Significant enhancement of power conversion efficiency for dye sensitized solar cell using 1D/3D network nanostructures as photoanodes

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The single–crystalline TiO₂ nanorod arrays with rutile phase have attracted much attention in the dye sensitized solar cells (DSSCs) applications because of their superior chemical stability, better electron transport properties, higher refractive index and low production cost. However, it suffers from a low surface area as compared with TiO₂ nanoparticle films. In order to enlarge the surface area of TiO₂ nanorod arrays, the 1D nanorods/3D nanotubes sample was synthesized using a facile two-step hydrothermal process involving hydrothermal growth 1D/3D nanorods and followed by post-etching treatment. In such bi-layer structure, the oriented TiO₂ nanorods layer could provide direct pathway for fast electron transportation, and the 3D nanotubes layer offers a higher surface area for dye loading, therefore, the 1D nanorods/3D nanotubes photoanode exhibited faster electron transport and higher surface area than either 1D or 3D nanostructures alone, and an highest efficiency of 7.68% was achieved for the DSSCs based on 1D nanorods/3D nanotubes photoanode with further TiCl₄ treatment.

Dye-sensitized solar cells (DSSCs) have attracted extensive research attention due to its low-cost, high-efficiency, and non-pollution, it has been considered as one of the most promising alternatives to Si-based photovoltaic cells in the last two decades. Typically, DSSCs consists of nanoporous TiO₂ films, a monolayer of dye molecule, counter electrode, and I⁻/I₃⁻ redox electrolyte solution. Among them, TiO₂ films serves as the transport media for photo-generated electrons and take charge for dye-loading and charge-collection. Therefore, the shape and structure of TiO₂ layer play an importance role in the photoperformance of DSSCs, and continuous efforts have been made for synthesizing different structure of TiO₂ photoanode to improving the PCE of solar cells. The TiO₂ films with shape of cactus-like, treelike, forest-like, pine tree-like have been successfully synthesized and applied as photoanode in DSSCs, these exhibited dramatic potential in improving performance for applications in solar cells.

Recently, TiO₂ photoanode with 1D/3D bi-layer structure have attracted much attention, such a structure may render fewer grain boundaries, larger surface area and better light scattering properties. For example, Hong et al. synthesized 1D vertically aligned rutile TiO₂ nanorods and 3D TiO₂ nanostars by a single step hydrothermal route, the 3D nanostars/1D nanorods based DSSCs cell exhibited 5.39% power conversion efficiency, which is remarkably higher than that of bare 1D nanorods based (3.74%) photoelectrode. Wang et al. reported a new type of crystalline rutile TiO₂ nanorod based photoanode prepared by using a facile two-step hydrothermal process, the bilayer photoanode has a bottom layer composed of oriented single-crystalline rutile nanorods and a top layer composed of loosely packed nanorods which not only increases the dye loading with a significantly increased surface area but also improves light scattering without sacrificing the electron-transport efficiency. Therefore, the resultant new structures delivered light-to-electricity conversion efficiency of 6.31% as photoanodes in DSSCs. Kim et al. reported 1D/3D nanorod network consisting of 1D nanowires bottom arrays and a three-dimensional (3D) dendritic microsphere top layer. These bilayer nanostructures simultaneously possess the incompatible features such as high specific area, fast electron transport, and a pronounced light-scattering effect, and demonstrated a high energy conversion efficiency of 5.6%. In addition, as we known, nanotubes structure exhibited bigger specific surface area than that of nanorod. Shao et al. reported 3D porous architecture composed of
TiO₂ nanotubes shown a large surface area of 502.9 m²/g has been obtained. So the transformation nanorods into nanotubes is a available method for lengthening the surface area.

