Highly efficient dye-sensitized solar cell using nanocrystalline titania containing nanotube structure

Supachai Ngamsinlapasathian, Singto Sakulkhaemaruethai, Sorapong Pavasupree,
Athapol Kitiyanan, Thammanoon Sreethawong, Yoshikazu Suzuki, Susumu Yoshikawa*

Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611 0011, Japan

Abstract

Nanocrystalline titania containing nanotube structure (TiNT) was synthesized by surfactant-assisted templating mechanism using tetraiso-propyl orthotitanate (TIPT) modified with acethylacetone (ACA)/laurylamine hydrochloride (LAHC). The electrode of dye-sensitized solar cell using TiNT exhibited higher short-circuit photocurrent density (J_{sc}) and solar energy conversion efficiency (η) than that of P25 titania electrode in thin film region. To obtain highly efficient cell, the thickness of TiNT electrode must be increased to attain high amount of dye. Blending TiNT gel with P25 was proved to be effective way for increasing the thickness. Increasing amount of P25 more than 5% decreased the J_{sc} of solar cells. However, TiNT + 2% P25 was the most suitable composition to obtain well-balanced properties. The open-circuit voltage (V_{oc}) and fill factor (ff) of the cell decreased with increasing thickness of the electrode due to increasing electron recombination and series resistance of the cell. The solar energy conversion efficiency (η) of 8.43% with a J_{sc} of 18.1 mA cm^{-2}, a V_{oc} of 0.72 V and a ff of 0.642 was attained by using TiNT + 2% P25 electrode with 8.2 μm film thickness.

1. Introduction

Dye-sensitized solar cell is expected as a low cost alternative to conventional solid state devices [1]. Several works have been directed toward improving the efficiency of dye-sensitized solar cells by developing new dyes, suppressing charge recombination and improving the nanocrystalline titania film. Generally, titania electrode is made from nanocrystalline titania which is prepared by sol–gel process or commercially available titania such as P25 (Degussa AG), ST2-02 (Ishihara), and Ti-Nanoxide HT (Solaronix). Sol–gel process is favored as appropriate process for preparing nanomaterials because particle size, film thickness and porosity can be controlled by adjusting parameters such as hydrothermal growth temperature, sintering condition, and sol concentration.

Preparation of anatase type nanocrystalline titania is normally achieved by using alkoxide as a precursor. Li et al. [2] prepared anatase type titania nanoparticles by using titanium butoxide in butanol. They showed that the electrode made from P25 titania powder displayed the same cell characteristic as one made from a sol–gel process. Kambe et al. [3] synthesized single-phase anatase nanocrystalline by hydrolysis of titanium butoxide in toluene under high pressure at high temperature (150–300 °C). The photovoltaic properties of the cell using transparent titania with 16 μm film thickness were superior to that of P25 titania with 11 μm film thickness. Grätzel and coworkers [4] used titania anatase nanoparticles of 16 nm, which were prepared by hydrolysis of titanium(IV) isopropoxide, as an electrode for dye-sensitized solar cells. This electrode was covered by black dye showing solar energy conversion efficiency (η) of 10.4% [5].

Titania nanotube is expected as a promising material for being used as electrodes of dye-sensitized solar cell, since the boundaries among particles could be reduced. Thus, facile electron transport from the titania layer to the current collecting electrode could be attained by using nanotube with high aspect ratio. Uchida et al. [6] also prepared titania nanotube by using Kasuga's method [7,8] and applied it for the electrode of dye-sensitized solar cells. However, the solar cell performance of this material was not different from that of P25 titania. Surfactant-assisted templating is an alternative method for preparing highly active nanocrystalline titania nanotube. We synthesized nanocrystalline titania nanotube by using this method. The details of titania

* Corresponding author. Tel.: +81-774-38-3507; fax: +81-774-38-3508.
E-mail address: s-yoshi@iae.kyoto-u.ac.jp (S. Yoshikawa).

nanotube formation was ascribed in previous paper [9]. Nanocrystalline titania nanotube had been applied for the electrode of dye-sensitized solar cell [10]. We reported that dye-sensitized solar cell with titania nanotube showed the fairly high efficiency especially in the thin film region. Titania nanotube was a good alternative for thin film electrode in the application of dye-sensitized solar cell.

