Nanoscale Research Letters
a SpringerOpen Journal

**NANO EXPRESS**                                                    **Open Access**

# Effect of TiO$_2$ rutile nanorods on the photoelectrodes of dye-sensitized solar cells

Young Hee Jung[1], Kyung-Hee Park[2], Jeong Seok Oh[3], Do-Heyoung Kim[1] and Chang Kook Hong[1,2*]

## Abstract

In order to enhance the electron transport on the photoelectrodes of dye-sensitized solar cells, one-dimensional rutile nanorods were prepared using electrospun TiO$_2$ nanofibers. The grain size of the nanorods increased with increasing temperature. Electrochemical impedance spectroscopy measurements revealed reduced interface resistance of the cells with the one-dimensional rutile nanorods due to the improved electron transport and the enhanced electrolyte penetration. Intensity-modulated photocurrent/photovoltage spectroscopy showed that the one-dimensional rutile nanorods provided the electrons with a moving pathway and suppressed the recombination of photogenerated electrons. However, an excessive quantity of rutile nanorods created an obstacle to the electrons moving in the TiO$_2$ thin film. The photoelectrode with 7 wt.% rutile nanorods optimized the performance of the dye-sensitized solar cells.

**Keywords:** One-dimensional TiO$_2$ nanorods, Photoelectrode, Electron transfer, Dye-sensitized solar cells

## Background

One-dimensional (1-D) structured TiO$_2$ nanorods show improved electrical and optical properties in the photoelectrodes of dye-sensitized solar cells (DSSCs) [1]. They can provide straight moving paths for electrons and reduce the $e^-/h^+$ recombination [2-4]. Further, they scatter sunlight so that the incident light stays longer in the cell [5]. As these properties enhance the solar energy conversion efficiency, much research into the effects of the 1-D structured TiO$_2$ on the photoelectrode have been conducted [6-8].

In principle, photoexcited electrons from dye molecules move on a TiO$_2$ nanocrystal undergoing a series of trapping and de-trapping events during diffusion. The 1-D nanorods, which are densely packed TiO$_2$ nanoparticles, could act as a single crystal and be involved in rapid electron transport, thereby reducing the chances for electron recombination. Furthermore, the TiO$_2$ film with random packing of 1-D rods helps the electrolyte to penetrate into the photoelectrode because of the porosity [9,10]. The enhanced interpenetration of electrolyte leads to the dye

regeneration by redox process of the electrolyte and enhances the energy conversion efficiency with improved photocurrent.

Few grain boundaries in the TiO$_2$ nanorods induce fast electron transport and decrease the electron recombination due to the reduced number of trapping sites in the interfaces [11]. In order to reduce grain boundaries in the nanorods, the crystal size should be increased. TiO$_2$ crystal structure (anatase and rutile) and size can be controlled by sintering temperature. The anatase phase has been reported to be developed at temperatures below 800°C, and above the temperatures, it transforms to the more stable rutile phase [12]. Also, the TiO$_2$ nanorods sintered at a high temperature have high crystallinity, meaning reduced grain boundaries and decreased trap sites. Electrons moving through the rutile structure undergo less stress because of the reduced number of trap sites on the grain boundaries [13,14]. In addition, the transported electrons can easily migrate from the rutile to anatase phase [15,16]. As the conduction band of the pure anatase phase is typically 0.2 eV more negative than that of the rutile phase, photoexcited electrons injected into the rutile phase migrate to the conduction band of the anatase phase, before passing through the external circuit. The resulting synergistic effects between the anatase and

* Correspondence: hongck@chonnam.ac.kr
[1]School of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, South Korea
[2]The Research Institute for Catalysis, Chonnam National University, Gwangju 500-757, South Korea
Full list of author information is available at the end of the article

Springer

rutile phases lead to energetic electron flows and enhanced photocurrents [17-19].

However, even though the rutile 1-D nanorods provide the electrons with a better moving path and improve electrolyte penetration, a large number of rutile phases simultaneously can become a barrier for electron transport [8]. The increased amount of rutile phase increases the probability of the moving electrons facing a higher energy level, which increases the internal resistance.

