FULL PAPER

Effects of the addition of surfactants on the direct fabrication of a CuFeO_2/Fe photocathode by hydrothermal method

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CuFeO_2 is a prospective photocathode material for water or CO_2 reduction, but satisfactory performance has not been achieved yet. This has been ascribed to the large size of the CuFeO_2 particles obtained by growing a CuFeO_2 film on an Fe substrate when using hydrothermal method for enhanced adhesion between film and substrate. This study evaluates the effect of adding oleic acid or acetic acid as surfactants in the hydrothermal fabrication process with the expectation of controlling the crystal growth. The investigation of the shape and the size of the obtained CuFeO_2 particles by scanning electron microscopy and X-ray diffraction and the evaluation of the photoelectrochemical performance of the CuFeO_2 photoelectrodes by electrical conductivity and photoelectrochemical measurements demonstrate that, although an increase in the particle surface area can be achieved, the performance is highly affected by the grain boundary resistance.

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1. Introduction

Photoelectrochemical water splitting is a promising way for the clean production of hydrogen, in which 10% of solar to hydrogen energy conversion efficiency is considered to be required for practical use.¹⁾ Although relatively high performance has been achieved, this is still insufficient, which has prompted numerous studies aimed at improving the performance of photoanodes and photocathodes.²⁾ In these systems, materials such as CIGS, commonly used for solar cells, have been employed as photocathode materials.³⁾ To this aim, other materials including Cu_2O , CuO , and CdS have also been explored; however, they exhibit inferior stability.³⁾ Therefore, the development of low-cost photocathode materials having more stable performance is an area of research of high interest.

In our group, we have been interested in evaluating cheaper and more stable materials as the photocathode for hydrogen evolution, focusing on CuFeO_2 because it is comprised of the earth-abundant and inexpensive metals Cu and Fe.^{4)–9)} CuFeO_2 is also attractive due to its delafossite-type structure. Delafossite compounds of general formula CuMO_2 ($M = \text{Al, Fe, Ga, etc.}$) have been reported to be p-type semiconducting materials. In these compounds, the electron-filled Cu-3d orbitals are very close in energy to the O-2p orbitals; therefore, both types of orbitals interact with each other and dominate the upper valence band.⁴⁾ The conduction band, in turn, is comprised

of Cu-3d orbitals. Consequently, the M^{3+} cation plays no direct role in the energy band diagram,⁵⁾ which prevents self-oxidation or corrosion and ensures the photoelectrochemical stability of the CuMO_2 material.⁶⁾

Other interesting features of CuFeO_2 are its responsiveness to visible light (Band gap energy = 1.55 eV) and hydrogen evolution activity.⁷⁾ For CuFeO_2 film fabrication, methods such as sol-gel⁸⁾ and electrodeposition⁷⁾ have been employed to date, affording a maximum photocurrent of $-0.71 \text{ mA} \cdot \text{cm}^{-2}$ ($0.6 V_{\text{RHE}}$).⁹⁾ (RHE: reversible hydrogen electrode) However, this value does not reach the desired 10% efficiency, which prompted us to evaluate the hydrothermal method as an alternative approach for the direct fabrication of CuFeO_2 . In this method, an iron substrate is used as both Fe source and conductive substrate.¹⁰⁾ The direct fabrication by hydrothermal method allows to lower the reaction temperature,¹¹⁾ affording CuFeO_2 films with enhanced adhesion to substrates. Unfortunately, the optimization of the reaction conditions to obtain CuFeO_2 films having high performance is difficult due to the large number of parameters involved.

Recently, we reported the successful direct fabrication of CuFeO_2 films on Fe substrates,¹⁰⁾ although the obtained photocurrent was low (about $150\text{--}200 \mu\text{A} \cdot \text{cm}^{-2}$, $0.4 V_{\text{RHE}}$). This limited photocurrent was ascribed to the small surface area of the $10 \mu\text{m}$ thick CuFeO_2 film grown on the Fe substrate, which is considered to be disadvantageous for photoelectrode applications. Furthermore, the carrier diffusion distance has been reported to be about 200 nm in CuFeO_2 ,¹²⁾ indicating that the particles were too large. Therefore, we were interested on reducing the CuFeO_2

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particle size. Our previous efforts toward decreasing the particle size and film thickness involved varying the hydrothermal conditions (the reaction time etc.);¹⁰⁾ however, this resulted in an increase of impurities. Other approaches such as metal cation doping also proved unsuccessful.