In this article, we precisely examined the photovoltaic properties of nanocrystalline titania containing nanotube structure, abbreviated as TiNT, comparing with commercially available P25 titania. Since the high quality films of TiNT were limited to less than 7 μm thickness. Blended TiNT with P25 titania was selected to increase the film thickness. The effect of film thickness and amount of P25 titania in TiNT on photovoltaic properties were investigated. Currently, the solar energy conversion efficiency of 8.43% has been attained by controlling film thickness and amount of P25. This is the first report on TiNT for dye-sensitized solar cells with precise observation.

2. Experimental

2.1. Preparation method of TiNT

TiNT was synthesized by surfactant-assisted templating mechanism using tetraisopropyl orthotitanate (TIPT) modified with acethylacetone (ACA)/lauryalmine hydrochloride (LAHC) [9]. Titania sol was obtained from the reaction between TIPT and ACA at the same molar concentration. This sol was mixed to 0.1 M LAHC aqueous solution (pH 4–4.5). The molar ratio of titania sol to LAHC aqueous solution was 4. Titania sol was stirred at 40 °C for 24 h until it became transparent yellow sol. Then, the sol in sealed bottle was kept in the oven at 80 °C. After 5 days, the obtained gel sample was washed with 2-propanol to remove LAHC.

2.2. Characterizations of TiNT

The morphology of titania was investigated by transmission electron microscopy (TEM). Samples for TEM observation were prepared by scratching a small powder from titania films. Crystal structure of titania was analyzed by X-ray diffraction (XRD) with Cu Kα radiation (Rigaku-A2). BET surface area of titania samples was determined by nitrogen adsorption isotherm (Belsorp 18 Plus).

2.3. Preparation of titania electrode

TiNT gel was coated on an ITO/SnO$_2$ conducting glass (5 Ω/□ Geomatec Co. Ltd.), by using a doctor-blading technique. After air-drying, the electrode was sintered at 400 °C in air for 2 h. For some samples, P25 was added to TiNT gel to prevent cracking of titania film when the film thickness was increased. TiNT gel was mixed with 2, 5 and 10 wt.% P25. Titania electrodes were soaked in a 0.3 mM of *cis*-di(thiocyanate)bis (2,2′-bipyridyl-4,4′-di-carboxylate) ruthenium(II) (R535, N3 dye), produced by Solaronix, in ethanol solution. The redox electrolyte, consisting of 0.6 M dimethylpropylimidazolium iodide, 0.1 M LiI, and 0.05 M I$_2$ in acetronitrile (AN), was introduced to the gap between electrode and counter one by capillary force. The 4-*tert*-butylpyridine (TBP) was added into the electrolyte at 0.5 M in order to increase the voltage of the cell [5,11,12].

### 2.4. Evaluation of amount of dye, film thickness, and photovoltaic characteristics

The amount of anchored dye was determined by desorbing the dye from the titania surface into a mixed solution of 0.1 M NaOH and ethanol (1:1 in v/v) and measuring its absorption spectrum. The concentration of anchored dye was analyzed by UV-Vis spectrophotometer (UV-2450 SHIMADZU). The cell size was 0.25 cm^2 (∼0.5 cm × 0.5 cm). The thickness of titania films was investigated with a Tencor Alpha-step profiler, which is considered to provide more reliable results than the values in previous report [10]. The solar cell is composed of titania electrode on a conducting glass plate, a platinum electrode, and an electrolyte between titania electrode and platinum counter elcetrode. The photovoltaic property was measured by using a potentiostat (Hokuto Denko HA-501G, HB-105) by irradiating with simulated solar light, i.e. AM 1.5, 100 mW cm^{-2} (Oriel 100 W91192).

3. Results and discussion

3.1. Characterization of TiNT

TiNT was synthesized by using the LAHC and TIPT modified with ACA as reported in previous works [9,10]. Fig. 1(a) shows a TEM image and electron diffraction pattern of TiNT, which was prepared by scratching a small powder from TiNT film. The titania film consisted of titania nanotube and nanoparticle. In Fig. 1(b), the size of single titania nanotube was 9 nm in diameter and at least several hundreds of nanometers in length. The electron diffraction of single titania nanotube, sintered at 400 °C for 2 h in Fig. 1, displays the Debye–Scherrer rings of anatase.

