JTTEE5 16:893–897
DOI: 10.1007/s11666-007-9090-z
1059-9630/$19.00 © ASM International

Fabrication of Nano-TiO_2 Coating for Dye-Sensitized Solar Cell by Vacuum Cold Spraying at Room Temperature

Sheng-Qiang Fan, Chang-Jiu Li, Guan-Jun Yang, Ling-Zi Zhang, Jin-Cheng Gao, and Ying-Xin Xi

(Submitted March 9, 2007; in revised form May 21, 2007)

Deposition of nanocrystalline TiO_2 coating at low temperature is becoming more attractive due to the possibility for continuous roll production of the coating for assembly lines of dye-sensitized solar cell (DSC) at a low cost. In this study, porous nano-TiO_2 coating was deposited by vacuum cold spraying (VCS) at room temperature on a conducting glass substrate using commercial P25 nanocrystalline TiO_2 powder. The microstructure of TiO_2 coating was characterized by field emission scanning electron microscopy (FESEM) and nitrogen adsorption test. A commercial dye (N719) was adsorbed on the surface of TiO_2 particles within the coating to assemble a DSC. The cell performance was evaluated by employing simulated solar light at an intensity of 100 mW/cm^2. The results showed that TiO_2 coating was deposited by the agglomerates of nano-TiO_2 powders. The Brunauer-Emmett-Teller (BET) test of the as-sprayed TiO_2 coating yielded a porosity of 49% and an average pore size of 17 nm. The assembled solar cell yielded a short-circuit current density of 7.3 mA/cm^2 and an energy conversion efficiency of 2.4%. The test results indicate that VCS was a promising method to deposit nanocrystalline TiO_2 coatings at low temperature applied to DSCs.

Keywords agglomerates, dye-sensitized solar cell, nanocrystalline material, porosity, TiO_2, vacuum cold spray

1. Introduction

At the beginning of 1990s, Grätzel and coworkers (Ref 1) reported a promising dye-sensitized solar cell (DSC) assembled using nanocrystalline TiO_2. High amounts of dye-molecules can be adsorbed due to large internal surface area of porous nanocrystalline coating. Consequently, the cells of a high light harvesting efficiency have been assembled. The solar power conversion efficiency of the cell reached a value higher than 11%, which makes it a possible competitor of silicon solar cell because of its low cost (Ref 2). Nano-TiO_2 coating is usually prepared through at least two steps. At first step, TiO_2 is deposited on a conducting glass substrate using a suspension or a paste containing nano-TiO_2 particles in a desired size (Ref 3, 4). Organic binders, surfactants, and porosity controlling agents are usually added to the suspension to optimize the microstructure of the resulting nanocrystalline coating. In the second step, the sintering at a temperature of above 400 °C is commonly employed to promote the formation of a continuous nanoparticle network with sufficient cohesion, and electrical contact to the substrate and between the nanoparticles as well (Ref 5). The organic additives are burnt off during the sintering.

Transparent conducting oxide (TCO) coated glass is usually employed as substrate material of the DSC due to its excellent optical, electrical and encapsulation barrier properties, and compatibility with high-temperature processing. Recently, it is considered that flexible plastic substrates can be potentially used as the substrate for DSC. Using such substrates, roll-to-roll production techniques can be applied to cost-effective mass production of thin film solar cells (Ref 6). However, the usage of plastic substrates limits the selection of TiO_2 suspension and additives because polyethyleneterephtalate (PET) as a typical plastic substrate of DSC can only be processed at a temperature lower than 150 °C. Hence, with a plastic substrate, a simple suspension of TiO_2 nanoparticles in ethanol or water (Ref 6, 7) without any organic additive is required to deposit TiO_2 coatings. Due to the high surface tension of TiO_2 suspension without surfactants (Ref 8), it is difficult to form a uniform TiO_2 coating by conventional

---

This article is an invited paper selected from presentations at the 2007 International Thermal Spray Conference and has been expanded from the original presentation. It is simultaneously published in *Global Coating Solutions, Proceedings of the 2007 International Thermal Spray Conference*, Beijing, China, May 14-16, 2007, Basil R. Marple, Margaret M. Hyland, Yuk-Chiu Lau, Chang-Jiu Li, Rogerio S. Lima, and Ghislain Montavon, Ed., ASM International, Materials Park, OH, 2007.

