NOTE

Photocatalytic hydrogen evolution from water over hafnium oxyphosphate

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Hafnium oxyphosphate was prepared as a novel photocatalyst for hydrogen production from water. Here, Hf^{4+} with d^0 electronic configuration was selected as the constituent cation, because efficient photocatalysts generally contain d^0 or d^{10} metal cations. In addition, most phosphates are reported to have high photoreduction ability of water due to their wide bandgap compared to oxides. By using $\text{Hf}_2\text{O}(\text{PO}_4)_2$, hydrogen gas was generated from water under the ultraviolet light irradiation, while a simple hafnium oxide, HfO_2 , did not show a hydrogen evolution ability. The hydrogen production rate of $\text{Hf}_2\text{O}(\text{PO}_4)_2$ was estimated to be $800 \mu\text{mol}\cdot\text{h}^{-1}$. Also, oxygen gas evolution was observed for $\text{Hf}_2\text{O}(\text{PO}_4)_2$.

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The development of renewable and clean energy source is important to solve the environmental issues, such as the fossil fuel depletion and the emission of carbon dioxide. Hydrogen gas has received attention as a next generation fuel, because the emission gas is only water. In particular, fuel cell systems can effectively convert hydrogen fuel into electricity, and they have been already applied for fuel cell vehicles. Today, the hydrogen fuel is generally produced by steam reforming of natural gas with emitting carbon dioxide; however, this process does not solve the fundamental problems. The photocatalytic hydrogen production from water using solar energy has a great advantage owing to the inexhaustible abundant, environmentally harmonious, and sustainable technology.^{1)–4)}

Photocatalysts have been widely studied, since the photocatalytic property for titanium oxide was discovered.⁵⁾ It has been well-known that efficient photocatalysts contain d^0 or d^{10} metal cations,^{3)–8)} such as Ti^{4+} , Zr^{4+} , and Nb^{5+} for d^0 ions and Ga^{3+} , Sn^{4+} , and Sb^{5+} for d^{10} ions, because the electronic configuration of metal oxides is suitable for water splitting; that is, the bandgap straddles the reduction and oxidation potentials of water. For realizing the high photocatalytic efficiency, an effective and easy method is the introduction of various elements into the photocatalyst previously reported.^{9)–11)} This material design requires the mother solid with photocatalytic ability; however, relatively less studies have been reported for novel photocatalysts, which can be the mother solids.

In this study, we focused on hafnium oxyphosphate, $\text{Hf}_2\text{O}(\text{PO}_4)_2$, as a novel photocatalyst for the hydrogen evolution from water. Here, we selected the Hf^{4+} ion as the d^0 metal cation. To our best knowledge, no photocatalytic property has been reported for the materials, which contain the Hf^{4+} ion as the main component, not as the dopant. In addition, most phosphate materials possess a relatively wide bandgap,^{12),13)} which would cause the high photoreduction ability of water. Therefore, the $\text{Hf}_2\text{O}(\text{PO}_4)_2$ solid was synthesized, and its photocatalytic activity for the hydrogen evolution was investigated.

$\text{Hf}_2\text{O}(\text{PO}_4)_2$ was prepared by evaporative drying method. Stoichiometric amounts of HfCl_4 (Aldrich) and $(\text{NH}_4)_2\text{HPO}_4$ (Aldrich) were dissolved into 5 mL of ethanol and 10 mL of water, respectively. These solutions were mixed, stirred at 80°C for 12 h, and then the solvents were vaporized at 130°C . The obtained precursor was preheated at 800°C for 12 h in air, and calcined at 1000°C for 12 h under the air flow. For comparison purpose, hafnium oxide (HfO_2) was also prepared using the same method without using $(\text{NH}_4)_2\text{HPO}_4$.

X-ray powder diffraction (XRD) measurement (SmartLab, Rigaku) was performed with $\text{Cu K}\alpha$ radiation (40 kV, 30 mA). Ultraviolet visible (UV–vis) reflection spectra were recorded by a UV–vis spectrophotometer (UV-2600, Shimadzu) with barium sulfate as a reference. The absorption spectra were represented using the reflection spectra by the Kubelka–Munk function:

$$f(R_\infty) = (1 - R_\infty)^2 / 2R_\infty$$

where $f(R_\infty)$ is Kubelka–Munk function and R_∞ is the absolute reflectance. From the absorption edge of the absorption spectra, the apparent bandgap energies were estimated.

