

## Growing TiO<sub>2</sub>-Based Pillars by Chemisorbed Nanotitania Followed by Annealing

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A templateless, efficient, and straightforward method is developed for the growth of TiO<sub>2</sub>-based microstructures perpendicular to the desired substrate. A variety of substrates coated by nanoparticles of TiO<sub>2</sub>, soaked in a 5 M NaOH solution for 2 h (chemisorption), and further annealed under air at 450 °C (4 h) fabricated a novel oriented, TiO<sub>2</sub>-based microarray comprised of nanotubes. Moreover, we verified that there is no need for both autoclaving (hydrothermal synthesis) and maintaining a lengthy reaction time for the growth of TiO<sub>2</sub>-based structures. The effect of several reaction parameters (solvent concentration, substrate nature, thickness and density of the seed nanotitania, and deposition of amorphous or crystalline TiO<sub>2</sub>) on the growth of the titania array is also demonstrated. The experimental results yielded the crystalline structure of anatase TiO<sub>2</sub>, and the previously anticipated mechanism for titania nanotubes synthesized by a soft chemical route supports the proposed growth mechanism. The electrodes grown on fluorine-doped tin oxide (FTO) glass substrates showed a moderate performance in dye-sensitized solar cells.

### Introduction

Titania and TiO<sub>2</sub>-based nanostructures are attractive materials for a wide variety of applications.<sup>1,2</sup> These applications include photovoltaic cells, batteries, separations, sensing, optical emissions, photonic crystals, catalysis and efficient photocatalysis, selective adsorption, ion exchange, ultraviolet blockers, smart surface coatings, and functional filling materials in textiles, paints, paper, and cosmetics. TiO<sub>2</sub> has been demonstrated as a promising electron-transport material of a dye-sensitized, oxide semiconductor solar cell.<sup>3</sup> Recently, the use of one-dimensional (1-D) nanostructures instead of nanocrystalline films in photoelectrochemical cells has been considered.<sup>4,5</sup> In addition, a more than 2-fold increase in maximum photoconversion efficiency for water splitting has been observed by replacing TiO<sub>2</sub> nanocrystalline films with TiO<sub>2</sub> nanowires.<sup>4</sup> For the dye-sensitized solar cell (DSSC), it is considered that extending the current collector by growing titania pillars perpendicular to the substrate may result in efficient electron transfer.

Among the different chemical methods available for titania nanotube fabrication, a method introduced by Kasuga et al.<sup>6,7</sup> triggered a wide discussion in the literature. Kasuga and co-workers applied a hydrothermal treatment to titania particles soaked in a NaOH solution at 110 °C, with the resulting product washed with water and hydrochloric acid to form titania nanotubes. They concluded that this washing procedure was critical in the formation of titania nanotubes.<sup>6</sup> However, Du and co-workers,<sup>9</sup> using the same hydrothermal process at 130 °C, obtained nanotubes without washing with water and HCl. Moreover, Du et al. concluded that the resulting nanotubes were not TiO<sub>2</sub> but rather H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>. Sun and Li, following a similar process, concluded that washing with water helps in nanotube formation and argued that the resulting nanotubes were not titania but a titanate<sup>10</sup> composition, Na<sub>x</sub>H<sub>2-x</sub>Ti<sub>3</sub>O<sub>7</sub> (with  $x \approx 0.75$ ). Yao et al. recently<sup>11</sup> contradicted the claims of Sun and Li<sup>10</sup> and tried to establish that the resulting nanotubes are TiO<sub>2</sub>.

