



Third-order optical nonlinearity of multi-armed CdS nanorods measured by the Z-scan method

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ABSTRACT

The multi-armed CdS nanorods were synthesized by aqueous chemical growth route at room temperature. The nonlinear optical properties of CdS nanorods dispersed in ethanol solution were investigated using the Z-scan method at a wavelength of 532 nm with pulse duration of 25 ps. The third-order nonlinear optical susceptibility, $\chi^{(3)}$, was determined to be 1.6×10^{-13} esu. Accounting for the CdS concentration and the effect of the dielectric confinement, $\chi^{(3)}$ was extrapolated to be $\sim 10^{-9}$ esu, which is over one order of magnitude larger than that of bulk material.

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1. Introduction

Semiconductor nanostructures have attracted much attention during the last decades for the study of fundamental physics as well as the potential novel device applications [1,2]. The ultrafast optical and electronic responses of semiconductor nanocrystals are different from bulk materials mainly originating from quantum confinement effects. Different shapes, sizes and dielectric surroundings of semiconductor nanomaterials can give rise to great differences of electronic states and correlated properties [3–8]. Therefore, much attention has been paid to control these parameters to manipulate the properties of semiconductor nanocrystals [4,5,9,10]. Recently, the more complicated one-dimensional (1D) nanostructure such as multi-armed nanorods, which have two or more limbs connected at a central core, were synthesized by many groups [11–14]. The unique structures have more challenges for shape control studies and would provide more opportunities to the applied field. The improvement of efficiency of hybrid photovoltaic devices consisting of branched CdSe nanorods and conjugated polymers has been reported by Greenham and his co-workers [15]. Cui et al. [16] have demonstrated a new single-electron transistor operation scheme

enabled by multi-armed CdTe nanorods indicating a very useful structure for electric devices. The linear optical properties, such as optical absorption, photoluminescence spectra of the multi-armed nanorods have also been widely studied [13,17]. However, the nonlinear optical properties of the multi-armed nanorods have not been investigated thus far.

In this paper, we report the third-order optical nonlinearity of the multi-armed CdS nanorods dispersed in ethanol solution measured by the Z-scan technique.

2. Experimental

The CdS nanorods with multi-arms were synthesized via aqueous chemical growth route at room temperature. The typical procedure has been described elsewhere [14]. The product was obtained by centrifugation and washed with deionized water and ethanol. The final solution comprising purified CdS nanorods dispersed in ethanol was placed in a 1 mm quartz cuvette for all optical measurements. The concentration of CdS nanorods was about 0.5 mg/ml.

The nanostructure of CdS nanorods was investigated by transmission electron microscopy (TEM). Linear optical absorption of the sample was measured from 300 to 800 nm using a SpectraPro-500i spectrophotometer (Acton Research Corporation)

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at room temperature. The third-order optical nonlinear susceptibility of the CdS colloidal solution was characterized using the single-beam Z-scan technique. In our experiment, a mode-locked Nd:YAG laser with frequency doubled at a wavelength of 532 nm and 25 ps duration was used as the light source. The repetition rate was set to 1 Hz. The laser beam was focused onto the sample by a 150 mm focal length lens, leading to a measured beam waist of about 24 μm . The peak intensities used in the experiments were in the range 9–18 GW/cm^2 . The on-axis transmitted beam energy, the reference beam energy, and the ratios of them were measured using an energy ratiometer (EPM 2000, Coherent Inc.).

3. Results and discussion

Fig. 1 presents a TEM image showing the size and the shape of CdS quantum-confined nanorods (with diameters of $<6\text{ nm}$). There is a mixture of one-, two-, three-, and four-armed rods. The lengths of the arms are not very uniform, while their widths have a relatively narrow size distribution (about 5 nm).

The linear optical absorption spectrum of the multi-armed CdS nanorods is shown in Fig. 2. The absorption band for the CdS nanorods is at around the wavelength of 450 nm, which is blue-shifted compared to the absorbance of the CdS bulk material (around 512 nm). The optical bandgap (E_g) was determined using the Tauc's formula. The relation $(\alpha h\nu)^2$ versus $h\nu$ is shown in the inset in Fig. 2. The bandgap of the nanorods can be calculated to be about 2.9 eV.

The Z-scan measurements were carried out at the on-axis peak intensity I_0 , varied from 9 to 18 GW/cm^2 . Fig. 3 shows typical closed-aperture (CA) Z-scan curves, normalized transmittance as a function of the sample position Z at peak irradiance $I_0 = 9.2, 12.2,$ and $15.3\text{ GW}/\text{cm}^2$ on the same spot. The filled squares, dots, and triangles indicate the measured data, with each point corresponding to the average value of 10 pulses. The corresponding solid lines represent their theoretical fittings [18]. Because the fused quartz of the cuvette in our experiment has a very small nonlinear optical response (nonlinear refractive index $n_2 \sim 10^{-14}\text{ esu}$), the nonlinear optical properties observed here resulted from the CdS nanorods. The curves of CA have the valley-peak configuration, corresponding to a positive nonlinear refractive index. The linear relation of

