

Facile Fabrication of Highly Porous Photoanode at Low Temperature for All-Plastic Dye-sensitized Solar Cells with Quasi-Solid State Electrolyte

Nianqing Fu^{† a, b, c}, Yandong Duan^{† b}, Yanyan Fang^b, Xiaowen Zhou^b, Yanchun Liu^c, Feng Peng^c, Yuan Lin^{b} and Haitao Huang^{a*}*

^aDepartment of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China.

^bBeijing National Laboratory for Molecular Sciences, Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

^cSchool of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

E-mail address: aphhuang@polyu.edu.hk (H, Huang), Tel: +852-2766-5694; Fax: +852-2333-7629

E-mail address: linyuan@iccas.ac.cn (Y, Lin), Tel: +86 10 8261-5031; fax: +86 10 8261-7315

Abstract

Fabrication of stable plastic dye-sensitized solar cells (DSSCs) is interesting, but still remains a big challenge. In this study, we develop a facile technique to prepare highly porous TiO₂ hybrid film on plastic substrate for flexible DSSCs with quasi-solid state electrolyte, employing an inorganic binder contained TiO₂ paste. Compared with a pristine P25 electrode, the obtained photoanode exhibits excellent mechanical stability and improved charge transport property. The semiconductor film also shows a highly porous structure with porosity up to 58%, guaranteeing the unhindered infiltration of viscous quasi-solid state electrolyte and thus the high performance of the cells. The obtained all-plastic DSSCs with quasi-solid state electrolyte demonstrate a high efficiency up to 3.6% which is 76% higher than the devices based on pristine P25 electrodes. The cell efficiency is further increased to 4.05% by depositing an insulating Al₂O₃ layer on the TiO₂ surface to suppress electron recombination. The effects of the inorganic binder on the performance of the hybrid electrodes as well as the DSSCs are investigated by diverse techniques and measurements.

Keywords: Plastic dye-sensitized solar cells; working electrode; macroporous; low temperature; quasi-solid state electrolyte; inorganic binder.

1. Introduction

Dye-sensitized solar cells (DSSCs) continue to attract increasing amount of attention as promising and inexpensive alternatives to conventional Si-based solar cells [1-8]. High power conversion efficiency (PCE) over 12% has been achieved for the rigid DSSCs [2]. Recently, many research efforts have been made to replace the rigid glass substrates with plastic ones, featuring a roll to roll manufacturing process for flexible, conformable, thin and light-weight photovoltaic devices [6-14].

A photoanode for high performance DSSCs should have a porous structure with large surface area, display efficient electrical connectivity, and exhibit tight adhesion of the semiconductor film to the substrate. Conventional nanocrystalline TiO₂ electrodes are usually prepared by coating the conductive glass with an organic binder contained TiO₂ paste, followed by high-temperature sintering (>450 °C) to remove any organic additives present in the TiO₂ paste and guarantee an efficient coalescence between the particles [14,15]. However, this traditional technique is not feasible when a plastic substrate such as ITO coated PEN (polyethylene naphthalate, ITO/PEN) or PET (polyethylene, ITO/PET) is used to replace the glass one, owing to the thermal instability of the plastic substrates.

Many alternative techniques have been proposed to prepare TiO₂ films at low temperatures [16-25]. Even some of these approaches show great promise, the PCE of those DSSCs prepared by the above techniques were still very low because of the poor TiO₂ film performance. Hagfeldt *et al.* pioneered a simple mechanical compression method to fabricate plastic DSSCs which yielded a PCE of 4.9% under

0.1 sun irradiation [6]. The cell efficiency was further improved to above 7% by other researchers [26-28], using the mechanical compression technique.

As one of the three key components of the DSSCs, electrolyte plays a crucial role on not only the PCE, but also the durability of the cell system. Till now, most of the high efficiency DSSCs (except the novel solid-state perovskite solar cells) employ volatile liquid solution as electrolytes [2,3,28]. Unfortunately, the presence of this kind of electrolyte substantially limits the practical application of the devices because of the evaporation and leakage of the electrolyte [4,29]. Replacing the liquid electrolyte with quasi-solid or solid state ones seems to be promising approaches to solve this problem [4,29]. Usually, the quasi-solid and solid state electrolytes have poor permeability and a highly porous photoanode is required for the electrolyte infiltration. Although certain progress has been made to fabricate quasi-solid or solid state DSSCs on rigid glass substrate, little work has been reported on the fabrication of plastic DSSCs with quasi-solid and solid state electrolytes [30-32], owing to the big challenge in fabrication of highly porous photoanode with high performance at low temperature. Therefore, developing simple techniques to fabricate plastic photoanode with high performance at low temperature for quasi-solid or solid DSSCs is still in highly demand.

