Control of the Photoluminescence Bandwidth of ZnTeSe Quantum Dots by Suppressing Te Cluster Effect

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Experiment

- Materials

Diethylzinc (Et_2Zn, 15% in Hexane, ca. 1mol/L), selenium (Se, 99.99%), tellurium (Te, shot ≤2 mm, 99.999%), diphenylphosphine (DPP, 98%), zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$, 99%), sulfur (S, ≥ 99.998%), zinc chloride ($ZnCl_2$, 99.999%), hydrofluoric acid (HF, 48% in water), oleic acid (OA, technical grade 90%), oleylamine (OAm, technical grade, 70%), trioctylphosphine (TOP, 97%) were purchased from Sigma-Aldrich. Tri-octylamine (TOA, 95.0%) was purchased from SAMCHUN CHEMICALS. Toluene (anhydrous, 99.8%) was purchased from Thermo Fisher Scientific. Acetone (99.8%) was purchased from DAEJUNG.

- Preparation of precursor

In general, to prepare 0.5 M zinc oleate ($Zn(OA)_2$), 60 mmol of OA was added in 40 ml of TOA in 100 ml flask and evacuated at 120°C for 60 min. Then, 20 mmol of Et_2Zn was carefully injected into the mixture to make $Zn(OA)_2$ and cool down to 80°C with 1ml of TOP. 2 M SeDPP were prepared 10 mmol of Se in 5 ml of DPP in a 25 ml flask and heated to 80°C. 0.5 M SeTOP, 0.5 M TeTOP and 1 M STOP were prepared by separately dissolving 6 mmol of selenium, 6 mmol of tellurium and 12 mmol of sulfur in 12 ml TOP in a N_2 filled glove box.

- Synthesis of evenly distributed Te doped ZnTeSe quantum dots

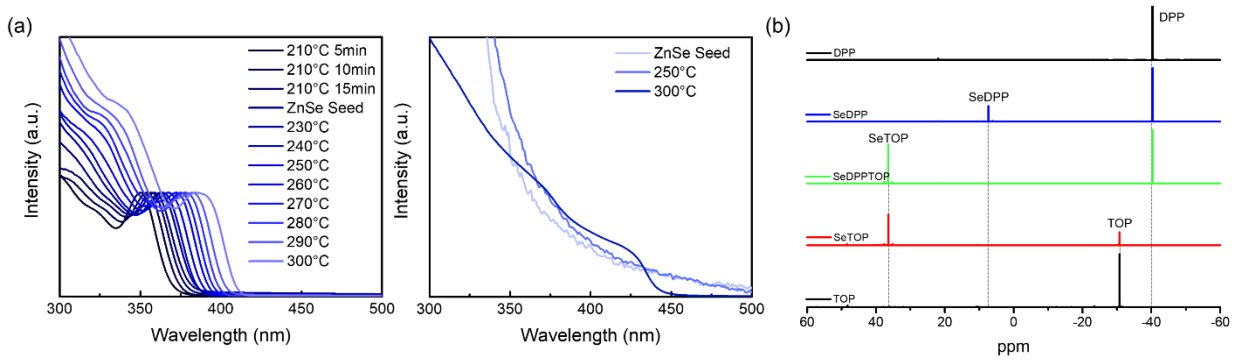
4 mmol of OAm and 5.8 mmol of OA in 40 ml of TOA was prepared in a 100 ml flask with stirring and degassing at 120°C for 60 min and heated to 210°C under N_2 flow (800 cc/min). 4 mmol of Et_2Zn was injected after degassing. Then, mixture of 2 M SeDPP and 0.5 M of TeTOP was rapidly injected into the flask at 210°C. In this stage, the total molar amount of the SeTOP and TeTOP mixture was fixed at 2 mmol, and the molarity of Te/TOP was adjusted to achieve the desired Te/(Se+Te) ratio. Then, the flask was reacted at 210°C for 30 minutes, followed by heating to 300°C for an additional 30 minutes, and then cooled down to room temperature with the addition of 1 ml of TOP. The uniform Te doped ZnTeSe QDs were repeated purified with anhydrous toluene and acetone by centrifugation at 6000rpm for 5 min and redispersed in anhydrous toluene.

