Synthesis and characterization of CdSe/ZnS core/shell quantum dots for optimal shell thickness

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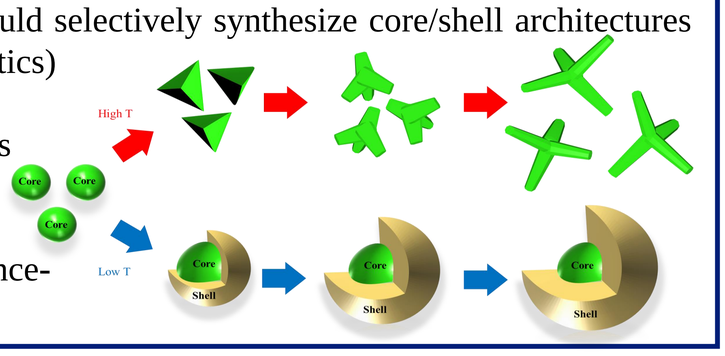
Introduction

Quantum dots (QDs) are semiconductor nanoparticles which emit light with different color depending on the sizes. QDs have been of great interest for potential materials to optoelectronic devices. However, synthesis of QDs with high quantum yield (QY) and long fluorescence lifetime is still a remaining challenge. Core/shell QDs with 'Type I' band gap structure, are coated with higher band gap inorganic materials and they have been shown to improve the photoluminescence quantum yields by passivating surface trap sites and confining the excitons in the core region. Here, this study investigated enhancement of optical properties of CdSe core adopted with ZnS shell layers.

Two different nanostructures (tetrapod and core/shell) can be induced from zinc-blende (cubic) CdSe core and we could selectively synthesize core/shell architectures by controlling the temperatures (kinetics) during the shell growth. Finally, we figured out optimal shell thickness of CdSe/ZnS core/shell QDs by-measuring various optical properties such as UV-vis absorption, fluorescence-spectra, lifetime, and QY.



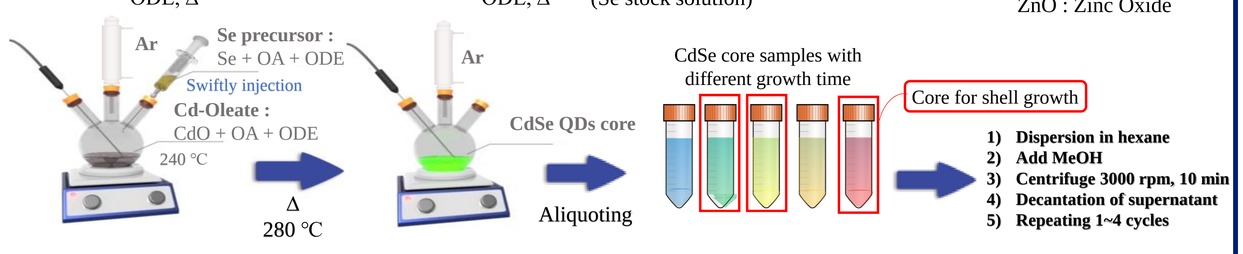
Experimental Methods

Synthesis of CdSe nanocrystals

CdO : Cadmium Oxide
OAc : Oleic acid
ODA : Octadecylamine
ODE : 1-Octadecene
ZnO : Zinc Oxide

a) CdO —(OAc, ODE, Δ)→ $Cd(Oleate)_2$

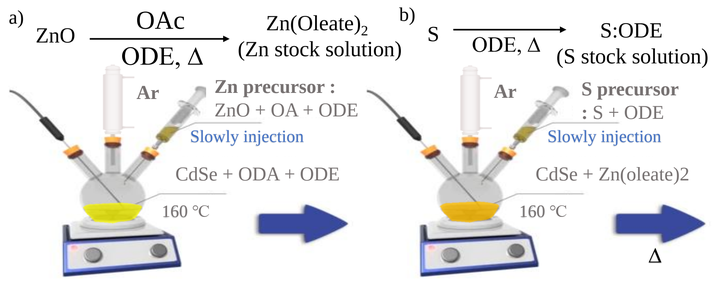
b) Se —(OAc, ODE, Δ)→ Se:OAc (Se stock solution)



Synthetic procedure of ZnS shell & arm on as-synthesized CdSe quantum dots

a) ZnO —(OAc, ODE, Δ)→ $Zn(Oleate)_2$ (Zn stock solution)

b) S —(ODE, Δ)→ S:ODE (S stock solution)



