Review

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TiO₂ nanotube structures for the enhancement of photon utilization in sensitized solar cells

Abstract: The nano- and microstructures of titanium dioxide (TiO₂) photoanodes in photovoltaic cells have a large impact on their photon to electron performances, including light harvesting, photogenerated electron separation, transport and recombination. This review will focus on anodic TiO₂ nanotubes (NTs) for the enhancement of photon conversion or light harvesting when incorporated in sensitized solar cells, which is valuable for increased photocurrent densities and solar cell efficiencies. By modulating the electrochemical processes which have a great impact on TiO₂ NT geometry, excellent optical properties can be achieved, resulting in the enhanced absorption of incident light and reduced light loss via reflection, penetration or transformation. The results indicate that the control of structures and morphologies of TiO₂ NTs is critical to the optimization of their applications in sensitized solar cells.

Keywords: light harvesting; light scattering; micro-structure; photonic crystal; TiO₂ nanotubes.

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1 Introduction

Titanium dioxide (TiO₂) is a multi-functional material with high chemical stability, and can be easily integrated in a variety of devices for photovoltaic and photocatalytic applications. TiO₂ nanoparticles (NPs) form a homogeneous n-type, large band-gap oxide semiconductor network (anatase ~3.2 and rutile ~3.0 eV), which is a promising electrode material for sensitized (organic and inorganic) composite solar cells with high surface roughness for photo-sensitive material loading [1–4]. On the other hand, the unique band structure allows the interfacial transfer of photogenerated electrons, which can further diffuse through the network and be efficiently collected by a conductive substrate. The sensitizer (such as dye molecules) usually absorbs light in the visible region, with strong absorption peaks around 530 nm (N3 or N719 dyes). The application of TiO₂ in quantum dot (QD)-sensitized heterojunction photovoltaic cells and organic solar cells (small molecules, polymers) has also been demonstrated. A major factor limiting the improvement of solar cell efficiency is that the photons in solar irradiation are not fully captured. Only a part of them can be intercepted by a light-absorbing layer to create electron-hole pairs, and a significant portion is lost by reflection, penetration or transformation to heat via phonon emission. Especially the low-energy photons (650–1000 nm) which capture a large percent (~1/3) of the total energy of solar irradiation that arrives at the earth surface have not been fully utilized for various sensitizers [5–7]. Consequently increasing photon absorption in the visible, particularly long wavelength region has become the most important task to improve the energy conversion efficiencies.

To realize the effective light absorption of sensitized solar cells, engineering the absorption spectrum of a single absorber to match solar irradiation as largely as possible has been demonstrated, such as new dyes [8–11] or perovskite [12–16]. Promoting the creation of multiple excitons in QDs [17–19] is also a hot spot. The concept of co-sensitization includes a mixture of absorbers with complementary spectra (such as dyes+QDs and QDs+QDs)

[20–24], and cascaded or tandem multiple layers with different layer absorbs photons of different energies [25–28]. Recently, by a proper combination with nano-sized gold or silver particles, hot electron transfer or near-field optical field enhancement originated from surface plasmon resonance (SPR) has been proposed [29–34]. Furthermore, the additional physical methods for the enhancement of incident photon absorption in the desired spectrum range are also helpful, which have unsubstituting advantages of simple fabrication and excellent compatibility.

Anodic TiO₂ nanotubes (NTs), similar to other one-dimensional (1D) nanomaterials (such as nanowire, nanorod or nanofiber) [35–44], in principle, can be used as the substitute to conventional nanocrystals as photoanode materials, which can provide superior electron collection properties in sensitized solar cells. After decades of development, the fabrication methodology of NTs has been fully studied. These NTs feature the self-organized configuration with the advantages of a regular, aligned and open structure. During anodization of Ti metal foil in hydrogen and fluoride ion containing electrolytes, the applied potentials drive the reactive ions through the barrier layer at the oxide/metal interfaces, leading to continuous NT growth into the Ti metal substrate, forming closely packed, vertically oriented and regular arranged arrays in an inherent self-ordering process [45–48]. Anodization is a highly controllable technique with the advantages of high efficiency, low cost and mass production [49, 50], and has been utilized to fabricate Al₂O₃, TiO₂, Fe₂O₃, WO₃, Nb₂O₅, Ta₂O₅, SnO₂, ZrO₂ metal oxide nanostructures, and so on [51–57].

During the working process of solar cells, the NPs on the electrode surface pile up irregularly, and electrons (majority carriers) injected by excited sensitizers go through numerous NPs before being collected. Thus, the path that electrons take to pass through the mesoporous layer is very long, increasing the recombination probability of electrons with holes in the electrolyte. Apparently, photogenerated electrons can be transported vectorially along the NT wall to the electron-collecting layer. The random movement of electrons is limited, and thus the electrons will meet fewer grain boundaries. Also, the electron-hole recombination in TiO₂ NT-based photoanodes is largely retarded as reported [58–60]. These electron-transport and recombination characteristics are key factors influencing their performances in nanostructured photoelectric applications. And the feasibility and superiority of the integration of such a structure to the photoanodes of dye [61–67], QD [68–73] or perovskite solar cells [74], with redox electrolytes or solid-state hole conductors [75], and on flexible substrates [76–80], have been largely

concerned. The TiO₂ NT array structure suffers from non-ideal crystallinity with trap states originated from fluoride containing electrolyte and non-oxidized Ti, which is peculiar to TiO₂ NTs as compared with NPs [81–84], and insufficient inner surface areas for dye adsorption [85]. Some convenient strategies have been proposed to solve the above problems. The crystallinity of high-quality TiO₂ NTs has been enhanced by various strategies to improve the charge collection [86–88], and the geometry of the tubes can be tailored to enlarge the surface area [89–94].

As a very important application, TiO₂ NTs can be used as a light-harvesting enhancement assembly in several ways. Through the control of electrical or chemical conditions during anodization, NTs with desired structures and geometries (such as lengths, diameters and regularities) and corresponding unique optical properties are introduced. The strategies are outlined below.

2 Light scattering

For sensitized solar cell devices, the preferred materials for the mesoporous photoanode or working electrode are TiO₂ metal oxide NPs with anatase phase (or, less often, SnO₂, WO₃, ZnO, Nb₂O₅, etc.) [57, 95–97], which can be made into pastes, deposited onto a variety of conductive substrates such as fluorine-doped tin oxide (FTO), indium tin oxide or Ti foil, and sintered to enhance inter-particle binding force. Meanwhile, the additional light scattering component with high diffuse reflectivity is also commonly added, forming the hybrid structures. The scattering appears as a wide-band effect which enhances light absorption and quantum efficiencies in the entire visible region [98]. The typical structure of solar cell photoanodes based on double-layered nanocrystalline TiO₂ films is as follows: a transparent layer that adsorbs light-harvesting dye molecules, and a non-transparent scattering layer deposited on top of the transparent layer.

2.1 Various scattering elements

Construction of a scattering layer from large particles (200–400 nm) [99–103] over a typical transparent nanocrystalline layer with small TiO₂ NPs (20–30 nm) has been a widely used technique to improve the solar cell efficiencies. In this configuration, large-sized particles serve as the scattering source, which lead to the better photon absorption in the red or near infrared (NIR) wavelength regions in a photovoltaic cell, especially low-energy

photons at 600–800 nm [104–106]. The scattering ability is markedly affected by the particle size, which has been described based on the Mie theory [107–110]. By adjusting synthesis conditions (e.g., hydrothermal temperature or reactant concentration), various-sized NPs can be obtained, leading to transparent, semi-transparent or non-transparent films based on these particles. First, the conventional transparent electrode is fabricated by doctor-blade coating, screen printing or spin coating. Then another white, opaque scattering layer is coated above the TiO_2 thin film. The parameters with respect to double-layered TiO_2 photoanodes in a sensitized solar cell have been largely optimized. For example, a typical “double-layered” high-efficiency sensitized solar cell is composed of a 14- μm -thick TiO_2 NP layer with a diameter of 20 nm as the dye-adsorption and electron-transport layer, and a 5- μm -thick scattering layer with 400-nm-sized NPs [111].

The above scattering particles, however, contribute little to the dye loading as a result of small surface areas, and thus deteriorate the photocurrent of solar cells. Some advanced building blocks, such as large-sized hierarchical hollow structures (nanoplates [112] and nanospheres [113–116]), rods [117, 118], fibers [119, 120], mesoporous nanospheres composed of nanocrystallite clusters [121–126], core/shell spheres [127] and other structures [128–130], can also be used as the scattering centers. The schematic of various scattering structures is shown in Figure 1. Such layers usually present dual functions when applied in sensitized solar cells, with light scattering and additionally

enhanced dye loading. Some typical TiO_2 photoanodes with scattering capacity in double-layered configuration are listed in Table 1.

Another type of architecture is the embedment or dispersion of the above-mentioned scattering elements, such as particles, spheres, rods, fibers, hierarchical aggregates or core/shell structures, directly in conventional TiO_2 NP films [134–140], acting as scattering centers and/or additional electron-transport pathways. Spherical or multiscale voids inside the photoanode have also been demonstrated to have good scattering ability [133, 141, 142]. Compared with double-layered structures where scattering is provided by a separated layer, this strategy has the advantage of simple synthesis and scale-up by using a hybrid TiO_2 paste, but would affect dye adsorption as random voids are formed concomitantly inside the films during deposition.

2.2 Conventional TiO_2 NTs

The scattering effect of NTs has been largely concerned [60, 143–147]. Normally synthesized TiO_2 NTs are in the film form. Recently, Fahim et al. first reported that by using potentiostatic rapid breakdown anodization in aqueous electrolytes [148–150], NTs in the powder form can be obtained in a very efficient way, which facilitates the utilization of NTs in sensitized solar cells. However, the quality of the NT powders fabricated by this strategy is not very satisfactory. NTs are still severely aggregated, resulting in the low packing density inside photoanodes. This would lead to the existence of large voids and the poor attachment and connectivity of aggregates, affecting the dye loading and electron transport. As a result, the solar cells based on pure NT powder showed inferior performances [151, 152].

By further physical milling treatment, TiO_2 NTs can be well dispersed into a high-quality powder form [131]. The characteristic diameter decreased from 800–1000 nm of as-formed NT powder to 100–500 nm after trituration, and the resultant NT powders can act as scattering layers on top of the NP layer to form the double-layered photoanode in sensitized solar cells (Figure 2A–C). From the color contrast of sensitized photoanodes (Figure 2C), the scattering layer based on NT powders (right, dark red) can also well adsorb dye molecules, while the commercialized large-diameter NP scattering layer shows poor dye anchoring (left, gray), indicating that the NT layer plays multi-functional roles in sensitized solar cells. The enhanced light harvesting with NT powder as a scattering layer can also be observed in the incident photon-to-current conversion

Figure 1 Schematic representation of various scattering components, such as large TiO_2 NPs, nanoplates, hollow spheres, mesoporous spheres, core/shell spheres, NTs, nanorods and nanofibers.

Table 1 Some double-layered configurations with advanced TiO₂ scattering structures.

Nanostructure	Size	Detailed description	Solar cell configuration	Efficiency and enhancement	Reference
Microsphere	350 nm	Mesoporous spheres	6 μ m microsphere+10 μ m octahedral nanocrystal	8.72%, 15%	[121]
Microsphere	Tunable from 260 to 980 nm	Mesoporous sphere	11 μ m sphere+9 μ m NP	9.04%, 31%	[122]
Microsphere	Diameter 3 μ m	Mesoporous spheres composed of 10 nm NPs	Total thickness 8 μ m	7.94%, 12%	[126]
Nanoplate	~200 nm	Hollow hexagonal structure with tunable shell numbers	4 μ m nanoplate+8 μ m P25 NP	6.53%, 24%	[112]
Nanotube	Aggregate, 100–500 nm	NT array powder	7 μ m NT+12 μ m NP	8.7%, 20%	[131]
Nanotube	Diameter 10–20 nm	Hydrothermally synthesized NT	7 μ m NT+14 μ m P25 NP	8.77%, 17%	[132]
Hollow microsphere	Diameter 1–3 μ m, wall thickness 0.25 μ m	Hollow spheres	4.3 μ m sphere+6 μ m NP	9.43%, 21%	[114]
Hollow microsphere	Diameter ~500 nm, thickness 50–80 nm	Hollow spheres composed of 10–15 nm NP	10 μ m sphere+10 μ m P25 NP	7.5%, 20%	[116]
Core/shell structure	Shell diameter 2.5 μ m, wall thickness 100 nm, core diameter 2 μ m	Monodisperse core-shell microsphere	4 μ m core/shell sphere+8 μ m NP	8.22%, 29%	[127]
Spherical void	Diameter 800 nm	Voids in NP	5 μ m NP with voids+5 μ m NP	5.76%, 22%	[133]
Porous Nanofiber	Diameter 200–300 nm, length >50 μ m	Voids in nanofiber	5 μ m porous nanofiber with voids+3 μ m NP	8.5%, 42%	[120]
Nanorod	Diameter tens of nm to ~800 nm, length <2 μ m	Ultraporous nanorod	5 μ m nanorod+15 μ m P25 NP	8.53%, 9%	[118]
Shell-in-shell sphere	Outer shell diameter 1–2 μ m, inner shell ~0.5 μ m	Shell-in-shell hollow sphere	5 μ m sphere+11 μ m P25 NP	9.10%, 19%	[130]

NP, nanoparticle; NT, nanotube.

efficiency (IPCE) spectra in Figure 2D, which shows the higher efficiency over the entire visible range. As a result, the greatly improved overall conversion efficiency of 8.7% can be achieved.

2.3 Large-diameter TiO₂ NTs

TiO₂ NTs have oriented configuration with outer diameters typically in the range of ~100–200 nm (Figure 3A), much larger than the size of TiO₂ NPs (~20–30 nm), thus showing inherent scattering properties. It is noted that the incident photon is strongly scattered at wavelengths close to the NT diameters, while the weaker light scattering appears when the tube diameters are well below the wavelength of incident light. As a result, the NT size should be further enlarged to enhance scattering.

During high-field anodization, simply increasing the applied voltage would lead to the great enlargement of the tube size [155–158]. In fact, in most conditions, the outer diameter of NTs (D) is proportional to the applied anodization voltage (U) in a large range, which can be expressed as $D \approx 2f_g \times U$, where f_g denotes the growth factor [159, 160]. Thus by incorporating other anodization parameters

suitably, such as the organic solvent and fluoride ion concentration of the anodization electrolyte and anodization duration, NTs with diameters comparable to the wavelengths of visible light can be obtained under high-voltage anodization (Figure 3B, C) [153, 154]. In the high-voltage condition, large-diameter NTs (LNTs) with multipodal or defined morphologies can be obtained, depending on the complex chemical etching of the NTs in the anodization process. Due to severe dissolution, the fabrication of LNTs with a large length and a regular top surface is still a challenge. Figure 3D shows that in the high-voltage region (120–240 V), the outer tube diameter still has the linear relationship with the applied voltage during anodization. As can be observed in the simulation of light transmission in the direction of NTs [161], LNTs significantly reduce the film transparency due to the strong light scattering effect over the entire visible range, and thus suitable for the enhancement of light harvesting in sensitized solar cells.

