

Preparation of p-Type CaFe_2O_4 Photocathodes for Producing Hydrogen from Water

Shintaro Ida,^{*,†,‡} Keisuke Yamada,[†] Takuya Matsunaga,[§] Hidehisa Hagiwara,[†]
Yasumichi Matsumoto,[§] and Tatsumi Ishihara[†]

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan, PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan, and Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

Received August 3, 2010; E-mail: s-ida@cstf.kyushu-u.ac.jp

Abstract: An (*hk*0)-oriented p-type CaFe_2O_4 (E_g : 1.9 eV) photocathode was prepared, and hydrogen and oxygen gases were produced from a photocell short-circuited by connecting the CaFe_2O_4 and n-type TiO_2 electrodes under illumination without applying an external voltage. The open-circuited voltage was 0.97 V and the short-circuit current was about $200 \mu\text{A}/\text{cm}^2$, and the amount of evaluated hydrogen and oxygen gases after 2 days of reaction were about 70 and $4 \mu\text{mol}$, respectively.

The challenge of generating hydrogen and electric power from water using solar energy has attracted considerable interest since it promises clean, environmentally friendly energy generation. The first report of photoelectrochemical decomposition of water into hydrogen used an n-type semiconductor TiO_2 -Pt system and required UV illumination and application of an external voltage of about 0.5 V.¹ Development of a hydrogen generation system that does not require an external voltage is critical for efficiently exploiting solar energy. Use of the above system to generate hydrogen gas from water without applying an external voltage requires p- and n-type semiconductor electrodes that can respectively decompose water into hydrogen and oxygen when illuminated by UV or visible light.² Such a system is an artificial photosynthesis system that generates hydrogen and oxygen gases separately. There have been many studies of high-efficiency n-type semiconductor photoanodes,³ whereas there have been comparatively few reports on high-efficiency photocathodes (oxides) for generating hydrogen. Examples of the latter include Cu_2O and Mg- or Zn-doped Fe_2O_3 photocathodes, which are p-type semiconductors with visible light responses.^{4–6} CaFe_2O_4 is a p-type semiconductor with a band gap of 1.9 eV and conduction and valence band edges of -0.6 and $+1.3$ V vs NHE, respectively, which are suitable for reducing water.⁷ In addition, it can be prepared from low-cost materials such as iron and calcium. However, it has a low photoresponse due to recombination of photogenerated carriers in polycrystalline CaFe_2O_4 electrodes.

This communication reports an (*hk*0)-oriented p-type CaFe_2O_4 film that exhibits a relatively high photocathodic current for reducing water. In addition, we describe wet photovoltaic cells with p- CaFe_2O_4 and n- TiO_2 electrodes that can generate hydrogen and oxygen gases without a voltage being applied.

CaFe_2O_4 powder was prepared by a solution method according to a procedure given in the literature.⁸ The CaFe_2O_4 photocathode

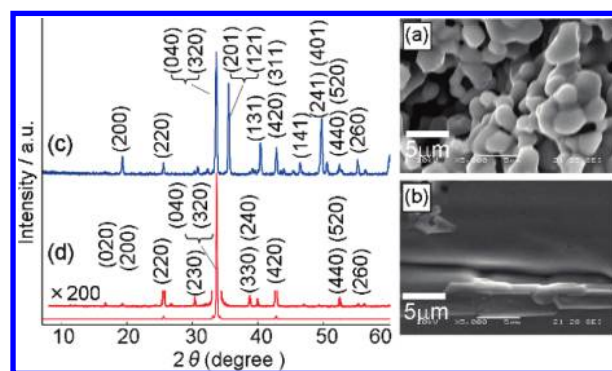


Figure 1. SEM images of CaFe_2O_4 electrodes after calcination at (a) 1100 and (b) 1200 °C. XRD patterns of CaFe_2O_4 electrodes after calcination at (c) 1100 and (d) 1200 °C.

was prepared as follows. CaFe_2O_4 powder (50 mg) was suspended in ethanol ($100 \mu\text{L}$), and the suspension was dried on a Pt substrate (1 cm^2) by heating the substrate at 80 °C. The substrate was calcined at 1100–1200 °C for 2 h. The TiO_2 electrode was prepared by annealing of the metal Ti substrate at 600 °C for 1 h.

