

Hierarchical Rutile TiO₂ Flower Cluster-Based High Efficiency Dye-Sensitized Solar Cells via Direct Hydrothermal Growth on Conducting Substrates

Meidan Ye, Hsiang-Yu Liu, Changjian Lin,* and Zhiquan Lin*

Dye-sensitized solar cells (DSSCs) based on hierarchical rutile TiO₂ flower clusters prepared by a facile, one-pot hydrothermal process exhibit a high efficiency. Complex yet appealing rutile TiO₂ flower films are, for the first time, directly hydrothermally grown on a transparent conducting fluorine-doped tin oxide (FTO) substrate. The thickness and density of as-grown flower clusters can be readily tuned by tailoring growth parameters, such as growth time, the addition of cations of different valence and size, initial concentrations of precursor and cation, growth temperature, and acidity. Notably, the small lattice mismatch between the FTO substrate and rutile TiO₂ renders the epitaxial growth of a compact rutile TiO₂ layer on the FTO glass. Intriguingly, these TiO₂ flower clusters can then be exploited as photoanodes to produce DSSCs, yielding a power conversion efficiency of 2.94% despite their rutile nature, which is further increased to 4.07% upon the TiCl₄ treatment.

1. Introduction

Semiconductor nanocrystals have emerged as new building blocks to construct desired functional assemblies for miniaturized devices. Among them, *n*-type wide band gap semiconductor TiO₂ stands out as one of the most widely studied nanocrystals for use in gas sensors, photocatalyst, catalyst

supports, Li-ion battery materials, and solar cells due to its outstanding physical and chemical properties, including chemical stability, photostability and appropriate electronic band structure.^[1–5] Over the past decades, great interest has been received in controlling the size, shape and dimension of nanostructured TiO₂ materials as many potential applications are correlated heavily with these parameters.^[6–13] To date, various TiO₂ nanostructures in the forms of spheres, tubes, wires, rods, sheets, belts, flowers, and trees have been produced.^[14–24] Recently, hierarchically structured TiO₂ composed of nanoscale building blocks has received considerable attention due to its elaborate shape-dependent features stemming from different morphological nanostructures.^[25–27] More importantly, hierarchical structures directly improve the photocatalytic activity of TiO₂-based catalysts. Because they possess abundance of voids as a result of the stacking growth of building blocks that largely increases their specific surface area, such three-dimensional structures have been proven to serve as efficient photocatalyst as compared to low dimensional counterparts.^[27–30] In particular, when employed as the photoanode in a dye-sensitized solar cell (DSSC), hierarchical architectures effectively enhance light scattering and trapping for efficient photon harvesting and offer a larger surface area for dye adsorption, thereby resulting in improved

M. D. Ye, Prof. Z. Q. Lin
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332, USA
E-mail: zhiquan.lin@mse.gatech.edu

M. D. Ye, Prof. C. J. Lin
Department of Chemistry
College of Chemistry and Chemical Engineering
Xiamen University
Xiamen, Fujian 361005, China
E-mail: cjlin@xmu.edu.cn

H.-Y. Liu
Department of Materials Science and Engineering
University of Delaware
Newark, DE 19716, USA

DOI: 10.1002/smll.201201590



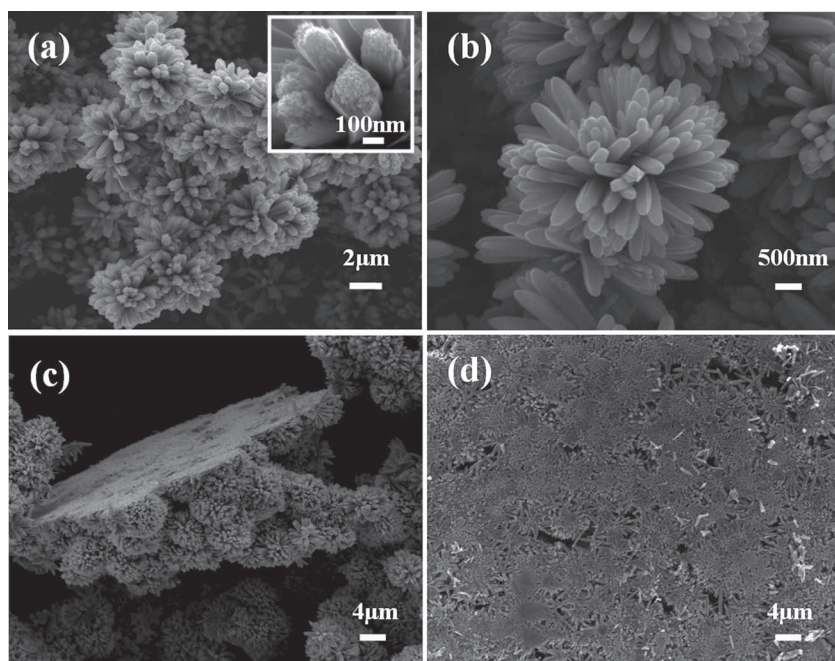


Figure 1. FESEM images of hierarchical rutile TiO₂ flowers. (a) Top view of flower clusters; inset show the close-up of nanopetals. (b) Top view of a flower. (c-d) Flower clusters removed from the FTO substrate by mechanical scratching; (c) cross-sectional view of flower clusters, and (d) bottom view of flower clusters.

power conversion efficiency.^[31,2] Notably, in most cases, the mechanism of the formation of these unique hierarchical structures is complicated and far less understood.

Hydrothermal synthesis is a simple yet effective method among other various strategies to produce a wide diversity of hierarchical TiO₂ architectures. The variation of hydrothermal conditions such as temperature, pH, concentration and molar ratio of reactants and additives imparts tunable morphologies and crystalline films of TiO₂ at the nano- and micro-scale.^[26,28,33,34] For example, rectangular parallelepiped rutile TiO₂ was synthesized via hydrothermal treatment in aqueous TiCl₃ solutions containing a large amount of NaCl that retarded the formation of TiO₂ and influenced the morphology through the adsorption of Cl[−] onto the (110) plane of rutile TiO₂.^[35] By changing the reaction solution to dilute HCl containing TiCl₃ and sodium dodecyl sulfate (SDS), a nano-micro chestnut-like morphology composed of rutile nanopin TiO₂ on the octahedral anatase TiO₂ surface was obtained.^[25] Recently, an acid vapor oxidation (AVO) strategy was developed to yield multilayered rutile TiO₂ nanostructures^[15] and ordered tree-like TiO₂ nanoarrays^[16] by reacting the Ti surface with vapor generated from a HCl solution in a Teflon lined autoclave. In this work, the use of HCl played an important role in the growth of hierarchical rutile superstructures, serving as both a catalyst and a chemical corrosive agent to enable the generation of rutile phase and in the meantime induce defects on the surface for the introduction of twin structures, respectively.^[16]

Herein, we report on, for the first time, a facile, one-step, bottom-up hydrothermal route to directly grow a wide range of hierarchical TiO₂ flower-shaped clusters made of rutile

nanorod petals on transparent conducting FTO glasses assisted by the addition of cations of different valence and size. The influence of growth parameters on the resulting complex structures was systematically scrutinized. A growth mechanism was proposed in which the small lattice mismatch between the FTO substrate and rutile TiO₂ rendered the epitaxial growth of a compact rutile TiO₂ layer on the FTO glass, while the intercalation of added cations and their interaction with the rutile chains composed of [TiO₆] units led to hierarchical flower-like architectures. The hierarchical TiO₂ flower clusters were then utilized as a photoanode and assembled into DSSCs. Rutile TiO₂ had remarkably close photocurrent-voltage responses as compared to anatase TiO₂ in DSSC with additional advantages such as better chemical stability and higher refractive index.^[36] A power conversion efficiency, PCE of 2.94% was achieved despite their rutile nature, which was further increased to 4.07% upon the TiCl₄ treatment.

