

Highly Efficient Dye-Sensitized Solar Cells with a Titania Thin-Film Electrode Composed of a Network Structure of Single-Crystal-like TiO₂ Nanowires Made by the “Oriented Attachment” Mechanism

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Abstract: In this study, single-crystal-like anatase TiO₂ nanowires were formed in a network structure by surfactant-assisted self-assembling processes at low temperature. The crystal lattice planes of the nanowires and networks of such wires composed of many nanoparticles were almost perfectly aligned with each other due to the “oriented attachment” mechanism, resulting in the high rate of electron transfer through the TiO₂ nanonetwork with single-crystal-like anatase nanowires. The direction of crystal growth of oriented attachment was controlled by changing the mole ratio of acetylacetone to Ti, that is, regulating both the adsorption of surfactant molecules via control of the reaction rate and the surface energy. A single-crystalline anatase exposing mainly the {101} plane has been prepared, which adsorbed ruthenium dye over 4 times higher as compared to P-25. A high light-to-electricity conversion yield of 9.3% was achieved by applying the titania nanomaterials with network structure as the titania thin film of dye-sensitized solar cells.

Introduction

Nanosize materials sometimes have peculiar properties that are not expected in the bulk phase, and elucidation of these properties has already led to breakthroughs in various fields of science and technology. The electrical and optical properties of nanoparticles are often size- and shape-dependent, and, hence, it is essential to be able to control the particle size, shape, and distribution.^{1–3} This requires a detailed understanding of the mechanisms of nucleation and growth, as well as processes such as aggregation and coarsening.

Nanosize semiconductor ceramics are useful materials for photoactive systems such as dye-sensitized solar cells (DSC), as shown by Grätzel in 1991.⁴ A porous thin film composed of titania nanosize particles accumulated on a transparent conducting glass has been used as an electrode to achieve a high specific surface area for adsorption of a large number of dye molecules. However, the electron diffusion coefficient determined by laser flash-induced transient photocurrent measurement^{5–7} and intensity modulated photocurrent spectroscopy^{8,9} was more than

2 orders of magnitude smaller than the value for bulk anatase crystal. These small diffusion coefficients can be roughly understood by the hypothesis of electron traps in the porous TiO₂ with a very broad distribution of release rate. Defects in the porous TiO₂ may act as electron traps and exist in grain boundaries at the contacts between nanosize particles. Thus, the use of a network structure of TiO₂ single-crystal-like nanowires instead of TiO₂ nanoparticles is expected to result in a great improvement for rapid electron transfer and high efficiency.

In this paper, we present the preparation of a TiO₂ network structure of single-crystal-like nanowires by an “oriented attachment” mechanism^{10–13} using surfactant-assisted processes at low temperature, 353 K. The direction of crystal growth could be controlled by changing the adsorption of surfactant molecules on the TiO₂ surface due to the reaction rate and the surface energy. These structures were characterized by high-resolution transmission electron microscopy (HRTEM) images, together with fast Fourier transform (FFT), selected area electron diffraction (SAED), X-ray diffraction (XRD), and nitrogen adsorption isotherm. We applied this anatase single-crystal-like

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tiania network structure exposing the {101} plane as a semiconductor thin-film electrode in DSC and attained a high light-to-electricity conversion yield of 9.3%.

Experimental Section

Formation of TiO₂ Network Structure of Single-Crystal-like Nanowires. In a typical synthesis process, laurylamine hydrochloride (LAHC) was dissolved in distilled water, and tetraisopropylorthotitanate (TIPT) was mixed with acetylacetone (ACA) to decrease the hydrolysis and condensation rates of TIPT. When TIPT was mixed with the same molar ratio of ACA, ACA coordinated to the titanium atom, with one isopropoxyl group unbound. The coordination number of the titanium atom changed from 4 to 5, resulting in a color change from colorless to yellow.¹⁴ This yellow TIPT solution was added to 0.1 M LAHC aqueous solution (pH 4–4.5). The molar ratio of TIPT to LAHC was 4. When the two solutions were mixed, precipitation occurred immediately. The precipitates were dissolved completely by stirring the solution for several days at 313 K, and the solution became transparent, indicating that the precipitates were finely divided; that is, the size became smaller than the wavelength of light, and surfactant molecules interacted well with the titania compounds. The temperature was then changed to 353 K. After 3 h at 353 K, the solution became a hard gel. After 5 h, the gel became weak and shrank with the proceeding condensation reaction, releasing isopropyl alcohol and ACA. After 3 days, the solution became a white gel with a thin yellow liquid layer. The titania products were separated by centrifugation. After being washed with 2-propanol and successive centrifugation, the titania powders were dried in a vacuum.