Figure 1 shows SEM images and XRD patterns of the CaFe_2O_4 electrodes after calcination at 1100 and 1200 °C, respectively. The powder size was in the range 2–4 μm after calcination at 1100 °C. In contrast, a flat surface rather than a powder was observed after calcination at 1200 °C, which indicates that the CaFe_2O_4 powder melted at 1200 °C. The films were about 60–100 μm thick. The XRD pattern after calcination at 1100 °C corresponds to that of CaFe_2O_4 powder. One intense diffraction peak and several weak peaks were observed for the electrode calcined at 1200 °C as shown in Figure 1d. The intense peak was assigned to the (320) and (040) peaks of CaFe_2O_4 , and the weak peaks were assigned to other (*hk*0) diffraction peaks of CaFe_2O_4 . These results indicate that calcination at 1200 °C produces an (*hk*0)-oriented CaFe_2O_4 film.

Figure 2a shows current–potential curves in 0.1 M NaOH solution for CaFe_2O_4 electrodes calcinated at 1100 and 1200 °C. When the electrode was heated at 1200 °C, it produced a photocurrent that was about 10–50 times higher than that when it was heated at 1100 °C. The SEM image in Figure 1b clearly shows that the grain boundary density in the film is reduced by calcination at 1200 °C. In addition, the CaFe_2O_4 layer adhered strongly to the Pt substrate after heat treatment at 1200 °C. These improvements in film quality are expected to greatly increase the photoresponse. Figure 2b shows an incident photon to current efficiency (IPCE) spectrum and UV–vis absorption spectra for CaFe_2O_4 electrodes. The IPCE was in the range 5–15% in the UV region, and it was less than 5% in the visible light region. A photocurrent was observed

[†] Kyushu University.

[‡] PRESTO, Japan Science and Technology Agency.

[§] Kumamoto University.

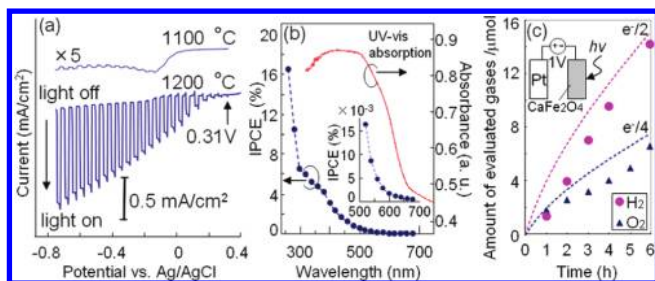


Figure 2. (a) Current–potential curves in 0.1 M NaOH solution under chopped light illumination (500 W Xe lamp) for CaFe₂O₄ electrodes treated at 1200 and 1100 °C. (b) IPCE spectrum of CaFe₂O₄ electrodes treated at 1200 °C with -0.8 V vs Ag/AgCl in 0.1 M NaOH and UV–vis absorption spectrum of CaFe₂O₄. (c) Time course of gases evolution from CaFe₂O₄(cathode, 10 cm²)-Pt(anode, 4 cm²) electrode system with 1 V of applied bias in 0.1 M NaOH solution under irradiation (500 W Xe lamp).

up to 650 nm, which corresponds to the UV–vis absorption edge of CaFe₂O₄ (band gap: 1.9 eV). The IPCE in the visible region was lower than that expected from the adsorption intensity. With regard to UV–vis absorption of an iron oxide such as Fe₂O₃, in general, absorptions of UV light (<400 nm) and visible light (>400 nm) correspond to a direct transition ($O^{2-} 2p \rightarrow Fe^{3+} 3d$ charge transfer) and an indirect transition (spin-forbidden $Fe^{3+} d \rightarrow d$ excitation), respectively.⁹ Presumably, the photogenerated electrons and holes related to the indirect transition of the CaFe₂O₄ tend to recombine. Figure 2c shows a time course of gas evolution from the CaFe₂O₄ (cathode)–Pt (anode) electrode system with 1 V of applied bias in 0.1 M NaOH solution under irradiation. H₂ and O₂ were evolved in a nearly stoichiometric ratio, and the Faraday efficiencies for H₂ and O₂ production after reaction were 92 and 89%, respectively.

Next, we prepared wet photovoltaic cells by connecting p-type CaFe₂O₄ and n-type TiO₂ electrodes to produce hydrogen without an external applied voltage. Figure 3a shows the reaction and the band model for the photocell. Bands generally bend upward (n-type) or downward (p-type) close to the interface between the aqueous electrolyte solution and the semiconductor electrode. Theoretically, photogenerated electrons in p-type CaFe₂O₄ reduce water to hydrogen and photogenerated holes in an n-type TiO₂ oxidize water to oxygen when the two electrodes are illuminated by light with a sufficiently high photon energy. The open-circuit voltage (OCV) of a photocell is equal to the difference between the Fermi levels of the p- and n-type semiconductor electrodes. Figure 3b shows current–potential curves in 0.1 M NaOH solution and an SEM image of the TiO₂ electrode that was used as an anode electrode in the photocell. The photooxidation current was observed, and the onset potential was -0.75 V. The surface was not smooth, and island shaped crystals were observed. The crystal type was rutile-type TiO₂ (see Supporting Information). Figure 3c shows the I – V curve of a photocell with p-type CaFe₂O₄ and n-type TiO₂ electrodes in 0.1 M NaOH aqueous solution under illumination. These data were obtained from a two-chamber system, in which the anode and cathode electrodes are immersed into separate quartz cells divided by a Nafion 117 film. The OCV was 0.97 V, and the short-circuit current ($V = 0$ V) was about 220 μ A. The difference between the two onset potentials of CaFe₂O₄ (0.31 V) and TiO₂ (-0.75 V) was 1.06 V, which was almost the same as the OCV value of the photocell in Figure 3c. Figure 3d shows the amounts of H₂ and O₂ gases generated from the photocell, which was short-circuited by connecting the CaFe₂O₄ and TiO₂ electrodes, as a function of the irradiation time. This result demonstrates that the photocell generates H₂ and O₂ gases without applying an external

