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Photocurrent Properties of TiO_2 Nanorods Grown on FTO by Hydrothermal Method

Hyun Kim and Bee Lyong Yang†

School of Advanced Materials and System Engineering, Kumoh National Institute of Technology, Gumi 39177, Korea

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ABSTRACT

In this work, we undertake a comparative study of the crystallographic microstructures and photo-catalytic properties of rutile TiO_2 nanorods grown on FTO facing up and down by a hydrothermal method. An analysis of the fine structures showed that TiO_2nanorods grown on FTO facing up were mixed with sea urchin and microsphere. These structures induced a vertical orientation of the nanorods on FTO. The saturated photocurrent densities of the TiO_2 nanorods grown both up and down were 1.5 mA/cm^2 in the former case, the IPCE was increased to 10% at 300~350 nm. The onset potential (?flat band potential) of the nanorods grown on FTO facing up is negatively shifted to a value of –0.31 V. This is caused by an increase in the surface state, in this case the number of oxygen vacancies, and by the formation of Ti^{3+}. Therefore, the FTO facing direction is considered as a critical factor during the hydrothermal reaction for TiO_2 growth so as to develop an efficient photo-catalytic system.

Key words : Titanium dioxide(TiO_2) nanorod, Hydrothermal method, FTO facing, Photo-activity

1. Introduction

As the energy exhaustion problems caused by industry development based on fossil fuels as a consumable energy source and the environmental problems due to byproducts of the fossil fuels are highlighted, continuous large-scale governmental support is being realized for development of eco-friendly renewable energy technologies. Solar energy is recognized as the ultimate source for renewable energy allowing eco-friendly and continuous development, and interests in key material technologies for the solar energy system have been increased as the importance of studies on development of high-efficiency energy systems using solar energy has emerged domestically and overseas. Electromagnetic radiation energy emitted from the sun is absorbed by semiconductors having a smaller band gap than that of the incident radiation energy to generate active charge carriers(electron and hole) inside the semiconductor, enabling power generation by using this phenomenon or energy production through chemical reaction(representatively hydrogen production reaction through water splitting).[1-2] Particularly, development of a solar energy system based on titanium dioxide(TiO_2) which is relatively harmless to human body showing high chemical stability and photo activity characteristics is under spotlight, and development of the high-efficiency solar energy systems has been facilitated through analytical studies of photoelectrochemical characteristics at photocatalyst/electrolyte interfaces by production of 1-dimensional nano-structured TiO_2 nanorod (NR) electrodes which have wide active surfaces and easy transfer of charge carriers in comparison with the bulk as the nano processing technology is developed. Studies are being reported on the solar energy systems using TiO_2 nanorod produced by hydrothermal process on the fluorine doped tin dioxide (FTO, F:SnO_2) electrode with high work function(high electron capture characteristics), low sheet resistance and high-temperature stability among transparent electrodes. Advantages of the hydrothermal process include control of product's microstructure characteristics through composition changes of solution, ease of crystal production at relatively low temperatures(< 250°C) and low unit costs of processing.[3] While most reports are concerned with production of TiO_2 nanorod electrodes by obliquely fixing the FTO electrode face so as to face down toward the bottom of reaction vessel among the study reports on production of TiO_2 nanorod using such hydrothermal process, there are almost no study reports on differences in microstructures and photocatalyst characteristics as a function of coordination orientations for the FTO electrode face which correspond to the reason for facing toward the bottom. Thus, in the present article, microstructures and photocatalyst characteristics of the grown TiO_2 nanorods upon production of 1-dimensional TiO_2 nanorod electrodes using hydrothermal process were compared between the case where the orientation of the FTO electrode face was facing down toward the bottom in teflon synthesis vessel of the autoclave and when it was placed to be facing up toward the vessel cover. According to the analysis results of microstructures, TiO_2 nanorods and TiO_2 sea urchin, microspheres

†Corresponding author : Bee Lyong Yang
E-mail : blyang@kumoh.ac.kr
Tel : +82-54-478-7741 Fax : +82-54-478-7769

were mixed when the FTO electrode face was facing up toward the vessel cover, and the onset potential(≒ flat band potential) was negatively shifted to -0.31 V compared with the electrode produced with the FTO electrode face facing down toward the bottom of teflon vessel according to the measurement results of photocurrent density. However, recombination rates of the photo-produced charge carriers were reduced by 7 seconds, reducing the life of charge carriers.