Characterization of the produced materials was made by X-ray diffraction (XRD) (Rigaku Goniometer PMG-A2, CN2155D2), transmission electron microscopy (TEM) (JEOL 200 CX), fast Fourier transform (FFT), selected-area electron diffraction (SAED), field emission scanning electron microscope (FE-SEM) (JEOL 2JSM-6500), and isotherm of nitrogen adsorption (BEL SORP 18 PLUS).

Preparation of Titania Thin Films and Solar Cells. Thin titania films were made by applying a titania sample on an electric conducting glass plate. Indium-tin-oxide (ITO) glass plates and fluorine-doped tin oxide (FTO) were used as an electric conducting glass plate. The ITO and FTO glass plates were kindly donated by Geomatec Co. Ltd. and by Asahi Glass Co., respectively. We used a gel with a white color, which was obtained after reactions at 353 K for 3 days, as the starting titania sample. Because the titania gel contained surfactant molecules, they were removed from the gel by washing with isopropyl alcohol. We controlled the alcohol content and viscosity of the gel simultaneously by changing the centrifugation speed, causing the sample to be separated from the alcohol solution. Next, titania gel sample 1 was prepared by mixing the washed gel with poly(ethylene glycol) (PEG: MW 20 000, Wako Chemicals) in the range from 5 to 10 wt %. Titania gel sample 2 was prepared by mixing the gel sample 1 with titania nanoparticle Degussa P-25 (P-25) in the range from 5 to 10 wt %. These gel samples were applied repetitively to the conducting glass (ITO) as follows. The conducting glass was covered on two parallel edges with adhesive tape to control the thickness of the TiO₂ film and to provide a noncoated area for electrical contact. The titania gel sample 1 was applied to the free edges of the conducting glass and distributed with a glass rod sliding over the tape-covered edges. Gel sample 1 was coated several times (usually three times) on the coating film as mentioned above. In several cases, gel sample 2 was then coated several times (usually two times) on the coated gel sample 1. After each coating, the sample was calcined at 723 K for 30 min after drying. The last time the sample was calcined at 723 K for 60 min. Dye was introduced to the titania thin films by soaking the film for about 20 h in a 3 × 10⁻⁴ M solution of ruthenium dye in ethanol. *cis*-Di(thiocyanate)bis-

(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II) (N3) and *cis*-di(thiocyanate)bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II) bis-tetra-butylammonium (N719) (Solaronix SA and Kojima Chemical Reagents, Inc.) produced by Grätzel's group¹⁵ were used as the dye.

The DSC was comprised of a titania thin-film electrode on a conducting glass plate, and a platinum electrode made by sputtering on the conducting glass and electrolyte between the titania thin film and the platinum. We used two kinds of electrolyte, that is, electrolyte 1, 0.1 M of LiI, 0.6 M of 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPII), 0.05 M of I₂, 1 M of 4-*tert*-butylpyridine (TBP) in methoxyacetonitrile, and electrolyte 2, 0.03–0.05 M of I₂, 0.3–0.5 M of LiI in 3-methyl-2-oxazolidinone (NMO)/acetonitrile solution in some cases. The volume ratio of NMO to acetonitrile was 1/9. The photocurrent–voltage characteristics were measured using a potentiostat (Hokuto Denko HA-501G, HB-105) by irradiating with simulated solar light, that is, AM1.5 100 mW/cm² (ORIEL 1000 W 91192). The cell size was 1 or 0.25 cm². Cells made of P-25 were also prepared according to the method reported by Grätzel¹⁵ for comparison, and the photocurrent–voltage characteristics of P-25 cells were measured under the same conditions. The incident photon-to-current conversion efficiency (IPCE) was measured using the IPCE evaluation system for a dye-sensitized solar cell (Bunkoh-Keiki Co. Ltd., CEP-2000).

Results and Discussion

Formation of the Network Structure of Single-Crystal-like TiO₂ Nanowires. There are only a few examples reported where nanorods and nanowires could be prepared in a controllable manner using evaporation or colloid-chemical techniques.^{16,17} Rod formation requires anisotropic crystal growth, which is realized usually when the free surface energies of the various crystallographic planes differ significantly. For wet chemical synthesis, Puentes et al.^{18a} recently showed that the formation of a tetra-pod structure could be realized in the case of CdSe by using two different surface ligands, which probably bind selectively to the respective surface planes. Thus, an “oriented attachment” mechanism can control the formation of rather complicated structures using the crystal plane of nanoparticles. Furthermore, organic molecules such as surfactants also act as surface ligands and have the ability to control the shape and size of the growing particles, as was shown recently by Banfield et al.^{18b}

