Hydrothermal Preparation of Anatase TiO₂ Nanoparticles for Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) have recently attracted intensive interest because of their simple construction, low cost, and high efficiency of sunlight to electricity conversion. Usually, a mesoporous titanium oxide (TiO₂) film deposited on a transparent electrode is used as a photoanode on which the ruthenium complex dye molecules adsorb. The aim of this work is to prepare pure anatase phase TiO₂ nanoparticles with high surface area for DSSCs application. We used the titanium (IV) *n*-butoxide as the precursor and acetic acid as a peptizer, after the hydrothermal treatment at 200°C, the anatase TiO₂ (a-TiO₂) can be obtained. The effect of hydrothermal duration on the properties of a-TiO₂ was studied. The TiO₂ products were characterized by XRD, TEM, and BET. The a-TiO₂ particles showed two distinct particle features: the irregular polyhedron and the elongated shaped as observed by TEM. Increasing the hydrothermal reaction time increased the average particle size for both cases and the surface area decreased as well. The a-TiO₂-based DSSCs were prepared with different thickness for the photovoltaic characteristics study. The best efficiency of ~6.61% was obtained for thickness of 24 µm ($V_{oc} = 0.77$ V, $J_{sc} = 16.48$ mA/cm², $FF = 0.56$).

Introduction

Titanium dioxide (TiO₂) is one of the most commonly used materials in many light induced processes such as a semiconductor for working electrode in dye-sensitized solar cells (DSSCs), and a photocatalyst for degrading the harmful molecules, and a sensor material for molecule detection (Grätzel, 2003; Hsiao *et al.*, 2007). The functional properties of TiO₂ is governed by many factors: crystallinity, particle morphology, particle size, and surface area which are all affected by the TiO₂ preparation method and condition. While the high crystallinity of TiO₂ helps to prolong the recombination rate of the photoexcited electron and hole, the large surface area of TiO₂ nanoparticles give large amount of photon generated electron-hole pairs as well as the active site concentration, thus the solar cell efficiency can be enhanced (Palomares *et al.*, 2003). The morphology of TiO₂ controls the electron conducting channels. The crystal of TiO₂ exists in two major forms: rutile and anatase (Park *et al.*, 2000). Anatase TiO₂ (a-TiO₂), due to the pres-

ence of large percentage of reactive facets, is generally considered to be more active than rutile in both photochemical reactions and photoelectrochemical cell (Yang *et al.*, 2008). A number of methods have been used to prepare anatase TiO₂ nanoparticle, such as microemulsion, precipitation method, hydrothermal crystallization, and sol-gel (Kim *et al.*, 2001; Zhang and Gao, 2002; Castro *et al.*, 2008; Li and Demopoulos, 2008; Mohammadi *et al.*, 2008). In this study, the a-TiO₂ nanocrystals were synthesized under hydrothermal condition and applied in the DSSCs. Titanium (IV) *n*-butoxide was used as a precursor of TiO₂, in conjunction with acetic acid (CH₃COOH) as a peptizer, the pure anatase phase TiO₂ nanoparticles with high surface area were successfully obtained. It was found that the TiO₂ films fabricated by such-made anatase nanocrystallines were efficiently sensitized by Ru-bipyridine dye, which showed the enhanced DSSCs performance compared with the photoelectrode made from commercial Degussa P 25 TiO₂ nanocrystallines. The detail microstructure, photovoltaic properties, and the effect of the TiO₂ film thickness on photo-conversion efficiency in DSSCs will be reported.

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Fig. 1 The flow chart of the method for preparing a-TiO₂ powder and a-TiO₂ photoanode

1. Experimental

1.1 The hydrothermal preparation of anatase TiO₂ nanoparticles

Figure 1 shows the schematic diagram for preparation of a-TiO₂ nanoparticles. To prepare a-TiO₂ nanoparticles, titanium (IV) *n*-butoxide (Ti(O-Bu)₄, ACROS) was mixed with 2 M CH₃COOH (pH = 2.1) at room temperature under magnetic stirring for 4–5 days until a homogeneous sol solution was obtained. The TiO₂ sol was then transferred to a Teflon-lined autoclave to perform the hydrothermal treatment at 200°C for various durations (3, 5, 10, 24, 36 h). The resulted sol was dried at 150°C for 8 h to form a-TiO₂ nanopowders. The formation of a-TiO₂ was confirmed by electron spectroscopy for chemical analysis (ESCA, VG Scientific ESCALAB 250 system) for chemical composition and X-ray diffraction (XRD, MXP 18, Japan MAC Science) for crystal phase and domain size. All measured XRD peaks were assigned by comparing with those of JCPDS data. The domain size of a-TiO₂ was determined according to the Scherrer equation using the full width at half maximum of (101) reflection peak. The morphology and particle size of a-TiO₂ particles were determined by transmission electron microscopy (TEM, H-7100, Hitachi Ltd.). The BET (Brunauer–Emmitt–Teller) surface area was obtained from nitrogen adsorption–desorption measurement