In this study, in order to make photoelectrodes with the 1-D rutile nanorods, the electrospun $TiO_2$ nanofibers were sintered at various temperatures. The photoelectrodes considerably improved the DSSC energy conversion efficiency, depending on the amount of $TiO_2$ nanorods. The intensity-modulated photocurrent spectroscopy, intensity-modulated photovoltage spectroscopy, charge-transfer resistance, and *I-V* characteristics of the DSSCs were investigated in order to study the effects of the rutile $TiO_2$ nanorods on the cell performance. The purpose of this study is to investigate the effects of the crystal size and amount of the rutile $TiO_2$ nanorods on the electron transport in the photoelectrodes of dye-sensitized solar cells.

## Methods

### Preparation of electrospun nanorods

Three grams of polyvinylpyrrolidone (PVP K90, $M_W$ = 130,000) was dissolved in 27 g of ethanol (Daejung Chemical & Metal Co., Ltd., Shiheung, South Korea), while the $TiO_2$ precursor was prepared by adding 12 ml of acetic acid (Kanto Chemical Co., In., Tokyo, Japan) and 12 ml of ethanol into 6 ml of titanium(IV) isopropoxide (Junsei Chemical Co., Ltd., Tokyo, Japan), successively. The solutions were mixed and stirred for 12 h to obtain homogeneity. The solution was loaded into a syringe (SGE Analytical Science, Ringwood, Victoria, Australia) under an applied voltage of 9 kV. $TiO_2$ nanofibers were electrospun on Al foil. The spinning rate was controlled by a syringe pump (KDS-100, KD Scientific, Holliston, MA, USA) at 2 ml/h. The tip-to-collector distance was maintained at 20 cm. The obtained $TiO_2$ nanofibers were calcined at 450°C, 650°C, 750°C, 850°C, and 1,000°C.
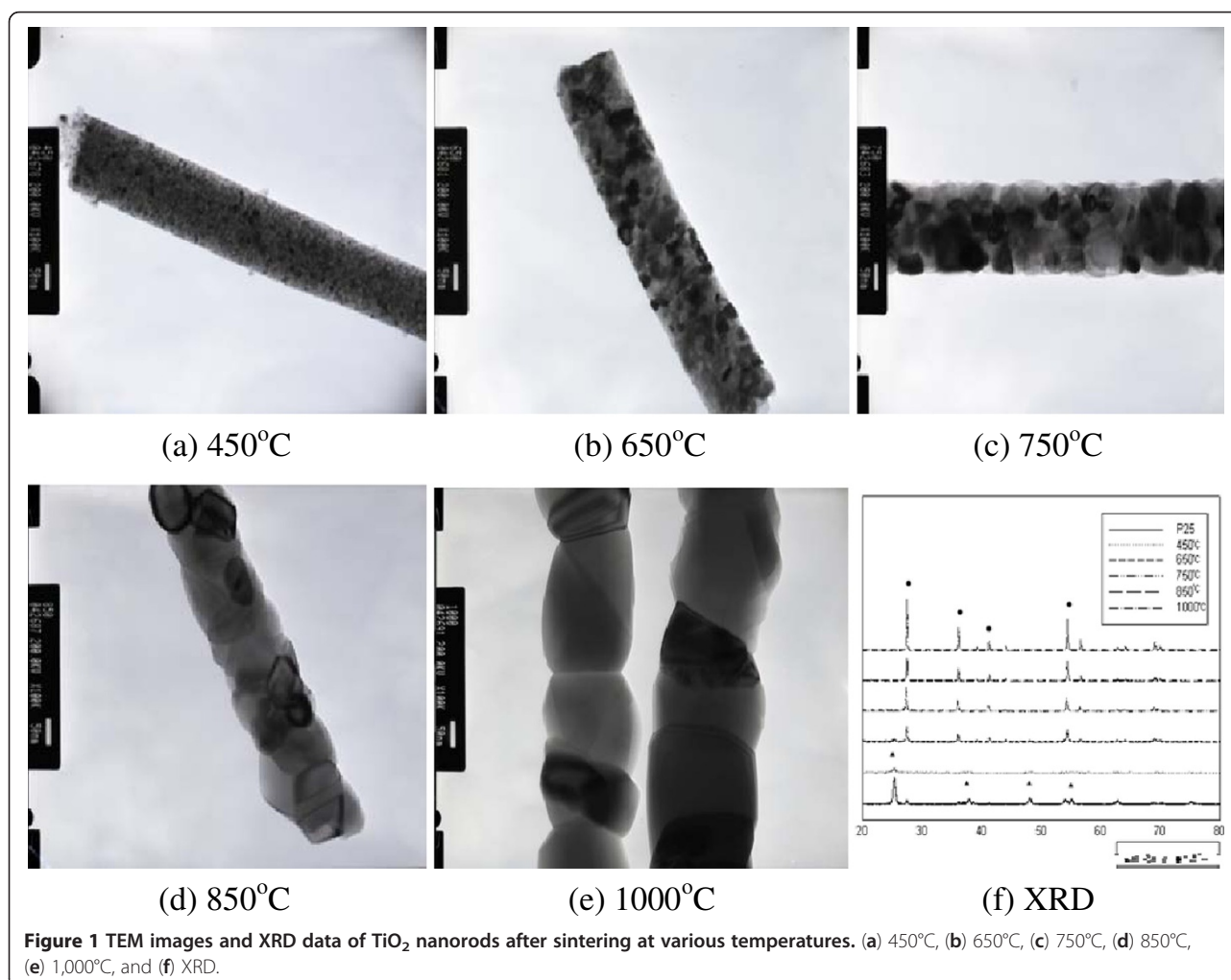


