

The Application of TiO₂ Hollow Spheres on Dye-sensitized Solar Cells

H. J. Cho and D. Jung*

Department of Chemistry and Institute of Basic Natural Sciences, Wonkwang University, Iksan, Jeonbuk 570-749, Korea

*E-mail: djung@wku.ac.kr

Received August 3, 2011, Accepted October 22, 2011

TiO₂ hollow spheres were fabricated by using SiO₂ as an inorganic template. Spherical SiO₂ particles were coated by TiO₂ through the nucleation process, and then the core SiO₂ part was eliminated by using HF solution. Finally, TiO₂ hollow spheres were obtained. The size of the TiO₂ hollow spheres was about 300-400 nm and the thickness of the hollow wall was about 20-30 nm. The hollow has several holes whose diameters were within 100-200 nm. Dye-sensitized solar cells fabricated by using the TiO₂ hollow spheres were characterized. The solar conversion efficiency of the cell was 8.45% when TiO₂ hollow spheres were used as a scattering material, while it was 4.59% when TiO₂ hollow spheres were used as a normal electrode material.

Key Words : Template method, Hollow TiO₂, Electronic materials, Dye-sensitized solar cells

Introduction

In recent years, the field of solar energy conversion to electricity and its storage has become one of the most interesting research fields. Among the different form of photovoltaic cells, the dye-sensitized solar cells (DSSCs) have attracted considerable attention over the past decade since they offer the possibility of low cost production of photovoltaic devices alternative to the conventional silicon-based junction devices¹⁻⁴ and also provide the opportunity to produce the transparent flexible devices. Typically, the electron collecting layer in these systems is a 10 nm thick nanocrystalline film comprising of three-dimensional network of interconnected semiconducting particles sintered onto a conductive glass substrate. As opposed to silicon-based devices where the semiconductor absorbs the light and transport the released charge carriers, the two tasks are separated in a DSSC system. Upon illumination, the dye molecules are excited and initial charge separation occurs by injection of an electron from the dye into the conduction band of the semiconductor resulting in charge separation. The oxidized dye is quickly reduced by the redox electrolyte before it can recapture the injected electron. Meanwhile, the injected electron is transported in the conduction band of the semiconductor by diffusion⁵ to the charge collecting conductive glass substrate from where it performs useful work in an external circuit before returning to the cell through the counter electrode to reduce the electrolyte.

For preparing high efficiency DSSCs, a high surface area of the nanostructured TiO₂ layer is essential, because it allows adsorption of sufficiently large number of dye molecules needed for efficient light harvesting. Extensive research has been conducted on TiO₂ materials with various structures, such as nanowire,⁶ nanorod,⁷ and nanotube.⁸⁻¹⁰ Besides the high surface area of the TiO₂ layer, good connections between TiO₂ grains as well as a good adhesion to transparent conducting oxide (TCO) are required to

diminish the reactions of photogenerated electrons with electrolyte material and to assure good electrical conductivity. Therefore, the optimization of the morphology of TiO₂ is a prerequisite for the realization of high efficiency DSSCs.^{11,12} The conventional DSSC is made from nanoporous TiO₂ photoelectrode with organo-ruthenium dye as a light harvesting component. The second generation of DSSCs adopts double electrode system consisting of a semiconducting layer which is made of TiO₂ particles having about 15-20 nm-sized diameter and a light scattering layer which is made of TiO₂ particles having about 400 nm-sized diameter.¹³⁻¹⁷ The purpose of using larger size TiO₂ particles is to increase the conversion efficiency by absorbing scattered light. The morphology of TiO₂ can be widely tuned to achieve the best efficiency. Grätzel *et al.* introduced mesoporous TiO₂ particulate films as semiconducting photoanodes to enhance the effective surface area so as to absorb more dye molecules and thus more light absorption which leads to better efficiency. The photoelectrodes are commonly the three-dimensional networking of interconnected TiO₂ nanoparticles, the band gap of which matches well with the sensitized dyes. TiO₂ photoanodes are also easily prepared through environmental design at low cost.

The TiO₂ hollow spheres were synthesized by using SiO₂ as a template. The obtained hollow powders were applied for preparing DSSCs to see if they could absorb more dye molecules using their empty spaces. In this paper, the preparation of TiO₂ hollow spheres and their applications on DSSCs are investigated.