SnO_2 have demonstrated itself as alternative host material for DSSCs because of its high electronic conductivity and electron mobility (up to $200 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, which is 100 times higher than that of TiO_2) [33-35]. Herein, we present the fabrication of all-plastic DSSCs with quasi-solid state electrolyte, employing a highly porous plastic

photoanode derived from a In/Sb doped SnO₂ sol (SITO-sol) contained TiO₂ paste. Owing to the chemical bridging-effects among the P25 particles by the more conductive In/Sb doped SnO₂ (SITO), the obtained semiconductor film exhibits enhanced mechanical stability as well as improved electron transport property, compared with the pristine P25 electrode. More importantly, the produced electrode demonstrates a high porosity up to ~58%, which will facilitate the infiltration of the viscous electrolyte. The quasi-solid DSSCs employed plastic hybrid photoanodes with optimized SITO yield a PCE of 3.6% which is 76% higher than the devices based on pristine P25 electrodes. Depositing an Al₂O₃ insulating layer on TiO₂ surface can further enhance the PCE to 4.05% by suppressing the charge recombination.

2. Experimental Section

2.1. Preparation of the (Sb, In) doped SnO₂ sol and TiO₂ paste.

The preparation of the (Sb, In)-doped SnO₂ sol (denoted as SITO-sol) was prepared according to our previous work [36]. In short, 9.6 g tin (II) dichloride dihydrate was dissolved in 50 mL anhydrous ethanol, and 3 mL distilled water was added subsequently. This mixture was refluxed at 80 °C for 7 h. Then, another 10 mL C₂H₅OH solution containing 0.66 g antimony chloride and 0.38 g indium chloride was added dropwise into the tin chloride mixture and refluxed at 80 °C for 3 h. The resulting mixture was aged for one week at room temperature to yield a light yellow sol.

TiO₂ powder (P25, Degussa) was subjected to a pre-sintering at 450 °C for 30 min

before use [15]. 0.6 g P25 powder was dispersed in a mixture of anhydrous ethanol and *n*-butanol (v/v=1:1) by 12 h magnetic stirring, followed by 1 h ultrasonic dispersion to form a uniform TiO₂ colloid. For the SITO-sol incorporated TiO₂ paste (SITO-sol/P25), a certain volume of SITO-sol (0, 50, 100, 200, 300, 400 μL) was added into the as-prepared pristine TiO₂ colloid, followed by 1 h of gentle stirring before coating onto the substrate. The solid content of the total metal oxide (TiO₂+doped SnO₂) in all paste was kept at 16 wt% by varying the amount of dispersants.

2.2 Fabrication of photoanode and assembly of plastic DSSCs.

Before film coating, a very thin TiO₂ compact layer (about 10 nm) was deposited on the well cleaned ITO/PEN substrates according to our previous work [13]. SITO-sol/P25 pastes with varying amounts of SITO-sol were spread on the substrates by the doctor-blade technique. The film thickness for all electrodes was controlled to be 10±0.2 μm. After drying in air, the films were exposed to UV irradiation (300 W) for 30 min. The as-prepared SITO contained electrodes were immersed in 100 °C distilled water for 30 min to remove any residues introduced by the SITO-sol. We refer to the electrodes derived from a pristine P25 colloid and the SITO-sol/P25 paste as P25 and SITO/P25, respectively. The coating of a thin Al₂O₃ layer was carried out by dipping the as-prepared films into a hot 2-propanol-based solution of aluminum sec-butoxide (20 mM, 50 °C) for 3 min, followed by air drying (80% humidity) and immersing in 100 °C distilled water for 30 min. All electrodes were dried at 100 °C in an oven for 1 h and then sensitized in 0.5 mM N719 dye/ethanol solution overnight.

