Densely aligned rutile TiO2 nanorod arrays with high surface area for efficient dye-sensitized solar cells†

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One-dimensional (1-D) TiO2 nanorod arrays (NRAs) with large inner surface area are desired in dye-sensitized solar cells (DSSCs). So far, good performance of DSSCs based on 1-D rutile TiO2 NRAs remains a challenge mainly owing to their low dye-loading ability resulting from the insufficient specific surface area of 1-D TiO2 nanostructures. In this paper, densely aligned TiO2 NRAs with tunable thickness were grown directly on transparent conductive fluorne-doped tin oxide (FTO) substrates by hydrothermal method, followed by a facile chemical etching route to further increase the specific surface area of the TiO2 NRAs. The etching treatment leads to the split of TiO2 nanorods into secondary nanorods with a reduced diameter, which markedly enlarges the inner surface area of the TiO2 NRAs. The formation of 1-D rutile TiO2 nanotube arrays (NTAs) is observed as well in the etched TiO2 films. Finally, a DSSC efficiency of 5.94% was achieved by utilizing an etched TiO2 NRA as the photoanode, which is so far the best DSSC efficiency that has been reported for the 1-D rutile TiO2 NRA films.

Introduction

Dye-sensitized solar cells (DSSCs) have been considered as one of the most promising solar energy conversion devices since the significant breakthrough in the efficiency that Michael Grätzel and Brian O’Regan contributed in 1991.1 TiO2 nanomaterials with different morphologies such as nanoparticles,2 nanotube arrays,3,4 nanorod or nanowire arrays,5-9 nanosheets,10,11 etc. have been prepared in application of DSSCs. Although the high efficiency achieved up to now has still been dominated by TiO2 nanoparticle-film based DSSCs, one-dimensional (1-D) nanostructures such as nanotube, nanorod or nanowire are recognized to be promising for further improvement of the efficiency of DSSCs due to their better electron transport behaviour by providing direct electrical pathways, suggesting an effective solution to the inevitable photo-generated charge recombination problem in the nanoparticle-film based solar cells.5-8,12-19 At present, TiO2 nanotube arrays (NTAs) has attracted much attention and relatively high efficiencies have been achieved by finely optimizing fabrication conditions and structure of TiO2 NTA photoanodes.4,17,20 Among these 1-D architectures, the TiO2 nanorod arrays (NRAs) with single-crystalline rutile phase have attracted much attention as well because of their superior chemical stability, better electron transport properties, structure controllability and low cost.21-30 It is traditionally considered that among the three polymorphs of TiO2, anatase is superior to the rutile phase mainly because of ~0.1 eV higher Fermi level for the former, which may be favourable for achieving a higher Voc (open-circuit voltage) in DSSCs.31 However, preparation of 1-D single-crystalline anatase NRAs on TCO glass is still a challenge and recent studies show that rutile TiO2 can achieve a similar or even higher Voc value by proper doping treatment.12,33 Furthermore, faster electron transport in 1-D single-crystalline rutile TiO2 NRAs has been previously reported compared with TiO2 nanoparticle film.14,15 Various synthetic techniques have been reported for preparing single-crystalline rutile TiO2 NRAs, including chemical vapour deposition (CVD),16,17 metal–organic chemical vapour deposition method (MOCVD),22 hydrothermal method,5,7,21,23,38 chemical bath deposition,39 solvothermal method4 and so on. Feng et al. first reported the synthesis of single-crystalline rutile TiO2 NRAs on TCO glass by solvothermal method and relatively high efficiency of DSSCs was obtained with such nanostructures.8 However, the toxic solvent toluene was used in the fabrication process, which becomes an obstacle in industrial applications. Accordingly, hydrothermal methods with an environmentally-benign solution were extensively explored recently. Liu et al. introduced a facile hydrothermal method for fabricating single-crystalline rutile TiO2 NRAs directly on FTO substrates.8 While 4 μm long TiCl4-treated TiO2 nanorod array (NRA) film was used in DSSCs, an efficiency of 3% was achieved. Owing to the limited inner surface area in such rutile TiO2 NRAs, the light-to-electricity conversion efficiency of DSSCs based on such photoanodes is
significantly confined. In addition, 1-D TiO₂ NRAs with a high inner surface are of great significance in their applications in various devices such as quantum-dot-sensitized solar cells (especially in solid-state DSSCs), sensors, photocatalysts, electrochromism materials and photoelectrochemical water splitting and so on.27,40–42 A number of reports have been published aiming to enhance the surface area of 1-D rutile TiO₂ NRAs. For example, rutile TiO₂ NRAs with ZnO branches or TiO₂ branches have been reported and rutile TiO₂ nanorod/nanoparticle composite photoanodes have been fabricated as well, where the nano-branches and nanoparticles are supposed to enhance the surface area of TiO₂ NRA film so that more adsorption of dye molecular can be realized.43,44 In spite of the enhanced light scattering effect and enlarged inner surface area by incorporating nanoparticles into 1-D nanostructure photoanodes, electron recombination is normally promoted compared to bare 1-D nanostructure photoanodes and thus a balance between electron transport and dye-loading amount should be carefully considered.45 Therefore, developing 1-D oriented nanostructure photoanodes should possess both properties of facilitated electron transport and a large inner surface area. Recently, Liu et al. reported the fabrication of V-shaped TiO₂ nanotube arrays with rutile phase by a selective etching route.46 Since such tube-like rutile TiO₂ nanostructures enlarged its inner surface area, a DSSC efficiency of around 2.62% was obtained, compared with that of 0.93% using rutile TiO₂ NRAs without any etching treatment.49 Although the above-mentioned methods can, to some extent, enlarge the surface area of the 1-D rutile TiO₂ NRAs, it is still a challenge to efficiently increase the surface area and improve the performance of DSSCs based on 1-D rutile TiO₂ NRAs. Herein, we report a facile strategy for construction of single-crystalline rutile TiO₂ NRAs directly on FTO substrates with high surface area by hydrothermal method combined with a chemical etching route. The chemical etching treatment is expected to remarkably enhance the surface area of 1-D rutile TiO₂ NRAs, which in turn allows more dye-loading on TiO₂ surface and improves the light-harvesting ability of the assembled DSSCs. The optimized efficiency of DSSCs using etched 1-D rutile TiO₂ NRA films as photoanodes has been demonstrated to be 5.94% in present study. Notably, such a preliminary high efficiency has been achieved without any further treatment of TiCl₄, NbCl₅ or exposure to O₂ plasma, which has been frequently used in the previous reports to further improve the fill factor, open circuit voltage and photocurrent density of the DSCs.4,5,8,12,30,50,51