Experimental

Preparation and Characterization of TiO₂ Hollow Spheres. An appropriate amount of TiCl₄ was added slowly into the flask which was filled with distilled water, under magnetic stirring. The temperature of the solution was kept under 5 °C by using an ice-bath. After adding TiCl₄

thoroughly, the flask was left with continuous stirring for 1 hour to produce TiOCl₂ mother solution. 5 g of purchased SiO₂ particles whose diameters ranged from 200 to 400 nm were dispersed into water in a 300 mL vial, and after 150 mL of already made TiOCl₂ mother solution was added into the vial. The capped vial was kept at 80 °C for 2 hours under magnetic stirring to obtain TiO₂-coated SiO₂ particles. The final white precipitate was filtered and washed with de-ionized water several times. The dried particles were dispersed into already prepared 4.8% HF solution under vigorous stirring for 1 hour to eliminate SiO₂ so that TiO₂ hollow spheres were prepared. After the reaction, the sediment was filtered, washed and dried. The sample obtained after the treating with HF solution was annealed at 500 °C for 2 hours.

The crystal structures and morphologies of the products were characterized with an X-ray diffractometer (XRD) and a scanning electron microscopy (SEM), before and after the treatment with HF solution. The amount of residual SiO₂ inside the TiO₂ hollow spheres was investigated by analyzing with an X-ray fluorescence spectrometer (XRF, Bruker S4-Pioneer), also before and after the treatment with HF solution.

Preparation of Solar Cell with TiO₂ Hollow Spheres.

Since the size of the prepared TiO₂ hollow spheres is about 300–400 nm, this sample was tested for two different applications; it was used as a scattering material (type B) and was used as an electrode material (type C and type D). When it was used as an electrode material, also two different types of cells were prepared; the first cell type was prepared by using TiO₂ hollow spheres as an electrode material without any scattering layer (type D) and the other cell type was with a scattering layer which was made of 400 nm sized spherical anatase TiO₂ (type C). When the sample was used as a scattering material, the electrode layer was constructed by using 13 nm sized anatase TiO₂ particles. For comparison, the standard cell which was made of 13 nm anatase TiO₂ film as an electrode layer and 400 nm sized anatase TiO₂ film as a scattering layer (type A), was also fabricated. Before preparing each layer, fluorine-doped tin oxide (FTO) glass plates (Pilkington TEC Glass-TEC 8, Solar 2.3 mm thickness) were cleaned in a detergent solution using an ultrasonic bath for 30 min and then rinsed with water and ethanol. A transparent nanocrystalline electrode layer was prepared on the FTO glass plates by using a doctor blade printing of 13 nm sized TiO₂ (type A: Solaronix, Ti-Nan-oxide T/SP) or hollow TiO₂ paste (type C: with a scattering layer; type D: without a scattering layer), which was then dried for 2 h at 25 °C. The TiO₂ electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and finally at 500 °C for 15 min. The gradual temperature raising is needed to evaporate the organic solvents step by step so that the coated TiO₂ layer does not make any crack. The thickness of the transparent layer was measured by using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, CA). The paste containing 400 nm sized anatase particles (type A, C: CCIC,

PST-400C) and the paste made of hollow TiO₂ particles (type B, C) as scattering layers were deposited by means of doctor blade printing, and then dried for 2 h at 25 °C. The TiO₂ scattering layers were also gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min, respectively. The TiO₂ electrodes were immersed again in TiCl₄ aqueous solution at 70 °C for 30 min and sintered at 500 °C for 30 min. Then, they were immersed in N719^{18,19} dye solution (0.3 mM in Ethanol, EtOH) and kept at room temperature for 24 h. Spherical TiO₂ (25 nm size) and hollow TiO₂ samples were immersed in dye solution (0.3 mM in Ethanol) for same time, and then each sample was filtered and dried. Dye absorbed in each sample was desorbed by dispersing the powders in ethanol with magnetic stirring. Two ethanol solutions were investigated by using a UV spectroscopy (Shimadzu UV 2450). Finally, the amount of dye absorbed in each sample was quantitatively examined by analyzing the peak area. FTO plates for the counter electrodes were cleaned in an ultrasonic bath in H₂O, acetone, and 0.1 M aqueous HCl, subsequently. The counter electrodes were prepared by placing a drop of H₂PtCl₆ solution (2 mg Pt in 1 mL ethanol) on an FTO plate and heating it (at 400 °C) for 15 min. The dye-adsorbed TiO₂ electrodes and the Pt counter electrodes were assembled into a sealed sandwich-type cell by heating at 80 °C using a hot-melt ionomer film (Surlyn) as a spacer between electrodes. A drop of the electrolyte solution was placed in the drilled hole of the counter electrode and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass (0.1 mm thickness). The electrolyte was then introduced into the cell, which was composed of 0.6 M 3-hexyl-1,2-dimethyl imidazolium iodide, 0.05 M I₂, 0.1 M LiI and 0.5 M *tert*-butylpyridine in acetonitrile. The photocurrent-voltage (*I*-*V*) curves were measured using a source measure unit under irradiation of white light from a 1,000 W Xenon lamp (class AAA K3000 solar cell I-V measurement system). The incident light intensity and the active cell area were 100 mW/cm² and 1.0 cm², respectively. The I-V curves were used to calculate the short-circuit current (*I*_{sc}), open-circuit voltage (*V*_{oc}), and overall conversion efficiency (η_{eff}) of DSSCs. The standard spectral coincidence of this equipment was AM 1.5G. The solar simulator was calibrated by using the KG5 filtered Si reference solar cell.