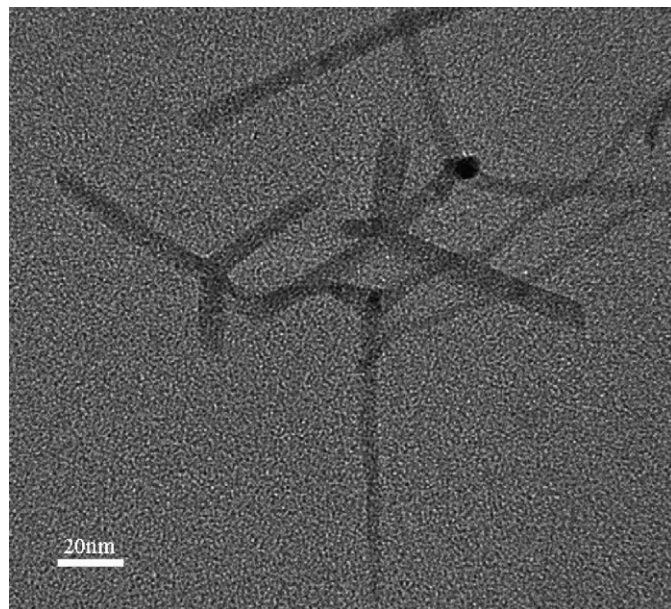


Fig. 1. TEM image of multi-armed CdS nanorods.

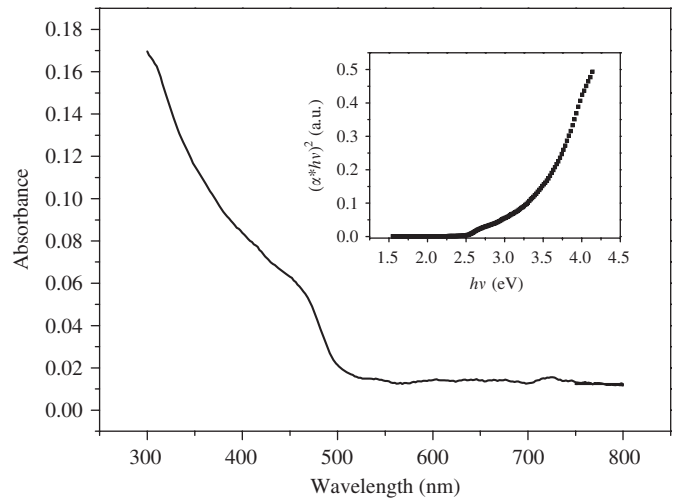


Fig. 2. The optical absorption property of CdS nanorods dispersed in ethanol solution and $(\alpha h\nu)^2$ versus $h\nu$ plot (inset).

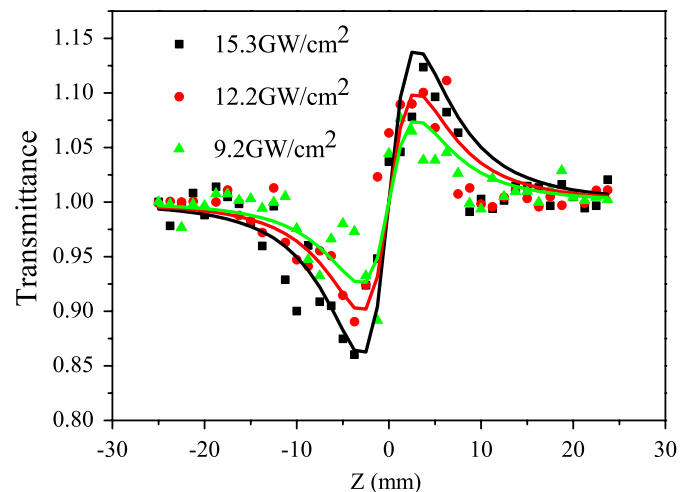


Fig. 3. Z-scan data of the sample with a closed-aperture at different intensities. The solid lines indicate the theoretical fit.

ΔT_{p-v} , the difference between the normalized peak and valley transmittance, and I_0 depicted in Fig. 4 indicated the third-order optical nonlinearity. The error bar in the figure is indicative of the maximum experimental error, which was about 20% in our case. The data were analyzed using the procedures described by Sheik-Bahae et al. [18]. The nonlinear refractive index n_2 , and the real part of the third-order nonlinear susceptibility, $\text{Re}\chi^{(3)}$, are given by the following equations:

$$n_2(\text{m}^2/\text{W}) = \frac{\lambda \Delta T_{p-v}}{0.812\pi(1-S)^{0.25} L_{\text{eff}} I_0} \quad (1)$$

$$\text{Re}\chi^{(3)}(\text{esu}) = \frac{cn_0^2}{120\pi^2} n_2(\text{m}^2/\text{W}) \quad (2)$$

where λ is the wavelength of light, c is the velocity of light, n_0 is the linear refractive index of the sample, S is the linear transmittance of the far-field aperture, defined as the ratio of the pulse energy passing the aperture to the total pulse energy, was measured to be 0.2, and $L_{\text{eff}} = 1 - \exp(-\alpha L)/\alpha$ is the effective thickness of the sample (L is the sample thickness, α is the linear optical absorption coefficient). The values of n_2 and $\text{Re}\chi^{(3)}$ were calculated to be $3.2 \times 10^{-19}\text{ m}^2/\text{W}$ and $1.6 \times 10^{-13}\text{ esu}$, respectively. The open-aperture (OA) profiles have no obvious valleys or peaks,

