

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Photovoltaic Performance Enhancement in Dye-Sensitized Solar Cells with Periodic Surface Relief Structures

Fadong Yan^a; Pilho Huh^a; Lian Li^b; Yanping Wang^a; Lynne A. Samuelson^b; Jayant Kumar^a

^a Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA ^b U.S. Army Natick Soldier Research, Development and Engineering Center, Natick, MA

To cite this Article Yan, Fadong , Huh, Pilho , Li, Lian , Wang, Yanping , Samuelson, Lynne A. and Kumar, Jayant(2009) 'Photovoltaic Performance Enhancement in Dye-Sensitized Solar Cells with Periodic Surface Relief Structures', Journal of Macromolecular Science, Part A, 46: 12, 1213 – 1216

To link to this Article: DOI: 10.1080/10601320903340283

URL: <http://dx.doi.org/10.1080/10601320903340283>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Photovoltaic Performance Enhancement in Dye-Sensitized Solar Cells with Periodic Surface Relief Structures

FADONG YAN¹, PILHO HUH¹, LIAN LI², YANPING WANG¹,
LYNNE A. SAMUELSON² and JAYANT KUMAR^{1,*}

¹Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA

²U.S. Army Natick Soldier Research, Development and Engineering Center, Natick, MA

One-dimensional and two-dimensional periodic TiO₂ relief structures were incorporated in dye-sensitized solar cells. The periodic TiO₂ structures were fabricated using surface relief gratings photoinscribed on azobenzene functionalized polymer films as templates and TiO₂ sol-gel solution. Enhancement of power conversion of the solar cells made with the relief TiO₂ structures was achieved. This enhancement suggests that the relief TiO₂ structures can offer efficient light-trapping with the increased effective optical-path length in the solar cells.

Keywords: Dye-sensitized solar cell, relief TiO₂ structure, template, light-trapping

1 Introduction

The urgent need for inexpensive renewable energy sources has attracted a great attention for developing new materials and technologies for efficient photovoltaic devices. Dye-sensitized solar cells (DSSCs) have drawn substantial interest as candidates for next generation photovoltaic devices due to their simple architecture and great potential for low-cost and easy manufacturing (1–3). It has been demonstrated that the DSSCs can offer power conversion efficiency more than 10% with ruthenium based dyes (4, 5). Extensive investigations have been carried out to increase the light absorption in the DSSCs. Incorporating dyes that can absorb a broad spectral range of the solar radiation has been reported and enhancement of the power conversion efficiency was accomplished (6, 7). Hammond et al. have demonstrated the ability to pattern TiO₂ on the micron and submicron scale using micro-contact printing of a copolymer combined with solution synthesis of TiO₂ thin films (8). The DSSCs with patterned TiO₂ exhibited almost 10 times larger power conversion efficiencies than a similar device without patterning due to the increased optical-path length in the solar cells. However, this multi-step approach is complicated, and time-consuming. In this

paper, we reported photovoltaic performance enhancement of the DSSCs fabricated with structured TiO₂. The DSSCs with periodic TiO₂ structures exhibited increased power conversion efficiency comparing to that without the structure. The experimental details and results are presented.

2 Experimental

Fluorine-doped tin oxide (FTO) glasses were acquired from Hartford Glass Company, Hartford City, Indiana. 1,4-Dioxane, isopropanol, nitric acid, acetonitrile, tert-butanol, and 4-tert-butylpyridine were purchased from Sigma Aldrich, USA. Poly(disperse orange 3) (PDO3), an azobenzene functionalized polymer, was synthesized from diglycidyl ether of bisphenol A and disperse orange 3 following the procedure reported elsewhere (9). The glass transition temperature of the azo polymer is about 106°C (10). A ruthenium dye, Z907 as a sensitizer was used in this investigation. The ruthenium dye absorbs broadly in the visible with an absorption peak around 514 nm (11).

