Hindawi Publishing Corporation
International Journal of Photoenergy
Volume 2013, Article ID 807931, 6 pages
http://dx.doi.org/10.1155/2013/807931

Research Article

Integration of High-Performance Nanocrystalline TiO_2 Photoelectrodes for N719-Sensitized Solar Cells

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Received 12 February 2013; Accepted 21 April 2013

Academic Editor: Theodoros Dimopoulos

We report on enhanced performance of N719-sensitized TiO_2 solar cells (DSCs) incorporating size and photoelectron diffusion-controlled TiO_2 as sensitizer-matched light-scatter layers on conventional nanocrystalline TiO_2 electrodes. The double-layered N719/TiO_2 composite electrode with a high dye-loading capacity exhibits the diffused reflectance of more than 50% in the range of $\lambda = 650$–800 nm, even when the films are coupled with the titania nanocrystalline underlayer in the device. As a result, the increased near-infrared light-harvesting produces a high light-to-electricity conversion efficiency of over 9% mainly due to the significant increase of J_{sc}. Such an optical effect of the NIR-light scattering TiO_2 electrodes will be beneficial when the sensitizers with low molar extinction coefficients, such as N719, are introduced in the device.

1. Introduction

Dye-sensitized solar cells (DSCs) have been explored from both academic and industry world as a promising alternative to the conventional silicon-based photovoltaic devices [1–3], and efficiencies of over 12% have been achieved [4]. In this cell, a wide band-gap nanostructured semiconductor electrode (typically, TiO_2) is employed to support a large surface area, on which dye molecules are assembled to improve the light harvesting of the dyed electrode. A great deal of effort has been focused on the development of effective panchromatic sensitizers or cosensitizers for efficient solar light harvesting in DSC devices. On the other hand, the light-harvesting efficiency of DSC can be promoted by introducing a sophisticated structure in the photoelectrode, in which the photon path length is increased by the confinement of incident solar energy light. Usami made the theoretical finding that lightscattering in DSCs will be optimized if the diameter of TiO_2 nanocrystals is twice the size of the wavelength of incident light [5]. The effect has been verified in the DSCs, in which a TiO_2 layer built from submicrometer-sized TiO_2 particles was employed in combination with a transparent nanostructured TiO_2 layer [6–8]. In addition, TiO_2 (or ZnO) photoelectrodes with submicrometer-sized beads, hollow spheres, and tubes have been widely investigated [9–15].

As an alternative to such a large particle light-scattering material, TiO_2 layers with periodic pore structures exhibiting photonic band gaps have been applied for DSCs to enhance light harvesting efficiency [16–21]. Such light scattering TiO_2 layers, however, required an elaborate multistep synthesis. On the other hand, Hore et al. reported scattering of light on disordered spherical voids in TiO_2 electrodes for enhanced DSC performance. The DSC with 400 nm void layers gave a higher efficiency (6.7%) as compared to the cavity-free layer (5.4%) [22]. While the overall efficiency was improved, a slight increase of J_{sc} was observed and the appreciable increase of fill factors resulted in the 18% increment of conversion efficiency. Despite a number of nanostructured TiO_2 photoelectrodes reported as mentioned previously, the cell performance originated from spherical void-centered TiO_2 has still been poorly understood. Most importantly,

little has been reported on an enhancement of near-infrared- (NIR-) light response in IPCE [22, 23]. As organic dye molecules with large extinction coefficients even in the red region were used, the results represent a compromise between slight light scattering and enhanced mobility of viscous electrolytes in the large hollow cavities [23]. In this paper we demonstrate optimized effects of scattering on submicron TiO_2 particles with spherical cavities on quantum efficiencies of light-to-electricity conversion of N719-sensitized solar cells at a NIR region, where the N719 dye has a low extinction coefficient. Accordingly, we prepared a TiO_2 layer containing 600 nm large spherical cavities and combined successively with the conventional nanocrystalline TiO_2 layer. We then applied the hollow-cavity-based TiO_2/nanocrystalline TiO_2 double composite electrodes to N719-sensitized DSC. The DSC exhibited a maximum conversion efficiency of 9.25% versus 6.38% for the reference cell with single conventional TiO_2 electrodes. We demonstrated that the hollow-cavity-based TiO_2 contributes not only to the enhanced absorption of near-infrared photons but also to effective dye sensitization as evidenced by the remarkable enhancement of J_{sc} in the performance. It should be noted that the effective electron diffusion coefficient of the dye-coated light-scattering TiO_2 layer also plays a crucial role in the improved DSC performance.

