Photocatalytic water splitting and CO_2 reduction over Nb- and Ta-containing metal oxide photocatalysts with a laminated structure

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Abstract: Development of new photocatalysts for water splitting and CO_2 reduction is an important research topic to achieve highly efficient artificial photosynthesis. In the present study, we found that $A_{10}Ta_{29.2}O_{78}$ and $A_8Nb_{22}O_{59}$ (A = Cs, Rb) with a laminated structure were active photocatalysts for water splitting and CO_2 reduction. Both oxides showed activities for water splitting even without any cocatalyst. The activities were drastically improved by loading of NiO and $Rh_{0.5}Cr_{1.5}O_3$ cocatalysts. When Ag was loaded as a cocatalyst, $A_{10}Ta_{29.2}O_{78}$(A = Cs, Rb) produced CO and H_2 as reduction products of CO_2 and H_2O, respectively, and O_2 as an oxidation product of H_2O.
Keywords: Water splitting, CO_2 Reduction, Laminated structure.

1. Introduction

Photocatalytic water splitting and CO_2 reduction have been extensively studied as a promising process to convert light energy to chemical energy. Various metal oxides with wide band gaps have been reported as an active photocatalyst for water splitting and CO_2 reduction under UV irradiation.[1] For example, we have reported that $CaTa_4O_{11}$ and $LaTa_7O_{19}$ with a laminated structure show activities for water splitting and CO_2 reduction under UV irradiation.[2,3,4] $A_{10}Ta_{29.2}O_{78}$ and $A_8Nb_{22}O_{59}$ (A = Cs, Rb) also possess the laminated structure,[5,6] and hence are expected to show activities for photocatalytic water splitting and CO_2 reduction. In the present study, we investigated the photocatalytic properties of $A_{10}Ta_{29.2}O_{78}$ and $A_8Nb_{22}O_{59}$ (A = Cs, Rb) with the laminated structure.

2. Experimental

$A_{10}Ta_{29.2}O_{78}$ and $A_8Nb_{22}O_{59}$ (A = Cs, Rb) were prepared by a polymerized complex method. NiO, $Rh_{0.5}Cr_{1.5}O_3$, and Ag cocatalysts were loaded by an impregnation method. The prepared materials were characterized using XRD, DRS, SEM, BET, and PL. Photocatalytic water splitting and CO_2 reduction were carried out in 1 atm of Ar and CO_2, respectively. Photocatalyst powder was dispersed in reactant solutions in an inner-irradiation cell made of quartz. A 400 W high-pressure mercury lamp was used as a light source. Gas products were determined using gas chromatographs.

3. Results and discussion

XRD measurements indicated that single phases of $A_{10}Ta_{29.2}O_{78}$ and $A_8Nb_{22}O_{59}$ (A = Cs, Rb) were obtained by a polymerized complex method. The band gaps of $A_{10}Ta_{29.2}O_{78}$ and $A_8Nb_{22}O_{59}$ (A = Cs, Rb) were estimated to be 4.4 eV and 3.6 eV, respectively, from the absorption edges of the diffuse reflectance spectra. Photoluminescence spectra at 77 K of the samples were also evaluated. $A_{10}Ta_{29.2}O_{78}$ (A = Cs, Rb) showed a broad blue emission with a maximum around 450 nm. The onset of the excitation spectrum agreed with that of the absorption spectrum.

Table 1 shows photocatalytic activities for water splitting over $A_{10}Ta_{29.2}O_{78}$ and $A_8Nb_{22}O_{59}$ (A = Cs, Rb). All of the metal oxides produced H_2 and O_2 even without any cocatalyst. It is noteworthy that the pristine $A_8Nb_{22}O_{59}$ (A = Cs, Rb) showed the activity for water splitting, because the niobates except $K_4Nb_6O_{17}$[7] require cocatalysts to achieve water splitting. The activities for water splitting were drastically improved when either an NiO or an $Rh_{0.5}Cr_{1.5}O_3$ cocatalyst was loaded. The turnover numbers reacted electron to molar quantities of photocatalysts were greater than unity, indicating that the water splitting

proceeded photocatalytically. When Ag cocatalyst was loaded, $A_{10}Ta_{29.2}O_{78}$ (A = Cs, Rb) showed the activity for CO_2 reduction to form CO accompanied by H_2 and O_2 evolution due to water splitting.

Table 1. Water splitting over $Rh_{0.5}Cr_{1.5}O_3/A_8Nb_{22}O_{59}$ and $NiO/A_{10}Ta_{29.2}O_{78}$ (A = Cs, Rb) photocatalysts

Photocatalyst	Cocatalyst (wt %)	BG / eV	S.A. / $m^2 g^{-1}$	Activity / μmol h^{-1}	
				H_2	O_2
$Cs_{10}Ta_{29.2}O_{78}$	None	4.4	4.3	10	4
$Cs_{10}Ta_{29.2}O_{78}$	NiO (0.2)	4.4	4.3	453	234
$Rb_{10}Ta_{29.2}O_{78}$	None	4.4	4.4	8	4
$Rb_{10}Ta_{29.2}O_{78}$	NiO (0.2)	4.4	4.4	369	188
$Cs_8Nb_{22}O_{59}$	None	3.6	2.4	4	3
$Cs_8Nb_{22}O_{59}$	$Rh_{0.5}Cr_{1.5}O_3$ (0.5)	3.6	2.4	212	112
$Rb_8Nb_{22}O_{59}$	None	3.6	1.4	5	3
$Rb_8Nb_{22}O_{59}$	$Rh_{0.5}Cr_{1.5}O_3$ (0.5)	3.6	1.4	343	175

Photocatalyst: 0.5 g, solution: pure water (340 mL), light source: 400-W high-pressure mercury lamp,
cell: inner irradiation cell made of quartz, cocatalyst: NiO (Impregnation 543K-1h), $Rh_{0.5}Cr_{1.5}O_3$ (Impregnation 623K-1h).

4. Conclusions

$A_{10}Ta_{29.2}O_{78}$ and $A_8Nb_{22}O_{59}$ (A = Cs, Rb) with a laminated structure have arisen as a new photocatalyst for water splitting and CO_2 reduction under UV light irradiation. $A_{10}Ta_{29.2}O_{78}$ and $A_8Nb_{22}O_{59}$ (A = Cs, Rb) showed activity for water splitting even without a cocatalyst. In addition, loading of either NiO or $Rh_{0.5}Cr_{1.5}O_3$ drastically improved the water splitting activities of $A_{10}Ta_{29.2}O_{78}$ and $A_8Nb_{22}O_{59}$ (A = Cs, Rb). Ag-loaded $A_{10}Ta_{29.2}O_{78}$ (A = Cs, Rb) photocatalysts was also active for CO_2 reduction to CO accompanied by O_2 evolution in an aqueous medium. Thus, we have successfully developed new photocatalysts for artificial photosynthetic water splitting and CO_2 reduction.

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