

Supporting Information for

**Pressure-dependent optical behaviors of colloidal
CdSe nanoplatelets**

Bo Zhou,^a Guanjun Xiao,^a Xinyi Yang,^a Qianjun Li,^a Kai Wang^{*a} and Yingnan Wang^{*a}

^a State Key Laboratory of Superhard Materials, Jilin University, Changchun, 130012, P. R. China

* Correspondence and requests for materials should be addressed to Y.W.

(email: ynwang@jlu.edu.cn)

Synthesis of 4&5 ML CdSe NPLs: 0.17 g (0.3 mmol) of Cd(myristate)₂, 0.012 g (0.15 mmol) of Se and 15 ml of ODE are introduced in a three neck flask and string under N₂ flow at 120 °C for 30 minutes. After that, the mixture is heated to 195 °C and keep for several minutes. 0.08 g (0.30 mmol) of Cd(Ac)₂•2H₂O is added into the flask. The mixture is brought up to 240 °C for 10 minutes.

Synthesis of 3&4 ML CdSe NPLs: 0.17 g (0.3 mmol) of Cd(myristate)₂, 0.012 g (0.15 mmol) of Se and 15 ml of ODE are introduced in a three neck flask and string under N₂ flow at 120 °C for 30 minutes. Then the mixture is brought up to 160 °C. 0.04 g of Cd(Ac)₂•2H₂O (0.15 mmol) is added into the flask and the mixture is brought up to 200 °C for 10 minutes.

Figure S1 shows the pressure-dependent PL spectra of CdSe NPLs samples containing two different thicknesses NPLs. It is noted that the compression process exhibit a quasi-hydrostatic condition, as these compressed samples are crude colloidal solution (unpurified) with no additional other pressure medium employed. PL spectra of crude 3&4 ML CdSe NPLs were recorded under loading pressure up to ~2.1 GPa (Figure S1a). Because the PL peak centered at around 463 nm of 3 ML CdSe NPLs is vulnerable to the interference of PL spectra of the diamonds, corresponding high-pressure experiment is carried out using Sapphire-anvil cell with culet diameter of 600 μm (copper gasket is drilled for the sample). PL spectra of 3 ML NPLs underwent more transient blue-shift than 4 ML NPLs at lower pressure range (below 0.7 GPa). Corresponding peak position of PL passed through a maximum of ~5 nm ($\Delta E = 0.029$ eV). With increasing pressure, PL peak shifted toward higher wavelength until the pressure reaches to 2.1 GPa. The 4 ML NPLs exhibited the similar behavior compared with pure 4 ML NPL samples in silicone fluid pressure medium because of the low pressure applied. Upon the release of pressure from 2.1 GPa, the PL spectra of 3&4 ML NPLs entirely recovered to their respective original states at ambient conditions, indicating a reversible process when low pressure employed. In comparison, when more than 7.5 GPa of the pressure was applied to compress the crude 4&5 ML CdSe NPLs in DAC, the emission spectra of

both 4 and 5 ML NPLs completely disappeared after releasing pressure to ambient conditions, indicating an irreversible process (Figure S1b). Corresponding pressure-depended PL peak position are summarized in Figure S2. For the pure 4 and 5 ML CdSe NPLs samples, not only the pressure-dependent PL peak position changing but also the irreversible changing of PL shows the similar results under quasi-hydrostatic condition (Figure S3). All these results indicated that the qualitative behaviors are the same under two different pressure environments. This was probably because "soft" long-chain organic acid could provide a nearly hydrostatic condition comparing to silicone fluid at relative low pressure.

A series of experimental results indicate that the irreversible changes in optical properties could only be observed when the CdSe NPLs released from the pressure higher than ~ 7.0 GPa (Figure S4 and S5). In contrast, when the employed pressure is lower than ~ 7.0 GPa and the PL of NPLs is not disappear completely, the PL spectra exhibit a reversible process (e.g. Figure S4a and 4b). According to a series of experiments on the release pressure, we located the critical pressure at around 7.0 GPa. In addition, the irreversible change of CdSe NPLs could also be observed by optical photos (Figure S5). After high pressure treatment, the color of sample turned from salmon to black.