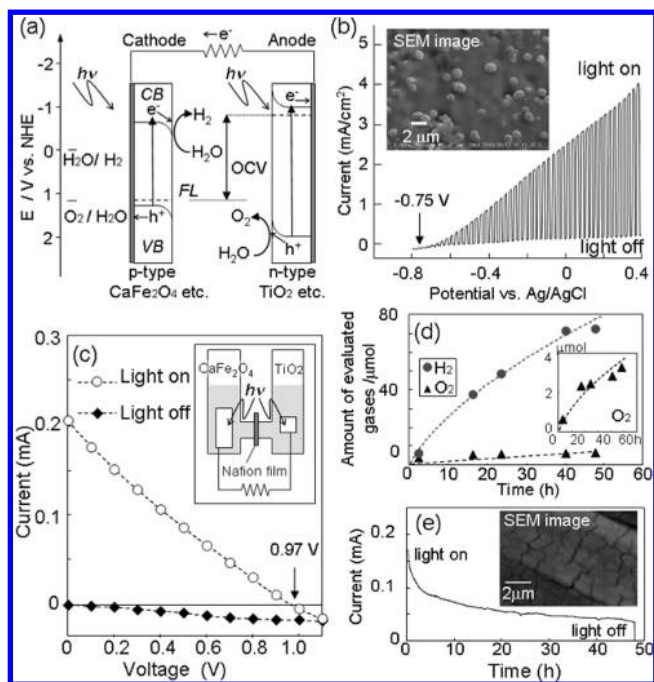


Figure 3. (a) Reaction and band model in photovoltaic cells using p-type and n-type semiconductor electrodes. (b) Current–potential curve and SEM image for TiO₂ electrode. (c) Current–potential curve of a photocell with CaFe₂O₄ (2 cm²) and TiO₂ (0.5 cm²) electrodes and model structure of measurement cell. (d) Amount of hydrogen and oxygen gases generated from the photocell short-circuited by connecting the CaFe₂O₄ and TiO₂ electrodes as a function of illumination time. (e) Current–time evolution for the photocell short-circuited by connecting the CaFe₂O₄ and TiO₂ electrodes and SEM image of CaFe₂O₄ after 48 h reaction. All reactions were carried out in 0.1 M NaOH (aq) under illumination (500 W Xe lamp).

bias by water splitting. The ratio of H₂/O₂ was around 10–20. The amount of H₂ evolved almost corresponded to half of the electrons passing through the outer circuit, while the amount of O₂ evolved was less than one fourth of the electrons. The Faraday efficiency for the O₂ production was 12%. This may be due to oxidation or oxygen absorption on the TiO₂/Ti electrode. On the other hand, the gas production rates decreased with increasing irradiation time. Figure 3e shows a current–time curve for the CaFe₂O₄–TiO₂ photocell and an SEM image of CaFe₂O₄ after reaction. The photocurrent slowly decreased with illumination time. After 48 h of reaction, many cracks were observed on the CaFe₂O₄ surface as shown in Figure 3e. In addition, the reaction solution after reaction contained 2.3 μ mol of Fe, indicating that the CaFe₂O₄ electrode was slightly decomposed during the reaction. This might be the main cause for the observed reduction in the photocurrent. However, we believe the decomposition will be suppressed by the loading of cocatalyst.

In conclusion, ($hk0$)-oriented p-type CaFe₂O₄ photocathodes were prepared and hydrogen gas was produced from a photocell containing a p-type CaFe₂O₄ electrode and an n-type TiO₂ electrode under illumination without applying an external voltage. This result indicates that the present CaFe₂O₄ is a promising p-type semiconductor photocathode for producing hydrogen.

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Supporting Information Available: Experimental procedure and other information for CaFe₂O₄–TiO₂ system (S1–S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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