(ASAP-2010, Micromeritics).

1.2 Preparation of anatase TiO₂ photoanodes and DSSCs performance measurement

Anatase TiO₂ films were made by spreading a-TiO₂ pastes on fluorine-doped tin oxide (FTO) conducting glass (8 Ω/square, Solaronix) followed the procedure in Figure 1. The a-TiO₂ paste was prepared by mixing the a-TiO₂ sample, distilled water, acetylaceton (acac), Triton X-100, and poly(ethylene glycol) (PEG: MW 20,000) (Nazeeruddin *et al.*, 1993). Adhesive tapes were placed on the edges of FTO to form a guide for spreading the paste using doctor-blade technique which is a fast, convenient, and non-energy-consuming procedure for thin film deposition. After drying in air, the a-TiO₂ electrode was heated at 100°C for 15 min followed by calcination at 450°C for 30 min. The resulted electrode was cooled to 80°C and immediately soaked in a 0.3 mM solution of N3 dye (RuL₂(NCS)₂(ruthenium(II)*cis-bis*(thiocyanate) bis(2,2'-bipyridyl-4,4'-dicarboxylic acid), Solaronix) in ethanol for overnight. Thickness of the film was controlled by multiple coating process as shown in Figure 1 (dashed line). The thickness of a-TiO₂ films were measured by a Alpha-step profiler (Perthometer S2) and confirmed by SEM (SEM, S-2400, Hitachi Ltd.) images of cross-sections. The surface morphology and crystal phase of a-TiO₂ films were investigated by SEM and XRD respectively. The apparent cell areas of the a-TiO₂ electrode was 0.25 cm² (0.5 cm × 0.5 cm). The Pt counter electrodes with mirror finish were prepared by sputtering-deposition (E-1045 ion sputter, Hitachi Ltd.) of a 20 nm layer of Pt on top of FTO substrates. To assemble the DSSCs, the electrolyte of 0.5 M lithium iodide (LiI), 0.05 M iodide (I₂), and 0.5 M 4-*tert*-butylpyridine (4-TBP) in acetonitrile was applied to the Pt electrode which was then placed over the dye-coated a-TiO₂ electrode. The liquid ion electrolyte (I[−]/I₂/I₃[−]) redox couple was applied in the DSSCs because it is the most widely used redox system in DSSCs investigation and also due to the faster electron transfer kinetics compared to that of gel-phase or solid-phase redox couple. The edges of the cell were sealed with a 50 μm polyimide tape spacer.

1.3 Dye-sensitized solar cell performance measurement

The photocurrent-voltage characteristics were performed using a Keithley model 2400 source measuring unit. A solar simulator with 300 W Xenon lamp (Oriel) served as a light source, and its light intensity was adjusted by using a NREL-calibrated monocrystalline silica solar cell (PVM134 reference cell, PV Measurement Inc.) for approximating AM1.5 radiation. The amount of adsorbed dye was determined by desorbing the dye from a-TiO₂ surface into a solution of 0.1 M NaOH. The concentration of the adsorbed dye was analyzed by UV-visible spectrophotometer (V-630, JASCO Corp.).