- **Synthesis of center/surface Te doped ZnTeSe quantum dots**

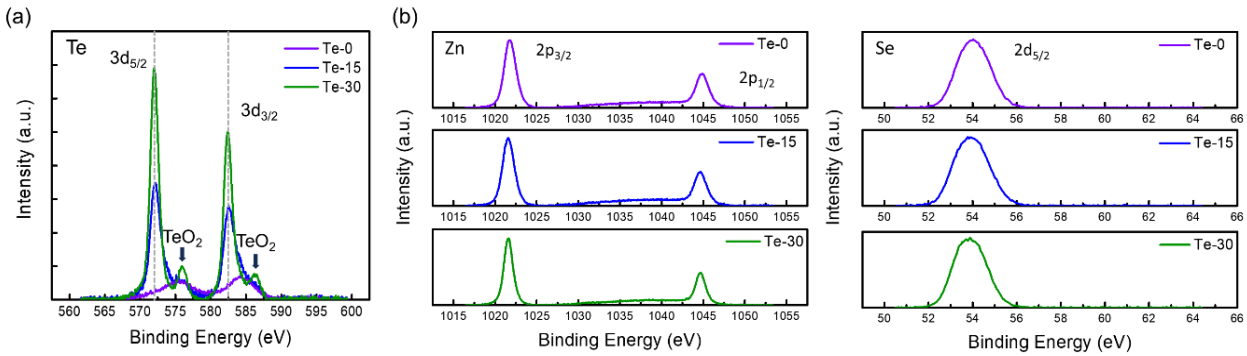
0.5 mmol of $Zn(Ac)_2$ and 1.2 mmol of OA in 20 ml of TOA was prepared in a 100 ml flask with stirring and degassing at 120°C for 60 min and heated to 260°C for 5 min under N_2 flow (800 cc/min). After cooling to 220°C, 3 nm of $ZnTe_xSe_{1-x}$ QDs (optical density at 100-fold dilution was 0.54 at the first absorption peak, 2 ml) was quickly injected and wait for 30 seconds to remove the toluene. Then, HF (10 vol% in acetone, 0.11 ml) and $ZnCl_2$ (0.5 M in acetone, 0.05 mmol, 0.1 ml) were added to the reaction pot, and the temperature increased to 300°C. For 1 nm thickness of exterior growth, the mixture of 0.5 M SeTOP and 0.5 M TeTOP, corresponding to a total of 0.7 mmol, was slowly injected together with 1.8 mmol of 0.5 M $Zn(OA)_2$ into the reaction mixture at 300°C for 40min. Same as the uniform Te doped ZnTeSe QDs synthesis method, the molarity of TeTOP was adjusted to achieve the desired Te/(Se+Te) ratio. ZnS passivation shell was grown by adding 1 mmol of 1 M STOP and 1 mmol of 0.5 M $Zn(OA)_2$ and reacted for 1h at 300°C. Purification method is same with uniform $ZnTe_xSe_{1-x}$ QDs purification.

- **Characterization**

The absorption and PL spectra were obtained by UV-Vis spectrophotometer (V-650; Jasco) and fluorescence spectrophotometer (Cary Eclipse; Agilent), respectively. The PLQY was measured by absolute PLQY spectrometer (QE-2100, Otsuka). Transmission electron microscopy (TEM) analysis was carried out by JEOL JEM-F200 operated at 200kV. The inductively coupled plasma optical emission spectrometer (ICP-OES) was conducted using Agilent 5100 for atomic analysis of Zn, Se and Te. X-ray photoelectron spectroscopy (XPS) spectra were acquired using a ESCALAB250 (Thermofisher). The conversion from the local Te ratio to the total Te ratio was calculated based on the volume ratio. Nuclear magnetic resonance (NMR) was conducted by Avance III 700 (Bruker), using Chloroform-d ($CDCl_3$). X-ray diffraction (XRD) patterns were obtained by SmartLab (Rigaku). Ultraviolet photoelectron spectroscopy (UPS) was conducted using EXSA G2 (Thermofisher Scientific).