TiO₂ sol-gel solution was obtained by slowly dropping 10 mL of titanium (IV) isopropoxide and 1.6 mL of isopropanol into 60 mL of 0.1 M aqueous nitric acid solution under vigorous stirring. The mixture was fluxed at 80°C for 8 h. The TiO₂ sol-gel solution was first spin-coated onto FTO glass substrates at 1000 rpm to form a compact layer of TiO₂. The TiO₂ coated FTO glass was then heated at 420°C for 10 min. The final TiO₂ film has a thickness of

Dedicated to the memory of Professor Sukant K. Tripathy

*Address correspondence to: Jayant Kumar, Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA 01854. E-mail: jayant_kumar@uml.edu

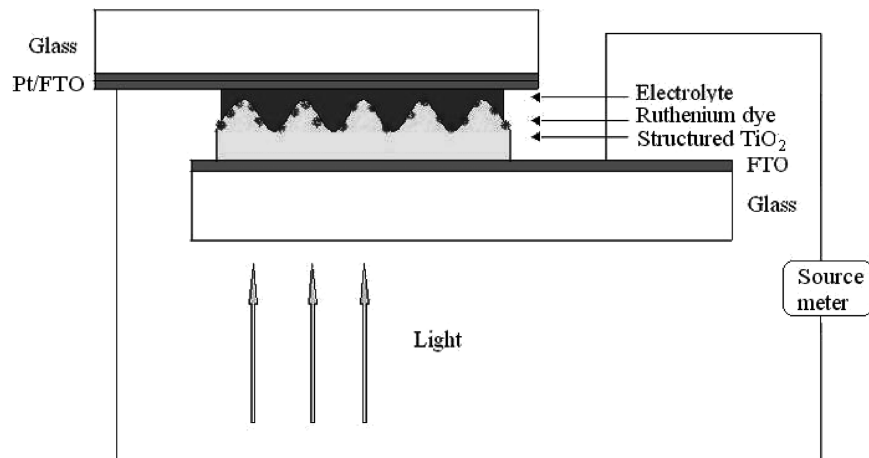


Fig. 1. Schematic of the DSSC with relief TiO_2 structure.

approximately 100 nm. The periodic TiO_2 relief structures using the SRGs templates were fabricated following the procedure described elsewhere (12–14).

PDO3 films were prepared on the compact TiO_2 films by spin-coating 5 wt% PDO3 in 1,4-dioxane solution. The films were dried in a vacuum oven at 60°C overnight. One-dimensional (1D) surface relief gratings (SRGs) on the PDO3 films were photoinscribed with two interfering laser beams at 514.5 nm from an Ar⁺ laser ($100\text{ mW}/\text{cm}^2$). The polarizations of the laser beams were chosen to be 45° polarized with respect to s-polarization. It is well-known that azobenzene chromophores can undergo reversible trans-cis isomerization process under illumination. This trans-cis photoisomerization in an azobenzene functionalized polymer can lead to the formation of large relief patterns on the polymer film (15, 16). The period of an SRG can be controlled by varying the incident angle and the wavelength of the laser beams. SRGs with periods about 400 nm, 600 nm and $1\ \mu\text{m}$ were recorded

and used as the templates. Two-dimensional (2D) SRGs were fabricated by writing two SRGs perpendicular to each other.

TiO_2 sol-gel solution was then spin-coated on the SRG templates on the TiO_2 compact films. The relief TiO_2 structures were formed via calcination at 450°C for 2 h. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were utilized to measure the periods and modulation depths of the templates and the periodic TiO_2 structures. X-ray diffraction (XRD) and Raman spectroscopy were used to examine the crystalline structure of the structured TiO_2 .

The structured TiO_2 films were dipped into a dye solution (Z907, 0.3 mM in acetonitrile:tert-butanol, 1:1 by volume) overnight. The films were rinsed with absolute ethanol to remove excess dye molecules on the TiO_2 surfaces and dried by blowing nitrogen gas. The liquid I^-/I_3^- electrolyte was prepared by dissolving 0.0254 g I_2 and 0.1358 g LiI in 2 mL acetonitrile and 0.3 mL