We present the formation of single-crystal-like titania nanowires made of crystalline spherical titania nanoparticles in aqueous solution based on oriented attachment. Figure 1a shows a TEM image of the vacuum-dried titania powders heated at 353 K for 1 day. We can see the titania nanonetwork consisting of nanowires with diameters of 5–15 nm. The titania nanowires have very high crystallinity as can be seen on selected area electron diffraction (SAED) patterns (Figure 1b) in a wide area, showing the Debye–Sherrer rings of {101}, (004), (200), (105), (204), (220), and (215) diffractions of the anatase phase. Thus, the titania nanowires had a crystalline structure of the anatase phase. In Figure 1c, the SEM image of the TiO₂ nanowire film is shown. As shown by the TEM image, we can see that most of the particles connected with each other and made a network

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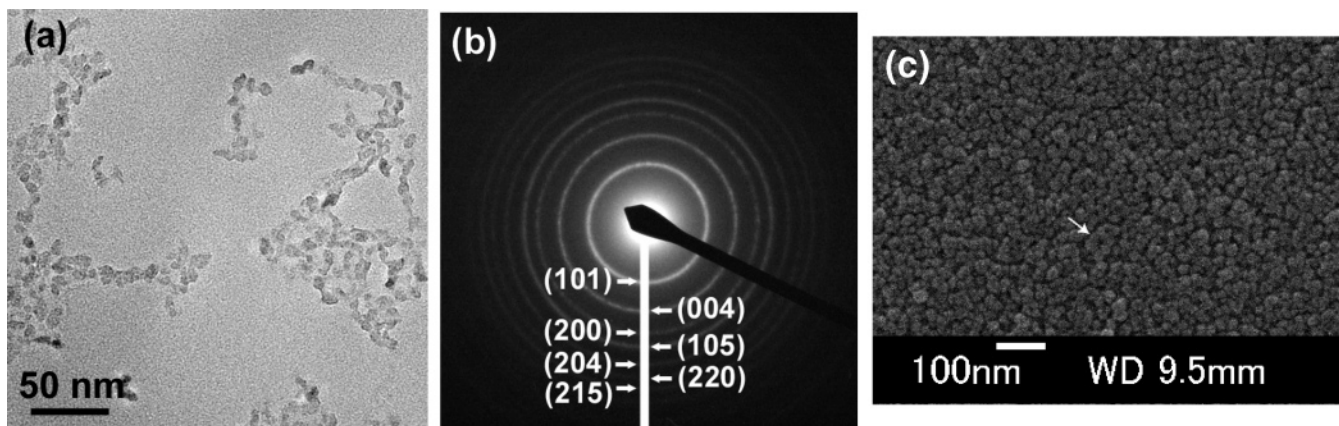


Figure 1. TEM images of vacuum-dried sample prepared at 353 K for 1 day. (a) Titania of the wire and the network structure were observed. (b) SAED pattern of titania nanowires. (c) SEM image of the TiO_2 nanowire film.

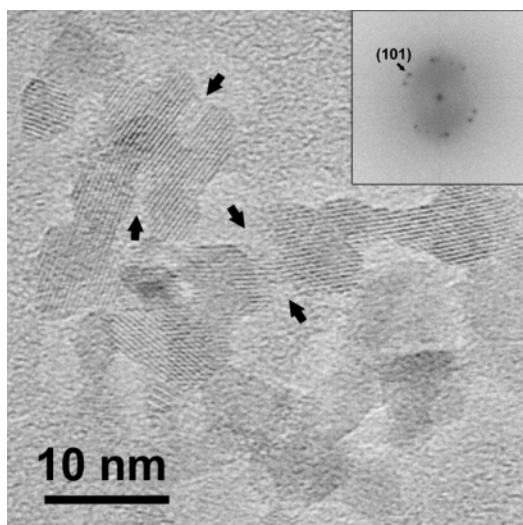


Figure 2. HRTEM image of several titania nanowires with single anatase structure formed by oriented attachment. Arrows in the HRTEM image indicate the indentations. Inset: FFT pattern obtained from HRTEM. The spacing of the lattice was calculated as 3.51 Å by FFT analysis, corresponding to {101} spacing of the anatase phase of titania.

of nanowires (shown by an arrow), although the magnification and resolution of the SEM image are limited.