Fig. 2 shows XRD patterns of P25 and TiNT deposited films. The result indicated that TiNT mainly consist of an anatase phase while the P25 titania film is compose of anatase and rutile phase. Generally, the bandgap of titania was reported to be 3.2 eV (the absorption edge at 388 nm) for anatase and 3.0 eV (the absorption edge at 413 nm) for rutile [13]. A wider bandgap of anatase prevents a bandgap absorption of blue light by titania. This also indicated that only dye absorbs the incident visible light, which improves the overall performance [2].
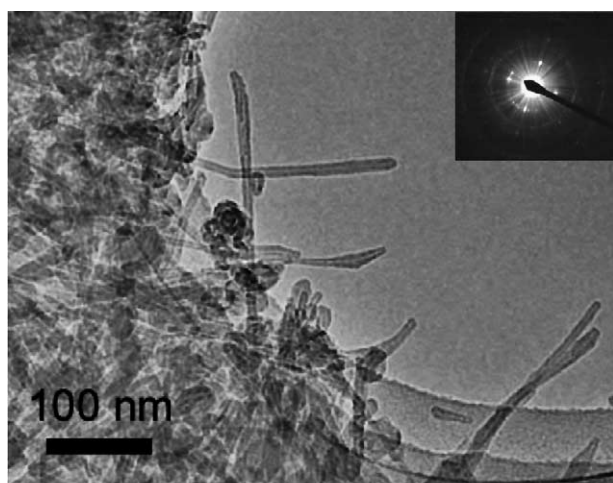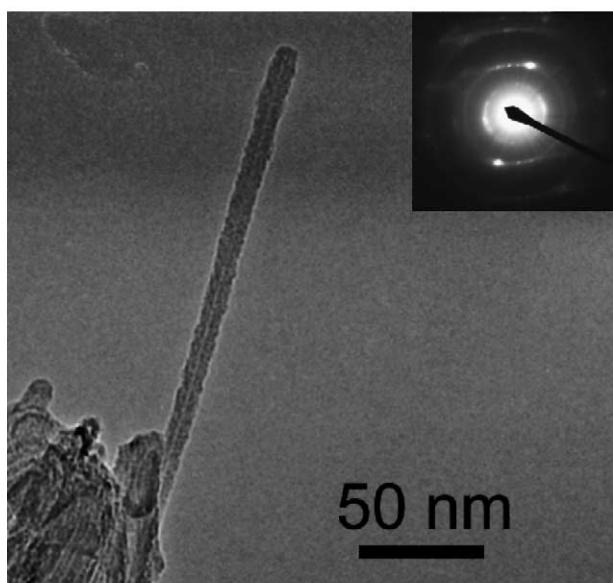
Fig. 1. TEM images and electron diffraction patterns of (a) titania nanotube and (b) single titania nanotube sintered at 400 °C for 2 h.

3.2. Dye-chemisorption onto the titania films and photocurrent–voltage characteristics of TiNT comparing with P25

The BET surface area of P25 and TiNT powder is 59 and 139 $m^2 g^{-1}$, respectively. The TiNT powder had obtained two times higher surface area than that of P25 powder. From the nitrogen adsorption–desorption isotherm, TiNT showed the IUPAC type IV isotherm which can be indicated that this material has a prevalent mesoporous structure.

Fig. 3 shows dependence of the amount of chemisorbed dye on the thickness of TiNT and P25 titania films. The amount of dye adsorption on titania surface is proportional to the thickness of the TiNT and P25 titania. The dye quantity of TiNT was higher than that of P25 titania film by approximately three times. This was resulted from the surface
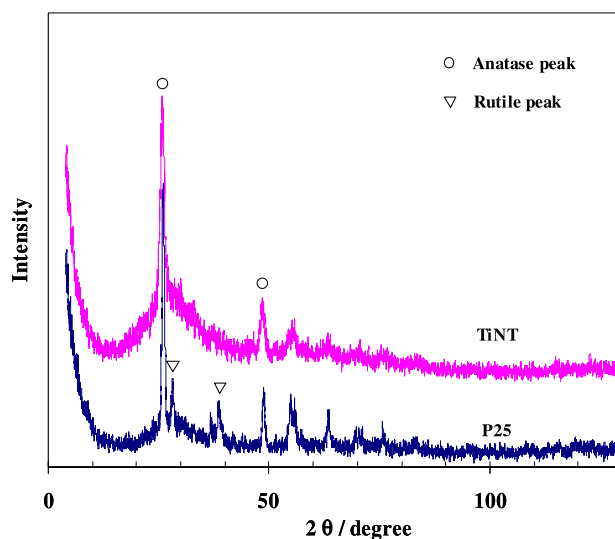

Fig. 2. XRD patterns of P25 and TiNT coated on a normal glass.

area of TiNT, which was higher than that of P25 titania as discussed earlier. The amount of adsorbed dye strongly depended on the surface area of titania film.

