Vertically aligned hexagonal WO₃ nanotree electrode for photoelectrochemical water oxidation

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Key words: hexagonal WO₃, photocatalysis, nanotree, visible light, oxygen evolution.

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Abstract

Thin films of aligned hexagonal WO_3 nanotrees were fabricated on metal tungsten substrates by hydrothermal treatment. In the presence of a sacrificial reduction agent, the fabricated WO_3 nanotree films oxidized water to evolve oxygen under visible-light irradiation. The photocatalytic water oxidation activity of the WO_3 nanotree was higher than that of a dense monoclinic WO_3 electrode, and had a quantum efficiency of 3.2% under visible-light irradiation. With the application of an anodic bias potential, the WO_3 nanotree electrode produced both hydrogen and oxygen in the absence of a sacrificial agent under visible-light irradiation.

Graphical Abstract

1. Introduction

Photocatalytic solar water splitting is a promising approach for renewable fuel production. The water splitting reaction involves the reduction of protons into hydrogen and the oxidation of water to molecular oxygen. Thus, an efficient photocatalyst should simultaneously drive reduction and oxidation reactions by photoexcited electrons and holes, respectively. In particular, the subtraction of electrons from water molecules to evolve oxygen is an important process for developing artificial photosynthesis systems that mimic natural plants.[1] Although the thermodynamic potential to generate oxygen by water oxidation is +1.23 V versus the standard hydrogen electrode, it is difficult to initiate this reaction due to the high over-potential resulting from the four electron and deprotonation reactions.

One approach to overcome the high over-potential for the water splitting reaction is the use of metal oxides, such as TiO_2 [2] and SrTiO_3 [3], because they have deep valence bands, consisting of an oxygen 2p orbital with strong oxidative power. However, because these metal oxides typically have a wide bandgap, they cannot be activated by visible light. Among metal oxides, visible-light-responsive pristine photocatalysts that are potentially

suitable for water oxidation are limited as those with a deep valence band, such as tungsten trioxide (WO_3) [4-9] and bismuth vanadate (BiVO_4). [10-13] Although numerous studies have examined the photocatalytic properties of WO_3 , this metal oxide can adopt one of several polymorphic crystalline forms, including monoclinic, triclinic, and hexagonal structures. [14-17] Most studies to date have investigated the visible-light sensitivity of the more stable monoclinic [6, 8, 18, 19] and triclinic [20, 21] phases of WO_3 , and the characterization of hexagonal WO_3 has been limited to material synthesized under non-equilibrium conditions, such as high-pressure hydrothermal reactions in the presence of alkaline earth elements. [22-24] Hexagonal WO_3 , has potential applications in super-capacitors, [25] electrochromic devices, [26, 27] sensors, [28, 29] and lithium ion batteries. [30] In addition, hexagonal WO_3 is reported to have photocatalytic water oxidation activity; [11, 31] however, quantitative performance data based on the number of generated oxygen molecules, such as quantum efficiency, have not yet been determined. Further, most previous reports on hexagonal WO_3 have investigated the properties of dispersed powder or particulate forms, which are disadvantageous for industrial process, as the collection of powder and the separation of evolved hydrogen and oxygen gasses are technically complex. In contrast to the powdered or particulate forms of metal oxide

photocatalysts, a thin-film electrode structure permits the application of a bias potential and allows for evolved oxygen and hydrogen to be easily separated using a membrane. Recently, the facile synthesis of hexagonal WO_3 nanotrees aligned on a metal tungsten substrate has been reported. [32] Notably, this configuration exhibited super-hydrophilic conversion under visible-light irradiation and was shown to be suitable for self-cleaning applications.[32]

