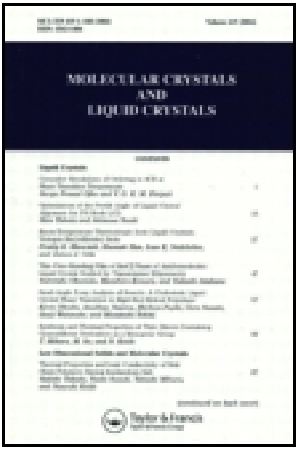

## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Hyo Jeong Jo [a] , Young Cheol Choi [a] , Do Kyung Lee [b] , Sun Hwa Lee [a] , No-Kuk Park [a] , Tae Jin Lee [a] & Jae Hong Kim [a]

[a] School of Display and Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk, Republic of Korea

[b] R&D Affairs Department, Gumi Electronics & Information Technology Research Institute, Gumi, Republic of Korea

Version of record first published: 10 Nov 2009

To cite this article: Hyo Jeong Jo, Young Cheol Choi, Do Kyung Lee, Sun Hwa Lee, No-Kuk Park, Tae Jin Lee & Jae Hong Kim (2009): Synthesis and Photovoltaic Properties of Mesophorous $TiO_2$ for the Dye-Sensitized Solar Cell, Molecular Crystals and Liquid Crystals, 514:1, 92/[422]-98/[428]

To link to this article: http://dx.doi.org/10.1080/15421400903228451

*Mol. Cryst. Liq. Cryst.*, Vol. 514, pp. 92/[422]–98/[428], 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903228451





# Synthesis and Photovoltaic Properties of Mesophorous $TiO_2$ for the Dye-Sensitized Solar Cell

**Hyo Jeong Jo[1], Young Cheol Choi[1], Do Kyung Lee[2], Sun Hwa Lee[1], No-Kuk Park[1], Tae Jin Lee[1], and Jae Hong Kim[1]**
[1]School of Display and Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk, Republic of Korea
[2]R&D Affairs Department, Gumi Electronics & Information Technology Research Institute, Gumi, Republic of Korea

*Nanocrystalline mesoporous titania was synthesized by using the surfactant assisted templating method with different temperatures. The energy conversion efficiency of 5.9% was achieved in the dye sensitized solar cell (DSSC) based on the 400°C sintered $TiO_2$ electrode with treatment of $TiCl_4$ aqueous solution. We found that the amount of dye adsorbed in $TiO_2$ surface was affected significantly with the temperature during the sintering process.*

**Keywords:** dye-sensitized solar cell; energy conversion efficiency; mesoporous titania; sintering process; wide band-gap semiconductor

## INTRODUCTION

The search for efficient solar energy conversion devices continues to be an important area of research. Since Gratzel and co-workers developed a new type of solar cell based on the nanocrystalline $TiO_2$ electrode, dye-sensitized solar cell (DSSC) has attracted much attention due to their high performance (over 10% at a very competitive cost) and easy manufacturing process [1–3]. Photoinduced electron transfer between photosensitizers and colloidal wide band gap semiconductors such as $TiO_2$ plays an important roll in DSSC cell [4,5]. A schematic

This work was supported by Grant No. R01-2007-000-20815-0 from the Basic Research Program of the Korea Science and Engineering Foundation.

Address correspondence to Prof. Jae Hong Kim, School of Display and Chemical Engineering, Yeungnam University, 214-1, Dae-dong, Gyeongsan, Gyeongbuk 712-749, Korea (ROK). E-mail: jhkim@ynu.ac.kr

