Hierarchical Oriented Anatase TiO₂ Nanostructure arrays on Flexible Substrate for Efficient Dye-sensitized Solar Cells

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The vertically oriented anatase single crystalline TiO₂ nanostructure arrays (TNAs) consisting of TiO₂ truncated octahedrons with exposed [001] facets or hierarchical TiO₂ nanotubes (HNTs) consisting of numerous nanocrystals on Ti-foil substrate were synthesized via a two-step hydrothermal growth process. The first step hydrothermal reaction of Ti foil and NaOH leads to the formation of H-titanate nanowire arrays, which is further performed the second step hydrothermal reaction to obtain the oriented anatase single crystalline TiO₂ nanostructures such as TiO₂ nanoarrays assembly with truncated octahedral TiO₂ nanocrystals in the presence of NH₄F aqueous or hierarchical TiO₂ nanotubes with walls made of nanocrystals in the presence of pure water. Subsequently, these TiO₂ nanostructures were utilized to produce dye-sensitized solar cells in a backside illumination pattern, yielding a significant high power conversion efficiency (PCE) of 4.66% (TNAs, JSC = 7.46 mA cm⁻², VOC = 839 mV, FF = 0.75) and 5.84% (HNTs, JSC = 10.02 mA cm⁻², VOC = 817 mV, FF = 0.72), respectively.

In a modern-day society, energy needs is increasingly urgent and thus emerging ecological concerns are invariably ensue. Since the pioneering report of Grätzel in 1991, dye-sensitized solar cells (DSSCs) are generally recognized as one of the most promising alternatives to conventional p-n junction photovoltaic devices. Subsequently, extensive researches have been conducted due to their low cost (relatively inexpensive raw materials and manufacturing processes), facile fabrication process (environmental friendly), stable photovoltaic properties as well as outstanding photoelectrical conversion efficiency. Currently, the highest power conversion efficiency up to 12% has been achieved for DSSCs based on zinc porphyrin sensitizer, Co(II/III)tris(bipyridyl) based redox electrolyte and TiO₂ nanoparticle photoanode. The typical TiO₂ nanoparticle based photovoltaic device has been found to limit the electron transport and reduce the electron lifetime because of the random network of crystallographically misaligned crystallites, and lattice mismatches at the grain boundaries. It has been widely accepted that the photovoltaic performance of TiO₂ is highly dependent on its morphological and structural characteristics. Hence, the effort towards TiO₂ nanostructures with desirable shape and crystallinity is of great interest. Recently, vertically aligned one-dimensional nanostructures such as nanorods (NRs), nanowires (NWs) or nanotubes (NTs) have been employed as photoanode materials because they can provide direct electrical transport pathways for photogenerated electrons. Moreover, TiO₂ with tailored crystalline facets has drawn extensive attention since both theoretical and experimental studies have reported that the [001] facets of anatase TiO₂ is much more reactive than the thermodynamically more stable [101] facets, which may be the dominant source of active sites for photovoltaic application as such [001] faceted single crystals could effectively retard the charge recombination. More recently, DSSCs assembled using the TiO₂ powder with various morphologies (nanosheets, nanosheet-based hierarchical spheres, hollow spheres, etc) and different percentage of exposed [001] facets demonstrated impressive PCE (~4.5–8.5%). However, up to date, there is no report on the direct fabrication of vertically aligned anatase single crystalline TiO₂ nanostructure arrays consisting of exposed [001] facet TiO₂ nanocrystals on Ti foil substrate, which can combine the advantages of 1D nanostructured materials as well as unique geometrical and electronic characteristics of nanosized anatase TiO₂ crystals with exposed [001] facets that rendered effective electron transport and light scattering. On the other hand, large surface area also...
plays a salient role in boosting the efficiency\textsuperscript{24–27}. It is well known that smooth 1D TiO\textsubscript{2} nanostructure (such as NW or NT) possess a lower roughness factor for sufficient dye attachment\textsuperscript{28,29}. To tackle this issue, increasing the surface roughness of 1D TiO\textsubscript{2} nanostructures is an effective strategy to enhanced surface areas for dye adsorption and sunlight harvesting\textsuperscript{31}. Hence, it is desirable to fabricate hierarchical TiO\textsubscript{2} nanotubes with walls made up of small nanocrystals.