In addition, the quenching of their PL might due to formation of large amount of crystalline defect, which play a role of the centers for non-radiative recombination. Moreover, after high pressure treatment, samples tend to minimize their volume. Assembly by stacking is an efficient way for NPLs with large lateral size and small uniform thickness (Fig S6). The stacking of NPLs significantly increases the nonradioactive recombination rate, due to the efficient exciton migration among the NPLs via homo Förster resonance energy transfer. Therefore, these subtle changes lead the photo generated holes to be trapped and quench the PL of NPLs. In contrast, when the employed pressure is lower than the critical pressure, these subtle changes could not generate.

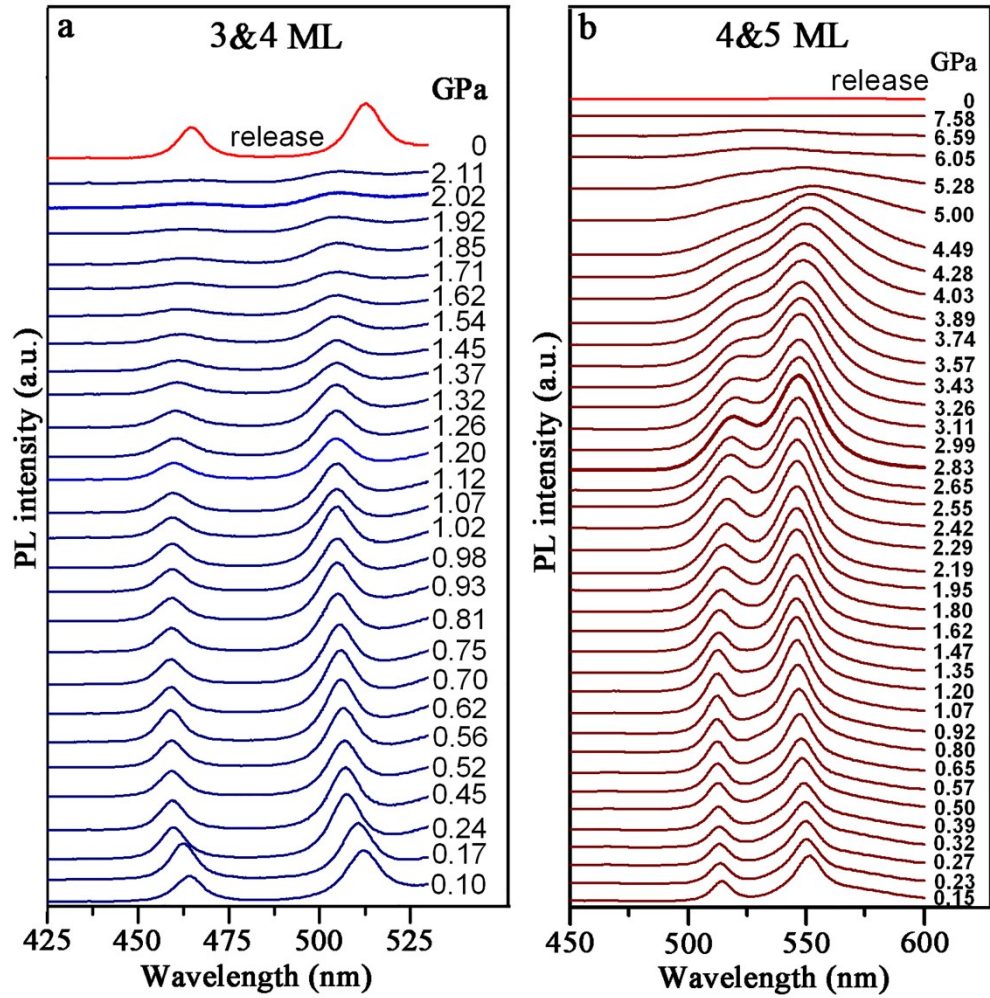


Figure S1. Pressure-dependent PL spectra of CdSe samples containing two different thicknesses NPLs. (a) 3&4 ML CdSe NPLs; (b) 4&5 ML CdSe NPLs. The red spectral lines are corresponding recovered PL spectra, respectively.