Sheng-Qiang Fan, Chang-Jiu Li, Guan-Jun Yang, Ling-Zi Zhang, and **Jin-Cheng Gao**, State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, P.R. China; and **Ying-Xin Xi**, Applied Chemistry Department, School of Science, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, P.R. China. Contact e-mail: licj@mail.xjtu.edu.cn.

methods, including spin coating (Ref 9, 10), doctor blading (Ref 11, 12), and electrophoretical deposition (Ref 13, 14). The resultant TiO_2 coatings are generally crack-rich with a porosity of even as high as 80% (Ref 13).

Therefore, with plastic substrates, the low temperature processes were attempted to immobilize nanocrystalline TiO_2. The methods include low-temperature sintering (Ref 9, 12), hydrothermal crystallization (Ref 15, 16), chemical vapor deposition of Ti alkoxides (Ref 13), microwave irradiation (Ref 17, 18), UV light irradiation (Ref 13, 19), electron bombardment (Ref 20), and the room temperature compressing process (Ref 6, 21, 22). However, only a weak contact between TiO_2 particles is present in the TiO_2 coatings deposited by low temperature processes mentioned above. As a result, the assembled cell attained an energy conversion efficiency about half of the cells assembled using the TiO_2 coatings sintered at a high temperature (Ref 7, 14, 15). On the other hand, those reported results suggest that the nanocrystalline TiO_2 deposited by low temperature process can be applied to DSC.

Recently, a new spray deposition system, vacuum cold spraying (VCS), has been installed in our laboratory (Ref 23). In VCS, dry TiO_2 powder is directly deposited on a solid glass substrate to form a uniform coating under a reduced-pressure atmosphere at room temperature. TiO_2 coatings could be deposited through solid particle impact of high velocity achieved by high pressure gas. The high dynamic pressure on impact makes it possible to form TiO_2 coatings with "good" mechanical stability and contact between particles even without any post-treatment. Our previous study showed that the VCS TiO_2 coatings could be deposited using nano-TiO_2 powder to a thickness from several micrometers to several tens of micrometers through controlling deposition parameters.

In this study, TiO_2 coatings were deposited by VCS and employed to assemble DSC. For comparison, a cell was also assembled using the VCS TiO_2 coating post-sintered at 450 °C for 30 min in order to examine the contact condition between TiO_2 particles in the as-deposited coating through cell performance. F-doped tin oxide (FTO) conducting glass was used as a substrate. The microstructure of VCS TiO_2 coating was characterized by field emission scanning electron microscopy (FESEM) and nitrogen adsorption apparatus. The performance of the cells was investigated using a simulated solar light at an intensity of 100 mW/cm^2 generated by a 500 W Xe lamp.

2. Experimental

2.1 Materials

P25 (Degussa, Dusseldorf, Germany) TiO_2 powder was used as a feedstock for coating deposition by VCS. A transparent FTO conducting glass (TEC-15, LOF, Toledo, Ohio, USA) of 15 Ω/cm^2 was employed as a substrate with dimensions of 1.5 cm × 2 cm. The FTO substrate was cleaned, before spraying in an ultrasonic acetone bath. LiI with a purity of >98% (Lancaster Synthesis, Lancaster, UK), I_2 (A.R, Sanpu, Xi'an, China), and acetonitrile (G.R, Kermel, Tianjin, China) were used to prepare electrolyte. A commercially available dye-sensitizer (N719, Solaronix, Aubonne, Switzerland) was employed in this study.

