Electronic Supplementary Information

The Effects of Discrete and Gradient Mid-Shell Structures on Photoluminescence of Single InP Quantum Dots

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1. Experimental

Materials

Indium acetate ($In(OAc)_3$, 99.99%), lauric acid (LA, 98%), zinc acetate (99.99%), oleic acid (OA, 90%), sulfur (99.98%), selenium (99.99%), 1-octadecene (ODE, 90%), trioctylamine (TOA, 95%) and toluene (anhydrous 99.8%) were purchased from Sigma-Aldrich. Tris(trimethylsilyl)phosphine (TMS_3P, 98%) and trioctylphosphine (TOP, 90%) were purchased from Strem. Acetone (HPLC grade) was purchased from Samchun. All chemicals were used as purchased.

Synthesis of InP core

InP core was prepared by quickly injecting a phosphine precursor to a solution containing indium and zinc precursors. Briefly, zinc acetate (1.2 mmol) and OA (2.4 mmol) were mixed in 10 mL of ODE. The mixture was evacuated at 120°C for 1 h, then refilled with N_2 and cooled to RT. After adding indium acetate (0.6 mmol) and LA (1.8 mmol), the reaction mixture was evacuated again at 120°C for 1 h, refilled with N_2, and heated to 150°C. TMS_3P (0.4 mmol) dissolved in TOP (1 mL) was quickly injected into the reaction mixture, which was then heated to 240°C for successive growth. The reaction was monitored by measuring the absorption spectrum of the aliquot, and quenched by rapid cooling below 200°C. The resulting InP core was precipitated and washed with acetone.

Preparation of InP/ZnSeS/ZnS core/shell/shell quantum dots (GS-QDs)

A ZnSeS/ZnS gradient alloy shell was grown over InP core by stepwise reaction of $Zn(OA)_2$, Se/TOP and S/TOP. The $Zn(OA)_2$ solution was prepared by dissolving zinc acetate (2.4 mmol) and oleic acid (4.8 mmol) in 10 mL of TOA at room temperature, degassing at 120°C under vacuum, and refilling with N_2 gas. The reaction mixture was heated to 180°C. The InP core dissolved in toluene was injected into the solution. Then Se/TOP (0.4 M, up to a total amount of 1.8 mL) and S/TOP (1.0 M, 0.8 mL) was divided into four steps and sequentially injected by raising the temperature to 320°C. The Se:S ratios of each step were gradually changed from Se-rich to S-rich, 4:1, 4:3, 1:2, and 0:1. Successively, the ZnS shell was grown in the same reaction flask. After cooling to 280 °C, another 1.7 mL of 1.0 M S/TOP was injected and maintained for 1 h.

Preparation of InP/ZnSe/ZnS core/shell/shell QDs (DS-QDs)

The InP/ZnSe/ZnS QDs were prepared using a similar method as described above, but no gradual change of Se:S ratio. The $Zn(OA)_2$ solution was prepared in the same way, the InP core dissolved in toluene was also injected into the solution at 180°C. Then Se/TOP (0.4 M, up to a total amount of 1.8 mL) was added stepwise by raising the temperature to 320°C. The shell growth was done by reacting at 320°C for 1 h. Successively, the ZnS shell was grown in the same reaction flask. A S/TOP solution (1.0 M, 0.8 mL) was injected to the above reaction solution at 320°C and kept at that temperature for 40 min. After cooling to 280 °C, another 1.7 mL of 1.0 M S/TOP was injected and maintained for 1 h.

Structural analysis

Scanning transmission electron microscopy (STEM) images were obtained with a Titan ChemiSTEM system operated at 200 keV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out with a Shimadzu ICPS-8100 sequential spectrometer. X-ray diffraction (XRD) patterns were taken with a Bruker D8 Advance instrument using a Cu Kα X-ray source ($\lambda = 1.5418$ Å).

