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Components-dependent optical nonlinearity in a series of $CdSe_xS_{1-x}$ and $CdSe_xS_{1-x}$/ZnS QDs

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ABSTRACT

The different compositions of the ternary alloyed $CdSe_xS_{1-x}$ and $CdSe_xS_{1-x}$/ZnS core/shell quantum dots (CSQDs) have been synthesized by the chemical routes. The nonlinear optical properties of these QDs were investigated using Z-scan technique under the excitation of the 1064 nm picosecond laser pulse. The Z-scan results reveal that the nonlinear refractive indices of these QDs can be tuned by changing the ratio of Se and S components. Nonlinear optical (NLO) properties have been shown to be enhanced in CSQDs as compared to their core semiconductor counterparts. These QDs exhibit the components-tuned nonlinear refraction indices, which lead to a wide application in the photonic field.

1. Introduction

Semiconductor quantum dots(QDs) have gained intense attention due to their unique physical and chemical properties [1,2]. The quantum confinement and dielectric confinement effect makes QDs a promising kind of nonlinear optical(NLO) material with large nonlinear susceptibilities and fast response time [3–7]. In the application to electronic and photonic devices, it is of extreme importance to adjust the NLO parameter. In general, the optical properties of QDs mainly depend on the size and the composition. Changing the size of semiconductor QDs is a useful method commonly used for adjusting their band-gap energy and these QDs often exhibit size-dependent NLO properties as a few articles reported [8–11]. The other method is that the electrical and optical properties of QDs is tuned by changing their composition. Thus, the multi-component alloy quantum dots were wanted in order to achieve the component-tuned the NLO parameters. For II–VI group of QDs, this small difference of CdSe and CdS in the lattice constant benefits the formation of $CdSe_xS_{1-x}$ alloy QDs, which are promising candidates in the optoelectronic applications with the tunable optical and electronic properties in a wide range. Recently, most investigations on $CdSe_xS_{1-x}$ QDs have focused on theoretical calculations, spectral research, the electro-optical properties, and the optical nonlinearity of $CdSe_xS_{1-x}$-doped glasses [12–20]. Moreover, recent experimental investigations have demonstrated that the surface passivation can improve the optical properties by formation of a core/shell structure [3,21–23]. However, there are few reports on the component-dependent NLO properties of the ternary alloy $CdSe_xS_{1-x}$ QDs and core/shell counterparts. Since the physical and optical properties of alloy QDs depend on both size and composition, it is possible to tune the NLO parameters by altering component ratios in the alloyed QDs while maintaining a small size. For the view of NLO design, the ternary alloyed QDs afford us the other approach to control the NLO parameters by altering component ratios. In this letter, the NLO properties of the ternary alloy $CdSe_xS_{1-x}$ and the core/shell counterpart with the same size was investigated by Z-scan technique 1064 nm ps laser pulse. The aim of the present work is to study component-tuned NLO properties suitable for opto-electronic devices. It was found that the nonlinear refractive indices of these QDs can be tuned by changing the ratio of Se and S components and the shell coating play a role in the enhancement of the NLO effect.

2. Experimental details

Three different compositions of $CdSe_xS_{1-x}$ QDs were synthesized by the similar method reported earlier [24]. The cadmium acetate dihydrate and oleic acid were heated to 260–330 °C under mm Ar gas and make a stock solution having a concentration of 0.4 mmol g^{-1} in Cd. And then, the prepared mixture of trioctylphosphine sulfide (TOPS) and trioctylphosphine selenide(TOPSe) was rapidly injected into the the cadmium solution and stirred for 10–15 min at the temperature of 300 °C. At last, the reaction

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solution was cooled to about 30 °C and dropped into the flask containing the methanol or ethanol solution. The reaction product of $CdSe_xS_{1-x}$ QDs was obtained by removing the supernatant liquid and the centrifugal sedimentation for 3 min.The three samples of $CdSe_xS_{1-x}$ QDs were labeled as S1, S2,and S3, whose feed mole ratios of Cd, Se and S are 1:0.28:29.02, 1:0.50:26.69 and 1:0.81:24.58, respectively. The oleic acid and trioctylamine were added into the flask containing ZnO and the ZnS stock solution were prepared. Then, ZnS shell was coated on the as-synthesized $CdSe_xS_{1-x}$QDs using the as-prepared ZnS stock solution. The core/shell $CdSe_xS_{1-x}$/ZnS QDs were labeled as S1′, S2′ and S3′. The resulting yellow precipitate was separated by centrifugation and washed several times with ethanol. After drying in vacuum, the solid was dissolved in some amount of chloroform and their concentration was 5×10^{-3}mol/L.

The size of $CdSe_xS_{1-x}$ QDs and $CdSe_xS_{1-x}$/ZnS CSQDs was inspected by the transmission electron microscope(TEM, Philip TZOST) operating at 190 kV.The linear absorption spectrum of these QDs was recorded on the UV–vis spectrometer (TU-1901). Z scans were employed to characterize the nonlinear optical properties at the different input intensity. The incident light source was the fundamental frequency of the Nd:YAG laser (YG901C, Quantel Co.) operating at 1064 nm wavelength, 35 ps pulse width and 10 Hz repetition rate. The detailed description of the Z-scan setup was presented in Ref. [25]. Thermal effect could be ignored since the low repetition rate of 10 Hz was used. Pure solvent was also examined at the same experimental condition and its nonlinear response was found to be insignificant. The main source of the uncertainty in the measured data is due to the fluctuation of the laser energy. In order to reduce the error, all Z-scan experimental data were average values of the 20 pulses. So the measured data had a high reliability and the relative error was estimated to be no more than 5%.

