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Optical Characterization of Colloidal Zinc Selenide Quantum Dots Prepared through Hydrothermal Method

(Pencirian Optik Titik Kuantum Koloid Zink Selenida Disediakan melalui Kaedah Hidroterma)

FAKHRURRAZI ASHARI, JOSEPHINE LIEW YING CHYI*, ZAINAL ABIDIN TALIB, W. WAHMOOD WAN YUNUS, LEONG YONG JIAN, LEE HAN KEE, CHANG FU DEE & BURHANUDDIN YEO MAJLIS

ABSTRACT

Zinc selenide (ZnSe) quantum dots (QDs) have been synthesized through a hydrothermal method using $ZnCl_2$ and Na_2SeO_3 powder as the precursor in the presence of oleylamine as capping agent. The hydrothermal route was conducted at a moderate temperature (150°C) for 8 h. Optical properties of ZnSe QDs were studied through ultraviolet-visible spectroscopy (UV-Vis) and photoluminescence (PL) while the structural properties of ZnSe QDs were characterized using transmission electron microscope (TEM). The photoluminescence (PL) characterization on ZnSe QDs showed that the QDs emit light in blue range region at around 440 nm with optical band gap energy at 3.68 eV. The TEM results showed that the average particle size is around 8.9 nm. It is a good candidates for optoelectronic devices such as light emitting diodes (LED).

Keywords: Absorption; morphology; optical band gap; photoluminesnce

ABSTRAK

Titik kuantum(QDs) zink selenida (ZnSe) telah disintesis melalui kaedah hidroterma menggunakan serbuk $ZnCl_2$ dan Na_2SeO_3 sebagai sumber asal dengan kehadiran oleilamina sebagai agen penutup. Kaedah hidroterma telah dijalankan pada suhu sederhana (150°C) selama 8 jam. Sifat optik ZnSe QDs telah dikaji melalui spektroskopi ultraungu/boleh nampak (UV-Vis) dan spektroskopi fotoluminesen (PL) manakala sifat struktur ZnSe QDs dicirikan menggunakan mikroskop trasmisi elektron (TEM). Pencirian fotoluminesen (PL) pada QDs menunjukkan bahawa QDs memancarkan cahaya di rantau julat biru sekitar 440 nm dengan jurang jalur optik pada 3.68 eV. Keputusan TEM ini menunjukkan bahawa purata saiz zarah adalah sekitar 8.9 nm. Ia adalah satu calon yang baik untuk peranti optoelektronik seperti diod pemancar cahaya (LED).

Kata kunci: Fotoluminesen; jurang jalur optik; penyerapan; morfologi

INTRODUCTION

Semiconductor is important in daily life because it can become neither conductor nor insulator and it depends on the surrounding conditions. Semiconductor is the basis for the fundamental part of computer, switching and amplification. The modern scientist need the understanding of quantum physics to explain the movement of electrons and holes, electrical, thermal and optical properties of semiconductor inside a lattice. An increased knowledge of semiconductor materials and fabrication processes among the researches made it possible in increasing understanding in materials behavior, the complexity and speed of integrated semiconductor devices.

In semiconductor clusters, researchers are interested to know the changes on fundamental behavior of quantum dot through their electrical and optical properties. Quantum dots is a nanocrystal material which diameter is small than its exciton Bohr radius, which lead to quantum properties and confinement effect (Murray et al. 2000). Quantum dot is closely related to the size and shape. The size of quantum dot is inversely related to the band gap (Eg) value which determined the frequency range of emitted light.

In the present study, we report the synthesis of ZnSe QDs via hydrothermal route in presence of oleylamine. Hydrothermal route has been chosen as the synthesis route due to its advantages of low temperature reaction, simple equipment and also less consumption of energy. The objective of this project were to investigate the concentration effect of zinc chloride in synthesizing ZnSe QDs colloidal as well as study the optical phenomenon of quantum dots for optoelectronic devices. Characterizations such as UV-Vis spectroscopy, photoluminescence (PL) and TEM used to examine the absorption value, band gap energy (Eg), emission value and the particle size of colloidal ZnSe QDs.