In this work, a novel 1D nanorods/3D nanotubes network structure was synthesized on a transparent conducting oxide substrates (TCO) by two-step hydrothermal. Relative to previous work and other related works¹⁻³, the 1D nanorod/3D nanotubes network structure was proposed as a derived structure of 1D/3D nanorod network. Compared with the nanorod network, the 1D nanorod/3D nanotubes network structure exhibited obvious advantages of larger specific surface area, due to the hollow of the 3D nanotubes. To the best of our knowledge, there is no report on 1D nanorod/3D nanotubes for DSSCs. The new structures delivered the highest power conversion efficiency of 7.68% to date for the DSSCs based on 1D rutile TiO₂ nanorods photoanodes with further TiCl₄ treatment. In addition, we have compared the photovoltaic performance of 1D nanorods/3D nanotubes structure with 3D nanotubes photoanode, and the detailed transient properties and electron transport resistance of these network structure in DSSCs were analyzed by open circuit voltage decay (OCVD) measurements and electrochemical impedance spectra (EIS), the 1D nanorods/3D nanotubes sample exhibits superior characteristics with longer life time and smaller electron transport resistance, indicating rapid electron transport rate than 3D nanotubes sample, which attributed to the electron pathway provided by 1D nanorod arrays.

### Results and Discussion

Figure 1 shows field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of 1D/3D TiO₂ nanorods prepared by hydrothermal method using a solution of 0.9 ml titanium butoxide, 16 ml hydrochloric acid, 16 ml deionized water at 150°C for 10 h while the FTO substrate lied flat on the bottom of the reactor with the conductive side facing up. Figure 1(a) shows the cross-sectional SEM image of the sample. As the image shown, after a single-step hydrothermal synthesis, a bi-layer network nanostructure has been formed, which consists of the upper layer of 3D TiO₂ nanorods and the bottom layer of 1D TiO₂ nanorod arrays. The figure 1(b) and the inset of figure 1(b) present the cross-sectional and top views of the 1D nanorod arrays, respectively. It reveals that the 1D TiO₂ nanorod arrays are very dense and little space exists between adjacent TiO₂ nanorods. The average length of the nanorods is ~4.4 μm with the average diameter of 150 nm. In addition, it can be seen from the plan view of 3D nanorods layer (figure 1c) that the upper layer of the structure consists of TiO₂ flower-like clusters. A close-up of a flower looks like a natural chrysanthemum. Each flower was composed of a large number of nanorods, and every individual nanorod is tetragonal in shape with square top facets. The void in the bottom nanorod arrays provide nucleation site for the upper 3D nanorods layer, which grow randomly and subsequently form a flow-like structure. These spokewise nanorods radiated from a common central zone. The nanorods were roughly 3 μm long and 450 nm wide with an aspect ratio of about 6.7. Moreover, the top surface of a nanorod appeared to contain many step edges, which are the substrates for further growth of sub-nanorods, while the side surface was smooth. Clearly a fully grown flower possessed a spherical symmetry with an average diameter of approximately 7.5 μm. From the SEM image at low magnification (Figure 1d), the TiO₂ flower-like clusters uniformly distributed on the surface of substrate, and enough space emerged between two adjacent TiO₂ clusters which are benefit for dye loading. Moreover, during the hydrothermal process, while the FTO substrate lied flat on the bottom of the reactor with the conductive sides facing down, a network nanostructure of 3D TiO₂ nanorods can be synthesized as figure 1f shown. The morphological and structural properties of 1D/3D nanorods are further characterized by TEM analysis. Figure 1 e shows that the single flower made of several nanorod petals. The close

Figure 1. The cross-sectional (a) and plan (c, d) SEM images of 1D/3D TiO₂ nanorods, image (b) and the inset image of (b) correspond to the cross-sectional and top view of the bottom layer of 1D TiO₂ nanorod arrays. TEM (e) and SAED (f) characterization of the 3D nanorods; TEM image (g) and SAED image (h) of the bottom layer 1D nanorods.
Logical transformation of rutile TiO\(_2\) nanorods through etching can a 1D nanorods/3D nanotubes structure is formed. The morpho-tubes with an average diameter of 8 nm, which markedly enlarged the surface area of the sample, and no additional phases were observed. It is known that the crystal defect has been directly synthesized without annealing treatment. Figure 3 shows the schematic diagram of TiO\(_2\) films with different network structures. The structures of 1D/3D nanorods and 3D nanotubes were successfully synthesized by a single-step hydrothermal route. When the conductive side of FTO glass faces up during the hydrothermal process, a 1D/3D nanorods structure was obtained, on the contrary, a 3D nanorods structure would be presented when the conductive surface face down. In order to further improve the surface area of the TiO\(_2\) films for DSSCs application, the network structure suffered from etching treatment. Finally, the structures of 3D nanorods and 1D/ 3D nanorods were successfully transformed into 3D nanotubes and 1D nanorods/3D nanotubes through the etching treatment.