Shell & arm layer	Injection Amount	Temperature (Tetrapod)	Temperature (core/shell)	Time
1st	0.52 mL	~180 °C	~140 °C	10 min
2nd	0.77 mL	~200 °C	~160 °C	10 min
3rd	1.1 mL	~220 °C	~180 °C	10 min
4th	1.45 mL	~240 °C	~200 °C	10 min
5th	2 mL	240 °C	200 °C	30 min

Results

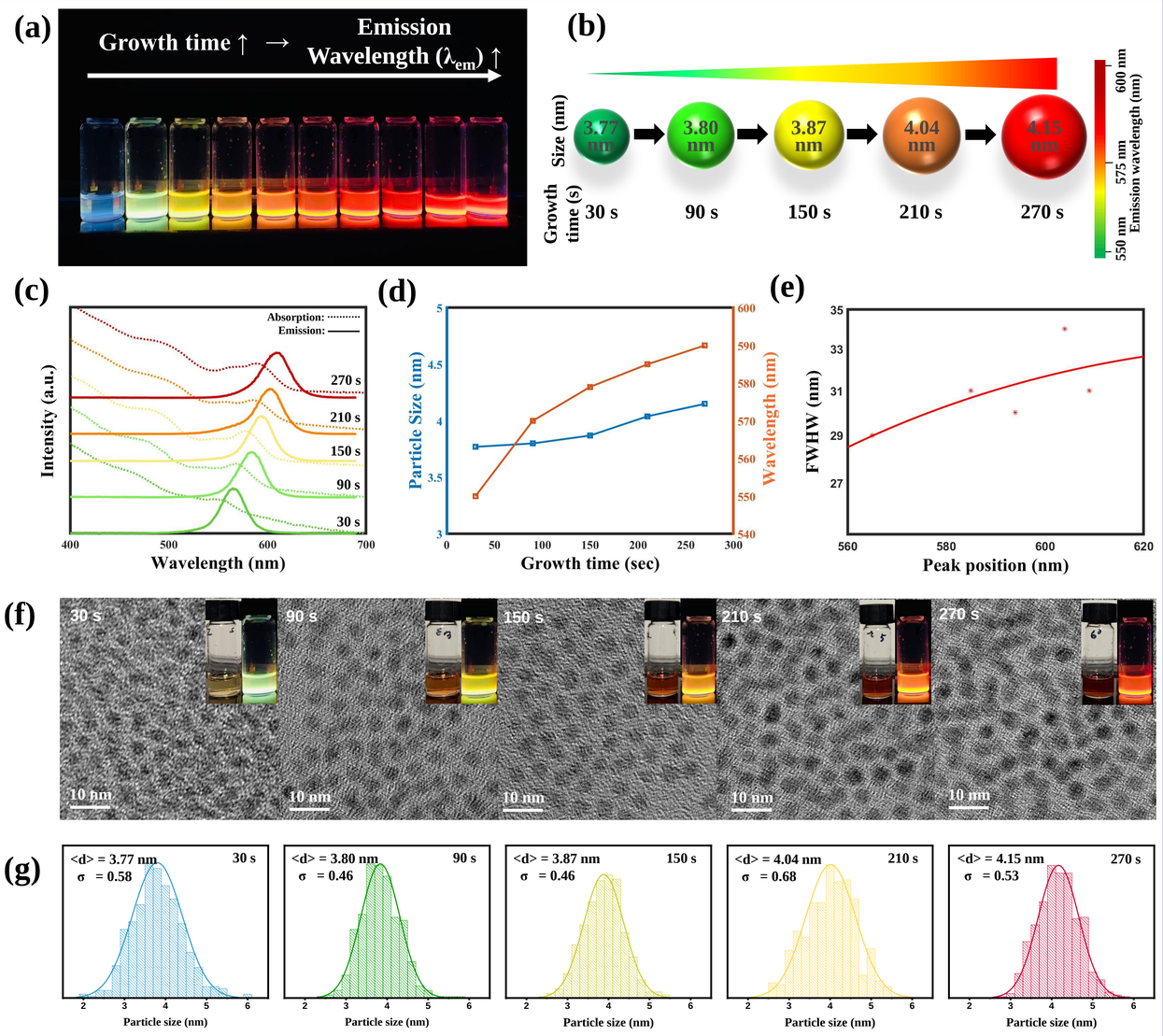


Fig 1. (a) Microscopic image of CdSe QDs under 365nm excitation. (b) Schematic illustration of QDs size with different growth time. (c) Optical properties of as-synthesized CdSe QDs. (Solid line: emission spectra, Dashed line: absorption spectra) (d) The relationship between growth time and quantum dots particle size, PL wavelength, and (e) full width at half-maximum (FWHM) of the emission peaks. (f) Transmission electron microscopy (TEM) images and (g) Size distribution of as-synthesized CdSe QDs at a different growth time (insert) microscopic image for each synthetic time.

