Photocatalytic Water Splitting into H_2 and O_2 over $R_2Ti_2O_7$ (R = Y, Rare Earth) with Pyrochlore Structure

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Titanate pyrochlores $R_2Ti_2O_7$ (R = Y, rare earth) were synthesized by a polymerized complex (PC) technique and used as photocatalysts for the splitting of water into H_2 and O_2. NiO_x-loaded $Y_2Ti_2O_7$, the first example of an active photocatalyst with a pyrochlore structure, demonstrated efficient evolution of H_2 and O_2 in a stoichiometric ratio from pure water under UV-light irradiation, whereas $R_2Ti_2O_7$ compounds with partly filled 4f orbitals showed quite low activity.

Photocatalytic water splitting has received much attention because of its potential application for the direct production of H_2 for clean energy.[1] The development of new photocatalysts is indispensable for revealing the essential properties of active photocatalysts. Some mixed oxides are reported to show reasonable activities for splitting water into H_2 and O_2 in a stoichiometric ratio under UV irradiation. However, the number of photocatalytic materials that have been found is still limited, and most of the active materials are perovskite-type compounds, such as $SrTiO_3$,[2–4] $K_2La_2Ti_3O_{10}$,[5] $KTaO_3$,[6] $NaTaO_3$,[7] $Sr_2M_2O_7$ (M = Nb, Ta),[8] $RbNdTa_2O_7$,[9] and $La_2Ti_2O_7$.[10] There have been no reports of photocatalytic or stoichiometric water splitting over materials with pyrochlore structure, despite the existence of a wide variety of pyrochlore compounds. Various pyrochlores can be derived in principle from appropriate substitution in materials of empirical formula $A_2B_2O_7$. In the present study, we report the photocatalytic and stoichiometric splitting of water into H_2 and O_2 over a $Y_2Ti_2O_7$ photocatalyst, the first example of an active pyrochlore compound.

Powdered $R_2Ti_2O_7$ samples were prepared by a polymerized complex (PC) technique.[11] First, 0.01 mol of titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) was dissolved in 0.4 mol of ethylene glycol (EG). Subsequently, 0.3 mol of anhydrous citric acid (CA) was added to the solution with continuous stirring. After complete dissolution of the CA, 0.01 mol of $R(NO_3)_3 \cdot nH_2O$ (R = Y, rare earth) was added, and the mixture was magnetically stirred for 1 h to produce a transparent solution. The solution was heated at ca. 130 °C to accelerate esterification reactions between CA and EG. After a transparent glassy resin was formed, the resin was fired in an electric furnace for 2 h at 350 °C. The resulting black solid mass was ground into a powder, which was calcined on an Al_2O_3 plate at 1000 °C for 4 h in air. The structures of the synthesized materials were confirmed by powder X-ray diffraction (MAC Science, MX Labo). The surface area was determined by BET surface area measurement (Shimadzu, Gemini2360). The diffuse reflectance spectrum was measured by UV–vis spectrometry (JASCO, V-570) to estimate the band gap of the photocatalysts.

A NiO_x cocatalyst was loaded on the photocatalyst powder to promote H_2 production.[4] The photocatalytic reaction was examined using a closed gas circulation system. The photocatalyst powder (0.5 g) was dispersed in distilled water (400 mL) with a magnetic stirrer in an inner-irradiation reaction cell. The light source (400-W high-pressure mercury lamp, Riko Kagaku Japan) was insulated with a water jacket (quartz glass; cutoff $\lambda < 200$ nm) to keep the reactor temperature constant at 20 °C. The gases evolved were analyzed on an on-line gas chromatograph (TCD, molecular sieve 5A) connected with the circulation system. Apparent quantum yield was measured using reactor cell with side window made of quartz and a 500-W high-pressure mercury lamp attached with a band-pass filter (Asahi Spectra Co. Ltd., HG0313). The incident light intensity was measured with a thermopile power meter (SCIENTECH, S310).

