



# Hydrothermal synthesis of titanate nanoparticle/carbon nanotube hybridized material for dye sensitized solar cell application

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## ABSTRACT

With the hydrothermal treatment, titanate nanostructure with distinctively different morphology and surface characteristics was successfully synthesized from commercial rutile titania powder dispersed in accommodating media which were deionized water or NaOH solution. Hybridized materials of titanate nanoparticles and carbon nanotubes (CNT) were also synthesized by the hydrothermal treatment process. Intrinsic interaction of titanate nanoparticles and CNTs could be confirmed by spectroscopic analysis. The synthesized titanate nanoparticle/CNT hybridized material was then employed for fabricating a working electrode of dye-sensitized solar cells (DSSC). Based on experimental results, DSSC fabricated from the hybridized titanate nanoparticles and carbon nanotubes could provide the highest photoconversion efficiency of approximately 3.92%.

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) or titania has widely been examined and employed due to its excellent photocatalytic activity, relatively cheap cost, non-toxicity, and high chemical stability [1–4]. It is well recognized that anatase TiO<sub>2</sub> with a specific band gap energy of 3.2 eV, which allows it to absorb photon with wavelength shorter than ca. 390 nm, could exhibit a much better photocatalytic activity when compared with that of rutile TiO<sub>2</sub> [3,4]. Meanwhile, many attempts have also been made for further improvement of TiO<sub>2</sub> nanostructures characteristics by various techniques, such as wet chemical impregnation, template replication and hydrothermal methods [5–9]. With the template replication method, well aligned and uniform TiO<sub>2</sub> nanotubes could be fabricated but there is difficulty in separating the tubular product from the residual template materials. Meanwhile, the hydrothermal treatment of TiO<sub>2</sub> powders in an alkali solution could distinctively provide slender titanate nanostructures [8,9]. The sonication pretreatment was also proposed to improve some characteristics which are length and specific surface area of titanate nanotubes fabricated by the hydrothermal method [9].

With such distinctive difference, it is recognized that titanate nanostructures could provide some promising applications including dye-sensitized solar cell [3,10]. At the same time, carbon nanotubes (CNT) are also recognized as unique nanomaterials with various applications due to their electrical and mechanical properties [5]. However, preparation of these hybridized materials has not been clearly understood and reported. This motivates many research teams to explore simple means to fabricate such hybridized material of titanate and carbon nanostructures.

Dye sensitized solar cells (DSSC) has gained tremendous interests from many research teams because of its promising characteristics which would contribute to endlessly renewable energy generator. DSSC has exhibited many advantages of the facile way to fabricate, low cost production and effective conversion of solar energy [1–4]. There are many previous works reporting that working electrodes fabricated from nanostructure with high surface area could provide a significant increase in the solar energy conversion of DSSC. The enhancement of DSSC efficiency are generally attributed to electron transport inside its electrode incorporating with novel nanomaterials, such as nanosized titania or zinc oxide [4,5]. It is well recognized that CNTs could be employed as charge carrier transport material because of its excellent conductivity, resulting in a potential in enhancing electron transport from dye to electrodes in a DSSC. Therefore, an increase in current density could be anticipated if CNTs are incorporated with such nanosized metal oxide as electrode material for DSSC applications.

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In this work, we aimed to synthesize hybridized material of titanate nanoparticles and CNTs for applying as photoelectrode of DSSC. Hydrothermal process was employed to synthesize various titanate nanostructures from rutile  $\text{TiO}_2$  powder which was commercially available. Two kinds of liquid (deionized water and 10.0 M NaOH solution) were utilized in the hydrothermal treatment which could provide nanostructures with different characteristics. Phase crystallinity, morphology and specific surface area of all representative nanostructures were characterized by XRD, TEM and BET, respectively. Based on our preliminary experimental results, deionized water could provide titanate nanostructures with much higher surface area so that the hybridized material of the titanate nanoparticles and CNTs were further prepared by the hydrothermal treatment using deionized water. Finally, the prepared composites were employed for fabrication of thin film electrodes of DSSC which were experimentally examined for its efficiency in a simulated solar irradiating set-up.

