SYNTHESIS AND OPTICAL PROPERTIES OF QDs CdSe FOR APPLICATION IN SOLAR CELLS

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Abstract: **In this paper we present experimental results for technology prepared quantum dots (QDs) to purpose the research for the next application. QDs were made with this process by Colloidal method at low temperature. Experimental research and manufacture of QDs obtained very good results, QDs were made with small size and sphere equally (shows at TEM images), the particle size change from 1.6nm to 2.5nm related to change in color from pale yellow to heavy red. Average deviation in size uniformly distributed are $\pm 2\%$ in the solution. Results were obtained for UV-Vis spectra, PL spectra (photoluminescence spectra) Stokes shift are approximate 0.61eV to 1.2eV correspond effective radius change 1.6nm to 2.5nm between the two spectra. This shift is attributed to two causes: the status of disability within the QDs and movement related to the optical dark state of the fine structure. Furthermore, we have surveyed the solution stability over time by measuring the absorption spectra in three months, and absorbance was unchanged much to compare with the original.**

Keywords - Nanocrystals; Defect states; CdSe nanocrystals.

I. INTRODUCTION

There were many methods which has been employed to synthesize semiconductor quantum dots (QDs) in recent years. These methods include the reverse micelle [1,2], epitaxial, colloidal, hydrothermal [3,4]… to depend on aims of the applications different. The quantum dots has shown potential applications in thin film light emitting devices (LED) [5,6], non linear optical devices [7], flourescent labels for biological applications [8], solar cells [7], displays, sensors or biosensors, lasers [2]… A large of number of hight quality quantum dots as such CdS, CdSe, CdTe were successfully synthesized.

In this paper, we present the fabrication technology CdSe QDs using Colloidal method, using thyoglycol agent. Provide important keys to success in the process to synthesize QDs for high luminescence are the molecular surface agent with three purposes: Firstly is the control over development of the QDs. The QDs used to trap molecules which must have functional groups are compatible with positive ion (cation) or negative ion (anion) of quantum dots. Such as TOPO, thiols or amines associated with the Cd^{2+} ion and the TOP solvent will bind Se^{2-} negative ions. To better control the formation and development of CdSe QDs, the process complicated of molecules are very important. If the surface of the QDs linking is so weak with agents that result uncontrol development of particle size. Also the linking is so trong that have been formulated fewer QDs. Therefore, to obtain QDs in size nanomer, you will choose the molecular surface agent that they are not trong but not so weak. Choice should be suiable the molecular surface agent that particle size of growth will depend on the rate between chemical precursors and molecular surface agent, reaction temperature.

The secondly, prevent aggregation between QDs together. The QDs are usually unstable in the environment thermodynamic. In this environment, QDs tend aggregation together and increasing the particle size. Because of this, we use the molecular surface agent to trap QDs. Furthermore, QDs are more stable when both electrons and holes are converted through the molecular surface agent.

Thirdly does passivation at the surface of QDs. When the particle size is small, the rate of surface area to volume of QDs is huge. Surface of the crystal no period, which results appear the states within the enegry gap (enegry between the lowest level of conduction band and the top of the valence band). The surface state trapped the electrons can radiation or no radiation. In the case of radiation, emission wavelengths are longer than the excitation wavelengths, often at non-radiative. The loss ennegry due to radiation will decrease the luminescence efficiency of QDs [9,10]. All the experiments were repeated many times to confirm the experimental results are correct. we also measured stored times of the solution through the absorption spectrum in long time.

