**Synthesis of Titanium Oxide Nanowires and their Application for Dye Sensitized Solar Cells**

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Highly efficient dye-sensitized solar cells become feasible using single crystalline anatase titania nanowires (TiNWs) and their network structures for semiconductor thin film instead of titania nanoparticles.We used laurylamine hydrocholoride(LAHC) / tetraisopropylortho-titanate(TIPT) modified with acetylacetone(ACA)system[1].

We optimized the cell using various electrolyte. The conversion efficiency obtained by the six times repetitive coating resulted in over 8%. This data promise realization of highly efficiency dye-sensitized solar cells using TiNWs as semiconductor thin film through further improvement.

TIPT-ACA solution was mixed with 0.1 M LAHC aqueous solution at 313K, and the solution was stirred until the solution became transparent. Then, temperature was changed to 353K. After 96 h the solution became a white gel with a yellow liquid thin layer on the gel. Preparation of titania thin films was carried out as follows. We used gel samples before calcinations. Surfactant molecules in TiNWs can be removed by washing with alcohol. Standard Titania sample was prepared by mixing TiNWs with PEG(10%). Another samples were prepared by mixing TiNWs with both PEG(10%) and P-25(with various concentration). These samples were applied repetitively to the conduction glass and distributed with a glass rod. Every time the sample was calcined at 723K for 30 min. The photocurrent-voltage characteristics was measured using a potentiostat by irradiating with simulated solar light (bunko-keiki), i.e., AM1.5. IPCE was also measured. Titania particle P-25 was used as reference titania for comparison.

Figure 1a shows a TEM image of the vacuum-dried titania powders heated at 353 K for 1 day. We can see the titania nano-network consisting of nanowires with diameter 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 anatase phase.

An HRTEM image of nanowires and nano-networks with single anatase crystal is shown in Figure 2. Most of the aggregated particles form a wire shape with a single crystalline structure. A lattice spacing of 3.51 Å was determined by fast Fourier transfer pattern (Inset) and corresponded to the lattice spacing of {101} plane of anatase phase. 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.

Figure 3(a) shows the current-voltage characteristics obtained for the cell with $TiO_2$ thin film composed of network structure of single crystalline anatase nanowires. The titania thin film was prepared as follows. Titania gel was first coated three times on ITO conductive glass. And Titania gel(mixed p-25 5-10wt%) was then coated three times on to coated Titania gel. The sample was calcined after every coating at 723 K for 30min. The cell size was 0.25 $cm^2$. After calcinations, N719 was introduced to the titania thin film. The photocurrent voltage characteristics were measured using electrolyte (0.1 M of LiI, 0.5 M of 1,2-dimethyl- 3-n-propylimidazolium iodide (DMPImI), 0.05 M of $I_2$, 1 M of 4-tert-butylpyridine (TBP) in methoxyacetonitride) by irradiating with simulated solar light, i.e., AM1.5 100mW/$cm^2$ (Bunkoh-keiki). A high light to electricity conversion rate of 8.37 % was obtained for the cell with a $TiO_2$ network of single crystalline anatase nanowires. Short-circuit photocurrent density, open-circuit voltage, and fill factor were obtained as 15.8 mA/$cm^2$, 0.74 V, and 0.72, respectively. The IPCE result of this dye-sensitized solar cell is shown in Figure 3(b), together with the result reported by Grätzel et al. 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 $TiO_2$ network structure of single crystalline anatase nanowires.

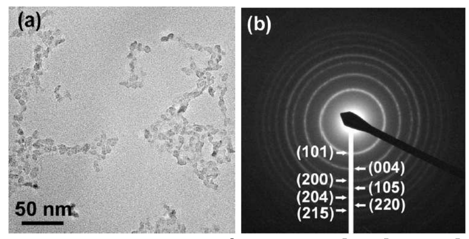


Figure 1. TEM images of vacuum-dried sample prepared at 353 K for 1 day.
(a) Titania of wire and network structure were observed.
(b) SAED pattern of titania nanowires.

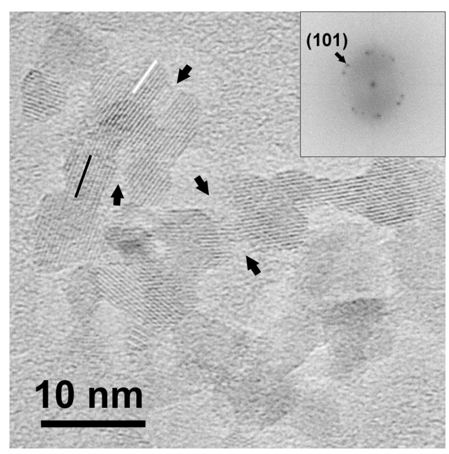


Figure 2. HRTEM image of several titania nanowires with single anatase structure formed by oriented attachment. Arrows in HRTEM image indicate the indentations.

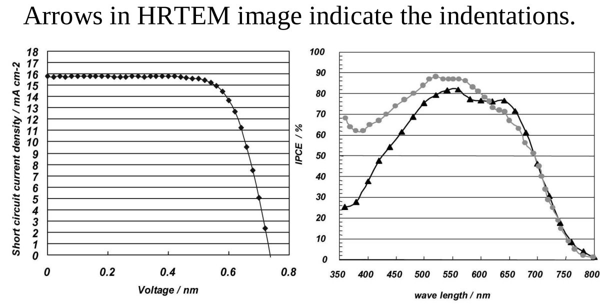


Fig.3 (a) Photocurrent-voltage characteristics of the dye-sensitized solar cells.
(b) IPCE of the cell with titania thin film composed of TiO2 network structure of single crystalline anatase nanowires (▲). Grätzel et al., JACS **1993**.

1. Motonari Adachi, Yusuke Murata, Issei Okada, and Susumu Yoshikawa, *Journal of The Electrochemical Society*, **150** (8) G488-G493 (2003)