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# Hierarchical Nanostructures of Metal Oxides for Enhancing Charge Separation and Transport in Photoelectrochemical Solar Energy Conversion Systems

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Photoelectrochemical solar energy conversion systems, including photoelectrochemical water splitting and photoelectrochemical solar cell (dye-sensitized solar cells, DSSCs), are under intensive development aiming at efficiently harvesting and utilizing solar energy. Metal oxides carved into hierarchical nanostructures are thought to be promising for improving photoelectrochemical performance by enhancing charge separation and transport. Herein, we review the recent progress in the research on the design and applications of metal oxide hierarchical nanostructures in water splitting and DSSCs systems with a view to understanding how they improve the device performance in terms of the enhanced charge separation and transport properties. This review will end with a conclusion on the metal oxide hierarchical nanostructures together with potential future research directions thereof.

## 1. Introduction

As a clean and inexhaustible energy source, solar energy is the most important alternative to non-renewable fossil fuels to solve the problems of energy shortage, global warming and environmental pollution. The key issue is how to efficiently harvest and utilize solar energy. Photoelectrochemical (PEC) solar energy conversion is regarded as one of the most promising technologies for solar energy conversion and application<sup>1-7</sup>. There are mainly two embodiments of the PEC solar energy conversion, as defined in Ref. 7: PEC water splitting and PEC solar cell. The PEC water splitting system is aimed to convert solar energy into chemical energy in terms of fuels such as H<sub>2</sub><sup>7-10</sup>. On the other hand, the PEC solar cell system, such as dye-sensitized solar cells (DSSCs) and quantum dot-sensitized solar cells (QDSCs)<sup>7,11,12</sup>, directly converts solar energy to electric energy. Thus far, much progress has been made from both fronts on PEC water splitting and PEC solar cells, primarily driven by the rapid advance of nanomaterials and nanotechnologies.

What the PEC water splitting and PEC solar cells systems have in common are the main device structure and working principle<sup>6,7</sup>. In particular, photoelectrodes are at the core of these devices, which absorb light to generate electrons and holes, and sequentially separate and transport these charges<sup>8,12</sup>. Metal oxide semiconductors (such as TiO<sub>2</sub>, ZnO, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, BiVO<sub>4</sub>, etc.) are widely explored and used

for the photoelectrodes, or more precisely photoanodes, because of their suitable semiconducting properties, high stability, material abundance and facile nanostructuring<sup>13,14</sup>. The charge separation and transport processes occurring at the photoelectrode/electrolyte interface and within the photoelectrode, respectively, are critical to device performance, which in turn greatly depends on the structure and morphology of the metal oxide semiconductor<sup>7,8,12,15</sup>. In principle, a large contact area between the photoelectrode and the electrolyte is necessary to increase the areal density of separated electron-hole pairs generated from photoabsorption. Following this line of thinking, nanoparticle building blocks with high surface-to-volume ratio are used to construct the photoelectrode<sup>11,15</sup>. However, the catch is that the small nanoparticle size is associated with numerous surface states and grain boundaries, which would hinder electron transport within the photoelectrode<sup>15-17</sup>.

Confronted by the conflicting issue of the nanoparticle photoelectrode, researchers have resorted to the integral nanostructure design that can ensure both a high surface area and good charge transfer/transport. In this context, well-aligned nanoarrays have been exploited as a general photoelectrode structure, including nanowire<sup>18-21</sup>, nanorod<sup>22-27</sup>, nanotube<sup>28-32</sup> and nanosheet<sup>33-38</sup> arrays, which efficiently shortened the electron transport path for charge collection. The improved electron transport is due to the single-crystalline nanounits in the nanoarrays and the elimination of grain boundaries<sup>12,15,25</sup>. It should be pointed out that such nanoarray photoelectrodes are still limited by their relatively low surface area for charge separation and/or sensitizer deposition, arising from the difficulty in controlling the packing density and the size parameters of the nanounits<sup>1,15</sup>. In the last few years, researchers started to focus on constructing hierarchical

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nanostructures in the interest of a large surface area for maximizing charge separation without compromising the electron transport rate. These hierarchical nanostructures are commonly composed of the trunks (highway transport) with high charge transport rate and the branches with high surface-to-volume ratio (local transport)<sup>15,39-41</sup>.

This review article attempts to document the important research progress in the last few years on the hierarchical nanostructures of metal oxides for PEC solar energy conversion systems. Because of the breadth of the area, we are obliged to be selective by focusing on unique hierarchical nanostructural designs for enhancing charge separation and transport. Therefore, many important works on metal oxide hierarchical nanostructures may be unfortunately omitted here, for which we refer the readers to other relevant review articles<sup>1,39,41-49</sup>. In addition, since QDSCs themselves have formed a new branch with a similar working principle to DSSCs as well as similar nanostructures, they are not included in this review, and interested readers are referred to some recent reviews in this area<sup>49-52</sup>.

In the following, we will start by briefly introducing the working principles of the hierarchical nanostructure photoelectrodes in PEC solar energy conversion systems with emphasis on the charge separation and transport behaviors. Then the most recent research progresses on the metal oxide hierarchical nanostructures for PEC water splitting and DSSCs will be sequentially presented and discussed. Finally, we will draw a conclusion and present potential future research directions for higher performance metal oxide hierarchical nanostructure photoelectrodes.

## 2. PEC Solar Energy Conversion with Metal Oxide Hierarchical Nanostructures

The general working principles for the PEC solar energy conversion systems (water splitting and DSSCs) are rather similar. Figure 1 illustrates the charge separation and transport processes together with the energy level diagrams for the PEC water splitting and DSSCs systems with an n-type oxide semiconductor. In the water splitting system (Figure 1(A)), photons with an energy exceeding the band gap of oxides generate electron-hole pairs, which are separated by the electric field present in the space-charge layer<sup>7</sup>. Electrons move across the oxide semiconductor to the current collector and reach the counter electrode through external circuit to reduce water to H<sub>2</sub>, while holes are driven toward the surface to oxidize water to O<sub>2</sub><sup>8</sup>. Therefore, the electron transport in oxide semiconductor and the hole transfer across the surface of oxide semiconductor are two important processes in the water splitting photoelectrode. Clearly, a rapid electron transport and efficient hole transfer will reduce charge recombination loss, which are consequently prerequisite for designing high performance water splitting devices.

In the DSSCs system, as shown in Figure 1(B), dye molecules are used as sensitizers to harvest sunlight. In the photoelectrode, therefore, photons are mainly absorbed by

the sensitizers to generate electron-hole pairs<sup>11,12</sup>. The electrons are then injected into the conduction band (CB) of oxide semiconductor and transport toward counter electrode through external circuit to reduce the oxidized form of redox relay molecules (I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple<sup>11,12</sup>), while holes are scavenged at the surface by the reduced form of the redox relay molecules. In this kind of system, the processes of the electron injection to and transport in the oxide semiconductor and the hole transfer to electrolyte should be all efficient to avoid charge recombination losses and thereby obtain an overall high-performance. Fortunately, the charge separation (electron injection into metal oxide and hole extraction by electrolyte) in DSSCs are commonly efficient due to the monolayer of dyes separating the two parts and the judicious design of dye molecules. Thus the remaining critical issue for device performance is electron transport in the metal oxide semiconductor. A faster electron transport would lead to a lower recombination between energetic electrons in the metal oxide and the electrolyte and thus a higher device performance.