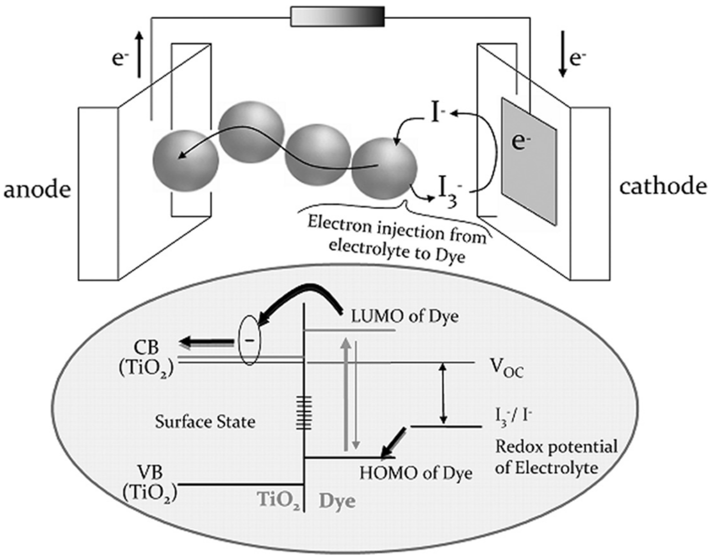


**FIGURE 1** A schematic representation of operating principles and energy level diagram of DSSC.

representation of operating principles and energy level diagram of DSSC components with the chemical structure of sensitizer (N3) were shown in Figure 1. The nanocrystalline titania is a most promising semi-conductor for DSSC electrode because the conduction band of titania is well optimized to inject electrons from the excited state of dye [6–9]. To achieve high performance of DSSC, the titania electrode should have the high crystalline anatase phase and wide surface area to increase the mobility of electron injected from the LUMO of dye and the amount of dye absorbed on the $TiO_2$ surface, respectively.

In this study, we prepared the nanocrystalline mesoporous titania by the surfactant assisted templating method with different temperature of sintering process, and the photovoltaic properties of DSSC based on $TiO_2$ electrode synthesized were evaluated to optimize the cell performance.

## EXPERIMENTAL

### Synthesis of Mesoporous $TiO_2$

In this study, $TiO_2$ nano-particles were synthesized by the sol-gel and hydrothermal method [10,11]. TTIP (titanium tetra-isopropoxide, Sigma-Aldrich, 97%) and ethyl alcohol (Duksan Pure Chemicals Co. Ltd, 99.9%) were used as the starting material and the solvent for the preparation of $TiO_2$ nano-particle, respectively. Ethyl alcohol and TTIP were mixed to the suitable mol ratio (EtOH/TTIP mol ratio = 5/1) for the dilution and this solution was stirred for 30 min. The ionized water ($H_2O$/TTIP mol ratio = 20) was added slowly in TTIP solution at the room temperature for the sol-gel process. The precipitate of white slurry was obtained and treated for 3 h at 200°C in the autoclave. After the filtration, the precipitate was dried for 24 h at 100°C, and then calcined for 4 h under air condition at various temperature (400, 500, 600, 700, 800°C) by the electric furnace. $TiO_2$ anatase and rutile structures of the different crystal-size and surface area were produced with various temperatures for calcinations which were characterized with SEM and XRD.

## Preparation of Dye-Sensitized Solar Cell

The transparent nanocrystalline-$TiO_2$ layer was coated on the Fluorine-doped Tin Oxide (FTO, sheet resistance: 10 Ω per square) glass plates by screen printing, and then 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 30 min. After cooling to 100°C, the $TiO_2$ electrodes were immersed into the $TiCl_4$ aqueous solution for treatment of surface of electrodes. The $TiCl_4$ treatment increases the necking between particles of the $TiO_2$, thus facilitating the percolation of photoinjected electrons from one particle to another and lowering the probability of recombination [12]. After the resultant electrode was washed with water and acetonitrile, it immersed into the N3 dye solution (50 mM of N3 in ethanol solution) at room temperature for 24 h to adsorb dyes on the surface. The dye-adsorbed $TiO_2$ electrode and Pt counter electrode (platinum-sputtered conducting glass) were assembled into a sealed sandwich-type cell, and then, a drop of the electrolyte solution (e.g., 0.1 M of LiI, 0.6 M of 1,2-dimethyl-3-propylimidazoleium iodide (DMPImI), 0.05 M of 4-tert-butylpyridine in methoxyacetonitrile) was placed on a drilled hole in the counter electrode of the assembled cell and was driven into the cell by means of vacuum backfilling. Finally, the hole was sealed using additional cover glass.

