Development of NIR Emitted CdTe Quantum Dots by Concentration Control Method

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Recently, much research has been performed on quantum dots (QDs) due to the promising applications of LED, laser and bio-imaging.[1] They can show the tunable fluorescent property between UV and IR via the control of particle size. Especially, near-infrared emission between 780-880 nm have attracted attention in bio-imaging area due to the deep penetration of emitted light and avoiding the window between the absorption band of hemoglobin and water.[2] Until now, CdTe/CdSe core-shell type-II QDs, InAs/ZnSe, and $InAs_xP_{1-x}$/InP/ZnSe core-shell QDs were developed and applied for sentinel lymph node mapping as an example of a bio-imaging application.[3] In particular, we are interested in CdTe QDs which have a smaller bandgap than the other II-VI QDs and which, therefore, can emit near-infrared light and provide high quantum efficiency.[4] Bulk CdTe is a typical II-VI QDs with a bandgap of 824 nm, which becomes larger than that of bulk semiconductor with decreasing particle size. Several methods have been reported to tune the bandgap of CdTe QDs: 1) growth temperature and time control,[4] 2) additional precursor injection[5] and 3) chemical surface modification using different surfactants.[6] In this paper, we present a new bandgap engineering method of CdTe QDs with controlling precursor concentration. A similar experiment has been conducted by Peng *et al.*,[7] but they studied size- and shape-controlled QDs with surfactant change. The synthetic procedure used in the present study is similar to the method developed by Bawendi *et al.*[8] for the production of CdSe QDs, using Cd(acac)₂ and TOP-Te as cadmium and tellurium precursors, respectively. The mixture solution of cadmium and tellurium precursors was injected into the surfactant solution of TOP (trioctylphosphine), TOPO (trioctylphosphine oxide) and HDA (hexadecylamine) at 350 °C and then cooled to room temperature.
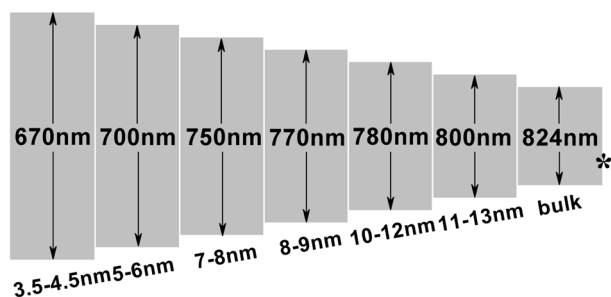
The concentration of precursors was controlled serially from one (9.64 mM of Cd) to six (57.84 mM of Cd). The detailed experimental procedures can be found in the Supporting Information. Scheme 1 depicts the bandgap variation versus size control, which were obtained from the emission peaks and TEM images, respectively. CdTe QDs with similar bandgap size to bulk semiconductors could be obtained by our method. Figure 1 shows that the CdTe QDs which were presented by the concentration control method were engineered to emit in the 670 to 800 nm range and that longer wavelength emission could be obtained at a high concentration than at a low concentration. A longer wavelength emission indicates larger particle size due to the Ostwald ripening[9] in the high concentration. In other words, the monomers react very fast with each other and form nuclei when the precursors are injected at high temperature (350 °C). The nuclei number in high concentration is larger than that in low concentration because of the high collision frequency in high concentration.[10]

Next, monomer depletion occurs very fast and the nuclei concentration decreases due to the Ostwald ripening which includes the decomposition of emission peaks move to a longer wavelength at high nuclei to monomer and re-growth in another nuclei. The monomer depletion and Ostwald ripening occur faster in high nuclei concentration. A few studies have reported on similar research about kinetics in QDs synthesis.[11] Table 1 and Figure 2 show the emission peak positions and quantum yields (QYs) according to the concentration and molar ratio. The emission peaks appear in
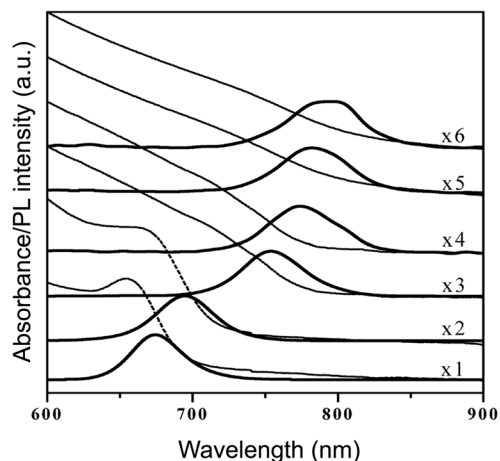
Scheme 1. Bandgap variation of CdTe QDs derived from emission peak. Sizes were obtained from TEM images. *Bulk value calculated from typical bulk value. (1.50 eV).

