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# Photo-electrochemical properties of amorphous $WO_3$ supported on $TiO_2$ hybrid catalysts

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In this work, we have carried out ivestigations on photo-electrochemical energy conversion and storage on $WO_3/TiO_2$ hybrid materials. The band gap excitation of the hybrid $WO_3/TiO_2$ having an amorphous $WO_3$ phase led to an effective photo-charging to form a tungsten bronze structure by the intercalation of protons while a reversible discharging through de-intercalation could also be observed.

**KEY WORDS:** photo-charging; discharging; $WO_3/TiO_2$; amorphous $WO_3$.

## Introduction

The photo-electrochemical conversion and storage of solar (photo) energy using semiconductors have attracted considerable interest over the last decades. Tungsten trioxide ($WO_3$) is especially interesting as a photo-anode and electro- or photo-chromic material [1–6]. On the other hand, the bicomponent $WO_3/TiO_2$ has been found to exhibit higher photocatalytic reactivity for the decomposition of organic compounds than either $TiO_2$ or $WO_3$ itself [7]. Moreover, the $WO_3/TiO_2$ system, with its energy storage ability, could also be applied for anticorrosion or bactericidal effects [8–10]. The photo-induced charge separation on $WO_3/TiO_2$ to produce a hole and an electron initiates the oxidation and slow reduction of the substrates even under dark conditions, respectively. Our aim is to design such photo-functional devices as photo-chargeable batteries using a hybrid $WO_3/TiO_2$ that can operate as an effective UV-light driven photo-anode for charge separation as well as charge accumulation. Here, we report on the effects of the crystallinity of $WO_3$, i.e., polycrystalline or amorphous, on its photo-charging and discharging abilities using hybrid $WO_3/TiO_2$ materials.

## Experimental

A polycrystalline $WO_3$ (referred to as c-$WO_3$) and an amorphous $WO_3$ (a-$WO_3$) were prepared by the thermal decomposition of ammonium tungstate at 873 K for 6 h and tungstic acid ($H_2WO_4$) at 573 K for 1 h, respectively. An a-$WO_3/TiO_2$ and c-$WO_3/TiO_2$ with 20 wt% $WO_3$ were prepared by the impregnation of ammonium tungstate into $TiO_2$ (anatase structure, Kanto Chemicals), and by a physical mixing of c-$WO_3$ with $TiO_2$, respectively. Each sample was spread over a conductive indium tin oxide glass (ITO, 10 $\Omega$) with triethyleneglycol as the binder, and was then calcinated in air at 773 K for 15 min. The powder X-ray diffraction (XRD) patterns of all the samples were obtained with a RIGAKU RINT2000 using Cu $K_\alpha$ radiation ($\lambda = 1.5417$ Å).

The charge–discharge characteristics of these materials were measured by a potentiostat (HA-501, HOKUTO DENKO) used as a potentiometer. A black light (UV-light: 365 nm, 0.50 mW/cm$^2$) was used as the light source for the photo-charging. In the charge–discharge cycle tests, all of the electrodes were discharged at a constant current density of 10 $\mu$A/cm$^2$ between the photo-electrode (working electrode) and Pt wire (counter electrode). The electrolyte was adjusted to 0.5 M $(COOH)_2$ and 0.1 M $LiClO_4$ in $CH_3OH$ solution. The electrolyte was bubbled with $N_2$ gas for 30 min under vigorous stirring.

## Results and discussion

The characteristics of the charge–discharge properties for the photo-electrodes of $TiO_2$, c-$WO_3$, a-$WO_3$, c-$WO_3/TiO_2$ and a-$WO_3/TiO_2$ are shown in figure 1. The photo-irradiated $TiO_2$ exhibits a negative shift to −0.12 V and subsequent remarkable self-discharging takes place under dark conditions. When a-$WO_3/TiO_2$ was illuminated, it exhibited blue coloration, its potential shifting negatively to 0 V. Even after UV-light was turned off, the potential could be retained for a while. Subsequently, discharging at 10 $\mu$A/cm$^2$ of the photo-charged a-$WO_3/TiO_2$ led to a typical Faradic discharging process and its color turned white. On the other hand, c-$WO_3/TiO_2$ exhibited less efficient blue coloration but could retain its blue color even after discharging

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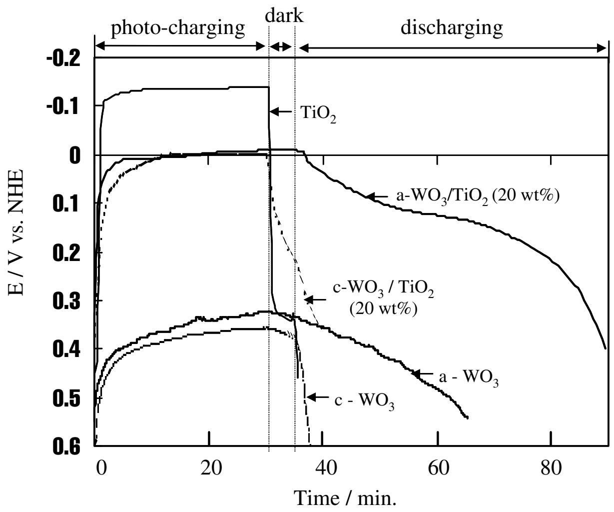