Results and Discussion

Structure and Shape of the Particle. The XRD patterns of TiO₂-coated SiO₂ particles and TiO₂ hollow spheres after the elimination of SiO₂ are shown in Figure 1(a) and 1(b), respectively. Anatase-type TiO₂ and SiO₂ peaks are clearly shown in TiO₂-coated SiO₂ particles (see Fig. 1(a)). Sharp peaks positioned at typical 2 θ of anatase and SiO₂ represent the TiO₂-coated SiO₂ powders are successfully synthesized and crystallized. Although SiO₂ is surrounded by TiO₂, the typical SiO₂ peak at 2 θ = 27° is sharply appeared since the

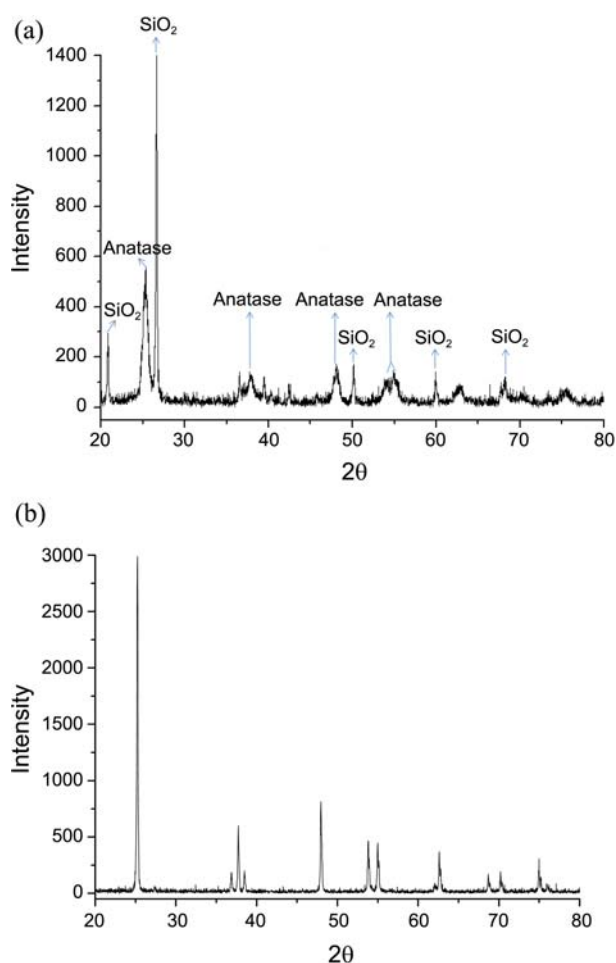


Figure 1. XRD pattern of (a) TiO₂-coated SiO₂ particles and (b) hollow TiO₂ after the elimination of SiO₂. All anatase peaks showed in Fig. 1(a) are disappeared.

major component in the particle is SiO₂ before the HF treatment. Only typical peaks of anatase phase are shown in the XRD result after the elimination of SiO₂ by treating the particles in the HF solution, as represented in Fig. 1(b). All reflections are assigned to anatase structure of TiO₂ and are indexed on the basis of JCPDS card No. 21-1272. Any peak corresponding to second phase is not detected, which means that all SiO₂ was eliminated.