Fig. 2 The ESCA survey spectra of a-TiO₂ sample

2. Results and Discussion

2.1 Characterization of anatase TiO₂ nanoparticles

The sol-hydrothermal reaction employed in the present work led to the formation of TiO₂ nanocrystallites which were characterized by various kinds of techniques. ESCA is an effective method to investigate the surface composition and chemical states of all kinds of solid samples. **Figure 2** shows the typical ESCA spectra of the above-synthesized TiO₂ samples. The peaks appearing in the spectra include the Ti2p doublet and O1s photoelectron peaks. The observed binding energies for Ti(2p_{3/2}) and Ti(2p_{1/2}) at 458.1 and 464.3 eV are in good agreement with the reported values of 458.2 eV and 464.3 eV for TiO₂ within the experimental error (Lou and Zeng, 2003). The O1s peak around 530 eV corresponds to O²⁻ bonding state in TiO₂. It is noted that the O1s peak is asymmetric which can be deconvoluted to two peaks centered at 529.4 and 530.6 eV. Detailed analysis of the integrated peak area of these two peaks showed that the peak ratio (Area_{529.4}/Area_{530.6}) increases from 1.36 to 2.22 with increase of hydrothermal duration from 0 to 48 h as well as the simultaneous decrease of BET surface area (see below). These two deconvoluted peaks are thus assigned to the lattice oxygen (529.4 eV) and the surface oxygen (530.6 eV) which was consistent with the ESCA assignment on sol-gel prepared TiO₂ (Jing *et al.*, 2003).

In the hydrothermal synthesis of TiO₂, the presence of acid as a peptizer material affects final crystal phase and the morphology (Yin *et al.*, 2001). **Figure 3** shows XRD spectra of TiO₂ samples after hydrothermal treatment at 200°C for various duration. It can be seen that the TiO₂ prepared using CH₃COOH as a peptizer for hydrothermal treatment up to 36 h, only exhibits XRD peaks that correspond to the anatase phase. For convenience, the a-TiO₂ samples are hereinafter abbreviated as Ht-A-B where A and B represent the hydrothermal temperature [°C] and heating duration [h], respectively. It can be seen that upon increasing the duration of hydrothermal treatment up to 36 h, only pure anatase TiO₂ was formed. Note that prolong hydrothermal treatment promoted the crystallization of a-TiO₂ as demonstrated by the increase of

Table 1 Results of particle size of a-TiO₂ samples obtained from TEM, BET, and XRD

a-TiO ₂ sample	XRD [nm]	TEM [nm]		BET [m ² /g]
		Polyhedron	Elongated width×length	
Ht-200-0	1.75	3.05	14 × 44	255.3
Ht-200-3	10.73	10.42	23 × 60	149.6
Ht-200-5	12.22	13.43	32 × 70	116.0
Ht-200-10	14.56	14.81	25 × 65	105.2
Ht-200-24	15.68	19.03	21 × 56	81.97
Ht-200-36	18.11	20.99	20 × 47	74.24

Fig. 3 A series of XRD peaks for the prepared a-TiO₂ powders by various duration of hydrothermal treatment

the diffraction peak intensities and decrease of the peak width. The calculated size of crystal domain for various samples of a-TiO₂ was summarized in **Table 1**. The a-TiO₂ nanocrystals can also be synthesized by a general sol-gel process using CH₃COOH as a acid catalyst (Tong *et al.*, 2008). To obtain the comparable crystal size of a-TiO₂, however, the heat treatment by calcination has to be higher than 500°C. This result infers that the complete formation of anatase phase could be accomplished in the solution at relatively low temperatures under hydrothermal conditions. The parallel study was carried by calcination of the same initial TiO₂ sol (results not shown). High calcination temperature of at least 600°C is required to achieve the a-TiO₂ with comparable crystal domain.

The crystal growth in different stage of hydrothermal treatment was analyzed by TEM. **Figure 4** shows the TEM micrographs of a-TiO₂ samples hydrothermally treated at 200°C for (a) 0, (b) 3, (c) 5, (d) 10, (e) 24, and (f) 36 h. The a-TiO₂ particles grew gradually with increasing autoclaving time. Before the hydrothermal treatment, the a-TiO₂ sol was observed as a bunch of rotten oatmeal with undefined shape (Figure 4(a)). After hydrothermal treatment, the TEM (Figures 4(b)–(f)) shows two distinct particle shapes: irregular polyhedron which is the typical shape for anatase phase TiO₂; and the elon-