2. Materials and Methods

Polyethyleneglycol (PEG, Mw = 20,000) was purchased from Fluka Co. The Ru dye, N719 (cis-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium) was purchased from Solaronix S.A. Iodine, 1-propyl-3-methylimidazolium iodide, valeronitrile, lithium iodide, and *tert*-butylpyridine were purchased from Aldrich without purification.

2.1. Preparation of DSCs. A 60 nm dense TiO_2 layer was deposited on a patterned ITO-coated glass substrates (10 Ω/□, Nippon Sheet Glass) by spin coating technique with tetraisopropyl orthotitanate in ethanol, as reported previously [24]. The TiO_2 films, served as a blocking layer in DSCs, were annealed in air at 500°C for 30 minutes. Following this, a TiO_2 paste with 20 nm particle size was deposited by doctor blade technique on the blocking layer, where the TiO_2 paste was prepared according to the previous report [25]. A transparent TiO_2 underlayer was achieved after the calcination at 500°C for 30 minutes. Functional polystyrene spheres (PS) (560 nm in size) were synthesized according to our previous method [26]. The resulting latex spheres were used directly without purification. The polystyrene spheres (PS) were fabricated via batch emulsion polymerization, where styrene was mixed with methyl methacrylate (MMA) and acrylic acid (AA). For the preparation of the spherical cavity-based light-scattering TiO_2 layer, as prepared spheres were dispersed in the TiO_2 colloid with the particle size of about 20 nm as a coating paste for the preparation of the overlayer. The PS sphere, the previously mentioned TiO_2 colloid, and PEG were mixed in water with ratio of 1/0.5/0.3 (TiO_2/PS/PEG, by weight) and homogenized with a stirring bar and ultrasonication. The resulting paste was deposited as a light-scattering layer on the underlayer, followed by the same calcination procedure mentioned previously. Finally, the double-layered TiO_2 film was impregnated with 0.2 M $TiCl_4$ aqueous solution at room temperature overnight and then calcinated again at 500°C for 30 minutes. After cooling to about 120°C, the films were emerged overnight in 1 : 1 v/v acetonitrile and *tert*-butyl alcohol solvent mixture containing N719 dye at a concentration of 0.3 mM. A Pt-sputtered FTO glass was used as a counter electrode. The electrolyte was composed of 0.6 M 1-propyl-3-methylimidazolium iodide, 0.1 M LiI, 0.04 M I_2, and 0.5 M tert-butylpyridine in the mixture of acetonitrile and valeronitrile (1 : 1, by volume).

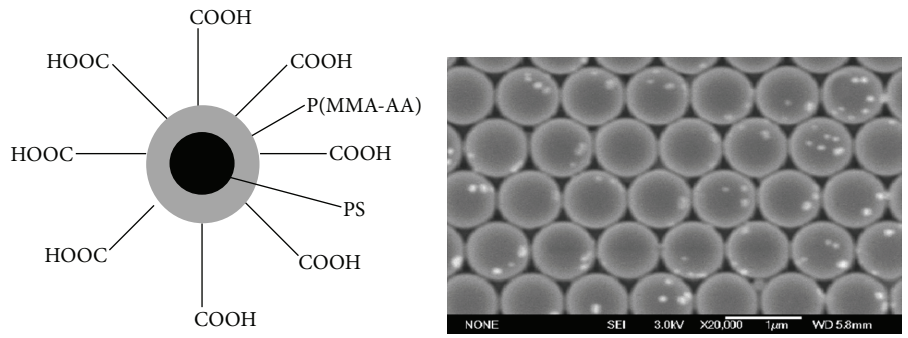
2.2. Characterization and Photoelectric Measurements. The SEM images of titania films were obtained with a field-emission SEM (JEOL JSM-4800, Japan). The optical reflection measurement was performed using an UV-vis spectrophotometer (U-3010, HITACHI) equipped with an integrating sphere.

