J Sol-Gel Sci Technol (2014) 72:67–73
DOI 10.1007/s10971-014-3427-0

ORIGINAL PAPER

Effect of titanium isopropoxide addition in low-temperature cured TiO_2 photoanode for a flexible DSSC

Hohyoung Kim · Taejin Hwang

Received: 21 February 2014 / Accepted: 7 June 2014 / Published online: 17 June 2014

Abstract In this study, titanium isopropoxide (TIPP) was employed as a binder for low-temperature processed photoanode of a flexible dye sensitized solar cell. The coating paste for dip-coating method was prepared comprising commercially available TiO_2 nanoparticles, TIPP and small amount of water. Effect of binder addition was compared at three different TIPP to TiO_2 nanoparticle molar ratios; 0.05, 0.1 and 0.3. By adding TIPP molecules directly to the coating paste, flexible photoanodes were successfully prepared. An optimum TIPP to TiO_2 particle ratio was selected considering the particle dispersion stability in the paste and the microstructure of prepared photoanode. The photoanode prepared using the paste with optimized composition showed highest photoconversion efficiency of 1.96 % from a unit cell.

Keywords Dye-sensitized solar cell · Photoanode · Low-temperature · Flexible · Titanium isopropoxide

1 Introduction

Dye sensitized solar cell (DSSC) is considered as one of the most feasible alternative to the conventional silicon-based solar cell devices due to the easiness of fabrication and the lower material cost. Ever since the groundbreaking discovery by Grätzel et al. [1], the energy conversion efficiency of the state-of-the-art DSSC has long been glued to around 10 % [2, 3, 4]. Unlike the conventional silicon-based solar cells, DSSC could easily be fabricated into a flexible form, and it is once again considered as a distinguished advantage. Together with the world-wide efforts to increase the energy harvesting efficiency, many tries to expand the application range of DSSC have also been performed including the preparation of flexible devices [5–9].

In most of the cases, where glass substrate is employed, a high temperature preparation method at such as 500 °C is frequently used to fabricate the TiO_2 photoanode. The high temperature sintering is to induce the necking of TiO_2 particles while maintaining the porous structure, which provides the electron diffusion pathway [10, 11]. However, when plastic substrate such as polyethylene naphthalate (PEN) or polyethylene terephthalate (PET) is used for the flexible DSSC, the photoanode deposited on the substrate should be processed under 150 °C [12–14]. The low-temperature processing of photoanode inevitably produces poor consolidation of particles, consequently sacrificing the photoconversion efficiency of the device. This is, in many cases, a big problem blocking prompt application of flexible DSSC to daily devices.

To tackle this low-temperature processing problem, sintering aids such as binder is frequently used, which helps the necking of TiO_2 particles even after low-temperature treatment. Pasquier demonstrated that a sol–gel prepared TiO_2 sol holds nanoparticles together after a heat treatment at around 130 °C [15]. Park et al. [16] showed a possibility of using binder-free TiO_2 paste for fabricating the photoanode just by drying at 150 °C. $CaCO_3$ coating also helped the TiO_2 nanoparticles to be cemented with

H. Kim · T. Hwang (✉)
Surface Technology R&BD Group, Korea Institute of Industrial Technology (KITECH), Gaetbeol-ro 156, Yeonsu-gu, Incheon Metropolitan City 406-840, Republic of Korea
e-mail: greathtj@kitech.re.kr

T. Hwang
Department of Electronic Packaging Engineering, Korea University of Science and Technology (UST), Gajeong-ro 217, Yuseong-gu, Daejeon 305-350, Republic of Korea

each other eventually to produce higher efficiency from the device [17, 18]. In some cases, the post treatment with Ti, In, Zr oxide precursor solution was tried to induce hydrolysis of the precursor after the TiO_2 photoanode is deposited on substrate [19]. As a novel trial, the anodized nanotube array was transferred to the flexible substrate to induce the efficiency improvement by the nanostructuring [6]. The aerosol deposition method was also tried to deposit TiO_2 layer without undergoing thermal treatment at elevated temperatures [20]. Not only the low-temperature deposition but also high-temperature sintering of TiO_2 on the surface of stainless steel mesh was tried to elucidate the possibility as the photoanode without transparent conductive electrode [21]. However, in spite of all these efforts, the flexible DSSC still needs more improvement in efficiency for the successful daily application.