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The photocatalytic performances were evaluated using an inner irradiation type cell with a 400 W high-pressure Hg lamp (250–577 nm; UVL-400HA, Ricoh), surrounded by quartz jacket. Before the photoirradiation, the dissolved gas was removed and argon gas (14 kPa) was filled into the closed system. The produced gas was analyzed by an online gas chromatograph with a thermal conductivity detector (GC-8A, Shimadzu). The hydrogen production was performed in 10 vol % methanol solution (200 mL), where the platinum co-catalyst (0.7 wt %) was loaded on the surface of the photocatalyst (0.15 g) using H_2PtCl_6 by an in situ photodeposition method. The oxygen production measurement was carried out in $0.01 \text{ mol} \cdot \text{L}^{-1}$ AgNO_3 aqueous solution (200 mL) containing La_2O_3 (0.2 g) as a pH buffer. The turnover number (TON) is generally defined by following Eq. (1).

$$(\text{TON}) = \frac{\text{Number of reacted photoelectrons}}{\text{Number of active sites in a photocatalyst}} \quad (1)$$

The number of active sites is often replaced by the number of a photocatalyst. In addition, the number of reacted electrons is estimated from the number of produced hydrogen molecules. Therefore, the TON is given as follows [Eq. (2)].

$$(\text{TON}) = \frac{2 \times \text{Number of evolved hydrogen}}{\text{Number quantity of a photocatalyst}} \quad (2)$$

Figure 1 shows the XRD pattern of $\text{Hf}_2\text{O}(\text{PO}_4)_2$, for comparison with the result of a simple hafnium oxide (HfO_2). The $\text{Hf}_2\text{O}(\text{PO}_4)_2$ and HfO_2 solids possessed the single-phases of the $\text{Hf}_2\text{O}(\text{PO}_4)_2$ phase (space group: $C2/m$, PDF#01-076-4743¹⁴) and the HfO_2 phase (space group: $P2_1/c$, PDF#00-034-0104¹⁵), respectively.

Figure 2 shows the absorption spectra of $\text{Hf}_2\text{O}(\text{PO}_4)_2$ and HfO_2 , estimated from the UV–vis reflectance spectra using the Kubelka–Munk function. Based on the spectra, the apparent bandgap energies of $\text{Hf}_2\text{O}(\text{PO}_4)_2$ and HfO_2 were calculated to be 5.67 and 5.55 eV, respectively, where the energy of HfO_2 was consistent with the previous

data.¹⁶ As expected, the apparent bandgap energy of $\text{Hf}_2\text{O}(\text{PO}_4)_2$ was higher than that of HfO_2 ; therefore, $\text{Hf}_2\text{O}(\text{PO}_4)_2$ is considered to have a high photoreduction ability compared to HfO_2 . In addition to the bandgap absorption, both samples absorbed light with a wavelength of 220–400 nm (Fig. 2), likely due to an additional level. It is considered that the band structure was affected by lattice defects generated via the sample preparation, because each solid has the single-phase. This additional absorption of $\text{Hf}_2\text{O}(\text{PO}_4)_2$ showed a higher intensity than the HfO_2 case.

The hydrogen evolution was evaluated by using methanol (10 vol %) as an oxidizable reagent and 0.7 wt % platinum as a co-catalyst for $\text{Hf}_2\text{O}(\text{PO}_4)_2$ and HfO_2 under UV irradiation (400 W Hg lamp; 250–577 nm). **Figure 3** shows the amount of the hydrogen evolution as a function of reaction time. For $\text{Hf}_2\text{O}(\text{PO}_4)_2$, hydrogen gas was obviously generated, and the amount of the evolution was linearly increased with operation time, where the average hydrogen production rate was estimated to be $800 \mu\text{mol} \cdot \text{h}^{-1}$. After the photocatalytic experiment, no change of the crystal structure was confirmed from the XRD measurement. Under dark condition, the hydrogen evolu-

Fig. 2. UV–vis absorption spectra of $\text{Hf}_2\text{O}(\text{PO}_4)_2$ and HfO_2 .