Table 1 Vacuum cold spraying parameters

Vacuum chamber pressure, Pa	2.3×10^2
Pressure of the aerosol room, Pa	1×10^6
He gas flow, L/min	2
Distance from nozzle exit to substrate, mm	5
Orifice size of nozzle, mm × mm	2.5×0.2
Substrate traverse speed, mm/s	5

2.2 Preparation of TiO_2 Coating

The TiO_2 coating was deposited using a home-developed VCS system (Ref 23). The system mainly constituted of a vacuum chamber, an accelerating gas feeding unit, a particle-accelerating nozzle, a two-dimensional worktable, and a control unit. The acceleration of TiO_2 particles was performed by high-pressure He gas. The coating thickness was about 15 μm. Spray parameters are given in Table 1.

2.3 Characterization of TiO_2 Powder and Coating

P25 TiO_2 powder consisted of agglomerates of primary nano-TiO_2 particles in a size of 25 nm in the diameter. The agglomerate size was measured by laser diffraction particle size analyzer (Mastersizer2000, Malvern Instruments Ltd., Malvern, UK). The topographic and cross-sectional morphologies of VCS TiO_2 coating were examined by FESEM (JSM-6700F, JEOL, Japan).

The porosity of VCS TiO_2 coating was estimated using a nitrogen adsorption-desorption apparatus (Coulter SA 3100 plus, Beckman Coulter, USA). The specific surface area was estimated by the Brunauer-Emmett-Teller (BET) equation and the pore size distribution was calculated by applying the Barret-Johner-Halenda (BJH) treatment to the desorption isotherm (Ref 24).

2.4 Fabrication of DSC

TiO_2 coating fabricated by VCS process was rinsed by absolute alcohol for anhydration. Then, it was soaked in a 3×10^{-4} mol L^{-1} N719 dye solution of alcohol for 24 h at room temperature. A Pt counter electrode was prepared in a way given elsewhere (Ref 25). The counter electrode was placed on the top of the dye-coated TiO_2 coating and separated by a 40 μm thick tape (Zhengtai, Fujian, China) to assemble a sandwich-type solar cell. An electrolyte with 0.5 mol L^{-1} LiI and 0.05 mol L^{-1} I_2 in acetonitrile was employed.

2.5 Photoelectrochemical Measurement

The performance of the DSC was examined under the illumination of a Xe lamp (CHF-500 W, Chuangtuo, Beijing, China) with a RGB-3 filter for simulating solar light at an intensity of 100 mW/cm^2. The photocurrent-voltage curves were measured through using a 1000 Ω slide rheostat as a load in the outer circuit (Ref 26). The conversion efficiency (η) was characterized by the short-circuit photocurrent density (I_{SC}), the open-circuit voltage (V_{OC}), the fill factor of the cell (ff), and the intensity of the incident light ($I_s = 100$ mW/cm^2) as follows:

$$\eta = I_{SC} \times V_{OC} \times \mathrm{ff}/I_s \qquad \text{(Eq 1)}$$

3. Results and Discussion

3.1 Microstructure of TiO$_2$ Coating by VCS

Figure 1 shows the cross-sectional morphology of nanocrystalline TiO_2 coatings deposited by VCS using P25 TiO_2 powder. The coatings were deposited on the FTO glass substrates and then fractured. Figure 1a was the as-sprayed TiO_2 coating and Fig. 1b was the sintered one at 450 °C for 30 min. It can be seen that the coatings were uniform in thickness. The thickness was 15 μm.

