Supplementary information: Thickness-modulated optical nonlinearity of colloidal CdSe/CdS core/shell nanoplatelets: Large two-photon absorption and self-focusing effects

1. Fitting of exciton binding energy

By using the quantum well absorption model mentioned in the references[1] to fit the low energy part of the absorption spectrum of the nanoplatelets (NPLs), the exciton binding energy of the sample can be roughly estimated. The absorption A_{HH} and A_{LH} for the heavy hole HH and the light hole LH can both be written in the following form:

$$A(E) = p(E) + c(E)$$

Where $p(E)$ is the absorption of quantum well excitons with asymmetric broadening η due to localization, and $c(E)$ is the absorption contribution of free carrier transitions, respectively:

$$p(E) = \frac{1}{2\eta}\left[erf\left(\frac{E-E_0}{\gamma} - \frac{\gamma}{2\eta}\right) + 1\right]\exp\left(\frac{\gamma^2}{4\eta^2} - \frac{E-E_0}{\eta}\right)$$

$$c(E) = \frac{A_c}{2}\left[erf\left(\frac{E-E_0-E_{B,X}}{\gamma_C}\right) + 1\right]$$

Where E_0 and $E_{B,X}$ are absolute exciton energy and exciton binding energy, respectively. γ is the line width of the exciton absorption peak, A_c and γ_C are the height and width of the continuous edge corresponding to the free carrier absorption, respectively, and erf is the error function.

Therefore, the total absorption of the sample can be expressed as:

$$A_{total}(E) = h_{HH}A_{HH}(E) + h_{LH}A_{LH}(E)$$

h_{HH} and h_{LH} are the proportion factors of different hole absorption. According to the above formula, the absorption curve of the sample is fitted, and the obtained parameter $E_{B,X}$is the exciton binding energy shown in the text.

2. Z-scan results of sample

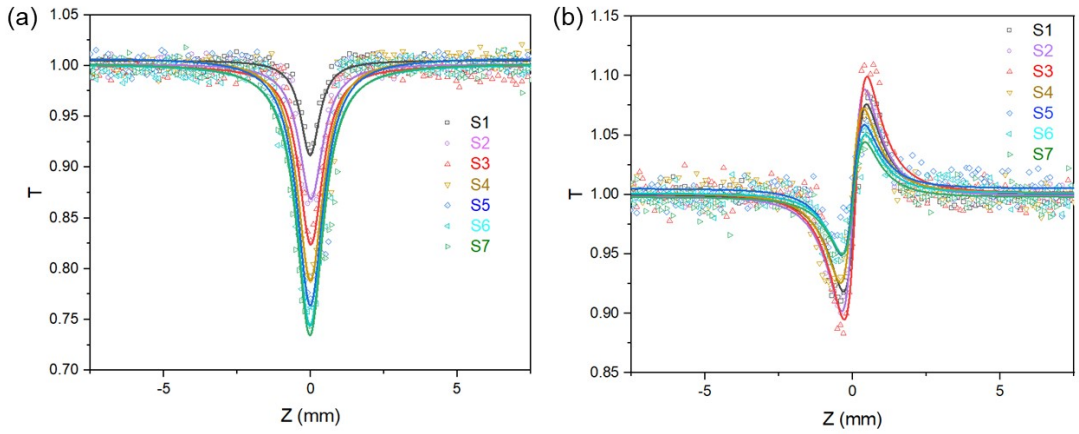

Figure S1 The open-aperture curves and (b) closed/open-aperture curves of samples with CdS shell, the solid line is the fitted curve.

Fitting equations:

Open aperture curve[2]:

$$T(z) = 1 - 0.33839 * \left[\frac{F_{TPA}}{1+x^2}\right] + 0.13326 * \left[\frac{F_{TPA}}{1+x^2}\right]^2 - 0.03446 * \left[\frac{F_{TPA}}{1+x^2}\right]^3 + 0.00377 * \left[\frac{F_{TPA}}{1+x^2}\right]^4$$

Closed/open aperture curve[3]:

$$T(z) = 1 + \frac{4 * \Delta\Phi_0 * x}{2^{0.5}(x^2+1)(x^2+9)} + \frac{4 * {\Delta\Phi_0}^2 * (3x^2-5)}{3^{0.5}(x^2+1)^2(x^2+9)(x^2+25)} + \frac{32 * {\Delta\Phi_0}^3 * (x^2-11)x}{2(x^2+1)^3(x^2+9)(x^2+25)(x^2+49)}$$