An HRTEM image of nanowires and nanonetworks with a single anatase crystal is shown in Figure 2. Most of the aggregated particles form a wire shape with a single-crystalline structure. There were almost no isolated particles observed. Lattice images were clearly observed, indicating that these nanowires composed of fused nanoparticles with diameters of 2–5 nm had high crystallinity despite the small size. Because the lattice images aligned perfectly, the orientations of crystals of fused nanoparticles were completely aligned. This feature shows that nanowires were made by an oriented attachment mechanism. A lattice spacing of 3.51 Å was determined by fast Fourier transfer pattern (inset) and corresponded to the lattice spacing of the {101} plane of the anatase phase. The lattice images in this figure may be directly related to the crystal growth of nanowires. Two arrows indicate the bond between two particles. These indentations are a feature of crystal growth by the oriented attachment mechanism. This suggested that the oriented attachment occurred in the [010] or $\langle 101 \rangle$ direction and made a network structure. In this case, the {101} plane is mainly exposed. The network of nanowires formed by oriented attach-

ment had an irregular shape as shown in Figure 2 because of the bonding process as mentioned above. It is known that the {101} plane is the one being mainly exposed, but that would be probably in a rather random fashion on the spherical particle. Yet, in our experimental conditions, the lattice planes always aligned with each other in all observed cases of fusion of nanoparticles. Oriented attachment seemed to always occur when nanoparticles fused with each other under our experimental conditions. This finding was very interesting, because crystal growth by oriented attachment mechanism was observed below 373 K. Usually much higher temperature is needed, for example, 433–523 K.^{21,22} This observation confirmed a remarkable characteristic of our surfactant-assisted synthesis method using ACA.

The particle size distribution in the system can be modified by oriented attachment of primary particles, leading to the formation of wire-shaped structures. There is certainly a strong thermodynamic driving force for oriented attachment, because the surface energy is reduced substantially when the interface is eliminated.¹² The driving force for the assembly process is thus the reduction of surface energy, and this mechanism has been reported already for a variety of metal oxide systems.^{19,20} In the titania system under hydrothermal conditions (433–523 K, 15–40 bar),^{21,22} crystal growth was reported to occur along [001]. Oriented attachment in common titania systems occurs occasionally on (001), and rarely on {101}. This mechanism effectively serves to reduce the overall surface energy by eliminating the surfaces at which the crystallites join. We thought that organic molecules such as surfactants might hinder or modify oriented attachment. Organic molecules adsorbed on a crystallographically specific surface can modify the oriented attachment mechanism by changing the surface energy and also preventing contact between the faces on which adsorption has selectively occurred. In our surfactant-assisted system, the observed attached planes in the image are not (001) with high surface energy but {101} with low energy. We supposed that the surface energy was decreased by the adsorbed surfactants to the (001) planes. It has been reported that the surface density of six-fold-coordinated Ti atoms with the hydroxyl of the (001)

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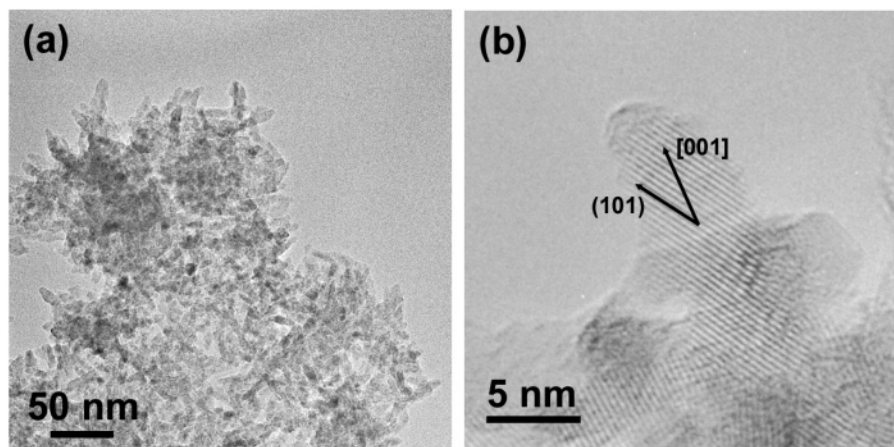


Figure 3. TEM (a) and HRTEM (b) images of titania nanorods prepared with ACA/Ti = 0.2 at 353 K for 1 day.

surface structure is high as compared to the {101} surface. The numbers of hydroxyl groups are 7.0 nm^{-2} for (001) surfaces and 5.1 nm^{-2} for {101} surfaces, respectively.²³ The (001) plane thus adsorbed much more surfactants than the {101} plane and hindered the contact between (001) planes, resulting in oriented attachment occurring on the {101} plane.

