Influence of TiO$_2$’s (101) crystal facet exposure on the photoelectroactivity of TiO$_2$ nanooctahedra/BiVO$_4$ nanocomposite

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Abstract. This work studies a research regarding the effect of exposing (101) crystal facet of anatase TiO$_2$ to photoelectroactivity of photoanode composed of TiO$_2$ nanooctahedra/BiVO$_4$ nanocomposite film. Here, the photoanode was fabricated by depositing the nanocomposite on the surface of FTO via doctor blade technique. In this study, anatase TiO$_2$ nanooctahedra were synthesized via solvothermal method in the presence of hydrazine hydrate as a directing agent. Furthermore, the as-prepared TiO$_2$ nanooctahedra was characterized using X-Ray Diffractometer (XRD), Transmission Electron Microscopy (TEM), Brunauer-Emmelt-Tellers (BET) and UV-Vis diffuse reflectance spectra (DRS). Based on the result, the diffraction peaks revealed characteristic for the pure anatase phase with exposure (101) crystal facet. Additionally, photoelectrochemical response of the photoanode was also evaluated using a three-electrode system and exhibited a significantly high current density value of 0.26 mA/cm$^2$.

Keywords: Anatase TiO$_2$ nanoctahedra, BiVO$_4$, crystal facet, photoelectrochemical

1. Introduction

Crisis energy issues due to the lack of fossil fuels lead to an idea to substitute petroleum based energy with hydrogen based energy by using water as electron and proton sources. Photoelectrochemical (PEC) devices convert water to oxygen and hydrogen using photon and semiconductor as photoanode. Since the photoanode plays an important role in PEC, visible light responsive, high efficiency, and low cost are crucial to the performance of PEC [1, 2]. One of the promising semiconductors type-n, titanium dioxide (TiO$_2$), is generally applied, owing to its superior photocatalytic activity, environmentally friendly, and low cost [3]. However, TiO$_2$ with wide band gap can only absorb ultraviolet energy, which contains only about 4 % of the solar energy [4]. This phenomenon will decrease the efficiency for PEC usage due to the maximum current will increase in the range of photon absorption. Hence, the new materials with photoactive nature in visible light were developed to shift the energy band gap of TiO$_2$. Bismuth vanadate, (BiVO$_4$) based photoanode is an interesting candidate due to visible-light activity, good stability, and effective charge separation properties. Combining the BiVO$_4$ that has small optical bandgap (2.4 eV) with TiO$_2$ would improve the light absorption in the visible region[5, 6]. Moreover, the formation of TiO$_2$/BiVO$_4$ prolongs the carrier lifetime and then promotes the separation of
photoelectron and holes that exhibit an excellent performance for photocatalytic water splitting and pollutant degradation [7].

Recently, controlled synthesis of TiO$_2$ to form a specific morphology with specific exposed crystal facet has gained much attention. Anatase TiO$_2$ crystal phase is known to have the highest photoactivity among the others phase, rutile and brookite [8]. According to the Wuff construction, the most available facets on the anatase TiO$_2$ crystals is dominated by (101) facets rather than (001) facets due to its less reactivity and thermodynamically more stable [9]. Therefore, (101) facets found naturally for about 90% of the total exposed surface on the anatase TiO$_2$ [10]. In this work, the effect of morphology and exposure (101) crystal facet of anatase TiO$_2$ nanoctahedra on the photoelectrochemical response of TiO$_2$ nanoctahedra/BiVO$_4$ nanocomposite film as photoanode were investigated. Here, anatase TiO$_2$ nanoctahedra were synthesized by a simple solvothermal method with the addition of directing agent into the reaction, followed by loading the as-prepared TiO$_2$ nanoctahedra onto BiVO$_4$ paste and deposition on the FTO via doctor blade technique to obtain the photoanode film.