## The Dye Desorption from $TiO_2$ Photo-Anode

The dye absorbed photo-anode was treated with the desorption solution for 1 hr to determine the amount of dye absorbed on $TiO_2$ surface, and then, the amount of dye on the photo-anode was detected from

UV-Vis absorption spectral intensity of dye desorpted solution. The dye desorption experimental was conducted by immersion of dye absorbed $TiO_2$ photo-anode in 1 M of NaOH aqueous 50% ethanol solution. The amount of dye uptake calculated from the molar extinction coefficient of N3 dye.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Mesoporous $TiO_2$

It is well known that the thermal treatment condition during $TiO_2$ nano particle preparation affect significantly the crystallinity, surface area, and particle size of $TiO_2$ which could determine the photovoltaic performance of the DSSC. We synthesized the $TiO_2$ nano particles prepared with different annealing temperatures from 400°C to 800°C to investigate the relationship between the thermal treatment and energy conversion efficiency in DSSC.

The effect of annealing temperatures on the properties of mesoporous $TiO_2$ was evaluated with the SEM, XRD, as shown in Figures 2 and 3, respectively. Most importantly, with increasing annealing temperature, the crystalline size of $TiO_2$ increased significantly (Fig. 2).

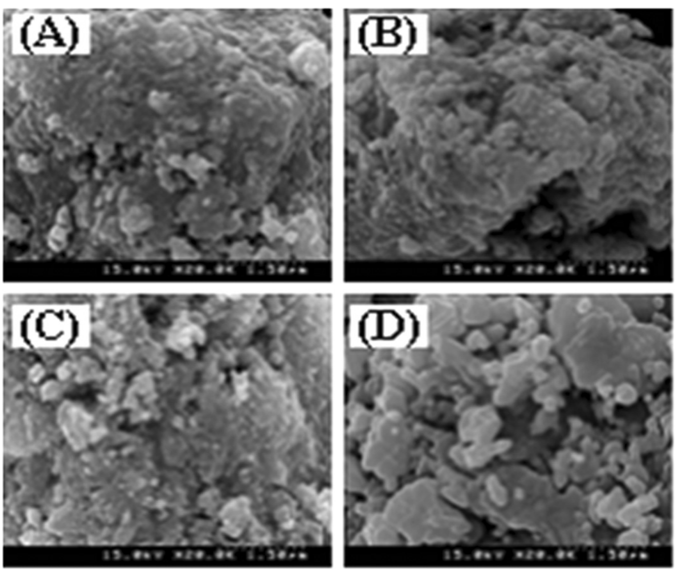


**FIGURE 2** Morphologies of $TiO_2$ prepared with different temperature. (A) Sol-gel method; (B) 400°C; (C) 600°C; and (D) 800°C.

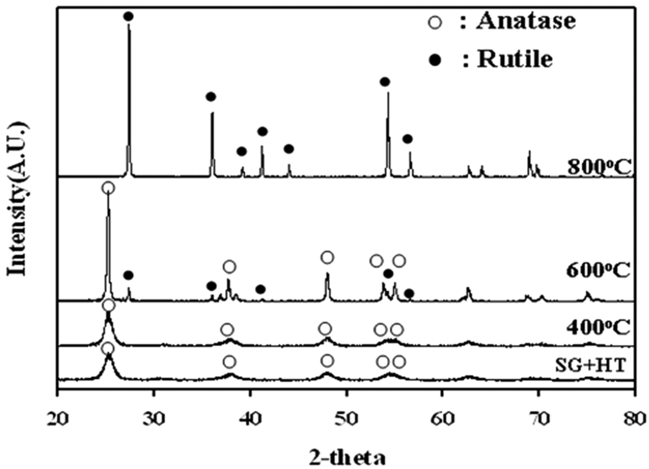


**FIGURE 3** XRD patterns of $TiO_2$ electrode prepared with different sintering temperatures.

Thus, the surface area of $TiO_2$ nano particles was decreased significantly with increasing annealing temperature as shown in Table 1.

And Figure 3 shows that the broad peaks of anatase phase became intense and sharp by elevating the sintering temperature to 600°C due to the enhancement of crystallinity. Above 600°C, the anatase phase started to be weakened and then, disappeared at 800°C. In stead of that, the peak from the rutile phase of $TiO_2$ became dominant. It was generally known that the electron mobility on the anatase phase of nanocrystalline $TiO_2$ was higher then that of rutile phase which could affect the photovoltain performance in DSSC, significantly [13].

Thus, the higher sintering process over 600°C could decrease the amount of dye adsorbed on the $TiO_2$ surface and reduce the electron mobility injected from the LUMO of dye due to the particle size and the phase transformation to rutile phase.