II. EXPERIMENT

Materials

Cd(CH$_3$COO)$_2$.2H$_2$O (99%), Dimethyl formamide (DMF) C$_3$H$_7$NO (99%), Mercaptoethanol (Thioglycol) HOCH$_2$CH$_2$SH (99%), Sodium selenite pentahydrate Na$_2$SeO$_3$.5H$_2$O (98%), Ti(OC$_4$H$_9$)$_4$ (99%), obtained from Merck.
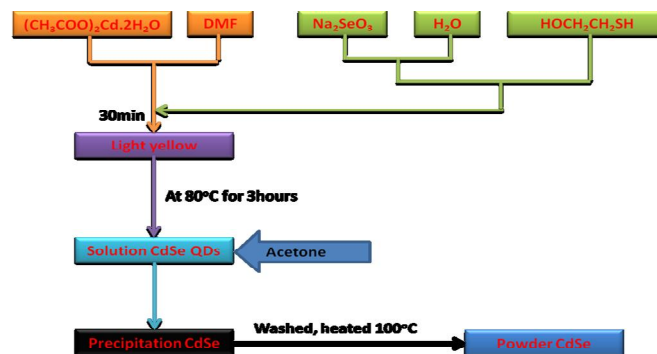

Figure 1. *Diagram synthesis of CdSe QDs.*

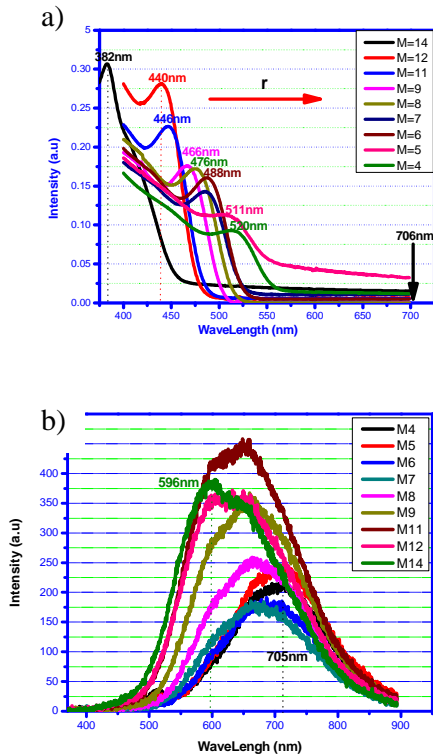## III. RESULTS AND DISCUSSION

Figure 2. *Shows the absorption spectra and PL of CdSe QDs corresponding M=4,5,6,7,8,9,11,12,14.*

Figure 2 shows absorption spectra of CdSe QDs with the different values M (M = Cd^{2+}/thioglycol), all samples are shown effects quantum that is very strong, peak of the absorption spectrum changed from 382nm to 520nm corresponding size particle changed from 1.6nm to 2.5nm (shows in Table 1) smaller than the radius of Borh (a_B = 5nm of CdSe bulk material) is calculated by the approximate equation [11]. Related to the shift in color from light yellow to dark red. Therefore, the results obtained with CdSe QDs are applied model strong confinement quantum (R<a_B) [12]. In semiconductor bulk, radius Borh of the exciton free is determined by the extension space wave function of electrons in the conduction and holes in the valence (*with a_B=5nm*). When the particle size can be compared with the radius of the exciton Bohr, wave functions of electrons and holes confined in nanometer space, the kinetic enegry of electrons and holes increases. As a result, causes a shift peak of absorption spectra towards higher energy while reducing the size of the QDs CdSe [11]. In this figure, the radius of the CdSe samples increase correspond with M value from 14 to 4. The organic molecules -thiol- group limited interaction between the QDs CdSe and therefore reducing link between the QDs together, QDs stabilized because electric charge moved from the QDs to ligand field [Sachleben 1998]. During this process we chosen thioglycol, it enveloped the QDs CdSe when the newly formed. When M values increasing, the thioglycol less envelopment than so the particle size increases correspond with the shift peak absorption of light torward red (the color change to red). Peak of absorption spectra of the samples was attributed to the shift that is due to shift between the two basic excitron $1S_{3/2}$-$1S_e$ [11].

Meanwhile the right picture is the PL spectra of QDs shows the process that moving the top of the PL spectrum is compared to the absorption spectrum.