Herein, we report a green step-by-step hydrothermal method to synthesize vertically oriented anatase TiO\textsubscript{2} nanostructure arrays (TNAs) consisting of TiO\textsubscript{2} nanocrystals with exposed \{001\} facets or hierarchical TiO\textsubscript{2} nanotubes (HNTs) with tube walls made of numerous TiO\textsubscript{2} nanocrystals directly on Ti-foil substrate. Specifically, H-titanate nanowires were employed as titanium precursor to hydrothermally fabricate TNAs in the presence of ammonium fluoride (NH\textsubscript{4}F) as shape-capping reagents, and HNTs in pure deionized water, respectively. Structural characterizations were undertaken to investigate the correlation between hydrothermal conditions and surface morphology of the anatase TiO\textsubscript{2} nanoarrays. Notably, DSSC based on such photoelectrodes exhibits the PCE of 4.66\% (TNAs) and 5.84\% (HNTs), respectively, which are much higher than that of commercial P25 TiO\textsubscript{2} nanoparticles photovoltaic (4.17\%).

Results
Structure of TNAs and HNTs film. Figure 1 shows the XRD patterns of the as-grown H-titanate nanowire film after alkali hydrothermal reaction and an ion-exchange process as well as TNAs film and HNTs film after second-step hydrothermal reaction. The diffraction peaks of the H-titanate nanowires in Fig. 1 (curve a) correspond well to the H\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} (OH\textsubscript{2}) phase. After further hydrothermal treatment of the H-titanate nanowires precursors in 0.1 M NH\textsubscript{4}F aqueous solution (TNAs), a pure anatase phase of TiO\textsubscript{2} (tetragonal, I\textsubscript{4}/amd, JCPDS 21-1272) was observed, as shown in Fig. 1, curve b). The (200) reflection of this sample is markedly more intense and sharper than (101) peaks, indicating a domain crystalline growth along (200) axis\textsuperscript{20}. In addition, after second-step hydrothermal reaction of the H-titanate nanowire in pure deionized water (without NH\textsubscript{4}F), the obtained samples (HNTs) were again indexed as anatase TiO\textsubscript{2} phase (Fig. 1, curve c) in accordance with the PDF card (JCPDS 21-1272). Since no diffraction peak belonging to impurities is observed, indicating that all the H\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4}(OH\textsubscript{2})\textsubscript{2} is completely converted to anatase TiO\textsubscript{2}.

The vertically aligned nanowire morphology is formed during the alkali hydrothermal reaction and is preserved throughout the ion-exchange process. After the second-step hydrothermal growth, the oriented nanostructure is still maintained, which eventually leads to TiO\textsubscript{2} nanostructure arrays (TNAs) consisting of TiO\textsubscript{2} nanocrystals with exposed \{001\} facets or hierarchically TiO\textsubscript{2} nanotubes (HNTs) consisting of numerous nanocrystals. Figure 2 displays the cross-sectional scanning electron microscopy (SEM) images of the as-prepared samples. Figure 2a and b show the longitudinal SEM image of H\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} (OH\textsubscript{2})\textsubscript{2} nanowire arrays. The mean diameter and length of H\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} (OH\textsubscript{2})\textsubscript{2} nanowires observed from SEM are 95 nm and 15 μm (Fig. 2b), respectively\textsuperscript{15}. After hydrothermal treatment of the as-prepared H\textsubscript{2}Ti\textsubscript{2}O\textsubscript{4}(OH\textsubscript{2})\textsubscript{2} nanowires in 0.1 M NH\textsubscript{4}F aqueous solution as a capping reagent at 200°C for 24 h, the morphology and length of nanowire arrays (Fig. 2c and d) undergone significant change. Specifically, as seen in Fig. 2c, TiO\textsubscript{2} nanostructure arrays are made up of TiO\textsubscript{2} truncated octahedral nanocrystals (50 ± 5 nm in diameter), which piles up randomly along certain growth axis. And the length of TiO\textsubscript{2} nanoarrays decreases to nearly half of the original H\textsubscript{2}Ti\textsubscript{2}O\textsubscript{4}(OH\textsubscript{2})\textsubscript{2} nanowire (from 15 μm to 8 μm, Fig. 2d).

