Influence of loading of brownmillerite-type Ca_2FeCoO_5 on photocatalytic activity of iron oxide for oxygen evolution reaction

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Abstract: Brownmillerite-type Ca_2FeCoO_5 was synthesized by a sol-gel method and loaded on Fe_2O_3 by an electrophoretic deposition method. The influence on photocatalytic activity for oxygen evolution reaction (OER) was investigated. The photocurrent density on the Ca_2FeCoO_5/Fe_2O_3 electrode was higher than that on pure Fe_2O_3 electrode. From the estimation of band levels, it is speculated that the charge separation of photogenerated holes and electrons was accelerated by formation of heterojunction at the Fe_2O_3-Ca_2FeCoO_5 interface. In addition, it was found that, in addition to OER, some side reactions related to OH^- were also promoted by Ca_2FeCoO_5 loading.

Keywords: Photocatalytic oxygen evolution reaction, brownmillerite, Fe_2O_3.

1. Introduction

The photoelectrochemical (PEC) water splitting on a photocatalyst has been studied as one of clean methods for hydrogen production. However, the reaction rate of OER, which is a counter reaction of hydrogen evolution, has been slow, limiting the efficiency of total process. It should be unavoidable to overcome the inactivity for OER to apply the photocatalysis to the practical solution of energy problem. Enhancement of the photocatalytic activity has been attempted by loading of a promotor which has been known to be active for OER. RuO_2 and IrO_2 have been known to be active for OER, but the supply of these noble metals is insufficient. Recently, we found that brownmillerite (BM)-type Ca_2FeCoO_5, consisting only of non-noble metals, exhibited distinct OER catalytic activity higher than the noble metal oxides.[1] Subsequently, we try to combine BM-type Ca_2FeCoO_5 with Fe_2O_3, which is one of the most efficient photocatalysts driven by visible light, and enhance the PEC activity.

2. Experimental

Fe_2O_3 electrodes were prepared by an electrodeposition method as reported.[2] $FeCl_3\cdot 6H_2O$, KCl, KF and H_2O_2 were dissolved in deionized water at 40 ºC. The Fe_2O_3 precursor was electrodeposited on a fluorine-doped tin oxide (FTO) glass substrate by potential sweep from 0.042 to 0.242 V vs. Ag/AgCl/KCl (satd.) for 30 cycles in the resultant solution at 40 ºC. A platinum foil and an Ag/AgCl/KCl (satd) electrode were used as a counter electrode and a reference electrode, respectively. The obtained substrates were annealed at 450 ºC in air for 1 h. Ca_2FeCoO_5/Fe_2O_3 electrodes were prepared by an electrophoretic deposition method using a two electrode sytstem.[3] BM-type Ca_2FeCoO_5 particles were synthesized by a sol-gel method [1] and dispersed in acetone with I_2. A Fe_2O_3 electrode and a FTO substrate were immersed in the suspension and applied -10 V between them for electrophoretic deposition of Ca_2FeCoO_5 on the Fe_2O_3 electrode. The amount of loaded Ca_2FeCoO_5 was controlled by adjusting the electric charge passing across the electrode. The yielded Ca_2FeCoO_5/Fe_2O_3 was annealed at 450 ºC in air for 1 h. PEC activity was evaluated by using a three electrode system with irradiation of simulated solar light (AM 1.5 G, 100 mW cm^{-2}). The fabricated photoanodes, a platinum foil and a Ag/AgCl/KCl (satd.) electrode were used as the working, counter and reference electrodes, respectively. A 0.05 mol dm^{-3} Na_2SO_4 was used as an electrolyte. The energy levels of the valence band (VB) and conduction band (CB) of Ca_2FeCoO_5 were estimated by Mott-Schottky analysis and ultraviolet-visible-near infrared (UV-vis-NIR) spectroscopy.