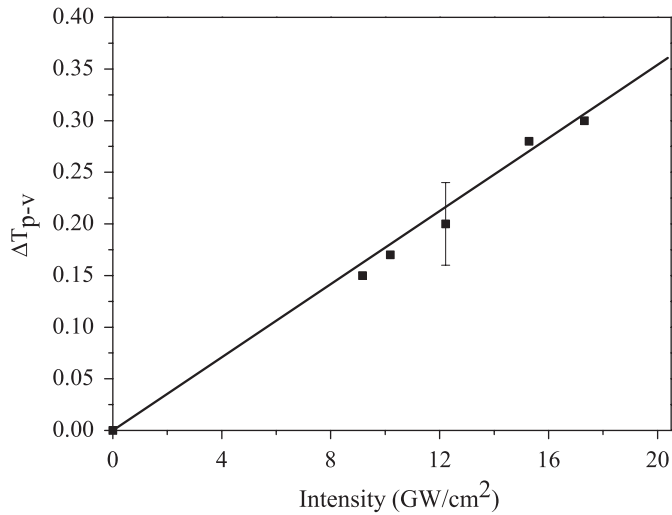


Fig. 4. The relationship of ΔT_{p-v} versus the peak irradiance I_0 . The line represents a cubic (n_2 type) nonlinearity.

which indicate that the imaginary part $\chi^{(3)}$ is very small to be determined.

The dielectric confinement due to the difference between dielectric constants of semiconductor crystallites and surrounding medium plays an important role in the optical properties [9,19]. In order to compare the optical nonlinearity of the sample with different low concentrations, and in view of the comparison of the result with that of the bulk material, a normalized nonlinear susceptibility of the sample was defined, which accounted for the nanorods concentration and the effect of the dielectric confinement. For nanoparticles in low concentration, the interaction between the light field and the particle can be calculated via the Lorentz–Mie theory [20]. The effective $\chi^{(3)}$ can be written as

$$\chi_{eff}^{(3)} = (1 - p)\chi_m^{(3)} + |f|^4 p\chi_s^{(3)} \quad (3)$$

where $\chi_{eff}^{(3)}$ is the effective nonlinear susceptibility of semiconductor nanocrystals dispersed in some matrix, and $\chi_m^{(3)}$, $\chi_s^{(3)}$ are nonlinear susceptibility of matrix and semiconductor nanocrystals, respectively. p is filling factor and f is local field factor, $f = E_i/E_0$, E_i is electric field inside the rods and E_0 is external field. Because the diameter of the CdS nanorod is much smaller than the wavelength of the light, so when the incident field is polarized parallel to the rods, the inside electric field of the rods is not reduced, $E_i = E_0$. While when polarized perpendicular to the rods, the electric field inside the rods is written [21]

$$E_i = \frac{2\varepsilon_m}{\varepsilon_s + \varepsilon_m} E_0 \quad (4)$$

where ε_m and ε_s are the dielectric constant of matrix and CdS semiconductor nanorods. The dielectric constants of bulk CdS and ethanol are 5.7 and 1.93, respectively. The filling factor p was about 8×10^{-4} . Assuming all the rods are perpendicular or parallel to the incident field polarization completely, f was calculated to be about 0.51 or 1, respectively. The value of $\chi_s^{(3)}$ of the CdS nanorods

was extrapolated to be about 4.3×10^{-9} or 0.2×10^{-9} esu accordingly. However, the nanorods are dispersed randomly in the solution and not be perpendicular or parallel to the incident field totally. So the local field factor f was estimated to be between 0.51 and 1, and the value of $\chi_s^{(3)}$ of multi-armed CdS nanorods was between 4.3×10^{-9} and 0.2×10^{-9} esu accordingly, which was over one order of magnitude larger than that of the CdS bulk material ($n_2 = -5.0 \times 10^{-11}$ esu and the calculated value of $|\chi^{(3)}| = 1.3 \times 10^{-11}$ esu at 610 nm) [22].

4. Conclusions

Multi-armed CdS nanorods were synthesized by aqueous chemical growth route at room temperature. The third-order optical nonlinearity of CdS nanorods dispersed in ethanol solution was determined by the Z-scan method at 532 nm wavelength with 25 ps pulse duration. The third-order nonlinear optical susceptibility, $\chi^{(3)}$, was determined to be 1.6×10^{-13} and $\sim 10^{-9}$ esu when accounting for the nanorods concentration and the effect of the dielectric confinement, which is over one order of magnitude larger than that of the bulk material.

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