The incident photon-to-current conversion efficiency (IPCE) for solar cells was measured by using a commercial setup (PV-25 DYE, JASCO) equipped with a monochromator. A 300 W Xenon lamp was employed as a light source for the generation of a monochromatic beam. Calibrations were performed with a standard silicon photodiode. IPCE is defined by $\mathrm{IPCE}(\lambda) = hc\,J_{sc}/e\varphi\lambda$, where h is Planck's constant, c is the speed of light in a vacuum, e is the electronic charge, λ is the wavelength in meters (m), J_{sc} is the short-circuit photocurrent density (A m^{-2}), and φ is the incident radiation flux (W m^{-2}). The photocurrent-voltage (*I-V*) characteristics were recorded using a computer-controlled Keithley 2400 source meter under air mass (AM) 1.5 simulated illumination (100 mw cm^{-2}, Oriel, 67005). The active area of the samples was about 0.2 cm^2, controlled by an aperture mask to prevent extra light from coming through the lateral space. *I-V* data were well within experimental error.

3. Results and Discussion

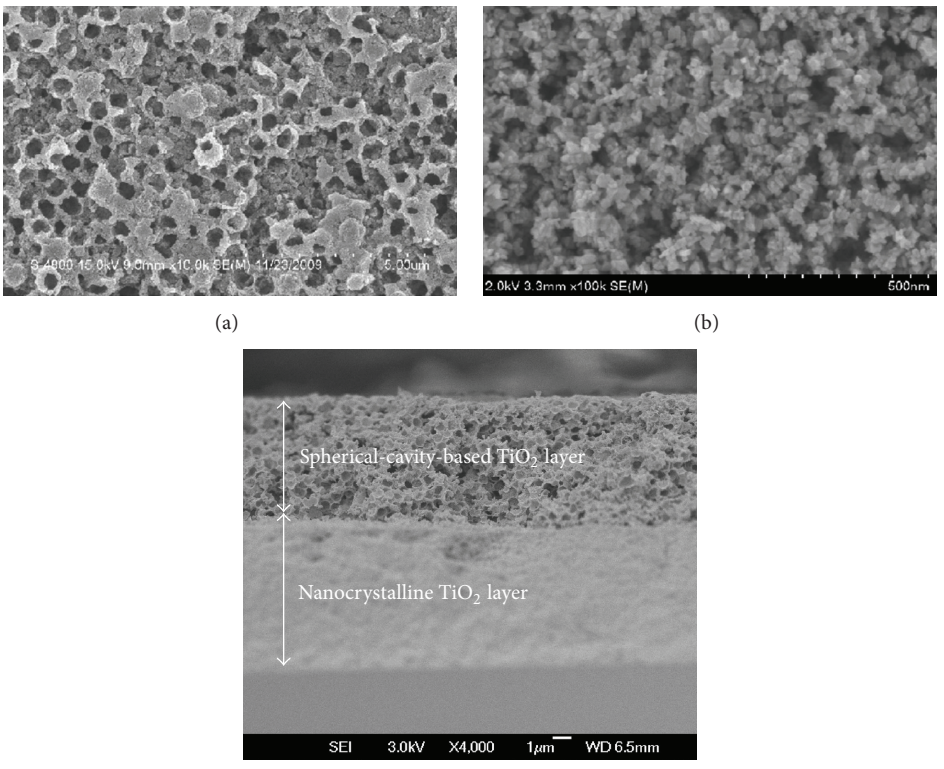
As shown in Figure 1(a), the latex PS sphere holds a hard PS core with an elastomeric PMMA/PAA shell and presents a monodispersity with the size of about 560 nm (Figure 1(b)). The TiO_2 overlayer was prepared through a simple mixing of submicrometer-size polystyrene (PS) spheres and nano sized TiO_2 particles, followed by subsequent coating and calcinations on a transparent TiO_2 underlayer. The PS spheres vanish during the calcination process.

The SEM image in Figure 2(a) shows a top surface image of the TiO_2 overlayer. It is very clear that homogeneous spherical voids spread on the whole surface with the size of around 600 nm. Figure 2(b) shows a top surface image of the TiO_2 transparent layer, which presents a porous structure comprised of 20 nm sized TiO_2 particles. The cross-sectional image of the corresponding double-layer electrode is shown in Figure 2(c), where the 8 μm thick transparent nanoporous TiO_2 underlayer and the 6 μm thick TiO_2 overlayer are formed without cracks.



(a) (b)

Figure 1: (a) A schematic structure of the functionalized polystyrene spheres. (b) A SEM image of the PS spheres with a diameter of 560 nm.



