D = K\lambda / B_{1/2} \cos\theta \quad (1)$$

Where D is the diameter of the quantum dot particle, K is the diffraction peak constant, λ is the wavelength, $B_{1/2}$ is the full width at half maximum of the diffraction peak, and θ is the diffraction angle. The calculated results show that the particle size of the sample is about 4nm.

Fig.2 The XRD Spectrum of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ Quantum Dots

A and B in Figure 3 are high-resolution transmission electron microscopy pictures of quantum dots with different resolutions. It can be intuitively seen from Figure 3 that the quantum dots are well dispersed, and the diameter is about 4nm, which is more uniform, which is in good agreement with the data calculated by Deby-Scherrer formula.

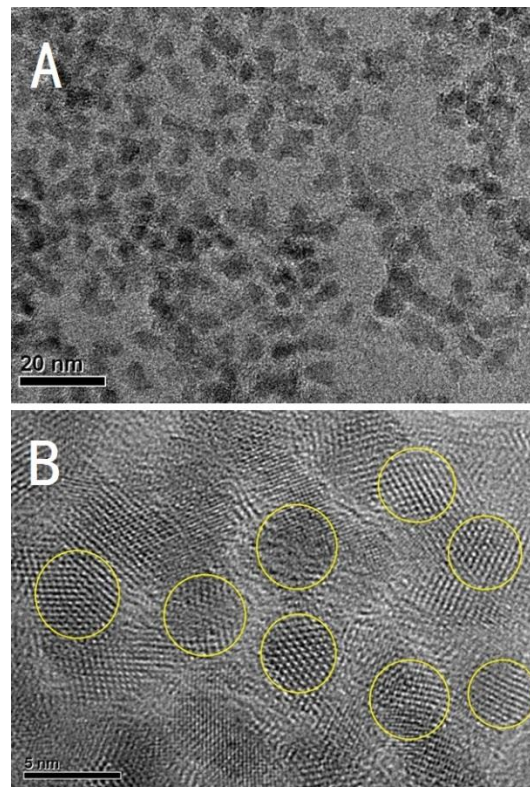


Fig.3 Transmission Electron Microscopy Images of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ Quantum Dots

Figure 4 shows the Energer Dispersive Spectrum (EDS) and energy spectrum data of the sample QDs. The results show that the atomic percentages of Zn and Cd in the QDs are relatively close and have no other impurities. Quantum dots with high quality and low impurity also provide a good foundation for the preparation of nano-quantum dot film.

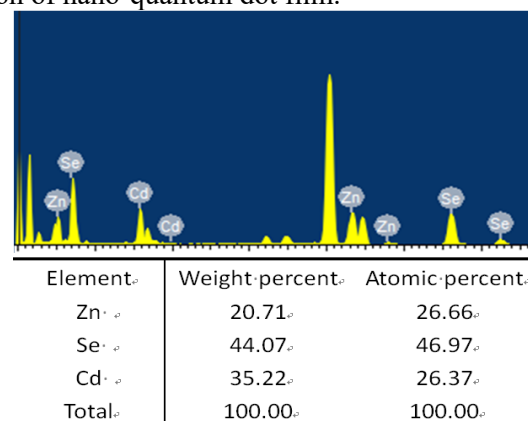


Fig.4 EDS Analysis of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ Quantum Dots

3.2 Quantum dot film thickness, surface appearance and absorption spectrum

Figure 5 shows the experimental curve of the quantum dot film thickness measured by a Step Profiler, where the two valleys are the Y-axis values of engraved marks on the film. From the above figure, the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dot film has a thickness of 40nm, and the measured values at two scratches are close to each other, indicating that the thickness of the prepared three-dimensional quantum dot film is relatively uniform.