Table 1. Describes the change of the particle size on the concentrate of M

Sample	λ (nm)	E_g^{eff} (ev)	R (nm)
M=4	520	2.384	2.471
M=5	511	2.426	2.393
M=6	488	2.540	2.211
M=7	488	2.540	2.211
M=8	476	2.605	2.126
M=9	466	2.660	2.060
M=11	446	2.780	1.936
M=12	440	2.818	1.901
M=14	428	3.246	1.605

Figure 3 shows the difference in energy between the two absorption spectrum and the PL spectrum of the same sample is called the Stokes shift. Figure 3 shows the relationship of the Stokes shift energy within the quantum dot to depend on effective radius. Energy shift changes from 0.6eV to 1.2eV corresponds to the change of the effective radius from 1.6nm to 2.5nm. Figure 3 shows a Stokes shift decreased when the size of the quantum dot increased when compared with the theoretical calculation results and experiments of the group Efros (Fig. 3.b). We know the cause of a Stokes shift inside the quantum dots are attributed to two causes:

- The existence of the surface states in CdSe quantum dots. The state is the main surface defect inside the QDs, resulting in recombination with electrons. When electrons receive excitation energy from the valence to conductor band and then returned immediately reombenation with state surface inside enerngy gap of CdSe QDs.

- Due to ±2 dark exciton states (passive optical) in the fine structure of quantum dots. Experiment shows that the Stokes shift is due to differences between ±2 and ±1^L energy levels, underlying cause is due to the shift between two basic levels by thermo dynamics by a phonon - assisted. As a result, causing shift peak of PL spectra compared to the peak of absorption spectrum [12]. In the fine structure of quantum dots, so spherical, structure, spin-orbit interaction that caused the spliting $1S_{3/2}$-$1S_e$ level into five levels corresponding to the moment angle total ±2, ±1^L, ±1^U, 0^L, 0^U. In this, ±2, 0^L exciton states are passive optical (dark) and ±1^L, ±1^U, 0^U exciton states are active optical (bright). Clealy when looked at in isolation, the ±2 exciton state has an in nite lifetime in the electric dipole approximation, since there is the requirement that the emitted photon is not allowed to take away an angular momentum of ±2 but only ±1. Optical process were found inside the quantum dots related to the difference in energy between two states ±2 and ±1^L, this is the lowest two energy in the 5 levels of the fine structure. Experiments Efros group in Figure 3 (b) have demonstrated that the optical switch in general or a Stokes shift in particular related directly with this two energy levels. According to calculations by Efros for spherical quantum dots, the difference in energy between the two levels ±2 and ±1^L about 20meV[13]. Therefore in his experiments he used pump source corresponds to the energy of two items to observe resonance Stokes. As well as, the transition to this state is then followed by relaxation to the dark ±2 exciton state via a thermal mechanism, from which recombination is now allowed and takes place by a phonon-assisted [14].
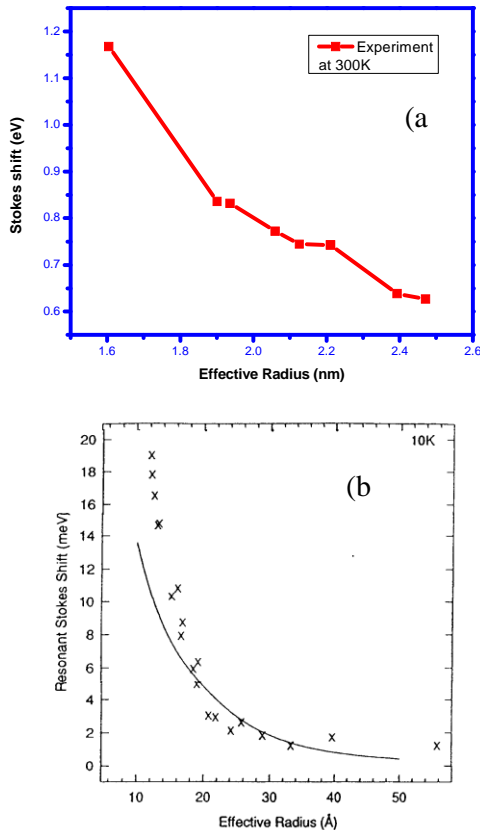
Figure 3. Shows the size dependence of Stokes shift (a) experimental values at 300K, (b) experimental values at 10K by Efros (1996)[29].
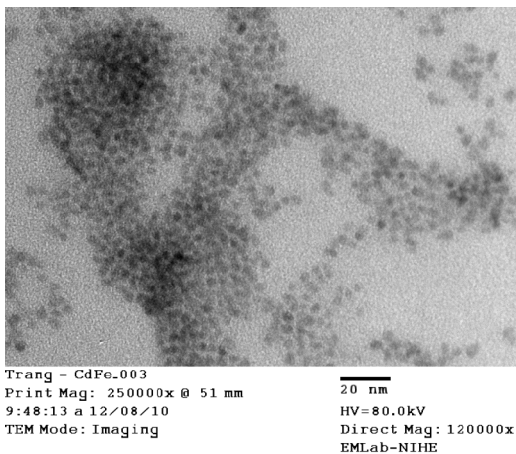