Dependence of the short-circuit photocurrent density (J_{sc}) on the thickness of the TiNT and P25 titania films is shown in Fig. 4. The J_{sc} of thin TiNT film was rapidly increased when the thickness increased in the range of 1–3 μm. This might be attributed to high surface area and rapid electron transport in the thin film of TiNT due to the short distance from the generated electron level to the current collecting electrode [14]. The J_{sc} of TiNT electrodes was gradually increased when increasing the film thickness from 3 to 7 μm. Although, the film thickness was increased up to 7 μm, the J_{sc} was improved only 30% comparing with film thickness
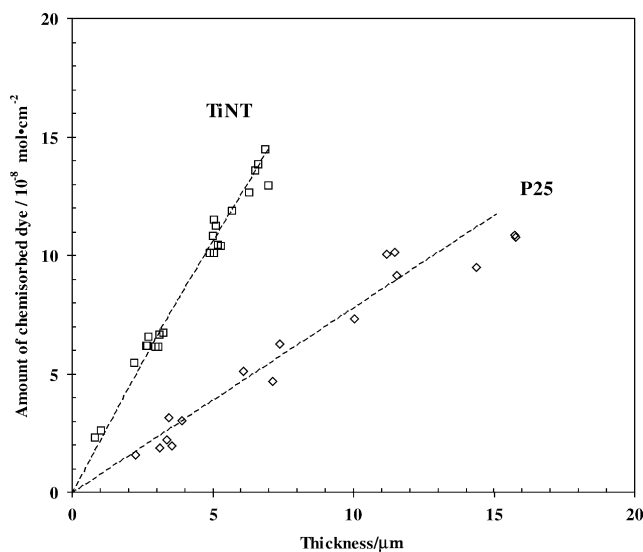

Fig. 3. Dependence of the amount of chemisorbed dye on the thickness of TiNT and P25 titania films.
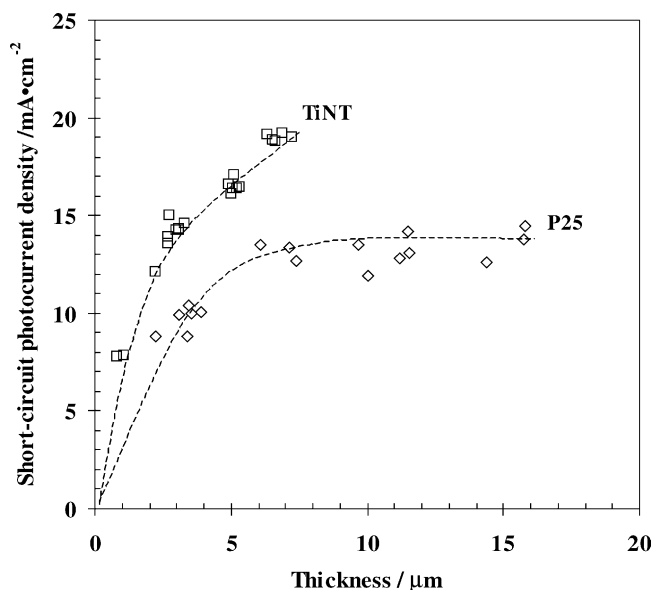
Fig. 4. Dependence of the short-circuit photocurrent density on the thickness of TiNT and P25 titania films.