In this study, we employed a precursor of TiO_2, titanium isopropoxide, as the binder for low-temperature consolidation of TiO_2 nanoparticles. Binder incorporated TiO_2 coating paste was prepared for the application of dip-coating method. Three sets of coating paste were prepared to investigate the effect of titanium isopropoxide (TIPP) content on photoconversion efficiency. To utilize the reactivity, the precursor molecules were added to the paste without prior hydrolysis, by which better chance of bonding among particles was intended.

2 Experiments

Commercially available TiO_2 nanopowder (Degussa, Aeroxide® P25) was used as the main material for the preparation of active electrode. The used nanoparticle is of 21 nm in average primary particle size and 80 wt% anatase: 20 wt% rutile in crystallographic phase. Titanium isopropoxide (TIPP, 98+ %, ACROS) was used as the precursor of sol–gel chemical synthesis to form binding bridges among the TiO_2 particles. All the chemicals and materials were used as received without further purification.

Coating paste was prepared as follows. 10 g of TiO_2 nanopowder was first dispersed into an ethanolic solution (1.4 g of D.I. water and 86.8 g of ethanol) importantly by using ultrasonication for 20 min. A simple stirring with either magnetic bar or mechanical screw was not enough to obtain stable dispersion of TiO_2 particles for at least 7 days, which is frequently requested under the mass production environment. Instead a high power (1 kW) ultrasonication is indispensable. Into the dispersion, 1.8 g of TIPP was added dropwise. Then the mixture was kept under mild stirring for about 5 h to achieve the further homogenization. For finding the optimized processing condition, the composition of the coating paste was varied in terms of molar ratio of TIPP:P25 powder, and the detailed compositions are given in Table 1.

Table 1 The composition of each prepared coating pastes

TIPP:P25 (molar ratio)	TIPP (g)	P25 (g)	Ethanol (g)	D.I. water (g)
0.05:1	1.8	10	86.8	1.4
0.1:1	3.6	10	85	1.4
0.3:1	10.7	10	77.9	1.4

Using the above prepared coating pastes, TiO_2 active electrode were dip-coated on flexible substrate, which is, in this study, ITO-coated PEN film (20–25 Ω/□, OIKE Co., Japan). To make the films thick enough for the operation as the active electrode for flexible DSSC, dipping was done 4 times so as the thickness of the prepared films to reach up to a certain extent. The deposited films were dried in air for about 15 min, and then heat treated in a convection oven at 120 °C for 1 h. The microstructure of the prepared films was investigated by using scanning electron microscopy (SEM).

For the comparison of energy conversion efficiency of the low-temperature processed active electrodes, unit cells were also assembled using the obtained films. The photoanodes were kept in the dye solution of 0.3 mM N719 in ethanol for 21 h for the adsorption of dye onto the surface of porous TiO_2 films. The dye-adsorbed TiO_2 films were then washed with ethanol and subsequently dried in air at 60 °C for 30 min. The preparation of the unit cell followed standard preparation process; the dye-coated photoanodes were sealed (Surlyn, Dupont) into the unit cells together with the counter electrode (Pt coated on the ITO-coated PEN) and the injected electrolyte (0.6 M BMII, 0.05 M I_2, 0.1 M LiI, and 0.5 M TBP in methoxypropionitrile). Photoconversion efficiency was investigated by the J–V measurement method under 1 Sun (Air Mass 1.5) illumination condition by a solar simulator (SS-200XIL, EKO Instruments Co.).

3 Results and discussion

For the comparison of the effect of TIPP:P25 ratio on TiO_2 film properties, the pastes were prepared at varying TIPP:P25 ratios as given in Table 1. The hydrolysis and condensation of TIPP were carried out without the addition of catalyst such as HCl or HNO_3, since the reactivity of TIPP was fast enough at room temperature. The TEM image of the TiO_2 particles in the paste of TIPP:P25 = 0.1:1 is given in Fig. 1. TiO_2 network that was formed by the hydrolysis of TIPP with the water in the paste and condensation into solid phase was also seen as in the inset of Fig. 1. As a whole, the