## 2. Experimental

Based on our previous reports, titanate nanotubes (TNTs) were prepared by the 1st hydrothermal treatment of commercially available rutile titania powder (Aldrich 99%, BET surface area of ca.  $3.5 \text{ m}^2/\text{g}$ ) with NaOH (10 M, 50 ml) in an autoclave reactor at  $150^\circ\text{C}$  for 72 h [11]. Then, the prepared slurry was rinsed repeatedly with HCl (0.1 M) until neutralized and dried in an oven at controlled temperature. Then, particulate product which contains TNTs was utilized as the precursor in the 2nd step hydrothermal treatment for preparing titanate nanoparticles using two different liquid media which were 10.0 M NaOH and deionized water. Similarly, pristine multi-walled carbon nanotubes or CNTs (Bayer Material Science, BET surface area of ca.  $209 \text{ m}^2/\text{g}$ ) were ultrasonicated with the anatase  $\text{TiO}_2$  and titanate nanostructures before being subject to the hydrothermal treatment for synthesizing hybridized material of titanate nanotube-CNT (TNT-CNT) and rice-shaped titanate nanoparticles-CNT (Rice-CNT), respectively. All hybridized materials were characterized by transmission electron microscopy (TEM, JEM-1230, JEOL) for assessing their size and morphology, X-ray diffraction spectroscopy (XRD, D-500 X-ray diffractometer with  $\text{Cu K}\alpha$  ( $\lambda = 1.544 \text{ \AA}$ ), SIEMENS) for crystalline phase and lattice of the nanostructure and nitrogen adsorption (Mini-Belsorp) for specific surface area and pore size distribution.

For fabrication of photoelectrode of DSSC, a suspension of hybridized material was prepared by adding 49.75 g of terpineol (Fluka, M. 154.25,  $\text{C}_{10}\text{H}_{18}\text{O}$ ) and 0.25 g of sodium dodecyl sulfate (Merck shuchardt,  $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$ ) with a designated amount of the particulate material. As a reference, a suspension of anatase  $\text{TiO}_2$  powder (Aldrich 99%, BET surface of  $158.0 \text{ m}^2/\text{g}$ ) was stirred for 30 min to ensure its uniform mixing. The prepared suspension was further sonicated for 1 h before adding ethyl cellulose (EC, Fluka biochemical) as binder. A screen-printing block and a rubber blade were employed for preparing thin film of the prepared suspension and platinum precursor (Solartec, Thailand) onto the surface of conductive glass plates (FTO, sheet resistance  $15 \Omega/\text{m}^2$ , Asahi Glass Co. Ltd.) with a designated area of  $1.5 \text{ cm} \times 2.0 \text{ cm}$ . The photoelectrodes were sintered at  $500^\circ\text{C}$  for 1 h before being immersed in N719 dye solution (Solarnic) for 1 h at  $65^\circ\text{C}$ . 0.5 M dimethylpropylimidazolium iodide, 0.1 M LiI, and 50 mM  $\text{I}_2$  dissolved in acetonitrile was employed as the redox electrolyte which was introduced to the gap between electrode and counter one by capillary force.

Similarly, suspensions of the synthesized TNT, TNT-CNT and Rice-TNT hybridized materials were also employed instead of the anatase titania suspension with the same fabricating procedures. Finally a set of five cells of DSSC was fabricated by assembling the

