THE EFFECT OF THE THICKNESS OF TiO$_2$ NANOSHEETS FILM WITH EXPOSED (001) FACETS ON THE PERFORMANCE OF DYE-SENSITIZED SOLAR CELLS

Xia Wu, Gaoqing Lu, Lianzhou Wang

ARC Centre of Excellence for Functional Nanomaterials,
School of Chemical Engineering and Australian Institute of Bioengineering and Nanotechnology, The University of Queensland, St Lucia QLD 4072, Australia
E-mail: l.wang@uq.edu.au

ABSTRACT
Nanosized anatase TiO$_2$ nanosheets with highly exposed (001) facets (ca. 80%) were prepared via hydrothermal reaction with the addition of hydrofluoric acid and characterized by various techniques like TEM, XRD, XPS and BET. High-quality TiO$_2$ nanosheets films with various thicknesses (ca. 5-20µm) were successfully fabricated by doctor blading and the effect of film thickness on the performance of DSSCs was investigated by I-V characterization and dark current potential scan. The results show each parameter of DSSCs performance depends strongly on the thickness of the TiO$_2$ nanosheets films. An optimised DSSCs performance of 8.39% was obtained by the TiO$_2$ nanosheets film with a thickness of ca. 15µm.

Introduction
Since the significant progress has been achieved on low-cost dye-sensitized solar cells by Professor Michael Grätzel in 1991 (Oregan and Gratzel, 1991), the DSSCs have attracted extensively attention and been regarded as a promising candidate for the next-generation solar cells. The overall solar to current conversion efficiency over 11% have been reached under standard AM1.5 solar illumination (Gratzel, 2009) exceeding that of the amorphous silicon solar cells. The most extensively explored type of DSSCs are comprised of four main component (1) a sensitizer attached to (2) a porous semiconductor film on conducting glass substrate which forms the photoanode, (3) a Pt-sputtered conducting glass known as counter electrode and (4) an electrolyte solution in-between. Basically TiO$_2$ is the most commonly used semiconductors in DSSCs due to its advantages in terms of its low cost, non-toxicity, and high chemical stability (Fujishima et al., 1979). Among all kinds of morphology, nanosized TiO$_2$ materials have attracted widespread attention as it provides a high specific surface area for dye absorption, thus efficiently increases light harvesting yield compared with the same bulk material. Recently, extensive interest has been drawn in the synthesis of anatase TiO$_2$ nanosheets with exposed (001) facets as the (001) surface of anatase TiO$_2$ is much more
reactive than the thermodynamically more stable (10 1) counterpart indicated by both theoretical and experimental studies, which would be favourable for photovoltaic cells, photodegradation of organic molecules, and photocatalytic water splitting applications (Herman et al., 2003, Vittadini et al., 1998). Lu et al. reported the preparation of micro-sized anatase single crystals with 47% of exposed (001) facets in 2008 (Yang et al., 2008). Most recently, TiO₂ nanosheets with exposed (001) facets were synthesized and was proven to show enhanced photo-conversion efficiency in DSSCs (Yu et al.).

In this study, nanosized anatase TiO₂ nanosheets with highly exposed (001) facets were prepared and fully characterized for DSSCs application. High-quality TiO₂ nanosheets films on FTO glass substrates with different thickness (ca. 5-20 µm) were fabricated by doctor blading. The effect of the film thickness of TiO₂ nanosheets films on the photovoltaic performance of DSSCs was investigated by photocurrent-voltage (I-V) characterization and dark current potential scan, the results shows each parameter of DSSCs performance depends strongly on the thickness of the TiO₂ nanosheets films. The efficiency was found to reach a maximum value of 8.39% at the thickness of about ca. 15 µm.