**TABLE 1** The BET Surface Area and Photovoltaic Properties of DSSCs Composed of $TiO_2$ Electrode Prepared with Different Sintering Temperatures

| Temp (°C) | BET ($m^2/g$) surface area | $V_{oc}$ (V) | $J_{oc}$ ($mA/cm^2$) | FF | Amount of dye ($mol/cm^2$)($10^{-5}$) | Efficiency (%) |
|---|---|---|---|---|---|---|
| 400 | 107.91 | 0.725 | 11.09 | 0.72 | 20.31 | 5.9 |
| 500 | 75.87 | 0.725 | 8.59 | 0.89 | 18.10 | 4.3 |
| 600 | 20.58 | 0.725 | 4.79 | 0.64 | 14.41 | 2.3 |
| 700 | 6.0 | 0.775 | 1.34 | 0.65 | 2.85 | 0.7 |
| 800 | – | 0.625 | 0.48 | 0.57 | 2.10 | 0.2 |

We prepared DSSCs composed of $TiO_2$ electrodes treated with different sintering process to demonstrate the effect of temperature dependency of the electrode on photovoltaic performances.

## Photovoltaic Performances of $TiO_2$ Electrodes

The synthesized $TiO_2$ was applied for the electrode in DSSC. The $TiO_2$ electrodes were pre-treated with $TiCl_4$ aqueous solution to improve photovoltaic properties [12]. Figure 4 shows the current-voltage characteristics of DSSC composed of $TiO_2$ electrode treated with different temperatures in the sintering process. The performances of DSSCs under AM1.5 illumination at 100 mW/cm$^2$ are summarized in Table 1. The amount of absorbed dye was determined by spectroscopic measurements of the desorbed solution from the concentrated NaOH in a mixture of water and ethanol (1/1, v/v) solution which also shown in Table 1 for the comparison. It shows clearly that with increasing annealing temperature, the amount of dye absorbed on $TiO_2$ surface decrease due to the increase of $TiO_2$ particle size.

Obviously, the efficiency of DSSC based on the electrode treated with the higher temperature above 600°C decreased, significantly without any considerable differences in Voc and fill factor. The significant difference of Jsc in DSSC performance was interpreted mainly as the difference in the amount of adsorbed dye on $TiO_2$ electrode as shown in Table 1, which affects the cell performance in DSSC, dominantly.

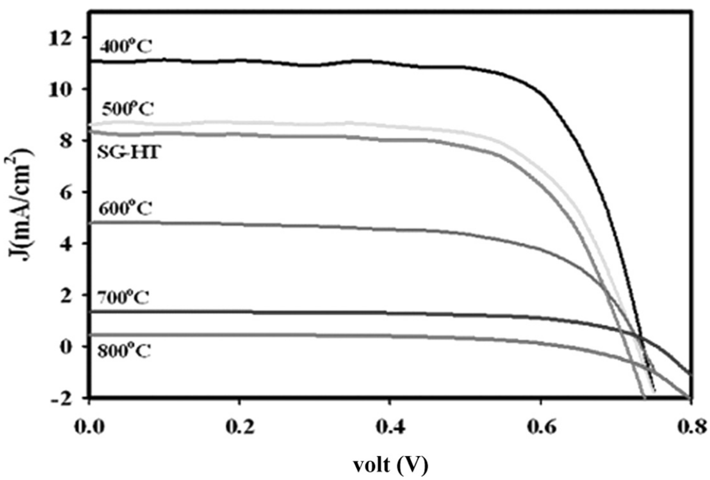


**FIGURE 4** The photocurrent-voltage characteristics in DSSC composed of $TiO_2$ electrodes prepared with different temperatures.

## CONCLUSIONS

We synthesized the nanocrystalline mesoporous $TiO_2$ with various temperatures which had the anatase phase during relative low temperature (400∼500°C) process. The experiments and measurements of DSSC disclose that the optimum sintering condition for $TiO_2$ electrode was determined to 400°C in which photovoltaic performance attained 5.9% of energy conversion efficiency with $J_{sc}$ of 11.09 mA/cm$^2$, a $V_{oc}$ of 0.725, and a fill factor of 0.72. Further studies to improve the energy conversion efficiency due to the increase of surface area and the optimization of DSSC structure are in progress.

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