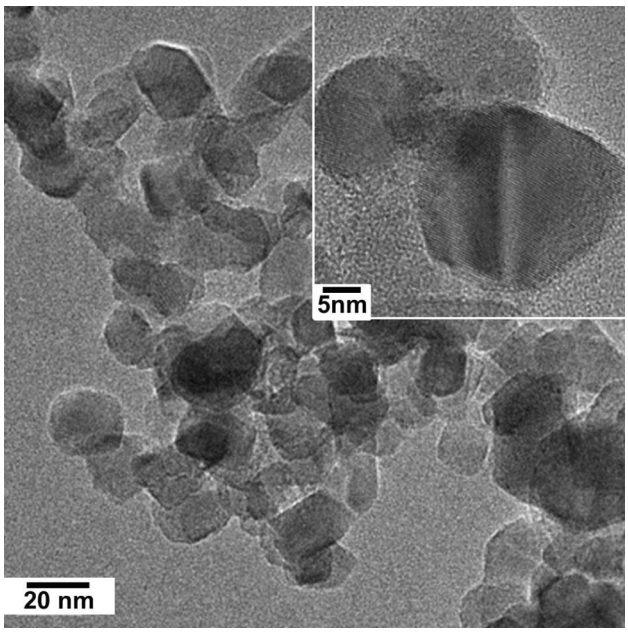

Fig. 1 TEM image of TiO_2 particles dispersed in the coating paste (TIPP:P25 = 0.1:1)

paste showed comparably stable dispersion after the ultrasonication regardless of given TIPP:P25 ratio. The addition of TIPP into the TiO_2 paste produced stable sols and the formation of bridging network between the particles was verified by the SEM microscopy.

Apparently, the pastes with TIPP:P25 = 0.05:1 and 0.1:1 exhibited stable dispersion as in Fig. 2a and b, respectively, while the sample with TIPP:P25 = 0.3:1 showed agglomeration of particles that were observed on the glass tube wall as in Fig. 2c. The excess amount of TIPP was found to produce agglomeration of P25 particles, due to an extended TiO_2 network formation among the particles [22]. This type of agglomeration was also reported when the paste was stored certain period of time [23]. The film made by the paste with TIPP:P25 = 0.1:1 showed highest quality as shown in Fig. 2b. The quality of the deposited films were compared by the UV/VIS spectra as given in Fig. 2e. The film by the paste with TIPP:P25 = 0.1:1 showed highest transparency, which could be attributed to the uniform dispersion of particles that was observed in the paste as in Fig. 2a. The transparent film also showed noticeable flexibility as in Fig. 2d.

The other samples with lesser or higher amount of TIPP than the one in Fig. 2b showed much different properties. The film with lesser amount of binder (TIPP) showed poor adhesion as in Fig. 2a showing exfoliation at some parts of the sample. The adjusted TIPP:P25 ratio at 0.05:1 simply meant insufficient addition of binder in the film. On the contrary, the excess amount of TIPP (TIPP:P25 = 0.3:1) produced translucency of the obtained film. This is because of the particles agglomeration that was observed from the paste (Fig. 2c) [22].

Surface microstructure of the films was investigated by SEM and the micrographs are given in Fig. 3. As intended, porous nature of films were observed for all samples, however, the microstructure was somehow different according to the TIPP:P25 ratio. It could be easily noticed that the film with TIPP:P25 = 0.1:1 has most uniform surface without much apparent cracks as in Fig. 3c and d. Uniform dispersion of particles in the paste and the high transparency of the film that was observed with bare eyes were once again supported by the most uniform SEM microstructure of the prepared film. In contrast, the sample