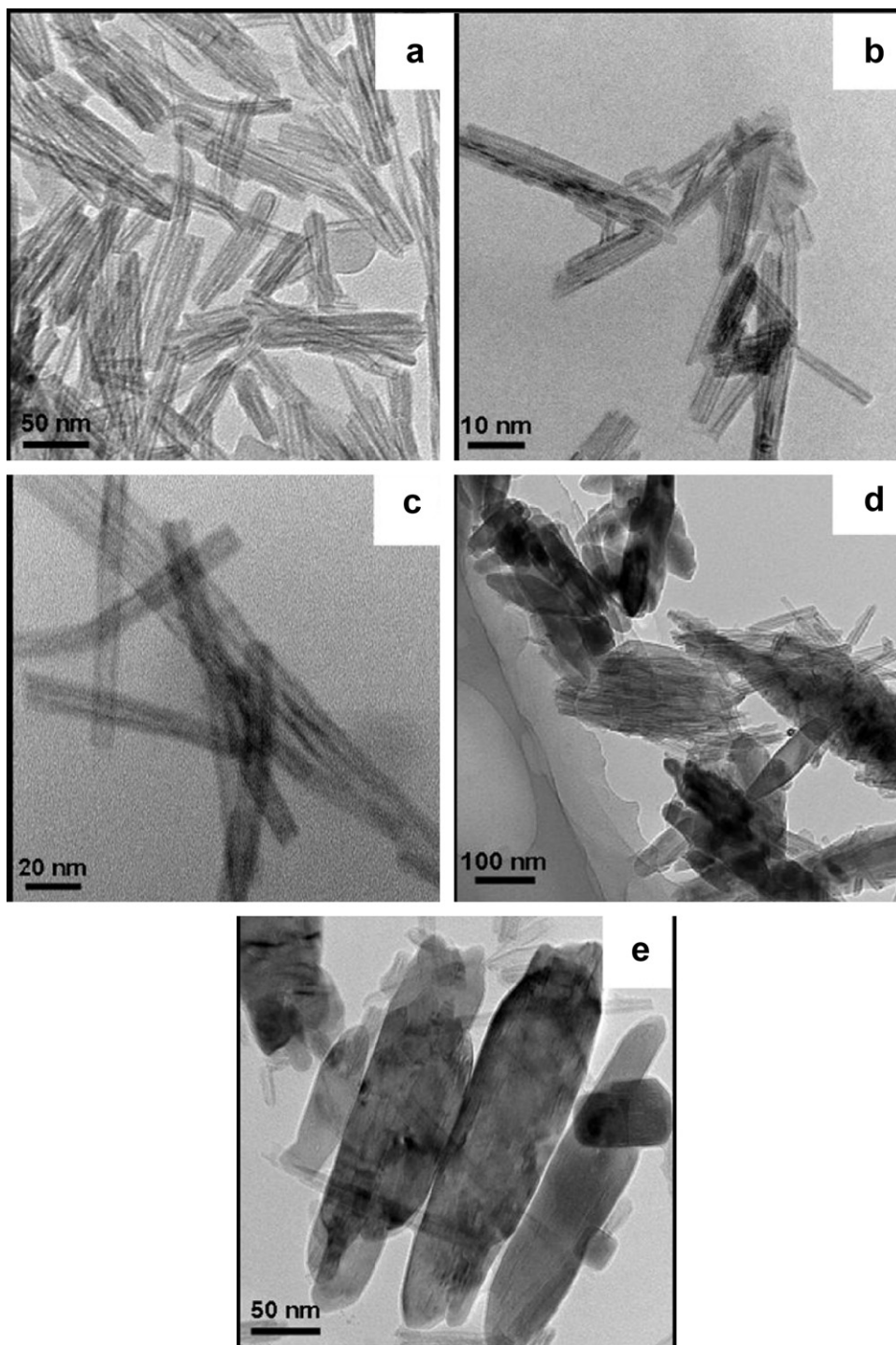
photoelectrodes made of each hybridized material with the counter electrodes and filling with the electrolyte before putting into the simulated solar irradiation set-up for its photoconversion efficiency assessment.