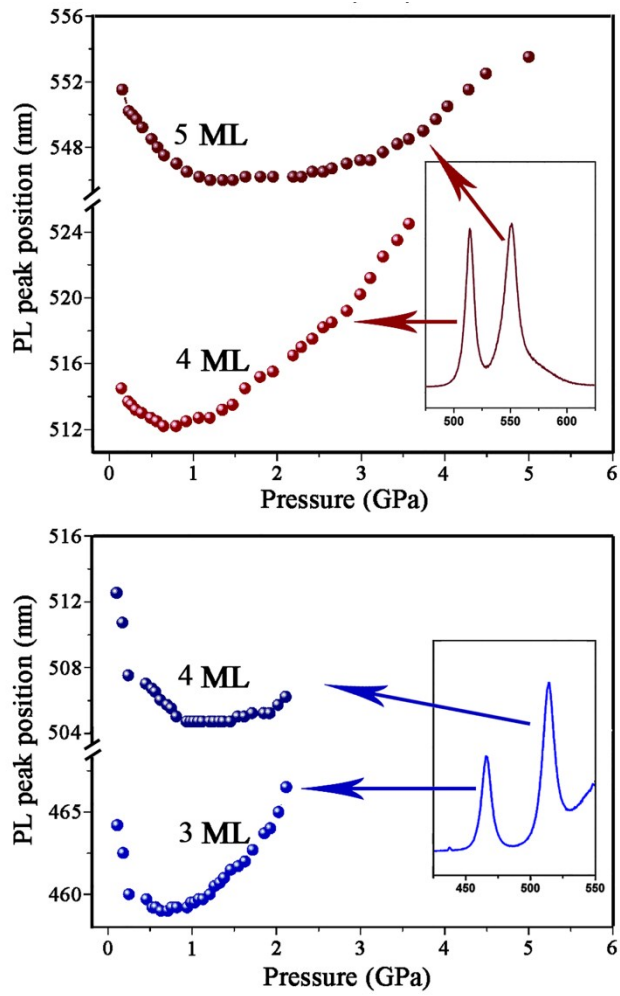


Figure S2. Pressure-dependent PL peak positions of different CdSe NPLs samples shown in Figure S1. (a) 4&5 ML CdSe NPLs; (b) 3&4 ML CdSe NPLs.

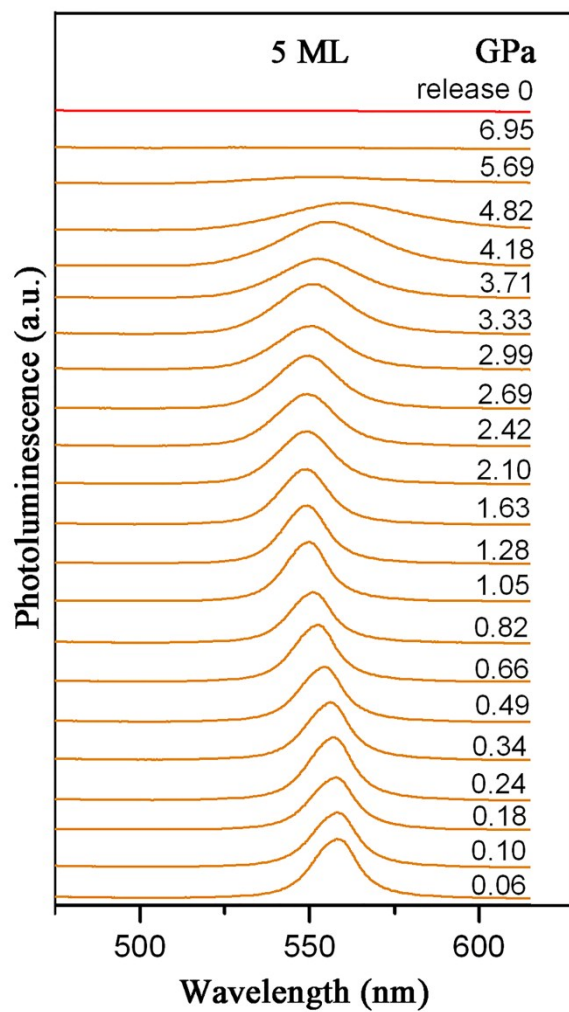


Figure S3. Pressure-dependent PL spectra of crude colloidal 5 ML CdSe NPLs.