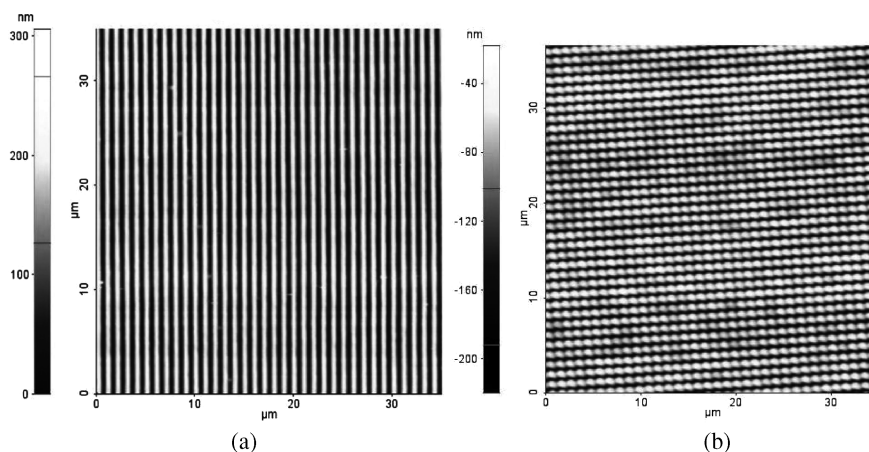


Fig. 2. AFM images of 1D (a) and 2D (b) SRGs with $1\ \mu\text{m}$ period.

Table 1. Photovoltaic characteristics of the DSSCs

	Period (nm)	Depth (nm)	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor	Efficiency (%)
Non-structured			0.45	0.30	0.56	0.078
1D	1000	270	0.53	0.70	0.52	0.19
	600	80	0.57	1.18	0.58	0.39
	400	50	0.61	1.04	0.56	0.36
2D	1000	230	0.58	0.97	0.57	0.32
	600	60	0.61	1.45	0.59	0.52
	400	35	0.59	1.70	0.55	0.55

4-tert-butylpyridine. Thick platinum (100 nm) coated FTO glasses were used as the counter electrodes and reflectors. The schematic of the DSSC made with relief TiO₂ structures is shown in Figure 1. A DSSC without the relief TiO₂ structure was also fabricated for comparison.

I-V characteristics of the DSSCs were evaluated under simulated AM 1.5 illumination (100 mW/cm²) in conjunction with a Keithley SMU2400 source meter. The active area of the DSSCs was controlled to be 0.25 cm² with a mask.

3 Results and Discussion

It is believed that during calcination the polymer templates tended to planarize above the glass transition temperature and the coated TiO₂ sol-gel migrated into the template grooves and aggregated. At higher temperature, the polymer templates were degraded and pyrolyzed, leaving the periodic relief TiO₂ patterns on the FTO substrates. Topography of the SRGs and the relief TiO₂ structures was investigated by AFM and SEM. Figure 2 shows the AFM images of 1D and 2D SRGs of 1 μm period. The SEM images of fabricated 1D and 2D relief TiO₂ structures are shown in Figure 3. The periodicities of the relief TiO₂ patterns are about the same as those of the

templates. The periods and modulation depths of the TiO₂ structures are summarized in Table 1.

The XRD study of the periodic TiO₂ pattern confirmed the anatase phase of the TiO₂ with one diffraction peak observed at $2\theta = 25.2^\circ$ (d -spacing of 3.53 Å). This peak corresponds to the diffraction from the (101) plane. The characteristic Raman peaks of the anatase TiO₂ at 402, 518 and 640 cm⁻¹ were measured. The strongest Raman peak at 143 cm⁻¹ was not observed due to the limitation of the Raman spectrometer.