2. Results and Discussion

Figure 1a shows a typical field emission scanning electron microscopy (FESEM) image of TiO₂ flower-like clusters synthesized in a tightly sealed 45 mL Teflon-lined autoclave containing a mixture of 15 mL deionized water and 10 mL HCl (~4.78 M) with the addition of 0.5 g (CH₃COO)₂Ba and 0.5 mL precursor TTIP at 140 °C for 9 h. Such flower-like clusters were developed by preferentially oriented nucleation and densely distributed over the surface of the FTO substrate. A close-up of a flower revealed that this superstructure resembled a natural chrysanthemum (Figure 1b). Each flower was composed of a large number of tetragonal nanorod petals with top square-shaped facets. These spokewise nanopetals radiated from a common central zone. The nanopetals were roughly 2 μm long and 250 nm wide with an aspect ratio of about 8. Moreover, the top surface of a nanopetal appeared to contain many step edges (inset in Figure 1a), which are the substrates for further growth of sub-nanorods, while the side surface was smooth. Quite intriguingly, the morphological feature of an individual nanopetal resembled that of the oriented TiO₂ nanorod grown normal to the FTO substrate, which was produced under the same experiment condition but without the addition of barium salt (Figure S1). Clearly, a fully grown flower possessed a spherical symmetry with an average diameter of approximately 7 μm (Figure 1c; the clusters were removed from the FTO substrate by a gentle mechanical scratching, and the bottom of flower clusters was shown in Figure 1d).

To scrutinize the detailed structures of an individual flower, transmission electron microscopy (TEM) was performed. The sample was subjected to mild ultrasonication

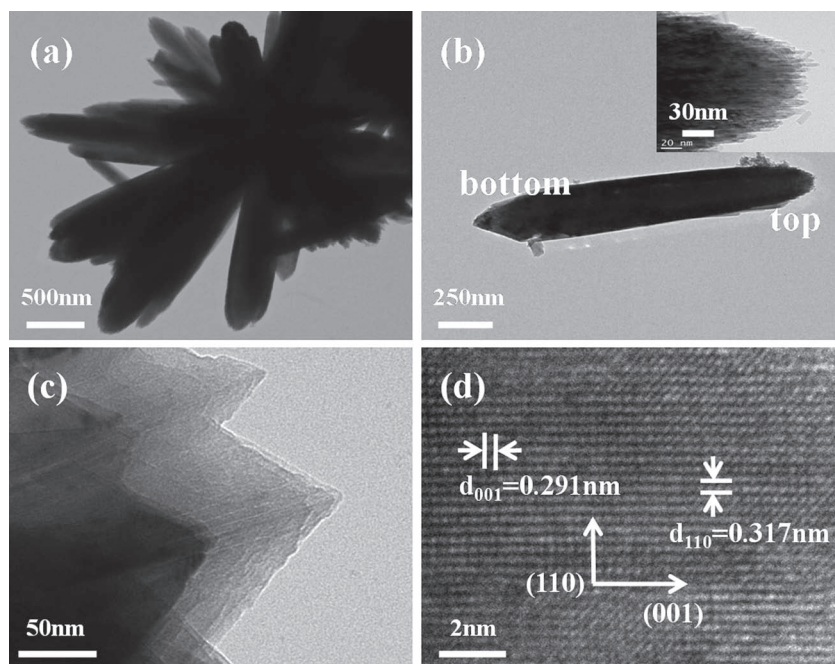


Figure 2. TEM images of hierarchical rutile TiO_2 flowers. (a) A flower. (b) A single nanopetal; inset shows the close-up of a nanopetal top. (c) Close-up of the bottom of a few nanopetals. (d) HRTEM image of a nanopetal.

in ethanol solution to yield an individual flower. **Figure 2a** shows a single flower made of several nanorod petals. Close examination revealed that each petal was composed of numerous parallel ultrathin nanoneedles (inset in Figure 2b) and had a sharp wedged bottom and an obtuse cambered top (Figure 2b). Notably, the sharp wedged bottom was beneficial to place the nanopetal firmly on the substrate surface and facilitated the growth together with other nanopetals from a focused center (Figure 2c), ultimately forming a stable bouquet. The nanopetals were completely crystalline as confirmed by high-resolution TEM (HRTEM). Lattice fringes with interplanar spacings, $d_{110} = 3.17 \text{ \AA}$ and $d_{001} = 2.91 \text{ \AA}$ can be indexed to tetragonal rutile phase (Figure 2d). The (110) crystal plane was perpendicular to the (001) plane, indicating that the nanorod petals grew along the (110) crystal plane with a preferred [001] orientation.

Subsequently, X-ray diffraction (XRD) analysis in conjunction with energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were performed to investigate the composition of TiO_2 flowers. XRD studies suggested that both ordered nanorod arrays and hierarchical flower films were pure rutile TiO_2 (**Figure 3**). They possessed the same diffraction peaks regardless of a difference in intensity, and were indexed to tetragonal rutile phase (space group, $P4_2/mnm$; JCPDS No.21-1276, $a = b = 0.459 \text{ nm}$ and $c = 0.294 \text{ nm}$), in accordance with the HRTEM measurement (Figure 2d).

In addition, the chemical stoichiometry of the flower film was measured by EDS (Figure S2) and XPS (Figure S3), showing that the atomic ratio of the added cation (i.e., Ba^{2+}) was minimal ($\sim 0.1\%$, which was likely due to a noisy signal). Accordingly, it can be concluded that the flowers were completely made of rutile TiO_2 , and no cation doping or formation of

other crystals (e.g., BaTiO_3) occurred, suggesting that the added cation served most likely as a catalyst. In the work that follows, the growth parameters were scrutinized in order to reveal the prominent factors that governed the formation of hierarchical architectures.

As noted above, the presence of $(\text{CH}_3\text{COO})_2\text{Ba}$ in hydrothermal synthesis resulted in hierarchical flower-like structures (Figure 1 and Figure S4a), while its absence only gave rise to the nanorod arrays (Figure S1), signifying that the Ba^{2+} salt play a crucial role in the creation of hierarchical TiO_2 architectures. Thus, the effect of Ba^{2+} amount was first examined. As clearly evidenced in **Figure 4**, at the low $(\text{CH}_3\text{COO})_2\text{Ba}$ amount ($c = 0.01 \text{ g}$), numerous flower bud-like structures emerged (Figure 4a). As the Ba^{2+} amount increased ($c = 0.2 \text{ g}$), the buds began to extend and gradually evolved into flower-like features (Figure 4b). Finally they came into full blooms at the high Ba^{2+} amount ($c = 0.5 \text{ g}$; Figure 4c). The flower features remained unchanged as the Ba^{2+} amount

exceeded 0.5 g ($c = 1.0 \text{ g}$; Figure 4d). Obviously, the addition of $(\text{CH}_3\text{COO})_2\text{Ba}$ significantly disrupted the oriented growth of rutile nanorods and remarkably imparted versatile hierarchical morphologies by varying its amount.

It is noteworthy that the density and thickness of TiO_2 flower films depended heavily on the hydrothermal reaction time. When 0.5 mL precursor TTIP and 0.5 g $(\text{CH}_3\text{COO})_2\text{Ba}$ were allowed to react at 140°C in the mixture of 15 mL deionized water and 10 mL HCl for less than 3 h , the FTO substrate remained transparent, and no TiO_2 nanostructures

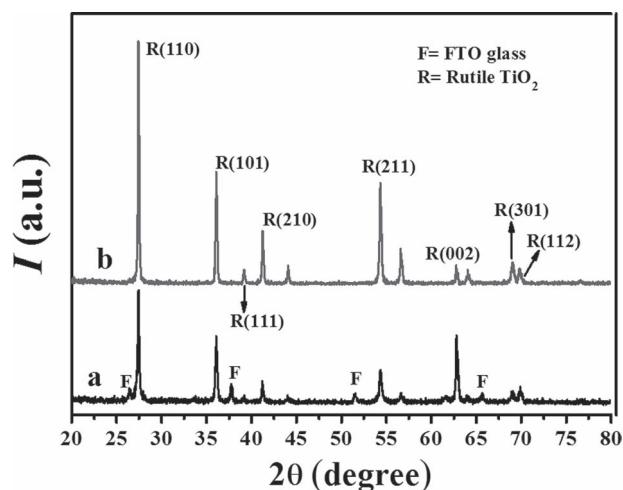


Figure 3. XRD patterns of (a) TiO_2 nanorod film prepared on an FTO substrate at 140°C for 9 h in a mixture of 15 mL deionized water and 10 mL HCl with the addition of 0.5 mL precursor TTIP only, and (b) TiO_2 flower film prepared on an FTO substrate under the same reaction condition as in (a) but with the addition of 0.5 g $(\text{CH}_3\text{COO})_2\text{Ba}$.