**Figure 1 TEM images and XRD data of TiO₂ nanorods after sintering at various temperatures.** (**a**) 450°C, (**b**) 650°C, (**c**) 750°C, (**d**) 850°C, (**e**) 1,000°C, and (**f**) XRD.
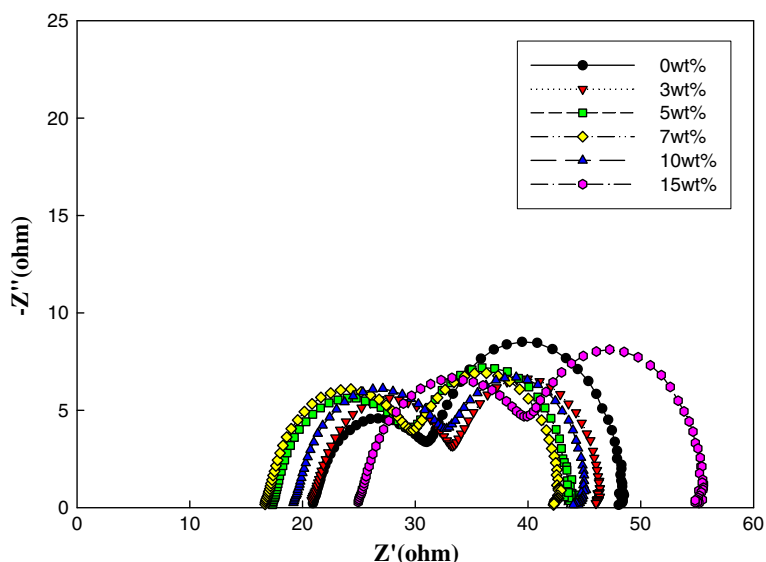
**Figure 2 Impedance spectra of the cells with the rutile nanorods.**

Transmission electron microscopy (TEM) was used to examine the $TiO_2$ nanorods, and the crystal structures were characterized by X-ray diffraction (XRD).