## 3. Results and discussion

### 3.1. Preparation and characterization of titanate nanoparticles

For comparison, typical microscopic images of specimens prepared under each condition are depicted in Fig. 1(a)–(e). First, titanate nanotubes (TNT) with a uniform diameter of 20 nm and length of 150 nm could repeatedly be prepared by the 1st hydrothermal treatment of the commercial rutile titania powder (Fig. 1(a)). The formation of the uniform TNTs would be attributed to the reaction involving with  $\text{Na}^+$  ions which could play a role in peeling surface of rutile titania into sheet of titanate compounds and rolled them to form a tubular shape [11]. These TNTs exhibit low crystalline characteristics with relative large specific surface area. With the 2nd hydrothermal treatment using 10.0 M NaOH solution for 12 h, much slimmer and shorter TNTs were prepared as shown in Fig. 1(b). This result would suggest that the 2nd hydrothermal treatment with the aqueous solution of  $\text{Na}^+$  ions would not provide any internal change of prepared product. Therefore, as an alternative deionized water was employed in the 2nd hydrothermal treatment. As depicted in Fig. 1(c), the 2nd hydrothermal treatment with deionized water for 12 h resulted in a product with tubular characteristics similar to the original TNTs obtained from the 1st hydrothermal treatment. However, with an increase in the treatment time from 12 to 48 h the 2nd hydrothermal treatment with deionized water could provide a partial formation of rice-shaped titanate nanoparticles (average short diameter of 80 nm and longer diameter of 250 nm) with some remaining TNTs as could be observed in Fig. 1(d). Finally, the 2nd hydrothermal treatment with deionized water for 72 h could result in distinctively different products which exhibit uniform rice-shaped titanate nanoparticles with significantly smaller size (average shorter diameter of 60 nm; Fig. 1(e)). Distinctive difference in morphological characteristics of these nanoparticles is attributed to their different crystallinity which could provide significant effects on their electron transferring [7].

Fig. 2 reveals the XRD patterns of samples a–e which correspond to each product of which typical micrograph is already shown in Fig. 1. As a reference, a commercial anatase  $\text{TiO}_2$  (sample f) was also characterized. It is worth noticing that the intensity of the rutile diffraction peaks could be observed in samples a and b. The crystallite sizes estimated from the broadening of the rutile phase (0 0 2) reflection plane ( $2\theta = 27.2^\circ$ ) of samples a and b are 8.2 and 7.8 nm, respectively (JCPDS no. 21-1272). However, the peaks presenting in the diffraction pattern of samples c and d are correspond to the anatase phase with reflection planes at  $2\theta = 25.4^\circ$ ,  $38.1^\circ$ , and  $48.2^\circ$ , while sample e exhibits additional peaks at the reflection planes at  $54.2^\circ$ ,  $62.7^\circ$ ,  $70.3^\circ$ , and  $75.3^\circ$ , respectively (JCPDS no. 77-0441). The high intensity and the small width at the half height of the diffraction peaks indicate the significant portion of the crystallized anatase phase on the surfaces of the nanoparticles. Based on these analyses, the crystallinity of the prepared nanoparticles is lower than that of the commercial anatase  $\text{TiO}_2$ . These results would suggest that the shielding of peaks of other titanate nanostructures would be affected by the presence of remaining anatase  $\text{TiO}_2$  which was transformed from the rutile precursor [11]. Regarding to these spectra, it could be confirmed that the results consistent with the increase in the treatment time from 12 to 72 h, which would favor the increase in the crystallinity of titanate nanostructures and the significant



