MNK Publication

International Journal of Latest Research in Science and Technology **ISSN (Online):2278-5299**
Volume 4, Issue 3: Page No.34-38, May-June 2015
https://www.mnkpublication.com/journal/ijlrst/index.php

SYNTHESIS AND OPTICAL PROPERTIES OF THIOGLYCOL-CAPPED CdSe QUANTUM DOTS EMBEDDED IN TiO_2 FILMS FOR SOLAR CELL APPLICATIONS

H. T. Tung and Nguyen Thanh Nguyen
Faculty of physics, Dong Thap University, Dong Thap Province, Vietnam

Abstract*- *CdSe quantum dots have been prepared via a colloidal route using Mercaptoethanol (Thioglycol) ($HOCH_2CH_2SH$) as a capping agent. The stability of the particles in solution and embedded in TiO_2 matrices has been followed by optical absorption and photoluminescence. Both the size and the size distribution of the particles are well controlled by ratio mole and temperature, thus allowing a tunable emission. Room temperature photoluminescence (PL) studies are reported, the band is assigned to recombination through defect states, whose energy depends on the nanocrystallite size and so depend the optical band gap on the nanocrystallite. X-ray, UV-Vis spectroscopies, and TEM have been used to characterize colloidal CdSe. With CdSe nanoparticles as seeds on TiO_2 film, a highly efficient of CdSe/TiO_2 thin films photoanode was prepared by dip coating deposition technique.

Keywords **-** nanocrystals; thin film; defect states; CdSe nanocrystals; TiO_2, solar cell.

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 [4,5], epitaxial, colloidal, hydrothermal [2,3]… to depend on aims of the applications different. The quantum dots has shown potential applications in thin film light emitting devices (LED) [6,7], nonlinear optical devices [8], flourescent labels for biological applications [9], solar cells [8], displays, sensors or biosensors, lasers [11]… A large of number of hight quality quantum dots as such CdS, CdSe, CdTe were successfully synthesized.

In this paper, CdSe QDs and TiO_2/CdSe thin films have been prepared via a colloidal route using Mercaptoethanol (Thioglycol) as a capping agent. We has fabricated successfully the CdSe QDs and TiO_2-CdSe thin films. We reseach optical characteristic of CdSe QDs and TiO_2-CdSe thin films for the application in solar cells device. Dye sensitized solar cells bases wide band gap semiconductors have the potential advantages of lower cost production and versatility in comparision to the conventional solid state cells. The photoanodes in such cells constituted by TiO_2 layer sensitized to the visible radiation by an absorbed dye. Instead of using dye, the sensitization of TiO_2 electrodes can achieved through modification of the oxide TiO_2 with CdSe QDs of the lower band gap semiconductor materials. Light is absorbed by the dye and an electron is excited to a higher energy level in the dye. This excited electron is rapidly injected into the titanium dioxide nanoparticles and travels to one of the solar cell electrodes by hopping from particle to particle. The positively charged dye undergoes an electrochemical reaction with I^- in the electrolyte to form I^{3-} which shuttles the the hole to the counter electrode where it is reduced back to I^- to repeat the cycles.

Publication History

Manuscript Received	:	*19 May 2015*
Manuscript Accepted	:	*12 June 2015*
Revision Received	:	*25 June 2015*
Manuscript Published	:	*30 June 2015*

II. EXPERIMENT

Materials

$Cd(CH_3COO)_2.2H_2O$ (99%), Dimethyl formamide (DMF) C_3H_7NO (99%), Mercaptoethanol (Thioglycol) $HOCH_2CH_2SH$

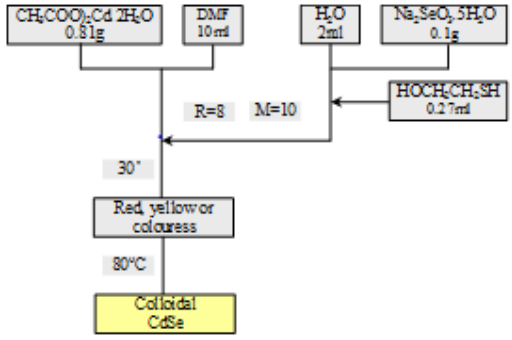

Figure 1. *Diagram synthesis of CdSe QDs.*

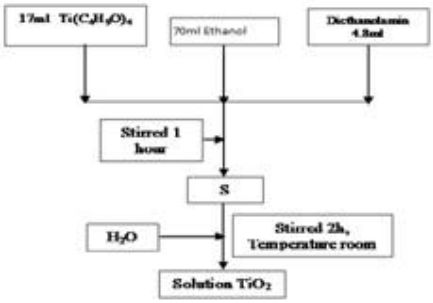

Figure 2. *Diagram fabricates of the TiO_2 solution.*

(99%), Sodium selenite pentahydrate $Na_2SeO_3.5H_2O$ (98%), $Ti(OC_4H_9)_4$ (99%), obtained from Merck

We investigated the effect of thioglycol capping agent(M = thioglycol/Cd^{2+} molar ratio) on the morphology of the QDs while keeping Cd^{2+}/Se^{2-} at 8 in all samples.

