Supporting information

Highly Luminescent Blue-emitting CdZnS/ZnS nanorods having Electric Field Induced Fluorescence Switching

property

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Fig. S1 TEM images of high quality CdZnS nanocrystals used in this work.



Fig. S2 TEM images of the products obtained with an injection of S-ODE solution at 330 °C with the reaction time of (a) 30 s, (b) 60 s, (c) 180 s, and (d) 300 s. TEM images of the products by injection of S-TOP solution with the reaction time of (e) 180 s, (f) 300 s, and (g) 60 min.



Fig S3 Time-evolution of absorption spectra of the products obtained with an injection of (a) S-TOP, and (b) S-ODE.



Fig. S4 (a) TEM image of CdZnS nanocrystals synthesized with 2 mmol of OA was used leaving other reaction parameters fixed. AR of NRs was reduced by addition of more OA ligands.



Fig. S5 Schematic diagram of energy level of optically excited CdZnS QD and CdZnS QR.

Annealing of CdZnS core to identify origin of defect emission (Fig. S6 ~ S7)

For annealing of the CdZnS cores with various reagents, 5.5 ml of OAm was commonly used and the reaction temperature was 230oC in each case. Specifically, 0.17mmol of sulfur was used for S-containing OAm, and 0.094 mmol of zinc sulfate heptahydrate was used for Zn-containing OAm, 0.094 mmol of cadmium acetate dihydrate was used for Cd-containing OAm, and both 0.17mmol of sulfur and 0.094 mmol of zinc sulfate heptahydrate were used for Zn and S containing OAm. Please see the Tab. S6 below for details about procedure of the core annealing with various reagent.

For defect emission of CdS-based NCs, some researchers have ascribed it to sulfur vacancy, 1~3 while others have vaguely attributed it to surface-related trap states or the recombination of electrons and holes at some defects.^{4~5} To investigate the origin of the defectrelated broad emission from the CdZnS core, we annealed the core at 230°C with various reagents (see experimental section for details). The obtained results are presented in Fig. S6 and S7. For the CdZnS cores annealed with OAm only, the PL and absorption peak were blueshifted (Fig. S6a and S6b). It turned out that the peak shifts were caused by etching of CdZnS core in the presence of oleylamine (Fig. S7b). Etching of inorganic nanocrystals by OAm is consistent with the results of a previous study.⁶ Annealing of the cores in a flask containing both zinc and sulfur precursors resulted in the formation of ZnS shells, and this can be verified by both an increase in ZnS absorption band (~ 300 nm)⁷ and TEM image (Fig. S7f). The addition of the zinc precursor only rarely changed the morphological characteristics and PL QY of the NRs compared to the case annealed with OAm, but it led to the blue-shift of the PL peak. The blue-shift of the PL peak might have been caused by zinc diffusion into the cores during annealing. Interestingly, the CdZnS cores annealed under sulfur containing OAm gave rise to noticeable changes. Both the first excitonic peak seen in the absorption spectra and the PL peak were red-shifted, and the PL QY was increased to 6.4% accompanied by the elimination of the broad defect emission. Such changes were found analogously in the case of ZnS shell formation, but no obvious ZnS peak (~ 300 nm) was observed in the absorption spectra for the core only annealed with sulfur dissolved in OAm. In the TEM image shown in Fig. S7e, the diameter of the nanocrystals increased, while their length decreased, unlike the case of the CdZnS/ZnS core/shell structures (Fig. S7f). A detailed explanation is given below related to the optical and morphological characteristics of the CdZnS/ZnS NRs. When CdZnS cores were annealed with cadmium-containing OAm, the PL QY slightly improved, but irregular shaped NCs were observed as shown in Fig. S7d. Judging from a variety of obtained results, it can be inferred that most of the defect-related emission of CdZnS NRs arises from the presence of sulfur vacancy on the surface.