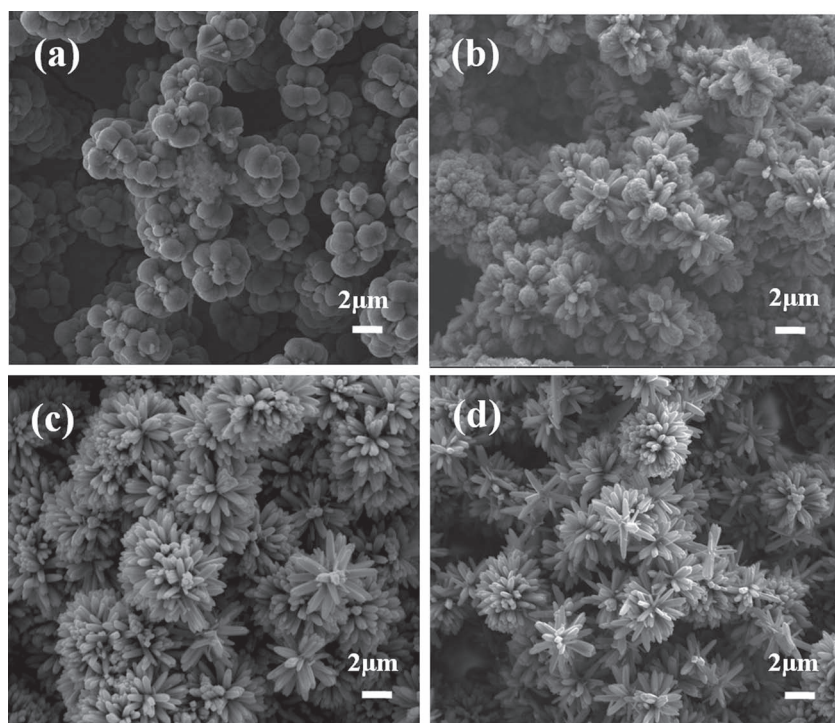


Figure 4. FESEM images of hierarchical rutile TiO₂ flower films grown at 140 °C for 9 h in a mixture of 15 mL deionized water and 10 mL HCl with the presence of 0.5 mL precursor TTIP and different amount of (CH₃COO)₂Ba. (a) 0.01 g, (b) 0.20 g, (c) 0.50 g, and (d) 1.00 g (CH₃COO)₂Ba.

were observed, consistent with the report on the preparation of vertical nanorod arrays.^[23] This was attributed partially to the need of a supersaturated process of TiO₂ precursor as a

and Figure S4a). The prolonged reaction to 15 h yielded denser and thicker flower clusters comprised of homogeneous nanorods (Figure 5d), due primarily to the crystal growth and Ostwald ripening process.^[38,39] However, when the growth time was extended more than 20 h, a white film composed of TiO₂ flowers started to detach from the FTO substrate (Figures S4c and S4d), most likely because of a competition between the crystal growth due to the hydrolysis of Ti⁴⁺ and the dissolution of TiO₂ by acidic solution.^[23]

In general, the TiO₂ flower-like morphology can be tuned by the hydrothermal temperature that profoundly influenced the crystal growth rate. When the temperature was lower than 100 °C, well defined flower clusters cannot be developed. Instead, some agglomerations on the FTO substrate were observed (Figure S4b). As the temperature increased to 120 °C, bud-like clusters emerged (Figure 6a). With further increase in temperature (140 °C in Figures 6b and 160 °C in Figures 6c), the hierarchical structure underwent intensive flourish due to a faster crystal growth rate. However, when the temperature was at 180 °C, the film started to detach from the substrate due to a faster equilibrium between the crystal growth and the chemical dissolution of TiO₂. In particular,

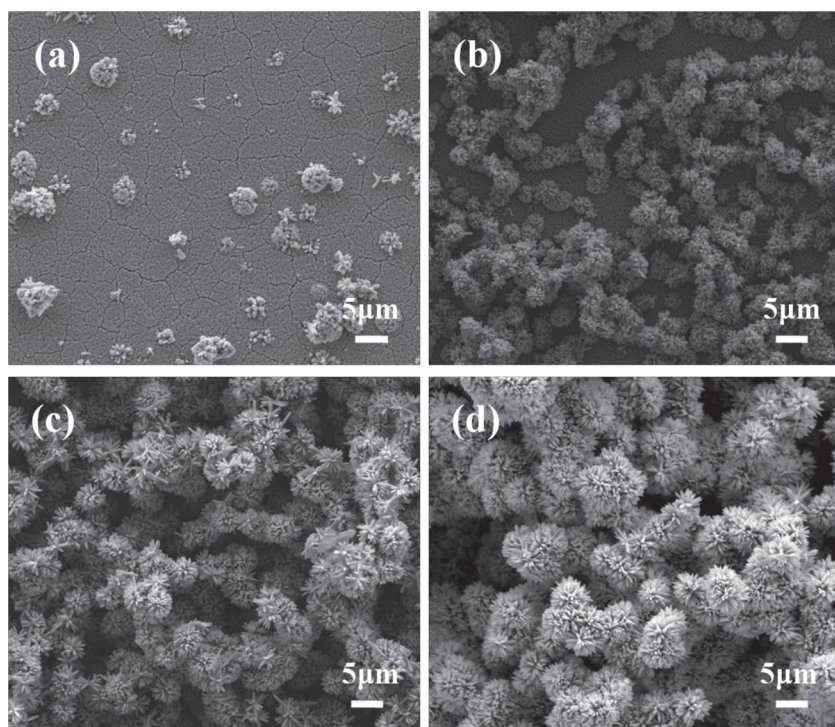


Figure 5. FESEM images of hierarchical rutile TiO₂ flower films grown at 140 °C in a mixture of 15 mL deionized water and 10 mL HCl with the addition of 0.5 g (CH₃COO)₂Ba and 0.5 mL precursor TTIP at different times. (a) 3 h, (b) 6 h, (c) 9 h, and (d) 15 h.

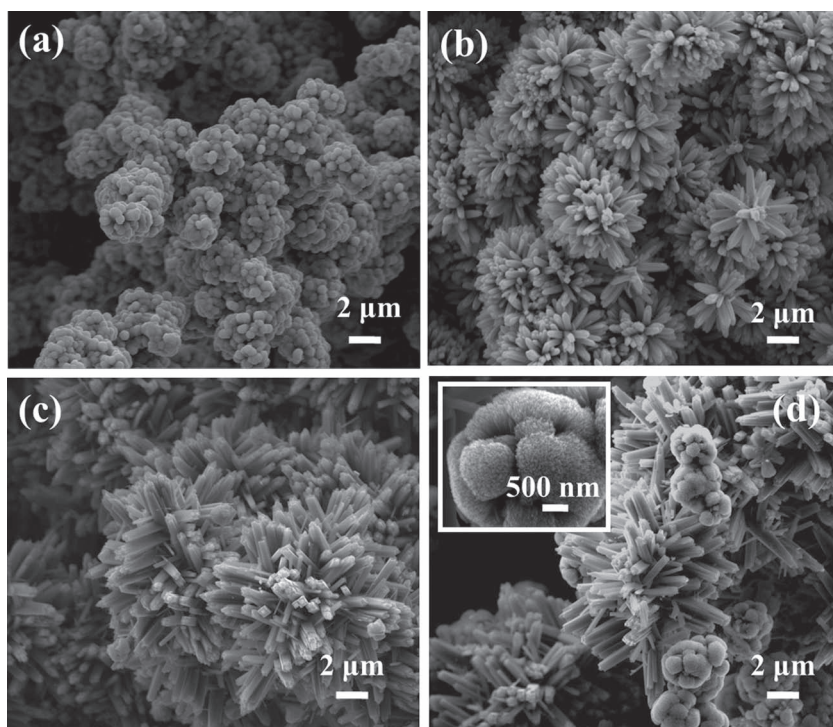


Figure 6. FESEM images of hierarchical rutile TiO_2 flower films grown for 9 h in a mixture of 15 mL deionized water and 10 mL HCl with the presence of 0.5 g $(\text{CH}_3\text{COO})_2\text{Ba}$ and 0.5 mL precursor TTIP at different temperatures: (a) 120 °C, (b) 140 °C, (c) 160 °C, and (d) 180 °C.

at this temperature, fruit-like structures composed of hundreds of nanoneedles emerged (inset in Figure 6d) and adhered on the clusters (Figure 6d), reflecting that high temperature was favorable for the formation of smaller-scale building blocks.