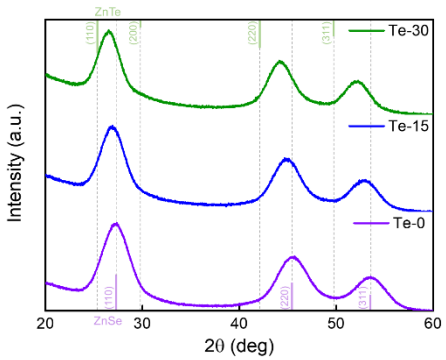
Supporting information 1 (a) Absorption spectra of nucleation and growth of ZnSe core with SeDPP (left) and SeTOP (right) as the reaction time and temperature increase. (b) ^{31}P NMR of DPP, SeDPP, SeDPPTOP, SeTOP and TOP, presented sequentially from top to bottom.



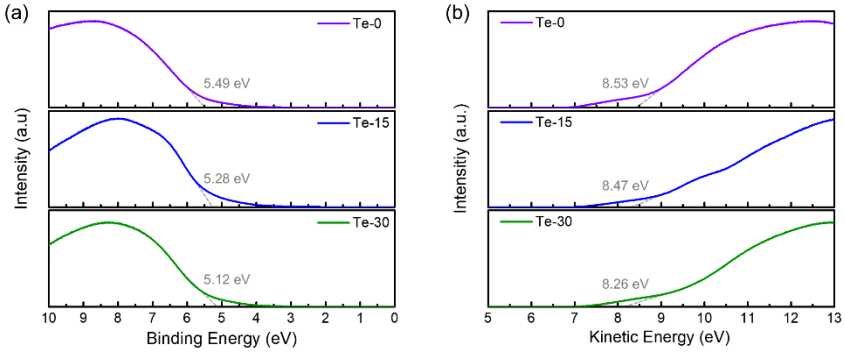
(c)

	Te- 0	Te-15	Te-30
Zn/(Se+Te) mole ratio	1.2	1.2	1.1
Te/(Se+Te) mole ratio	-	0.13 (XPS 0.18)	0.27 (XPS 0.27)

Supporting information 2 XPS spectra of (a) Te binding energy of the Te-0, Te-15, Te-30 after purification. The Te peak observed in the Te-0 spectrum is identified as the Zn Auger peak.[1] XPS spectra of (b) Zn2p and Se2d binding energy of the Te-0, Te-15, Te-30 after purification. (c) XPS elemental ratio and ICP-OES of the Te-0, Te-15, Te-30 after purification.



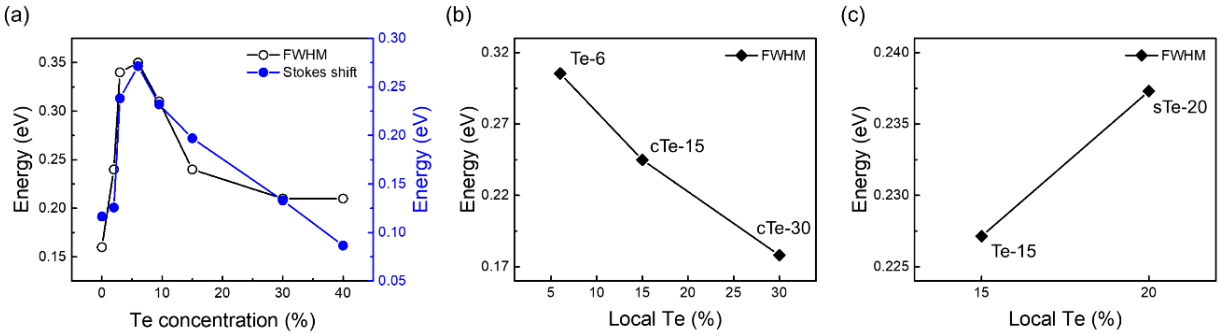
Supporting information 3 XRD patterns of Te-0 (violet), Te-15 (blue), Te-30 (green) after ZnSe/ZnS passivation. The representative diffraction peaks of bulk zincblende ZnSe (violet, bottom; JCPDS No. 65-9602) and ZnTe (green, top; JCPDS No. 15-0746) are included as references for comparison.



