

CdSe Quantum Dots Sensitized TiO₂ Electrodes for Photovoltaic Cells

Jun-Ho Yum[†], Sang-Hyun Choi^{††}, Seok-Soon Kim, Dong-Yu Kim, and Yung-Eun Sung^{††*}

Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, S. Korea

[†]Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of basic Sciences, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland, ^{††}School of Chemical Engineering and Research Center for

Energy Conversion and Storage, Seoul National University, Seoul 151-744, S. Korea

(Received October 11, 2007 : Accepted November 1, 2007)

Abstract : The electronic properties of quantum dots can be tuned by changing the size of particles without any change in their chemical composition. CdSe quantum dots, the sizes of which were controlled by changing the concentrations of Cd and Se precursors, were adsorbed on TiO₂ photoelectrodes and used as sensitizers for photovoltaic cells. For applications of CdSe quantum dot as sensitizers, CdSe/TiO₂ films on conducting glass were employed in a sandwich-type cell that incorporated a platinum-coated conductive glass and an electrolyte consisting of an I⁻/I₃⁻ redox. The fill factor (FF) and efficiency for energy conversion (ζ) of the photovoltaic cell was 62 % and 0.32 %, respectively.

Keywords : Quantum dot, Quantum dot-sensitized solar cell, CdSe, Nanostructured TiO₂

1. Introduction

The photosensitization of nanocrystalline TiO₂ by an adsorption of a dye was pioneered by O'Regan and Grätzel and investigations continued during the past three decades because the potential as a low cost alternative to conventional silicon solar cells.¹⁻³⁾ In this system, a very large surface-to-volume ratio of nanocrystalline TiO₂ is used for coverage of the dye onto a TiO₂ surface. Quantum sized semiconductor materials (quantum dots) such as CdS, PbS, InP, CdSe have recently been reported for possible use as a photosensitizer absorbing photons on TiO₂.⁴⁻⁸⁾ Considerable interest has developed regarding quantum dots because of their unique electronic and optical properties. When their size is sufficiently small (below the exciton radius), they exhibit a quantum confinement effect leading to a size-dependent separation between the valence and conduction band. Thus, their band gap can be widened as their size is increased, permitting the optical and electronic properties of materials to be tailored for specific applications. That is, the electronic properties of quantum dots can be tuned by changing the size of the particles without changing their chemical composition. The use of quantum dots as sensitizers have advantages compared to organic dyes that are an adjustable band gap or band edge, effective light harvesting, and their possible stability under sun light. Most quantum dots for use as sensitizers can be produced by in situ-precipitation on the TiO₂.⁴⁻⁷⁾ InP quantum dots as sensitizers were obtained by synthesis in a desired size following their adsorption to the surface of TiO₂ nanoparticles.⁸⁾

In this work, CdSe quantum dots having a desired size

were synthesized and used as sensitizer of TiO₂ nanoparticles. CdSe quantum dots have been widely studied and methods of controlling their size are well established.⁹⁻¹²⁾ The final size of CdSe dots was controlled by changing the concentration of the Cd and Se precursors. For sensitization of TiO₂, CdSe quantum dots, the sizes of which were 5.5 ± 0.4 nm, with a corresponding band gap of 2.08 eV were used. CdSe quantum dots/TiO₂ photoelectrodes were then applied for use in photovoltaic cells.

2. Experimental

CdSe quantum dots were synthesized by rapidly injecting a solution of dimethylcadmium (Me₂Cd) (Strem) and selenium (99.999%, Aldrich) in trioctylphosphine (TOP) (95%, Aldrich) into trioctylphosphine oxide (TOPO) (90%, Fluka) at 350°C with subsequent heating at 250-280°C. Complete details have been described elsewhere.⁹⁾ The final size of the CdSe dots was controlled by changing the concentration of Cd and Se precursors when the precursors were injected under conditions of maintaining the temperature of the TOPO. The growth of CdSe quantum dots was achieved by secondary injection of concentrated precursors into the solution to obtain the desired size (5.5 nm) with an acceptable size distribution. After washing and removing the TOPO, monodispersed CdSe quantum dots were produced, dispersed in hexane, and were used as sensitizers of TiO₂.

