Enhancement of photocatalytic activity of tungsten oxide for water splitting by modification with brownmillerite-type Fe-Co oxide

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Abstract: Brownmillerite-type Ca_2FeCoO_5 synthesized by a sol-gel method and loaded by an electrophoretic deposition method on WO_3 and TiO_2 as a cocatalyst, and photoelectrochemical activity for water splitting was evaluated. The photocurrent density of WO_3 was increased by loading Ca_2FeCoO_5, while that of TiO_2 was decreased by the loading. Ultraviolet-visible-near infrared spectroscopy and Mott-Schottky analysis revealed that the higher conduction band level of Ca_2FeCoO_5 than that of WO_3, inducing the charge separation, the oxygen evolution on the surface of Ca_2FeCoO_5 and enhancement of the PEC activity.

Keywords: PEC water splitting, brownmillerite, cocatalyst.

1. Introduction

Enhancement of activity of a photocatalyst for water splitting and related reactions by modification with a cocatalyst for oxygen evolution reaction (OER) has been attempted. Recently, Tsuji et al. found Brownmillerite (BM)-type Ca_2FeCoO_5 with remarkably high OER activity, higher than those of noble metal oxides such as RuO_2.[1] The interface between the BM-type Ca_2FeCoO_5 and a semiconductor photocatalyst like WO_3 should be "semiconductor-semiconductor" type, whereas the interface between the photocatalyst and a conventional cocatalyst such as RuO_2 is "semiconductor-metal like" interface. In the former case, the energy levels of conduction bands (CB) and valence bands (VB) of BM-type Ca_2FeCoO_5 and the photocatalysts control the direction of electron transfer, significantly affecting the photoelectrochemical (PEC) activity. In this work, we report the effect of loading BM-type Ca_2FeCoO_5 on the photocatalysts with different band positions, i.e., WO_3 and TiO_2, on the PEC activity.

2. Experimental

A photoanode was prepared by an electrophoretic deposition (EPD) method on a fluorine-doped tin oxide (FTO) glass substrate in a constant voltage mode.[2] WO_3 or TiO_2 powder (40 mg) was dispersed in acetone (50 ml) with iodine (10 mg). Two FTO glasses were immersed in the solution and applied at -10 V between the electrodes using a DC power supply (thickness of the films; TiO_2 1.5 ~ 2.5 μm, WO_3 0.6 ~ 0.9 μm). Then, BM-type Ca_2FeCoO_5 synthesized by a sol-gel method[1] was loaded and annealed at 450 °C for 1 h in air. The PEC performance was studied by using a three electrode system. The fabricated photoanodes, a platinum foil and a saturated Ag/AgCl/KCl electrode were used as the working, counter and reference electrodes, respectively. The simulated solar or ultraviolet (UV) illumination was carried out by passing light from a 500 W Xe arc lamp equipped with an AM 1.5G filter (100 mW/cm^2) or a 33U filter (cut more than 330 nm, 60 mW/cm^2). The light was irradiated from the back side of the FTO glasses for all cases. The surface area of each photoanode was 1 cm^2. A 0.05 mol dm^{-3} Na_2SO_4 aqueous solution was used as an electrolyte for the PEC measurements. UV-visible-near infrared (UV-Vis-NIR) spectrum was obtained with JASCO V-770 spectrometer by a diffuse reflectance method in the wavelength range of 190 - 2500 nm and converted to the absorption spectrum by using Kubelka-Munk function.

3. Results and discussion

The current density-potential (*J-V*) curves for OER are shown in Figure 1. The photocurrent density of WO_3 irradiated with the simulated solar light at > ca. 1 V vs. RHE was obviously increased (from 0.46 mA cm^{-2} to 0.78 mA cm^{-2} at 1.23 V vs. RHE) by loading BM-type Ca_2FeCoO_5. On the other hand, the photocurrent density of TiO_2 irradiated with UV at 0.4-1.7 V vs. RHE was decreased by the loading. Thus, the PEC activity of WO_3 was enhanced by the loading of BM-type Ca_2FeCoO_5, while that of TiO_2 was suppressed.