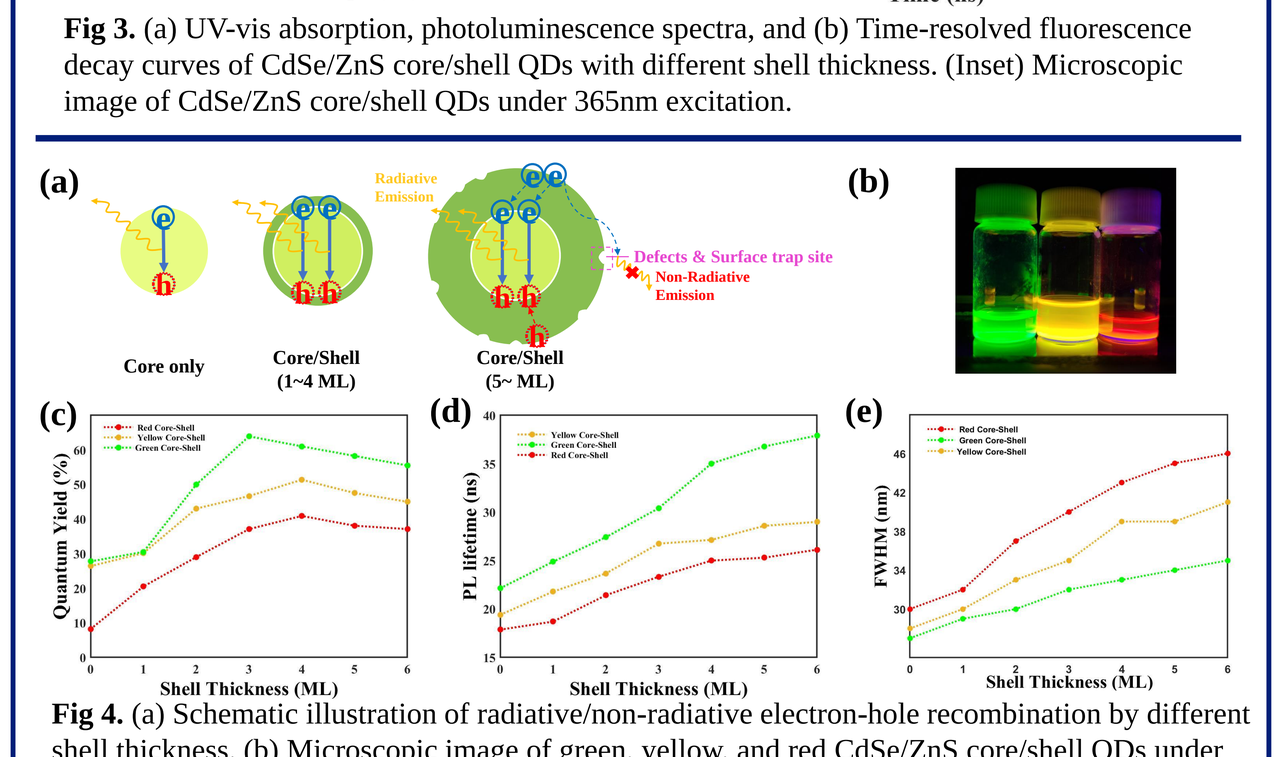


Fig 3. (a) UV-vis absorption, photoluminescence spectra, and (b) Time-resolved fluorescence decay curves of CdSe/ZnS core/shell QDs with different shell thickness. (Inset) Microscopic image of CdSe/ZnS core/shell QDs under 365nm excitation.

Fig 4. (a) Schematic illustration of radiative/non-radiative electron-hole recombination by different shell thickness. (b) Microscopic image of green, yellow, and red CdSe/ZnS core/shell QDs under 365nm excitation. (c) Quantum yields (d) Lifetime and (e) FWHM of CdSe/ZnS core/shell QDs with different shell thickness under excitation wavelength of 475 nm, green, yellow, and red emission, respectively.