Figure 4. *Image TEM of the solution of CdSe QDs as M=8, R=10*

Figure 4 shows image of CdSe QDs in solution. We see that particlesize are very equally, shape of spherical QDs. The particle size changed from 1nm to 5nm smaller than the radius of Borh (a_B= 5nm for CdSe bulk). Therefore, the results obtained which can be applied model strong confinement quantum (R<a_B) (Effos, 1996).
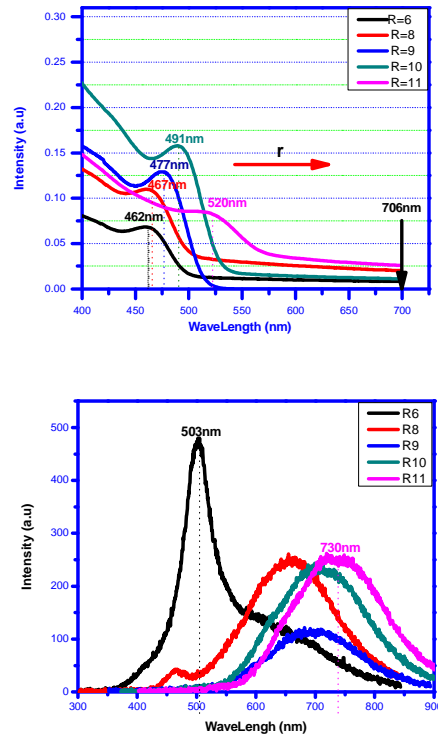

Figure 5. *Shows the absorption spectra and PL spectra of CdSe QDs corresponding R=6,8,9,10,11.*

Figure 5 describes the absorption spectra and PL spectra of CdSe QDs corresponds to change in the value R = Cd^{2+}/Se^{2-} from 6 to 11. The peak of absorption spectrum shift toward the red when R increases, correspond with increasing of the particle size. This related to change in color from light yellow to heavy red. Particle size change from 1.73nm to 2.11nm (***Table 2***), the difference about average radius is approximate 1.083%. when fewer amount of Cd^{2+} cation, CdSe QDs were created fewer. Small particle size corresponds to the shift peak of absorption spectrum toward shorter waves. By contrast, the particle size increases due to the link between QDs together, resulting shift peak of absorption spectra toward longer waves (red). The results obtained from absorption spectrum are again check back with the results obtained from PL spectra and completely suiable together.

