Electronic Supplementary Information

Composition-Tunable Nonlinear Optical Properties of Alloy Ternary

\[ \text{CdSe}_{x}\text{S}_{1-x} \ (x = 0-1) \cdot \text{Quantum Dots} \]

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1. The Z-scan experimental results obtained with an open aperture

Fig. ESI1 The open-aperture Z-scan curves of the CdSe$_x$S$_{1-x}$ QDs with different compositions: (A) CdS, (B) CdSe$_{0.14}$S$_{0.86}$, (C) CdSe$_{0.33}$S$_{0.67}$, (D) CdSe$_{0.43}$S$_{0.57}$, (E) CdSe$_{0.56}$S$_{0.44}$, (F) CdSe$_{0.76}$S$_{0.24}$ and (G) CdSe.
2. The Z-scan experimental results obtained with an closed aperture

Fig. ESI2 The closed-aperture (S=0.054) Z-scan curves of the CdSe$_{x}$S$_{1-x}$ QDs with different compositions: (A) CdS, (B) CdSe$_{0.14}$S$_{0.86}$, (C) CdSe$_{0.33}$S$_{0.67}$, (D) CdSe$_{0.43}$S$_{0.57}$, (E) CdSe$_{0.56}$S$_{0.44}$, (F) CdSe$_{0.76}$S$_{0.24}$ and (G) CdSe.
3. Calculation of the nonlinearity of CdSe$_x$S$_{1-x}$ QDs

The purely nonlinear refraction Z-scan data are obtained by dividing the closed-aperture data with the corresponding open-aperture data. $\Delta\Phi_0$ can be obtained from the purely nonlinear refraction Z-scan data by fitting the open aperture data using Eq. (1):

$$T = 1 + \frac{4x}{(x^2 + 9)(x^2 + 1)} \Delta\Phi_0$$  \hspace{1cm} (1)$$

where $T$ is the normalized transmittance of the sample with, $\Delta\Phi_0$ is the phase shift at the focus, $x = z/z_0$, $z_0 = \pi\omega_0^2/\lambda$ is the laser diffraction length.

The nonlinear refractive index $\gamma$ of the CdSe$_x$S$_{1-x}$ QDs is determined according to Eq. (2) and (3):

$$|\Delta\Phi_0| = (2\pi/\lambda)\gamma I_0 L_{\text{eff}}$$  \hspace{1cm} (2)

$$n_2(\text{esu}) = (cn_0/40\pi)\gamma(m^2/\text{W})$$  \hspace{1cm} (3)$$

where $I_0$ is on-axis pulse peak intensity on sample in the form of $I_0 = E/\pi\omega_0^2\tau$ where $E$ is the pulse energy, $\omega_0$ is the radius of the beam waist, $\tau$ is the pulse width, $\lambda$ is the laser wavelength, $L_{\text{eff}}$ is the effective length of the sample, which is related to the sample thickness $L$ and the linear absorption coefficient $\alpha$, in the form of $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$, $c$ is the speed of light, and $n_0$ is the linear index of refraction of the quantum dots.

The nonlinear absorption, $\beta$ of the CdSe$_x$S$_{1-x}$ quantum dots can be obtained from Z-scan data by fitting the open aperture data using Eq.(4):

$$T(z, S=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^n}{(m + 1)^{1/2}}$$  \hspace{1cm} (4)$$
Where $q_0 = \beta_1 L_{\text{eff}} / (1 + z^2 / z_0^2)$, $z_0 = \pi \omega_0^2 / \lambda$. is the laser diffraction length.

The nonlinear susceptibility is a result of interaction between light wave field and medium. It can be evaluated through measuring $n_2$ or $\gamma$. To the sample having the nonlinear absorption, the nonlinear susceptibility is considered to be a complex number. For CdSe$_x$S$_{1-x}$ quantum dots, the value of third-order nonlinear susceptibility $\chi^{(3)}$ is calculated by Eq.(5):

$$\chi^{(3)} = \chi^{(3)}_R + i\chi^{(3)}_I$$

(5)

The real and imaginary parts of the third-order nonlinear susceptibility were deduced by using the values $\gamma$ and $\beta$, as shown in Eqs.(6), (7) and (8).

$$\text{Re}\chi^{(3)} = 2n_0^2 \varepsilon_0 c \gamma$$

(6)

$$\text{Im}\chi^{(3)} = n_0^2 \varepsilon_0 c \lambda \beta / 2\pi$$

(7)

$$\chi^{(3)} = \left\{(\text{Re}\chi^{(3)})^2 + (\text{Im}\chi^{(3)})^2\right\}^{1/2}$$

(8)

Where $n_0$ is the linear refractive index of the quantum dots, $\varepsilon_0$ is the permittivity of free space.
4. Nonlinearity of CdSe$_{0.43}$S$_{0.57}$ with different sizes

Fig. ESI3 Z-scan curves of CdSe$_{0.43}$S$_{0.57}$ with different sizes: (A) 2.0 nm, (B) 2.3 nm, (C) 2.6 nm, (D) 2.9 nm, (E) 3.1 nm.
Table. ESI1 Calculated values of the nonlinearity of CdSe\textsubscript{0.43}S\textsubscript{0.57} with different sizes.

<table>
<thead>
<tr>
<th>Average size (nm)</th>
<th>CdSe\textsubscript{0.43}S\textsubscript{0.57}</th>
<th>β (m/W)</th>
<th>n\textsubscript{2} (esu)</th>
<th>Im(χ\textsuperscript{(3)})</th>
<th>Re(χ\textsuperscript{(3)})</th>
<th>χ\textsuperscript{(3)} (esu)</th>
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<tr>
<td>2.0</td>
<td>170°C</td>
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<td>-5.15×10\textsuperscript{-11}</td>
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<td>-1.76×10\textsuperscript{-19}</td>
<td>2.44×10\textsuperscript{-19}</td>
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<tr>
<td>2.3</td>
<td>190°C</td>
<td>-3.60×10\textsuperscript{-11}</td>
<td>-5.38×10\textsuperscript{-11}</td>
<td>-1.82×10\textsuperscript{-19}</td>
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<td>2.59×10\textsuperscript{-19}</td>
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<tr>
<td>2.6</td>
<td>210°C</td>
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<td>-5.28×10\textsuperscript{-11}</td>
<td>-1.78×10\textsuperscript{-19}</td>
<td>-1.80×10\textsuperscript{-19}</td>
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</tr>
<tr>
<td>2.9</td>
<td>230°C</td>
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<td>250°C</td>
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<td>-1.86×10\textsuperscript{-19}</td>
<td>2.61×10\textsuperscript{-19}</td>
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