**Fabrication of DSSCs with the $TiO_2$ nanorods**
The ground nanorods, sintered at 450°C, 650°C, 750°C, 850°C, and 1,000°C, were mixed into a homemade $TiO_2$ (P25, Degussa-Hüls, Frankfurt/Main, Germany) paste at a loading of 3 wt.% as a preliminary experiment in order to choose the best nanorod. The ground nanorods sintered at 850°C were chosen and mixed into a commercial $TiO_2$ anatase paste (Dyesol, Queanbeyan, New South Wales in Australia) at ratios of 0, 3, 5, 7, 10, and 15 wt.%. The $TiO_2$ paste with the electrospun nanorods was cast on pre-cleaned fluorine-doped tin dioxide (FTO; Pilkington TEC glass, 8 Ω cm$^{-2}$, Pilkington Group Limited, St Helens, UK) using a squeeze printing method. The $TiO_2$ films were sintered at 450°C for 30 min. The thickness of the $TiO_2$ films was about 10 μm, and the active area of the $TiO_2$ electrode was 0.25 cm$^2$. The obtained $TiO_2$ film was immersed in 0.5 mmol ethanol solution of N719 dye (Solaronix, Aubonne, Switzerland) for 24 h to adsorb the dye molecules. A Pt counter electrode was fabricated by squeeze printing of the Pt-Sol (Solaronix) on an FTO substrate. The sandwich-type solar cell was assembled by placing a Pt counter electrode on the dye-sensitized $TiO_2$ electrode. The redox electrolyte (Dyesol) was injected between the electrodes.
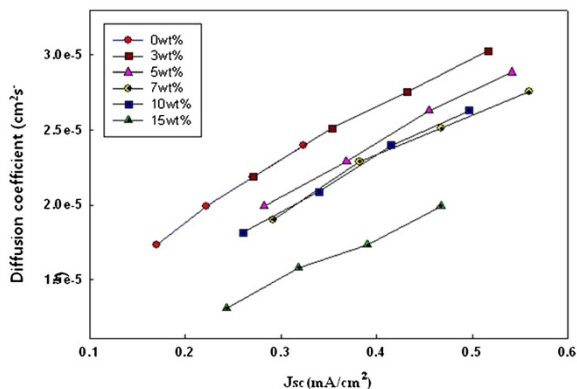


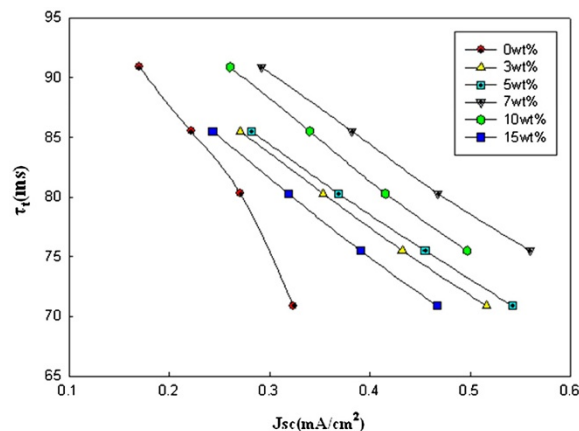**Figure 3 Electron diffusion coefficients ($D_n$) for the DSSCs with the 1-D rutile nanorods.**



**Figure 4 Electron lifetimes ($\tau_r$) for the DSSCs with the 1-D rutile nanorods.**

**Table 1 Diffusion coefficients and lifetime values of the DSSCs with 1-D rutile nanorods at 1-V light intensity**

|  | 0 wt.% | 3 wt.% | 5 wt.% | 7 wt.% | 10 wt.% | 15 wt.% |
|---|---|---|---|---|---|---|
| Diffusion coefficient ($cm^2 s^{-1}$) | 2.40E−05 | 3.03E−05 | 2.89E−05 | 2.76E−05 | 2.63E−05 | 1.99E−05 |
| Lifetime ($\tau_r$) (ms) | 70.9 | 70.9 | 70.9 | 75.5 | 75.5 | 70.9 |

## Characterization

An AM 1.5 solar simulator (white light from a 150-W Xenon lamp, McScience, Suwon-si, South Korea) was used as the light source. The incident light intensity was calibrated with a standard Si solar cell (Japan Quality Assurance Organization, Tokyo, Japan). Electrochemical impedance spectroscopy (EIS) was conducted using Iviumstat (Ivium Technologies B.V., Eindhoven, the Netherlands) at an open-circuit potential at frequencies ranging from $10^{-1}$ to $10^5$ Hz with an AC amplitude of 10 mV. The diffusion coefficients and electron lifetime of the electrons in the $TiO_2$ films were determined using ModuLight-module under a red LED ($\lambda$ = 625 nm) as light source (Ivium Technologies). The values of the diffusion coefficient and electron lifetime were obtained under 0.55-, 0.7-, 0.85-, and 1-V light intensity.