Plastic counter electrodes (CEs) were prepared through a photoplatinization technique [13]. In short, ITO/PEN substrates was modified by ~25 nm TiO₂ layer produced by spin-coating and hydrolysis of tetra-n-butyl titanate. The modified substrates were immersed in 0.13 mM H₂PtCl₆/2-propanol solution and exposed to UV irradiation for about 1 h to deposit Pt on the TiO₂ surface. Plastic DSSCs were assembled using the as-prepared photoanodes and the plastic CEs, employing a quasi-solid state electrolyte which was prepared according to our previous work [29].

2.3 Measurements and Characterizations of the TiO₂ electrodes and DSSCs

The surface morphology of the electrodes was investigated by scanning electron microscopy (SEM/EDX, Hitachi S-4800, 15 kV) and high resolution transmission electron microscopy (TEM, JEM 2011, Japan; 200 kV). The mechanical adhesion strength of the TiO₂ photoelectrode was measured by scratching the TiO₂ film with a standard pencil, according to the ISO/DIS 15184 method [28]. The adhesion strength of the film was measured by the bending test similar to the reported work [37]. The surface area and porosity were evaluated using a Quantachrome NOVA 2000e analyzer. The Brunauer–Emmett–Teller (BET) and Barrent-Joyner-Halenda (BJH) methods were used to estimate the specific surface area (SSA) and the porosity, respectively. The photocurrent-voltage curves were recorded using a computer-programmed Keithley 2611 SourceMeter under simulated sunlight illumination (AM 1.5, 100 mW cm⁻²) supplied by a solar simulator (Oriel, 91160-1000 91192, Perccell Technologies). The intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS)

measurements were performed on the same sandwiched cells, using a green light emitting diode (LED, peak wavelength 520 nm) driven by a Solartron 1255B frequency-response analyzer. The LED provides both dc and ac components of the illumination. The light intensities were modulated ($\pm 8\%$) by modulating the voltage applied to the LED.

3. Results and Discussion

3.1 Formation of hybrid electrodes and their mechanical properties.

Scheme 1 represents the technique for preparation of the plastic electrode at low temperature. When the SITO-sol (Fig. S1 in Supplementary Materials) is added into the liquid TiO₂ colloid, the Sn-OH active head groups of the HO-(Sn-O-Sn)_n-OH chains react with the hydroxyl groups on the TiO₂ particles surface to form cross-linked network. The SITO-sol in the paste acts both as an inorganic binder and a kind of surfactant. After the SITO-sol/P25 paste was spread onto the substrate and dried in the air, the SITO-sol shrinks gradually at the grain boundaries by capillary force upon solvent evaporation. During the subsequent UV-irradiation, the dried SITO-sol was converted into SITO crystals with a tetragonal rutile structure [36] which bridged the individual TiO₂ particles and also formed connections between the film and the TiO₂ modified ITO/PEN substrate.

The mechanical rigidity is one of the most important properties of the electrode, especially for plastic devices with quasi-solid state electrolyte since the semiconductor films in contact with the viscous gel-state electrolyte is more liable to

be damaged during the shape wrench of the devices. The hardness and bending tests were employed to evaluate the mechanical stability of the films. Fig. 1 illustrates the effect of the SITO content on the hardness of the hybrid film. The pristine P25 film was easily destroyed by a 6B pencil, while the incorporation of the SITO continuously increased the hardness of the films. The hybrid film with 4 wt% SITO demonstrates a hardness up to HB grade, and this value further increases to 3H with 10 wt% SITO incorporation. The increased film hardness can be attributed to the formation of rigid bridges between TiO_2 particles by SITO crystals, which will be discussed later. The excellent adhesion of the SITO/P25 film to the substrate was confirmed by bending test. The inset in Fig. 1 shows that no changes could be observed for the SITO/P25 (4 wt%) hybrid electrode after fifty cycles of concave and convex bending. In contrast, the P25 film was desquamated by just one cycle of bending.