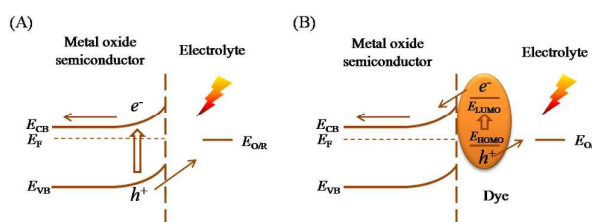


Figure 1. Schematic illustrating the charge separation and transport processes in photoelectrochemical solar energy conversion systems: (A) PEC water splitting and (B) DSSCs systems.  $E_{CB}$ ,  $E_{VB}$  and  $E_F$  represent the bottom of the conduction band (CB), the top of the valence band (VB), and the Fermi level of oxide semiconductor, respectively, while  $E_{O/R}$  represents the energy level of the water oxidation or the regenerating species in the electrolyte.

In photoelectrochemical systems, a large specific surface area is usually necessary for the photoelectrodes to achieve high performance because it will provide ample sites for separating the photogenerated charges in water-splitting devices and for dye loading in DSSCs. Therefore nanostructured photoelectrodes are usually adopted. Figure 2 illustrates three typical oxide nanostructure photoelectrodes used in photoelectrochemical systems and their corresponding charge transfer and transport behaviors. The first photoelectrode consists of randomly assembled nanoparticles (NPs), in which a large surface area (a specific surface area of 780 cm<sup>2</sup> per cm<sup>2</sup> of geometric surface for the film fabricated by 15 nm NPs)<sup>7,41</sup> could afford numerous charge separation sites at the photoelectrode/electrolyte interface for water-splitting devices and allow to deposit a large amount of sensitizers for DSSCs. However, charge transport in such NP electrode is greatly limited due to the presence of numerous grain boundaries and high surface state density. For example, the electron diffusion coefficient ( $D_n$ ) of a TiO<sub>2</sub> NP film is about 5×10<sup>-5</sup> cm<sup>2</sup>/s, which is several orders of magnitude lower than

that of a single crystalline  $\text{TiO}_2$  ( $0.4 \text{ cm}^2/\text{s}$ ), and hence limits its diffusion length ( $L_n$ ) to about  $7\text{--}30 \mu\text{m}$ <sup>53–55</sup>.

The second photoelectrode is made of nanoarrays, in which well-aligned and/or single-crystalline nanostructures would favor the charge transport. Indeed, a diffusion length  $L_n$  up to  $100 \mu\text{m}$  has been reported for such nanoarrays<sup>56</sup>. However, the remaining challenge is the relatively low surface area of such nanoarrays which is insufficient for efficiently separating the photogenerated charge carriers and for depositing a large amount of dyes. This challenge can be taken up by the third photoelectrode, which is characterized by hierarchical nanostructures such as branched-nanoarrays. In a hierarchical nanostructure, the trunk can act as a rapid charge transport pathway while the branches outreach to increase the interfacial charge separation and/or dye deposition. Therefore, in the photoelectrochemical systems, the hierarchical nanostructures are usually designed to increase the surface area of nanoarray photoelectrodes but without obviously compromising their charge transport rates. By careful design, such hierarchical nanostructures should be able to achieve higher performance than the NP and nanoarray counterparts. Up to now, the nanoarrays have been extended to nanorod (NR), nanowire (NW), nanotube (NT), nanosheet (NS) and nanotetrapod (NTP) arrays, while branched arrays have comprised nanounits of NP, NR, NW, NT and NS.

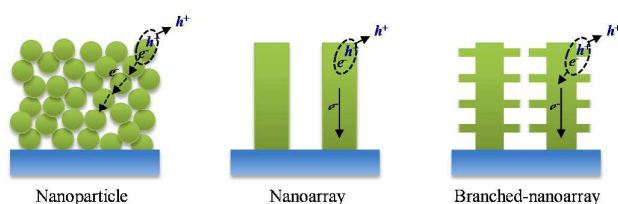


Figure 2. Schematic illustrating the three typical photoelectrodes and their corresponding charge separation/transport behaviors.

### 3. Hierarchical Nanostructures in water splitting systems

We focus on PEC water splitting systems using metal oxides as the photoelectrode for both light absorption and charge transfer/transport. As mentioned above, charge separation in a NP film is commonly efficient. However, charge transport in NP film is obviously limited by the large number of grain boundaries. In fact, in addition to the low charge transport rate, another serious problem faced by NP films is their significantly lower light scattering capacity than nanoarray films and hence the much lower light absorptivity, as shown in Figure 3<sup>57</sup>. As a result, NP films usually give a considerably lower water splitting performance than NR films.

However, the small surface area of a nanoarray film due to its large unit size means limited sites for driving the charge separation processes, compromising the water splitting performance, especially when water oxidation kinetic is sluggish. This becomes more serious for metal oxides with

short hole diffusion lengths ( $L_n$ ), such as  $\alpha\text{-Fe}_2\text{O}_3$  ( $L_n = 2\text{--}4 \text{ nm}$ )<sup>58</sup> and  $\text{BiVO}_4$  ( $L_n = 70\text{--}100 \text{ nm}$ )<sup>59</sup>. Therefore, it is highly desirable to increase the surface area of the nanoarrays for efficient charge separation, and building branching nanoarrays with small nanounits is widely thought to be a promising strategy in that direction.

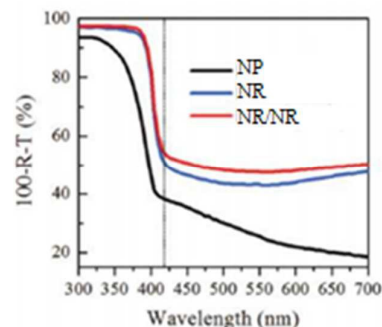


Figure 3. Light absorption plus scattering curves of the  $\text{TiO}_2$  NP, NR, and NR/NR in the wavelength range from 300 nm to 700 nm. Reproduced with permission from ref. <sup>57</sup>.

#### 3.1 Branched-1D nanoarray photoelectrodes

1D nanoarrays are the most common kind of nanoarrays that provide a direct and rapid electron transport pathway toward the collection substrate, and over the past few years, branching 1D nanoarrays widely explored in water splitting systems. In 2011, Zheng et al. first applied branched- $\text{TiO}_2$  NR (NR/NR) arrays for water splitting and systematically compared the performance of NP, NR, and NR/NR photoelectrodes, which are illustrated in Figure 4(A)<sup>57</sup>. Both the NR trunk and NR branches were prepared by seed-assisted hydrothermal method using FTO and FTO/NRs as substrates, respectively, which were both single-crystalline rutile  $\text{TiO}_2$ . As indicated in Figures 4(B), the needle-shaped NR branches with about 50 nm long and 10 nm wide were grown uniformly on the NR trunks whose diameter was about 100 nm. After branching, the roughness factor of NR/NR was greatly increased from 32 to 130, though were still lower than that of NP film (210).  $\text{TiO}_2$  NRs and NR/NRs exhibited similar light absorption property, obviously higher than  $\text{TiO}_2$  NPs, especially at  $\lambda < 420 \text{ nm}$ , as shown in Figure 3, due to the enhanced light scattering between NRs. From the  $J$ - $V$  curves in Figure 4(C), the photocurrent densities of the NPs, NRs, and NR/NRs are 0.01, 0.31 and  $0.83 \text{ mA}/\text{cm}^2$  at 0.8 V (vs. RHE), respectively. The very low photocurrent density for NPs was thought to be due to the low light absorption and slow charge transport. The  $J$ - $V$  curve for  $\text{TiO}_2$  NR/NRs exhibits a steeper increase in current as the potential scanning in positive direction with a saturated photocurrent density at 0.6 V (vs. RHE), suggesting the much more efficient charge separation and transport.