The morphological and structural characterizations of TNAs and HNTs are further characterized by using transmission electron microscopy (TEM). Figure 3a is a typical TEM image of TNAs consisting of TiO\textsubscript{2} nanocrystals with exposed \{001\} facets which agrees

![Figure 1](image-url) X-ray diffraction patterns of as-prepared samples. (a) H\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4}·H\textsubscript{2}O nanowire film formed after alkali hydrothermal growth process and an ion-exchange process, which corresponds well to the H\textsubscript{2}Ti\textsubscript{2}O\textsubscript{4}(OH\textsubscript{2})\textsubscript{2} phase. (b) TNAs film and (c) HNTs film obtained after the second-step hydrothermal reaction, which indicates that the obtained samples were indexed as anatase phase.

![Figure 2](image-url) Cross-sectional SEM images of as-prepared products. (a, b) H\textsubscript{2}Ti\textsubscript{3}O\textsubscript{4}·H\textsubscript{2}O nanowire arrays. (c, d) TiO\textsubscript{2} nanostructure arrays consisting of TiO\textsubscript{2} truncated octahedron nanocrystals and (e, f) hierarchical TiO\textsubscript{2} nanotubes consisting of numerous nanocrystals.
with the SEM observation. The individual nanocrystals that made up of oriented arrays are truncated octahedrons with two \{001\} planes and eight \{101\} planes. The inset image in Fig. 3a shows that the interfacial angle between the truncated facet and the surrounding facet is 68.3°, which matches well with the angle between the \{001\} and \{101\} of anatase \(^{30,31}\). HRTEM image taken from the interfacial region of adjacent truncated octahedrons displayed in Fig. 3b further show that the lattice fringe parallel with the truncated plane has an interplanar spacing of 0.48 nm, corresponding to \{001\} facets. And the other interplanar spacing of 0.35 nm are in accordance with the \{101\} facets. The TiO\(_2\) nanostructure arrays (TNAs) were assembled by linkage of truncated octahedrons with the high energy \{001\} facets in less thermodynamically feasible manner, and the nanocrystals are aligned with each other along growth orientation of \{100\} direction. Figure 3c shows the typical TEM images of the as-prepared hierarchical TiO\(_2\) nanotubes (HNTs). It can be seen that these one-dimensional nanostructures are composed of small TiO\(_2\) octahedrons (~20 nm in width and ~50 nm in length). The HRTEM displayed in Fig. 3d shows an interplanar spacing of 0.35 nm, indicating that the exposed facets of all octahedrons were dominated by \{101\} facets and there is an excellent alignment among the individual nanocrystals along \{100\} direction.