SEM images of particles before and after the treatment with HF solution are shown in Figure 2(a) and Fig 2(b), respectively. TiO₂ is coated well onto the surface of SiO₂ and the size of the TiO₂-coated particles is about 300 nm diameter before the treatment with HF solution. Although not shown, the size of the TiO₂-coated particles depends on the temperature of the solution and the nucleation time of TiO₂ on the surface of a SiO₂ particle. After the treatment with HF solution, the core material (SiO₂) was eliminated and finally the TiO₂-coated spheres became hollow-structured TiO₂ particles. The wall of the hollow TiO₂ consists of hundreds of small TiO₂ particles whose sizes are within 20 nm. The thickness of the hollow wall is about 20-30 nm and the hollow is open through a hole whose diameter is about 150 nm. TEM image of the sample also demonstrates that

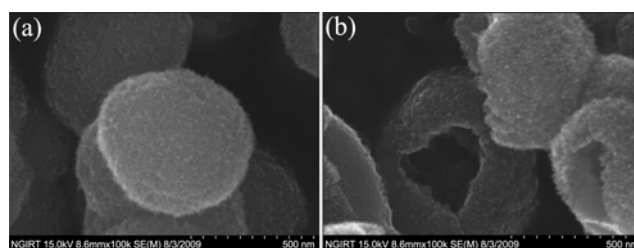


Figure 2. SEM images of (a) TiO₂-coated SiO₂ particles and (b) hollow TiO₂ after the elimination of SiO₂.

Table 1. XRF data of TiO₂ powders before and after the elimination of SiO₂

Element	Before elimination	After elimination
Ti	74.8%	99.8%
Si	24.0%	0.07%
Cl	1.0%	0%

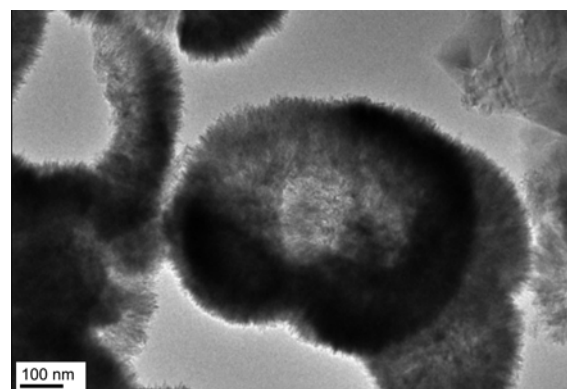


Figure 3. TEM image of hollow TiO₂.

the center of the particle is empty (see Fig. 3). The XRF analysis on the particles before and after the treatment with HF solution clearly shows that SiO₂ was completely eliminated after the treatment with HF solution (see Table 1). The SEM and TEM results are consistent with the XRF analysis data of TiO₂ hollow.

The UV spectroscopic data for the amount of dye absorbed by spherical and hollow TiO₂ samples are illustrated in Figure 4. The N719 dye shows typical absorbance peak at 230 nm in UV region. The peak area representing the amount of desorbed dye from spherical and hollow TiO₂ samples are 107 and 118, respectively. This means that hollow TiO₂ sample absorbs dye molecule more than 15% compared with spherical TiO₂ sample.

Application of the Synthesized Hollow TiO₂ Spheres to DSSCs. The performance of the DSSCs fabricated by using hollow TiO₂ powders was tested. Figure 5 shows the I-V characteristics of the cells made of hollow TiO₂ powders and that of a reference cell. The solar conversion efficiency of the reference cell (type A) which was prepared with 13 nm anatase as an electrode layer and 400 nm anatase as a scattering layer, was 9.29 %. The short-circuit photocurrent