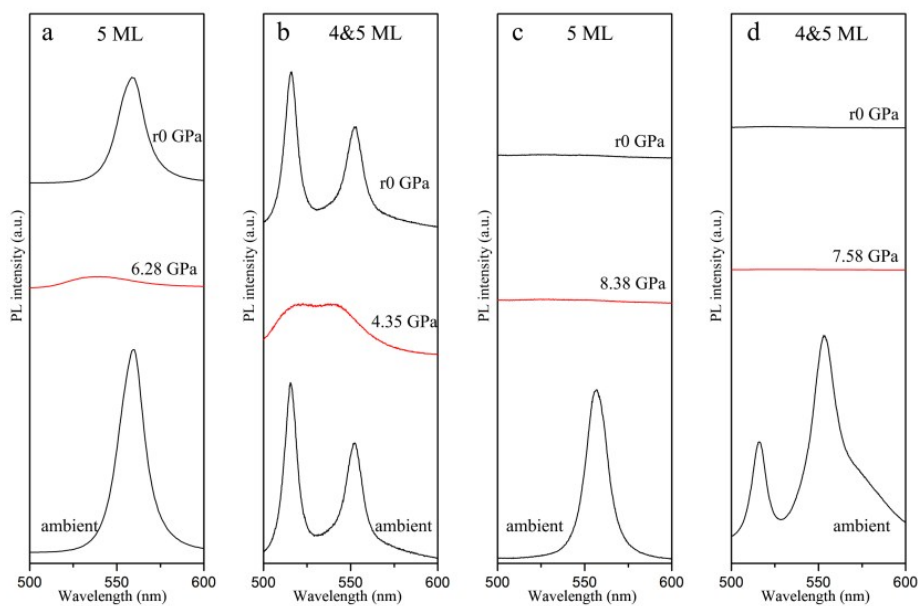


Figure S4. CdSe NPLs sample released at different pressure a, 6.28 GPa; b, 4.35 GPa; c, 8.38 GPa; d, 7.58 GPa.

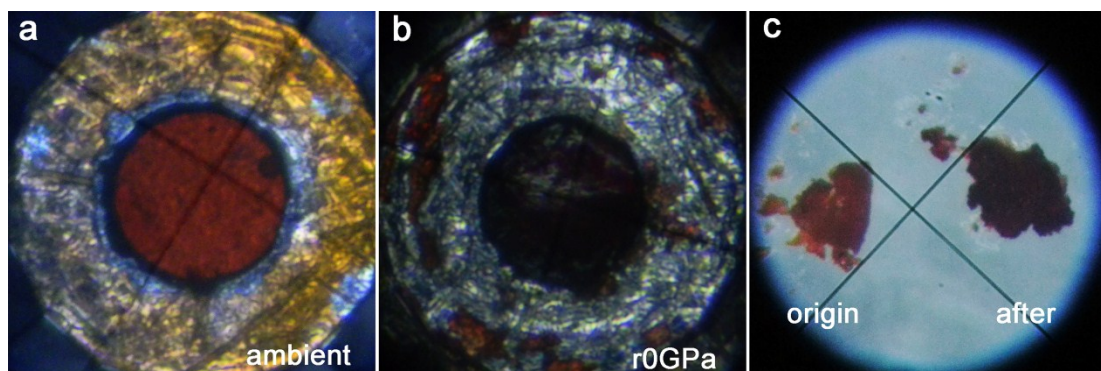


Figure S5. Optical pictures of 5 ML CdSe NPLs before and after high pressure treatment. a, ambient pressure. b, released to 0 GPa from 10 GPa. c, two samples of Fig. R2a and R2b were transferred onto a glass slide.