In this regard, addition of a surfactant can be envisaged as an alternative method for controlling particle size or morphology. This approach is mainly used in homogeneous nucleation systems such as powder synthesis by hydrothermal method.^{13),14)} In this method, surfactants surround the growing crystals in solution, hindering their growth and aggregation. Additionally, the morphology of the particles may change depending on the size of the surfactant.¹⁵⁾ In this study, we added a surfactant especially for reducing the size of particle composing films.

Herein, we describe the evaluation of acetic acid (AA) (CH_3COOH) and oleic acid (OA) [$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$] as surfactants to control the CuFeO_2 crystal growth and the investigation of their effects on the photoelectrochemical performance of the resulting materials. Since the reduction of the particle size can induce the formation of secondary particles and the occurrence of grain boundary resistance, we also subjected the photoelectrodes to electrical conductivity measurement to estimate the resistance.¹⁶⁾ This allows to measure the interfacial resistance between CuFeO_2 films and Fe substrates and the grain boundary resistance separately, and to evaluate the effects of the latter on the performance of the CuFeO_2/Fe photocathode.

2. Experimental procedures

Since the aim of this work was to analyze the effects of the addition of a surfactant, in particular, of the carboxylate anion, we utilized CuO as the Cu source instead of the previously used $\text{Cu}(\text{NO}_3)_2$ to avoid interferences with other anions.

0.02 M of CuO (>98.0%, JUNSEI Chemical Co. Ltd., Japan) was added into 20 mL of deionized water in a 50 mL Teflon-lined beaker. Then, 2.0 g of NaOH (>97.0%, JUNSEI Chemical Co. Ltd., Japan) was added to the dispersion. Fe substrates (>99.5%, The Nilaco Corp., Japan, $0.5 \times 10 \times 20 \text{ mm}^3$) were polished with a polishing paste (NIHON MARYO KOGYO Co. Ltd., Japan) and washed with acetone using an ultrasonic bath before being added to the dispersion. Then, 0, 25, or 50 μL of OA or 0, 10, 50, 100, 500, or 1000 μL of AA was added into the suspension, which was then sealed in an autoclave (HU-50, SAN-AI Kagaku Co. Ltd., Japan). Hydrothermal treatment was then performed at 160°C for 24 h. Finally, the hydrothermally treated substrates were washed with deionized water. The Fe substrate was also treated in a similar manner replacing the Cu source with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.0–105.0%, JUNSEI Chemical Co. Ltd., Japan). Hereinafter, the samples treated with OA will be referred to as OA-0, OA-25, and OA-50, and the samples treated with AA as AA-0, AA-10, AA-50, AA-100, AA-500, and AA-1000.

The films deposited on the Fe substrates were characterized by X-ray diffraction (XRD, Ultima IV, Rigaku

Fig. 1. Schematic for the electrical conductivity measurements.

Corporation, Japan) with $\text{Cu K}\alpha$ radiation and by scanning electron microscopy (SEM, VE-9800, KEYENCE Corp., Japan). Photoelectrochemical (PEC) measurements were made with an automatic polarization system (HSV-110, HOKUTO DENKO Corp., Japan) in a three-electrode configuration and a cell comprising of the prepared photocathode as the working electrode, an Ag/AgCl reference electrode, a Pt counter electrode, and a 0.1 M Na_2SO_4 (>99.0%, FUJIFILM Wako Pure Chemical Corp., Japan) solution (pH 13) as the electrolyte. Prior to the PEC measurements, the electrolyte was bubbled with Ar gas for 15 min. The working electrode was irradiated by AM 1.5G solar simulated light.

Electrical conductivity measurements were performed using the setup depicted in Fig. 1 and a chemical impedance analyzer (IM3570, HIOKI E.E. Corp., Japan). The conditions for the measurements were as follows: amplitude of AC voltage, 10 mV; frequency, 0.01–200000 Hz; DC voltage, 0 V. Conductive cables were attached to the prepared films with conductive paste (TK PASTE CN-7120, KAKEN TECH Co. Ltd., Japan).