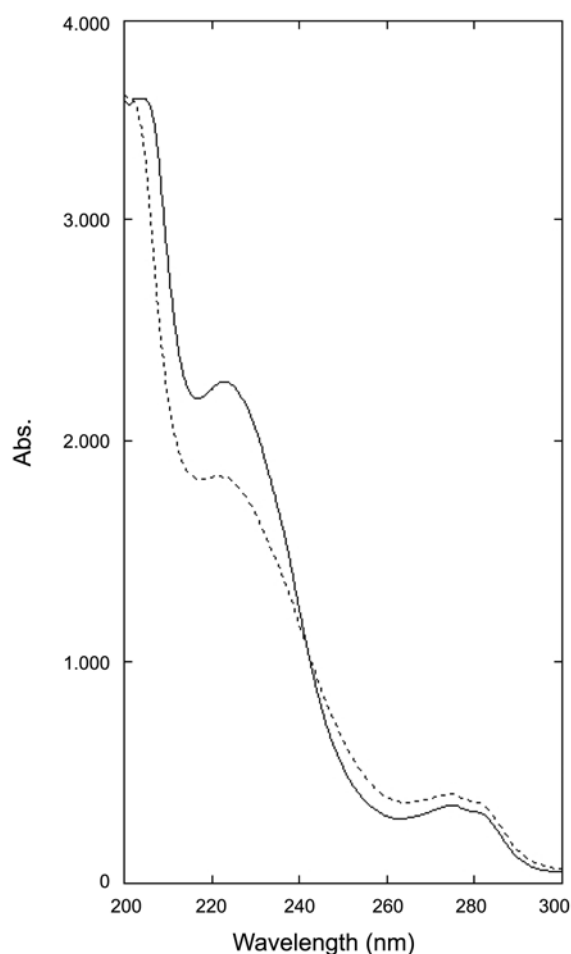


Figure 4. UV spectroscopy data for the amount of desorbed dye from hollow TiO₂ (solid line) and spherical TiO₂ (dotted line).

density (J_{sc}) and open circuit photovoltage (V_{oc}) were 17.8 mA/cm² and 0.73 V, respectively as shown in Figure 5(a). This result is consistent with the values obtained by other DSSCs research group when the same dye was used. The solar conversion efficiency of the cell was decreased to 3.58% when the hollow TiO₂ powders were used as an electrode layer material without any scattering layer (type D) as illustrated in Figure 5(d). The short-circuit photocurrent density (J_{sc}) and open circuit photovoltage (V_{oc}) were also decreased to 7.17 mA/cm² and 0.70 V, respectively (see Fig. 5(d)). The solar conversion efficiency of the cell (type C) which was fabricated with TiO₂ hollow spheres and 400 nm anatase spherical powders as an electrode layer and a scattering layer, respectively, was 4.59% as shown in Figure

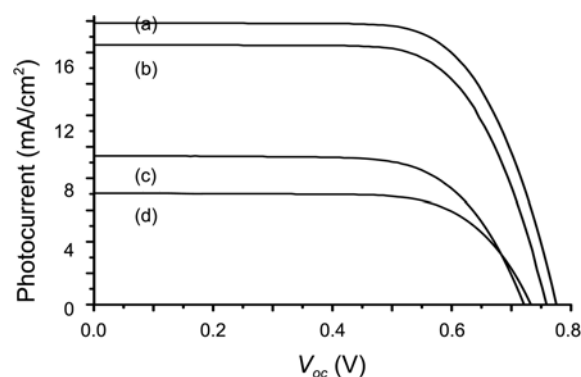


Figure 5. I-V characteristics of the different cells made of (a) 13 nm anatase and 400 nm anatase as electrode and scattering layer (type A), (b) 13 nm anatase and hollow TiO₂ as electrode and scattering layer (type B), (c) hollow TiO₂ and 400 nm anatase as electrode and scattering layer (type C), and (d) hollow TiO₂ only (type D).

5(c). Although the efficiency of this cell is higher than that of type D cell, it is still low compared with that of the reference cell. This means that large size (> 300 nm) anatase is not appropriate for the electrode material in a DSSC in spite of the shape of the powder. The conversion efficiency of the cell (type B) prepared with 13 nm anatase and hollow TiO₂ powders as electrode material layer and scattering layer, respectively, is shown in Figure 5(b). The solar conversion efficiency of type B cell is 8.45%, and the short-circuit photocurrent density (J_{sc}) and open circuit photovoltage (V_{oc}) were 16.5 mA/cm² and 0.72 V, respectively, which is similar to those of the reference cell. This result clearly shows that the size of the electrode material should be small to have the large surface area. The results of solar conversion efficiency, the short-circuit photocurrent density (J_{sc}) and open circuit photovoltage (V_{oc}) of each cell is summarized in Table 2. The photocatalytic efficiency of the hollow TiO₂ powders was slightly higher than that of P-25 sample.²⁰ It was proposed in the reference²⁰ that the hollow shape could contribute to absorb more light by using its empty space thereby increasing its photocatalytic efficiency. The DSSC result is contrary to the expectation that the solar conversion efficiency of the cell made of hollow-type TiO₂ spheres might be also increased by absorbing more dye molecules inside their empty cavities. It could be concluded, therefore, that submicron TiO₂ hollow spheres themselves cannot increase the solar efficiency of the DSSC as long as they were used as electrode material although they may absorb more amount of dye molecule.