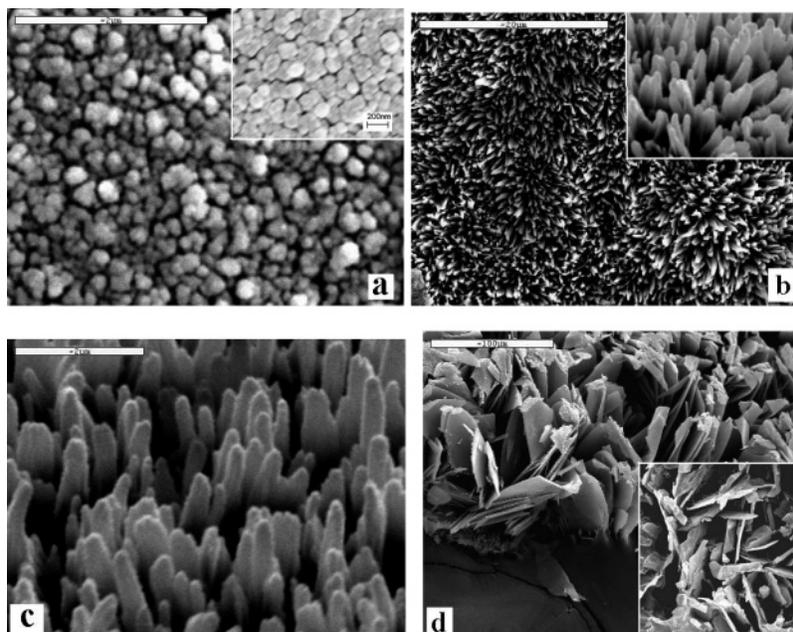
Consequently, as indicated by the above chronological records, there is still considerable ambiguity regarding both the underlying mechanism of nanotube growth using the process initially reported by Kasuga and co-workers<sup>6,7</sup> and a lack of consensus on the chemical composition of the resulting nanotubes. A simplified process to fabricate titania nanotubes was performed by the alkali treatment of the initial TiO<sub>2</sub> nanoparticles in a glass beaker<sup>12</sup> at 180 °C for 30 h. This process is in contrast to other soft-chemical nanotube fabrication processes reported in the literature requiring hydrothermal treatment in an autoclave.<sup>6,7,10,11,13</sup> The literature survey confirmed that titanates and not titania are the layered structure, and therefore, growing titania still remains a challenge.

In this paper, we report on a new straightforward, efficient, templateless approach for growing large oriented arrays of TiO<sub>2</sub>-based structures on desired substrates. A variety of substrates coated with nanoparticles of TiO<sub>2</sub>, soaked in a 5 M NaOH solution for 2 h and annealed under air at 450 °C, result in an oriented TiO<sub>2</sub>-based array. Moreover, we showed that there is no need of autoclaving (hydrothermal synthesis) and a lengthy reaction time for the growth of TiO<sub>2</sub>-based structures in the presence of NaOH. The effect of several reaction parameters, solvent concentration, substrate nature, thickness and porosity of the coated nanotitania, and deposition of amorphous or crystalline TiO<sub>2</sub> is discussed with respect to the titania-array growth. The nanostructured TiO<sub>2</sub> electrodes grown by the new procedure on FTO glass were tested in dye-sensitized solar cells, showing a reasonable performance.

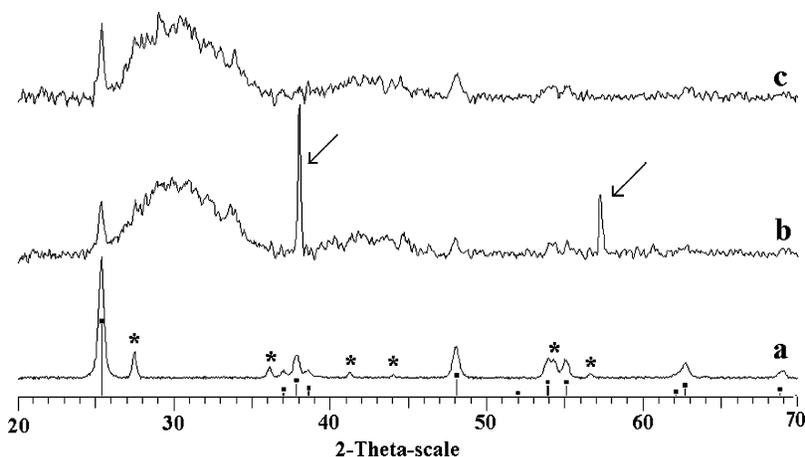
### Experimental Section

The oriented arrays of TiO<sub>2</sub> were grown on various substrates that were seeded with TiO<sub>2</sub> nanoparticles rather than in the bulk solution phase. Two methods to deposit the seed layer were used. In the first approach, a dilute TiO<sub>2</sub> suspension was prepared by sonicating 1.0 g of Degussa P25 TiO<sub>2</sub> powder in 15 mL of absolute ethanol for 5 min under cooling. TiO<sub>2</sub> nanoparticles were deposited on clean ITO, FTO glass, micro-

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**Figure 1.** SEM images of (a) bare TiO<sub>2</sub> nanoparticles deposited on FTO glass (inset: TiO<sub>2</sub> nanoparticles soaked in 5 M NaOH), (b) a top view of grown titania that was soaked in 5 M NaOH and heated to 450 °C/4 h (inset demonstrates a close view), (c) high-resolution image of the side view of the grown titania pillars that were soaked in 5 M NaOH and heated to 450 °C/4 h, and (d) side view of the grown TiO<sub>2</sub> walls using 10 M NaOH (inset: top view).