**Growth mechanism.** Figure 4 illustrates the schematic hydrothermal growth process of the TNAs and HNTs film on Ti-foil substrate by using oriented H-titanate nanowires precursors under different aqueous solution. In this process, the original H-titanate can act as a template to facilitate the shape conversion, while the one-dimensional orientation was still maintained. For HNTs with walls made up of octahedrons (bound with eight \{001\} planes) prepared in pure water, it is generally believed that H-titanate experiences a dissolution and nucleation process during the hydrothermal treatment \(^{32}\). Since the nucleation may occur at any time during the dissolving stage, numerous octahedrons with a broad size distribution were obtained and aligned with each other along \{100\} directions. Interestingly, channel-like interiors were appeared along the crystal arrays afterwards. As for the TNAs consisting of TiO\(_2\) nanocrystals with exposed \{001\} facets obtained in the NH\(_4\)F system, the existing of F\(^-\) ions not only can easily to bond with Ti atom to form Ti-F bonds, which can markedly reduce the surface free energy of the \{001\} facets to lower than that of the \{101\} facets \(^{33}\), but also act as the capping reagent to stabilize the high energy \{001\} facets and impede the growth along the \{001\} direction, which eventually forms the truncated octahedrons \(^{27}\). After the dissolving and nucleation process, individual adjacent truncated octahedrons are inclined to connect with other one with high energy \{001\} facets \(^{34}\), which lead to intelligent assembly of such novel one-dimensional TiO\(_2\) nanoarrays.

**Photovoltaic performance.** To evaluate the photovoltaic performance of the TNAs and HNTs, the as synthesized products were applied as photoanode for DSSCs applications. Since the TiO\(_2\) nanowire nanoarrays based DSSC has been previously investigated \(^{35}\), which also has different length with the TNAs or HNTs, hence the commercial P25 nanoparticle with ~8 μm in thickness was used here as comparison. The J-V curves and corresponding detailed photovoltaic performance parameters of the DSSCs based on the three photoelectrodes (P25, TNAs and HNTs) are shown in Fig. 5a and Table 1. Evidently, the DSSCs assembled with the TNAs or HNTs film photoelectrode demonstrated higher power conversion efficiency than that of P25 photoelectrode. Specifically, it reveals that the TiO\(_2\) photoelectrode made from TNAs shows a short-circuit current density \(J_\text{sc}\) of 7.46 mA cm\(^{-2}\) and a photovoltage \(V_\text{oc}\) of 839 V with a PCE of 4.66%, and TiO\(_2\) photoelectrode made from HNTs shows a \(J_\text{sc}\) of 10.02 mA cm\(^{-2}\) and a \(V_\text{oc}\) of 817 V with a PCE of 5.84%, whereas P25 NP cell only
gives a $J_{sc}$ of 6.91 mA cm$^{-2}$ and a $V_{oc}$ of 807 V with a PCE of 4.17%. Obviously, the enhancement of photovoltaic performance for TNAs or HNTs based DSSCs compared with P25 NP based DSSCs is due to the improvement of $J_{sc}$ and $V_{oc}$. Despite that P25 NP photoelectrode exhibits the higher amount of dye uptakes (66.06 nmol cm$^{-2}$) than that of TNAs (61.11 nmol cm$^{-2}$) and HNTs (65.61 nmol cm$^{-2}$), the enlargement of $J_{sc}$ can be mainly attributed to the superior light scattering ability and fast electron transport for TNAs and HNTs based DSSC (seen in subsequent UV-vis and IMPS measurement). Clearly, the reflectance of the films made of TNAs or HNTs film are higher than that of the traditional P25 film in the wavelength range from 400 to 800 nm (seen in Fig. 5c), emphasizing the improvement of light scattering capabilities in this kind of novel vertically aligned photoanode. In addition, Fig. 5b shows the IPCE as a function of wavelength for those three cells. It is well known that IPCE was dominated by light-harvesting efficiency, quantum yield of electron injection and the efficiency of collecting the injected electrons. Compared to P25 NP cell, the IPCE of TNAs or HNTs increase from 30% to 42% or 64% at 520 nm, respectively. The film of both TNAs and HNTs has a higher IPCE from 450 nm to 700 nm wavelength range than P25 film, which correlate well with the increased photocurrent density for the former. The enhancement of the $J_{sc}$ for TNAs based DSSCs can be attributed to the following features: (i) For TNAs consisting of TiO$_2$ truncated octahedrons with exposed [001] facets, the crystals with [001] facets exposed electrode exhibited a great advantage in the light harvesting performance, since the anatase [001] surfaces with high surface energy can increase the electronic coupling between the dyes sensitizer and the TiO$_2$ and favour electron injection from the excited state of sensitizer in to TiO$_2$ conduction band$^{34,35}$. (ii) The unique vertically aligned structure built from random stacking with large particle sizes and exposed [001] facets can effectively minimize the grain interface effect and thus reduce the electron loss, leading to higher charge collection efficiency$^{20}$. Compared with TNAs based DSSCs, further enhancement of $J_{sc}$ for HNTs film can be attributed to larger amount of dye uptakes and better light scattering ability, because HNTs possess tube structure with a comparable larger inner diameter, which can utilize the light in a multi-reflections mode, leading to the enhancement of the light harvesting efficiency. As seen in Fig. 5c, in the light wavelength range of 400–800 nm, HNTs films depicted strongest light-scattering effects, which would improve the light-harvesting efficiency resulting in a higher $J_{sc}$.