**Experimental**

Anatase TiO₂ nanosheets with exposed (001) facets were prepared by a hydrothermal method reported previously (Han et al., 2009). Typically, 10mL of Ti(O₂C₂H₅)₄ (Aldrich) and 1.2mL of hydrofluoric acid solution (with a concentration of 50 wt %) were mixed in a Teflon-lined 35mL autoclave at room temperature, and then kept at 200 °C for 24h. After hydrothermal reaction, the white precipitates were collected and washed with deionized water and ethanol for several times, and then dried in oven at 50 °C overnight. The as-prepared sample was further sintered at 450 °C for 30min and 500 °C for 30min to remove fluoride species.

For DSSCs working electrodes fabrication, cis-bis (isothiocyanato) bis (2, 2'-bipyridyl-4, 4'-dicarboxylato) – ruthenium (II) bis-tetrabutylammonium (N719 dye, Dyesol), acetonitrile (HPLC, Lab-scan), tert-butanol (LR, Ajax Chemicals) were used for the preparation of the dye solution. The I/I₃ organic solvent based electrolyte (EL-HSE) and Pt sputtered counter electrode used in DSSC fabrication were supplied by Dyesol (Australia). The fluorine-doped tin oxide FTO glass (2.3 mm thickness, 8Ω/sq, Dyesol Glass) was cleaned with 2-propanol and deionized water successively using an ultrasonic bath for 30min, and then thoroughly rinsed with deionized water. The TiO₂ paste was prepared by an improved method depicted in (Ito et al., 2008). Typically, 1g of Degussa P25 was mixed in 20mL of ethanol with the addition of 0.17mL of acetic acid and 0.83mL of deionized water. This mixture was then sonicated using an ultrasonic probe, alternating stirring, and sonication, for three consecutive times before adding 4.056g of Terpineol and 0.5g of Ethyl Cellulose successively. After that, ethanol was removed by rotary-evaporator (initial temperature 40 °C and pressure 175 mbar, subsequently reduced to a final pressure of 40 mbar at 40 °C). The resulting slurry was casted on the FTO glass plates by doctor-blade method (Mills et al., 2003), and kept in a
clean box for 30 min so that the paste can relax to reduce the surface irregularity and mechanical stress, and then dried at 100°C for 6 min. This doctor-blading procedure (with coating, storing and drying) was repeated to increase the thickness of the TiO₂ working electrode. The TiO₂ films were cut into 4×4 mm squares and then gradually heated at 325°C for 5 min, at 375°C for 5 min, at 450°C for 15 min and 500°C for 15 min. When the films had cooled to 80°C, they were immersed into a 0.5 mM N719 dye solution in a mixture of acetonitrile and tert-butanol (volume ratio: 1:1) and kept at room temperature for 24 h to complete the sensitizer uptake. Subsequently, the dye-covered TiO₂ electrode and Pt-counter electrode (Dyesol) were assembled into a sandwich type cell and sealed with a thermoplastic membrane of 30 µm thickness (Surlyn, DuPont). In the sealed cell, a drop of electrolyte solution was introduced via vacuum backfilling (Ito et al., 2007). Finally, the hole was sealed using an Al-backed thermoplastic membrane (Bynel, DuPont).

I-V curves of the constructed solar cells were measured by using a Keithley 2420 Source Meter under illumination of simulated sunlight (100 mW cm⁻²) provided by an Oriel Solar simulator with an AM 1.5G type filter (Newport, 81094). The I-V curve is obtained by applying an external bias to the cell and measuring the generated photocurrent under simulated solar illumination, while the dark current potential scan is performed as the same but without illumination.

The measurements were repeated three times for each sample, and the experimental error was found to be within ca. 3%.