Raman spectroscopy

Samples for Raman spectroscopy were prepared by drop-casting QD solution on cleaned coverslips and drying in ambient conditions. Raman spectra were recorded by using confocal micro-Raman spectrometer (LabRam Aramis, Horiba).

Ensemble spectroscopy

Steady-state absorption spectra were recorded by using a UV/Vis spectrometer (Cary5000, Varian). Steady-state photoluminescence (PL) of quantum dots (QDs) in toluene was measured by using a fluorescence spectrophotometer (F-2500, Hitachi).

Single-dot confocal microscopy

Samples for single-dot confocal measurements were prepared by spin-coating QD solutions on rigorously cleaned coverslips at 2000 rpm for 60 s. QD solutions were composed of QDs in toluene containing 20 mg ml^{-1} polystyrene (Aldrich, average M.W. = 44,000). Confocal microscope (TE2000-U, Nikon) was equipped with a sample scanning stage at RT. Circular polarized light from a picosecond pulsed diode laser (LDH-D-C-450, Picoquent, 1 MHz repetition rate, prepared using a Berek compensator (5540, New Focus)) excited the samples. It was passed through a laser line filter (FF01-450/10-25, Semrock) and collimating lens. Then, it subsequently focused on the sample via an oil immersion objective (Plan Fluor, 1.3 NA, 100×, Nikon) with a power density corresponding to an average number of excitons per pulse, $\langle N_x \rangle$ = 0.1. Fluorescent signals were passed through a dichroic mirror (Z458rdc, Chroma Technology), spectrally filtered using a notch filter (HNPF-450.0-1.0, Kaiser optical systems) and a band pass filter (LP02-473RU-25, Semrock), and then split by using a non-polarizing 50:50 beam splitter. Half of the fluorescence was dispersed via a spectrograph (SpectraPro 2150i, Princeton Instruments) and projected onto an EMCCD camera (PL PROEM:512B EMCCD, Princeton Instruments). The other half was detected by an avalanche photodiode (APD) module (SPCM-AQR-16-FC, EG&G). The fluorescent signal detected by the APD was registered by a time-correlated single photon counting (SPC 830, Becker & Hickl). The TCSPC was operated in first-in-first-out regime in which the arrival time after the beginning of acquisition and the time lag with respect to the excitation pulse were stored for each detected photon. The the full-width half maximum (FWHM) of the overall instrumental response function approximately corresponded to 500–600 ps. The data were processed by using a BIFL data analyzer software

(Scientific Software Technologies Center) to obtain fluorescence intensity trajectories and the time-resolved fluorescence decays.

Probability density plots

Probability distributions for *on*- and *off*-times, calculated by over 100 individual QDs to exclude any artifacts introduced by unexpected events. According to previously reported probability density plots, the probability densities for *off*-time events consistently followed a power law distribution, whereas those for *on*-times showed “bending” structures for long *on*-time durations.[1] In our study, the *off*-time (blinking recovery) kinetics were observed to not be governed by a single rate constant for all samples because the probability densities were broadly distributed over a wide range of durations. Indeed, the blinking recovery kinetics were fitted to a power law equation, $P\left(\tau_{off}\right) \propto \tau^{-\alpha_{off}}$. Conversely, the *on*-time kinetics followed a truncated power law behavior, $P(\tau_{on}) \propto \tau^{-\alpha_{on}}e^{-\tau/\tau_{fall-off}}$, which shows a “bent” curvature for long τ_{on}, as previously reported by Wang et al. In log–log plots, the power law coefficient is the slope of the linear fit, and the fall-off time ($\tau_{fall\text{-}off}$) indicates the start of exponential truncation.[2,3]