**Figure 2.** XRD patterns of (a) the starting P-25 TiO<sub>2</sub> nanoparticles obtained from Degussa, (b) TiO<sub>2</sub> nanoparticles soaked with an alkaline solution of 5 M NaOH for 2 h, and (c) the NaOH-soaked TiO<sub>2</sub> annealed at 450 °C for 4 h under air.

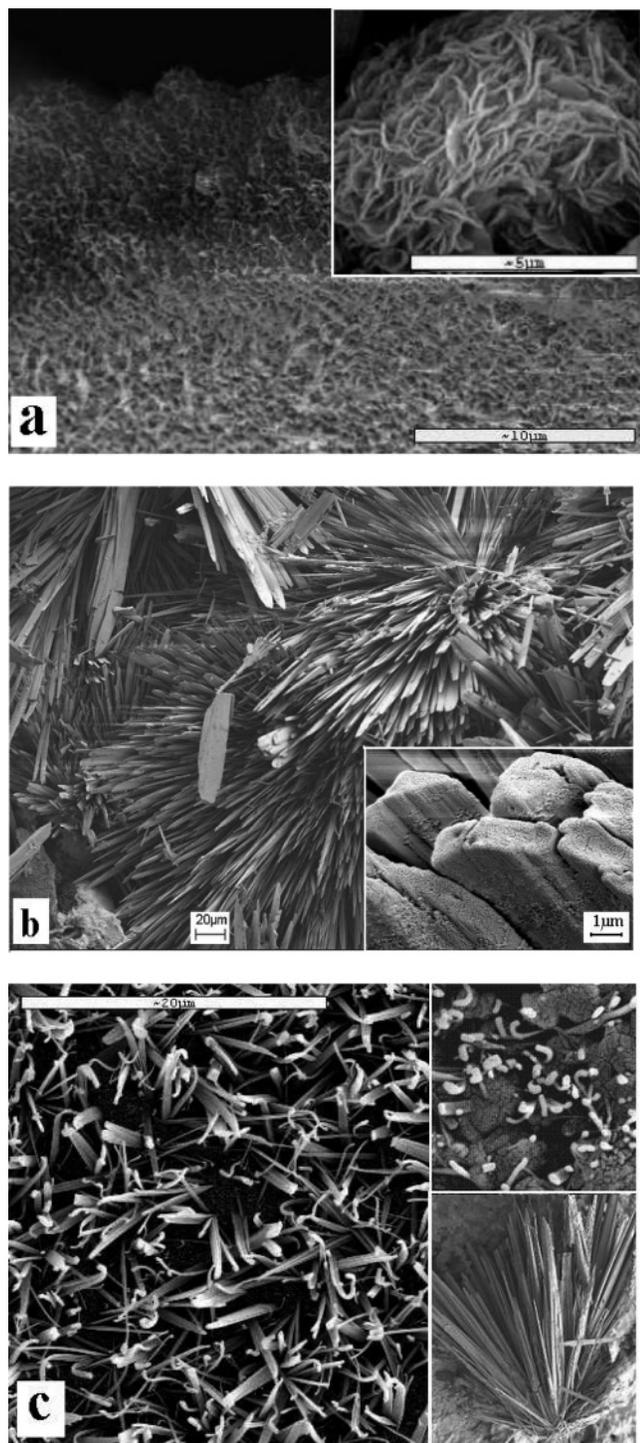
scope slides, titanium, and copper plates by a doctor blade method. In the second method, an electrophoretic deposition (EPD) process<sup>14</sup> was employed for the uniform deposition of amorphous and Degussa P25 TiO<sub>2</sub> nanoparticles on a FTO substrate. These predeposited TiO<sub>2</sub> nanoparticle substrates were mechanically pressed at 0.8 T/cm<sup>2</sup> and then soaked with an alkaline solution of 5 M NaOH for 2 h. The soaked substrates were directly heated to 450 °C for 4 h under air atmosphere and then cooled to room temperature. After annealing, all the substrates were washed with ethanol and diluted HCl. This morphology was studied with scanning electron microscopy, while the composition was measured by XPS surface analysis. The grown, washed TiO<sub>2</sub>-oriented arrays were detached from the substrate for morphological (SEM, TEM), structural (HR-TEM, XRD), and surface area (BET) analysis.