Experimental

Preparation of rutile TiO₂ NRAs

Rutile TiO₂ NRA films were prepared directly on FTO (fluorine-doped tin oxide) substrates by a modified hydrothermal method according to a previous report.52 In a typical synthesis process, FTO substrates were ultrasonically cleaned sequentially in acetone, ethanol and deionized (DI) water each for 15 min and were dried in air. 1 mL of titanium tetrachloride (TiCl₄) was added dropwise to a mixture of 30 mL DI water and 30 mL concentrated hydrochloric acid (36.0–38.0 wt%), by which magnetically stirring for 20 min to obtain a transparent solution. Three pieces of FTO substrates (1 cm × 1.5 cm) were fixed on a home-made Teflon®-socket at an angle of around 75° with respect to the horizontal plane with their conductive sides facing down. The Teflon®-socket and the previous mixed solution were transferred into a Teflon®-liner (100 mL volume), and the Teflon®-liner was loaded in an autoclave, which was then placed in an electric oven. The hydrothermal reaction was carried out at 150 °C for various times (6–48 h). After synthesis, the autoclave was cooled to room temperature in air. Then the samples were rinsed with DI water extensively and dried in air. The TiO₂ NRA films with thickness around 6 μm and 8 μm were prepared in our study.

Chemical etching treatment

The as-prepared samples were immersed into a solution containing 30 mL DI water and 30 mL concentrated hydrochloric acid (36.0–38.0 wt%). The chemical etching reaction was conducted by hydrothermal method at 150 °C for 1–13 h. After the autoclave cooled to room temperature, the etched samples were rinsed with DI water and dried in air.

