A Novel Photodeposition Method in the Presence of Nitrate Ions for Loading of an Iridium Oxide Cocatalyst for Water Splitting

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IrO_2 cocatalysts for water splitting were photodeposited from aqueous solution of $(NH_4)_2[IrCl_6]$ or $Na_3[IrCl_6]$ in the presence of nitrate ions on La-doped $NaTaO_3$ (denoted as $NaTaO_3$:La) photocatalysts, while metallic iridium particles were deposited in the absence of nitrate ions. The IrO_2-loaded $NaTaO_3$:La showed the activity for water splitting 2.5 times higher than the nonloaded $NaTaO_3$:La. In contrast, the steady activity was not obtained for the metallic iridium-loaded photocatalyst, because the back reaction quickly proceeded.

Photocatalytic water splitting into H_2 and O_2 is an attractive reaction from the viewpoint of the solution of energy and environmental issues. It has been reported that many oxide photocatalysts show reasonable activities for water splitting into H_2 and O_2 in a stoichiometric ratio under UV irradiation.[1–3] Most photocatalysts require loading of cocatalysts in order to obtain high activities. Pt,[4] Rh,[5,6] NiO,[7] and RuO_2[3,8] cocatalysts that assist H_2 evolution are often employed for overall water splitting. It has been reported by Inoue that an IrO_2 cocatalyst loaded by an impregnation method is also effective for water splitting as well as RuO_2.[9] In contrast, the cocatalyst for O_2 evolution using a powdered photocatalyst is limited. Hara and Mallouk reported that a colloidal IrO_2 cocatalyst works as an active site for O_2 evolution.[10–12] However, the loading procedure of the colloidal IrO_2 is somewhat complicated. In addition, there are no reports on the O_2-evolution cocatalyst which improves the photocatalytic activity for overall water splitting. In the present paper, we report a novel photodeposition method of iridium-based cocatalysts which are effective for water splitting on a La-doped $NaTaO_3$ photocatalyst.

$NaTaO_3$ powder doped with 2 mol % of La was prepared by a solid-state reaction according to the previous report.[13] Photocatalytic reactions were carried out in a gas-closed circulation system. For the photocatalytic decomposition of water, an inner irradiation reaction cell made of quartz was used. The $NaTaO_3$:La powder (1.0 g) was dispersed in a reactant solution (350 mL) containing a certain amount of iridium species, $(NH_4)_2[IrCl_6]$ (Wako Pure Chemical) and $Na_3[IrCl_6]$ (Wako Pure Chemical). $NaNO_3$ (Kanto chemical; 99%) was added into the solution, if necessary. The suspension was irradiated using a 400 W high-pressure mercury lamp (SEN; HL400EH-5). Photodeposition of an iridium-based cocatalyst was carried out in situ at the beginning stage of photocatalytic reactions. $NaTaO_3$:La powder loaded with a cocatalyst in the aqueous $NaNO_3$ solution was washed and collected by a centrifugal method when it was employed for photocatalytic reactions in the absence of $NaNO_3$. Half reactions of H_2 and O_2 evolution were also tested in aqueous methanol and silver nitrate solutions, respectively. The reaction cell with a top window made of quartz and a light source of a 300 W Xe lamp (ILC-technology, CERMAX·LX-300BUV) were used for these sacrificial reactions. The amounts of evolved H_2 and O_2 were determined using gas chromatography (Shimadzu, GC-8A). Diffuse reflection spectra were obtained using a UV–vis–NIR spectrometer (JASCO, Ubest-570) and were converted from reflection to absorbance by the Kubelka–Munk method.