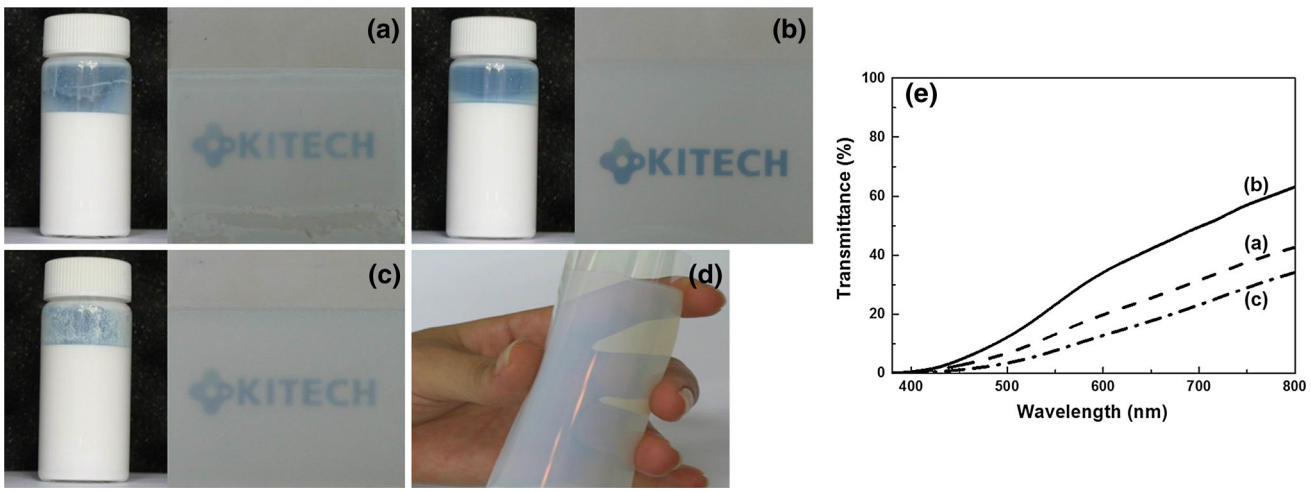

Fig. 2 Prepared TiO_2 pastes with different molar ratios of TIPP:P25 and corresponding film samples; **a** TIPP:P25 = 0.05:1, **b** TIPP:P25 = 0.1:1 and **c** TIPP:P25 = 0.3:1. **d** Flexibility of TiO_2 film casted on the flexible substrate with the paste in **b**. **e** The UV/VIS spectra of the films **a**, **b** and **c**