Of particular interest is that the addition of $(\text{CH}_3\text{COO})_2\text{Ba}$ resulted in the formation of flower clusters, however, there was no special trace of Ba^{2+} detected in the flowers in light of the collective results from HRTEM, XRD, EDS, and XPS measurements. Therefore, in the hydrothermal synthesis, Ba^{2+} most likely only acted as a catalyst to promote the production of hierarchical structures. As such, it is of key importance to explore the effect of cation salts on the structure transformation. Remarkably, the addition of a multitude of cation salts, including CH_3COONa , NaCl , KCl , MgCl_2 , $(\text{CH}_3\text{COO})_2\text{Ca}$, $(\text{CH}_3\text{COO})_2\text{Sr}$, $(\text{CH}_3\text{COO})_2\text{Zn}$, CuCl_2 , FeCl_3 , ErCl_3 , and $(\text{CH}_3\text{COO})_4\text{Sn}$, exerted a noteworthy influence on the creation of TiO_2 flower-like films (**Figures 7** and **Figure 8**), although a detailed study to account for the obtained varied flower-like

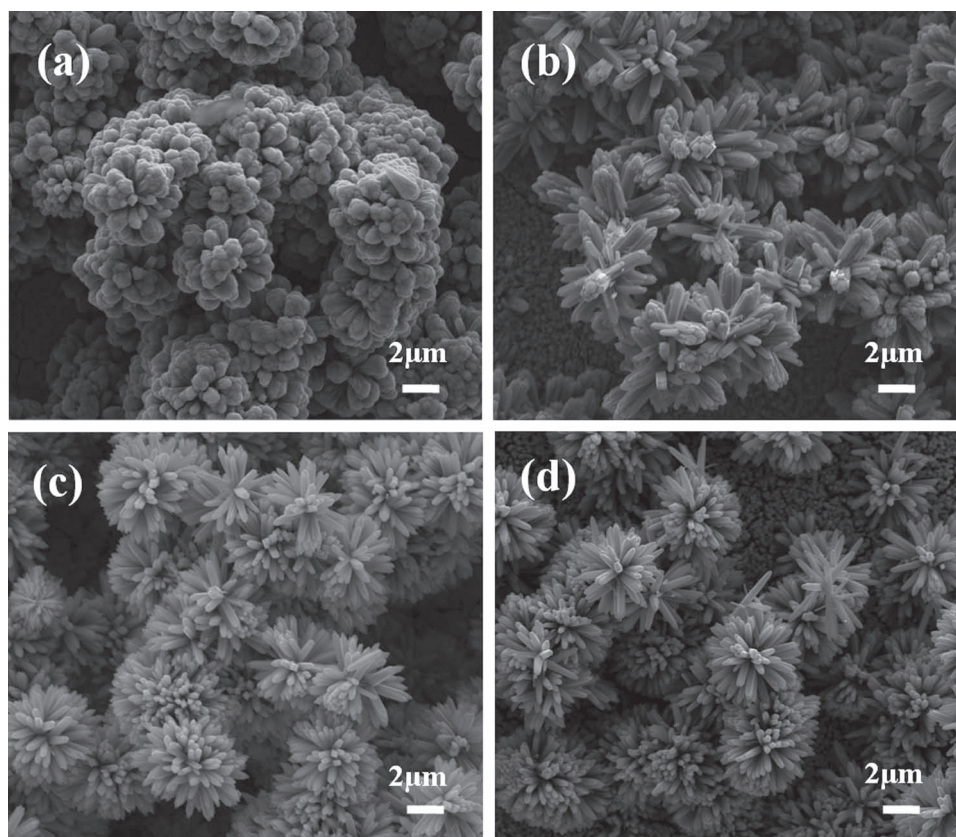


Figure 7. FESEM images of hierarchical rutile TiO_2 flower films grown at 140 °C for 9 h in a mixture of 15 mL deionized water and 10 mL HCl in which 0.5 mL precursor TTIP and 0.1 M different cation salts were present. (a) CH_3COONa , (b) MgCl_2 , (c) CH_3COOK , and (d) $(\text{CH}_3\text{COO})_2\text{Ca}$.

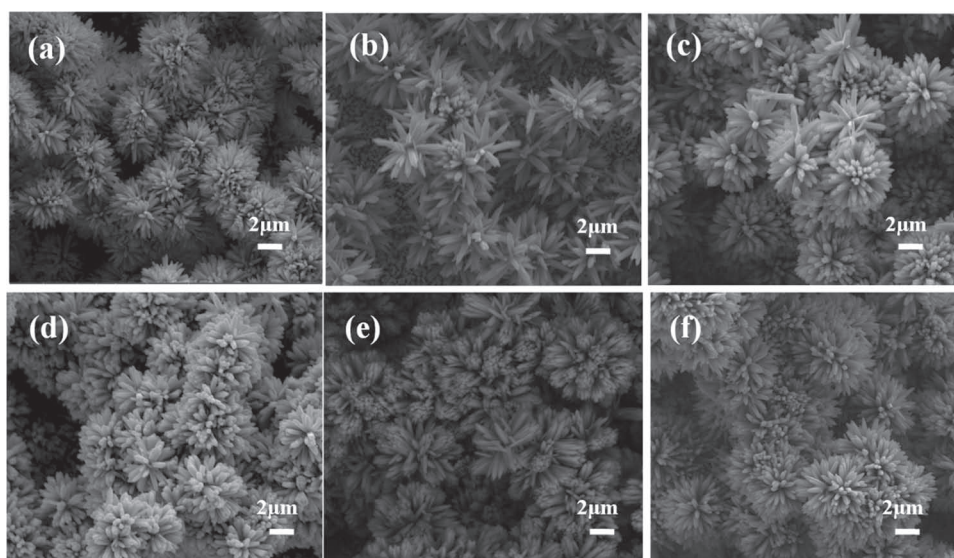


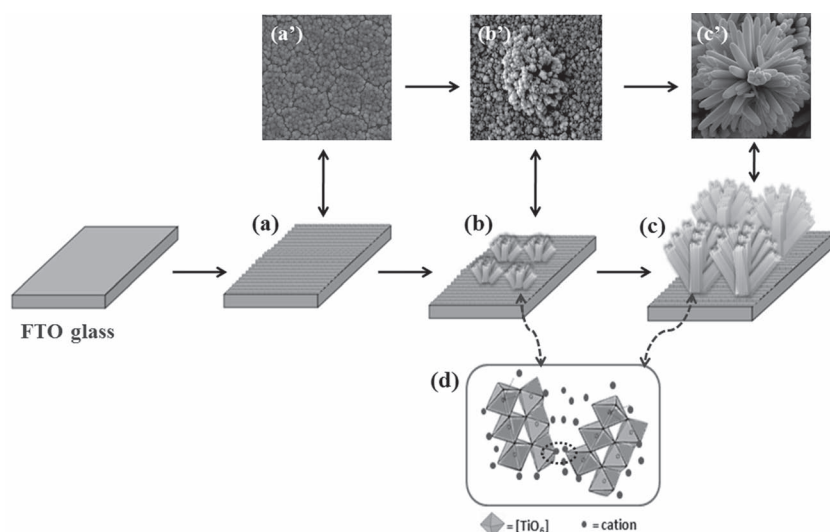
Figure 8. FESEM images of hierarchical rutile TiO₂ flower films grown at 140 °C for 9 h in a mixture of 15 mL deionized water and 10 mL HCl in which 0.5 mL precursor TTIP and 0.1 M different cation salts were present. (a) FeCl₃·6H₂O, (b) CuCl₂·2H₂O, (c) (CH₃COO)₂Zn, (d) (CH₃COO)₂Sr, (e) (CH₃COO)₄Sn, and (f) ErCl₃.

