Synthesis of CdTe-CdSe Core-Shell Quantum Dots with Luminescence in the Red
(Sintesis Titik Kuantum Teras Dalaman-luaran CdTe-CdSe yang Memberikan Luminesen Merah)

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ABSTRACT
This paper reports on the synthesis and characterization of CdTe-CdSe core-shell quantum dots (QDs) with luminescent from 650 to 720 nm. The QDs were synthesized using a wet-chemical process at a moderate temperature (300 °C) following two-steps process of core and shell synthesis. The photoluminescence characterization on the QDs showed that the QDs emitted light in the range of red regime with quantum yield as high as 37%. Owing to their unique photoluminescence characteristics (high quantum yield and narrow spectrum), the QDs may find a potential application in a variety of applications such as LED, solar cell and bio-labeling.

Keywords: CdTe-CdSe core-shell; narrow spectrum; photoluminescence; quantum dots; quantum yields.

INTRODUCTION
The synthesis of colloidal semiconductor nanocrystals has received considerable attention since the last two decades due to their unique optical, optoelectronics, magnetic and electrical properties that are different from their bulk structure counterpart (Alivisatos 1996 & Lee et al. 2006). For example the binary systems of Quantum Dots (QDs), such as CdTe and CdSe, have been synthesized and used as active agent due to their rich luminescent properties with unique tunable, narrow emission spectrum and high-quantum yield photoluminescence (Abu Bakar et al. 2008; Chen & Nie 1998; Han et al. 1998; Klostranec & Chan 2006; Klimov et al. 2000; Wang et al. 2001) characteristics. These characteristics make it possible for the production of pure-colour light-emission in LED application (Sepeai et al. 2008; Tengku Aziz et al. 2008).

For LED application, the QDs should have high quantum yield and narrow spectrum. To enhance the quantum yield and improve the spectrum purity, the QDs must suppress the non-radiation recombination on the surface and improve the confining potential. One of the ways to achieve this condition is by capping the core-QDs with inorganic material as a shell with higher energy gap. The electrons and holes are expected to be fully trapped inside the core. This may also effectively suppress the non-radiative recombination of electrons and holes on the QDs surface due to the pressure of shell materials (Steckel et al. 2004). Hence the quantum yield could be increased.

Here, we synthesized CdTe-CdSe core-shell QDs with luminescent from 650 to 720 nm. The QDs exhibited high quantum yield and relatively narrow spectrum, typically, 37 % and 40 nm, respectively. The CdTe-CdSe core-shell QDs have potential applications in laser (Fafard et al. 1995), photonic devices, solar cell, bio labeling and LED (Lodahl et al. 2004; Miliron et al. 2004).

EXPERIMENTAL DETAILS

MATERIALS
Cadmium acetate hydrate, octadecene, tellurium and selenium powders were purchased from Sigma-Aldrich. Meanwhile, oleic acid, tri-n-octylphosphine (TOP), and tri-n-octylphosphine oxide (TOPO) were procured from Wako Company. The chemicals were directly used without any further purification process.

PREPARATION OF CdTe-CdSe CORE-SHELL QDS
There are two synthesis steps for the preparation of core-shell, namely preparation of CdTe-core QDs and secondly,
preparation of CdSe-shell structure. The CdTe-core QDs was prepared using the following procedure. In a typical process, the CdTe was prepared by dissolving 40 mg of cadmium acetate hydrate and 0.8 gm of TOPO with 8.5 mL TOP, 0.6 mL oleic acid, in 10 mL of octadecene in the flask and heated at 350 °C in a heating mantle. The solution was called as cadmium precursor. Meanwhile, the tellurium precursor (a yellowish TOPe) was prepared by mixing 26 mg of tellurium powder and 3 mL of TOP at temperature of about 200 °C. The CdTe QDs was prepared by quickly injecting 1 mL of room-temperature TOPe into the hot solution of cadmium precursor. Then, the reaction was started. Next, the aliquots amount of reaction solution were extracted from the reaction at several period of time, namely 10, 20 and 30 s after addition of TOPe and quenched the reaction by injecting them into ice-cooled 4 mL hexane solution. The as-prepared QDs were then washed using centrifuge and dispersed in octadecene.

The CdSe-shell structure was prepared as follow: After the CdTe-core QDs was prepared, the CdSe shell was grown on the CdTe core surface, by following similar procedure as indicated in the preparation of CdTe-core QDs. However, at this stage, the TOPe was replaced with TOPSe as selenium powder meanwhile the cadmium precursor remains unchanged. To prepare CdTe-CdSe core-shell, 1 mL of the CdTe QDs seed and 1 mL of TOPSe were concurrently injected into hot solution (350 °C) of cadmium precursor and the reaction immediately started. The samples were extracted and quenched at seven different growth time namely 10 s, 10 mins, 15 mins, 20 mins, 30 mins, 50 mins and 1 hour 30 mins to observe the relationship between the CdSe shell thickness and photoluminescence properties. The as-prepared CdTe-CdSe core-shell QDs were further washed by repeated centrifugation in methanol. The precipitate was then washed using centrifuge and dispersed in octadecene.

CHARACTERIZATION OF QDS

The photoluminescence properties of the core-shell QDs were characterized using Perkin Elmer LS 55 Luminescence Spectrometer at an excitation and emission slits of 10 and 2.5 nm, respectively. The optical absorptions were measured using Perkin Elmer Lambda 900/UV/VIS/NIR Spectrometer. The transmission electron microscopy analysis was carried out using a CM 12 Philips TEM instrument.