Table 1. Water splitting activities of $R_2Ti_2O_7$ photocatalysts

Photocatalyst	Electrons in R^{3+}	Band gap /eV	Activity/μmol h^{-1}	
			H_2	O_2
$Y_2Ti_2O_7$	[Kr]	3.0	280	140
$Lu_2Ti_2O_7$	[Xe] $4f^{14}$	3.0	45	15
$Yb_2Ti_2O_7$	[Xe] $4f^{13}$	3.0	19	0
$Tm_2Ti_2O_7$	[Xe] $4f^{12}$	3.0	17	3
$Er_2Ti_2O_7$	[Xe] $4f^{11}$	3.5	4	tr.
$Ho_2Ti_2O_7$	[Xe] $4f^{10}$	3.5	14	0
$Dy_2Ti_2O_7$	[Xe] $4f^{9}$	3.5	8	0
$Tb_2Ti_2O_7$	[Xe] $4f^{8}$	3.0	0.5	0
$Gd_2Ti_2O_7$	[Xe] $4f^{7}$	3.0	8	1
$Eu_2Ti_2O_7$	[Xe] $4f^{6}$	3.6	3	0

The mineral pyrochlorite ($CaNaNb_2O_6F$) has as a face-centered cubic structure. The XRD reflections of $R_2Ti_2O_7$ (R = Eu–Lu) samples prepared by the PC technique at temperatures >800 °C indicated they had pure cubic-pyrochlore structure, like that of $Y_2Ti_2O_7$ reported previously.[11,12] In contrast, $Pr_2Ti_2O_7$, $Nd_2Ti_2O_7$, and $Sm_2Ti_2O_7$ samples prepared by the PC technique possessed monoclinic perovskite structure like that of $La_2Ti_2O_7$.[10] Table 1 summarizes the photocatalytic activities of NiO_x (1 wt %)–$R_2Ti_2O_7$ samples prepared by the PC technique at 1000 °C for the splitting of distilled water. The band gaps of the $R_2Ti_2O_7$ samples estimated from the UV–vis spectra are also included. Among the $R_2Ti_2O_7$ photocatalysts, NiO_x-loaded $Y_2Ti_2O_7$, $Lu_2Ti_2O_7$, $Tm_2Ti_2O_7$, and $Gd_2Ti_2O_7$ showed activity for the simultaneous evolution of H_2 and O_2. However, the rates of gas evolution were low, and the H_2:O_2 ratio was not stoichiometric (2:1) with $Lu_2Ti_2O_7$, $Tm_2Ti_2O_7$, and $Gd_2Ti_2O_7$. In contrast, simultaneous evolution of H_2 and O_2 at a steady rate was observed over the $Y_2Ti_2O_7$ photocatalyst calcined at 1000 °C, as shown in Figure 1. When long-term photoirradiation was carried out for 18 h over a NiO_x (1 wt %)–$Y_2Ti_2O_7$ sample (0.5 g, ca. 1.3 mmol) with periodic evacuation of the gas phase, the total amounts of evolved H_2 and O_2 reached ca. 2.8 and 1.3 mmol, respectively. The amount of H_2 evolved exceeded the stoichiometric amount with respect to the $Y_2Ti_2O_7$ sample (0.5 g, ca. 1.3 mmol). No structural change of the $Y_2Ti_2O_7$ sample was observed after the reaction. These results indicate that both H_2 and O_2 formation occurred photocatalytically over NiO_x–$Y_2Ti_2O_7$ by means of water splitting. The apparent quantum yield of the NiO_x–$Y_2Ti_2O_7$ photocatalyst was calculated to be ca. 3% at 313 nm. As shown in Table 1, all the $R_2Ti_2O_7$ pyrochlore photocatalysts containing 4f electrons showed low activity, whereas the $Y_2Ti_2O_7$ photocatalyst, which contains no 4f electrons, exhibited high photocatalytic activity. $Lu_2Ti_2O_7$, which has fully filled 4f orbitals ($4f^{14}$), showed higher activity than the catalysts with partly filled 4f orbitals (R = Yb–Eu). This result might indicate that the R^{3+} species with partly filled 4f orbitals serve as recombination centers for photoexcited electrons and holes and consequently decrease the photocatalytic activity of $R_2Ti_2O_7$.