2.4 The NP layer coupled with LNTs

With the addition of lactic acid into the used organic anodization electrolyte, LNTs can be obtained with regular

Figure 2 (A) A schematic drawing of the double-layered structure with the dispersed TiO₂ NTs as the light scattering layer. (B) The pore size distribution of highly dispersive NT powders. The inset shows the corresponding transmission electron microscope (TEM) image of the randomly accumulated NTs. (C) The scanning electron microscope (SEM) cross-sectional image of the assembled photoanode. The thicknesses of the upper NT layer and underlying NP layer are about 7 and 12 μm, respectively. The inset is the pictures of the sensitized photoanodes (left: nc-TiO₂+CCIC: NP-absorbing layer with a commercialized NP scattering layer; right: nc-TiO₂+TNT: NP-absorbing layer with a NT scattering layer). (D) The IPCE spectra of the solar cells based on the double-layered structure, indicating the superior scattering effect of the dispersed NTs (nc-TiO₂ only: 12-μm-thick NP-absorbing layer). Reprinted with permission from Ref. [131]. Copyright (2012) American Chemical Society.

top and side morphologies (Figure 4A, B). By anodization at 180 V, NTs with an outer diameter of ~500 nm are formed, which is comparable to the wavelength of visible light [162]. The lactic acid added here successfully avoids the dielectric breakdown of NTs during high-voltage anodization [49]. After anodization, the LNT layer can be detached from the underlying Ti metal substrate to obtain robust and free-standing membranes [163–166], followed by transfer and adhesion of the LNT membranes onto the FTO substrate by a layer of TiO₂ NPs to fabricate the photoanode [167–170]. In this configuration (see Figure 4C, D), incident photons first reach the dye-adsorbed layer and are partially absorbed. The remaining photons would be scattered by the LNTs back into the dye-adsorbed TiO₂ layer and recaptured. That is to say, the photons are recycled

properly inside the photoanode and the light path length is increased. This recycling process leads to more effective absorption of coming photons, and thus more electrons are generated. Visually, for photoanodes integrated with larger sized NTs, the transparency of the films decreases strongly, which is also obvious from the transmission spectra (Figure 4E). The visible and particularly desirable red or NIR photons will be reflected back into the absorbing layer. Compared with sensitized solar cells based on single-layered electrodes, those consisting of LNTs as the scattering layer show improved photocurrents and power conversion efficiencies. Also, it is observed that the light scattering effect within NTs is insensitive to irradiation angles (as is shown in Figure 4F) and occurs in the entire angle range.

Figure 3 (A) The SEM image of the morphology of a TiO₂ NT array synthesized under traditional conditions (at a low voltage of 60 V for 1.5 h in ethylene glycol (EG) electrolyte with 0.5% NH₄F and 3% H₂O). (B) The TiO₂ NTs with surface diameter >600 nm, which were fabricated by anodization at 120 V for 44 h in diethylene glycol (DEG) electrolyte with 0.25% HF and 2% water. The arrows indicate the presence of multipodal NTs. (C) The defined tube arrays with diameters of 680–750 nm, fabricated at 225 V for 7 h in used EG electrolyte with 0.5% NH₄F and 10% water. (D) The outer diameter of large-sized NTs increases almost linearly with increasing applied voltage at the high-voltage anodization conditions. (B) Reprinted with permission from Ref. [153]. Copyright (2010) American Chemical Society. (C, D) Reprinted with permission from Ref. [154]. Copyright (2013) Elsevier.

2.5 Stacked multi-layered photoanodes

In a photoanode, (1) sufficient light harvesting and electron generation, and (2) fast electron transport to the external circuit without recombination loss are both required for efficient solar cells. However, different nanostructures have their unique advantages and disadvantages. These features can rarely be realized by a single given multi-functional structure in a monolayer. For example, TiO₂ NTs feature excellent electron recombination and collection properties but suffer from insufficient internal surface areas for dye adsorption, while TiO₂ NPs show the opposite characteristics. To realize photoanodes with these multi-functions simultaneously to promote solar cell performances, multi-layered (two, three or more layers) structures can be designed, in which nanostructures of various morphologies and sizes are combined together in series, and each layer plays different roles in

photon to electron conversion processes, including sufficient dye adsorption, fast electron diffusion and proper light recycling [98, 171–176].

For example, Kuang et al. fabricated a photoanode configuration with three different layers, with the schematic shown in Figure 5A [177]. This structure is constructed by first hydrothermal growth of a 1D NT and three-dimensional (3D) hierarchical microflower double layers based on the Ti metal substrate, and then coating a conventional NP layer onto the top of the resultant 1D-3D structure. From the SEM images of the structure (Figure 5B–D), the microflower is assembled by nanosheets consisted of small-diameter nanocrystals, and underlying NTs are nearly perpendicularly oriented. The NT, microflower and NP layers mainly serve as electron-transport, light scattering and dye-adsorption components, respectively. However, in the tri-layered configuration, micrometer-sized scattering flowers are in the intermediate region,

Figure 4 (A, B) The SEM top and side views of large-sized NTs, showing the flat, regular surface morphologies and aligned tube arrays with good quality. (C) The SEM cross-sectional image of the integrated photoanode, with the upper layer composed of LNTs and the underlying layer of porous NPs on FTO glass. The adhesion between NT and NP layers is excellent. (E) The transmission spectra and the photographs (inset) of various integrated photoanodes. TP(3L), TP(3L)+LTNA and TP(3L)+STNA represent a 14 μm NP layer only, an NP layer coupled with LNTs and STNs, respectively. The NP layer without any scattering layer shows high transparency over the visible region. By the coupling of the STN scattering layer to the NP layer, the transmission is lowered and the photoanode becomes semi-transparent. After the coupling of LNTs, the photoanode converts to opaque one, and nearly no light can be transmitted through. (F) The dependence of the solar cell efficiency on the angle of the incident light. The effect of efficiency enhancement through the scattering of LNTs is not affected by the incident angle, indicating the effectiveness of this structure in the application in various irradiation conditions. Reprinted with permission from Ref. [162]. Copyright (2014) Springer.

which is not the optimized architecture to achieve the maximum scattering effect. Also, solar cells should be assembled with backside illumination, that is, the incident light enters the cell through the Pt-coated counter electrode and electrolyte and finally reaches the NP layer of the photoanode. This illumination configuration, as has been reported previously, suffers from the light energy loss through reflection and absorption by the counter electrode and the dark color electrolyte, which would deteriorate the solar cell efficiency [179–182]. They further improved the configurations of this kind of multi-layered structures through the layer-by-layer assembly on the FTO glass substrate, consisting of TiO_2 nanowires, submicrometer hollow spheres and microspheres (viewing from the

light incident direction). And by further hydrothermal treatment of the ensemble, the three-layer structures are hyperbranched with large surface areas for improved dye loading capability. Also, the nanowire structure underlayer acts as an electron-transport medium which ensures the efficient electron collection, and the upper two layers (hollow spheres and microspheres) provide excellent light scattering. The cross-sectional SEM image of the tri-layered photoanode on the transparent FTO substrate is shown in Figure 5E, and the corresponding microstructures of each layer are presented in Figure 5F–H. The synergetic effects of the individual component of the multi-layered structure would lead to great improvement in solar cell performances [178]. Compared with the reference NP layer with

Figure 5 (A) The schematic diagram of the tri-layered photoanode on the Ti foil substrate. 0D NPs: conventional NPs; 3D HTFs: 3D hierarchical TiO₂ flowers; 1D TNTs: 1D TiO₂ NTs. Incident light arrives at the NP layer first. (B–D) The 1D-3D double-layered structure (flower+NT) formed by a two-step hydrothermal method. (E) The SEM cross-sectional images of the tri-layered hyperbranched TiO₂ photoanode on the FTO substrate. HTS-Branches: branched hierarchical TiO₂ microspheres; MPT-Branches: branched macroporous TiO₂ hollow spheres; AHTNW-Branches: branched anatase hierarchical TiO₂ nanowires. The three layers form well-interconnected networks. (F–H) The enlarged SEM images of the above three types of structures, showing the hyperbranched characteristics. The right column is the schematic drawing of the corresponding structures. (A–D) Reprinted with permission from Ref. [177]. (E–H) Reprinted with permission from Ref. [178]. Copyright (2014) American Chemical Society.

similar thickness, the multi-stacked photoanode achieved an efficiency of 11.01%, enhanced by 44%.

Recently, Chen et al. fabricated a kind of hybrid structure based on this synergetic concept by utilizing multifunctional TiO₂ NTs through simple synthesis [183]. The schematic and the corresponding cross-sectional images of this structure are presented in Figure 6A, which is divided into three parts. The incident light enters the photoanode through the FTO glass coated with a layer of TiO₂ NPs (layer 1). This layer provides a large internal surface area which mainly adsorbs light absorbers. Layer 2 upon layer

1 consists of small-diameter NTs (SNTs, ~130 nm) with great crystallinity. As highly crystallized TiO₂ NTs have a very fast electron-transport rate, this layer can act as both the light-harvesting and electron-transport layer. Finally, layer 3 on the top consists of LNTs (~520 nm tube diameter at the bottom), which acts as the scattering layer. The surface morphologies of SNTs and LNTs and the bottom of LNTs are shown in Figure 6B. Layers 2 and 3, i.e., the SNT and LNT array films, are fabricated in a single anodization process (with the change of anodization electrolytes in between), and thus the two parts are firmly connected.

Figure 6 (A) The schematic drawing (left) and the cross-sectional SEM image (right) of the multi-layered photoanode. From bottom to top: FTO glass substrate; layer 1 is NPs; layer 2 is SNTs; layer 3 is LNTs. The incident sunlight enters the solar cell from the bottom side. The thicknesses of layers 1, 2 and 3 are about 9, 15 and 2 μm, respectively. (B) The SEM images showing the morphologies of the top of SNTs and LNTs and the bottom of LNTs (with remnant of SNTs). The diameters of large tubes at the top and bottom are about 320 and 520 nm, respectively. That is to say, the diameters from top to bottom are not uniform, with a “tapered” NT morphology. And the diameter of small tubes is about 130 nm. (C) The dependence of the solar cell efficiency on the thickness of each layer. NP5+SNT15+LNT2, for example, denotes that the layer thicknesses of NPs, SNTs and LNTs are about 5, 15 and 2 μm, respectively. Reprinted with permission from Ref. [183]. Copyright (2014) The Royal Society of Chemistry.

As shown in Figure 6B, the surface of SNTs and the bottom of LNTs (with remnant of SNTs in the intertube region, showing the hexagonal shape) are originally connected together. This demonstrates that after the formation of an LNT layer, SNTs can continuously grow under the bottom and in the intertube regions of LNTs. In fact, the as-formed two types of NTs can be regarded as a whole, or so-called bi-layered NT film, which is then detached from the Ti metal substrate, subjected to high-temperature annealing

simultaneously to enhance the crystallinity and further transferred to the NP layer (layer 1) using the techniques as mentioned above. After the optimization of the thicknesses of each layer (the thicknesses of layers 1, 2 and 3 are ~9, 15 and 2 μm, respectively, Figure 6C), the achieved efficiency was as high as 6.52%, with an enhancement of 38% as compared with pure NPs and 29% as compared with the NP+SNT double-layered structure, resulting from the combined effects of more dye loading, faster electron transport and strong light scattering in sensitized solar cells. The scattering layer, which is necessary for sensitized solar cells as an additional component for light harvesting, has the tendency to be designed to play multiple roles in the solar cell working process, and would not introduce any side effect. The above strategy based on TiO₂ NTs features the advantages of simple synthesis and multi-functions, and has the room for further improvement.

3 Photonic crystal-assisted solar cells

It is well known that TiO₂ possesses a very high refractive index (2.4–2.7), which therefore can serve as photon-active material, for example, structural color materials duplicated from butterfly wings [184–187] and the photonic crystals (PCs). The incorporation of PCs is also a common method to enhance light harvesting in given spectrum ranges. PCs are structures with periodically changed refractive indices, which can strongly affect the light propagation through photoanode materials at photon energies within photonic band gaps (PBGs), and thus can strengthen the absorption of photons in the visible region in sensitized solar cells and broaden the range of light harvesting to the red or NIR region. Unlike scattering components which are nontransparent, the utilization of a PC layer would preserve the electrode transparency of sensitized solar cells, a unique characteristic valuable for certain applications, such as integration to building windows. In addition, the incorporation of this optical element would have little influence on the charge collection in solar cells [188].

3.1 Alternate layered materials and self-assembly

PCs normally consist of inorganic, organic, polymer or hybrid materials and can be divided into 1D, two-dimensional (2D) or 3D structures. The effects of PCs in sensitized

solar cells have been investigated in 1D configuration by using alternate layered materials, either TiO₂ or other high reflective index metal oxide materials such as SiO₂ [188–192]. The band gaps could only be adjusted in a narrow range, and the integration is also complicated. 3D and 2D PCs can be developed by state-of-the-art self-assembly approaches, such as artificial opals [193] and higher refractive index inverse opals using colloidal spheres as templates [194–197]. Other more precise but complex methods such as ion-beam or photolithography [198–200] and direct laser writing [201, 202] have also been used, but the existence of intrinsic disadvantages when coupled to sensitized solar cells impedes the wide usage of these techniques.

The PC structures are used in photoanodes in double-layered configuration, accompanied by the following inherent disadvantages. (1) The single functional PC layer contributes little to the adsorption of sensitizers. (2) It is difficult for electrolyte, especially solid-state hole transport materials, to penetrate through the layer-layer interface since the upper PC layer may block the underlying porous films during the coating or templating process. (3) Since the two layers are heterogeneous, the adherence of the PC layer on the underlying layer is rather weak, adversely affecting the photovoltaic processes. (4) The interface flatness has to be taken into account when PCs are deposited. (5) The optical properties of PCs can hardly be adjusted freely.

3.2 Secondary structures along the NT axis

By anodization, a hexagonal or round TiO₂ NT (nanopore) array structure into the Ti metal can be prepared. During the fabrication in fluoride ion containing organic electrolytes, the TiO₂ growth at the metal/oxide interface becomes equal to the TiO₂ dissolution at the oxide/electrolyte interface near the NT bottom. Typically under the constant voltage (namely potentiostatic anodization), the tube walls are smooth or with ripples on the outer wall surfaces [203, 204]. This external geometry of NT walls depends on whether or not the current has the tendency of spontaneous random fluctuations during anodization and also the amplitude of the fluctuations [205]. This phenomenon has also been observed in porous aluminum oxide under hard anodization [206]. For example, in the conditions of adding a large amount of water in an organic electrolyte, the recorded current response during anodization shows strong oscillations, and the ripple formation on the outside of the tube wall surface is evident (Figure 7A) [207]. This additional secondary structures on

the tube walls show defined interference patterns under white light illumination. Inspired by the spontaneous formation of tube wall structures, many more advanced and controllable TiO₂ NT morphologies, such as bamboo-type (Figure 7B, C) [208, 209, 211–214] and multi-layered structures (Figure 7D) [210, 215–217], have been designed and fabricated through pulse or cyclic anodic oxidation. The careful investigation demonstrates that the shaped TiO₂ NT walls display small-large diameter alternations. The so-called superlattice NTs have the similar bamboo-shaped morphology, but are composed of alternating types of metal oxides [218, 219].