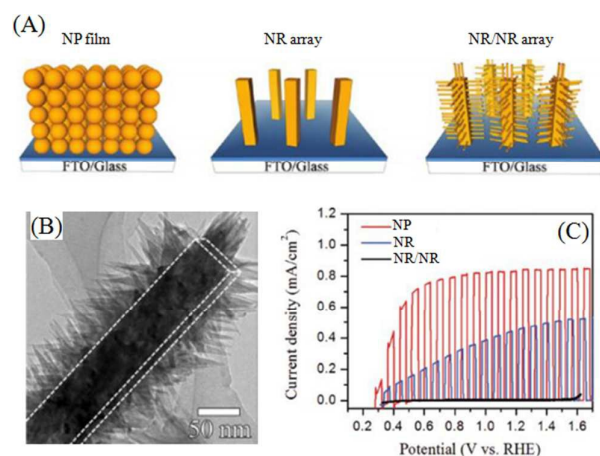


Figure 4.  $\text{TiO}_2$  NR/NR nanostructure arrays as water splitting photoelectrodes. (A) Schematic description of  $\text{TiO}_2$  NP, NR, and NR/NR photoelectrodes. (B) TEM image of  $\text{TiO}_2$  NR/NR nanostructure. (C) Chopped  $J$ - $V$  curves under the Xenon lamp (UV portion of spectrum matched to AM 1.5G, 88  $\text{mW}/\text{cm}^2$ ) illumination. Reproduced with permission from ref. <sup>57</sup>.

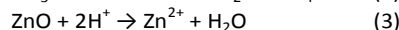
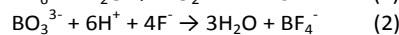
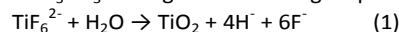
Besides branched- $\text{TiO}_2$  NR arrays, branched- $\text{ZnO}$  NR arrays ( $\text{ZnO}$  NR/NR) were also fabricated and tested as water splitting photoelectrodes<sup>60</sup>. Similarly, a two-step seed-assisted hydrothermal method was exploited for NR trunk and NR branch growth. The  $\text{ZnO}$  NR/NR photoelectrode exhibited more than twice the photocurrent density of the  $\text{ZnO}$  NR photoelectrode at 1.2 V (vs. Ag/AgCl) under one-sun illumination. The highest solar-to-hydrogen conversion efficiency (STH) value for  $\text{ZnO}$  NR/NR photoelectrode was 0.299 %, obviously higher than that of  $\text{ZnO}$  NR photoelectrode (0.236 %). Therefore, branched-1D nanoarrays have well proved to be promising photoelectrode structures for water splitting.

### 3.2 Branched-nanotetrapod hierarchical nanostructures.

In addition to 1D nanoarrays, other nanostructures have also been exploited as trunks for oxide hierarchical nanostructures. Nanotetrapod (NTP) is one of the promising trunk structures, which consist of four rod-shaped nanostructures joining at a central core with tetrahedral angles. Size-tunable  $\text{ZnO}$  NTPs were successfully synthesized in our laboratory in 2007<sup>61</sup> and recently, we explored them to construct various types of photoelectrodes<sup>62-66</sup>. However,  $\text{ZnO}$  NTP alone is still limited by the small surface area. In order to solve this problem, we further branched  $\text{ZnO}$  NTP for water splitting systems<sup>67</sup>. Figure 5(A) shows the structure and charge generation, transfer and transport processes of a branched tetrapod array electrode<sup>1</sup>. NR branches increased the surface area for enhancing charge separation and NTP served as the charge transport pathway. For the construction,  $\text{ZnO}$  NTP film was first prepared by a doctor-blade method and a seed-assisted hydrothermal process was exploited to grow NR branches on the NTP trunks. However, the surface of NTP was really smooth, which made it hard to deposit  $\text{ZnO}$  seeds by simply coating seed solution. Therefore, an etching method was used to in-situ produce

seeds on the NTP trunks<sup>68</sup>. Figure 5(B) illustrated the typical final morphology of  $\text{ZnO}$  NTP/NR photoelectrode. The  $J$ - $V$  curves in Figure 5(C) indicated that the  $\text{ZnO}$  NTP photoelectrode only got a photocurrent density of 0.046  $\text{mA}/\text{cm}^2$  at 0.31 V (vs. Ag/AgCl) under one-sun illumination, while  $\text{ZnO}$  NTP/NR photoelectrode promoted the photocurrent density to 0.12  $\text{mA}/\text{cm}^2$  at 0.31 V (vs. Ag/AgCl). The increase in the surface area for NTP/NR photoelectrode was the main reason for the improvement in photocurrent density, which could enhance the charge separation at the photoelectrode/electrolyte interface. After being doped with N element, the photocurrent density was further increased up to 0.99  $\text{mA}/\text{cm}^2$  at 0.31 V (vs. Ag/AgCl) due to the enhanced light absorption and utilization in visible region.

Recently, we also synthesized and exploited hollow  $\text{TiO}_2$  NTP/NR hierarchical nanostructures as water splitting photoelectrodes. The synthesis was achieved by dissolution and nucleation processes on a  $\text{ZnO}$  NTP template<sup>69</sup>. The reaction was conducted in an aqueous solution containing  $(\text{NH}_4)_2\text{TiF}_6$  and  $\text{H}_3\text{BO}_3$  through the following steps<sup>70,71</sup>:



The dissolution of  $\text{ZnO}$  in the midst of  $\text{TiO}_2$  deposition led to a hollow  $\text{TiO}_2$  NTP, as shown in Figure 5(D). Interestingly, tiny  $\text{TiO}_2$  NR branches about several nanometers in diameter and tens of nanometers in length were also generated on the hollow  $\text{TiO}_2$  NTP. As the water splitting photoelectrode, hollow  $\text{TiO}_2$  NTP/NR obtained obviously higher photocurrent density than NP counterparts regardless of substrates (Figure 5(E)). Besides, a steeper increase in current as the potential scanning in positive direction and a saturated photocurrent density at about 0.3 V (vs. RHE) was observed for hollow  $\text{TiO}_2$  NTP/NR, which was not observed for NP counterparts, well suggesting the much more efficient charge separation<sup>57</sup>. This should be attributed to the tiny  $\text{TiO}_2$  NR branches with sizes smaller than those of P25  $\text{TiO}_2$  NPs (about 20-30 nm in diameter). The charge transport characteristics of hollow NTPs/NR was also studied by the intensity modulated photocurrent spectroscopy (IMPS) technique and as shown in Figure 5(F), we obtained a shorter transport time (or transit time) for the  $\text{TiO}_2$  NTPs/NR photoelectrodes than that for the NP counterpart.