3. RESULTS AND DISCUSSION

Synthesis of TiO_2/CdSe thin films corresponding concentration different of CdSe quantum dots: 10%; 20%; 30%; 50% and temperatures different: Final, we obtain TiO_2/CdSe thin films by using dip coating technique.

Analysis instrument: X ray diffraction pattern is using CuKα radiation (λ=0.1542nm) at 40kV and 60mA in Sceinces and technology institute of Ho Chi Minh city. UV-Vis absorption spectra in faculty of chemistry, university of sceinces of Ho Chi Minh city. TEM images in institute of epidemic prevention, Yesin road, Ha Noi capital city. Photoluminescence spectra FL3 – 22 excited by using laser Xenon XFOR – 450, power 450W, 25A in spectrum application, faculty of physics, university of sceinces of Ho Chi Minh city..

1. Optical characteristic and structure of the CdSe quantum dots.

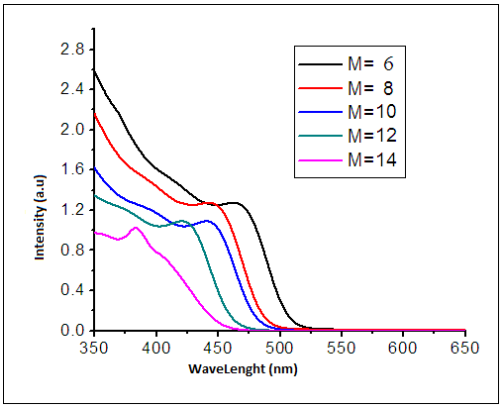

Figure 3. *Shows the absorption spectra of CdSe QDs corresponding M=6,8,10,12,14.*

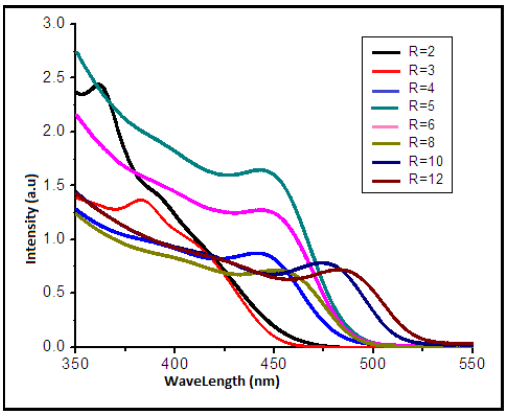

Figure 4. *Shows the absorption spectra of CdSe QDs corresponding M=2,3,4,5,6,8,10,12.*

Figure 3 shows that all cases the CdSe QDs appeared the absorption shouder in different positions to depend on molar of the thioglycol with Cd^{2+} (M = thioglycol/Cd^{2+} molar ratio). The thioglycol capping agent is too important to grow the CdSe QDs in the reaction. In figure 3, we can be seen the peaks of absorption spectra of CdSe QDs, both of the peaks shift in the energy as a functional of size. This indicates that one or the other of two charge carries might be in a confined interior state of the nanocrystal when recombination occurs. The stokes of the band egde emission increases with decreasing particle size due to the larger coupling of the electron and hole pair in the emitting state to phonons LO in the polar CdSe lattice for the smaller nanoparticles [9]. The nonresonant Stokes shift might also be influenced by dispersions in sharp, inhomogeneity in structure and phonons effect [9,10].

When we dissolve the thioglycol surfactant into solution of Na_2SeO_3 to result thioglycol formed ligands field, it envelops the Se^{2-} anion and hinders the direcly recombination of Se^{2-} anion with Cd^{2+} cation. Morever, thioglycol also envelops the CdSe QDs when it was already formed. The results obtain that the CdSe QDs are monodiperse and the smaller particles size. From figure 3, the absorption peaks of CdSe quantum dots were blue-shifted when the thioglycol concentration is dicreasing and precitation at M=1 to 3 (red-shifted, no show).