Herein, we report that a hexagonal WO_3 nanotree film-based electrode functions as a water oxidation photocatalyst under visible-light irradiation. The WO_3 nanotree electrode was fabricated by attaching copper wire to the backside on a metal tungsten substrate of a WO_3 nanotree film synthesized by a facile hydrothermal method. Photo-electrochemical analyses of the fabricated electrode were conducted to examine the charge transport and trapping processes in the WO_3 nanotree structured crystals. We also examined the effect of sacrificial agents in the aqueous electrolyte solution on the photocatalytic water oxidation activity and optimized the experimental conditions to achieve the high quantum efficiency for water oxidation. Consequently, the quantum efficiency of the hexagonal WO_3 nanotree electrode was 3.2% under visible-light irradiation and without the application of bias

potential. Further, we examined the potential of the hexagonal WO_3 nanotree electrode to completely split water into oxygen and hydrogen under an applied anodic bias potential.

2. Experimental section

Three-dimensional hierarchical WO_3 nanotree film was fabricated on a metal tungsten substrate by a facile hydrothermal synthesis. The metal tungsten substrate (0.5-mm thickness) was cut into 4-cm² squares and were then annealed in air at 773 K for 1 h to oxidize the tungsten surface. For hydrothermal treatment, the oxidized tungsten metal plates were placed in an aqueous solution of 0.2 M nitric acid (HNO_3 , 25 ml) containing oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$, 1.56 g) and rubidium sulfate (Rb_2SO_4 , 0.2 g), and heated at 423 K for 30 h in an autoclave. After the hydrothermal reaction, the substrates were gently washed with 1 M HNO_3 solution and pure water, and were then dried at room temperature. The dried samples were annealed in air at 973 K for 1 h to reduce oxygen defects in WO_3 . For comparison, polycrystalline monoclinic WO_3 electrodes were fabricated by annealing metal tungsten plates in air at 973 K for 2 h.

The crystal structures of the WO_3 nanotree films were determined using an X-ray

diffraction meter (XRD; Rigaku SmartLab SPI/TISM). The morphologies of the WO₃ nanotree films were examined using a scanning electron microscope (SEM; model S-4500, Hitachi Co.). UV–Vis spectra of the electrodes were recorded using a spectrophotometer (V-660, Jasco Ltd.) in diffuse reflectance mode.

For photo-electrochemical measurements, a copper wire was attached using silver paste to the reverse side of the tungsten metal substrate. The copper wire and exposed metal substrate on the reverse side of the electrode were covered with an epoxy resin, leaving only the surface of the WO₃ nanotrees exposed. Electrochemical measurements were conducted using a potentiostat (HZ-5000, Hokuto Denko Co.) in an aqueous solution containing 0.5 M Na₂SO₄ as an electrolyte and 0.01 M Fe³⁺ ions as a sacrificial agent for the reduction reaction. The WO₃ nanotree film functioned as the working electrode, and a platinum (Pt) plate and saturated Ag/AgCl were used as the counter and reference electrodes, respectively. The WO₃ nanotree film was illuminated with a light source supplied from a 150-W Xe lamp equipped with a UV cutoff filter, which cutoff below 430 nm wavelength to excite the WO₃ nanotree film. Photocurrent action spectra for the WO₃ nanotree films were recorded using a potentiostat (HSV-110, Hokuto Denko Co.) under a monochromatic light source generated from a 300-W Xe lamp (Bunko Keiki, Ltd.). The

action spectra were measured as function of wavelength from 400 to 700 nm under an applied anodic bias of +0.5 V. Intensities of the monochromatic light source were recorded using a spectro-radiometer (USR-40D, Ushio, Ltd.), and the measured spectra are shown in the Supporting Information (Figure S1).