Nanocrystalline TiO₂ films were prepared as described elsewhere.^{2,13)} A slurry was prepared by mixing commercial TiO₂ powders (P25, Degussa) with Triton X-100 and acetylacetone and the slurry was then deposited onto conducting glass (F-doped SnO₂ (FTO), Asahi glass). After air drying, the TiO₂ films were sintered at 425°C for 1 h. For adsorption

*E-mail: ysung@snu.ac.kr

of CdSe quantum dots to TiO₂ electrodes, the electrodes were immersed into a colloidal solution of CdSe quantum dots in hexane. The adsorption process required several hours before the electrodes became opaque or optically scattered.

In the photoelectrochemical cell configuration, CdSe/TiO₂ electrodes were employed in a sandwich-type cell incorporating a Pt sputtered indium tin oxide (ITO) coated glass and a non aqueous electrolyte consisting of 0.3 M LiI and 0.03 M I₂ in an acetonitrile solution. The cell was not sealed, but simply pressed and fixed by clamps. The cell was tested under AM 1.5 solar conditions using Xe (Müller, 500 W) lamp and an AM 1.5 filter without an IR or UV cut off. The photochemical behavior was investigated by means of a 1287A potentiostat/galvanostat (Solatron).

Optical absorption spectra of CdSe quantum dots were collected at room temperature on a Hewlett-Packard 8452 diode array spectrometer using 1 cm quartz cuvettes. Photoluminescence experiments were carried out on an ACTON spectrometer (SpectraPro-300i) connected to a photomultiplier tube (Acton Research, PD-438) with a Xe lamp as an excitation source connected with another monochromator (SpectraPro-150i). Wide angle XRD patterns were obtained using a Rigaku X-ray diffractometer. To investigate the optical properties of CdSe/TiO₂ electrodes, absorbance experiments were carried out using a UV-Visible spectrophotometer (Cary 1E, Varian). The morphologies and compositions of the films were observed by SEM (S-4700, Hitachi) and EDX (Digital Instruments). Transmission electron microscopy (TEM) images of CdSe quantum dots were obtained using a Philips technai F 20 electron microscope. CdSe quantum dots, dissolved in hexane, were dropped onto the thin amorphous carbon supported by a copper grid and dried at 60°C in the vacuum for TEM images.

3. Results and Discussion

Fig. 1 shows the absorbance (dot line) and photoluminescence (solid line) of CdSe quantum dots in hexane. The absorbance of the CdSe quantum dots showed a broad spectrum having a peak at 596 nm with a corresponding band

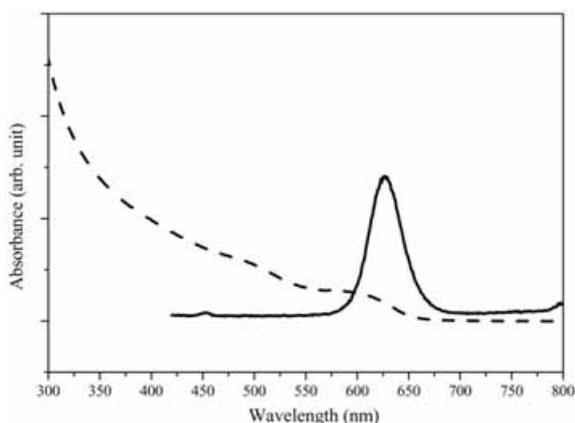


Fig. 1. Absorbance and photoluminescence of CdSe quantum dots with a size of 5.5 ± 0.4 nm.

gap of 2.08 eV. The sizes of CdSe quantum dots could be estimated from the absorbance values. In the tight confinement limit (Bohr diameter of CdSe is about 6 nm), the bandgap size is dependent on the radius (R) of particles based on equation (1).¹⁴⁾

$$E(R) = E_g + \frac{h^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{4\pi\epsilon R} \quad (1)$$