of 3 μm. The J_{sc} of TiNT film was higher than that of P25 titania film by 28% at film thickness of 5 μm. At the high film thickness region (>6 μm), the J_{sc} of thick P25 film seems to be almost constant while J_{sc} of TiNT tends to level off more slowly than P25 film. This might be due to facile electron transport of TiNT. In general, the photocurrent that is generated by the solar cell is directly corresponded to the amount of dye adsorption on titania electrode. Therefore, the increase in surface area of titania electrode resulted in an increase in not only increase amount of adsorbed dye but also photocurrent. Furthermore, the other factors such as film thickness, crystallinity and electron transport should be considered. The thick film exhibited high light harvesting efficiency due to increasing the dye concentration, but it has also high electron recombination losses compared to thin film. To obtain high solar conversion efficiency, titania electrodes should have high surface area and facile electron transport. A high J_{sc} of TiNT films could be due to high surface area and its pure anatase phase, which offers higher electron transport than rutile phase [15,16]. Besides, the high aspect ratio of nanotube structure can assist in electron transfer more efficient than that of only P25 titania particle because boundaries among particles have a noticeable effect on reducing the photocurrent [17]. To evaluate the efficiency of the dye molecules that generate photocurrent, the dependence of J_{sc} on the amount of adsorbed dye on both of titania films is plotted in Fig. 5. The J_{sc} of TiNT film was higher than that of the P25 film by 30% at the dye concentration of 5×10^{-8} mol cm^{-2} and 27% at the dye concentration of 1×10^{-7} mol cm^{-2}. This could be attributable to its pure anatase phase and high aspect ratio of nanotube, which cause the decrease in the number of grain boundaries and the facile electron transport.
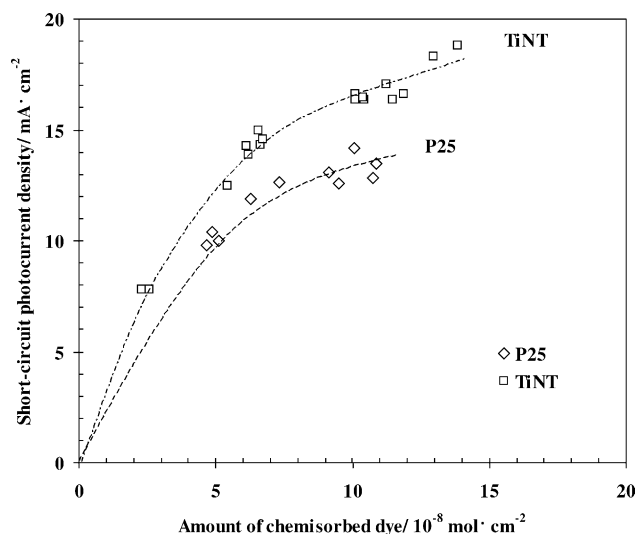

Fig. 5. Dependence of the short-circuit photocurrent density on the amount of chemisorbed dye of TiNT and P25 titania films.

Preliminary photovoltaic property revealed that they had relatively low photovoltage. Open-circuit photovoltage (V_{oc}) was found to be in the range of 550–585 mV for TiNT electrodes with increasing thickness from 0.8 to 7.2 μm and 540–590 mV for P25 electrodes with increasing thickness from 3 to 16 μm. The V_{oc} of TiNT and P25 electrodes are relatively consistent. The low V_{oc} of both cells is a major problem for lowering solar energy conversion efficiency (η). Charge recombination may play a significant role in lowering the photovoltage [18]. The electron recombination can be retarded by treated electrode with TBP [12,18]. Fig. 6 shows comparison between photocurrent–voltage characteristics of the cell using TiNT and P25 titania with and without TBP. To improve the photovoltage of the cell, TBP was introduced into the electrolyte. Although, the added TBP
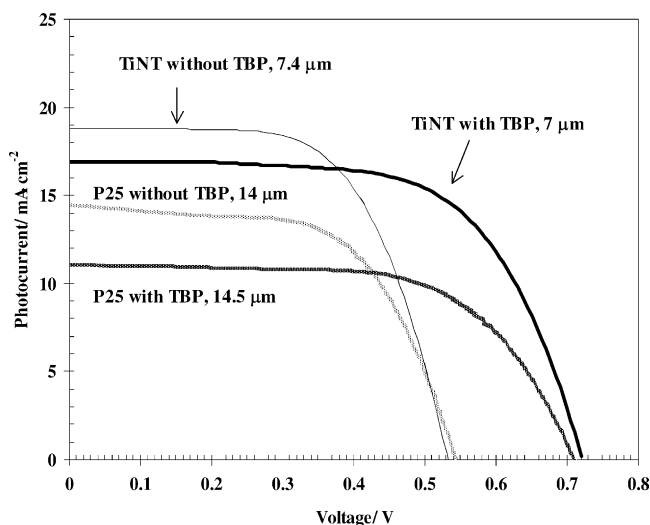