Charge transfer dynamics. In order to acquire better insight into dynamics of interfacial charge transfer process within the DSSCs, electrochemical impedance spectroscopy (EIS) was carried out for the DSSCs based on different photoanodes in the dark under a forward bias of $\approx$−0.82 V. $J$-$V$ characteristics show that TNAs or HNTs based cell exhibits higher $V_{oc}$ value compared to P25 NPs cell. Generally, it is believed that the $V_{oc}$ value is quite sensitive to the recombination resistance and electron lifetime in the conduction band of TiO$_2$$^{36,37}$. Figure 6a depicts the Nyquist plots of DSSCs based on above three photoelectrodes. The larger semicircles in the Nyquist plots are attributed to the electron recombination at TiO$_2$/dye/electrolyte interface, and the recombination resistance ($R_2$) as well as electron lifetime ($\tau_e$) were analyzed by Z-view software using an equivalent circuit (summarized in Table 1). As seen in Fig. 6a and Table 1, the results illustrate that the recombination resistance ($R_2$) of cell TNAs (137.6 $\Omega$) or HNTs (103.7 $\Omega$) is larger than that of cell P25 (70.26 $\Omega$), indicating a slower electron recombination process for TNAs or HNTs based DSSCs. And this can be ascribed to their unique one-dimensional structure which provide a direct pathway for facilitating electron transport and thus reduce recombination reaction. Moreover, the cell TNAs possesses the longest electron lifetime (~76 ms), which is agreement with the highest open circuit voltage for the DSSC based on such kind of photoelectrode. This reflects lower trap state density existing within TNAs based DSSC leading to slower recombination reaction, which is mainly due to the fact that there is fewer grain boundaries and surface defects existing in vertically aligned TiO$_2$ nanostructure arrays (TNAs) consisting of TiO$_2$ truncated octahedron nanocrystals with exposed [001] facets based film framework$^{34}$.

| Cell  | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (mV) | $\eta$ (%) | $FF$ | Dye adsorption (nmol cm$^{-2}$) | $R_2$ (ohm) | $\tau_e$ (ms) |
|-------|------------------------|--------------|-----------|------|-------------------------------|--------------|-------------|
| P25   | 6.91                   | 807          | 4.17      | 0.75 | 66.06                         | 70.26        | 57.0        |
| TNAs  | 7.46                   | 839          | 4.66      | 0.75 | 61.11                         | 137.6        | 76.0        |
| HNTs  | 10.02                  | 817          | 5.84      | 0.72 | 65.61                         | 103.7        | 68.0        |