This equation depends upon known bulk parameters: two effective masses, m_e (0.13 m) and m_h (0.6 m), the ϵ is product of ϵ_r (9.7) and ϵ_0 (The values of parameters are taken from the CRC Handbook.¹⁵⁾ The bandgap size of bulk CdSe is 1.74 eV, as a result, the size of the CdSe quantum dots is approximately 5.6 nm, based on the above equation. The photoluminescence of CdSe quantum dots was measured using an excitation wavelength of 550 nm. Fig. 1 shows the photoluminescence of CdSe quantum dots having an excitation spectrum in the range of 580 to 680 nm at a maximum

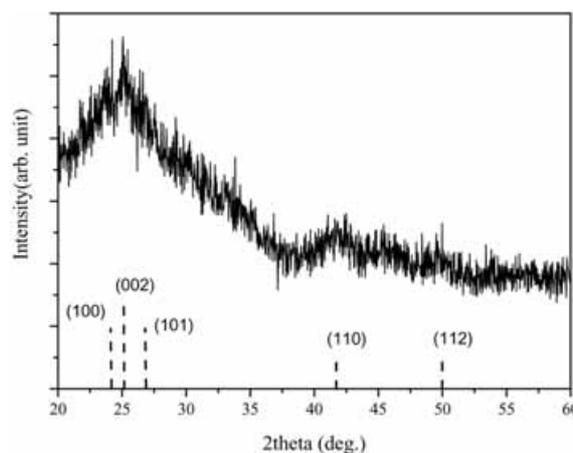


Fig. 2. XRD spectra of CdSe quantum dots.

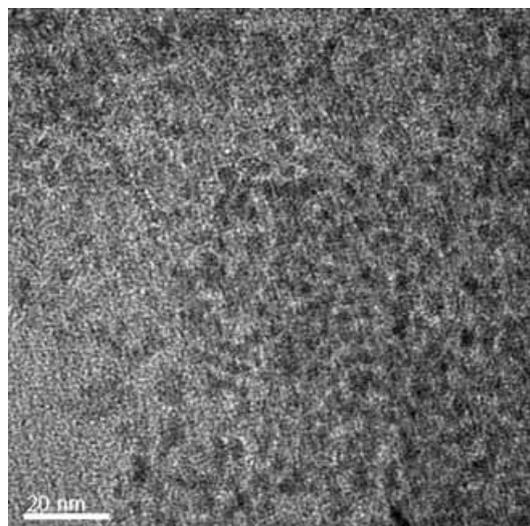


Fig. 3. TEM image of CdSe quantum dots.

emission of approximately 630 nm. Narrow emission line widths indicate the growth of crystallites with few electronic defect sites. The sizes were confirmed by investigating XRD measurements, as shown in Fig. 2. The diameter of the CdSe quantum dots was approximately 5.4 nm based on the (110) reflection at 2θ of 41.95° . The main (002) reflection of the CdSe at $2\theta = 25.34^\circ$ was not used because it was obscured by overlapping (100) and (101) reflections. The sizes of the CdSe quantum dots were confirmed by TEM, as shown in Fig. 3. From the TEM images, the average size and deviation of CdSe quantum dots was about 5.5 nm and ± 0.4 nm, respectively. This is in good agreement with XRD and absorbance data. The success in fabrication of CdSe quantum dots with a size of 5.5 ± 0.4 nm was verified by XRD and the sizes of quantum dots were investigated by XRD, TEM, and absorbance.

CdSe quantum dots were adsorbed on a nanocrystalline TiO_2 electrode having a thickness of about $5 \mu\text{m}$ for a photovoltaic cell. Fig. 4 shows the absorption spectra of the TiO_2 electrode and CdSe quantum dots which are adsorbed to the TiO_2 electrode. The absorption spectrum of CdSe quantum dots on the TiO_2 electrode was coincident with the combination of the spectra of the TiO_2 electrode and the CdSe quantum dots. In the absorption spectrum, the absorption of CdSe quantum dots in the visible range was not high in comparison with a typical dye adsorbed to a TiO_2 electrode. This result is presumably caused by less loading of sensitizer, quantum dots when compared to organic dyes. This may result in a low photocurrent due to a low light-harvest and conversion to current, as mentioned below.