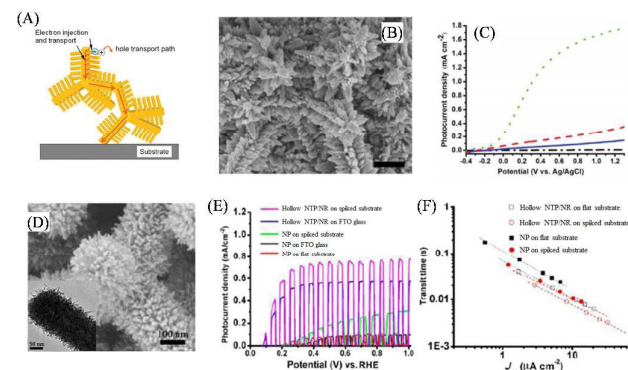


Figure 5. NTP-based hierarchical nanostructure as water splitting photoelectrode. (A) Schematic illustrating charge generation, transfer and transport in NTP/NR. Reproduced with permission from ref. 1. (B) SEM image of ZnO NTP/NR nanostructure. (C)  $J$ - $V$  curves of the ZnO NTP in the dark (dot-dashed line), ZnO NTP (solid line), ZnO NTP/NR (dashed line), and N-doped ZnO NTP/NR (dotted line). Reproduced with permission from ref. 67. (D) SEM image of hollow  $\text{TiO}_2$  NTP/NR. Inset was the TEM image. (E)  $J$ - $V$  curves and (F) transit time (transport time) of the water splitting photoelectrodes based on different nanostructures on different substrates. Reproduced with permission from ref. 69.

### 3.3 Treelike hierarchical nanostructures.

Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) with a band gap of 2.1 eV has attracted broad interest as a water splitting photoelectrode material because of its low-cost, earth-abundance and high theoretical STH of 14-17 %, corresponding to a photocurrent density of 11-14  $\text{mA}/\text{cm}^2$  under one-sun illumination<sup>72</sup>. However, its disadvantages are also obvious, such as a relatively low absorption coefficient, poor majority carrier conductivity and short diffusion length ( $L_D=2\text{-}4$  nm) of minority carriers, meaning that enhancing light absorption by increasing film thickness would result in serious charge recombination losses<sup>58</sup>. As such, nanostructure design strategy is important to increase light absorption without increasing hole transfer distances and electron transport pathway lengths. In 2006, Grätzel and coworkers developed the promising treelike  $\alpha\text{-Fe}_2\text{O}_3$  hierarchical nanostructures by the vapor phase deposition (VPD) method<sup>73</sup>. This treelike nanostructure is highly porous with the topmost nanocrystals about 20-40 nm in diameter for undoped  $\alpha\text{-Fe}_2\text{O}_3$  and 10-20 nm in diameter for Si-doped  $\alpha\text{-Fe}_2\text{O}_3$ , which could afford efficient charge separation. Oriented attachment of these nanocrystals during growth was thought to lead to the efficient charge transport. As a result, the Si-doped  $\alpha\text{-Fe}_2\text{O}_3$  treelike nanostructure achieved a photocurrent density of 2.2  $\text{mA}/\text{cm}^2$  at 1.23 V (vs. RHE) under one-sun illumination. And it was revealed that the VPD parameters (e.g., air flow rate) greatly influenced the oriented attachment of  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles in the treelike nanostructure, thus impacting the PEC performance. By increasing the air flow rate from the previous 2 L/min (2L photoelectrode) to 6 L/min (6L photoelectrode), the gas residence time was shortened and the particle/precursor ratio was reduced, resulting in a better adhesion between the particles while attached to the growing film. The better particle attachment has endowed the 6L photoelectrode with an obviously enhanced photocurrent density of over 3  $\text{mA}/\text{cm}^2$  while using  $\text{IrO}_2$  as the catalyst<sup>74</sup>.

Although that treelike nanostructure (especially the 6L photoelectrode) has achieved a promising performance, the structural characteristics of this hematite structure responsible for the performance most was not clear at the time. For example, the reason as to why the 2L and 6L photoelectrodes with similar morphologies exhibited the obviously different performances still need more in-depth investigations. To

clarify this issue, Warren et al. adapted a dark-field TEM (DF-TEM) in combination with conducting atomic force microscopy (C-AFM) to get the information about the correlation between the spatial distribution of crystalline and current-carrying domains<sup>75</sup>. The 2L and 6L photoelectrodes were chosen as the research subjects. Although the morphologies of the two samples were similar (Figure 6(A) and (B)), the water-splitting performance was significantly different, as mentioned above. According to DF-TEM results (Figure 6(C) and (D)), the nanocrystal aggregates in 2L photoelectrode had about 75% high-angle grain boundaries, significantly higher than that in 6L photoelectrode (18%). From the C-AFM results (current maps in Figure 6(E) and (F)), high-angle grain boundaries mainly decreased photocurrent by generating a potential barrier and hence blocking the transport of majority carrier between adjacent crystals. Therefore this study suggests that it is important to reduce the high-angle grain boundaries in nanocrystal aggregates to get high photocurrent.

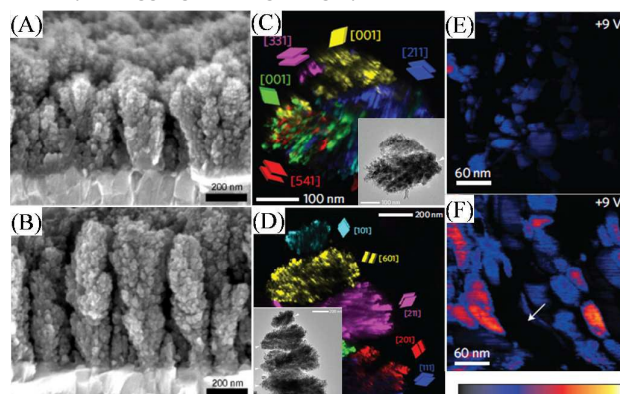


Figure 6.  $\text{Fe}_2\text{O}_3$  nanotree as water splitting photoelectrode. Cross-sectional SEM images of (A) 2L and (B) 6L photoelectrodes. Reproduced with permission from ref. 74. DF-TEM images of (C) 2L and (D) 6L photoelectrodes. Insets in (C) and (D) were the corresponding BF-TEM images. Each set of parallelograms defined the crystallographic orientation of the corresponding region of the DF-TEM. C-AFM current maps of (E) 2L and (F) 6L photoelectrodes at a tip-sample voltage of 9 V. The color scales represented a current variation from 0 (black) to 5 nA. Reproduced with permission from ref. 75.