It is also noted that in anodic Al₂O₃ (AAO), whose fabrication method is similar to that of TiO₂ NTs, partially branched nanostructures are synthesized to be used as PCs [220–224]. Although the ordering and regularity are not quite satisfactory, the porous Al₂O₃ shows structural colors and PBGs in the visible region, and can be tailored by anodization parameters and/or post-chemical etching. Lee et al. utilized alternating mild and hard anodizations for the preparation of periodically structured AAOs and also novel 3D architectures [225, 226]. By controlling anodization current profiles, even complex pore structures inside the films are formed [227]. Similar to Al₂O₃ nanopores, anodic TiO₂ NTs can be fabricated in a straightforward and controllable way as discussed above. By exploration of special TiO₂ NT architectures with the variation of anodization conditions, the incorporation of PBG structures in NTs could be possible.

3.3 Periodically structured NTs by current pulse anodization

Chen et al. first reported in 2011 the work on the potential capability of periodically structured TiO₂ NTs for photonic applications (or the so-called 1D anodic TiO₂ NT PC) [228]. Since then intensive studies have been devoted to the controlled growth of this kind of structures, and utilization of these NT PCs as photoanode materials for sensitized solar cells. The morphologies of PC structures sensitively depend on the pulse profiles.

When pulsed anodization is applied, the periodic structure along the tube longitudinal or axis direction is formed. The interface of the periods is typically voids or ridges, resulting in the required periodic modulation of the refractive index for PCs. To achieve the defined PC effect, the regularity of the periods is very important. However, the NT growth under a fixed voltage is nonuniform, with gradually decreased anodic current density with time during the oxidation process [229, 230]. As a result, for

Figure 7 (A) The NTs with apparent ripples on the sidewall surface, grown by adding a large amount of water (~8%) to the fluoride containing organic electrolyte. The density of ripples is related directly to the water content. Reprinted with permission from Ref. [207]. Copyright (2010) Elsevier. (B) The nanobamboo-shaped NTs formed under voltage pulse anodization. The inset shows that the adjacent NTs are connected together with nanorings while the inner part of the tube wall is smooth. Reprinted with permission from Ref. [208]. Copyright (2008) American Chemical Society. (C) The double-walled NTs with bamboo-type morphologies. Reprinted with permission from Ref. [209]. Copyright (2011) Elsevier. (D) The multi-layered NTs with branches. The top and underlying layers are relatively large-sized NTs formed at a high applied voltage, and the intermediate layer is small-sized NTs formed when the voltage is decreased to a lower value. The (1) schematic and (2) SEM images on the right side show that from top to bottom, one large-sized NT first splits into four branched small tubes when the applied voltage is decreased. Then when the voltage is increased, some small-sized tubes enlarge to large ones while the growth of other tubes would be terminated. Reprinted with permission from Ref. [210]. Copyright (2012) American Chemical Society.

voltage pulse anodization to fabricate periodic TiO₂ NTs, the current profile also shows a decreasing tendency with anodization time. For example, during the 1.25 h voltage pulse anodization, the current density decreased by a factor of 3 from a stable peak value (not consider the sharp current rise in the initial stage) to the lowest value where the anodization process was terminated. The tube growth becomes slower and slower, and the difference of the period length between the top and bottom parts of the NT films can be very large (Figure 8A), which cannot meet the regularity requirement for PCs.

By using current pulse anodization, in contrast, nearly constant tube growth rate is realized, and the corresponding voltage response maintains almost the same waveform and value. Thus, the regularity and geometry of structural periods along NTs can be precisely tuned, which is crucial for PCs. Two samples of periods with

different average lengths (292 and 352 nm, ~20 periods) are shown in Figure 8B, C, where the interfaces are denoted by arrows. It can be observed that the spacing between interfaces (i.e., period length) remains unchanged from the top to the bottom side (the detailed variation curve is shown in Figure 8D). The period length can be adjusted simply by changing the lasting time of the high current limit during the current pulse, which shows an almost linear relationship (Figure 8E). For comparison, the period length of a representative sample fabricated under voltage pulse anodization decreases from about 470 to 260 nm in ~20 periods (Figure 8D), a large variation consistent with the apparent anodization current decrease. To take the advantage of the PC effect and facilitate the device integration, TiO₂ NT arrays with periodic structures have to be utilized based on the membrane architecture. This could be achieved by detaching TiO₂ NT array layers from the

Figure 8 The SEM images of NT microstructures showing the variation of the period length along the tube direction. (A) NTs with irregular periods fabricated under voltage pulse anodization, and (B, C) regular periods by current pulse anodization, with two different average lengths of 292 and 352 nm. (D) The detailed variation of the period length with the period number of the samples shown in (A)–(C). (E) The variation of the period length with the duration of high current limit, showing a linear relationship. (F) The tunable colors of films over the entire visible region with different period lengths. The film at the bottom side of the white color is common NTs fabricated by constant current anodization with no period along the tube axis. (G) By changing the incident or viewing angles, the film color of a specific sample changes greatly through the entire visible spectrum: purple, green and red. And the lower part shows the colorful films with the excellent flexibility. (H) The reflection measurements showing the optical properties of representative colorful films. The black curve is the reflection of the white sample shown in (F). Reprinted with permission from Ref. [228]. Copyright (2011) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Ti metal foil substrate [163]. Since TiO₂ NTs without longitudinal periods only absorb ultraviolet light (above the nominal wide band gap), NT films are of high transparency in the visible region and suitable for photonic applications. The obtained NT films show vivid and uniform colors, including green, yellow and red, which are distributed across the whole visible range (Figure 8F). The film colors are perceived to be from the structural periodicity of NTs, which results in the modulation of the relative refractive index. As can be observed in Figure 8G, the film color of one sample varies greatly from purple, blue to red by changing the incident or viewing angles, which is the characteristic of structural colors. Also the colorful film has excellent flexibility, and can be bent to a large angle without crack. The color and transparency of the films depend on the period length and total thickness. The period length determines in which part of the wavelength region light will be strongly reflected (PBGs), back to the

TiO₂-absorbing layer. Figure 8H shows the representative reflection peaks of colorful films over the entire visible region. Several models have been proposed to explain the effect of PC structures in photoanodes, such as reflection, multiple scattering, resonances and photon localization [231, 232].

During the current pulse, when the anodization current drops to the lower value (not necessarily equal to zero), the tube size also decreases. The lower current process corresponds to the interface between periods, and directly leads to the formation of voids in the interface region. The critical factor for the successful adjustment of tube wall morphologies is the abruptness of the established equilibrium by changing the applied voltage or current during the anodization process. When the situations of field-assisted oxidation and dissolution change, the local reaction ions would suffer from redistribution. Under different pulse conditions, various NT

structures can be obtained. The detailed morphologies in the interface region using triangular, sinusoidal or square current profiles show great disparity, which would affect the dye loading capacity when applied in sensitized solar cells [233]. Li et al. fabricated periodic structures in Si, Fe and Ti substrates by anodization etching using sinusoidal, square or multi-step voltage or current pulses, and various porous structures of these materials with structural colors can be obtained [234–236]. Table 2 summarizes some representative oxide periodic structures with broad applications.

PCs based on TiO₂ NTs have various outstanding advantages. (1) By adjusting the anodization parameters, including the pulse shape, high/low voltage or current value, duration, number and pause time, etc., the period geometry, length, number and total thickness can be tuned in a highly controllable way, realizing the continuous engineering of PBGs. (2) Furthermore, free-standing PC films are very flexible and are of high mechanical strength in the crystallized form, which can withstand post-processing, be easily handled and readily integrated for device applications. (3) As the TiO₂ NT film can be used as multi-functional material, such as biologically adaptive coating, biofilter, microfluidic catalysis, and super-hydrophilicity or hydrophobicity surfaces, the newly introduced PC effect in TiO₂ NTs combined with one or more of the above-mentioned functions will promote future important applications of TiO₂ NTs.

3.4 Single-step synthesis of double-layered NTs with PCs

Among various oxide materials, TiO₂ has the required large refractive index, ensuring the complete band gaps in PCs. Furthermore, the photoanode material itself consists of TiO₂ in sensitized solar cells, and thus TiO₂ NT PCs can be perfectly integrated into solar cell devices with excellent compatibility. In fact, NT PCs typically act as multi-functional materials when applied in sensitized solar cells. Besides the PC effect, this layer can also absorb dyes and scatter light as mentioned above. Various kinds of configurations can be assembled coupled with TiO₂ NTs with photonic feature, indicating the easy integration of such structures for device applications.

Huang et al. tried to fabricate a double-layered NT structure (PC+absorbing layers) through one single anodization step (current pulse+constant current) [238]. The schematic diagram of the double-layered structure and cell assembly, and the SEM images of the NT structure can be seen in Figure 9A, B, respectively. The NT-absorbing

layer of normal smooth-walled NTs mainly adsorbs dye molecules. And the PC layer of periodically structured TiO₂ NTs not only reflects light into the absorbing layer, but also loads dyes, an additional sensitizer adsorbing component. The thicknesses of the PC and absorbing layers are about 4.5 and 5.5 μm , respectively. The reflection spectra of two kinds of samples with 150 and 190 nm period lengths (or lattice constants) are shown in Figure 9C, D, respectively. By changing the period length or the number of PC structures, the locations of reflection peaks and peak intensities vary greatly. With this architecture of a PC coupled photoanode, the above-mentioned drawbacks of previous PC coupling strategies can be overcome. It should be noted that the PC properties (or more evidently, colors) of films when applied in sensitized solar cells (in organic solvents) would be different from the as-synthesized ones in air since the refractive index of the surrounding medium changes (Figure 9C, D, insets). For example, when transferring the 150 nm period length PC film from air to ethanol, the color of the film changed from purple to green, a red shift of the reflection peaks. This discrepancy has to be considered during the design of a PC structure to enhance light harvesting in a given spectrum range. With the optimization of structural features of NTs to match the absorbing spectrum of dye molecules (from visible to NIR), improved photocurrent and superior photoconversion efficiency in the solar cell application can be achieved, up to more than 7% under AM 1.5G sunlight, and the output open-circuit voltage remains almost unchanged. As this double-layered structure is formed in a single anodization step, the two layers can be regarded as an entirety, and thus the electrical contact and material transportation between the two layers are straightforward.

The origin of the increased photocurrent of the double-layered structure is further analyzed by using finite-element simulation, with the parameters similar to the real experimental conditions [239]. It is concluded that the enhancement of photon absorption could happen both in the PBGs and near the band edges. This investigation can be used to design new NT PC structures and search for optimized structural parameters.

3.5 Application of NT PCs to an NP layer

PCs based on TiO₂ NTs can also be used individually to enhance the solar cell efficiency constructed of conventional NPs [240]. The schematic of the fabrication processes is shown in Figure 10A. NT PCs are designed to have the reflection (infiltrated with electrolyte) in the active spectrum region of sensitizers. After that, the PCs

Table 2 Different oxide periodic structures fabricated by anodization and their applications.

Periodic structure	Electrolyte	Pulse method	Regularity	Application	Reference	Image
Al ₂ O ₃ branching pores	0.3 m H ₂ SO ₄	Square current pulse, gradually descended duration of high and low current limits	Periodically branched	Chemical sensor	[222]
Porous Al ₂ O ₃	0.3 m H ₂ SO ₄	Alternating potentials in mild and hard anodization regions	Regular multilayer	Distributed Bragg reflector	[237]
Porous Al ₂ O ₃	0.1 m H ₃ PO ₄	Multiprofiled current cycles with variable periods and amplitudes	Multilayer, controllable	Complex 3D structure	[227]

(Table 2 Continued)

Periodic structure	Electrolyte	Pulse method	Regularity	Application	Reference	Image
TiO ₂ NT	0.3 wt.% NH ₄ F+2 wt.% H ₂ O in EG	Square voltage pulse	Multilayer, not regular	Photocatalysis	[215]
Periodic TiO ₂ NT	0.3 wt.% NH ₄ F+2 vol.% H ₂ O in EG	Square/ sinusoidal/ triangular-wave current pulse	Regular	Solar cell	[233]

(Table 2 Continued)

Periodic structure	Electrolyte	Pulse method	Regularity	Application	Reference	Image
Porous TiO ₂	0.27 wt.% NH ₄ ⁺ F in EG	Multipulsed voltage, impurity driven	Multilayered nanoporous structure, not regular	Electrochromic device	[236]
Porous Fe ₂ O ₃	0.1 M NH ₄ ⁺ F+ 1.5 vol.% H ₂ O in EG	Sinusoidal-wave current pulse	Partially regular	Chemical sensor	[235]

EG, ethylene glycol; NT, nanotube.

Figure 9 (A) The schematic of the solar cell device assembly. The main part of the photoanode is double-layered NTs of upper-region NT PCs with periods on tube walls and lower-region normal NTs with smooth tube walls (viewing from the light incident direction). (B) The SEM images of the NTs fabricated by a single anodization step, including one layer of PCs based on NTs and another layer of normal NTs. From the SEM image of the interface region shown in the inset, distinct variation of tube wall morphologies can be observed. (C) The reflection of the samples (period length ~ 150 nm) with 40 or 20 periods in air, ethanol and electrolyte. The optical images in the inset show the film colors in air or ethanol. (D) The reflection of the samples (period length ~ 190 nm) with 20 or 10 periods. Reprinted with permission from Ref. [238]. Copyright (2011) Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

are transferred onto the NP layer, and the microstructures of the resulting double-layered electrode are presented in Figure 10B. As compared with the direct self-assembly of colloidal PCs on top of the NP layer, the requirement of surface flatness and homogeneity could be lowered by using this strategy of incorporating PCs. The excellent optical properties and good quality of NT PC films are maintained after integration (Figure 10C). As has been discussed above, the crystallized and closely packed photonic NT layer has superior mechanical stability after it is detached from the Ti metal substrate, and thus flexible free-standing membranes can be easily transferred and integrated onto porous NP layers. Strong reflection is observed by coupling NT PCs, as can be observed in the reflection spectra of integrated photoanodes, and the peak position depends on the PC period length (Figure 10D). This means by precisely tuning the PBGs of PCs, more light could be coupled by NT PCs into solar cells,

realizing the significant enhancement of light-harvesting efficiency. The energy conversion efficiencies of solar cells without and with NT PC layers were further compared to verify the PC effect, which significantly increased from 4.99% to 6.96%.

3.6 Engineering the band gaps

Although much success has been achieved based on the NT PC concept, creation of ideal PCs and optimization of composite structures still need to be further investigated, which may facilitate the search for broader applications of such unique structures. Inspired by the above PC structures with a single kind of period lengths, which enhance light absorption far below the theoretical limit, the investigation of multi-, quasi- or even gradient band gap structures in TiO₂ NTs by using modified electrochemical

Figure 10 (A) Schematic of the fabrication of the NT PC layer and transferring of this layer to an independently processed porous NP layer. 1: NT PC layer is first grown on a Ti metal substrate by current pulse anodization; 2: The PC layer is detached from the substrate to obtain free-standing PC films; 3: A porous NP layer is coated on the FTO substrate by a doctor-blade method; 4: The preformed PC film is transfer onto the NP layer, forming the double-layered structure; 5: The tight connection between the two layers is obtained after calcination. (B) The cross-sectional SEM image of the integrated structure, with a 2.3-μm-thick top NT PC layer on a 10-μm-thick underlying porous NP layer. The scale bar is 100 nm. (C) Photographs of the colorful photoanodes after the assembly, exhibiting large crack-free films with uniform colors. (D) The experimental and calculated reflection spectra. Samples of 120, 150, 180, 230-PC denote that the period lengths of incorporated PCs in the photoanodes are 120, 150, 180 and 230 nm, respectively. Reprinted with permission from Ref. [240]. Copyright (2012) The Royal Society of Chemistry.

anodizations, with the intent of enhancing the light-harvesting efficiency in the broader band or even the full spectrum region of incident sunlight (where different PC components enhance light absorption in different bands), would have the bright prospects.