The surface coverage of CdSe quantum dots onto TiO_2 electrodes was observed by means of SEM, as shown in Fig. 5. Fig. 5a shows an SEM image of a TiO_2 electrode and fig. 5b shows an SEM image of CdSe quantum dots adsorbed to a TiO_2 electrode, in which the quantum dots (small spots having a brighter color than TiO_2) were uniformly adsorbed and covered the surface of the TiO_2 electrode. But, this SEM image is not clear to figure out adsorption of quantum dots on TiO_2 surface. To make sure, the adsorption of CdSe quantum

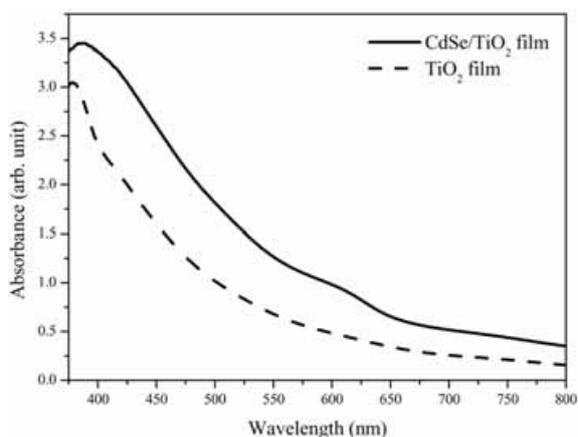
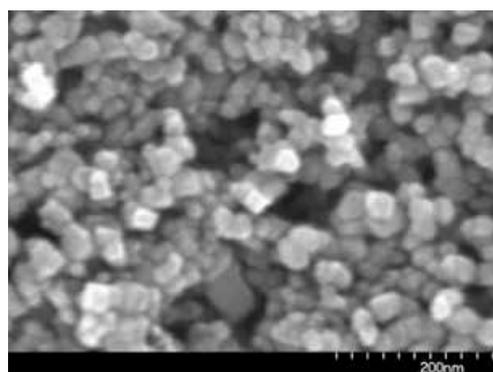
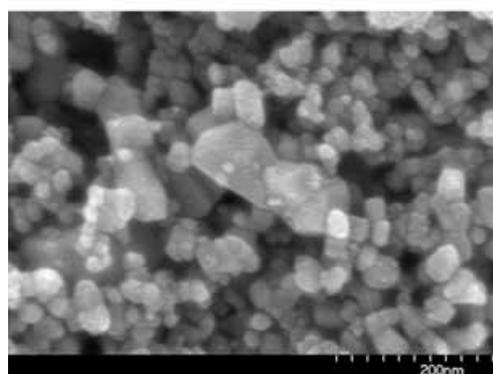


Fig. 4. Absorption spectra of a nanocrystalline TiO_2 film on a FTO (dashed line) and CdSe quantum dots on a TiO_2 film (solid line).

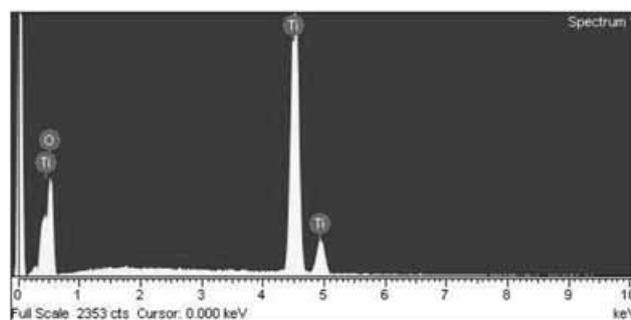


(a)

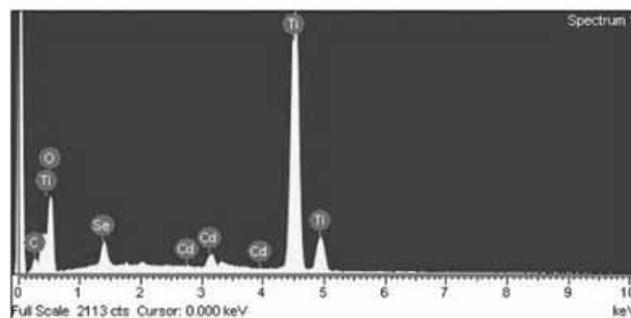


(b)

Fig. 5. SEM images: (a) nanocrystalline TiO_2 film on a FTO, and (b) CdSe quantum dots adsorbed to a TiO_2 film.