Fig. 4 The TEM micrographs of a-TiO₂ samples hydrothermally treated at 200°C for (a) 0, (b) 3, (c) 5, (d) 10, (e) 24, and (f) 36 h

gated shaped a-TiO₂. Similar structures have been observed by Wu *et al.* (2008) for anatase TiO₂ nanoparticles prepared by hydrolysis of titanium isopropoxide followed by crystal growth under hydrothermal conditions. A ball-like tetragonal anatase TiO₂ was obtained in nitric acid solution while a bipyramid rod-like shaped anatase TiO₂ was obtained in tetramethylammonium hydroxide solution. From the size distribution analysis in terms of estimated diameter for irregular polyhedron shaped a-TiO₂ particles and width × length for elongated ones, it is found that increasing the reaction time increased the average particle size for both cases (Table 1). As expected from the previous XRD analysis, prolonging the autoclaving time promotes the tendency of crystal growth. The proportion of elongated (rod-like) feature increases with increasing hydrothermal duration as shown in Figures 4(b)–(f). Based on the calculations by Penn and Zhang, the elongated TiO₂ nanocrystal is more stable than other shapes (Wu *et al.*, 2008). It is also noted that the morphology of irregular polyhedron shaped a-TiO₂ is uniform with narrow size distribution (the plot of statistic analysis is not shown) indicating the faster nucleation compared to the crystal growth. The elongated a-TiO₂, on the other hand, a broader particle size distribution with various morphology was observed indicating the slower nucleation than its growth. BET surface area measurement

was carried out to further confirm the size variation of a-TiO₂ nanoparticles on the hydrothermal duration. The results listed in Table 1 showed the steady decrease of surface area for increasing hydrothermal reaction time indicating an increase of a-TiO₂ particle size after longer heat treatment. These results are also consistent with the particle size variation from XRD and TEM (Table 1).

2.2 Characterization and application of a-TiO₂ electrode to DSSCs

DSSCs is a quite complicated system and there are many factors influencing the cell efficiency (Jiu *et al.*, 2006). One of the most important parameter is the TiO₂ electrode. The crystal phase, particle shape, diameter, and surface composition of TiO₂ samples used will affect the dye adsorption, electron transport, and electrolyte diffusion in the cell as well as the light-to-electricity conversion efficiency. The film preparation procedure and condition also play significant effect in the resultant electrode property, in particular, the film morphology and porosity. The a-TiO₂ electrodes for DSSCs were prepared according to the procedures described in Section 2. We chose Ht-200-5 as a-TiO₂ sample for DSSCs study because of high surface area and good crystallinity. As seen in previous section, increasing hydrothermal time period increased the crystallinity of a-TiO₂. Better crystallinity could enhance the electron transportation (Kambe *et al.*,

Fig. 5 The XRD pattern for a-TiO₂ film after calcination at 450°C, under atmospheric conditions

Fig. 6 The SEM images of (a) small area scan of a-TiO₂ film, (b) larger area scan of a-TiO₂ film

2002) as well as the cell efficiency. However, the high surface area of a-TiO₂ is also important to be a good DSSCs electrode materials since more dye molecules can adsorb on higher surface area TiO₂ to generate larger photocurrent in DSSCs. Since prolong hydrothermal treatment caused the aggregation of a-TiO₂, the particle size of a-TiO₂ increased while the BET surface area decreased. To compromise the consideration on the effects of crystallinity and surface area, we chose Ht-200-5 as the a-TiO₂ sample for further DSSCs study.

The XRD pattern of a-TiO₂ electrode was shown in **Figure 5** which exhibited peaks corresponding to anatase TiO₂ indicating the presence of stable anatase phase after 30 min calcination at 450°C. Several small peaks appear at $2(\theta) = 26.6, 33.9, \text{ and } 51.8$ are assigned to SnO₂ from FTO substrate. It was found that the domain size of a-TiO₂ film (12.22 nm) was almost identical to that of a-TiO₂ (13.43 nm) nanoparticles. It was known that calcination treatment in general makes nanoparticle aggregated as well as the crystal growth. On a-TiO₂ film, however, one of the dimension for a-TiO₂ to freely move is restricted so the extent for anatase domain to grow is limited. We thus concluded that the SnO₂ has no significant effect on the physical property of a-TiO₂. **Figure**

Table 2 The photocurrent-voltage characteristics of a-TiO₂ DSSCs with different film thickness

Sample	Thickness [μm]	$\overline{Dye_{ads}}$ [μm/cm ²]	J_{sc} [mA/cm ²]	V_{oc} [V]	FF	η [%]
a-TiO ₂	8	0.42	9.42	0.76	0.63	4.51
	15	0.47	10.64	0.76	0.65	5.27
	17	0.53	13.53	0.75	0.61	6.23
	24	0.77	16.48	0.72	0.56	6.61
	38	0.99	16.72	0.66	0.48	5.31
P 25	14	0.37	7.80	0.76	0.63	3.74