The crystallinity of the hydrothermally deposited network structures were examined by X-ray diffraction (XRD) measurement. Figure 4 (a) shows the XRD patterns of the 1D/3D nanorods as prepared, which can be easily indexed to the tetragonal rutile structure of TiO\(_2\) (JCPDS No.89-4920), indicating that a crystalline structure has been directly synthesized without annealing treatment. Figure 4 (a), (c) and (d) show the XRD patterns of TiO\(_2\) 1D/3D nanorods, 3D nanotubes and 1D nanorods/3D nanotubes samples respectively. The three curves exhibited the same diffraction peaks locations which match well with the pure rutile phase. All of the four samples present rutile TiO\(_2\) single crystals, where the growth direction is along [001] orientation, side surfaces exhibit [110] facets, and no additional phases were observed. It is known that the crystalline rutile phase can be advantageous for reducing the electron transport resistance and thus the electron-recombination rate in the photoanode of DSSCs\(^{23}\). In addition, compared the XRD patterns of un-etched sample with that of the etched one, it can be found that they possessed the same diffraction peaks regardless of difference in intensity, indicating etching treatment does not destroy the single-crystalline rutile properties of TiO\(_2\) nanorods.

Three kinds of network structures including 1D/3D nanorods (sample I), 3D nanotubes (sample II), and 1D nanorods/3D nanotubes (sample III) are further used as photoanodes in DSSCs. Figure 5 shows typical current density versus voltage (J-V) curves of the three network structure bases DSSCs irradiated by AM 1.5 G simulated sunlight (100 mW cm\(^{-2}\)), and the detailed photovoltaic parameters are listed in table 1. As shown in figure 5 and table 1, the open-circuit photovoltage (\(V_{oc}\)) of the DSSCs based on the three films have no significant variations. DSSCs with sample I exhibited a relatively low short-circuit current density (\(J_{sc}\)) of 5.96 mA/cm\(^2\), an \(V_{oc}\) of 0.76 V, and a fill factor (FF) of 62\%, which gives an overall light-to-electricity conversion efficiency of 2.80\%. The cells based on sample II and III present a significant enhancement in the \(J_{sc}\) values comparison with sample I, which reach 7.68 and 13.40 mA/cm\(^2\), respectively.

\[
\text{TiO}_2 + \text{HCl} \rightarrow \text{TiCl}_4 + \text{H}_2\text{O} \quad (1)
\]

The 3D TiO\(_2\) nanorods begin to dissolve on the relatively unstable crystal faces. The dissolve rate of different crystal faces in rutile TiO\(_2\) nanorods follows the sequence (110) < (100) < (101) < (001)\(^{20,21}\). Thus, the (001) planes of rutile TiO\(_2\) nanorods are the preferential etching planes\(^2\). Rutile TiO\(_2\) nanorods dissolved along the [001] direction, which leads to TiO\(_2\) transform from 3D nanorods to 3D nanotubes. Moreover, there are more crystal defects existing in the grain boundaries among 1D rutile TiO\(_2\) nanorod arrays and these sites are favored etching position as well, so that the bottom layer of densely packed TiO\(_2\) nanorod arrays split into secondary nanorods with small diameter.