EXPERIMENTAL DETAILS

SAMPLE PREPARATION

Zinc chloride, $ZnCl_2$ (98%, HmBG) and sodium selenite, Na_2SeO_3 (≥99%, Sigma) powder were used as the precursor in the preparation. $ZnCl_2$, Na_2SeO_3, 15 mL ethanol and 0.3 g hydrazine hydrate, N_2H_2(≥99%, Fluka) were added sequentially in 30 mL distilled water under stirring condition until the solution become cloudy. Four mL of oleylamine (≥70%, Sigma) were then added into the mixture under stirring condition. The mixture was then transferred into autoclave for hydrothermal reaction under 150°C for 8 h. The autoclave was naturally cooled to room temperature. The light yellow liquid formed will undergo centrifugation process using ethanol for several times. The samples have been prepared based on the ratio $ZnCl_2$: Se as shown in Table 1.

TABLE 1. The experimental condition with different concentration of $ZnCl_2$: Se

Sample	$ZnCl_2$: Se ratio
1	1:1
2	2:1
3	3:1
4	4:1

CHARACTERIZATION

The photoluminescence properties of the QDs were characterized using luminescence spectrometer (Perkin Elmer LS 55 Luminescence) with excitation source at 350 nm. The optical absorptions were measured using ultraviolet-visible NIR spectrometer (Shimadzu UV-3600) at room temperature. The morphology properties were investigated using TEM (TEM H-9500) and HRTEM (Tecnai S-TWIN LaB6 with 200 kV).

RESULTS AND DISCUSSION

OPTICAL PROPERTIES

Figure 1 shows the absorption spectra for the ZnSe QDs synthesized with different concentrations of $ZnCl_2$. The $ZnCl_2$: Se ratio is varied from 1:1, 2:1, 3:1 to 4:1. From the result obtained, we observed that the absorption spectra for each sample with different concentrations ratio of $ZnCl_2$: Se is slightly different. The absorption peak is 316 nm for 1:1 sample ratio, ratio 2:1 and 3:1 sample ratio is about 313 nm and ratio 4:1 is 314 nm, respectively. This is due to different concentrations ratio between $ZnCl_2$ and Se as a starting material which further indicates that the higher concentration ratio of $ZnCl_2$.

By extracting the UV-Vis data, optical energy band gap for the samples have been calculated using classical Tauc equation (Liu et al. 2013),

$$\alpha hv = K(hv - Eg)^n \quad (1)$$

where α is absorption coefficient; hv is photon energy; Eg is band gap energy; K is constant; and n is different possible electronic transitions.

Figure 2 shows the Tauc plot of $(\alpha hv)^2$ vs energy (eV) for all sample concentrations with $ZnCl_2$:Se ratio 1:1 until 4:1. The absorption peak value and optical band gap energy for sample concentration with different $ZnCl_2$: Se ratios have been tabulated in Table 2. It can be seen in Figure 3 that when the $ZnCl_2$: Se ratio increases, the optical band gap energy increases (Eg). This can be explained by the relation between the concentrations of the precursor of $ZnCl_2$: Se with the optical band gap energy (Eg). According to Gupta and Ramrakhiani (2009), it was related to the energy dependence of electron transitions between quantized level of the valence and conduction bands, furthermore it was also related with the kinetic energy and Coulomb energy that were produced.

Photoluminescence (PL) spectra of ZnSe QDs sample with different $ZnCl_2$: Se ratios are shown in Figure 4. The sample is excited with excitation source at 350 nm using ethanol as solvent. A single and strong emission

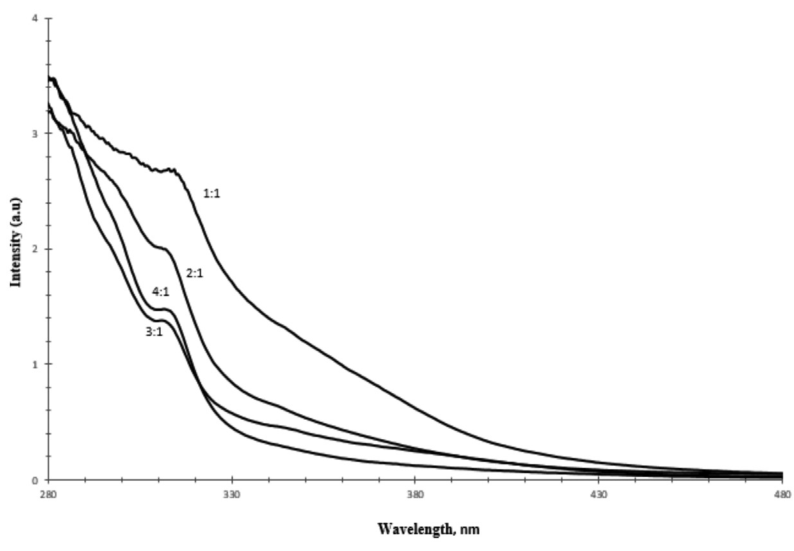


FIGURE 1. UV-Vis absorption spectra for ZnSe QDs synthesized with different concentrations of $ZnCl_2$: Se ratio