Fig. 6. Comparison of photocurrent–voltage characteristics of the cell using TiNT and P25 with and without TBP.

can help increase photovoltage, it decreases photocurrent of both TiNT and P25 cell. However, the overall cell performance was improved by using electrolyte with added TBP. The solar energy conversion efficiency (η) of TiNT using TBP electrolyte reached 7.83% with J_{sc} of 16.6 mA cm^{-2}, V_{oc} of 0.72 V and ff of 0.655; while η of P25 using TBP electrolyte reached 5.01% with J_{sc} of 11.07 mA cm^{-2}, V_{oc} of 0.71 V and ff of 0.637. The TiNT was found to be superior solar energy conversion efficiency to P25 titania. This material possesses high potential for further development in the application of dye-sensitized solar cells.

3.3. Blending TiNT with P25 titania

Although, TiNT films have a potential for fabrication of highly efficient dye-sensitized solar cells, TiNT films without crack were limited the thickness up to 7 μm. The P25 titania was blended with TiNT gel for increasing the thickness. Fig. 7(a) illustrates relationship between the J_{sc} and the
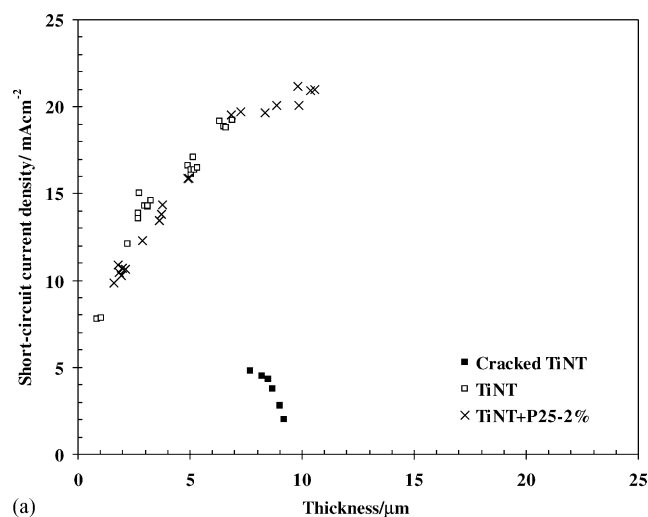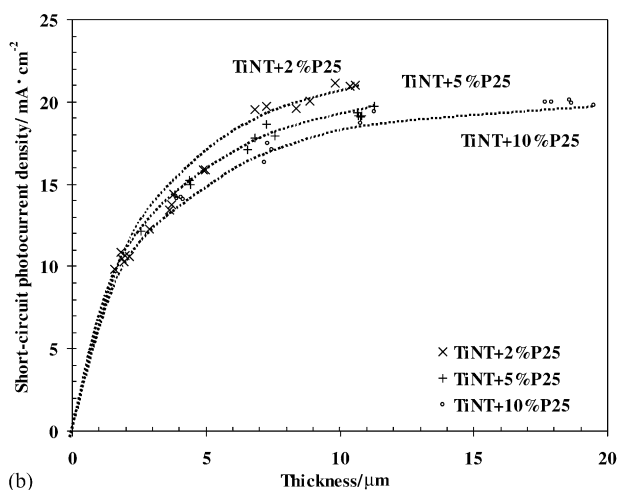
Fig. 7. Relation between the short-circuit photocurrent density and the thickness of (a) TiNT films comparing with TiNT + 2% P25 films and (b) blended TiNT with 2, 5 and 10% P25 titania.
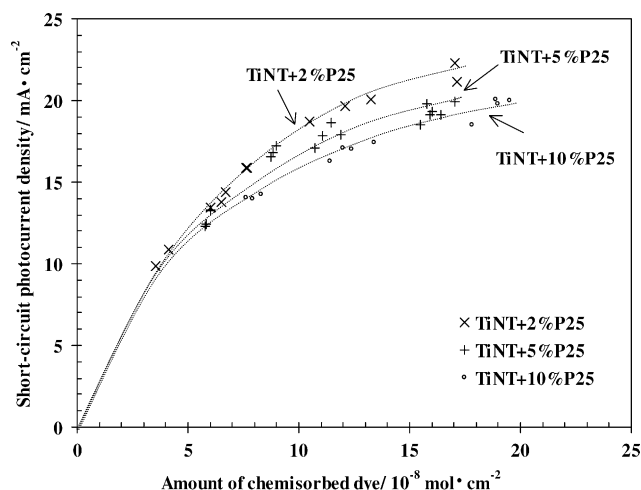