3.2 Influence of SITO on the surface morphology of the TiO_2 electrodes

Fig. 2 shows the cross-sectional SEM images of the electrodes with various amount of SITO (ca. 0, 4, 6, and 10 wt%, respectively), which demonstrate that both the pore number and pore size can be altered by the SITO amount. Appropriate amount of SITO (ca. 4 wt%, Fig. 2b) in TiO_2 increases the number of pores and enlarge the pore size as well. However, excessive SITO (ca. 10 wt%) will obstruct the pores, decreasing the pore size and pore number (Fig. 2d). The pore structure of the film is crucial to the infiltration of the viscous electrolyte and affects the cell performance subsequently. The TEM images in Fig. 3a and 3b reveal that continuous network morphology still remained even though the SITO/P25 film had been

subjected to two hours of strong ultrasonication. By contrast, the P25 film disintegrated into small aggregates after the similar treatment. High magnification TEM images (Fig. 3c and 3d) confirm that the TiO₂ particles in SITO/P25 hybrids are bridged by SITO while the stacking of the TiO₂ particles in the pristine P25 film relies only on their physical contact. The formation of SITO/P25 network not only promises the semiconductor film excellent mechanical stability but also provides a continuous pathway which facilitates the efficient and fast charge transport in the hybrid films.

BET specific surface area (SSA), porosity, scattering property and dye-loadings of the films were tested to further evaluate the effects of SITO on the electrode performance. As shown in Table 1, the SSA decreases from 57.7 to 42.4 m²/g with the amount of incorporated SITO increased from 0 to 10 wt%, since the SITO covers the joints of TiO₂ particles or even fills into the pores (Fig. 2 and Fig. 3), decreasing the SSA consequently. The porosity of the film first increases with the addition of a small amount of SITO, achieving a peak value of 58.5% at 4 wt% SITO incorporation, and then decreases significantly. This result is in accordance with that observed in SEM. As shown in Table 1, the addition of SITO lowers the dye-loading of the films because of (1) the reduced SSA and (2) the relative poorer dye-absorption capacity of the SnO₂, as compared to TiO₂ [38]. The decrease of dye-loading will, in principle, decline the light harvesting of the photoanode employing SITO/P25. The light scattering property of the films was shown in Fig. 4. It reveals that the incorporation of the SITO leads to an appreciable enhancement in the diffuse light scattering, since the SITO connects the TiO₂ particles to form aggregates with mixed sizes, leading to

light-scattering and light-confinement effects [19,27]. The light scattering and confinement effects can extend the optical path length of the film, which enhances the probability of photons being captured by the dye molecules and finally improves the short-circuit current (J_{sc}) of the device.

3.3 The photovoltaic performance of DSSCs

The photovoltaic characteristics of the plastic quasi-solid DSSCs as a function of the SITO contents are shown in Fig. 5. The open-circuit voltage (V_{oc}) of the devices first increases slightly and then decreases with further increasing of SITO content. The formation of continuous pathway and tight adhesion of the SITO/P25 film to the substrate will facilitate fast charge transport and transfer and suppresses charge recombination consequently, leading to higher V_{oc} at low SITO content. However, since SITO has a lower conduction band than TiO_2 , which should, in principle, lower the Fermi levels of the film and decreases the V_{oc} [33,34]. Additionally, too much SnO_2 with deeper conduction band will form electronic traps which lead to faster interfacial electron recombination and thus further lowers the V_{oc} as well [33]. The short-circuit current density (J_{sc}) of the DSSCs increases at low SITO concentration, reaching a peak value at 4wt%, and then begins to decrease with further increasing of SITO. The increased J_{sc} at low SITO concentration (no more than 4 wt%) results from the positive effects of the SITO incorporation, such as enhanced electron transport and transfer, improved electron collection efficiency (will be discussed later) and enhanced light-scattering. However, in the case of high SITO concentration, the decreased dye-loading, increased electron recombination and poor electrolyte

infiltration will decline the J_{sc} . The PCE of the DSSCs exhibits a similar trend to the J_{sc} values, attaining the maximum value with 4 wt% SITO.