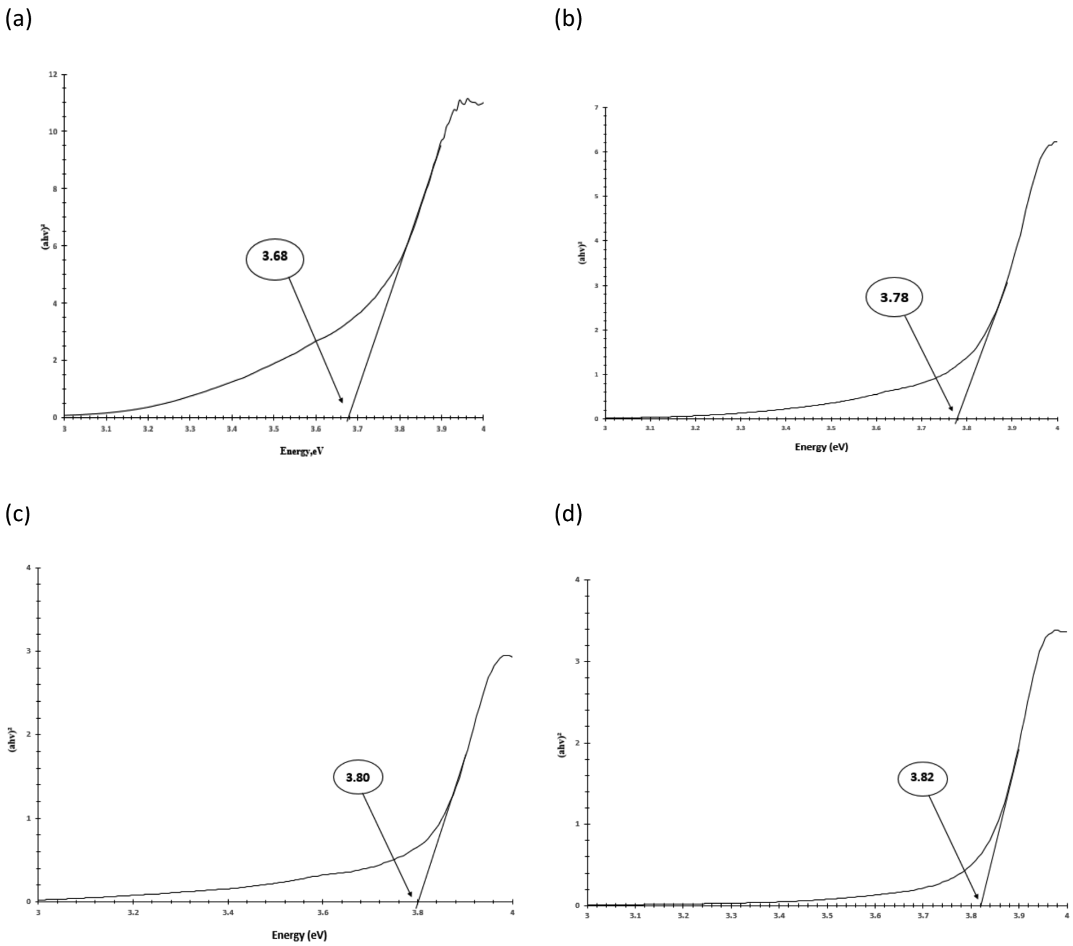


FIGURE 2. Optical band gap energy (Eg) for sample with different concentrations of $ZnCl_2$: Se ratio (a) 1:1 (b) 2:1 (c) 3:1 and (d) 4:1

TABLE 2. Absorption peak and Band Gap values of ZnSe QDs with different concentrations of $ZnCl_2$: Se

$ZnCl_2$: Se Ratio	Absorption peak (nm)	Optical band gap energy (Eg)
1:1	316	3.68 eV
2:1	313	3.78 eV
3:1	313	3.80 eV
4:1	314	3.82 eV