(a) (b) (c)

Figure 2: Scanning electron micrographs of (a) the top view of a spherical-cavity-based TiO_2 film, (b) the top view of a nanocrystalline TiO_2 film, (c) cross-sectional view of the double-layer TiO_2 film with a nanocrystalline TiO_2 layer and a spherical-cavity-based TiO_2 layer.

In order to investigate the light-scattering ability of the overlayer, UV-vis reflectance spectra were recorded for a 6 μm thick spherical-cavity-based TiO_2 film with and without sensitization by using a standard N719 dye, and an 8 μm-thick nanostructured TiO_2 film was employed for comparison, as shown in Figure 3. For the film without the dye loading, the reflectance of the overlayer is more than 70% in the whole UV-vis region, indicating that more than 90% of the light reflecting efficiency can be achieved by the overlayer when considering the absorption and reflection by the FTO glass substrate. By contrast the reflectance of the transparent nanostructured TiO_2 underlayer is less than 30%. After the dye adsorption, the reflectance was significantly decreased in the spectral range by around 535 nm for both the layers, where N719 dye has the maximum absorption, indicating that the reduction is mainly ascribed to the light absorption by the dye. Most importantly, the diffused reflectance of the TiO_2/dye composite film is found to be more than 50% in the range of λ = 650–800 nm after the dye loading for the overlayer.

We tested the double composite films as DSC photoelectrodes (denoted as sample 1) consisting of a 8 μm thick nanostructured TiO_2 underlayer and a 6 μm thick overlayer, in which a single-layer TiO_2 electrode only with the 8 μm

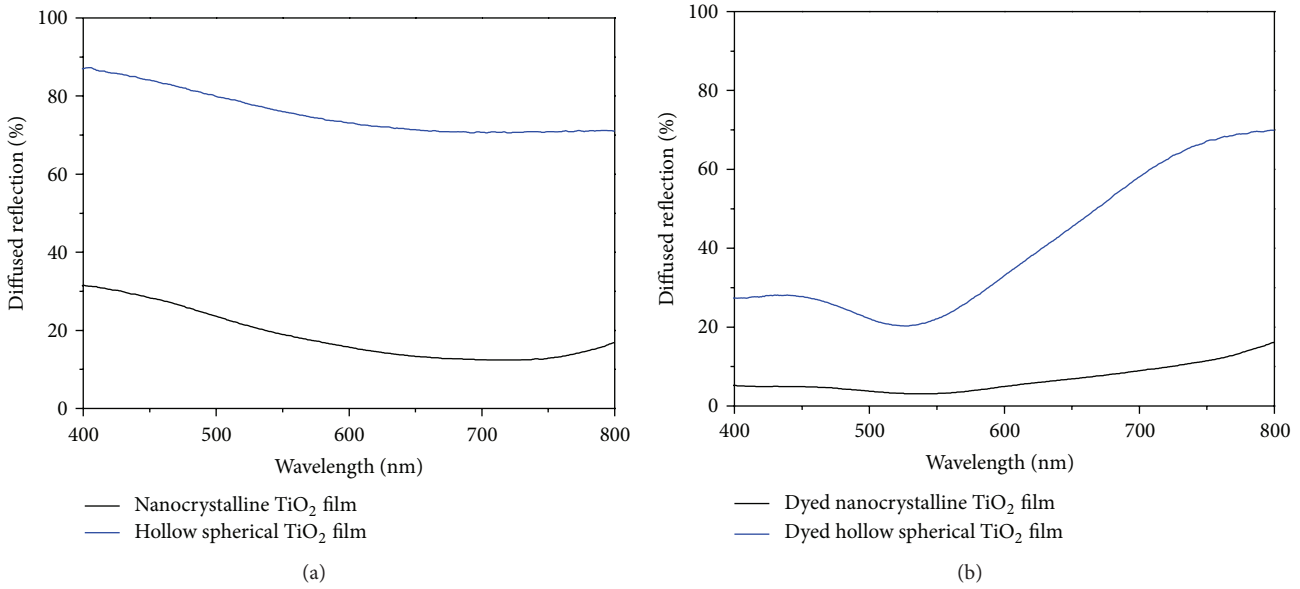


FIGURE 3: Diffused reflectance spectra of a nanocrystalline TiO_2 film (8 μm thick) and a spherical-cavity-based TiO_2 film (6 μm thick) without (a) and with (b) N719 dye loading.

TABLE 1: Photovoltaic characteristics of samples 1, 2, and 3 measured under AM1.5 illumination (100 mW cm^{-2}). Each data represents the average of three cells with active area of 0.2 cm^2.