The results show that the CdSe QDs are larger (d=4.79-5.44nm). From the effective mass model, we obtained the equation[1]:

$$E_R = E_g + \frac{\hbar^2 \pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.786e^2}{\varepsilon R} - 0.248E^*_{Ry}$$

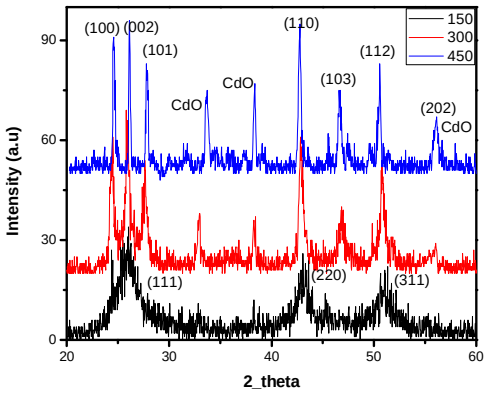

Figure 5. *Shows X-ray diffraction pattern of CdSe QDs with M=7, annealed at 150°C, 300°C, 450°C for 30min.*

In the figure.4, the peaks show at 25.7°, 42.2° and 50° corresponding to the (111), (220) and (311) planes of the cubic structure. The size obtained from the broadening of XRD pattern agrees well with size estimate obtained from SEM images and absorption spectra. It has been improved that CdSe crytallization in the cubic phase is possible due to the low growth temperature (80°C) comparing with papers different.

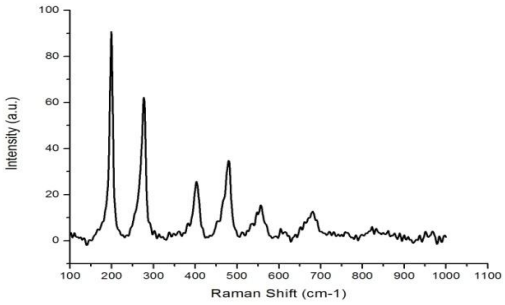

Figure 6. *Raman spectrum of powder CdSe with M = 7, annealed at 100 ^{0}C for 30min.*

In the Raman spectrum, there are 3 peaks at 201 cm^{-1}, 402 cm^{-1} and 601 cm^{-1}. These are the peaks corresponding to the phonon of longitudinal optical vibration in CdSe, the first lies at 201 cm^{-1} (longitudinal optical-LO), the second at 402 cm^{-1} is the second harmonic of the first peak (2LO), the third at 601 cm^{-1} is the third harmonic of the first peak (3LO). Origin of branch LO and the interactions between phonons with suface of CdSe QDs depend on thi size of electron-hole pair interaction. Each peak is asymmetrical tends to stretch toward the low frequency, which is attributed to the surface vibration. Blue-shifted were also seen in the two peaks LO and 2LO at 201cm^{-1} and 402cm^{-1} of CdSe powder in comparing with the peaks 210cm^{-1} và 418cm^{-1} [2] of bulk CdSe. The red-shifted proved that CdSe QDs, with high ratio area/volume, were created in the sample.

