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Fabrication by Fine Particles and Evaluation of WO_3 Photo Semiconductor Electrode

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ABSTRACT

Application of semiconductor particles has been noticed to solve energy problems as photocatalysis for O_2 evolution in water splitting etc. We are trying fabrication of semiconductor electrode by n-WO_3 particle toward O_2 evolution in water splitting. The electrode obtained high photooxidation properties of water as preventing effective recombination between electrons and holes by utilizing fine semiconductor particles. Particularly, application of suspension prepared by ball milling was able to obtain fine n-WO_3 thin film and the remarked semiconductor properties.

Keywords: Semiconductor; Electrode; WO_3; Photocatalysis; Photoelectrochemistry; Water Splitting

1. Introduction

We have noticed that water splitting by the use of a semiconductor electrode or photocatalysis is utilized for alternative energy resources by solar energy. At present, the efficiency is very low in order to absorb only ultraviolet ray for a titanium oxide or other metal oxide etc. as the semiconductors. Therefore, development of photo semiconductor materials is required to absorb broad visible light region toward high efficiency [1-8].

The evaluation has performed photoelectrochemically toward utilization of solar energy [9-14], and we have attempted fabrication a complex semiconductor electrode consisting of n-Si and n-WO_3. The n-Si/WO_3 semiconductor electrode is expected to absorb long wavelength at n-Si and short wavelength at WO_3 in solar lights for water splitting efficiency, which is called for Z-scheme as known to two steps electron transport chain of photosynthesis. At first, we attempted fabrication of highly active n-WO_3 electrode on FTO substrate in this study, and the n-WO_3 properties was evaluated photoelectrochemically.

2. Methodology

2.1. Photoelectrochemical Measurements

The n-WO_3 thin film semiconductor electrode was fabricated by a doctor blade method, and evaluated photoelectrochemically by forming the thin film on FTO substrate. Current-voltage (j-V) measurements of the WO_3 electrode was performed by illuminating it with 100 mW/cm^2, A.M. 1.5 Xe lamp with imposing anodic bias at 50 mV/s, which was constructed with potentiostat, Ag/AgCl reference electrode and Pt counter electrode in 0.1 mol/l Na_2SO_4 electrolyte as shown in **Figure 1**. Action spectra were measured by 300 W Xe lamp filtered out UV ray (UV-33) through a monochromator.

2.2. Fabrication of WO_3/FTO Electrode

WO_3 suspension was prepared with the WO_3 powder (Wako Pure Chemical Industries, Ltd.) at ca. 200 nm particle size, which was obtained by mixing 1 g WO_3 + 0.1 g HNO_3 (60%) + 0.2 g H_2O and a small amount of surfactant (Triton-X 100, MP Biomedicals, Inc.). The WO_3 thin film was formed by applicating the suspension with doctor blade method on FTO substrate, and was calcinated at 450˚C for 30 min in air. Furthermore finer WO_3 powder (Aldrich) was also utilized as ca. 30 - 50 nm particle size.

2.3. Fine WO_3 Powder Preparation by Ball Milling

A ball milling was applied to prepare a finer WO_3 powder with ZrO_2 balls at 3 mm diameter. The finer WO_3 suspension was produced by mixing 6 g WO_3

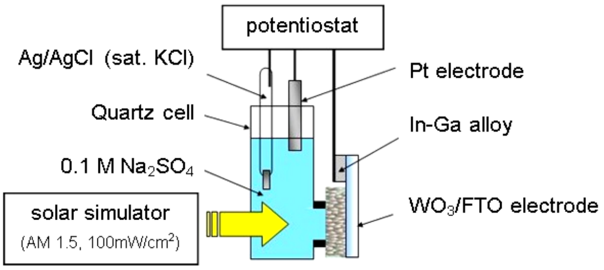

Figure 1. Photoelectrochemical evalutation system to measure n-WO$_3$ semiconductor electrode on the FTO substrate.

powder (Aldrich) + 14 ml H_2O + 70 g ZrO_2 balls in 30 ml bottle at 24 h in the ball milling. The WO_3/FTO electrode was fabricated by applicating the suspension on the FTO substrate at 450˚C for 30 min sintering in air similarly.

3. Results and Discussion

3.1. Photoelectrochemical Properties

The j-V curves were shown about WO_3/FTO electrode under dark, illumination and illumination in adding methanol as a reducing agent in **Figure 2**, which obtained anodic photocurrent, and indicated water photooxidation. The photocurrent in the presence of methanol was about twice and means giving knowledge as following sentences. Photooxidation of methanol was known to two processes for electron transfer at direction and secondary. In the case of the direct process, methanol adsorbed on the WO_3 surface reacts with hole [15,16].

$$\mathrm{CH_3OH}(\mathrm{ads}) + h^+_{(V.B.)} \rightarrow \cdot\mathrm{CH_2OH}\ (\mathrm{ads}) + H^+(\mathrm{aq})$$

The hole makes photooxidaton of methanol proceed preferentially in comparison to that of water. Hence recombination between electrons and holes is prevented efficiently, and the generation of $\cdot CH_2OH$ radical caused injection of electrons to conduction band in WO_3 to indicate enough negative redox potential
$E_0(\cdot CH_2OH/CH_2OH) = -0.97$ V in following equation, and double photocurrent is observed.

$$\cdot\mathrm{CH_2OH}\ (\mathrm{ads}) \rightarrow \mathrm{CH_2O} + \mathrm{H}^+(\mathrm{aq}) + e^-_{(C.B.)}$$

The electron transfer corresponds with the j-V curves in **Figure 2**. In addition, the secondary electron transfer by electrolyte diffused into WO_3 thin film etc. except the photocurrent would not occur not to decrease the photocurrent remarkably in the absence of methanol [15,16]. Consequently, the fabricated WO_3/FTO electrode would show good semiconductor properties for water photooxidation.