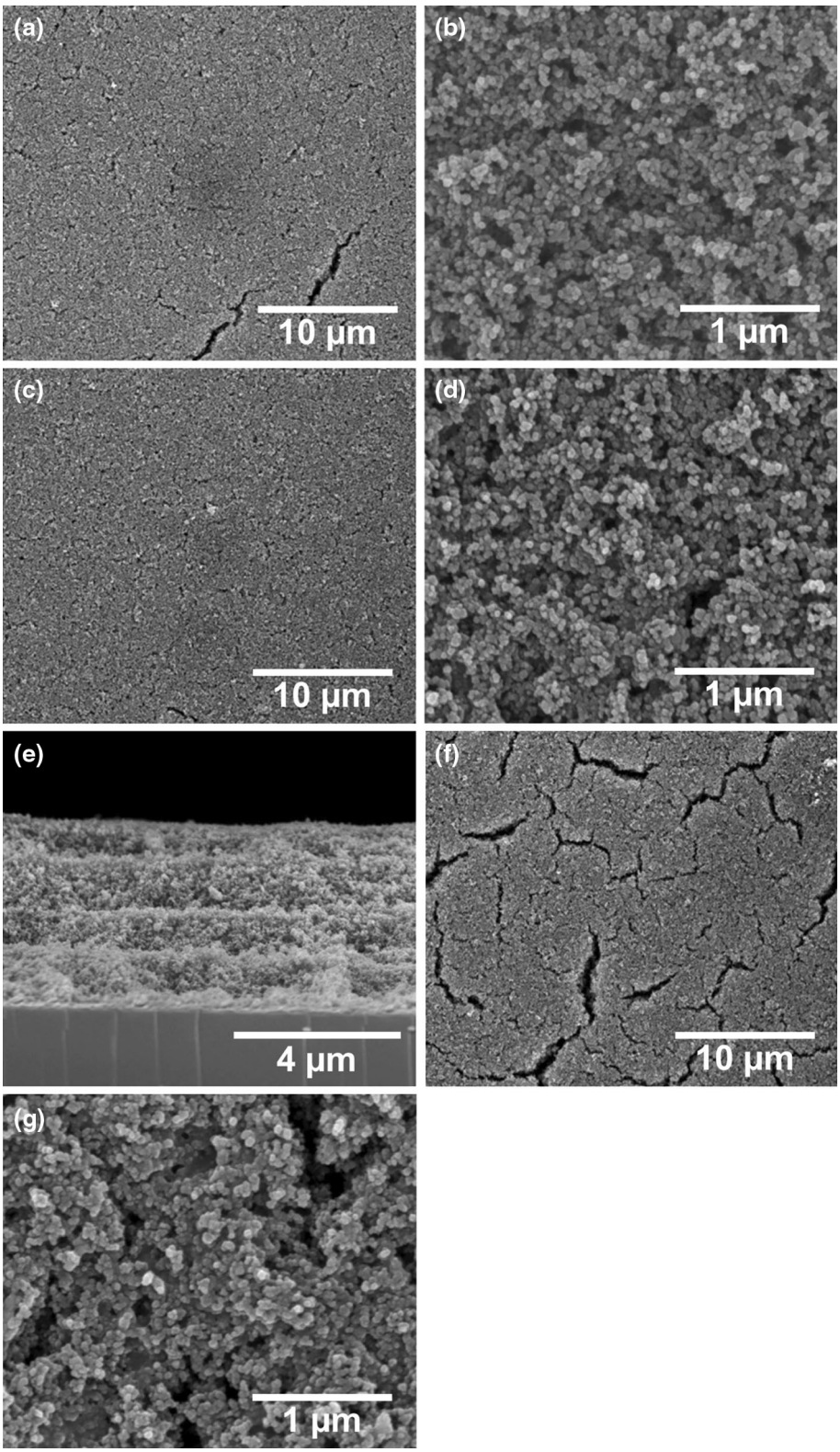

Fig. 3 SEM images of porous TiO_2 films prepared with the pastes of different molar ratios; **a** and **b** TIPP:P25 = 0.05:1, **c**–**e** TIPP:P25 = 0.1:1 and **f** and **g** TIPP:P25 = 0.3:1. **e** is the cross-sectional view of the film prepared with the paste of TIPP:P25 = 0.1:1

with lower (Fig. 3a, b) or higher amount of TIPP addition (Fig. 3f, g) showed much cracks on the surface. Insufficient addition of TIPP could produce cracks because of the poor binding of the particles, and the extended formation of TiO_2 network by the excess amount of TIPP could also cause the cracks because of the stiffness of film layer [24].

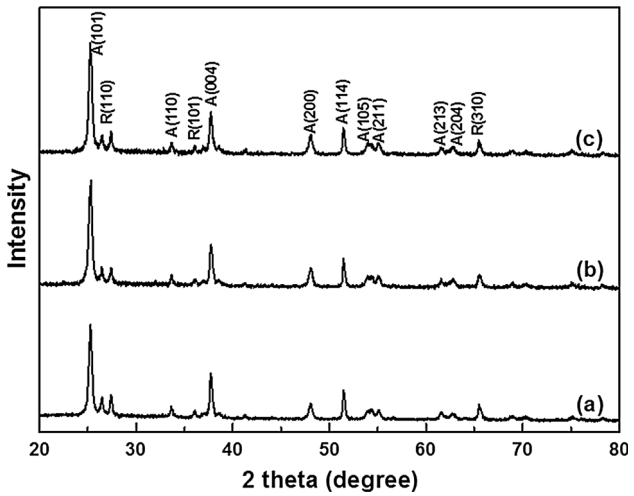

Fig. 4 XRD patterns of the prepared photoanodes with different TIPP:P25 ratios; **a** TIPP:P25 = 0.05:1, **b** TIPP:P25 = 0.1:1 and **c** TIPP:P25 = 0.3

This phenomenon of crack formation with the excess addition of sol–gel precursor could be understood by a development of the surface tension of pore fluid during the gel formation and the subsequent drying of gel [25]. The incorporated precursor molecules are ready to form the gel network via the hydrolysis and condensation reaction, which is subject to a drying after the film deposition. During the evaporation of the solvent from the gel network in ambient atmosphere inevitably produces stress in the network because of the surface tension, which is strong enough to break the network. To reduce the surface tension, many works employed the treatments such as addition of surfactant or dispersant [26, 27]. In the case of nanoparticle binding, the stress built-up in the TiO_2 film is of course proportionally increasing with the increasing portion of gel network by the addition of TIPP. The crack formation in the TiO_2 film with the excess amount of TIPP addition as in Fig. 3f could be attributed to this stress built up in the binder network. In contrast, the proper amount of TIPP (in our experiment, TIPP:P25 = 0.1:1) that produced endurable amount of stress gave uniform crack-free film as in Fig. 3c. From the observation, we could select TIPP:P25 = 0.1:1 as the optimum composition of paste. Thickness of the films was around 5 μm within the selected range of TIPP addition, as was shown in the cross-sectional view (Fig. 3e) of the film with TIPP:25-0.1:1.