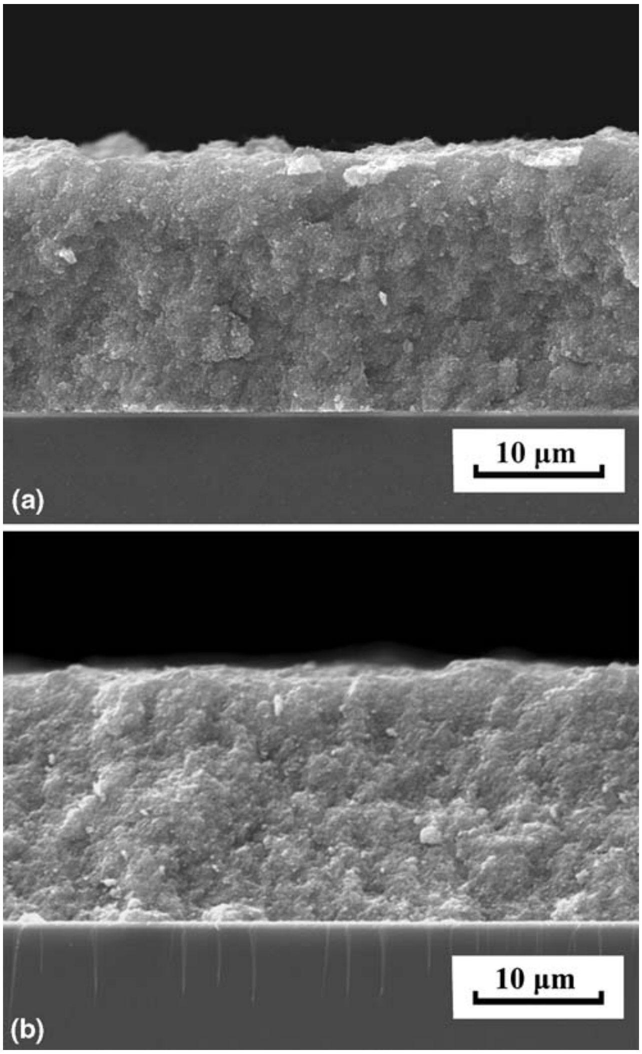

Fig. 1 Cross-sectional view of the nanocrystalline TiO_2 coating deposited on FTO glass substrate using P25 TiO_2 powders by vacuum cold spraying. (a) The as-sprayed TiO_2 coating, (b) the sintered TiO_2 coating at 450 °C for 30 min

P25 TiO_2 powder with a primary mean diameter of 25 nm was naturally agglomerated. The particle size distribution of agglomerates from the starting powders was characterized by laser diffraction particle analyzer (Fig. 2). Most agglomerated particles were in a size of several micrometers. Figure 3 shows typical surface morphology of TiO_2 coating prepared by the VCS process using P25 TiO_2 powder on the FTO substrate with the parameters shown in Table 1. It can be seen that TiO_2 coating was relatively compact in micrometer-sized scale, which was comparable with that deposited on ITO substrate (Ref 23). No obvious cracks were present in the