As the SEM images present, we can control the morphology and dimension of TiO\(_2\) films by experiment condition. It can be found that the TiO\(_2\) films contain only 1D nanorod arrays while the mount of titanium precursor is less than 0.5 ml as we previously reported\(^{16-18}\), and the films present 1D/3D nanorods network structure as adequate titanium precursor is added. Figure 3 shows the schematic diagram of TiO\(_2\) films with different network structures. The structures of 1D/3D nanorods and 3D nanotubes were successfully synthesized by a single-step hydrothermal route. When the conductive side of FTO glass faces up during the hydrothermal process, a 1D/3D nanorods structure was obtained, on the contrary, a 3D nanorods structure would be presented when the conductive surface face down. In order to further improve the surface area of the TiO\(_2\) films for DSSCs application, the network structure suffered from etching treatment. Finally, the structures of 3D nanorods and 1D/ 3D nanorods were successfully transformed into 3D nanotubes and 1D nanorods/3D nanotubes through the etching treatment.

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Figure 2a and Figure 2e) clearly show that they have similar thicknesses of 72 μm, so the effect of the thickness on photovoltaic performance can be ignored. The differences of photovoltaic properties are mainly attributed to increased dye loading due to the larger surface area after the etching post-treatment. It is worth noting that the Jsc of sample III is ~2.3 times higher than that of the un-etched one, and a most efficient photovoltaic performance of 6.43% is achieved for 1D nanorods/3D nanotubes cells without any further post-treatment of TiCl4, which has frequently been used in a previous report to further improve the performance of DSSCs24,25. Comparing the sample II with sample III, it can be found that the Jsc increases from 7.67 mA/cm² to 13.40 mA/cm², the enhanced Jsc may ascribed to the bottom layer of 1D TiO2 nanorod arrays in sample III, which can provide a direct current pathway for electrons to the external circuit with few grain boundaries. As a result, the power conversion efficiency varies from 3.57% for sample II, to 6.43% for sample III.

To obtain better insight into the factors contributing to efficiency, the specific surface area and pore volume of TiO2 photoanode with different network structures were measured by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis using a nitrogen adsorption-desorption apparatus. The measured specific surface areas of the three sample were 75.53 m²g⁻¹, 103.42 m²g⁻¹, 134.06 m²g⁻¹, respectively. This BET result is in accordance with the SEM image in Fig 1 and Fig 2. The two etching samples showed a larger surface area than that of the unetching sample. This indicates that the etching samples should provide larger sensitizer surface coverages than the unetching photoelectrodes. The amounts of dyes adsorbed on the three samples were measured by the UV-vis absorption spectra of the N719 dye-desorption solution, which were prepared by immersing the sensitized electrodes into a 0.1 M NaOH in a mixed solvent (water: ethanol = 1 : 1). The amount of dye adsorbed was determined by the molar extinction coefficient of 1.41 × 10⁴ dm³mol⁻¹ cm⁻¹ at 515 nm26. It is found that the two etched samples exhibit higher dye-loading capacity than the un-etchetd film. Especially for 1D nanorods/3D nanotubes sample, it has the largest amount of dye adsorption (236.16 nmol/cm²) and is about 3.6 times larger than that of the un-etched 1D/3D nanorods films (65.97 nmol/cm²), which result from the enlarged internal surface area via etching treatment, definitely contribute to the enhanced photocurrent density and thus higher DSSC efficiencies. This is well in agreement with J-V data.

In order to better understand the different photovoltaic performances of the three DSSCs, the UV/Vis reflectance spectra were further characterized and shown in figure 6 (a). The light-scattering ability of the photoanode is crucial for efficient harvesting of the incident light, the sample with inferior light-scattering ability have a better chance to capture incident light. As the figure 6 (a) shown, the reflectance of the 1D nanorods/3D nanotubes film (sample III) is
about 85% in the range of 400–900 nm, which is higher than the other two films. It is worth noting that sample III and sample II, with etching treatment, shows higher diffuse reflection capabilities in the visible and near infrared regions compared to that of un-etched one (sample I), suggesting that the incident light was significantly scattered within film III and II, which can maximize the use of solar light to improve the light harvesting efficiency, and definitely result in a higher photocurrent for DSSCs based on sample III and II. In addition, the reflectance of the 3D nanotubes (sample II) is about 70% in the range of 400–800 nm, it presents a little lower than that of sample III which fabricated by an aligned bottom layer of 1D nanorod arrays with better light-scattering capacity. The absorption spectra of the three TiO2 network structure photoanodes sensitized with N719 dye have been shown in figure 6 (b). It is found that the dye-sensitized 1D nanorods/3D nanotubes film have best light-harvesting capabilities in the range from 400–700 nm and the peaks around 530 nm are the characteristic absorption of the N719 dye. It reveals that the etched films show much higher light absorption, especially during the visible and near infrared regions compared to that without any etching treatment, which is consistent with result of the amount of dye molecules measurement in which etching sample showed the higher dye-loading.