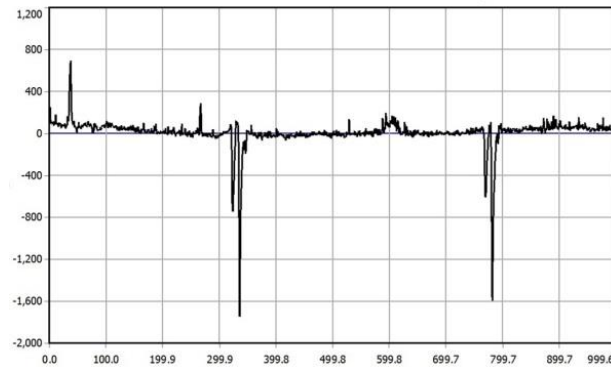
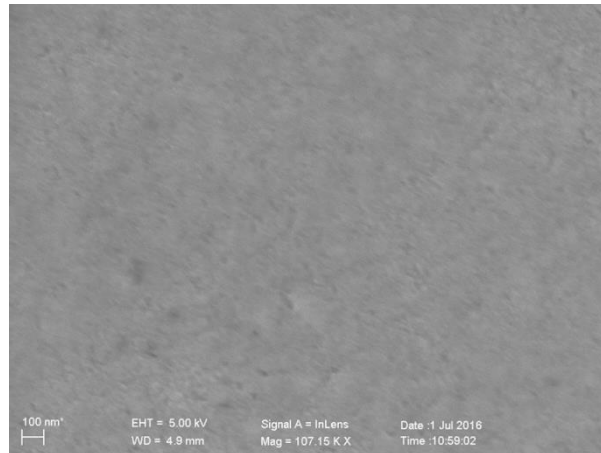


Fig.5 Thickness measurement of step

High-resolution scanning electron microscopy was used to observe the surface morphology of the quantum dot films. As shown in figure 6, we can see that there are no obvious cracks and collapses on the surface of the films. The films were relatively flat, which indicated the high quality of the prepared nano-film.

Fig.6 Scanning electron microscopy images of Cd_{0.5}Zn_{0.5}Se quantum dot films

The upper part of Fig. 7 shows the ultraviolet visible absorption spectrum of the Cd_{0.5}Zn_{0.5}Se ternary quantum dot film, and the lower part shows the ultraviolet visible absorption spectrum of the FTO glass. The results show that the FTO glass almost absorbs no light in the 350nm to 600nm band, and the absorption mainly comes from the quantum dot film. According to the absorption spectrum data, the band gap of the quantum dot film can be calculated as 2.31eV from the following formula.

$$(\alpha h\nu)^2 = k(h\nu - E_g)^2 \quad (2)$$

(Where α is the absorptivity, $h\nu$ is the energy of the incident photon, k is a constant, and E_g is the forbidden band width.)

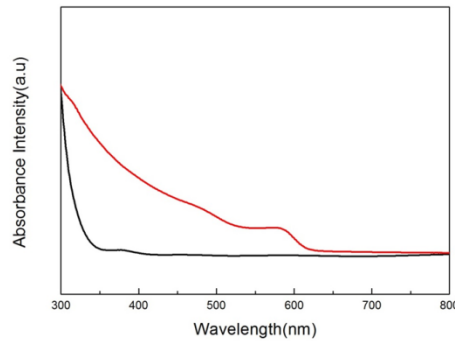


Fig.7 UV-Vis absorption spectra of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ quantum dot films

3.3 Nonlinear optical properties of quantum dot film

The Z-scan method was used to test the non-linear optical properties of the experimental samples and blank samples without the quantum dot film.