## Results and discussion

TEM images and XRD data of the $TiO_2$ nanorods sintered at various temperatures are shown in Figure 1. The phase transition of the $TiO_2$ was observed depending on the sintering temperatures. With increasing sintering temperature, the amorphous $TiO_2$ underwent phase transition to anatase and rutile structures. The crystallinity increased and the crystal size in the nanorods grew with increasing temperature. Comparison with the XRD peaks of P25, which contains both anatase and rutile phases, confirmed that the sintered nanorods at 750°C, 850°C, and 1,000°C had rutile peaks. During the high-temperature thermal treatment, the average crystal size increased, reducing the grain boundaries and crystal defects. The decreased number of trap sites on the nanorods reduced the number of obstacles on the fast electron moving paths. These effects influenced the charge trap conditions and consequently increased the electron diffusion speed [20]. Among the nanorods sintered at various temperatures, those sintered at 850°C had the highest energy conversion efficiency in DSSCs. The photoelectrodes using a homemade paste with P25 $TiO_2$ and 3 wt.% nanorod sintered at 450°C, 650°C, 750°C, 850°C, and 1,000°C exhibited efficiencies of 3.32%, 3.12%, 3.16%, 3.47%, and 3.41%, respectively.

The internal resistance was investigated by EIS. The impedance spectra of the cells prepared using various amounts of nanorods sintered at 850°C are presented in Figure 2. The semicircles are related to the electron transfer resistance and the tendency of recombination at the $TiO_2$/electrolyte interface [21]. The arc decreased with increasing amount of nanorods until 7 wt.% and then increased. The 1-D nanorods improved the charge transport and decreased electron recombination by providing fast moving paths for electrons. Although 1-D nanostructured nanorods have been proven to deliver a higher short-circuit photocurrent density ($J_{sc}$) than $TiO_2$ nanoparticles, too many large rutile nanorods could become a barrier for the electrons due to the higher energy level of the rutile phase.

Figures 3 and 4 show the electron diffusion coefficients ($D_n$) and lifetimes ($\tau_r$) of the rutile $TiO_2$ nanorods as a function of $J_{sc}$. The $D_n$ and $\tau_r$ values were determined by the photocurrent and photovoltage transients induced by a stepwise change in the laser light intensity controlled with a function generator. The trends of diffusion coefficients by $TiO_2$ structures are known to be reasonably consistent with the resistances in the $TiO_2$ film determined by EIS [22,23]. In Figure 3, all the DSSCs with 1-D rutile nanorods have a higher $J_{sc}$ than the 0 wt.% $TiO_2$ electrode. Table 1 shows that the diffusion coefficients of the electrode with the 1-D rutile nanorods are higher than those of the electrode without the nanorods. However, the value of the diffusion coefficient at the electrode with 15 wt.% nanorods decreased due to the higher energy level of the rutile phase in the nanorods. In Figure 4, the $J_{sc}$ of the electrode with the 1-D nanorods is also increased. The lifetime of the electrodes with rutile nanorods is relatively similar to the 0 wt.% electrode at 3, 5, and 15 wt.% and higher at 7 and 10 wt.%. The 1-D nanorods with the increased $\tau_r$ values can provide an electron pathway. The improved diffusion coefficient and the provided electron pathway result in a synergistic effect that increases the $J_{sc}$.

Table 2 shows the performances of the DSSCs with the 1-D structured rutile nanorods. The $J_{sc}$ value increased with increasing amount of nanorods until 10 wt.% and then decreased at 15 wt.%. The conversion efficiency of the cells using the rutile-phase nanorods was improved depending on the amount of nanorods. In the

