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, Hf⁴⁺ with d⁰ electronic configuration was selected as the constituent cation, because efficient photocatalysts generally contain d⁰ or d¹⁰ 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 Hf₂O(PO₄)₂, hydrogen gas was generated from water under the ultraviolet light irradiation, while a simple hafnium oxide, HfO₂, did not show a hydrogen evolution ability. The hydrogen production rate of Hf₂O(PO₄)₂ was estimated to be 800 µmol·h⁻¹. Also, oxygen gas evolution was observed for Hf₂O(PO₄)₂.

Key-words : Photocatalyst, Hydrogen evolution, Hafnium oxyphosphate, Oxygen evolution, UV irradiation

In this study, we focused on hafnium oxyphosphate, Hf₂O(PO₄)₂, as a novel photocatalyst for the hydrogen evolution from water. Here, we selected the Hf⁴⁺ ion as the d⁰ metal cation. To our best knowledge, no photocatalytic property has been reported for the materials, which contain the Hf⁴⁺ ion as the main component, not as the dopant. In addition, most phosphate materials possess a relatively wide bandgap, which would cause the high photoreduction ability of water. Therefore, the Hf₂O(PO₄)₂ solid was synthesized, and its photocatalytic activity for the hydrogen evolution was investigated. Hf₂O(PO₄)₂ was prepared by evaporative drying method. Stoichiometric amounts of HCl₄ (Aldrich) and (NH₄)₂HPO₄ (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 (HfO₂) was also prepared using the same method without using (NH₄)₂HPO₄.

X-ray powder diffraction (XRD) measurement (SmartLab, Rigaku) was performed with Cu Kα 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:

\[ f(R_\infty) = \frac{1 - R_\infty}{2R_\infty} \]

where \( f(R_\infty) \) is Kubelka–Munk function and \( R_\infty \) is the absolute reflectance. From the absorption edge of the absorption spectra, the apparent bandgap energies were estimated.
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 H2PtCl6 by an in situ photodeposition method. The oxygen production measurement was carried out in 0.01 mol·L⁻¹ AgNO3 aqueous solution (200 mL) containing La2O3 (0.2 g) as a pH buffer. The turnover number (TON) is generally defined by following Eq. (1).

\[
(TON) = \frac{\text{Number of reacted photoelectrons}}{\text{Number of active sites in a photocatalyst}}
\]  

(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)].

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

(2)

Figure 1 shows the XRD pattern of Hf2O(PO4)2, for comparison with the result of a simple hafnium oxide (HfO2). The Hf2O(PO4)2 and HfO2 solids possessed the single-phases of the Hf2O(PO4)2 phase (space group: C2/m, PDF#01-076-4743⁴) and the HfO2 phase (space group: P21/c, PDF#00-034-0104⁵), respectively.

Figure 2 shows the absorption spectra of Hf2O(PO4)2 and HfO2, estimated from the UV–vis reflectance spectra using the Kubelka–Munk function. Based on the spectra, the apparent bandgap energies of Hf2O(PO4)2 and HfO2 were calculated to be 5.67 and 5.55 eV, respectively, where the energy of HfO2 was consistent with the previous data.⁶ As expected, the apparent bandgap energy of Hf2O(PO4)2 was higher than that of HfO2; therefore, Hf2O(PO4)2 is considered to have a high photoreduction ability compared to HfO2. 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 Hf2O(PO4)2 showed a higher intensity than the HfO2 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 Hf2O(PO4)2 and HfO2 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 Hf2O(PO4)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 μmol·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. 1. XRD patterns of prepared Hf2O(PO4)2 and HfO2.

Fig. 2. UV–vis absorption spectra of Hf2O(PO4)2 and HfO2.

Fig. 3. Hydrogen evolution from the aqueous methanol solution over Hf2O(PO4)2 and HfO2 with 0.7 wt % platinum loading under UV irradiation.
Hf$_2$O(PO$_4$)$_2$ and HfO$_2$ under UV irradiation.

The difference in the photocatalytic activity between Hf$_2$O(PO$_4$)$_2$ and HfO$_2$ was higher for exciting both of Hf$_2$O(PO$_4$)$_2$ and HfO$_2$. One of the reasons is that Hf$_2$O(PO$_4$)$_2$ possessed the high apparent bandgap energy compared to the HfO$_2$ case, suggesting that Hf$_2$O(PO$_4$)$_2$ might have the high photoreduction ability for the hydrogen generation from water. The other reason is that Hf$_2$O(PO$_4$)$_2$ absorbed light of wavelength of 220 to 400 nm efficiently compared to HfO$_2$. Hf$_2$O(PO$_4$)$_2$ also possessed the oxygen generation ability. Therefore, it is demonstrated that Hf$_2$O(PO$_4$)$_2$ is the novel photocatalyst capable of generating hydrogen and oxygen from water.

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

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