(a)



(b)

Fig. 6. EDX data: (a) nanocrystalline TiO_2 film on FTO, and (b) CdSe quantum dots adsorbed to a TiO_2 film.

dots onto the TiO_2 electrode was confirmed by EDX, as shown in Fig. 6. The EDX data for a TiO_2 electrode and a CdSe/TiO_2 electrode are shown in Fig 6(a) and (b), respectively. Cd and Se elements, which are not shown in the EDX of the TiO_2 electrode, appear in the EDX of CdSe/TiO_2 electrode. It is known that the pores of a TiO_2 are sufficiently large for small quantum dots to penetrate and are loaded in the TiO_2 .⁸⁾ CdSe quantum dots were well adsorbed into the TiO_2 electrode in this work.

In the photoelectrochemical cell configuration, CdSe quantum dots adsorbed TiO_2 electrodes were employed in a sandwich-type cell incorporating a Pt sputtered ITO and a non aqueous electrolyte including I^-/I_3^- . The current density-voltage characteristics of the photovoltaic cell using CdSe quantum dots under conditions of illumination are shown in Fig. 7. Open-circuit voltage (V_{oc}) and short circuit current density (J_{sc}) of the cell under $10 \text{ mW}/\text{cm}^2$, AM 1.5 solar conditions was 0.59 V and $88 \text{ } \mu\text{A}/\text{cm}^2$, respectively. The corresponding fill factor (FF) and efficiency for energy conversion (η) of the

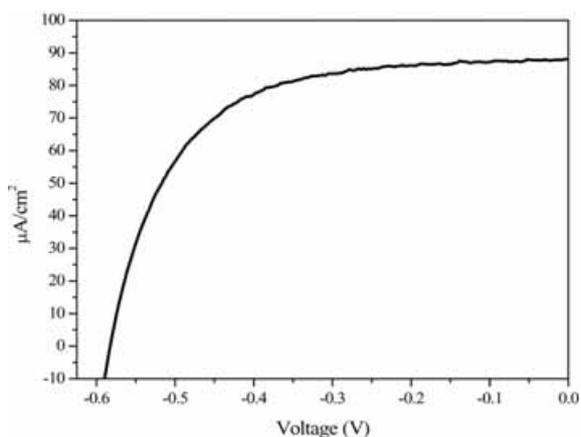


Fig. 7. Current-voltage characteristics of a photovoltaic cell using a CdSe quantum dots/ TiO_2 photoelectrode. The counter electrode is Pt-coated ITO-glass. The electrolyte consists of 0.3 M LiI and 0.03 M LiI_2 in acetonitrile. The cell was tested under conditions of $10 \text{ mW}/\text{cm}^2$, AM 1.5 solar.

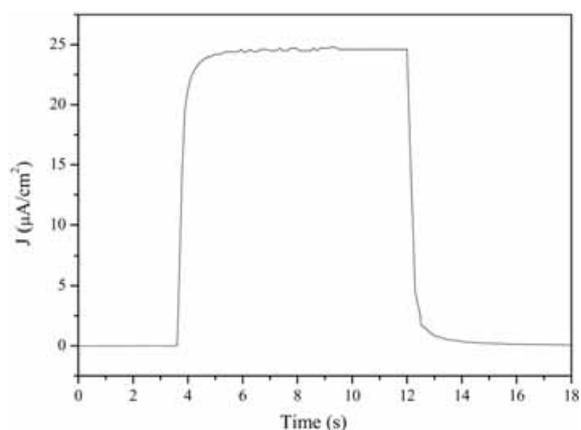


Fig. 8. Current response to light (AM 1.5, $2 \text{ mW}/\text{cm}^2$) at a potential of 0 V .