**Characterizations.** We measured the X-ray diffraction pattern of the products with a Bruker AXS D\* Advance Powder X-ray diffractometer (using Cu K $\alpha$  = 1.5418 Å radiation). The particle morphology and structure were studied by transmission electron microscopy on a JEOL-JEM 100 SX microscope,

working at an 80 kV accelerating voltage, and a JEOL-2010 HRTEM, using an accelerating voltage of 200 kV. The scanning electron micrographs (HR-SEM) were obtained with an LEO Gemini 982 field emission gun SEM (FEG-SEM) operating at a 4 kV accelerating voltage. X-ray photoelectron spectra (XPS) were measured with an AXIS, HIS 165, Kratos Analytical, ULTRA. An hydraulic programmable press (Bivas Hydraulic Industries Ltd.) was used to press substrates deposited by nano-TiO<sub>2</sub>. The thickness of the TiO<sub>2</sub> films was measured with a SurfTest SV 500 Profilometer from Mitutoyo Co.

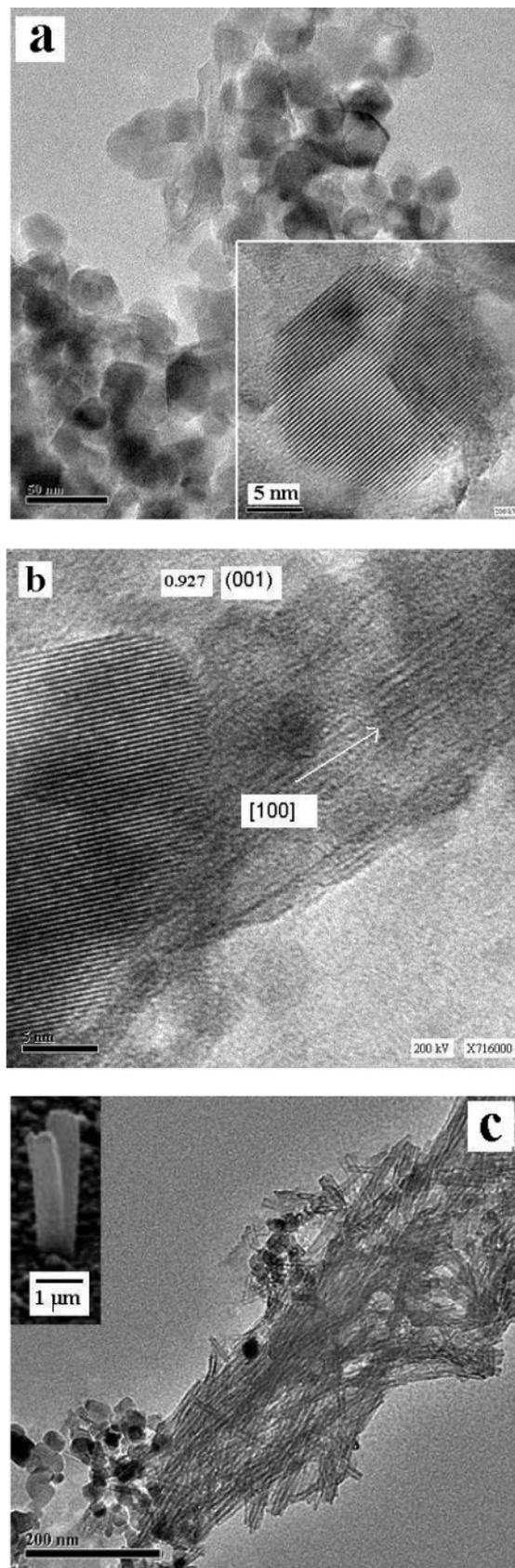
## Results and Discussion

Figure 1a shows a SEM image of P-25 Degussa TiO<sub>2</sub> nanoparticles deposited on clean FTO glass, with a diameter in the range 25–50 nm. The substrate, containing a 9  $\mu$ m thick layer of the nanoTiO<sub>2</sub>, was soaked in an alkaline solution of 5 M NaOH for 2 h, resulting in swollen TiO<sub>2</sub> particles attached to the FTO surface (see inset of Figure 1a). The soaked substrate was directly heated at 450 °C for 4 h under air and then cooled