4 Pre patterning of the Ti surface for 2D NT PCs

TiO₂ NTs could be successfully fabricated as 2D PC structures with periodicity close to the visible wavelength by using a ZnO nanorod template [241] or an ordered AAO template [242]. With such an AAO membrane as a template, anodic TiO₂ nanorod arrays with regular top morphologies

are formed [243]. In TiO₂ NT films synthesized by anodization, although regular periodical structures in the tube direction by current pulse anodization have been achieved as discussed above, the NT mouth has a wide pore distribution in the film plane. It has been explored that in AAO nanopore structures, 2D PCs can be realized due to their regularly arranged characteristics in the 2D direction with a long-range order [244–247]. By changing the lattice constant from 200 to 220 nm or from 436 to 513 nm, the peak positions in the transmission spectra of polarized light show a significant red shift. Furthermore, this 2D Al₂O₃ PC structure with ideal periodicity and high aspect ratio was applied to generate laser emission at the band edge of the PBG. As compared with Al₂O₃, TiO₂ has a higher refractive index as mentioned above, and thus can exhibit excellent PC properties. As a result, the improvement of

2D regularity of TiO₂ NTs is critical for their applications in PC-assisted sensitized solar cells.

4.1 Large-area 2D PCs

Various methods have been proposed to improve the 2D regularity parallel to the hexagonal and closely packed NT film surface in a large area. For example, the strategy of two- or multi-step anodization [204, 229, 248–250] forms initial concaves by first-step anodization and ultrasonication, which will guide the tube growth afterwards. Wang et al. fabricated hierarchically structured TiO₂ NTs with two-step anodization [251, 252], resulting in the defined patterns of top large pores and inside small ones on the top surface (nanoring+NT, Figure 11A). They further deposited Au NPs with the plasmonic effect on the NT surface (Figure 11B) and also utilized the hierarchical NT

surface with improved periodicity and uniformity as the PC layer to enhance the SPR effect of Au NPs [253]. The schematic of the fabrication processes is shown in Figure 11C. The results in Figure 11D demonstrate that the TiO₂ NT top surface structure could well serve as a PC layer, which shows defined multi-peaks in the reflectance absorption spectra. Also, by changing the surrounding environment of the 2D PC structure, for example, from air to ethanol, the absorption peaks show a red shift, indicating the successful formation of PC structures on the NT surface. The insets in Figure 11D show the structural colors originated from the top regular surface of NTs. When incorporating Au NPs with 556 nm SPR peaks on the 2D NT PC surface, the absorption intensity is increased over the visible region. That is to say, the plasmonic effect could be enhanced – the PC assisted SPR effect. The enhancement of SPR by a PC layer on the NT surface can also be seen in Figure 11E. Compared with Au NPs deposited on the NT surface

Figure 11 (A) The hierarchical porous NTs with large pores on surface and underlying small pores formed inside the large pores. The upper inset is the cross-sectional SEM image of the NTs and lower is the tilted view of the concave-shaped surface. (B) The porous NTs loaded with Au NPs. (C) The schematic of the fabrication processes of 2D NT PCs with Au NPs. 1: The first step anodization forms irregular top NTs. 2: The as-formed NT layer is removed from the Ti substrate by ultrasonication. Nanoimprint is formed on the Ti metal surface. 3: The second step anodization is performed to fabricate NTs with hierarchical nanopores as shown in (A). 4: Au NPs are deposited on the NT surface as shown in (B). Consequently, a TiO₂ NT layer on the Ti substrate coupled with both PC layer and Au NPs is obtained. The schematic on the bottom left shows that the PC effect can enhance the SPR of Au NPs. (D) The diffuse reflectance absorption of three samples. TiO₂ NTPC in air: TiO₂ NTs with the porous surface layer as PCs in air. Au(556)/TiO₂ NTPC in air: TiO₂ NTs with the PC layer and Au NPs of 556 nm SPR peak. TiO₂ NTPC in ethanol: TiO₂ NTs with the PC layer in ethanol. (E) The SPR absorption of three samples: Au NPs on TiO₂ NTPC with the 556 nm SPR peak; larger Au NPs on TiO₂ NTPC with the 590 nm peak and Au NPs with the 556 nm SPR peak on TiO₂ NTs without the PC layer. Reprinted with permission from Ref. [253]. Copyright (2013) American Chemical Society.

without a PC layer, the SPR absorption intensities of two types of Au NPs (SPR peaks locating at 556 and 590 nm, respectively) are greatly enhanced, and 556 nm Au NPs show greater enhancement than the 590 nm ones. The 2D PCs on the top surface will trap incident light inside the layer where Au NPs are coated and thus the SPR effect could be enhanced, and by matching the PC band gap to the absorption peak of Au NPs, the maximized enhancement can be achieved.

Pre-anodization polishing is another kind of strategy for the improvement of 2D periodicity [254–257], which aims at the modification of the surface flatness of the Ti metal substrate to improve the local electric field distribution during anodization [258]. Although the short-range order has been improved, the results are not quite satisfactory. The biggest obstacle is that unlike Al₂O₃, the self-ordering of TiO₂ nanopores or NTs is in the short range. This is possibly due to the fact that the chemical dissolution of TiO₂ NTs during the rapid growth process with the presence of fluoride ions is severe, while this process is suppressed in Al₂O₃ nanopore formation.

4.2 Patterns by guided anodization

To further improve the regularity, various strategies have been adopted including pre patterning organization by focused ion beam (FIB) etching and nanoimprinting, etc. FIB etching has been used to form desired regular patterns on the Ti metal surface prior to anodization. These patterns will guide the following TiO₂ NT growth, and regular arrays can be successfully obtained [259–265]. The interpore distances at the surface can be varied from 150 to 500 nm, and NT cells are of hexagonal, square and triangular shapes (Figure 12A–C). Moreover, by FIB etching even alternating-sized (Figure 12D) and sophisticated sunflower (Figure 12E, F) arrangements of NTs can be realized. That is to say, the guiding effect is universally applicable to fabricate various shapes and arrangements. Seeding the initial pores by nanoimprinting under high pressure has also been utilized to create very regular but shallow nanopores below the breakdown potential [266]. These strategies enable us to restrict the tube growth, and the NT initiates preferentially at designated locations, resulting in the formation of desired 2D periodic architectures with a long-range order. The possible drawbacks of these methods are complex manipulation procedures, high cost and limitation to a small active area in the micrometer scale, and thus large-scale production is difficult when applied for the enhancement of photon absorption in sensitized solar cells. Furthermore, to fabricate deep pores

under the conditions of high fluoride concentration, large anodization voltage or prolonged anodization duration, the NT top and side would be gradually etched out [267], forming the bunching and destroying the surface guiding layer.

5 Perspectives

This review presents various strategies to enhance the interaction of the incident light with the absorbing layer by using TiO₂ NT structures. TiO₂ NTs, when applied in sensitized solar cells, enhance light harvesting by trapping the incident light inside the solar cells, and usually exhibit multi-functional properties. The unique characteristics of TiO₂ NTs make them show one or more features of light scattering, dye anchoring or photogenerated electron transport in photon management.

Various novel NT structures are expected to be developed in future work. Especially in sensitized solar cells, the configuration of the incorporation of the strong and tunable scattering effect of TiO₂ NTs in composite films combining the advantages of each component can be further optimized, which will lead to the enhanced light harvesting of the films loaded with photon-active materials. The investigation of reliable and cost-effective pre patterning methods on the Ti substrate to synthesize 2D periodic structures of large-sized NTs for visible response, with advantages of easy manipulation, large-area production and high throughput would be beneficial for the coupling of 2D NT PCs in sensitized solar cells for photon utilization. By the combination of 1D and 2D periodicities as discussed above, 3D PC structures based on TiO₂ NTs can be realized. With the omni-directional response of the 3D structures to the incident light, the light would be perfectly harvested, which is very important for the enhancement of solar energy conversion efficiency. Other strategies include the anti-reflection coating by using TiO₂ NTs. TiO₂ thin films have been largely reported as anti-reflection coatings in silicon solar cells to enhance light transmission. The investigation of the use of NTs as an outer-face anti-reflection coating is underway, with the intent of reducing reflection of the incident light entering sensitized solar cells. Grating of the Ti metal surface by lithography [268–270], laser patterning [271] or mechanical ruling [272] methods can introduce micropatterning on the photoanode surface, and also has the great potential to harvest the incident light more efficiently. The application of TiO₂ nanostructures with the enhancement of photon utilization, in combination with proper sensitizers, would be expected to realize the efficient utilization of solar energy and wider device applications.

Figure 12 Various NT morphologies by FIB-guided anodization. (A, B) The hexagonal or square arrangement of closely packed NT arrays with excellent pore periodicity. Insets (1) and (2) are the bottom and cross-sectional SEM images, respectively. The scale bars are all 500 nm. (C) Triangular-shaped NTs guided by patterns arranged in a graphite lattice. The interpore distance is 225 nm and no new tubes form at the lattice center. (D) The hexagonal arrangement of alternating-sized NTs fabricated by patterned graphite lattice. As a result, the self-compensating effect, small-sized NTs grow at the centers of the lattice. (E, F) The top and bottom morphologies of TiO_2 NT sunflower grown from FIB guiding patterns, respectively. Insets (1) and (2) in (F) show the counterclockwise and clockwise spirals in NT sunflowers, respectively. (A, B, D) Reprinted with permission from Ref. [260]. (C, E, F) Reprinted with permission from Ref. [263]. Copyright (2011) The Royal Society of Chemistry.

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References

- [1] O'regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* 1991, 353, 737–740.
- [2] Yella A, Lee H-W, Tsao HN, Yi C, Chandiran AK, Nazeeruddin MK, Diau EW-G, Yeh C-Y, Zakeeruddin SM, Grätzel M. Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. *Science* 2011, 334, 629–634.
- [3] Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells. *Chem. Rev.* 2010, 110, 6595–6663.
- [4] Grätzel M. Recent advances in sensitized mesoscopic solar cells. *Acc. Chem. Res.* 2009, 42, 1788–1798.
- [5] Snaith HJ, Schmidt-Mende L. Advances in liquid-electrolyte and solid-state dye-sensitized solar cells. *Adv. Mater.* 2007, 19, 3187–3200.
- [6] Nazeeruddin MK, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, Ito S, Takeru B, Grätzel M. Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers. *J. Am. Chem. Soc.* 2005, 127, 16835–16847.
- [7] Chen C-Y, Wang M, Li J-Y, Pootrakulchote N, Alibabaei L, Ngoc-le C-h, Decoppet J-D, Tsai J-H, Grätzel C, Wu C-G. Highly efficient light-harvesting ruthenium sensitizer for thin-film dye-sensitized solar cells. *ACS Nano* 2009, 3, 3103–3109.
- [8] Burke A, Schmidt-Mende L, Ito S, Grätzel M. A novel blue dye for near-IR 'dye-sensitized' solar cell applications. *Chem. Commun.* 2007, 234–236.
- [9] Yum J-H, Walter P, Huber S, Rentsch D, Geiger T, Nüesch F, De Angelis F, Grätzel M, Nazeeruddin MK. Efficient far red sensitization of nanocrystalline TiO₂ films by an unsymmetrical squaraine dye. *J. Am. Chem. Soc.* 2007, 129, 10320–10321.
- [10] Hardin BE, Hoke ET, Armstrong PB, Yum J-H, Comte P, Torres T, Fréchet JM, Nazeeruddin MK, Grätzel M, McGehee MD. Increased light harvesting in dye-sensitized solar cells with energy relay dyes. *Nat. Photonics* 2009, 3, 406–411.
- [11] Humphry-Baker N, Driscoll K, Rao A, Torres T, Snaith HJ, Friend RH. Time-evolution of poly(3-hexylthiophene) as an energy relay dye in dye-sensitized solar cells. *Nano Lett.* 2012, 12, 634–639.
- [12] Kim H-S, Lee C-R, Im J-H, Lee K-B, Moehl T, Marchioro A, Moon S-J, Humphry-Baker R, Yum J-H, Moser JE, Grätzel M, Park N-G. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Sci. Rep.* 2012, 2, 591.
- [13] Lee MM, Teuscher J, Miyasaka T, Murakami TN, Snaith HJ. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science* 2012, 338, 643–647.
- [14] Pellet N, Gao P, Gregori G, Yang TY, Nazeeruddin MK, Maier J, Grätzel M. Mixed-organic-cation perovskite photovoltaics for enhanced solar-light harvesting. *Angew. Chem. Int. Ed.* 2014, 53, 3151–3157.
- [15] Bi D, Yang L, Boschloo G, Hagfeldt A, Johansson EM. Effect of different hole transport materials on recombination in CH₃NH₃PbI₃ perovskite-sensitized mesoscopic solar cells. *J. Phys. Chem. Lett.* 2013, 4, 1532–1536.
- [16] Fan J, Jia B, Gu M. Perovskite-based low-cost and high-efficiency hybrid halide solar cells. *Photon. Res.* 2014, 2, 111–120.
- [17] Kongkanand A, Tvrdy K, Takechi K, Kuno M, Kamat PV. Quantum dot solar cells. Tuning photoresponse through size and shape control of CdSe-TiO₂ architecture. *J. Am. Chem. Soc.* 2008, 130, 4007–4015.
- [18] Sambur JB, Novet T, Parkinson B. Multiple exciton collection in a sensitized photovoltaic system. *Science* 2010, 330, 63–66.
- [19] Kamat PV. Quantum dot solar cells. The next big thing in photovoltaics. *J. Phys. Chem. Lett.* 2013, 4, 908–918.
- [20] Lan C-M, Wu H-P, Pan T-Y, Chang C-W, Chao W-S, Chen C-T, Wang C-L, Lin C-Y, Diau EW-G. Enhanced photovoltaic performance with co-sensitization of porphyrin and an organic dye in dye-sensitized solar cells. *Energy Environ. Sci.* 2012, 5, 6460–6464.
- [21] Wu H-P, Ou Z-W, Pan T-Y, Lan C-M, Huang W-K, Lee H-W, Reddy NM, Chen C-T, Chao W-S, Yeh C-Y. Molecular engineering of cocktail co-sensitization for efficient panchromatic porphyrin-sensitized solar cells. *Energy Environ. Sci.* 2012, 5, 9843–9848.
- [22] Li L-L, Diau EW-G. Porphyrin-sensitized solar cells. *Chem. Soc. Rev.* 2013, 42, 291–304.
- [23] Li Y, Wei L, Chen X, Zhang R, Sui X, Chen Y, Jiao J, Mei L. Efficient PbS/CdS co-sensitized solar cells based on TiO₂ nanorod arrays. *Nanoscale Res. Lett.* 2013, 8, 67.
- [24] Zhang S, Islam A, Yang X, Qin C, Zhang K, Numata Y, Chen H, Han L. Improvement of spectral response by co-sensitizers for high efficiency dye-sensitized solar cells. *J. Mater. Chem. A* 2013, 1, 4812–4819.
- [25] Miao Q, Wu L, Cui J, Huang M, Ma T. A new type of dye-sensitized solar cell with a multilayered photoanode prepared by a film-transfer technique. *Adv. Mater.* 2011, 23, 2764–2768.
- [26] Zhang X, Deng Y, Liao W, Mu W, Zheng D, Zhou Y, Liu W, Lin Z. Rational design of hybrid dye-sensitized solar cells composed of double-layered photoanodes with enhanced power conversion efficiency. *J. Mater. Chem. A* 2014, 2, 11035–11039.
- [27] Bailey ZM, McGehee MD. Modeling low cost hybrid tandem photovoltaics with the potential for efficiencies exceeding 20%. *Energy Environ. Sci.* 2012, 5, 9173–9179.
- [28] Park SW, Lee K, Lee D-K, Ko MJ, Park N-G, Kim K. Expanding the spectral response of a dye-sensitized solar cell by applying a selective positioning method. *Nanotechnology* 2011, 22, 045201.
- [29] Chang S, Li Q, Xiao X, Wong KY, Chen T. Enhancement of low energy sunlight harvesting in dye-sensitized solar cells using plasmonic gold nanorods. *Energy Environ. Sci.* 2012, 5, 9444–9448.
- [30] Brown MD, Suteewong T, Kumar RSS, D'Innocenzo V, Petrozza A, Lee MM, Wiesner U, Snaith HJ. Plasmonic dye-sensitized solar cells using core-shell metal-insulator nanoparticles. *Nano Lett.* 2010, 11, 438–445.
- [31] McFarland EW, Tang J. A photovoltaic device structure based on internal electron emission. *Nature* 2003, 421, 616–618.
- [32] Xu Q, Liu F, Liu Y, Cui K, Feng X, Zhang W, Huang Y. Broadband light absorption enhancement in dye-sensitized solar cells with Au-Ag alloy popcorn nanoparticles. *Sci. Rep.* 2013, 3, 2112.