The incident-photo-to-current efficiency (IPCE) spectra could provide further evidence on the light-harvesting efficiency of the DSSCs. Figure 7 displays the IPCE spectra as a function of wavelength from 400 to 800 nm for those three cells. As can be seen, the IPCE curves of the three cells exhibit similar spectrum shape, and get a maximum efficiency at 530 nm corresponding to the absorption peak of the N719 dye. The data of IPCE have an order of sample I < sample II < sample III at the visible light wavelength range, which is consistent with Jsc order. The DSSCs fabricated from 1D nanorods/3D nanotubes photoanode displays the highest IPCE value over a wide range from 400–700 nm among these three cells. Moreover, the IPCE of the etching sample III increased from 58% to 90% around 530 nm compared to the un-etching sample I. The higher IPCE of cell sample III over a wide range contribute to the increase in efficiency of light harvesting (larger dye molecular loading and higher light reflectance), which could lead to a higher short-circuit current density. In addition, it can be found that the IPCE data of cell sample III shows an obvious red-shift to a longer wavelength compared to the cell sample I and II due to the better light-scattering ability.

Table 1 | Detail photovoltaic parameters of the DSSCs based on TiO2 photoanode with different network structures (1D/3D nanorods, 3D nanotubes, 1D nanorods/3D nanotubes) under illumination of simulated solar light (100 mW/cm², AM 1.5 G)

| Sample                  | V oc (V) | J sc (mA/cm²) | η (%) | FF | Dye-loading (nmol/cm²) |
|-------------------------|---------|--------------|-------|----|------------------------|
| 1D/3D nanorods          | 0.76    | 5.96         | 2.80  | 0.62| 65.97                  |
| 3D nanotubes            | 0.78    | 7.67         | 3.57  | 0.60| 138.3                  |
| 1D nanorods/3D nanotubes| 0.76    | 13.40        | 6.43  | 0.63| 236.16                 |

(a) Diffused reflectance spectra of different network structures films before dye adsorption without electrolyte and illuminated from the TiO2 side with integrating sphere. (b) UV-Vis absorbance spectra of dye-sensitized photoanode with different network structures (1D/3D nanorods, 3D nanotubes, 1D nanorods/3D nanotubes).

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Figure 7 | Incident photon to current conversion efficiency (IPCE) curves of DSSCs based on TiO2 photoanodes with different network structures.
and the electron lifetime. We carried out the experiment according to the technique reported by Zaban et al.\textsuperscript{27,28}. For the photoinduced OCVD measurements, the cell was irradiated with AM 1.5 solar light for 10 s to a steady voltage, then the illumination was turned off using a shutter, the OCVD was recorded with an electrochemical work station, typically the measurement interval was 10–50 ms. The response time is obtained by the reciprocal of the derivative of the decay curve normalized by the thermal voltage as equation (2)

$$\tau_n = \frac{K_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}$$  \hspace{1cm} (2)