Photocatalytic oxygen and hydrogen evolution were examined in a glass cell connected to a closed gas-circulating system. For the measurements, a 4-cm² WO₃ nanotree film was placed in 20 mL aqueous solution containing 0.5 M Na₂SO₄ with 0.01 M Fe³⁺ as a sacrificial agent. After purging the electrolyte aqueous solution and headspace with argon gas, the cell was illuminated with light from a 150-W Xe lamp equipped with a 430-nm cutoff filter, similar to the photo-electrochemical experiment. Evolved H₂ and O₂ gasses were detected using an on-line gas chromatograph (GC-8A, Shimadzu Co.) equipped with a 5-Å molecular sieve-packed column and using Ar as the carrier gas. The photocatalytic reaction was also evaluated without the addition of the sacrificial agent and under a bias potential at +1.0 V versus the Pt counter electrode in a glass reactor. Both O₂ and H₂ gasses were measured by on-line gas chromatography, as mentioned above. Quantum efficiency was determined according to the following equation (1) [33-35]:

$$\text{Quantum efficiency} = \frac{(\text{number of reacted electrons})}{\int (\text{photon flux}) \times (\text{absorption coefficient}) \cdot d\lambda} \quad (1)$$

The photon flux and absorption coefficient of the WO₃ nanotree films were measured using a spectro-radiometer (USR-40D, Ushio Co.) and spectrophotometer (V-660, Jasco, Ltd.), respectively. The number of reacted electrons was determined based on the assumption that for water splitting, oxygen evolution involves the four-electron oxidation of water molecules.

3. Results and discussion

Figure 1 shows the XRD pattern for the fabricated WO₃ nanotree film. The diffraction peaks related to the [002] direction were clearly detected for the WO₃ nanotree film, whereas the [200] peak was the strongest in the powder diffractions of hexagonal WO₃ (ICDD, 85-2460).[36] These results indicated that the [001] orientation of the WO₃ thin film was perpendicular to the tungsten substrate. The hexagonal WO₃ structure contains large tunnels that are formed by octahedral sharing (WO₆) in the crystal.[37] As ions are easily exchanged into these tunnels, Rb⁺ ions were intercalated into the hexagonal WO₃

during the present hydrothermal synthesis of the nanotree films. Although our previous X-ray photoelectron spectroscopy (XPS) analysis indicated that Rb^+ ions were intercalated into these tunnels, [32] the atomic percentage of Rb in the hexagonal WO_3 nanotree films fabricated here was only 5 atom%, as the films were gently washed in acid solution and pure water after the hydrothermal reaction.

Figure 2 shows SEM images of the fabricated hexagonal WO_3 nanotree thin film on the tungsten metal substrate. Numerous WO_3 nanotrees, which were composed of “trunks” and “branches,” were uniformly distributed and aligned on the substrate. The diameters of the trunks ranged from approximately 100 to 200 nm, whereas those of branches were approximately several tens of nanometers. The branches were formed along the hexagonal symmetry axis on the sides of the trunks. Our previous transmission electron microscopy analysis revealed that the trunks and branches were single crystals, with the long length of the axes oriented toward the [001] direction,[32] that were consistent with the observed crystal orientation in the present XRD pattern (Figure 1). The hexagonal WO_3 nanotree film had a thickness of several micrometers.

Here, we discuss the mechanism for the formation of the aligned WO_3 nanotree film. Yao and coworkers reported that a rodlike hexagonal WO_3 powder was produced by the

hydrothermal reaction of sodium tungstate (Na_2WO_4) in an aqueous solution of $\text{H}_2\text{C}_2\text{O}_4$, Rb_2SO_4 , and hydrochloric acid (HCl). [24] Although we treated the metal tungsten plate with the same aqueous solution and at the identical temperature, only a small number of aligned WO_3 nanotrees were produced. In the initial stages of the hydrothermal reaction, a dense oxidative layer was formed on the tungsten substrate, but further hydrothermal treatment resulted in the dissolution of this oxidative layer, as well as the nuclei, thereby promoting the growth of the single-crystalline hexagonal WO_3 nanotrees. Notably, the use of HNO_3 , which has highly oxidative properties as compared to HCl , as an acid for the hydrothermal treatment was critical for forming the nanotree structures. In addition, the dense incubation layer of the fabricated WO_3 films acted as a binder between the nanotree arrays and the tungsten substrate, leading to strong adhesion to the substrates. Further, the addition of alkali salts in the hydrothermal solution was required for the formation of the WO_3 nanostructure. Consistent with this finding, Michailovskiet et al. [22] demonstrated that smaller alkali cations promoted the formation of fibrous structures of hexagonal WO_3 with nanometer length, whereas larger cations yielded stacked nanorods that exhibit hierarchical patterns. In addition, Gu et al. [24] synthesized WO_3 nanostructure by adding metal salts in a hydrothermal solution containing either Rb_2SO_4 , which led to nanorod and