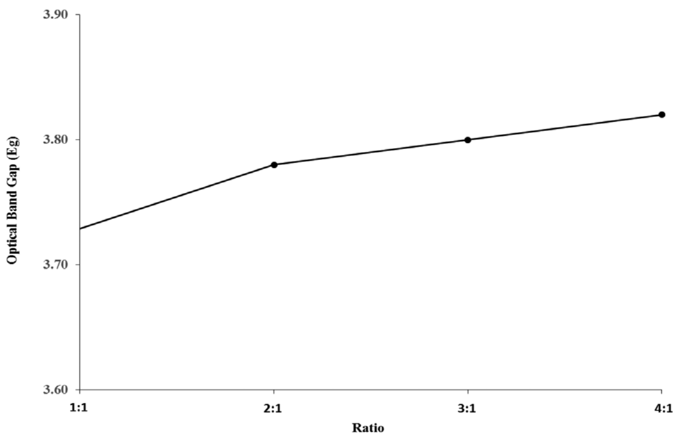


FIGURE 3. Optical bang gap energy (Eg) vs ratio of $ZnCl_2$: Se

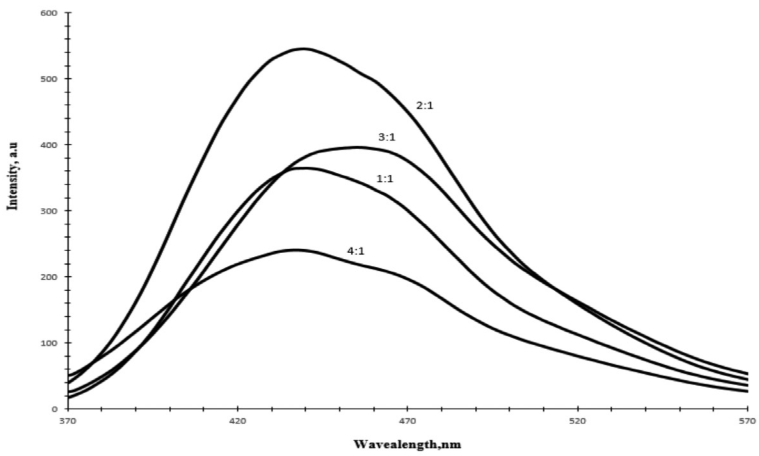


FIGURE 4. Photoluminescence emission peak of ZnSe QDs synthesized with difference ratio of $ZnCl_2$: Se

peak has been observed at 440 nm for sample with $ZnCl_2$: Se ratio 1:1, 2:1 and 4:1 which falls under violet region (380 until 450 nm). The sample with $ZnCl_2$: Se ratio 3:1 shows the emission peak at 460 nm. The peak was shifted to the blue region (450 until 495 nm). This was due to the aggregation and non-homogeneous of particle in the solvent. When the particle size increases, the emission peak will have red shift. The pH value for sample with different $ZnCl_2$: Se have been studied and shown in Figure 5. As the concentration of $ZnCl_2$ increases, the pH value for the sample decreases from 10.98 to 5.15. According to Murase and Gao (2004), the PL intensity of ZnSe solution will decrease from alkaline range to acidic range due to the strongly hydroxyl ions negative charge in the ZnSe solution.

MORPHOLOGY ANALYSIS

Figure 6 shows a typical TEM image of ZnSe QDs for sample ratio 1:1. It can be seen that, the average diameter of the sample is around 8 nm (Figure 9) and is dispersed well without any aggregation. The inset (top left) shows a selected area electron diffraction (SAED) pattern, the rings of which could be assigned to (002), (022) and (004) of cubic ZnSe, respectively. The clear reflection ring of the SAED pattern indicate that the products synthesized were polycrystalline by observing HRTEM image as shown in Figure 7. Figure 8 shows a typical HRTEM image of ZnSe QDs with different concentrations of $ZnCl_2$: Se from 1:1 until 4:1 ratio. The average diameter has been calculated for every different concentrations of $ZnCl_2$: Se ratio where, ratio 1:1 is 8.9 nm, ratio 2:1 is 22.0 nm, ratio 3:1 is 20.6 nm and 4:1 is 49.1 nm, respectively. The QDs can be easily dispersed in nonpolar solvents such as ethanol and chloroform to form a stable homogenous solution (bottom left in Figure 6) that can be preserved for several months without any changes in their properties (Jiao et al. 2007). According to Jiao et al. (2007), oleylamine played a multiple roles by acting as stabilizing agent, surfactant and also as a shape controller. In the absence of oleylamine, the products was a mixture of elemental Se and ZnSe at the same synthetic conditions, while a pure phase of ZnSe was obtained when more than 1.8 mL of oleyamine was introduced.