photovoltaic cell was 62% and 0.32%, respectively. In a view of stability, the efficient I^-/I_3^- redox system could not give stability in quantum dots-sensitized cells because of a fast dissolution of quantum dots. So, finding and incorporating alternative good redox couple for quantum dots-sensitized solar cells is under issue. The reason of the low efficiency with respect to energy conversion in photoelectrochemical cells using quantum dots such as the high photoconductivity of quantum dots / TiO_2 films was introduced by Zaban et al.⁸⁾ In our work, the low loading of CdSe quantum dots in the range of visible light constitutes another important reason for the low efficiency of energy conversion because the size of quantum dots is much larger than sensitizers. The efficiency of energy conversion is the product of three key factors: (a) light harvesting efficiency (related to a spectral and photo-physical properties of sensitizers), (b) charge injection yield (related to a desorption of sensitizer or the excited state redox potential), and (c) charge collection efficiency (related to a structure and morphology of TiO_2 films).¹⁶⁻¹⁷⁾ The light harvesting efficiency of CdSe quantum dots was lower than that of the dye because the absorption of visible light was low as evidenced by the absorption spectrum as mentioned above. The charge injection yield might have no or little effect on the low efficiency of energy conversion. The charge transfer from CdSe quantum dots to TiO_2 films was indirectly defined by investigating photocurrent response. When the pulse of light source ($2 \text{ mW}/\text{cm}^2$ with AM 1.5 filter) was turned onto the photovoltaic cell comprised of CdSe/TiO_2 photoelectrode, a photocurrent response was shown in Fig. 8. The photocurrent at the moment of illumination was generated in below 1 sec. This rapid response of photocurrent indicates a rapid charge injection. When the light was turned off, the current decayed to zero after a longer time, in excess of 15 sec, in comparison with the moment of illumination. The reason for this is the long lifetime of injected electrons. The charge collection efficiency is dependent on the rapid recombination of injected electrons into TiO_2 with redox mediator.¹⁷⁾ The fill factor of the photovoltaic cell comprised of a CdSe/TiO_2 photoelectrode was not low, as mentioned above. Thus, the low light harvesting due to low loading of sensitizers was a major factor and made the efficiency of energy conversion to be low value.

4. Conclusions

CdSe quantum dots with a desired size were fabricated and used as sensitizers of photovoltaic cells. CdSe quantum dots, as the sensitizers, were adsorbed to TiO_2 and open-circuit voltage (V_{oc}) and short circuit current (I_{sc}) of the cell including CdSe quantum dots under $10 \text{ mW}/\text{cm}^2$, AM 1.5 solar conditions were found to be 0.59 V and $88 \text{ } \mu\text{A}/\text{cm}^2$, respectively. The corresponding fill factor (FF) and efficiency for energy conversion (η) of the cell was 62% and 0.32%, respectively. However, the efficiency of the photovoltaic cell was much low in comparison with typical dye-sensitized solar cells. This result may be induced from low light harvesting efficiency of CdSe quantum dots in visible light due to low

loading of quantum dots. However, CdSe quantum dots can be used for supplement of dye or other quantum dots such as CdS to increase the efficiency of photovoltaic cells. Studies directed at addressing this issue are now in progress.

Acknowledgments

This work was supported by the Energy Research Center for Energy Conversion and Storage and the Sol-Gel Innovation Project (SOLIP) funded by Ministry of Commerce, Industry, and Energy (MOCIE), and the Brain Korea 21 project from the Ministry of Education.