- [33] Li Y, Wang H, Feng Q, Zhou G, Wang Z-S. Gold nanoparticles inlaid TiO₂ photoanodes: a superior candidate for high-efficiency dye-sensitized solar cells. *Energy Environ. Sci.* 2013, 6, 2156–2165.
- [34] Jia B, Chen X, Saha JK, Qiao Q, Wang Y, Shi Z, Gu M. Concept to devices: from plasmonic light trapping to upscaled plasmonic solar modules. *Photon. Res.* 2013, 1, 22–27.
- [35] Wu W-Q, Lei B-X, Rao H-S, Xu Y-F, Wang Y-F, Su C-Y, Kuang D-B. Hydrothermal fabrication of hierarchically anatase TiO₂ nanowire arrays on FTO glass for dye-sensitized solar cells. *Sci. Rep.* 2013, 3, 1352.
- [36] Que L, Lan Z, Wu W, Wu J, Lin J, Huang M. High-efficiency dye-sensitized solar cells based on ultra-long single crystalline titanium dioxide nanowires. *J. Power Sources* 2014, 266, 440–447.
- [37] Wang F, Wang Y, Zhan X, Safdar M, Gong J, He J. Pt nanoparticle and CdS quantum dot assisted WO₃ nanowires grown on flexible carbon fibers for efficient oxygen production. *CrystEngComm* 2014, 16, 1389–1394.
- [38] Zhan X, Wang Q, Wang F, Wang Y, Wang Z, Cao J, Safdar M, He J. Composition-tuned ZnO/Zn_xCd_{1-x}Te core/shell nanowires array with broad spectral absorption from UV to NIR for hydrogen generation. *ACS Appl. Mater. Interfaces* 2014, 6, 2878–2883.
- [39] Melcarne G, De Marco L, Carlino E, Martina F, Manca M, Cingolani R, Gigli G, Ciccarella G. Surfactant-free synthesis of pure anatase TiO₂ nanorods suitable for dye-sensitized solar cells. *J. Mater. Chem.* 2010, 20, 7248–7254.
- [40] Kang SH, Choi SH, Kang MS, Kim JY, Kim HS, Hyeon T, Sung YE. Nanorod-based dye-sensitized solar cells with improved charge collection efficiency. *Adv. Mater.* 2008, 20, 54–58.
- [41] Ghadiri E, Taghavinia N, Zakeeruddin SM, Grätzel M, Moser JE. Enhanced electron collection efficiency in dye-sensitized solar cells based on nanostructured TiO₂ hollow fibers. *Nano Lett.* 2010, 10, 1632–1638.
- [42] Chandrasekar R, Zhang L, Howe JY, Hedin NE, Zhang Y, Fong H. Fabrication and characterization of electrospun titania nanofibers. *J. Mater. Sci.* 2009, 44, 1198–1205.
- [43] Liao J-Y, He J-W, Xu H, Kuang D-B, Su C-Y. Effect of TiO₂ morphology on photovoltaic performance of dye-sensitized solar cells: nanoparticles, nanofibers, hierarchical spheres and ellipsoid spheres. *J. Mater. Chem.* 2012, 22, 7910–7918.
- [44] Wang H, Guo Z, Wang S, Liu W. One-dimensional titania nanostructures: synthesis and applications in dye-sensitized solar cells. *Thin Solid Films* 2014, 558, 1–19.
- [45] Su Z, Zhou W. Formation mechanism of porous anodic aluminum and titanium oxides. *Adv. Mater.* 2008, 20, 3663–3667.
- [46] Huang S, Peng W, Ning C, Hu Q, Dong H. Nanostructure transition on anodic titanium: structure control via a competition strategy between electrochemical oxidation and chemical etching. *J. Phys. Chem. C* 2012, 116, 22359–22364.
- [47] Kowalski D, Kim D, Schmuki P. TiO₂ nanotubes, nanochannels and mesosponge: self-organized formation and applications. *Nano Today* 2013, 8, 235–264.
- [48] Zhou X, Nguyen NT, Özkan S, Schmuki P. Anodic TiO₂ nanotube layers: why does self-organized growth occur – a mini review. *Electrochem. Commun.* 2014, 46, 157–162.
- [49] So S, Lee K, Schmuki P. Ultra-fast growth of highly ordered anodic TiO₂ nanotubes in lactic acid electrolytes. *J. Am. Chem. Soc.* 2012, 134, 11316–11318.
- [50] Wang D, Liu L. Continuous fabrication of free-standing TiO₂ nanotube array membranes with controllable morphology for depositing interdigitated heterojunctions. *Chem. Mater.* 2010, 22, 6656–6664.
- [51] Roy P, Berger S, Schmuki P. TiO₂ nanotubes: synthesis and applications. *Angew. Chem. Int. Ed.* 2011, 50, 2904–2939.
- [52] Lee W, Park S-J. Porous anodic aluminum oxide: anodization and templated synthesis of functional nanostructures. *Chem. Rev.* 2014, 114, 7487–7556.
- [53] Pervez SA, Kim D, Farooq U, Yaqub A, Choi J-H, Lee Y-J, Doh C-H. Comparative electrochemical analysis of crystalline and amorphous anodized iron oxide nanotube layers as negative electrode for LIB. *ACS Appl. Mater. Interfaces* 2014, 6, 11219–11224.
- [54] Teh JJ, Guai GH, Wang X, Leong KC, Li CM, Chen P. Nanoporous tin oxide photoelectrode prepared by electrochemical anodization in aqueous ammonia to improve performance of dye sensitized solar cell. *J. Renew. Sustain. Energy* 2013, 5, 023120.
- [55] Shin Y, Lee S. A freestanding membrane of highly ordered anodic ZrO₂ nanotube arrays. *Nanotechnology* 2009, 20, 105301.
- [56] El-Sayed HA, Birss VI. Controlled growth and monitoring of tantalum oxide nanostructures. *Nanoscale* 2010, 2, 793–798.
- [57] Ou JZ, Rani RA, Ham M-H, Field MR, Zhang Y, Zheng H, Reece P, Zhuiykov S, Sriram S, Bhaskaran M. Elevated temperature anodized Nb₂O₅: a photoanode material with exceptionally large photoconversion efficiencies. *ACS Nano* 2012, 6, 4045–4053.
- [58] Baker DR, Kamat PV. Photosensitization of TiO₂ nanostructures with CdS quantum dots: particulate versus tubular support architectures. *Adv. Funct. Mater.* 2009, 19, 805–811.
- [59] Kuang DB, Brillet J, Chen P, Takata M, Uchida S, Miura H, Sumioka K, Zakeeruddin SM, Grätzel M. Application of highly ordered TiO₂ nanotube arrays in flexible dye-sensitized solar cells. *ACS Nano* 2008, 2, 1113–1116.
- [60] Zhu K, Neale NR, Miedaner A, Frank AJ. Enhanced charge-collection efficiencies and light scattering in dye-sensitized solar cells using oriented TiO₂ nanotubes arrays. *Nano Lett.* 2007, 7, 69–74.
- [61] Mir N, Lee K, Paramasivam I, Schmuki P. Optimizing TiO₂ nanotube top geometry for use in dye-sensitized solar cells. *Chem. Eur. J.* 2012, 18, 11862–11866.
- [62] Tao L, Xiong Y, Liu H, Shen W. Chemical assisted formation of secondary structures towards high efficiency solar cells based on ordered TiO₂ nanotube arrays. *J. Mater. Chem.* 2012, 22, 7863–7870.
- [63] Ye M, Zheng D, Lv M, Chen C, Lin C, Lin Z. Hierarchically structured nanotubes for highly efficient dye-sensitized solar cells. *Adv. Mater.* 2013, 25, 3039–3044.
- [64] Roy P, Kim D, Lee K, Spiecker E, Schmuki P. TiO₂ nanotubes and their application in dye-sensitized solar cells. *Nanoscale* 2010, 2, 45–59.
- [65] Varghese OK, Paulose M, Grimes CA. Long vertically aligned titania nanotubes on transparent conducting oxide for highly efficient solar cells. *Nat. Nanotechnol.* 2009, 4, 592–597.
- [66] Galstyan V, Vomiero A, Concina I, Braga A, Brisotto M, Bontempi E, Faglia G, Sberveglieri G. Vertically Aligned TiO₂ nanotubes on plastic substrates for flexible solar cells. *Small* 2011, 7, 2437–2442.
- [67] Choi J, Park S-H, Kwon YS, Lim J, Song IY, Park T. Facile fabrication of aligned doubly open-ended TiO₂ nanotubes, via a selective etching process, for use in front-illuminated dye sensitized solar cells. *Chem. Commun.* 2012, 48, 8748–8750.

- [68] Sheng P, Li W, Cai J, Wang X, Tong X, Cai Q, Grimes CA. A novel method for the preparation of a photocorrosion stable core/shell CdTe/CdS quantum dot TiO₂ nanotube array photo-electrode demonstrating an AM 1.5 G photoconversion efficiency of 6.12%. *J. Mater. Chem. A* 2013, 1, 7806–7815.
- [69] Ye M, Gong J, Lai Y, Lin C, Lin Z. High-efficiency photoelectrocatalytic hydrogen generation enabled by palladium quantum dots-sensitized TiO₂ nanotube arrays. *J. Am. Chem. Soc.* 2012, 134, 15720–15723.
- [70] Jung SW, Park J-H, Lee W, Kim J-H, Kim H, Choi C-J, Ahn K-S. Enhanced electron lifetime in CdS quantum dot-sensitized solar cells with nanoporous-layer-covered TiO₂ nanotube arrays. *J. Appl. Phys.* 2011, 110, 054301.
- [71] Huang S, Zhang Q, Huang X, Guo X, Deng M, Li D, Luo Y, Shen Q, Toyoda T, Meng Q. Fibrous CdS/CdSe quantum dot co-sensitized solar cells based on ordered TiO₂ nanotube arrays. *Nanotechnology* 2010, 21, 375201.
- [72] Yang H, Fan W, Vaneski A, Susha AS, Teoh WY, Rogach AL. Heterojunction engineering of CdTe and CdSe quantum dots on TiO₂ nanotube arrays: intricate effects of size-dependency and interfacial contact on photoconversion efficiencies. *Adv. Funct. Mater.* 2012, 22, 2821–2829.
- [73] Wang X, Zheng J, Sui X, Xie H, Liu B, Zhao X. CdS quantum dots sensitized solar cells based on free-standing and through-hole TiO₂ nanotube arrays. *Dalton Trans.* 2013, 42, 14726–14732.
- [74] Gao X, Li J, Baker J, Hou Y, Guan D, Chen J, Yuan C. Enhanced photovoltaic performance of perovskite CH₃NH₃PbI₃ solar cells with freestanding TiO₂ nanotube array films. *Chem. Commun.* 2014, 50, 6368–6371.
- [75] Kang SH, Kim J-Y, Kim Y, Kim HS, Sung Y-E. Surface modification of stretched TiO₂ nanotubes for solid-state dye-sensitized solar cells. *J. Phys. Chem. C* 2007, 111, 9614–9623.
- [76] Bella F, Lamberti A, Sacco A, Bianco S, Chiodoni A, Bongiovanni R. Novel electrode and electrolyte membranes: towards flexible dye-sensitized solar cell combining vertically aligned TiO₂ nanotube array and light-cured polymer network. *J. Membr. Sci.* 2014, 470, 125–131.
- [77] Kuo Y-Y, Chien C-H. Sinter-free transferring of anodized TiO₂ nanotube-array onto a flexible and transparent sheet for dye-sensitized solar cells. *Electrochimica Acta* 2013, 91, 337–343.
- [78] Jang N-S, Kim MS, Kim S-H, Lee S-K, Kim J-M. Direct growth of titania nanotubes on plastic substrates and their application to flexible gas sensors. *Sensor. Actuat. B-Chem.* 2014, 199, 361–368.
- [79] Vomiero A, Galstyan V, Braga A, Concina I, Brisotto M, Bontempi E, Sberveglieri G. Flexible dye sensitized solar cells using TiO₂ nanotubes. *Energy Environ. Sci.* 2011, 4, 3408–3413.
- [80] Liu Y, Cheng Y, Chen K, Peng Z, Yang G, Zakharova GS, Chen W. Fabrication of TiO₂ nanotube arrays and its application in flexible dye-sensitized solar cells. *RSC Adv.* 2014, 4, 45592–45597.
- [81] Richter C, Schmuttenmaer CA. Exciton-like trap states limit electron mobility in TiO₂ nanotubes. *Nat. Nanotechnol.* 2010, 5, 769–772.
- [82] Zhang Q, Celorrio V, Bradley K, Eisner F, Cherns D, Yan W, Fermín DJ. Density of deep trap states in oriented TiO₂ nanotube arrays. *J. Phys. Chem. C* 2014, 118, 18207–18213.
- [83] Guo Z, Prezhdov OV, Hou T, Chen X, Lee S-T, Li Y. Fast energy relaxation by trap states decreases electron mobility in TiO₂ nanotubes: time-domain ab initio analysis. *J. Phys. Chem. Lett.* 2014, 5, 1642–1647.
- [84] Docampo P, Guldin S, Steiner U, Snaith HJ. Charge transport limitations in self-assembled TiO₂ photoanodes for dye-sensitized solar cells. *J. Phys. Chem. Lett.* 2013, 4, 698–703.
- [85] Kang T, Smith A, Taylor B, Durstock M. Fabrication of highly-ordered TiO₂ nanotube arrays and their use in dye-sensitized solar cells. *Nano Lett.* 2009, 9, 601–606.
- [86] Lin J, Guo M, Yip CT, Lu W, Zhang G, Liu X, Zhou L, Chen X, Huang H. High temperature crystallization of free-standing anatase TiO₂ nanotube membranes for high efficiency dye-sensitized solar cells. *Adv. Funct. Mater.* 2013, 23, 5952–5960.
- [87] Kuo Y-Y, Li T-H, Yao J-N, Lin C-Y, Chien C-H. Hydrothermal crystallization and modification of surface hydroxyl groups of anodized TiO₂ nanotube-arrays for more efficient photoenergy conversion. *Electrochimica Acta* 2012, 78, 236–243.
- [88] Jung M-H, Ko KC, Lee JY. Single Crystalline-like TiO₂ nanotube fabrication with dominant (001) facets using poly (vinylpyrrolidone) for high efficiency solar cells. *J. Phys. Chem. C* 2014, 118, 17306–17317.
- [89] Lin J, Liu X, Guo M, Lu W, Zhang G, Zhou L, Chen X, Huang H. A facile route to fabricate an anodic TiO₂ nanotube-nanoparticle hybrid structure for high efficiency dye-sensitized solar cells. *Nanoscale* 2012, 4, 5148–5153.
- [90] Liu X, Lin J, Chen X. Synthesis of long TiO₂ nanotube arrays with a small diameter for efficient dye-sensitized solar cells. *RSC Adv.* 2013, 3, 4885–4889.
- [91] Liu N, Albu SP, Lee K, So S, Schmuki P. Water annealing and other low temperature treatments of anodic TiO₂ nanotubes: a comparison of properties and efficiencies in dye sensitized solar cells and for water splitting. *Electrochimica Acta* 2012, 82, 98–102.
- [92] Ye M, Xin X, Lin C, Lin Z. High efficiency dye-sensitized solar cells based on hierarchically structured nanotubes. *Nano Lett.* 2011, 11, 3214–3220.
- [93] Choi J, Kwon YS, Park T. Doubly open-ended TiO₂ nanotube arrays decorated with a few nm-sized TiO₂ nanoparticles for highly efficient dye-sensitized solar cells. *J. Mater. Chem. A* 2014, 2, 14380–14385.
- [94] Bavykin DV, Passoni L, Walsh FC. Hierarchical tube-in-tube structures prepared by electrophoretic deposition of nano-structured titanates into a TiO₂ nanotube array. *Chem. Commun.* 2013, 49, 7007–7009.
- [95] Hardin BE, Snaith HJ, McGehee MD. The renaissance of dye-sensitized solar cells. *Nat. Photonics* 2012, 6, 162–169.
- [96] Fukai Y, Kondo Y, Mori S, Suzuki E. Highly efficient dye-sensitized SnO₂ solar cells having sufficient electron diffusion length. *Electrochem. Commun.* 2007, 9, 1439–1443.
- [97] Zhang Q, Chou TP, Russo B, Jenekhe SA, Cao G. Polydisperse aggregates of ZnO nanocrystallites: a method for energy-conversion-efficiency enhancement in dye-sensitized solar cells. *Adv. Funct. Mater.* 2008, 18, 1654–1660.
- [98] Chang Y-J, Kong E-H, Park Y-C, Jang HM. Broadband light confinement using a hierarchically structured TiO₂ multi-layer for dye-sensitized solar cells. *J. Mater. Chem. A* 2013, 1, 9707–9713.
- [99] Wang P, Zakeeruddin SM, Comte P, Charvet R, Humphry-Baker R, Grätzel M. Enhance the performance of dye-sensitized solar cells by co-grafting amphiphilic sensitizer and hexadecyl-malonic acid on TiO₂ nanocrystals. *J. Phys. Chem. B* 2003, 107, 14336–14341.