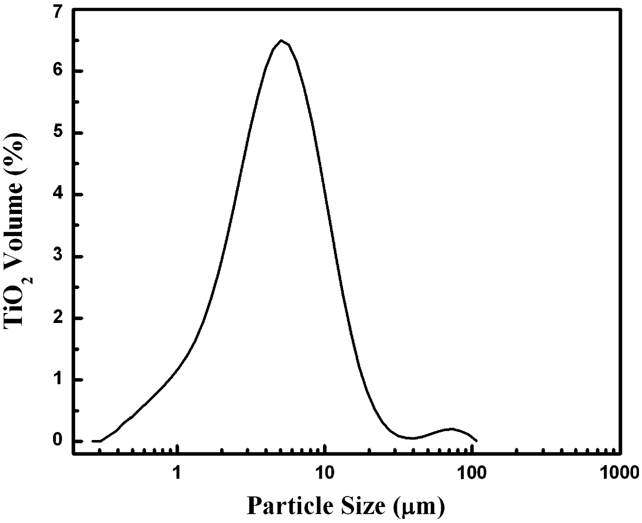

Fig. 2 Size distribution of agglomeraters in P25 TiO_2 feedstock powder

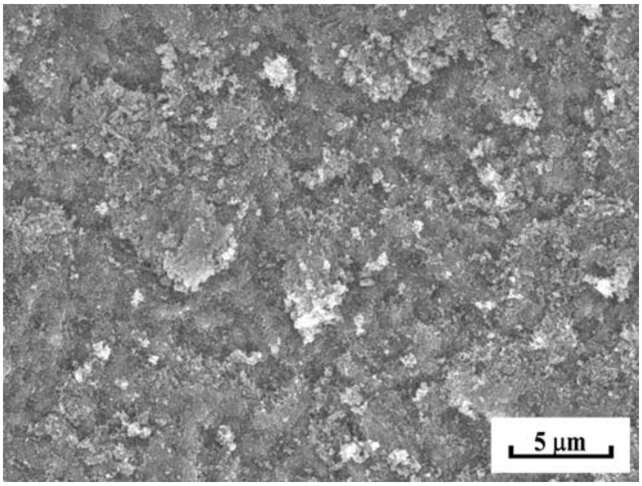

Fig. 3 Surface morphology of the nanocrystalline TiO_2 coating deposited on FTO glass substrate using P25 TiO_2 powders by vacuum cold spraying

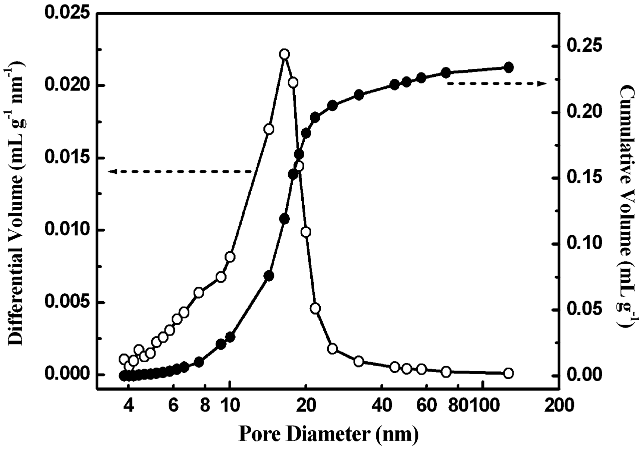

Fig. 4 Pore size distribution of TiO_2 coating deposited on FTO substrate by VCS using P25 TiO_2 powder

coating. Some large particles on the surface of the VCS TiO_2 coating have diameter of several micrometers comparable to that of TiO_2 agglomerates shown in Fig. 2. Therefore, possibly the deposition of TiO_2 nanocrystalline coating using P25 TiO_2 powder was achieved through the impact of the agglomerated particles. The compactness of the coating surface as shown in Fig. 3 implies that high contact pressure of impacting agglomerates at high velocity induced effectively the tamping effect on the deposited coating.

The pore size distribution of the VCS TiO_2 coating measured by the N_2 adsorption approach is presented in Fig. 4. The pore size ranged from 4 to 40 nm and the mean size was around 17 nm. The BET specific surface area was 56 m^2/g, which was the same as that of the starting P25 TiO_2 powder. From the cumulative pore volume of about 0.24 cm^3/g, the porosity of 49% was obtained, by taking 4.00 g/cm^3 as the density of P25 TiO_2 (Ref 14).

3.2 Performance of DSC

Figure 5 shows photocurrent-voltage curve of a DSC assembled using the as-deposited TiO_2 coatings by VCS on the FTO conducting glass substrate. It can be seen that the test of the cell's performance yielded a short-circuit current density of 7.3 mA/cm^2, an open circuit voltage of 0.54 V and an overall conversion efficiency of 2.4%. These values are comparable to that of the cells assembled using TiO_2 coatings prepared by other methods at low temperature, such as mechanical compression (Ref 7) and hydrothermal crystallization (Ref 27). This fact indicates that vacuum cold spaying was an effective low-temperature deposition method for nanocrystalline TiO_2 coating applied to DSC.