2. Supporting Tables

Table S1. Atomic molar ratio, thickness of shell and PL QY at each growth step

Step	GS-QD						DS-QD					
	P/In	S/In	Zn/In	Se/In	Thickness (nm)	PL QY (%)	P/In	S/In	Zn/In	Se/In	Thickness (nm)	PL QY (%)
1	0.61	0.95	8.39	6.93	1.1	39	0.55	0.00	8.82	7.48	1.1	36
2	0.64	1.69	13.92	10.53	1.4	43	0.56	0.00	14.82	13.3	1.4	40
3	0.73	2.90	16.40	12.30	1.5	60	0.57	0.00	17.07	14.67	1.5	65
4	0.82	7.59	23.82	12.23	1.8	67	0.72	7.89	30.22	15.72	1.9	72
5	0.78	13.11	28.44	12.22	2.0	88	0.92	14.73	34.93	15.33	2.1	95

Table S2. The full-width half maximum (FWHM) values of PL, single frame, averaged spectra, and emission frequency shift histograms, respectively. All fwhm values were determined by Gaussian fitting.

Sample	**FWHM$_{PL}$ (meV)**	**FWHM$_{each}$ (meV)**	**FWHM$_{avg}$ (meV)**	**FWHM$_{\Delta shift}$ (meV)**
GS-QD	184	118	135	16.2
DS-QD	164	113	122	12.7

Table S3. Calculated probabilities for creating single- and multi-excitons in a single pulse and the Auger ionization efficiencies.

	$\tau_{\text{fall-off}}$ (s)	P_{SX} ($\times 10^{-2}$)	P_{BX} ($\times 10^{-4}$)	P_{MX} ($\times 10^{-4}$)	P_{ionize} ($\times 10^{-4}$)	P_{ionize}/P_{MX}
GS-QD	6.4	1.81	1.68	1.69	9.3	5.5
DS-QD	13.7	1.79	1.64	1.65	4.4	2.7

3. Supporting Figures

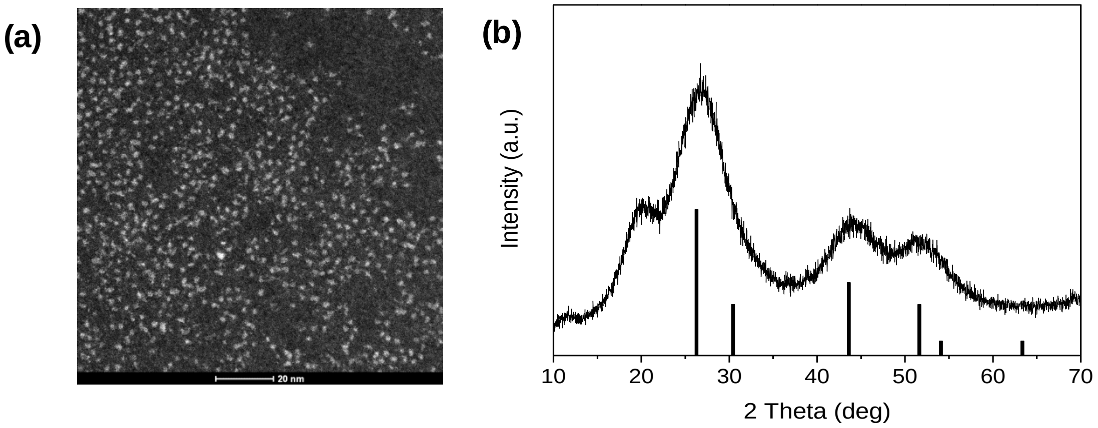

Figure S1. (a) TEM image and (b) Powder XRD pattern of InP core. Lattice parameter (5.87 Å) The black vertical bars represent the diffraction pattern for bulk zinc-blende InP (JCPDS 00-032-0452)