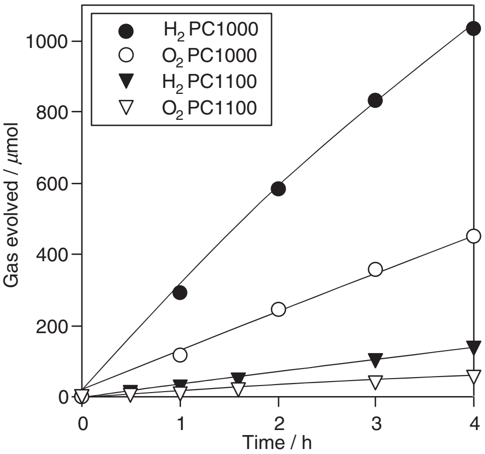

Figure 1. Gas evolution from distilled water over NiO_x (1 wt %)–$Y_2Ti_2O_7$ photocatalysts prepared by calcination at 1000 °C for 4 h (H_2: ●, O_2: ○) and at 1100 °C for 4 h (H_2: ▼, O_2: ▽).

To investigate the effect of calcination temperature on the photocatalytic activity, we prepared $Y_2Ti_2O_7$ samples at temperatures ranging from 800 to 1200 °C by the PC technique. We confirmed that all the $Y_2Ti_2O_7$ samples calcined at above 800 °C had pure cubic-pyrochlore structure, as reported by Kakihana et al.[11] The rates of H_2 and O_2 evolution for the NiO_x (1 wt %)–$Y_2Ti_2O_7$ samples are plotted as a function of the calcination temperature in Figure 2, along with the specific surface area of each sample. The rate of gas evolution increased monotonously with calcination temperature in the range from 800 to 1000 °C. The surface area of $Y_2Ti_2O_7$ significantly decreased in the range from 800 to 900 °C, which indicates the increase in crystallinity. The increase in crystallinity was also confirmed by the XRD patterns of the $Y_2Ti_2O_7$ samples. Therefore, the increase of the photocatalytic activity in going from 800 to 1000 °C is certainly associated with the increase in the crystallinity of the $Y_2Ti_2O_7$ photocatalyst. The activity of $Y_2Ti_2O_7$ significantly decreased at calcination temperatures higher than 1000 °C, in spite of the slight change in surface area from 900 to 1200 °C (Figure 2).

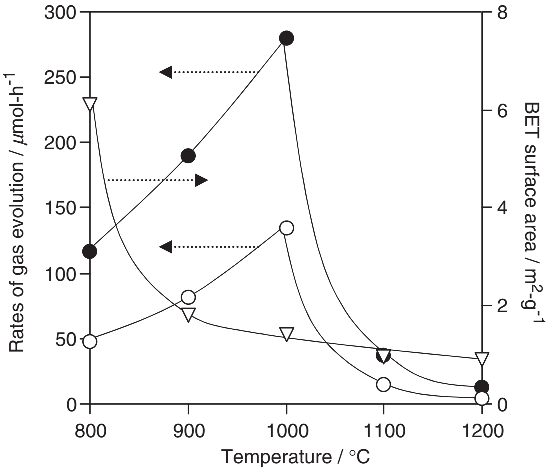

Figure 2. Gas evolution rates (H_2: ●, O_2: ○) and specific surface areas (▽) of NiO_x (1 wt %)–$Y_2Ti_2O_7$ samples as a function of calcination temperature.

As shown in Figure 1, the activity of the $Y_2Ti_2O_7$ photocatalyst prepared at 1100 °C was much lower than that of the $Y_2Ti_2O_7$ photocatalyst prepared at 1000 °C. We believe that another crucial change occurred on the $Y_2Ti_2O_7$ photocatalyst during calcination above 1000 °C. Recently, Kudo et al. have reported that the presence of certain surface structures, such as nanosteps, significantly affects the activity of $NaTaO_3$ photocatalyst for water splitting.[7] The surface structure of $Y_2Ti_2O_7$ might change during the calcination above 1000 °C, although the change was not confirmed by XRD measurement. Further studies are required for an understanding of the effects of calcination temperature on the activity of the $Y_2Ti_2O_7$ photocatalyst.

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