It was considered that the contacts between TiO_2 agglomerates formed in a VCS TiO_2 coating resulted from mechanical impact of agglomerates. Such contacts are weak, which limits the improvement of cell performance. Generally, the contacts between nano-TiO_2 particles can be improved by a sintering treatment. In order to investigate the influence of particle contacts in the coating on DSC cell's performance, a post-sintering at a temperature of 450 °C was applied to VCS TiO_2 coating for 30 min before assembly of solar cell. The performance of the cell composed of the annealed TiO_2 coating was shown in Fig. 5 for comparison. It is obvious that the short-circuit current density and conversion yield increased to 14.0 mA/cm^2 and 4.9%, respectively. Compared with the cell assembled using a sintered TiO_2 coating, the cell assembled with the as-sprayed TiO_2 coating reached about 50% of the short-circuit current density and the conversion yield. It was considered that the improvement of cell performance after sintering was attributed to the improvement of the contacts between nano-TiO_2 particles in the coating. On the other hand, this fact indicates that the contacts between nano-TiO_2 particles in the present coating attained only by impact were limited. Therefore, the improvement of cell performance should be attempted through improving the contacts between nano-TiO_2 particles in the as-sprayed coating by controlling deposition conditions.

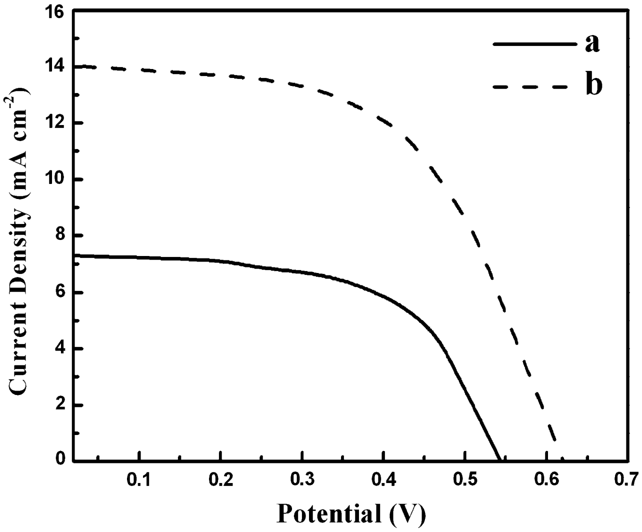

Fig. 5 Photocurrent-voltage characteristics of dye-sensitized solar cells composed of TiO_2 coating deposited by vacuum cold spraying on FTO substrate using P25 TiO_2 powder. (a) The cell assembled using the as-sprayed coating, (b) the cell assembled using the sintered coating at 450 °C for 30 min

4. Conclusions

TiO_2 coating was deposited by VCS at room temperature using 25 nm nano-TiO_2 feedstock powders. The porosity of the as-sprayed coatings estimated using N_2 adsorption method was 49% and the average pore size was 17 nm. The assembled solar cell yielded a short-circuit current density of 7.3 mA/cm^2 and an energy conversion efficiency of 2.4%. These results clearly indicated that VCS was a promising method to deposit nanocrystalline TiO_2 coatings at low temperature for DSC applications. Moreover, it was found that sintering the as-sprayed TiO_2 coating at a temperature of 450 °C for 30 min increased the short-current density and energy conversion efficiency of the cell by a factor of 2. This result clearly suggests that the contact between nano-TiO_2 particles in the nanocrystalline deposit significantly influences the cell's performance. It can be considered that the controlling of particle contact through deposition conditions benefits the improvement of DSC performance.

Acknowledgment

The present project is supported by the National Natural Science Foundation of China (Grant No.: 50602035).