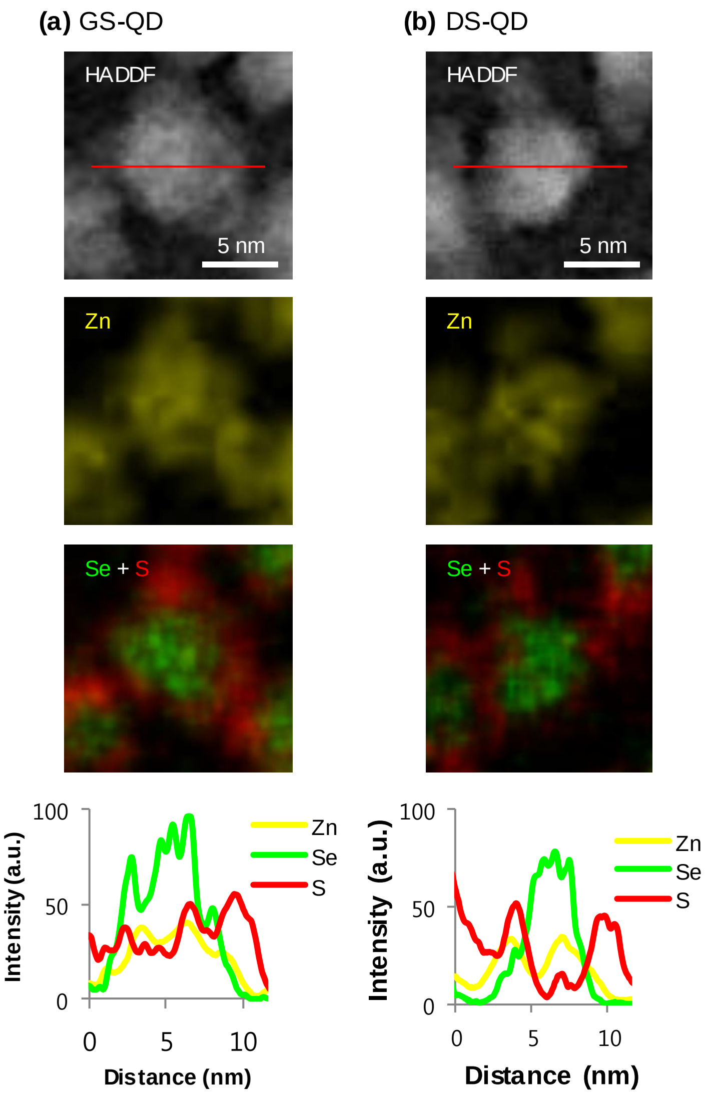

Figure S2. STEM EDS mappings and the line profiles of the Zn, Se and S atom across the red line in the HADDF images of the (a) GS-QD and (b) DS-QD.

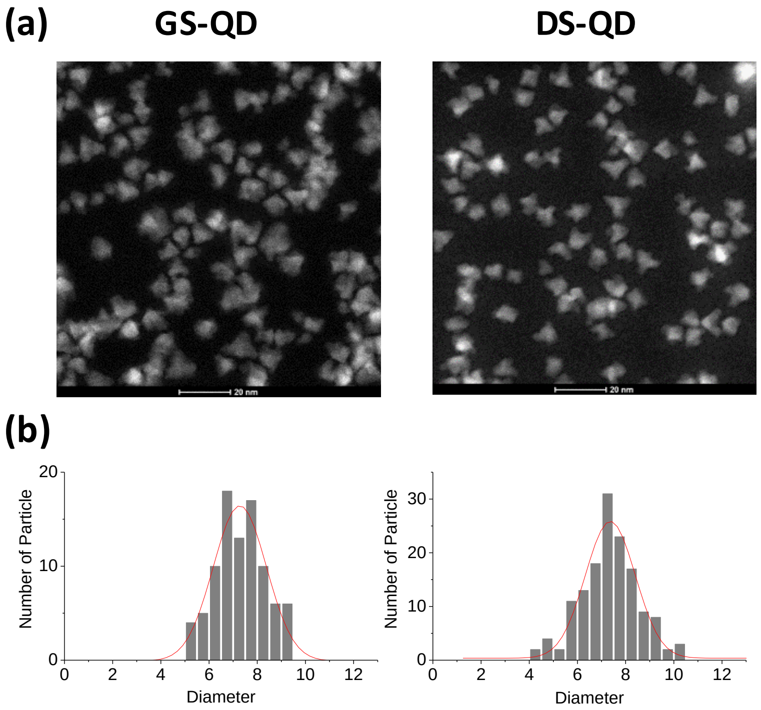

Figure S3. (a) TEM images and, (b) the diameter histograms of GS- and DS-QDs.