2. Experimental Procedure

2.1. Production of TiO_2 nanorods/FTO electrodes

2 × 2 cm FTO (TEC7, Jindol tech co. ltd) transparent electrodes were cleaned ultrasonically for 5 minutes in trichloroethylene (DC Chemical, 99.5%) - acetone (OCI Company Ltd, 99.5%) - methanol (OCI Company Ltd, 99.6%), followed by drying on a hot plate at 80°C for 10 minutes. For a hydrothermal solution for TiO_2 nanorod, 60 ml of the mixed solution of deionized water and hydrochloric acid (Duksan, 35 %) in a volume ratio of 1:1 was mixed with 1.0 mL of titanium(IV) n-butoxide (Sigma Aldrich) and agitated for 5 minutes. After arranging the FTO electrode faces to be facing toward the bottom and the cover of teflon vessel, respectively, the vessel was filled with the agitated synthesis solution for growth of TiO_2 nanorods at 150°C for 6 h. After 6 h, the vessel was cooled to room temperature using water, and then the electrode was removed from the autoclave with the synthesis solution left on the electrode surface being removed by using deionized water and subsequently dried at room temperature for 15 minutes, followed by annealing at 450°C for 4 h in air atmosphere.

2.2. Analysis procedure

Microstructure changes in TiO_2 nanorods as a function of FTO electrode orientations were analyzed using FE-SEM (JSM / 6500F) and XRD (Rigaku / SWXD) while photocurrent densities were measured in the three-electrode system consisting of 0.1 M $Na_2S \cdot 9H_2O$ (Sigma Aldrich, ≥ 99.99 %), water-soluble electrolyte (pH = 12.4), Nafion (Dufont / NR211), Platinum(Pt) mesh (AT Frontier), Ag/AgCl reference electrode (AT Frontier) and TiO_2 nanorod electrode by using Potentiostat (AT Frontier / VERSASTAT3). In the Cyclic voltammetry (single) mode, photocurrent densities(mA/cm^2) were measured under irradiation of 100 mW/cm^2 of white light using 1 kW xenon lamp (Newport) and Silicon photo-detector (Newport). Photocurrent densities(mA/cm^2) at wavelengths of 300 ~ 700 nm were measured with application of constant voltage at 0.5 V in the Chronoamperometry mode using Monochromator (Newport / 74000), and Incident Photon to Current Efficiency (IPCE) was calculated. For the measurement of recombination times for electron and hole, chopping was conducted (measurement method with light source being turned on, off) under the condition where a constant voltage of 0.5 V was applied in the Chronoamperometry mode.

3. Results and Discussion

FE-SEM images of surface and cross section of TiO_2 nanorods grown on FTO electrodes arranged so as to face toward the bottom and the cover of reaction vessel are shown in Figs. 1(a), (b) and (c), (d), respectively. The nanorods grown on FTO facing toward the bottom had an average diameter of 150 nm and an average length of 2.4 μm, while the nanorods grown on FTO facing toward the cover had an average diameter of 250 nm and an average length of 3 μm, and TiO_2 in the form of sea urchin, microsphere is mixed with TiO_2 nanorods in Fig. 1(c). When FTO was facing toward the cover, flow rates on the substrate surface were slow and pressures high to facilitate the chemical reaction of Ti precursors making the longitudinal growth rate to be about 1.3 times as fast, and sea urchin and microsphere grown by nuclei formed in the solution are considered to have been transferred to the surfaces of TiO_2 nanorods by thermal convection of the solution. In the x-ray diffraction patterns of two electrodes, rutile-TiO_2 (space group: P42/mnm, a = b = 4.593 Å, c = 2.961 Å) peaks[4] for crystal planes of (101) at 45° and (002) perpendicular to the longitudinal growth orientation of nanorods were measured.(See Fig. 2) The peak intensity from (002) diffraction plane measured at 2θ of 62.8° was affirmed to be increased when grown on FTO facing toward the cover. Such increase in the peak intensity was presumably caused by much diffraction from (002) crystal plane as TiO_2 microspheres were formed between nanorods and arranged in the orientation perpendicular to FTO in the array of nanorods grown obliquely on FTO with high surface roughness (See Figs. 1(b) and (d)). The measurement results of photocurrent densities for two electrodes are shown in Fig. 3. Saturated photocurrent densities of the two electrodes were identical at 1.5 mA/cm^2, and the onset potential (≒ flat band potential) of the electrode grown on the FTO facing toward the cover was