Where $K_B$ is the Boltzmann constant taken to be $1.38 \times 10^{-23}$ J/K, $T$ is the temperature, $K_B T$ gives the thermal energy, $e$ is the positive elementary charge to be $1.69 \times 10^{-19}$ C and $dV_{oc}/dt$ is the derivative of the open circuit voltage transient. The data shown in figure 8 (a) consist of three OCVD curves based on different network structures TiO\textsubscript{2} photoanodes. For a linearly with time, the curves indicate a supralinear decay where the lifetime recedes to larger values. Figure 8 (b) shows the lifetime values obtained from figure 8 (a) using equation (2). It can be seen from figure 8 (b) that the lifetimes of DSSCs based on sample III are longer than that of sample II at the voltage range of 0.4 V–0.7 V, which may be due to the bottom layer of 1D nanorods arrays that provide the electron pathway with few boundary. It is worth noting that the two etched samples exhibit superior characteristics with longer lifetime than the un-etched film, indicating fewer recombination centers in the etched sample. The grain boundaries among rutile TiO\textsubscript{2} nanorods are favored etching positions, owing to their higher concentration of defects. So the etching-treatment reduces the defects of samples, which suppress the recombination pathway at the electrode-electrode and electrode-electrolyte interface.

Electrochemical impedance spectroscopy (EIS) is a powerful tool to clarify the transport resistance in DSSCs. Figure 9 shows the electrochemical impedance spectra of the above different DSSCs at the open circuit voltage illuminated with AM 1.5 solar light of 100 mW cm\textsuperscript{-2} and a frequency range from 0.1 Hz to 10\textsuperscript{5} Hz. Generally, the first gap (R\textsubscript{s}) is related to the sheet resistance on the transparent conductive oxide (TCO) substrates and the contact resistance between TCO and TiO\textsubscript{2}. In addition, three semicircles can be observed from the impedance spectra, the semicircle in high frequency region represents the charge transfer resistance at the electrolyte/Pt-electrode interface (R\textsubscript{pt}), the second semicircles are assigned to electron transfer at the interface between the TiO\textsubscript{2}/dye/electrolyte (R\textsubscript{ct}), and the third semicircle observed in the low frequency region correspond to the characteristics of diffusion of the I\textsuperscript{3}/I\textsuperscript{−} redox electrolytes electron\textsuperscript{−}\textsuperscript{29}. As shown in table 2, the three DSSCs show similar values of $R_s$ and $R_{pt}$, which ascribes to the use of the same electrolyte and counter electrodes. However, the charge transfer resistance $R_{ct}$ of two etched samples is obviously smaller than that of unetched samples, hence denoting the more superior charge transport characteristics after etching treatment. It is worth mentioning that the smaller value of $R_{ct}$ is observed from sample III, as compared to the sample II, this indicated that the addition of TiO\textsubscript{2} nanorod arrays contributes to the reduction of charge transfer resistance, which leading to an increase of the $J_{sc}$\textsuperscript{30,31}.

The performance of the DSSCs can be improved through many ways. One well-known method is post-treatment the TiO\textsubscript{2} photoanode with titanium tetrachloride (TiCl\textsubscript{4}) solution. The TiCl\textsubscript{4} treatment can results in an improvement of 10–30% in photocurrent. It is claimed that the treatment by TiCl\textsubscript{4} could introduce 3–10 nm nanoparticles onto TiO\textsubscript{2} photoanode to increase the surface area. Accordingly, it improves the dye-loading capacity of the photoanode. In addition, the TiCl\textsubscript{4} surface treatment can improve the electron transport and light scattering. In this work, the as-prepared TiO\textsubscript{2} 1D nanorods/3D nanotubes sample was immersed in 0.2 M TiCl\textsubscript{4} aqueous solution at room temperature for 48 h, and then was annealed in air at 450 °C for 30 min. FE-SEM images of the modified sample are shown in Figure 10 (a, b, c). As the plan-views shown, the sample maintains the flower cluster structures which composed of a
large number of nanotubes, the inside and outside surface of the nanotubes are covered with a mass of TiO₂ nanoparticles and the surfaces become rough. From the top view at high magnification (Figure 10c), the diameter of nanoparticle is about 10–20 nm. Figure 10 (c) gives the cross-sectional image of TiO₂ 1D nanorod arrays at the bottom layer, which shows a lot of TiO₂ nanoparticles also attach on surface of the nanorod arrays. Figure 10 (d) presents the J-V curves and photovoltaic parameters of DSSCs based on the TiCl₄ modified 1D nanorods/3D nanotubes photoanode. After the TiCl₄ treatment at room temperature for 48 h, the cell attained an over efficiency of 7.68% with Jₘₜ of 18.3 mA/cm², Vₜₐₚ of 0.72 V, and an FF of 58.29%, the Jₘₜ and conversion efficiency of the cell were increased through the TiCl₄ treatment by 36% and 20%, respectively, whereas the Vₜₐₚ and FF decreased a little after the TiCl₄ treatment, this result suggests that the increase in the solar cell performance was mostly derived from the increase in current density. The large increase of Jₘₜ can be explained as follows. After TiCl₄ post-treatment, a dense amorphous TiO₂ particles forming on the surface of bare anotubes or nanorods will facilitate electron transfer and increase the surface area for more light capture. The procedure leads to increased dye adsorption due to increased roughness. A thin blocking layer of TiO₂ is deposited on the naked FTO surface that reduces the recombination loss between accumulated electrons and electrolyte. All these factors help to achieve higher energy conversion efficiency after TiCl₄ treatment.