Results and discussion

Transmission electron microscopy (TEM) image shown in Fig 1a and b revealed that the as-prepared TiO₂-NS showed an average size of ca. 50 nm and thickness of ca. 6 nm. Figure 1d demonstrates a typical top-viewed square shape particle indicative of (001) facet, while the HRTEM image (Fig 1c) shows the lattice spacing parallel to the top and bottom facets is ca. 0.235 nm, representing the (001) atomic planes of the anatase TiO₂ (Yang et al., 2008), the calculated percentage of exposed (001) facets was ca. 80%. The corresponding X-Ray Diffraction (XRD) pattern (Fig 1e) indicates the as-prepared and calcined TiO₂-NS both showed well-resolved diffraction peaks which are dominated by anatase phase (tetragonal, I₄₁/amd, JCPDS card No. 21-1272). The relative ratio of (004) peak diffraction intensity to that of the (101) peak of the as-prepared TiO₂-NS was estimated to be ca. 50%, implying the oriented growth of the TiO₂-NS along the (001) axis. The (004) / (101) ratios of the TiO₂-NS were decreased to ca. 38.6% after calcination, which might be attributed to the increased thickness of the nanosheets due to the fusion of several neighboring nanosheets during the calcination. The Brunauer-Emmett-Teller (BET) surface areas of the as-prepared TiO₂-NS were determined by the nitrogen sorption isotherms with the value of 89.2 m²/g. The X-ray Photoelectron Spectroscopy (XPS) was employed to investigate the chemical composition and status of the as-prepared TiO₂-NS before and after calcination. As indicated in Fig 1f, the existence of F1s peak (684.8 eV) can be easily observed in the as-prepared TiO₂-NS due to surface fluorination, whereas the F1s peak disappeared after calcination, suggesting the F in TiO₂ is completely removed.
Fig. 1: TEM images of (a) Top-view and (b) side view of TiO$_2$ nanosheets (designated as TiO$_2$-NS); (c) high-resolution TEM image of TiO$_2$-NS; (d) schematic crystallographic structure of TiO$_2$-NS; (e) XRD patterns and (f) XPS survey spectra of pristine TiO$_2$-NS and calcined TiO$_2$-NS.

To investigate the effect of the thickness of the TiO$_2$-NS films on the photovoltaic performance of DSSCs, TiO$_2$-NS films with various thicknesses of ca. 5, 10, 15 and
20µm were fabricated by doctor blading and designated as TiO$_2$-NS-5, TiO$_2$-NS-10, TiO$_2$-NS-15 and TiO$_2$-NS-20, respectively. Five cells were fabricated under identical condition for each thickness and the average values of the DSSCs performance were summarized in Table 1. The surface SEM image of porous TiO$_2$-NS film with the thickness of ca. 10 µm after calcination (Fig 2) revealed that the film was uniform, smooth and crack-free over the large area with minor aggregates. The TiO$_2$ film also exhibits a nanoporous structure which consists of interconnected nanoparticles. The other films also exhibit a similar smooth and crack-free morphology as the TiO$_2$-NS-10 film.

Fig. 2: SEM image of the surface morphology of porous TiO$_2$-NS film with thickness of ca. 10 µm on the FTO glass substrate.

The I–V curves and photovoltaic properties of DSSCs assembled with various thicknesses of TiO$_2$-NS films (ca. 5–20µm) were depicted in Fig 3 and Table 1. Photovoltaic-characteristics variations of short-circuit photocurrent density (a, $J_{sc}$), open-circuit voltage (b, $V_{oc}$), fill factor (c, $FF$) and conversion efficiency (d, $\eta$) with layer thickness of TiO$_2$-NS film were demonstrated in Fig 4. A clear trend could be observed that both $V_{oc}$ and $FF$ decrease with increasing film thickness, whereas $J_{sc}$ increased with the increase of film thickness, resulting an optimised $\eta$ of 8.39% with a $J_{sc}$ of 20.75 mA/cm$^2$, a $V_{oc}$ of 0.741V and a $FF$ of 54.6% was obtained by the TiO$_2$-NS-15 film with a thickness of ca. 15µm. Since the dye adsorption capacity and the light scattering property of the TiO$_2$-NS films is directly proportional to the film thickness (Wang et al., 2004), they both play essential roles in determine the performance of DSSCs. Therefore, the enhanced $J_{sc}$ with increasing film thickness could be mainly attributed to the improved dye loading capacity and light scattering properties of the TiO$_2$-NS films with the increased thickness. On the other hand, as a result of the improved dye loading with increasing film thickness, more electrons were generated under illumination, thus the back reaction of photo-generated electrons at the surface of TiO$_2$-NS films with oxidized species such as I$_3^-$ in the electrolyte increased (Nazeeruddin et al., 1993), leading to the decreased $V_{oc}$ and $FF$ with increasing film thickness.
Table 1: Comparison of photovoltaic properties of the DSSCs fabricated with various thicknesses of TiO$_2$ films.