The J - V characteristic curves and the corresponding photovoltaic parameters of the quasi-solid plastic DSSCs employing pristine P25 and SITO/P25 hybrid (4 wt% SITO) photoanodes are displayed in Fig. 6 and Table 2. The J_{sc} , V_{oc} , FF and PCE of the P25 cells are 4.66 mA cm⁻², 660 mV, 0.674 and 2.04%, respectively. The J_{sc} and FF of the SITO/P25 cells are 7.25 mA cm⁻² and 0.741, respectively, which are significantly higher than those of the P25 ones. As a result, the SITO/P25 devices demonstrate a PCE up to 3.6%, improved by 76%, as compared with the P25 cell. The enhanced light-scattering property (as shown in Fig. 4), faster electron transport and improved charge collection efficiency (which will be discussed in section 3.4) account for the improved J_{sc} . The decreased series resistance of the SITO/P25 electrode results in a higher FF . Noticeably, though the carefully handled pristine P25 cells yield efficiency of 2.04%, the bending tests reveal that they are not practically useful as flexible devices because the electrolyte infiltrated film are easily detached off from the substrate during the shape wrench, owing to the poor adhesion of the semiconductor film to the substrate. In contrast, as shown in Fig. 7, there is almost no efficiency deterioration can be observed after the SITO/P25 (4 wt% SITO) cells were subjected to fifty circles of concave and convex bending, indicating that the plastic DSSCs produced by the proposed technique have the potential for practical application as flexible devices. It was reported that the recombination rate increases by 2–3 orders of magnitude when a high mobility material, such as SnO₂, is in direct

contact with the sensitizer and/or the electrolyte [33-35]. In this case, further improvement in the DSSC performance can be anticipated by depositing a thin insulating layer to suppress the electron recombination arose from the introduction of the SITO. As shown in Fig. 6 and Table 2, the J_{sc} , V_{oc} , and FF of the Al_2O_3 coated SITO/P25 cells (Al_2O_3 /SITO/P25) are 7.71 mA cm^{-2} , 715 mV , and 0.732 , respectively, leading to a PCE improvement from 3.6% to 4.05% . Compared with the SITO/P25 cell, the PCE improvement of the Al_2O_3 /SITO/P25 cell results from the enhanced V_{oc} and J_{sc} . The improvement of V_{oc} is attributed to the combination of reduced recombination and/or shifts in Fermi levels. On one hand, the charge-blocking effect of the Al_2O_3 insulating layer prohibits the electron recombination from the SITO/P25 to the redox electrolyte and increases the V_{oc} in return. On the other, the insulating Al_2O_3 layer will shift the Fermi levels of the Al_2O_3 /SITO/P25 film and enlarges the difference between the Fermi levels and the redox potential of the I_3^-/I^- , leading to the increase of the V_{oc} . The increase in the J_{sc} value is ascribed to (1) the improved dye adsorption (from 0.62×10^{-7} to $0.66 \times 10^{-7} \text{ mol cm}^{-2}$) due to the more favorable dye adsorption on the surface of Al_2O_3 than TiO_2 [38] and (2) decreased electron loss resulting from the suppressed electron recombination.

3.4 Electrochemical and electrical properties of the photoanodes and DSSCs

IMPS and IMVS, which are commonly employed in the characterization of DSSCs [39,40], were used to investigate the charge transport and recombination process in the DSSCs with different photoanodes. The IMPS and IMVS plots display

a semicircle in the complex plane. The electron recombination and transport behavior can be evaluated by the electron lifetime (τ_n) and the electron transport time (τ_d), respectively. τ_n and τ_d can be estimated from the $\tau = (2\pi f_{\min})^{-1}$, where f_{\min} is the frequency corresponding to the bottom of the semicircle at the IMVS and IMPS plots respectively. Fig. 8 shows the IMPS and IMVS spectrum of pristine P25, SITO/P25, and Al₂O₃/SITO/P25 photoanodes based plastic DSSCs. The electron transport time (τ_d) for the SITO/P25 cell is 22.4 ms, much shorter than that of the P25 cell (46 ms). As demonstrated in Fig. 3, the existence of the more conductive SITO among TiO₂ particles forms a continuous network which facilitates the efficient and fast charge transport in the semiconductor hybrid film. The I - V curves of the P25 and the SITO/P25 films are shown in Fig. S2 (Supplementary Materials). The current response at 10 V for the SITO/P25 film is 12.2 μ A, almost 30-fold higher than that of the P25 film (0.43 μ A), implying that the more conductive SITO has formed a continuous network with significantly decreased film resistance. The significant decrease of charge transport resistance in the SITO/P25 electrode was also revealed by electrochemical impedance spectroscopy (EIS) measurements in real DSSCs system, as demonstrated in our previous work [36]. The decreased charge transport resistance results in shorter τ_d . The electron lifetime (τ_n) of the SITO/P25 is 79.6 ms, higher than that of P25 (63.2 ms). The faster charge transport in the SITO/P25 film than the P25 one will decrease the possibility of the electrons being recombined and leads to longer τ_n in turn. The coating of insulating Al₂O₃ layer on SITO/TiO₂ surface can suppress the electron recombination remarkably, hence increasing the τ_n from 79.6

to 126.4 ms. The charge collection efficiency η_{cc} can be determined by the equation $\eta_{cc}=1-\tau_d/\tau_n$ [40]. It increases from 49.8% for P25 to 71.9% for 4 wt% SITO/P25 photoanode based cells. It further improves to 84.1% when an insulating Al_2O_3 layer was deposited on the SITO/P25 surface to suppress electron recombination. The high η_{cc} is a crucial factor for the SITO/P25 DSSCs to yield a high efficiency.