In conclusion, TiO₂ 1D/3D nanorods network structure are grown directly on transparent conductive fluorine-doped tin oxide substrates by a single-step hydrothermal route. Followed by a secondary hydrothermal etching treatment, the bottom layer of TiO₂ nanorod arrays split into secondary nanorods with a reduced diameter, and the up layer of 3D nanorods have been hollow, which markedly enlarge the surface area of the sample, and a 1D nanorods/3D nanotubes bi-layer structure is formed. The 1D nanorods/3D nanotubes sample are further applied as the photoanodes in dye sensitized solar cells (DSSCs). Compared to a 1D/3D nanorods based cell, the photovoltaic performance of the 1D nanorods/3D nanotubes TiO₂ cell

| Sample                  | Rs/Ω  | Rpt/Ω | Rct/Ω |
|-------------------------|-------|-------|-------|
| 1D/3D nanorods          | 20.18 | 1.434 | 26.73 |
| 3D nanotubes            | 21.75 | 1.524 | 12.48 |
| 1D nanorods/3D nanotubes| 19.21 | 1.738 | 4.874 |

Table 2 | Series resistance (Rs), charge transfer resistance (Rpt), and electron transfer and recombination (Rct) of the DSSCs fabricated using different photoanodes.

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Figure 10 | The plan (a) and cross sectional (c) SEM images of 1D nanorods/3D nanotubes photoanode modified with TiCl₄ treatment, image (b) correspond to the top view of the TiCl₄ modified sample at high magnification. Image (d) presents the J-V curves and photovoltaic parameters of DSSCs based on the TiCl₄ modified 1D nanorods/3D nanotubes photoanode.
exhibits excellent DSSC performance, which results from the large dye-loading, the superior light scattering, rapid electron transport and lower electron recombination rate. The DSSCs based on 1D nanorods/3D nanotubes exhibits a high power conversion efficiency of 7.68% with TiCl4 treatment, which is remarkably higher than that of the 1D/3D nanorods (2.80%) photoelectrode. In order to understand the specific role of TiO2 nanorod arrays in the 1D nanorods/3D nanotubes structure, we have compared the photovoltaic performance of 1D nanorods/3D nanotubes structure with 3D nanotubes photoanode, and the detailed transient properties of these network structure in DSSCs are analyzed by open circuit voltage decay measurements, the 1D nanorods/3D nanotubes sample exhibits superior characteristics, with longer life time indicating rapid electron transport rate than 3D nanotubes sample, which attributed to the electron pathway provided by 1D nanorod arrays.