Table 2. *Describes the change of the particle size on the concentrate of R.*

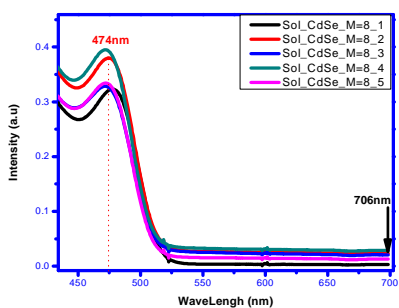| Sample	R=6	R=8	R=9	R=10	R=11
λ (nm)	462	467	477	491	520
E_g^{eff} (ev)	2.68	2.65	2.59	2.52	2.384
R (nm)	1.73	1.76	1.82	1.90	2.112

Figure 6. *Absorption spectra of CdSe QDs as diferent temperatures(left) and absorption spectra of CdSe QDs with cycle measure to research the stable of them.*

In addition to the parameters M, R we also research dependant of the CdSe QDs on temperature during the formation. From this results, we find that peak of the absorption spectrum change when we change temperature, and the peak of the absorption spectrum shift toward red.
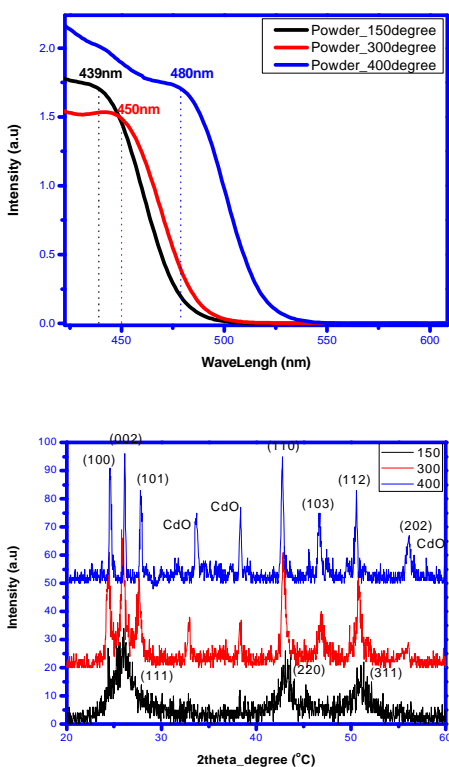

Figure 7. *Absorption spectrum and X- ray spectrum of CdSe QDs powder as 150ºC,300ºC,400ºC.*

After fabrication completed the solution, we carried out for CdSe solution into the solvent acetone, the solution obtained for precipitation of CdSe QDs. This solution into a centrifuge at 5,000 cycle/minute, collecting precipitate and repeatedly washed with acetone to clean and heating at different temperatures in a vacuum environment. From the absorption spectra, when the samples were heated from 100^oC to 300^oC, CdSe powder transfer from the cubic structure to hexagonal structure in the X-ray diffraction correspond to shifts peak of the absorption spectrum toward longer waves. The results obtained that particle size increase [15].

Table 3. Describes the change of the particle size on the temperature.

Temperature	Δ(2θ) (degree)	Peak 2θ (Degree)	d (nm)	Structure	Space group
150^0C	2.30	26.03	3.55	Zincblende	F $\overline{4}$ 3m
300^0C	1.64	25.85	5.00	Zincblende	F $\overline{4}$ 3m
400^0C	0.52	25.84	15.67	Wurzite	P6₃mc

IV CONCLUSIONS

In summary, we have successfully controlled particle size of CdSe QDs through the parameters M, R and temperature. We have determined the stability of the solution in three months. The results of the absorption spectra and PL spectra are suible together, Stokes shift between the peak of the absorption and PL spectrum were from 0.6eV to 1.2eV to depend on effective radius. The experimental value for the Stokes shift is taken to be the difference in energy between the $\pm1^L$ bright and ±2 dark exciton states, which is found to increase as the dot radius R decreases, and the values are in reasonable agreementwith the theoretical estimates [13,14].

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