Figure 1 shows overall water splitting on iridium-loaded $NaTaO_3$:La which was prepared by photodeposition in pure water without nitrate ions (denoted as Ir(water)-$NaTaO_3$:La). The water splitting reaction stopped immediately although the photocatalytic activity of Ir(water)-$NaTaO_3$:La (H_2: 1210 $\mu mol\,h^{-1}$, O_2: 484 $\mu mol\,h^{-1}$) was 3 times higher than that of native $NaTaO_3$:La (H_2: 404 $\mu mol\,h^{-1}$, O_2: 187 $\mu mol\,h^{-1}$) at the beginning stage. In addition, evolved H_2 and O_2 decreased

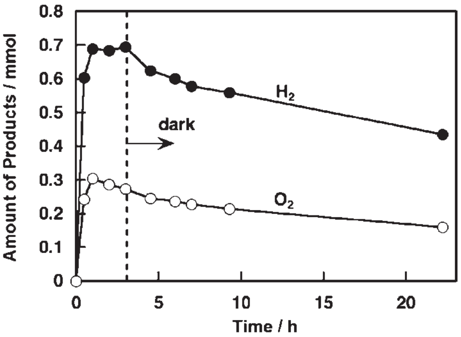

Figure 1. Photocatalytic water splitting into H_2 and O_2 over Ir(water)-$NaTaO_3$:La; closed circle: H_2, open circle: O_2. Catalyst: 1.0 g, pure water: 350 mL, a 400 W high-pressure Hg lamp, an inner irradiation cell made of quartz.

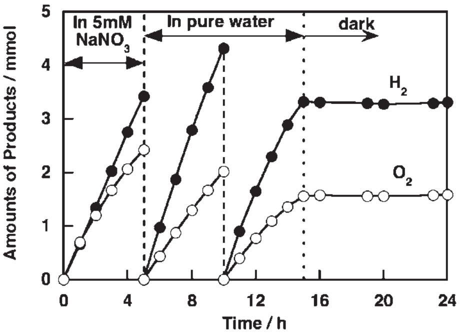

Figure 2. Photocatalytic water splitting over Ir(nitrate)-$NaTaO_3$:La in 5 $mmol\,L^{-1}$ $NaNO_3$ (1st run) and pure water (2nd and 3rd runs); closed circle: H_2, open circle: O_2. Catalyst: 1.0 g, reactant solutions: 350 mL, a 400 W high-pressure Hg lamp, an inner irradiation cell made of quartz.

at the ratio of 2:1 in the dark. XPS measurements revealed that metallic iridium existed on Ir(water)-$NaTaO_3$:La. The back reaction was not observed for native $NaTaO_3$:La. Therefore, the deactivation was due to the back reaction on the metallic iridium cocatalyst photodeposited in pure water. Figure 2 shows overall water splitting on iridium-loaded $NaTaO_3$:La which was prepared by photodeposition in the presence of nitrate ions (denoted as Ir(nitrate)-$NaTaO_3$:La). Water splitting steadily proceeded on Ir(nitrate)-$NaTaO_3$:La. In the 1st run in the presence of nitrate ions, the rate of H_2 evolution was 2.5 times higher than that of native $NaTaO_3$:La even if the reduction of nitrate ions competed with that of water judging from the evolution of an excess amount of O_2. When the reactant solution was changed to pure water (2nd and 3rd runs), the ratio of evolved H_2 and O_2 became two. The rate of H_2 evolution on Ir(nitrate)-$NaTaO_3$:La in pure water was higher than that in the aqueous nitrate solution. No back reaction was observed for Ir(nitrate)-$NaTaO_3$:La in the dark. Thus, the property of Ir(nitrate)-$NaTaO_3$:La was quite different from that of Ir(water)-$NaTaO_3$:La. These results indicate that the nitrate ions were necessary when the iridium cocatalysts which assisted steady water splitting were photodeposited on $NaTaO_3$:La. In the case of 2nd and 3rd runs, the total amount of H_2 evolved from pure water was 7.6 mmol. The turnover numbers of the reacted electrons/holes to the amount of $NaTaO_3$:La and Ir were 4 and 600, respectively. It indicates that the water splitting proceeded photocatalytically.