3. Results and discussion

Figure 1 shows the photocurrent density - potential curves of the Ca_2FeCoO_5/Fe_2O_3 and Fe_2O_3. The photocurrent density shown here is (the current density under light irradiation) - (density in a dark measurement). On the Fe_2O_3 electrode, photooxidation current density for OER was observed from around 0.7 V vs. RHE, and saturated to be 2 nA cm^{-2} at more than 0.9 V vs. RHE. On the Ca_2FeCoO_5/Fe_2O_3 electrode, the response with light irradiation was quite different from that of Fe_2O_3; large photooxidation and photoreduction peaks were observed at 0.8 V vs. RHE in the positive sweep and at 0.6 ~ 0.7 V vs. RHE in the negative sweep, respectively. The peak intensities of the photooxidation and photoreduction increased with the loading of Ca_2FeCoO_5. Here it is noteworthy that pure Ca_2FeCoO_5 possessed no photocatalytic activity, but the above enhancement of current by introduction of Ca_2FeCoO_5 on Fe_2O_3 was thus found.

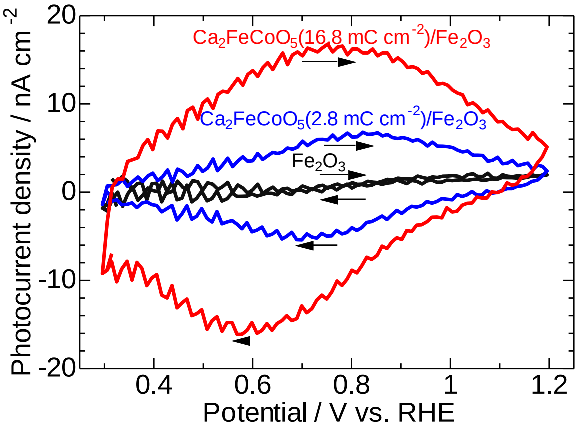

Figure 1 Photocurrent density on Fe_2O_3 and Ca_2FeCoO_5/Fe_2O_3 electrodes.

Figure 2 shows CB and VB levels of Ca_2FeCoO_5 and Fe_2O_3 estimated from the Mott-Schottky analysis and the UV-vis-NIR spectroscopy. The bottom edge of VB of Fe_2O_3 is more positive than that of Ca_2FeCoO_5. Therefore, it is predicted that the holes photogenerated at VB of Fe_2O_3 moved to VB of Ca_2FeCoO_5 through the heterojunction, resulting in the charge separation and suppressing the rate of recombination of electrons and holes. The SEM and DES indicated that the coverage of surface by Ca_2FeCoO_5 increased with the loading of Ca_2FeCoO_5, and therefore it is suggested that the charge separation was promoted at higher loading.

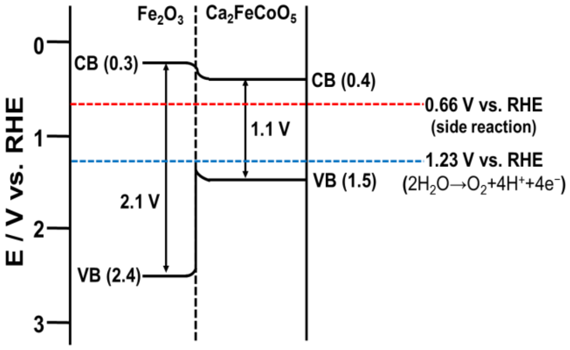

Figure 2 Estimated energy levels of CB (conduction band) and VB (valence band) of Fe_2O_3 and Ca_2FeCoO_5.

On the Ca_2FeCoO_5/Fe_2O_3 electrodes, the photocurrent density did not saturate but showed the volcano shape curves, implying that side reactions took place under light irradiation. In 0.1 mol dm^{-3} NaOH aqueous solution in place of Na_2SO_4, i.e., at higher pH, the photo redox peaks shifted to the negative side at a rate corresponding to about 60 mV/pH. The photocurrent density in the NaOH solution was twice higher than that in the Na_2SO_4 solution. Therefore, it is considered that some side reactions related to OH^- were also promoted by the loading of Ca_2FeCoO_5 on Fe_2O_3.

4. Conclusions

The photocurrent density on the Fe_2O_3 electrode increased with loading of BM-type Ca_2FeCoO_5. It is speculated that photogenerated holes at VB of Fe_2O_3 moved to that of Ca_2FeCoO_5 via the heterojunction, suppressing the rate of recombination of electrons and holes. In addition, some side reactions under visible light related to OH^- were also promoted by the loading of Ca_2FeCoO_5.

Acknowledgments

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