Figure 5 | Photovoltaic characteristics using P25 and as-prepared TNAs and HNTs samples as photoanode. (a) Photocurrent density ($J_{sc}$) - photovoltage ($V_{oc}$) characteristics of DSSCs composed of P25, TNAs and HNTs photoelectrodes measured under AM 1.5 G one sunlight (100 mW cm$^{-2}$) illumination. (b) IPCE spectra of DSSCs based on P25, TNAs and HNTs photoanodes. (c) Diffused reflectance spectra of P25, TNAs and HNTs with similar film thickness of around 8 µm.
Intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) have been further employed to probe the electron transport and charge recombination dynamics within DSSCs based on P25, TNAs and HNTs photoelectrode under different incident light intensities. Figure 6b presents the plots of time constant including electron transport time (IMPS) and electron lifetime (IMVS) as a function of light intensity. Notably, all time constant decreases with increasing light intensity due to a larger injected electron density at a higher light intensity. An obvious discrepancy in both electron transport time and electron life time is observed. Specifically, as compared with P25 based cell, the electron transport time is shorter in DSSCs based on TNAs or HNTs film, which means faster electron transport rate within the TNAs or HNTs cells. This is mainly attributed to the one-dimensional structures of TNAs or HNTs film, in which the electron can transit through an ordered direction and the grain boundaries would decrease significantly when compared with P25 nanoparticles, and thus facilitate electron transport in the film. Moreover, the electron lifetime for DSSCs based on TNAs or HNTs film is lengthened, which is quite consistent with above EIS results. And the electron lifetime decreases in an order of TNAs, HNTs and P25 (IMVS and EIS) correlates with the continuing decreased $V_{OC}$. Among which, the TNAs film consisting of truncated octahedron nanocrystals with exposed [001] facets showcase the longest electron lifetime (slowest charge recombination) and shortest electron transport time. The fact can be explained by following facts. Firstly, the TNAs with reactive surface facet [001] of the TiO$_2$ exposed are believed to effectively decrease the surface trap sites and recombination centers for the efficient electron transport and suppress charge recombination. Secondly, adjacent truncated octahedrons are considered to be linked together in a manner of one by one with the exposed high surface energy [001] facets, leading to superior interparticle connectivity and conductivity and thus would possibly reduce the occurrence possibility of charge recombination during the electron transport process. Thirdly, with reactive facet [001], the dye molecules were favorably adsorbed on the energy active [001] facet rather than deleterious extrinsic surface states including large amount of trap sites, where photoelectrons can be trapped or recombined with $I_3^–$ in the electrolyte. Therefore, recombination was suppressed and longer electron lifetime (higher $V_{OC}$) was obtained in DSSC based on TNAs films. Overall, the enhancement of power conversion efficiency for the TNAs or HNTs based cell compared with P25 based cell can be attributed to superior light scattering capability for boosting light-harvesting efficiency and faster electron transport as well as slower charge recombination rate within DSSCs due to unique one-dimensional nanostructure for efficient electron transport. The present work opens up a promising avenue for the fabrication of such novel one-dimensional single crystalline TiO$_2$ nanostructured arrays composed of the nanocrystals with well-defined facets on flexible metal substrate and we anticipate that this method could be transplanted to other substrates for potentially high-efficiency DSSCs or QDSSCs.