CONCLUSION

In summary, colloidal ZnSe QDs was successfully synthesized via hydrothermal method at moderate

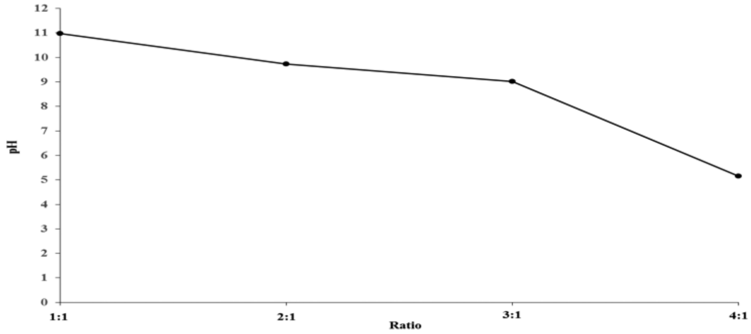


FIGURE 5. Relation between pH value with $ZnCl_2$: Se ratio

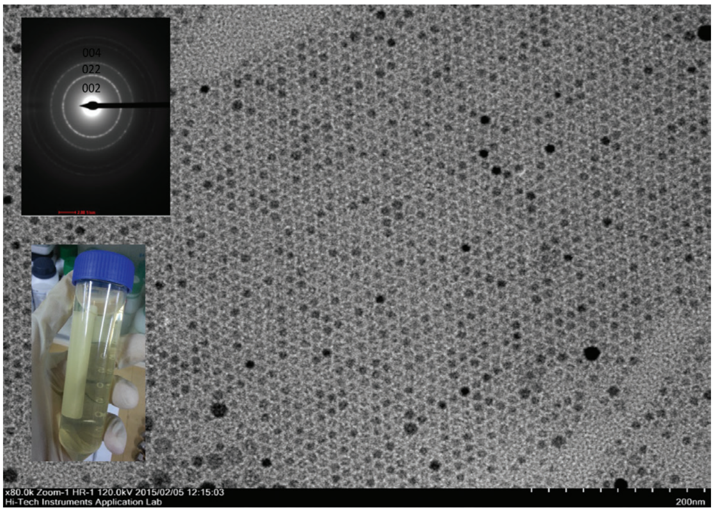


FIGURE 6. A typical TEM image of sample with $ZnCl_2$: Se at ratio 1:1 insert a SAED pattern (left top corner) and a photo of ZnSe QDs (bottom left corner)

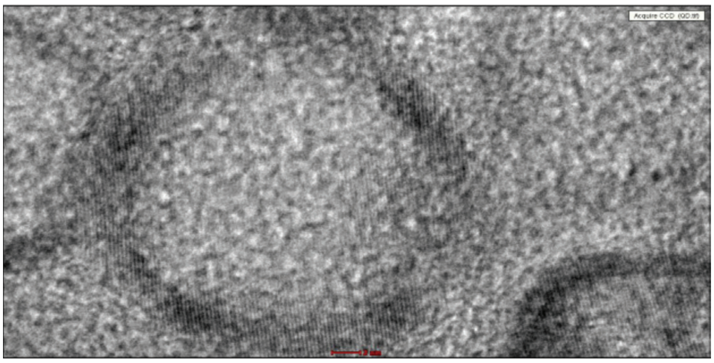
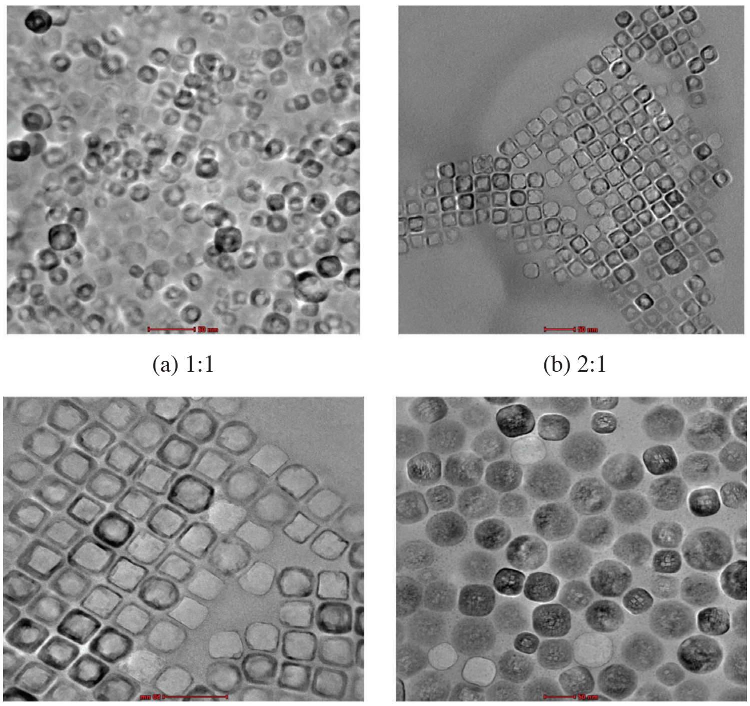