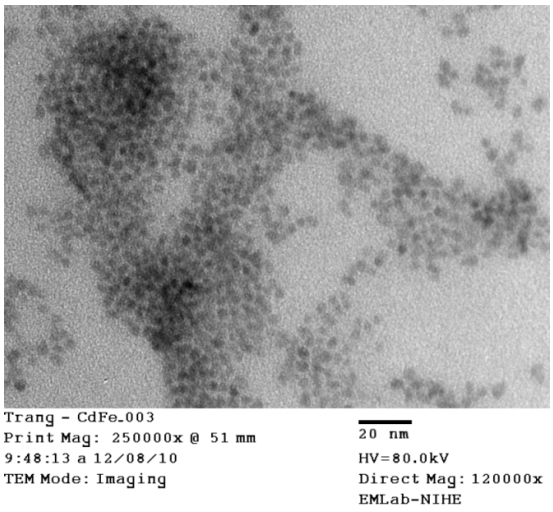

Figure 6. *SEM images of the powder CdSe QDs as M=4.*

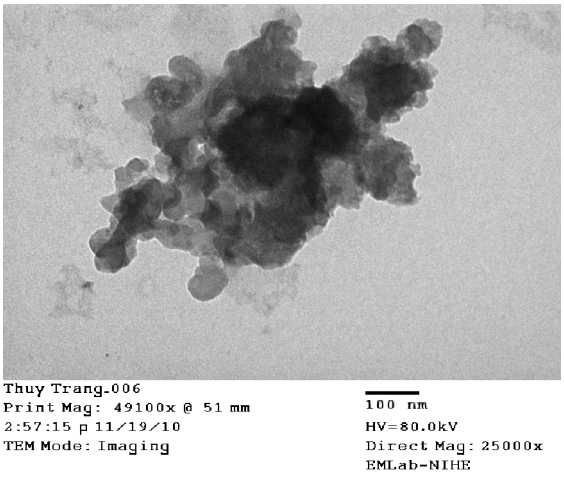

Figure 7. *TEM images of the solution CdSe QDs as M=4.*

The molar of thioglycol is key parameter in controlling the morphology of the CdSe quantum dots. We thus investigated the effect of thioglycol capping agent on the morphology of the QDs while keeping Cd^{2+}/Se^{2-} at 8. TEM images show the CdSe QDs synthesize with different M. The size of CdSe QDs determined from the TEM image is from 2nm to 5nm and this is in agreement well with X-ray diffraction and absorption spectra results. In all cases CdSe QDs appeared spherical and relatively monodisperse and high strable.

An estimate average nanoparticle size can be obtained from peaks of the photoluminescence. Assuming that the photoluminescence is due to band to band emission, thus the wavelength at the PL can be used to obtain the band gap. The average particle size might be estimated from band gap using a suitable model for confinement quantum (no show).

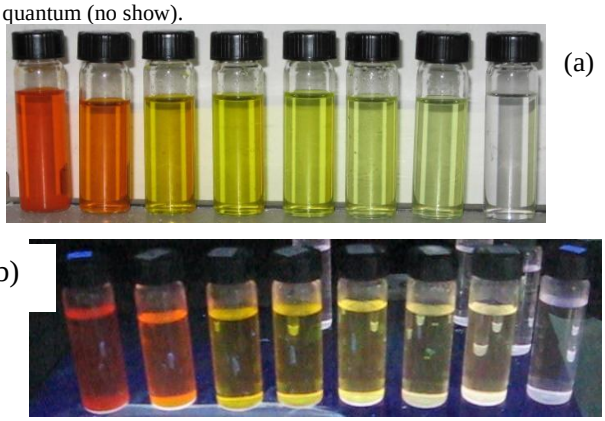

Fig 8. The CdSe nanoparticles with original colour different (a) and under UV lamp (b).

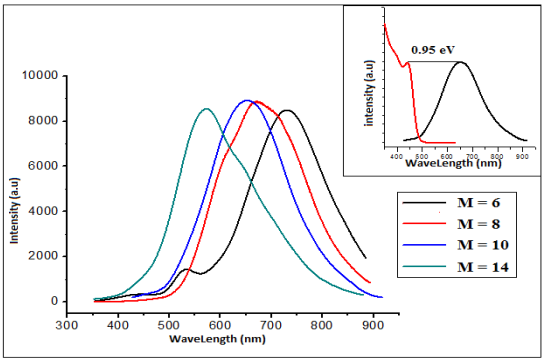

Figure 9. *PL spectra of the CdSe quantum dots correspond M=6;8;10;14.*

Figure.8 shows such change in the engery gap CdSe QDs by giving a red - shifted in the photoluminescence peaks, agrees well absorption spectra, with the increasing of M ratio. The peaks of absorption of CdSe QDs is asymmetrical at M=10 because they are uniform. Morever, our results also showed that the intensity of PL spectra increased with the dicreasing of M value. This might be attributed to the increase in the nonradiative recombination of electrons and holes on the suface state of the CdSe QDs as size particles increase [9]. The differences in PL spectra can be directly associated with change in the CdSe QDs size, hence the energy gap. The effect of the surfactant concentration on the photoluminescence characteristic of CdSe QDs was studied by using thioglycol concentration different (M=2,3,4,5,6,7,8,9,10,11,12,14,16,20) in the same condition reaction. This changed QDs characteristic, hence the change in the color of the solution were different each other even at the same reaction period.

Therewith, in figure 9 (small fig) we survey a large shift – stokes of photoluminescence spectra in comperision with absorbtion spectra about 0.9eV. This might be attributed to the increase in the nonradiative recombination of electrons and holes on the suface state of the CdSe QDs as size particles increase[9].