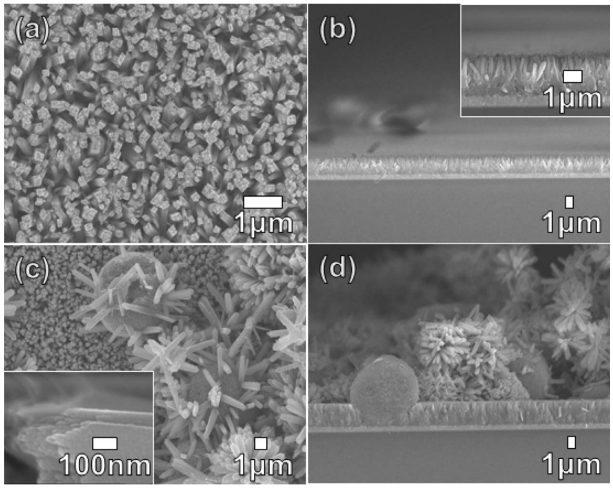

Fig. 1. FE-SEM images of the TiO_2 nanorods are grown on the FTO (a), (b) facing down and (c), (d) up by hydrothermal method, respectively.

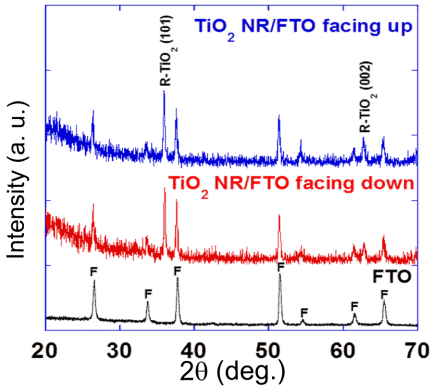

Fig. 2. X-ray diffraction patterns of the TiO_2 nanorods are grown on the FTO facing up and down, respectively.

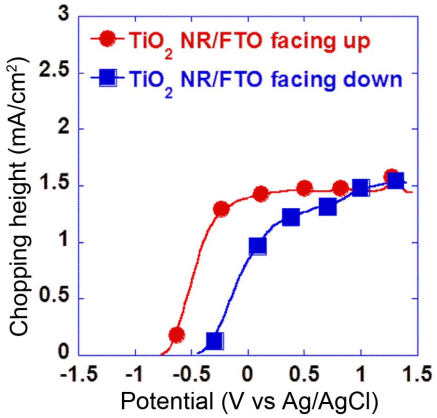

Fig. 3. Chopping height (on-off) versus applied potential plot of TiO_2 nanorods are grown by hydrothermal synthesis measured under the white light illuminations (100 mW/cm^2) in 0.1 M Na_2S (pH = 12.4) electrolyte.

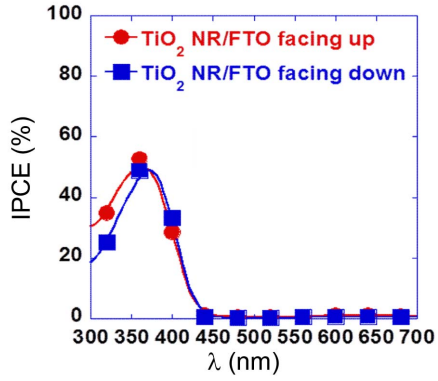

Fig. 4. Incident photon to current efficiency (IPCE) of TiO_2 nanorods are grown by hydrothermal synthesis measured under the white light illuminations (100 mW/cm^2) in 0.1 M Na_2S (pH = 12.4) electrolyte at 0.5 V.