features is yet to be unraveled and may be rather complex. Specifically, the use of cations from the same main group (e.g., Ca²⁺, Ba²⁺, Sr²⁺, belonging to IIA in the periodic table of elements) with the same valence state yielded similar features (Figure 7d, 6b, and 8d). Moreover, the addition of Fe³⁺ and Er³⁺ with the same valence state but different molar weight produced kindred flower features (Figure 8a and f). Sn⁴⁺ having high valence induced exquisite bouquets composed of smaller nanorod petals (Figure 8e). Despite the complexity, an important piece of information can be already gained from these entertaining experimental observations: these flowers were formed as a direct consequence of a synergistic effect of the valence state (i.e., ionic strength) and the molar

weight (i.e., the size of cation) of added cations. On the basis of these results, we anticipate that the use of other types of cation salts would produce similar flower structures.

We note that the influence of other growth parameters, including initial TTIP amount (Figure S5), acidity (Figure S6), anion species (Figure S7), and two-step hydrothermal growth process (Figure S8) on the resulting complex structures was also scrutinized (see Supporting Information).

We now turn our attention to elucidate the possible growth mechanism of the hierarchical flower-like architecture, which probably involves three steps: (1) formation of a compact TiO₂ nucleus layer (panel a in **Scheme 1**); (2) growth of initial bouquets of flowers (panel b and c in **Scheme 1**); (3) ripening into flower clusters. The SEM images corresponding to panels a-c are shown in panels a'-c'. It is widely recognized that the epitaxial and anisotropic nucleation and growth can be induced by the atom arrangement at the nucleation site on substrate and precursor.^[15,40] Notably, the FTO substrate has a tetragonal rutile structure and the lattice mismatch between the tetragonal FTO (*a* = *b* = 0.4687 nm) and rutile TiO₂ (*a* = *b* = 0.4594 nm) is only 2%.^[23] Such small lattice mismatch promoted the epitaxial nucleation and growth of rutile TiO₂ film compactly on the FTO substrate. At the early stage of hydrothermal reaction, the high concentration of precursor led to a burst of homogeneous nucleation. Then the supersaturated TiO₂ nuclei tended to aggregate to minimize the surface energy. As a result, the anisotropic growth process was restricted, and a compact TiO₂ layer



Scheme 1. Schematic illustration of the growth mechanism. (a) Formation of a compact TiO₂ nucleus layer on the FTO glass. (b) Emergence of initial flower buds. (c) Growth of the bouquets of flowers. (d) Interaction between rutile [TiO₆] octahedra and cation.

was thus *first* developed on the FTO substrate (panel a in Scheme 1 and the corresponding SEM images are shown in panel a' and Figure 6a), from which the flowers grew subsequently.

It is well known that the formation of each phase in TiO₂ nanostructures is governed by the arrangement of distorted [TiO₆] octahedra.^[41] Previous work suggested that, in strong acidic solution under hydrothermal condition, tetragonal rutile TiO₂ phase was formed by the mode of edge sharing.^[42–44] The structure of rutile constitutes chains of [TiO₆] octahedra along the *c*-axis. The [TiO₆] octahedra in the chain are linked to one another through a shared edge to form a zigzag chain-like structure, while the [TiO₆] octahedra between two chains connect each other through a point, as depicted in panel d in Scheme 1, implying that the chemical bond in the chain is stronger than that between the chains.^[6,42] According to periodic bond chain (PBC) theory,^[45–47] periodic bond chains construct the crystal, and the direction of the strongest chemical bond is usually the one at which the crystal has the fastest growth rate. Moreover, theoretical calculation shows that for a rutile lattice, the surface energy is on the order of $E_{(110)} < E_{(100)} < E_{(001)}$.^[48] Thus, crystal growth along the [001] direction (i.e., *c*-axis) would have the fastest growth rate compared to other directions. On the other hand, it has been demonstrated that Cl[−] played an important role in the growth of TiO₂ grains into nanorods instead of nanoparticles.^[42] This is because the (110) plane of rutile has a positive polar face and Cl[−] can be preferentially adsorbed on its surface to restrain the contact of the TiO₂ grains on the (110) surface and thus greatly retarded the crystal growth along the (001) plane.^[42] As a result, TiO₂ grain growth was suppressed in the [110] direction and accelerated in the [001] direction, thereby forming a rod-like structure.^[23,35,42] In this work, the addition of cation salt led to the creation of hierarchical flower-like TiO₂ architectures instead of vertical nanorod arrays. We propose that [TiO₆] octahedra in a chain tended to connect with another octahedra in an adjacent chain through a point (dashed black circle in panel d, Scheme 1), thus the cation may easily locate in the interchain spaces due to the electrostatic interaction between [TiO₆] and cation, and formed a diffusion barrier around the chains, retarding the diffusion of the precursor TTIP to the surface of [TiO₆] chains. Moreover, the addition of cation greatly increased the ionic strength of the reaction solution, which favored the formation of small crystals of TiO₂ through electrostatic screening.^[23,49] Consequently, several crystal nuclei developed from active sites that possess many defects on the preformed compact TiO₂ layer (panel b in Scheme 1; the corresponding SEM image is shown in panel b') and were separated due to the intercalation of cation. The grain growth from these crystal nuclei tended to tilt from the original nucleation center zone at an identical speed along the [001] direction and branched out into multi-arms (i.e., nanorod-like petals) due to the space limitation as evidenced in Figure 2c where the bottom of nanopetals were closely contacted each other, and eventually grew into radially symmetric flower-like features.^[37,50]

On the basis of the principle of crystal growth, secondary nucleation occurs preferentially at sites with more defects.^[39] The nanorod petals provided many step edges for

Table 1. The performance of dye-sensitized solar cells prepared at different conditions.

Sample		Voc [V]	Jsc [mA cm ^{−2}]	FF	PCE [%] ^{a)}
TiO ₂ nanorods (15 h)		0.76	5.25	0.46	1.84
TiO ₂ nanorods +TiCl ₄ treatment (15 h)		0.80	6.88	0.55	3.03
TiO ₂ flowers	3 h	0.67	2.10	0.70	0.98
	6 h	0.69	4.55	0.63	2.00
	9 h	0.76	7.32	0.44	2.47
	15 h	0.76	9.59	0.40	2.94
TiO ₂ flowers +TiCl ₄ treatment	3 h	0.77	3.68	0.57	1.61
	6 h	0.77	6.15	0.53	2.51
	9 h	0.79	8.78	0.54	3.72
	15 h	0.79	10.98	0.47	4.07

^{a)} (PCE (%) = $J_{sc} \times V_{oc} \times FF / P_{in}$, where $P_{in} = 100 \text{ mW cm}^{-2}$ (AM 1.5)).

the subpetal growth (inset in Figure 1a). Thus, it is not surprising that individual flower first grew from the formed bouquet layers. As the reaction progressed, such process caused the assembled flowers to flourish, and ultimately transform into considerably dense flower clusters. The use of different cations yielded diversified flower features (Figures 7 and 8). In the light of the intriguing experimental observations, these flowers may be formed as a direct consequence of a synergistic effect of the valence state (i.e., ionic strength) and the molar weight (i.e., the size of cation) of added cations. For example, the cation size of Na⁺ was small than K⁺, and thus was unable to effectively isolate the grain, thereby resulting in flowers made of coarse nanopetals (Figure 7a). It is worth noting that regardless of the small size of the added cation, the influence of its valence state dominated, that is, a cation with higher valence state favored stronger interaction with the grain to promote the formation of thinner nanopetals (e.g., flowers produced using Sn⁴⁺ shown in Figure 8e).