### 3.4 Single-crystalline hierarchical nanostructures.

In the above, we have shown that branching 1D nanoarrays and NTP was an effective approach to promote water splitting performance. However, grain boundaries were present between the trunks and branches, which still limited the charge transport rate. In our recent work, we exploited an epitaxial growth strategy to eliminate the grain boundary between trunk and branches, which is actually also in the spirit of reducing the aforementioned high-angle grain boundaries. Specifically, the ZnO nanodisk (ND) was epitaxially grown on ZnO NW to form a single-crystalline ZnO NW/ND nanostructure, as illustrated in Figure 7(A). ZnO ND was epitaxially grown on NW by a modified hydrothermal process, in which sodium citrate was added into the reaction solution

as additive. As presented in Figure 7(B), ZnO NW was uniformly covered with tiny ND that was vertical to the NW. The ND was about tens of nanometers thick, which obviously increased the roughness factor from 219 to 363. The spotted electron diffraction pattern (Figure 7(C)) proved the single-crystalline structure of ZnO NW/ND, which was further supported by the coincident lattice fringes (such as (0001) planes) between NW and ND in the HRTEM image (Figure 7(D)). The formation of ND resulted from the absorption of citrate anions on the (0001) planes to form complexes with  $\text{Zn}^{2+}$  ions, which greatly suppressed the growth rate along the [0001] direction. And as a result, the ND had large exposed (0001) and (000-1) facets. The electron diffusion coefficients ( $D_n$ ) determined by IMPS technique (Figure 7(E)) indicated that at the same current density, the NW/ND had very close  $D_n$  with NW, suggesting that rapid charge transport property of NW was retained after single-crystalline branching. As water splitting photoelectrode, the single-crystalline ZnO NW/ND got a significantly higher photocurrent density than ZnO NW in the whole potential range (Figure 7(F)). The enhanced light utilization and the larger surface area (about 66 % enlargement) for charge separation in the single-crystalline ZnO NW/ND photoelectrode were the important causes. And the observation of a steeper increase in photocurrent density with respect to potential scanning and a saturated photocurrent density at 0.7 V (vs. Ag/AgCl) confirmed the much more efficient charge separation and collection in ZnO NW/ND photoelectrode. Besides, the polar facet of ZnO ND was also proposed to favor the charge separation at the interface.

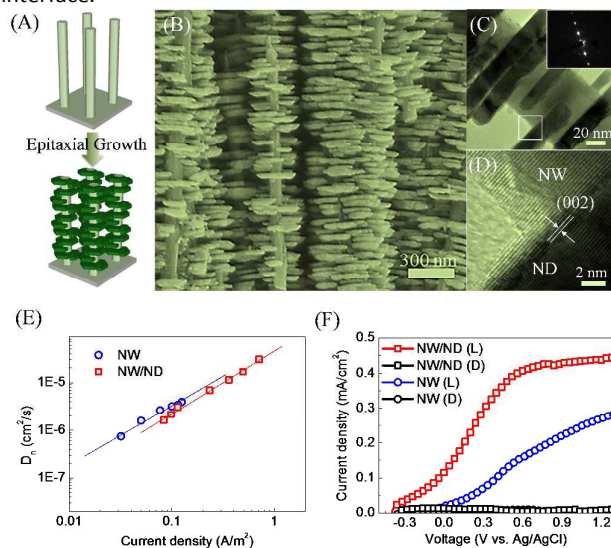


Figure 7. Single-crystalline ZnO NW/ND nanostructure as water splitting photoelectrode. (A) Schematic illustrating the epitaxial growth of ZnO ND on NW. (B) SEM, (C) TEM and (D) HRTEM images of single-crystalline ZnO NW/ND nanostructure. (E) Electron diffusion coefficient ( $D_n$ ) as a function of current density. (F)  $J$ - $V$  curves of ZnO NW/ND and ZnO NW obtained under dark (D) and one-sun illumination (L). Reproduced with permission from ref. <sup>76</sup>.

#### 4. Hierarchical Nanostructures in DSSCs system

In DSSCs, light absorption and electron transport are performed by a monolayer of dye molecules and the host metal oxides separately, and because of such a unique structure, the charge separation at the photoelectrode/electrolyte interface is typically rather efficient. Since a sufficient amount of dye molecules in the form of a monolayer is necessary to absorb most of the sunlight, the metal oxide electrode needs to have a large surface for dye loading and should be able to rapidly transport the injected electrons for collection while avoiding recombination. The commonly used NP films could offer large specific surface area but the film thickness was usually limited to about 10  $\mu\text{m}$  due to its poor electron transport property, resulting in low current densities which are about 55-75 % of their theoretical maximum value for full sunlight illumination<sup>12,21</sup>. The strategy to exploiting the long well aligned nanoarray whose electron diffusion length is considerably longer than that of NPs was not very successful because the large size of nanounits and large gaps between them compromised the specific surface area.

Hierarchical nanostructures were developed for DSSCs systems aiming to utilize small size branches to increase the specific surface of the nanoarray trunks without obviously sacrificing their electron transport rate. Such hierarchical nanostructures include  $\text{TiO}_2$ - and ZnO-based photoelectrodes, such as  $\text{TiO}_2$  NW/NR<sup>77-80</sup>,  $\text{TiO}_2$  NT/NR<sup>81</sup>,  $\text{TiO}_2$  NT/NP<sup>82</sup>,  $\text{TiO}_2$  NT/NS<sup>83</sup>, ZnO NW/NR<sup>84-87</sup>, ZnO NS/NR<sup>88,89</sup>, ZnO NW/NS<sup>90,91</sup>. However, the larger size trunks and/or branches than the NP counterparts did not provide a sufficient specific surface area for dye deposition. This can be appreciated from Figure 8, which makes a surface area comparison between some different hierarchical nanostructures and NP films using data from the literatures.<sup>21,80,81,84,88,90,92-95</sup> As a result, the early reported  $\text{TiO}_2$  or ZnO hierarchical nanostructures usually exhibited lower photocurrent density and PCE than their NP counterparts in DSSCs<sup>96-98</sup>.

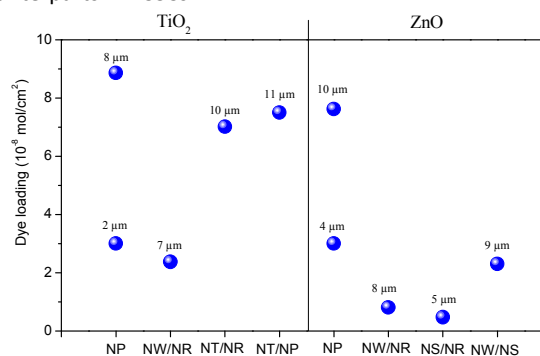


Figure 8. Surface area comparison among different hierarchical nanostructures and NP films based on the loading amount of N719 dye molecules<sup>21,80,81,84,88,90,92-95</sup>. The dye loading using other dyes was converted to N719 dye according to their relative molecule area. The corresponding film thicknesses are marked. The sizes of  $\text{TiO}_2$  and ZnO NP are typically about 15-30 nm in diameter<sup>21,93,95</sup>.

In recent years, some promising hierarchical nanostructures have been reported with larger specific surface areas and/or strong light scattering features that can compensate surface area losses, such as multi-level hierarchical nanostructures and hierarchical spherical aggregate nanostructures. Besides, the application of hierarchical nanostructures in solid-state DSSCs is gaining interest because the well-aligned nanoarrays are amenable to deep penetration of electrolyte in comparison to the NP films. In addition, single-crystalline hierarchical nanostructures were also successfully synthesized as a promising photoelectrode candidate for DSSCs.