We carried out the experiment while varying the reaction rate to investigate the relationship between the adsorption of the surfactants and crystal growth. The mole ratio of ACA to TIPT was changed from 1 to 0.2, and the reaction behavior drastically changed. When LAHC solution was added to TIPT-ACA solution at a mole ratio of 0.2, a white colloidal suspension was formed immediately. A transparent supernatant was formed after the precipitation. Although the temperature was changed to 353 K, gelation did not occur, indicating that surfactant molecules did not affect the formation process of TiO_2 . The structure of the product heated at 353 K for 1 day was examined on TEM and HRTEM images. A rodlike morphology with an average diameter of $5 \pm 2 \text{ nm}$ and an average length of $20 \pm 10 \text{ nm}$ (aspect ratio $\cong 5$) was observed as shown in Figure 3a. The diameter of nanorods was not constant throughout their length. The SAED pattern of this sample indicated Debye–Scherrer rings corresponding to lattice planes of anatase phase. The lattice configuration of the nanorods is clearly shown in HRTEM images of Figure 3b, and the lattice spacing was found to be 3.52 \AA in agreement with the lattice spacing of the {101} planes of the anatase phase. As shown in Figure 3b, it was observed that the direction of crystal growth was not the $\langle 101 \rangle$ but the [001] direction. This result suggested that the attachment occurs mostly in the (001) plane.

The XRD pattern of titania nanorods prepared in the same way was measured under the conditions of 35 kV and 20 mA and is shown in Figure 4, indicating formation of the anatase phase. Comparing the intensity of the (004) peak of this sample to that of the standard TiO_2 sample shown in JCPDS, it was found that the relative intensity of (004) had increased 2.5 times from 20% to 50%. This implied that crystal growth of the titania nanorod occurs along the [001] direction, consistent with the HRTEM images in Figure 3b. Figure 5 clearly shows the crystal growth along the [001] direction under ACA/Ti = 0.2. The lattice spaces in Figure 5a were determined to be 4.75, 3.52, and 2.38 \AA , corresponding to the (002), {101}, and (004) planes

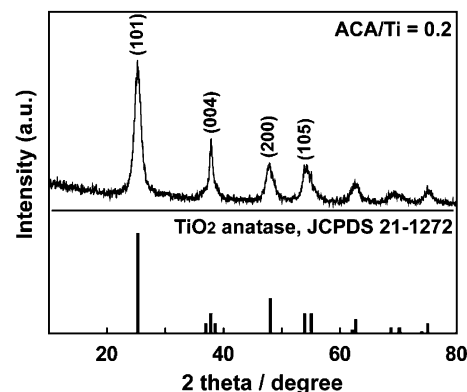


Figure 4. XRD pattern of titania nanorods prepared with ACA/Ti = 0.2.

of the anatase phase, respectively. The HRTEM image without the lattice image of the {101} plane in Figure 5a was obtained by masking the {101} plane by the inverse FFT method as shown in Figure 5b. These results show that the surface energy of crystal growth differs with the reaction conditions. Because the condensation reaction speed was much faster under ACA/Ti = 0.2, it is predicted that the crystal growth occurred before the surfactant molecules were adsorbed on the titania nanoparticles. Therefore, the crystal growth occurred along the [001] direction, which is a common oriented growth in the titania system. The result is also consistent with the findings of Banfield and Penn in the absence of ACA.^{21,22}

Thus, it can be concluded that the direction of crystal growth of oriented attachment can be controlled by regulating the adsorption of surfactant molecules via control of the reaction rate and can make a single-crystalline anatase exposing mainly the {101} plane by the surfactant-assisted oriented attachment mechanism at a low temperature, 353 K.

Application of Single-Crystalline Anatase Exposing Mainly the {101} Plane to DSC. To increase the efficiency of DSC, improvement in both open-circuit voltage and short-circuit current is essential. To accomplish this, a breakthrough in the preparation of a thin semiconductor film of titania is expected. Among many possible approaches, the use of a {101} exposure plane with a network structure of single-crystal-like anatase nanowires is one of the most promising ways, because the intercrystalline titania contacts are greatly decreased by using a single-crystal-like network structure in comparison with a porous titania thin film composed of accumulated nanosize

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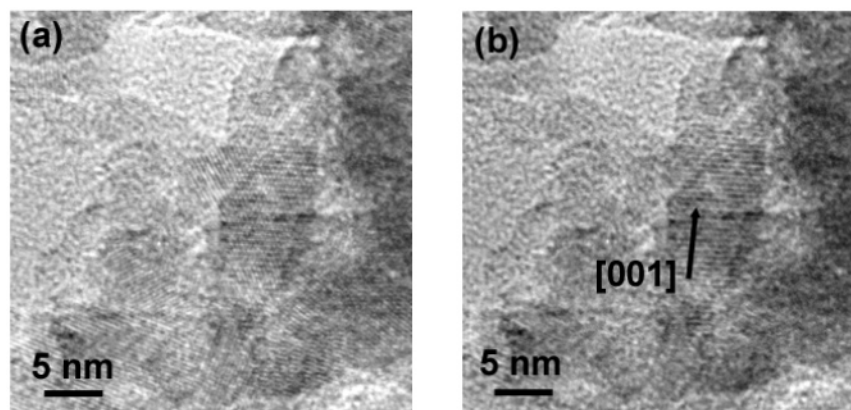


Figure 5. (a) HRTEM image of the aggregated titania nanorods prepared with ACA/Ti = 0.2 at 353 K for 1 day. (b) HRTEM image masked the {101} plane in (a) by the inverse FFT method.