The rutile TiO₂ flower films prepared at different times were then exploited as photoanodes to produce DSSCs (see Experimental section). As noted in **Table 1**, the power conversion efficiency (PCE) of the resulting DSSCs increased from 0.98% to 2.94% with a short circuit current, J_{sc} of 9.59 mA cm^{−2}, an open circuit voltage, V_{oc} of 0.76 V, and a fill factor, FF of 0.40 when the time for TiO₂ flower growth extended from 3 h to 15 h. The largely enhanced PCE can be attributed to the increase in film thickness as the growth time increased, leading to higher dye loading. However, as mentioned above, extreme reaction could induce the separation of flower film from the substrate; thus, in the present study even thicker film was not used for producing DSSCs. Furthermore, TiCl₄ treatment has been employed as an effective strategy to increase the surface roughness of nanostructured TiO₂ and improve the device performance by providing an increased surface area for dye adsorption in conjunction with a modification of structural defects on TiO₂.^[51] Thus, the TiCl₄ treatment was performed; the samples then exhibited

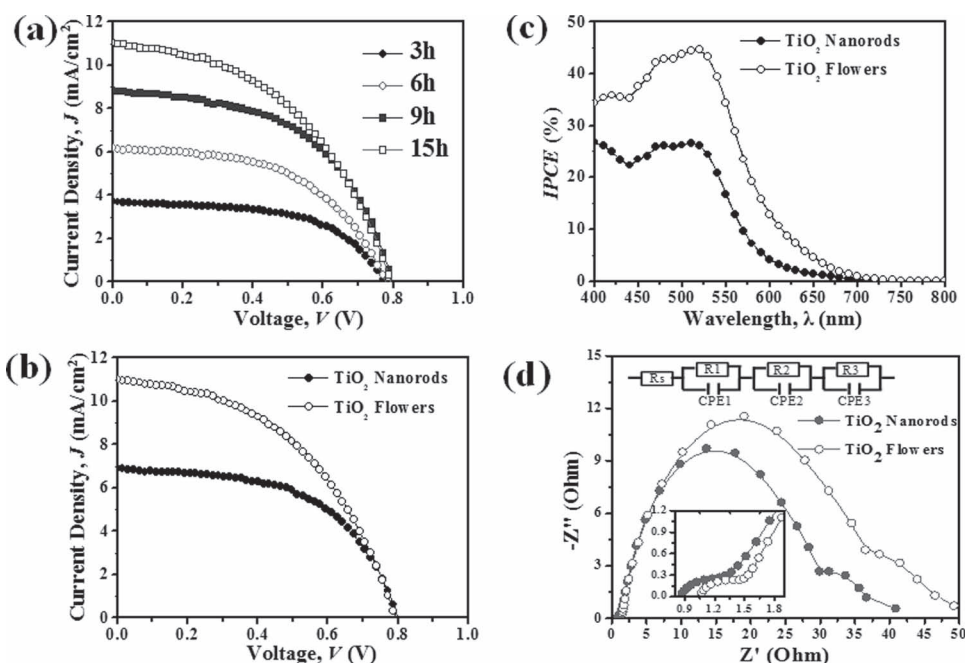


Figure 9. (a) Current-Voltage (J-V) characteristics of dye-sensitized solar cells assembled from (a) rutile TiO₂ flower films with TiCl₄ treatment. The films were hydrothermally grown for 3 h, 6 h, 9 h, and 15 h, respectively. (b) J-V characteristics, (c) IPCE curves, and (d) Nyquist plots of rutile TiO₂ flower film (open circles) and rutile TiO₂ nanorod film (solid circles) fitted based on the equivalent circuit (shown in the inset), respectively. The lower inset in (d) is the close-up in the low Z' region. Both films were prepared by hydrothermal growth for 15 h. The films were then treated by TiCl₄ prior to the fabrication into DSSCs.

substantially improved PCEs (**Figure 9a**). For example, TiCl₄-treated flower film prepared by hydrothermal growth for 15 h showed a highest PCE of 4.07% with J_{sc} of 10.98 mA cm⁻², V_{oc} of 0.79 V, and FF of 0.47 (Table 1).

It is interesting to note that the DSSCs fabricated by capitalizing on rutile TiO₂ nanorod films (prepared = under the same condition but without the addition of cation salts; see Experimental section) as photoanodes had PCEs of only 1.84% (J_{sc} = 5.25 mA cm⁻², V_{oc} = 0.76 V, and FF = 0.46 without the TiCl₄ treatment) and 3.03% (J_{sc} = 6.88 mA cm⁻², V_{oc} = 0.80 V, and FF = 0.55 with the TiCl₄ treatment), respectively (Table 1, Figure 9b). Obviously, the hierarchical flower film (20 μ m, Table S1) was thicker than the nanorod arrays (5 μ m, Table S1) under the same growth time, implying that the cation addition supported thicker film for higher dye adsorption as confirmed by the measurement of dye loading (i.e., 1.82×10^{-8} mol cm⁻² and 2.27×10^{-8} mol cm⁻² for the flower film vs. 1.15×10^{-8} mol cm⁻² and 1.75×10^{-8} mol cm⁻² for the nanorod film, without and with TiCl₄ treatment, respectively; Table S1). It is worth noting although the thickness of the hierarchical film was 4 times the nanorod film, the amount of dyes adsorbed was only 1.58 times that of the nanorod film, indicating that the existence of interspaces between the flower clusters restrained the corresponding increase of their surface area. Accordingly, the 3D hierarchical architecture may also promote the scattering of photons for light harvesting. As dye molecules situated on the TiO₂ flower surface, the hierarchical TiO₂ architecture can scatter and trap light to enhance the light harvesting via the dye absorption. A comparison of

UV-vis spectra of these two different photoanodes composed of flowers and nanorods respectively is shown in Figure S9. It is clearly evident that the absorbance of the flower-based photoanode was larger than the nanorod-based counterpart, especially in the long wavelength region, which may be due primarily to the enhanced light scattering resulting from the presence of voids in the 3D hierarchical film.

To understand the different photovoltaic performance of two TiCl₄-treated DSSCs (i.e., flower-based and nanorod-based DSSCs), the incident-photon-to-current efficiency (IPCE) spectra were measured (Figure 9c). The IPCE spectra of both cells with N719 dye displayed a maximum at approximately 535 nm. Moreover, the IPCE over the entire wavelength region for the flower-based DSSC was higher than the nanorod-based DSSC, suggesting that the flower-based DSSC generated more photoelectrons because of greater dye loading, which was correlated well with the aforementioned dye-loading measurement.

To further elucidate the electrochemical characteristics of both flower- and nanorod-based DSSCs, electrochemical impedance spectroscopy (EIS) measurements were performed. Figure 9d depicts the Nyquist plots under the open-circuit voltage condition for DSSCs. The fitted results are summarized in Table S2 (see Experimental section). The EIS spectra exhibited three semicircles with a contact series resistance (R_s) on the FTO substrate of approximately 0.9 Ω for both cells. The first semicircle in the high frequency range represents the resistance at the counter electrode (R_f) for the reduction reaction of I₃⁻ ions in the electrolyte using Pt

as the counter electrode. The second semicircle in the intermediate frequency range reflects the charge transfer resistance (R_2) at interfaces among the electrolyte, dye, and TiO_2 . The third semicircle in the low frequency range offers the information regarding the resistance of finite diffusion of the electrolyte (R_3).^[22,32] The close values of R_1 , 0.83 Ω and 0.65 Ω for flower- and nanorod-based DSSCs, respectively were obtained as the counter electrodes (i.e., Pt) were prepared in the nearly same manner. Interestingly, the R_2 , widely considered to be primarily determined by the charge recombination resistance with a partial contribution from the transport resistance, exhibited distinct difference, i.e., 32.09 Ω and 26.94 Ω for flower- and nanorod-based DSSCs, respectively, signifying a higher recombination rate for the nanorod-based cell, which may due most likely to their dense array-like feature constructed with tightly connected nanorods for easy recombination (Figure S1a-c). Finally, appreciably larger R_3 was found for the flower-based cell, which can probably be ascribed to its considerably thickness as compared to that of the nanorod-based cell, thus imposing a mass diffusion difficulty for electrolyte.