3. Results and discussion

Fig. 1(a) presents the TEM image and the size distribution of $CdSe_xS_{1-x}$ QDs in the sample S1and the size distribution with the average diameter of 4.0 ± 0.3 nm is shown in Fig. 1(b). The solid line is a lognormal fit to the size distribution. The TEM images of the other samples and the size distribution was similar to the sample S1, which was not present in this paper. The size of the $CdSe_xS_{1-x}$/ZnS CSQDs is larger than the corresponding core $CdSe_xS_{1-x}$ QDs due to the ZnS shell formation on the surface of the core QDs.

Optical absorption spectra of the $CdSe_xS_{1-x}$ QDs in the sample S1 and S1′ are shown in Fig. 2(a) and (b), respectively.The absorption onsets are localized at 493 and 500 nm for core QDs (sample S1) and core/shell QDs(sample S1′) respectively. A red-shift of 7 nm with respect to sample S1 stems from the dielectric confinement due to the ZnS shell encapsulation. The similar red-shift was observed in the other samples, of which the absorption spectra were not shown in this letter. The Gaussian fitting present the lowest transition $1S_{3/2}(h) \rightarrow 1S(e)$ and the higher transition $2S_{3/2}(h) \rightarrow 1S(e)$ for these QDs. According to the lowest transition $1S_{3/2}(h) \rightarrow 1S(e)$, the bandgap of sample S1 and sample S1′ were determined to be 2.51 eV and 2.48 eV, respectively.The sharp absorption increase of the exciton absorption peak reveals narrow size distribution. The broadening of optical transitions in the absorption spectra of $CdSe_xS_{1-x}$ and $CdSe_xS_{1-x}$/ZnS QDs primarily is due to inhomogeneity arising from size dispersion, which is in close agreement with the size distribution of these QDs measured by TEM as shown Fig. 1(b). In the strong confinement regime, Brus proposed the following expression for the band gap of the finite-sized system [26]:

$$E = E_g + \hbar^2\pi^2(1/m_e + 1/m_h)/2R^2 - 1.8e^2/\varepsilon R - 0.248E^*_{RY} \quad (1)$$

where R is the nanocrystal radius and E_g is the bulk band gap. The second term is the kinetic-energy term containing the effective masses, m_e and m_h, of the electron and the hole, respectively. The third term arises due to the Coulomb attraction between the electron and the hole, and the fourth term due to the spatial correlation between the electron and the hole which is generally small compared to the other two terms. For the ternary alloyed $CdSe_xS_{1-x}$ bulk semiconductor, their bandgap can be estimated by the following formula [27]:

$$E_g = E_g^{CdSe}\cdot(1-x) + E_g^{CdS}\cdot x - bx(1-x) \quad (2)$$

where b is the direct gap bowing parameter, $E_g^{CdSe}$and $E_g^{CdS}$are the bandgap energy of CdSe and CdS bulk semiconductors, respectively. Based on the (Eqs. (1) and 2), the components x of the sample S1 was determined to be 0.3. The components x of the sample S1 was determined to be 0.3. In the same way, the bandgap and the components x of the other samples were also obtained, which were summarized in the Table 1. It was found that the bandgap of these QDs can be tuned by the compositional ratio of Se and S.

In order to determine the nonlinear refraction and nonlinear absorption of $CdSe_xS_{1-x}$ QDs and $CdSe_xS_{1-x}$/ZnS CSQDs QDs, we performed close-aperture(CA) and open-aperture(OA) Z-can measurements. The CA Z-scan curves of $CdSe_{0.5}S_{0.5}$/ZnS CSQDs at the input intensity of 6.8 GW/cm^2 was given in Fig. 3(A). The configuration of the symmetric valley and peak indicates self-focused effect and no nonlinear absorption. The Z-scan curves of the

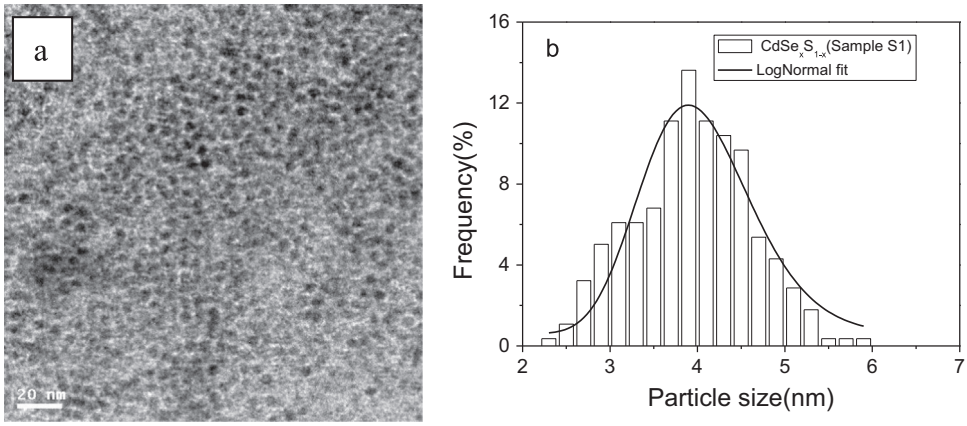

Fig. 1. (a) TEM image and (b) size distribution of the sample S1. The solid line is a lognormal fit.