XRD analysis was done on the prepared photoanodes, and the results are given in Fig. 4. Both anatase and rutile phase that are the phase found in the P25 TiO_2 powder (80 wt% anatase : 20 wt% rutile) were also detected in our experiment. Since the photoanodes were prepared by binding the P25 powder with TIPP through the low-temperature sol–gel process, the crystallographic phase of the photoanodes followed that of source powder, and the addition of TIPP does not exert any remarkable change in phase.

The unit cells with a dimension of 0.6 mm × 0.6 mm were built using the prepared porous TiO_2 active electrodes. The photoconversion efficiency of the cells was investigated by the J–V measurement method using the unit cells having the sandwich type structure as in Fig. 5a, and the results are given in Fig. 5b, and the efficiency from the flexible unit cell was also compared with the rigid device, where ITO-coated glass used as the substrate. The photoconversion efficiencies of the TiO_2 electrodes with different binder contents, and the fill factors (FF), open circuit voltages (V_{oc}) and short circuit currents (J_{sc}) are compared in Table 2. The unit cell assembled with the TiO_2 film of TIPP:P25 = 0.1:1 with the thickness ~5 μm exhibited the highest efficiency of 1.96 %, which is noticeably low when compared with the rigid cell (2.93 %). This lowered efficiency could be attributed to the higher sheet resistance of the ITO-PEN (20–25 Ω/□) than ITO-glass (~5 Ω/□). The sheet resistance of the ITO PEN leads to high series resistance and hence to a lower J_{sc} which is shown in Table 2 (4 mA/cm^2). From this it is suitable to give a future R&D route to reduce the ITO-PEN sheet resistance to reach higher current density. Also, we think that the TiO_2 photoanode contains micro cracks, which increase the recombination component in the TiO_2 layer. The J_{sc} is still lower in this study regarding values obtained in other research works (14–20 mA/cm^2, V_{oc} = 0.8 Volts, η = 7.29 %) [28–30].

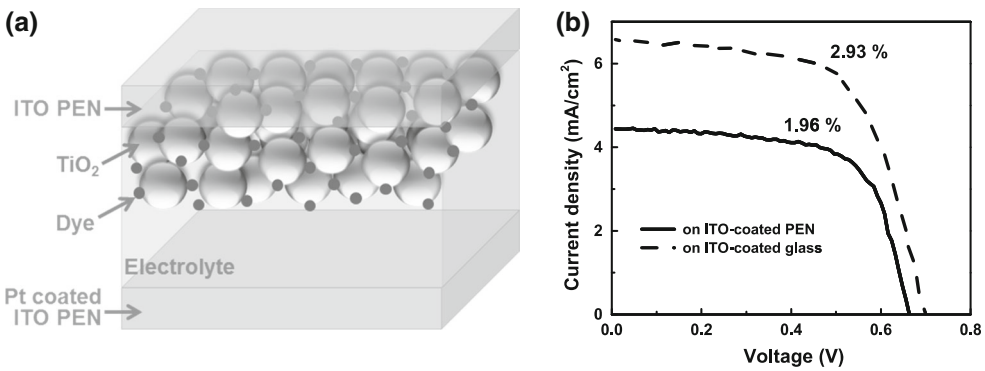

Fig. 5 **a** The unit cell structure prepared in this study, and **b** the J–V curve of the unit cells comprising the porous TiO_2 film prepared with the paste of TIPP:P25 = 0.1:1

Table 2 Efficiency of DSSC unit cells (0.6 × 0.6 cm)

Samples	FF (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	ŋ (%)
TIPP:P25 = 0.05:1	58.8	0.645	4.18	1.59
TIPP:P25 = 0.1:1	67.1	0.657	4.44	1.96
TIPP:P25 = 0.3:1	62.4	0.636	3.14	1.24

FF for all the unit cells prepared was around 60 % and V_{oc} was in the same range, while J_{sc} differs with the variation of binder content; from 3.14 mA/cm^2 for TIPP:P25 = 0.3:1 to 4.44 mA/cm^2 for TIPP:P25 = 0.1:1. It was shown that the enhancement of efficiency for TIPP:P25 = 0.1:1 mainly comes from the enhancement of short circuit current, which was induced from the optimized binding among the TiO_2 particles providing better pathway for the diffusion of injected electron.

In this study, the binder (TIPP addition into the paste) effect on the low-temperature-prepared active electrode of flexible DSSC was demonstrated. By comparing the photoconversion efficiency of the prepared unit cells, we found that the appropriate composition of binder (TIPP:P25 = 0.1:1), which exhibited the best dispersion of particles in the coating paste and the most transparent film with uniform microstructure, resultantly produced the best unit cell performance.