2. Materials and method

2.1. Materials
Titanium(IV) fluoride (TiF$_4$, Sigma-Aldrich), hydrazine hydrate (N$_2$H$_4$.H$_2$O, 60%, Sigma-Aldrich) and ethanol (C$_2$H$_5$OH, Merck) were used to synthesize the anatase TiO$_2$ nanoctahedra. Bismuth(III) nitrate pentahydrate (Bi(NO$_3$)$_3$.5H$_2$O, Wako Ltd.), ammonium vanadate (NH$_4$VO$_3$, Sigma-Aldrich), polyethylene glycol (PEG, MW 20000, Sigma-Aldrich), and Triton-X (Tokyo Chemical Industry Ltd.) were used to synthesize the photoanode film.

2.2. Synthesis of TiO$_2$ nanoctahedra
Anatase TiO$_2$ nanoctahedra were synthesized through a solvothermal method as previously reported [8]. For the typical synthesis, 2 mmol TiF$_4$ was added to 5 mL distilled water forming a clear solution. Then, 35 mL of hydrazine hydrate was added to the solution with magnetic stirring. The solution mixture was transferred into a Teflon lined autoclave and heated at 200 °C for 24 h. After the reaction, the products were separated by centrifuge and rinsed with distilled water and ethanol for several times. Finally, the products were dried in an oven at 70 °C for 6 h and calcined at 450 °C for 2 h.

2.3. Fabrication of TiO$_2$ nanoctahedra/BiVO$_4$ nanocomposite
The photoanode was prepared via doctor blade technique according to the previous literature [11]. Bi(NO$_3$)$_3$.5H$_2$O (2 mmol), NH$_4$VO$_3$ (2 mmol) were mixed with 2 mL of 13 M HNO$_3$ and grinded in an agate mortar followed by the addition of as-prepared TiO$_2$ nanoctahedra (1 mmol). Then, polyethylene glycol (0.2 mmol) was added gradually to the above mixed solution. After the solid was dissolved, one drop of Triton-X was added and grinded to form yellow-brownish paste. The resulting paste was coated on FTO and calcined at 450 °C for 3 h.

2.4. Characterizations
In order to determine the crystallinity of the as-prepared TiO2, the X-Ray diffraction (XRD) analysis was employed by using PANanalytical X’Pert Pro MPD with Cu-Kα radiation. To determine the morphology and the particle size, transmission electron microscopy (TEM) was performed on a TECNAI G2 Spirit Twin High-Resolution. To investigate the porosity and surface area, Brunauer-Emmett-Teller (BET) surface area, Barret-Joyner-Halenda (BJH) pore volume and BET N2 adsorption-desorption isotherm were recorded on a QUADRASOB evo (Quanatchrome Instruments). To determine the optical properties, diffuse reflectance spectroscopy (DRS) was carried out using Shimadzu UV-2450 spectrophotometer and the band gap (Eg) was calculated using Kubelka-Munk method.
2.5. Photoelectrochemical measurements

The photoelectrochemical response of the photoanode film was carried out with a three-electrode system by using Hokuto Dento Hz-3000 Potentiostat. TiO₂ nanooctahedra/BiVO₄ nanocomposite (0.9 cm × 0.9 cm) film was used as working electrode, Ag/AgCl (3 M NaCl) as reference electrode, and coiled Pt as counter electrode. An 500 W Xenon lamp was used as the visible light source with an intensity 160 mW/cm² measured by TENMARS TM-208 solar light meter and Na₂SO₄ 0.5 M (pH 7) was added into the phosphate buffer 0.1 M as the electrolyte solution [12].

3. Results and discussion

3.1. Fabrication and characterization of anatase TiO₂ nanooctahedra

The crystalline structure of the as-prepared TiO₂ was analyzed by XRD as shown in figure 1a. According to the XRD patterns, the as-prepared TiO₂ was believed to show the anatase crystalline phase, which corresponds to the reference (JCPDS Card No. 21-1272) [13]. Furthermore, the morphology of the as-prepared TiO₂ nanooctahedra was observed by TEM analysis. From the TEM image in Figure 1b, the as-prepared TiO₂ with addition of hydrazine hydrate as directing agent was found to be an octahedral shape structure with edge width in the range of 200–300 nm and length between the two-pointed ends in the range of 400–500 nm. In addition, to investigate the exposure of the (101) crystal facet, Fast Fourier Transform (FFT) analysis of the TEM images is shown in the inset in figure 1b. As shown, the result confirms that the as-prepared TiO₂ nanooctahedra did expose more (101) crystal facet.