Furthermore, WO_3/FTO electrode based on a finer WO_3 powder at 30 - 50 nm diameter (Aldrich) was evaluated as shown in **Figure 3**. The photocurrent increased

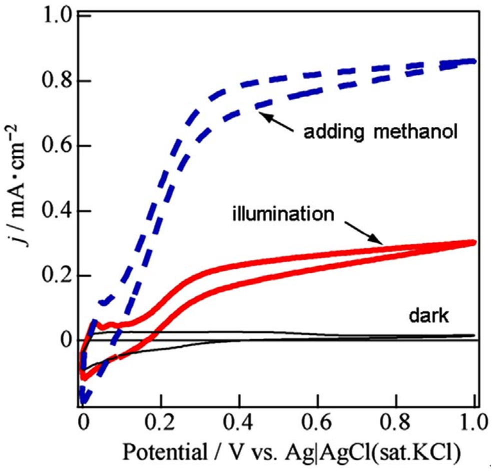

Figure 2. Current-voltage curves about WO$_3$/FTO electrode under dark (black line), illumination (red line) and the illumination in adding a small amount of methanol (dashed blue line) in 0.1 mol/l Na$_2$SO$_4$.

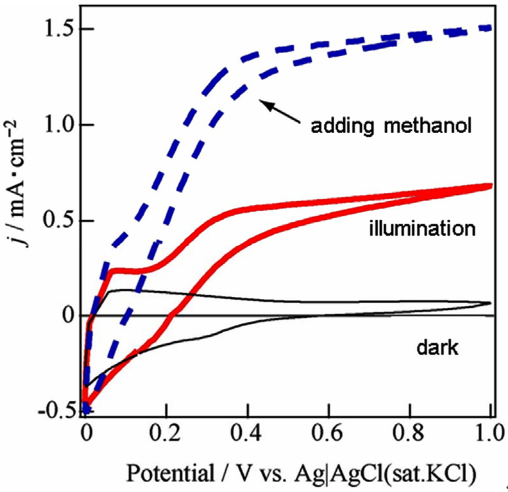

Figure 3. Current-voltage curves about WO$_3$/FTO electrode based on fine WO$_3$ powder under dark (black line), illumination (red line) and the illumination in adding a small amount of methanol (dashed blue line) in 0.1 mol/l Na$_2$SO$_4$.

as compared with that of the WO_3/FTO electrode based on the previous WO_3 powder, which would suggest that carrier transfer was faster to be deposited with high density and homogeneous. Hence, the finer powder will be required to obtain the excellent semiconductor properties.

3.2. Application of Ball Milling

We attempted fabrication of excellent WO_3/FTO electrode by a ball milling to prepare most homogeneous WO_3 suspension from the WO_3 powder at 30 - 50 nm diameter (Aldrich) without the surfactant. The suspendsion was markedly homogeneous without separation or precipitation. The j-V curves of the WO_3/FTO electrode indicated increase of photocurrent in the presence of methanol particularly in **Figure 4**. The results will suggest that the fabrication method by utilizing the ball milling process of WO_3 powder is very effective for the excellent semiconductor properties. Absorbance of the WO_3 thin film indicated a large absorption at short wavelength within ca. 440 nm as shown in **Figure 5**, and corresponded to band gap at 2.8 eV. Moreover, an action spectrum in **Figure 6** also accorded with the absorption spectrum, and the results would indicate that the ball milling method was one of valid fabrication methods to prepare the thin film for ideal photo semiconductor properties.

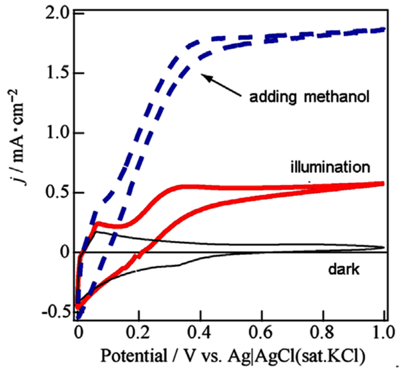

Figure 4. Current-voltage curves about WO_3/FTO electrode based on WO_3 suspension prepared by ball milling under dark (black line), illumination (red line) and the illumine-tion in adding a small amount of methanol (dashed blue line) in 0.1 mol/l Na_2SO_4.

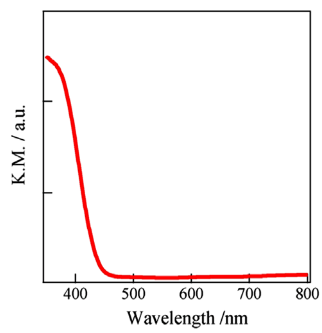

Figure 5. Absorption spectrum of WO_3 thin film fabricated by utilizing ball milling on Kubelka-Munk analysis.

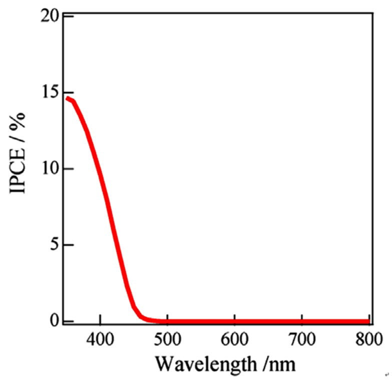

Figure 6. Action spectrum of WO_3/FTO electrode fabric-cated by utilizing ball milling in 0.1 mol/l Na_2SO_4.

4. Conclusion

Application of the fine WO_3 particle improved photo-electrochemical properties, which was more effective by ball milling process for WO_3/FTO electrode. These results suggested that the recombination between electrons and holes was prevented and anodic current was improved in the presence of methanol, and would expect for water photo splitting.

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