4 Conclusions

We investigated the effect of TIPP addition on the photoconversion efficiency as the binder for the TiO_2 particles in a low-temperature processed photoanode for flexible DSSC. By a direct addition of TIPP, a stable TiO_2 coating paste of low-temperature curable photoanode was prepared. The formation of bridging network between the particles was observed by TEM, and the crack-free uniformly porous film was obtained with the optimized composition of the paste as TIPP:P25 = 0.1:1. The photoconversion efficiency obtained by using the optimized film of thickness ~5 μm was 1.96 %.

Acknowledgments This work was fully supported by KITECH Institutional Program (Grant No. EO-14-0023). The authors also appreciate the professors of Department of Electronic Packaging Engineering of University of Science and Technology (UST) for the active exchange of technical and theoretical discussions.

References

1. O'Regan B, Gratzel M (1991) A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. Nature 353:737–740. doi:10.1038/353737a0
2. Upadhyaya HM, Senthilarasu S, Hsu M-H, Kumar DK (2013) Recent progress and the status of dye-sensitised solar cell (DSSC) technology with state-of-the-art conversion efficiencies. Sol Energy Mater Sol Cells 119:291–295. doi:10.1016/j.solmat.2013.08.031
3. Narayan MR (2012) Review: dye sensitized solar cells based on natural photosensitizers. Renew Sustain Energy Rev 16:208–215. doi:10.1016/j.rser.2011.07.148
4. Gong J, Liang J, Sumathy K (2012) Review on dye-sensitized solar cells (DSSCs): fundamental concepts and novel materials. Renew Sustain Energy Rev 16:5848–5860. doi:10.1016/j.rser.2012.04.044
5. Pagliaro M, Ciriminna R, Palmisano G (2008) Flexible solar cells. ChemSusChem 1:880–891. doi:10.1002/cssc.200800127
6. Liao J-Y, Lei B-X, Chen H-Y et al (2012) Oriented hierarchical single crystalline anatase TiO2 nanowire arrays on Ti-foil substrate for efficient flexible dye-sensitized solar cells. Energy Environ Sci 5:5750–5757. doi:10.1039/C1EE02766B
7. Zou D, Wang D, Chu Z et al (2010) Fiber-shaped flexible solar cells. Coord Chem Rev 254:1169–1178. doi:10.1016/j.ccr.2010.02.012
8. Li Y, Yoo K, Lee D-K et al (2010) Highly bendable composite photoelectrode prepared from TiO2/polymer blend for low temperature fabricated dye-sensitized solar cells. Curr Appl Phys 10:e171–e175. doi:10.1016/j.cap.2010.01.014
9. Weerasinghe HC, Huang F, Cheng Y-B (2013) Fabrication of flexible dye sensitized solar cells on plastic substrates. Nano Energy 2:174–189. doi:10.1016/j.nanoen.2012.10.004
10. Lee J-W, Choi JO, Jeong J-E et al (2013) Energy harvesting of flexible and translucent dye-sensitized solar cell fabricated by laser assisted nano particle deposition system. Electrochim Acta 103:252–258. doi:10.1016/j.electacta.2013.04.050
11. Balraju P, Suresh P, Kumar M et al (2009) Effect of counter electrode, thickness and sintering temperature of TiO2 electrode and TBP addition in electrolyte on photovoltaic performance of dye sensitized solar cell using pyronine G (PYR) dye. J Photochem Photobiol A 206:53–63. doi:10.1016/j.jphotochem.2009.05.014
12. Gutiérrez-Tauste D, Zumeta I, Vigil E et al (2005) New low-temperature preparation method of the TiO2 porous photoelectrode for dye-sensitized solar cells using UV irradiation. J Photochem Photobiol A 175:165–171. doi:10.1016/j.jphotochem.2005.04.031
13. Wessels K, Wark M, Oekermann T (2010) Efficiency improvement of dye-sensitized solar cells based on electrodeposited TiO2 films by low temperature post-treatment. Electrochim Acta 55:6352–6357. doi:10.1016/j.electacta.2010.06.059
14. Kovash CS Jr, Hoefelmeyer JD, Logue BA (2012) TiO2 compact layers prepared by low temperature colloidal synthesis and deposition for high performance dye-sensitized solar cells. Electrochim Acta 67:18–23. doi:10.1016/j.electacta.2012.01.092
15. Pasquier AD (2007) An approach to laminated flexible dye sensitized solar cells. Electrochim Acta 52:7469–7474. doi:10.1016/j.electacta.2007.06.028
16. Park N-G, Kim KM, Kang MG et al (2005) Chemical sintering of nanoparticles: a methodology for low-temperature fabrication of dye-sensitized TiO2 films. Adv Mater 17:2349–2353. doi:10.1002/adma.200500288
17. Lee S, Kim JY, Youn SH et al (2007) Preparation of a nanoporous CaCO3-coated TiO2 electrode and its application to a dye-sensitized solar cell. Langmuir 23:11907–11910. doi:10.1021/la701826v
18. Chen J, Luo J, Jin X et al (2013) Promotion of charge transport in low-temperature fabricated TiO2 electrodes by curing-induced compression stress. Electrochim Acta 100:85–92. doi:10.1016/j.electacta.2013.03.127
19. Menzies DB, Dai Q, Bourgeois L et al (2007) Modification of mesoporous TiO2 electrodes by surface treatment with