nanoplate structures, or K_2SO_4 , which promoted for the formation of ribbon-like structures. In the present hydrothermal conditions, Rb^+ ions played an important role in the one-dimensional growth of the WO_3 nanotrees, as demonstrated by the fact that the treelike structures were only formed in the presence of Rb_2SO_4 .

Figure 3 shows photocurrent action and absorption spectra for the hexagonal WO_3 film. Both the action and absorption spectra revealed that the signals steeply increased at 500 nm, corresponding to the band gap excitation of hexagonal WO_3 . Although broad absorption was observed above 500 nm, no photo-current generation was detected in this region of the action spectrum, indicating that the broad absorption above 500 nm does not contribute to the photochemical water-splitting reaction. According to a previous report, the broad absorption from 500 nm to the infrared region is attributable to trapped electrons forming small polarons.[38] In the presently synthesized WO_3 nanotree, Rb^+ ions remained as an impurity; therefore, trapped electrons were present in the crystal to compensate for the charge imbalance. In photochromic or electrochromic devices, electrons localize at tungsten ions to form W^{5+} species, resulting in coloration from the visible to near-infrared region.[39] The fabricated WO_3 nanotree film appeared blue just after hydrothermal treatment, but turned yellowish-green in color after the washing and annealing treatment in

air. Although trapped electrons can absorb visible light by optical transition or plasmonic excitation, these excited carriers in the WO_3 nanotree do not contribute to the photocatalytic reaction because of their low oxidation or reduction potentials and their strong localization.

Figure 4 shows the current-voltage curves under dark and chopped visible-light irradiation of the WO_3 nanotree film electrode in aqueous electrolyte solution. Anodic photocurrent was observed under visible-light irradiation, indicating that the hexagonal WO_3 nanotree is an n-type semiconductor. The potential threshold of the photocurrent was approximately +0.25 V versus Ag/AgCl, which corresponds to +0.45 V versus the normal hydrogen electrode (NHE). These results indicate that the conduction band of the WO_3 nanotree is more positive than the redox potential required for hydrogen generation; thus, this material cannot generate hydrogen without the application of bias potential. The UV-Vis spectrum results suggest that the bandgap of the WO_3 nanotree structure is approximately 2.5 eV (Figure 3) and indicate that the valence band of the WO_3 nanotree is sufficiently deep to oxidize water. Therefore, the photocurrent generated by the WO_3 nanotree film electrode under anodic bias is attributed to the water oxidation reaction at the surface of the WO_3 nanotrees.

Figure 5 shows the oxygen evolution properties of the WO_3 nanotrees in the presence

and absence of Fe^{3+} as a sacrificial agent. In electrolyte solution without sacrificial agent, the amount of oxygen evolved did not exceed 5 μmol , whereas oxygen molecules were continuously produced and reached approximately 17 μmol in the presence of Fe^{3+} . In addition, the sample color changed to blue in the absence of sacrificial agent after visible-light irradiation (Figure 5, inset), suggesting the formation of trapped electrons in the hexagonal WO_3 crystal and indicative of a photochromic color change. In contrast, when the sacrificial agent was added to the aqueous electrolyte solution, the WO_3 nanotree remained yellowish-green in color. Without the sacrificial agent, photogenerated electrons in the conduction band of WO_3 cannot react with electron acceptor and therefore accumulate at W^{6+} sites to form W^{5+} species, which act as color centers. Because these trapped electrons function as recombination centers and deteriorate the photocatalytic reaction, oxygen evolution was saturated below 5 μmol . In contrast, excited electrons in the conduction band of WO_3 nanotrees reacted with Fe^{3+} ions to form Fe^{2+} ions and were consumed without forming trapped electrons in the crystal structure. Therefore, oxygen molecules were continuously evolved in the presence of the sacrificial agent.