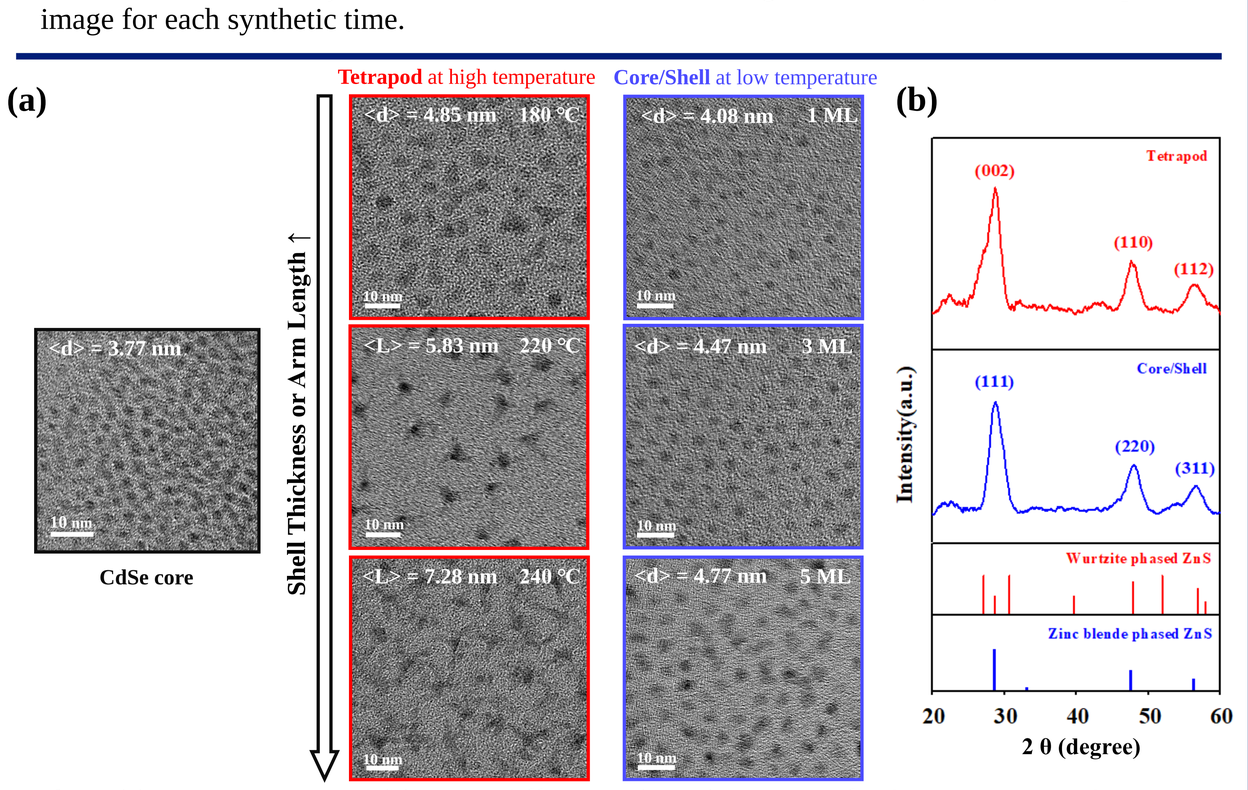


Fig 2. (a) TEM images and (b) X-ray diffraction (XRD) patterns of CdSe-ZnS nanoarchitecture under different synthetic temperature. (Red) tetrapod and (blue) core/shell, respectively.

Conclusion

We have synthesized the well-defined CdSe nanocrystals as a core material with various sizes under different growth time. We adopted the ZnS as a shell layer on the Zinc-blende based CdSe core and conducted kinetic control to synthesize two different crystal structures. Tetrapod-like nanostructure with Wurtzite phased ZnS and core/shell nanostructure with Zinc-blende phased ZnS have been synthesized under high and low temperature, respectively. Furthermore, we measured quantum yield and fluorescence decay curve to figure out a relationship between the shell thickness and optical properties of the CdSe/ZnS QDs. We suggest that the optimal shell thickness of CdSe/ZnS core/shell QDs to be 4th monolayer. We confirmed that QY and lifetime increased due to passivation of surface trap site and effective exciton confinement.

Reference

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