3. Results and discussion

3.1 Effects of adding OA

Figure 2 shows the XRD patterns of the samples treated with OA. Most of the diffraction peaks of the samples are attributable to 3R- CuFeO_2 delafossite. From these results, it can be extracted that the formation of the crystal phase of CuFeO_2 proceeds in the presence of OA. In the samples OA-0 and OA-25, peaks derived from 2H- CuFeO_2 were also observed. The 2H- CuFeO_2 type is known to generate when the ratio of CuFeO_2 deviates from stoichiometry,^{17),18)} which suggests that a single phase product cannot be obtained using the conditions of OA-0 and OA-25, regardless of the presence or absence of OA.

A change in the strength ratio of the two strongest peaks (006 and 012) was confirmed between the samples OA-0 and OA-25. Although the oleate ion covering the 006 crystal plane could hinder the crystal growth in that plane, irregularities in the crystal growth were detected in several experiments.

Fig. 2. XRD patterns of the samples treated with 0, 25, and 50 μL OA (OA-0, OA-25, and OA-50) and the ICDD data of 3R- CuFeO_2 (ICDD No. 00-039-0246).

Fig. 3. SEM images of the samples treated with 0, 25, and 50 μL OA (OA-0, OA-25, and OA-50).

As can be seen in the SEM images depicted in Fig. 3, a white part appeared in the sample OA-50, and the shape of the particles was more unclear than that of the samples OA-0 and OA-25. Additionally, in the XRD pattern of the sample OA-50, the presence of peaks attributable to Fe_2O_3 was also confirmed. This is most likely due to the low solubility of OA in water affording an inhomogeneous solution under hydrothermal condition, which would prevent the reaction between the Cu ion and the Fe substrate and hence the formation of the CuFeO_2 crystal phase. However, the PEC performance almost unchanged (Fig. 4) compared to the sample OA-0, thus the CuFeO_2 film was prepared, even which was not pure.

On the other hand, no peaks arising from impurities were observed in the XRD pattern of the sample OA-25. Furthermore, this sample gave rise to smaller particles than OA-0 and a slight improvement on the PEC performance for water splitting (Fig. 4), which can be attributed to an increase in the surface area.

Fig. 4. Current–potential curves for the samples treated with 0, 25, and 50 μL OA (OA-0, OA-25, and OA-50) under chopped light irradiation (AM 1.5G solar simulated light) in 0.1 M Na_2SO_4 solution (pH 13).

These results demonstrate that the addition of a surfactant has an effect on the direct fabrication of the oxide films on the metal substrate.

Next, to circumvent the problem of the low solubility of OA in water, we evaluated the effect of changing the surfactant to the smaller AA.

3.2 Effects of adding AA

AA can be dissolved to deionized water. Thus, pH conditions of precursor solution can change. Therefore when the precursor solution was prepared, the pH condition was also measured to investigate the effects of pH on the CuFeO_2 crystal growth. No changes in the pH value were observed when less than 100 μL of AA was added (pH about 13.9). In contrast, a slight decrease was confirmed when adding more than 500 μL of AA (pH 13.7–13.8, repeatability of the pH meter (D-51, HORIBA, Ltd.): $\pm 0.01 \text{ pH} \pm 1 \text{ digit}$).

Figure 5 shows the XRD patterns of the samples AA-0–AA-1000. As can be seen, the CuFeO_2 crystal phase was obtained in all cases. However, in the sample AA-1000, peaks arising from Fe_2O_3 were detected, which can be ascribed to reaction inhibition induced by the decrease in pH when adding excess AA.

Additionally, the full-width at half maximum of the strongest peak at about 35° of the sample treated with AA became wider than that of the sample without the surfactant, suggesting that a decrease in particle size can occur by adding AA.

The change in particle size was confirmed from the corresponding SEM images (Fig. 6). The exposed plane of the particles also changed, especially that of the sample AA-10. Moreover, upon adding more than 100 μL of AA, a collapse of the particle shape was detected. These results indicate that even the presence of a small surfactant such as AA can affect the particle size in the oxide films directly fabricated by hydrothermal method. It is also worth men-

Fig. 5. XRD patterns of the samples treated with 0–1000 μL AA (AA-0–AA-1000) and the ICDD data of 3R- CuFeO_2 (ICDD No. 00-039-0246).

Fig. 6. SEM images of the samples treated with 0–1000 μL AA (AA-0–AA-1000).

tioning that a noticeable difference in the particle morphology existed between the samples AA-500 and AA-1000. This phenomenon can be attributed to the coexistence of Fe_2O_3 in the film.

Figure 7 shows the cyclic voltammogram (CV) of all the AA-treated samples. The shape of the voltammogram changed by adding AA. Therefore, adding OA can affects surface state more than particle shape and size.