The WO_3 nanotree film has a large surface area and is expected to have higher photocatalytic activity than conventional dense WO_3 electrodes. To confirm this speculation

experimentally, we also prepared a dense polycrystalline monoclinic WO_3 electrode by annealing tungsten substrate at 973 K. SEM image and XRD pattern of the prepared monoclinic WO_3 electrode are shown in the Supporting Information (Figures S2 and S3). Comparison of the photocatalytic water oxidation activity of the WO_3 nanotree film electrode with that of the dense monoclinic WO_3 film revealed that the former exhibited more efficient oxygen production than the latter (Figure S4). Based on the oxygen generation rate determined for the WO_3 nanotree (Figure 5), the quantum efficiency of this material was estimated to be 3.2%. Previous studies also reported the quantum efficiencies of WO_3 photoanode for water oxidation. Theoretical maximum quantum efficiency of WO_3 based photoelectrochemical devices is 6 % for solar-to-hydrogen conversion because the bandgap of WO_3 is 2.8 eV.[40] Experimentally, Liu et al. the maximum solar energy conversion efficiencies were approximately 3.24 % and 2 % at 1.23 V (vs. Ag/AgCl) for a WO_3 photoanode.[41] These studies determined quantum efficiencies by photocurrent generation and did not examined Faradaic efficiency, which should be determined by actual oxygen production rate measured by a gas chromatograph.[42] In our paper, we have estimated our quantum efficiency by actual oxygen evolution rate under visible light with cutoff below 430 nm versus absorbed photon numbers according to the equation (1). Miseki

et al. reported that their apparent quantum efficiency of Cs modified WO₃ reached 9 % under the visible light irradiation with the wavelength of 440 nm.[43] Waller et al also reported the quantum efficiency of single crystal WO₃ nanosheet by the same method with the present paper, and its value was 1.55 %.[44] The quantum efficiency of our hexagonal WO₃ nanotree is comparable to the previously reported efficient WO₃ photoanodes. The hexagonal WO₃ film had a thickness of several micrometers, which is a similar order of magnitude to the depth of visible light penetration and the distance of the space charge layer of WO₃. [45] Therefore, excited charge carriers are likely generated in WO₃ nanotrees from the bottom to the top, and are efficiently separated for chemical reactions at the film surface.

The above-described results indicate that the hexagonal WO₃ nanotree film efficiently oxidizes water molecules to evolve oxygen under visible-light irradiation in the presence of Fe³⁺ as a sacrificial agent, but hydrogen is not generated because of the low conduction band of WO₃. According to the threshold of photocurrent generation shown in Figure 4, the flat band potential of the WO₃ nanotree film is more positive than that needed for hydrogen production; therefore, this material cannot generate hydrogen without the application of a bias potential. We next attempted to split water under visible-light irradiation by applying a

bias potential in the absence of added sacrificial agent in the electrolyte solution. To investigate photocatalytic water splitting, the applied bias potential must be lower than +1.23 V, which is the theoretical potential value for electrolysis (water splitting). Thus, we applied an anodic bias of +1.0 V on the WO₃ nanotree electrode versus a Pt counter electrode, and then measured photocatalytic oxygen and hydrogen production in the absence of a sacrificial agent (Figure 6). Under visible-light irradiation, both oxygen and hydrogen molecules were evolved from the WO₃ nanotree electrode. When the light irradiation was stopped, oxygen and hydrogen production ceased, indicating that the reaction proceeded photocatalytically. Notably, the ratio of evolved hydrogen to oxygen was less than the expected value for complete water splitting.