Figure 1. Absorbance (dash line) and photofluorescence (solid line) control of CdTe QDs by change precursor concentration.

Table 1. Emission peak positions and quantum yields on the basis of precursor concentration and molar ratio

| Relative concentration | Cd(acac)$_2$ *vs* TOPTe precursor molar ratio | | | | | |
| | 1:1 | | 1.5:1 | | 2:1 | |
	PL (nm)	QY (%)	PL (nm)	QY (%)	PL (nm)	QY (%)
× 1	674.5	14.8	678.8	13	674.3	11.4
× 2	691.3	14.8	699.4	20.4	698.8	15.4
× 3	753.8	4.8	746.2	13.4	748.8	13
× 4	773.8	< 1	772.3	7.4	775.8	5.1
× 5	781.9	<< 1	788.4	3.9	794.1	4.4
× 6	796	<< 1	797.3	<< 1	799	1.2
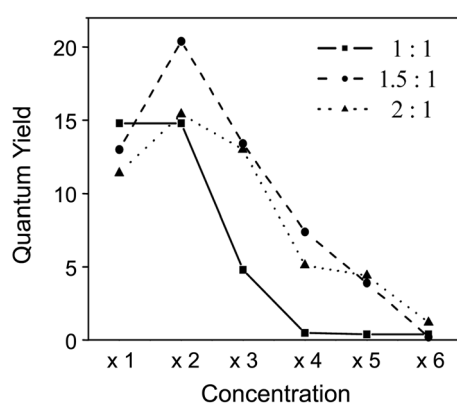
Figure 2. Plot of quantum yield vs precursor concentration.
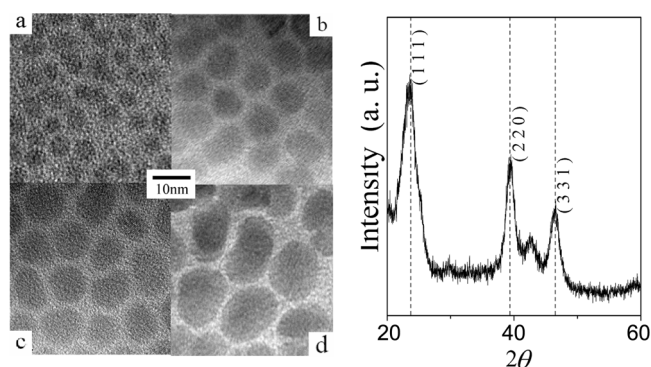
Figure 3. (a-d) TEM image of CdTe QDs (a; 5.5-6 nm, X2, b; 7-7.5 nm, X3, c; 8-9 nm, X4, d; 10-13 nm, X6) e) PXRD patterns of CdTe QDs. Dash line are for bulk CdTe with zinc blende.

a similar position although the molar ratios of cadmium and tellurium are different. The difference in QYs is clearly observed with increaing particle sizes, with the results indicating that smaller particles have equal or higher QYs. (× 2 concentration show the best QY). The tendency of QY versus molar ratio is not convincing; however, a higher cadmium ratio results in better overall QYs. The reason can be found in the high oxidative property of tellurium com-

pared to that of cadmium. TEM images show the CdTe QDs of about 3.5 nm-13 nm diameter (Figure 2a, 2b, 2c and 2d). All sizes of CdTe QDs by concentration control method have a zinc blende structure, which is more stable at room temperature than is wurzite structure.[12]

In conclusion, NIR-emitted CdTe quantum dots were synthesized by concentration control method, and larger particles resulted from a higher concentration.

Experimental details are available on request from the correspondence author.

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