#### 4.1 Multi-level hierarchical nanostructures.

During the last few years, Kuang and coworkers established a systematical strategy to grow  $\text{TiO}_2$  multi-level hierarchical nanostructures based on anatase  $\text{TiO}_2$  NWs. Figure 9(A) illustrates the evolution of a typical  $\text{TiO}_2$  NW/NR/NR hierarchical nanostructures<sup>99</sup>. The long anatase  $\text{TiO}_2$  NW array with a smooth surface were grown by their self-developed hydrothermal method using the reaction solution of potassium titanium oxide oxalate dehydrate (PTO)/ $\text{H}_2\text{O}$ /diethylene glycol (DEG). And  $\text{TiO}_2$  NW/NR and  $\text{TiO}_2$  NW/NR/NR nanostructures were synthesized by immersing  $\text{TiO}_2$  NW and  $\text{TiO}_2$  NW/NR nanostructures in the above PTO/ $\text{H}_2\text{O}$ /DEG reaction solution, respectively. The trunks of the final  $\text{TiO}_2$  NW/NR/NR photoelectrode was about 8  $\mu\text{m}$  in length with a diameter of about 200–400 nm (Figure 9(B)), while the NR branches formed at the second step were about 300–500 nm in length and about 10–20 nm in diameter. At the third step, numerous tiny NR with an average size of 3–5 nm were randomly grown on the aforementioned nanorod branches. Dye absorption test experiment for different photoelectrodes with the similar thickness of 8  $\mu\text{m}$  indicated that dye uptakes have the following order of NW ( $3.76 \times 10^{-8} \text{ mol/cm}^2$ ) < NW/NR ( $6.35 \times 10^{-8} \text{ mol/cm}^2$ ) < NP ( $8.86 \times 10^{-8} \text{ mol/cm}^2$ ) < NW/NR/NR ( $9.01 \times 10^{-8} \text{ mol/cm}^2$ ). The multi-level hierarchical nanostructure of  $\text{TiO}_2$  NW/NR/NR has obtained a larger surface area than the NP counterpart at the similar thickness. The charge transport and recombination property measurements indicated that  $\text{TiO}_2$  NW/NR/NR also owned the lower transport time and longer electron lifetime than  $\text{TiO}_2$  NP (Figure 9(C) and (D)) due to the presence of the fast charge-transport  $\text{TiO}_2$  NW trunks. As a consequence,  $\text{TiO}_2$  NW/NR/NR got the highest PCE (8.11 %) among different photoelectrodes, obviously higher than that of NP photoelectrodes (6.32 %), as presented in Figure 9(E).

Very recently, they exploited a relatively large size  $\text{TiO}_2$  NS (named as  $\text{TiO}_2$  NW/NS/NR) as the first-level branches for enhancing light scattering to build a balance between specific surface area and light trapping capacity. Though final  $\text{TiO}_2$  NW/NS/NR nanostructure own a slightly smaller surface area than the NP film ( $1.51 \times 10^{-7} \text{ mol/cm}^2$  vs.  $1.58 \times 10^{-7} \text{ mol/cm}^2$ ), it still got a considerably higher  $J_{\text{sc}}$  ( $16.71 \text{ mA/cm}^2$ ) and PCE (9.09 %) in DSSCs than NP film ( $J_{\text{sc}} = 13.53 \text{ mA/cm}^2$  and PCE = 7.55 %)<sup>99</sup>. And soon afterwards, through layer-by-layer assembly of hyperbranched hierarchical tree-like  $\text{TiO}_2$  NWs (under layer), branched hierarchical rambutan-like  $\text{TiO}_2$  hollow

submicrometer-sized spheres (intermediate layer) and hyperbranched hierarchical urchin-like  $\text{TiO}_2$  micrometer-sized spheres (top layer), their newly developed multi-layer hierarchical nanostructure photoelectrode successfully boosted the PCE of DSSCs up to 11.01 %<sup>100</sup>.

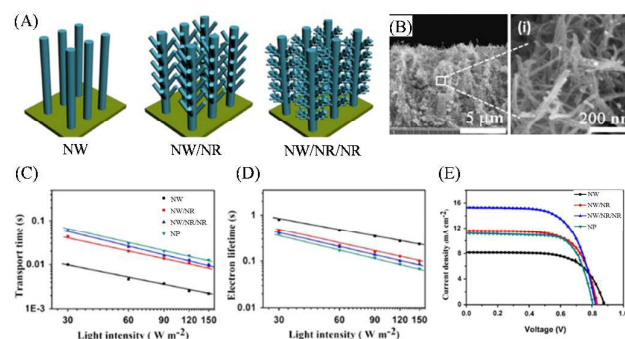


Figure 9.  $\text{TiO}_2$  NW/NS/NR nanostructure as DSSCs photoelectrode. (A) Schematic illustrating the structures of  $\text{TiO}_2$  NW, NW/NR and NW/NR/NR. (B) SEM images of  $\text{TiO}_2$  NW/NR/NR nanostructure. (C) Transport time, (D) electron lifetime and (E)  $J$ - $V$  curves of the DSSCs based on different nanostructures. Reproduced with permission from ref.<sup>99</sup>.

#### 4.2 Hierarchical spherical aggregate nanostructures

Hierarchical spherical aggregates have emerged as a promising photoelectrode structure to enhance the light harvesting efficiency of nanoparticle-based photoanodes and to accelerate electron transport without having to sacrifice the specific surface area. A typical hierarchical spherical aggregate nanostructure (ZnO) is illustrated in Figure 10(A), which was first explored as the photoelectrode in DSSCs by Cao et al. and was synthesized (Figure 10 (B)) by hydrolysis of zinc salt in a polyol medium at an elevated temperature (160  $^{\circ}\text{C}$ )<sup>48,101</sup>. The ZnO aggregate photoelectrode exhibited a considerably higher light scattering capacity than the ZnO nanoparticle photoelectrode, which as a result led to a greatly enhanced PCE (3.51 %) than that with the nanoparticle photoelectrode (0.6 %). The researchers pushed the PCE to 5.4 %<sup>102</sup> by employing polydisperse ZnO aggregates and further boosted the PCE to 6.3 % by coating the ZnO aggregates with a thin  $\text{TiO}_2$  layer to suppress recombination<sup>103</sup>. By employing the spray pyrolysis method to deposit the polydispersed ZnO aggregates in-situ on a substrate, Sberveglieri et al. have successfully promoted the PCE of ZnO-based DSSCs to a record value of 7.5 %<sup>104</sup>.

In parallel,  $\text{TiO}_2$  spherical aggregates have also been well documented with the structure similar to that of the aforementioned ZnO aggregates. For such materials, solvothermal treatment of amorphous precursor  $\text{TiO}_2$  spheres is a well established synthesis method<sup>105–110</sup>. Dye loading measurement has demonstrated an obviously higher loading amount of about  $8.69 \times 10^{-5} \text{ mol/g}$  for  $\text{TiO}_2$  aggregate powder than that for P25  $\text{TiO}_2$  nanoparticles ( $4.25 \times 10^{-5} \text{ mol/g}$ )<sup>105</sup>. Besides the high light scattering capacity and larger surface area,  $\text{TiO}_2$  aggregates were confirmed to accelerate the electron transport in the photoelectrode (Figure 10(E))<sup>108</sup>,

possibly due to the enhanced interconnection between different aggregates. So far, the TiO<sub>2</sub> nanoparticle aggregates have garnered a high PCE of over 10 %<sup>108</sup>.

Most recently, Zhao et al. have exploited a simple evaporation-driven oriented assembly method to synthesize a new kind of TiO<sub>2</sub> spherical aggregates—three-dimensional open mesoporous TiO<sub>2</sub> microspheres—as shown in Figure 10 (F)<sup>111</sup>. This kind of TiO<sub>2</sub> microspheres exhibited well-controlled radially oriented hexagonal mesochannels and crystalline anatase walls, which greatly enhanced the surface area of the photoelectrode with an N719 dye uptake of  $2.13 \times 10^{-7}$  mol/cm<sup>2</sup>, about twice those of P25 TiO<sub>2</sub> ( $1.12 \times 10^{-7}$  mol/cm<sup>2</sup>) as well as the above mentioned TiO<sub>2</sub> aggregates ( $1.45 \times 10^{-7}$  mol/cm<sup>2</sup>). At the same time, this photoelectrode also exhibited an obviously longer electron lifetime and higher  $D_n$ , leading to a record certified PCE value of over 12 %.