References

1. B. O'Regan and M. Grätzel, A Low-Cost, High Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO_2 Films, *Nature*, 1991, **353**, p 737-740
2. R.D. McConnell, Assessment of the Dye-Sensitized Solar Cell, Renew, *Sust. Energ. Rev.*, 2002, **6**, p 273-295
3. M. Grätzel, Sol-Gel Processed TiO_2 Films for Photovoltanic Applications, *J. Sol-Gel. Sci. Technol.*, 2001, **22**, p 7-13
4. S. Burnside, S. Winkel, K. Brooks, V. Shklover, M. Grätzel, A. Hinsch, R. Kinderman, C. Bradbury, A. Hagfeldt, and H. Pettersson, Deposition and Characterization of Screen-Printed Porous Multi-Layer Thick Film Structures from Semiconducting and Conducting Nanomaterials for Use in Photovoltaic Devices, *J. Mater. Sci.: Mater. Electron.*, 2000, **11**, p 355-362
5. M. Grätzel, Conversion of Sunlight to Electric Power by Nanocrystalline Dye-Sensitized Solar Cells, *J. Photoch. Photobio. A: Chemistry*, 2004, **164**, p 3-14
6. H. Lindström, A. Holmberg, E. Magnusson, S. E. Lindquist, L. Malmqvist, and A. Hagfeldt, A New Method for Manufacturing Nanostructured Electrodes on Plastic Substrates, *Nano. Lett.*, 2001, **1**, p 97-100
7. A. Hagfeldt, G. Boschloo, H. Lindström, E. Figgemeier, A. Holmberg, V. Aranyos, E. Magnusson, and L. Malmqvist, A System Approach to Molecular Solar Cells, *Coordin. Chem. Rev.*, 2004, **248**, p 1501-1509
8. J. Halme, J. Saarinen, and P. Lund, Spray Deposition and Compression of TiO_2 Nanoparticle Films for Dye-Sensitized Solar Cells on Plastic Substrates, *Sol. Energ. Mat. Sol. C.*, 2006, **90**, p 887-899
9. S. Ito, T. Takeuchi, T. Katayama, M. Sugiyama, M. Matsuda, T. Kitamura, Y. Wada, and S. Yanagida, Conductive and Transparent Multilayer Films for Low-Temperature-Sintered Mesoporous TiO_2 Electrodes of Dye-Sensitized Solar Cells, *Chem. Mater.*, 2003, **15**, p 2824-2828
10. F. Pichot, J.R. Pitts, and B.A. Gregg, Low-Temperature Sintering of TiO_2 Colloids: Application to Flexible Dye-Sensitized Solar Cells, *Langmuir*, 2000, **16**, p 5626-5630
11. S. Nakade, M. Matsuda, S. Kambe, Y. Saito, T. Kitamura, T. Sakata, Y. Wada, H. Mori, and S. Yanagida, Dependence of TiO_2 Nanoparticle Preparation Methods and Annealing Temperature on the Efficiency of Dye-Sensitized Solar Cells, *J. Phys. Chem. B*, 2002, **106**, p 10004-10010
12. C. Longo, J. Freitas, and M.-A. De Paoli, Performance and Stability of TiO_2/dye Solar Cells Assembled with Flexible Electrodes and a Polymer Electrolyte, *J. Photoch. Photobio. A: Chemistry*, 2003, **159**, p 33-39
13. T.N. Murakami, Y. Kijitori, N. Kawashima, and T. Miyasaka, Low Temperature Preparation of Mesoporous TiO_2 Films for Efficient Dye-Sensitized Photoelectrode by Chemical Vapor Deposition Combined with UV Light Irradiation, *J. Photoch. Photobio. A: Chemistry*, 2004, **164**, p 187-191
14. J.H. Yum, S.S. Kim, D.Y. Kim, and Y.E. Sun, Electrophoretically Deposited TiO_2 Photo-Electrodes for Use in Flexible Dye-Sensitized Solar Cells, *J. Photoch. Photobio. A: Chemistry*, 2005, **173**, p 1-6