FIGURE 7. A typical HRTEM image of ZnSe QDs for sample with $ZnCl_2$: Se at ratio 1:1



(a) 1:1 (b) 2:1

(c) 3:1 (d) 4:1

FIGURE 8. HRTEM image of ZnSe QDs with different concentration of $ZnCl_2$: Se ratio

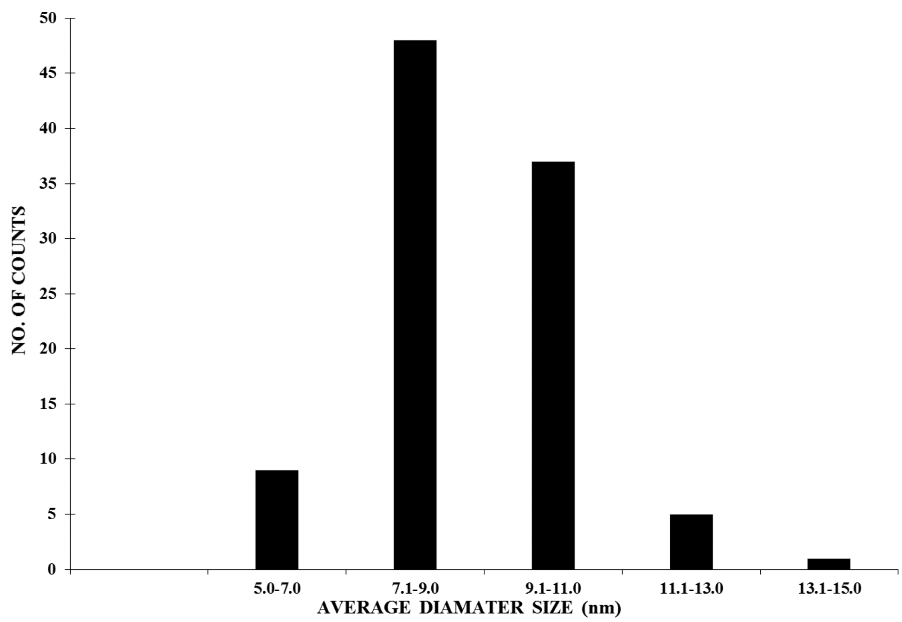


FIGURE 9. Tabulation average particle size of ZnSe QDs for $ZnCl_2$: Se at ratio 1:1

temperature (150°C). Different concentrations of $ZnCl_2$: Se ratio in preparing the colloidal ZnSe QDs has been studied. From the absorption result, the absorption peak was shifted from 316 to 313 nm when the concentrations of $ZnCl_2$ increased and the optical band gap energy (Eg) was also increased due to the shifted of the absorption spectra. The emission peak at 440 nm in violet region had been detected for sample with $ZnCl_2$: Se ratio 1:1, 2:1 and 4:1 but blue region (460 nm) for sample ratio 3.0. The optimum condition to synthesized colloidal ZnSe QDs was at ratio 4:1 with absorption spectrum at 314 nm and optical band energy at 3.82 eV.

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Fakhrurrazi Ashari, Josephine Liew Ying Chyi*,
Zainal Abidin Talib, W. Wahmood Wan Yunus,
Leong Yong Jian & Lee Han Kee
Department of Physics, Faculty of Science
Universiti Putra Malaysia
43400 Serdang, Selangor Darul Ehsan
Malaysia

Chang Fu Dee & Burhanuddin Yeo Majlis
Institute Microengineering and Nanoelectronics
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor Darul Ehsan
Malaysia

*Corresponding author; email: josephine@upm.edu.my

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