Table 2. Characteristics of different solar cells

Cell type	V_{oc} (V)	J_{sc} (mA/cm ²)	η (%)
Reference Cell (13 nm TiO ₂ + 400 nm TiO ₂)	0.78	17.8	9.29
Hollow TiO ₂ as an electrode layer without a scattering layer	0.74	7.17	3.58
Hollow TiO ₂ + 400 nm TiO ₂ as a scattering layer	0.72	9.49	4.59
13 nm TiO ₂ + hollow TiO ₂ as a scattering layer	0.76	16.5	8.45

Conclusions

TiO₂ hollow spheres were successfully fabricated by using an inorganic template. The thickness of the hollow wall is about 20-30 nm and the hollow is open through a hole whose diameter is about 150 nm. As the nucleation time of the mother solution (TiOCl₂) increased, the thickness of the hollow wall also increased. It is important, therefore, to control the time and the temperature of the crystallization process to obtain the appropriate TiO₂ hollow spheres. Obtained samples were applied for the fabrication of dye-sensitized solar cells. Since the size of the prepared TiO₂ hollow spheres is about 300-400 nm, this sample was tested in several ways; the sample was used as an electrode material (type C and type D) and was used as a scattering material (type B). When it was used as an electrode material, also two different type cells were prepared; first cell type was prepared by using TiO₂ hollow spheres as an electrode material without any scattering layer (type D), and the other cell type was prepared by adding a scattering layer which was made of 400 nm sized spherical anatase TiO₂ (type C). The results of solar conversion efficiencies, the short-circuit photocurrent densities (J_{sc}) and open circuit photovoltages (V_{oc}) of type C and type D cells were inferior to those of the type A reference cell and type B cell. The solar conversion efficiency of type B cell was similar to that of the reference cell. In conclusion, the solar conversion efficiency of the cell was low when TiO₂ hollow spheres were used as an electrode layer.

Acknowledgments. This work was supported by Wonkwang Research Fund of 2011. Authors thank to professor

Ko at Korea university for invaluable discussions.

References

1. Kay, A.; Grätzel, M. *Sol. Energy Mater. Sol. Cells* **1996**, *44*, 99.
2. O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
3. Nazeeruddin, M. K.; Pechy, P.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613.
4. Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.
5. Grätzel, M. *Inorg. Chem.* **2005**, *44*, 6841.
6. Adachi, M.; Murata, Y.; Takao, J.; Jiu, J. T.; Sakamoto, M.; Wang, F. M. *J. Am. Chem. Soc.* **2004**, *126*, 14943.
7. Jiu, J. T.; Isoda, S.; Wang, F. M.; Adachi, M. *J. Phys. Chem. B* **2006**, *110*, 2087.
8. Mor, G. K.; Shankar, K.; Paulose, M.; Varghese, O. K.; Grimes, C. A. *Nano Lett.* **2006**, *6*, 215.
9. Paulose, M.; Shankar, K.; Varghese, O. K.; Mor, G. K.; Hardin, B.; Grimes, C. A. *Nanotechnology* **2006**, *17*, 1446.
10. Mor, G. K.; Varghese, O. K.; Paulose, M.; Shankar, K.; Grimes, C. A. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2011.
11. Park, N. K.; Schlichthol, G.; van de Lagemaat, J.; Cheong, H. M.; Mascarenhas, A.; Frank, A. J. *J. Phys. Chem. B* **1999**, *103*, 3308.
12. Grunwald, R.; Trbutsch, H. *J. Phys. Chem. B* **1997**, *101*, 2564.
13. Ferber, J. Dissertation, University of Feiberg, 1999.
14. Ferber, J.; Luther, J. *Sol. Energy Mater. Sol. Cells* **1998**, *54*, 265.
15. Rothenberger, G.; Comte, P.; Grätzel, M. *Sol. Energy Mater. Sol. Cells* **1999**, *58*, 321.
16. Wang, Z. S.; Kawauchi, H.; Kashima, T.; Arakawa, H. *Coordinat. Chem. Rev.* **2004**, *248*, 1381.
17. Hore, S.; Vetter, C.; Kern, R.; Smit, H.; Hinsch, A. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 1176.
18. Choi, H.; Baik, C.; Kang, S. O.; Ko, J.; Kang, M.-S.; Nazeeruddin, M. K.; Grätzel, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 327.
19. Kim, C.; Choi, H.; Kim, S. H.; Baik, C.; Song, K. H.; Kang, M.-S.; Kang, S. O.; Ko, J. *J. Org. Chem.* **2008**, *73*, 7072.
20. Cho, H. J.; Hwang, P.-G.; Jung, D. *J. Phys. Chem. Solids* submitted.