**Figure 3.** SEM images of grown  $\text{TiO}_2$  structures on (a) a copper substrate (inset: close view), (b)  $3 \mu\text{m}$  thick compact  $\text{TiO}_2$  layer coated on FTO glass (inset: close up view of the pillars), and (c) thickness effect on the growth of a titania-based array.

to room temperature, thus fabricating the oriented array shown in Figure 1b (top view). The inset (Figure 1b) demonstrates a closer view of the grown titania pillars. The same sample was tilted up by  $60^\circ$  to see a side view of the grown titania (Figure 1c). The diameter of the grown pillars is  $\sim 200 \text{ nm}$  with a height of  $\sim 2 \mu\text{m}$ . There is no detectable effect on the shape and size of the resulting morphology after carefully washing with ethanol and diluted HCl. The distance between the two as-grown titania pillars is  $\sim 300 \text{ nm}$  on the FTO substrate. The surface area of the titania layer decreases upon the one-dimensional growth from  $50$  to  $7.5 \text{ m}^2/\text{g}$ . We observed an accumulation of the  $\text{TiO}_2$



**Figure 4.** (a) TEM image of nano- $\text{TiO}_2$  used for the growth of the titania microarray (inset: crystalline anatase titania particle soaked with an alkaline solution of  $5 \text{ M NaOH}$  for  $2 \text{ h}$ ). (b) HR-TEM image of the growth occurring along the  $[100]$  direction of the anatase phase, resulting in a zigzag structure. (c) HR-TEM of an ultrasonically dispersed microarray of titania (inset: before dispersion of individual pillars).

pillars when we provided an additional heat treatment up to 500 °C. The perpendicularly grown titania arrays are fragile and could be damaged by pressing (0.8 T/cm<sup>2</sup>). An increase in the concentration of NaOH from 5 to 10 M leads to the fabrication of TiO<sub>2</sub>-based walls instead of pillars. Figure 1d shows that the grown walls are ~2 μm thick, ~50 μm long, and ~80 μm high. The inset designates the top view of the irregularly grown, titania-based walls.

Figure 2a shows the XRD pattern of the starting P-25 TiO<sub>2</sub> material obtained from Degussa AG, Germany. This figure reveals that the P-25 TiO<sub>2</sub> material is a mixture of 70% body-centered tetragonal anatase (PDF No. 1-89-4921) and 30% tetragonal rutile (PDF No. 1-89-8304). The match of the peak position and the respective intensity is indicated for anatase, while peaks denoted by stars belong to rutile titania. For the XRD measurements of the grown titania pillars, samples were performed by detaching them from the FTO glass to avoid overlapping with the diffraction lines of the FTO substrate. The XRD pattern of nanotitania soaked with an alkaline solution of 5 M NaOH for 2 h (chemisorption) is shown in Figure 2b. In addition to the pure anatase and rutile titania, new diffraction lines are observed, showing the presence of NaOH (marked by an arrow). Figure 2c shows the XRD pattern of the NaOH-soaked TiO<sub>2</sub> followed by annealing at 450 °C for 4 h under air. Figure 2c reveals that the NaOH peaks completely disappeared, while a peak at  $2\theta = 25.4^\circ$  belonging to anatase titania became more intense. The XRD pattern does not change after washing with ethanol and diluted HCl. Figure 2b,c shows that there is no phase transformation from the starting anatase titania material. Similar XRD patterns were reported by Grimes<sup>12</sup> et al. for the formation of titania nanotubes after NaOH treatment in an autoclave. The XRD patterns, Figure 2b,c indicates that the anatase-TiO<sub>2</sub> structures (PDF No. 1-89-4921) were formed during the alkali treatment followed by annealing, and no acidic or other treatment was necessary for the fabrication of TiO<sub>2</sub> arrays on the substrates. The as-grown and lightly washed TiO<sub>2</sub> microstructures on the FTO substrates are termed a “TiO<sub>2</sub>-based array” since they possess some Na impurity, as confirmed by XPS surface analysis. The mass concentration of Na was found to be 50% after soaking the nano-TiO<sub>2</sub> in 5 M NaOH for 2 h. Heating the soaked nanotitania to 450 °C/4 h reduced the Na mass concentration to 44.5%. Mild washing with diluted HCl prior to applying the heat treatment resulted in an 18.5% mass concentration of Na in the TiO<sub>2</sub> microstructures. This Na impurity could be completely removed only by the mechanical detachment of the TiO<sub>2</sub>-based array, followed by thorough washing with diluted HCl and ethanol over a few centrifugation cycles.