- [100] Gao F, Wang Y, Shi D, Zhang J, Wang M, Jing X, Humphry-Baker R, Wang P, Zakeeruddin SM, Grätzel M. Enhance the optical absorptivity of nanocrystalline TiO₂ film with high molar extinction coefficient ruthenium sensitizers for high performance dye-sensitized solar cells. *J. Am. Chem. Soc.* 2008, 130, 10720–10728.
- [101] Shi D, Pootrakulchote N, Li R, Guo J, Wang Y, Zakeeruddin SM, Grätzel M, Wang P. New efficiency records for stable dye-sensitized solar cells with low-volatility and ionic liquid electrolytes. *J. Phys. Chem. C* 2008, 112, 17046–17050.
- [102] Ito S, Zakeeruddin SM, Humphry-Baker R, Liska P, Charvet R, Comte P, Nazeeruddin MK, Péchy P, Takata M, Miura H. High-efficiency organic-dye-sensitized solar cells controlled by nanocrystalline-TiO₂ electrode thickness. *Adv. Mater.* 2006, 18, 1202–1205.
- [103] Ito S, Takahashi K, Yusa S-i, Imamura T, Tanimoto K. Effects of homogenization scheme of TiO₂ screen-printing paste for dye-sensitized solar cells. *Int. J. Photoenergy* 2012, 2012, 405642.
- [104] Koo H-J, Park J, Yoo B, Yoo K, Kim K, Park N-G. Size-dependent scattering efficiency in dye-sensitized solar cell. *Inorganica Chimica Acta* 2008, 361, 677–683.
- [105] Zhang Q, Myers D, Lan J, Jenekhe SA, Cao G. Applications of light scattering in dye-sensitized solar cells. *Phys. Chem. Chem. Phys.* 2012, 14, 14982–14998.
- [106] Tian Z, Tian H, Wang X, Yuan S, Zhang J, Zhang X, Yu T, Zou Z. Multilayer structure with gradual increasing porosity for dye-sensitized solar cells. *Appl. Phys. Lett.* 2009, 94, 031905.
- [107] Ferber J, Luther J. Computer simulations of light scattering and absorption in dye-sensitized solar cells. *Sol. Energy Mater. Sol. Cells* 1998, 54, 265–275.
- [108] Rothenberger G, Comte P, Grätzel M. A contribution to the optical design of dye-sensitized nanocrystalline solar cells. *Sol. Energy Mater. Sol. Cells* 1999, 58, 321–336.
- [109] Usami A. Theoretical simulations of optical confinement in dye-sensitized nanocrystalline solar cells. *Sol. Energy Mater. Sol. Cells* 2000, 64, 73–83.
- [110] Vargas WE, Niklasson GA. Optical properties of nano-structured dye-sensitized solar cells. *Sol. Energy Mater. Sol. Cells* 2001, 69, 147–163.
- [111] Ito S, Murakami TN, Comte P, Liska P, Grätzel C, Nazeeruddin MK, Grätzel M. Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%. *Thin Solid Films* 2008, 516, 4613–4619.
- [112] Shao W, Gu F, Gai L, Li C. Planar scattering from hierarchical anatase TiO₂ nanoplates with variable shells to improve light harvesting in dye-sensitized solar cells. *Chem. Commun.* 2011, 47, 5046–5048.
- [113] Dadgostar S, Tajabadi F, Taghavinia N. Mesoporous submicrometer TiO₂ hollow spheres as scatterers in dye-sensitized solar cells. *ACS Appl. Mater. Interfaces* 2012, 4, 2964–2968.
- [114] Koo HJ, Kim YJ, Lee YH, Lee WI, Kim K, Park NG. Nano-embossed hollow spherical TiO₂ as bifunctional material for high-efficiency dye-sensitized solar cells. *Adv. Mater.* 2008, 20, 195–199.
- [115] Lv F, Xiao S, Zhu J, Li H. Dye-sensitized solar cells with enhanced efficiency using hierarchical TiO₂ spheres as a scattering layer. *RSC Adv.* 2014, 4, 36206–36211.
- [116] Hongchang P, Hongbin Y, Chun Xian G, Jinlin L, Chang Ming L. Nanoparticle self-assembled hollow TiO₂ spheres with well matching visible light scattering for high performance dye-sensitized solar cells. *Chem. Commun.* 2012, 48, 8832–8834.
- [117] Park Y, Lee JW, Ha S-J, Moon JH. 1D nanorod-planted 3D inverse opal structures for use in dye-sensitized solar cells. *Nanoscale* 2014, 6, 3105–3109.
- [118] Chen H-Y, Zhang T-L, Fan J, Kuang D-B, Su C-Y. Electrospun hierarchical TiO₂ nanorods with high porosity for efficient dye-sensitized solar cells. *ACS Appl. Mater. Interfaces* 2013, 5, 9205–9211.
- [119] Yang L, Leung WWF. Application of a bilayer TiO₂ nanofiber photoanode for optimization of dye-sensitized solar cells. *Adv. Mater.* 2011, 23, 4559–4562.
- [120] Hwang SH, Kim C, Song H, Son S, Jang J. Designed architecture of multiscale porous TiO₂ nanofibers for dye-sensitized solar cells photoanode. *ACS Appl. Mater. Interfaces* 2012, 4, 5287–5292.
- [121] Yan K, Qiu Y, Chen W, Zhang M, Yang S. A double layered photoanode made of highly crystalline TiO₂ nanooctahedra and agglutinated mesoporous TiO₂ microspheres for high efficiency dye sensitized solar cells. *Energy Environ. Sci.* 2011, 4, 2168–2176.
- [122] Yu IG, Kim YJ, Kim HJ, Lee C, Lee WI. Size-dependent light-scattering effects of nanoporous TiO₂ spheres in dye-sensitized solar cells. *J. Mater. Chem.* 2011, 21, 532–538.
- [123] Park Y-C, Chang Y-J, Kum B-G, Kong E-H, Son JY, Kwon YS, Park T, Jang HM. Size-tunable mesoporous spherical TiO₂ as a scattering overlayer in high-performance dye-sensitized solar cells. *J. Mater. Chem.* 2011, 21, 9582–9586.
- [124] Kim YJ, Lee MH, Kim HJ, Lim G, Choi YS, Park NG, Kim K, Lee WI. Formation of highly efficient dye-sensitized solar cells by hierarchical pore generation with nanoporous TiO₂ spheres. *Adv. Mater.* 2009, 21, 3668–3673.
- [125] Huang F, Chen D, Zhang XL, Caruso RA, Cheng YB. Dual-function scattering layer of submicrometer-sized mesoporous TiO₂ beads for high-efficiency dye-sensitized solar cells. *Adv. Funct. Mater.* 2010, 20, 1301–1305.
- [126] Miao X, Pan K, Liao Y, Zhou W, Pan Q, Tian G, Wang G. Controlled synthesis of mesoporous anatase TiO₂ microspheres as a scattering layer to enhance the photoelectrical conversion efficiency. *J. Mater. Chem. A* 2013, 1, 9853–9861.
- [127] Feng J, Hong Y, Zhang J, Wang P, Hu Z, Wang Q, Han L, Zhu Y. Novel core-shell TiO₂ microsphere scattering layer for dye-sensitized solar cells. *J. Mater. Chem. A* 2014, 2, 1502–1508.
- [128] Lan C-M, Liu S-E, Shiu J-W, Hu J-Y, Lin M-H, Diau EW-G. Formation of size-tunable dandelion-like hierarchical rutile titania nanospheres for dye-sensitized solar cells. *RSC Adv.* 2013, 3, 559–565.
- [129] Yang L, Lin Y, Jia J, Li X, Xiao X, Zhou X. Cauliflower-like TiO₂ rough spheres: synthesis and applications in dye sensitized solar cells. *Microporous Mesoporous Mater.* 2008, 112, 45–52.
- [130] Wu X, Lu GQM, Wang L. Shell-in-shell TiO₂ hollow spheres synthesized by one-pot hydrothermal method for dye-sensitized solar cell application. *Energy Environ. Sci.* 2011, 4, 3565–3572.
- [131] Lee KS, Kwon J, Im JH, Lee CR, Park N-G, Park JH. Size-tunable, fast, and facile synthesis of titanium oxide nanotube powders for dye-sensitized solar cells. *ACS Appl. Mater. Interfaces* 2012, 4, 4164–4168.
- [132] Sun KC, Qadir MB, Jeong SH. Hydrothermal synthesis of TiO₂ nanotubes and their application as an over-layer for dye-sensitized solar cells. *RSC Adv.* 2014, 4, 23223–23230.