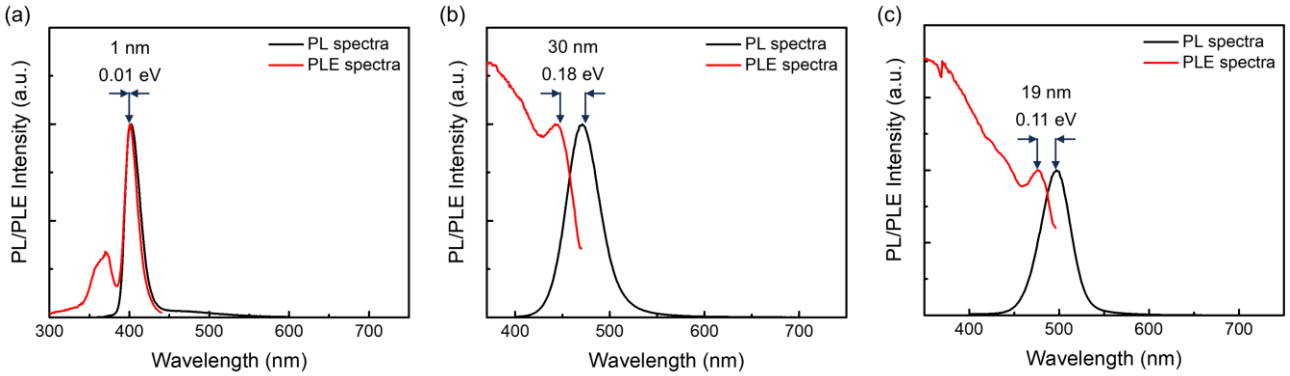
Supporting information 4 UPS spectra of Te-0, Te-15, Te-30 QDs showing (a) valence band edge regions (BE) and (b) secondary electron cutoff (KE)

Te Concentration (Te/(Te+Se))	First Absorption Peak (nm)	PL Wavelength (nm)	FWHM (nm)	Stoke Shift (nm)
0	379	393	20 (0.16 eV)	14
0.02	401	418	34 (0.24 eV)	17
0.03	404	438	52 (0.34 eV)	34
0.06	408	448	57 (0.35 eV)	40
0.095	421	457	52 (0.31 eV)	36
0.15	433	465	42 (0.24 eV)	32
0.30	461	485	37 (0.21 eV)	24
0.40	485	502	39 (0.21 eV)	17

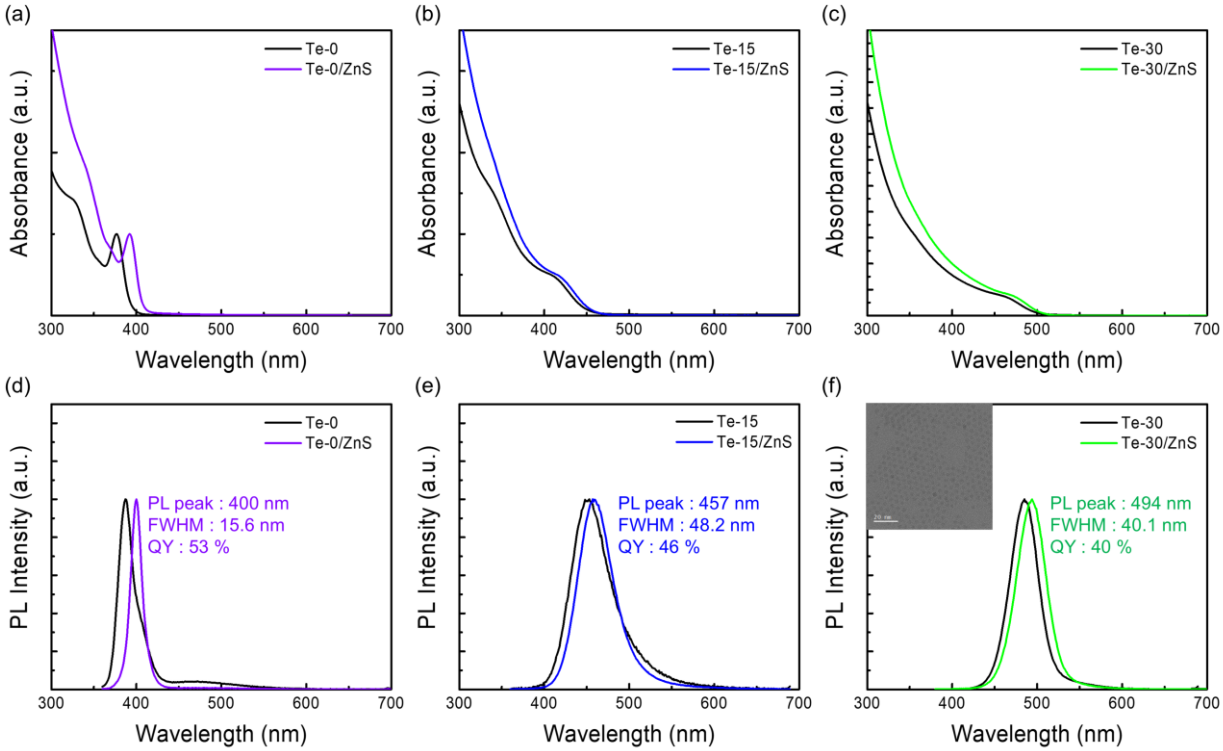
Supporting information 5 Characteristics of the evenly distributed Te-doped $ZnTe_xSe_{1-x}$ QDs ($0 \leq x \leq 0.40$)