Fig. S6 (a) Absorption and (b) PL spectra of the core annealed with various conditions, oleylamine(OAm), zinc precursor dissolved in oleylamine (Zn+OAm), cadmium precursor dissolved in oleylamine (Cd+OAm), sulfur precursor dissolved in oleylamine (S+OAm), and zinc and cadmium precursor dissolved in oleylamine (Zn+OAm). (c) PL QY and PL peaks arising from band edge emission of NCs with various annealing conditions.



Fig. S7 TEM images of the core (a) and the products annealed with various conditions, (b) oleylamine(OAm), (c) zinc precursor dissolved in oleylamine (Zn+OAm), (d) cadmium precursor dissolved in oleylamine (Cd+OAm), (e) sulfur precursor dissolved in oleylamine (S+OAm), and (f) zinc and cadmium precursor dissolved in oleylamine (Zn+OAm).



Fig. S8 (a) PL spectra, (b) absorption spectra, (c) PL QYs, (d) PL peaks, and (e) FWHMs of the short core/shell NRs obtained without core pre-annealing (S1) and with (S2).

Time-resolved PL decay (Fig. S9)

Time-resolved PL studied were conducted for CdZnS rod core and CdZnS/ZnS core/shell NRs obtained with OAm and shell precursors (Fig. S9). The PL decays were characterized at three spectral wavelengths of ~440 nm, ~460 nm and ~700 nm for the CdZnS core and ~460 nm for the CdZnS/ZnS core/shell NRs. The emission lifetimes were de-convoluted into three exponential decay components, a shorter one, τ_1 and longer ones, τ_2 , τ_3 . The average lifetime at ~460 nm were recorded as 194.42 ns for the CdZnS core, and 85.72 ns for the CdZnS/ZnS core/shell NRs. The longer average lifetime of the core is attributed to the longer lifetime and the larger decay amplitude fraction of the longest component (τ_3 : 583.00 ns, 27.89%), and it seems that the longer components could be closely related to the defect emission on the surface. The PL decay curve was taken at ~ 700 nm where the surface defect-related emission was centered, and the PL lifetime was 1007.47 ns. The value was much larger than that measured at 460 nm, and the fraction and lifetime of the largest component were increased to 1780.18 ns and 45.12%, respectively (Fig. S9e). Please note that the fraction of the longest component for the case measured 440 nm of which emission was less affect by defect emission was reduced to 17.55% (Fig. S9c). The fast decay components could result from the non-radiative surface states of the NCs, and the longer components could be related to the spatially localized states at lower energy such as structural imperfections and morphological irregularities.⁸ Even though the lifetime of the core/shell structure was smaller than the CdZnS core measured at 460 nm, the shortest decay component, τ_1 , was lengthened and more occupied from 3.25 ns (40.39%) for the core to 16.19 ns (50.94%) for core/shell NRs. This may mean that the fast decay channels associated with the trap states were reduced with the passivation of the ZnS shell.⁹



Fig. S9 (a) PL spectra of CdZnS core and CdZnS/ZnS core/shell NRs. (b) PL emission decays of CdZnS core monitored at 440nm, 460 nm and 700 nm, and CdZnS/ZnS core/shell structures monitored at 460 nm. Deconvoluted exponential decay components and fraction and average lifetime of (c) CdZnS core monitored at 440nm, and (d) CdZnS core monitored at 460nm, (e) CdZnS core monitored at 700nm and (f) CdZnS/ZnS core/shell NRs monitored at 460nm.



Fig. S10 (a) Atomic structure of (CdS)₃(ZnS)₃ core/shell NR in the (0001) plane and along the [0001] direction. (b) The local wurtzite unit cell of CdS core in the (CdS)₃(ZnS)₃ model (c) Wurtzite unit cells of equilibrium bulk CdS(left) and ZnS(right), Blue, yellow, red, and white balls represent Cd, Zn, S, and pseudo H atoms, respectively.