**Table 2 Cell performances of the DSSCs with the 1-D rutile nanorods**

|  | 0 wt.% | 3 wt.% | 5 wt.% | 7 wt.% | 10 wt.% | 15 wt.% |
|---|---|---|---|---|---|---|
| $V_{OC}$ | 0.71 | 0.72 | 0.74 | 0.73 | 0.74 | 0.74 |
| $J_{SC}$ | 10.55 | 11.97 | 11.32 | 12.29 | 11.13 | 10.07 |
| Fill factor | 63.17 | 61.71 | 69.38 | 68.52 | 69.43 | 67.24 |
| Efficiency | 4.75 | 5.35 | 5.79 | 6.16 | 5.68 | 4.99 |

cells with nanorods, more electrons could move along the 1-D rutile nanorods due to the enhanced electron diffusion and the reduced electron recombination. Furthermore, the conversion efficiency was improved due to the enhanced electrolyte penetration. The electrolyte could easily penetrate into the photoelectrode due to the random packing of 1-D nanorods because of the porosity. The enhanced interpenetration of the electrolyte led to dye regeneration by redox process of the electrolyte and thus enhanced the energy conversion efficiency with improved photocurrent. As a result, the increased $J_{sc}$ affected the enhancement of the energy conversion efficiency. However, the efficiency of the cell with 15 wt.% nanorods was decreased because the random distribution of a large number of rutile nanorods created a barrier to the electron transport due to the higher energy level of the rutile phase. An excessive amount of 1-D $TiO_2$ nanorods can limit the DSSC performance.

## Conclusions

1-D rutile nanorods can provide a fast moving pathway for electrons and decrease electron recombination. In this study, the nanorods with high crystallinity showed enhanced energy conversion efficiency with reduced $TiO_2$/electrolyte interface resistance. However, an excessive amount of randomly distributed rutile nanorods could create an obstacle to the moving electrons and reduce the internal surface area, even though they provided the electron moving paths. The charge-transfer resistance was decreased with increasing rutile nanorod loading up to 7 wt.%, but the electrical resistance was increased as the loading exceeded 10 wt.%. A 7 wt.% loading of 1-D rutile nanorods was considered the best condition for optimizing the performance of the DSSCs. The energy conversion efficiency of the optimized cell was 6.16%.

### Abbreviations
1-D: one-dimensional; DSSCs: dye-sensitized solar cells; EIS: electrochemical impedance spectroscopy; FTO: fluorine-doped tin dioxide; TEM: transmission electron microscopy; XRD: X-ray diffraction.

### Competing interests
The authors declare that they have no competing interests.

### Authors' contributions
YHJ fabricated the DSSCs. KP and JSO performed the spectroscopic study. DK and CKH drafted the manuscript. All authors read and approved the final manuscript.

### Author details
[1]School of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, South Korea. [2]The Research Institute for Catalysis, Chonnam National University, Gwangju 500-757, South Korea. [3]Materials Development Center, R&D Division for Hyundai Kia Motors, Hwaseong, Gweonggi-do 445-130, South Korea.