Sample	Thickness [μm]	J_{sc} [mA/cm^2]	V_{oc} [V]	FF	η [%]	Adsorbed dye [μ mol cm^{-2}]
1	8 + 6	18.40 ± 0.05	0.73 ± 0.02	0.69 ± 0.01	9.25 ± 0.05	1.163
2	8	13.04 ± 0.03	0.73 ± 0.02	0.67 ± 0.01	6.38 ± 0.05	1.012
3	10	14.86 ± 0.03	0.70 ± 0.02	0.68 ± 0.01	7.07 ± 0.05	1.171

thick TiO_2 underlayer (sample 2) was used for comparison. The current-voltage characteristics are shown in Figure 4 and Table 1. The conversion efficiency (η) was improved from 6.38% for sample 2 to 9.25% for sample 1, corresponding to the 45% increment. The improved efficiency was mainly caused by the increase of the short-circuit current density (J_{sc}) from 13.04 mA cm^{-2} to 18.40 mA cm^{-2}, while the V_{oc}s and fill factors are the same or comparable for the two samples. It should be noted that, in the overlayer, the submicro-meter sized voids are surrounded by the nanostructured TiO_2 film with the TiO_2 particles of 20 nm. The dye molecules can be absorbed on the overlayer to contribute to the increment of J_{sc} in the double layer. In order to evaluate the effect of dye absorption in the overlayer on J_{sc}, the one-layer nanostructured TiO_2 electrode with a thickness of 10 μm was prepared (sample 3), by considering the amount of the dye loading for fair comparison (the porosity of TiO_2 overlayer : ~80%). The amounts of the absorbed dyes were determined for the three different electrodes by measuring the eluted dye concentration from the TiO_2 electrodes as shown in Table 1. The dye adsorption capacity was comparable for samples 1 and 3, suggesting that the scattering layer maintains a high dye-adsorption capacity. As shown in Table 1, sample 3 with the 10 μm thick TiO_2 electrode gave 14.86 mA cm^{-2} of J_{sc}, which was much lower than that of sample 1. A further comparison between sample 2 and sample 3 showed only a slight increase (1.82 mA cm^{-2}) in J_{sc}. On the other hand, the reflectance for sample 1 was significantly higher across the visible part of the spectrum than that of a single-layer TiO_2 cell as mentioned previously. Therefore, these results indicated that the marked increment in J_{sc} for sample 1 as compared to 3 is ascribed to the stronger light scattering, particularly at a red to near-infrared light region. It is thus postulated that both the light-scattering property and high dye-loading capacity from the integrated nanocrystalline composite electrodes resulted in the significant increase of IPCE as shown in Figure 5. In addition, it should be noted that the unaffected and effective electron diffusion coefficient in the double-layered TiO_2 is essential for the improved IPCE in sample 1.

4. Conclusions

We applied a facile colloidal template method for the preparation of spherical-cavity-based TiO_2/nanocrystalline TiO_2 double composite layers as a strong near-infrared light-scattering layer for N719-sensitized solar cells, which is particularly useful for the significant gain of photocurrents. The DSC fabricated by using double-layered electrodes composed of the scattering layer and the nanocrystalline TiO_2 layer produced a higher conversion efficiency of 9.25% versus 6.38% for the reference cell with a single TiO_2 electrode

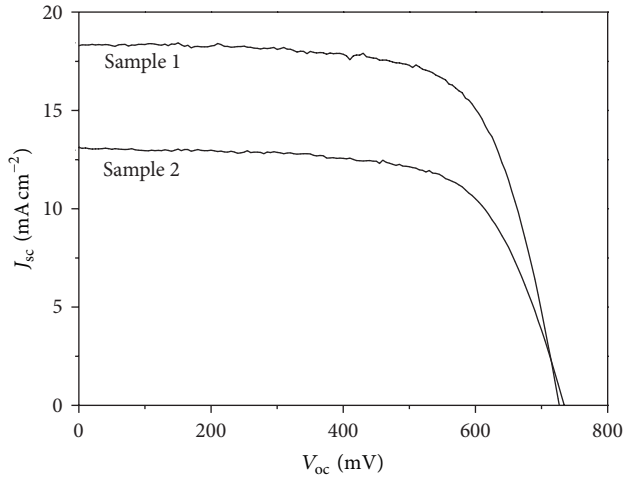


Figure 4: Photocurrent and voltage curves for samples 1 and 2. Both measurements were performed under AM 1.5 G with the active area of 0.2 cm^2.