Figure 2 (a) displays a UV-Vis-NIR absorbance spectra of BM-type Ca_2FeCoO_5, showing the absorption in a wide infrared range. Figure 2 (b) shows a Tauc plot, indicating a direct optical band gap of 1.1 eV. The Mott-Schottky analysis provided the band energy levels as shown in Figure 3. The bottom edge of CB of Ca_2FeCoO_5 was located between the bottom edges of CB of WO_3 and TiO_2, making the CB of Ca_2FeCoO_5 more negative than that of WO_3 but more positive than that of TiO_2. The upper edge of VB of Ca_2FeCoO_5 was more positive than those of both WO_3 and TiO_2. This tells us that that photogenerated holes moved from WO_3 to Ca_2FeCoO_5, and therefore the BM-type Ca_2FeCoO_5 with the OER activity oxidized water to form oxygen, while photogenerated electrons were not moved to Ca_2FeCoO_5. In contrast, not only the holes but also the electrons moved from TiO_2 to Ca_2FeCoO_5, probably resulting in the recombination. Thus, the BM-type Ca_2FeCoO_5 enhanced the PEC activity of a photocatalyst for water splitting through the OER on the Ca_2FeCoO_5 surface in the case where the both levels of CB and VB were more negative than those of the photocatalyst.

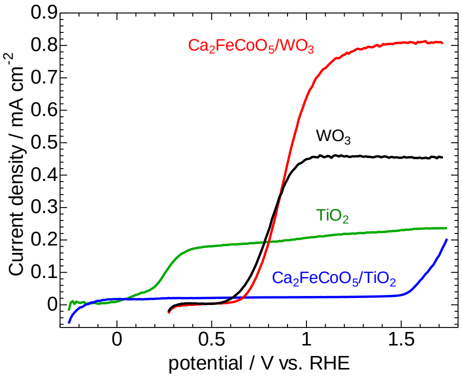

Figure 1. Photocurrent densities of WO_3 and Ca_2FeCoO_5/WO_3 under AM1.5G irradiation and those of TiO_2 and Ca_2FeCoO_5 under UV irradiation in 0.05 mol dm^{-3} Na_2SO_4.

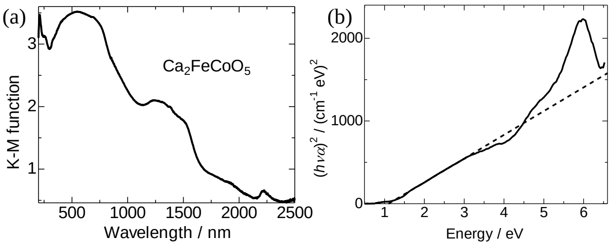

Figure 2. (a) UV-Vis-NIR spectrum and (b) Tauc plots of Ca_2FeCoO_5.

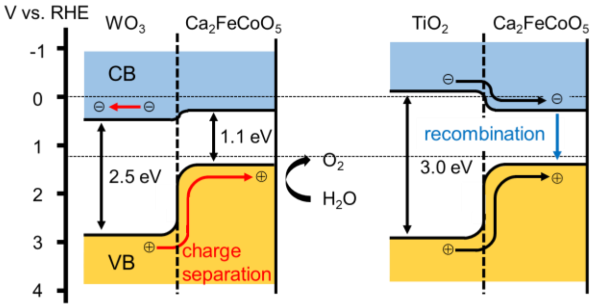

Figure 3. Conduction and valence band levels of WO_3, TiO_2 and Ca_2FeCoO_5 analyzed from UV-vis-NIR spectroscopy, redox potentials of H^+/H_2 and O_2/H_2O and speculated charge flow.

4. Conclusions

The photocurrent density of WO_3 was increased to about 1.7 times by loading of the BM-type Ca_2FeCoO_5, whereas that of TiO_2 was decreased. The Tauc plot of Ca_2FeCoO_5 showed a direct optical band gap 1.1 eV. Mott-Schottky analysis showed that the upper edge of CB of Ca_2FeCoO_5 was more negative than that of WO_3 and more positive than that of TiO_2, whereas the bottom edge of VB of Ca_2FeCoO_5 was more negative than those of WO_3 and TiO_2. Therefore, it is speculated that the photogenerated electrons and holes in Ca_2FeCoO_5/WO_3 were effectively separated by the moving of holes from WO_3 to Ca_2FeCoO_5, while the electrons were trapped in WO_3. It is thus shown that the BM-type Ca_2FeCoO_5 played a role of OER cocatalyst to enhance the PEC activity for water splitting in the case where the band positions were suitably located.

Acknowledgments

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References

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