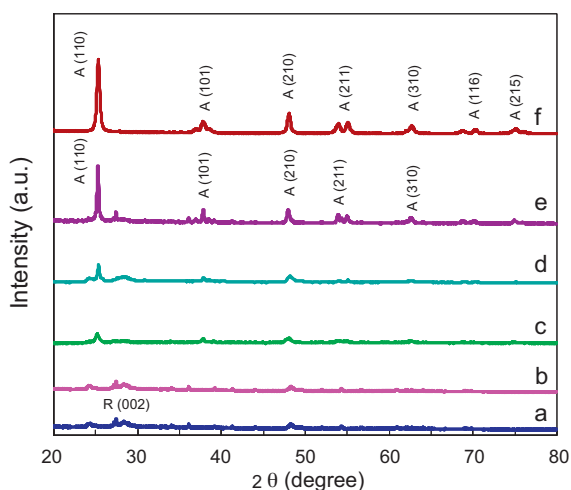
**Fig. 1.** Typical TEM micrographs of titanate nanoparticles synthesized with different conditions: (a) 1st treated TNTs, (b) TNTs treated with NaOH for 12 h, (c) TNTs treated with deionized water for 12 h, (d) TNTs treated with deionized water for 48 h, and (e) TNTs treated with deionized water for 72 h.

decrease in the particle agglomeration [12]. Also, it could be clearly observed that the reference anatase  $\text{TiO}_2$  nanoparticles (sample f) exhibit characteristic peaks at the same reflection planes as those of sample e. In addition, our XRD analyses suggest that the rice-shaped titanate nanoparticles would exhibit semiconductive property similar to that of anatase  $\text{TiO}_2$  nanoparticles. For further examination, commercial anatase  $\text{TiO}_2$ , TNT and rice-shaped titanate nanoparticles were employed as precursor for fabricating photoelectrodes of DSSC of which solar energy conversion efficiency would be experimentally examined and discussed later.

### 3.2. Synthesis and characterization of titanate nanoparticles/CNT hybridized material

**Fig. 3** illustrates morphology of typical samples of two different hybridized materials which are titanate nanotubes (TNT) with CNTs (TNT-CNT) and rice-shaped titanate nanoparticles with CNTs (Rice-CNT). CNTs with diameter of 25 nm were uniformly mixed with TNTs which had almost the same diameter. SEAD analysis shown as the inset of **Fig. 3(a)** reveals that TNTs within the TNT-CNT hybridized material exhibit amorphous characteristics. On the





**Fig. 2.** XRD spectrum of each particulate material: (a) 1st treated TNTs, (b) TNTs retreated with NaOH for 12 h, (c) TNTs retreated with deionized water for 12 h, (d) TNTs retreated with deionized water for 48 h, (e) TNTs retreated with deionized water for 72 h, and (f) commercial anatase titania.

other hand, relatively large rice-shaped titanate nanoparticles were found to entangle with CNTs of smaller diameter. In addition, the SEAD diffraction pattern in Fig. 3(b) suggests that rice-shaped titanate nanoparticles in Rice-CNT hybridized material possess a certain level of crystallinity [12]. No significant defect on the surface of CNTs could be detected by our TEM analyses. This is attributed that  $\text{TiO}_2$  and TNT would be more reactive to the hydrothermal reaction with de-ionized water when compared with pristine CNTs.

For further characterization, pristine CNTs, hybridized TNT-CNTs and hybridized rice-shaped titanate nanoparticle-CNTs (Rice-CNT) were subject to FT-IR for analyzing the existence of functional groups on their surface. Based on IR spectra shown in Fig. 4, the presence of carboxylic acid group ( $-\text{C}=\text{O}$ ) which correspond to the wave number of  $1700\text{ cm}^{-1}$  and the peak of broad OH vibration at  $3400\text{ cm}^{-1}$  could be found in all samples. These results would suggest that the presence of carboxylic acid group on the surface of each hybridized material was confirmed. According to the existence of carboxylic acid group on the surface of CNTs within TNT-CNT or Rice-CNT hybridized material, it could be implied that the CNTs would play an important role in hindering the recombination of electrons because the carboxylic acid group