Figure 1. Changes in potential by the photo-charge and discharge on $TiO_2$; c-$WO_3$; a-$WO_3$; c-$WO_3/TiO_2$; and a-$WO_3/TiO_2$.

under the same conditions. The potential of c-$WO_3$ or a-$WO_3$ by itself was observed to shift to around +0.35 V under UV-irradiation, accompanied by photo-induced reactions for $(COOH)_2$ to produce $CO_2$. It was found that a-$WO_3$ exhibited larger discharging capacity than c-$WO_3$, indicating that the former has more surface trapping sites to form tungsten bronze than the latter. The photo-charging potential, discharging capacity and the efficiency of W utilization for the photo-electrodes are summarized in table 1. The accumulated charge on the photo-induced a-$WO_3/TiO_2$ for 2 h was about 22.7 C/g, indicating that 18.4% $WO_3$ was converted to tungsten bronze. The efficiency of W utilization ($\eta_W$) was estimated to be in the following order: a-$WO_3/TiO_2$ $\gg$ a-$WO_3$ > c-$WO_3/TiO_2$ $\gg$ c-$WO_3$.

XRD analysis showed that the $WO_3$ included in a-$WO_3/TiO_2$ had an amorphous structure while that in c-$WO_3/TiO_2$ had a monoclinic polycrystalline structure, as shown in figure 2. On a-$WO_3/TiO_2$, the diffraction peaks of the amorphous $WO_3$ changed to those of a tungsten bronze ($H_{0.23}WO_3$) structure after UV irradiation for 2 h. Moreover, the structure could be reversibly recovered to that of the original amorphous $WO_3$ after discharging until reaching the original potential. On the other hand, although the photo-charged polycrystalline $WO_3$on c-$WO_3/TiO_2$ exhibited diffraction peaks of tungsten bronze, these peaks could not be recovered to the original peaks of $WO_3$ even after discharging under the same conditions. It should be noted that $Li^+$ ions could not be detected in the photo-charged samples by analysis with atomic absorption spectroscopy. These results clearly show that the photo-induced tungsten bronze, through the intercalation of protons of an amorphous $WO_3$ phase, could exhibit de-intercalation much more effectively than through intercalation with protons of a polycrystalline $WO_3$ phase. In this work, we have found that a-$WO_3/TiO_2$ is superior to c-$WO_3/TiO_2$ as well as to c-$WO_3$ and a-$WO_3$ in terms of such properties as: (i) photo-charging accumulation; (ii) more negative potential shift; and (iii) reversible charge-discharging abilities.

The system of photo-induced charge separation and charge accumulation for a-$WO_3/TiO_2$ is shown in figure 3. UV-light is harvested by $TiO_2$ and/or a-$WO_3$ to

Table 1

Photo-charging potential, discharging capacity and efficiency of tungsten utilization on the photo-electrode

| Photo-electrode | Photo-charging potential/V | Discharging capacity[a]/ C/g | Efficiency of W utilization/$\eta_W$[c] |
|---|---|---|---|
| $TiO_2$ | −0.12 | 0.03 | – |
| a-$WO_3$ | +0.32 | 10.8 | 0.017 |
| c-$WO_3$ | +0.35 | 0.3 | 0.00047 |
| a-$WO_3/TiO_2$ | −0.01 | 16.5 | 0.13 |
| a-$WO_3/TiO_2$ | −0.01 | 20.7 [b] | 0.18 |
| c-$WO_3/TiO_2$ | 0.00 | 1.3 | 0.010 |

[a] The discharging capacity accumulated until the potential reached its original value at 10 $\mu A/cm^2$ after photo-irradiation for 30 min.

[b] The photo-irradiation was performed for 2 h.

[c] $\eta_W$ = number of accumulated electrons/number of W atoms.