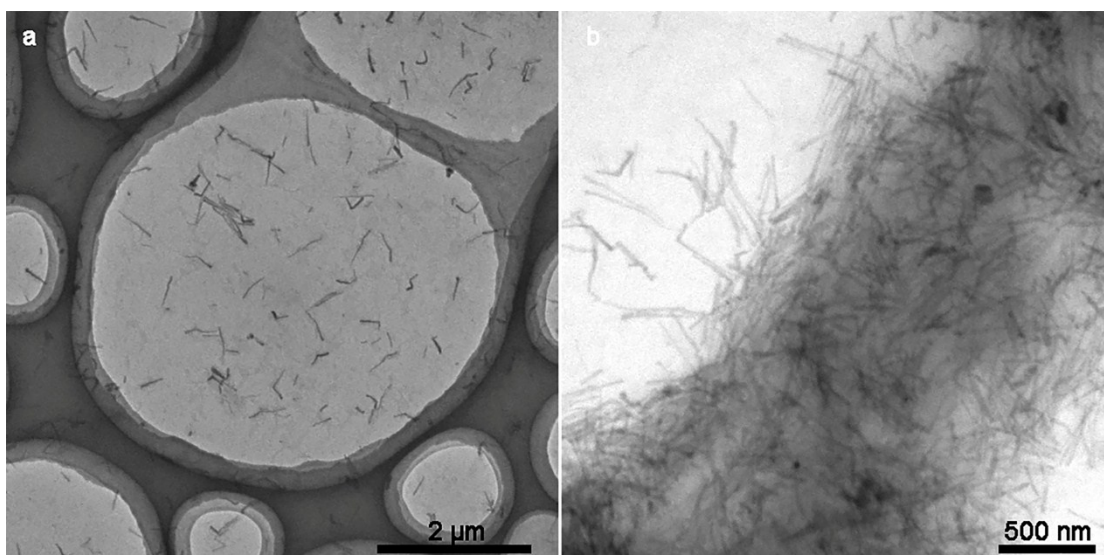


Figure S6. TEM images of large scale assemblies by stacking after high pressure treatment. a, low magnification TEM image; b, high magnification TEM image.

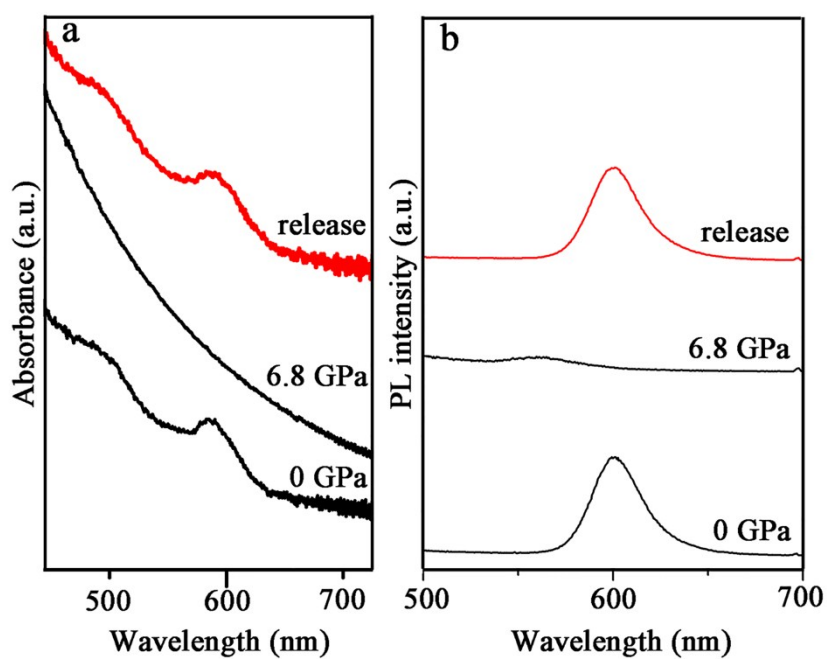


Figure S7. Absorption (a) and PL (b) spectra of 3.6 nm CdSe QDs, indicating reversible processes.