- [133] Ha S-J, Moon JH. In-situ fabrication of macroporous films for dye-sensitized solar cells: formation of the scattering layer and the gelation of electrolytes. *Sci. Rep.* 2014, 4, 5375.
- [134] Liu Z, Su X, Hou G, Bi S, Xiao Z, Jia H. Mixed photoelectrode based on spherical TiO₂ nanorod aggregates for dye-sensitized solar cells with high short-circuit photocurrent density. *RSC Adv.* 2013, 3, 8474–8479.
- [135] Lee KE, Charbonneau C, Demopoulos GP. Thin single screen-printed bifunctional titania layer photoanodes for high performing DSSCs via a novel hybrid paste formulation and process. *J. Mater. Res.* 2013, 28, 480–487.
- [136] Son S, Hwang SH, Kim C, Yun JY, Jang J. Designed synthesis of SiO₂/TiO₂ core/shell structure as light scattering material for highly efficient dye-sensitized solar cells. *ACS Appl. Mater. Interfaces* 2013, 5, 4815–4820.
- [137] Yoon J-H, Jang S-R, Vittal R, Lee J, Kim K-J. TiO₂ nanorods as additive to TiO₂ film for improvement in the performance of dye-sensitized solar cells. *J. Photochem. Photobiol. A* 2006, 180, 184–188.
- [138] Mohammadpour R, Hagfeldt A, Boschloo G. Investigation on the dynamics of electron transport and recombination in TiO₂ nanotube/nanoparticle composite electrodes for dye-sensitized solar cells. *Phys. Chem. Chem. Phys.* 2011, 13, 21487–21491.
- [139] Wang X, Karanjit S, Zhang L, Fong H, Qiao Q, Zhu Z. Transient photocurrent and photovoltage studies on charge transport in dye sensitized solar cells made from the composites of TiO₂ nanofibers and nanoparticles. *Appl. Phys. Lett.* 2011, 98, 082114.
- [140] Tan B, Wu Y. Dye-sensitized solar cells based on anatase TiO₂ nanoparticle/nanowire composites. *J. Phys. Chem. B* 2006, 110, 15932–15938.
- [141] Pham TTT, Bessho T, Mathews N, Zakeeruddin SM, Lam YM, Mhaisalkar S, Grätzel M. Light scattering enhancement from sub-micrometer cavities in the photoanode for dye-sensitized solar cells. *J. Mater. Chem.* 2012, 22, 16201–16204.
- [142] Hore S, Nitz P, Vetter C, Prah C, Niggemann M, Kern R. Scattering spherical voids in nanocrystalline TiO₂ – enhancement of efficiency in dye-sensitized solar cells. *Chem. Commun.* 2005, 2011–2013.
- [143] Li LL, Tsai CY, Wu HP, Chen CC, Diau EWG. Fabrication of long TiO₂ nanotube arrays in a short time using a hybrid anodic method for highly efficient dye-sensitized solar cells. *J. Mater. Chem.* 2010, 20, 2753–2758.
- [144] Yun HG, Park JH, Bae BS, Kang MG. Dye-sensitized solar cells with TiO₂ nano-particles on TiO₂ nano-tube-grown Ti substrates. *J. Mater. Chem.* 2011, 21, 3558–3561.
- [145] Zheng Q, Kang H, Yun J, Lee J, Park JH, Baik S. Hierarchical construction of self-standing anodized titania nanotube arrays and nanoparticles for efficient and cost-effective front-illuminated dye-sensitized solar cells. *ACS Nano* 2011, 5, 5088–5093.
- [146] Luo J, Gao L, Sun J, Liu Y. A bilayer structure of a titania nanoparticle/highly-ordered nanotube array for low-temperature dye-sensitized solar cells. *RSC Adv.* 2012, 2, 1884–1889.
- [147] Zhang Y, Khamwannah J, Kim H, Noh SY, Yang H, Jin S. Improved dye sensitized solar cell performance in larger cell size by using TiO₂ nanotubes. *Nanotechnology* 2013, 24, 045401.
- [148] Fahim NF, Sekino T. A novel method for synthesis of titania nanotube powders using rapid breakdown anodization. *Chem. Mater.* 2009, 21, 1967–1979.
- [149] Liao Y, Que W. Preparation and photocatalytic activity of TiO₂ nanotube powders derived by a rapid anodization process. *J. Alloys Compd.* 2010, 505, 243–248.
- [150] Arunchandran C, Ramya S, George R, Kamachi Mudali U. Corrosion inhibitor storage and release property of TiO₂ nanotube powder synthesized by rapid breakdown anodization method. *Mater. Res. Bull.* 2013, 48, 635–639.
- [151] Zhong P, Liao Y, Que W, Jia Q, Lei T. Enhanced electron collection in photoanode based on ultrafine TiO₂ nanotubes by a rapid anodization process. *J. Solid State Electrochem.* 2014, 18, 2087–2098.
- [152] Fahim NF, Sekino T. Anodic TiO₂ nanotubes powder and its application in dye-sensitized solar cells. *J. Nanopart. Res.* 2011, 13, 6409–6418.
- [153] Mohammadpour A, Waghmare PR, Mitra SK, Shankar K. Anodic growth of large-diameter multipodal TiO₂ nanotubes. *ACS Nano* 2010, 4, 7421–7430.
- [154] Ni J, Noh K, Frandsen CJ, Kong SD, He G, Tang T, Jin S. Preparation of near micrometer-sized TiO₂ nanotube arrays by high voltage anodization. *Mater. Sci. Eng. C* 2013, 33, 259–264.
- [155] Wang D, Liu Y, Yu B, Zhou F, Liu W. TiO₂ nanotubes with tunable morphology, diameter, and length: synthesis and photo-electrical/catalytic performance. *Chem. Mater.* 2009, 21, 1198–1206.
- [156] Wang X, Zha C, Ji C, Zhang X, Shen L, Wang Y, Gupta A, Yoriya S, Bao N. Synthesis of highly-ordered TiO₂ nanotube arrays with tunable sizes. *Mater. Res. Express* 2014, 1, 035031.
- [157] Yoriya S, Grimes CA. Self-Assembled TiO₂ nanotube arrays by anodization of titanium in diethylene glycol: approach to extended pore widening. *Langmuir* 2009, 26, 417–420.
- [158] Valota A, Curioni M, Leclerc D, Skeldon P, Falaras P, Thompson G. Influence of applied potential on titanium oxide nanotube growth. *J. Electrochem. Soc.* 2010, 157, K243–K247.
- [159] Ghicov A, Schmuki P. Self-ordering electrochemistry: a review on growth and functionality of TiO₂ nanotubes and other self-aligned MO_x structures. *Chem. Commun.* 2009, 2791–2808.
- [160] Macak J, Hildebrand H, Marten-Jahns U, Schmuki P. Mechanistic aspects and growth of large diameter self-organized TiO₂ nanotubes. *J. Electroanal. Chem.* 2008, 621, 254–266.
- [161] Mohammadpour A, Shankar K. Anodic TiO₂ nanotube arrays with optical wavelength-sized apertures. *J. Mater. Chem.* 2010, 20, 8474–8477.
- [162] Liu X, Guo M, Cao J, Lin J, Tsang YH, Chen X, Huang H. Large-diameter titanium dioxide nanotube arrays as a scattering layer for high-efficiency dye-sensitized solar cell. *Nanoscale Res. Lett.* 2014, 9, 362.
- [163] Lin J, Chen J, Chen X. Facile fabrication of free-standing TiO₂ nanotube membranes with both ends open via self-detaching anodization. *Electrochem. Commun.* 2010, 12, 1062–1065.
- [164] Paulose M, Peng L, Popat KC, Varghese OK, LaTempa TJ, Bao N, Desai TA, Grimes CA. Fabrication of mechanically robust, large area, polycrystalline nanotubular/porous TiO₂ membranes. *J. Membr. Sci.* 2008, 319, 199–205.
- [165] Liu G, Wang K, Hoivik N, Jakobsen H. Progress on free-standing and flow-through TiO₂ nanotube membranes. *Sol. Energy Mater. Sol. Cells* 2012, 98, 24–38.
- [166] Ouyang HM, Fei GT, Zhang Y, Su H, Jin Z, Xu SH, De Zhang L. Large scale free-standing open-ended TiO₂ nanotube arrays: stress-induced self-detachment and in situ pore opening. *J. Mater. Chem. C* 2013, 1, 7498–7506.

- [167] Lin J, Chen J, Chen X. High-efficiency dye-sensitized solar cells based on robust and both-end-open TiO₂ nanotube membranes. *Nanoscale Res. Lett.* 2011, 6, 475.
- [168] Li L-L, Chen Y-J, Wu H-P, Wang NS, Diau EW-G. Detachment and transfer of ordered TiO₂ nanotube arrays for front-illuminated dye-sensitized solar cells. *Energy Environ. Sci.* 2011, 4, 3420–3425.
- [169] Lamberti A, Sacco A, Bianco S, Manfredi D, Cappelluti F, Hernandez S, Quaglio M, Pirri CF. Charge transport improvement employing TiO₂ nanotube arrays as front-side illuminated dye-sensitized solar cell photoanodes. *Phys. Chem. Chem. Phys.* 2013, 15, 2596–2602.
- [170] Zhang J, Li S, Ding H, Li Q, Wang B, Wang X, Wang H. Transfer and assembly of large area TiO₂ nanotube arrays onto conductive glass for dye sensitized solar cells. *J. Power Sources* 2014, 247, 807–812.
- [171] Wu H-P, Lan C-M, Hu J-Y, Huang W-K, Shiu J-W, Lan Z-J, Tsai C-M, Su C-H, Diau EW-G. Hybrid titania photoanodes with a nanostructured multi-layer configuration for highly efficient dye-sensitized solar cells. *J. Phys. Chem. Lett.* 2013, 4, 1570–1577.
- [172] Xin XK, Wang J, Han W, Ye MD, Lin ZQ. Dye-sensitized solar cells based on a nanoparticle/nanotube bilayer structure and their equivalent circuit analysis. *Nanoscale* 2012, 4, 964–969.
- [173] De Marco L, Manca M, Giannuzzi R, Belviso MR, Cozzoli PD, Gigli G. Shape-tailored TiO₂ nanocrystals with synergic peculiarities as building blocks for highly efficient multi-stack dye solar cells. *Energy Environ. Sci.* 2013, 6, 1791–1795.
- [174] Wu W-Q, Xu Y-F, Su C-Y, Kuang D-B. Ultra-long anatase TiO₂ nanowire arrays with multi-layered configuration on FTO glass for high-efficiency dye-sensitized solar cells. *Energy Environ. Sci.* 2014, 7, 644–649.
- [175] Wang X, Sun L, Zhang S, Zhao D. On seeding of the second layer in growth of double-layered TiO₂ nanotube arrays. *Electrochimica Acta* 2013, 107, 200–208.
- [176] Tu W-K, Lin C-J, Chatterjee A, Shiau G-H, Chien S-H. A novel nanocomposite TiO₂ photoanode for highly efficient dye-sensitized solar cells. *J. Power Sources* 2012, 203, 297–301.
- [177] Wu W-Q, Xu Y-F, Rao H-S, Su C-Y, Kuang D-B. Trilayered photoanode of TiO₂ nanoparticles on a 1D-3D nanostructured TiO₂-grown flexible Ti substrate for high-efficiency (9.1%) dye-sensitized solar cells with unprecedentedly high photocurrent density. *J. Phys. Chem. C* 2014, 118, 16426–16432.
- [178] Wu W-Q, Xu Y-F, Rao H-S, Su C-Y, Kuang D-B. Multi-stack integration of three-dimensional hyperbranched anatase titania architectures for high-efficiency dye-sensitized solar cells. *J. Am. Chem. Soc.* 2014, 136, 6437–6445.
- [179] Mor GK, Shankar K, Paulose M, Varghese OK, Grimes CA. Use of highly-ordered TiO₂ nanotube arrays in dye-sensitized solar cells. *Nano Lett.* 2006, 6, 215–218.
- [180] Shankar K, Bandara J, Paulose M, Wietasch H, Varghese OK, Mor GK, LaTempa TJ, Thelakkat M, Grimes CA. Highly efficient solar cells using TiO₂ nanotube arrays sensitized with a donor-antenna dye. *Nano Lett.* 2008, 8, 1654–1659.
- [181] Stergiopoulos T, Ghicov A, Likodimos V, Tsoukleris D, Kunze J, Schmuki P, Falaras P. Dye-sensitized solar cells based on thick highly ordered TiO₂ nanotubes produced by controlled anodic oxidation in non-aqueous electrolytic media. *Nanotechnology* 2008, 19, 235602.
- [182] Kim JY, Noh JH, Zhu K, Halverson AF, Neale NR, Park S, Hong KS, Frank AJ. General strategy for fabricating transparent TiO₂ nanotube arrays for dye-sensitized photoelectrodes: illumination geometry and transport properties. *ACS Nano* 2011, 5, 2647–2656.
- [183] Liu X, Guo M, Lin J, Chen X, Huang H. Design of multi-layered TiO₂ nanotube/nanoparticle hybrid structure for enhanced efficiency in dyesensitized solar cells. *RSC Adv.* 2014, 4, 45180–45184.
- [184] Sato O, Kubo S, Gu Z. Structural color films with lotus effects, superhydrophilicity, and tunable stop-bands. *Acc. Chem. Res.* 2009, 42, 1–10.
- [185] Zhang W, Zhang D, Fan T, Gu J, Ding J, Wang H, Guo Q, Ogawa H. Novel photoanode structure templated from butterfly wing scales. *Chem. Mater.* 2008, 21, 33–40.
- [186] Han J, Su H, Song F, Zhang D, Chen Z. Controllable reflection properties of nanocomposite photonic crystals constructed by semiconductor nanocrystallites and natural periodic biomatrices. *Nanoscale* 2010, 2, 2203–2208.
- [187] Lou S, Guo X, Fan T, Zhang D. Butterflies: inspiration for solar cells and sunlight water-splitting catalysts. *Energy Environ. Sci.* 2012, 5, 9195–9216.
- [188] Colodrero S, Mihi A, Häggman L, Ocana M, Boschloo G, Hagfeldt A, Míguez H. Porous one-dimensional photonic crystals improve the power-conversion efficiency of dye-sensitized solar cells. *Adv. Mater.* 2009, 21, 764–770.
- [189] Colodrero S, Ocana M, Míguez H. Nanoparticle-based one-dimensional photonic crystals. *Langmuir* 2008, 24, 4430–4434.
- [190] Colonna D, Colodrero S, Lindström H, Di Carlo A, Míguez H. Introducing structural colour in DSCs by using photonic crystals: interplay between conversion efficiency and optical properties. *Energy Environ. Sci.* 2012, 5, 8238–8243.
- [191] Colodrero S, Mihi A, Anta JA, Ocaña M, Míguez Hn. Experimental demonstration of the mechanism of light harvesting enhancement in photonic-crystal-based dye-sensitized solar cells. *J. Phys. Chem. C* 2009, 113, 1150–1154.
- [192] Colodrero S, Forneli A, López-López C, Pellejà L, Míguez H, Palomares E. Efficient transparent thin dye solar cells based on highly porous 1D photonic crystals. *Adv. Funct. Mater.* 2012, 22, 1303–1310.
- [193] Gu Z-Z, Fujishima A, Sato O. Fabrication of high-quality opal films with controllable thickness. *Chem. Mater.* 2002, 14, 760–765.
- [194] Guldin S, Hüttner S, Kolbe M, Welland M, Müller-Buschbaum P, Friend R, Steiner U, Tétreault N. Dye-sensitized solar cell based on a three-dimensional photonic crystal. *Nano Lett.* 2010, 10, 2303–2309.
- [195] Lee S-HA, Abrams NM, Hoertz PG, Barber GD, Halaoui LI, Mallouk TE. Coupling of titania inverse opals to nanocrystalline titania layers in dye-sensitized solar cells. *J. Phys. Chem. B* 2008, 112, 14415–14421.
- [196] Mihi A, Zhang C, Braun PV. Transfer of preformed three-dimensional photonic crystals onto dye-sensitized solar cells. *Angew. Chem. Int. Ed.* 2011, 123, 5830–5833.
- [197] Shin J-H, Kang J-H, Jin W-M, Park JH, Cho Y-S, Moon JH. Facile synthesis of TiO₂ inverse opal electrodes for dye-sensitized solar cells. *Langmuir* 2010, 27, 856–860.