Figure 3 shows diffuse reflection and absorption spectra of Ir(water)-$NaTaO_3$:La, Ir(nitrate)-$NaTaO_3$:La, and colloidal IrO_2. Ir(nitrate)-$NaTaO_3$:La gave the characteristic absorption band around 600 nm as well as the IrO_2 colloids whereas Ir(water)-$NaTaO_3$:La did not. The similarity indicates that the iridium species photodeposited in the presence of nitrate ions was colloid-like IrO_2. Therefore, the Ir(nitrate)-$NaTaO_3$:La photocatalyst can be denoted as IrO_2-$NaTaO_3$:La. Although we tried to load $NaTaO_3$:La with IrO_2 by an impregnation method, it was not effective. Thus, the present aqueous process was superior to the conventional impregnation method, at least for the $NaTaO_3$:La photocatalyst. Hara et al. have reported that the colloidal IrO_2-loaded photocatalysts are active for O_2 evolution.[11] According to their report, the colloidal IrO_2 is prepared by the pH-controlled hydrolysis, and colloidal IrO_2 is adsorbed on a photocatalyst. In contrast to it, the simple photodeposition method by an aqueous process, which gave good performance for water splitting, was developed in the present study.

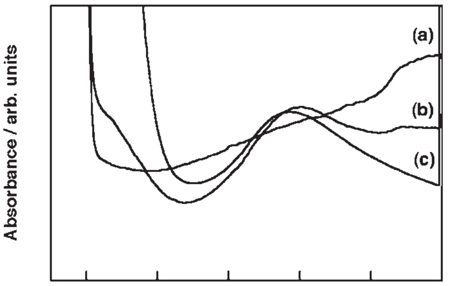

Figure 3. Diffuse reflection spectra of (a) Ir(water)-$NaTaO_3$:La and (b) Ir(nitrate)-$NaTaO_3$:La, and absorption spectrum of (c) colloidal IrO_2.

Table 1. Photocatalytic activities of IrO_2-$NaTaO_3$:La for H_2 and O_2 evolution from aqueous solutions containing sacrificial reagents

Photocatalyst	Activity/μmol h^{-1}	
	H_2[a]	O_2[b]
$NaTaO_3$:La	191	44
IrO_2 (0.26 wt %)/$NaTaO_3$:La	37	76

300 W Xe lamp, a top window cell made of quartz. [a]Catalyst: 0.3 g, 10 vol % CH_3OH (aq) 150 mL. [b]Catalyst: 0.5 g, 0.05 mol L^{-1} $AgNO_3$ (aq) 150 mL.

Table 1 shows the activities of IrO_2-$NaTaO_3$:La for H_2 and O_2 evolution from aqueous solutions containing sacrificial reagents. The IrO_2-loaded $NaTaO_3$:La photocatalysts were prepared by photodeposition in the presence of nitrate ions and washed by a centrifugal method before use. The activity of $NaTaO_3$:La for O_2 evolution was increased by 1.5 times by loading of the IrO_2 cocatalyst, while the activity for H_2 evolution was decreased. It is considered that the low activity for H_2 evolution is due to the charge recombination facilitated by partly reduced IrO_2 in the presence of CH_3OH as a hole scavenger. These results indicated that the present IrO_2 cocatalyst assisted O_2 evolution as well as the IrO_2 colloid previously reported.[10–12] It is considered that the IrO_2 cocatalyst plays important roles for the formation of active sites for O_2 evolution and the suppression of the charge recombination. It results in the improvement for overall water splitting.

In conclusion, the IrO_2 cocatalyst that was effective for overall water splitting was loaded on a La-doped $NaTaO_3$ photocatalyst by a simple photodeposition method from an aqueous solution of $(NH_4)_2[IrCl_6]$ or $Na_3[IrCl_6]$ in the presence of nitrate ions. It is noteworthy that photocatalytic water splitting was enhanced by loading of a cocatalyst not for H_2 evolution but for O_2 evolution.

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