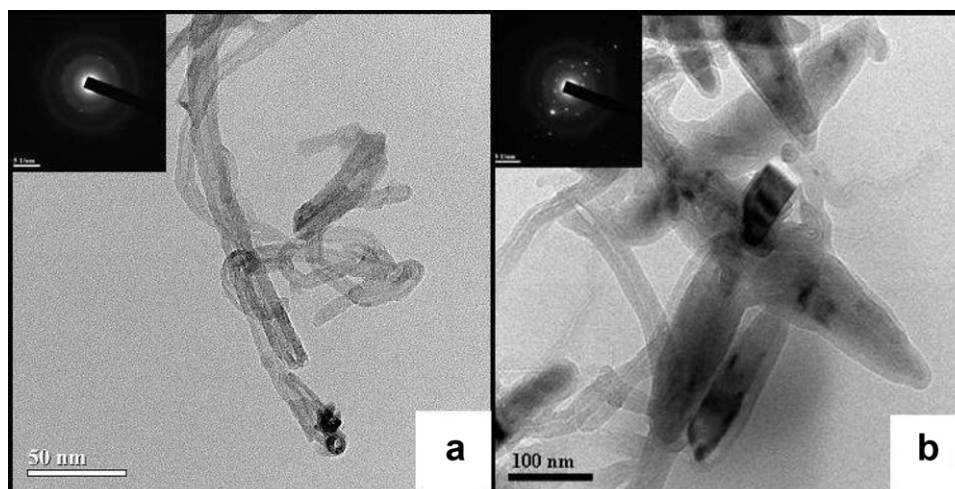
located on their surface could enhanced their polar properties. Additionally, some previous literatures also report that CNTs could preferably attach dye molecule which would help increase electron transfer process [13–16]. It would conceptually be implied that the faster electron transfer would be represented by the higher electrical current density flowing through a cell. Therefore, it could be anticipated that the addition of CNTs to semiconductive  $\text{TiO}_2$  or its derivatives would be suitable for application of DSSC.

However, it should be noted that specific surface area of particles which are employed as electrode material is a key parameter playing role in adsorption of dye molecules in DSSC. Therefore, BET surface area analyses were also conducted for examining specific surface area of all typical hybridized material samples in comparison with other reference materials which were rutile titania, anatase titania, pristine CNT and rice-shaped titanate nanoparticles. Fig. 5 reveals the comparison of BET surface area of all samples. It could be clearly observed that rutile titania possesses the lowest BET surface area of  $3.5\text{ m}^2/\text{g}$  while anatase titania contains much higher BET surface area of  $158.0\text{ m}^2/\text{g}$ . With the 1st hydrothermal treatment, TNT would lose its crystallinity and certain level of its specific surface area but the 2nd hydrothermal treatment would reverse its crystallinity once the TNT was treated in de-ionized water [11]. Based on our investigation, TNT possessed significantly lower BET surface area of  $137.4\text{ m}^2/\text{g}$ , when compared with that of rice-shaped titanate nanoparticles (BET surface area of ca.  $182.1\text{ m}^2/\text{g}$ ). With introduction of CNTs (BET surface area of ca.  $209.0\text{ m}^2/\text{g}$ ) into TNT or rice-shaped titanate nanoparticles before their hydrothermal treatment, an observable improvement of BET surface area of TNT-CNT or Rice-CNT hybridized material could be achieved. BET surface area of TNT-CNT and Rice-CNT hybridized materials were  $175.8$  and  $202.3\text{ m}^2/\text{g}$ , respectively.

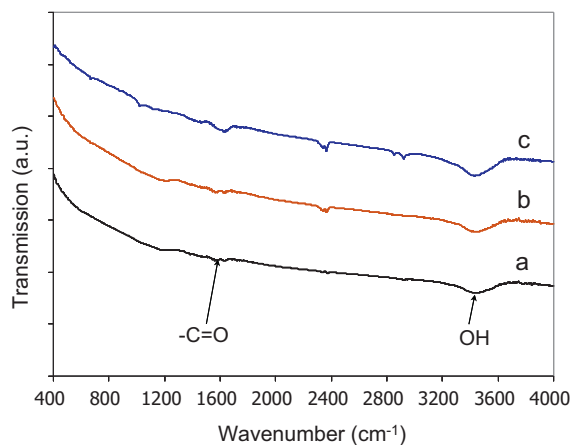
Based on all of our characterization results, we could come up with an implication that TNT-CNT and Rice-CNT would have potential for being employed as electrode materials of DSSC. Also, based on other previous literatures, anatase titania and TNT were also employed for fabrication of DSSC electrode for the sake of comparison.