Fabrication of DSSCs

The as-prepared samples were annealed in air at 450 °C for 2 h with heating rate of 5 °C min⁻¹. Then, the annealed TiO₂ NRAs and etched TiO₂ NRAs on FTO substrates were immersed in 0.3 mM ethanolic solution of cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(n)(II)tetrabutylammonium dye (N719, Solaronix) for 24 h. Platinum-coated FTO substrates were used as counter electrodes, which were prepared by thermal decomposition of 2 mg mL⁻¹ ethanolic solution of chloroplatinic acid hexahydrate under 400 °C for 10 min. The DSSCs were fabricated through assembling the dye-sensitized TiO₂ NRA films as photoanodes and Pt-coated FTO substrates as counter electrodes, separated by a 25 μm thick parafilm as the spacer. The electrolyte used here was iodide/triiodide redox system in acetonitrile, which can be commercially available (CJX-EH, CasJuxin Solar Technology Co., LTD., China) and was introduced into the space of the sandwich-like DSSCs by capillary action.

Characterization

The morphologies of the as-prepared samples were observed by a field-emission scanning electron microscope (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100) with an accelerating voltage of 200 kV. The crystal structure was examined by X-ray diffraction (XRD, Panalytical X’pert PRO). The XRD patterns were recorded from 20° to 70° at a scanning speed of 12.5’’ min⁻¹ with Cu Kα radiation (λ = 0.15406 nm). Performance of assembled DSSCs was obtained by measuring photocurrent density–voltage (J–V) curves under AM 1.5G simulated solar light (100 mW cm⁻², Oriel 300 W Xe lamp and Newport AM-1.5G filter) and an active area of 0.14 cm² was used. Incident photon-to-current efficiency (IPCE) spectra were recorded with the help of Oriel QE/IPCE Measurement Kit (equipped with 150–300 W full spectrum solar simulator). Diffuse reflectance spectra of TiO₂ NRAs were measured by a UV-vis-NIR spectrophotometer (Varian Cary5000). UV-vis
absorption spectra of N719 dye-desorption solutions were measured on a UV-vis absorption spectrophotometer (Shimadzu 2550).

Results and discussion

Fig. 1(a) and (b) show FESEM images of TiO$_2$ NRAs prepared by hydrothermal method using a solution of 1 mL TiCl$_4$, 30 mL DI water and 30 mL concentrated hydrochloric acid (36.0–38.0 wt%) at 150 °C for 6 h. It can be seen that densely aligned TiO$_2$ NRA with a thickness of ~6.2 μm grew uniformly on the FTO substrate after 6 h hydrothermal reaction at 150 °C. Some cracks with wideness ranging from 200–400 nm can be observed from the top view of the FESEM image, which may have resulted from the tension force existing in the compactly aligned TiO$_2$ NRAs (see Fig. 1a). While measured at the tip, TiO$_2$ nanorods are of an average diameter of ~250 nm. Actually, the TiO$_2$ nanorods with diameter from 60 to 300 nm can be found in the film and closer observation reveals a nearly square cross section at the tip but a circular cross section at the middle and bottom of the TiO$_2$ nanorods (see inset of Fig. 1a). From the cross-sectional view of TiO$_2$ NRAs, it can be found that little space exists between adjacent TiO$_2$ nanorods, especially at the bottom of the film (see Fig. 1b). Furthermore, during hydrothermal process, a thick layer of dandelion-shaped TiO$_2$ nanorod clusters was also deposited both on the glass side of FTO and the inner surface of the Teflon®-liner (see Fig. S1†).