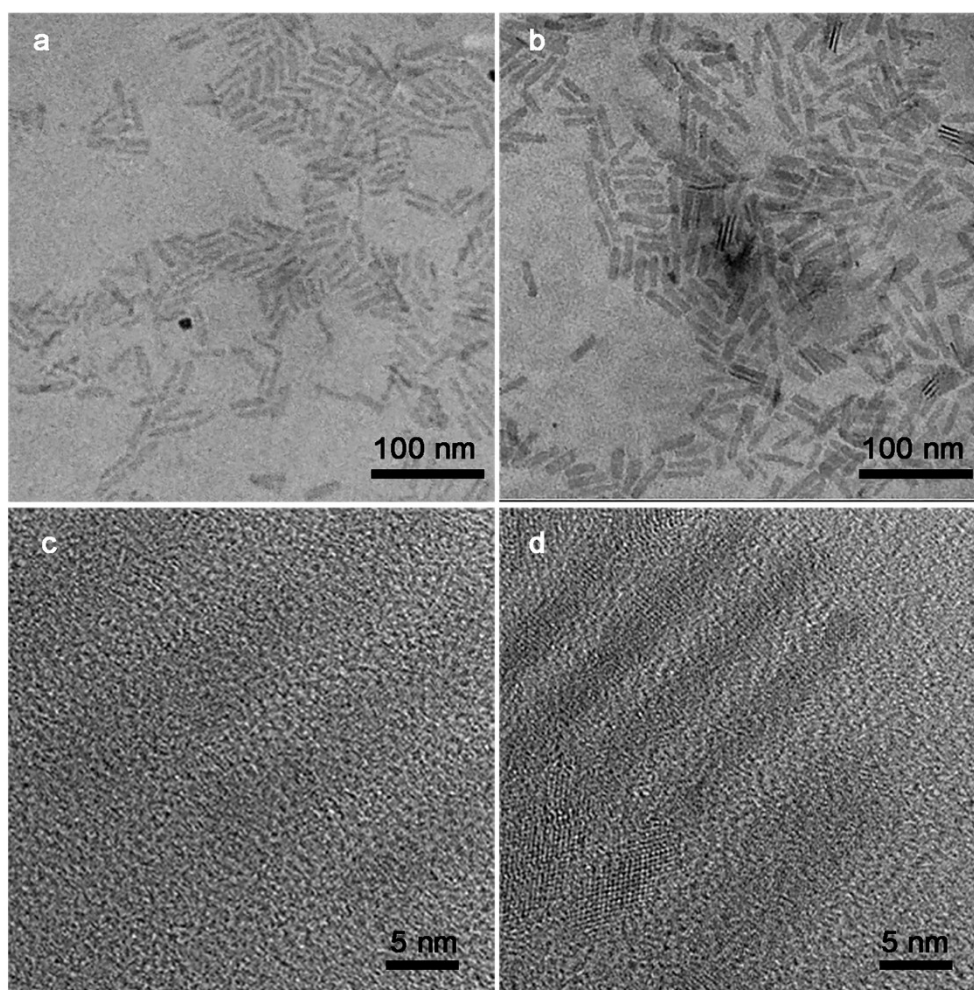


Figure S8. TEM and HRTEM images of 5 ML CdSe NPLs. a, TEM of origin sample. b, TEM of sample after high pressure treatment. c, HRTEM of origin sample. d, HRTEM of sample after high pressure treatment.