### References
1. Cozzoli PD, Kornowski A, Weller H: **Low-temperature synthesis of soluble and processable organic-capped anatase $TiO_2$ nanorods.** *J Am Chem Soc* 2003, **125**:14539–14548.
2. Ramakrishna S, Jose R, Archana PS, Nair AS, Balamurugan R, Venugopal J, Teo WE: **Science and engineering of electrospun nanofibers for advances in clean energy, water filtration, and regenerative medicine.** *J Mater Sci* 2010, **45**:6283–6312.
3. Manna L, Scher EC, Li LS, Alivisatos AP: **Epitaxial growth and photochemical annealing of graded CdS/ZnS shells on colloidal CdSe nanorods.** *J Am Chem Soc* 2002, **124**:7136–7145.
4. Enache-Pommer E, Boercker JE, Aydil ES: **Electron transport and recombination in polycrystalline $TiO_2$ nanowire dye-sensitized solar cells.** *Appl Phys Lett* 2007, **91**:123116-1-3.
5. Cuangchote S, Sgawa T, Yoshikawa S: **Efficient dye-sensitized solar cells using electrospun TiO2 nanofibers as a light harvesting layer.** *Appl Phys Lett* 2008, **93**:033310-1-3.
6. Song MY, Kim DK: **New application of electrospun TiO2 electrode to solid-state dye-sensitized solar cells.** *Synth Met* 2005, **153**:77–80.
7. Fujihara K, Kumar A, Jose R, Ramakrishna S, Uchida S: **Spray deposition of electrospun TiO2 nanorods for dye-sensitized solar cell.** *Nanotechnology* 2007, **18**:365709.
8. Thavasi V, Renugopalakrishnan V, Jose R, Ramakrishna S: **Controlled electron injection and transport at materials interfaces in dye sensitized solar cells.** *Mater Sci Eng* 2009, **63**:81–99.
9. Park NG, van de Lagemaat J, Frank AJ: **Comparison of dye-sensitized rutile- and anatase-based $TiO_2$ solar cells.** *J Phys Chem B* 2000, **104**:8989–8994.
10. Jiu JT, Isoda S, Wang F, Adachi M: **Dye-sensitized solar cells based on a single-crystalline $TiO_2$ nanorod film.** *J Phys Chem B* 2006, **110**:2087–2092.
11. Berger T, Teresa LV, Damian MS, Gomez R: **An electrochemical study on the nature of trap states in nanocrystalline rutile thin films.** *J Phys Chem C* 2007, **111**:9936–9942.
12. Sen S, Mahanty S, Roy S, Heintz O, Bourgeois S, Chaumont D: **Investigation on sol–gel synthesized Ag-doped $TiO_2$ cermet thin films.** *Thin Solid Films* 2005, **474**:245–249.
13. Lee KM, Suryanarayanan V, Ho K-C: **A study on the electron transport properties of TiO2 electrodes in dye-sensitized solar cells.** *Sol Energ Mater Sol Cells* 2007, **91**:1416–1420.
14. Lee BH, Song MY: **Charge transport characteristics of high efficiency dye-sensitized solar cells based on electrospun $TiO_2$ nanorod photoelectrodes.** *J Phys Chem C* 2009, **113**:21453–21457.
15. Hurum DC, Agrios AG, Gray KA, Rajh T, Thurnauer MC: **Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase $TiO_2$ using EPR.** *J Phys Chem B* 2003, **107**:4545–4549.
16. Leytner S, Hupp JT: **Evaluation of the energetics of electron trap states at the nanocrystalline titanium dioxide/aqueous solution interface via time-resolved photoacoustic spectroscopy.** *Chem Phys Lett* 2000, **330**:231–236.
17. Li GH, Richter CP, Brudvig GW, Batista VS: **Synergistic effect between anatase and rutile $TiO_2$ nanoparticles in dye-sensitized solar cells.** *Dalton Trans* 2009, **10**:10078–10085.
18. Barbe CJ, Arendse F, Comte P, Jirousek M, Lenzmann F, Shklover V, Gratzel M: **Nanocrystalline titanium oxide electrodes for photovoltaic applications.** *J Am Ceram Soc* 1997, **80**:3157–3171.
19. Kang SH, Choi SH, Kang MS, Kim JY, Kim HS, Hyeon TG, Sung YE: **Nanorod-based dye-sensitized solar cells with improved charge collection efficiency.** *Adv Mater* 2008, **20**:54–58.
20. Nakade S, Saito Y, Kubo W, Kanzaki T, Kitamura T, Wada Y, Yanagida S: **Enhancement of electron transport in nano-porous TiO2 electrodes by dye adsorption.** *Electrochem Commun* 2003, **5**:804–808.
21. Park KH, Hong CK: **Morphology and photoelectrochemical properties of $TiO_2$ electrodes prepared using functionalized plant oil binders.** *Electrochem Commun* 2008, **10**:1187–1190.

22.  Kang SH, Kim JY, Kim HS, Koh HD, Lee JS, Sung YE: **Influence of light scattering particles in the TiO$_2$ photoelectrode for solid-state dye-sensitized solar cell.** *J Photochem Photobio A: Chem* 2008, **200:**294–300.
23.  Kim YJ, Lee MH, Kim HJ, Lim G, Choi YS, Park NG, Kim KK, Lee WI: **Formation of highly efficient dye-sensitized solar cells by hierarchical pore generation with nanoporous TiO$_2$ spheres.** *Adv Mater* 2009, **21:**3668–3673.