The as-prepared TiO$_2$ NRA film was etched in a solution containing 30 mL DI water and 30 mL concentrated hydrochloric acid (36.0–38.0 wt%) at 150 °C for different hydrothermal durations. When etched for 1 h, there was no significant change in the bulk of TiO$_2$ nanorods (see Fig. 1d), but the morphology at the top of the nanorods changed a little. As shown in Fig. 1c, there are many small “islands” appearing at the top of each individual TiO$_2$ nanorod and apparent space between adjacent “islands” can be observed. For 3 h etched samples, nanorods with diameters larger than 100 nm disappeared and were replaced by numerous uniformly distributed rectangular TiO$_2$ nanotubes. Interestingly, it can be found that the tube wall is assembled by TiO$_2$ nanorods with diameter ranging from 15–60 nm (Fig. 1e). It seems that the original TiO$_2$ nanorods were split into a secondary structure of nanorods with smaller diameters during the etching process and the split nanorods were developed from the above mentioned “islands”. By further prolonging the etching duration to 5 h, the amount of secondary nanorods began to reduce, leaving enlarged space across the entire TiO$_2$ NRA film and such space was further widened in the case of 7 h etching (see Fig. 1g and i). That is, the cracks across the entire film, with width in range of 200–400 nm before etching treatment, shrunk to smaller than 100 nm after the etching process was carried out but widened again with a etching duration as long as 7 h. After etching for 7 h, many TiO$_2$ nanotubes were damaged severely and the tube walls collapsed, which should be responsible for the enlarged space between the adjacent nanotubes across the film. Obviously, after etching post-treatment, the compactly aligned nanorods were replaced by loosely distributed secondary nanorods with diameter of 15–60 nm (insets in Fig. 1f, h and j). Along with the 1-D architecture, a porous structure can be observed at the middle and bottom of the TiO$_2$ NRA film from the cross-sectional views of etched TiO$_2$ NRAs prepared in the solution of 1 mL TiCl$_4$, 30 mL DI water and 30 mL concentrated hydrochloric acid at 150 °C for 6 h (a and b), followed by etching treatment in a solution of 30 mL DI water and 30 mL concentrated hydrochloric acid at 150 °C for (c and d) 1 h, (e and f) 3 h, (g and h) 5 h and (i and j) 7 h, respectively.

The hydrothermal reactions were as follows: 
\[
\text{TiCl}_4 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{Ti(IV) complex} \quad (1) \\
\text{Ti(IV) complex} \xrightarrow{\text{dehydration}} \text{TiO}_2 \quad (2)
\]

During the initial hydrothermal process, the Ti$^{4+}$ precursor is abundant, so that rutile TiO$_2$ nanorods form quickly. As the reactions go on, the concentration of the Ti(IV) complex reduces...
gradually and finally achieves its equilibrium. However, once the hydrothermal solution is replaced by chemical etching solution containing 30 mL DI water and 30 mL concentrated hydrochloric acid, the reverse reactions are favoured. Then, TiO$_2$ nanorods begin to dissolve on the relatively unstable crystal faces. The growth rate of different crystal faces in rutile TiO$_2$ nanorods follows the order: (110) < (100) < (101) < (001).

Thus, the (001) planes of rutile TiO$_2$ NRs are the preferential growth, as well as etching, planes. Rutile TiO$_2$ nanotubes are formed because of such selective etching of (001) planes. In addition, it is worth noting that the grain boundaries among rutile TiO$_2$ nanorods are favoured etching positions as well, owing to their higher concentration of defects, so that densely packed TiO$_2$ nanorods with original diameter of ~250 nm split...
into thinner TiO$_2$ NRs with diameter of 15–60 nm under the etching environment. In fact, even if the hydrothermal solution was not replaced by chemical etching solution, a similar etching process could still happen by simply extending hydrothermal reaction duration (see Fig. S7†). This phenomenon is analogous with the Ostwald ripening. The etching process has been reported before. However, in the previous study, only a 1.5 µm thick film was achieved after 10 h etching process, which was far from enough for high performance DSSCs. In our case, the thickness of rutile TiO$_2$ NRA did not change significantly even after 13 h etching treatment. Such difference can be primarily attributed to two points. First, the etching conditions used here are properly chosen. Second, the TiO$_2$ NRA prepared using TiCl$_4$ as the Ti$^{4+}$ precursor is much more densely aligned compared with the film prepared using tetrabutyl titanate as the Ti$^{4+}$ precursor, which can significantly reduce the damages to the wall of TiO$_2$ nanotubes during etching process and thus almost preserve the thickness of the TiO$_2$ NRA.

The growth parameters of bare TiO$_2$ NRAs were investigated as well, such as growth temperature, growth duration and initial Ti$^{4+}$ concentration, and the detailed results were mentioned in the attached ESI.† It is found that the elevated temperature, the prolonged growth duration and the increased initial Ti$^{4+}$ concentration can accelerate the growth speed of TiO$_2$ NTAs.

Fig. 2 shows the XRD patterns of the FTO substrate (curve c), TiO$_2$ NRA film grown on FTO substrate (curve a) and 5 h etched TiO$_2$ NRA film (curve b). It is confirmed from the XRD patterns that both of the TiO$_2$ NRAs before and after etching treatment are rutile phase and agree well with the standard tetragonal rutile structure of TiO$_2$ (PDF file #01-086-0147, $P4_2/mnm$, $a = 4.594$ Å and $c = 2.958$ Å). The high intensity of (002) peak indicates that the as-prepared TiO$_2$ NRAs is highly oriented against FTO substrates. It is also observed that the intensity of (002) peak becomes weaker after TiO$_2$ NRA films suffered from etching, which can be ascribed to the selective etching of (001) planes of the TiO$_2$ nanorods.