Discussion

We demonstrate a simple hydrothermal process to prepare single crystalline anatase TiO$_2$ nanostructure arrays (TNAs) consisting of TiO$_2$ truncated octahedrons with exposed [001] facets and hierarchical TiO$_2$ nanotubes (HNTs) consisting of numerous nanocrystals by hydrothermal treatment of H-titanate nanowire precursors in the presence of NH$_4$F aqueous solution. To the best of our knowledge, it is the first report on fabricating such vertically aligned TiO$_2$ nanoarrays on Ti foil substrate and their application in DSSCs. The DSSC based on such TNAs or HNTs film showed an impressive power conversion efficiency of 4.66% and 5.84%, respectively, which is higher than that of P25 based cell (4.17%). The detailed investigations of UV-vis reflectance, IMPS, IMVS and EIS revealed the enhancement of $J_{SC}$, $V_{OC}$ and $\eta$ for TNAs, HNTs based cell compared with P25 based cell can be attributed to superior light scattering capacity for boosting light-harvesting efficiency and faster electron transport as well as slower charge recombination rate within DSSCs. Moreover, the electron lifetime for DSSCs based on TNAs or HNTs film is lengthened, which is quite consistent with above EIS results. And the electron lifetime decreases in an order of TNAs, HNTs and P25 (IMVS and EIS) correlates with the continuing decreased $V_{OC}$. Among which, the TNAs film consisting of truncated octahedron nanocrystals with exposed [001] facets showcase the longest electron lifetime (slowest charge recombination) and shortest electron transport time (fastest electron transport). The fact can be explained by following facts. Firstly, the TNAs with reactive surface facet [001] of the TiO$_2$ exposed are believed to effectively decrease the surface trap sites and recombination centers for the efficient electron transport and suppress charge recombination. Secondly, adjacent truncated octahedrons are considered to be linked together in a manner of one by one with the exposed high surface energy [001] facets, leading to superior interparticle connectivity and conductivity and thus would possibly reduce the occurrence possibility of charge recombination during the electron transport process. Thirdly, with reactive facet [001], the dye molecules were favorably adsorbed on the energy active [001] facet rather than deleterious extrinsic surface states including large amount of trap sites, where photoelectrons can be trapped or recombined with $I_3^–$ in the electrolyte. Therefore, recombination was suppressed and longer electron lifetime (higher $V_{OC}$) was obtained in DSSC based on TNAs films. Overall, the enhancement of power conversion efficiency for the TNAs or HNTs based cell compared with P25 based cell can be attributed to superior light scattering capability for boosting light-harvesting efficiency and faster electron transport as well as slower charge recombination rate within DSSCs due to unique one-dimensional nanostructure for efficient electron transport. The present work opens up a promising avenue for the fabrication of such novel one-dimensional single crystalline TiO$_2$ nanostructured arrays composed of the nanocrystals with well-defined facets on flexible metal substrate and we anticipate that this method could be transplanted to other substrates for potentially high-efficiency DSSCs or QDSSCs.

Methods

Preparation of hydrogen-exchanged Titanate nanowire arrays. Sodium titanate nanowires were firstly prepared by alkali hydrothermal growth process of titanium foil in NaOH solution. Typically, a piece of titanium foil (2.5 × 3.0 cm$^2$) was ultrasonically cleaned in water, acetone and ethanol for 15 min, respectively, and then placed against the wall of a 50 mL Teflon-lined stainless steel autoclave filled with 30 mL 1 M NaOH aqueous solution. After that, the sealed autoclave was kept inside in an electric oven at 220 °C for 24 h. After the first-step hydrothermal reaction, titanium foil covered with sodium titanate nanowire was immersed in 0.1 M HCl solution for 10 min to replace Na$^+$ with H$^+$. Finally, the obtained H-titanate were rinsed with deionized water, pure ethanol and dried in ambient conditions.

Synthesis of TiO$_2$ nanoarrays with different structures. In a typical experiment, the as-prepared H-titanate nanowire was placed into a 50 mL Teflon-lined autoclave containing 40 mL deionized water or with the addition of 0.1 M ammonium fluoride (NH$_4$F) as shape-capping reagents. The autoclave was heated at 200 °C for 24 h. After naturally cooling to room temperature, the obtained vertically oriented anatase TiO$_2$ nanostructure arrays (TNAs) consisting of TiO$_2$ nanocrystals with exposed [001] facets (in the presence of 0.1 M NH$_4$F) or hierarchical TiO$_2$ nanotubes (HNTs)
consisting of numerous octahedrons with round edges (in the absence of NH4F) on Ti-foil substrate were taken out from the solution and subsequently rinsed with deionized water and ethanol.