The photovoltaic characteristics of the DSSCs with or without 1D and 2D periodic TiO₂ structures were measured and summarized in Table 1. Figure 4 shows the I-V characteristic of a solar cell made with a 2D 600 nm periodic TiO₂ structure. The DSSCs with the relief TiO₂ structures showed much higher photovoltaic performance than that without the relief TiO₂ structure. This enhancement indicates that the TiO₂ relief structures can offer efficient light-trapping in the solar cells, leading to higher photocurrent. The photocurrent and power conversion efficiency of the cells made with the 2D TiO₂ structures are higher than those with 1D TiO₂ structures of the same periods. This result suggests that the 2D TiO₂ structures can provide more efficient light-trapping. The power conversion efficiency of the DSSCs with the TiO₂ structures of 400 and 600 nm periods are higher than those of the DSSCs with 1 μm TiO₂ structures, implying that the relief TiO₂ structures of 400

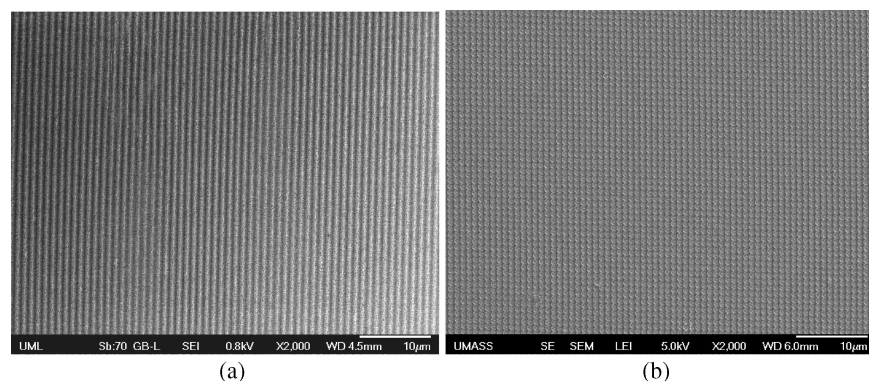


Fig. 3. SEM images of 1D (a) and 2D (b) relief TiO₂ structures with 1 μm period.

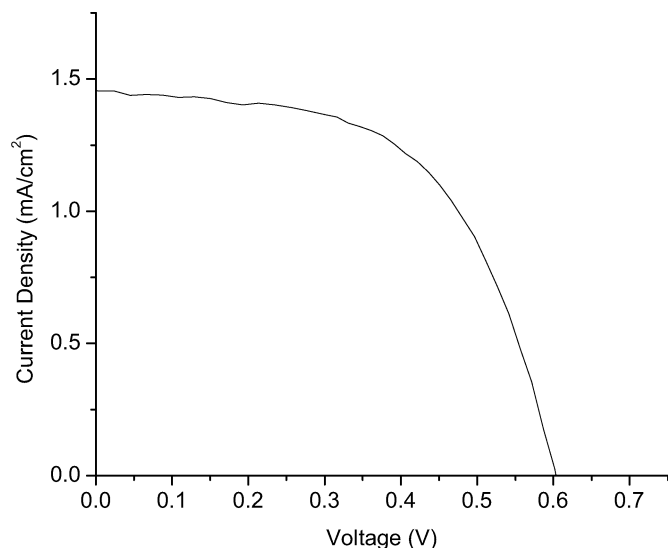


Fig. 4. I-V curve of a DSSC made with a 2D TiO₂ structure of 600 nm period.

and 600 nm periods offer better diffraction in the spectral range where the Z907 dye absorbs.

The relief TiO₂ structures in the solar cells act as diffractive elements. The normal incident light can diffract according to the following equation:

$$n\Lambda \sin \theta = m\lambda$$

Where n is the refractive index of the liquid electrolyte, Λ is the period of the TiO₂ structure, θ is the angle of diffraction, m is the order of diffraction, and λ is the wavelength of the incident light. Through reflection from the thick platinum coating and total internal reflection (if the diffraction angle is larger than a critical angle at the air/glass interface), the diffracted light beams can be confined inside the solar cell. The critical angle is estimated to be 42° using refractive index of 1.5 for the glass. These multiple reflections would consequently increase optical-path length, resulting in efficient light-trapping and absorption, and significant enhancement in the photovoltaic performance. The TiO₂ structures with the smaller periods provide larger diffraction angles, leading to better light harvesting and higher photocurrents. It is expected that these diffractive effects to be effective at most thorough out the visible spectrum due to the fact that the liquid electrolyte has an index around 1.5 (17), thereby effectively reducing the wavelength of the light in the medium.