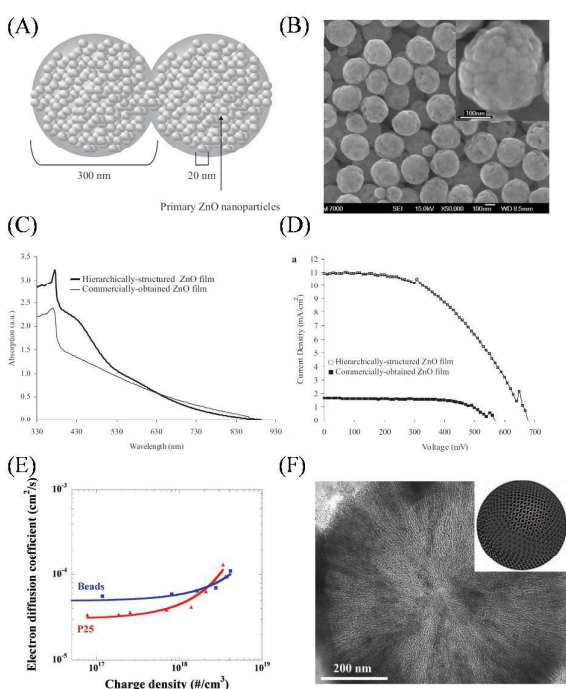


Figure 10. Hierarchical spherical aggregate nanostructures studied for DSSCs photoelectrodes. (A) Scheme and (B) SEM image of ZnO aggregates. (C) UV-vis spectra of a ZnO aggregate film and a ZnO nanoparticle film. (D)  $J$ - $V$  curves of the DSSCs based on ZnO aggregate film and ZnO nanoparticle film. Reproduced with permission from ref.<sup>101</sup>. (E)  $D_n$  vs. charge density curves of the photoelectrodes based on a TiO<sub>2</sub> aggregate film and a P25 TiO<sub>2</sub> nanoparticle film. Reproduced with permission from ref.<sup>108</sup>. (F) TEM image and scheme of oriented mesoporous TiO<sub>2</sub> microspheres. Reproduced with permission from ref.<sup>111</sup>.

#### 4.3 Hierarchical nanostructures in solid-state DSSCs.

For high performance solid-state DSSCs (ssDSSCs), the thorough penetration of solid-state electrolyte into the mesoscopic photoelectrode is an important challenge. The difficulty has limited the NP film thickness to a few

micrometers. On this point, hierarchical nanostructures have obvious advantages over NP films since well-aligned nanoarray allow deep penetration into the solid-state electrolyte. And through careful optimization, the hierarchical nanostructures are expected to permit large amount of dye deposition together with good electrolyte penetration.

Kim et al. have shown that pine tree-like TiO<sub>2</sub> NT arrays (PTT), which were grown by an one-step hydrothermal method in a PTO/DEG/H<sub>2</sub>O solution<sup>112</sup>, are a promising hierarchical nanostructure for ssDSSCs. As shown in Figure 11 (A), the NT trunks in the PTT arrays grew almost vertically from the FTO substrate and NR branches were uniformly covered on the NTs. By changing the H<sub>2</sub>O/DEG volume ratio, the structure parameters of PTT arrays could be well controlled. The length of NT, length of NR and diameter of NR for the samples obtained at the H<sub>2</sub>O/DEG ratio of 1:4.7 (PTT1), 1:3.4 (PTT2) and 1:2.6 (PTT3) were (13.5  $\mu$ m, 430 nm and 40 nm), (13.5 to 16  $\mu$ m, 300 nm and 30 nm) and (19  $\mu$ m, 230 nm and 20 nm), as shown in Figure 11(A), (B) and (C), respectively. The specific area measured by dye absorption experiment has the order of NP ( $8.32 \times 10^{-8}$  mol/cm<sup>2</sup> for 8.5  $\mu$ m) < PTT1 ( $8.35 \times 10^{-8}$  mol/cm<sup>2</sup>) < PTT2 ( $9.41 \times 10^{-8}$  mol/cm<sup>2</sup>) < PTT3 ( $1.06 \times 10^{-7}$  mol/cm<sup>2</sup>), respectively. It should be noted that the thickness of the NP film was the optimized value in their ssDSSCs. For the application of these branched TiO<sub>2</sub> NT arrays in DSSCs, N719 dye and the solid-state electrolyte of poly ((1-(4-ethenylphenyl) methyl)-3-butyl-imidazolium iodide) were chosen as sensitizer and electrolyte, respectively. The charge transfer resistance at the photoelectrode/electrolyte interface, corresponding to the low-frequency semicircle in Nyquist plots (Figure 11(D)), showed the order of PTT1 < PTT2 < PTT3, which was well related with their surface area. The larger area was expected to increase dye deposition and photoelectrode/electrolyte interface contact area, which would favor light absorption and efficient charge separation. Besides, PTT3 photoelectrode also exhibited the highest  $D_n$  (Figure 11(E)), demonstrating the highest electron transport rate. And the high concentration but short NR branches were proposed to shorten the electron transport pathway and concentrate the electrons from NR branches to NT trunks, which resulted in the most rapid electron transport. The ssDSSCs based on these PTT photoelectrodes were observed to achieve much higher PCE than that of TiO<sub>2</sub> NP device (4.0 %), attributable to the higher  $J_{sc}$  and FF values (Figure 11(F)). The improved  $J_{sc}$  values resulted from the larger dye loading due to the larger surface area and more rapid charge transport, while the 1D well-aligned TiO<sub>2</sub> NT allowed for the deep penetration of solid electrolyte to improve the photoelectrode/electrolyte interfacial contact and charge separation efficiency, improving FF values. And the PCE obtained by PTT3 (8.0 %) was one of the highest values observed for N719-based ssDSSCs.

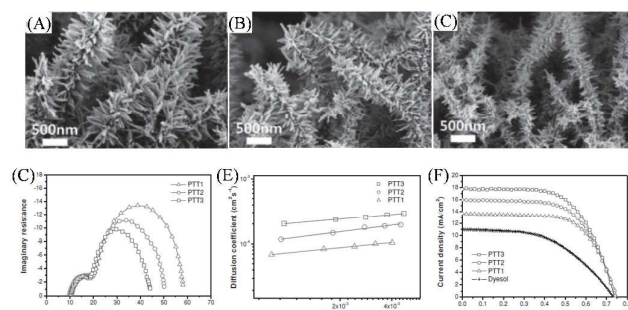


Figure 11. Pine tree-like  $\text{TiO}_2$  NT-based hierarchical nanostructure as DSSCs photoelectrode. SEM images of (A) PTT1, (B) PTT2 (C) PTT3. (D) Nyquist plots, (E) electron diffusion efficient ( $D_n$ ) as a function of current density and (F)  $J$ - $V$  curves of the solid-state DSSCs based on different nanostructures. Reproduced with permission from ref. <sup>112</sup>.