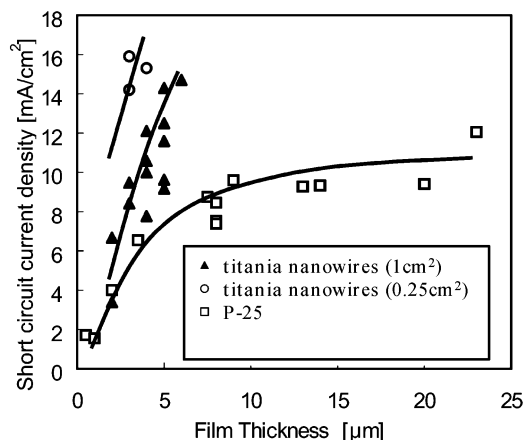


Figure 6. Relationship between the short-circuit current density and the film thickness. Electrolyte 2 was used.

particles. This might be useful for easier electron transfer through the titania layer, suppression of back reaction of photoinjected electrons with I_3^- , and also high dye adsorption on the titania surface, as shown later in detail. We succeeded in the preparation of such a network of single-crystal-like anatase nanowires and successfully used it in a thin film for DSC with high efficiency.

To compare a cell composed of a titania network of nanowires with one composed of standard titania particles P-25, we measured the photocurrent–voltage characteristics of both cells under the conditions described in the Experimental Section using FTO glass as the electric conducting glass and electrolyte 2. Figure 6 shows the short-circuit current density obtained from the cells made of the titania network of nanowires, together with those of P-25, against the film thickness. In the thin-film region, the current density of the cell made of a network of nanowires was more than 2 times higher than that of P-25. The high current density in the thin-film region might be attributable to both the high adsorption of N3 dye due to the large surface area mainly exposing {101} plane and the very high rate of electron transfer through the single-crystal-like TiO_2 nanonetwork, which is shown in Figure 2 by HRTEM. The use of a TiO_2 nanonetwork with single-crystal-like anatase nanowires instead of TiO_2 nanoparticles also contributes to the decreased number of contacts between titania materials, which make grain boundaries and act as electron traps.

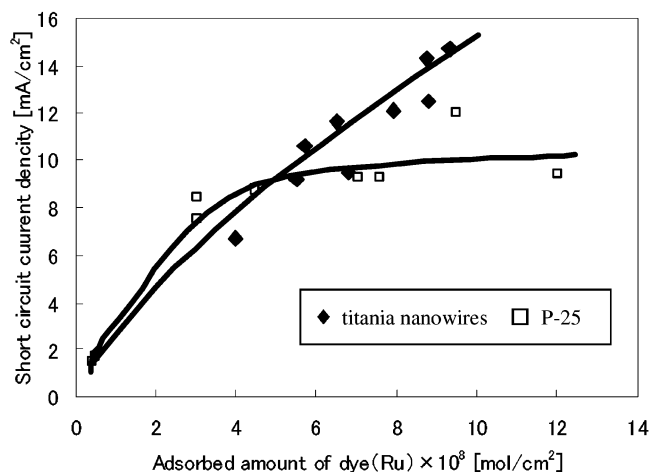


Figure 7. Relationship between the short-circuit photocurrent density and the dye amount. Electrolyte 2 was used.

Figure 7 shows the short-circuit current density obtained for both cells against the amount of dye adsorbed on the titania thin film on the unit area of the conducting glass. In the range $(0-6) \times 10^{-8}$ mol/cm², both cells gave almost the same photocurrent density. In the higher dye amount range, the photocurrent density of the P-25 cell stopped increasing and became constant. On the other hand, the photocurrent density of the network cell gave a linear increase. This linear increase in the high dye concentration region shows the potential higher efficiency of this cell with the TiO_2 network of nanowires. The film thickness of the cell with the TiO_2 network of nanowires is significantly thin in comparison with the cell made of P-25 for the same amount of dye adsorbed, especially in the high amount range. This might bring the above results.