The assumed band structure of the WO₃ nanotree electrode under a bias potential is schematically illustrated in Figure 7. When a bias potential is applied between the WO₃ nanotree electrode and the Pt counter electrode, the Fermi level of Pt is comparable to the potential required for hydrogen production. Under visible-light irradiation and an anodic bias of +1.0 V, photogenerated holes diffuse to the surface of the WO₃ nanotrees and react with water to produce oxygen, and electrons are transferred to the Pt counter electrode, where they react with protons to produce hydrogen. However, our experimental results

indicate that a portion of the electrons are trapped in WO_3 itself and do not react with protons, as the hydrogen production rate was lower than the expected value for complete water splitting. One possible approach for improving hydrogen production is to increase the potential gap between the anode and cathode to minimize the trapping of electrons. Besides bias potential application, the construction of Z-scheme is very promising, because the potential gap is increased by the photo-voltage of the WO_3 anode as well as photo-cathodes comprised of p-type semiconductors. The combination of a hexagonal WO_3 nanotree photo-anode with a visible-light responsive p-type photo-cathode such as $\text{Cu}_2\text{ZnSnS}_4$ [46] or CaFe_2O_4 [47-49] is currently being examined in our laboratory for hydrogen production and the potential for complete water splitting.

4. Conclusions

This paper represents the first report of photocatalytic water oxidation activity by a hexagonal WO_3 nanotree electrode, which was shown to efficiently oxidize water to produce oxygen under visible-light irradiation in the presence of a sacrificial agent for photo-reduction. The water photo-oxidation activity of the WO_3 nanotrees was higher than

a conventional dense monoclinic WO_3 film and was determined to have a quantum efficiency under visible light of 3.2%. When an anodic bias potential was applied to the hexagonal WO_3 nanotree electrode under visible-light irradiation, hydrogen molecules were also evolved, indicating that the WO_3 nanotree is a good candidate as a photo-anode for constructing Z-scheme systems. In addition, because the WO_3 nanotree electrode was fabricated by the facile hydrothermal treatment of a metal tungsten substrate, it is possible to use this fabrication process for the production of nano-structured thin film electrodes with large surface areas for industrial applications. Thus, the hexagonal WO_3 nanotree structure described here is expected to contribute to the development of artificial photosynthesis systems.

Acknowledgement

This work was supported by a grant from the Advanced Catalytic Transformation Program for Carbon utilization (ACT-C), Japan Science and Technology Agency (JST). We also acknowledge Mr. Greg Newton for the critical reading of the manuscript.

Figure Captions

Figure 1. XRD pattern for the hexagonal WO₃ nanotree film.

Figure 2. SEM images of the hexagonal WO₃ nanotree film on a tungsten substrate. (a) Cross section of the edge of the thin film viewed from a 45° tilt angle, and (b) surface image viewed from a 60° tilt angle.

Figure 3. UV-Vis absorption and action spectra of the WO₃ nanotree film. The action spectrum was recorded under irradiation from a monochromatic light source.

Figure 4. Current-voltage relationship under dark and chopped visible-light irradiation using an Xe lamp with a 430-nm UV cutoff filter.

Figure 5. Oxygen evolution from the hexagonal WO₃ nanotree film under visible-light irradiation in aqueous solution with and without Fe³⁺ as a sacrificial agent. Bias potential was not applied on the film. Inset photos show the color change of the WO₃ nanotree films before and after visible-light irradiation in the absence of a sacrificial agent.

Figure 6. Photocatalytic oxygen and hydrogen evolution from the hexagonal WO₃ nanotree film under an applied anodic bias potential of +1.0 V in the absence of a sacrificial agent.

Figure 7. Schematic band diagram of the WO₃ nanotree electrode under a bias potential.

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