Fig. S11 Atomic structures (top panel), spatially resolved LDOS along the radial direction (left panels) and band structure (right panels) of (a) the pristine, (b) shell S vacancy, (c) core Cd vacancy, and (d) shell Zn vacancy (CdS)₂(ZnS)₂ NRs. On the top of the atomic structures, we overlay the LDOS for the energy ranges marked by shaded regions in the band plots at the isovalues of 5×10^{-4} e Å⁻³. In LDOS plot, the origin is defined as the geometric center of core/shell NRs. The energetically less favorable shell S vacancy defect reduced the band gap value to 2.21 eV (561.01 nm). For the Cd core and Zn shell vacancies with much higher

formation energies, the defect states appear directly above the valence band minimum and the degree of band gap reduction is much higher (band gap of 2.15 eV or 576.67 nm in both cases)

Tab. S1 Optical and morphogical characteristics of CdZnS NCs described in detailed that were synthesized under various reaction conditions. * Samples are the ones shown in Fig. 1 (a) \sim (d) and Fig. S3.

Sample	Band edge emission peak (nm)	Defect emission peak (nm)	Peak difference (nm)	Diameter (nm)	Length (nm)	AR
1. 370 °C 120 s	442	641	199	Spherical	(3.5 nm)	-
2. 370 °C 30 s (+HPA)	466	739	273	3.5	12.1	3.5
3. 330 °C 30 s (+HPA)	452	727	275	2.4	12.0	5.0
4. 300 °C 30 s (+HPA)	442	720	278	2.0	10.0	5.0
5. 370 °C 30 s (+HPA+OA)	471	731	260	4.1	7.5	1.8

Tab. S2 Elemental composition of Cd and Zn measured by ICP-OES. CdZnS NCs were synthesized in a flask containing 1) Zn acetate, CdO, sulfur, OA, TOPO, ODPA, ODE or 2) Zn sulfate heptahydrate, Zn nitrate hextahydrate, Cd nitrate tetrahydrate, sulfur, oleylamine. Actual compositional ratio of Zn/Cd in the NC is different from the Zn/Cd precursors ratio in a flask due to difference in reactivity of zinc. In the former case where various common ligands except for amine were used, the actual component ratio of zinc was far below that of cadmium (12.6:1), even though the ratio of Cd precursor to Zn precursor put into the flask was similar (2:1). In the latter one where OAm ligand was used, however, there was no big difference between the actual ratio of Cd:Zn measured by ICP-OES (1:3) and the precursor ratio of Cd:Zn (1:3).

Atomic %	1) Zn, Cd precursors /OA, TOPO, PA, ODE	2) Zn, Cd precursors /Oleylamine
Cd:Zn(precursor)	2:1	1:3
Cd:Zn(ICP-OES)	12.6:1	1:3
Reactivity	Cd>>Zn	Cd≒Zn

Tab. S3 PL quenching efficiency of CdZnS/ZnS NRs grown from long, short CdZnS seed, and short one with PA as a function of an applied electric field.

For long core/shell NRs having an AR of 5.8, 35% of the PL emission was reduced at an applied field of 125 kV/cm, and the PL quenching efficiency was increased to 79% at an applied field of 500 kV/cm. The maximum PL QY (see Tab. 1) and PL quenching efficiency at an applied field of 500 kV/cm of short NRs were 40% and 41%, respectively, whereas those of long NRs was 18% and 79%, respectively. For short (long) NRs, the probability of electron-hole recombination increased (decreased) due to strong (weak) quantum confinement by the reduced (enlarged) dimension in the length leading to increased (decreased) PL QY.