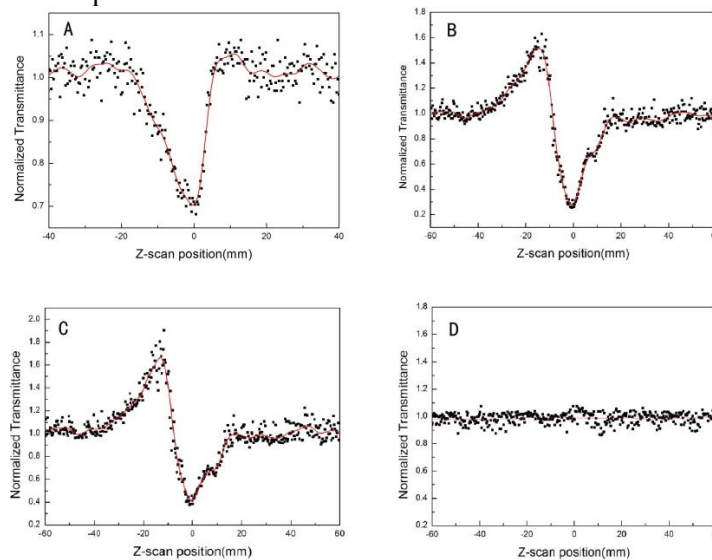


Fig.8 Z-scans: (A)Open-aperture Z-scanning curve; (B)Closed-aperture Z-scanning curve; (C)Open/Close-aperture Z-scan curve; (D)Z-scanning curve of FTO glass

Figure 8 is the Z-scan curve of the sample. The scatter plot in the figure is the experimental data, and the curve is the fitted data. Where A is the open-hole Z-scan curve of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dots, which reflects the nonlinear absorption characteristics of the sample. The curve is about the focal symmetry valley, indicating that the absorption coefficient of light increases with the increase of light intensity, is the reverse saturation absorption, and the nonlinear absorption coefficient is positive. B is a closed-hole Z-scan experimental curve of a $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dot film, and the curve was observed after the first peak hysteresis, indicating that the sample has a self-defocusing characteristic and the nonlinear refractive index is negative. C is closed-hole / open-hole Z-scan normalized experimental curve, closed-hole Z-scan experimental data divided by open-hole Z-scan experimental data obtained. As can be seen from the graph curve that the first half of the curve is the valley of the second half of the peak. The analysis shows that the material has the property of self-defocusing and the refractive index is negative. And D is the nonlinear scanning curve of FTO glass. It is clear that FTO glass does not possess nonlinear optical properties under such experimental conditions. Therefore, the nonlinear characteristics of the samples are all caused by the nonlinear characteristics of the ternary quantum dot film.

From the equations (3)-(5), we can calculate the nonlinear absorption coefficient of the sample

through the Z-scan aperture data. [10]

$$L_e = (1 - T_s) / \alpha_0 \quad (3)$$

$$I_0 = 4E\sqrt{\ln 2} / \tau \omega_0^2 \sqrt{\pi^3} \quad (4)$$

$$\beta = A / I_0 L_e \quad (5)$$

(Where L_e is the effective thickness of the sample, T_s is the transmittance, α_0 is the absorption coefficient, I_0 is the power density at the focal point of the laser, E , τ and ω_0 is the pulse energy, pulse width, and beam waist radius, respectively, of the laser, A is derived from the experimental data)

Substituting into the parameters to calculate the third-order nonlinear absorption coefficient of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ternary quantum dot films: $\beta = 2.3 \times 10^{-5} \text{ m/W}$.

The nonlinear refractive index of the sample can be calculated by equation (6) and equation (7) [10].

$$|\Delta\Phi_0| = 2\pi / n_2 I_0 L_e \lambda \quad (6)$$

$$\Delta T_{p-v} = 0.406(1-s)^{1/4} |\Delta\Phi_0| \quad (7)$$

(Where $|\Delta\Phi_0|$ is the nonlinear phase shift caused by the nonlinear refraction, ΔT_{p-v} is the peak-to-valley difference of the transmittance curve, and s is the linear transmittance of the small hole)

Substitute the data into the nonlinear refractive index of the available sample : $n_2 = 8.2 \times 10^{-12} \text{ esu}$.

4. Conclusion

In this paper, the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ quantum dots were prepared by one pot boiling method, and the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ quantum dot film were prepared by rotating coating method. The results show that the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ quantum dot have uniform particle size and high purity, and the diameter is about 4nm. The thickness of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ quantum dot film is 40nm, and at a wavelength of 532 nm laser induced, it perform out of the excellent reverse saturable absorption effect, the third order nonlinear refractive index n_2 is $8.2 \times 10^{-12} \text{ esu}$, third-order nonlinear absorption coefficient β is $2.3 \times 10^{-5} \text{ m/W}$. Next we will prepare a series of ternary quantum dot films and explore their applications in laser protection and other fields.

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