Fig. 8. Dependence of the short-circuit photocurrent density on the amount of chemisorbed dye of blended TiNT with 2, 5 and 10% P25.

film thickness of unblended TiNT compared with blended TiNT with 2% P25 (TiNT + 2% P25). In Fig. 7(a), the J_{sc} of pure TiNT electrodes was insignificantly differ from that of TiNT electrodes up to 7 μm thick, while the film thickness was increased, leading to decrease in J_{sc} because some parts of TiNT film were cracked. However, the thick crack-free films can be obtained by using TiNT + 2% P25. Fig. 7(b) shows the relation between the J_{sc} and the thickness of blended TiNT with 2, 5 and 10% P25. The J_{sc} of TiNT + 5% P25 and TiNT + 10% P25 electrodes were lower than that of TiNT + 2% P25 electrodes. That clearly showed the increasing amount of P25 further decreased the J_{sc} of the cell prepared from blended TiNT with P25. This can be explained by the coexistence of rutile phase, which is 30% lower J_{sc} than anatase phase [13]. Other reasons are considered not only a decrease in surface area but also an increase in grain boundaries that retard the electron transport from one grain to another as mentioned earlier. Fig. 8 illustrates dependence of J_{sc} on the amount of dye adsorption on the surface of blended TiNT with P25 film. Increasing amount of P25 tended to decrease the J_{sc} at the same amount of dye-concentration. This can be concluded that increasing amount of P25 leaded to increase the necking between particles and decrease the surface area.

Fig. 9(a) and (b) shows dependence of V_{oc} and ff against thickness of TiNT + 2% P25 films treated with and without TBP. The addition of TBP dramatically improved the V_{oc}, ff, and solar energy conversion efficiency (η) but reduced the J_{sc} of the cell. This could be due to the suppression of dark current and a negative shift of the conduction band level [19]. In Fig. 9(a), the V_{oc} of electrode treated with TBP decreased from 750 to 700 mV with increasing thickness from 3.7 to 11.8 μm and the V_{oc} of untreated electrode decreased from 620 to 540 mV with increasing thickness from 3 to 10.3 μm. In Fig. 9(b), the ff of electrode treated with TBP decreased from 0.694 to 0.601 with increasing thickness from 3.7 to 11.8 μm and the ff of untreated electrode decreased
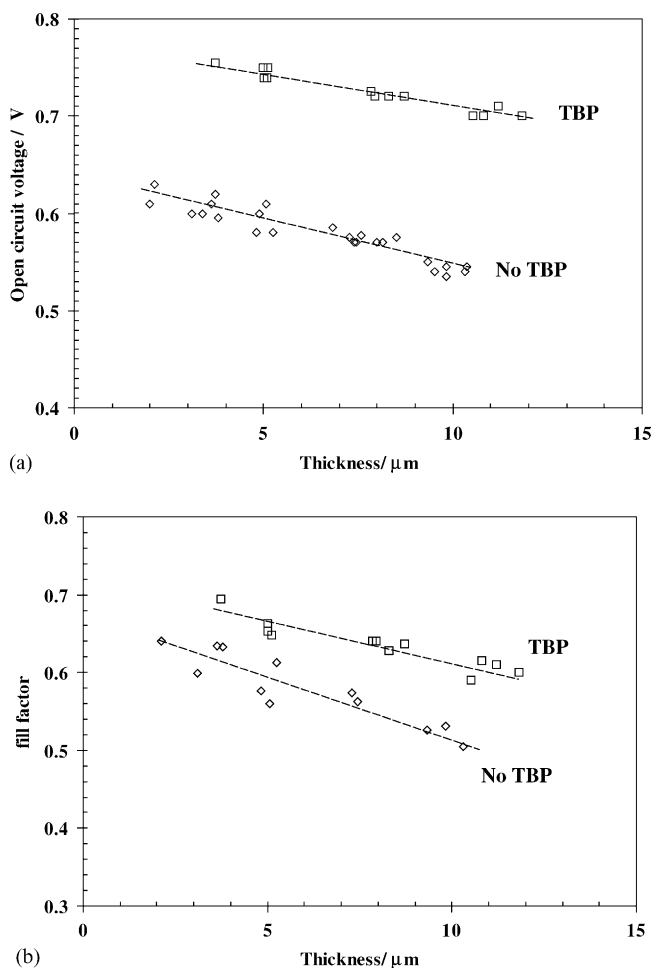
(a)