### 3.3. Performance of DSSC fabricated from titanate nanoparticles/CNT composite

$J$ - $V$  characteristics of DSSCs with an active area of  $3.0\text{ cm}^2$  which were subject to AM 1.5 illumination standard are illustrated in Fig. 6. For comparison, DSSCs with working electrodes fabricated



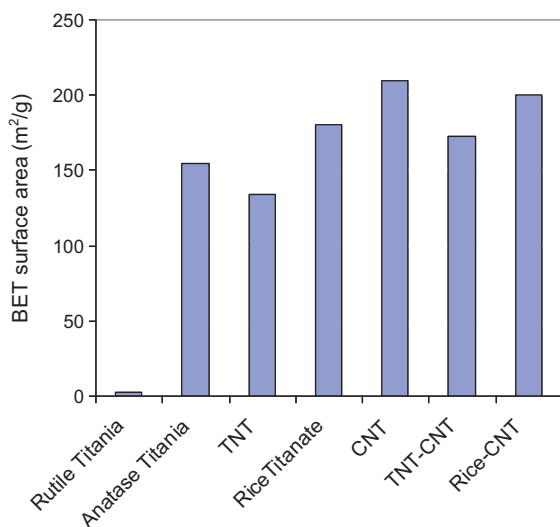
**Fig. 3.** Typical TEM micrographs of (a) TNT-CNT and (b) Rice-CNT hybridized materials.



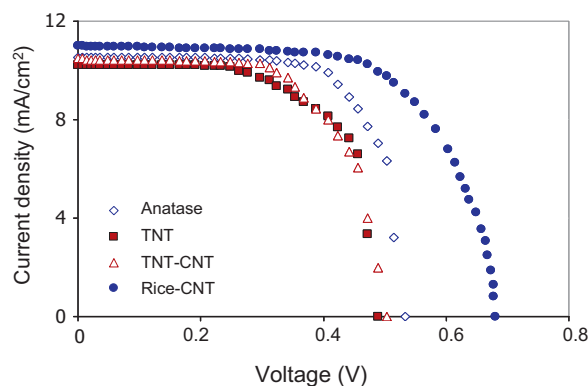
**Fig. 4.** FT-IR spectra of (a) pristine CNT, (b) TNT-CNT hybridized material, and (c) Rice-CNT hybridized material.

from commercial anatase titania exhibited the short-circuit current density ( $J_{sc}$ ) of 10.52 mA/cm<sup>2</sup>, open-circuit voltage ( $V_{oc}$ ) of 0.53 V, and filling factor (FF) of 0.44 while those of DSSC using TNT as electrode material were 10.23 mA/cm<sup>2</sup>, 0.49 V and 0.40, respectively. These are equivalent to the overall photoconversion efficiency ( $\eta$ ) of 2.93 and 2.39%, respectively. Meanwhile, it should be noted that DSSCs using electrodes fabricated from TNT-CNT or Rice-CNT exhibited remarkably better  $J$ - $V$  characteristics. With the working electrodes made of TNT-CNT, the DSSC exerted  $J_{sc}$  of 10.48 mA/cm<sup>2</sup>,  $V_{oc}$  of 0.52 V, and FF of 0.42. Finally, the DSSC using Rice-CNT working electrodes exhibited the best characteristics which were  $J_{sc}$  of 11.00 mA/cm<sup>2</sup>,  $V_{oc}$  of 0.65 V, and FF of 0.46. Overall comparison of  $J_{sc}$ ,  $V_{oc}$ , FF, and  $\eta$  of each cell fabricated from different electrode materials is summarized in Table 1. These data are illustrative of 5 solar cell samples with the same active area mentioned above. It could be confirmed that DSSCs with electrodes fabricated from Rice-CNT hybridized material exhibited the highest photoconversion efficiency of 3.92% while the DSSC with working electrodes made of TNT had the lowest efficiency of 2.39%. Incorporation of CNT with TNT could help increase the photoconversion efficiency of DSSC to 2.73% but it was still lower than the DSSC with electrodes fabricated from anatase titania (2.93%).