To explain the amount of adsorbed dye on the film, the nitrogen adsorption measurement was applied to analyze the properties of titania samples. The nitrogen adsorption–desorption isotherm of the titania sample taken from a semiconductor layer in the DSC system calcined at 723 K for 30 min is shown in Figure 8a, together with that of a bulk sample of vacuum-dried titania. The isotherm pattern for the calcined sample was IUPAC type IV, indicating that meso-size pores were formed, like the bulk sample. However, the hysteresis loop for the calcined one was of H1 type; that is, the loop was relatively narrow, and the adsorption and desorption branches were nearly

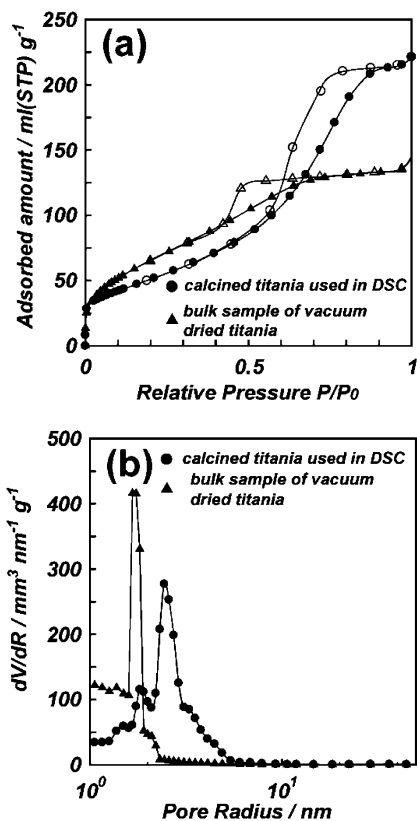


Figure 8. (a) Nitrogen adsorption–desorption isotherms of titania using dye-sensitized solar cells calcined at 723 K for 30 min and vacuum-dried titania nanowires. Filled and open symbols represent adsorption and desorption, respectively. (b) Pore size distribution obtained from Figure 8a.

parallel. A hysteresis loop of this type is shown by adsorbents with a narrow distribution of uniform pores, for example, open-ended tubular pores. The BET (Brunauer–Emmett–Teller) specific surface area of the calcined powders was 189 m²/g, and the peak pore size and the pore volume obtained from the Barrett–Joyner–Halenda method were 5.04 nm and 0.420 cm³/g, respectively (see Figure 8b). Thus, the network structure of titania nanowires became more rigid by calcinations, and the pore size and the pore volume increased in comparison with the bulk sample of vacuum-dried titania, which had a BET specific surface area of 248 m²/g, a pore size of 3.48 nm, and a pore volume of 0.267 cm³/g.

The relationship between the film thickness and the adsorbed N3 dye amount is shown in Figure 9. The adsorbed N3 dye was dissolved completely from TiO₂ to the sodium hydroxide aqueous solution, and the concentration of N3 was determined by the spectroscopic method. In the range of 0–10 μm, the amount of dye adsorbed to the titania network of nanowires was about 4–5 times higher than that of P-25 film. The BET specific surface areas of the calcined titania network of nanowires and P-25 were 189 and 55 m²/g, respectively. Thus, the titania network of nanowires adsorbed dyes more than the increase in the BET specific surface area. This finding suggests the importance of the control of interaction of dye molecules at the interface with the titania nanosize materials.

The interaction of the dye with the nanocrystalline TiO₂ electrode and the photophysical and electrochemical properties of the dye have been investigated.^{24–30} Recently, the anchoring

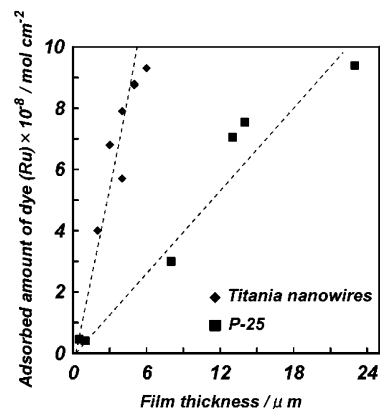


Figure 9. Relationship between the film thickness and the adsorbed dye amount.

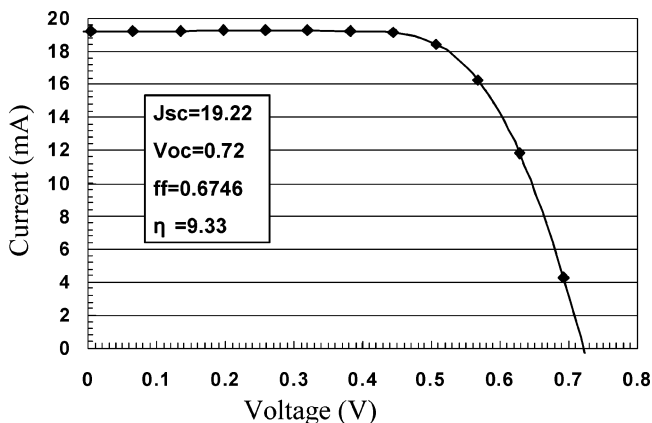


Figure 10. Illustration of photocurrent–voltage characteristics of the cell with titania thin film composed of a TiO₂ network structure of single-crystal-like anatase nanowires. A high light-to-electricity conversion of 9.3% was achieved. Electrolyte 1 was used.