<table>
<thead>
<tr>
<th>Thickness of the TiO$_2$-NS film [µm]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>$FF$ [%]</th>
<th>$\eta$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>14.24</td>
<td>0.755</td>
<td>58.9</td>
<td>6.33</td>
</tr>
<tr>
<td>10</td>
<td>19.09</td>
<td>0.747</td>
<td>58.7</td>
<td>8.37</td>
</tr>
<tr>
<td>15</td>
<td>20.75</td>
<td>0.741</td>
<td>54.6</td>
<td>8.39</td>
</tr>
<tr>
<td>20</td>
<td>21.72</td>
<td>0.729</td>
<td>51.4</td>
<td>8.15</td>
</tr>
</tbody>
</table>

Fig. 3: I-V curve of DSSCs assembled with various thicknesses of TiO$_2$-NS films.

Fig. 4: Photovoltaic-characteristics relationship with layer thickness of TiO$_2$-NS film: (a) $J_{sc}$, (b) $V_{oc}$, (c) $FF$ and (d) conversion efficiency ($\eta$).
The dark current potential scans were performed to investigate the back electron transfer process in the TiO$_2$-NS films with various thicknesses (Fig 6). This technique could be employed to qualitatively describe the extent of the back electron transfer as the origination of the dark current arises from the reduction of I$_3^-$ ion by the electrons on the FTO substrate and therefore lead to electron recombination and the loss of photocurrent (Ito et al., 2005). It could be observed that the dark current onset of the TiO$_2$-NS films shifted to a lower potential and produced a higher dark current at the same potential above 0.6 V with increasing film thickness, reflecting a higher recombination rate between transferred electrons and I$_3^-$ ions with the increase of film thickness, which is in good agreement with the decreased $V_{oc}$ and $FF$ with increasing film thickness obtained in I-V characterization.

Fig. 6: Dark current potential scans of DSSCs assembled with various thicknesses of TiO$_2$-NS films.

Conclusions

In summary, nanosized anatase TiO$_2$ nanosheets with highly exposed (001) facets (ca. 80%) were successfully synthesized via hydrothermal reaction with the addition of hydrofluoric acid. High-quality crack-free TiO$_2$ nanosheets films were fabricated using doctor blading with various thicknesses (from ca. 5-20µm) and the effect of film thickness on the performance of DSSCs was investigated by I-V characterization and dark current potential scan. A clearly trend of increased $J_{sc}$ and decreased $V_{oc}$ and $FF$ were observed with increasing film thickness, resulting peak efficiency of 8.39% at ca. 15µm thickness for TiO$_2$ nanosheets films.

REFERENCES


**Brief Biography of Presenter**

Xia Wu is currently a PhD student at ARC Centre of Excellence for Functional Nanomaterials, School of Chemical Engineering, the University of Queensland. Prior to this, Xia was working as a technical engineer and marketing assistant at Thermo Fisher Scientific in Shanghai, China (Since July, 2006).

She received her Bachelor of Science from the School of Chemistry and Chemical Engineering, Nanjing University, China, and graduated in June 2006. Xia’s research interest focuses on the morphology and structure design of novel photoanode for dye-sensitized solar cells. The strategy employed includes morphology design of novel nanostructured semiconducting materials for achieving sufficient visible to near-infrared sunlight harvesting efficiency and structure design and modification of photoanode film to improve the electron transfer efficiency and suppress the recombination of photogenerated electrons.