- [198] Juodkazis S, Rosa L, Bauerdick S, Peto L, El-Ganainy R, John S. Sculpturing of photonic crystals by ion beam lithography: towards complete photonic bandgap at visible wavelengths. *Opt. Exp.* 2011, 19, 5802–5810.
- [199] Kang J, Moon J, Lee S, Park S, Jang S, Yang S, Yang S. Thermoresponsive hydrogel photonic crystals by three-dimensional holographic lithography. *Adv. Mater.* 2008, 20, 3061–3065.
- [200] Shir D, Liao H, Jeon S, Xiao D, Johnson H, Bogart G, Bogart K, Rogers J. Three-dimensional nanostructures formed by single step, two-photon exposures through elastomeric Penrose quasicrystal phase masks. *Nano Lett.* 2008, 8, 2236–2244.
- [201] Anscombe N. Direct laser writing. *Nat. Photonics* 2010, 4, 22–23.
- [202] Deubel M, Von Freymann G, Wegener M, Pereira S, Busch K, Soukoulis C. Direct laser writing of three-dimensional photonic-crystal templates for telecommunications. *Nat. Mater.* 2004, 3, 444–447.
- [203] Macak JM, Tsuchiya H, Taveira L, Aldabergerova S, Schmuki P. Smooth anodic TiO₂ nanotubes. *Angew. Chem. Int. Ed.* 2005, 44, 7463–7465.
- [204] Li S, Zhang G, Guo D, Yu L, Zhang W. Anodization fabrication of highly ordered TiO₂ nanotubes. *J. Phys. Chem. C* 2009, 113, 12759–12765.
- [205] Liu H, Tao L, Shen W. Controllable current oscillation and pore morphology evolution in the anodic growth of TiO₂ nanotubes. *Nanotechnology* 2011, 22, 155603.
- [206] Lee W, Kim J, Gösele U. Spontaneous current oscillations during hard anodization of aluminum under potentiostatic conditions. *Adv. Funct. Mater.* 2010, 20, 21–27.
- [207] Song Y, Schmuki P. Modulated TiO₂ nanotube stacks and their use in interference sensors. *Electrochem. Commun.* 2010, 12, 579–582.
- [208] Kim D, Ghicov A, Albu SP, Schmuki P. Bamboo-type TiO₂ nanotubes: improved conversion efficiency in dye-sensitized solar cells. *J. Am. Chem. Soc.* 2008, 130, 16454–16455.
- [209] Ji Y, Lin K-C, Zheng H, Zhu J-j, Samia ACS. Fabrication of double-walled TiO₂ nanotubes with bamboo morphology via one-step alternating voltage anodization. *Electrochem. Commun.* 2011, 13, 1013–1015.
- [210] Chen B, Lu K. Hierarchically branched titania nanotubes with tailored diameters and branch numbers. *Langmuir* 2012, 28, 2937–2943.
- [211] Zhang F, Chen S, Yin Y, Lin C, Xue C. Anodic formation of ordered and bamboo-type TiO₂ nanotubes arrays with different electrolytes. *J. Alloys Compd.* 2010, 490, 247–252.
- [212] Albu SP, Kim D, Schmuki P. Growth of aligned TiO₂ bamboo-type nanotubes and highly ordered nanolace. *Angew. Chem. Int. Ed.* 2008, 47, 1916–1919.
- [213] Wang S, Zhou X, Xiao X, Fang Y, Lin Y. An increase in conversion efficiency of dye-sensitized solar cells using bamboo-type TiO₂ nanotube arrays. *Electrochimica Acta* 2014, 116, 26–30.
- [214] Luan X, Guan D, Wang Y. Facile synthesis and morphology control of bamboo-type TiO₂ nanotube arrays for high-efficiency dye-sensitized solar cells. *J. Phys. Chem. C* 2012, 116, 14257–14263.
- [215] Liu Y, Wang D, Cao L, Chen S. Structural engineering of highly ordered TiO₂ nanotube array by periodic anodization of titanium. *Electrochem. Commun.* 2012, 23, 68–71.
- [216] Xiong F-Q, Wei X, Zheng X, Zhong D, Zhang W-H, Li C. Fabrication of multilayered TiO₂ nanotube arrays and separable nanotube segments. *J. Mater. Chem. A* 2014, 2, 4510–4513.
- [217] Yang D-J, Park H, Kim H-G, Cho S-J, Choi W-Y. Fabrication of a patterned TiO₂ nanotube arrays in anodic oxidation. *J. Electroceram.* 2009, 23, 159–163.
- [218] Wei W, Jha H, Yang G, Hahn R, Paramasivam I, Berger S, Spiecker E, Schmuki P. Formation of self-organized superlattice nanotube arrays-embedding heterojunctions into nanotube walls. *Adv. Mater.* 2010, 22, 4770–4774.
- [219] Yang M, Yang G, Spiecker E, Lee K, Schmuki P. Ordered “superlattice” TiO₂/Nb₂O₅ nanotube arrays with improved ion insertion stability. *Chem. Commun.* 2013, 49, 460–462.
- [220] Wang B, Fei G, Wang M, Kong M, Zhang L. Preparation of photonic crystals made of air pores in anodic alumina. *Nanotechnology* 2007, 18, 365601.
- [221] Hu X, Ling Z, Sun T, He X. Tuning optical properties of photonic crystal of anodic alumina and the influence of electrodeposition. *J. Electrochem. Soc.* 2009, 156, D521–D524.
- [222] Guo D-L, Fan L-X, Wang F-H, Huang S-Y, Zou X-W. Porous anodic aluminum oxide Bragg stacks as chemical sensors. *J. Phys. Chem. C* 2008, 112, 17952–17956.
- [223] Liu Y, Chang Y, Ling Z, Hu X, Li Y. Structural coloring of aluminum. *Electrochem. Commun.* 2011, 13, 1336–1339.
- [224] Zheng WJ, Fei GT, Wang B, De Zhang L. Modulation of transmission spectra of anodized alumina membrane distributed Bragg reflector by controlling anodization temperature. *Nanoscale Res. Lett.* 2009, 4, 665–667.
- [225] Lee W, Schwirn K, Steinhart M, Pippel E, Scholz R, Gösele U. Structural engineering of nanoporous anodic aluminium oxide by pulse anodization of aluminium. *Nat. Nanotechnol.* 2008, 3, 234–239.
- [226] Lee W, Scholz R, Gösele U. A continuous process for structurally well-defined Al₂O₃ nanotubes based on pulse anodization of aluminum. *Nano Lett.* 2008, 8, 2155–2160.
- [227] Losic D, Lillo M, Losic D Jr. Porous alumina with shaped pore geometries and complex pore architectures fabricated by cyclic anodization. *Small* 2009, 5, 1392–1397.
- [228] Lin J, Liu K, Chen X. Synthesis of periodically structured titania nanotube films and their potential for photonic applications. *Small* 2011, 7, 1784–1789.
- [229] Wang D, Yu B, Wang C, Zhou F, Liu W. A novel protocol toward perfect alignment of anodized TiO₂ nanotubes. *Adv. Mater.* 2009, 21, 1964–1967.
- [230] Prakasam H, Shankar K, Paulose M, Varghese O, Grimes C. A new benchmark for TiO₂ nanotube array growth by anodization. *J. Phys. Chem. C* 2007, 111, 7235–7241.
- [231] O’Brien PG, Kherani NP, Chutinan A, Ozin GA, John S, Zukotynski S. Silicon photovoltaics using conducting photonic crystal back-reflectors. *Adv. Mater.* 2008, 20, 1577–1582.
- [232] Lozano G, Colodrero S, Caulier O, Calvo ME, Míguez H. Theoretical analysis of the performance of one-dimensional photonic crystal-based dye-sensitized solar cells. *J. Phys. Chem. C* 2010, 114, 3681–3687.
- [233] Xie Y-L, Li Z-X, Xu H, Xie K-F, Xu Z-G, Zhang H-L. Fabrication of TiO₂ nanotubes with extended periodical morphology by alternating-current anodization. *Electrochem. Commun.* 2012, 17, 34–37.

- [234] Cheng H, Tsang CK, Li H, Cheng J-W, Liang F, Li YY. Facile fabrication of porous nickel films with tunable colors. *J. Electrochem. Soc.* 2012, 159, H928–H931.
- [235] Cheng H, Zheng L, Tsang CK, Zhang J, Wang H, Dong Y, Li H, Liang F, Zapfen JA, Li YY. Electrochemical fabrication and optical properties of periodically structured porous Fe₂O₃ films. *Electrochem. Commun.* 2012, 20, 178–181.
- [236] Zheng L, Cheng H, Liang F, Shu S, Tsang CK, Li H, Lee S-T, Li YY. Porous TiO₂ photonic band gap materials by anodization. *J. Phys. Chem. C* 2012, 116, 5509–5515.
- [237] Sulka GD, Hnida K. Distributed Bragg reflector based on porous anodic alumina fabricated by pulse anodization. *Nanotechnology* 2012, 23, 075303.
- [238] Yip C-T, Huang HT, Zhou LM, Xie KY, Wang Y, Feng TH, Li J, Tam WY. Direct and seamless coupling of TiO₂ nanotube photonic crystal to dye-sensitized solar cell: a single-step approach. *Adv. Mater.* 2011, 23, 5624–5628.
- [239] Guo M, Yong Z, Xie K, Lin J, Wang Y, Huang H. Enhanced light harvesting in dye-sensitized solar cells coupled with titania nanotube photonic crystals: a theoretical study. *ACS Appl. Mater. Interfaces* 2013, 5, 13022–13028.
- [240] Guo M, Xie KY, Lin J, Yong ZH, Yip C-T, Zhou LM, Wang Y, Huang HT. Design and coupling of multifunctional TiO₂ nanotube photonic crystal to nanocrystalline titania layer as semi-transparent photoanode for dye-sensitized solar cell. *Energy Environ. Sci.* 2012, 5, 9881–9888.
- [241] Song H, Jo K, Jung BY, Jung GY. Fabrication of periodically aligned vertical single-crystalline anatase TiO₂ nanotubes with perfect hexagonal open-ends using chemical capping materials. *Nano Res.* 2014, 7, 104–109.
- [242] Tevis ID, Stupp SI. Patterning of periodic high-aspect-ratio nanopores in anatase titanium dioxide from titanium fluoride hydrolysis. *Nanoscale* 2011, 3, 2162–2165.
- [243] Chang Y-H, Lin H-W, Chen C. Ultrafast initial growth rate of self-assembled TiO₂ nanorod arrays fabricated by Ti anodization. *Electrochem. Solid-State Lett.* 2011, 14, K1–K4.
- [244] Masuda H, Ohya M, Asoh H, Nakao M, Nohtomi M, Tamamura T. Photonic crystal using anodic porous alumina. *Jpn. J. Appl. Phys.* 1999, 38, L1403–L1405.
- [245] Masuda H, Yamada M, Matsumoto F, Yokoyama S, Mashiko S, Nakao M, Nishio K. Lasing from two-dimensional photonic crystals using anodic porous alumina. *Adv. Mater.* 2006, 18, 213–216.
- [246] Masuda H, Ohya M, Asoh H, Nishio K. Photonic band gap in naturally occurring ordered anodic porous alumina. *Jpn. J. Appl. Phys.* 2001, 40, L1217–L1219.
- [247] Král Z, Vojtkůvka L, Garcia-Caurel E, Ferré-Borrull J, Marsal LF, Pallarès J. Calculation of angular-dependent reflectance and polarimetry spectra of nanoporous anodic alumina-based photonic crystal slabs. *Photonic. Nanostruct.* 2009, 7, 12–18.
- [248] Lin J, Chen X. Synthesis of high-aspect-ratio, top-open and ultraflat-surface TiO₂ nanotubes through double-layered configuration. *Phys. Status Solidi-R* 2012, 6, 28–30.
- [249] Zhang G, Huang H, Zhang Y, Chan H, Zhou L. Highly ordered nanoporous TiO₂ and its photocatalytic properties. *Electrochem. Commun.* 2007, 9, 2854–2858.
- [250] Shin Y, Lee S. Self-organized regular arrays of anodic TiO₂ nanotubes. *Nano Lett.* 2008, 8, 3171–3173.
- [251] Zhang Z, Wang P. Optimization of photoelectrochemical water splitting performance on hierarchical TiO₂ nanotube arrays. *Energy Environ. Sci.* 2012, 5, 6506–6512.
- [252] Zhang Z, Yu Y, Wang P. Hierarchical top-porous/bottom-tubular TiO₂ nanostructures decorated with Pd nanoparticles for efficient photoelectrocatalytic decomposition of synergistic pollutants. *ACS Appl. Mater. Interfaces* 2012, 4, 990–996.
- [253] Zhang Z, Zhang L, Hedhili MN, Zhang H, Wang P. Plasmonic gold nanocrystals coupled with photonic crystal seamlessly on TiO₂ nanotube photoelectrodes for efficient visible light photoelectrochemical water splitting. *Nano Lett.* 2013, 13, 14–20.
- [254] Wei W, Berger S, Shrestha N, Schmuki P. Ideal hexagonal order: formation of self-organized anodic oxide nanotubes and nanopores on a Ti-35Ta Alloy. *J. Electrochem. Soc.* 2010, 157, C409–C413.
- [255] Lu K, Tian Z, Geldmeier JA. Polishing effect on anodic titania nanotube formation. *Electrochimica Acta* 2011, 56, 6014–6020.
- [256] Albertin K, Tavares A, Pereyra I. Optimized Ti polishing techniques for enhanced order in TiO₂ NT arrays. *Appl. Surf. Sci.* 2013, 284, 772–779.
- [257] Zhou H, Zhang Y. Electrochemically self-doped TiO₂ nanotube arrays for supercapacitors. *J. Phys. Chem. C* 2014, 118, 5626–5636.
- [258] Apolinario A, Sousa CT, Ventura J, Costa JD, Leitão D, Moreira JM, Sousa JB, Andrade L, Mendes A, Araujo JP. The role of the Ti surface roughness in the self-ordering of TiO₂ nanotubes: a detailed study of the growth mechanism. *J. Mater. Chem. A* 2014, 2, 9067–9078.
- [259] Lu K. Newfound capability of focused ion beam patterning guided anodization. *Electrochimica Acta* 2012, 63, 256–262.
- [260] Chen B, Lu K, Tian Z. Effects of titania nanotube distance and arrangement during focused ion beam guided anodization. *J. Mater. Chem.* 2011, 21, 8835–8840.
- [261] Chen B, Lu K. Influence of patterned concave depth and surface curvature on anodization of titania nanotubes and alumina nanopores. *Langmuir* 2011, 27, 12179–12185.
- [262] Chen B, Lu K, Tian Z. Novel patterns by focused ion beam guided anodization. *Langmuir* 2010, 27, 800–808.
- [263] Chen B, Lu K, Geldmeier JA. Highly ordered titania nanotube arrays with square, triangular, and sunflower structures. *Chem. Commun.* 2011, 47, 10085–10087.
- [264] Tian Z-P, Lu K, Chen B. Unique nanopore pattern formation by focused ion beam guided anodization. *Nanotechnology* 2010, 21, 405301.
- [265] Chen B, Lu K. Selective focused-ion-beam sculpting of TiO₂ nanotubes and mechanism understanding. *Phys. Chem. Chem. Phys.* 2013, 15, 1854–1862.
- [266] Choi J, Wehrspohn RB, Lee J, Gösele U. Anodization of nanoimprinted titanium: a comparison with formation of porous alumina. *Electrochimica Acta* 2004, 49, 2645–2652.
- [267] Lim JH, Choi J. Titanium oxide nanowires originating from anodically grown nanotubes: the bamboo-splitting model. *Small* 2007, 3, 1504–1507.
- [268] Berger S, Kunze J, Schmuki P, LeClere D, Valota AT, Skeldon P, Thompson GE. A lithographic approach to determine volume expansion factors during anodization: using the example of initiation and growth of TiO₂-nanotubes. *Electrochimica Acta* 2009, 54, 5942–5948.

- [269] Albu SP, Ghicov A, Berger S, Jha H, Schmuki P. TiO₂ nanotube layers: flexible and electrically active flow-through membranes. *Electrochem. Commun.* 2010, 12, 1352–1355.
- [270] Pittrof A, Park J, Bauer S, Schmuki P. ECM spreading behaviour on micropatterned TiO₂ nanotube surfaces. *Acta Biomater.* 2012, 8, 2639–2647.
- [271] Wang D, Hu T, Hu L, Yu B, Xia Y, Zhou F, Liu W. Microstructured arrays of TiO₂ nanotubes for improved photo-electrocatalysis and mechanical stability. *Adv. Funct. Mater.* 2009, 19, 1930–1938.
- [272] Xu T, Lin J, Chen J, Chen X. The effect of pre-pattern on the morphology and growth speed of TiO₂ nanotube. *Appl. Surf. Sci.* 2011, 258, 76–80.

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