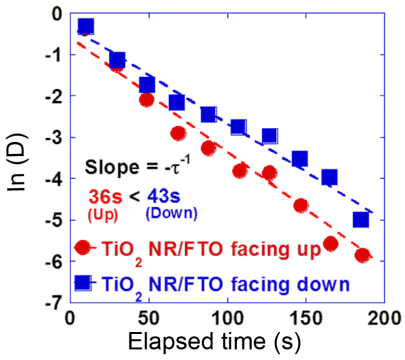

Fig. 5. Normalized photocurrent density-time dependence plot of TiO_2 nanorods are grown by hydrothermal synthesis measured under the white light illuminations (100 mW/cm^2) in 0.1 M Na_2S (pH = 12.4) electrolyte at 0.5 V.

negatively shifted to -0.31 V. Such shift phenomenon is presumed to be the result of a difference in growth rates of TiO_2 nanorods or increased oxygen vacancies due to generation of TiO_2 in the form of sea urchin and microsphere, an increase in surface states of Ti^{3+}. By substitution of the photocurrent density measured under monochromatic irradiation of 300~700 nm in the following equation(1), IPCE(%) was calculated.(See Fig. 4) (I: intensity of light, J: photocurrent density, λ: wavelength of incident light).[5]

$$IPCE(\%) = \frac{1240 \times J(mA/cm^2)}{I(mW/cm^2) \times \lambda(nm)} \quad (1)$$

The IPCE of TiO_2 nanorods electrode grown on FTO facing toward the cover at 300~350 nm was higher by 10%, and such result is presumably attributable to a difference in light absorption characteristics due to scattering effect of the incident light caused by sea urchin on the surface. At 0.5 V, photocurrent densities were measured as a function of time by the chopping method and substituted in the following equation (2) for calculation of time taken for recombination (transient time)(See Fig. 5). (t: time, τ: recombination time, I: photocurrent density at i(0 sec), f(t sec)).[6]

$$D = \exp\left(-\frac{t}{\tau}\right) \quad (2)$$

The D(defining parameter for photocurrent relaxation) in the equation (2) is defined as shown in the following equation(3).

$$D = \frac{I(t) - I(f)}{I(i) - I(f)} \quad (3)$$

In the equation (2), the recombination reactions were affirmed to occur after 36 seconds in the nanorods electrode grown on FTO facing toward the cover, and after 43 seconds in the nanorods electrode grown on FTO facing toward the vessel bottom. Through the above analysis, it was ascertained that the life of electrons and holes optically stimulated due to an increase in oxygen vacancies and Ti^{3+} defect densities was reduced by 7 seconds, whereas the photo activity at TiO_2 interfaces was increased by TiO_2 sea urchin and microsphere when the orientation of FTO crystal plane was facing up toward the cover rather than down toward the vessel bottom upon direct growth of TiO_2 nanorods on

FTO electrode by a hydrothermal method.

4. Conclusions

In the present article, differences in microstructures and in photocurrent characteristics were compared as a function of the orientations of FTO electrode face when TiO_2 nanorods/FTO electrodes were produced by a hydrothermal method. In the microstructure analysis, when FTO was facing up toward the vessel cover, TiO_2 nanorods and TiO_2 sea urchin, microsphere were mixed while it was affirmed through diffraction measurement that the nanorods had crystal growth perpendicular to FTO. According to the photocurrent measurements, the saturated photocurrent density for two electrodes was 1.5 mA/cm^2,and the onset potential was affirmed to be negatively shifted to -0.31 V due to the change in surface states of TiO_2 grown as a function of FTO orientation conversion. Consequently, differences in the microstructures and the photocurrent characteristics as a function of substrate orientation may also be presumed to be shown in production of the photocatalyst electrodes of other (transition) metal oxides using the hydrothermal method.

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