(b)

Fig. 9. Dependence of (a) V_{oc} and (b) fill factor against thickness of TiNT + 2% P25 films with and without TBP.

from 0.640 to 0.505 with increasing thickness from 2.1 to 10.3 μm. It can be noticed that an increasing in the thickness of electrode had significant effects on V_{oc} and ff. This is resulted from increasing vanished electrons due to recombination and increasing series resistance of the cell [9,20]. The electron recombination depends on the reduction of I_3^- electrons injected backward to combine with I^- [18]. Moreover, the probability of electron recombination may be increased by the increment of non-dye-adsorbed titania sites and grain boundaries [13]. The V_{oc} and ff were effectively increased after treated electrode with TBP. The substituted TBP plays an important role in blocking the electron when its adsorbed on the non-dye-titania surface [13].

Fig. 10 shows photocurrent–voltage characteristic of the cell using TiNT + 2% P25 treated with and without TBP. TiNT + 2% P25 without TBP exhibited higher J_{sc} but lower V_{oc} than those of TiNT + 2% P25 with TBP. The solar energy conversion efficiency (η) of TiNT + 2% P25 with TBP electrolyte reached 8.43% with J_{sc} of 18.1 mA cm^{-2}, V_{oc} of 720 mV and ff of 0.642. A small amount of P25 was added in TiNT, aiming to increase in the film thickness and subsequently increase J_{sc} and solar energy conversion
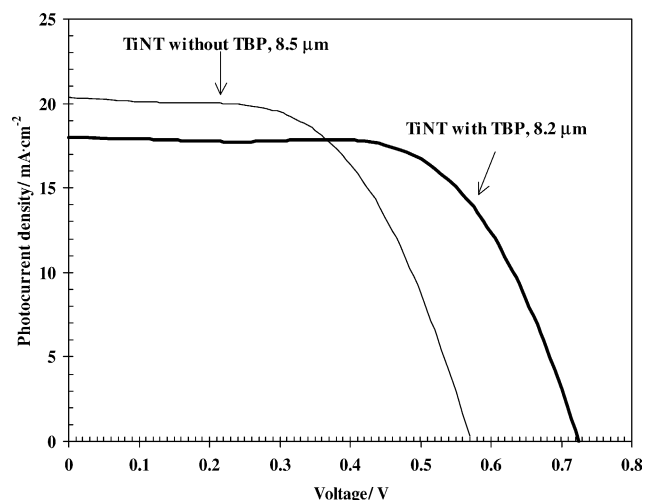

Fig. 10. Photocurrent–voltage characteristic of the cell using TiNT + 2% P25 treated with and without TBP.

efficiency (η) of the cell. Therefore, highly efficient solar cell can be obtained by using TiNT + 2% P25 as an electrode.

4. Conclusions

TiNT with high surface area and anatase phase was synthesized by surfactant-assisted templating mechanism in LAHC/TIPT with ACA system. Transparent films of TiNT electrode were superior in solar energy conversion efficiency to that of P25 electrode in thin film region. The addition of P25 to TiNT could prevent the cracking of film. Increasing amount of P25 more than 5% further decreased the J_{sc} of the cell. The J_{sc} of TiNT + 2% P25 electrodes was slightly different from that of TiNT electrodes. The thickness of TiNT + 2% P25 electrode and treatment of electrode with TBP had great effects on V_{oc} and ff. This could be due to increasing in electron recombination and series resistance of the cell. TiNT + 2% P25 electrode has been suitably utilized for highly efficient dye-sensitized solar cells. The optimal thickness of this electrode should be further investigated.

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