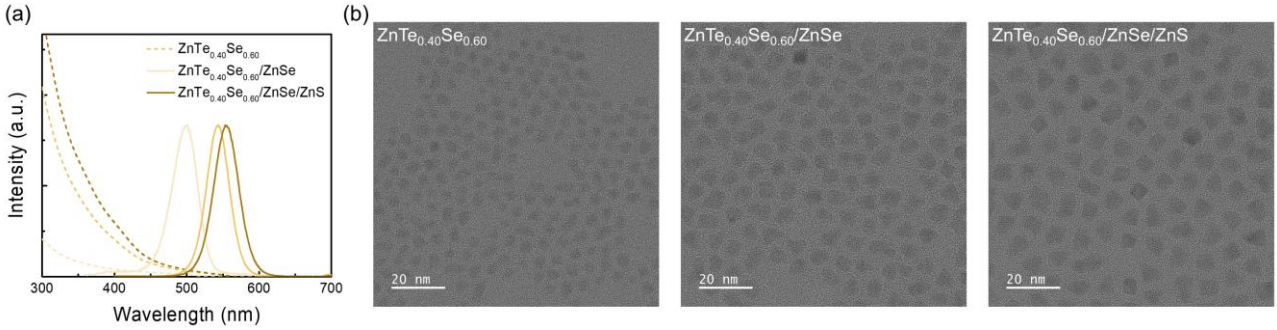
Supporting Information 6 (a) Change in FWHM (black) and Stokes shift (blue) of the evenly distributed Te doped in overall 3 nm $ZnTe_xSe_{1-x}$ QDs ($0 \leq x \leq 0.40$) (b) Change in FWHM of Te-6, cTe-15 and cTe-30 (c) Change in FWHM of Te-15 and sTe-20.



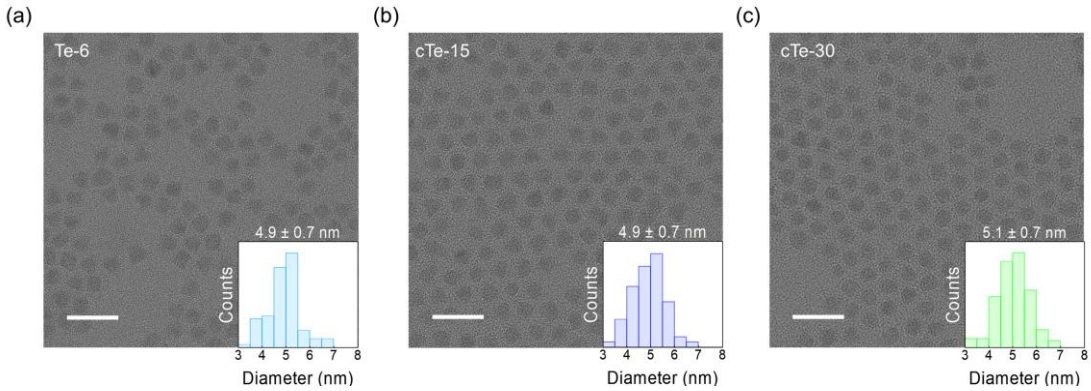
Supporting information 7 PLE (red solid line) and PL (black solid line) of the (a) Te-0, (b) Te-15, (c) Te-30. (PL and PLE intensity were measured under 365 nm excitation and PL emission wavelength, respectively)