nature of the dye on the semiconductor surface has been investigated mainly by FTIR.²⁵ A carboxylate group can coordinate to the TiO₂ surface²⁸ in mainly three ways:^{25,29} unidentate mode, chelating mode, and bridging bidentate mode. The possible anchoring models of the dye on the TiO₂ were proposed by Shklover et al.²⁴ on the basis of the crystal structure of the N3 dye. For N719, the most stable anchoring on the TiO₂ was determined as follows. The FTIR spectra of N719 showed the presence of mainly carboxylate groups, demonstrating that N719 was being adsorbed on the surface using the two carboxylic groups, which are trans to the SCN ligands. However, the presence of a small band (around 5%) at the carboxylic position indicated that around 5% of N719 was being adsorbed on the surface, employing one carboxylic acid and one carboxylate group. The distances between these two binding carboxylate groups and between one carboxylate and one carboxylic groups agreed quite well with the distance between Ti atoms on the anatase (101) plane.^{24,27} Thus, the anatase (101)

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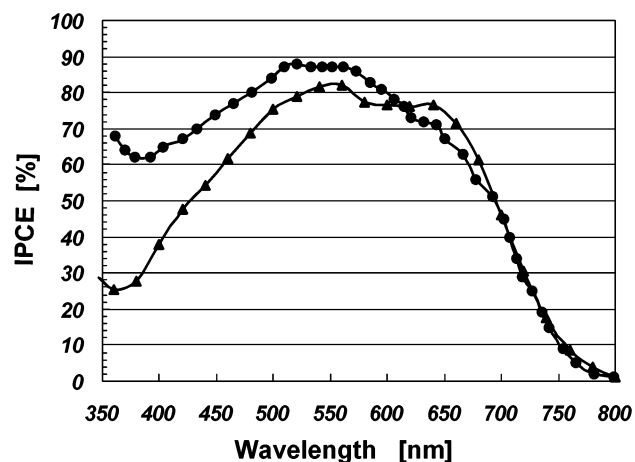


Figure 11. ▲: IPCE of the cell with titania thin film composed of the TiO₂ network structure of single-crystal-like anatase nanowires. ●: Grätzel, et al. *J. Am. Chem. Soc.* **1993**, *115*, 6382–6390. Electrolyte 1 was used.

plane is the best surface for adsorbing N3 or N719, indicating the reason the TiO₂ network of nanowires adsorbed much more dye than did P-25. The area occupied by the dye at the surface was determined as 1.6 nm²/molecule.²⁷

Figure 10 shows the current–voltage characteristics obtained for the cell with TiO₂ thin film composed of the network structure of single-crystal-like anatase nanowires. The titania thin film was prepared as follows. Titania gel sample 1 (see Experimental Section) was first coated three times on ITO conductive glass. Gel sample 2 was then coated two times onto coated gel sample 1. The sample was calcined after every coating at 723 K for the times described in the Experimental Section. The cell size was 0.25 cm². After calcinations, N719 was introduced to the titania thin film. The photocurrent voltage characteristics were measured using electrolyte 1 (see Experi-

mental Section) by irradiating with simulated solar light, that is, AM1.5 100 mW/cm² (ORIEL). A high light-to-electricity conversion rate of 9.3% was obtained for the cell with a TiO₂ network of single-crystal-like anatase nanowires. Short-circuit photocurrent density, open-circuit voltage, and fill factor were obtained as 19.2 mA/cm², 0.72 V, and 0.675, respectively. This high light-to-electricity conversion was attributed to the network structure of single-crystal-like anatase nanowires shown in Figure 2. The IPCE result of this dye-sensitized solar cell is shown in Figure 11, together with the result reported by Grätzel et al.¹⁵ The obtained IPCE spectrum for our titania network structure gave almost the same efficiency as the curve reported by Grätzel et al., confirming the high light-to-electricity conversion yield of our cell composed of a TiO₂ network structure of single-crystal-like anatase nanowires.

Conclusion

A titania nanonetwork structure composed of single-crystal-like anatase nanowires was successfully synthesized by a surfactant-assisted “oriented attachment” mechanism at a low temperature of 353 K. A high light-to-electricity conversion yield of 9.3% was achieved by applying the titania nanonetwork structure of single-crystal-like anatase nanowires as the titania thin film of dye-sensitized solar cells.

Acknowledgment. We gratefully acknowledge Professor S. Isoda (The Institute for Chemical Research, Kyoto University) for his assistance with TEM experiments. This work was supported by the Strategic University/Industry Alliance of the International Innovation Center, Kyoto University. The conductive ITO and FTO glasses were kindly donated by Geomatec Co. Ltd. and by Asahi Glass Co. LTD, respectively.

JA048068S