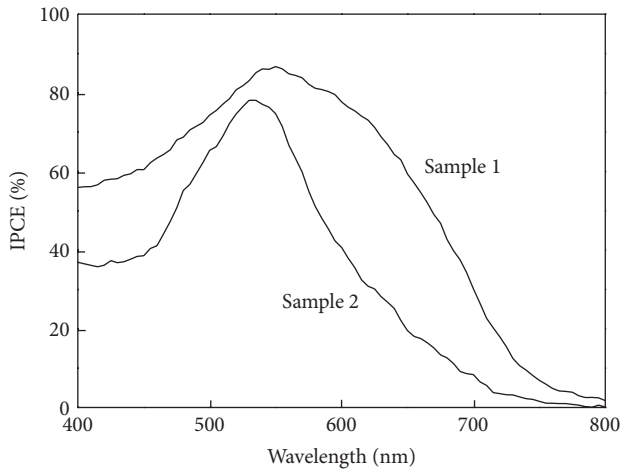


Figure 5: Incident monochromatic photon-to-current conversion efficiency (IPCE) as a function of excitation wavelength for samples 1 and 2.

with the comparable thickness. The results obtained from our facile photon capture approach could open up new perspectives of exploiting low-cost and high-efficiency DSCs with a wide range of newly developed dye molecules and electrolytes.

Conflict of Interests

The authors declare that there is no conflict of interests.

Acknowledgments

The authors would like to acknowledge the National 863 Program (no. 2011AA050521) and 973 Program (no. 2006CB806200), National Science Foundation of China (nos. 20774103, 50625312, 60601027, 20421101, and U0634004), (No. 50973105), and the Koshiyama Research Grant in Japan for financial support.

References

[1] B. O.'Regan and M. Grätzel, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films," *Nature*, vol. 353, pp. 737–740, 1991.

[2] S. Yanagida, Y. You, and K. Manseki, "Iodine/Iodide-Free Dye-Sensitized Solar Cells," *Accounts of Chemical Research*, vol. 42, no. 11, pp. 1827–1838, 2009.

[3] J. Xia and S. Yanagida, "Strategy to improve the performance of dye-sensitized solar cells: Interface engineering principle," *Solar Energy*, vol. 85, no. 12, pp. 3143–3159, 2011.

[4] A. Yella, H. W. Lee, H. N. Tsao et al., "Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency," *Science*, vol. 334, no. 6056, pp. 629–634, 2011.

[5] A. Usami, "Theoretical simulations of optical confinement in dye-sensitized nanocrystalline solar cells," *Solar Energy Materials and Solar Cells*, vol. 64, no. 1, pp. 73–83, 2000.

[6] C. J. Barbé, F. Arendse, P. Comte et al., "Nanocrystalline titanium oxide electrodes for photovoltaic applications," *Journal of the American Ceramic Society*, vol. 80, no. 12, pp. 3157–3171, 1997.

[7] S. Ito, P. Comte, P. Chen et al., "Fabrication of screen-printing pastes from TiO_2 powders for dye-sensitised solar cells," *Progress in Photovoltaics*, vol. 15, no. 7, pp. 603–612, 2007.

[8] Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, and L. Han, "Dye-sensitized solar cells with conversion efficiency of 11.1%," *Japanese Journal of Applied Physics*, vol. 45, no. 24-28, pp. L638–L640, 2006.

[9] T. P. Chou, Q. Zhang, G. E. Fryxell, and G. Cao, "Hierarchically structured ZnO film for dye-sensitized solar cells with enhanced energy conversion efficiency," *Advanced Materials*, vol. 19, no. 18, pp. 2588–2592, 2007.

[10] D. H. Chen, F. Z. Huang, Y. -B. Cheng, and R. A. Caruso, "Mesoporous anatase TiO_2 beads with high surface areas and controllable pore sizes: a superior candidate for high-performance dye-sensitized solar cells," *Advanced Materials*, vol. 21, no. 21, pp. 2206–2210, 2009.

[11] I. G. Yu, Y. J. Kim, H. J. Kim, C. Lee, and W. I. Lee, "Size-dependent light-scattering effects of nanoporous TiO_2 spheres in dye-sensitized solar cells," *Journal of Materials Chemistry*, vol. 21, no. 2, pp. 532–538, 2011.