4. Conclusion

In this study, we have demonstrated a simple and effective method for the fabrication of porous and robust SITO/ TiO_2 hybrid electrode on ITO/PEN substrate at low temperature for plastic DSSC applications. In addition to flexibility and mechanical stability, the produced films exhibit other meritorious characteristics, such as, excellent porosity, improved light-scattering, enhanced electron transport and decreased electron recombination. Owing to the complete infiltration of the quasi-solid state electrolyte and high charge collection efficiency, the obtained all-plastically quasi-solid DSSCs yield a PCE up to 3.6%, 76% higher than the device based on pristine P25 electrode. The SITO/P25 also demonstrates outstanding stability toward shape wrench. The deposition of an insulating Al_2O_3 layer on the SITO/ TiO_2 surface further improves the efficiency of the SITO/P25 device to 4.05% by suppressing the electron recombination. The encouraging performance of the DSSCs with gel electrolytes suggests that the method developed in this work is promising for the fabrication of plastic electrodes for solid state plastic-DSSCs or flexible perovskite solar cells.

ASSOCIATED CONTENT

Supplementary Materials

Digital image of the SITO/sol, method and result of the electrical test of the semiconductor films. Those material is available free of charge via the Internet

AUTHOR INFORMATION

Corresponding Author

E-mail: aphhuang@polyu.edu.hk (H, Huang), Tel: +852-2766-5694; Fax: +852-2333-7629; E-mail: linyuan@iccas.ac.cn (Y, Lin), Tel: +86 10 8261-5031; fax: +86 10 8261-7315

Notes

†Nianqing Fu and Yandong Duan contribute equally to this article. The authors declare no competing financial interest.

Acknowledgements

This work was financially supported by National Research Fund for Fundamental Key Project (2012CB932903), Foundation of Chinese Academy of Sciences (KGCX2-YW-386-2). This work was also partially supported by grants received from the Research Grants Council of the Hong Kong Special Administrative Region (PolyU5159/13E and PolyU5163/12E).

Notes and references

- [1] B. O'Regan, M. Grätzel, *Nature* 353 (1991) 737-740.
- [2] A. Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* 334 (2011) 629-634.
- [3] C. T. Yip, H. T. Huang, L. M. Zhou, K. Y. Xie, Y. Wang, T. Feng, J. Li, W.Y. Tam, *Adv. Mater.* 23 (2011) 5624-5628.
- [4] I. Chung, B. Lee, J. Q. He, R. P. H. Chang, M. G. Kanatzidis, *Nature* 485 (2012) 486-490.
- [5] M. Guo, K. Y. Xie, J. Lin, Z. Yong, C. T. Yip, L. M. Zhou, Y. Wang, H. T. Huang, *Energy Environ. Sci.* 5 (2012) 9881-9888.
- [6] H. Lindström, A. Holmberg, E. Magnusson, S. E. Lindquist, L. Malmqvist, A. Hagfeldt, *Nano letters* 1 (2001) 97-100.
- [7] M. Dürr, A. Schmid, M. Obermaier, S. Rosselli, A. Yasuda, G. Nelles, *Nat. Mater.* 4 (2005) 607-611.
- [8] S. So, K. Lee, P. Schmuki, *J. Am. Chem. Soc.* 134 (2012) 11316–11318.
- [9] J. H. Wu, Y. M. Xiao, Q. W. Tang, G. T. Yue, J. M. Lin, M. L. Huang, Y. F. Huang, L. Q. Fan, Z. Lan, S. Yin, T. Sato, *Adv. Mater.* 24 (2012) 1884–1888.