4 Conclusions

A series of DSSCs using the periodic 1D and 2D TiO₂ relief structures were fabricated. The relief TiO₂ structures were readily made using the SRGs photoinscribed on the azobenzene functionalized polymer films as the templates.

The photocurrent and power conversion efficiency of the DSSCs with the periodic TiO₂ structures are higher than those without the structures, suggesting that the diffractive effects from the periodic TiO₂ structures can increase the optical-path length and offer efficient light-trapping and absorption in the DSSCs. The 2D TiO₂ structures provide higher ability to trap light in the solar cells, resulting in better power conversion efficiency. The DSSCs with the TiO₂ structures of the smaller periods show better performance than those with 1 μm TiO₂ structures.

Acknowledgements

This research was supported by U.S. Army Natick Soldier Research, Development and Engineering Center (W911QY-06-C-0060) and National Science Foundation (ECCS-0601602). Part of the research was performed while LL held the Senior National Research Council Research Associateship at U.S. Army Natick Soldier Research, Development and Engineering Center.

References

- O'Regan, B. and Grätzel, M. (1991) *Nature*, 353, 737–740.
- Lyon, J.E., Rayan, M.K., Beerbom, M.M. and Schlaf, R. (2008) *J. Appl. Phys.*, 104(7), 073714.
- Grätzel, M. (2003) *J. Photochem. Photobiol. C: Photochem. Rev.*, 4(2), 145–153.
- Chiba, Y., Islam, A., Kakutani, K., Komiya, R., Koide, N. and Han, L. *Technical Digest of the 15th International Photovoltaic Science and Engineering Conference*, Shanghai, 2005; pp 665–666.
- Gao, F., Wang, Y., Shi, D., Zhang, J., Wang, M., Jing, X., Humphry-Baker, R., Wang, P., Zakeeruddin, S.M. and Gratzel, M. (2008) *J. Am. Chem. Soc.*, 130(32), 10720–10728.
- Renouard, T., Fallahpour, R.A., Nazeeruddin, M.K., Humphry-Baker, R., Gorelsky, S.I., Lever, A.B.P. and Grätzel, M. (2002) *Inorg. Chem.*, 41(2), 367–378.
- Nazeeruddin, M.K., Kay, A., Rodicio, I., Humphry-Baker, R., Muller, E., Liska, P., Vlachopoulos, N. and Grätzel, M. (1993) *J. Am. Chem. Soc.*, 115(14), 6382–6390.
- Tokuhisa, H. and Hammond, P.T. (2003) *Adv. Funct. Mater.*, 13(11), 831–839.
- Mandal, B.K., Jeng, R.J., Kumar, J. and Tripathy, S.K. (1991) *Makromol. Chem., Rapid Commun.*, 12 (11), 607–612.
- Bian, S., Williams, J.M., Kim, D.Y., Li, L., Balasubramanian, S., Kumar, J. and Tripathy, S. (1999) *J. Appl. Phys.*, 86(8), 4498–4508.
- Petrozza, A., Groves, C. and Snaith, H.J. (2008) *J. Am. Chem. Soc.*, 130 (39), 12912–12920.
- Kim, M., Kang, B., Yang, S., Drew, C., Samuelson, L.A. and Kumar, J. (2006) *Adv. Mater.*, 18(12), 1622–1626.
- Yan, F., Li, L., Huh, P., Wang, Y., Samuelson, L.A. and Kumar J. (2008) *Mater. Res. Soc. Symp. Proc.*, 1059, 1059-KK10-27.
- Huh, P., Yan, F., Li, L., Kim, M., Mosurkal, R., Samuelson, L.A. and Kumar, J. (2008) *J. Mater. Chem.*, 18(6), 637–639.
- Kim, D.Y., Tripathy, S.K., Li, L. and Kumar, J. (1995) *Appl. Phys. Lett.*, 66 (10), 1166–1168.
- Rochon, P., Batalla, E. and Natansohn, A. (1995) *Appl. Phys. Lett.*, 66(2), 136–138.
- Ferber, J. and Luther, J. (1998) *Solar Energy Mater. Solar Cells*, 54(1–4), 265–275.