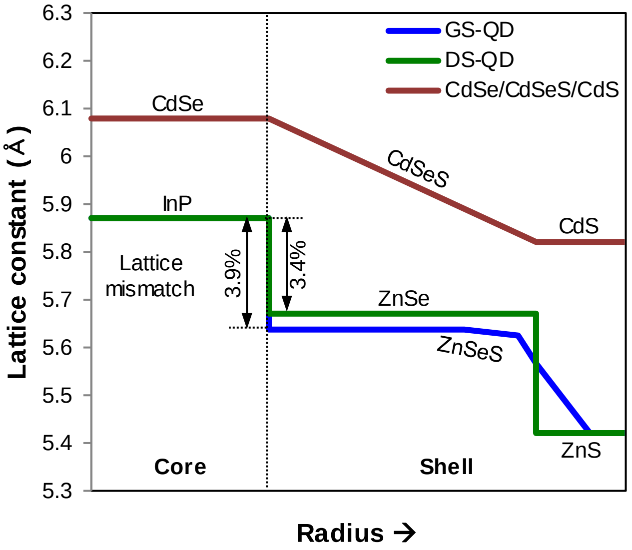

Figure S4. The change of bulk lattice constants according to the core and shell composition in GS-, DS-QDs and comparative schematic drawing of the CdSe/CdSeS/CdS gradient alloy structure.

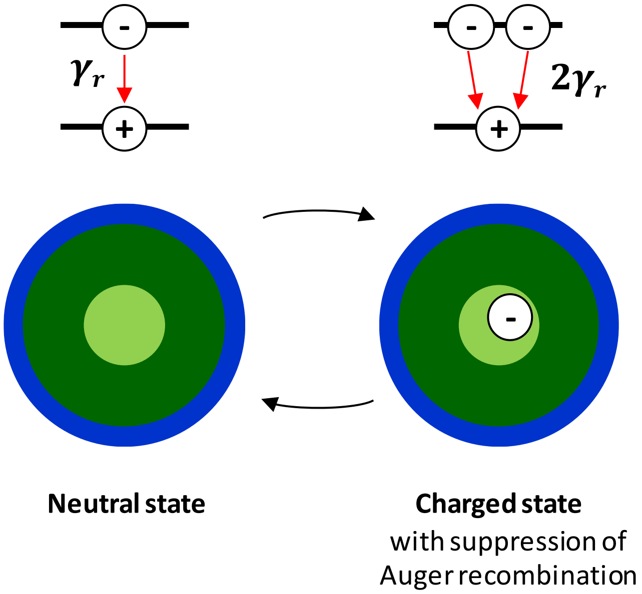

Figure S5. Schematic representation of the lifetime blinking behavior when the γ_r represent the radiative decay rate.

4. References for Supporting Information

1 K. T. Shimizu, R. G. Neuhauser, C. A. Leatherdale, S. A. Empedocles, W. K. Woo and M. G. Bawendi, *Phys. Rev. B*, 2001, **63**, 205316.

2 S. Wang, C. Querner, M. D. Fischbein, L. Willis, D. S. Novikov, C. H. Crouch and M. Drndic, *Nano Lett.*, 2008, **8**, 4020–4026.

3 S. Wang, C. Querner, T. Emmons, M. Drndic and C. H. Crouch, *J. Phys. Chem. B*, 2006, **110**, 23221–23227.