RESULTS AND DISCUSSION

Prior to the preparation of CdTe-CdSe core-shell, the CdTe QDs seed was firstly prepared. The colour of the solutions was drastically changed upon the injection of TOPe from light orange to brown with the increasing of the growth times during the reaction, reflecting the formation of QDs. Under the UV lamp irradiation, the solution glows giving reasonably bright red color emission. The brightness was found to decrease with the increase of the growth time. The results are shown in Figures 1(a) and 1(b) for the QDs grown up at three different growth times, namely 10, 20 and 30 seconds. Photoluminescence spectroscopy characterization on the QDs samples showed emissions centered at 664, 670 and 673 nm for the QDs grown at 10, 20 and 30 s, respectively (Figure 1c). From the photoluminescence results a typical quantum yield of the QDs is ca. 25 %. Figure 1(ii) shows the absorption spectra of the QDs. It was found that the QDs give absorption band in the range of 600 to 750 nm, which agrees with the photoluminescence peaks as shown in Figure 1c. From the absorption spectra, it can also be seen that the absorbance of the QDs increased with the increase of growth time, inferring the increase in the QDs size. It was also found that the absorption peaks was red-shifted when the growth time was increased. Using this absorption spectrum, we can calculate the direct optical band gap energy of the QDs by simply plotting $(\alpha h\nu)^2$ versus $h\nu$, obtained from the relation of $\alpha h\nu = A (h\nu - E_g)^{1/2}$, where $\alpha$ and $A$ are the absorption coefficient and a constant, respectively. The result is shown in Figure 2. From this analysis, by extrapolating a straight line at the linear part of the curve, the direct optical band gap energy of the QDs was calculated to be 1.825, 1.838 and 1.847 eV for the QDs grown at 10, 20 and 30 s respectively.

The shell structure of CdSe was grown on the as–prepared CdTe-core QDs. In the preparation of the

![Figure 1](image1.png)

**Figure 1.** i) Photoluminescence spectra of QDs of CdTe with different aging times namely a) 10 s, b) 20 s, c) 30 s and ii) the corresponding UV-Vis spectra.
core-shell structure, the CdTe QDs grown for 10 s were used as the seed. Figure 3 shows the absorption and photoluminescence spectra of the core-shell QDs that were prepared at several growth times. It was found that the absorption peak of the core-shell QDs was laid in the range of 500 to 650 nm. These absorption peaks value lower than the CdTe core only or blue-shifted from the original QDs core photoluminescence peak, which is in the range of 600 to 750 nm. The related energy band gap the core-shell structures were 2.031, 2.050, 2.063, 2.075, 2.093 and 2.181 eV at growth times namely 10, 15, 20, 30, 50 and 90 min. Figure 4 shows the comparison for the photoluminescence and absorption spectra of the QDs core and core-shell structure that grown at the same period. It can be clearly seen that the photoluminescence intensity of the core-shell structures is much higher than the QDs core for about 1.5 times. It was also found that the width of the emission spectra is narrower than the QDs core, inferring the improvement of the quantum efficiency of the QDs as a result of core-shell structure formation. Calculation on the quantum yield of the core-shell structure QDs found the value as high as 37%, much higher compared to the QDs core only, namely 25%.

The blue-shifting in the photoluminescence peaks upon the formation of core-shell structure could be due to the decrease in the core-particle size during the reaction prior to the formation of shell structure. The decrease in the particles size caused the increase in the energy gap. In the preparation of core-shell structure, we firstly prepared the core seed particles. The seed were then injected into the reactor that contained the shell precursors. Because of relatively high-temperature and high-chemical potential condition, the seed particles might undergo an Oswald annealing process. The transmission electron microscopy analysis on the quantum dots particle further confirmed such assumption by through the decrease in the particles size upon the formation of core-shell structure. The result is shown in Figure 5.

Owing to the limitation of the detail analysis of the core-shell QDs, the exact core-shell structure image or the compounds mapping of the core-shell QDs were not obtained. However, based on the optical properties analysis, we confirmed that the core-shell CdTe-CdSe QDs was successfully obtained. It is proven by the improvement of the photoluminescence quantum yield of the quantum dots. From the photoluminescence spectra, it can also be seen that the width of the photoluminescence spectrum decreased when compared to the CdTe core only. These two phenomena are general indicators for the formation of core-shell structure. The formation of shell structure at the surface of the QDs core causes the improvement of the confining potential of the electrons and hole at the inner QDs core. This also caused an effective suppression of the non-radiative recombination of electrons and holes on the surface of the QDs core due to successful caption by the CdSe shell. These cases resulted in the increase in the quantum yield of the quantum dots and improve the quality of QDs emission by showing a narrower spectral width.

The actual mechanism of CdTe-CdSe core-shell formation was not yet well-understood, but the following assumption can be considered. In a typical synthesis, the
CdTe cores were firstly synthesized. The QDs were then purified by centrifugation. After that the CdTe QDs cores were injected into a reactor that contained CdSe precursor. Due to a relatively low lattice mismatch, namely as lower as 6.7% (Zeng et al. 2009), we expected that the CdSe may easily crystallize on the surface of CdTe seed. Based on the result of CdTe-CdSe, absorption and photoluminescence spectra, it can be concluded that the core-shell structures were successfully formed.

**CONCLUSION**

The QDs of CdTe-CdSe core-shell has been successfully synthesized using the present technique. Based on the results, the quantum yield and colour purity of the QDs can be successfully improved indicated by the increase in the photoluminescence intensity and the decrease in the spectral width by the formation of the core-shell structure. This is believed due to the effective of confinement of electron and holes inside the core and the effective suppression on the non-radiative recombination of electron and holes in the surface of the QDs core. The CdTe-CdSe core-shell may find use in the LED and other light source applications.

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