Fig. 7 Photocurrent-voltage curves of solar cells for various thickness fabricated from a-TiO₂

6(a) showed an SEM micrograph of deposited a-TiO₂ particles which are mostly spherical and the size distribution ranges from 20 to 30 nm. For a large area SEM scan (**Figure 6(b)**), a rough surface layer containing large and almost smooth TiO₂ chunks develops in which the individual a-TiO₂ particles are hardly visible anymore. The irregular cracks appearing on the a-TiO₂ layer are probably stress-induced and are caused by the fast cooling rate after 450°C calcination.

Figure 7 showed the typical current-voltage characteristics of N3-sensitized a-TiO₂ solar cells measured at 1 sun light intensity for various film thickness. **Table 2** lists the photoelectric data of the DSSCs in Figure 7. It can be seen that the film thickness greatly affects the DSSCs performance. First, the photocurrent density, J_{sc} , increased from 9.42 to 16.72 mA/cm² as the film thickness increased from 8 to 38 μm. This is due to the increase of total surface area and thus the amount of dye adsorbed by the film ($\overline{Dye_{ads}}$) from 0.42 to 0.99 μmole/cm². This result indicates that the dye loading dominates the photocurrent generation. Concomitantly, the efficiency increased from 4.51 to 6.61% for thickness up to 24 μm. Further increasing the thickness to 38 μm, although the amount of dye adsorption increases, the efficiency dropped to 5.31%. It is generally believed that thicker film will create larger number of recombination centers, the longer path of the injected electron to travel inside

the cell, and more difficult ionic motion of electrolyte through the TiO₂ film, leading to the decrease of V_{oc} to 0.66 V as well as the cell performance. Comparing the performance of a-TiO₂ and degussa P 25 fabricated photoanodes (Figure 7 and Table 2), a higher DSSCs efficiency was achieved for the former one. Higher J_{sc} of a-TiO₂ DSSCs was responsible for the higher efficiency due to the presence of full anatase domain with higher surface area and greater amount of dye adsorbed on a-TiO₂ electrode (Table 2). Park *et al.* (2000) have reported that the effective electron diffusion coefficient for the rutile phase is about one order of magnitude lower than that of the anatase due to the poor interparticle connection of rutile TiO₂ network. The SEM measurement (image not shown) showed the looser arrangement of P 25 film morphology, thus slow electron transportation rate and lower cell efficiency are expected. A more definitive determination of electron diffusion coefficient will require further experimental works. Kartini *et al.* (2004) have applied the hydrothermal-based technique to prepare the TiO₂ nanoparticles with mixed crystal phase of anatase (major), rutile (minor), and brookite (minor). The rutile-free TiO₂ sample showed higher DSSCs performance with efficiency of 5.05% than the rutile-phase mixed TiO₂ samples which showed the efficiency up to 4.67%. Huang *et al.* (2006) have studied the effects of hydrothermal temperature on the preparation of TiO₂ colloids, and their film thickness on FTO glass, toward the performance of DSSCs. With the increase of hydrothermal temperature from 85 to 240°C, the DSSCs efficiency increased from 4.9 to 5.8%. Further increase of temperature to 260°C, the efficiency decreased. The efficiency was found to reach a maximum value when the TiO₂ film thickness was about 10 µm. The results in this work showed the comparable DSSCs performance with those found in the literature using the hydrothermal approach. To the best of our knowledge, this paper reported the first work of using Ti(O-Bu)₄ to be the TiO₂ precursor in the DSSCs application.

Conclusions

In summary, using sol-hydrothermal process, we successfully synthesized TiO₂ nanoparticles which possessed good properties for DSSCs, such as pure anatase phase for superior electron transportation and high surface area for enhanced dye adsorption. The solar conversion efficiency of DSSCs made from above prepared a-TiO₂ film was higher than that of the cell made from P 25 TiO₂. This work also discussed the correlation between the film thickness, the associated film properties and DSSCs efficiency.

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Nomenclature

Dye_{ads}	=	N3 dye adsorption	[µm/cm ²]
FF	=	fill factor	
J_{sc}	=	photocurrent density	[mA/cm ²]
V_{oc}	=	voltage	[V]
η	=	conversion efficiency	[%]

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