The differences in the voltammograms are particularly evident between the samples AA-10 and AA-0; the anodic current and cathodic current at low and high potential were much larger for the former than for the latter. This difference confirms the changes of the surface state upon addition of AA. Thus, the addition of the surfactant would

Fig. 7. CV of the samples treated with 0–1000 μL AA (AA-0–AA-1000).

Fig. 8. Current–potential curves for the samples treated with 0–1000 μL AA (AA-0–AA-1000) under chopped light irradiation (AM 1.5G solar simulated light) in 0.1M Na_2SO_4 solution (pH 13).

expose the Cu atom on the surface of the CuFeO_2 crystal, and hence it would become electrochemically active. Since the CuFeO_2 crystal has a layered crystal structure along the c -axis direction composed of an FeO_6^- layer and a Cu^+ layer, this Cu^+ exposure can occur if AA covers the 006 (003, 009) crystal plane.

Figure 8 shows the results of the PEC measurements for the samples AA-0–AA-1000. No apparent differences were observed, despite the changes in particle size and surface area. This means that the effect of the grain boundary resistance is larger than that of the surface area. To confirm the effect of grain boundary resistance, we subjected the photoelectrodes to electrical conductivity measurements, as discussed below.

3.3 Electrical conductivity measurements

Figure 9 shows an assumed equivalent circuit estimated from the electrical conductivity system depicted in Fig. 1.

Fig. 9. The assumed equivalent circuit for the CuFeO_2 photocathodes fabricated by hydrothermal method.

Fig. 10. Nyquist plots of the sample treated with $\bullet$ $\text{Cu}(\text{NO}_3)_2$ and $\blacksquare$ the sample AA-10 and SEM images of the sample treated with $\text{Cu}(\text{NO}_3)_2$ and the sample AA-10.

As can be seen in Fig. 9, the circuit is composed of four components: two interface resistances (one between the CuFeO_2 film and the conductive paste and another between the CuFeO_2 film and the Fe substrate), resistance in the bulk of the CuFeO_2 particles, and the grain boundary resistance, which is the focus of this study. Therefore, ideally, four semicircles would be observed in the Nyquist diagram of the present conductivity measurements. The results obtained for the sample AA-10 were compared with those of that treated with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ as the Cu source, which has the highest performance ever obtained.

Figure 10 shows the Nyquist diagram of both samples, in which two semicircles attributable to bulk resistance (high frequency side) and grain boundary resistance (low

Fig. 11. Current-potential curves for the sample treated with $\text{Cu}(\text{NO}_3)_2$ and the sample AA-10 under chopped light irradiation (AM 1.5G solar simulated light) in 0.1M Na_2SO_4 solution (pH 13).

frequency side) were obtained. As can be seen, the value of the grain boundary resistance obtained for the sample treated with $\text{Cu}(\text{NO}_3)_2$ is smaller than that of the sample AA-10.

According to the results of the PEC measurements for the same two samples (Fig. 11), the value corresponding to the photocurrent of the $\text{Cu}(\text{NO}_3)_2$ sample is much larger than that of the sample AA-10. Therefore, it seems reasonable to conclude that the grain boundary resistance is the main factor affecting the performance of the present CuFeO_2 photocathode, which suggests that further optimization of the reaction conditions to prevent the formation of secondary particles is required for the fabrication of high-performance CuFeO_2 photocathodes by hydrothermal method.

4. Conclusions

In this study, we evaluated the effect of the addition of surfactants on the fabrication of CuFeO_2 photocathodes by hydrothermal method, finding that the use of 25 μL of OA or 10 μL of AA led to a decrease in particle size compared to the sample with no surfactant. An increase in surface area can be then expected by using this method.

However, no clear effect on the performance of the CuFeO_2 photocathodes could be demonstrated, due presumably to the grain boundary resistance exerting a larger influence on the performance than the surface area. This was confirmed by subjecting CuFeO_2 photocathodes fabricated with different copper sources [$\text{Cu}(\text{NO}_3)_2$ and CuO] to electrical conductivity measurements and corroborated by PEC measurements. From these results, it can be concluded that electrical conductivity measurements can be applied for the estimation of the photoelectrode resistance, and that optimization of the reaction conditions to prevent the formation of secondary particles is required for the fabrication of high-performance CuFeO_2 photocathodes.

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