Fig. 1. XRD patterns of prepared $\text{Hf}_2\text{O}(\text{PO}_4)_2$ and HfO_2 .

Fig. 3. Hydrogen evolution from the aqueous methanol solution over $\text{Hf}_2\text{O}(\text{PO}_4)_2$ and HfO_2 with 0.7 wt % platinum loading under UV irradiation.

Fig. 4. Oxygen evolution from aqueous AgNO_3 solution over $\text{Hf}_2\text{O}(\text{PO}_4)_2$ and HfO_2 under UV irradiation.

tion was not observed, indicating that the hydrogen gas was produced by the photoirradiation. In order to confirm that this reaction is a catalytic reaction, the TON was estimated from the amount of evolved hydrogen. As a result, the TON for $\text{Hf}_2\text{O}(\text{PO}_4)_2$ after the reaction for 2.5 h reached up to ca. 14, which is larger than 1; therefore, the hydrogen evolution occurred catalytically. In the case of HfO_2 , however, no hydrogen generation was observed as shown in Fig. 3. There are two possible reasons for the difference in the photocatalytic activity between $\text{Hf}_2\text{O}(\text{PO}_4)_2$ and HfO_2 . One of the reason is that $\text{Hf}_2\text{O}(\text{PO}_4)_2$ possessed the high apparent bandgap energy compared to the HfO_2 case, suggesting that $\text{Hf}_2\text{O}(\text{PO}_4)_2$ might have the high photoreduction ability for the hydrogen generation from water. The other reason is that $\text{Hf}_2\text{O}(\text{PO}_4)_2$ absorbed light of wavelength of 220 to 400 nm effectively rather than the HfO_2 case (Fig. 2). Here, since the apparent bandgap energies for exciting both of $\text{Hf}_2\text{O}(\text{PO}_4)_2$ and HfO_2 were higher than the light source energy, this additional absorption (220–400 nm) might be necessary to excite an electron.

In order to investigate the water oxidation ability, the photocatalytic oxygen evolution was carried out by using AgNO_3 ($0.01 \text{ mol} \cdot \text{L}^{-1}$) as a sacrificial reagent and La_2O_3 (0.2 g) as a pH buffer, and the results are shown in Fig. 4. The oxygen evolution was clearly observed for $\text{Hf}_2\text{O}(\text{PO}_4)_2$, and the average oxygen evolution rate was $211 \mu\text{mol} \cdot \text{h}^{-1}$. Here, the oxygen evolution rate decreased with irradiation time, due to the deposition of metallic silver on the photocatalyst. This oxygen gas evolution reveals that $\text{Hf}_2\text{O}(\text{PO}_4)_2$ holds the photooxidation ability of water. For HfO_2 , the oxygen generation was not observed. From these results, it is clear that the $\text{Hf}_2\text{O}(\text{PO}_4)_2$ solid possesses the photocatalytic activity to produce hydrogen and oxygen gases from water.

In conclusion, we developed $\text{Hf}_2\text{O}(\text{PO}_4)_2$ as a novel photocatalyst for hydrogen production from water. For $\text{Hf}_2\text{O}(\text{PO}_4)_2$, the hydrogen generation was clearly observed and the average hydrogen production rate was estimated to be $800 \mu\text{mol} \cdot \text{h}^{-1}$, while hydrogen generation for HfO_2 was not observed. One reason is the large apparent bandgap energy of $\text{Hf}_2\text{O}(\text{PO}_4)_2$ (5.67 eV) compared to HfO_2 (5.55 eV); that is, $\text{Hf}_2\text{O}(\text{PO}_4)_2$ might have a high photoreduction ability. The other reason is that $\text{Hf}_2\text{O}(\text{PO}_4)_2$ absorbed light efficiently compared to HfO_2 . $\text{Hf}_2\text{O}(\text{PO}_4)_2$ also possessed the oxygen generation ability. Therefore, it is demonstrated that $\text{Hf}_2\text{O}(\text{PO}_4)_2$ is the novel photocatalyst capable of generating hydrogen and oxygen from water.

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