These testing results suggested that utilization of the Rice-CNT hybridized material in DSSC, which could provide the very high short-circuit current densities of 11.00 mA/cm<sup>2</sup>, would reasonably



**Fig. 5.** Comparison of BET surface area of each electrode material.



**Fig. 6.** Short-circuit current–voltage curves of DSSC with electrodes fabricated from different electrode materials.

be attributed to the high surface area of the hybridized material (referring to data in Fig. 5). In addition, upon illumination the large concentration of injected electron was efficiently collected at the contact within the heterogeneous interface of rice-shaped titanate nanoparticles and CNTs, leading to high  $J_{sc}$ . Bwana also reported that high  $J_{sc}$  would also be attributed to the entangling of the titanate nanotubes and CNTs arrays which would considerably reduce the trap-site effects seen in sintered film by providing a short electron diffusion path to the contact [17]. In addition, reduction of the so-called band bending effect of the conduction band of anatase phase caused by accumulation of electron in the deep trap states would also enhance the electron collection once the specific surface area of electrode material would be efficient. The existence of titania nanostructure may lead to rough surface which would consequently enhance the absorption in dye remediation process [18]. Our microscopic analyses also revealed the presence of titanate nanoparticles within the electrode which could be persistent with the sintering temperature (500 °C). Regarding to all of these experimental results, we would conclude that the efficiency of the fabricated DSSC would require further improvement. Uniformity of the hybridized materials would potentially provide faster electron transport and higher surface area essential for dye deposition. The faster electron transport in each DSSC fabricated from different nanostructure would be implied from the increase in current density of the DSSC which is summarized in Table 1. Anyway it would be essential to further examine this characteristics using electrochemical tunneling spectroscopy (ETS). Based on typical microscopic analyses shown above, though the hybridized materials of Rice-CNT exhibited the BET surface area which was comparable with that of pristine CNT, there is possibility to increase surface area by avoiding its agglomeration and generating its internal porosity [11]. In addition, the roughness factor of Pt counter electrode and sheet resistance of FTO should also be considered as they are related to the charge transfer and internal resistance of device [16]. FF would also be further improved by post-treatment of the DSSC electrodes to limit carrier recombination of electron. There are plenty of rooms for further improvement of these parameters which would be a challenge for researchers to gain practical application of DSSC.

**Table 1**  
Comparison of overall photoconversion efficiency of DSSC fabricated from each electrode material.

Materials	$J$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	$\eta$ (%)
Anatase	10.52	0.53	0.44	2.93
TNT	10.23	0.49	0.40	2.39
TNT-CNT	10.48	0.52	0.42	2.73
Rice-CNT	11.00	0.65	0.46	3.92

#### 4. Conclusion

Consecutive hydrothermal treatment of commercial rutile titania powder within de-ionized water could provide rice-shaped titanate nanoparticles with anatase characteristics and improved specific surface area. Regarding to spectroscopic analysis, intrinsic interaction of titanate nanoparticles and CNTs could be confirmed. Based on simulated sun irradiation, the DSSC with working electrodes fabricated from hybridized materials of titanate nanotube-CNT and rice-shaped titanate nanoparticles-CNT exhibited remarkably increasing efficiency when compared with that of anatase titania. The highest photoconversion efficiency of approximately 3.92% was achieved when the rice-shaped titanate nanoparticles-CNT hybridized material was employed as DSSC working electrode.

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