2. Optic characteristic of the TiO_2-CdSe thin film.

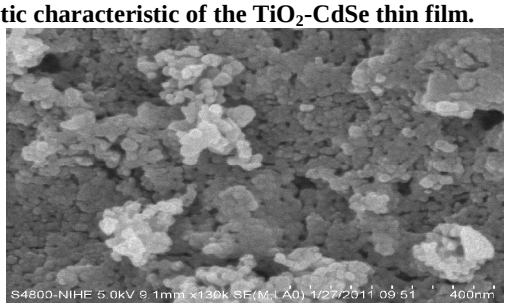

Figure 10. *SEM images of the TiO_2 thin film.*

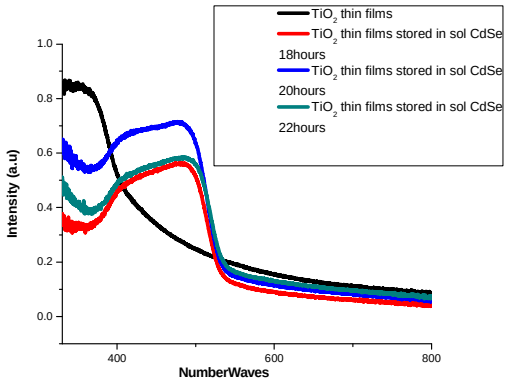

Figure11. *Shows absorption spectra of TiO_2/CdSe thin films corresponding diped time:18hours, 20hours, 22hours.*

Figure 11 shows the absorption spectra of CdSe QDs embeded in TiO_2 thin films. The intensity of absorption peaks increases stored time at 20 hours of TiO_2 thin films in the solution of CdSe QDs. The peaks of TiO_2/CdSe thin films are shifted litle or constant.The absorption spectra shows one egde at 455nm for TiO_2/CdSe thin films. The amount of CdSe QDs adsorbed onto TiO_2 is dependent on the charging effect in solution. This is very suitable for TiO_2/CdSe thin films in solar cells application.

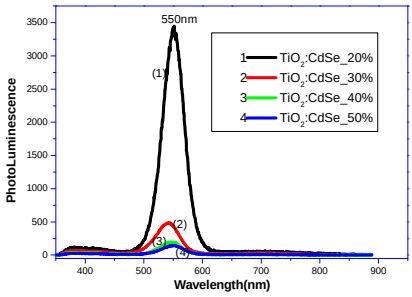

Figure 12. *Shows the PL spectra of CdSe nanoparticles doped TiO_2 thin films corresponding 20%, 30%, 40%, 50%CdSe.*

Figure 12 shows the photoluminescence spectra of CdSe QDs embeded in TiO_2 thin films with 20%, 30%, 40%, 50%CdSe. All samples appear peak of PL spectra at 550nm, position of peaks is not change. The sample have the strongest intensity corresponding 20% and the intensity of samples decrease when concentration of CdSe nanoparticle increase. We want to make the TiO_2/CdSe thin film which absorb a lot of the light visible for solar cell applications. So that, we choose the sample with 20%CdSe. Because the sample have the strongly intensity photoluminescence, it may be absorbed more the light visible. The next work, we will apply TiO_2/CdSe thin films to prepare Dye – sensitized solar cells by using CdSe QDs.

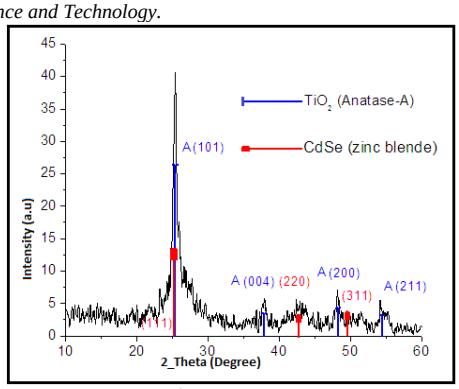

Figure 13. *Shows XRD spectra of CdSe nanoparticles doped TiO_2 thin films corresponding.*

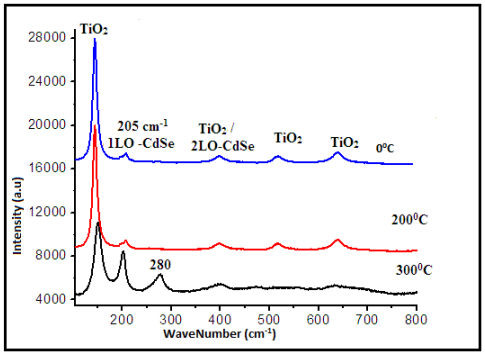

Figure14. *Shows Raman spectra of TiO_2/CdSe thin films corresponding 0^oC, 200^oC,300^oC of CdSe* QDs.