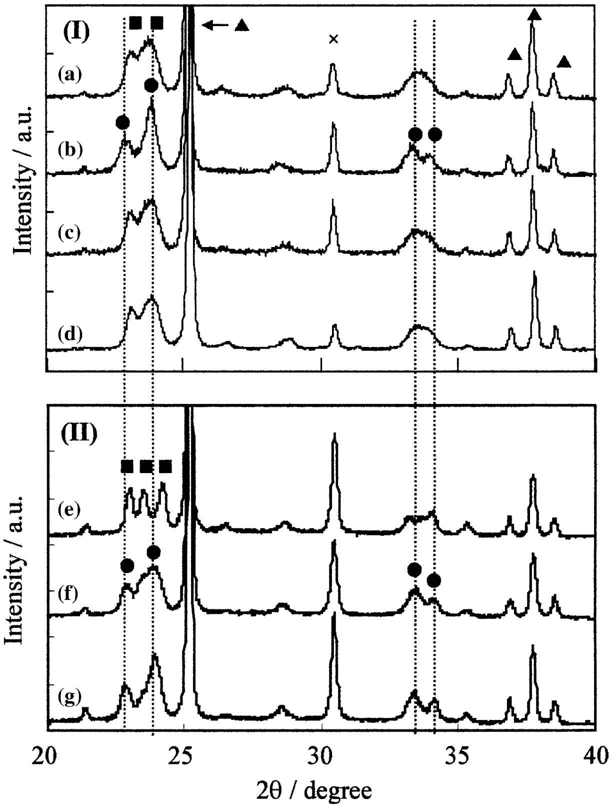

Figure 2. XRD patterns of a-$WO_3/TiO_2$ (I) and c-$WO_3/TiO_2$ (II). (I) a) before charging; b) after photo-charging; c) after discharging; d) after 20 cycles for charge-discharging. (II) e) before charging; f) after photo-charging; g) after discharging. (■: $WO_3$; ●: $H_{0.23}WO_3$; ▲: $TiO_2$ (anatase); x : ITO glass; dotted lines show the diffraction peaks attributed to $H_{0.23}WO_3$).

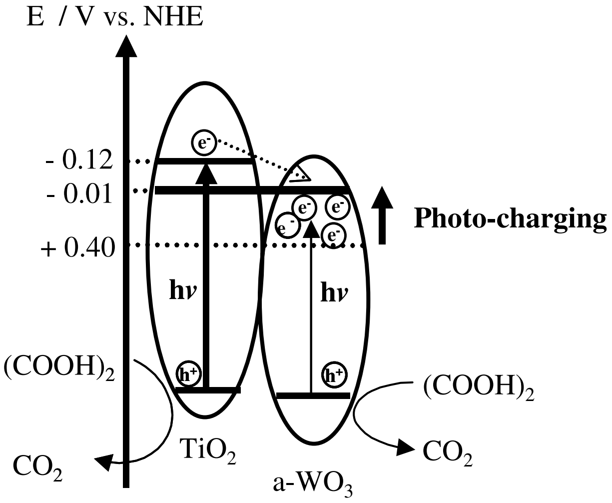

Figure 3. Photo-induced charge separation and charge accumulation on a-$WO_3/TiO_2$.

produce an electron and a hole. The hole is effectively scavenged by the photoreaction of $(COOH)_2$ to form $CO_2$ and protons, so that the recombination of the photo-generated carriers is suppressed. The photo-induced electrons, thus, accumulate to form tungsten bronze, resulting in the photo-charging.

The results of the charge–discharge cycles of a-$WO_3/TiO_2$ exhibited relatively good durability of about 75% within 20 cycles in an organic electrolyte, as shown in figure 4. In fact, it could be observed from the XRD data that the amorphous $WO_3$ phase on $TiO_2$ was retarded to transform into a polycrystalline $WO_3$ phase even after the charge–discharge cycles, as shown in figure 2d.

## Conclusions

A hybrid $WO_3/TiO_2$ involving an amorphous $WO_3$ phase was shown to exhibit efficient photo-electrochemical charging properties to form tungsten bronze through the intercalation of protons as well as efficient reversible discharging through de-intercalation. Such unique hybrid materials are promising for applications in photo-functional catalytic systems as well as for such useful devices as photo-chargeable batteries.

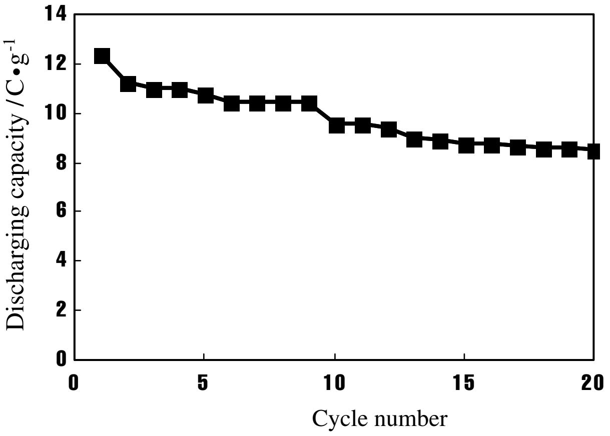

Figure 4. Discharging capacity as a function of the number of cycles for a-$WO_3/TiO_2$.

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