References

1. B. O'Regan and M. Grätzel, "A low-cost, high efficiency solar cell based on dye-sensitized colloidal TiO₂ films" *Nature*, **353**, 737 (1991).
2. M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry Backer, E. Mueller, P. Liska, N. Vlachopoulos, and M. Grätzel, "Conversion of Light to Electricity by *cis*-X₂Bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium(II) Charge-Transfer Sensitizers (X = Cl-, Br-, I-, CN-, and SCN-) on Nanocrystalline TiO₂ Electrodes" *J. Am. Chem. Soc.*, **115**, 6382 (1993).
3. C. J. Barbé, F. Arendse, P. Comte, M. Jirousek, F. Lenzenmann, V. Shklover, and M. Grätzel, "Nanocrystalline Titanium Oxide Electrodes for Photovoltaic Applications" *J. Am. Ceram. Soc.*, **80**, 3157 (1997).
4. R. Vogel, P. Hoyer, and H. Weller, "Quantum-Sized PbS, CdS, Ag₂S, Sb₂S₃, and Bi₂S₃ Particles as Sensitizers for Various Nanoporous Wide-Bandgap Semiconductors" *J. Phys. Chem.*, **98**, 3183 (1994).
5. R. Plass, S. Pelet, J. Krueger, M. Grätzel, and U. Bach, "Quantum Dot Sensitization of Organic-Inorganic Hybrid Solar Cells" *J. Phys. Chem. B*, **106**, 7578 (2002).
6. L. M. Peter, K.G. U. Wijayantha, D. J. Riley, and J. P. Waggett, "Band-Edge Tuning in Self-Assembled Layers of Bi₂S₃ Nanoparticles Used To Photosensitized Nanocrystalline TiO₂" *J. Phys. Chem. B*, **107**, 8378, (2003).
7. P. Yu, K. Zhu, A. G. Norman, S. Ferrere, A. J. Frank, and A. J. Nozik, "Nanocrystalline TiO₂ Solar Cells Sensitized with InAs Quantum Dots" *J. Phys. Chem. B*, **110**, 25451, (2006).
8. A. Zaban, O. I. Miäiä, B. A. Gregg, and A. J. Nozik, "Photosensitization of Nanoporous TiO₂ Electrodes with InP Quantum Dots" *Langmuir*, **14**, 3153 (1998).
9. C. B. Murray, D. J. Norris, and M. G. Bawendi, "Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites" *J. Am. Chem. Soc.*, **115(19)**, 8706 (1993).
10. M. Danek, K. F. Jensen, C. B. Murray, and M. G. Bawendi, "Synthesis of Luminescent Thin-Film CdSe/ZnSe Quantum Dot Composites Using CdSe Quantum Dots Passivated with an Overlayer of ZnSe" *Chem. Mater.*, **8(1)**, 173 (1996).
11. M. A. Hines and P. Guyot-Sionnest, "Synthesis and Characterization of Strongly Luminescing ZnS-Capped CdSe Nanocrystals" *J. Phys. Chem.*, **100**, 468 (1996).
12. X. Peng, J. Wickham, and A. P. Alivisatos, "Kinetics of II-VI and III-V Colloidal Semiconductor Nanocrystal Growth: "Focusing" of Size Distributions" *J. Am. Chem. Soc.*, **120(21)**, 5343 (1998).
13. S. -S. Kim, J. -H. Yum, and Y. -E. Sung, "Improved performance of a dye-sensitized solar cell using a TiO₂/ZnO/Eosin Y electrode" *Sol. Energy Mater. Sol. Cells*, **79**, 495 (2003).
14. G. Timp, "Nanotechnology", 264, Springer-Verlag, New York (1998).
15. D. R. Lide, "CRC Handbook of Chemistry and Physics 81st edition", 12-105, CRC Press, Boca Raton.
16. K. Kalyanasundaram and M. Grätzel, "Applications of functionalized transition metal complexes in photonic and optoelectronic devices" *Coord. Chem. Rev.*, **177**, 347 (1998).
17. J. van de Lagemaat, N. -G. Park, and A. J. Frank, "Influence of Electrical Potential Distribution, Charge Transport, and Recombination on the Photopotential and Photocurrent Conversion Efficiency of Dye-Sensitized Nanocrystalline TiO₂ Solar Cells: A Study by Electrical Impedance and Optical Modulation" *J. Phys. Chem. B*, **104(9)**, 2044 (2000).