Fig 13 and 14 corresponding XRD and Raman spectra of TiO_2/CdSe thin films. XRD spectra is suitable well with Raman pectra, both are description anatase of TiO_2 and zince blenbe of CdSe QDs structure. Morever, Sample at 300^0C appears a peak at 280 cm^{-1}, This peaks is oscillate of linking -Se-Se- or ligands of CdS_xSe_{1-x} [12,13,14].

4. CONCLUSIONS

The CdSe QDs and TiO_2/CdSe thin films were fabricated by colloidal method in low temperature (80^oC). The particles size of CdSe QDs and TiO_2/CdSe thin films were determined from 2nm to 5nm by using XRD, TEM images and absorption spectra. The change in the energy gap of CdSe QDs by the blue-shifted in the absorption spectra and photoluminescence. The edge absorption of TiO_2/CdSe thin films is at 500nm, thus It is suitable to prepare solar cells.

Acknowledgment. *We acknoledge the university of sceince of Ho Chi Minh city for technical assistance and university of Dong Thap for helping about research grant.*

REFERENCES

[1] Murray. C. B, Kagan. C. R and Bawendi. M. G, Annu. Rev. Mater. Sci. **30**,545 (2000).

[2] Peng. Q, Dong. Y.J, Deng. Z.X, Li. Y.D. Inorg. Chem. 41 (2002) 5249.

[3] Chen.M.H, Gao. L, Am. J.Ceram.Soc.**88** (2005) 1643.

[4] Xi. L.F, Lam. Y.M, J. Colloid Interface Sci. **316** (2007) 771.

[5] Maillard. M, Giorgio. S, Pileni. M.P.Adv. Mater. **14** (2002) 1084.

[6] (a) Alivisatos.A.P. Nat. Biotechnol,2004, **22**,47; (b) Jaiswal. J. K and Simon. S. M.Trends Cell Biol, 2004, 14, 497.

[7] Nanda. J, Narayan. K. S, Kuruvilla. B. A, Murthy. G. L and Sarma.D.D. Appl. Phys. Lett. 1998, **72**, 1335.

[8] (a) Koktysh. D. S, Gaponik. N, Reufer. M. Crewett. J, Scherf. U, Eychmuller. A, Lupton. J. M, Rogach. A. L and Feldmann. J, ChemPhysChem, 2004, **5**, 1435; (b) Gao. M.Y, Lesser. C, Kirstein. S, Mo. H. Rogach. A. L and Weller. H. J. Appl. Phys.2000,**87**,2297.

[9] Klimov. V. I, Mikhailovsky. A. A, Xu. S, Malko. A, Hollingsworth. J. A, Leatherdale. C. A, Eisler. H. J and Bawendi. M. G. Science. 2000, **290**, 314.

[10] Efros.A.L, Rosen.M, Kuno.M, Nirmal.M, Norris.d.J and Bawendi.M.Phys. Re .B 1996,**54**, 4843.

[11] Kuno.M, Lee.J.K, Dabbousi.B.O, Mikulec.F.V, Bawendi.M.G.J.Chem.Phys.1997, **106**, 9869.

[12] Klimov.V.I, Mikhailovsky.A.A, Xu.S, Malko.A, Hollingsworth.J.A, Leatherdale.C.A, Eisler.H.J and Bawendi.M.G. Science.**290**, 314 (2000).

[13] Iván Mora-Seró, Vlassis Likodimos, Sixto Giménez, Eugenia Martínez-Ferrero, Josep Albero, Emilio Palomares, Athanassios G. Kontos, Polycarpos Falaras, and Juan Bisquert (2010), "Regeneration of CdSe Quantum Dots by Ru Dye in Sensitized TiO_2 Electrodes", J. Phys. Chem. C XXXX, xxxx, 000.

[14] Jin Young Kim, Sung Bum Choi, Jun Hong Noh, Sung HunYoon, Sangwook Lee, Tae Hoon Noh, Arthur J. Frank, and Kug Sun Hong (2009), "Synthesis of CdSe-TiO2 Nanocomposites and Their Applications to TiO2 Sensitized Solar Cells", *Langmuir*, American Chemical Society

[15] Kevin Tvrdy and Prashant V. Kamat (2009), "Substrate Driven Photochemistry of CdSe Quantum Dot Films: Charge Injection and Irreversible Transformations on Oxide Surfaces", *J. Phys. Chem. A* , *113*, 3765–3772.