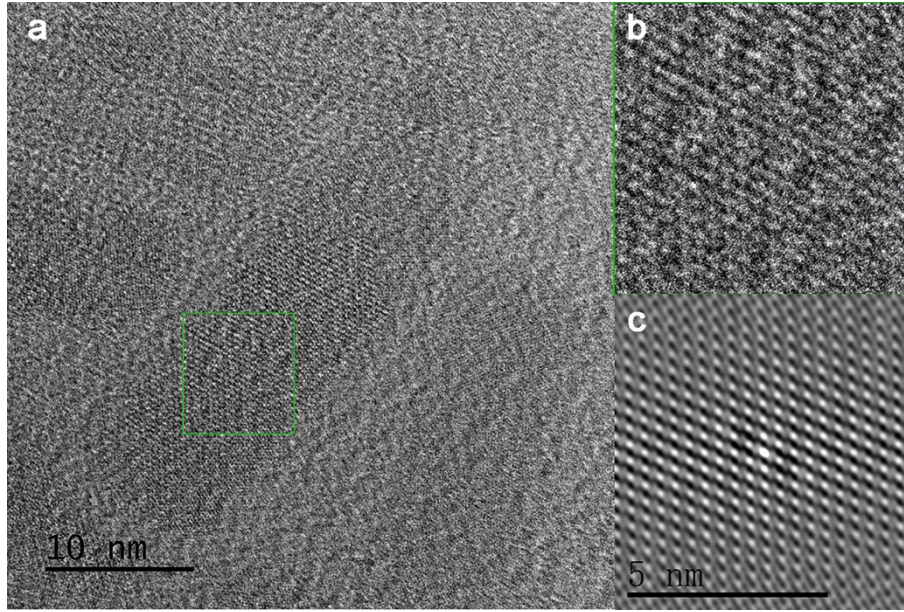


Figure S9. a, HRTEM picture of 5 ML CdSe NPLs after high pressure treatment; b, the selected crystal lattice area; c, corresponding image after filter process.

Table S1: The formula and fit parameters used for 5ML NPLs.

Formula: $y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2} + A_3 e^{-x/t_3}$		$\tau = A_1 t_1 + A_2 t_2 + A_3 t_3$					
Pressure (GPa)	0.22	0.71	1.25	2.65	3.47	4.59	5.92
A₁	0.402	0.344	0.123	0.252	0.149	0.233	0.253
t₁	1.343	0.845	5.578	1.189	6.531	4.693	5.412
A₂	0.398	0.344	0.139	0.267	0.149	0.233	0.235
t₂	1.342	0.845	5.567	1.188	6.530	4.694	0.986
A₃	0.192	0.286	0.738	0.401	0.611	0.481	0.129
t₃	5.955	3.861	1.157	5.562	1.316	0.547	0.069
τ (ns)	2.22	1.69	2.31	2.85	2.75	2.45	1.61

Table S2: The formula and fit parameters used for 4ML NPLs

Formula: $y = y_0 + A_1 e^{-x/t_1} + A_2 e^{-x/t_2} + A_3 e^{-x/t_3}$		$\tau = A_1 t_1 + A_2 t_2 + A_3 t_3$				
Pressure (GPa)	0.39	1.50	2.32	3.21	4.38	5.69
A₁	0.411	0.428	0.374	0.230	0.420	2.664
t₁	0.794	0.514	0.564	0.900	0.635	0.025
A₂	0.411	0.420	0.374	0.196	0.420	0.451
t₂	0.794	0.514	0.564	3.753	0.634	0.567

A_3	0.411	0.137	0.187	0.509	0.131	0.167
t_3	0.794	3.198	3.197	0.428	3.795	2.740
τ (ns)	0.98	0.87	1.02	1.09	1.03	0.78

Synthesis of CdSe QDs with Different Sizes.

The detailed synthetic methods are described as follows: a mixture of CdO powder (0.0385 g, 0.3 mmol), TOPO (2.32 g, 6 mmol), myristic acid (3 mmol), and ODE (7.0 ml) was added to a 50 ml three-neck flask. This mixture was heated to 260 °C under a nitrogen flow till CdO powder was completely dissolved under stirring. A Se solution containing 0.05 g (0.6 mmol) of Se, 1.0 ml of TOP and 1.0 ml of ODE prepared in a glovebox was swiftly injected into the vigorously stirred growth solution. After the injection, the temperature was dropped to 240 °C for the growth of CdSe QDs. At different reaction moments, aliquots were taken from the flask.