**Methods**

**Hydrothermal Synthesis of 1D/3D nanorods and 3D nanotubes on FTO substrate.** The procedure for obtaining TiO2 nanorods network architecture on FTO substrate that developed by Liu et al using hydrothermal method11. All the chemicals were of analytic grade and used without further purification. Titanium butoxide, concentrated hydrochloric acid (HCl, 36.5%-38% by weight) and deionized water were used as titanium precursor, acidic medium and solvent, respectively. In a typical synthesis, 16 ml of deionized water, 0.9 ml of titanium butoxide and 16 ml of hydrochloric acid were mixed in a Teflon-lined autoclave of 50-ml capacity under magnetic stirring. A piece of FTO substrate (2 × 2 cm²), through an ultrasonically cleaning with acetone, anhydrous alcohol, and deionized water, was lied flat on the bottom of the reactor with the conductive side facing up. Subsequently, the autoclave was sealed and maintained at 150°C for 10 h. After cooling the autoclave to room temperature, the TiO2 films were rinsed extensively with deionized water and dried in ambient air and designated as 1D/3D nanorods. For the synthesis of 3D nanotubes, the FTO substrate was place in the autoclave as the conductive side facing down.

**Preparation of 1D nanorods/3D nanotubes and 3D nanotubes.** The as-prepared rutile 1D/3D nanorods and 3D nanotubes were immersed into a solution of 5 ml DI water and 11 ml HCl (36.0~38.0 w%) and hydrothermally treated at 150°C for 12 h. After the hydrothermal reaction finished, the sample rinsed extensively with deionized water, and dried in ambient air. The samples were annealed at 500°C for 2 h in the air atmosphere.

**Transferring the TiO2 network structure to FTO substrate.** After the chemical etching treatment, the TiO2 network structure were separated from the FTO substrate, the detached free standing TiO2 film with network structure were carefully handled with tweezers and subsequently transferred to a new FTO glass which were coated as a self-prepared ultra-thin adhesive TiO2 paste. For a practical application, the adhesive TiO2 paste is needed to have a good adhesion property. The TiO2 network structure photoanodes were obtained after an annealing process of 500°C for 2 h in the air atmosphere.

**Solar cell fabrication.** In order to fabricate the DSSC, the calcined TiO2 network structure photoanode was immersed in ethanol solution of 0.03 mM Ruthenium dye (N719) for 24 h. The dye-adsorbed TiO2 photoanode was washed with ethanol to remove the redundant dye molecules without adsorption and dried under nitrogen flow at room temperature. A DSSC was fabricated using a standard two electrode configuration, comprising dye loaded TiO2 network structure as the photoelectrode and platinum coated FTO as the counter electrode. Afterward, the iodide-base electrolyte was used as the redox couple and was injected from the edge of the DSSCs to evaluate their photovoltaic performance.

**Characterization.** SEM and XRD were utilized to characterize the morphology and structure of the TiO2 nanostructure. The diffuse reflectance spectra and the amount of dye adsorbed on TiO2 nanostructures were measured by UV-3600 spectrophotometer. Photocurrent density-voltage (J-V) curves of the DSSCs were recorded using a Keithley 2420 digital multimeter under the simulated AM 1.5 illumination (100 mW cm⁻²) and an active area of 0.16 cm² was used. J-V spectra were recorded with the help of Oriel QE/IPCE Measurement Kit (equipped with 150–300 W full spectrum solar simulators). OCVD measurements were obtained with CHI Electrochemical work station (model-CHI-660D). EIS characteristics were carried out using an electrochemical workstation (CHI-660D) with a 10 mV AC signal over the frequency range of 0.1~10⁵ Hz under 100 mW cm⁻² illumination.
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Author contributions
W.H. contributed to establishing the scientific principles of the 3D network DSSCs, supervising the work, analyzing the data, commenting and editing the manuscript. W.B.Y. contributed to the design of the experiment, analysis of the data and writing the manuscript with the help of Z.J. and Y.J.C. synthesized the TiO$_2$ network nanostructure. X.C. performed the etching treatment with TiO$_2$ films. H.Y.X. carried out the fabrication and the characterization of the solar cells. L.R. contributed to the OCVD measurement and the analysis of the data.

Additional information
Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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