Further structure characterization of the samples was carried out using transmission electron microscope (TEM), high-resolution TEM (HRTEM) and selected-area electron diffraction.
(SAED). It is indicated that both the TiO$_2$ nanorods and etched TiO$_2$ nanorods are single-crystalline along their entire lengths from the HRTEM images and SAED patterns examined along the [110] zone axis (Fig. 3a and b). The lattice fringes can be clearly distinguished from the HRTEM images and the inter-planar spacing is around 3.2 Å, which corresponds to the (110) plane, suggesting that TiO$_2$ nanorods have preferential growth along the [001] direction. As proven by the HRTEM images and SAED patterns (Fig. 3a and b), the etching procedure does not change the single-crystalline rutile properties of the TiO$_2$ nanorods.

Interestingly, the un-etched TiO$_2$ nanorods with diameters of around 150 nm are found to be a continuous unit (see Fig. 3c), while the etched nanorods seem to be assembled by several individual rod building blocks with diameters of around 15 nm (see Fig. 3d), which is consistent with a similar observation from the corresponding SEM images (see Fig. 5g and h). Thus, the etching process transforms a single TiO$_2$ nanorod into a bundle of TiO$_2$ building blocks with diameters of around 15 nm while the etched nanorods seem to be assembled by several nanorods. Therefore, the etched nanorods are a continuous unit (see Fig. 3c), while the etched nanorods seem to be assembled by several individual rod building blocks with diameters of around 15 nm (see Fig. 3d), which is consistent with a similar observation from the corresponding SEM images (see Fig. 5g and h).

In order to study the light-harvesting behaviour of the TiO$_2$ NRA photoanodes sensitized with the N719 dye, the diffuse reflectance absorption spectra of TiO$_2$ NRA films before and after etching treatment were compared (see Fig. 4). It is found that the dye-sensitized TiO$_2$ NRA films have better light-harvesting capabilities in the range from 300–600 nm and the peaks around 380 nm and 510 nm are the characteristic absorption of the N719 dye. The etched TiO$_2$ NRA films show much higher light absorption, especially during the visible and near infrared regions compared to that without any etching treatment. Moreover, the 3 h etched film shows the best light-harvesting ability, while a longer etching duration (e.g., 5 h and 7 h) weakens such light absorption ability.

For a further comparison, the TiO$_2$ NRA films without N719 dye sensitizing were characterized as well using UV-vis diffuse reflectance spectra (see Fig. S3f). The reflectance of the bare TiO$_2$ NRA film without etching is much higher than the etched films in the range of 400–800 nm and the 3 h etched film has the lowest reflectance value, suggesting that etched TiO$_2$ NRA films have inferior light-scattering capabilities, leading to insufficient utilization of light transmitted through the films.

Fig. 5a shows the photocurrent density–voltage ($J$–$V$) characteristics of DSSCs assembled by un-etched and etched TiO$_2$ NRA films and the corresponding photovoltaic parameters are listed in Table 1. The DSSCs based on the un-etched TiO$_2$ NRA films achieved an efficiency of 1.30% with a relatively low short-circuit photocurrent density ($J_{sc}$) of 4.29 mA cm$^{-2}$. The $J_{sc}$ values are 7.63, 11.55, 11.27 and 10.06 mA cm$^{-2}$ for the TiO$_2$ NRA films etched for 1, 3, 5 and 7 h, respectively, and the corresponding power conversion efficiencies are 2.56, 5.36, 5.15 and 4.06%. It is worth noting that the $J_{sc}$ values increase initially with the etching duration from 0 h to 3 h but reduce when further extending etching time to 5 h or 7 h. The open circuit voltage ($V_{oc}$) values show no apparent change (see Table 1). The maximum fill factor values (FF) are achieved by the DSSCs based on the 3 h and 5 h etched photoanodes.