3.2. Surface and optical properties of anatase TiO₂ nanooctahedra

The BET isotherms graphs in figure 2a shows a typical type (III) like with type (IV) hysteresis loops that presence at high pressure [14]. Furthermore, the pore size distribution (PSD) plot was also determined using Barrett-Joyner-Halenda (BJH) method from the desorption of the isotherm (figure 2b). According to the result, the obtained PSD plot exhibited similar features with isotherm plot, having peaks of microporous (< 2 nm) and mesoporous (2–50 nm). Additionally, the result also demonstrated that the average pore volume and BET surface area for the as-prepared TiO₂ nanooctahedra were 0.026 cc/g and 16.133 m²/g, respectively. Furthermore, the optical properties of the samples were also investigated using UV-Vis spectroscopy. As it can be seen in figure 3, the absorbance of TiO₂ nanooctahedra increases in the UV region and displays an absorption edge at 413 nm, which corresponds to a band gap of 3.0 eV.

![Figure 1. (a) XRD pattern, and (b) TEM images of the as-prepared TiO₂ nanooctahedral (inset: FFT pattern).](image-url)
3.3. Photoelectrochemical measurements

In order to gain the information about the film response to the light irradiation, the linear sweep voltammetry (LSV) was carried out both under dark and light exposure conditions. Figure 4a shows the obtained J-V characteristics of the as-prepared TiO$_2$ nano-octahedra/BiVO$_4$ photoanode. According to the result, it is obvious that there is a significant increase in the photocurrent in light irradiation, indicating the film photoactive response. Additionally, result also showed that the film produced about 0.14 mA/cm$^2$ of photocurrent at the thermodynamic water oxidation potential of 1.23 V. Further investigation was also carried out to evaluate the stability of the photoanode film. Here, photocurrent measurements were performed under the applied potential bias (1.4 V$_{RHE}$) and light illumination. According to the result in figure 4b, the photocurrent spikes of TiO$_2$ nano-octahedra/BiVO$_4$ nanocomposite film reached the value of 0.26 mA/cm$^2$. Nevertheless, it is also worth to note that these photocurrents were quickly decreased during the first 200 sec of light exposure before gradually reached the equilibrium. This photocurrent was found to be significantly higher than the value of bare BiVO$_4$ photoanode film, 0.5 $\mu$A/cm$^2$, under illumination of simulated sunlight (AM 1.5, 100 mW/cm$^2$) and
Figure 4. (a) J-V plot under dark and light irradiation, and (b) J-t plot of the as-prepared TiO$_2$ nanooctahedra/BiVO$_4$ nanocomposite photoanode.

active area of photoanode 2 cm × 2 cm without applied bias [11]. It is believed that the high-energy electrons of BiVO$_4$ that excited by the light would be energetically transferred to TiO$_2$ and enhanced the lifetimes and separation of visible-excited charge carriers of BiVO$_4$[7].

4. Conclusion
In summary, anatase TiO$_2$ nanooctahedra have been successfully synthesized via solvothermal method with the addition of hydrazine hydrate as a directing agent. This conclusion is confirmed by the evidence that the diffraction peaks of TiO$_2$ powder particles are corresponded to the characteristic peak of pure anatase phase and the morphology of the anatase TiO$_2$, found to be an octahedral shape, which preferentially exposed (101) facets. The TiO$_2$ nanooctahedra/BiVO$_4$ nanocomposite film has the potential to become a promising photoanode on PEC for water splitting and pollutant degradation due to its photoactive response and effective charge separation.

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