3. PL decay curve analysis

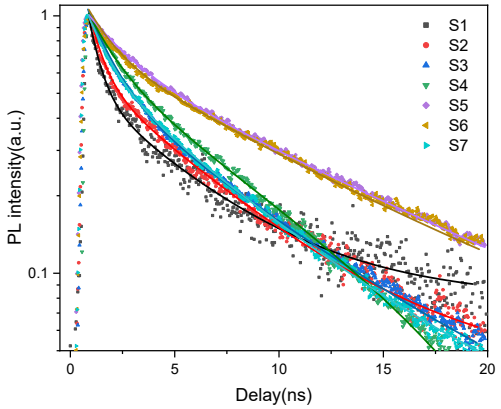

Figure S2 PL decay curves of CdSe/CdS core/shell NPLs with different thicknesses

Fitting equations:

$$y = A_1 \times e^{-\frac{x}{\tau_1}} + A_2 \times e^{-\frac{x}{\tau_2}} + y_0$$

$$\tau_{av} = A_1\tau_1 + A_2\tau_2$$

Table S1 Fitting results of PL decay curves

Sample	S1	S2	S3	S4	S5	S6	S7
A_1 (%)	0.82	0.74	0.64	0.45	0.42	0.48	0.60
τ_1 (ns)	0.57	0.66	1.28	1.44	1.97	1.29	1.12
A_2 (%)	0.18	0.26	0.36	0.55	0.58	0.52	0.40
τ_2 (ns)	5.36	5.76	7.16	9.68	10.62	9.43	6.36
τ_{av} (ns)	1.43	1.97	3.42	6.00	6.98	5.55	3.20

Note: For all fitting curves, the goodness of fitting parameter R^2>0.99.

The attenuation curve of the sample was fitted with double exponential attenuation to obtain the results in Table S1, in which the part with faster attenuation is believed to be related to the effect of defects. With the passivation of cladding, the proportion of this part from S1-S5 gradually decreases, and the life of both parts shows an increasing trend, while the proportion of S5-S7 increases, corresponding to the increase of stress-induced interface defects, and the life decreases accordingly.

4. Confront with other literatures

Table S2 List of third-order nonlinear coefficients of similar materials

Materials and structure	Wavelength	Pulse-Width	n_2/(cm^2/W)	β/(cm/GW)	Reference
SnS NPLs	800nm	-	-	-5.05×10^{-2}	[4]

Graphene oxide sheets	800nm	120fs	-1.1×10^{-15}	2.5×10^{-2}	[5]
h-BN NPLs	1064nm	10ns	1.20×10^{-13}	74.8	[6]
NbS_2 NPLs	800nm	100fs	3×10^{-16}	2.1×10^{-1}	[7]
$MoTe_2$ NPLs	1064nm	100ps	-1.60×10^{-13}	-2.99	[8]
$MoSe_2$ NPLs	1064nm	100ps	-1.20×10^{-13}	-2.05	[8]
MoS_2 NPLs	1064nm	100ps	-2.07×10^{-13}	-5.5	[8]
CdSe/CdS NPLs	1064nm	30ps	1.35×10^{-13}	1.79×10^{-1}	This work

In order to show the nonlinearity of our CdSe/CdS nanoplatelets, the nonlinearity coefficients of typical materials are selected and compared with other nanosheets and nanoplatelets (NPLs is used uniformly in the table). Since the research of colloidal NPLs is mainly focused on CdSe NPLs and its derivatives with relatively mature synthesis methods. In order to compare different NPLs, consider that colloidal NPLs are also known as quasi-two-dimensional nanocrystals, we selected some two-dimensional nanosheets as comparison objects. The results show that CdSe/CdS NPLs have excellent nonlinear properties compared with some two-dimensional materials. In addition, unlike most two-dimensional materials, the third-order nonlinear response of the CdSe/CdS NPLs is two-photon absorption (TPA) instead of saturated absorption (SA), corresponding to a positive two-photon absorption coefficient, demonstrating its potential for application in the field of optical limiting.

References

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