titanium(IV), indium(III) and zirconium(IV) oxide precursors: preparation, characterization and photovoltaic performance in dye-sensitized nanocrystalline solar cells. Nanotechnology 18:125608
20. Cho SH, Yoon YJ (2013) Multi-layer TiO2 films prepared by aerosol deposition method for dye-sensitized solar cells. Thin Solid Films 547:91–94. doi:10.1016/j.tsf.2013.04.107
21. Vijayakumar V, Du Pasquier A, Birnie DP III (2011) Electrical and optical studies of flexible stainless steel mesh electrodes for dye sensitized solar cells. Sol Energy Mater Sol Cells 95:2120–2125. doi:10.1016/j.solmat.2011.03.010
22. Hao Y, Rui Y, Li Y et al (2014) Size-tunable TiO2 nanocrystals from titanium (IV) bis (ammonium lactato) dihydroxide and towards enhance the performance of dye-sensitized solar cells. Electrochim Acta 117:268–275. doi:10.1016/j.electacta.2013.11.128
23. Syrrokostas G, Giannouli M, Yianoulis P (2009) Effects of paste storage on the properties of nanostructured thin films for the development of dye-sensitized solar cells. Renew Energy 34:1759–1764. doi:10.1016/j.renene.2008.12.029
24. Dhungel SK, Park JG (2010) Optimization of paste formulation for TiO2 nanoparticles with wide range of size distribution for its application in dye sensitized solar cells. Renew Energy 35:2776–2780. doi:10.1016/j.renene.2010.04.031
25. Bakhshayesh AM, Mohammadi MR (2013) Development of nanostructured porous TiO2 thick film with uniform spherical particles by a new polymeric gel process for dye-sensitized solar cell applications. Electrochim Acta 89:90–97. doi:10.1016/j.electacta.2012.11.060
26. Nam J-G, Lee E-S, Jung W-C et al (2009) Photovoltaic enhancement of dye-sensitized solar cell prepared from [TiO2/ethyl cellulose/terpineol] paste employing TRITON™ X-based surfactant with carboxylic acid group in the oxyethylene chain end. Mater Chem Phys 116:46–51. doi:10.1016/j.matchemphys.2009.02.037
27. Vishwas M, Sharma SK, Rao KN et al (2010) Influence of surfactant and annealing temperature on optical properties of sol–gel derived nano-crystalline TiO2 thin films. Spectrochim Acta Part A Mol Biomol Spectrosc 75:1073–1077. doi:10.1016/j.saa.2009.12.057
28. Thapa A, Zai J, Elbohy H et al (2014) TiO2 coated urchin-like SnO2 microspheres for efficient dye-sensitized solar cells. Nano Res. doi:10.1007/s12274-014-0478-z
29. Lee K-M, Hsu C-Y, Chiu W-H et al (2009) Dye-sensitized solar cells with a micro-porous TiO2 electrode and gel polymer electrolytes prepared by in situ cross-link reaction. Sol Energy Mater Sol Cells 93:2003–2007. doi:10.1016/j.solmat.2009.07.017
30. Opara Krašovec U, Berginc M, Hočevar M, Topič M (2009) Unique TiO2 paste for high efficiency dye-sensitized solar cells. Sol Energy Mater Sol Cells 93:379–381. doi:10.1016/j.solmat.2008.11.012