Electric field	0 kV/cm	62.5 kV/cm	125 kV/cm	187.5 kV/cm	250 kV/cm	500 kV/cm
Short NRs	0%	15%	18%	22%	27%	41%
Short NRs (PA)	0%	24%	26%	30%	37%	51%
Long NRs	0%	25%	35%	48%	59%	79%

Models	a [Å]	с [Å]	Core diameter [Å]	Total diameter [Å]	Quantum confinement effect [eV]	Strain effect [eV]
Bulk CdS	4.15	6.78	-	-	-	-
Bulk ZnS	3.82	6.25	-	-	-	-
$(CdS)_2(ZnS)_1$	4.19	6.42	12.6	19.9	-0.572	0.380
$(CdS)_2(ZnS)_2$	4.16	6.33	12.5	27.4	-0.845	0.615
$(CdS)_2(ZnS)_3$	4.14	6.30	12.5	34.9	-0.991	0.743
$(CdS)_2(ZnS)_4$	4.14	6.27	12.5	42.4	-1.080	0.828
$(CdS)_3(ZnS)_1$	4.17	6.50	20.8	28.1	-0.305	0.237
$(CdS)_3(ZnS)_2$	4.16	6.41	20.8	35.5	-0.489	0.412
(CdS) ₃ (ZnS) ₃	4.16	6.36	20.8	42.9	-0.610	0.536
(CdS) ₃ (ZnS) ₄	4.15	6.32	20.8	50.4	-0.685	0.619
$(CdS)_4(ZnS)_1$	4.16	6.55	29.1	36.3	-0.178	0.149
$(CdS)_4(ZnS)_2$	4.15	6.46	29.0	43.6	-0.323	0.295
$(CdS)_4(ZnS)_3$	4.15	6.40	29.1	51.1	-0.423	0.401
$(CdS)_4(ZnS)_4$	4.15	6.37	29.1	58.5	-0.499	0.494

Tab. S4 Local lattice constant of CdS core region, core and total diameter, electronic quantumconfinement, and strain effects of corresponding CdS/ZnS NRs.

Tab. S5 DFT-derived formation energies of various vacancy defect models at CdS/ZnS interface considered in this work.

Defect models	Formation energy [eV]
Core S vacancy	0.555
Shell S vacancy	1.426
Core Cd vacancy	4.080
Shell Zn vacancy	4.314

Tab. S6 Synthetic condition of CdZnS core with various reagents.

	OAm	Zn	Cd	S	Zn+S			
Oleylamine	5.5 ml							
Sulfur powder				0.17 mmol	0.17 mmol			
Zinc sulfate heptahydrate		0.094 mmol			0.094 mmol			
cadmium acetate dihydrate			0.094 mmol		0.094 mmol			
Reaction Temperature			230°C	-				

Reference

- Y. Wada, H. Kuramoto, J. Anand, T. Kitamura, T. Sakata, H. Mori and S. Yanagida, J. Mater. Chem. 2001, 11, 1936.
- [2] Q. Xiao and C. Xiao, *Appl. Surf. Sci.* 2009, **255**, 7111.
- [3] F. Wu, J. Z. Zhang, R. Kho and R. K. Mehra, *Chem. Phys. Lett.* 2000, **330**, 237.
- [4] D. Xu, Z. Liu, J. Liang and Y. Qian, J. Phys. Chem. B 2005, 109, 14344.
- [5] W.-S. Chae, H.-W. Shin, E.-S. Lee, E.-J. Shin, J.-S. Jung and Y.-R. Kim, *J. Phys. Chem.B* 2005, **109**, 6204.
- [6] B. Koo, R. N. Patel and B. A. Korgel, J. Am. Chem. Soc. 2009, 131, 3134.
- [7] Z. Deng, H. Yan and Y. Liu, Angew. Chem. Int. Ed. 2010, 49, 8695.
- [8] L. V. Titova, T. B. Hoang, H. E. Jackson, L. M. Smith, J. M. Yarrison-Rice, J. L. Lensch and L. J. Lauhon, *Appl. Phys. Lett.* 2006, **89**, 053119.
- [9] V. K. Komarala, C. Xie, Y. Wang, J. Xu and M. Xiao, J. Appl. Phys. 2012, 111, 124314.