The effect of the substrate on the titania-based microstructure growth was studied using copper, titanium, and FTO glass substrates. In all these cases, a 3 μm thick nanotitania layer was dipped in 5 M NaOH followed by annealing at 450 °C. The titania growth on the copper substrate resulted in a 15 μm thick porous layer (Figure 3a). The inset shows a HR-SEM image of the porous titania layer representing a typical flakelike morphology with a submicrometer size width and several micrometer size lengths. A similar type of growth was observed when a titanium metal plate was used as a substrate. The growth of the TiO<sub>2</sub>-based microstructures on FTO or glass was similar to the growth observed in the case of FTO substrates (Figure 1b). Consequently, this finding confirms that the growth of titania-based microarrays can happen on any substrate. This confirms that the surface of the substrate is indeed not important and only the chemisorbed (NaOH) titania grows while sintering.

We studied the effect of the density of the seed nanotitania on the array growth by pressure densification prior to chemisorption and annealing. The 9 μm thick TiO<sub>2</sub> layer was compressed to 3 μm using an hydraulic programmable press employing 0.8 T/cm<sup>2</sup>. The 3 μm densified titania film was soaked in 5 M NaOH/2 h followed by annealing at 450 °C/4 h. Figure 3b shows the resulting dense submicrometer size diameter and several micrometer long titania-based arrays formed on the FTO substrate. The HR-SEM depicts TiO<sub>2</sub>-based pillars that are arranged parallel to each other, possessing nanosized particles on the surfaces (inset). A similar nonpressed electrode forms smaller pillars with diameters of ~200 nm and a height in the range of 2 μm (Figure 1c). Comparing the array formed from the pressed electrode with that of the array formed on the basis of a similar nonpressed electrode leads to the understanding that the densification of the seed nanotitania increases the size of the resulting pillars.

The effect of thickness on the growth of the titania-based array was carried out using three similar nanotitania films that differ in their thickness: 700 nm; 2.7 μm; 9 μm. These three electrodes were pressed employing 0.8 T/cm<sup>2</sup> to a thickness of ~200 nm, 800 nm, and 3 μm, respectively. Figure 3c shows the effect of the thickness of the seed nanotitania layer on the growth. The 800 nm thick layer leads to the dense growth of titania pillars (Figure 3c). The 200 nm thick layer formed only a few oriented titania pillars, as shown in the top inset of Figure 3c. Finally, the 3 μm layer yielded a dense submicrometer size diameter and several micrometer long, titania-based arrays (the bottom inset of Figure 3c). Consequently, an increase in the thickness of the seed titania layer increases the growth of the titania pillars. The dependence of the amount of titania (thickness) on the growth is an important observation, and it further confirms that the whole titania layers grows.

A mechanism by which the anatase nano TiO<sub>2</sub> grows into microarrays is not fully clear yet, but it seems to be different from the reported mechanism that requires autoclaving.<sup>6–10</sup> In the following section, we suggest a mechanism on the basis of our experimental results and the crystalline structure of anatase TiO<sub>2</sub>. The TEM image of the nano-TiO<sub>2</sub> (diameters of 20–30 nm) used for the growth of the titania microarray is shown in Figure 4a. An HR-TEM image of the nanotitania soaked with 5 M NaOH/2 h is demonstrated in the inset of Figure 4a. The high-resolution insert image shows that the surface of the crystalline anatase nanotitania became disturbed during a 2 h soaking treatment, while the core of titania particles ~2–3 nm from the surface was still well crystalline. One of our control experiments verified that titania pillars do not grow when nanotitania was soaked in NaCl instead of NaOH. This finding confirms that the OH groups play an important role during the growth of the pillars.