3. Conclusion

In summary, a simple yet robust, one-step, bottom-up hydrothermal method was developed, for the first time, to directly grow hierarchical rutile TiO_2 flower clusters on transparent conducting substrates. This in-situ growth technique dispensed with the need for transferring and deposition of formed hierarchical structures onto transparent conducting substrates later as in copious past work.^[15,26,27,33,49] A comprehensive study on the effects of growth parameters, including growth time, the addition of cations of different valence and size, initial concentrations of precursor and cation, growth temperature, and acidity, on the creation of diversified forms of TiO_2 flower-like films with different thickness and density was presented. The small lattice mismatch between the FTO substrate and rutile TiO_2 allowed epitaxial growth of a compact TiO_2 layer on the FTO substrate and the intercalation of added cations and their interaction with the rutile chains composed of $[\text{TiO}_6]$ units led to the nucleation and growth of hierarchical flower-like architectures on the preformed TiO_2 layer. Intriguingly, despite their rutile nature, a PCE of 2.94% of DSSCs were yielded by capitalizing on TiO_2 flower clusters as photoanodes. The PCE was further increased to 4.07% upon the TiCl_4 treatment, which contrasted the PCE of 3.03% from a nanorod film prepared under the same synthesis conditions, representing a 34% efficiency improvement. While only TiO_2 flower-like architectures were studied here, this viable, one-pot hydrothermal method is not restricted to them alone, but can be easily extended to a broad range of other functional materials (e.g., ZnO , SnO_2 , etc.) to craft fine hierarchical architectures that provide a tremendous potential for use in optoelectronic devices, solar cells, solar hydrogen generation, hydrogen storage, self-cleaning and environmental remediation through solar excitation, gas sensors, photocatalysis, fuel cells, batteries, supercapacitors, and cell separation.

4. Experimental Section

Fabrication of Hierarchically Structured TiO_2 Flower Clusters: Hierarchical TiO_2 flower-like films on transparent conducting substrates were prepared based on a hydrothermal procedure^[23] with modifications. In a typical synthesis, a small amount of cation salts (i.e., $(\text{CH}_3\text{COO})_2\text{Ba}$, $(\text{CH}_3\text{COO})_2\text{Sr}$, $(\text{CH}_3\text{COO})_2\text{Ca}$, CH_3COONa , KCl , CH_3COOK , MgCl_2 , $(\text{CH}_3\text{COO})_2\text{Zn}$, CuCl_2 , FeCl_3 , ErCl_3 , and $(\text{CH}_3\text{COO})_4\text{Sn}$) were dissolved in deionized water (15 mL), which was further mixed with concentrated hydrochloric acid (HCl ; 15 mL, mass fraction = 36.5–38%). The mixture was stirred under ambient conditions for 5 min before adding titanium isopropoxide ($\text{TTIP} - \text{TiO}_2$ precursor; 0.5 mL, Sigma-Aldrich Co.). After stirring for an additional 5 min, an FTO substrate (F:SnO_2 , 2 cm $\times$ 2 cm, 14 Ω /square; Pilkington Glass, USA), which was ultrasonically cleaned for 30 min in a mixed solution of acetone and ethanol with a volume ratio of 1:1, followed by deionized water rinsing for 15 min, was placed in the mixture noted above at a 45° angle against the wall of the Teflon-lined stainless steel autoclave with its conducting side facing up (the volume of autoclave = 45 mL). The hydrothermal reaction was performed at 140 °C for 9 h in an oven. The autoclave was then cooled to room temperature in air. Subsequently, the FTO substrate was taken out, rinsed extensively with deionized water, and dried in air. The effects of growth parameters, including growth time (from 2 h to 20 h), initial concentrations of precursor and cation, growth temperature (from 90–180 °C), and acidity on the resulting hierarchical structures were systematically investigated. TiO_2 nanorod films were also fabricated under the same condition without the addition of cation salts and used as controls to assess the influence of the presence of cation on the formation of hierarchical architectures.

TiO_2 Film Solar Cell Fabrication: Dye-sensitized solar cells (DSSCs) were assembled using nanostructured TiO_2 films (both nanorod film and flower cluster film) grown on the FTO glass as photoanodes. Prior to dye adsorption, the photoanode was placed in TiCl_4 solution (0.2 M, 100 mL) at 70 °C for 1 h. After rinsing with deionized water, the TiCl_4 -treated sample was annealed at 450 °C for 30 min inside a furnace. The sample was then soaked in anhydrous ethanol containing commercially available N719 dye (0.2 mM, cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium); Solaronix Co.), and kept for 24 h at room temperature. Platinum (Pt)-coated counter electrode was prepared by dropping H_2PtCl_6 (0.5 mM) isopropanol solution on another piece of FTO glass, followed by heating at 400 °C for 20 min. The dye-sensitized TiO_2 film with an active area of approximately 0.12 cm² was assembled together with the Pt-coated FTO glass by applying a 25 μm thick hot-melt sealed film as the spacer (SX1170-25; Solaronix). The liquid electrolyte used here was acetonitrile solution containing the I_3^-/I^- redox couple and commercially available (CJX-EH, Casjuxin Solar Technology Co., LTD., China). The electrolyte was injected between two electrodes and driven by capillary force through the hole on the hot-melt sealed film.^[51]

Characterization: The morphology and lattice structure of TiO_2 films were examined by field emission scanning electron microscopy (FESEM; FEI Quanta 250, operated at 10 kV in high vacuum) and transmission electron microscopy (TEM; JEOL 2100, operated at 200 kV). An SEM equipped with an energy dispersive X-ray spectrometer (EDS) was used to analyze the composition of TiO_2 nanostructures. Phase identification of TiO_2 was conducted by X-ray

diffraction (XRD; SCINTAG XDS-2000, Cu K α radiation). XPS measurements were performed in a PHI 5500 multitechnique system to confirm the chemical stoichiometry of the sample. The light absorption of TiO₂ films and desorption of dyes were measured by UV-visible spectroscopy (Varian; UV-Visible spectrophotometer, Cary 5000). The current–voltage (J–V) characteristics of DSSCs were measured using a Keithley 2400 source meter under one sun AM 1.5 G (100 mW cm^{−2}) illumination with a solar light simulator (Oriel, Model: 91260). A 300 W xenon arc lamp (Oriel, Model: 91160) was used as a light source and its incident light intensity was calibrated with a NREL-calibrated Si solar cell equipped with an optical filter to approximate AM 1.5 G one sun light intensity prior to each measurement. The incident-photon-to-current efficiency (IPCE) spectra as a function of wavelength (λ = 400 to 800 nm) were measured by a monochromator (Oriel, Model: 74125). Impedance tests were performed in dark under open circuit voltage over a frequency range from 10⁵ to 10^{−2} Hz with an AC voltage magnitude of 10 mV. The impedance data were analyzed by Autolab electrochemical impedance spectroscopy (EIS) fitting software.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

M.Y. gratefully acknowledges the financial support from the Chinese Scholarship Council. Z.L. gratefully acknowledges the financial support from Georgia Institute of Technology. C.L. gratefully acknowledges the financial supports from the National Natural Science Foundation of China (51072170, 21021002) and the National Basic Research Program of China (2012CB932900), and Academic New Artist Ministry of Education Doctoral Post Graduate of China (2010).