15. D.S. Zhang, T. Yoshida, and H. Minoura, Low-Temperature Fabrication of Efficient Porous Titania Photoelectrodes by Hydrothermal Crystallization at the Solid/Gas Interface, *Adv. Mater.*, 2003, **15**, p 814-817
16. D.S. Zhang, T. Yoshida, K. Furuta, and H. Minoura, Hydrothermal Preparation of Porous Nano-Crystalline TiO_2 Electrodes for Flexible Solar Cells, *J. Photoch. Photobio. A: Chemistry*, 2004, **164**, p 159-166
17. S. Uchida, M. Tomiha, H. Takizawa, and M. Kawaraya, Flexible Dye-Sensitized Solar Cells by 28 GHz Microwave Irradiation, *J. Photoch. Photobio. A: Chemistry*, 2004, **164**, p 93-96
18. J. N. Hart, D. Menzies, Y.B. Cheng, G.P. Simon, and L. Spiccia, A Comparison of Microwave and Conventional Heat Treatments of Nanocrystalline TiO_2, *Sol. Energ. Mat. Sol. C.*, 2007, **91**(1), p 6-16
19. D. Gutiérrez-Tauste, I. Zumeta, E. Vigil, M.A. Hernández-Fenollosa, X. Domènech, and J.A. Ayllón, New Low-Temperature Preparation Method of the TiO_2 Porous Photoelectrode for Dye-Sensitized Solar Cells Using UV Irradiation, *J. Photoch. Photobio. A: Chemistry*, 2005, **175**, p 165-171
20. T. Kado, M. Yamaguchi, Y. Yamada, and S. Hayase, Low Temperature Preparation of Nano-Porous TiO_2 Layers for Plastic Dye Sensitized Solar Cell, *Chem. Lett.*, 2003, **32**(11), p 1056-1057
21. H. Lindstrom, A. Holmberg, E. Magnusson, L. Malmqvist, and A. Hagfeldt, A New Method to Make Dye-Sensitized Nanocrystalline Sola Cells at Room Temperature, *J. Photoch. Photobio. A: Chemistry*, 2001, **145**, p 107-112
22. H. Santa-Nokki, J. Kallioinen, T. Kololuoma, V. Tuboltsev, and J. Korppi-Tommola, Dynamic Preparation of TiO_2 Films for Fabrication of Dye-Sensitized Solar Cells, *J. Photoch. Photobio. A: Chemistry*, 2006, **182**, p 187-191
23. S.-Q. Fan, G.-J. Yang, C.-J. Li, G.-J. Liu, C.-X. Li, and L.-Z. Zhang, Characterization of Microstructure of Nano-TiO_2 Coating Deposited by Vacuum Cold Spraying, *J. Therm. Spray. Technol.*, 2006, **15**(4), p 513-517
24. Y. Saito, S. Kambe, T. Kitamura, Y. Wada, and S. Yanagida, Morphology Control of Mesoporous TiO_2 Nanocrystalline Films for Performance of Dye-Sensitized Solar Cells, *Sol. Energ. Mat. Sol. C.*, 2004, **83**, p 1-13
25. S.-Q. Fan, C.-J. Li, C.-X. Li, G.-J. Liu, G.-J. Yang, and L.-Z. Zhang, Preliminary Study of Performance of Dye-Sensitized Solar Cell of Nano-TiO_2 Coating Deposited by Vacuum Cold Spraying, *Mater. Trans.*, 2006, **47**(7), p 1703-1709
26. G.P. Smestad and M. Grätzel, Demonstrating Electron Transfer and Nanotechnology: A Natural Dye-Sensitized Nanocrystalling Energy Converter, *J. Chem. Educ.*, 1998, **75**, p 752-756
27. T. Oekermann, D.S. Zhang, T. Yoshida, and H. Minoura, Electron Transport and Back Reaction in Nanocrystalline TiO_2 Films Prepared by Hydrothermal Crystallization, *J. Phys. Chem. B*, 2004, **108**, p 2227-2235