- [10] F. Z. Huang, D. H. Chen, L. Cao, R. A. Caruso, Y. B. Cheng, *Energy Environ. Sci.* 4 (2011) 2803–2806.
- [11] W. Wang, Q. Zhao, H. Li, H. W. Wu, D. C. Zou, D. P. Yu, *Adv. Funct. Mater.* 22 (2012) 2775–2782.
- [12] Y. L. Li, D. K. Lee, J. Y. Kim, B. S. Kim, N. G. Park, K. Kim, J. H. Shine, I. S. Choi, M. J. Ko, *Energy Environ. Sci.* 5 (2012) 8950–8957.
- [13] N. Q. Fu, Y. Y. Fan, Y. D. Duan, X. W. Zhou, X. R. Xiao, Y. Lin, *ACS Nano* 6 (2012) 9596–9605.
- [14] V. Zardetto, F. D. Giacomo, D. Garcia-Alonso, W. Keuning, M. Creatore, C. Mazzuca, A. Reale, A. D. Carlo, T. M. Brown, *Adv. Energy Mater.* 3 (2013) 1292–1298.
- [15] D. S. Zhang, T. Yoshida, T. Oekermann, K. Furuta, H. Minoura, *Adv. Funct. Mater.* 16 (2006) 1228–1234.
- [16] F. Pichot, J. R. Pitts, B. Gregg, *Langmuir* 16 (2000) 5626–5630.
- [17] X. Li, H. Lin, J. B. Li, X. X. Li, B. Cui, L. Z. Zhang, *J. Phys. Chem. C* 112 (2008) 13744–13753.
- [18] K. Fan, T. Y. Peng, J. N. Chen, K. Dai, *J. Power Sources* 196 (2011) 2939–2944.
- [19] H. W. Chen, C. P. Liang, H. S. Huang, J. G. Chen, R. Vittal, C. Y. Lin, K. C. W. Wu, K. C. Ho, *Chem. Commun.* 47 (2011) 8346–8348.

- [20] H. W. Chen, Y. T. Liao, J. G. Chen, K. C. W. Wu, K. C. Ho, *J. Mater. Chem.* 21 (2011) 17511-17518.
- [21] S. Uchida, M. Tomiha, H. Takizawa, M. Kawaraya, *J. Photochem. Photobiol. A* 164 (2004) 93–96.
- [22] S. I. Cha, B. K. Koo, K. H. Hwang, S. H. Seo, D. Y. Lee, *J. Mater. Chem.* 21 (2011) 6300–6304.
- [23] H. Lee, D. Hwang, S. M. Jo, D. Kim, Y. Seo, D. Y. Kim, *ACS Appl. Mater. Interfaces* 4 (2012) 3308–3315.
- [24] N. G. Park, K. M. Kim, M. G. Kang, K. S. Ryu, S. H. Chang, Y. J. Shin, *Adv. Mater.* 17 (2005) 2349-2353.
- [25] H. C. Weerasinghe, G. V. Franks, J. D. Plessis, G. P. Simon, Y. B. Cheng, *J. Mater. Chem.* 20 (2010) 9954–9961.
- [26] W. H. Chiu, K. M. Lee, W. F. Hsieh, *J. Power Sources* 196 (2011) 3683–3687.
- [27] T. Yamaguchi, N. Tobe, D. Matsumoto, H. Arakawa, *Chem. Commun.* 45 (2007) 4767–4769.
- [28] T. Yamaguchi, N. Tobe, D. Matsumoto, T. Nagai, H. Arakawa, *Sol. Energy Mater. Sol. Cells* 94 (2010) 812–816.
- [29] Y. Y. Fang, J. B. Zhang, X. W. Zhou, Y. Lin, S. B. Fang, *Electrochim. Acta* 68 (2012) 235-239.