- [1] C. J. Barbe, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Gratzel, *J. Am. Ceram. Soc.* **1997**, *80*, 3157.
- [2] T. Beuvier, M. Richard-Plouet, M. Mancini-Le Granvalet, T. Brousse, O. Crosnier, L. Brohan, *Inorg. Chem.* **2010**, *49*, 8457.
- [3] X. S. He, C. G. Hu, B. Feng, B. Y. Wan, Y. S. Tian, *J. Electrochem. Soc.* **2010**, *157*, J381.
- [4] A. Wold, *Chem. Mater.* **1993**, *5*, 280.
- [5] M. Ye, J. Gong, Y. Lai, C. Lin, Z. Lin, *J. Am. Chem. Soc.* **2012**, *134*, 15720.
- [6] H. M. Cheng, J. M. Ma, Z. G. Zhao, L. M. Qi, *Chem. Mater.* **1995**, *7*, 663.
- [7] Y. H. Jang, X. Xin, M. Byun, Y. J. Jang, Z. Lin, D. H. Kim, *Nano Lett.* **2011**, *12*, 479.
- [8] W. Liu, L. Zhang, L. X. Cao, G. Su, Y. G. Wang, *J. Alloy. Compd.* **2011**, *509*, 3419.
- [9] G. K. Mor, O. K. Varghese, M. Paulose, C. A. Grimes, *Adv. Funct. Mater.* **2005**, *15*, 1291.
- [10] R. L. Penn, J. F. Banfield, *Geochim. Cosmochim. Acta* **1999**, *63*, 1549.
- [11] S. Seifried, M. Winterer, H. Hahn, *Chem. Vapor Depos.* **2000**, *6*, 239.
- [12] X. Xin, J. Wang, W. Han, M. Ye, Z. Lin, *Nanoscale* **2012**, *4*, 964.
- [13] M. Ye, X. Xin, C. Lin, Z. Lin, *Nano Lett.* **2011**, *11*, 3214.
- [14] X. Xin, M. Scheiner, M. Ye, Z. Lin, *Langmuir* **2011**, *27*, 14594.
- [15] X. F. Yang, C. J. Jin, C. L. Liang, D. H. Chen, M. M. Wu, J. C. Yu, *Chem. Commun.* **2011**, *47*, 1184.
- [16] W. G. Yang, F. R. Wan, Y. L. Wang, C. H. Jiang, *Appl. Phys. Lett.* **2009**, *95*, 133121.
- [17] J. G. Yu, J. J. Fan, K. L. Lv, *Nanoscale* **2010**, *2*, 2144.
- [18] J. Wang, Z. Q. Lin, *Chem. Mater.* **2008**, *20*, 1257.
- [19] J. Wang, Z. Q. Lin, *J. Phys. Chem. C* **2009**, *113*, 4026.
- [20] J. Wang, L. Zhao, V. S. Y. Lin, Z. Q. Lin, *J. Mater. Chem.* **2009**, *19*, 3682.
- [21] X. J. Feng, K. Shankar, O. K. Varghese, M. Paulose, T. J. Latempa, C. A. Grimes, *Nano Lett.* **2008**, *8*, 3781.
- [22] Y. J. Kim, M. H. Lee, H. J. Kim, G. Lim, Y. S. Choi, N. G. Park, K. Kim, W. I. Lee, *Adv. Mater.* **2009**, *21*, 3668.
- [23] B. Liu, E. S. Aydil, *J. Am. Chem. Soc.* **2009**, *131*, 3985.
- [24] K. Pan, Y. Z. Dong, C. G. Tian, W. Zhou, G. H. Tian, B. F. Zhao, H. G. Fu, *Electrochim. Acta* **2009**, *54*, 7350.
- [25] E. Hosono, S. Fujihara, H. Imai, I. Honma, I. Masaki, H. S. Zhou, *ACS Nano* **2007**, *1*, 273.
- [26] A. K. Sinha, S. Jana, S. Pande, S. Sarkar, M. Pradhan, M. Basu, S. Saha, A. Pal, T. Pal, *CrystEngComm* **2009**, *11*, 1210.
- [27] N. P. Thuy-Duong, E. J. Kim, S. H. Hahn, W. J. Kim, E. W. Shin, *J. Colloid Interface Sci.* **2011**, *356*, 138.
- [28] Q. Q. Cheng, Y. Cao, L. Yang, P. P. Zhang, K. Wang, H. J. Wang, *Mater. Res. Bull.* **2011**, *46*, 372.
- [29] Y. W. Wang, L. Z. Zhang, K. J. Deng, X. Y. Chen, Z. G. Zou, *J. Phys. Chem. C* **2007**, *111*, 2709.
- [30] J. Zhu, S. H. Wang, Z. F. Bian, C. L. Cai, H. X. Li, *Res. Chem. Intermed.* **2009**, *35*, 769.
- [31] J. K. Oh, J. K. Lee, H. S. Kim, S. B. Han, K. W. Park, *Chem. Mater.* **2010**, *22*, 1114.
- [32] F. Sauvage, F. Di Fonzo, A. L. Bassi, C. S. Casari, V. Russo, G. Divitini, C. Ducati, C. E. Bottani, P. Comte, M. Graetzel, *Nano Lett.* **2010**, *10*, 2562.
- [33] J. Q. Huang, Z. Huang, W. Guo, M. L. Wang, Y. G. Cao, M. C. Hong, *Cryst. Growth Des.* **2008**, *8*, 2444.
- [34] J. P. Wei, J. F. Yao, X. Y. Zhang, W. Zhu, H. Wang, M. J. Rhodes, *Mater. Lett.* **2007**, *61*, 4610.
- [35] E. Hosono, S. Fujihara, K. Kakiuchi, H. Imai, *J. Am. Chem. Soc.* **2004**, *126*, 7790.
- [36] N. G. Park, J. van de Lagemaat, A. J. Frank, *J. Phys. Chem. B* **2000**, *104*, 8989.
- [37] W. B. Hu, L. P. Li, W. M. Tong, G. S. Li, T. J. Yan, *J. Mater. Chem.* **2010**, *20*, 8659.
- [38] J. Huo, L. Wang, E. Irran, H. J. Yu, J. M. Gao, D. S. Fan, B. Li, J. J. Wang, W. B. Ding, A. M. Amin, C. Li, L. A. Ma, *Angew. Chem.-Int. Ed.* **2010**, *49*, 9237.
- [39] J. G. Yu, L. F. Qi, *J. Hazard. Mater.* **2009**, *169*, 221.
- [40] M. Shang, W. Z. Wang, W. Z. Yin, J. Ren, S. M. Sun, L. Zhang, *Chem. Eur. J.* **2010**, *16*, 11412.
- [41] J. Bokhim, A. Morales, M. Aguilar, J. A. Toledo-Antonio, F. Pedraza, *Int. J. Hydrog. Energy* **2001**, *26*, 1279.
- [42] Y. X. Li, M. Guo, M. Zhang, X. D. Wang, *Mater. Res. Bull.* **2009**, *44*, 1232.
- [43] H. Z. Zhang, J. F. Banfield, *J. Phys. Chem. B* **2000**, *104*, 3481.
- [44] H. Z. Zhang, J. F. Banfield, *J. Mater. Res.* **2000**, *15*, 437.
- [45] P. Hartman, W. G. Perdok, *Acta Crystallogr.* **1955**, *8*, 521.
- [46] P. Hartman, W. G. Perdok, *Acta Crystallogr.* **1955**, *8*, 525.
- [47] P. Hartman, W. G. Perdok, *Acta Crystallogr.* **1955**, *8*, 49.
- [48] B. J. Morgan, G. W. Watson, *J. Phys. Chem. C* **2009**, *113*, 7322.
- [49] B. Zhao, F. Chen, Q. W. Huang, J. L. Zhang, *Chem. Commun.* **2009**, 5115.
- [50] J. P. Liu, X. T. Huang, J. X. Duan, H. H. Ai, P. H. Tu, *Mater. Lett.* **2005**, *59*, 3710.
- [51] J. Wang, Z. Q. Lin, *Chem. Mater.* **2010**, *22*, 579.

Received: July 7, 2012
Published online: October 9, 2012