[12] H. J. Koo, Y. J. Kim, Y. H. Lee, W. I. Lee, K. Kim, and N. G. Park, "Nano-embossed Hollow Spherical TiO_2 as Bifunctional Material for High-Efficiency Dye-Sensitized Solar Cells," *Advanced Materials*, vol. 20, no. 1, pp. 195–199, 2008.

[13] S. C. Yang, D. J. Yang, J. Kim et al., "Hollow TiO_2 Hemispheres Obtained by Colloidal Templating for Application in Dye-Sensitized Solar Cells," *Advanced Materials*, vol. 20, no. 5, pp. 1059–1064, 2008.

[14] D. Li, P. C. Chang, C. J. Chien, and J. G. Lu, "Applications of tunable TiO_2 nanotubes as nanotemplate and photovoltaic device," *Chemistry of Materials*, vol. 22, no. 20, pp. 5707–5711, 2010.

[15] J. Yu, J. Fan, and L. Zhan, "Dye-sensitized solar cells based on hollow anatase TiO_2 spheres prepared by self-transformation method," *Electrochimica Acta*, vol. 55, no. 3, pp. 597–602, 2010.

[16] S. H. A. Lee, N. M. Abrams, P. G. Hoertz, G. D. Barber, L. I. Halaoui, and T. E. Mallouk, "Coupling of titania inverse opals to nanocrystalline titania layers in dye-sensitized solar cells," *Journal of Physical Chemistry B*, vol. 112, no. 46, pp. 14415–14421, 2008.

[17] A. Mihi, M. E. Calvo, J. A. Anta, and H. Miguez, "Spectral response of opal-based dye-sensitized solar cells," *Journal of Physical Chemistry C*, vol. 112, pp. 13–17, 2008.

[18] S. Nishimura, N. Abrams, B. A. Lewis et al., "Standing wave enhancement of red absorbance and photocurrent in dye-sensitized titanium dioxide photoelectrodes coupled to photonic crystals," *Journal of the American Chemical Society*, vol. 125, no. 20, pp. 6306–6310, 2003.

[19] L. J. Diguna, Q. Shen, J. Kobayashi, and T. Toyoda, "High efficiency of CdSe quantum-dot-sensitized TiO_2 inverse opal solar cells," *Applied Physics Letters*, vol. 91, no. 2, Article ID 023116, 2007.

[20] S. Guldin, S. Hüttner, M. Kolle et al., "Dye-sensitized solar cell based on a three-dimensional photonic crystal," *Nano Letters*, vol. 10, no. 7, pp. 2303–2309, 2010.

[21] S. Colodrero, A. Mihi, L. H*n*ggman et al., "Porous one-dimensional photonic crystals improve the power-conversion efficiency of dye-sensitized solar cells," *Advanced Materials*, vol. 21, no. 7, pp. 764–770, 2009.

[22] S. Hore, P. Nitz, C. Vetter, C. Prahl, M. Niggemann, and R. Kern, "Scattering spherical voids in nanocrystalline TiO_2 —Enhancement of efficiency in dye-sensitized solar cells," *Chemical Communications*, no. 15, pp. 2011–2013, 2005.

[23] T. T. T. Pham, T. Bessho, N. Mathews et al., "Light scattering enhancement from sub-micrometer cavities in the photoanode for dye-sensitized solar cells," *Journal of Materials Chemistry*, vol. 22, no. 32, Article ID 16201, 2012.

[24] P. Wang, S. M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker, and M. Gratzel, "Enhance the performance of dye-sensitized solar cells by co-grafting amphiphilic sensitizer and hexadecylmalonic acid on TiO_2 nanocrystals," *Journal of Physical Chemistry B*, vol. 107, no. 51, pp. 14336–14341, 2003.

[25] K. Manseki, W. Jarernboon, Y. Youhai et al., "Solid-state dye-sensitized solar cells fabricated by coupling photoelectrochemically deposited poly(3,4-ethylenedioxythiophene) (PEDOT) with silver-paint on cathode," *Chemical Communications*, vol. 47, no. 11, pp. 3120–3122, 2011.

[26] J. X. Wang, Y. Q. Wen, H. Ge et al., "Simple Fabrication of Full Color Colloidal Crystal Films with Tough Mechanical Strength," *Macromolecular Chemistry and Physics*, vol. 207, no. 6, pp. 596–604, 2006.