In order to further increase the inner surface area of TiO$_2$ NRA films, thicker films with length in the range of ~8.0 μm were prepared by prolonging hydrothermal duration from the previous 6 h to 12 h. However, the un-etched films with thickness ~8.5 μm showed poor adhesion with FTO substrates and easily detached when dried in air. Actually, the phenomena has been mentioned before and TiO$_2$ NRA films with their thickness around 8 μm were easily detached from the FTO substrates.$^{52}$ Notably, if the un-etched samples were directly transferred into another autoclave filled with a mixture of 30 mL DI water and 30 mL concentrated hydrochloric acid and followed by etching treatment for 5–9 h, excellent adhesion between etched TiO$_2$ NRA films and FTO substrates was achieved (see Fig. 6b and d). The enhanced adhesion may be attributed to reduced tension force across the TiO$_2$ NRA films after etching treatment for a certain period. The as-prepared TiO$_2$ NRA films were etched for 5, 9 and 13 h respectively according to the previous etching conditions. From the SEM images of 9 h etched TiO$_2$ NRA film, it can be found that TiO$_2$ nanorods with diameters around

### Table 2 Detailed photovoltaic parameters of DSSCs based on ~8 μm thick TiO$_2$ NRAs films

<table>
<thead>
<tr>
<th>Samples$^a$</th>
<th>Thickness/μm</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>Dye-loading/nmol cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
<td>~8.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5 h</td>
<td>~8.3</td>
<td>13.19</td>
<td>0.75</td>
<td>58.23</td>
<td>5.76</td>
<td>46.69</td>
</tr>
<tr>
<td>9 h</td>
<td>~8.3</td>
<td>14.68</td>
<td>0.73</td>
<td>55.77</td>
<td>5.94</td>
<td>52.62</td>
</tr>
<tr>
<td>13 h</td>
<td>~8.3</td>
<td>—</td>
<td>—</td>
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$^a$ Samples are listed according to the different etching times of TiO$_2$ NRAs.
250 nm before etching treatment split into secondary structures of nanorods with diameter ranging from 15–60 nm (see Fig. 6c), which is supposed to enhance the inner surface area of TiO2 NRA films. While etching for 13 h, the space between adjacent nanorods increased apparently (see Fig. 6g). Surprisingly, it was noted that the 13 h etched films were detached from FTO substrates. Thus, the etching treatment could only enhance the adhesion between the TiO2 NRA films and the FTO substrates to some extent. The dye loading measurement shows a value of 52.62 nmol cm⁻² for 9 h etched film (Table 2), which is nearly 10 times larger than that of the un-etched film prepared at 150 °C for 6 h. Consequently, the highest efficiency (5.94%) of DSSC was obtained when the 9 h etched films were applied as DSSC photoanodes. Furthermore, assuming that each Ni719 dye molecule occupies an area of 1 nm² on the surface of rutile TiO2 nanorods, the roughness factor (RF) can be calculated. In this case, the value of RF for 9 h etched rutile TiO2 NRA film was calculated to be 316.65 and the un-etched one was only 35.22. However, for 10 µm thick TiO2 nanoparticle films, a similar calculation showed a RF value of around 780, which is much larger than that of 9 h etched rutile TiO2 NRA films. Thus, the results shown above indicate that the performance of DSSCs based on 1-D TiO2 NRA photoanodes has much potential to be improved simply by enlarging their inner surface area and the method presented here will be a promising choice (Fig. 7).

Conclusions

In summary, vertically aligned single-crystalline rutile TiO2 NRA films with large internal surface area were prepared directly on FTO substrates by a facile two-step hydrothermal process, involving an initial hydrothermal step to grow TiO2 NRA films followed by chemical etching treatment to increase the surface area of the above-mentioned films. It was also found that etching post-treatment was beneficial to reinforce the adhesion between TiO2 NRA films and FTO substrates to some extent, providing a simple route to prepare thicker TiO2 NRA films on FTO substrates, which was crucial for various applications based on such nanomaterials. Finally, the marked enhanced efficiency up to 5.94% was achieved in the DSSCs based on the 9 h etched 1-D rutile TiO2 NRAs with thickness around 8.3 µm, compared to that of 1.30% in the DSSCs based on un-etched TiO2 NRAs. It is also demonstrated in this study that the performance of DSSCs can be significantly improved by enlarging the inner surface area of 1-D TiO2 NRAs. Further improvement can be focused on enhancing the adhesion between the TiO2 NRA film and the FTO substrate, so that thicker films with larger inner surface area can be utilized.

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Notes and references