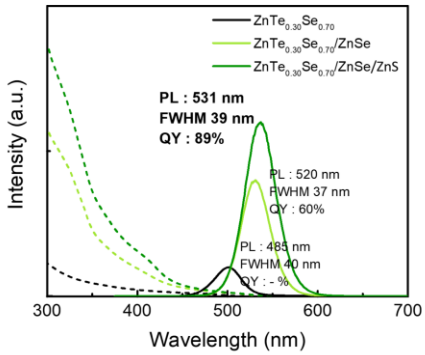
Supporting information 8 (a) Absorption and (b) PL spectra of the Te-0, Te-15, Te-30 before/after ZnS passivation, with inset TEM image.



Supporting information 9 (a) Absorption & PL spectra and (b) TEM images of $ZnTe_{0.40}Se_{0.60}$, $ZnTe_{0.40}Se_{0.60}$/ZnSe, $ZnTe_{0.40}Se_{0.60}$/ZnSe/ZnS



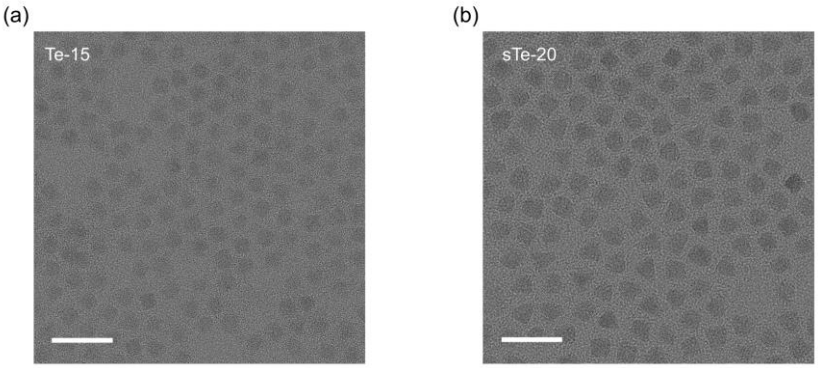
Supporting information 10 TEM image of the (a) Te-6, (b) cTe-15, (c) cTe-30 with inset diameter histogram based on TEM image of ZnTeSe QDs. (Scale bar is 20nm)



Supporting information 11 Absorption and PL spectra of the $ZnTe_{0.30}Se_{0.70}$ QDs.

Core diameter (nm)	Shell thickness (nm)	Center Te/(Te+Se)	Surface Te/(Te+Se)	Total Te/(Te+Se)
3.00	1.00	0.00	0.30	0.24
3.00	1.00	0.00	0.20	0.16
3.00	1.00	0.00	0.08	0.06
3.00	1.00	0.00	0.30	0.24
3.00	0.10	0.00	0.30	0.06
3.00	1.00	0.00	0.20	0.16
3.00	0.20	0.00	0.20	0.06
3.00	1.00	0.00	0.30	0.24
35.00	1.00	0.00	0.30	0.06
3.00	1.00	0.00	0.20	0.16
15.00	1.00	0.00	0.20	0.06

Supporting information 12 Calculated values for the surface Te doping ratio, shell thickness, and core diameter to achieve a Total Te/(Te+Se) ratio of 0.06.



Supporting information 13 TEM images of (a) 5 nm-diameter Te-15 and (b) sTe-20 after ZnS passivation. (scale bar is 20nm)

Reference

1. Xpsdatabase, https://xpsdatabase.net/zinc-zn-z30-chemicals, (accessed October 2021).