Preparation of TiO2 photoanode. The as-prepared TNA consisting of TiO2 nanocrystals with exposed [001] facets or HNTs consisting of numerous nanocrystals were soaked in 0.04 M TiCl4 aqueous solution for 30 min at 70 °C. After sintering at 520 °C for 30 min, the TiO2 photoelectrode films were immersed into 0.5 mM N719 dye ([Ru(NC)2(npy)]2+ · 2·2·2-bipyridyl), 4·4·4′-tetrabutylammonium carboxylate, Solaxon®) in acetonitrile/tert-butanol (volume ratio 1 : 1), and sensitized for about 16 h at room temperature. Afterward, these films were rinsed with acetonitrile in order to remove physical adsorbed N719 dye molecules. The active area of the TiO2 photoelectrode film was approximately 0.16 cm2.

Fabrication of Dye-sensitized solar cell. To investigate their photovoltaic performance, the as-prepared TNA/Ti and HNTs/Ti were use to fabricate dye-sensitized solar cells with Pt-coated FTO glass as counter electrode in a sandwich-type. Platinitized counter electrodes were fabricated by thermal depositing of H2PtCl6 solution (5 mM in isopropanol) onto FTO glass at 400 °C for 15 min. For comparison, reference P25 TiO2 photoanode based DSSCs on Ti-foil substrate with a similar thickness (≈8 μm) was prepared via screen-printing process. Meanwhile, Ti/In2O3-based liquid electrolyte containing 0.6 M 1-methyl-3-propylimidazolium iodide (PMII), LiI (0.05 M), 0.10 M guanidinium thiocyanate, 0.03 M I2, 0.5 M tertbutylpyridine in acetonitrile and valeronitrile (85 : 15) was injected into the space between the photoanode and counter electrode.

Characterization. The phase purity of the as-prepared products was characterized by X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). The Field emission scanning electron microscopy (FE-SEM, JSM-6330F), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEO-L-2010 HR transmission electron microscope to characterize the morphology, size and the crystalline structure of the samples. The current-voltage characteristics (open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF), and power conversion efficiency (η)) were performed using a Keithley 2400 source meter under simulated AM 1.5 G illumination (100 mW cm–2) provided by a solar light simulator (Oriel, Model: 91192). The incident light intensity was calibrated with a NREL-calibrated Si solar cell. The IPCE spectra were measured as a function of wavelength from 400 to 800 nm on the basis of a Spectral Products DK240 monochromator. To measure the adsorbed dye amount and the reflectance of the TiO2 films, diffuse reflectance spectra and absorption spectra of desorbed-dye solution from the as-prepared films (dyed-adsorbed TiO2 film was immersed in 0.1 M NaOH aqueous solution) were measured on a UV/Vis-NIR spectrophotometer (UV-3150). The electrochemical impedance spectra (EIS) were conducted with an electrochemical workstation (Zahner, Zennium) at a bias potential of −0.82 V in a dark with the frequency range from 10 mHz to 1 MHz. The magnitude of the alternating current was 10 mV. The Nyquist plot of the □-shape electrode (IMVS) and intensity-modulated photocurrent spectroscopy (IMPS) measurements were also performed on an electrochemical workstation (Zahner, Zennium) in a frequency range from 1 KHz to 0.1 Hz. The impedance parameters were determined by fitting of the impedance spectra with Z-view software.
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**Author contributions**

W.Q.W. and D.B.K. proposed and designed the experiments. W.Q.W. carried out the synthetic experiments and conducted the characterization. H.S.R., Y.F.W. and Y.F.X. performed the HRTEM, SEM characterization and structural analysis. W.Q.W. and D.B.K. analysed the data. W.Q.W., D.B.K. and C.Y.S. wrote the manuscript. All the authors participated in discussions of the research.

**Additional information**

Competing financial interests: The authors declare no competing financial interests.

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