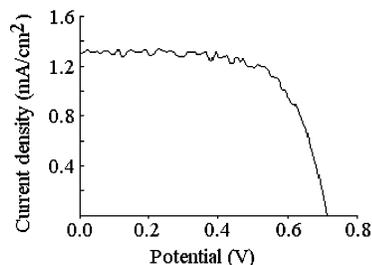
We partially considered the mechanism published by Grimes<sup>12</sup> et al. for the growth and structure of titania nanotubes synthesized by a soft chemical route. They added 2 g of anatase nanotitania to 150 mL of a 10 M NaOH aqueous solution, heated in a Pyrex beaker at 180 °C for 30 h without an autoclave. The constant volume of the aqueous solution was maintained during the heat treatment with the continual addition of a 10 M NaOH solution. Grimes et al. suggested that an alkali environment breaks the bonds between the anatase octahedra, which then link together through hydroxy bridging, leading to the growth in the anatase [100] direction. This process, along with the lateral growth through oxo bridge formation in the [001] direction, results in the formation of crystalline sheets that then roll up to form TiO<sub>2</sub> nanotubes. The HR-TEM image shown in Figure

4b indicates that the growth of anatase particles during heat treatment (450 °C) occurred along the [100] direction, probably through the connection of Ti–O–Ti, thus making use of the surface hydroxyl groups. Rajh et al. also demonstrated the pH dependence<sup>15</sup> on the self-coiling of TiO<sub>2</sub> sheets, supported by SAXS and WAXS data. Recoiling of the titania sheets resulted in the formation of a nanotubular titania structure, which also supports our claim. Recently, Wei et al. synthesized the tubular morphology of TiO<sub>2</sub> via a self-assembly and self-removal process<sup>16</sup> using NaOH. The formation of TiO<sub>6</sub> octahedra and weakened O–H bonds resulted in the formation of H<sub>2</sub>O, which further leads to the formation of a large number of cylinder-like TiO<sub>2</sub> sheets. Our results are also analogous to their observations and possible formation mechanism. The disordered system (amorphous TiO<sub>2</sub>) did not grow with chemisorbed NaOH, which might be due to the lack of formation of TiO<sub>6</sub> octahedra under identical reaction conditions. The TEM investigations confirm that the arrays were formed during the heat treatment of NaOH-soaked nanotitania, and neither subsequent acidic treatment nor washing with dilute HCl or ethanol had any effect on the structure and shape of the titania pillars.

The as-grown titania microarrays were detached from the FTO substrate and ultrasonically dispersed into absolute ethanol. A drop of the formed suspension was placed on a copper grid coated with an amorphous carbon film and allowed to air-dry for a HR-TEM study. Figure 4c shows that the formed titania microarrays (inset, diameter of ~200 nm and length of several micrometers) were comprised of much smaller nanotubes (diameter 10 nm and length of several micrometers) aligned along the pillars.

The titania pillars grown on the FTO electrode were sensitized by the N3 dye, *cis*-diisothiocyanatobis(4,4-dicarboxy-2,2-bipyridine)ruthenium(II) (Solaronic SA). For dye adsorption, a diluted HCl and water-washed electrode was immersed overnight in a 0.5 mM solution of dye in absolute ethanol. To avoid contact with water, the film was heated to 100 °C before immersion in the dye solution. A sandwich-type configuration was employed to measure the performance of the dye-sensitized solar cell (DSSC) using an F-doped SnO<sub>2</sub> film coated with Pt as a counter electrode.<sup>17</sup> The electrolyte solution consisted of 0.5 M *tert*-butylammonium iodine ((TBA)I), 0.05 M I<sub>2</sub>, and 2.7 mM 4-*tert*-butylpyridine (TBP) in 1:1 acetonitrile–3-methyl-2-oxazolidinone (NMO). The illumination of the cell was performed as described elsewhere.<sup>18</sup>

The DSSC performance of our titania pillar electrode exhibited  $J_{sc} = 1.32 \text{ mA/cm}^2$ ,  $V_{oc} = 0.72 \text{ V}$ ,  $ff = 0.56$ , and  $\eta = 0.64\%$  (Figure 5). The low current obtained was related to the low optical density of our sensitized electrode. The latter results from the low surface area of the TiO<sub>2</sub> pillars compared with the standard nanocrystalline electrodes. Further work toward the increase in the pillars' surface area will be reported when available.



**Figure 5.** Photocurrent–photovoltage characteristics of dye-sensitized titania pillars.

In conclusion, novel oriented, TiO<sub>2</sub>-based microarrays comprised of nanotubes are formed on the surface of various substrates using nanoTiO<sub>2</sub> coating, chemisorption, and heat treatment. The current report facilitates the understanding that a long reaction time and the autoclaving of the solute and solvent are not required to grow titania-based structures. The effect of several reaction parameters on the growth of titania arrays is also demonstrated. This templateless, efficient, and straightforward approach may help in growing other inorganic oxides on a variety of substrates.

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