#### 4.4 Single-crystalline hierarchical nanostructures.

Though many hierarchical nanostructures have been synthesized and applied in DSSCs, the grain boundaries between trunks and branches still limit the charge transport rate, which need to be eliminated to further enhance the charge transport. Along this direction, Feng et al. have taken a step by exploiting the epitaxial growth strategy to obtain the single-crystalline rutile phase  $\text{TiO}_2$  NW/NR<sup>113</sup>. Figure 12(A) shows the needlelike NR branches growing in four symmetrical directions with a length of tens of nanometers and the NR branches grow uniformly with a clear orientation along specific crystal facets of the trunk. The HRTEM image in Figure 12(C) taken from the region f in Figure 12(B) suggested the single-crystalline structure, which was illustrated by the atomic model in Figure 12(D). The DSSCs based on NW, NW/NR, and NP have been constructed for the characterizations of electron transport property and photovoltaic performance. At the same photoelectron density, the  $D_n$  for NW/NR was about 2 orders of magnitude higher than that of NP films Figure 12(E), which should be attributed to the elimination of grain boundaries for faster charge transport. The higher surface trap state density associated with the increase in the surface area of NW/NR led to the relatively low  $D_n$  with respect to that of NW. As shown in Figure 12(F), the NW/NR-based device obtained a  $V_{oc}$  of 0.71 V, FF of 0.64,  $J_{sc}$  of 10.14  $\text{mA}/\text{cm}^2$  and PCE of 4.61 %, while the NW based device show a  $V_{oc}$  of 0.73 V, FF of 0.63,  $J_{sc}$  of 6.57  $\text{mA}/\text{cm}^2$  and PCE of 3.02 %. The  $J_{sc}$  value for the former was about 54 % higher than that for the latter, which was due to the larger surface area of the NW/NR for more dye deposition and more efficient charge separation.

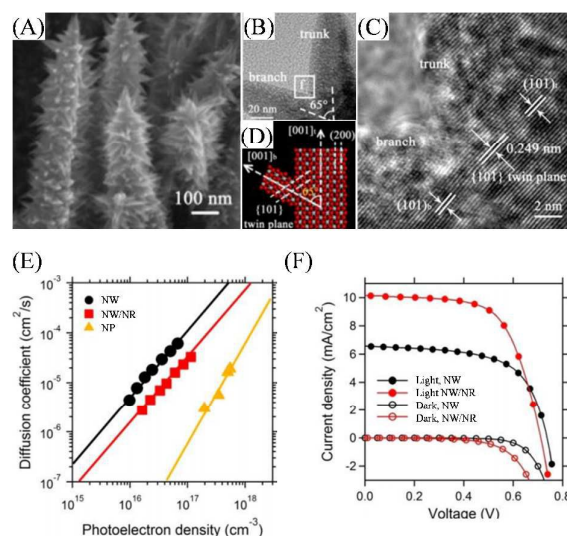


Figure 12. Single-crystalline  $\text{TiO}_2$  NW/NR nanostructure as DSSCs photoelectrode. (A) SEM, (B) TEM and (C) HRTEM images of the single-crystalline NW/NR nanostructure. (D) Schematic atomistic structure profile along the [010] zone axis of the trunk displayed in panel (C). (E) Electron diffusion coefficients ( $D_n$ ) as a function of the photoelectron density for NW, single-crystalline NW/NR and NP films-based DSSCs. (F)  $J$ - $V$  curves of the single-crystal NW/NR and NW-based DSSCs. Reproduced with permission from ref. <sup>113</sup>.

## 5. Conclusion and outlook

To sum up, hierarchical nanostructures of metal oxides have shown the expected advantages over the NP film and nanoarray counterparts in PEC solar energy conversion systems (water splitting and DSSCs systems). In the water splitting system, a high performance photoelectrode needs to have both high light absorptivity and efficient charge separation/transport. For hierarchical nanostructures, the increased specific surface area due to the small size branches create much more charge separation sites than in the nanoarray counterpart. In addition, the nanoarray trunk not only affords rapid charge transport but also enhances the light scattering capacity in comparison with the NP films. As a result, the hierarchical nanostructures usually exhibit a superior performance to the NP and nanoarray counterparts. As learned from the high performance hierarchical nanostructure photoelectrodes, the trunks should have a single-crystalline structure or a polycrystalline structure with few high angle grain boundaries for fluent charge transport. Besides, the branch size should be sufficiently small to favor charge separation. Ideally, eliminating the grain boundaries between trunk and branches to a single-crystalline structure should be a very promising strategy.

In the DSSCs system, the metal oxides play the dual roles of supporting dye molecules and transporting the injected photoinduced electrons from the dye molecules. The early reported hierarchical nanostructure usually exhibited a lower

performance than the NP counterparts due to their considerably smaller specific surface area for the dye deposition. However, the multi-level hierarchical nanostructures developed in recent years have largely solved this problem. Specifically, by introducing the high-level and much smaller branches into the hierarchical nanostructures, one could significantly increase the specific surface area. In addition, the hierarchical spherical aggregates have successfully promoted the cell efficiency to a record certified value by enlarging surface area, improving charge transport and enhancing light scattering capacity. Furthermore, the hierarchical nanostructures have proved to be superior for constructing ssDSSCs because the well-aligned nanoarray trunks favor penetration into the solid-state electrolyte to afford an excellent interface contact and charge separation. In a way similar to the water splitting system, a single-crystalline hierarchical nanostructure is highly desirable candidate for DSSCs.

Clearly, there is still much room for further developments of the hierarchical nanostructure photoelectrodes. In particular, we foresee the future developments in the following directions for both water splitting and DSSCs systems. (1) Passivating surface states on the hierarchical nanostructures. The small size branches usually induce higher surface state density, which not only increases charge recombination pathways but also suppress charge transport rates by trapping/detrapping events. Therefore, it is necessary to passivate the surface states by depositing a thin oxide nanolayer (such as  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}_2$  and  $\text{ZrO}_2$ ) on the surface of the hierarchical nanostructures. (2) Increasing carrier concentrations by doping the hierarchical nanostructure. Doping the metal oxide hierarchical nanostructures will increase the carrier concentration and effectively increase the conductivity, while the increase in band bending will also favor the charge separation at the surfaces. (3) Forming heterojunctions between the trunks and the branches. An appropriate energetic gradient formed by the heterojunction at the trunk/branch interface will favor charge separation, while the higher CB position of the branch oxides will decrease the recombination of the injected electrons with the electrolyte. (4) Introducing 3D conducting substrates into the hierarchical nanostructure. A 3D conducting substrate (ITO or FTO glasses) will reduce the trunk length to improve charge transport rate and collection efficiency, which will especially benefit the metal oxides with a short carrier diffusion length.

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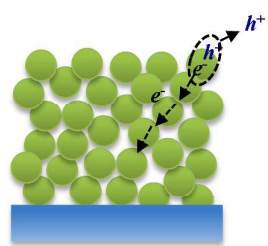
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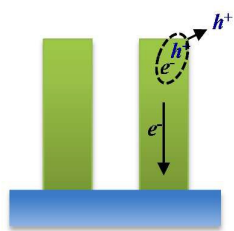
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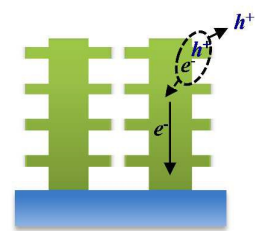
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Nanoparticle



Nanoarray



Hierarchical nanostructure