- [30] L. C. Chen, J. M. Ting, Y. L. Lee, M. H. Hon, *J. Mater. Chem.*, 22 (2012) 5596–5601.
- [31] S. A. Haque, E. Palomares, H. M. Upadhyaya, L. Otley, R. J. Potter, A. B. Holmes, J. R. Durrant, *Chem. Commun* 2003 3008–3009
- [32] Z. S. Xue, C. Y. Jiang, L. Wang, W. Liu, B. Liu, *J. Phys. Chem. C* 2013. DOI:10.1021/jp408663d
- [33] C. T. Gao, X. D. Li, B. G. Lu, L. L. Chen, Y. Q. Wang, F. Teng, J. T. Wang, Z. X. Zhang, X. J. Pan, E. Q. Xie, *Nanoscale* 4 (2012) 3475–3481.
- [34] N. Tétreault, É. Arsenault, L. P. Heiniger, N. Soheilnia, J. Brillet, T. Moehl, S. Zakeeruddin, G. A. Ozin, M. Grätzel, *Nano Lett.* 11 (2011) 4579–4584.
- [35] A. N. M. Green, E. Palomares, S. A. Haque, J. M. Kroon, J. R. Durrant, *J. Phys. Chem. B* 109 (2005) 12525-12533.
- [36] N. Q. Fu, Y. D. Duan, Y. Y. Fang, X. W. Zhou, X. R. Xiao, Y. Lin, *Electrochem. Commun.* 34 (2013) 254 – 257.
- [37] X. L. He, M. Liu, G. J. Yang, H. L. Yao, S. Q. Fan, J. Li, *J. Power Sources* 226 (2013) 173-178.
- [38] A. Kay, M. Grätzel, *Chem. Mater.* 14 (2002) 2930-2935.
- [39] D. S. Zhang, T. Yoshida, T. Oekermann, K. Furuta, H. Minoura, *Adv. Funct. Mater.* 16 (2006) 1228–1234.

[40] Y. D. Duan, N. Q. Fu, Q. P. Liu, Y. Y. Fang, X. W. Zhou, J. B. Zhang, Y. Lin, J.

Phys. Chem. C 116 (2012) 8888–8893.

Fig. captions

Scheme 1 Schematic representation of the preparation of hybrid TiO₂ electrodes, employing a Sb/In doped SnO₂ sol contained TiO₂ paste.

Fig. 1 The hardness of the semiconductor films with various SITO incorporation, tested according to the ISO/DIS 15184 method. The insets are digital images of P25 (top) and SITO/P25 (bottom) electrodes after one cycle and fifty cycles of bending test, respectively.

Fig. 2 Cross-sectional high-resolution SEM micrographs of SITO/P25 electrodes with (a) 0 wt%, (b) 4 wt%, (c) 6 wt%, and (d) 10 wt% SITO, respectively.

Fig. 3 TEM images of sample from (a, c) SITO/P25 (4 wt% SITO) and (b, d) P25 film. The samples for TEM tests were prepared by 2 hours' strong ultrasonication of the films.

Fig. 4 Reflectance spectra of P25 and STIO/P25 electrodes with different amounts of SITO incorporation.

Fig. 5 Open-circuit voltage (V_{oc} , ◆), fill factor (FF , ●), short-circuit current density (J_{sc} , ▲) and power conversion efficiency (PCE, ■) of the DSSCs as a function of SITO content in the TiO₂ paste, respectively.

Fig. 6 Current-voltage curves of DSSCs employing different photoanodes. P25, SITO/P25, Al₂O₃/SITO/P25, and P25-C represent the pristine P25 electrode, 4 wt% SITO incorporated SITO/P25 hybrid electrode, Al₂O₃ coated SITO/P25 hybrid

electrode, and P25 electrode prepared by 100 MPa mechanical compression, respectively.

Fig. 7 The efficiency variation of the SITO/P25 cells (4 wt% SITO) with the circles of bending test.

Fig. 8 (a) IMPS and (b) IMVS complex plane plots of plastic DSSCs based on P25, SITO/P25, Al₂O₃/SITO/P25, and P25-C electrodes.

Table 1 The BET surface area, porosity, and dye-loading of the P25 and SITO/P25 electrodes with 2, 4, 6, and 10 wt% SITO.

SITO content	Surface area	Porosity	Dye-loading
0	57.7	51.3	0.67
2	56.4	54.5	0.65
4	53.1	58.5	0.62
6	50.6	48.3	0.58
10	42.4	40.0	0.47

Table 2 Photovoltaic characteristics of DSSCs with different photoanodes, measured under AM 1.5 simulated illumination of 100 mW cm^{-2} .^a

Photoanodes	J_{sc} [mA cm ⁻²]	V_{oc} [mV]	FF	PCE [%]
P25	4.66	660	0.674	2.04
SITO/P25	7.25	670	0.741	3.60
Al ₂ O ₃ /SITO/P25	7.71	715	0.732	4.05

^aThe data in the table are the mean values of five samples